Oil-dispersed pH - responsive particle as Pickering Emulsifiers

by

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Abstract

In this work, the oil-dispersed polydimethylsiloxane (PDMS) sterically stabilised poly(Methl Methacrylate-2Vinyl Pyridine) p(MMA-2-VP) particles are investigated for use as Pickering emulsifiers with varied emulsification conditions (pH, particle concentrations and oil-water volume ratios) and their adsorption behaviours on 2-Dimensional curved oil-water interface. These particles are synthesised by dispersion polymerisation in dodecane and their particle content can be controlled by varying the initial MMA: 2-VP ratio (uncrosslinked particles with varied MMA-2-VP ratio in particle cores) and crosslinker concentrations (cross-linked particles with constant initial MMA-2-VP ratio).

Transitional phase inversion from w/o to o/w emulsions which are stabilised by oil-dispersed p(MMA-2-VP)-PDMS particles is induced by tuning pH from 6 to 2 in aqueous phase, regardless of particle concentrations. It is the first time reported of such phase inversion in emulsions stabilised with responsive emulsifiers by responding to the relevant environmental trigger. This phenomenon occurs only in the emulsion systems that prepared in the presence of such oil-dispersed particles containing more than 62% p2-VP in cores. The particles which synthesised with 5 mol% (respect to monomer concentration) cross-linkers can stabilise most stable emulsions than others, in particular the o/w emulsion, no released oil can be observed after 10 months preparation.

Pickering emulsions are also prepared by changing the oil-water volume ratio under different pHs. Catastrophic emulsion phase inversion from single emulsions to multiple emulsions are observed under certain experimental conditions, indicating that such phenomenon is not only controlled by increased dispersed phase fraction in emulsion systems but also governed by the proton concentration/quantity in aqueous phase. The o/w high internal phase emulsion gels are stabilised by such oil-dispersed pH responsive particles which synthesised with 5 mol% (respect to monomer concentration) cross-linkers at pH 2 with 70 vol% oil phase.

Eventually, the measurement of interfacial tension as a function of time in the presence of varied concentrations of oil-dispersed pH responsive particles are performed basing on a pendant drop method. Oil-dispersed pH responsive particles are more interfacially active at uncharged state than charged state. The adsorption coefficient value is large at charged state (pH2) than uncharged state (pH 6), implying the fact that such particle stabilised emulsion properties are governed mainly by their adsorption kinetics

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Chapter 1. Introduction

1.1 Introduction

The colloidal particle stabilised emulsion (so-called Pickering–Ramsden emulsion) has been discovered for more than a century(Pickering, 1907; Ramsden, 1903; Finkle et al., 1923). Comparing to the original surfactant stabilised emulsion, it has some more advantages such as super stability against collapse, good reproducibility, comparatively environmental friendly and low toxicity, etc., which are nowadays more and more familiarized and exploited by scientists(Binks, 2002; Aveyard et al., 2003). Generally, in addition to its high academic research value, the Pickering emulsion has also brought growing interests in industries given its promising applications in pharmaceutical, food, cosmetics and agricultural fields (Binks, 2002).

In particular, some practical applications like oil recovery and drug delivery often demand the relevant emulsion systems to be stabilized/destabilized or reversed in type (e.g. o/w to w/o) at more willing (or with simple control). For this, efforts have been devoted to the development of stimulus-responsive Pickering emulsions, which have extraordinary ability in controlling the stability and the type of emulsion by responding to environmental triggers. To meet the specific demands for different purposes, a variety of well-designed and tailored organic polymeric particles have been developed as smart Pickering emulsifiers with responsiveness to specific external stimuli such as pH (Nuopponen and Tenhu, 2007; Webber et al., 2005; Dupin et al., 2008; Delaittre et al., 2009; Binks et al., 2005a), temperature (Monteux et al., 2010; Tsuji and Kawaguchi, 2008; Binks et al., 2005a), magnetic field intensity

(Melle et al., 2005; Zhou et al., 2011; Nypelö et al., 2014; Peng et al., 2012) and light, etc. In principle, their ability of precisely controlling emulsion stabilization/destabilization is realized through the stimuli-triggering conformational changes of the responsive particles at the oil/water interface whereby their wettability (i.e. the interfacial contact angle) are correspondingly altered(Binks et al., 2007; Amalvy et al., 2003). Importantly, except from the wettability, the environmental triggers can also induce particle deformations at the interface especially in the cases of microgels, which is often argued to attribute to the emulsion stabilization or phase inversion (Ngai et al., 2005; Destribats et al., 2011a). Even so, the investigations of the stimulus-responsive Pickering emulsions particularly the knowledge about the interfacial properties of the responsive particles at the interface and their mystical relation with emulsion stability are far from enough (Ngai et al., 2005; Destribats et al., 2011a; Amalvy et al., 2003; Aveyard et al., 2003).

As known, most of the well-tailored polymeric particles designed as responsive Pickering emulsifiers are normally dispersed in aqueous solutions. This is perhaps due to the fact that lots of applications in cosmetics(Gichinga et al., 2010), pharmaceuticals(Supasuteekul et al., 2012; Gichinga et al., 2010; Fernandez-Nieves et al., 2011), catalysts(Mei et al., 2007), photochemistry(Sasa and Yamaoka, 1994) and in optical switches or sensors(Scheffold et al., 2010) require an aqueous environment. With emerging developments of new materials in various areas, more and more stringent requirements are needed one of which is the dispersion in non-aqueous solvent of colloidal particles especially for the responsive particulate systems. This is especially true in fields like coating industry (Saatweber and Vogt-Birnbrich, 1996; Ishikura et al., 1988; Bartsch et al., 1998), oil recovery(Fernandez-Nieves et al., 2011) and electrophoretic displays (EPD) where a low dielectric constant environment is required. However, it is rare to find examples of oil-dispersed responsive Pickering emulsifiers in previous studies reported within the past decades. Based on such circumstances, oil-dispersed responsive Pickering emulsifiers are becoming the theme of this thesis study with a purpose to combine the advantages of responsive colloidal particles as emulsion stabilisers and the feature of good dispersability in non-aqueous based system.

1.2 Aim of thesis

The aim of this work is to investigate the oil-dispersed core-shell p(MMA-2-VP)-PDMS particles as Pickering emulsifiers, in particular their core pH responsiveness at emulsion droplets' oil-water interface and the key aspects on influencing the properties of the corresponding stabilised emulsions. The core-shell particles are composed of p(MMA-2-VP) copolymer core stabilised by polydimethylsiloxane (PDMS) polymer chains as shells to be able dispersing in dodecane. Such oil-dispersed particles are synthesised by dispersion polymerization method. Methyl Methacrylate (MMA) and Vinyl 2-Pyridine (2-VP) are varied in a range of ratios, further systematically increased initial cross-linker is controlled with a fixed MMA-2-VP ratio, to constitute the particle cores. The synthesised particle suspensions are well-characterised to understand the particle core content, particle size and particle morphology. The role of such oil-dispersed particle adsorbed at oil-water interface and the pH-responsiveness of particles on affecting emulsion properties are studied as a function of particle concentrations, oil-water volume ratios and pH. Particle stabilised emulsion types, mean droplets diameter, stability and the observation of particle adsorbing layer are characterised and analysed to conclude and discuss the key aspects that influence the emulsion properties in our system. Eventually, to understand pH induced particle adsorption behaviours, the interfacial tension of dodecane-water interface in the presence of varied concentrations and different configurations of particles are examined as a function of time at different pH. Such investigation is purposed to potentially reveal the particle adsorbing kinetics and the influences of pH on particle interfacial behaviours.

1.3 Thesis structure

Chapter 2

This chapter provides a detailed background and literature review on related areas in colloidal science. The theoretical background and literature reviews can be divided into three parts. In the first part, the background of responsive polymeric particles and some typical responsive monomer/polymer examples have been introduced. The theory of emulsion, emulsion stability and Pickering emulsifiers are illustrated in second part. Especially, an elaborate review on responsive Pickering emulsifiers and oil-dispersed particular stabilisers are stated as well. Thirdly, this chapter is finished by presenting the method and related investigating techniques of responsive particle adsorbing at curved interface.

Chapter 3

Chapter 3 demonstrates the synthesis and characterisation of oil-dispersed p(MMA-2-VP)-PDMS particles. The oil-dispersed particles consist of either varied co-monomer contents or systematically increased cross-linker ratios. The effect of particle core content on final particle suspensions is paid attentions as well.

Chapter 4

The forth chapter is focusing on the use of synthesised oil-dispersed particles to fabricate Pickering emulsions as a function of particle concentrations at varied pH. In this part of work, all synthesised particles are employed as Pickering emulsifiers to stabilise emulsions at same conditions. The effect of pH in aqueous phase and particle configurations on emulsion properties and types are evaluated.

Chapter 5

Chapter 5 continuously investigate the role of such oil-dispersed particles in preparation of Pickering emulsions at varied oil-water volume ratio and pH. Four batches of oil-dispersed p(MMA-2-VP)-PDMS particle suspensions are selected to investigate the oil-water volume ratio influence on emulsion types and properties at different pH in the presence of two different particle concentrations (particle concentration of oil volume and constant particle quantity in whole system). The key aspect in our system that affect the emulsion types by varying oil-water volume ratio is revealed based on the experimental results.

Chapter 6

This chapter shows the initial investigation of particle interfacial adsorbing behaviours. The dodecane-water interfacial tension is presented as a function of time in the presence of varied particle concentrations of three selected oil-dispersed particles at different pH. The effect of pH and particle configurations on adsorption kinetics are studied and discussed as well.

Chapter 7

This final chapter contributes as a summary of the importance and achievement of this thesis and related experimental study and a future direction of further investigation and potential industrial development.

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Chapter 2. Theoretical background and literature review

2.1 Responsive particle system

In the late of 20th and beginning of 21st centuries, to sustain life and achieve the variation and diversity of daily common, specific tailored materials, which have varied chemical functions and structures that can be changed by responding to environmental triggers, are required by different industrial areas (Stuart et al., 2010; Cayre et al., 2011; Alarcon et al., 2005; Ahn et al., 2008; Crespy and Rossi, 2007). An increasing focus in functional materials research for high value liquid based chemical products are synthetic stimuli-responsive polymeric particle systems, which have been designed and studied for a wide range of emerging applications or potential uses, like: smart emulsion/foam stabilisers (Destribats et al., 2011a) for oil-harvesting(Tang et al., 2016) and personal products, controlled-drug delivery and release(Yuan et al., 2007; Frelichowska et al., 2009; Guo et al., 2008; Soppimath et al., 2005; Müller-Schulte and Schmitz-Rode, 2006; Veiseh et al., 2003), chemical/physical sensors(Shen et al., 2008; Nuopponen and Tenhu, 2007; Zhu et al., 2004) and coating(Cayre et al., 2011).

Responsive colloidal particle systems are defined as those that can respond to local environmental triggers, leading to conformational and chemical changes in the bulk liquid or at fluid-fluid interfaces(Stuart et al., 2010) . The key component which drives such change is the responsive polymer. Various polymers respond to corresponding triggers associated with the variation of their physical properties, for example: from hydrophilic to hydrophobic and structure changes(Stuart et al., 2010; Alarcon et al., 2005). Normally, those variation of responsive polymers are owing to the gain/loss of hydrogen bonding or progressive ionisation in bulk(Alarcon et al., 2005). There are many responsive polymers that can be incorporated in synthetic responsive particle systems, much of the research to date has involved pH(Amalvy et al., 2003; Amalvy et al., 2003; Binks et al., 2007; Fujii et al., 2010; Dai et al., 2008; Dupin et al., 2008), temperature(Monteux et al., 2010; Binks et al., 2005a; Nuopponen and Tenhu, 2007; Ngai et al., 2005) , light (Chen et al., 2014)or magnetic field(Veiseh et al., 2003) as the stimulus.(Alarcon et al., 2005; Cayre et al., 2011; Stuart et al., 2010).

This section focuses on the review and discussion of various chemical bonded responsive particle systems, although it is noted that for focus and clarity, self-assembled responsive micelle systems will not be included. Initially, the common responsive polymers/monomers involved as part of responsive particle systems are analysed for their structure, physical and chemical properties. In the next step, we look at how these monomers/polymers form particles with varied conformation. We then review literature studies on their responsive behaviour, as well as how particle architecture affects their bulk and interfacial changes. Finally, specific research area is focused to discuss studied oil-dispersed responsive particle systems, the potential challenges and research gap.

2.1.1 Responsive polymers

Responsive polymers have attracted significant attention over the last two decades, as there is a wide range of potential applications when the polymer itself is used as a responsive material, including analytical chemistry(Nishio et al., 2009), purification techniques(Mattiasson et al., 2007) and active molecule delivery (Dai et al., 2008). Also there is growing interest on their steric structures when polymers self-aggregate or graft on curved particle/planar surfaces(Cayre et al., 2011). The responsive polymer can be categorised as the stimulus that they can respond to; such as temperature, pH, ionic strength and (as discussed above)(Cayre et al., 2011; Dai et al., 2008; Stuart et al., 2010; Alarcon et al., 2005). The following paragraphs give a brief introduction on several categories of responsive polymers that are most commonly used in the process in designing responsive particles, including examples of each category with their related responsive mechanisms and review research activities on them.

Temperature-responsive polymers, as known, are those that be controlled through changes of some physical properties by or around a critical temperature degree. Such specific temperatures are defined as lower critical solution temperature (LCST) and upper critical solution temperature (UCST)(Stuart et al., 2010; Hocine and Li, 2013; Alarcon et al., 2005; Cayre et al., 2011). Below LCST, polymers become more hydrophobic because of the loss of hydrogen bonds, while polymers can be mixed better and easier in aqueous phase when the bulk temperature is above UCST(Hocine and Li, 2013; Stuart et al., 2010; Alarcon et al., 2005). This hydrophilic-hydrophobic variation, normally, leads a coil-globule transition of polymer conformation as well as a swell-deswell of its polymeric particle (Figure 2-1)(Hocine and Li, 2013).

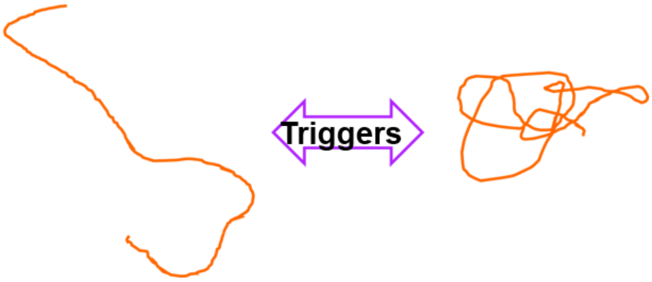

Figure 2-1 Schematic representation of the conformational change of temperature responsive polymer from a hydrated coil (left) to a dehydrated collapse globule (right) after answering triggers （inspired by (Hocine and Li, 2013)）.

There are many thermosensitive polymers and their derivatives, which have been studied for their critical transitional behaviour and for various potential applications recently (e.g. (Cayre et al., 2011; Hocine and Li, 2013)). There are several kinds of polymers which are especially attractive, based on their particular responsive behaviours and physical properties. The Poly(alkyl oxide) family that has the derivatives of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO)(Hocine and Li, 2013) are particularly popular, due to their bio-compatibility and the ability to reduce protein adsorption(Lasic, 1994; Needham et al., 1992; Gref et al., 2000; Vittaz et al., 1996). The so-called 'close-loop transition' induces the solubility variation of PEO upon LCST and UCST (Figure 2-1) (Saeki et al., 1976; Saeki et al., 1977). When the temperature increases above the LCST, PEO becomes insoluble in water and phase separates (Hocine and Li, 2013; Cayre et al., 2011). However, if the temperature increases over the UCST, the suspension state becomes stable again(Hocine and Li, 2013; Cayre et al., 2011). Poly(N,N-dimethylaminoethylmethacrylate) (PDMAEMA) is another common thermo-responsive polymer which belongs to the poly(aminoalkylmethacrylate) family(Cayre et al., 2011; Hocine and Li, 2013; Bütün et al., 2001; Fournier et al., 2007; Plamper et al., 2007). Such polymers are well known for their dual responsiveness, by responding to temperature variations as well as the pH changes in aqueous bulk(Wetering et al., 1998; Bütün et al., 2001; Fournier et al., 2007; Plamper et al., 2007).

Another widely studied and understood polymer is from the Poly(N-acrylamide) class(Scarpa et al., 1967; Heskins and Guillet, 1968; Hocine and Li, 2013), especially, poly(N-isopropylacrylamide) which is known as PNIPAM, and been extensively used to form well-documented temperature responsive microgels in past 5-10 years(Schild, 1992; Schild and Tirrell, 1990; Ngai et al., 2005). It has the advantage of its human body closed LCST (32 ^{o}C) and thus has been adapted for a potential drug delivery system(McCormick et al., 2006). Besides PNIPAM, some other polymers in Poly(N-acrylamide) family had been taken into consideration when they took part into the responsive particle system, like poly(acrylamide) (PAA) and Poly(N,N-dimethylacrylamide) (PDMA) (Liu and Zhu, 1999).

pH-responsive polymers are amongst the most intensely studied stimuli-responsive polymers and have been widely employed to form varied structures, like hydrogels, polymer brushes and responsive particle systems, for potential applications in drug/active molecule delivery and release, sensor and oil harvesting (e.g.(Stuart et al., 2010; Cayre et al., 2011; Dai et al., 2008)). pH-responsive polymers normally respond to weak acid or base triggers, depending on their chemical structures(Cayre et al., 2011; Dai et al., 2008). Their functional moieties are protonated and deprotonated by decreasing/increasing the pH in bulk phase, inducing variation of the charged or uncharged state(Cayre et al., 2011). Such chemical change of polymer structure leads to a final conformation transition accompanying with the variation of their physical properties in the bulk or at an interface(Stuart et al., 2010; Cayre et al., 2011). The most commonly used acidic and basic pH responsive polymers are shown in Figure 2-2.

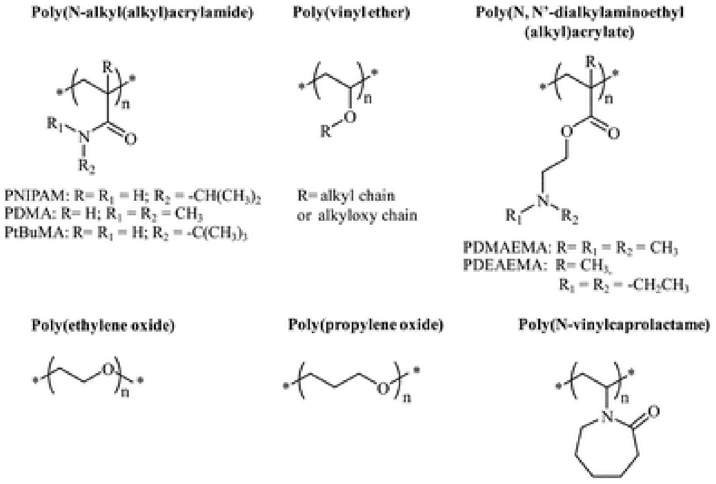

Figure 2-2 Most commonly used acidic and basic pH responsive polymers. (Taken from (Cayre et al., 2011))

Poly(methacrylic acid) (PMAA) and poly(acrylic acid) (PAA) are typical carboxylic acidic responsive polymers, and their carboxylic acid group can be protonated at high pH and deprotonated in acidic conditions(Nuopponen and Tenhu, 2007; Li et al., 2005). PDMAEMA and its derivative poly(N,B-diethylaminoethylmethacryalte) (PDEAEMA) both can respond to temperature and pH, which are popular dual stimuli-responsive polymers as mentioned(Cayre et al., 2011; Hocine and Li, 2013; Dai et al., 2008). The alkylamino is their basic group protonated at acidic condition, while the whole alkylamino alkyl(meth)acrylate group responds to temperature stimuli(Webber et al., 2005). Poly (2-vinylpyridine) (P2-VP) and Poly(4-vinylpyridine)(P4-VP) are another type of ammoniac chemicals, which are commonly involved as basic responsive polymeric systems (Dupin et al., 2008; Delaittre et al., 2009;

Vincent, 1997). The pyridine rings in poly(vinylpyridine) can be protonated in acidic conditions due to the electronegative nitrogen atoms(Tantavichet et al., 2001). In the p2-VP case, which has a pK_a of 4.92, protonated polymer becomes more hydrophilic owing to the loss of counterions (Roiter and Minko, 2005). Along with the protonation of p2-VP, polymer conforms into a coil balanced by coulomb repulsion and van der Waals attraction (Roiter and Minko, 2005). On the other hand, p2-VP coil transits into globule gradually with the increased deprotonation of polymer chain(Roiter and Minko, 2005; Puterman et al., 1979a; Puterman et al., 1979b).

Generally, those polymers are not only used and formed as responsive materials with themselves but also collaborated with same stimuli responsive polymers, unresponsive polymers and responsive polymer that responds to different triggers as multifunctional materials.

PS-b-PAA is one of highly focused pH responsive polymeric system. With the help of carboxylic acid, polymers are uncharged at low pH while becoming losing proton by increased pH(Dai et al., 2008). Polymers don’t dissolve in water when they are uncharged. Increased pH make such polymers more soluble in water until they self-assemble and aggregate into varied morphologies(Dai et al., 2008).

Simultaneously, temperature – sensitive polymer PNIPAM is usually combined with PAA or PMAA to meet the requirement of responding to both pH and temperature, which can be applied for biological, tissue engineering and drug delivery(Dai et al., 2008; Schilli et al., 2004). Polymers micelles can be formed by varying pH and temperature due to the influences of hydrogen-bond interactions between NIPAM and acrylic acid(Dai et al., 2008; Schilli et al., 2004). Such combination of PNIPAM and PAA/MAA were usually used to obtain famous responsive microgel as well, which has a strong temperature influence of particle conformation and interfacial adsorption ability(Li and Ngai, 2013; Dai and Ngai, 2013; Liu et al., 2014; Liu et al., 2013; Tokarev and Minko, 2009; Bayliss et al., 2011).

PDMAEMA-PMMA is a well-studied block polymer which combines thermos-pH dual responsive monomers and unresponsive monomers(Dai et al., 2008; Baines et al., 1996a). Deprotonated PDMAEMA has an increased affinity with water due to the formation of hydrogen bonds at high pH(Dai et al., 2008; Baines et al., 1996a). Such deprotonation of PDMAEMA also induce its micellization at pH 9.5 by adding electrolyte(Dai et al., 2008; Baines et al., 1996a). However, PDMAEMA can dissolve in water at low pH due to the protonation. It has a LCST in the range of 32-52 ^{o}C(Dai et al., 2008; Baines et al., 1996a).

Apart from the well-documented temperature and pH sensitive polymers discussed, there are still some other stimulus which specific polymers can respond to. The ionic strength of aqueous solution can lead to conformation changes of some pH-responsive polymers and other ionic-sensitive only polymers(Di et al., 2007; Cayre et al., 2011). UV light intensity also can be utilised as triggers for certain polymers, which has been discovered applications of release active chemicals(McCormick et al., 2006; Chen et al., 2014; Rijcken et al., 2007; Goodwin et al., 2005; Cayre et al., 2011). Such responsive polymers commonly have azobenzene, pyrene or 2-diazo-1,2-naphthoquinone (DNQ) which can reversibly form micelles by the controlling of UV light (Chen et al., 2014; McCormick et al., 2006; Cayre et al., 2011).In summary, the choice of responsive polymer is limited not only by the environmental triggers, but also the physical and chemical properties of polymer itself, for example: solubility in the solvent. If a responsive system is required by both responding to the pH change and dispersing in oil, 2-Vinylpyridine can meet the criteria.

2.1.2 Responsive polymer-particle systems

Traditionally, polymer chains can self – assemble into “soft” formations (polymer micelles or vesicles), be cross-linked for additional stability or grafted on the surface of other inorganic/polymeric particles to form chemical bonded structures (microgels/core-shell latexes etc.)(Cayre et al., 2011; Stuart et al., 2010). All those polymeric structures have been extensively studied and explored for their potential applications. Herein, the chemical bonded conformation of latex particle/microgel systems will be emphasized with their architecture, chemical/physical properties, bulk and interfacial behaviours.

Mostly, emulsion polymerization(Peng and Imhof, 2015; Chen and Lee, 1991; Bourgeat-Lami et al., 2002; Nagao et al., 2006; Morse et al., 2013; Morse et al., 2012; Mathew et al., 2012), suspension polymerization (Ugelstad et al., 1979; Okubo and Tsujihiro, 1991; Peng and Imhof, 2015) and precipitation polymerization (Barthet et al., 1999; Percy et al., 2000) are adopted to effectively synthesize the functional polymeric particles. The possibility to synthesize responsive polymeric particles, surely, opens a new potential area for the advanced and sophisticated applications, especially, in pharmaceutical, biological and petroleum industries(Cayre et al., 2011). Especially, the improvement of non-polar dispersion polymerization, reported recently, opens and supports a new research area by synthesizing oil-dispersed polymeric colloidal particles(Richez et al., 2013). (detailed review of responsive particle synthesis is introduced in Chapter 4 introduction section)

In past few decades, responsive colloidal systems had been discovered and studied a lot especially based on the involving of responsive polymers.

Responsive latex particles can be approximately divided into two categories based on their structures. The first type is known as 'Core-shell' particles, and normally consists of a sterically stabilised latex core with one or more monomers, with a pH or temperature responsive polymer being part of the steric shell (Amalvy et al., 2003; Dupin et al., 2008; Amalvy et al., 2004). As mentioned above, responsive polymers can respond to environmental changes by presenting a coil-globule transition(Stuart et al., 2010; Hocine and Li, 2013). The extension of polymer chains on surface of particle cores leads an increase of particle hydrodynamic diameter in bulk phase(Amalvy et al., 2003; Dupin et al., 2008; Amalvy et al., 2004). Simultaneously, the interfacial behaviour of responsive core-shell latex is driven by hydrophobic/hydrophilic transition, resulting in interfacial desorption and adsorption(Amalvy et al., 2003; Dupin et al., 2008; Amalvy et al., 2004).

The second type of responsive particles studied in emulsions are 'Microgels', which consist of a cross-linked stereoscopic polymeric network that can swell and shrink depending on solvent conditions (Li and Ngai, 2013). Generally, such conformation has been employed as simple soft particles or grafted with other responsive/unresponsive polymers/monomers becoming core-responsive shell structures (Destribats et al., 2011a). The responsive polymers/co-polymers extend leading to the swell of particles (cores) by responding to environmental triggers. The environmental triggers not only induce the swell or deswell of microgel itself and bulk behaviours, but also drive desorption and adsorption of microgel at interface, especially, as Pickering emulsifiers(Ngai et al., 2005; Ngai et al., 2006; Fujii et al., 2005).

The detailed responsive particle, their interfacial behaviour and properties as Pickering emulsifiers will be reviewed and discussed in next emulsion section. Here, we only give several representative examples of core-responsive particle system illustrating their structures, potential responsiveness in bulk and on potential applications. Fujii, Binks and co-workers reported a pH responsive Poly(4-vinylpyridine)/silica (P4VP/SiO_2) nanocomposite particle which could be swollen from 230 nm to 550 nm by lowering the pH from 8 to 2 (Fujii et al., 2005; Fujii et al., 2006; Binks et al., 2006). Simultaneously, the same pH reduction could induce phase separation of o/w emulsion when these nanocomposite particles were used as Pickering emulsifiers (Binks et al., 2006; Fujii et al., 2005; Fujii et al., 2006) (Figure 2-3).

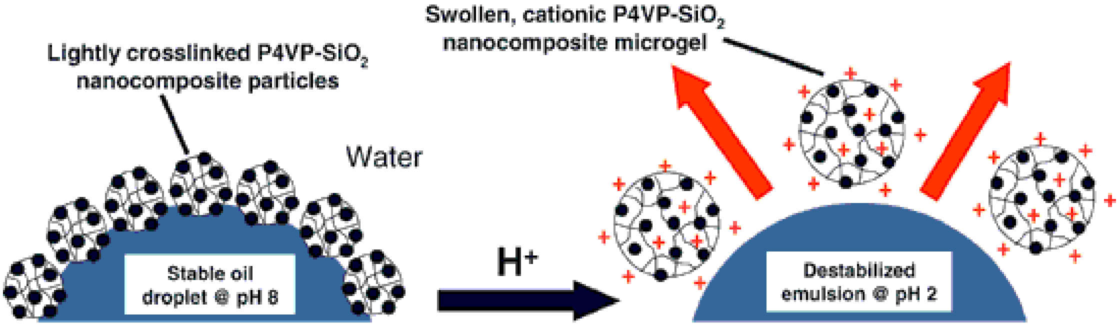

Figure 2-3 Schematic image of pH-induced desorption of P4VP/SiO_2 nanocomposite from pickering emulsion interface (Taken from (Fujii et al., 2006)).

Ngai and co-workers, designed both pH and temperature sensitive poly(N-isopropylacrylamide) –co-(methacrylic acid) (pNIPAM-co-MAA) microgels which swell or deswell depending on either stimulus (Ngai et al., 2005; Ngai et al., 2006) Their octanol in water (o/w) Pickering emulsions were stabilised by pNIPAM-co-MAA microgels at high pH and low temperature. However, either the increasing of temperature over LCST or lowering pH can cause droplet coalescence even demulsification (Figure 2-4) (Ngai et al., 2006; Ngai et al., 2005).. Following from this work, Destribats *et al.* (Destribats et al., 2011a; Destribats et al., 2013; Destribats et al., 2014; Destribats et al., 2012; Destribats et al., 2011b) and Richtering' group (Richtering, 2012; Brugger et al., 2010; Schmidt et al., 2011) carried a series of experiments, separately, on varied PNIPAM donated microgel system to understand their interfacial behaviour and controllability. This part of work will be reviewed in detail in Section 2.2.5.

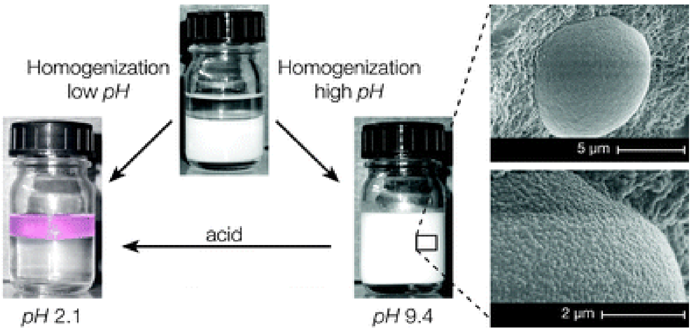

Figure 2-4 Influence of the solution pH on the formation of octanol-in-water emulsions after 48 h at *T* = 25 °C. (Taken from (Ngai et al., 2005))

Two pH-responsive monomethoxy-capped poly(ethylene glycol) methacrylate (PEGMA) stabilised microgels were copolymerized with 2-(diethylamino)ethyl methacrylate (DEA) and 2-(tert-butylamino)ethyl methacrylate (TBAEMA), respectively, by Morse and co-workers(Morse et al., 2013; Morse et al., 2012). Both microgels could achieve reversible stabilisation of o/w emulsion droplets by adjusting pH with acid and base (Morse et al., 2013; Morse et al., 2012) . Additionally, demulsification was also investigated on the PEGMA-PDEA stabilised emulsion by purging CO_2 (Morse et al., 2013)

It is necessary to emphasize that all responsive systems reported employed latexes dispersed in the aqueous phase, except Kasier and co-workers' magnetic responsive hybrid core-shell particles, which were transferred into cyclohexane (Kaiser et al., 2009). However, with emerging interest in oil dispersion systems, especially oil-dispersed Pickering emulsifiers (see section 2.2.5), and the requirement of certain low dielectric constant fields, exploration of oil-dispersed responsive particle system is rather a novel field, but, with a number of important formulation applications(Richez et al., 2014).

Of perhaps singular note in the area of responsive particles manufactured in the oil-phase ,is the work of Fujii et al. (Fujii et al., 2010) who synthesized crosslinked pure poly(2-vinylpyridine) pH responsive particles by dispersion polymerization employing monomethacrylate polydimethylsiloxane (PDMS) as particle stabilisers. Particles were dispersed in n-hexane and isopropanol mixtures initially and then dried into white powder (Fujii et al., 2010). They investigated the stability of so-called 'liquid marbles' at different pH by rolling aqueous drops onto particle powder beds, but did not explicitly investigate their use as Pickering emulsifiers (Figure 2-5).

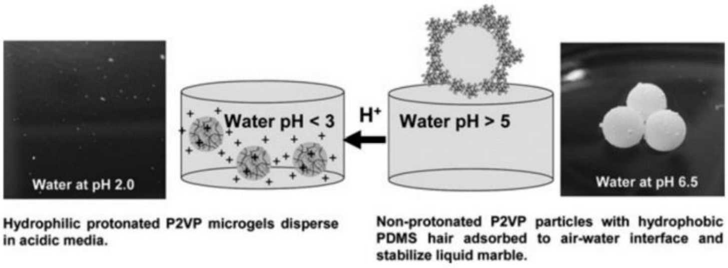

Figure 2-5 A schematic graph shows the pH-responsiveness of PDMS-P2-VP latex particles stabilised liquid marble. (Taken from (Fujii et al., 2010))

2.2 Pickering emulsions

Emulsions are a metastable system of two immiscible liquid phases, where one is dispersed in the other by forming droplets within colloidal size range (Binks and Horozov, 2007; Becher, 1988; Barnes and Gentle, 2011; Shaw, 1992). This kind of colloidal system plays a vital role in daily life and industrial applications. Food, personal products and pharmaceuticals are common emulsion systems(Stig et al., 2003; Becher, 1988; Binks and Horozov, 2007; Barnes and Gentle, 2011; Shaw, 1992). They are also used in a variety of industries, for example paintings, petroleum and agriculture(Binks and Horozov, 2007; Barnes and Gentle, 2011; Shaw, 1992).

In this part of review, the fundamental background of emulsion systems will be introduced initially. Secondly, the related theoretical concepts of emulsion stability, and practical phenomena will be concluded based on Pickering emulsions. Simultaneously, a brief summary and a detailed review will be focused on varied Pickering emulsifiers and responsive particulate stabilisers, respectively. Lastly, research on oil –dispersed particle emulsifiers will be considered.

2.2.1 Emulsion formation

Commonly, emulsions which are formed with two pure immiscible liquids are thermodynamically unstable(Barnes and Gentle, 2011; Binks and Horozov, 2007; Shaw, 1992; Sherman, 1968; Schramm, 2005). To avoid the fast phase separation, commonly surface active molecules are initially employed as ‘emulsifiers’ to maintain system stability(Aveyard et al., 2003; Barnes and Gentle, 2011; Binks and Horozov, 2007; Shaw, 1992; Schramm, 2005; Sherman, 1968). These types of emulsions are generally determined by the curve tendency towards oil or aqueous phase of surfactants, which is decided by a packing parameter, the system HLB (hydrophile-lipophile balance) (Binks, 2002; Aveyard et al., 1986; Shaw, 1992; Schramm, 2005; Sherman, 1968). Such parameters give the preferred residences of emulsion surfactants, indicating stabilised emulsion types (Binks, 2002; Aveyard et al., 1986; Shaw, 1992; Sherman, 1968; Schramm, 2005).

However, solid particles can act similar role as surfactants to efficiently stabilise emulsion droplets(Binks, 2002). This phenomenon has been discovered and recorded by Ramsden (solid stabilised foams) (Ramsden, 1903) and Pickering (Pickering, 1907)a century ago, and such solid colloidal particle stabilised emulsions are now known as ‘Pickering’ emulsions (Pickering, 1907). Solid particles do not stabilise the emulsion droplets in same way as surfactants do (Binks, 2002). They make an interfacial contact angle by adsorbing to water-air/water-oil interfaces(Binks, 2002; Aveyard et al., 2003; Binks and Horozov, 2007) to reduce the three-phase surface energies, but are not explicitly considered surface-active (as generally they do not contain both hydrophilic and lipophilic sections).

Equilibrium contact angles relate the affinity of particles to both phases, and indicate the emulsion/foam type preferentially formed (o/w or w/o; foam/ dry water) (Binks, 2002; Aveyard et al., 2003; Binks and Horozov, 2007; Binks and Murakami, 2006). If the contact angle is below 90^o, the larger part of particle is in the aqueous phase, which means it is a hydrophilic particle resulting in o/w emulsion droplets (or a/w foams) (Binks, 2002; Aveyard et al., 2003; Binks and Horozov, 2007; Binks and Murakami, 2006). Alternatively, hydrophobic particles with a contact angle $> 90^o$ will preferentially form w/o emulsions (or w/a ‘liquid marbles’ or ‘dry water’) (Binks, 2002; Aveyard et al., 2003; Binks and Horozov, 2007; Binks and Murakami, 2006). In comparison to surfactant system (which have rapid and dynamic adsorption and desorption on droplet interfaces) once a colloidal particle adsorbs at interface it can be treated as an irreversibly adsorbed, due to the extremely high detachment energy for particles leaving the interface(Binks, 2002; Aveyard et al., 2003; Binks and Horozov, 2007). This mechanism improves Pickering emulsions' stability in terms of coalescence of droplets, which extends their shelf-life beyond what is possible with surfactants.

2.2.2 Particle adsorption

In the previous section, the main differences between traditional surfactant and Pickering stabilised emulsions were briefly introduced. As mentioned above, Pickering emulsions have a longer shelf-life, due to the irreversibility of adsorbing of particle emulsifiers at interfaces (Binks, 2002; Aveyard et al., 2003; Binks and Horozov, 2007), and is critical to consider why this happens with particle stabilised emulsions. To understand the strong adsorption, it is better to consider how much energy is needed to *remove* a particle from an interface once it is adsorbed. Herein, an Equation 2-1 has been given by Binks and co-workers to explain the relationship between energy of detachment and particle size, contact angle and interfacial tension(Binks, 2002).

$$\mathrm{E} = \pi r^2 \gamma_{\alpha\beta} (1 \pm \cos\theta)^2 \qquad \text{Equation 2-1}$$

Which: $\mathrm{E} =$ Energy of detachment

$r =$ Radius of particles

$\theta =$ Contact angle

$\gamma_{\alpha\beta} =$ Interfacial tension

According to the equation, it is obvious that the adsorption of particles at interfaces is determined by particle size, oil type (oil-water interfacial tension) and particle wettability (contact angle). Among them, the square of particle radius has a liner relation with the required detach energy(Binks, 2002). The larger of particle size, the remarkable higher energy needed to remove it from the interface(Binks, 2002). A 20 nm diameter spherical particle once adsorbed, can be considered as irreversibly attached owing to the request of over 10^5 kT to remove particle, and indeed even a 20 nm particle requiring ~10^4 kT for detachment should not be removed (Binks, 2002). By contrast in surfactant systems, the necessary detachment energy of such molecules can be thought as particle which is smaller than 0.5 nm(Binks, 2002). Only several kT is needed to take particle/surfactant out of the interface leading to a really unstable adsorption comparing to colloidal particle system(Binks, 2002).

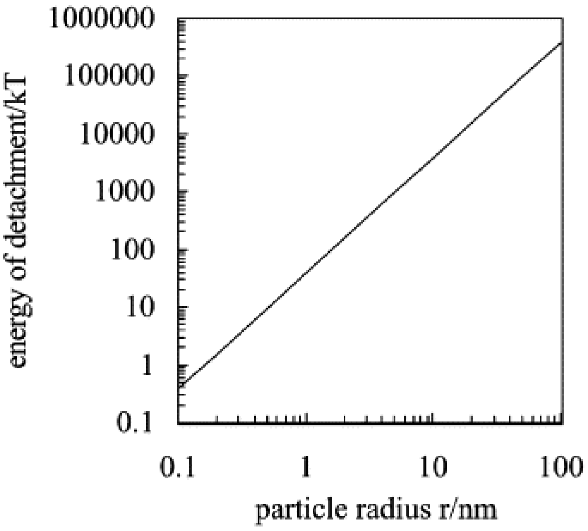

Figure 2-6 The relation between required detaching energy of an ideal spherical particle with a 90° contact angle at planar oil-water interface and such particle radius at 298K. (Taken from (Binks, 2002))

2.2.3 Emulsion types

In Pickering systems, particle interfacial contact angle θ predicts the emulsion types generally. Commonly, emulsions are either w/o ($\theta > 90°$) or o/w ($\theta < 90°$) (Binks, 2002; Aveyard et al., 2003; Binks and Horozov, 2007). However, some novel and complex emulsions can be formed with particles stabilisers as well, for example: multiple emulsions (o/w/o, w/o/w, w/o/w/o, o/w/o/w and so on), and o/o emulsions(Binks, 2002; Aveyard et al., 2003; Binks and Horozov, 2007; Binks and Tyowua, 2016). The formation of such emulsions not only relate to the two phases affinity of colloidal particles, but also have some other influences, like o-w ratios(Binks and Lumsdon, 2000a), particle concentrations(Binks et al., 2005b), oil types(Binks and Rodrigues, 2003), environmental changes of tailored stimuli-responsive particle emulsifier system etc. (Sun et al., 2010; Binks et al., 2005a).

Phase inversion

Emulsion type changes from w/o to o/w or vice versa by adjusting related parameters, is so-called phase inversion(Salager, 2005). The phase inversion of Pickering emulsion systems can be divided into two categories, one is o-w volume affected catastrophic phase inversion, the other one is the transitional phase inversion mainly owing to the variation of particle wettability(Binks, 2002; Aveyard et al., 2003; Binks and Horozov, 2007).

Catastrophic phase inversion

To understand catastrophic phase inversion, Binks and coworkers carried out a series of experiments with both hydrophilic and hydrophobic fumed silica stabilised emulsions, by varying the relative water-to-oil (w-o) volume fraction, particle concentration and preparation routes(Binks and Lumsdon, 2000a). Emulsions stabilized by hydrophobic silica particles could be inverted from w/o to o/w, while hydrophilic particle stabilised o/w emulsions were inverted to w/o type, both by increasing only the dispersed phase volume fraction(Binks and Lumsdon, 2000a). Although their emulsions were stable to coalescence, w/o types also did not sediment, while o/w creamed to the system top(Binks and Lumsdon, 2000a). The most stable w/o and o/w emulsions were investigated around the phase inversion point along with the maximum viscosity(Binks and Lumsdon, 2000a). Accompanying with increased water volume in each system, w/o types became more and more stable whereas the stability of o/w droplets after inversion decreased(Binks and Lumsdon, 2000a). Figure 2-7 shows the mean emulsion droplet size as function of initial system water ratio, where it is apparent there is a sharp difference in mean droplet diameters (larger/smaller) after emulsion type inversion(Binks and Lumsdon, 2000a). It can be confidently claimed that such phase inversion can be achieved only varying o-w volume ratio without altering particle wettability(Binks and Lumsdon, 2000a). The key phenomena to investigate catastrophic phase inversion of Pickering emulsions (droplet size differences, emulsion stability, viscosity) in their work offered a model for future studies.

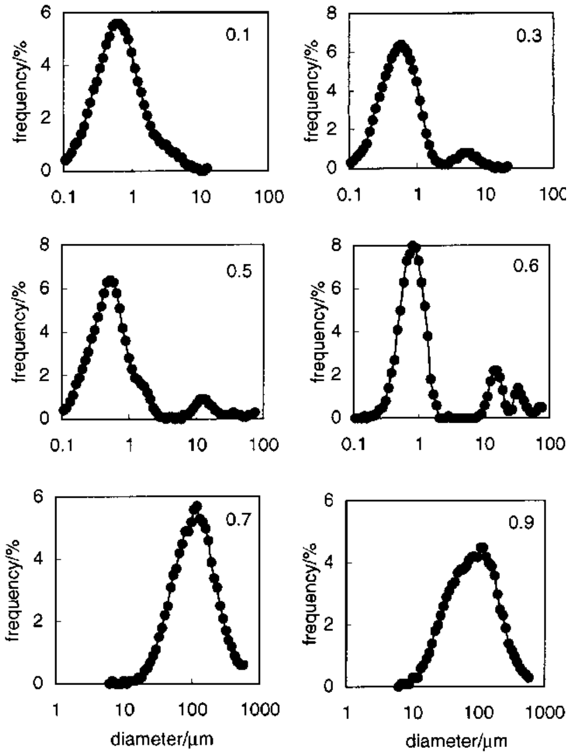

Figure 2-7 Pickering emulsion droplet size distribution with increased water fraction in system. Emulsion type was inversed from w/o to o/w after water ratio increased over 0.65 in the system. (Taken from (Binks and Lumsdon, 2000a))

To expand the understanding of aspects that affect phase inversion on Pickering emulsion systems, Binks' group varied initial particle positions, particle concentrations, preparation routs and even homogenization time, to look for the evidence of phase inversion(Binks and Rodrigues, 2003). Surprisingly, phase inversion is not only limited to the switch of simple emulsions, but also the inversion from w/o or o/w to multiple emulsions(Binks and Rodrigues, 2003). That was the first time that multiple emulsions were stabilised by only one kind of particle emulsifier(Binks and Rodrigues, 2003). Besides that, they also discovered that with same particle, the initial particle position has strong influence on emulsion types and stability(Binks and Rodrigues, 2003).

Transitional phase inversion

Except varying o-w volume ratio, particle wettability of o-w phases can be manipulated in different ways to achieve the inversion of emulsion types(Binks, 2002). Various polarities of oil(Binks et al., 2010), the concentration of SiOH modified silica particles(Binks et al., 2005b) and varied ratio of hydrophobic and hydrophilic particle mixtures (Binks and Lumsdon, 2000b) have been recorded to inverse emulsion types with equal volumes of oil and water. Particle interfacial wetting was the vital influence that affected the stabilised emulsion types. Binks *et al.* reported the transitional emulsion phase inversion as function of particle concentrations(Binks et al., 2005b). They also investigated that the smallest and most stable emulsions could be found around inversion conditions(Binks et al., 2005b). The trigger of such inversion was from the increased hydrophilicity, induced by increased concentration of coated silica, which declined the interfacial contact angle leading to the inversion(Binks et al., 2005b). However, particle interfacial contact angle was only changed by increasing particle concentration in their work, which cannot be controlled quantitatively once an emulsion has formed. To better control particle wetting or interfacial contact angles, tailored particles had been investigated in Pickering emulsion systems(Binks et al., 2005a; Cayre et al., 2011). Such particles may be manipulated through environmental triggers, as described Section 2.1. Emulsion types and stability would be able to be controlled with such smart system. Detailed review will be performed in Section 2.2.5.

2.2.4 Stability of Pickering emulsions

Pickering emulsion stability can be influenced by various parameters, for instance temperature, particle contact angle, o-w volume ratio and so on(Binks, 2002; Binks and Horozov, 2007). A stable emulsion is resistant to physical changes over a practical period of time(Binks and Horozov, 2007). In terms of emulsion instability, four key physical phenomena are generally responsible for final phase separation, as illustrated in Figure 2-8 (Binks and Horozov, 2007).

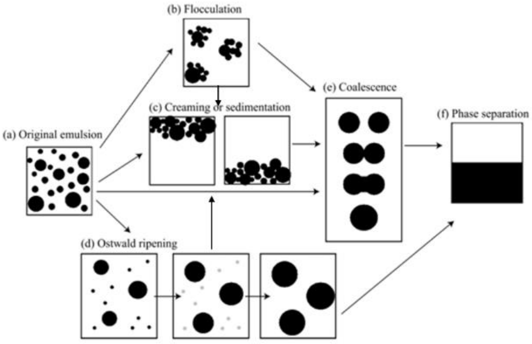

Figure 2-8 Various phenomena that leads to complete phase separation in emulsions(Binks and Horozov, 2007).

Creaming/sedimentation

Due to the density differences of oil-water, less density liquid formed droplets may be subject to creaming while high density phase formed droplets sediment to the bottom of the system(Binks and Horozov, 2007; Shaw, 1992; Barnes and Gentle, 2011). In this process, o-w density differences and gravity force are in charge, as well as the influences of system viscosity(Binks and Horozov, 2007; Shaw, 1992; Barnes and Gentle, 2011).

Ostwald ripening

In emulsion systems, instability arises from larger droplets growth at the expense of the smaller ones, due to the mass transportation of the soluble dispersed phase through the continuous phase(Binks and Horozov, 2007; Shaw, 1992; Barnes and Gentle, 2011), and is known as Ostwald ripening. This phenomenon is not as common as flocculation and coalescence in emulsion systems (except in systems with relatively high inter-phase miscibility), but it is still a vital influence that causes long term emulsion instability and eventually phase separation(Binks and Horozov, 2007; Shaw, 1992; Barnes and Gentle, 2011). This process can be reduced by controlling the droplet size distribution, and using emulsifiers that decrease the oil solubility to water(Binks and Horozov, 2007; Shaw, 1992; Barnes and Gentle, 2011).

Flocculation

Freshly prepared emulsion droplets are normally separated and well-dispersed(Binks and Horozov, 2007; Shaw, 1992; Barnes and Gentle, 2011), due to the high shear in production. However, if collisions of droplets occur over time in lower-shear environments, droplets may to interact together and aggregate into droplet clusters(Binks and Horozov, 2007; Shaw, 1992; Barnes and Gentle, 2011). From appearance, flocculated Pickering emulsions are often observed as a rigid chunk and unflowable due to the particle bridging between emulsion droplets(Binks and Horozov, 2007; Shaw, 1992; Barnes and Gentle, 2011; Ashby et al., 2004b; Ashby et al., 2004a; Stancik et al., 2004; Horozov and Binks, 2006) (Figure 2-9).

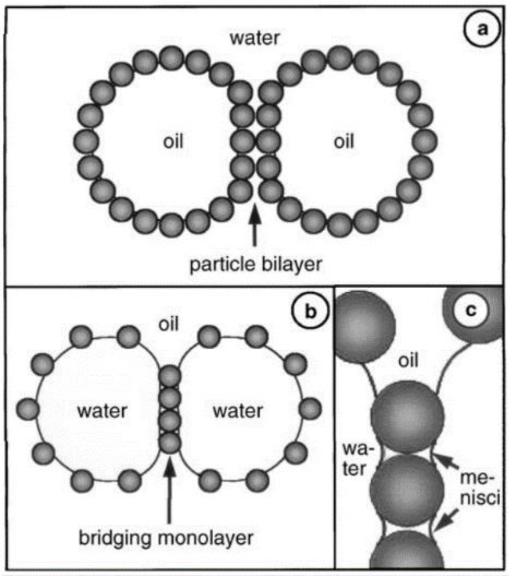

Figure 2-9 Schematic representation of a close look of flocculated droplets: a) particle bilayers exist in two fully covered emulsion droplets, and b) particle bridging exists in two unclosed packed emulsion droplets. In situation (b), the strong capillary attraction forces cause a close contacted bridging particle monolayer (c). (Taken from (Horozov and Binks, 2006))

Coalescence (limited/ arrested)

The collisions of emulsion droplets induce not only the flocculation, but also the merging of droplets into a single large one(Binks and Horozov, 2007). This process is so-called coalescence (Figure 2-8), and is the most dynamically important process for phase separation. Due to the Brownian motion, two droplets may contact with each other in the emulsion, with the interaction leading to a deformed and flattened contact area(Binks and Horozov, 2007; Barnes and Gentle, 2011). Van der Waals forces induces the draining of a thin interstitial film between two contacted interfaces, while on the other hand, thermal fluctuations also cause the film to be unstable. Thus, the film becomes thinner and thinner until it breaks and droplets merge with each other. The force that act on droplets contact area is the so-called disjoining pressure. If the disjoining pressure has negative value, the film is easy to rupture leading to the droplets coalescence, and vice versa(Schramm, 2005; Sherman, 1968; Becher, 1988; Binks and Horozov, 2007).

However, there is another type of droplets coalescence called arrested coalescence, which is more common in Pickering systems than other emulsions(Pawar et al., 2011). It is an intermediate stage that droplets neither occur complete coalescence not remain separately stable(Pawar et al., 2011). This phenomenon is observed if the rheological resistance of a droplet offsets the Laplace pressure driving force for coalescence(Pawar et al., 2012; Pawar et al., 2011). Droplets coalescence occurs initially, they remain stable and an irregular shape against further shape relaxation in half way of their coalescence process(Pawar et al., 2011). Nevertheless, the key parameter that affect this phenomenon in Pickering emulsion system is the droplet surface particle coverage (Pawar et al., 2011). According to Pawar’s works, the total surface coverage that can cause such arrested coalescence of two droplets is in range of 1.43 to 1.81(Pawar et al., 2011).

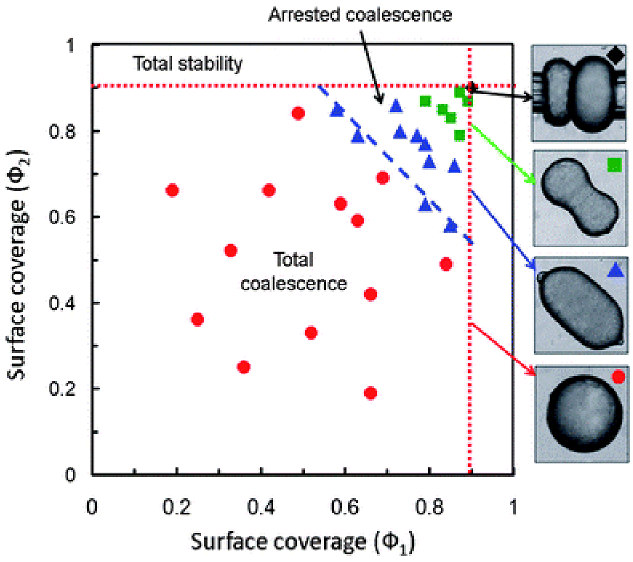

Figure 2-10 Various Pickering emulsion droplets coalescence (coalescence, arrested coalescence and stability of two droplets) with related particle surface coverage. (Taken from (Pawar et al., 2011))

2.2.5 Responsive and non-responsive Pickering Emulsifiers

A wide range of inorganic particles have been employed as Pickering emulsifiers either stabilising o/w or w/o emulsions(Shaw, 1992), for example: fumed silica(Binks and Rodrigues, 2003; Binks et al., 2005b; Binks and Lumsdon, 2000a; Midmore, 1998), carbon black(Schlaepfer, 1918; Moore, 1919; Gelot et al., 1984), clay(Abend et al., 1998; Ashby and Binks, 2000; Bon and Colver, 2007; Lagaly et al., 1999) (iron oxide, hydroxides, metal sulfates). Additionally, organic particles such as polystyrene latex(Binks and Lumsdon, 2001) and polytetrafluoroethylene (PTFE) (Aveyard et al., 2003) have been used as stabilisers for w/o emulsions.

Within those particular systems, the effectiveness of the solid in stabilising emulsions have been well-understood relying on the influences of particle size, shape, concentration and wettability(Aveyard et al., 2003). Two very important particle stabilising mechanisms have been studied in Pickering emulsion's, depending on various systems(Aveyard et al., 2003). The first, and major mechanism, is that the droplet can be stabilised because of single or multilayers of particles, that densely adsorb and pack at the interface(Aveyard et al., 2003). For example, Figure 2-11 shows a polystyrene particle monolayer film covering a water droplet in cyclohexane (Binks and Lumsdon, 2001). Both hexagonally close-packed regions and disordered particle packing regions can be investigated on this droplet (Binks and Lumsdon, 2001). A second mechanism, is based on a three-dimensional network that forms between adsorbed particles on multiple droplets in the continuous phase(Aveyard et al., 2003). Abend *et al*. illustrated the fact that oil drop was captured and immobilised by a clay-contained system in water(Abend et al., 1998).

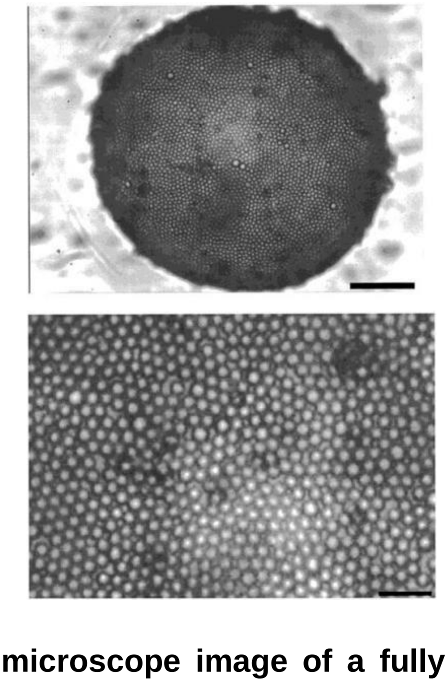

Figure 2-11 Optical microscope image of a fully covered water in oil emulsion droplet (upper). (Scale bar 50 μm) Closer sight of droplet surface showing particle packing at interface (lower) (scale bar 15μm). (Taken from (Binks and Lumsdon, 2001))

While the stabilities of most Pickering emulsions are very high in relation to surfactants, there is no ability to dynamically alter stability (e.g. to create colloidasomes that release actives) or even invert emulsions (either as an adaptive formulation trigger or for oil harvesting applications for example). Hence, the study of stimuli-responsive particles at emulsion oil-water interfaces has received increased attention in recent years. Served as particular emulsifiers, these responsive-particles can be controlled by stimulus to adsorb or desorb at emulsion droplets(Tang et al., 2015). For some specific kinds of responsive particles, such as microgels, their softness and deformability at oil-water interfaces are also a focus of research in understanding how they responding to environmental triggers(Richtering, 2012).

The study of responsive Pickering emulsions have particularly involved the use of particles created from monomers or polymers that respond to pH(Morse et al., 2013; Morse et al., 2012; Read et al., 2004; Dupin et al., 2006; Binks et al., 2007; Fujii et al., 2010; Soppimath et al., 2005; Amalvy et al., 2003), temperature (Ngai et al., 2006; Ngai et al., 2005; Richtering, 2012; Destribats et al., 2011b), magnetic field intensity (Kaiser et al., 2009; Müller-Schulte and Schmitz-Rode, 2006; Veiseh et al., 2003; Yuan et al., 2007; Guo et al., 2008) and light (Chen et al., 2014). Such particles can offer unprecedented various architectures (polymer chain extending/shrinking, swell/deswell and sphere/deformation) and interfacial behaviours (contact angle shifting and adsorption/desorption) (see section Chapter 2). Not only can the responsiveness of such particulate systems be used to control and trigger changes in emulsions, overall the types and stability of the stabilising Pickering emulsions are well in excess of what can be achieved by using small molecule surfactants or conventional solid particles.

Responsive particle systems were categorised into two types due to their architectures. Sterically stabilised core-shell solid particle system can respond to environmental triggers because of their surface grafted responsive polymer chains. In such system, polymer chains extended or shrank by answering pH or ionic strength changes leading to the adsorption or detachment of particle themselves at interface.

Mathew *et al.* (Mathew et al., 2012) synthesized a typical pH responsive polystyrene latex with poly(methylmethacrylate)-b-poly(dimethylaminoethyl methacrylate) [$pMMA_{16}$-co-$pDMAEMA_{254}$] stabilisers, to study its adsorption and desorption mechanism and kinetics at planar air-water interfaces by varying the pH of aqueous phase. Amalvy *et al.* (Amalvy et al., 2003) used poly[2-(dimethylamino)ethyl methacrylate-*block*-methyl methacrylate] [PDMA-PMMA] diblock copolymer sterically stabilized polystyrene (PS) latexes to stabilise o/w emulsion droplets, with proven reversible pH-responsiveness. To understand such pH responsive latex interfacial properties, Read *et al.* varied the polarity of emulsion oil phase, particle concentration, copolymer shell density, and pH in bulk phase to prepare different emulsion and investigate their types, stability and ability to be controlled by pH (Read et al., 2004). They demonstrated that emulsion types can be decided by polarities of oil phase, like lower polarity can form oil-in-water emulsions while water-in-oil droplets were in polar oil cases at higher pH(Read et al., 2004). Intermediate polar/non-polar oil leaded to transitional phase inversion of emulsion droplets from o/w to o/w by decreasing the pH with certain o-w volume ratio(Read et al., 2004). Binks *et al*. reported a temperature affected phase inversion on emulsion employing PS latexes sterically stabilised by PDMA-b-PMMA copolymer as particular emulsifiers(Binks et al., 2005a). The inversion from o/w, w/o/w to w/o, finally, were adjusted by increased temperature when latexes were at pH 8 (Binks et al., 2005a). A PS-co-MAA latex leaded phase inversion was investigated by Sun et al. by presenting three droplet states of gel, w/o and o/w emulsions with increased pH (Sun et al., 2010). Besides pH-responsive latex, Kasier and co-workers synthesized a novel magnetic responsive hybrid core-shell particle which polystyrene chains bonded on the surface of FeO_x dispersing in cyclohexane(Kaiser et al., 2009). Pickering emulsions were stabilised by such particles to exam the influence of magnetic field on emulsion stability (Kaiser et al., 2009). As well as that, magnetic-responsive capsules can be formed with same particles (Kaiser et al., 2009). Yang et al. modified surface of silica particles with hydrophobic $(MeO)_3Si(CH_2)_7CH_3$ and hydrophilic, pH responsive $(MeO)_3Si(CH_2)_3(NHCH_2CH_2)_2NH_2$ brushes (Yang et al., 2013). Pickering emulsion phase inversion stabilised by organosilane-functionalized silica particles had been investigated in their work by varying pH (Yang et al., 2013). Their emulsion system has a good reversibility by responding to pH (Yang et al., 2013).

Further, there is another type responsive particle system that responsive polymeric chains were crosslinked to be able swell/deswell by responding to environmental triggers. These are so-called microgels which were briefly introduced in section 2.1.2. Such soft particular stabilisers behaved very differently from the conventional solid spherical particles at oil-water interface according to some research groups' studies.

Firstly, Ngai *et al*. synthesised both temperature and pH responsive pNIPAM-MAA [Poly(N-isopropylacrylamide-co-methacrylic acid)] microgel to prepare the octanol in water (o/w) emulsions that can respond to pH and temperature changes(Ngai et al., 2005; Ngai et al., 2006). At high pH and low temperature (below VPTT), stable o/w emulsions could be obtained with their microgel systems. Such microgel stabilised emulsions were broken by, simply, decreasing the pH or increasing the temperature to 60 °C, which is over the VPTT of pNIPAM microgels. From their studies, the destabilisation of emulsions induced by pH and temperature change were mainly due to the increased hydrophobicity of microgel at oil-water interface. The wettability or contact angle change resulted in the moving of microgels into oil phase following with the demulsification of emulsions(Ngai and Bon, 2015).

Following from Ngai and co-workers studies, Richering's group carried out a series studies to understand such microgel's behaviour at emulsion interfaces(Brugger and Richtering, 2008; Ngai and Bon, 2015). Initially, Brugger and co-workers synthesized pNIPAM-MAA microgels under both acid and base(Brugger and Richtering, 2008). The unpurified microgel synthesized under basic condition stabilised o/w water emulsions better than purified microgels, due to the contribution of residual oligomers. Also, the incorporated MAA fraction in the microgel was observed to depend on the pH condition during synthesis. They concluded charged microgels can act as efficient stimuli-sensitive emulsifiers in various conditions. In their following works, Brugger and co-workers also demonstrated the stability and pH temperature responsiveness of such microgel stabilised emulsions relied on the polarity of oil phase, even at high pH and room temperature(Brugger et al., 2008). When a polar solvent was used as oil phase, demulsification could be achieved by either stimulus independently. However, emulsions produced with non-polar oils were broken only when both stimuli were switched together. Their also carried on a number of investigations on 2-D interfaces (droplet profiling measurement) and their related rheology properties, which will be introduced in section 2.3.

According to all studies on these types of "soft" microgel particles, it seems their emulsification and interfacial behaviour may appear very different from traditional rigid Pickering emulsifiers and surfactants(Richtering, 2012; Ngai and Bon, 2015). To highlight these differences, Schmidt *et al.* prepared two types of PNIPAM-MAA microgels with different conformations(Schmidt et al., 2011). They named one as MS microgels, which had a PNIPAM core with PNIPAM-co-MAA shell, and the other as MC with a PNIPAM-co-MAA core and a PNIPAM shell. Those two microgels offered varied emulsion properties compared to conventional emulsifiers. The location of charges on the microgels played a relevant important role to maintain the stability of emulsion, however, regardless of electrostatic repulsion. Their cryo-SEM data shown the variety of microgel deformation (soft and porous nature) at the o/w interface due to their varied configurations, which also dominated to emulsification ability and stability (Ngai and Bon, 2015; Schmidt et al., 2011)(Figure 2-12). Emulsions were not stable, when were emulsified with less soft microgels, and stability increased with greater microgel deformability. Based on those data, they implied that the contact angle of rigid Pickering emulsifiers is no longer applicable for soft microgels. The conformation, softness/deformability, the volume changes and osmotic pressure of counterions in microgels were proposed as key mechanisms in microgel stabilised emulsion properties(Ngai and Bon, 2015). Such specific emulsion kind were named as "mickering emulsions" to highlight the similarity and differences to traditional Pickering emulsions(Ngai and Bon, 2015).

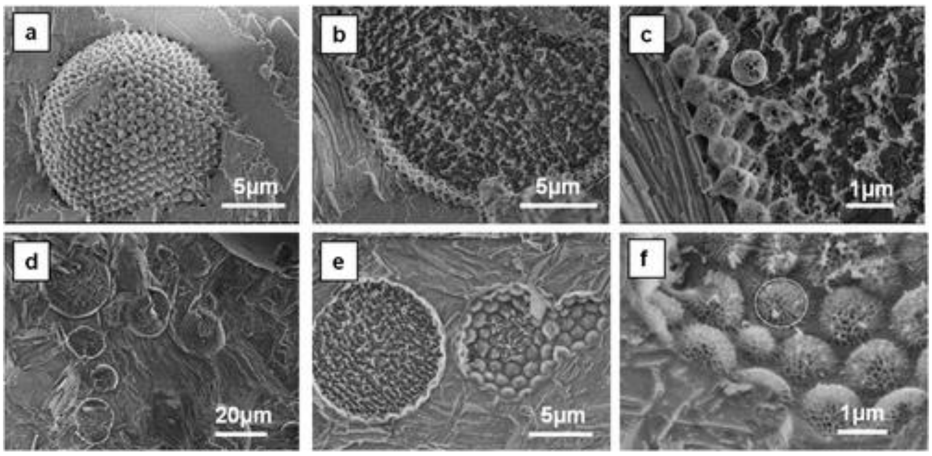

Figure 2-12 Porous and deformed microgel particles at emulsion droplet interface. (Image taken from (Schmidt et al., 2011))

In the later work with Liu, they again demonstrated the independence of emulsion stability and electrostatic interactions, by using two PNIPAM oppositely charged microgels with MAA and AEM respectively, to investigate noncoalescence properties of their emulsions(Liu et al., 2012). Interestingly, when the positively charged emulsion droplets were forced to encounter the negatively charged ones in a microfluide device, they didn't coalesce, in contrast to traditional emulsions whos stability would be greatly affected by the opposite charge(Liu et al., 2012; Ngai and Bon, 2015). However, such emulsion droplets could still be broken up by varying the pH.

With the increased attention on PNIPAM microgels, Schmitt's group synthesized pure PNIPAM microgels, to investigate its emulsion properties and interfacial behaviour(Destribats et al., 2013; Destribats et al., 2012; Destribats et al., 2011b; Destribats et al., 2014; Destribats et al., 2011a). Deformed "fried egg-like" structures were observed by cryo-SEM and convinced by comparing the diameter with microgel hydrodynamic diameter at 25° at heptane-in-water (o/w) emulsion interface by Destribats and co-workers(Destribats et al., 2011a). In their opinion, the crosslinking density has a negative influence on microgel deformability. Their microgel’s deformability could also be controlled by temperature, and such deformability also played a vital role in emulsion stability. Again, in accordance with Richtering group’s opinions (Schmidt et al., 2011), Destribats and co-workers suggested that the contact angle of Pickering emulsifiers adsorbing at an oil-water interface, is no longer applicable to a microgel system.

In following works, Destribats *et al.* varied several parameters of microgel stabilised emulsion systems, to understand such temperature responsiveness of soft microgels, (Destribats et al., 2012) and continued their investigation of PNPAM with varied cross-link densities. Microgels of a similar size, but increased crosslink density, stabilised more flocculated emulsion droplets than lower crosslinked microgels. It was hypothesised that such flocculation was due to inter microgel bridging. They observed that large flat films separated droplets, and employed microscopy methods to measure the adhesion angle at the junction. According to the cryo-SEM investigation, the adhesion angle, film structure and emulsion properties are highly relying on the particle softness. Finally, a special route to control the emulsion flocculation and microgel temperature sensitiveness was proposed (Figure 2-13).

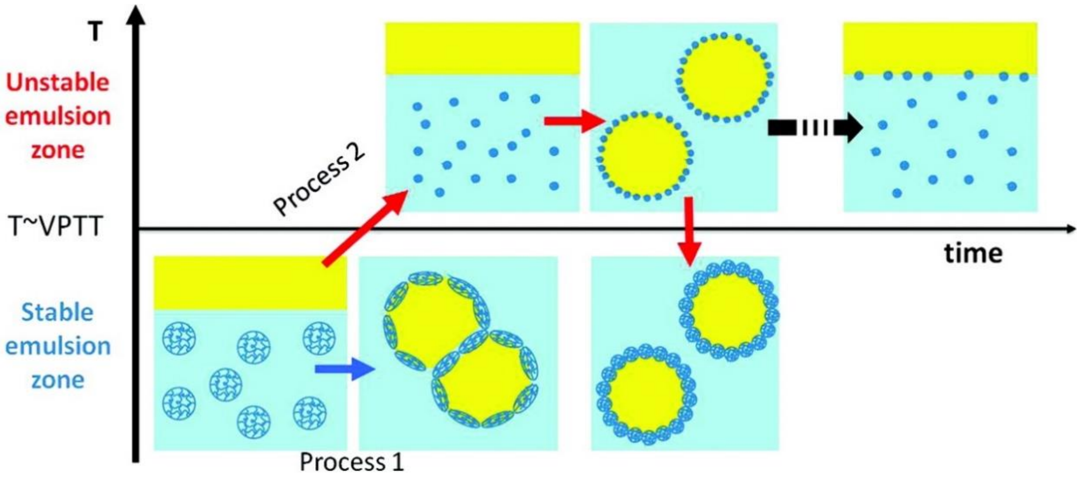

Figure 2-13 A schematic image shows a special pathway (red arrows) which can prepare unflocculated and stable emulsions. Emulsion are prepared with collapsed microgles above their volume phase transitional temperature (VPTT). After lowering temperature below VPTT, emulsion interfacial adsorbed microgels swell resulting in a more covered surface of droplets, which protects the emulsion droplets avoiding droplets bridging and coalescence (Taken from (Destribats et al., 2012)).

In the majority of studies discussed, aqueous based microgels have been used to stabilise o/w emulsions. However, w/o type can also be stabilised by PNIPAM microgels in the presence of fatty alcohols. The stabilisation principle in w/o emulsions was found with multi layers of nondeformed microgels from aqueous phase, which is opposite with the empirical Finkle rule. Finkle demonstrates that the dispersed of emulsifiers is commonly the preferred continuous phase of the emulsion they stabilised(Finkle et al., 1923). Under this state, the microgel lost its thermal responsiveness. As well as microgel crosslink density and oil polarity, the microgel size and emulsification shear rate were also studied of microgel stabilised (Destribats et al., 2014; Destribats et al., 2013). Based on Destribats's work, larger microgels led to higher deformability, but poorer stability of emulsion (higher flocculation) and vice versa. So does the shear rate, lower shear rate during emulsification process produced more dispersible emulsion droplets but less deformed microgel at interface. A series emulsion study with pure pNIPAM microgel as stabilisers by Destribats and co-workers gave a step forward understanding of such un-Pickering like emulsifiers' behaviour. However, due to the complex structure and interfacial interaction, pNIPAM microgel system haven't been comprehended properly. The further adsorption kinetics of such thermal responsive system at oil-water interface will be introduced in section 2.3.3.2

It is clear from the papers discussed, that microgel emulsifiers have attracted significant attention in recent years, and perhaps are the most common examples of soft responsive stabiliser systems. However, as mentioned in section 2.1.2, there are only rare examples of responsive 'soft' particulate systems which are based on oil as the disperse phase, and even less instances of oil dispersed *responsive* Pickering emulsifiers, and even among all general Pickering emulsifier systems, the majority of colloidal particles are dispersed in the water phase. Nevertheless, there are a handful of literature studies which have reported oil dispersed Pickering emulsifiers. Park et al. had published their work to synthesize MgO nanoparticles by precipitation polymerization in alkaline(Park et al., 2006). They are oil-dispersed particles. Unfortunately, they didn't carry out the further study on it like: use as Pickering emulsifiers. Binks and co-workers reported a series of emulsion study with both water dispersed and oil dispersed fumed silica particles(Binks and Lumsdon, 2000b; Binks and Lumsdon, 2001; Binks and Lumsdon, 2000a; Binks et al., 2005b; Binks and Tyowua, 2016; Binks and Rodrigues, 2003). They were all able to stabilise emulsion droplets, and even cause phase inversion of emulsion droplets by changing particle concentration(Binks et al., 2005b), oil-water volume ratio(Binks and Lumsdon, 2000a) and hydrophobicity of silica particles(Binks and Lumsdon, 2000b). In fact, o/o emulsions could actually be prepared with various oil types and oil-dispersible Pickering emulsifiers (Binks and Tyowua, 2016). All involved fumed silica particles, however, were dry powder when received, and then well dispersed into oil by high-intensity ultrasonic vibracell processor before emulsion preparation, and were not responsive to any particular environmental trigger.

As introduced in section 2.1.2, Fujii *et al.* synthesized crosslinked pure poly(2-vinylpyridine) pH responsive particles by dispersion polymerization employing monomethacrylate polydimethylsiloxane (PDMS) as particle stabilisers(Fujii et al., 2010). Particles were dispersed in n-hexane and isopropanol mixture initially and then dried into white powder. They investigated stability of so-called ‘liquid marble’ at different pH by rolling aqueous drop on particle powder bed. In their work, liquid marbles could be stabilised by uncharged PDMS-p2-VP powder at pH 6.5 while, below pH 3.8, drop covered with charged particles could only hold for few second. Similarly, their particles were specifically investigated as Pickering emulsifiers.

To conclude, majority of responsive particles/microgels are aqueous based. They attracted lots of attentions in the areas of cosmetics(Gichinga et al., 2010), pharmaceuticals(Supasuteekul et al., 2012; Gichinga et al., 2010; Fernandez-Nieves et al., 2011), catalysts(Mei et al., 2007), photochemistry(Sasa and Yamaoka, 1994) and in optical switches or sensors(Scheffold et al., 2010). However, with the increased requirement of applications from oil based industries, for example: oil recovery (Fernandez-Nieves et al., 2011) and low dielectric constant environment, oil-dispersed particles are becoming more and more attractive. Especially, the oil-dispersed responsive Pickering emulsifiers are very interesting and challenging by both meet the criteria of oil-dispersible and responsive, to study particle fundamental interfacial behaviours and understand potential applications.

2.3 Particles at curved oil-water interfaces

Emulsion is the bulk which are often complicated system to study mechanistically, due to the complex association between droplets, where various parameters can affect different emulsion properties in the system. However, generally a stable emulsion droplet is a sphere to keep their interfacial energy at very low level(Hunter and Chan, 1989). Therefore, to understand particle adsorption at droplet oil-water interface, the properties of spherical-like curved oil-water interface play a vital role in determining relevant emulsion stability and particle interactions at the interface(Barnes and Gentle, 2011), and thus single interface studies can provide an important bridge to quantifying bulk behaviour.

2.3.1 Interfacial tension

At a curved interface, interfacial tension/surface tension is often the most important parameter which is needed to be taken into consideration(Barnes and Gentle, 2011) (noting, there is no fundamental distinction between interfacial tension and surface tension(Shaw, 1992)). Here, interfacial tension will be mostly discussed, as related studies are focused on the oil-water interface. In daily life, interfacial tension exists everywhere. There are several examples to explain this term, for example: when we use a paint brush, if water is existing among the fibres of paint brush, the fibres will tend to get together(Barnes and Gentle, 2011). But if the brush has been pushed into bulk water, the fibres will try to move away from each other; And if we tried to build up a sandcastle on the beach, wet sands can be built to a castle or a figure due to droplet capillary attraction(Barnes and Gentle, 2011). In either case, the phenomenon of importance is that they are held together under tension.

Interfacial tension is also an important parameter to the stability of an interface. This is because that while an interface will attempt to form a spherical shape to reduce the system free energy and maintain stability, the interfacial tension can support the tendency of droplets to make the interface curved(Barnes and Gentle, 2011). This phenomenon can be explained by understanding molecule constraints (Figure 2-14). The forces in all directions act on each molecule within liquid bulk phase, which come from liquid phase itself. The molecule within the bulk phase, has no net force to make it move around, as these forces acting on the molecule are isotropic(Barnes and Gentle, 2011). However, interfacial molecules have unbalanced forces that make them be pulled into bulk phase, as essentially the surface area tries to minimize(Barnes and Gentle, 2011).

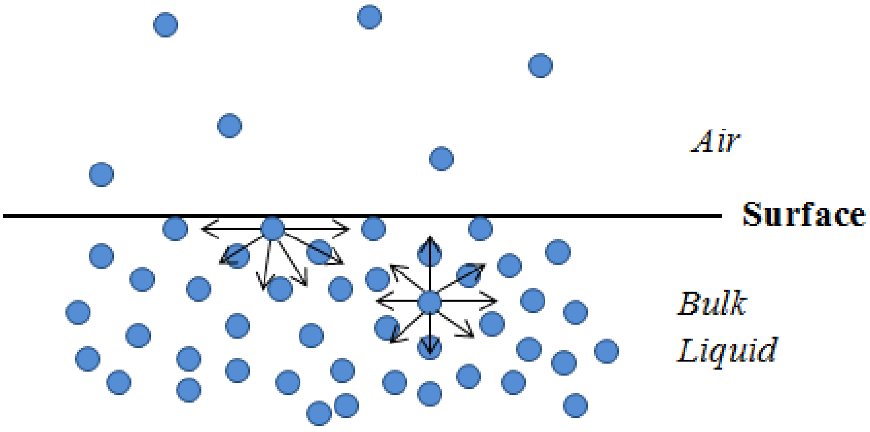

Figure 2-14: Forces acting on molecules near a surface (taken from (Barnes and Gentle, 2011)).

In the other way, the interfacial tension can also be explained as the energy differences between the molecules at the interface and bulk phases(Adamson and Gast, 1997). Interfacial tension can be thought as a force per unit length, while the free energy is defined on per unit area(Adamson and Gast, 1997), as given in Equation 2-2.

$$\mathrm{W} = \mathrm{\gamma dA} = \mathrm{\gamma ldx} \qquad \text{Equation 2-2 (Taken from (Adamson and Gast, 1997))}$$

Where W is the work required for an area change, and $dA = ldx$ is the change in area or width for a given length. From this equation, the interfacial tension γ has a unit of joules per square meter (J/m^2) or Newton per meter (N/m) (Adamson and Gast, 1997), where the later definition is the commonly used one. Interfacial tension is a uniform intensive parameter, which doesn’t depend on the extension of the interface.

2.3.2 Measurement of Surface tension

2.3.2.1 The method of Whilhemy plate

To understand the interfacial behaviour and related stability properties, interfacial tension must be quantified. The Wilhelmy plate method is a clear, convenient way to get the value of, normally, a planar interfacial tension (Barnes and Gentle, 2011). In 1863, Wilhelmy invented the method, which used a plate to dip into the water bulk phase, where the pulling force of the plate can be measured, and converted to surface tension (Figure 2-15). The perfect plate position is extremely vertical to the horizontal bulk phase. As it in this position, the contact area between plate and gas-liquid surface can be calculated as $2(x+y)$. Thus, the surface force, which is pulling down the plate can be summarized, as shown in equation 1; where *F* represents the pull force, *γ* the surface tension, *x* the plate thickness and *y* the bottom length of the plate (Figure 2-15).

$F = \gamma 2(x+y)$ E Equation 2-3 (taken from (Barnes and Gentle, 2011))

In this equation, $F, x,$ and y can be known by measurement, so it is obviously to obtain the interfacial tension(Barnes and Gentle, 2011). To improve, in 1970, Lane and Jordan suggested that the buoyancy force of the liquid surface and how deep the plate has been dipped into the liquid bulk phase should be taken into consideration as well (Barnes and Gentle, 2011). In past decades, Wilhelmy plates were made of various kinds of materials such as: mica, platinum and etched glass(Barnes and Gentle, 2011). The most important thing for making a Wilhelmy plate is to ensure its surfaces are extremely clean and form zero contact angle with the interface. Therefore, paper plates, or filter and chromatography paper were explored to make

Wilhelmy plate from 1977 by Gaines (George, 1977), and are now often used in standard practice.

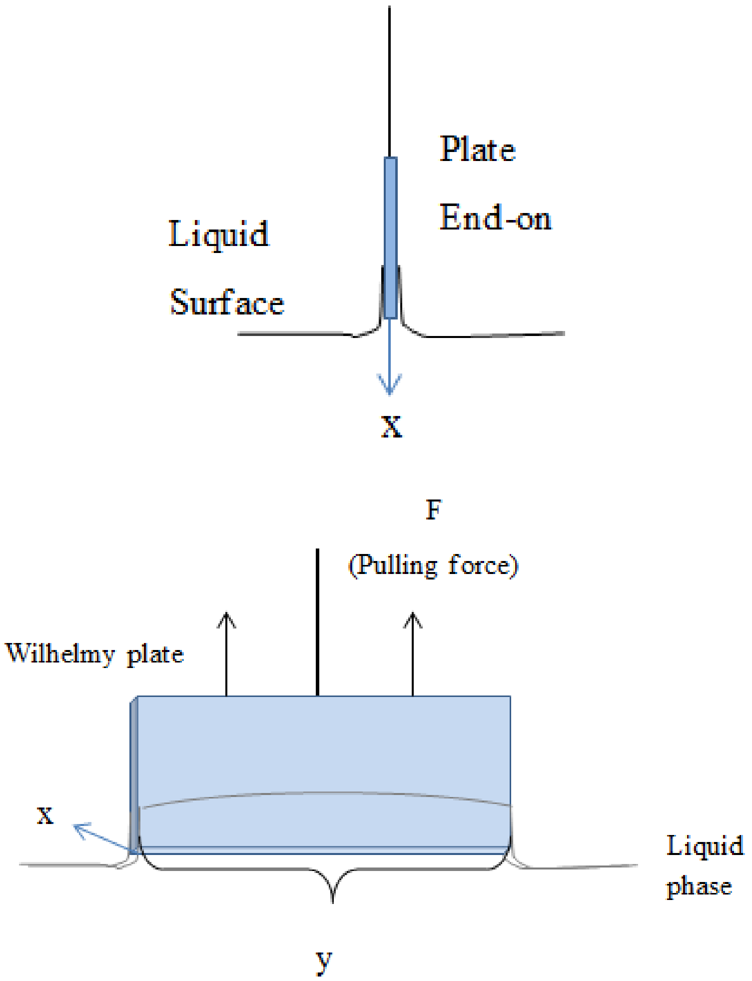

Figure 2-15: Measurement of interfacial tension

2.3.2.2 Pendant drop tensiometer

The method of Wilhelmy plate is used to measure the interfacial tension at planar interface, generally. However, the pendant drop tensiometer is another way to obtain interfacial tension based on a curved interface. The single droplet model can also be a specific way to understand bulk Pickering emulsion properties further by analysing interfacial particle behaviour.

Prior to the considering the principle of a pendant drop tensiometer, some fundamental knowledge need to be understood. At a curved interface, there always exist a pressure difference ΔP, which is known as capillary pressure P_c and Laplace pressure(Adamson and Gast, 1997). The curvature and interfacial tension can determine the ΔP at a curved interface, as shown in Equation 2-4.

$$\boldsymbol{\Delta P = \gamma[\frac{1}{r_1} + \frac{1}{r_2}]}$$ Equation 2-4 (Taken from (Adamson and Gast, 1997))

Where γ is the interfacial tension of such interface, and r_1 , r_2 are the principal radii of curvature which one is perpendicular to another(Adamson and Gast, 1997). In the case of a spherical interface, $r_1 = r_2 = r$, the sphere radius; if it is a plane interface, r_1 and r_2 are close to infinite, ΔP is equivalent to zero (Adamson and Gast, 1997). Given that, the differences between curved and planar interfaces, due to the interface curvature can be demonstrated here(Adamson and Gast, 1997). Equation 2-4, is known as the Young-Laplace equation. The pendant drop tensiometer is based on the analysis of pendant drop shape, and the Young-Laplace equation to determine various interfacial properties, most importantly the interfacial tension(Hoorfar and Neumann, 2006).

Generally, the measurement principle utilises a liquid droplet hanging from a straight syringe needle or holding on a hooked needle (depending on relative fluid densities). If the droplet is at hydro-mechanical equilibrium, the difference in liquid-liquid density can be balanced by the interfacial tension (Adamson and Gast, 1997; Hoorfar and Neumann, 2006). Due to the relationship between the interface curvature, capillary pressure and interfacial tension, as shown in the Young-Laplace equation (Equation 2-4) the measured interfacial tension between two designed liquids can be calculated by analysing the pendant drop shape directly(Adamson and Gast, 1997; Hoorfar and Neumann, 2006). The detailed principle and methodology of the specific pendant drop tensiometer that was used in this work will be introduced in Chapter 3.

2.3.3 Dynamic interfacial tension

Originally, the interfacial tension of a pure oil-water interface should be the same at any time point. With the addition of interfacial active substance like surfactants or polymers, the equilibrated interfacial tension will be changed, where , these changes to the interfacial tension γ_{eq} can be measured instantaneously(Chang and Franses, 2007; Li et al., 2007; Nagarajan and Wasan, 1993; Otis et al., 1994; Dukhin et al., 1995; Eastoe and Dalton, 2003). Once the oil-water interface is created in the presence of interfacial active agent, the transient interfacial tension γ is very close to the tension of pure oil-water system γ_0. After this momentary point, the interfacial actives start to diffuse from bulk phase to interface, then adsorb inducing a decrease in γ. The rate that drives interfacial actives from the bulk to adsorb at interface, is bulk diffusion(Chang and Franses, 2007; Eastoe and Dalton, 2003; Li et al., 2007; Nagarajan and Wasan, 1993; Otis et al., 1994; Dukhin et al., 1995). After the interfacial active substances rearrange with each other at an interface, γ reaches the equilibrium interfacial tension γ_{eq} (Chang and Franses, 2007; Eastoe and Dalton, 2003; Li et al., 2007; Nagarajan and Wasan, 1993; Otis et al., 1994; Dukhin et al., 1995). This process can take from milliseconds to days, depending on the concentration and types of actives(Chang and Franses, 2007; Eastoe and Dalton, 2003; Li et al., 2007; Nagarajan and Wasan, 1993; Otis et al., 1994; Dukhin et al., 1995). The interfacial tension measured as function of time, is known as the dynamic interfacial tension. The dynamic interfacial tension of interfacial active contained system can be used to understand the interfacial adsorption processes (Adamson and Gast, 1997). The fundamental Gibbs adsorption equation is applied to explain the relationship between the amount of adsorbed substances Γ and the oil-water interfacial tension(Adamson and Gast, 1997).

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{dlnC}$$ Equation 2-5 (Taken from (Adamson and Gast, 1997))

Where C is the concentration of actives, R and T represent the gas constant and absolute temperature, respectively(Adamson and Gast, 1997). After the initial adsorption of interfacial active substances, they accumulate on the interface. The accumulation and adsorption results in an interfacial pressure/surface pressure Π. The relationship is demonstrated as shown in Equation 2-6.

$$\Pi = \Delta\gamma = \gamma_{solvent} - \gamma_{after} = \gamma_0 - \gamma_t$$ Equation 2-6 (Taken from (Dukhin et al., 1995))

The Henry isotherm relates the surface pressure to the occupied area of an active at interface, as given in Equation 2-7, Where, R and T represent the gas constant and absolute temperature, respectively.

$\Pi = \Gamma RT$ Equation 2-7 (Taken from (Dukhin et al., 1995))

In section 2.2, the main properties of Pickering emulsions were introduced in detail. Especially, the use of responsive particles and microgels, which are the key parameters in charge of Pickering emulsion or so-called “mickering” emulsion stabilities. Understanding the adsorption kinetics of responsive rigid particles and soft microgels is vital to comprehend their oil-water interfacial behaviours(Ngai and Bon, 2015). The dynamic interfacial tension is an important property to investigate the link between the responsive emulsion properties, and the corresponding interaction of particles to stimulus at the interface (Ngai and Bon, 2015).

2.3.3.1 Adsorption mechanisms

To understand the preparation and physical properties of emulsions, the adsorption kinetics of the interfacial actives at oil-water interface are important(Ngai and Bon, 2015), where quantitative models can explain adsorption kinetics (Dukhin et al., 1995). Here, small molecular surfactants are selected as an example to illustrate two adsorption kinetic models(Dukhin et al., 1995). These two adsorption models, which are the diffusion and the kinetic controlled models, are used to interpret such surfactants’ interfacial adsorption behaviour(Dukhin et al., 1995). Figure 2-16 demonstrates the schematic processes of the adsorption of surfactants from bulk to the interface(Dukhin et al., 1995). Step 1 shows that diffusion is the determining process that transports surfactants from the bulk to an interface(Dukhin et al., 1995). Step 2 is the kinetic process, where surfactants are transferred from a dissolving state to their adsorbed state(Dukhin et al., 1995).

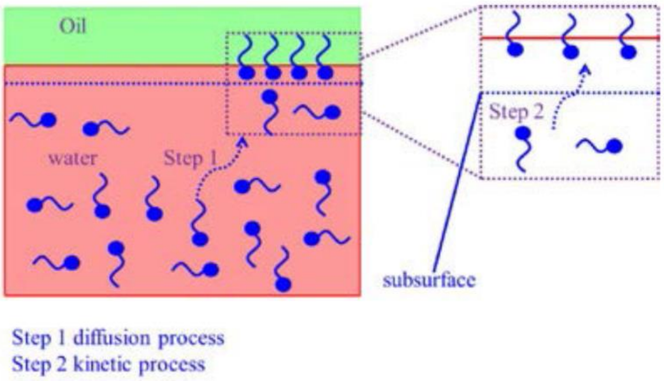

Figure 2-16 Schematic image of two adsorption processes using surfactants as an example (Taken from (Dukhin et al., 1995))

Ward and Tordai (Ward and Tordai, 1946) assume that the dynamic interfacial tension is dependent on the interfacial adsorbing concentration of actives ' Γ ', due to the transportation of surfactants from bulk to interface(Ward and Tordai, 1946). If there is no external influence, the transportation only relies on the diffusion process(Ward and Tordai, 1946). They concluded the diffusion controlled model based on the conditions above as given in Equation 2-8.

$$\Gamma = 2\sqrt{\frac{D}{\pi}}\left(C_0\sqrt{t} - \int_0^{\sqrt{t}} c(0, t-\tau)d\sqrt{\tau}\right)$$ Equation 2-8 (Taken from (Ward and Tordai, 1946))

Where D is the diffusion coefficient, C_0 is the surfactant concentration in bulk, and τ is a dummy variable.

The kinetic controlled adsorption can be shown as:

$$\frac{d\Gamma}{dt} = k_{ad}\ C_0\left(1 - \frac{\Gamma}{\Gamma_\infty}\right) - k_{des}\frac{\Gamma}{\Gamma_\infty}$$ Equation 2-9 (Taken from (Dukhin et al., 1995))

If $\frac{\Gamma_0}{\Gamma_\infty} \ll 1$ presents a small interfacial coverage, the Henry mechanism can be illustrated as:

$\frac{d\Gamma}{dt} = k_{ad}\ C_0 - k_{des}$ Equation 2-10 (Taken from (Dukhin et al., 1995))

Γ

$\boldsymbol{k_{ad}}$ and $\boldsymbol{k_{des}}$ represent the adsorbing and desorbing rate constant (Dukhin et al., 1995). If $\frac{\boldsymbol{d\Gamma}}{\boldsymbol{dt}} = \mathbf{0}$, it reaches the equilibrium state of adsorption (Dukhin et al., 1995). The two models described above are based on extreme conditions. The adsorption of surfactant at oil-water interface is relied on the combination of diffusion and kinetic controlled models.

2.3.3.2 The review of adsorption kinetics of microgels

In Section 2.1.2 and 2.2.5, the literature reviews were focused on the responsiveness of particle/microgel bulk/interfacial behaviour, and the properties of responsive emulsions stabilised by such systems. As mentioned above, the adsorption kinetics of such systems at oil-water interfaces can give a good indication of how they form and stabilise emulsions. For responsive systems, there are many factors could affect their interfacial adsorption kinetics, for instance: their related stimulus, concentrations and deformability.

Brugger, Richtering and co-workers(Brugger et al., 2009) have continually studied the dynamic interfacial tension of pNIPAM-MAA microgel particle systems at the heptane and water interface (Brugger et al., 2009), in addition to their demonstrated work investigating the properties of microgel stabilised emulsions (see section 2.2.5). In their work, microgel stabilised emulsions were less stable at pH 3 than pH 9 case. However, the equilibrium interfacial tension of same system at pH 3 was lower than pH 9 (Figure 2-17). Therefore, this result implied the reason for the lower stability of emulsions at pH 3 is *not* because of the desorption of microgel at the heptane-water interface, as the particles still strongly reduced the IFT in these conditions (Brugger et al., 2009; Ngai and Bon, 2015). With additional evidence from cryogenic scanning electron microscopy (cryo-SEM) results, they concluded that the dominant property which determines pH-dependent emulsion stability, is the interfacial viscoelastic properties rather than the wetting of the microgels. From there, they suggested that the stability of emulsion droplets is not because of the particle-particle electrostatic repulsion, which they concluded in their later work of microgel interfacial behaviour studies (Schmidt et al., 2011; Liu et al., 2012). However, the influence of interfacial tension as function of time and microgel adsorption kinetics hadn't been studied in detail within this other work.

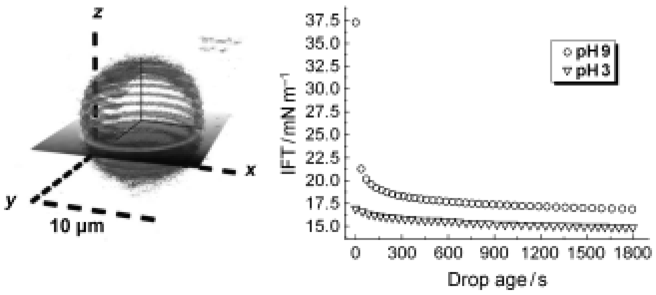

Figure 2-17 Dynamic interfacial tension of a pNIPAM-MAA contained water-heptane interface at pH 3 and pH 7 (Taken from (Brugger et al., 2009))

Li *et al*. studied the dynamic interfacial tension of 3.2% cross-linked PNIPAM microgels in a heptane-water system, at various concentrations both above and below the VPTT(Ngai and Bon, 2015; Li et al., 2013). The dynamic interfacial tension at both temperatures of such microgel systems reduced as function of time, indicating self-adsorption behaviour, which is similar to behaviour investigated in protein systems (Ngai and Bon, 2015; Li et al., 2013; Dickinson, 2003; Dickinson, 2001; Dickinson, 1998a; Dickinson, 1998b; Dickinson, 1999) (Figure 2-18). After the comparison of the normalized diffusion coefficients of such microgels at various concentrations and different temperatures, the diffusing process is necessary for microgel transport from bulk to heptane-water interface, which is similar to other interfacial active substances, like surfactants (Miller et al., 1994), polymers (Miller et al., 1994), proteins and colloidal stabilisers(Ngai and Bon, 2015; Li et al., 2013; Dickinson, 2003; Dickinson, 2001; Dickinson, 1998a; Dickinson, 1998b; Dickinson, 1999). This initial step is controlled by microgel concentrations(Li et al., 2013; Ngai and Bon, 2015). Secondly, they suggested that the conformation of microgel play a vital role in kinetic changes to the surface tension when at the interface. The increased temperature induced swell to deswell transitions in the microgels, which increased diffusion in the bulk, but decreased diffusion at the interface. When the microgels swelled in the bulk, the large amounts of dangling PNIPAM chains accelerated the diffusing process at the interface, but their correlated increase in size reduced their bulk diffusion(Cohin et al., 2013; Li et al., 2013; Stieger et al., 2004). When the microgel collapsed at higher temperature, they could diffuse more rapidly in the bulk(Cohin et al., 2013; Li et al., 2013; Stieger et al., 2004).

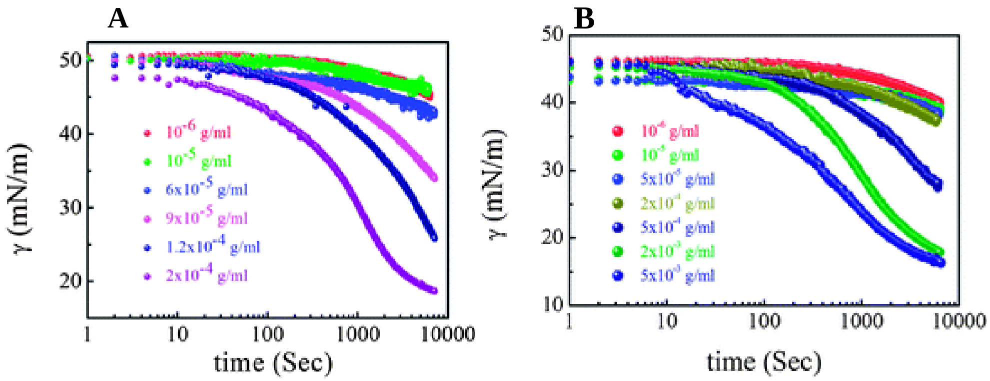

Figure 2-18 The dynamic interfacial tension of heptane-water interface with varied 3.2% cross-linker PNIPAM microgel concentrations at 298K (A) and 317K (B)

Li and co-workers also investigated the effect of stimuli on microgel interfacial adsorption behaviour(Li et al., 2014). They studied the dynamic interfacial tension as function of time with systematically increased temperature (below, around and above the VPTT) (Li et al., 2014) (Figure 2-19). According to their dynamic interfacial tension results, the minimum interfacial tension could be found around the VPTT, and independent of microgel aggregation (Figure 2-20). They suggested that microgel spreading at interface was due to the deformability of the PNIPAM, initially. However, the packing and particle-particle interactions of the microgel at the interface determined the equilibrium stage.

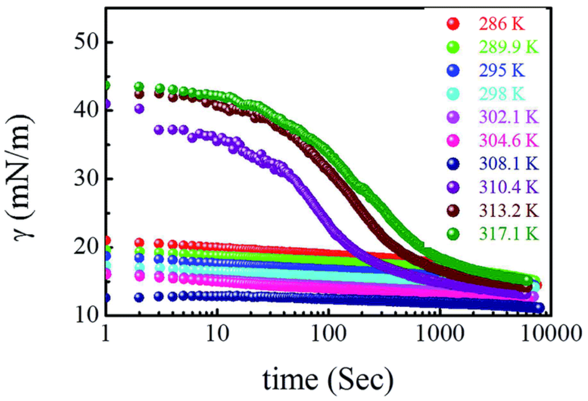

Figure 2-19 Temperature dependent dynamic interfacial tension of PNIPAM microgel contained heptane-water interface. (Taken from (Li et al., 2014))

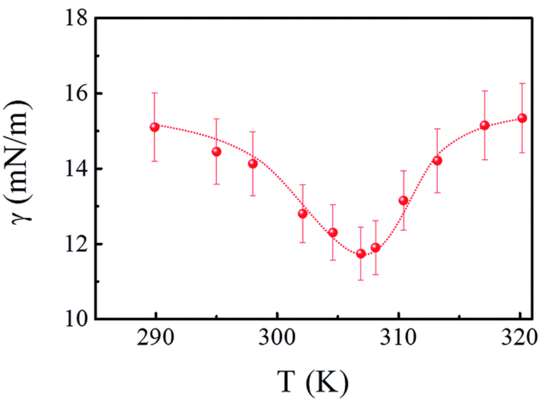

Figure 2-20 The meso-equilibrium interfacial tension of PNIPAM microgel contained heptane-water interface as function of temperate (Taken from (Li et al., 2014)).

Finally, they drew out three distinctive states illustrating microgel interfacial behaviour at temperatures below, around and above VPTT, from both interfacial tension and dilatational rheology studies (Li et al., 2014) (Figure 2-21). They also claimed that transition among those states is irreversible(Li et al., 2014).

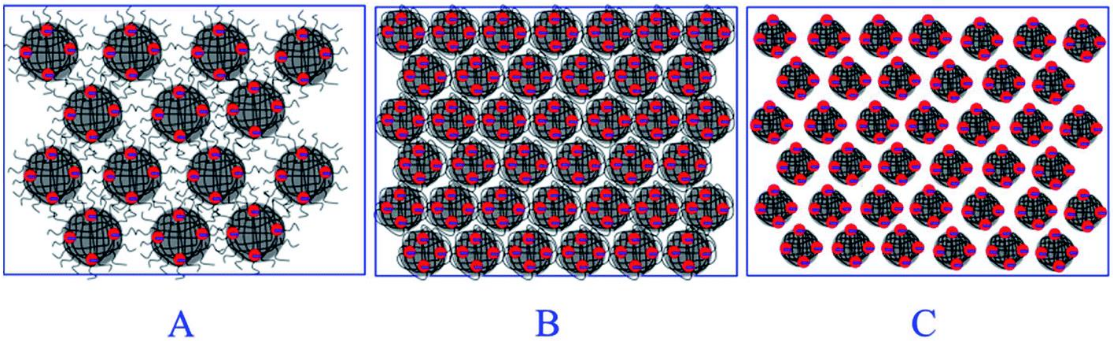

Figure 2-21 The schematic image shows the predicted three distinct microgel interfacial packing and interactions at the heptane-water interface (A) at temperature below VPTT; (B) at a temperature around VPTT; and (C) at temperature above VPTT (Taken from (Li et al., 2014)).

To understand the effect of deformability when microgels spontaneously adsorbed at interface, Li *et al*. prepared two types of microgels containing lower and higher cross-linking densities, to investigate the dynamic interfacial tension at various temperature(Li et al., 2013). They also studied the adsorption behaviour of core-shell particles, which had various ratios of polystyrene core and cross-linked PNPAM shell(Li et al., 2013). They claimed that the deformability of the responsive particles/microgels only affect the kinetic controlled model, whereas particles adsorbed at the interface alter both diffusion process and kinetic process(Ngai and Bon, 2015).

In conclusion, the interfacial behaviour of responsive microgel system has been studied under various the parameters and conditions, and in particular,the concentration, stimuli and conformation all have an influence on their interfacial adsorption kinetics. Based on this previous work, microgel concentration plasy an initial role while they are diffusing from bulk to the interface(Ngai and Bon, 2015; Li et al., 2013). In the kinetic control process, microgels then spread at interface to minimise the interfacial energy(Ngai and

Bon, 2015; Li et al., 2013). Temperature and deformability of microgel key parameters in this stage(Ngai and Bon, 2015; Li et al., 2013).

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Chapter 3. Synthesis of copolymer particles from dispersion polymerization in a non-polar solvent

3.1 Introduction

For several decades now, the synthesis of well-controlled monodisperse polymer particles has attracted a lot of attentions from academic and industrial researchers as these have found applications in paints, coatings recently, stimuli-responsive monomers have played a significant role in exploring the broader potential of such particles to expand their possible applications to oil recovery(Ezell and McCormick, 2007), drug or active molecule delivery(Veiseh et al., 2003; Yuan et al., 2007; Guo et al., 2008; Liu et al., 2002), purification system(Mattiasson et al., 2007) and smart emulsifiers or foam stabilisers(Fujii et al., 2004; Binks et al., 2006; Amalvy et al., 2004; Binks et al., 2005). The synthesis of such environmentally-responsive polymer particles has mostly been based on processes carried out in polar phases, where the continuous phase is either water or ethanol, typically through either emulsion or dispersion polymerisation(Lovell et al., 1997; Arshady, 1992; Bonham et al., 2014). With the increased interests and requirements of applications in low dielectric constant environment (e.g. electrophoretic displays, ink-jet printing, lubricant technologies) the synthesis of such responsive polymer particle systems in non-polar phases also represents an area of interest although very few articles have investigated their synthesis(Richez et al., 2013; Richez et al., 2014), likely due to the difficulty in demonstrating their response to environmental changes (as those typically are driven by H-bonding interactions with the polar solvents in which the particles are dispersed.

The work displayed in this chapter is concerned with the design and synthesis of polymeric particles that are able to fully disperse in non-polar solvents but also change their behaviour upon variation of some environmental conditions. For this purpose, we will design particles that specifically respond to different pH environments and as a result will change their behaviour when adsorbed at an interface with water.

Therefore, in this chapter, the emphasis is primarily on the synthesis of polymer particles dispersed in dodecane with a polymer core synthesised from systematically varied ratios of non-responsive (Methyl Methacrylate, MMA) and responsive (2-vinyl pyridine, 2-VP) monomers. These particles will be synthesised through a dispersion polymerisation process, which is explained detaily in the following sections. The resulting particles are purified and their particle morphology, mean diameter, hydrodynamic diameter and achieved monomer ratios are characterised. Here it is expected by the characterisation carried out in this chapter can demonstrate the effect of monomer ratios and other variables on particle properties. It is expected that particles containing a small amount of MMA in their core will not dissolve when adsorbed at a dodecane-water interface, even at pHs where the 2-VP components of the core protonate. However, the next step will explore the possibility of cross-linking the particles (to potentially prevent particle dissolution) and consequently the effect of cross-linking density on the particle properties. Therefore, particles with a fixed monomer ratio but varied cross-linking density will also be synthesised to explore the influence of cross-linking. Finally, crosslinked particles that contain pure 2-VP in its core will also be synthesised. This range of particles will subsequently be used in the following chapters as emulsion stabilisers to investigate their interfacial adsorption behaviour and their ability to respond to pH changes in the water phase.

The current chapter first briefly reviews the literature around the synthesis of environmentally-responsive polymer particles and in particular the dispersion polymerisation method as it is used in this work. Subsequently, the results of all the experiments described above are displayed and analysed.

3.2 Literature review

3.2.1 Responsive particle synthesis

As known, responsive colloidal particle system can be divided into several categories by the kind of environmental triggers they can response to, like pH(Fujii et al., 2005; Amalvy et al., 2004; Read et al., 2004), temperature(Ngai et al., 2005; Li et al., 2009) , magnetic (Zhou et al., 2011; Peng et al., 2012)and light(Chen et al., 2014). On the other hand, these particles can also be classified into groups basing on their structures, for instance: sterically stabilised solid particles with responsive polymer shell, core-responsive polymer shell particles/microgels, nanocomposite and so on. To obtain these specific particles, there are several synthesis protocols to meet the requirement depends.

Emulsion polymerization is, mostly, adopted to effectively synthesize the functional polymer particles(Peng and Imhof, 2015; Chen and Lee, 1991; Bourgeat-Lami et al., 2002; Nagao et al., 2006). Morse et al. used aqueous emulsion copolymerization to obtain PEGMA (Monomethoxy-capped poly (ethylene gloycol) methacrylate) stabilized PDEA (poly 2-Diethylamino ethyl methacrylate) core-shell latexes with the reversible pH-responsive cross-linked cores(Morse et al., 2013). Mathew et al.(Mathew et al., 2012) anchored poly(methyl methacrylate)-b-poly(dimethylaminoethyl methacrylate) [pMMA$_{16}$-b-pDMAEMA$_{254}$] on the surface of monodisperse polystyrene core by batch emulsion polymerization. Such particles demonstrated the pH responsive ability of [$pMMA_{16}$-b-$pDMAEMA_{254}$] polymer chains that drive particles to adsorb and desorb from interface(Mathew et al., 2012).

Simultaneously, some other synthesis methods were also used to obtain the monodisperse environmental-sensitive colloidal particles, such as suspension polymerisation(Ugelstad et al., 1979; Okubo and Tsujihiro, 1991; Peng and Imhof, 2015) and precipitation polymerization, etc. N-isopropyl acrylamide (NIPAM) is a mostly studied temperature sensitive monomer which, normally, polymerized by itself(Destribats et al., 2011b; Destribats et al., 2012; Destribats et al., 2011a; Destribats et al., 2013; Wu et al., 1994) or copolymerized with pH responsive monomer methacrylic acid (MAA) (Li et al., 2012; Li and Ngai, 2009; Ngai et al., 2006; Ngai et al., 2005; Snowden et al., 1996; Brugger et al., 2010) to form core-responsive particles, so-called microgel. Ngai et al.(Ngai et al., 2005; Ngai et al., 2006) and Li et al.(Li and Ngai, 2009) synthesized pNIPAM-co-MAA microgel with 5.0wt% MAA content in 200nm-250nm hydrodynamic diameter range while Brugger et al.(Cayre et al., 2011) presented some work with 6 mol% MAA copolymerized pNIPAM microgel by same technique. The synthesized pNIPAM-co-MMA microgels are both sensitive to temperature and pH which were investigated in lots different areas. pH-responsive nanocomposite microgel particles which have been combined with polymers and silica particles to build up a spherical network structure attract lots of attention recently. Binks et al.(Binks et al., 2006), Fujii and co-authors(Fujii et al., 2005) as well as Armes's group(Barthet et al., 1999; Percy et al., 2000) prepared poly 4-vinyl pyridine (P4VP)/SiO_2 nanocomposite microgel particles in 100-200nm size range with 35 wt% silica content by free-radical vinyl polymerization and, subsequently, studied their responsive emulsification properties.

Nevertheless, the particle synthesis methods above were all comparatively time and effort consuming(Peng and Imhof, 2015), particularly for the separation of required products from the other mixtures like emulsifiers used in the emulsion polymerization(Lovell et al., 1997; Peng and Imhof, 2015). Based on that, a more straightforward and concise synthesis procedure which can be taken into considerations, while its outcome still has a narrow and controllable size distribution and certain unique shape, is dispersion polymerization(Peng and Imhof, 2015; Barrett, 1974) .

3.2.2 Dispersion polymerization

Since the first appearance of dispersion polymerisation in coating industry, more than half century had been expended along with efforts of previous researchers on the improvement of the dispersion polymerization itself (Osmond and Thompson, 1962; Barrett, 1974; Richez et al., 2013). Nowadays, comparatively mature dispersion polymerization technique has been adopted to synthesis colloidal particles dispersed in non-polar solvent initially which can meet the requirement of low electronic constant environment or other specific areas.

Dispersion polymerization is defined as a kind of precipitation polymerization with an improvement of aggregation and flocculation of new generated particles(Barrett, 1974). The brief procedure of dispersion polymerization in non-polar media is shown in Figure 3-1. Initially, stabilisers and solvent are mixed in a reactor apart from the mixture of monomer and initiator. Both of them present a clean and transparent homogeneous phase until the real reaction starts with the system heating up to the reaction temperature, when the monomers are immediately added into the reactor. At very beginning of polymerization, some monomers are activated by initiators which can react with other inactivated ones to build up a polymer chain. The polymer chain starts to grow up and precipitate resulting in a cloudy looking of the continuous phase in the reactor. When the polymer chain reaches the critical chain length, it becomes a nucleus by self-aggregative. To avoid the aggregation of unstable new nuclei, the continuous soluble polymer stabilisers begin to graft at surface of the nuclei. The formation of particle seeds has occurred along with the milky white system. Currently, the so-called nucleation stage has completed(Barrett, 1974). In the following particle growth stage, polymer seeds capture or absorb activated oligomers from bulk phase to swell and grow until all oligomers and monomer are run out in the continuous phase or particle seeds grow up to critical size. Whole reaction has finished as long as mature polymer stabilised particles are obtained.

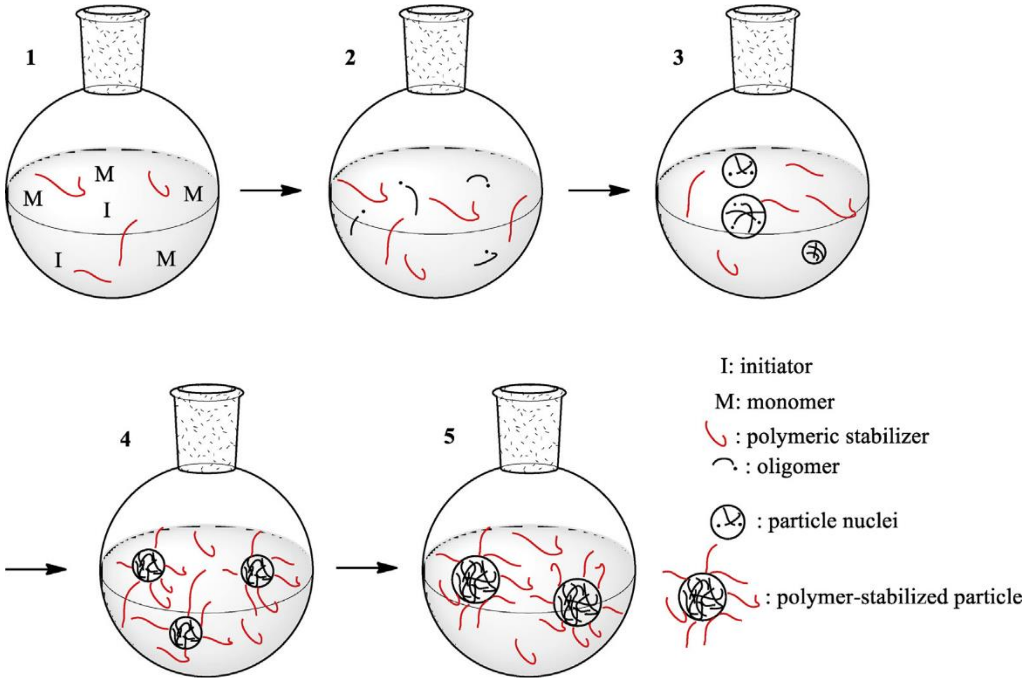

Figure 3-1 Dispersion polymerization mechanism in non-polar solvent: (1) initial homogeneous phase, (2) polymerization initiation (soluble oligomers), (3) oligomer precipitation and oligomer aggregation into particle nuclei, (4) particle stabilization by polymer adsorption, and (5) particle growth (Barrett, 1974; Richez et al., 2013)

Richez et al. ,successfully, synthesized a series of core-shell particles by dispersion polymerization in dodecane (Richez et al., 2014). He adopted two different molecular weight polydimethylsiloxane (PDMS) as steric stabiliser to synthesize particles by varying monomer concentration, stabiliser concentration and monomers' ratios. Particle stabilised with higher molecular weight PDMS are really monodisperse and spherical. The mean particle size can be well-controlled by monomer or stabiliser concentration in Richez's work.

Nevertheless, the same stabiliser was involved in Fujii's work to obtain his lightly cross-linked pH responsive latexes dispersed in a mixture of n-hexane and isopropanol by dispersion polymerization(Fujii et al., 2010). Unfortunately, it is easy to observe the comparatively polydispersity of such particle system as well as the non-spherical shape appears in his work. Undoubtedly, there are many reasons that can affect the final production of dispersion polymerization. Expect the purification of monomer, selection of solvent and other practical operation errors, the one that needs to be taken into consideration mostly is the involving of cross-linker during reaction.

As known, standard dispersion polymerization can be roughly divided into two stages (nucleation stage and particle growth stage)(Song and Winnik, 2005; Peng and Imhof, 2015). The nucleation stage is the most vital but sensitive stage as any parameter changes can affect the final products in this stage. Especially, the involvement of cross-linker can combine two linear polymers or two parts from same chain to build up a rigid structure leading to an interference of particulate forming(Song and Winnik, 2005). In literatures, lots of dispersion polymerization failed when cross-linkers were added into synthesis (Song and Winnik, 2005; Peng and Imhof, 2015; Tseng et al., 1986; Shen et al., 1993; Peng et al., 2012b; Thomson et al., 1995; Thomson et al., 1996; Dullens et al., 2004). The failed products were represented of flocculated and coagulated particles/seeds or the un-controlled, polydisperse and odd-shaped particle (Song and Winnik, 2005; Peng and Imhof, 2015). In 1986, Tseng et al. presented the initial work of polystyrene particles with systematic increased cross-linker (DVB) ratio by dispersion polymerization (Tseng et al., 1986). Below 0.3% DVB ratio, cross-linked polystyrene particles remained comparatively uniform shape and narrow size distribution(Tseng et al., 1986). However, the “mortarlike” polystyrene particle with 0.6% DVB was demonstrated in their work (Tseng et al., 1986). They also pointed out that the coagulated particle suspension was found while the cross-linking density increased. Nevertheless, they didn’t mention the cardinal principles of the formed cross-linked polystyrene particles with odd-shapes. Later, “deswelling” of particle seed was suggested by Ober to describe the pitted particle surface(Ober, 1990). But, Thomson and co-authors proposed “deformation” to explain accurately with the deep exploration on the morphology, particle stability, size distribution and size range of DVB cross-liked polystyrene particles(Thomson et al., 1996). Early addition, late addition and slow addition with systematic changed cross linker ratio at varied synthesis time point were tried in his experiments. In all conditions, infected particle suspension can be obtained in different degrees. Early one-shot and slow addition under 0.7% and 0.9% of DVB, respectively, both illustrated the coagulation system or deformed surface and shape of polystyrene particles (Figure 3-2) while particles can only keep relatively spherical shape with slowing adding method. Nevertheless, the stable higher density (1%-6%) of cross-linked polystyrene particles with spherical shape and slightly deformed surface can be synthesized when cross linker was added after 420mins to evade the nucleation stage. To summary his work, the solutions to improve the stability and morphology of cross-linked polystyrene particle suspension is either slow adding crosslinker or keeping the addition away from nucleation stage. Even his work deciphered a lot on the part that how the particle synthesis reaction is affected by the involution of cross-linker, he still didn't give a scenario to obtain smooth spherical high cross-linked density polystyrene particles.

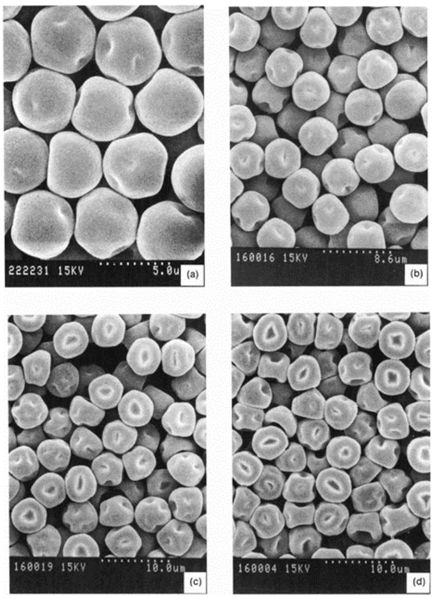

Figure 3-2 Scanning electron micrographs from ref (Thomson et al., 1996) which illustrate the deformed latex morphology of DVB cross-linked particles by dispersion polymerization . Clockwise from top left: (a) DISP578,0.68% DVB added over 615 min, (b) DISP658, 0.9% DVB added over 615 min; (c) DISP669,1% DVB added over 615 min; (d) DISP405,0.2% DVB in the charge, 0.8% added over 513 min, from 60-min mark (Thomson et al., 1996)

Based on their idea, song et al. dramatically improved the highly cross-linked particle shape and size distribution by using both late and slow addition methods at same time(Song and Winnik, 2005; Song et al., 2004). He also suggested that the quick consumption of crosslinker during the reaction can cause particle deformation or polydispersion(Song and Winnik, 2005; Song et al., 2004). Analogously, Peng and Imhof conclusively studied the surface morphology of cross-linked polystyrene and poly(methyl methacrylate) (PMMA) particles(Peng and Imhof, 2015). Differently, they adopted two different cross-linkers (DVB and ethylene glycol dimethacrylate, EGDMA) to synthesize polyvinylpyrriolidone (PVP) sterically stabilised particles. Nucleation stage had been circumvented initially, the improvement of higher cross-linked particle morphology and size distribution was found under the slow addition method (Figure 3-3). In peng's opinion, the reactivity ratio and chemical properties of cross-linkers' functional group can affect their cross-linking ability resulting varied configuration of particles as well (Peng and Imhof, 2015). Besides that, they also showed an excellent work to synthesize functional uniform PMMA particles with high cross-linking density (up to 10 wt %)(Peng et al., 2012b).

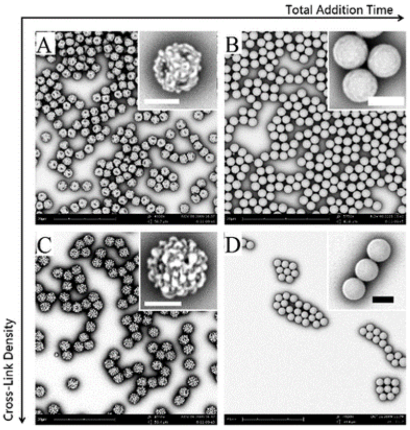

Figure 3-3 SEM micrographs of core–shell cross-linked PMMA particles prepared by the post-addition method, with different cross-link densities and total addition times (the cross-link density and total addition time increased in the direction of the arrows). Key: (A) batch 1, (B) batch 3, (C) batch 8, (D) batch 10. The cross-link densities in (A) and (B) were 1 wt%, and in (C) and (D) were 2 wt%, respectively. The total addition times were 2 h in (A) and (C), 4 h in (B) and 10.5 h in (D), and the addition start time was 1.5 h in all the cases. The scale bars are 20 µm and the insets are 2 µm (Taken from (Peng and Imhof, 2015))

To conclude, later addition of cross-linker in dispersion polymerization after particle nucleation stage can effectively avoid the effect of cross-linker and its concentration on final products' morphology and polydisperse index (PDI). Thus, this synthesis protocol was employed to produce our designed particle suspension. In 2rd chapter, the responsive monomers can be employed into stimuli-responsive polymer particles(Cayre et al., 2011) have been reviewed in detail. Among them, vinyl pyridine (VP) is the joint name of pyridine which are second or fourth substituted by vinyl group. They are both the weak basic monomers with a pK_a of 5 (2-vnyl pyridine)(Fernández-Nieves et al., 2000) and a pK_a of 5.62 (4-vinyl pryridine)(Kabanov et al., 1968). In this work, 2-VP was chosen to randomly co-polymerized with MMA of varied initial monomer ratios to form the particle cores. Since the PDMS chains are soluble in the dodecane, this macromonomer acts as an effective steric stabilizer during this latex synthesis. Besides that, divinylbenzene which is an oil-soluble cross-linker that had been chosen as cross-linker in lots of 2-VP involved particle synthesis, so that such monomer was selected to be employed as a cross-linker in MMA and 2-VP copolymerization.

In this part of work, the core-shell particles were synthesized with varied initial MMA and 2-VP ratios which were polymerized and dispersed in dodecane, firstly. Simultaneously, varied concentrations of DVB were added into the polymerization to cross-link fixed ratio of MMA and 2-VP to obtain similar core-shell dodecane dispersed particles. Finally, with the help of PDMS, designed sterically stabilised cross-linked p2-VP particles were formed and able to be dispersed into a non-polar media, dodecane.

3.3 Experimental materials and methodology

3.3.1 Materials

Dodecane ReagentPlus®, ≥99%, methyl methacrylate (MMA), 2-vinyl pyridine (2-VP), octanethiol (chain transfer agent), Hexane ReagentPlus®, ≥99%, Divinylbenzene (DVB, 80% mixture of isomers) and $CDCl_3$ for NMR were purchased from Sigma-Aldrich. Monomethacryloxypropyl terminated polydimethylsilaxane (PDMS-MA) (10000g.mol^{-1}) was purchased from Fluorochem and 2,2'-azobis (2-methylpropionitrile) (AIBN) from Molekula.

MMA, 2-VP and DVB were purified by passing through an alumina column to remove the polymerization inhibitors. All other chemicals were used as received. Water used here for all purposes was from a Milli-Q reagent water system.

3.3.2 Particle synthesis and characterisation

Non-polar media dispersion polymerisation

A typical synthesis of oil-dispersed core-shell polymer particles was conducted as follows. (1) 2.08g (20wt% vs MMA) PDMS-MA stabiliser macromonomer was weighted in a round-bottom flask, to which 100ml of dodecane was added. (2) The flask was sealed and degassed for 30 mins with nitrogen. (3) In the meantime, 107 mg ([Monomer]/[AIBN]=159) of AIBN, 126uL of octanethiol ([Monomer]/[octanethiol]=142) and 11ml of total monomers (varied ratio of MMA and 2-VP) (10% v/v vs dodecane) were added into second round bottom flask. Octanethiol is acting as a chain transfer agent (CTA) in the dispersion polymerization. This solution was also degassed under nitrogen for 30 mins in an ice bath. (4) After 15 minutes, the stabiliser and solvent mixture was heated to 80 °C in an oil bath and stirred at 300 rpm and once the temperature reached equilibrium, the monomer solution was injected. The reaction was thus initiated and stirring was continued at 300 rpm (at 80°C) under static nitrogen atmosphere for another 4 hours. (6) Subsequently, the obtained particle dispersion was purified by 3-4 cycles of centrifugation and redispersion in pure dodecane to ensure all remaining unreacted monomers and stabilisers was removed. The suspensions were subsequently stored at 3-5°C. The resulting particles were then characterized using the following methods.

Proton- Nuclear Magnetic Resonance spectroscopy (proton-NMR):

1ml of each purified particle suspension was placed into standard NMR testing tube and then labelled to be dried in 25°C vacuum oven. To help the drying of dodecane, approximately 1ml of hexane was added into sample tubes. Hexane has a comparatively low boiling point (50~70℃), which is an easily evaporated non-polar solvent(Clayden et al., 2012). As well as that, hexane can dissolve dodecane well(Clayden et al., 2012). Thus, all solvents can be removed properly with the addition of hexane. Proper dried samples were dissolved in deuterated chloroform ($CDCl_3$). And then, ^{1}HNMR analysis was carried on a 500 MHz Bruker spectrometer in room temperature. The experimental results were analysed in an NMR analysis software. The MMA-2-VP polymer composition (monomer ratio) can be determined upon that.

Scanning electron Microscope (SEM):

Particle suspension was ultra-sonicated in ultrasonic bath and then diluted with dodecane ten to fifth times. The diluted samples were deposited on aluminous stubs. Several drops of hexane were dropt on sample stubs to help the evaporation of dodecane in 25°C vacuum oven. Dried sample, then, were coated with carbon (with an approximate layer of 5 nm) and inserted in the SEM chamber. The SEM was running at 15 kV and room temperature. Synthesized particle morphology can be obtained from image immediately. Mean particle size was estimated from such analysis by averaging the diameter of over 200 particles by an Image J software.

Dynamic Light scattering (Malvern Zetasizer):

Initially, all particle suspension was diluted into target concentrations. The target concentration was determined by a first run measuring the same particle sample under different dilution conditions, which allowed to work out the necessary particle concentration to avoid multiple scattering in the system. Secondly, the diluted sample of each particle suspension was injected into a clean glass cuvette. Before each measurement, sample cuvettes contained the diluted suspension were ultra-sonicated in 25 °C water bath for 5 minutes. Hydrodynamic diameters of particles were measured at 25 °C in dodecane using a Malvern Nanosizer ZEN 3600 instrument equipped with a 4 mW He-Ne solid-state laser operating at 633 nm. Backscattered light was detected at 173° and the mean particle diameter was calculated from the quadratic fitting of the correlation function over 30 runs of 10 s duration. All measurements were performed in triplicate on highly dilute dispersions (0.01wt %).

3.4 Results and discussion

All particles in this thesis were synthesised through a dispersion polymerisation process in dodecane. In all cases, the stabiliser used for the polymerisation process was a poly(dimethyl siloxane), containing a methacrylate moiety at one end, which allows it to participate in the polymerisation reaction. A series of experiments was conducted where a range of variables were explored in order to affect the response of the particles when adsorbed at the interface with water at different pHs.

Initially, the stabilizer concentration was fixed to investigate the influence of systemically changing the 2-VP/MMA ratio on the particle properties. The mean particle diameter and morphology were investigated under SEM. Additionally, to understand the actual ratio of monomers in the final particles (as opposed to the ratio of monomer initially mixed in the solution prior to polymerisation), proton NMR was used on the purified particle systems.

Subsequently, a fixed 2-VP and MMA ratio was used to prepare particles with approximately a constant diameter but varied cross-linking densities.

Finally, we synthesized cross-linked pure 2-VP particles. The influence of cross-linked density on particle morphology and PDI were investigated.

3.4.1 Influence of Monomer Ratios on MMA-2-VP copolymer particles

In this particular study, the experimental work published by our research group (Richez et al., 2014) was extended to vary the initial monomers' ratio by a large range. The particles were synthesized using a concentration of 20.0wt% of PDMS-MA stabilisers as compared to the total monomer mixture. The initial monomer ratios used in the synthesis were as follows: 10:90, 25:75, 50:50, 75:25 and 100:0 of 2-VP versus MMA. A detailed description of all the synthesis parameters and the obtained data for the prepared particles are presented in Table 3-1. Additionally, Scanning Electron Micrographs of all these particle samples are shown in Figure 3-4. All particles obtained in this series were found to be stable against aggregation in the dodecane dispersions and were subsequently used to study their adsorption to dodecane-water interfaces.

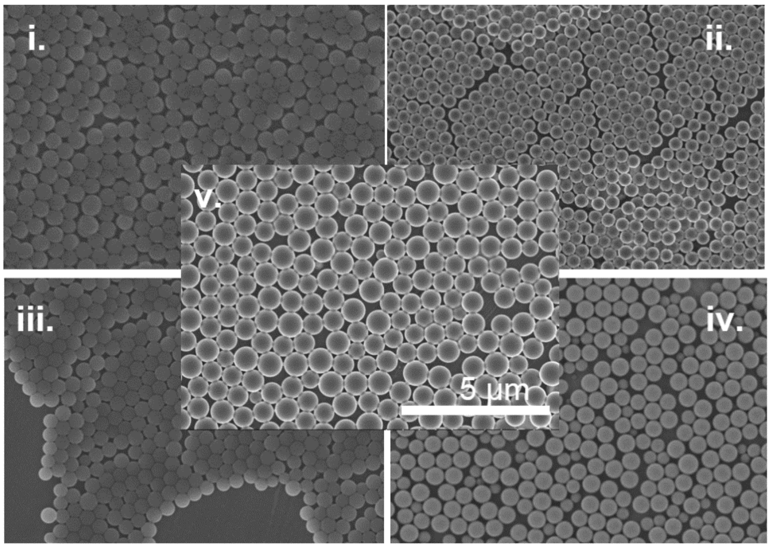

Figure 3-4. Scanning electron microscographs of p(MMA-co-2-VP) particles stabilised with PDMS where the MMA to 2-VP ratio is varied as follows: (i.) 100:0 MMA:2-VP; (ii.) 75:25 MMA:2-VP; (iii.) 50:50 MM:2-VP; (iv.) 25:75 MMA:2-VP; (v.) 10:90 MMA:2-VP. (Scale bar 5 µm)

Table 3-1. Particle size and Polydispersity of (pMMA-co-p2-VP)-PDMS particles with varied targeted monomer molar ratio obtained by dispersion polymerization in dodecane

Entry	Label	MMA/2-VP targeted molar ratio (actual[a])	[monomer] (v/v% vs dodecane)	Average particle size (nm)[b]	Particle Diam. nm (DLS)	PdI
1	MV0	100/0 (100/0)	10	500 ± 60	520± 10	0.05
2	MV25	75/25 (70/30)	10	490 ± 20	530 ± 8	0.03
3	MV50	50/50 (38/62)	10	505 ± 35	560 ± 10	0.08
4	MV75	25/75 (11/89)	10	630 ± 60	650± 60	0.08
5	MV90	10/90 (10/90)	10	680 ± 80	750 ± 30	0.08

[Monomer]/ [CTA]:142, [Monomer]/ [AIBN]:164, 80°C, N2, 300rpm, 4 h

[a]Estimated using ^{1}H NMR. [b]Estimated from SEM images approximately 200 particles

As seen in Figure 3-4, smooth and spherical polymer particles are obtained following the dispersion polymerisation procedure. Combined with the data presented in Table 3-1, these results demonstrate that the dispersion polymerization process in the non-polar solvent led to polymer particles successfully stabilised by the PDMS macromonomer(Richez et al., 2014). Both sets of data also confirm that for large levels of 2-VP monomers, the particles appear to grow to larger sizes. This directly correlates to the NMR data where it is confirmed that the amount of 2-VP present within the particle core tends to be higher than what is initially aimed for. These observations are characteristic of 2 monomers that possess different reaction rates within the same mixture. Indeed here, 2-VP polymerises faster than MMA and as a result for the same polymerisation time, it is expected that the particles created with a higher initial ratio of 2-VP will contain more polymer and therefore will grow to larger sizes, particularly as these experiments only run the polymerisation reaction for a limited period of time (Brandrup et al., 1998; Natansohn et al., 1979; Tamikado, 1960). An additional evidence of the difference in reaction rates of the two monomers (albeit much more practical and indirect) is the fact that the appearance of the polymerisation reaction vessel turned cloudy after the reaction was initiated at different times depending on the monomer ratio used in the initial mixture. Indeed, this occurred almost instantly for the mixtures containing high ratios of 2-VP, while for pure MMA and low ratios of 2-VP mixtures, the reaction vessel only turned cloudy after around 30 minutes

Be aware of the key procedure of dispersion polymerisation, monomers were activated by initiators to react with other monomers at beginning of dispersion polymerisation process(Barrett, 1974; Richez et al., 2013; Peng and Imhof, 2015; Richez et al., 2014). Polymer chains were growing up until the critical chain length(Barrett, 1974; Richez et al., 2013; Peng and Imhof, 2015; Richez et al., 2014). Following that, polymer chains self-aggregated into nucleus to complete the nucleation stage. In particle growth stage, particle seeds started to absorb and capture activated oligomers to enlarge particle volume until reaction stopped (Barrett, 1974; Richez et al., 2013; Peng and Imhof, 2015; Richez et al., 2014). The increasing of mean particle diameter on the basis of SEM images seems following the increased initial 2-VP content (Vincent, 1997). The higher reactivity ratio of 2-VP ($\gamma_{2vp} = 1.1;\ \ \gamma_{mma} = 0.27$) (Brandrup et al., 1998; Natansohn et al., 1979; Tamikado, 1960) and initial input pushed whole dispersion polymerisation proceed much quicker which gave larger particle than other cases in a limited reaction time. The polydispersity indexes of all cases are all below 0.1 by dynamic light scattering measurement, which indicated they were monodisperse particle suspension. This can also correlate with the SEM observation (Figure 3-4) that the particles are indeed monodispersed, visually.

Similar with literature results , the actual monomer ratios of all 2-VP contained particles vary from the original input (Richez et al., 2014) (Table 3-1). The final 2-VP composition is richer than the targeted in most of particles (MV25, MV50, MV75). This, as well, is owing to the higher reactivity ratio of 2-VP when it copolymerises with MMA. However, MV90 particles contained same MMA: 2-VP ratio after synthesis with the original input. This may be linked to the fact that all monomers had been taken part into the polymerization and then end up with a larger particle size.

3.4.2 Influence of cross-linker

The cross-linked p(MMA-2-VP)-PDMS polymeric particles

In the previous sections, successful dispersion polymerization processes in dodecane have been carried out. These batch polymerisations have resulted in oil-dispersed co-polymer core-shell monodisperse particles with good control over particle size and final core content. It is envisaged in this chapter that the adsorption of these particles at oil-water interfaces will be studied. In some of the conditions that these particles will be studies, it is also envisaged that the particle core will be protonated through contact with a low pH water interface. As a result it is possible that the high 2-VP content particles could dissolve into the water phase as the co-polymer forming the particle cores may become water soluble when fully protonated. Therefore this section will aim to investigate the possibility of including a cross-linker within the polymerisation reaction to prevent a potential dissolution of the particle core in interfacial studies. Because this challenge may arise mostly from high 2-VP content particles, only the highest tested ratio of 2-VP particles will be cross-linked.

Consequently here, MMA: 2-VP ratio of 10:90 was chosen for these experiments where total monomer concentrations of 10 % as compared to dodecane volume was used while the cross-linker concentration was systematically varied across 4 samples. In this part of work again, particle mean diameter, PDI and particle morphology were characterised to investigate the effect of cross-linker ratios.

It was decided that, in this case, the synthesis would follow previous work from the literature where addition of the cross-linker during the dispersion polymerization process was carried out after initiation of the reaction to ensure that the suspensions obtained remained monodisperse. (Peng and Imhof, 2015; Peng et al., 2012b; Song et al., 2004; Song and Winnik, 2005; Thomson et al., 1996). As mentioned in introduction section, the dispersion polymerization of particles can be divided into two stages in general, the nucleation stage and particle growth stage(Barrett, 1974). Nevertheless, the nucleation stage is really sensitive, complicated and vital, which lots of practical parameters can affect the formation of nuclei leading to the tremendous differences on final production (Peng and Imhof, 2015; Peng et al., 2012b; Song et al., 2004; Song and Winnik, 2005; Thomson et al., 1996). The addition of cross-linker during the nucleation process is certainly affecting the final particle's morphology (Wiley and Jin, 1968) The cross-linker DVB has a higher reactivity ratio than MMA ($r_{MMA} \cong 0.62, r_{DVB} \cong 1.3$)(Wiley and Jin, 1968). As well as that, DVB reacted faster than 2-VP(Pashkov et al., 1969). Once the reaction has been initiated, DVB will react rapidly. However, the quick consumption of crosslinker during the particle nucleation stage of dispersion polymerisation resulted in the deformation or polydispersion of particle suspension(Song et al., 2004; Song and Winnik, 2005). Thus, adding cross-linker after nucleation stage was suggested in literatures to avoid the influence of cross-linker on nucleation stage (Peng and Imhof, 2015; Peng et al., 2012b; Song et al., 2004; Song and Winnik, 2005; Thomson et al., 1996). Practically, the same reaction conditions as for the synthesis procedure described previously were followed, however degassed Di-Vinyl Benzene (DVB) was injected into the reaction mixture one hour after initiation of the reaction. Finally, the reaction was kept running for another 3 hours.

The effect of adding cross-linker in dispersion polymerization was investigated by comparing the particle morphology from SEM data initially. Figure 3-5 shows typical Scanning Electron Micrographs obtained for these 10:90 MMA-2-VP copolymer particles with varied initial cross-linker concentrations in the reaction mixture. Spherical and individual (i.e. non-aggregated) particles are observed in all micrographs. It seems that these particles didn’t present un-spherical shape and dented morphology in literatures(Peng and Imhof, 2015). This also can imply the very little influence of cross-linker adding in synthesis even on high cross-linked (up to 5 mol%) particles (Figure 3-5 vi and vii). The slightly wrinkled particle surface was owing to the influence of overexposing under SEM electron beam (Dullens et al., 2004).

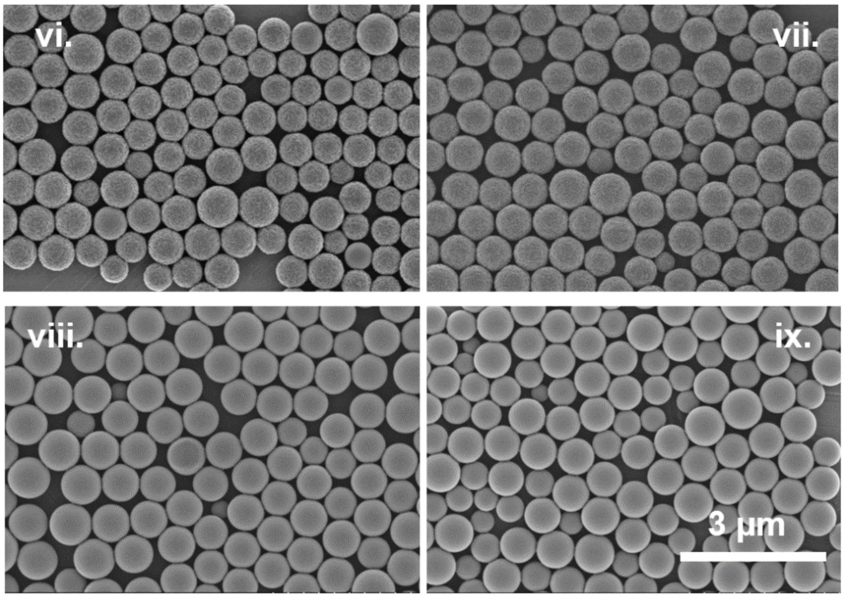

Figure 3-5. Scanning electron micrographs of DVB cross-linked (pMMA-co-p2-VP)-PDMS particles with varied cross-linker initial concentration: (vi.) 0.5 mol% ; (vii.) 1 mol% ; (viii.) 2.5 mol%; (ix.) 5 mol% with respect to monomer concentration; (Scale bar 3 μm)

Table 3-2 shows the average particle diameter measured by SEM images, mean hydrodynamic diameter by dynamic light scattering and associated polydispersity index. The initial monomer ratio of MMA-2-VP was kept at 10/90 with initial DVB concentration in the reaction mixture of 5 mol%, 2.5 mol%, 1 mol% and 0.5 mol% in entry 6 to 10. They illustrate that the copolymer particles with different cross-linking density were in the similar particle size range (from 680 ± 100 nm to 740 ± 50 nm), which was measured over 200 particles by SEM images. However, they didn’t show any obvious tendency of mean particle diameter relate to the decreased cross-linking density. Nevertheless, the mean particle diameter of such cross-linked particles tells a difference from the uncross-linked particles with same particle core content (680nm). The size difference is more likely due to the addition of DVB which forms a cross-linker shell around particle core, due to the reactivity differences and slow addition of DVB (Peng et al., 2012b).

Table 3-2. Particle size and Polydispersity of DVB cross-linked (pMMA-co-p2-VP)-PDMS particles with cross-linking density obtained by dispersion polymerization in dodecane

entry	MMA/2-VP targeted molar ratio	[DVB] (initial ratio, mol% vs 2-VP/MMA)	[monomer] (v/v% vs dodecane)	Average particle size (nm)[a]	Particle Diam. nm (DLS)	PdI (DLS)
6	10/90	5.0	10	700 ± 70	750 ± 25	0.04
7	10/90	2.5	10	740 ± 50	760 ± 30	0.04
8	10/90	1.0	10	730 ± 60	750 ± 30	0.05
9	10/90	0.5	10	680 ± 100	710 ± 80	0.03
10	0/100	2.5	10	750 ± 160	750 ± 15	0.02

[a]Estimated from SEM images over 200 particles

The Cross-linker pure p2-VP-PDMS particles

The synthesis and characterisation of comparatively monodisperse spherical cross-linked pMMA-2-VP-pDMS particles were demonstrated in the section above. Results show that neither the addition of cross-linker nor the high concentration affect particle morphology and structure. Based on that, a further synthesis was carried on obtaining cross-linked dodecane dispersed p2-VP-pDMS particle. This experiment was undertaking in exactly same conditions with previous synthesis by later cross-linker adding method. Non-polar media dispersion polymerization of 2-VP and DVB using the PDMS macromonomer at 80 °C for 4 h led to a colloidally stable p2-VP-pDMS latex with no coagulum (Figure 3-6). However, it is obviously to find out that the particles with 2.5 mol% cross-linked poly 2-VP core reveal the un-spherical shape and slightly dented surface with several obvious big hollows. The gentle polydispersity can be convinced both by SEM images and the standard deviation of its mean particle diameter (750 ± 160 nm) (Figure 3-6 and Table 3-2 entry 10). Here, with emphasis, the odd surface morphology of cross-linked pure 2-VP particles isn’t the fact of the damage of electron beam of SEM. Comparing Figure 3-6 and Figure 3-2a the hollow and deformation morphology is the affection of cross-linker even delaying the addition of cross-linker to after particle nucleation stage. As known, the nucleation stage is the most sensitive and complicated stage (Peng and Imhof, 2015; Thomson et al., 1996). Lots of parameters can affect this stage leading to the tremendous differences on production (Peng and Imhof, 2015). Of course, cross-linker does. Delaying the addition of crosslinker is an efficient way to avoid the influence to nucleation stage which has been convinced by literature and our previous study on the effect of cross-linker and its concentration (Peng and Imhof, 2015; Peng et al., 2012b; Song et al., 2004; Song and Winnik, 2005;

Thomson et al., 1996). However, big cavities can be observed clearly on each particle surface. This is because of the one-shot injection of DVB instead of slow adding. Huang et al suggested that the late and slow feeding of DVB can cause one cavity particle which is due to the long-time accumulated DVB on particle core likely polymerized to one point leading a deep shrink on surface(Huang et al., 2011). But, one shot gave different particle morphology as rapid injecting DVB into system make them staying in several separate location on particle surface resulting a surface with several hollows (Huang et al., 2011). Simultaneously, instead of smooth surface, particles are covered by light dents. When particle seeds have formed after nucleation stage, most polymerization locus were inside of the swollen nuclei by absorbing monomers and cross-linkers. Once monomer is consumed out and the polymers have been cross-linked into a rigid status, the surface of monomer-swollen particle cores start to deswell resulting in a deformed surface covered by little dents(Peng and Imhof, 2015; Song and Winnik, 2005; Thomson et al., 1996). In the other hand, 2-VP has a relatively higher reactivity ratio than DVB (Tanaka et al., 2014). At same time, later addition of DVB remains even more crosslinker at nuclei surface leading to deformed and fully dented particle morphology.

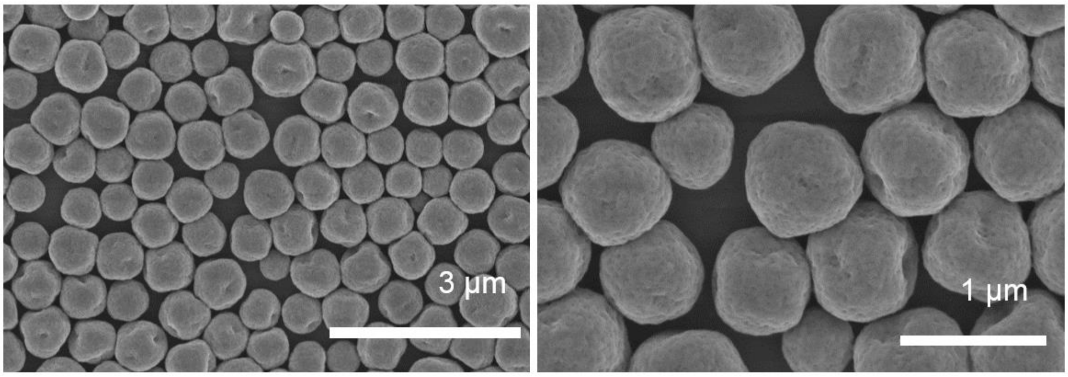

Figure 3-6. Scanning electron microscope images of DVB cross-linked p2-VP-PDMS particles with 2.5 mol% cross-linking density (Scale bar 3 µm and 1 µm)

On the other hand, 10:90 pMMA-2-VP particles with 2.5mol% DVB cross-linker (Figure 3-5 vii) were synthesized under same conditions with 2.5 mol% DVB cross-linked pure p2-VP-pDMS particles suspension. Table 3-2 entry 5 presents that the final products with such ratio of co-monomer are in similar size range (740 ± 50 nm) with cross-linked pure 2-VP (around 750nm). But, apparently, particle shape, morphology and polydispersity have the dramatic differences. We assumed the reason is due to the involved MMA which has a slower reactivity ratio than 2-VP and DVB. Peng in his paper indicated the slow injection of cross-linker is benefit for the formation of a relatively cross-linker well-distributed and thick shell cover the whole particle cores. Final products remain their spherical shape in certain degree (Peng et al., 2012b). The reactivity ratio of monomers have an influence on cross-linked particle morphology as well. Among 2-VP, MMA and DVB, 2-VP has the highest reactivity ratio and MMA is the one which reacts slowest (Tanaka et al., 2014; Wiley and Jin, 1968). Comparing to pure 2-VP system, the infusion of MMA in initial monomer solution is aim to avoid the quick consumption of monomer and slow down the cross-linking reactions. 2-VP, once initiated, run out quickly in the system. Slow reacted MMA and late added DVB both continue to react in similar period and are thereby keeping the spherical shape of products.

3.5 Conclusion

Non-polar solvent dispersion polymerization has been employed in this chapter to synthesize the designed particle suspension dispersed in dodecane initially. The PDMS was successfully stabilising particle cores to ensure the dispersible in dodecane. The systematically increased 2-VP ratio in particle core can be obtained by varying the initial monomer ratio during the synthesis. Due to the reactivity ratio differences, copolymer particle cores contained higher 2-VP ratio than initial input. Mean particle size of such particles increased with a decreased MMA ratio, which is owing to the higher reactivity ratio of 2-VP as well. Spherical and smooth cross-linked particle with different DVB density were synthesized successfully by later adding cross-linker of dispersion polymerization. Such particles have a fixed MMA and 2-VP ratio in their particle cores which lead to similar particle size even they have different cross-linking density. However, an unsuccessful batch of 100% 2-VP contained cross-linked particles were synthesized by same method. Particles present deformed and dented surface with obvious hollows. The odd shape and surface morphology of such particles are due to addition of cross-linker. But copolymer particles with same cross-linking density didn’t illustrate the similar morphology of pure 2-VP contained particles. This is can be concluded as the slower reactivity ratio of MMA which maintained the spherical shape at last stage of dispersion polymerization.

The combination of hydrophilic core and hydrophobic polymer shell is expected to give the remarkable particle interfacial properties at oil-water interface in following work. Especially, with the help of 2-VP which is a common responsive monomer has a pK_a below 5, particles will behave differently at different pH. And also these particle will give varied interfacial performance due to the 2-VP ratio in their cores. Besides that, cross-linked particles will be studied as well to understand the influence of cross-linking density on oil-water interfacial behaviours upon varied pH.

Reference

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Chapter 4. Performance of dodecane-dispersed particles as Pickering emulsifiers (effect of pH and concentration)

4.1 Introduction

In previous chapter, two sets of core-shell polymeric particles were synthesized via dispersion polymerization in dodecane. Firstly, uncross-linked particles were prepared, where the ratio of 2-VP to MMA within particle cores was systematically increased. Secondly, cross-linked particles were also synthesised with a fixed MMA to 2-VP content but varied initial cross-linker concentrations. In this chapter, these particles will be evaluated as Pickering emulsifiers with the aim of demonstrating that their pH-responsive core can influence their ability to stabilise emulsions.

Particle-stabilised emulsions (so-called Pickering – or Ramsden - emulsion) were first reported more than a century ago by W. Ramsden and shortly after by S.U. Pickering without extensively being explored.(Pickering, 1907; Ramsden, 1903; Finkle et al., 1923) Over the last 20 years however, their acclaimed advantages of high stability, good reproducibility and (comparatively to surfactant-stabilised emulsions) environmental friendly and low toxicity have driven a large amount of studies(Binks, 2002; Aveyard et al., 2003). There exists a large range of particles with the ability of stabilising oil-water interfaces and that are, as a result, good Pickering emulsifiers. Such particles include silicone dioxide or titanium dioxide (often after a process of chemical surface modification)(Binks and Whitby, 2004; Binks and Lumsdon, 2000a; Binks et al., 2005b; Stiller et al., 2001), or metallic particles such as gold, silver, iron-based particles (Nuopponen and Tenhu, 2007; Schwartz et al., 2001; Zhou et al., 2011)and polymer particles(Amalvy et al., 2003; Binks et al., 2005a; Fujii et al., 2005; Ngai et al., 2006), which are typically synthesised for this application in a range of sizes from a few nanometers to a few microns. Polymer-based Pickering emulsifiers have particularly attracted the attention of recent studies as they can be synthesized using a very large pool of monomers, typically allowing tuning of both their core and surface properties that are important features in controlling their interfacial behaviour. Particularly, polymeric nanoparticles that can change their interfacial behaviour in response to changes in pH (Nuopponen and Tenhu, 2007; Webber et al., 2005; Dupin et al., 2008; Delaittre et al., 2009; Binks et al., 2005a), temperature (Monteux et al., 2010; Tsuji and Kawaguchi, 2008; Binks et al., 2005a), magnetic field and/or light intensity (Melle et al., 2005; Zhou et al., 2011; Peng et al., 2012; Nypelö et al., 2014) have been used to control the characteristics of the emulsions they stabilise. However, in all previous cases such environment-responsive Pickering emulsifiers are dispersed in water. This is because typically their response is triggered by the way they interact with water.

In this chapter we expand the use of such particles to those synthesised in the previous chapter, which are dispersed in a non-polar phase acting as the oil phase in the Pickering emulsion systems. These particles are responsive to changes in pH but are only able to undergo some transition in their behaviour when adsorbed at the interface. Thus, this chapter will first explore the ability of the synthesised particles to adsorb at an oil-water interface and stabilise emulsions. Subsequently the ability of the particles to modify their interfacial adsorption properties upon changes in the pH of the aqueous phase is also thoroughly investigated.

By testing the ability of these particles to change the properties of the produced emulsions, it is expected that our observations will match some made for other Pickering systems in the past. This includes a process known as emulsion phase inversion, which has been introduced in Chapter 2. The inversion from dispersed phase to continuous phase of solely particle stabilised emulsion system is called phase inversion which can be achieved by changing oil-water volume ratio (catastrophic phase inversion)(Binks and Lumsdon, 2000a; Salager, 1988), particle concentrations (Binks et al., 2005b) or particle wettability (transitional phase inversion) (Binks and Rodrigues, 2005d; Read et al., 2004; Binks et al., 2010; Binks and Rodrigues, 2003; Sun et al., 2010; Binks et al., 2005a; Binks and Lumsdon, 2000b) (see Chapter 2). With the increased interests on responsive particles, the phase inversion of responsive particle stabilised emulsion systems has attracted lots of attentions due to the controllability of the transition of emulsion types via external factors, for example: environmental triggers.

<u>Phase inversion of shell-responsive particle stabilised emulsions</u>

Binks and Rodrigues demonstrated pH-induced Pickering emulsion phase inversion (Binks and Rodrigues, 2005d). They first prepared emulsions using ionisable carboxylic acid coated polystyrene latex particles as stabilisers in standard conditions (1:1 volume ratio of hexadecane and 1 M electrolyte solutions) but systematically varied the aqueous phase pH. W/O emulsions were inversed to O/W by increasing pH to 10.1. Simultaneously, the emulsion type can also be inverted by adding more NaCl up to 0.66 M in aqueous phase. In their opinion, the surface charge of ionisable carboxylic acid coated polystyrene latex particles can be controlled by either pH or electrolyte concentrations in aqueous phase. Such variation of particle surface charge drives the changing of particle wettability at oil-water interfaces, which eventually affect the type of emulsion they stabilised.

Sun et al. also demonstrated transitional Pickering emulsion phase inversion induced by changes in pH and ionic strength with the aim of forming high-internal-phase emulsions (HIPE). The particles they used for this purpose were based on copolymers of polystyrene and methacrylic acid (MAA) (Sun et al., 2010). Here, emulsions were prepared with 27vol% dichloromethane as the oil phase and 73vol% water. Three emulsion (w/o gel, w/o HIPE and o/w) can be stabilised by varying the pH or ionic strength in aqueous phase (Figure 4-1 and Figure 4-2).

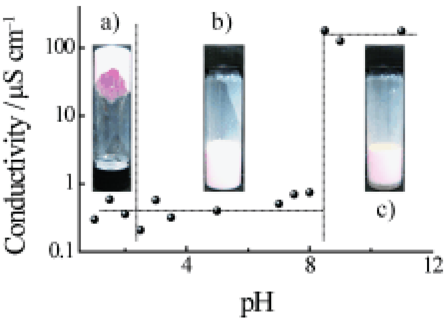

Figure 4-1 The conductivity and correlated appearance of 5.0 wt % of PS-co-MAA latex particles stabilised dichloromethane-water emulsions at varied pH. The formed emulsion types are a) gel, b) water/oil HIPE, c) oil/water. (Taken from (Sun et al., 2010))

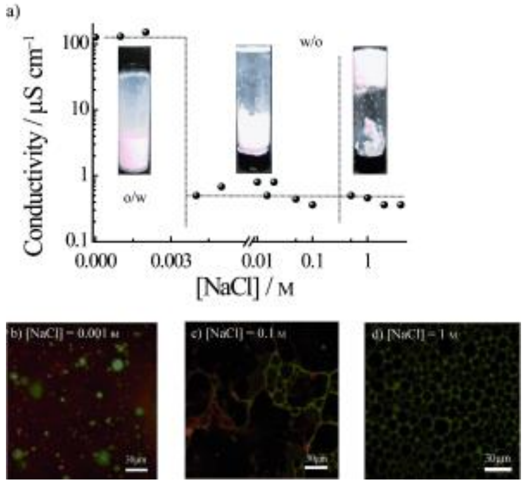

Figure 4-2: a) The conductivity and correlated appearance of 5.0 wt % of PS-*co*-MAA latex particles stabilised dichloromethane-water (pH 9) emulsions at varied electrolyte concentrations. The stabilisation of o/w, w/o HIPE and w/o gel emulsion are governed by the increased electrolyte concentrations. b-d) the confocal microscope images of correlated emulsions with b) 0.001 M, c) 0.1 M, and d) 1 M of electrolyte solutions.(Taken from (Sun et al., 2010))

Another example of transitional phase inversion of polystyrene based sterically stabilised latex stabilised emulsion system has been reported by Binks and co-workers(Binks et al., 2005a). In their work, they synthesized poly[2-(dimethylamino)ethyl methacrylate-block-methyl methacrylate] (PDMA-b-PMMA) stabilised polystyrene particles, which was used to prepare emulsions at varied temperature conditions. PDMA polymer block has the thermal sensitivity, which can respond to the increased temperature driven to the shifting of polystyrene particle contact angle at oil-water interface. Due to the thermal sensitivity of such particles, the transitional phase inversion from o/w, w/o/w and w/o emulsions had been investigated for conditions of 25, 55 and 65°C Figure 4-3.

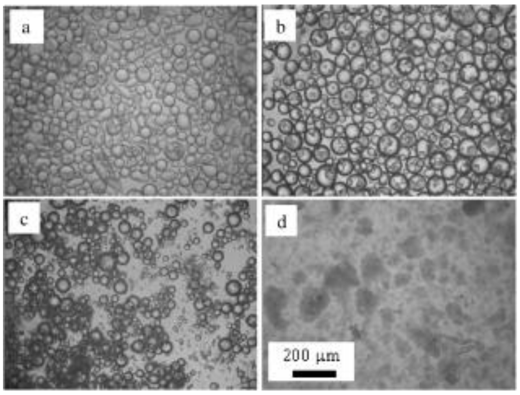

Figure 4-3 Optical microscope images of emulsions prepared with n-hexadecane and water in the presence of 2wt% PDMA-b-PMMA sterically stabilise polystyrene latex (pH 8.1) at a) 25 °C (o/w) b) 55 °C (w/o/w), and c) 65 °C (w/o). (Taken from (Binks et al., 2005a))

Three typical examples reviewed above show the possibility of transitional phase inversion induced by environmental triggers of shell-responsive particle latex stabilised emulsion systems. The main aspect suggested by all of the authors above is the contact angle shifting of particles resulting in a stabilisation of varied types of emulsions. Such variation of particle contact angle at oil-water interface is due to the changing of hydrophilicity-hydrophobicity of particle responsive shells by responding to environmental triggers.

There are some other cases of phase inversion observed in shell-responsive particle stabilised emulsion systems. Here is an example. Read et al. used different polarity of oils as examples of oil phases to prepare emulsions with (PDMA-PMMA) sterically stabilised polystyrene under different pH(Read et al., 2004). The phase inversion of emulsions from w/o to o/w, here, was not induced by the environmental trigger, but inverted by switching the oil phases (from higher polarity oils to lower ones, in their examples). In their opinion, the key aspect that driven such inversion is still owing to the contact angle shifting at oil-water interface. Such variation is due to the different polarities of oil phases rather than the function of the responsive properties of the particles. However, pH induced transitional phase inversion by decreasing pH can be observed only with intermediate polarity oils. Their work implies the vital role of particle interfacial wettability that affect the types of emulsion they stabilise with. Such wettability of shell-responsive particle adsorbed at interface can be governed not only by the environmental trigger but also the polarities of oil phases. All of the cases above were based on shell/surface responsive polystyrene solid latex system.

Phase inversion of Core-responsive particles/microgels stabilised emulsions

Core-responsive particles (often referred to as microgel particles) have also been used as pickering emulsifiers in recent years. However, it is surprisingly that there is no literature showing the transitional phase inversion of microgel/core-responsive particle stabilised emulsions, which is caused by the function of particle’s responsiveness. Destribats et al. discussed the possible microgel stabilization mechanism with varied nature of oil phases(Destribats et al., 2011b). Conventionally, their pNIPAM microgel stabilised o/w emulsions below volume phase transition temperature (VPTT)(Destribats et al., 2011a). W/o emulsion droplets can be formed by such microgels either increased the water ratio over 60% or switch the oil phase to fatty alcohols or dichlorobenzene. Simultaneously, they also observed a multi-layer structure of spherical microgel building inside of w/o emulsion droplet interfaces. In this condition, the aqueous based pNIPAM microgel lost its deformability. The stabilisation of water globules dispersing in oil phase by such water dispersed microgels broke the finkle rule in their suggestions. Furthermore, their emulsion phase inversion was only induced by changing water-oil volume ratio or oil nature rather than responding to the environmental trigger.

To the best of our knowledge, tit is worth to emphasize, again, that all the phase inversion reported were based of aqueous based responsive particle stabilised emulsion system. As mentioned previously, this project aims to use oil-dispersed core-shell particles as Pickering emulsifiers. In this chapter, the core pH-responsive particles synthesised in the previous chapter are investigated for their ability to stabilise emulsions of different types as a function pH change in the aqueous phase

This chapter demonstrates the investigation of emulsion stabilised by dodecane dispersed (PMMA-2-VP)-PDMS core-shell particles. There is a challenge on discovering the responsiveness of oil-dispersed core-shell particles. Commonly, the conformation of conventional water-dispersible microgels changed by responding to environmental triggers can be investigated with the variation of hydrodynamic diameter of particles in bulk directly. In our case, p2-VP within the cores of such oil-dispersed particles need to contact with aqueous solution at varied pH to be protonated/deprotonated. In the other word, the pH responsiveness of our oil-dispersed particles cannot be examined in bulk phase. As reviewed above, the types of emulsions and their stability can be dictates by responsive particle interfacial behaviours, which are termed as the wettability. Such wettability of responsive particle system can be, commonly, driven by their charge density when they respond to the environmental trigger. Therefore, the changes occurring to the particle structure/behaviours at the interface can be observed by the properties of the emulsions such particle stabilise in different conditions. Hence, oil-dispersed particles with varied comonomer ratios are attempted to use as pickering emulsifiers with fixed oil-water volume ratio but varied concentrations to understand their emulsification ability and their emulsion stability. Then, emulsions are stabilised with same parameters and conditions but under different pH in the aqueous phase. The effect of particle concentrations and pH on emulsion properties and particle interfacial behaviours are demonstrated as well as the influence of MMA and 2-VP ratios. Continually, particles with varied cross-linking density are explored with same parameters of emulsions base on the results of uncross-linked particles. Finally, cryo-SEM was employed to reveal the particle monolayer and potential behaviours at the interface of emulsion droplet.

4.2 Experimental materials and Methodology

4.2.1 Experimental materials

Table 4-1: Chemicals involved in this Chapter’s experiments

Entry	Materials	Standard	Supplier	Purpose
1	Water	Milli-q water	Milli-Q reagent water system	Cleaning Solvent Aqueous phase
2	Dodecane	Reagent Plus®, ≥99%	Sigma-Aldrich	Solvent Oil phase
3	Sodium hydroxide (NaOH)	reagent grade, ≥98%, pellets (anhydrous)	Sigma-Aldrich	Base solution
4	hydrogen chloride (HCl)	ACS reagent, 37%	Sigma-Aldrich	Acid solution
5	Nile red	suitable for fluorescence, BioReagent, ≥98.0% (HPLC)	Sigma-Aldrich	Oil soluble dye
6	Fluorescein sodium salt		Sigma-Aldrich	Water soluble dye
7	Decon			Cleaning
8	Ethanol	ACS reagent, absolute ≥99.8%	Sigma-Aldrich	Cleaning
9	Acetone	CHROMASOLV® Plus, for HPLC, ≥99.9%	Sigma-Aldrich	Cleaning

Involved chemicals are listed in Table 4-1. All chemicals are used as received. Milliq water and dodecane are employed as aqueous phase and oil phase, respectively. Sodium hydroxide and hydrogen chloride are dissolved in water to adjust the pH of aqueous phase. Decon, ethanol, Acetone and milliq water are cleaning agent and solvents.

4.2.2 Emulsion preparation and properties characterisation

Emulsion preparation and stability characterisation.

Prior to any emulsification activity, either water phase or oil phase is dyed by Fluorescein sodium salt (water soluble dye) and Nile red (oil soluble dye), respectively. For sake of optimal resolution and less effect on experimental results, the concentrations of both dyes are kept at $2.5\times\ 10^{-4}\ M$. As known, particles were dispersed in dodecane directly after synthesis. The diluted particle suspensions were used as oil phase directly. Experiments were carried out at pH 6 and pH 2. Preliminarily prepared acid solution (1mol/L HCl) and base solution (1mol/L NaOH) were employed to adjust the pH of milliq water.

Initially, 5 ml pH adjusted milliq water was added into a 20ml emulsion vial. The particle suspension was diluted with pure dodecane to the target concentrations (4wt%, 2wt%, 1wt% and 0.5 wt%) from the concentration obtained after synthesis (typically ~10 wt%) and 5 ml was placed on top of the water phase. Oil and water volumes were kept the same in all cases. The prepared mixture was homogenised using an IKA Ultra-Turrax T-25 homogenizer at 20,000rpm for 2 mins at room temperature. The resulting emulsion was kept in a water bath at 23°C for the duration of the experiment (typically 24 hours). Digital photographs of the emulsion vials were taken at different times (directly after emulsification and after 30 minutes, 60 minutes, 2 hours and 24 hours) and measurements of the height of the emulsion phase and the potentially separated oil and water phases were recorded to track emulsion stability as a function of time.

Emulsion characterisation.

Drop test

This was used to have an initial idea of the emulsion type (water in oil or oil in water). Just after emulsification, a drop of the prepared emulsion was placed into Milli-Q water or dodecane. The type of emulsion was deduced from the test.

Fluorescent Optical microscopy

An Olympus (BX51 model) optical microscope in transmitted mode was used to investigate emulsion droplet shapes and to determine droplet size for each of the emulsion sample prepared immediately. The same microscope was also used in reflected mode to monitor fluorescence of chemical dyes dissolved in either the oil or the water phase to further confirm the emulsion types obtained for each system. The emulsion sample were imaged both under transmission light and fluorescent light. Mean droplet size for each sample was calculated by taking into account at least 150 droplets from at least 3 optical micrographs using the Java-based image processing software Image J (developed at the National Institutes of Health).

Cryo-Scanning Electron Microscopy

An FEI Quanta 200 F FEG ESEM was used to image the prepared emulsion samples. The instrument used is a PolarPrep 2000 Cryo Transfer System supplied by Quorum Technologies. Two droplets (c. 20 μl) of sample were mounted onto rivets mounted on the stub/transfer shuttle of the transfer rod. And then the samples were plunging froze in liquid nitrogen slush (c. -180 degrees C) and inserted them into the cryo prep chamber at c. -180 degrees C. The samples were then fractured using a mounted razor blade and sublimed at -95 degrees C for 4 minutes. After which they were platinum coated for 30 seconds (c. 5nm) before transfer into the SEM and imaging on the SEM stage running at -135 degrees C.

4.3 Results and discussion

4.3.1 Emulsion stabilised by oil-dispersed particles with varied p(2-VP-MMA) ratios

All five batches of oil-dispersed core-shell particles with varied ratios of 2-VP and MMA co-monomers in their cores (as synthesized and characterised in the previous chapter) were used here to investigate their ability to act as Pickering emulsifiers.

4.3.1.1 Effect of particle concentrations

All four oil-dispersed samples of particles with varied MMA and 2-VP ratio were first diluted with dodecane to four concentrations (4wt%, 2wt%, 1wt% and 0.5wt%). Subsequently, a 50:50 water-oil volume ratio emulsion containing water was prepared using these dodecane suspensions of particles at different concentrations. All emulsions were initially prepared at a pH of 6, where the particle core is not expected to protonate when entering the interface with water. From fluorescent optical microscopy investigations and drop test results, the emulsion types for these particle samples at all particle concentrations were found to be water-in-oil (w/o). Optical microscopy images of the emulsions are shown in Figure 4-4 while droplet size distributions extracted from the images (by measuring the average of a minimum of 100 droplets, using Image J software) are shown in Figure 4-5. Generally, the optical micrographs in Figure 4-4 show a clear visualized trend that emulsion droplet size increased with decreasing particle concentrations. This is also be confirmed by Figure 4-5. However, it seems a decreasing trend of droplet size can be concluded with increased 2-VP ratio in emulsifier cores when emulsion were stabilised with lower than 2wt% particle suspensions (Figure 4-5). Mostly spherical emulsion droplets can be observed in all cases. However, it is apparent that few non-spherical droplets were found in the two systems using particles with the highest MMA ratio in cores and highest particle concentrations (4wt% and 2wt% of MV0 and MV25 - Figure 4-4 ai, aii, bi and bii).

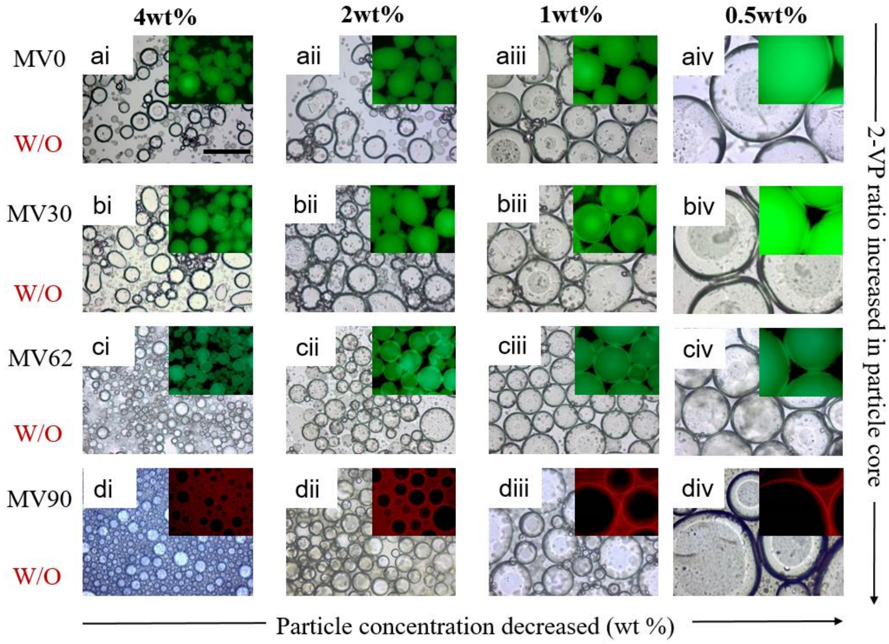

Figure 4-4. Optical micrographs of emulsion droplets stabilised with i). 4wt%; ii). 2wt%; iii). 1wt% and iv). 0.5wt% for the different particles synthesised in Chapter 4 a). MV0 (no VP present); b). MV30 (30% VP present in the core); c) MV62 (62% VP present in the core) and d). MV90 (90% VP present in the core) at pH 6 (scale bar of 500 μm in ai applies to all micrographs)

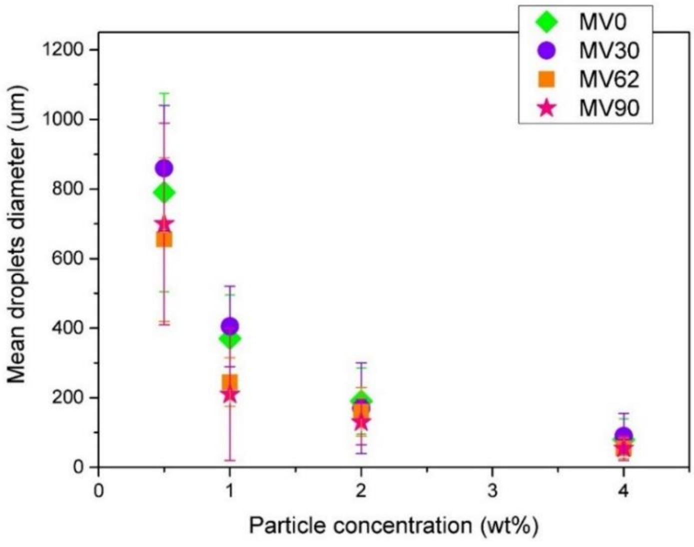

Figure 4-5 Mean emulsion droplets size as function of particle concentrations of w/o emulsion droplets stabilised by oil-dispersed particles with varied core content at pH 6.

W/O emulsion droplets stabilised by four batches of oil-dispersed particles in our cases are following the empirical Bancroft - finkle rule of Pickering systems, which states that the preferred continuous phase of emulsion droplets should be the phase in which the particle emulsifiers are initially dispersed (Finkle et al., 1923; Bancroft, 1912). The mean droplet size in all particle cases decrease as function of particle concentrations in accordance with conventional spherical particle stabilised emulsion systems from the literature (Binks, 2002; Binks and Horozov, 2006; Aveyard et al., 2003). This is typically explained by the fact that fewer particles cover less surface area, thus resulting in coalescence of the small droplets created during the emulsification step. Thermodynamically, the coalescence process occurs to decrease the total free energy in the system until a point where the droplets are sufficiently covered with particles to create a physical barrier preventing further coalescence.

All w/o droplets that appear non-spherical were most probably formed from an arrested coalescence process over time (Pawar et al., 2011; Morse et al., 2014). This is also supported by the fact that non-spherical droplets are only observed at high particle concentrations, thus suggesting that an arrested process is possible due to the large excess of particles present in the system. When two partially covered drops encounter with each other, they can begin to coalesce. The surface coverage of the combined droplet increases while interfacial area is decreased. Consequently, instead of a larger spherical drop, jammed particles may form a cohesive film leading to droplets remaining with shapes of higher curvature by the Laplace pressure gradient (Pawar et al., 2011).

The decreased mean droplet size by increased p2-VP in particle cores with lower particle concentrations implies decreased rate of droplet coalescence. Potentially, such oil-dispersed particles have an increased water affinity with increased p2-VP ratio in cores while particles adsorbed at oil-water interface. Therefore, the mean droplet size is lowering by increased 2-VP ratio in particle cores, which w/o emulsion were stabilised in the presence of lower particle concentrations. However, at higher particle concentrations, there are enough particles to stabilise the emulsion droplets showing little difference of mean droplet diameter regardless of 2-VP ratio in particle cores. The higher affinity of the particles for the interface at high VP ratios means that the likeliness of particles adsorbing at the interface upon contact during the emulsification step is higher and therefore that there are more particles adsorbed at the interface, thus more interfacial area was stabilised.

Figure 4-6 shows digital images of freshly prepared emulsions stabilised by decreasing particle concentrations and Figure 4-7 shows the same emulsions aged for 24 hours at constant temperature. To facilitate optical microscopy observations, either a water-soluble or oil-soluble dye was added to one of the phases prior to preparation of the emulsions. This allowed for additional determination of the type of emulsion produced under fluorescent optical microscope. The sedimentation of emulsion can be observed in the presence of varied particle concentrations regardless of the core content of the emulsifiers (Figure 4-7). When emulsions were freshly prepared at high particle concentrations (4wt% and 2wt% in most of cases), they presented the total milky status in vials. However, emulsion stabilised with lower particle concentration generally appeared a thin layer of clean oil on top of emulsion layers which indicated the rapid sedimentation coalescence just after emulsification in the systems. Such phenomenon can also be convinced by the visualized differences of droplets size between higher particle concentrations stabilised emulsion and lower ones in Figure 4-4. Emulsion, here, were stabilised with four batches of particles containing varied co-monomer ratios. The thin layer of clean oil existed in the MV0 and MV25 vials which convinced the rapid sedimentation and coalescence in their systems. After waited for a day, a significant reduction of emulsion volume can be found in emulsion sample vials.

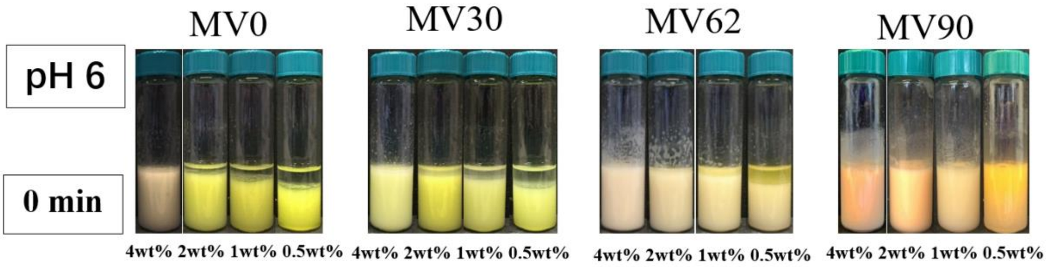

Figure 4-6. Appearances of sample vials containing emulsion droplets stabilised by varied concentration of MV0, MV30, MV62 and MV90 particles at pH 6 just after homogenisation

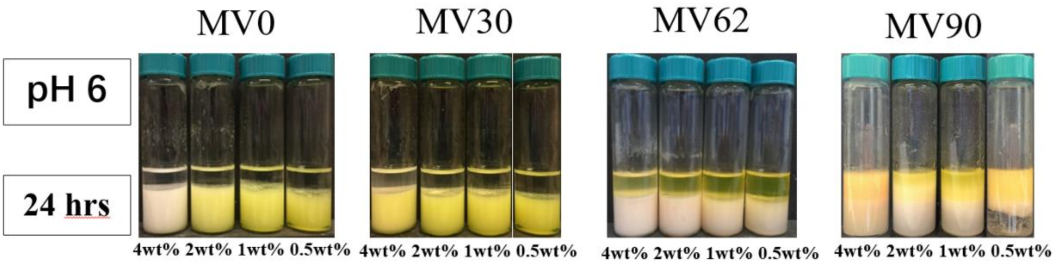

Figure 4-7. Appearances of sample vials containing emulsion droplets stabilised by varied concentration of MV0, MV30, MV62 and MV90 particles at pH 6 after waiting for 24 hours.

In MV0, MV25 and MV50 systems, the oil phases above were fairly clear indicating few or no residual particles. As explained above, the coalescence and droplets sedimentation occurred, here, in all oil-dispersed particles stabilised emulsion systems. However, MV90 didn’t show a clean oil phase after 24 hours and the magnifying image of emulsion layers illustrate a “foam-like” structure Figure 4-8.

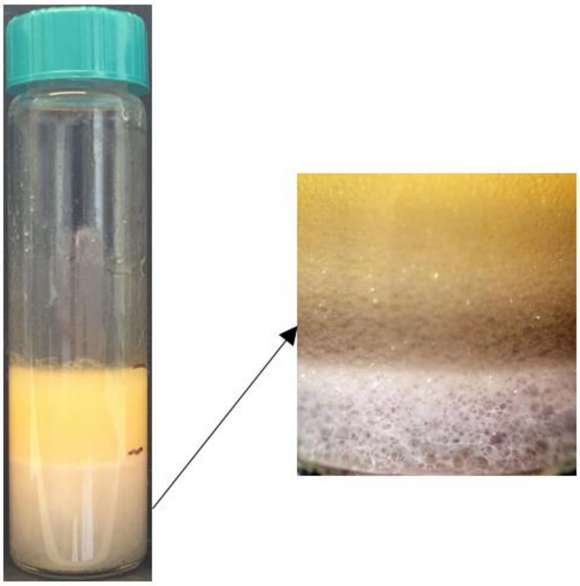

Figure 4-8 Appearance of an example emulsion vial containing a w/o emulsion stabilised by 2wt% MV90 particles at pH 6 after 24 hours and the magnified image of “foam-like” emulsions from same sample.

Traditional gel emulsion have single particle bridging or double particle layers between two droplets(Horozov and Binks, 2006). Unlikely, the large amount of particle dispersing in oil and accumulating to trap water droplets, in our case, were investigated. This reveals that first, the adsorption of MV 90 particles at interface from oil side was really poor, and second the emulsion stabilization mechanism of such system is different from other cases. Instead of fully covered and robust adsorbed at curved interface, MV90 particle formed a 3-D network with aggregated or dense particle layers to prevent the droplet-droplet interactions (Binks and Horozov, 2006). Our particles in current conditions follow Finkle - bancroft rule that particles were initially dispersed in oil which becomes the continuous phase of their emulsions(Finkle et al., 1923; Bancroft, 1912). Good solubility of Polydimethylsiloxane (PDMS) which is the stabiliser of particles to dodecane maintains particles dispersing in and helps the stabilisation of water droplets. On the contrary, 2-VP, as known, likes water inducing the more oil-hate particle cores with its increased content. Thus, these oil dispersed particles can stabilise smaller and smaller water globules with increased 2-VP ratio in their cores leading to a better stability of w/o emulsion. The unusual low stability and “gel-like” structure of the w/o emulsion stabilised by 90% 2-VP may be linked to the fact that such particle seems broke the balance of hydrophilicity-hydrophobicity induced by decreased MMA : 2-VP ratio in particle cores. It drives the lose of the interfacial adsorbing ability, thus, making particles easy to aggregate at interface.

4.3.1.2 Effect of pH

a) Emulsion performance at two different pH environment

In the previous section, the ability of these oil-dispersed particles as the Pickering emulsifiers has been proved, with obtained results indicating relatively stable w/o emulsions. However, an important question that needs to be taken into consideration, is whether there is any potential that if the aqueous environment changes, that particle behaviour differ due to the 2-vinylpridine’s natural chemical properties to protonate? To explore this behaviour more, a series of emulsion studies was carried out by varying the pH in the aqueous phase.

Emulsions were prepared under the same conditions of previous ones (see Section 4.3.1.1) but at pH 2 (Figure 4-9). Figure 4-10 shows appearances of the same emulsions after 24 hours’ preparation. Intuitively, there appears to be some differences, when comparing to Figure 4-6 (at pH 6) except for the MV0 stabilised system, which seems qualitatively consistent. MV30 appears with resolved oil and water even when just made, while emulsions stabilised by MV62 and MV90 particles appear to have creamed (from the clear evidence of water in the vial bases) which would imply an aqueous continuous phase at the lower pH.

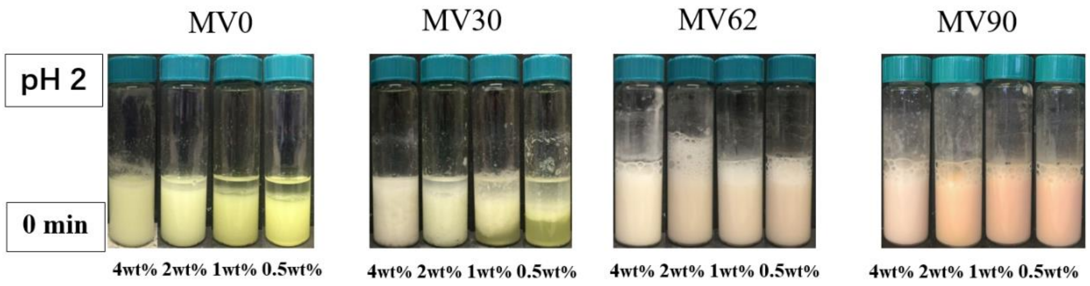

Figure 4-9. Appearances of sample vials containing emulsion droplets stabilised by varied concentrations of MV0, MV30, MV62 and MV90 particles at pH 2 just after homogenisation.

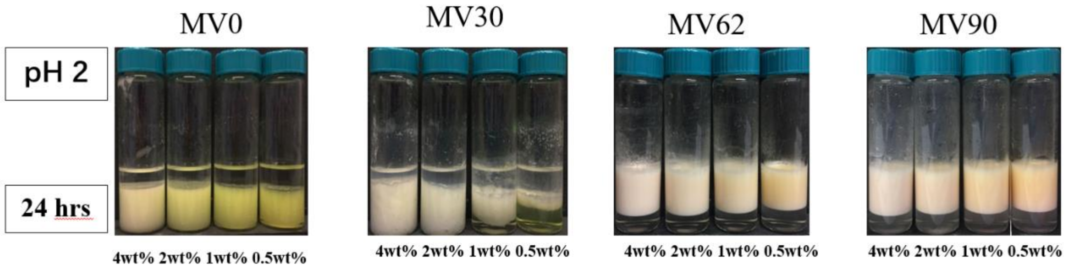

Figure 4-10. Appearances of sample vials containing emulsion droplets stabilised by varied concentrations of MV0, MV30, MV62 and MV90 particles at pH 2 after waiting for 24 hours.

As shown and discussed (in Section 4.3.1.1) only w/o emulsion droplets can be formed by all particles in all concentrations at pH6. To confirm w/o or o/w behaviour at pH 2, drop test and fluorescent microscope investigations were again performed, and are shown in Figure 4-11. MV0 particles still stabilised uniform, spherical water globules regardless of pH change in its aqueous phase. This was also true in the case of MV30, however microscopy evidence suggest that the w/o emulsion droplets were flocculated at pH 2 in this case (which was also shown as a rigid chunk in its appearance).

Transitional phase inversion from water in oil droplets (pH 6) to oil in water ones (pH 2) was observed for all particle samples containing more than 50 % 2-VP monomer in their core. These changes are shown in Figure 4-11from the fluorescence microscopy images. For MV62 and MV90 cases, red oil-soluble dye was used as a marker, which are seen clearly as the dispersed droplets (while the same green water soluble dye was used for the MV0 and

MV30 cases). It is worth to emphasize that this transitional phase inversion is only induced by the proton concentration variation in aqueous phase, and not changes with bulk electrolyte. This conclusion was checked by making emulsions which were homogenised with a pH 6 aqueous phase of 0.01 mol/L and 10^{-6} mol/L NaCl (see Appendix 4-1). Only w/o emulsion droplets were generated in those situations.

From the observation of emulsion vessels, w/o droplets are at the bottom of the vials with a clean oil layer on top, while o/w drops cream on top of a transparent water phase suggesting that sedimentation and creaming had been undertaking as function of time (Figure 4-10). From fluorescent microscope images it is also qualitatively evident (Figure 4-11 c and d), that the oil droplets are much smaller at pH 2 than their w/o emulsion droplets at pH6, a typical behaviour found in emulsion phase inversion phenomena(Binks et al., 2010; Binks and Lumsdon, 2000b; Binks and Lumsdon, 2000a; Binks et al., 2005b).

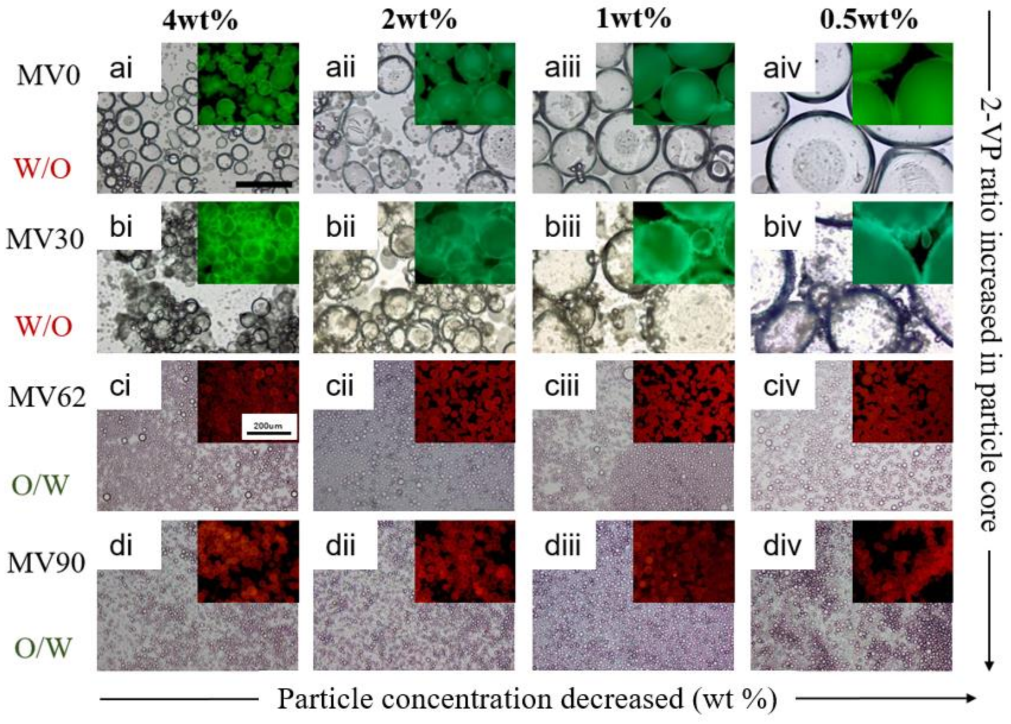

Figure 4-11. Optical microscope images of emulsion droplets stabilised with i) 4wt%; ii) 2wt%; iii) 1wt% and iv) 0.5wt% of a). MV0; b). MV30; c) MV62 and d). MV90 at pH 2 (scale bar 500 μm for all; ci to div and di to div fluorescent images scale bar 200 μm).

2-Vinylpyridine is a derivative of pyridine, with second –position substitution of the vinyl group. This structure induces the nitrogen on the pyridine ring to lose an electron in acidic environments, so that its deprotonation occurs at basic conditions and vice versa. Polymerized 2-VP has a pK_a around 4.7 (Fujii et al., 2010). Below its pK_a, p2-VP should be protonated and becoming water soluble. This pH responsive ability induces its polymeric particle to stabilise w/o or o/w interfaces. However, the particle only appears to be charged under pH 3 in our case (note; other emulsion tests at pH 3-4, only gave w/o types, similar to pH 6). This shift of p-2-VP contained particles is probably due to the participation of MMA and the oil-dispersed core-shell conformations. In Binks' work, the proton induced transitional phase inversion pH point (around pH 10) of the aqueous phase also had a shift comparing to the pK_a of carboxylic acid (4.8) in bulk(Binks and Rodrigues, 2005d). They explained this case was due to higher difficulty that the acid dissociation occurred on surface of particles rather than in bulk solutions, due to the generation of a particle surface potential. The pK_a shifting, here, can also be the aspect of particle conformation. Instead of a surface responsive particle, PDMS polymer chains do not bring the extra surface potential of oil-dispersed particles at the interface. However, higher reactivity ratio of 2-VP than MMA may lead to a more highly p2-VP contained centre and p(2-VP-MMA) shell in the particle core, which would further hinder proton interaction with the pyridine groups. Protonation of a weak basic group in such particle cores will therefore only be completed at decreased pH values in the aqueous phase, relative to that of a weak base in solution. On the other hand, the lower contact area of oil-dispersed particles in the water phase, when adsorbed at the oil- water interface, may decrease the chance of full protonation. The likely collapse of the PDMS polymer chains on the particle surface, at the water side (due to it being an unfavourable environment for the hydrophobic polymer) might further build-up a barrier that slows proton diffusion into particle cores, which would therefore require higher proton concentration in bulk.

In the MV30 stabilised emulsion systems at pH 2, the micrographs evidenced that droplets overlapped and connected with each other into small clusters indicating the possibility of particle bridging (Horozov and Binks, 2006) . When the particles charged at pH2, they became more hydrophilic, altering their contact angle and reducing the stability of the w/o droplets, leading to the observed clustering. Nonetheless, they were still water globule clusters surrounding by dodecane (w/o) according to relatively less content of 2-VP in particle cores, which wouldn't be able to stabilise a reversed curved interface. With increased 2-VP content in the particle core, charged MV 62 and MV 90 possess the ability to stabilise the oil-water interface by employing the phase they initially dispersed in as emulsion dispersed phase, which is known as anti-finkle rule (Destribats et al., 2011b; Golemanov et al., 2006). The comparatively constant droplets diameter regardless of particle concentration change can also imply this special emulsion stabilization mechanism.

Specific droplet sizes for all the systems were quantified by Image J, and concentration trends are shown in Figure 4-12. Water in oil emulsion droplets stabilised at pH 6, all presented a decrease trend of their mean droplets diameter while particle concentration increased. This change induced a less rapid sedimentation of emulsion droplets stabilised with higher particle concentrations in each case. In the MV0 case, there is no obvious evidence of mean droplet size differences between pH 2 and 6 at all particle concentrations (Figure 4-12). It implies that the wettability of MV0 particle which contains pure pMMA in the core cannot be changed by just varying pH in the aqueous bulk phase. The other cases all demonstrate a conspicuous variation of their average droplet diameters. This is due to the stability and type of their emulsion changing as the pH of their bulk phase is lowered.

MV30 stabilised w/o emulsions flocculated at pH 2. Alongside this phenomenon, the mean droplets diameter appears slightly decreased, but with significant standard deviation, which reveals the dramatic polydispersity in size when droplets become aggregated. Instead of individual particle stabilised droplets, the particles themselves appeared to be aggregated, which adsorbed collectively at the interface to maintain the shape and stability of emulsion. These changes can explain the extreme polydispersity with a broad range of emulsion droplets size in this case.

For the MV62 and MV90 systems, with higher 2-VP content, where phase inversion occurred from w/o to o/w, the droplet sizes dramatically reduce to around 20-30 µm, with comparatively little variation of their size in same system. This is a big difference comparing to pH 6‘s hundreds micron size. Besides this, there is not any dramatic difference of droplets diameter in each concentration between MV62 and MV90 particles system at pH 2. Due to their smaller size, the tiny droplets of pH 2 o/w emulsion creamed much slower than the sedimentation speed of their w/o emulsions at pH 6 (see Appendix 4-2). From here, a summary can be made that charged particles can stabilise relatively higher surface area o/w emulsion systems than w/o emulsions stabilised by their uncharged version. It perhaps surprising also that the emulsion droplets diameter of o/w with both MV 62 and MV 90 system seem don’t show a significant reduction as their particle concentrations are varied, and likely indicates a stability limit is being approached.

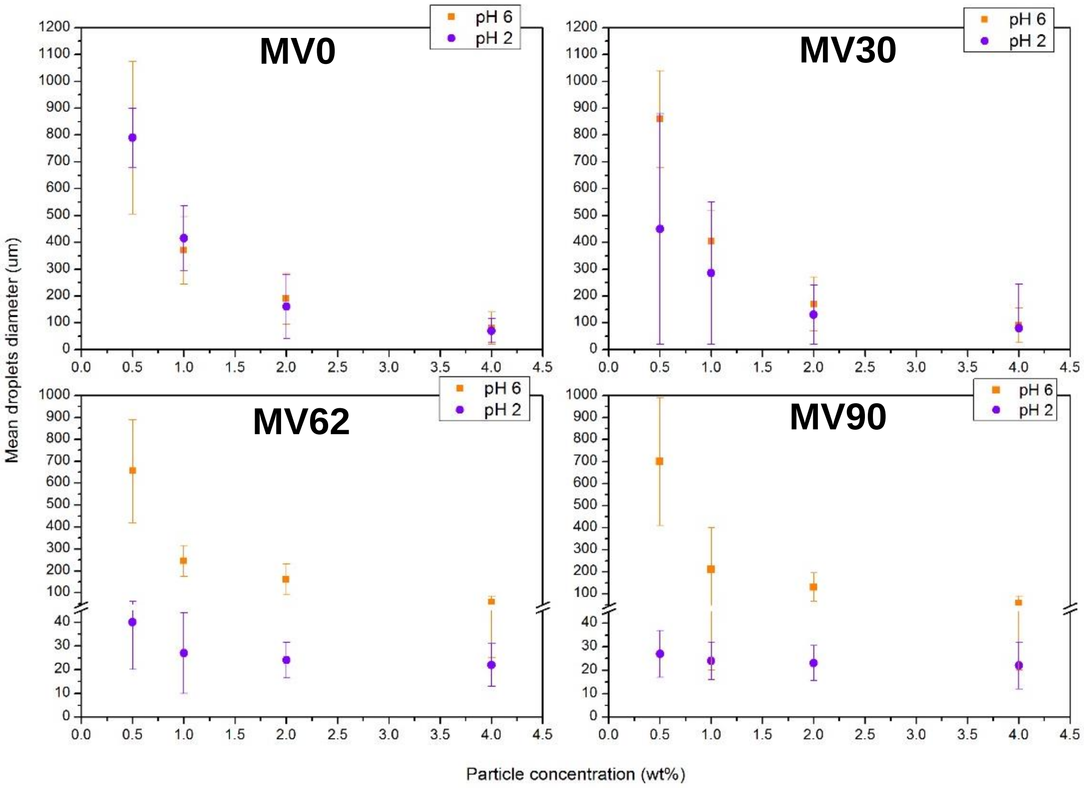

Figure 4-12. Mean droplets diameter vs. Particle concentration at both pH 2 and pH 6 with MV0, MV30, MV62 and MV90 particles (Estimated over 200 droplets from microscope image in each condition by Image J).

b). Emulsion performance by changing pH in vial

Using water–dispersed pH-responsive latex particles or microgel particles as Pickering emulsifiers has been well studied in the past (Ngai et al., 2006; Ngai et al., 2005). Thus, their pH – responsive ability can be investigated directly of hydrodynamic diameter and zeta potential variation according to pH change in water by dynamic light scattering. In other words, the responsiveness of those particles can be confirmed in bulk dispersion studies, even before they were as Pickering emulsifiers. Unfortunately, it is not the case for any our oil-dispersed particles. It is hard to test particle pH-responsiveness, due to the simple fact that they are dispersed initially in a non-polar non-aqueous solvent. Hence, in an attempt to better understand their pH responsive ability at an interface, a series of studies were completed by changing the in-vial environment of pre-formed o/w emulsions. The performance of emulsions, droplet size and stability were all taken into consideration.

Figure 4-13 (A) shows the process and emulsion vials of how pH change was affected in pre-formed emulsion environments. Initially, o/w emulsions were prepared in advance at pH 2 with 1 wt% MV90 particle suspensions. The emulsion samples then had same amount of concentrated pH 2 HCl and pH 12 NaOH solution separately added in each vial following with a gentle shake. Enough NaOH solution was added to alter the bulk pH to ~6 (while the vials with pH 2 HCl solution added were only in effect diluted). Note; the yellow colour in the pH 6 case is simply due to the addition of water soluble dye that was used as a tracer to confirm emulsion type.

From the appearance of emulsion vials at the bottom of Figure 4-13section A, the dense yellow milky part is the emulsion phase, which is creamed in both pH cases (indicating continued o/w emulsion types). However, the volume of the emulsion with environmental conditions altered to pH 6 is clearly reduced significantly, which suggests that t if the aqueous environment of such emulsions is neutralized by NaOH solution into pH 6, demulsification occurs rapidly with a gentle shake. Microscope images demonstrated the droplets size increased after added base into the system, which is evidence of the o/w emulsion droplets coalescencing (Figure 4-13 B). In our case, the demulsification happened immediately, indicating and extremely fast process of coalescence and final burst. MV90 particle owns an instant response to environmental trigger. On the other hand, a robust adsorption of charged MV90 particles at interface can be investigated on no oil-release in diluted and shaken o/w emulsion sample.

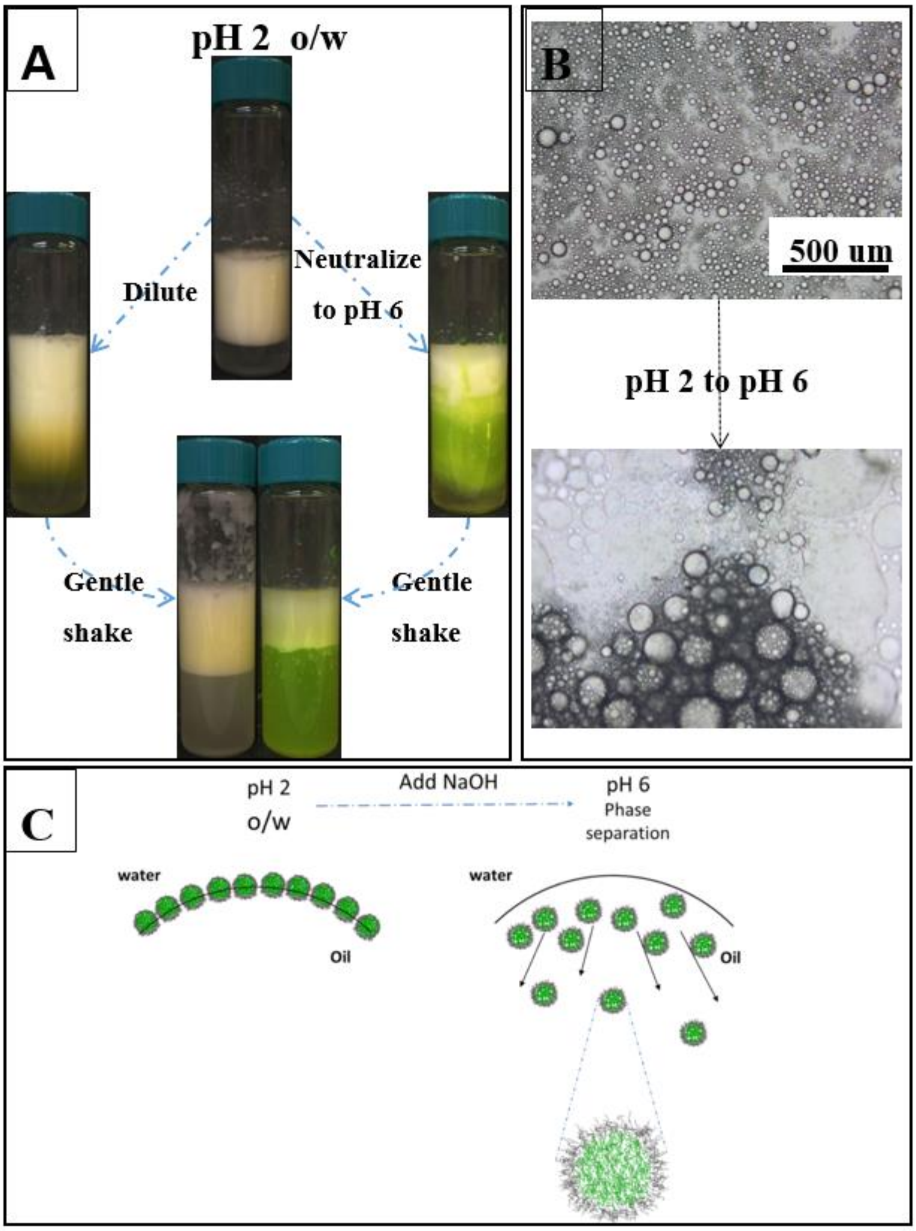

Figure 4-13 Digital photograghs of (A) demulsification or dilution of preformed o/w emulsion by 1wt% MV90 particles at pH 2 by adding same amount of 0.01M HCl and 0.01M NaOH, and (B) optical microscope images of o/w emulsion droplets and coalescence by adding tiny drop of 0.01M NaOH on sample. (C) Schematic representation of demulsification process on oil-dispersed pH responsive particles.

Initially, MV90 particles were synthesized and dispersed in dodecane with the help of particle stabilisers. PDMS has good solubility in dodecane which is the key content to keep particles in oil. Base on this, charged MV90 particles deprotonated by added NaOH which induce the contact angle shift at interface. Coalescence occurred from that. As mentioned above, MV90 particles prefer to disperse in oil or aggregate instead of adsorb at interface at pH 6. Coalesced droplet, finally, break down owing to the detachment of deprotonated MV90 particles. In consequence, particles re-disperse in dodecane Figure 4-13 C. This can explain the white turbid phase after demulsification in Figure 4-13 A.

4.3.1.3 Particle interfacial monolayers observed with cryo-SEM

In the previous sections, it was clear there were significant differences to the mechanics of particle stability, as water phase pH changes from low pH to high. What was not defined however, was whether particles deformed, in a similar way to many microgel particles, when pH is changed at an interface (Destribats et al., 2011a; Richtering, 2012); and to what extent particle contact angles may have shifted in response to the pH environment trigger. To answer these questions, prepared emulsion droplets in different conditions were investigated under cryo-status by Scanning Electron Microscopy (SEM)

Water in dodecane and dodecane in water emulsion droplets (50 % oil volume fraction) with pH 6 and pH 2, respectively, were prepared by with such oil-dispersed pH responsive particle (2 wt%) as emulsifiers. Typical freeze-fracture SEM images of w/o and o/w emulsion droplets with MV62 particle stabilised surface are shown in Figure 4-14. At pH 6 (ai and aii) the oil drops appear completely/ densely covered with a monolayer of the apparently spherical oil-dispersed particles, reflecting the robust stabilisation of w/o emulsion droplets by uncharged MV62 particles at oil-water interface.

Moving from the top images to the bottom line (bi and bii) in Figure 4-14, when the o/w droplets were prepared at pH 2, the packed spherical particle monolayer has been replaced by deformed and randomly adsorbed protonated particles. Appendix 4-3 also illustrate the residual MV62 particles at curved surface of water phase, which an oil globule has been removed. The residual MV62 particles are not spherical anymore appearing a flattened state at pH 2. As known, the deformability of responsive particle by environmental triggers were, mostly, discovered and studied in water-dispersed temperature-sensitive pNIPAM microgel system (Destribats et al., 2013; Destribats et al., 2014; Destribats et al., 2011a; Schmidt et al., 2011). Here, it is the first time to discover the deformation of oil-dispersed pH-responsive co-polymer particles at emulsion drop interface. Besides that, oil-dispersed pH responsive particle shown in Figure 4-14 was flattened uniformly as a “button” instead of “fried-egg” in most literatures. The strength and morphology of deformed microgels were determined by cross-linking density and architecture of particle itself (Schmidt et al., 2011; Destribats et al., 2011a). Thus, the “button” shape deformed oil-dispersed particle, here, is due to its uncross-linked design. It leads to the fact that randomly co-polymerized pMMA-2-VP polymer chains extended efficiently without the constraint by crosslinked structure when they were protonated at pH 2.

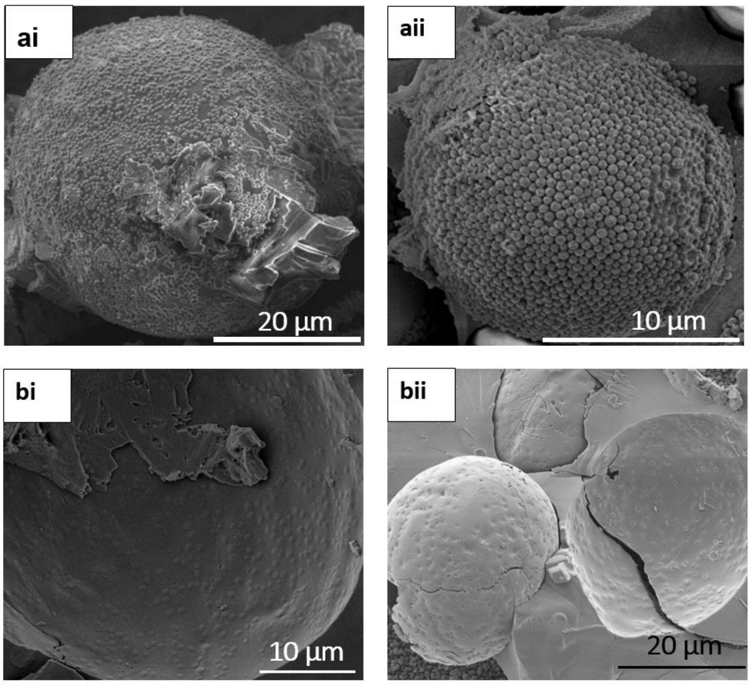

Figure 4-14. Cryo-SEM images of (ai and aii) two water in dodecane drops and (bi and bii) two dodecane in water droplets stabilised by oil dispersed pH responsive particles/microgels (MV62) at pH 6 and 2, respectively. (Scale bar shown on images)

Phase inversion of emulsion droplets from w/o to o/w by just changing pH of aqueous phase was also found in MV90 particle stabilised emulsion system.

Figure 4-15 gives an overall surface view of o/w emulsion droplet stabilised by MV90 at pH 2. The exposed part of droplet surface which was fractured (underneath an ice layer that covers the interface) by sampling process, shows the nearly- hexagonal packed spherical particles and particle pits (where it is assumed particles have been removed with the ice layer in the fracturing process). Apparently, particles are spherical when they were charged to stabilise o/w emulsion droplet in MV90 case differing from MV62. The initial monomer ratio of co-polymerized oil-dispersed responsive particles which gave varied architecture, can affect their deformability when polymers are protonated at droplet interface.

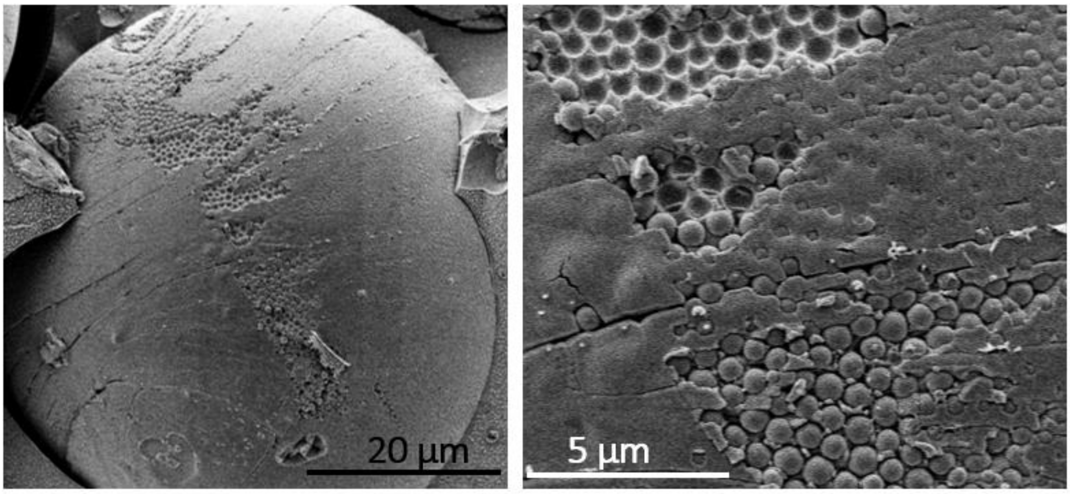

Figure 4-15. Cryo-SEM of a dodecane in water droplet stabilised by oil-dispersed pH responsive particles (10:90 (MMA-2-VP)-PDMS) at pH 2 (ai-ii) (Scale bar as shown on images);

Comparing with cryo-SEM image of w/o emulsion droplet in supporting information, these Cryo-SEM images appear to confirm the phase inversion of w/o to o/w is mainly due to the contact angle change of un-deformed responsive particles (MV90 case). As mentioned above, the thin layer of ice covered particles on the surface is due to water that has crystallised between the particles in the capillaries between them. The real interface is below the ice layer, and the particles are bigger than the pits (yellow circle in Figure 4-16. Due to the number of exposed particle 'pits', it was possible to extract some contact angle information from these images, although only in a relatively limited way. Figure 4-16 shows the method of how we calculated such particle contact angles, assuming an ideal flat interface according to the residual particle pits observed by cryo-SEM. The contact angle θ of MV90 at pH 2 was estimated as:

$$\theta = 90° - \theta_\alpha$$

Where θ_α and a right angle is the opposite angle representing for the value of particle contact angle. θ_α can be calculated by actual particle diameter and the diameter of particle pits. So the equation can be sorted as:

$$\theta = 90° - sin^{-1}\frac{d_p}{D_p}$$

Where D_p is the mean diameter of particles; d_p is the diameter of particle pit. The mean particle diameter of MV90 is $680 \pm 80\ nm$. The diameter of particle pits is measured between biggest (746 nm) and smallest (369 nm) in Figure 4-16. The approximately contact angle range according to the calculation is from $11°\ to\ 61°$. Charged particle became more hydrophilic at oil-water interface due to the estimated contact angle. At the same time, such particles protruded differently at droplet interface. This can be linked to the fact that randomly polymerized MMA and 2-VP built up varied core architecture. During the investigation under SEM, we didn’t find any evidence showing that charged MV90 particles can disperse in water phase. This is different from the findings of charged p2-VP-pDMS particles’ behaviour at liquid marble interface (air-water) in Fujii etcs’ work (Fujii et al., 2010).

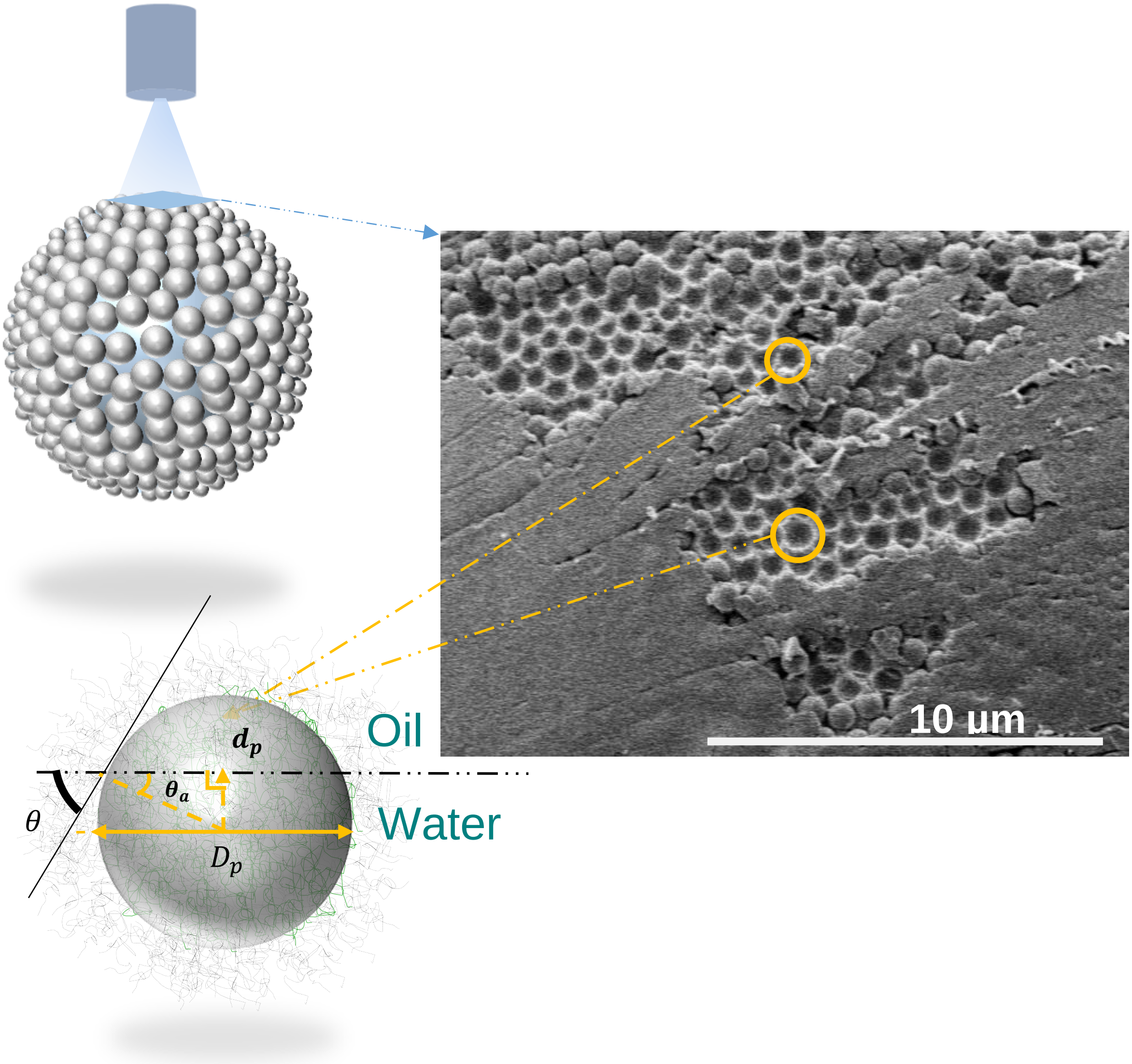

Figure 4-16. Schematic graph of how to estimate the particle contact angle range from cryo-SEM images. θ is the contact angle of particle. θ_α is the required angle to determine θ with a right angle next to it.

In summary, w/o emulsion can be stabilised under pH 6 with all four batches of oil-dispersed particles regardless of the co-monomer contents in cores. At pH 2, oil-dispersed particles which cores consisted of p2-VP can be charged leading to the stabilisation of varied types and status of emulsions. Flocculated w/o droplets can be stabilised by MV30 at charged. Emulsion phase inversion from w/o to o/w can be investigated by only changing pH in aqueous phase with MV62 and MV90 stabilised emulsion systems. This phenomenon also resulted in a sharp variation of mean droplets diameters. In general, increased particle concentration led to an apparent decreased mean droplets diameter of w/o emulsion systems. But, it is not really obvious in o/w emulsion systems, which imply different interfacial behaviours of charged MV62 and MV90 particles at interface. Instant demulsification was also discovered in MV90 stabilised o/w emulsions by neutralizing the system in vial which indicate the pH induced desorption of such particle from oil-water interface. Finally, two different interfacial stabilising behaviour have been demonstrated by cryo-SEM of MV62 and MV90 stabilised emulsion systems. The inversion of MV90 stabilised emulsion system by pH was supposed to be the shifting of contact angle at interface. However, the deformation of MV62 under pH 2 at interface played an important role to stabilise o/w droplets in this case. It is necessary to emphasize, here, that it is the first time that transitional emulsion phase inversion is reported by only changing the pH in aqueous phase of a sole particle stabilised emulsion system and the particles are dispersed in oil. And charged MV62 particle deformed at interface which is also the very initial case to demonstrate the deformation of oil-dispersed pH responsive core-shell Pickering emulsifiers.

4.3.2 Emulsion stabilised by oil-dispersed 10:90 p(2-VP-MMA) particles with varied cross-linking density

From previous emulsion study, transitional phase inversion from w/o (pH 6) to o/w (pH 2) were only induced with higher p2-VP contained particles by pH change in aqueous phase. Empirically, p2-VP polymer has a pK$_a$ at 4.7(Fujii et al., 2010). Our oil-dispersed p(2-VP-MMA) co-polymeric particles were charged at pH 2, which presents a shift of the pK$_a$ may due to the configuration of the core-shell particles. However, charged polymer chains from particle cores may potentially dissolve at pH 2 in aqueous phase. Since that, the other range of cross-linked particles were synthesized (see chapter 4). This range of particle are dispersing in dodecane with fixed initial input ratio of MMA and 2-VP (10:90) but varying the initial cross-linker density (DVB) within particle cores.

In this part of work, Pickering emulsions are stabilised such range of cross-linked particle with systematically increased particle concentration at pH 6 and pH 2. The similarity and differences of emulsion types, stability, droplets diameters and potential particle interfacial behaviours are demonstrated to compare and discuss with uncross-linked particle stabilised emulsion systems and within emulsion stabilised by particle containing varied cross-linking densities.

Firstly, MV90 with varied cross-linking densities (0.5mol%, 1mol%, 2.5mol% and 5mol% of DVB) were diluted into four concentrations (4wt%, 2wt%, 1wt% and 0.5wt%) to prepare emulsions at both pH 6 and pH 2. The freshly prepared emulsions under such conditions are shown in Appendix 4-4. Figure 4-17 shows same emulsions had been stored after 24 hours. From appearances, emulsion sedimented to the bottom after 24 hours in upper line while emulsion creamed to the top in lower line. The phase separation can be investigated in emulsion stabilised by MV90-0.5mol% and mv90-1mol% with lower particle concentrations at pH 6. Same systems which stabilised by higher particle concentrations illustrate the similar “foam-like” emulsion in accordance with the uncross-linked MV90 stabilised emulsion system in Figure 4-7. The foam-like emulsion phenomenon disappeared in higher cross-linked particle stabilised emulsion systems. Obvious oil release can also be found in MV90-0.5mol% stabilised emulsion system with 0.5wt% particle concentration at pH 2. Except this case, all emulsions formed with any concentrations and particles are fairly stable in terms of oil release.

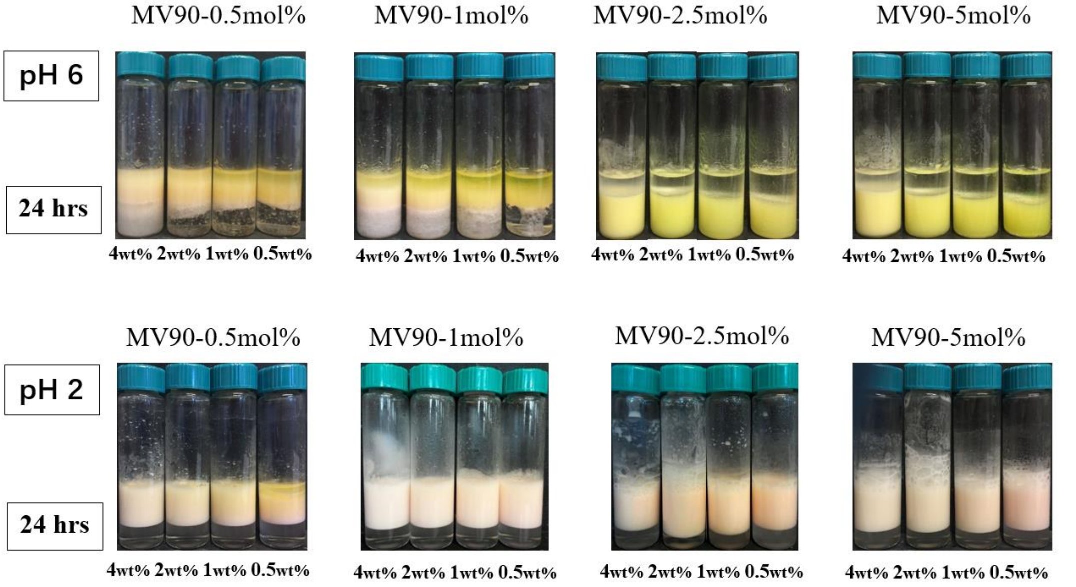

Figure 4-17. Appearances of sample vials containing emulsion droplets stabilised by varied concentration of cross-linking MV90-0.5mol%, mv90-1mol%, MV90-2.5mol% and MV90-5mol% particles at pH 6 (upper line) and pH 2 (lower line) after waiting for 24 hours.

W/o emulsion were stabilised at pH 6 with all cross-linked MV90 particles regardless of the variation of particle concentrations according to the drop test and florescent optical microscope investigations (Figure 4-18). Undoubtedly, emulsion type inversed to o/w by only switching pH in aqueous phase from 6 to 2 in all cases with an observed sharp decrease of droplet size in Figure 4-19. The positions of emulsions in sample vials can also indicate such transitional phase inversion of emulsion types, which are gave rise to the sedimentation of water globules to the bottom while that oil drop creamed Figure 4-17. In MV90-1mol% case, no emulsion stabilised with 0.5wt% particles can be handled to be observed under microscope. This may be due to either the droplets are too big or the emulsions are too unstable to bear the gentle force from the pipettes.

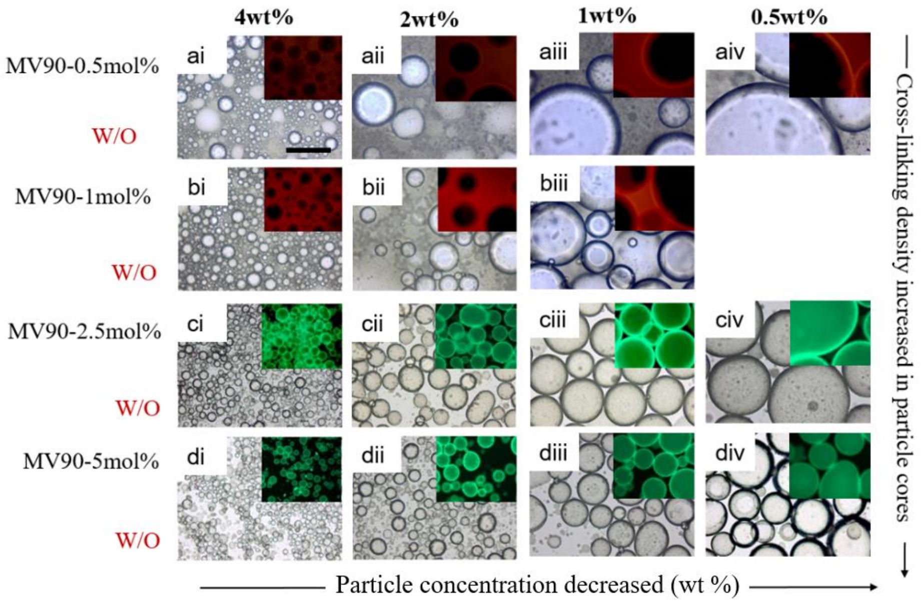

Figure 4-18. Optical microscope images of emulsion droplets stabilised with i). 4wt%; ii). 2wt%; iii). 1wt% and iv). 0.5wt% of MV90 a). 0.5 mol%; b). 1mol%; c). 2.5 mol% and d). 5 mol% cross-linked particles at pH 6 (scale bar 500 µm for all)

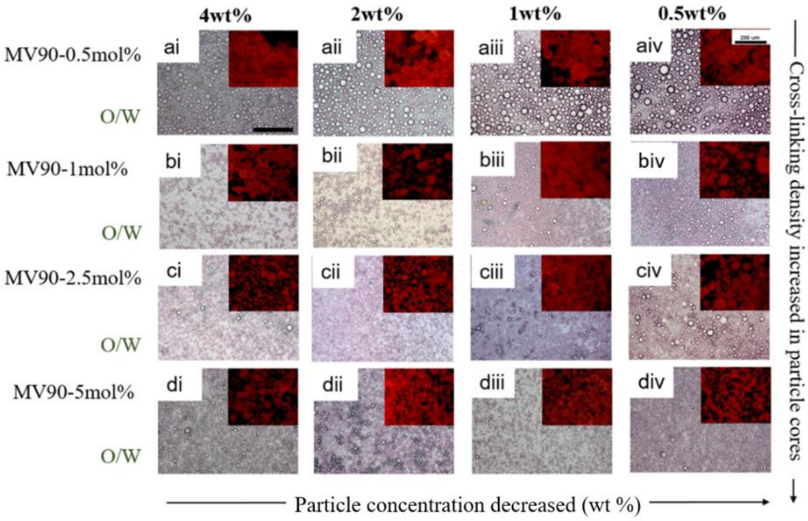

Figure 4-19. Optical microscope images of emulsion droplets stabilised with i). 4wt%; ii). 2wt%; iii). 1wt% and iv). 0.5wt% of MV90 a). 0.5 mol%; b). 1mol%; c). 2.5 mol% and d). 5 mol% cross-linked particles at pH 2 (scale bar 500 µm for all; scale bar 200 µm for fluorescent images)

W/o emulsion stabilised by cross-linked oil-dispersed core-shell particles has an increase of droplet size with decreased particle concentrations observed under microscope immediately (Figure 4-18). However, in Figure 4-19 inversed o/w emulsions seem don’t show the trend of droplet size as function of particle concentrations, which is in accordance with uncross-linked particle stabilised o/w emulsion system (Figure 4-12). The two observations under microscope can also be convinced by the mean droplet size estimation data in Figure 4-20. Furthermore, w/o emulsion droplet were getting smaller with each concentration while the crosslinking density increased in particle cores both, according to the microscopy image and mean droplet size estimation (Figure 4-18and Figure 4-20). MV90-0.5mol% stabilised relatively larger o/w droplets than other cases at pH 2. Except this, the crosslinking density in charged particle cores at pH 2 don’t affect the o/w droplet size as well as the o/w emulsion stability in terms of creaming and coalescence (Appendix 4-4). The influence of cross-linking density in cores were acting on the stability of w/o emulsions in terms of sedimentation and coalescence at pH 6. Overall, highly cross-linked particles can stabilise smaller droplets leading to higher stability of w/o emulsion in our case. Especially, there is no evidence of oil release from o/w emulsion with any particle concentrations of highest cross-linked MV90-5mol% system only even after 11 months (Figure 4-21).

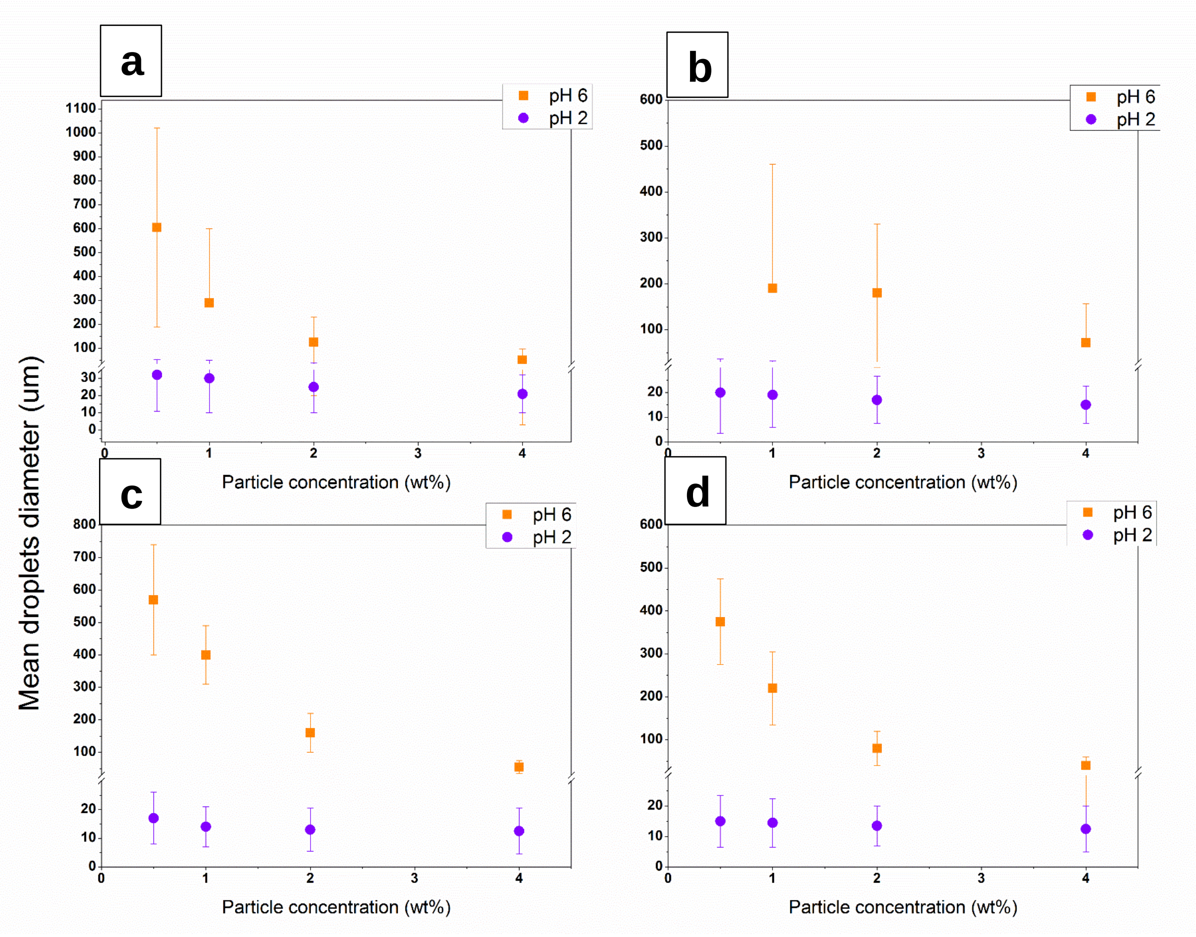

Figure 4-20. Mean droplets diameter of emulsion stabilised by a) MV90-0.5mol%; b) MV90-1mol%; c) MV90-2.5mol%; d) MV90-5mol% with 1:1 oil-water ratio at pH 2 and 6.

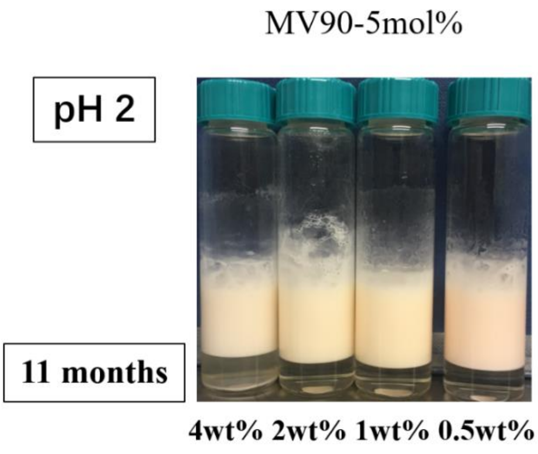

Figure 4-21 Appearances of emulsion vials contains emulsion stabilised by MV90-5mol% with varied concentrations at pH 2 and stored over 11 months since prepared.

The transitional inversion of particle-stabilised emulsion from w/o to o/w were observed by only changing pH in aqueous phase with oil-dispersed uncross-linked higher p2-VP contained core-shell particles. It has been discussed detailedly in former section. Either the shifting of particle contact angle at interface or the deformation of particle configuration upon pH change is in charge of the phase inversion phenomenon. Both the possibilities can be concluded as the variation of particle affinity to oil/water when the p2-VP is charged in cores. This is the reason why phase inversion occurred in the system while particle contains higher p2-VP. This also dominates the phase inversion of emulsion stabilised with 90% 2-VP contained cross-linked particle system.

The cross-linking density of such particle systems, undoubtedly, has no influence on emulsion types while the pH change in aqueous phase. Also in previous section, the potential interfacial behaviours of uncross-linked uncharged Pickering emulsifiers and charged particles which induced the inversion of emulsion types (MV62 and MV90) are different from each other. At pH 6, such oil-dispersed polymeric core-shell particles behaved as conventional Pickering emulsifiers having certain contact angle to stabilise curved interface. This is also the case of our cross-linked particles. The foam-like emulsions were also investigated in lower cross-linked particles implying the large particle contact angle and potential 3-D emulsion stabilising mechanisms(Binks and Horozov, 2006). With the increased cross-linking density in particle cores, emulsion was becoming more and more stable with smaller mean droplets diameter. This is supposed to be the contributions of both contact angle changing of particle itself and the variation of particle adsorption kinetics. The hypothesis of these reasons is due to the actual p2-VP content within the particle cores after synthesis and real allocations of DVB while they cross-linked particle cores during the reactions.

O/w emulsion droplets with cross-linked particle systems performed similar in almost evidences with uncross-linked MV62 and MV90 stabilised emulsions by comparing the mean droplets size, influence of particle concentrations and stability as function of time. The very stable o/w emulsions were obtained with MV90-5mol% only indicating the influence of cross-linking density in particle cores. This also can convince the conjecture of varied viscoelasticity dominated particle systems. The potential conclusion of stabilising mechanism, adsorption kinetics and influence of cross-linking density cannot be draw out at this stage. Thus, further study will be shown in following chapters to provide more evidences.

4.4 Conclusion

In this part of work, oil-dispersed polymeric particle with varied core content (different ratio of copolymers and cross-linked copolymers) stabilise w/o emulsion droplets at pH with all particle concentrations. Transitional phase inversion induced only by pH changing in aqueous phase of emulsion system stabilised by oil dispersed higher p2-VP contained particles (actual p2-VP ratio equals to 62% and higher) regardless of cross-linking density. This is first and only case of pH induced transitional phase inversion occurred with oil-dispersed core-responsive copolymeric Pickering emulsifiers. This practical phenomenon also proves the pH responsiveness of such particular emulsifiers. Such core-shell pH responsive emulsifier system is also the rare case that pH responsiveness works on non-polar oil based particles. Particles contained lower p2-VP ratio show the pH-dependence of emulsions. Flocculated w/o emulsion droplets have been discovered by switching water phase from pH 6 to pH 2 of MV30 stabilised emulsion system.

W/o emulsion droplets under pH 6 have an increase of mean droplet size diameter with decreased particle concentrations in all particle stabilised emulsion cases. The p2-VP ratio in particle cores has a moderate decrease of average droplet size at pH 6 except MV90. MV90 stabilised system implies a different 3-D network of emulsion stabilization mechanism. However, the increased cross-linking in particle cores improved emulsion stability showing as the decreased mean droplet size and the appearance of flowable spherical w/o drops. All of the evidences suggest the varied emulsion stabilisation mechanisms are dominated by p2-VP ratio and cross-linking density in particle cores even at uncharged states. Furthermore, mean droplet size of inversed o/w emulsion kept more or less constant regardless of particle concentrations, core content and cross-linking density. This implies a different particle stabilisation behaviours comparing to w/o system. With the data of Cryo-SEM, deformation of charged particle and contact angle shifting explain the possibility of particle interfacial behaviours when stabilise inversed o/w droplets. This only can adapt to MV62 and MV90 systems. It is also worth to highlight the fact that the deformation of core-responsive particles is firstly discovered on dodecane-dispersed pH responsive particular emulsifier system, here. But, the potential interfacial particle behaviour and emulsion stabilisation mechanism are only based on hypothesis which will be discussed further in following chapters.

Finally, this chapter is relied on the successful synthesis and characterisation of designed particle suspensions from chapter 4 to understand their interfacial behaviour on emulsion droplets as well as the proof of pH responsiveness at interface. During those investigations, lots of surprising and interesting phenomena were found. To further understand particles’ interfacial interactions, several typical particle examples are selected to carry on further emulsion behaviour investigations in next chapter.

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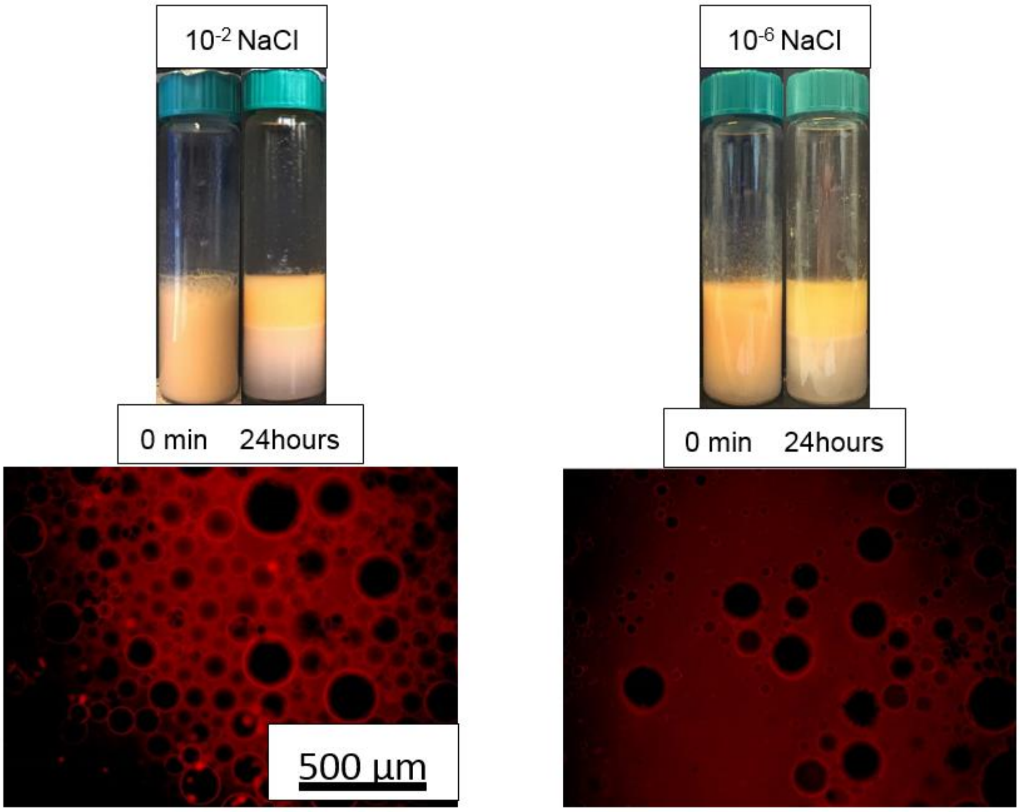
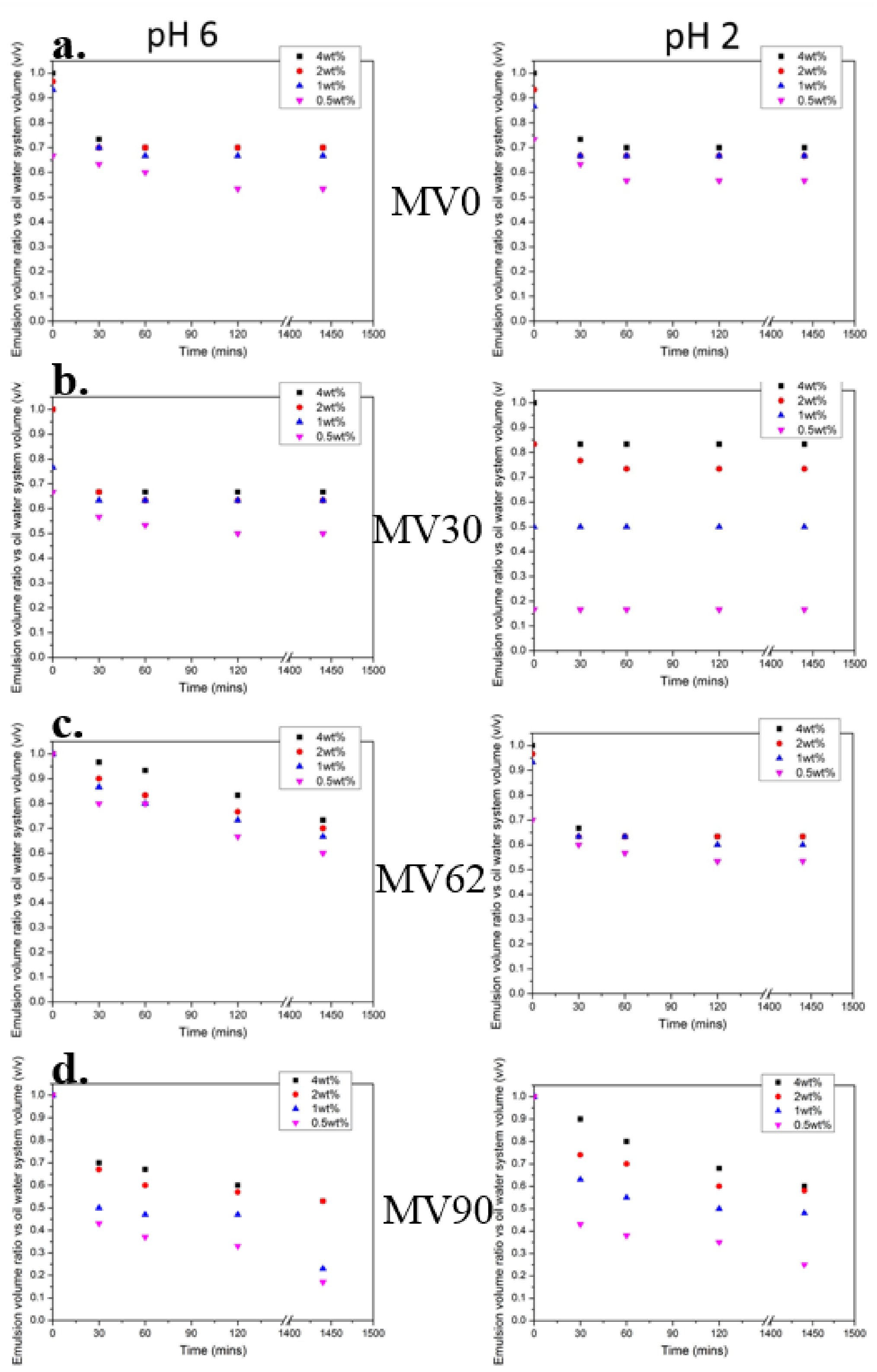
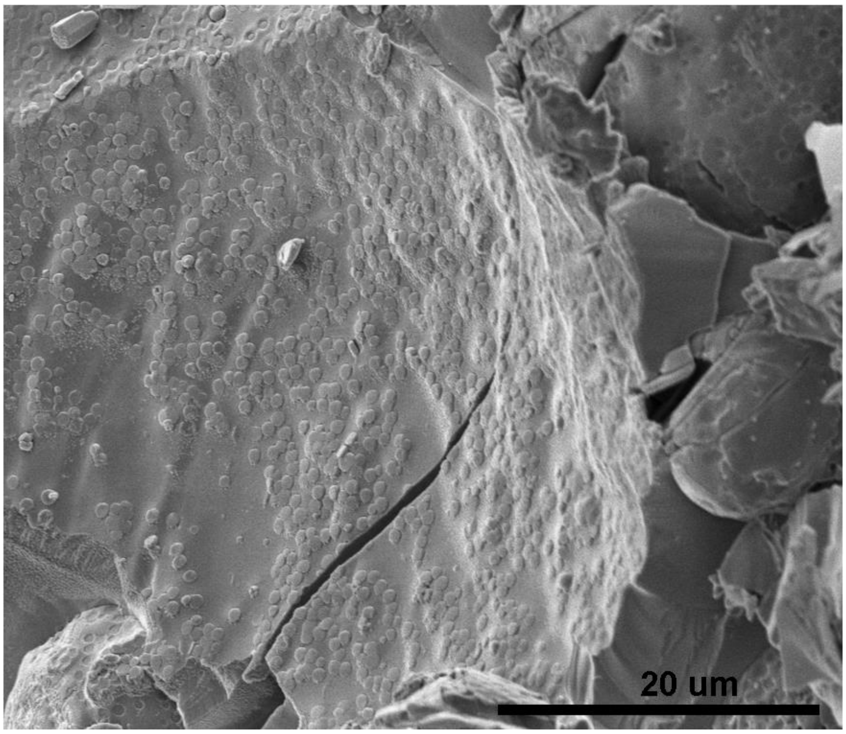
Appendix



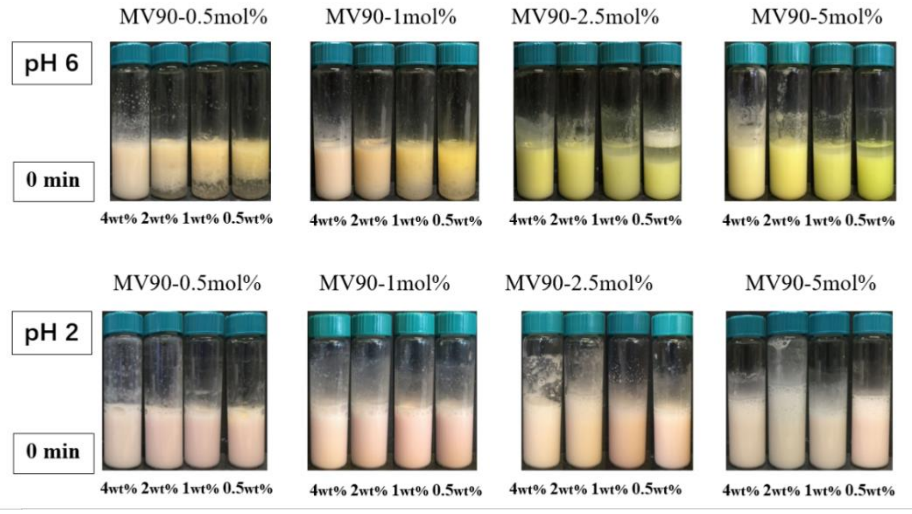
Appendix 4-1: The appearance of emulsion vials and fluorescent optical microscope images of emulsion stabilised with 2wt% 10:90 MMA-2-VP particles at pH 6 but with a). 0.01 mol/L NaCl solution (electrolyte concentration equal to pH 2 HCl solution); b). 10^{-6} mol/L NaCl solution (electrolyte concentration equal to pH 6 aqueous solution)



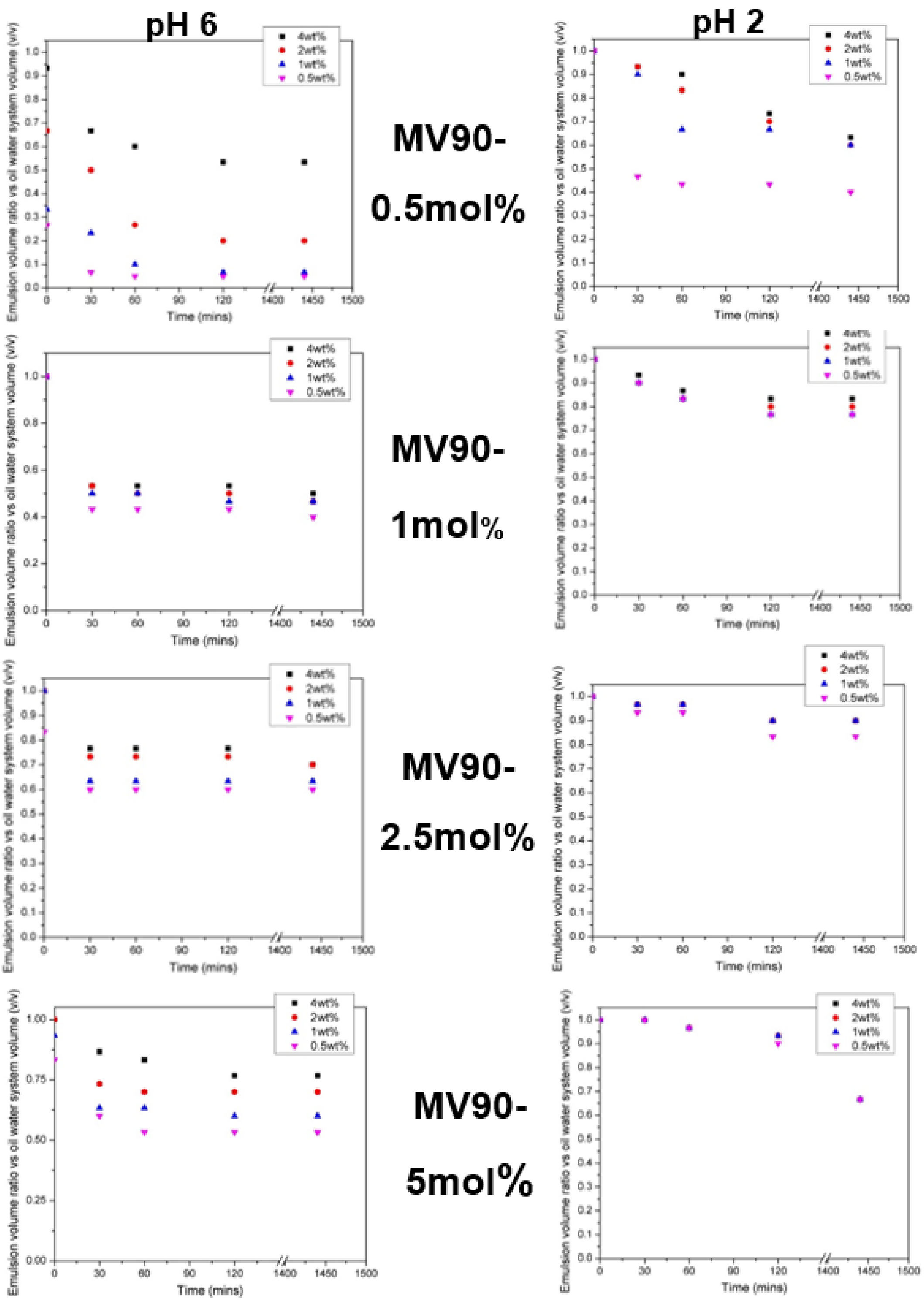
Appendix 4-2: Systematically changed particle concentration stabilised emulsion volume change as function of time at both pH 6 and pH 2; Emulsion were stabilised by a). MV0; b). MV30; c). MV62; d). MV90



Appendix 4-3: Cryo-SEM of 2wt% residual MV62 particle at curved oil-water interface while droplet has been removed at pH 2. Note, the residual particles are not spherical any more.



Appendix 4-4 Appearances of sample vials containing emulsion droplets stabilised by varied concentration of cross-linking MV90-0.5mol%, mv90-1mol%, MV90-2.5mol% and MV90-5mol% particles at pH 6 (upper line) and pH 2 (lower line) after just prepared.



Appendix 4-5 : Systematically changed particle concentration stabilised emulsion volume change as function of time at both pH 6 and pH 2; Emulsion were stabilised by a). MV90-0.5mol%; b). MV90-1mol%; c). MV90-2.5mol%; d). MV90-5mol%

Chapter 5. Performance of dodecane dispersed particles responsive polymer particles as Pickering emulsifiers: the effect of oil-water volume ratio and pH

5.1 Introduction

The transitional phase inversion of Pickering emulsions from w/o to o/w induced only by pH has been reported in chapter 5 when the oil-dispersed pH responsive core-shell particles were used as emulsifiers. It was demonstrated that Pickering emulsion types can be easily inverted from w/o to o/w by switching pH of aqueous phase from 6 to 2. However, this transition occurred on the emulsions stabilised with particles of high vinyl pyridine content only (MV62 and MV90). Additionally, MV30 particles showed pH-dependent behaviours in controlling emulsion stability. From the work in chapter 5, the Pickering emulsion properties were influenced by the composition and configuration of such oil-dispersed particles. However, experiments in the previous chapter were conducted using a 1:1 oil-water volume ratio. However, several studies in the literature have demonstrated the possibility of inverting emulsions stabilised by colloidal particles when varying the oil to water ratio (Aveyard et al., 2003; Binks and Lumsdon, 2000; Binks and Horozov, 2006).

For example, Binks et al. reported Pickering emulsions with varied water content by using both hydrophobic and hydrophilic silica particle emulsifiers(Binks and Lumsdon, 2000). Catastrophic phase inversion from w/o to o/w droplets was observed in the case of hydrophobically-modified silica particles as the emulsifiers for 70 vol% initial water fraction. The phase inversion was also accompanied by an increase in the mean droplet diameter (Binks and Horozov, 2006). Inverted o/w droplets creamed quickly but were stable to coalescence. In their study, the authors also observed that o/w emulsions stabilised by hydrophilic silica particles catastrophically inverted, without hysteresis, to w/o at oil fraction of 70vol%. They concluded that dramatic change in emulsion stability and drop diameter can be observed with both types of silica particles through phase inversion with typically an associated increase in emulsion viscosity. However, they didn't clearly evident theoretic support of such inversion, just suggested the influence of hydrophile-lipophile balance on particle stabilised emulsion inversion induced by oil-water volume ratio of the system, which is the key aspect that affect the phase inversion of surfactant stabilised emulsion system(Binks and Lumsdon, 2000).

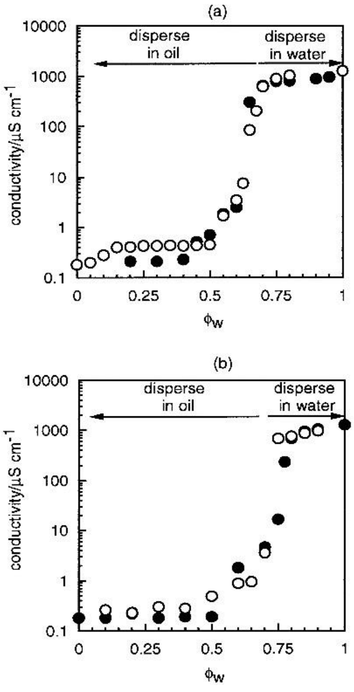


Figure 5-1: Hydrophobic silica particle stabilised emulsion conductivity as function of water volume fraction. (a) 2wt% silica particle of oil phase volume; sequentially adding water to oil (open points) or oil to water (close points). (b)Emulsion prepared in batch; 1wt% particle in emulsion (open points); 2wt% of oil volume (filled points). (taken from (Binks and Lumsdon, 2000))

Very hydrophobic silica or hydrophilic clay particles were also used to investigate phase inversion of Pickering emulsions (Binks and Lumsdon, 2001; Binks and Lumsdon, 2000). Despite these particles efficiently stabilising emulsions, it was shown that neither stabilisers allowed for phase inversion when varying dispersed/continuous phase volume ratios. In addition to investigating the behaviour of inorganic particles, Binks et al. also prepared emulsions with various sizes of polystyrene latex particles (Binks and Lumsdon, 2001). In this work, catastrophic phase inversion of w/o emulsions was again not observed upon increasing dispersed phase volume fraction with flocculation of w/o emulsion droplets occurring at higher water fraction (using cyclohexane as the oil phase).

With emerging interest in tailored responsive polymeric particle systems, such particle systems also showed some interesting phase inversion properties that could be made to be different depending on external parameters. For example, Ngai and co-workers demonstrated catastrophic phase inversion of octanol-water emulsions from o/w to w/o at 60 vol% oil volume fraction using PNIPAM-co-MAA microgels (Ngai et al., 2006). Li et al. reported the preparation of o/w high internal phase emulsions (HIPE) stabilised by 2wt% temperature-sensitive PNIPAM-co-MMA microgel particles with an oil phase volume of up to 90% of the total emulsion volume (Figure 5-2) (Li et al., 2009). The high internal phase emulsions (HIPE) is defined as that more than 74 vol% (Lissant defined as over 70 vol%(Lissant, 1966)) of emulsion is comprised of droplets(Cameron, 2005; Cameron and Sherrington, 1996; Ikem et al., 2008). Surprisingly, such microgel-stabilised HIPE can be stabilised in the presence of as low as 0.05wt% particles with a remarkable stability against coalescence and creaming.

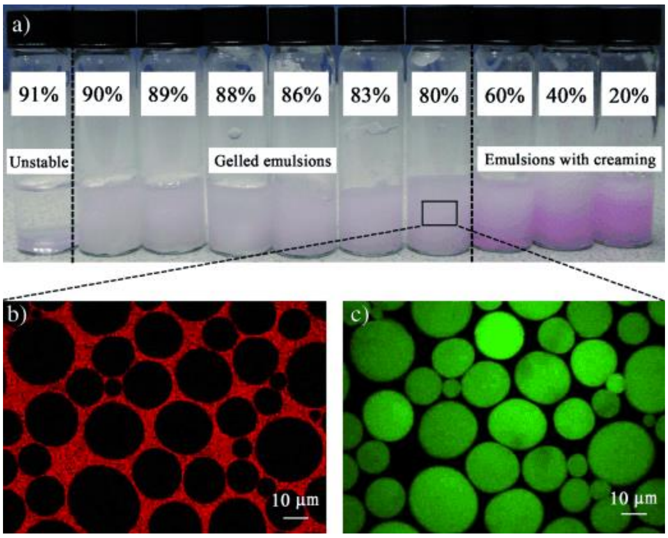


Figure 5-2: a) Appearances of emulsion vessels contained microgel stabilised emulsions with an internal oil phase fraction from 91vol% to 20vol% in presence of 2wt% microgel in pH 6 aqueous phase. b,c) florescent confocal images of emulsion stabilised with 2wt% microgel and 80vol% hexane. (Taken from (Li et al., 2009))

Additionally, Pickering emulsion types can be inverted by changing the oil/water fraction of the system not only from simple w/o or o/w to o/w to w/o but also into multiple emulsions (Binks et al., 2010; Binks and Rodrigues, 2003; Binks and Lumsdon, 2001; Binks and Whitby, 2004). Traditionally, multiple emulsions (o/w/o, w/o/w) are stabilised by particle mixtures to be desired, which indeed require varied types of particle wettability being able to stabilise both w/o and o/w in one system(Ngai and Bon, 2015). Binks and Rodrigues reported that multiple w/o/w emulsions could be inverted from w/o droplets by increased water fraction. The multiple emulsions were formed by pure oil-water system with a single particle stabiliser (hydrophobic silica) (Binks and Rodrigues, 2003) (Figure 5-3). However, authors didn’t draw out the key aspect which induce such stabilisation of multiple emulsions by one type of particle. Such w/o/w emulsions were stable to coalescence but creamed due to the gravity force. This is a novel phenomenon which was firstly reported differing from previous o/w/o and w/o/w multiple emulsions stabilised by particle mixture(Barthel et al., 2010). The stabilisation of such multiple emulsions by single particle type was driven by increased continuous phase volume fraction (Pacek et al., 1994; Groeneweg et al., 1998). On the contrary, multiple emulsion can also be stabilised by single type responsive particular emulsifiers by gradually changing the environmental trigger, like temperature. Binks and co-workers demonstrated the temperature responsive emulsion system which were stabilised by PDMA-b-PMMA sterically stabilised polystyrene latex(Binks et al., 2005a). The effective responsiveness of such latex at interface was govern by temperature leading to a transitional phase inversion from o/w to w/o. W/o/w multiple emulsions with equal initial volume of n-hexane and water phase were observed while temperature increased to 55 degree approaching to inversion point (Figure 5-4). Nevertheless, not many studies manage to obtain multiple emulsions with one particle type.

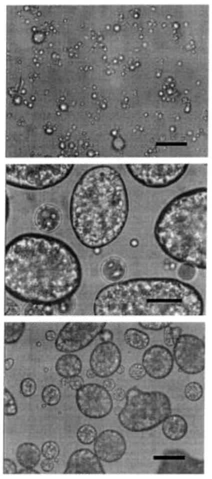


Figure 5-3: Optical microscopy images of emulsions stabilised with oil-dispersed 2wt% silica particles (79.9% SiOH). (upper) w/o of tricaprylin with 60vol% water, scale bar = 50µm; (middle) w/o/w of tricaprylin at 65vol% water fraction, scale bar = 25 µm; (lower) w/o/w of Miglyol 812 with same water fraction of middle one, scale bar is the same as well. (Taken from (Binks and Rodrigues, 2003))

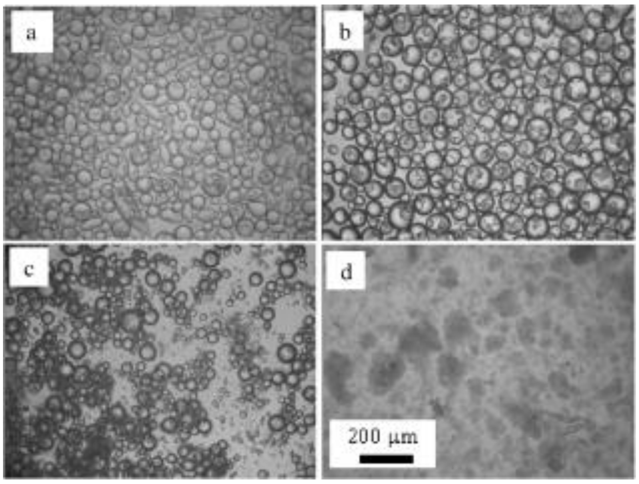


Figure 5-4: Optical microscopy image of emulsions stabilised with 2wt% temperature PS latex of 1:1 hexane and water ratio at a) 25 (o/w), b) 55 (w/o/w), and c) 65 °C (w/o). Also d) 2wt% PS latex at pH 8.1 which was held at 70 °C for 30 min on a microscopy slide. Scale bar = 200 µm of all image. (Taken from (Binks et al., 2005a))

Changing oil-water volume fraction in Pickering emulsions often leads to phase inversion and that in some (rare) cases, one can also obtain multiple emulsions. It is clear from the examples provided above, that the effect of oil-water volume fraction on Pickering emulsion has drawn lots of research attention recently, especially, resulting from catastrophic phase inversion and multiple emulsions (Binks and Rodrigues, 2003; Binks et al., 2010; Binks and Lumsdon, 2000; Sun et al., 2010). The mechanism of such phase inversion and the formation of multiple emulsions are complicated, particularly, in the case of tailored responsive particle/microgel stabilised systems. To better understand both the influence of oil-water volume fraction and environmental triggers on stabilised emulsion properties, it is worthy to present this part of the emulsion study here. Additionally, I intend to clarify the relationship between 2-VP content and cross-linking density in particle cores to stabilised emulsion properties, as well as the key aspect(s) driving the varied interfacial behaviour of particles.

Therefore, to further understand the ability of the synthesised responsive particles in this chapter, the influence of varied initial oil-water volume ratios on the properties of the corresponding Pickering emulsions is investigated. Four batches of dodecane dispersed (PMMA-2-VP)-PDMS core-shell particles were chosen to fabricate emulsions with varied oil-water volume ratios. They are MV30 (lowest 2-VP contained particles), MV90 (highest 2-VP contained particles), MV90-0.5mol% (particles with the lowest cross-linking density) and MV90-5mol% (particle with the highest cross-linking density). The study of MV30 and MV90 particles are subjected to identify the influences of 2-VP content in the particle cores on emulsion properties. However, the effect of cross-linking density is based on the study of emulsions stabilised with MV90-0.5mol% and MV90-5mol% particles. Two particle types in particular were chosen to investigate the influence of cross-linking of the particle cores. All the emulsion studies above in this part of work were focused on the investigation of emulsion properties affected by systematically changing oil-water volume ratios in the presence of two particle concentrations (2 wt% of oil phase volume and 1 wt% of entire system volume).

Initially, MV90 is used to stabilise emulsions with 1:1 water-oil volume ratio under pH 2, 2.5 and 3, respectively. The difference of emulsion types, droplet average diameter and stability are investigated and concluded. Further, emulsions are prepared with varied oil-water volume ratio under pH 2, 2.5 and 3 in presence of two concentrations of MV90 particles. The same study is also carried on emulsions stabilised by MV30 particles. Various emulsion properties upon these experimental conditions of both MV90 and MV30 stabilised systems are aimed to illustrate the influence of particle configurations and charging degree. Finally, Pickering emulsion with increased oil fraction are prepared with the cross-linked MV90-0.5mol% and MV90-5mol% particles at pH 2, 2.5 and 3. The catastrophic phase inversion from one type to another is observed for these particle emulsifiers by both changing oil-water volume ratio and varying pH. The influence of proton concentrations in the aqueous phases are then considered in the cases where the phase inversion is driven by pH changes as well as in the case where multiple emulsions are formed. Eventually, the influence of particle core cross-linking is also investigated.

5.2 Experimental materials and Methodology

5.2.1 Experimental Materials

See Chapter 4 section 4.2.1

5.2.2 Emulsion preparation and properties characterisation

Emulsion preparation and stability characterisation.

The emulsion preparation procedure is generally following the description in Chapter 4 section 4.2.2. However, the oil-water volume ratio is varied (1:9, 3:7, 7:3 and 9:1 Oil : Water) to prepare emulsions in the presence of two different concentrations (2wt% of oil phase volume and 1wt% of entire system) in each sample. As well as that, pH of aqueous phase is adjusted to pH 2, pH 2.5 and pH 3 in this part of work.

5.3 Result and discussion

5.3.1 Effect of pH and oil-water volume ratio

Effect of pH

As discussed in Chapter 4, at condition of pH 6, the MV90 particles form a water/oil emulsion, while at pH 2, the system turns into an oil/water emulsion. In this part of the work, the aqueous phase is varied below pH 3, on preparation of the MV90 stabilised emulsions with an oil-water volume of 1:1, initially (to define more exactly the inversion pH). Additionally, MV90 stabilised emulsions are fabricated under same conditions but in presence of increased oil fractions from 0.3 to 0.7. Finally, another batch of emulsions are prepared with constant quantity of MV90 particles (1 wt% of entire system) but varied oil-water volume ratios. The formation of the emulsions by using the MV90 particles at different pH conditions (pH 2, 2.5 and 3) are investigated in Figure 5-5. In this study, these MV90 particles were diluted to 2wt% (of oil volume), and used as Pickering emulsifiers with a ratio of 1:1 (oil-water) at pH 2 to 3. In the cases of pH=2 and pH=2.5, the resulting emulsions were found to cream after 2 hrs. Phase separation was observed in pH 3 emulsion system after 2hrs.

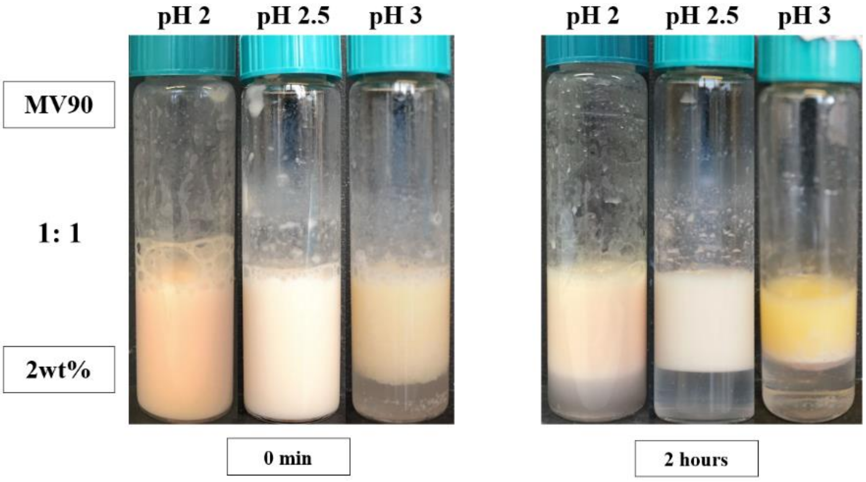


Figure 5-5 Appearance of emulsion stabilised by 2wt% (of oil phase volume) MV90 particles with 1:1 oil-water volume ratio under pH 2, pH 2.5 and pH 3, respectively. Left three vials contained freshly made emulsions, right three samples show the same emulsions after 2 hours.

The phase structure of the resulting emulsions at studied pH conditions (2, 2.5 and 3 respectively) were further explored by optical microscopy (Figure 5-6). Fluorescence optical micrographs (in which dodecane droplets were dyed in red) were also added for comparison purpose. These results clearly demonstrate the formation of oil/water emulsions at pH=2 and pH=2.5, with droplets at pH-2.5 being significantly larger. In contrast, water/oil type emulsion was observed at pH=3. The size of droplets for each system was estimated using the ImageJ software. The calculation showed the droplet size of formed emulsion decreased as tuning the system pH to more acidic condition.

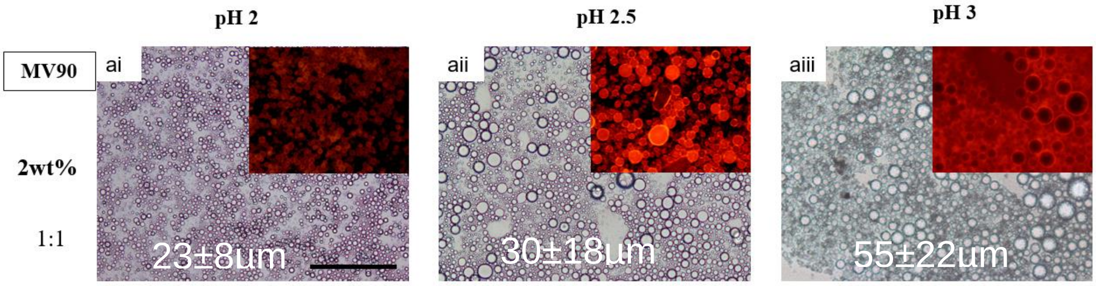


Figure 5-6 Optical microscope images of emulsion droplets stabilised by 2wt% (of oil phase volume) MV90 with a mean droplets diameter estimated by image J of approximately 150 drops, at ai) pH 2; aii) pH 2.5 and aiii) pH 3 (scale bar 500 µm for all)

The stability of emulsions prepared at pH 2, 2.5 and 3 were explored by measuring the changes in the emulsion volume (in terms of the fraction of the remaining emulsion volume against the volume of the entire system) as the function of time (shown in Figure 5-7). The decline in the emulsion volume as time elapsed indicates the instability of all three emulsions prepared at different pH (creaming for pH 2 and 2.5 emulsions and sedimentation for pH 3 emulsion). Compared with pH 2 and 2.5 emulsions, the slope of the decline line for pH 3 emulsion was greater, indicating the occurrence of phase separation in this system. With respect to the pH 2 and 2.5 emulsions, the less changes in the volume against the time indicated their advantages in stability. The consistency in volume declining lines demonstrated they had similar performance in stability which were proved by images shown in Figure 5-5.

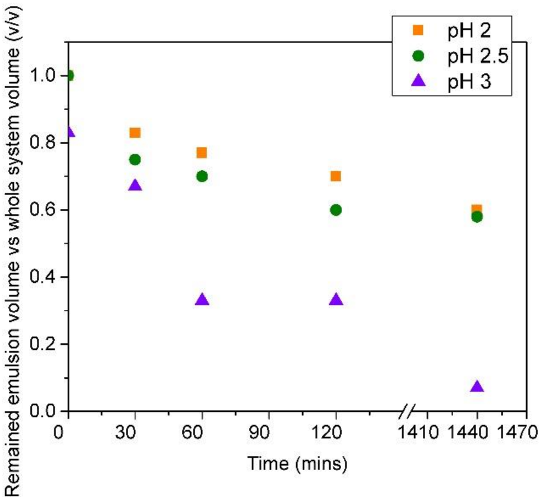


Figure 5-7: Remained emulsion ratio as function of time at varied pH (o/w at pH 2, o/w at pH 2.5 and w/o at pH 3). Emulsion were prepared with 2wt% (of oil phase volume) and 1:1 water-oil volume ratio.

Emulsions stabilised at pH 2.5 suffered slightly more rapid creaming than the droplets formed at pH 2 (Figure 5-7). The velocity of sedimentation and creaming of Pickering emulsions depends on the droplet size and viscosity of continuous phase (Binks and Lumsdon, 2000). The poorer emulsion stability in terms of creaming discovered at pH 2.5 is likely the consequence of droplets coalescence by forming larger o/w droplets than the emulsion stabilised at pH 2 (see average droplet sizes in Figure 5-6 inset). This may be considered as the main effect of increased pH in the aqueous phase, suggesting that the emulsions become last stable as they come closer towards the inversion point, as expected. On the other hand, the w/o emulsions stabilised at pH 3, where in accordance with the emulsions formed at pH 6 with same oil-water volume ratio and particle concentration (2wt% of oil phase volume, see Figure 4-4 in Chapter 4 section 4.3.1.1). However, dramatic oil-water phase separation was only observed with w/o emulsions at pH 3, while emulsions prepared at pH 6 are relatively more stable. This result is again indicative of a reduction in stability near the inversion point, but coming from the w/o side.

To clarify these predictions, emulsions were also fabricated with 50% volume ratio of 10^{-2}, 10^{-3} and 10^{-6} NaCl solution, and a particle concentration of 2 wt% (Appendix 5-1). All w/o emulsions stabilised by each concentration of NaCl in the aqueous phase had comparatively similar stability with emulsions fabricated at pH 6. This experiment was n performed to eliminate the influence of electrolyte concentration on particle interfacial behaviour further, resulting in a variation of emulsion properties. Therefore, the only determined aspect that was linked to stability changes is the variation of proton concentration in the aqueous phase and the findings are likely rationalized in terms of systematically changed particle wettability at the interface of the emulsion droplets, driven by different protonation degree of the pH responsive particles adsorbed at the interface by contacting varied concentrations of protons in aqueous phase.

The effect of oil-water volume ratio

The effect of oil-water ratio on the formation of the emulsions was investigated by using same particles (MV90) at pH 2, 2.5 and 3 respectively. In this study, the particles were diluted to 2wt% (of oil volume), and used as the Pickering emulsifiers for emulsion stabilisation. At each pH studied, three different oil-water ratios were investigated: 3:7, 5:5 and 7:3. Figure 5-8 and Figure 5-9show the appearance of emulsions after 0 min and 24 hrs preparation. With oil-water ratio of 3:7 and 5:5, creaming was observed at pH 2 and 2.5. However, with same ratios, phase separation was identified again at pH 3. When the oil-water ratio was raised to 7:3, *sedimentation* was found at all three pHs. Interestingly, the settled emulsion from this ratio (7:3) at pH 2.5 clearly had an aggregated “foam-like” structure which was very similar to the observation in the same particle based emulsions prepared at pH 6 with an oil-water ratio of 1:1 (discussed in Chapter 4, Section 4.3.1.1).

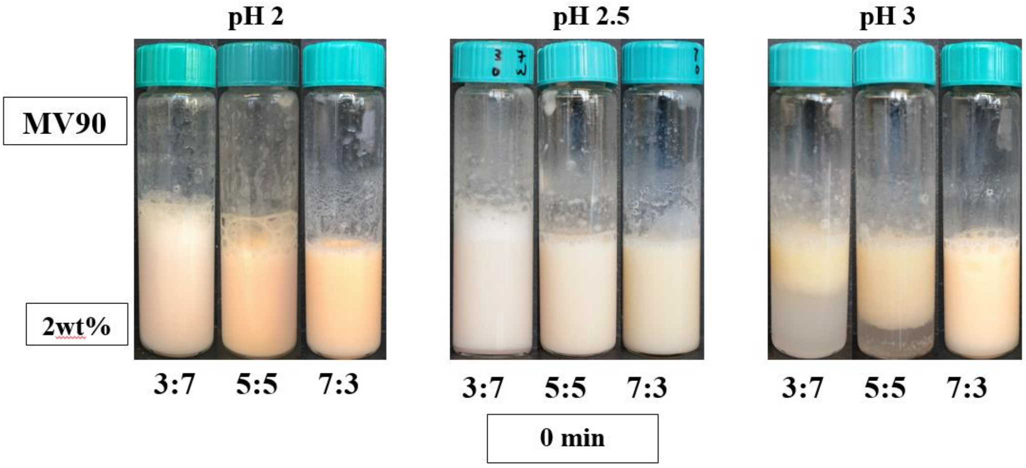


Figure 5-8 Appearance of fresh emulsion stabilised by 2wt% (of oil phase volume) MV90 particles with 3:7, 1:1 and 7:3 oil-water volume ratio under pH 2, pH 2.5 and pH 3, respectively.

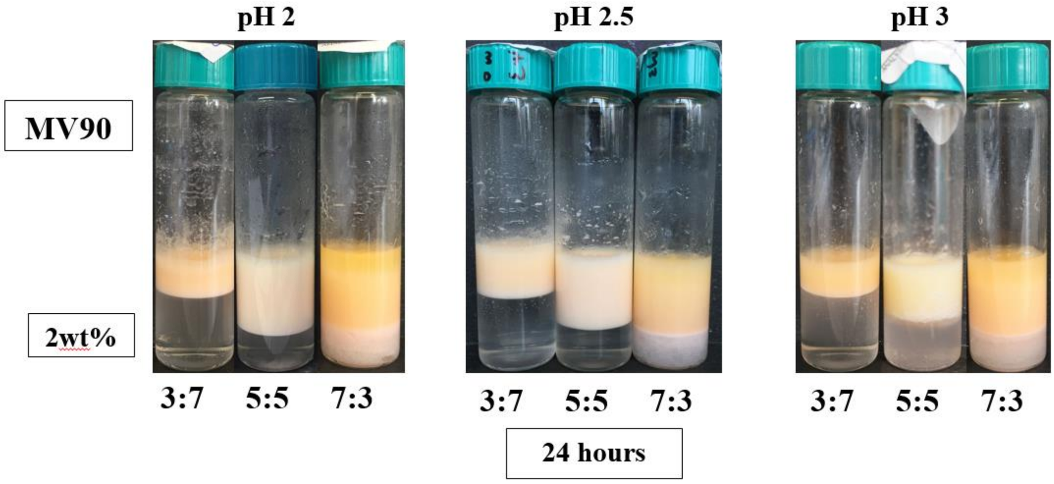


Figure 5-9 Appearance of emulsion which has been waited for 24 hours stabilised by 2wt% (of oil phase volume) MV90 particles with 3:7, 1:1 and 7:3 oil-water volume ratio under pH 2, pH 2.5 and pH 3, respectively.

The types of emulsions stabilised with varied oil-water volume ratio in presence of 2 wt% MV90 particles at pH 2, 2.5 and 3 were determined by drop test and observed under fluorescent optical microscope. At pH 2 and 2.5, o/w emulsions were stabilised with lower oil fractions (Φ equal to 0.3 and 0.5), while when oil ratio increased to 70 vol%, o/w/o multiple emulsions can be observed at both pH 2 and 2.5. This change is also evident from the representative images in Figure 5-10 for pH 2 system (aiii) with the similar behaviour occurring for pH 2.5 system (biii) at the higher Φ; inner oil drops are clearly visible within water globules. This is the first time we have observed the appearance of multiple emulsions in responsive particle/microgel systems by simply varying oil-water content. Aggregated Oil droplets in relatively empty water globules at pH 2.5 are shown while crowded oil drops in o/w/o existed under pH 2 status (Figure 5-10 aiii and biii). Results also showed undoubtedly, that w/o emulsion types were stabilised at pH 3 with all, although with clearly larger droplet sizes as oil fraction is increased (Figure 5-10 c).

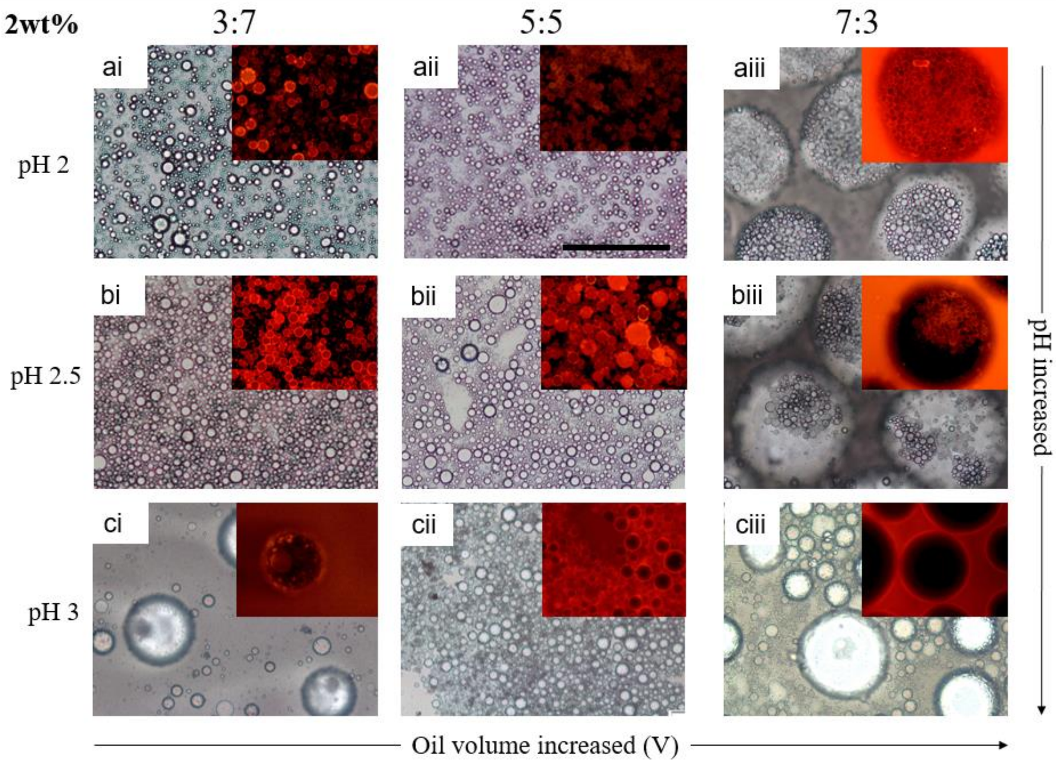


Figure 5-10 Optical microscope images of emulsion droplets stabilised with 2wt% (of oil phase volume) MV90 at a) pH 2; b) pH 2.5 and c) pH 3 of i) 3:7 oil-water volume ratio, ii) 5:5 oil-water volume ratio and iii) 7:3 oil-water volume ratio (scale bar 500 μm for all).

The mean droplets diameters of above emulsions are quantified in Figure 5-11. The mean droplets diameter with related standard deviation was gained by estimating over 150 droplets diameter from microscopy images on Image J. Generally, increased mean droplet diameters can be draw out with increased oil fraction at all pH. The larger droplet sizes at pH 2 and pH 2.5 is due to the formation of o/w/o emulsions, as described. Emulsions prepared with 30 vol% oil fraction have declining of mean diameters with decreased pH. In contrast, an increase of droplet size is observed at Φ =0.7 while the pH of aqueous phase decreases independent of emulsion types.

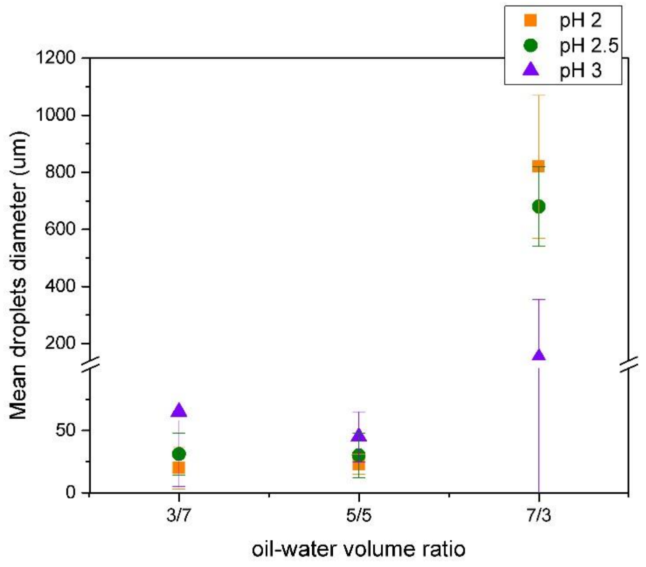


Figure 5-11 Mean droplets diameter of 2 wt% (of oil phase volume) MV90 stabilised emulsions at pH 2, pH 2.5 and pH 3 with varied oil-water volume ratios.

The inversion of emulsion type from o/w to o/w/o is induced by increased fraction of the dispersed phase, and results in a sudden change of bulk emulsion behaviour in terms of creaming and sedimentation as well as droplet size. As described in a number of sections throughout the thesis, converting one type of emulsion into another is so-called phase inversion. Generally, it involves two kinds: transitional and catastrophic phase inversions. The detailed information was introduced in Chapter 2 section 2.2.3. In Chapter 4, we demonstrated a really rare example of the transitional phase inversion from w/o to o/w only induced by environmental trigger (pH of aqueous phase) of emulsion stabilised by tailored oil-dispersed pH responsive core-shell particles. As discussed before, such pH induced particle interfacial behaviour is due to a wettability change by tuning pH resulting in a contact angle shift or a deformation of particle at interface. With the changing oil fraction studies however, the pH of aqueous phase is kept constantly as the oil-water volume fraction is changed, which is assumed to lead to the so-called catastrophic phase inversion(Binks and Lumsdon, 2000; Binks and Horozov, 2006). Such inversion was only found in emulsion systems prepared at pH 2 and pH 2.5, initially in o/w type, which may be forced towards inversion with the increase in the dispersed (oil) phase.

Emulsions fabricated with Φ_O = 0.3 and 0.7 both show an increase in droplet size followed by a more rapid creaming speed, when the pH switched from 2 to 2.5, which is consistent with the results gained from Figure 5-5 and Figure 5-6. Especially, the aggregated o/w droplets inside large w/o droplets were discovered with 70 vol% oil system at pH 2.5, while the produced oil globules didn't aggregate at pH 2. As discussed before, these visible differences of emulsion properties may be the fact that the increased protonation ratio of MV90 particles adsorbed at the interface, leading to more hydrophilic Pickering emulsifiers, eventually presenting as the stabilisation of smaller o/w droplets at different pH. Pure p2-VP-PDMS particles have a pK_a around 4.7 with increased air-water interfacial contact angle in pH range from 3 to 6 (Fujii et al., 2010). The oil-water interfacial behaviour of co-polymeric particle which contained 90% 2-VP is more likely to be consistent with the case of pure p2-VP-PDMS particles. The pH induced shifting of contact angle of p2-VP-PDMS and MV90 particles according to pH can be both concluded as the varied protonation degree within particle cores. Henderson-Hasselbalch equation (Weller et al., 2014; Housecroft and Sharpe, 2008)is normally employed to explain the relations between pK_a and pH in solution.

If the ionic equilibrium theory of base can be written as below:

$\mathrm{B} + \mathrm{H_2 0} \ \leftrightarrow \mathrm{B}H^{+} + OH^{-}$ Equation 5-1 ((Weller et al., 2014; Housecroft and Sharpe, 2008))

Henderson-Hasselbalch equation can be shown as:

$\mathrm{pH} = \mathrm{p}K_a + \log 10\left(\frac{[\mathrm{B}]}{[\mathrm{B}H^{+}]}\right)$ Equation 5-2 ((Weller et al., 2014; Housecroft and Sharpe, 2008))

Where $[\mathrm{B}]$ represents the concentration of base, $[\mathrm{B}H^{+}]$ represents the concentration of protonated base.

Pure p2-VP has a $\mathrm{pK_a}$ at pH 4.7, which means 50% of p2-VP chains/units within particle cores should have been protonated when particles are dispersing in aqueous phase. So ideally, if the pH decreases to 3, 2.5 and 2, the protonation degree of such particles can be estimated to 98%, 99.4% and 99.8%, respectively. And only 5% p2-VP will be protonated while pH of the aqueous bulk is at 6. In the work of Fujii *et al*., air-water interfacial contact angles of p2-VP-PDMS particles were measured by presenting an increasing trend as a function of increased pH, with a transition from hydrophilic to hydrophobic (Fujii et al., 2010). Nevertheless, MV90 particles consist of randomly co-polymerized MMA and 2-VP units, so that less 2-VP units can be obtained in comparison with same size pure p2-VP particles. In contrast with pure p2-VP microgel, dodecane dispersed MV90 particles have much less chance to contact water phase even when adsorbed at an oil-water interface, due to the good solubility of PDMS polymer chains in dodecane. These two aspects lead to the facts that MV90 may either have a different $\mathrm{pK_a}$ (potentially lower), or be shown as varied contact angle at oil-water interface by responding to same pH value, or both, comparing to pure p2-VP microgels. It certainly cannot be denied that gradually changed MV90 stabilised emulsion properties indicated the estimation and hypothesis of systematically increased protonation degree, driving the fact that particles behaved differently in terms of hydrophobicity-hydrophilicity at the interface, which is analogues to the pure p2-VP case.

5.3.2 Effect of particle concentrations and oil-water volume ratio

Catastrophic phase inversion of MV90 stabilised emulsions from o/w to o/w/o induced by varying oil-water volume ratio of the system was reported in the previous section. It only occurred in the emulsion system which was stabilised by 2 wt% charged particles (at pH 2 and 2.5). However, such particle concentrations was in reference to the volume of oil phase. Thus, total amount of particles involved in system before emulsification was changing with varied oil-water volume ratio (i.e higher oil fraction resulting in a larger number of total particles in the system). To further study the influence of oil-water volume ratio on emulsion properties, we then tested emulsions stabilised by a constant amount of particles (1 wt% of whole system) with varied oil-water volume ratios. Emulsion types and stability are characterised by optical fluorescent microscope and emulsion volume measurement as function of time.

The experiments were performed at pH 2 and pH 6 with Φ_O = 0.3, 0.5 and 0.7. Figure 5-12 and Figure 5-13 show the varied appearances of emulsions prepared with increased Φ_O and constant particle numbers just after emulsification and after storing for 24 hours. At pH 2, emulsions prepared with any Φ_O all creamed after 24 hours, while oil release only appeared with Φ_O =0.7. At pH 6, sedimentation of emulsion droplets can be observed with all the studied Φ_O meanwhile a dramatic phase separation happened to the Φ_O = 0.3 system and a foam-like emulsion was observed at Φ_O = 0.7.

Drop test and fluorescent optical microscope images illustrate that o/w emulsions (oil was dyed shown as red area) were stabilised by1 wt% MV90 at pH 2 regardless of Φ_O (shown in Figure 5-14). All Φ_O emulsions prepared at pH 6 were w/o. O/w emulsion droplets has an increase of size by increased Φ_O with constant particle concentration, which is similar to 2wt% (of oil volume) particle stabilised emulsion system. W/o droplets were becoming smaller as function of water volume fraction at pH 6. It is obvious that emulsion type wasn't inverted by increased oil volume fraction of 1 wt% (whole system) particle concentration (see Figure 5-14) differ from the 2 wt% (relative oil volume) case in Figure 5-10. This important finding suggests that not only water-oil volume ratio has the influence on catastrophic emulsion phase inversion, but also the relative particle concentrations, which are often interlinked variables in studies.

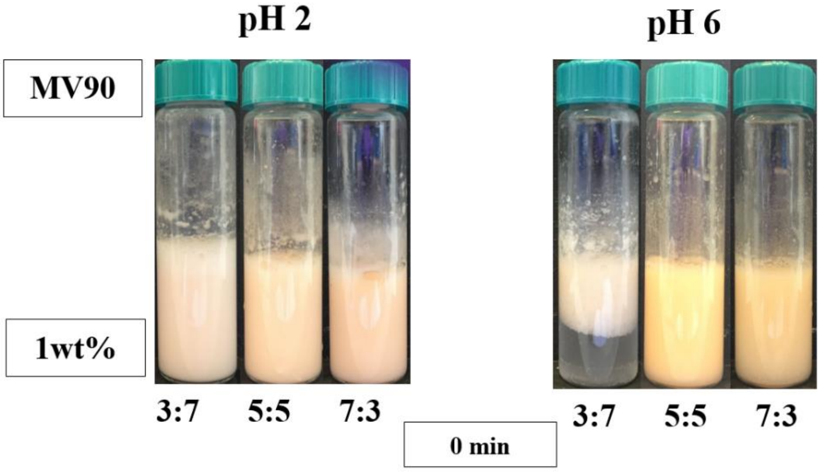


Figure 5-12 Appearance of fresh emulsion stabilised by 1wt% (of whole system) MV90 particles with 3:7, 1:1 and 7:3 oil-water volume ratio under pH 2 and pH 6, respectively.

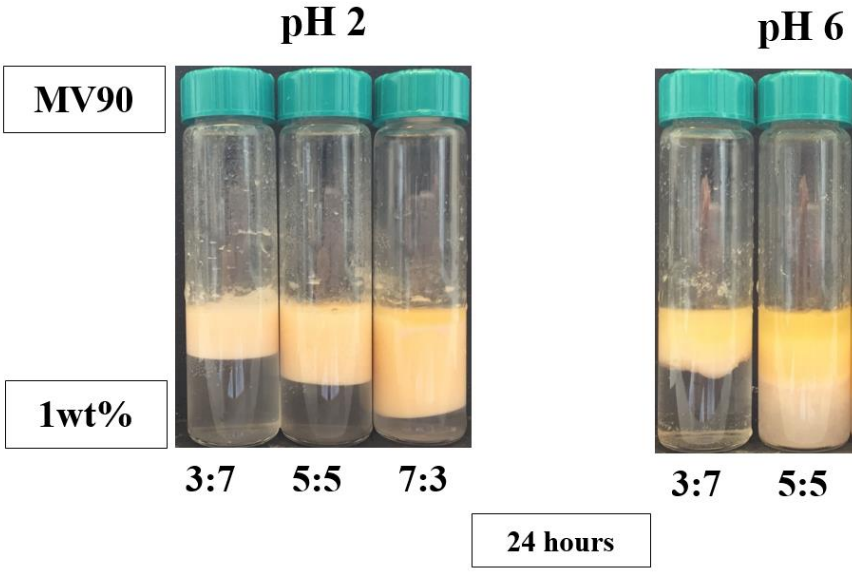


Figure 5-13 Appearance of emulsion vials stabilised by 1wt% (of whole system) MV90 particles with 3:7, 1:1 and 7:3 oil-water volume ratio under pH 2 and pH 6, respectively, after 24 hours.

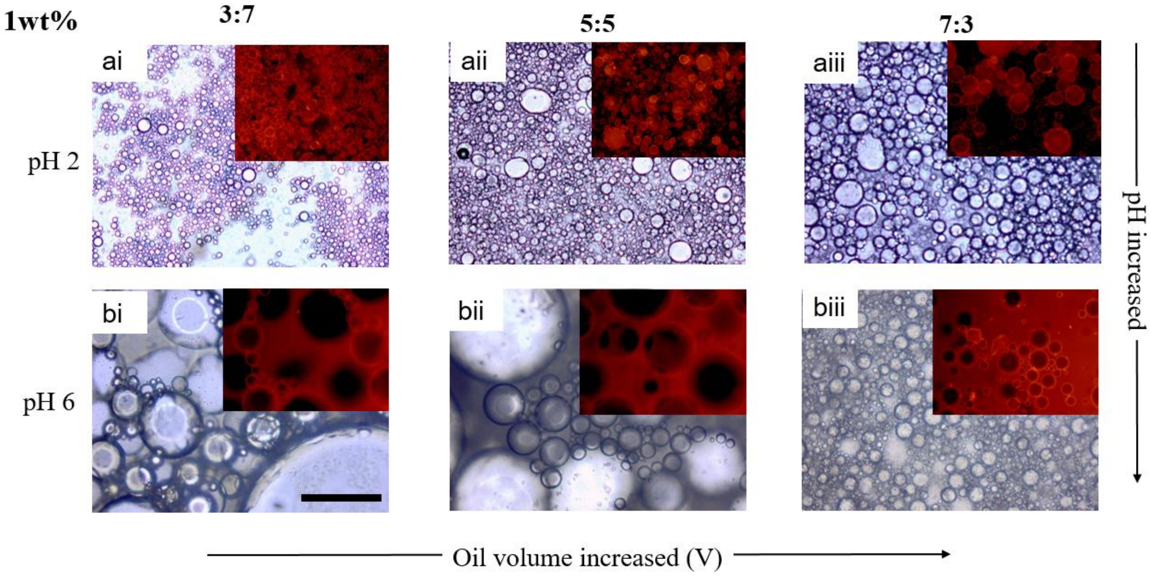


Figure 5-14 Optical microscope images of emulsion droplets stabilised with 1 wt% (of whole system) MV90 at a) pH 2; and b) pH 6 of i) 3:7 oil-water volume ratio, ii) 5:5 oil-water volume ratio and iii) 7:3 oil-water volume ratio (scale bar 500 μm for all)

As introduced before, 2 wt% particle concentration was based on oil volume in the system which means the total amount particle dispersed in system was changed by varying oil-water volume ratio. Thus, a conclusion cannot be made on various the droplet size of 2 wt% particle stabilised emulsions at each pH, due to both the influences of water-oil volume ratio and particle concentrations. Nevertheless, increased/decreased droplet size is presented as a function of increased oil content at a constant initial particle concentration of the whole system at 1 wt% under pH 2 and pH 6 (Figure 5-15). Surprisingly, mean o/w droplet diameters didn't appear to be significantly influenced by varying the initial particle concentrations at fixed system volume ratios, which was discussed in Chapter 4 (see Figure 4-12, Section 4.3.1.2). As shown in Figure 5-15, since the initial particle concentrations are kept constant in the system, it appears that different extent additional oil added creates a new interface which may not be covered sufficiently by adsorbed particles, so coalescence becomes possible for o/w emulsions at pH 2 during emulsification, and vice versa (Binks and Lumsdon, 2000), which increases droplet size with oil fraction.

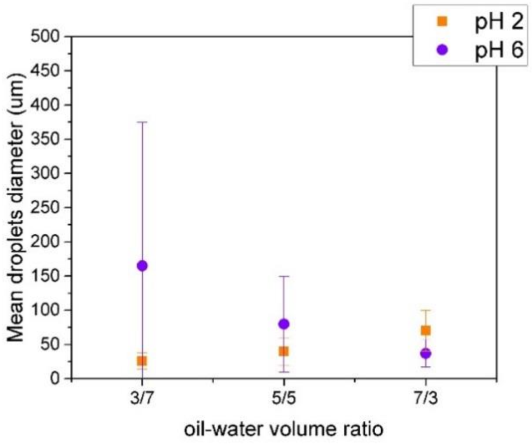


Figure 5-15 Mean droplet diameter of 1 wt% (of whole system volume) MV90 stabilised emulsions as function of oil-water volume ratio and pH.

It is known that catastrophic phase inversion of particle stabilised emulsion is generally induced by varying the oil-water volume ratio in the system(Binks and Lumsdon, 2000; Binks and Horozov, 2006). Besides, the inversion of emulsion type from one to another can be also affected by the system HLB due to the wettability of particles(Binks and Lumsdon, 2000; Groeneweg et al., 1998). As to this regard, the formation of o/w/o emulsions in our system is undoubtedly an interesting phenomenon. This finding only exists while the oil volume was increased to a certain ratio (i.e. 0.7) with 2 wt% particles (based on oil volume) at pH below 3. In other words, MV90 must be protonated until certain degree to stabilise multiple emulsions at lower water content system. Here, we questioned whether particle concentration has an influence on the formation of multiple emulsions and catastrophic phase inversion and whether it is possible to link the effect of particle concentration to the particle interfacial behaviour at varied oil-water volume ratios.

As discussed, particle concentrations of 2 wt% (oil volume) and 1 wt% (whole system volume) behave very differently. If one can be transferred into another, 2 wt% particle concentrations to each oil-water volume ratio can be considered as 0.6 wt% (of whole system) at Φ_O = 0.3, 1 wt% at Φ_O = 0.5 and 1.4 wt% at Φ_O = 0.7. In other words, when system contain 70 vol% oil, o/w/o emulsion can only be stabilised with 1.4 wt% (whole system) particles while 1 wt% particles can only fabricate o/w emulsions at pH 2. It is more likely that there are some particles which also haven't been protonated to certain ratio, thus are able to stabilise w/o droplet. This hypothesis may be based on the fact that water ratio is decreased and thus contains less protons for protonation of the particles in the system. As well as that, MV90 are *core* responsive Pickering emulsifiers. Theoretically, such core-responsive particles swell when they are protonated. When 70 vol% oil and 30 vol% water are homogenised, some particles which are adsorbed on the interface initially may be swelling, induced by the protonation of 2-VP units on polymer chains, while the rest of particles adsorbed at the interface later have less chance to be protonated properly, due to increasing diffusion hindrance of the other particles. Especially, protonated particle swells and then more protons will diffuse in. So that, the rest of particles have even less protonated degree to be able to stabilise o/w droplets due to the limited amount of protons in 30 vol% relative aqueous phase. This is one possible mechanism for the o/w/o emulsion being generated within such “particle mixtures” (relatively charged MV90 and uncharged MV90).

5.3.3 Oil-water volume ratio study on oil-dispersed cross-linked pH responsive particles

Since the pH, particle concentration and oil-water volume ratio are crucial in indicating the types of emulsion ultimately formed with the MV90 particles as emulsion stabilizers, it is of interest to investigate the influence of cross-linking extent in particle core with regard to the oil-water volume study. The cross-linked oil-dispersed pH responsive particles have been introduced in previous two chapters, which has a fixed theoretical composition of 90% 2-VP in particle cores. The extent cross-linking is ranging in term of initial DVB concentrations from 0.5 mol% to 5 mol% based on total amount of monomer. The transitional phase inversion of such particle stabilised emulsions were investigated by switching pH of aqueous phase from 6 to 2 whereby the particle wettability at interface was altered. In this part of work, two batches of cross-linked particle suspensions which theoretically contain 0.5 mol% and 5 mol% DVB in cores as expected from the initial cross-linker concentrations were chosen as model examples to examine the influences of oil-water volume ratio on emulsion properties under certain pH environment and particle amount.

As previously investigated, the aforementioned particles containing 0.5 mol% and 5 mol% DVB are lightly and highly cross-linked, respectively. As having been discussed in Chapter 4 (Section 4.3.2), the MV90-0.5mol% particles exhibited a very similar interfacial behaviour to the MV90 ones of no cross-linker as confirmed from their alike emulsion properties (both have slightly poor emulsion stability), implying no big difference in configuration between them. Nevertheless, the highly cross-linked particles (MV90-5 mol%) have been demonstrated to be good Pickering emulsion stabilisers not matter stabilising the w/o or the o/w typed droplets.

5.3.3.1 Oil-water volume study of MV90-0.5mol% particles

Emulsions were fabricated in a range of oil-water volume ratios with either 1 wt% particles (of whole system volume) or 2 wt% particles (of oil phase volume) at pH 2, pH 2.5 and pH 3. In an attempt to see if the extreme water/oil ratio is crucial in controlling emulsion properties of our particle systems, two emulsions have been prepared under same conditions but with one containing 90 vol% of oil and the other 90 vol% of water. Figure 5-16 shows the vessel images taken at 24 hours after preparation of emulsions stabilised with 2 wt% (of oil phase volume) MV90-0.5mol% particles with increased oil volume fraction ($\emptyset_O$ 0.1 to 0.9) at pH 2, pH 2.5 and pH 3. As can be seen, at both pH 2 and pH 2.5, the emulsion droplets with low $\emptyset_O$ creamed in 24h while those with high $\emptyset_O$ experienced sedimentations. At pH 3, phase separation happened in the cases of low $\emptyset_O$ while sedimentation was observed for those with $\emptyset_O$ exceeding 0.5.

This is further clarified quantitatively with the data of resolved oil/water fraction as shown in Figure 5-17. The resolved oil/water fraction is a good indicator to compare emulsion stability between different cases, regardless of their potentially different emulsion types. Here, the resolved dispersed phase, indicating the extent of the phase separation of clarified released oil from the o/w emulsion and water for the w/o ones, represents overall the emulsion stability against droplet coalescence. The volume fraction of the resolved continuous phase is indicating the stability against creaming and sedimentation. All the emulsions stabilised by MV90-0.5mol% creamed and sedimented regardless of oil-water volume ratio and pH. The relatively higher values of released dispersed phase at $\emptyset_O$ = 0.3, pH 3 and at $\emptyset_O$ = 0.7, pH 2 than the others at the same pH imply that the emulsions underwent droplet coalescences before the eventual phase separation (Binks and Lumsdon, 2000).

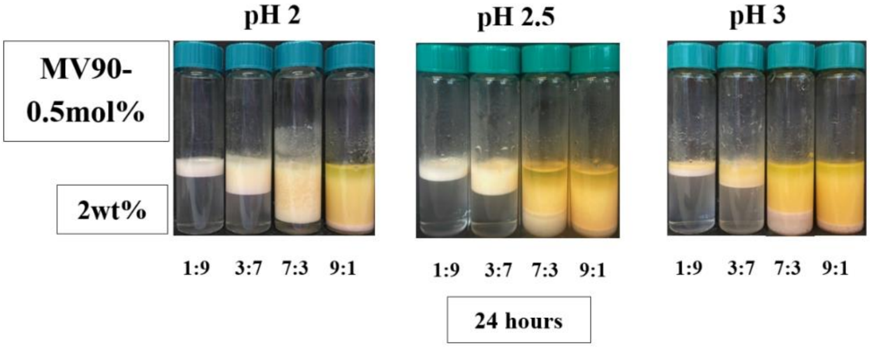


Figure 5-16 Appearance of emulsion vials stabilised by 2wt% (of oil phase) MV90-0.5mol% particles with 1:9, 3:7, 7:3 and 9:1 oil-water volume ratio under pH 2, pH 2.5 and pH 3, respectively, after 24 hours.

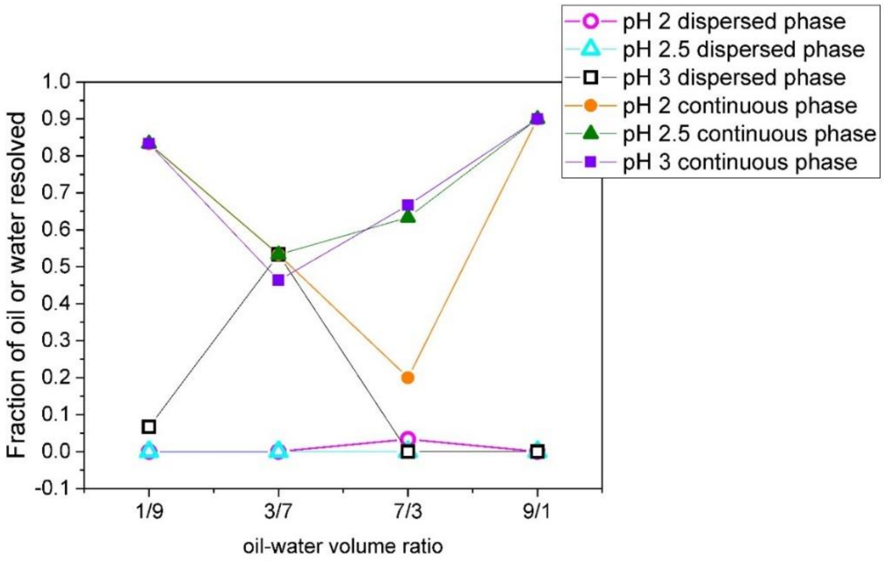


Figure 5-17 Stability after 24 hours of emulsions stabilised by 2 wt% MV90-0.5mol% at different pH as function of oil-water volume ratios. (open points) The variation of resolved dispersed phase volume ratio refer to coalescence; (filled points) fraction change of continuous phase refer to sedimentation for dodecane dispersed emulsion and creaming for o/w emulsions.

From the drop test and fluorescent optical microscope results shown in Figure 5-18, various emulsion types (oil was dyed shown as red area) can be prepared with the MV90-0.5mol% particle system by simply changing oil-water volume ratio and pH. Figure 5-19 depicts the corresponding variation of their mean droplets diameters, where a general trend of increment as a function of $\emptyset_O$ is evident, regardless of the emulsion type. Interestingly, catastrophic phase inversion can be achieved at each pH by only varying the water-oil volume ratio. At pH 2, o/w emulsion droplets can be inverted to o/w/o and w/o emulsions when the $\emptyset_O$ is more than 70 vol%. The mean droplet diameter of o/w droplets increased as a function of increased oil content. Nevertheless, the oil-water volume ratio for the phase inversion shifted to 7:3 if the pH was increased to 2.5. An increasing of o/w droplets mean diameter with a reduction of water ratio was accompanied with the fall of multiple emulsion droplet size beyond phase inversion. Strikingly, at pH 3, the case where w/o type emulsion was generally observed, a o/w emulsion was produced under the condition of low oil fraction, $\emptyset_o$= 0.1 with 2 wt% particles (based on oil phase). This is normally only possible in the cases that the pH in the aqueous phase is either 2 or 2.5. This observation, undoubtedly, indicates the occurrence of catastrophic phase inversion from w/o to o/w in the MV90-0.5mol% stabilised emulsion system as achieved by reducing the $\emptyset_o$ to 0.1 at pH 3. Meanwhile, a reduction of the w/o emulsion droplets mean diameter was observed as the $\emptyset_o$ was increased in the system, as expected. A conclusion may be drawn out at this stage, the phase inversion from w/o to o/w or o/w to o/w/o can be induced not only by switching the pH of aqueous bulk phase, but also by controlling of the initial oil-water volume ratio in our oil-dispersed pH-responsive particle system.

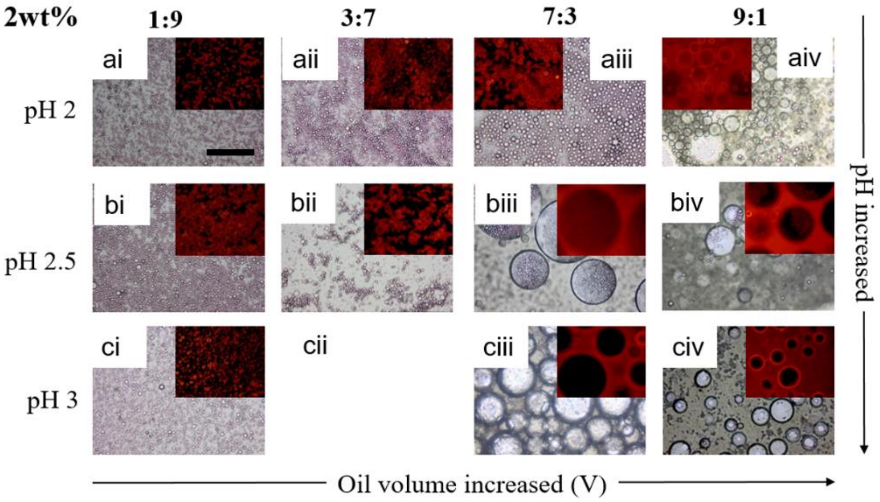


Figure 5-18 Optical microscope images of emulsion droplets stabilised with 2wt% (of whole system) MV90-0.5mol% at a) pH 2; b) pH 2.5 and c) pH 3 of i) 1:9; ii) 3:7 ; iii) 7:3; iv) 9:1 oil-water volume ratio (scale bar 500 µm for all)

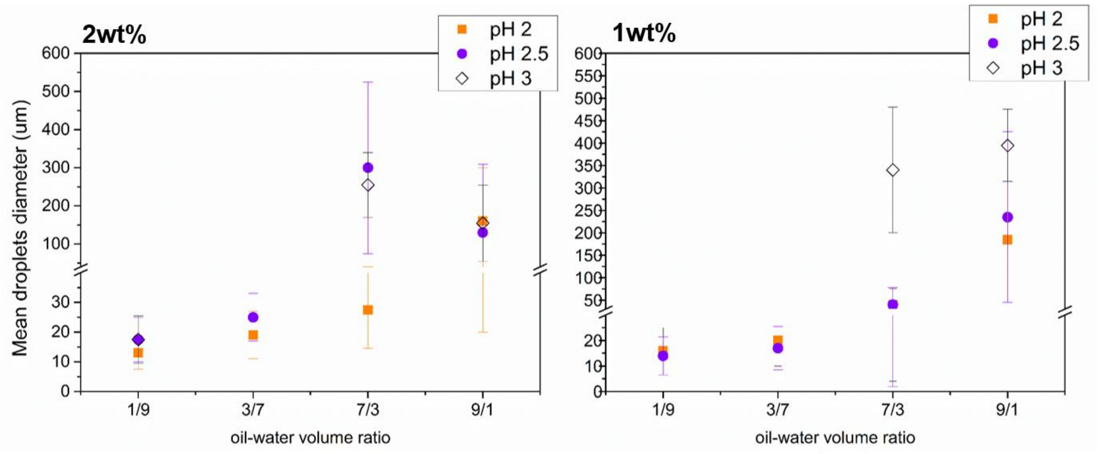


Figure 5-19 Mean droplets diameter of MV90-0.5mol% stabilised emulsions with varied particle concentrations and oil-water volume ratios at pH 2, pH 2.5 and pH 3.

It has been shown that the least stable emulsions were observed in the vicinity of inversion locus with a relevant larger droplets size compared to the same types of emulsion before or after the phase inversion(Binks and Horozov, 2006; Binks and Lumsdon, 2000). The same to our case of MV90-0.5mol% stabilised emulsions, severe phase separation and droplets coalescence have been reported around the catastrophic phase inversion locus in either o/w or w/o emulsions, as confirmed from the observation of relatively larger drops (see Figure 5-18 and Figure 5-19). Such poor stability of emulsions obtained around the phase inversion is reasonable provided that the sudden increased dispersed phase fraction is likely to cause coalescence and phase separations. As Binks and co-workers reported, catastrophic phase inversion of solid particle stabilised emulsion from w/o to o/w, normally, take place on the emulsions fabricated around with water fraction $\emptyset_W$ = 0.7 (Binks and Lumsdon, 2000). However, the inversion of MV90-0.5mol% stabilised emulsions from o/w to w/o and o/w/o occurs at a volume fraction of oil at 0.9.

On the other hand, it is worthy of questioning whether or not the particles behave differently in terms of emulsion properties if they are cross-linked. Comparing Figure 5-10 and Figure 5-18, one can see that in the MV90-0.5mol% stabilised system emulsion phase inversion never happened until the $\emptyset_O$was increased above 0.9 while the o/w was inverted to o/w/o at $\emptyset_O$ = 0.7 in the MV90 system at both pH 2 and pH 2.5. However, as compared to the MV90 stabilised emulsion at pH 3, the w/o emulsion in the MV90-0.5mol% system with water fraction $\emptyset_\mathrm{W}$ = 0.7 is more unstable and a phase inversion occurred when the $\emptyset_\mathrm{W}$ is increased further.

Conventional catastrophic phase inversion of emulsion stabilised by solid particles was induced by increased fractions of dispersed phase leading to a sudden transition of emulsion types and properties. This type of transition in Pickering system was generally defined as inversion of emulsion types without altering particle wettability. In Section 5.3.2, we have reported that the possible influential factors on such phase inversion in MV90 stabilised emulsions was not only limited to the dispersed/continuous phase ratio, but also the pH values. It can be anticipated that the particles' interfacial behaviour is greatly dictated by the actual proton concentrations, which is tuneable by the aqueous phase volume fraction and the pH value. Therefore, the real particle amount and its degree of protonation should play a crucial role. To further test this anticipation, in addition to the system containing 2 wt% particle suspension (of oil phase volume), here the water-oil volume ratio study of MV90-0.5mol% stabilised emulsions was also performed on the systems containing 1 wt% particle suspension (of whole system) with varied pH values in aqueous phase. Figure 5-20 illustrates the fluorescent optical microscope images of emulsion droplets stabilised with 1 wt% MV90-0.5mol%, data collected under same conditions as in Figure 5-18. For $\emptyset_O$= 0.7 at pH 2.5, dodecane becomes incorporated into the o/w emulsions (Figure 5-20 biii), other than the formation of o/w/o double emulsions with 2 wt% particles under same conditions (Figure 5-18 biii). The phase inversion at pH 2.5 of 1 wt% MV90-0.5mol% stabilised emulsion droplets only occurs at $\emptyset_O$= 0.9 as o/w/o emulsions indicating a hysteresis (Figure 5-20 biv). At pH 3, a rapid phase separation of w/o emulsions was observed at a lower oil/water ratio system (see Appendix 5-2 and Appendix 5-3). It is noticeable that the existence of o/w/o multiple emulsions at $\emptyset_O$= 0.7 is astonishing, which didn't appear in 2wt% system. Figure 5-19 shows the variation of emulsion droplet size with increased oil fraction with different pH and particle concentrations. Generally, emulsions prepared at pH 2 and 2.5 have an increase of mean droplet diameter with increased oil fraction due to the inversion from o/w to o/w/o. The biggest difference in droplet size between the two cases (i.e. 2 wt% in oil and 1 wt% in total) can be captured at $\emptyset_O$= 0.7, pH 2.5, where the former has a larger droplet size than the latter owing to the formation of o/w/o multiple emulsion in presence of the 2 wt% MV90-0.5mol% particles.

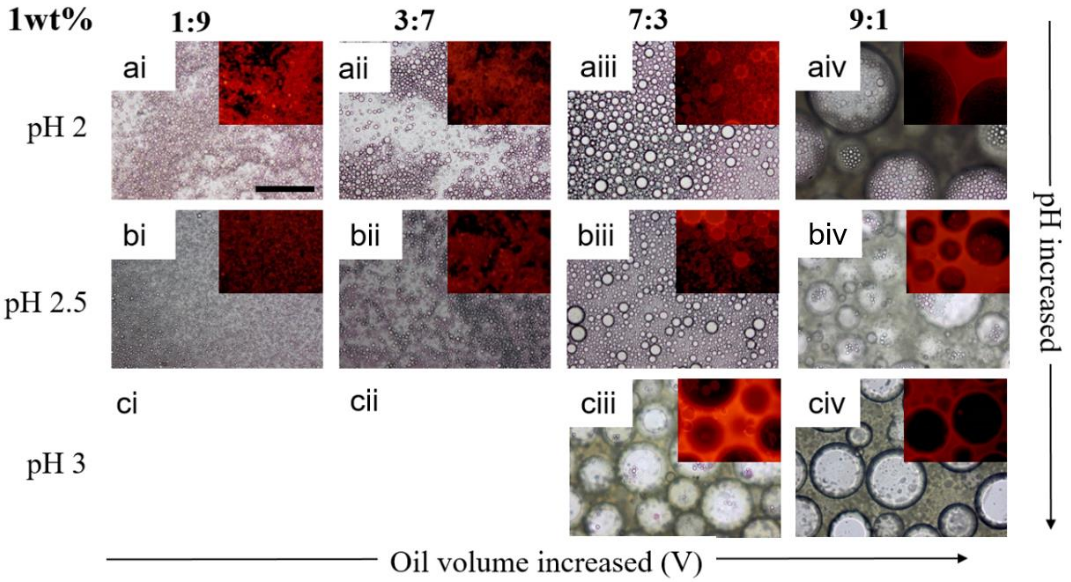


Figure 5-20 : Optical microscope images of emulsion droplets stabilised by 1wt% (of whole system) MV90-0.5 mol% cross-linked particle suspension with i). 1:9 o:w; ii) 3:7 o:w; iii) 7:3 o:w and iv) 9:1 o:w at a) pH 2; b) pH 2.5 and c) pH 3 of aqueous phase (scale bar 500 μm for all)

In Sections 5.3.1 and 5.3.2, the possible relations between particle protonation degree and pH, particle concentrations as well as proton concentrations with regard to their influence on the types and stability of emulsions stabilised by such oil-dispersed pH responsive particles have been introduced. In order to ascertain such hypothesis, we try to link the relations among pH, aqueous phase volume and particle concentrations together. Firstly, the quantity of protons of varied $\emptyset_W$ at each pH is calculated basing on equation below:

$$n_{H^+} = C_{H^+} \times V_W \times N_A \qquad \text{Equation 5-3}$$

Where n_{H^+} represents the total quantity of protons, C_{H^+} is the molarity of H^+, V_W is the volume of aqueous phase in such pH and N_A is the Avogadro constant.

Then, we transfer the particle concentrations into the same definition and calculate the quantity of particles in each condition based on the following equation:

$$n_{particle} = \frac{wt\%\times\rho_{dodecane}\times V}{\frac{4}{3}\pi(\frac{D}{2})^3\times\rho_{particle}} \qquad \text{Equation 5-4}$$

Where wt% represents the weight concentration of particle suspensions, V is the volume of whole system. For comparison purpose, the particle concentration of 2 wt% in oil phase has been converted to the whole system volume based concentration before eventually calculating the particle quantity. The D in equation is the particle diameter, which is around 680nm in average for the MV90-0.5mol% system. $\rho_{dodecane}$ is 0.75 g/ml and $\rho_{particle}$ can be estimated to be 1.05 g/ml. The influence of proton and particle quantity on the emulsion types is shown in Table 5-1.

Table 5-1: In MV90-0.5mol% stabilised emulsion system, estimated proton quantity, ideally participated particle amount in each particle concentrations and preferred emulsion types of varied water fractions at each pH.

	Oil-water volume ratio (O:W)	Proton quantity (n)	2 wt% (of oil volume) particle quantity (n) and preferred emulsion type	1 wt% (of whole system volume) particle quantity (n) and preferred emulsion type
pH 2 *(10^{-2}mol/L)*	9:1	6.02×10^{19}	o/w/o 0.774×10^{12}	o/w/o 0.43×10^{12}
	7:3	18.06×10^{19}	o/w 0.602×10^{12}	o/w 0.43×10^{12}
pH2.5 *($10^{-2.5}$mol/L)*	9:1	1.9×10^{19}	o/w/o 0.774×10^{12}	o/w/o 0.43×10^{12}
	7:3	5.7×10^{19}	o/w/o 0.602×10^{12}	o/w 0.43×10^{12}
pH 3 *(10^{-3}mol/L)*	1:9	5.42×10^{19}	o/w 0.086×10^{12}	w/o 0.43×10^{12}
	7:3	4.2×10^{19}	w/o 0.258×10^{12}	w/o 0.43×10^{12}

According to the data from Table 5-1 at pH 2 and 2.5, multiple emulsions can be stabilised at water volume fraction $\emptyset_W$ =0.1 regardless of particle concentrations. Meanwhile, o/w emulsions were stabilised at $\emptyset_W$=0.3except for the case of 2 wt% (in oil) at the same pHs. The dominated variation of such difference of emulsion types is due to the three times of proton quantity at $\emptyset_W$=0.3 comparing to the proton amount at $\emptyset_W$=0.1, which eventually results in an efficiently protonated particle system to form o/w emulsion in most of conditions. On the other hand, the formation of o/w/o emulsion is owing to inadequate proton amount in the system. Particles were protonated to be able to stabilise the o/w droplets at such pH while the low water volume brings less protons to protonate all particles, which have been taken part into the emulsifications.

In our previous experimental findings, MV90 particles stabilised w/o emulsions at pH 3, indicating a higher demand of protons on protonating the particles to adsorb at o/w interface. Thus, the stabilisation of large water globule containing small oil drops is attributed to the adsorbing of less/non-protonated particles in presence of $\emptyset_W$=0.1 at pH 2 and pH 2.5. At same moment, o/w droplets were stabilised with lower amount of particles while o/w/o emulsion were observed in 2 wt% (of oil phase volume) system, both at exactly same pH (2.5) and oil-water ratio (7:3). This can be easily explained by our hypothesis as same amount of protons were only enough to protonate appropriate quantity of particles, 1.4wt% is more than 1 wt%.

No simple w/o only emulsion system was stabilised at neither pH 2 nor pH 2.5 regardless of the oil-water ratio and the particle concentrations. This is also an evidence to confirm our explanation. Nevertheless, the unexpected o/w emulsions were observed in presence of 0.2 wt% of whole system volume with $5.42\times10^{19}\ H^+$ of 90 vol% water content (pH 3), but only w/o was existing with 1 wt% particles. The stabilisation of o/w in such system can be considered as behaviour of the proper protonated small amount MV90-0.5mol% particles.

But the reason of the stabilisation of w/o droplets under such conditions is questioned by comparing to the observation of o/w emulsion with same amount of particles and similar quantity of protons (pH 2.5, 7:3 o:w). We also notice that the o/w/o emulsion of pH 2 and $\emptyset_W$=0.1 was facing similar amount of protons with the system at pH 2.5 and 30v ol% water content, which formed o/w droplets only of exactly same particle concentrations. Those findings confirm the importance of the effect of pH in bulk phase, consistent with our hypothesis. In section 5.3.1, the effect of pH in bulk on emulsion types and properties have been studied and discussed. Herein, the eventual emulsion types and properties have been demonstrated to be determined not only by the amount of protons and related particles but also by the proton concentrations. Different pH of aqueous bulk phase cause varied protonation ratios of particles that adsorbed at the interface. As different pH of bulk phase brings varied levels of potential and osmotic pressure differences between particle and bulk solutions.

5.3.3.2 Oil-water volume study of MV90-5mol% particles

Emulsions were fabricated with oil-dispersed pH responsive particles synthesized with varied initial concentrations of cross-linkers in presence of systematically decreased particle concentrations and fixed oil-water volume ratio (1:1), firstly. In Chapter 4, results have shown that the transitional phase inversion from w/o to o/w of such cross-linked particle stabilised emulsions can be induced by the falling of pH in aqueous phase regardless of the particle concentrations and the cross-linking density in particle cores. Besides this, the stability of such emulsions is sensitive not only to the pH but also to the particles themselves that are with varied cross-linking densities (as expected from theory). The MV90-5mol% stabilised emulsions exhibited a better stability not matter in the o/w or the w/o types, obviously indicating the role of cross-linking density on emulsion properties. To further explore the role of the cross-linking density, here we will demonstrate the performance of the emulsions stabilised by the MV90-5mol% particles under varied pH, oil-water volume ratios and particle concentrations.

Starting with the emulsions stabilised at 2 wt% (of oil phase volume), Figure 5-21 shows the variation of emulsion type with $\emptyset_O$(oil was dyed shown as red area for pH2 and pH2.5, water was dyed shown in green for pH3). The experiments have been performed under three different pHs. Catastrophic phase inversion of emulsion from one type to another occurred only at pH 2 and pH 2.5. With increased oil fraction in the system, emulsions were suffering from transitions from o/w to o/w type high internal phase emulsion (HIPE) gels before transferring to the final o/w/o multiple emulsion at pH 2. O/w emulsions were formed at 70 vol% oil fraction, showing as an unspherical shape with oils being trapped in as a result of the stabilisation of HIPE gel emulsion. As well, such emulsions are stable to against creaming from the gravity force (Figure 5-22). The formation of dodecane dispersed multiple emulsions at $\emptyset_O$=0.9 indicated a postponing of conventional catastrophic phase inversion at pH 2. 'Instead of undergoing an o/w to oil-dispersed emulsion phase inversion as typically observed at high oil fraction (e.g. $\emptyset_O$=0.9) for the other particle systems, here the o/w emulsions stabilized by MV90-5mol% at pH2 are well dispersed again in oil at high $\emptyset_O$ (c.a. 0.7), forming an o/w/o type multiple emulsion. Phase inversion from o/w to o/w/o thus occurs at this volume fraction.

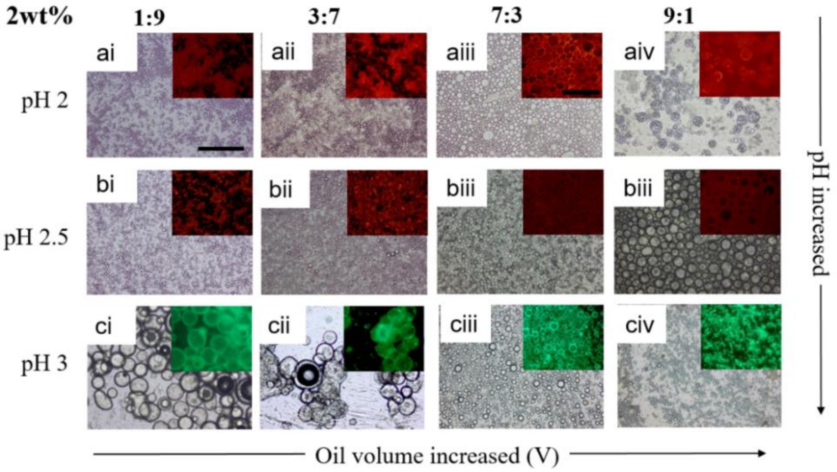


Figure 5-21: Optical microscope images of emulsion droplets stabilised by 2 wt% (oil phase) MV90-5 mol% cross-linked particle suspension with i) 1:9 o:w; ii) 3:7 o:w; iii) 7:3 o:w and iv) 9:1 o:w at a) pH 2; b) pH 2.5 and c) pH 3 of aqueous phase (scale bar 500 μm for all; aiii florescent image scale bar 100 μm)

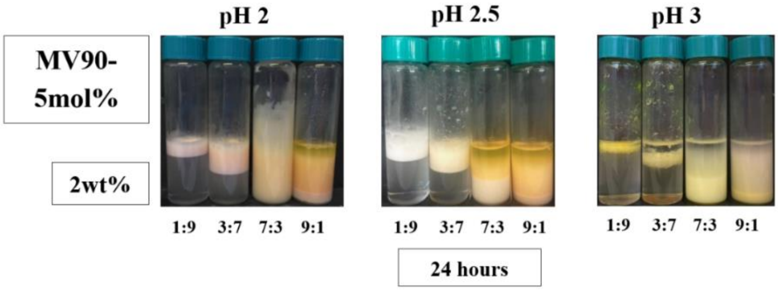


Figure 5-22 Appearance of emulsion vials stabilised by 2wt% (of oil phase) MV90-5mol% particles with 1:9, 3:7, 7:3 and 9:1 oil-water volume ratio under pH 2, pH 2.5 and pH 3, respectively, after 24 hours.

The dodecane dispersed emulsions are the mixture of o/w/o multiple droplets and w/o under pH 2.5. It is obvious that the multiple emulsions contained one or two oil drops in each water globule at pH 2.5 (biii and biv) while there were couple of oil droplets existing in 90 vol% oil formed multiple emulsions at pH

2 (aiv). In (c) line, emulsions were prepared at pH 3 showing a trend of big flocculated w/o droplets to tiny dispersed water globules in dodecane via decreased water content in the system. The evidence of multiple emulsion (o/w/o) can be found in some flocculated w/o droplets at lower oil fractions. The stability of the aforementioned emulsions is sensitive to the oil-water volume ratio as well. Despites of the creaming and sedimentation of o/w droplets and dodecane dispersed emulsions, the o/w HIPE gels are stable to resist coalescence and phase separations (Figure 5-22 and Figure 5-23). Severe aggregation of dodecane dispersed emulsions following with a phase separation was showing as a rigid chunk in emulsion vials of higher water fraction at pH 3.

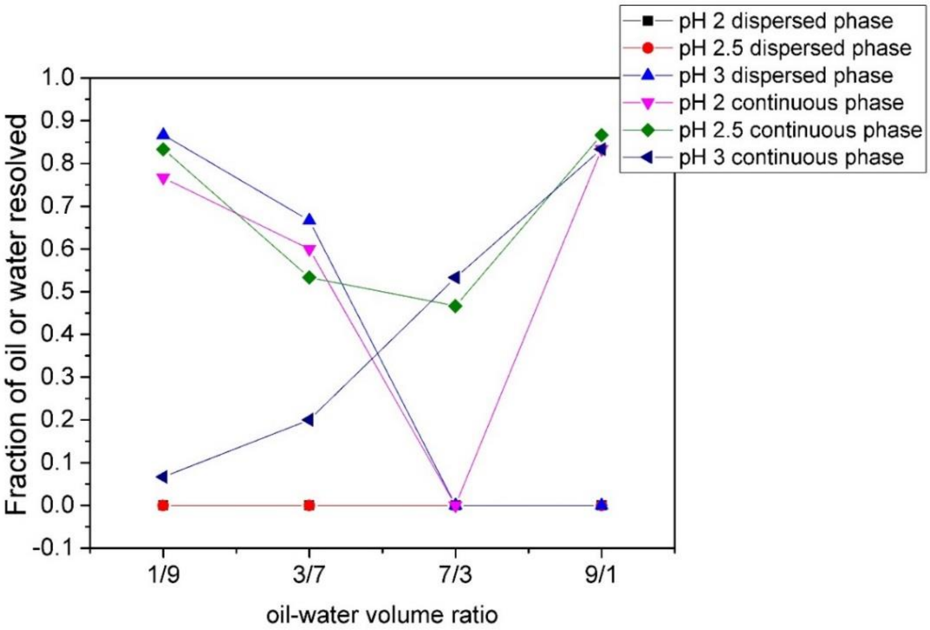


Figure 5-23 Stability after 24 hours of emulsions stabilised by 2wt% MV90-5mol% at different pH as function of oil-water volume ratios. The variation of resolved dispersed phase volume ratio refer to coalescence; fraction change of continuous phase refer to sedimentation for dodecane dispersed emulsion and creaming for o/w emulsions.

Following with the experiments of water-oil volume ratio study of emulsions with 2 wt% (of oil phase volume), MV90-5mol% stabilised emulsions were also performed with 1 wt% (of whole system), and such concentration indicates the constant particle quantity in system independent of oil-water volume fractions. Emulsion types of 1 wt% particle concentration are more or less following the trends of 2 wt% particle stabilised systems at each pH and increased $\emptyset_O$ (Figure 5-21). Especially, o/w HIPE was also observed with such concentrations, indicating the formation was owing to the charged MV90-5mol% particle interfacial behaviour itself. It is worthy to highlight not only the fact that the o/w HIPE was only discovered within MV90-5mol% stabilised emulsion systems under specific conditions, but also the truth that it was the first time of demonstration of such phenomenon in oil-dispersed pH responsive particle/microgel systems.

Nevertheless, the multiple emulsions (Figure 5-24 biii and biv) of 1 wt% that was inverted from o/w by increased oil fraction at pH 2.5 contained more oil globules inside the w/o droplets comparing to the 2 wt% cases (Figure 5-21). This also implies that the reduced particle amount in the 1 wt% (of the whole system) case results in an eventually increase of mean droplet size. This motivated us to investigate further in terms of mean drop size and emulsion stability to compare the two systems (Figure 5-25 and Appendix 5-4). At lower water fractions, the average emulsion drop diameter is larger in the 2 wt% particle stabilised system than the 1 wt% system at pH 3. Indeed, the 2 wt% particle concentration in oil is actually equal to 0.2 wt% and 0.6 wt% based on the whole system volume at $\emptyset_W$= 0.1 and 0.3, respectively. Undoubtedly, the 1 wt% (of whole system volume) fabricated smaller w/o droplets than the 0.2 wt% and 0.6 wt% cases, as confirmed from Figure 5-24. However, this did not happen on o/w emulsion systems, in which it has been stated that the particle concentrations have no obvious influence on o/w emulsion droplet size in Chapter 4 (Section 4.3.2)

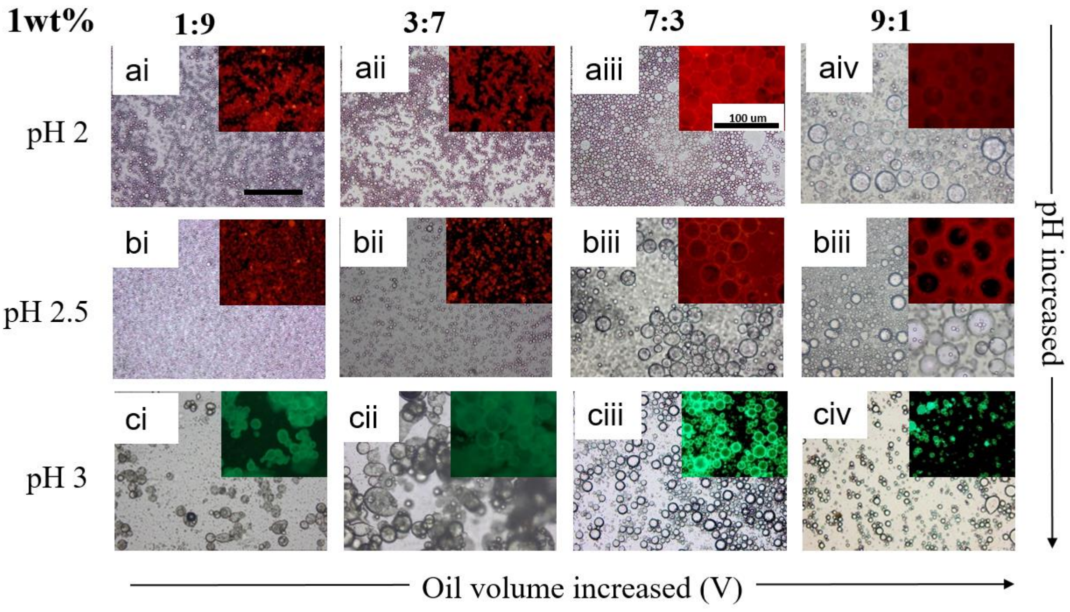


Figure 5-24: Optical microscope images of emulsion droplets stabilised by 1wt% (all oil and water phase) 10:90 MMA-2-VP 5 mol% cross-linked particle suspension with i). 1:9 o:w; ii) 3:7 o:w; iii) 7:3 o:w and iv) 9:1 o:w at a) pH 2; b) pH 2.5 and c) pH 3 of aqueous phase (scale bar 500 µm for all, aiii florescent image scale bar 100 µm)

Emulsion droplets are noticeably smaller in presence of the 2 wt% particle comparing to the 1wt% stabilised system in all pHs. This is not only due to the relatively more particles contained in the systems of 2 wt% at $\emptyset_O$=0.7 and 0.9 (equal to 1.4 wt% and 1.8 wt% of whole system volume) but also because of the type of emulsions. At higher oil contents, the majority of emulsions are dispersing in dodecane (w/o or/and o/w/o) which is following Finkle-Bancroft rule that indicated a decreased droplet size by increased particle concentrations as a typical Pickering emulsion property(Finkle et al., 1923;

Bancroft, 1912; Binks and Horozov, 2006). Further, when emulsion were stabilised by constant amount of particles, the decreased droplet size can be concluded as the increased volume of dispersed phase.

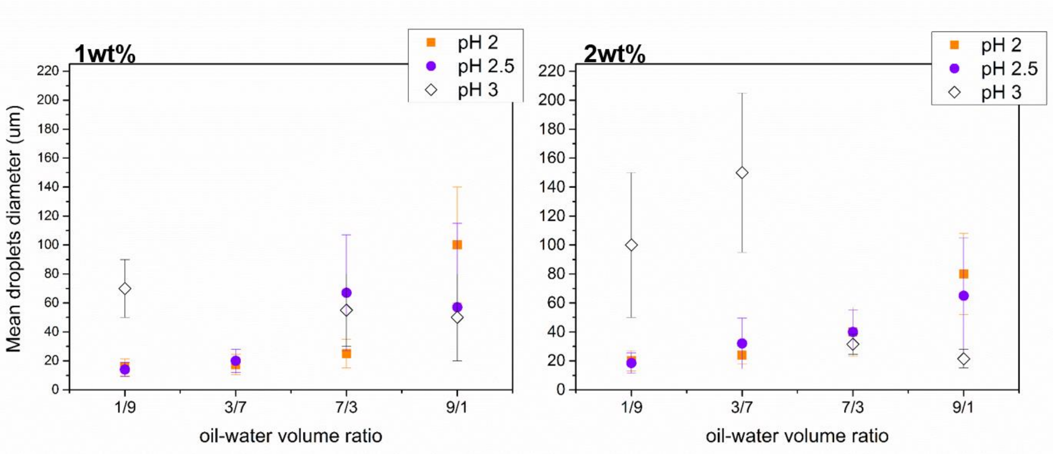


Figure 5-25 Mean droplets diameter of MV90-5mol% stabilised emulsions with varied particle concentrations and oil-water volume ratios at pH 2, pH 2.5 and pH 3.

Table 5-2 demonstrates the estimated particle and proton quantities and the preferential emulsion types as obtained with varied oil-water volume ratios at all the studied pHs. As aforementioned in the particle systems of MV90-0.5mol% and MV90, the formations of o/w/o multiple emulsions with high $\emptyset_O$ at pH 2 and pH 2.5, and the formations of flocculated o/w/o emulsions with low $\emptyset_O$at pH 3 again indicate the key roles of the charging degree of the particles at the interface and their corresponding interfacial behaviour. The interfacial properties are greatly associated with the particle quantity, the amount of protons and the protonation degree of the particle. Indeed, the experiments have been performed with four batches of particles (the data of MV30 stabilised emulsion are placed in the end from Appendix 5-5 to Appendix 5-13).

Table 5-2 In MV90-5mol% stabilised emulsion system, estimated proton quantity, ideally participated particle amount in each particle concentrations and preferred emulsion types of varied water fractions at each pH.

	Oil-water volume ratio (O:W)	Proton quantity (n)	2wt% (of oil volume) particle quantity (n) and preferred emulsion type	1wt% (of whole system volume) particle quantity (n) and preferred emulsion type
pH 2 *(10^{-2}mol/L)*	9:1	6.02×10^{19}	o/w/o 0.774×10^{12}	o/w/o 0.43×10^{12}
	7:3	18.06×10^{19}	o/w HIPE 0.602×10^{12}	o/w HIPE 0.43×10^{12}
pH2.5 *($10^{-2.5}$mol/L)*	9:1	1.9×10^{19}	o/w/o 0.774×10^{12}	w/o less o/w/o 0.43×10^{12}
	7:3	5.7×10^{19}	o/w/o contained single oil droplet 0.602×10^{12}	o/w/o 0.43×10^{12}
pH 3 *(10^{-3}mol/L)*	1:9	5.42×10^{19}	Flocculated w/o 0.086×10^{12}	Flocculated o/w/o 0.43×10^{12}
	7:3	4.2×10^{19}	Highly flocculated w/o 0.258×10^{12}	Flocculated o/w/o 0.43×10^{12}

Emulsion stabilised by oil-dispersed pH-responsive particles can be inverted from one type into another at some specific conditions (pH or particle concentrations) by increasing/decreasing the volume fraction of either phase. The evidences of changes from spherical and flowable droplets to gelled/flocculated emulsions indicate an emulsion viscosity increment peaking with a maximum near the inversion locus, as a typical phenomenon reported for the catastrophic phase inversion of conventional particle stabilised emulsions(Binks and Lumsdon, 2000). Nevertheless, comparing the emulsions prepared with MV90-0.5mol% and MV90-5mol% at each specific condition (e.g. 1 wt% particles in whole at pH 2.5), catastrophic phase inversion from o/w to o/w/o occurred above 70 vol% oil fraction regardless of particle concentrations for the latter case, greatly different from the hysteresis at $\emptyset_O$=0.9 for the former. Except from the noticeable formation of o/w/o multiple emulsions by decreasing oil content, no phase inversion has been found in the MV90-5mol% system at pH 3. MV90-0.5mol% can stabilise o/w droplets in presence of 2 wt% particles (in oil) with 10 vol% oil phase volume fraction at pH 3. In general, emulsions stabilised with MV90-5mol% particles are more stable with relatively smaller size of each type than the MV90-0.5mol% stabilised system. Especially, the remarkable stabilisation of o/w HIPE and more stable flocculated w/o (o/w/o) emulsion at certain conditions indicate a very good adsorbing ability of MV90-5mol% at both w/o and o/w interfaces, which haven't been observed in the MV90-0.5mol% system.

In aqueous based PNIPAM stabilised emulsion systems, the lower cross-linked microgels deformed stronger at interface leading to a better stability of emulsion they stabilised(Destribats et al., 2011a). However, this is not the case for our oil-dispersed pH responsive cross-linked particle system, since good stability of emulsions have been obtained with both the charged and the uncharged MV90-5mol% particles. It is more likely that some surface rheological properties such as shear or compression viscoelasticity of such particles at the interface become better with the increased cross-linking density in the particle cores, as also reported in the literature(Senff and Richtering, 2000). To figure out further more possibilities of our anticipations, the measurements of dynamic interfacial tension with such particular systems will be shown and discussed in next chapter.

5.4 Conclusion

In this chapter, based on the Pickering emulsions stabilized by oil-dispersed pH responsive p(MMA-2-VP)-PDMS particles as discussed in Chapter 4, in this chapter we have continually investigated the influences of oil-water volume ratios, particle concentrations and pH on the formation, structure and stability of the emulsion systems. In particular, the experiments were performed with four batches of particles, that is, MV90 containing the highest 2-VP ratio (90%), MV30 containing the lowest 2-VP ratio (30%), MV90-0.5mol% with the lowest cross-linker density(initial 0.5 mol% relative to monomer) and MV90-5mol% with the highest cross-linker density(initial 5 mol% relative to monomer). Specifically, the oil-water volume study regarding the emulsion properties and types is demonstrated in presence of constant particle amount of whole system (1wt%) and particle concentration of oil phase (2wt%) while particles subjected to different charging state (pH 2, pH 2.5 and pH 3).

Firstly, within a narrow pH range(2.0 to 3.0) the critical pH point that drives the phase inversion from w/o to o/w has been found to lie between pH 2.5 and pH 3.0 based on particle MV90(2wt% in oil) at a water/oil volume ratio of 50/50. By increasing the oil/water volume ratio in the emulsions with the particle concentration fixed at 2wt% (in oil), catastrophic phase inversion from o/w to o/w/o was induced when the oil fraction is approaching 70% at pH2 and pH2.5, where the particles are supposed to be at charged state. To the best of our knowledge, this is the first time multiple emulsion is achieved by simply varying oil/water phase ratio based on the responsive particle/microgel systems. However, the w/o emulsions at pH3 show not clear phase inversion within the studied oil/water volume ratios for these un-crosslinked particles, but only the emulsion stability and the droplet size are affected. Worthy to notice, the o/w/o was not observed in the systems with 1 wt% particles in whole even at high oil/water volume ratios (fewer particle amount compared to the case of 2wt% in oil). Hence, we would conclude that the as-prepared o/w/o multiple emulsion is likely to be attributed to the coexistence of both protonated and un-protonated particles in the system which stabilize either o/w or the o/w in oil.

Secondly, in the systems of cross-linked particles (i.e. MV90-0.5mol% and MV90-5mol%), the hysteresis of catastrophic phase inversion happened with emulsion inversion from o/w to o/w/o at pH2 and 2.5 taking place at a higher oil/water volume ratio of 9/1 compared to the un-crosslinked particles. One surprising finding is that for the w/o emulsion systems stabilized at pH3, only the case of MV90-0.5mol% (with 2wt% in oil) underwent a catastrophic phase inversion from w/o to simple o/w. Moreover, for the particles with potential highest crosslinking density (initial cross-linker concentration), namely the MV90-5mol%, a remarkable emulsion system of o/w HIPE (high internal phase emulsion) was formed at pH 2.0 regardless of the studied particle concentrations. Again, this is reported for the first time based on oil-dispersed pH responsive particle/gel systems. Meanwhile, an interesting flocculated o/w/o emulsions was found with lower oil fraction in presence of 1wt% MV90-5mol% at pH 3.

Furthermore, all these phenomena concerning the phase inversions have been confirmed by the measurements of mean droplet diameter and emulsion viscosity, which both show an increment in the vicinity of the inversion point. The viscosity increase was reflected from the phase appearances such as rigid chunk, flocculated and HIPE states, etc. Besides, as revealed from the data of the resolved dispersed/continuous phase (creaming/sedimentation) after 24 hours preparation, the stability of emulsion experiences a decrease within the critical regime of phase inversion. According to our estimations, the catastrophic phase inversion is induced by the variation of oil-water volume fraction, but dominated by the proton quantity and concentrations with the corresponding particle amount in the system. As far as the crosslinking effect is concerned, the MV90-5mol% prepared emulsions have better stability regardless of emulsion types at each pH, particle concentrations and oil-water fractions than the MV90 (uncross-linked) and MV90-0.5mol% (lower cross-linker density) stabilised emulsions, indicating stronger adsorption of MV90-5mol% at oil-water interface and greater interfacial properties to against coalescence.

In sum, taking advantage of the pH-responsiveness of the oil-dispersed p(MMA-2-VP)-PDMS particle, various emulsion types can be formed by just simply varying one or two parameters in the system. However, catastrophic phase inversion of such particle stabilised emulsion system is mainly associated with the relation between proton and particle quantity which is different from conventional catastrophic phase inversion mechanism. Interestingly, the better stability of MV90-5mol% stabilised emulsion implies the influence of cross-linker density on particle adsorption at oil-water interface, which will be further investigated based on dynamic interfacial tension measurement as will be presented in next chapter.

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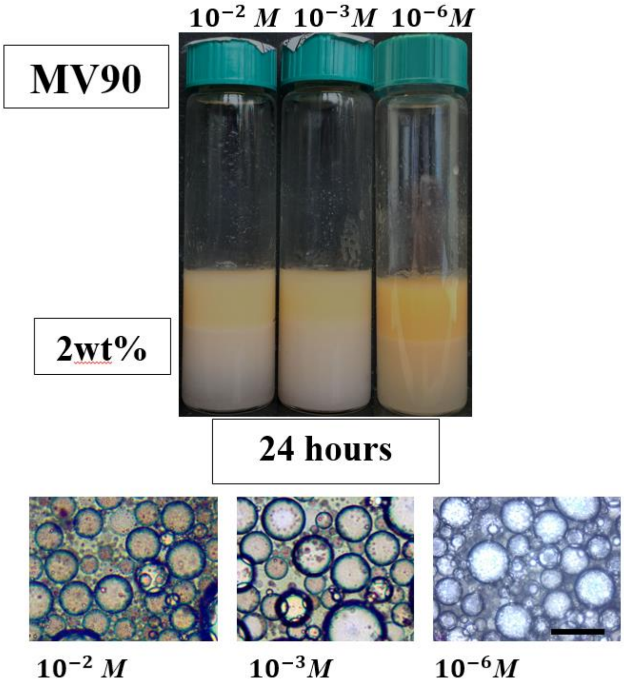
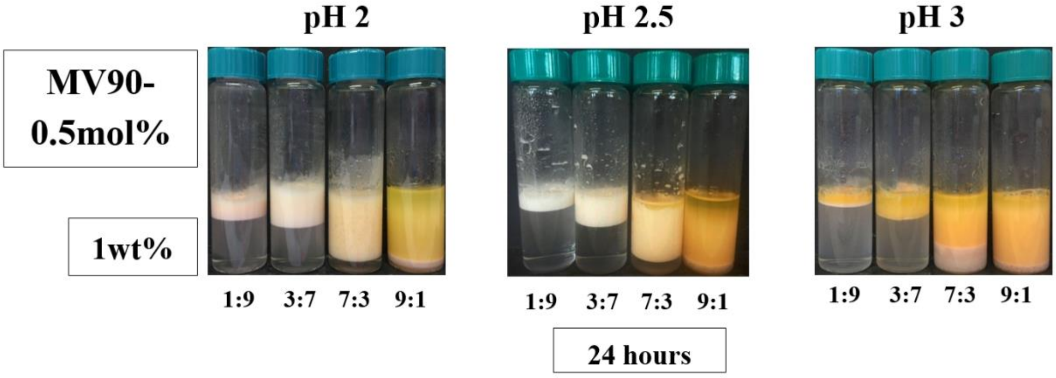
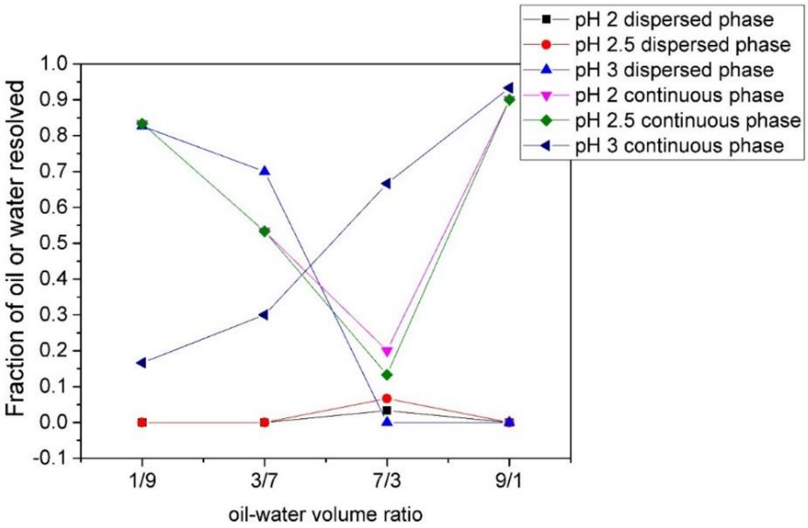
Appendix



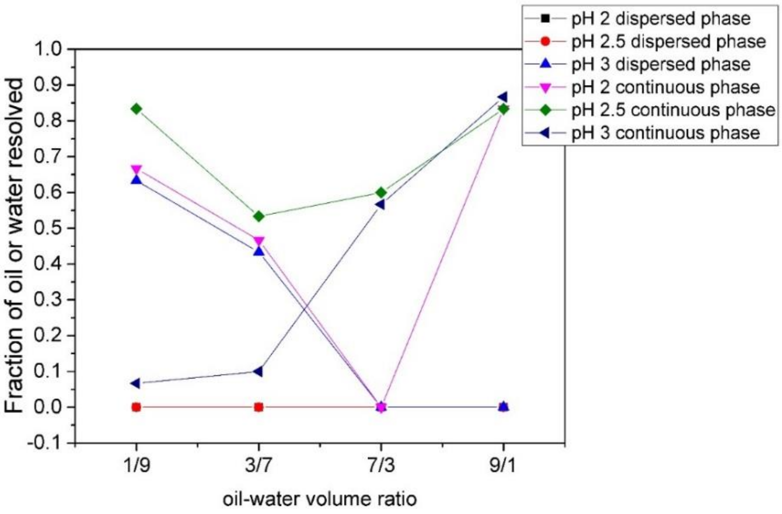
Appendix 5-1: (Upper) Appearance of vessels contained w/o emulsions stabilised by 2wt% MV90 at pH 6 with aqueous phase of 10^{-2} M, 10^{-3}M and 10^{-6}M NaCl solution after 24 hours. (Lower) optical microscopy images of w/o droplets in each condition.



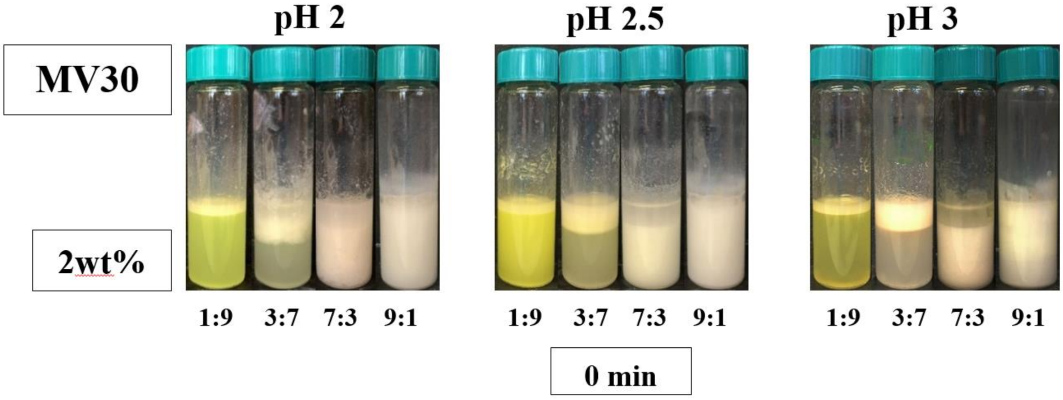
Appendix 5-2 Appearance of emulsion vials stabilised by 1wt% (of whole system) MV90-0.5mol% particles with 1:9, 3:7, 7:3 and 9:1 oil-water volume ratio under pH 2, pH 2.5 and pH 3, respectively, after 24 hours.



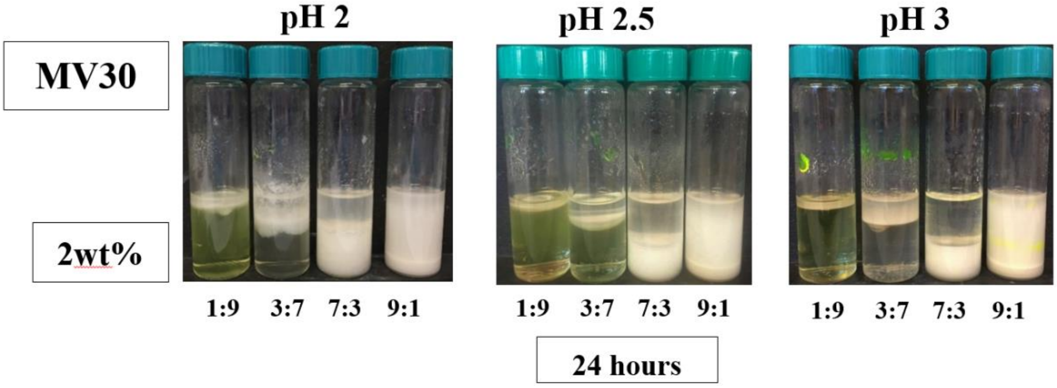
Appendix 5-3 Stability after 24 hours of emulsions stabilised by 1wt% MV90-0.5mol% at different pH as function of oil-water volume ratios. The variation of resolved dispersed phase volume ratio refer to coalescence; fraction change of continuous phase refer to sedimentation for dodecane dispersed emulsion and creaming for o/w emulsions.



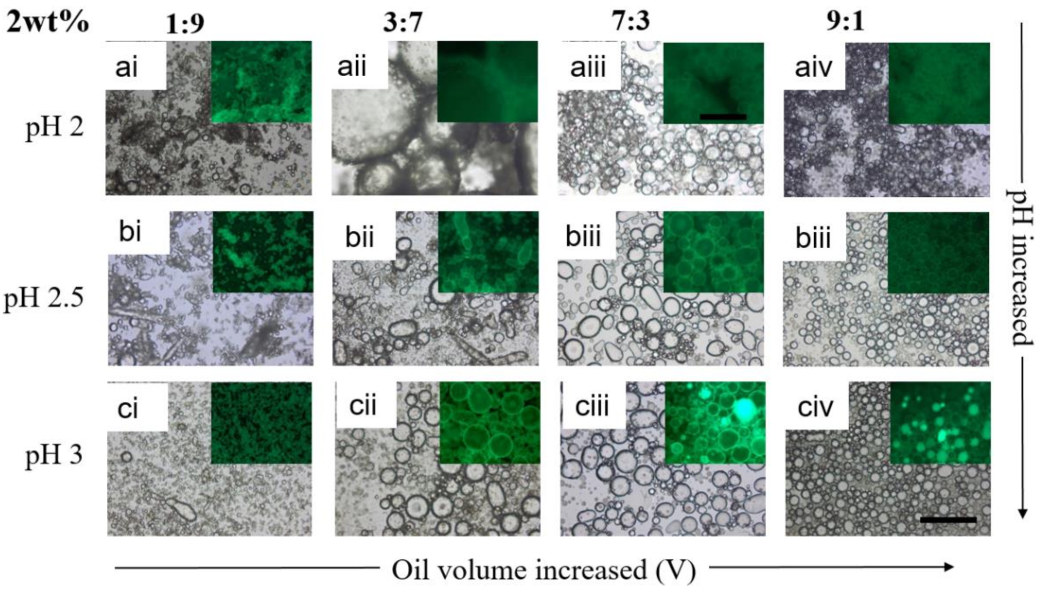
Appendix 5-4 stability after 24 hours of emulsions stabilised by 1wt% MV90-5mol% at different pH as function of oil-water volume ratios. The variation of resolved dispersed phase volume ratio refer to coalescence; fraction change of continuous phase refer to sedimentation for dodecane dispersed emulsion and creaming for o/w emulsions.



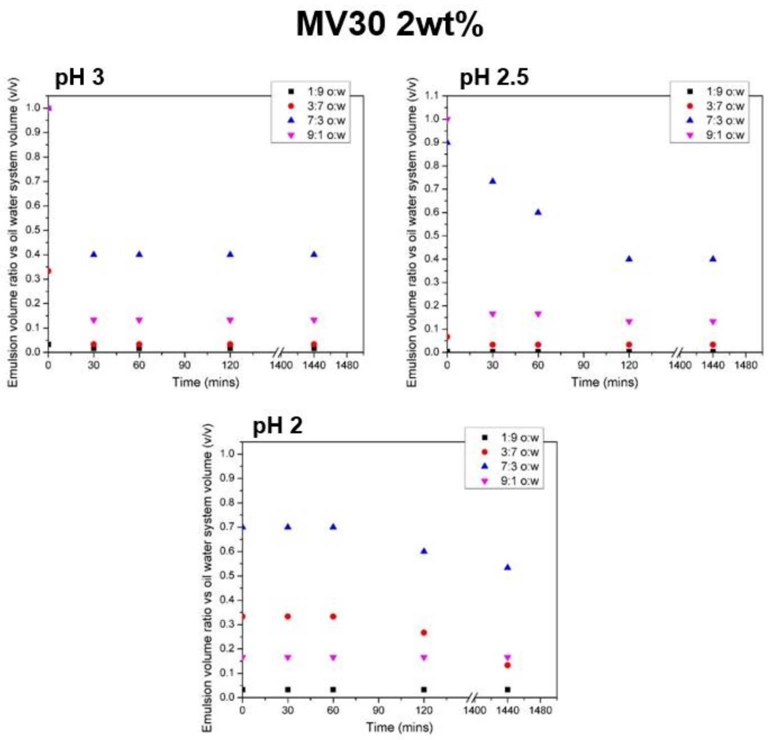
Appendix 5-5 Appearance of emulsion vials stabilised by 2wt% (of oil phase) MV30 particles with 1:9, 3:7, 7:3 and 9:1 oil-water volume ratio under pH 2, pH 2.5 and pH 3, respectively, just prepared.



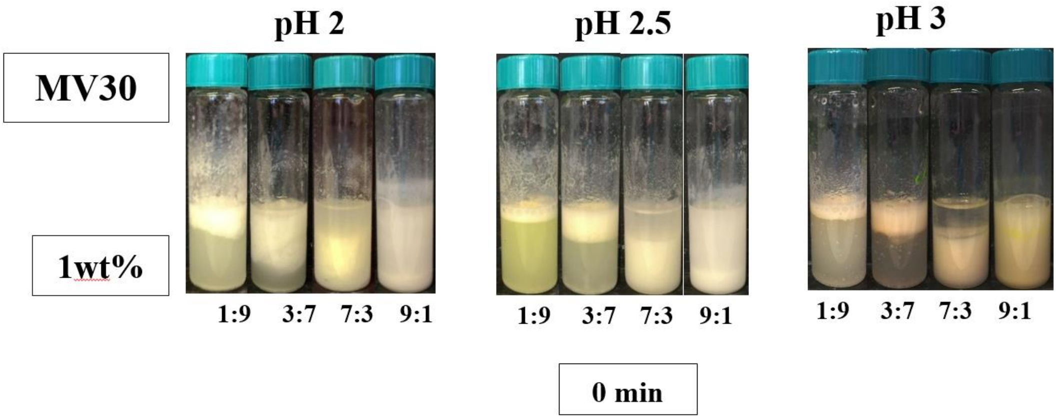
Appendix 5-6 Appearance of emulsion vials stabilised by 2wt% (of oil phase) MV30 particles with 1:9, 3:7, 7:3 and 9:1 oil-water volume ratio under pH 2, pH 2.5 and pH 3, respectively, after 24 hours.



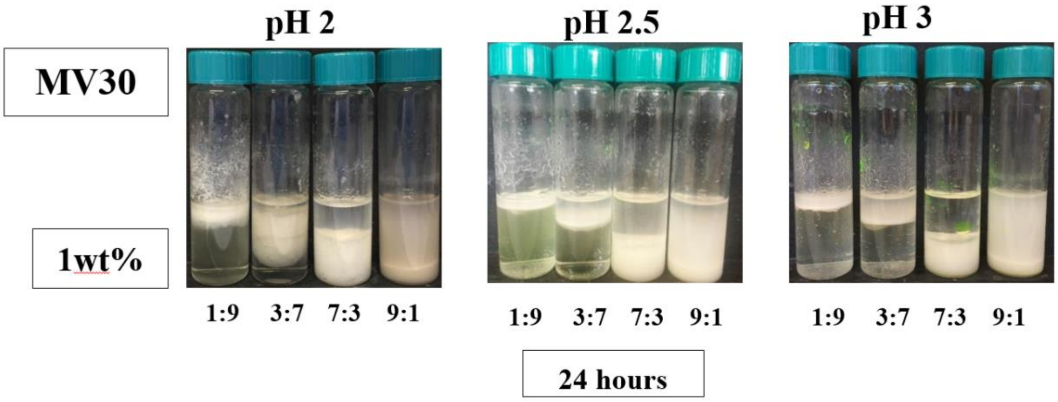
Appendix 5-7 Optical microscope images of emulsion droplets stabilised by 2wt% (oil phase) MV30particle suspension with a). 1:9 o:w; b) 3:7 o:w; c) 7:3 o:w and d) 9:1 o:w at i) pH 2; ii) pH 2.5 and iii) pH 3 of aqueous phase (scale bar 500 um for all)



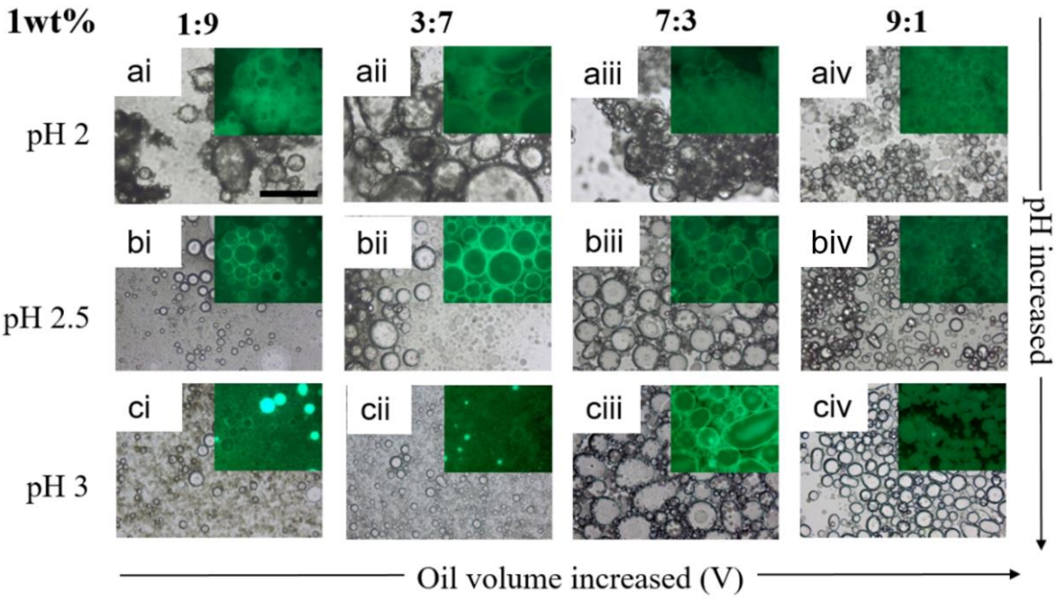
Appendix 5-8 Emulsion volume fraction as function of time at varied pH and different oil-water volume ratio of emulsion stabilised by 2wt% MV30 particles.



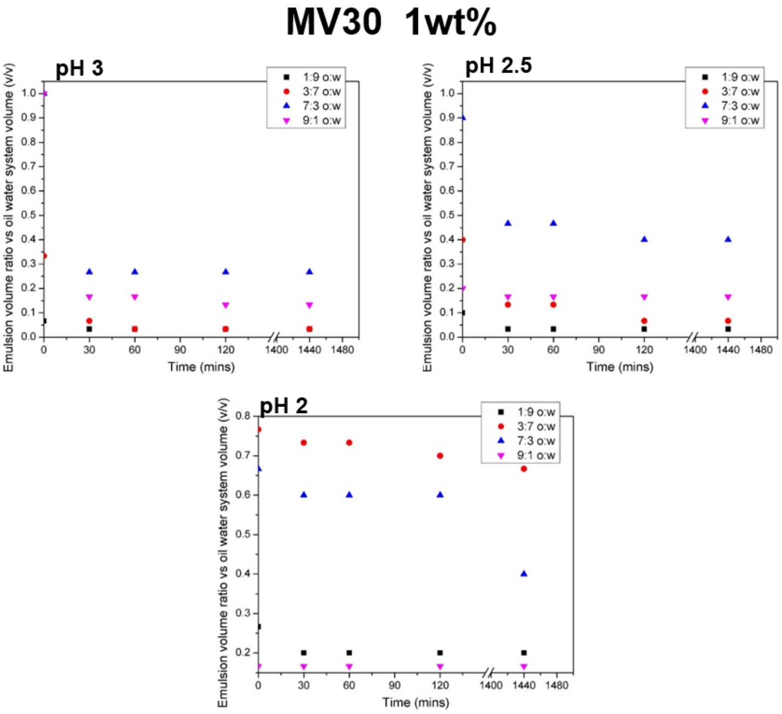
Appendix 5-9: Appearance of emulsion vials stabilised by 1wt% (of whole system volume) MV30 particles with 1:9, 3:7, 7:3 and 9:1 oil-water volume ratio under pH 2, pH 2.5 and pH 3, respectively, just prepared.



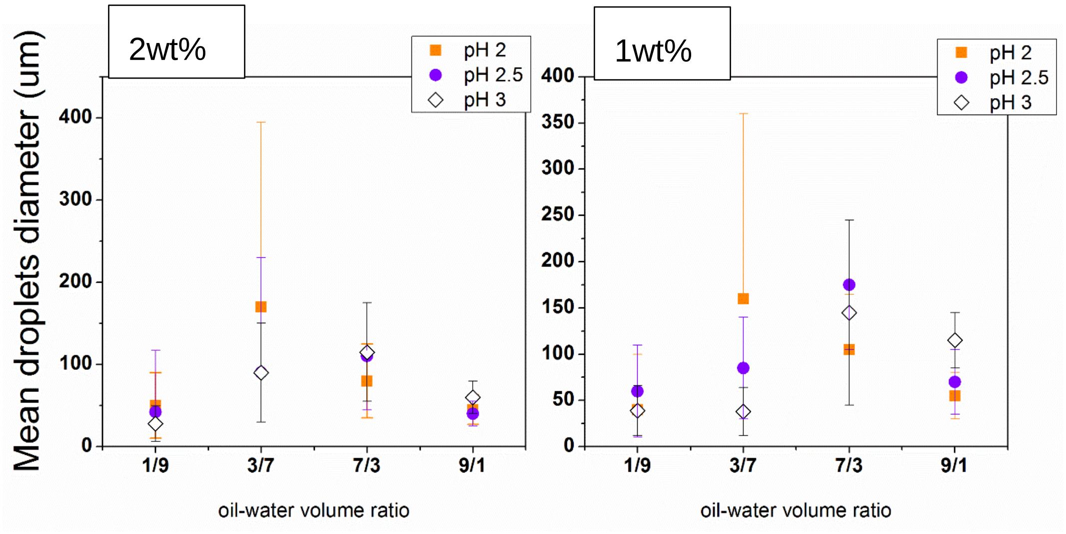
Appendix 5-10: Appearance of emulsion vials stabilised by 1wt% (of whole system volume) MV30 particles with 1:9, 3:7, 7:3 and 9:1 oil-water volume ratio under pH 2, pH 2.5 and pH 3, respectively, after 24 hours



Appendix 5-11: Optical microscope images of emulsion droplets stabilised by 1wt% (of whole system volume) MV30 particle suspension with i). 1:9 o:w; ii) 3:7 o:w; iii) 7:3 o:w and iv) 9:1 o:w at a) pH 2; b) pH 2.5 and c) pH 3 of aqueous phase (scale bar 500 um for all)



Appendix 5-12 Emulsion volume fraction as function of time at varied pH and different oil-water volume ratio of emulsion stabilised by 1wt% MV30 particles



Appendix 5-13 Mean droplets diameter of MV30 stabilised emulsions with varied particle concentrations and oil-water volume ratios at pH 2, pH 2.5 and pH 3.

Chapter 6. Oil-dispersed pH responsive particle adsorption kinetics

6.1 Introduction

In previous chapters, the behaviour of newly developed core-responsive silicone-based shell particles has been shown to drastically influence the properties of the emulsions they stabilise. Large variations in the type, stability and droplet diameters of such emulsions where seen (from simple o/w and w/o to o/w/o, including gelled HIPE) when changes to external parameters such as pH and oil/water volume fractions were made. It is clear that the behaviour of these responsive particles in response to changes in these parameters have a drastic influence on the resulting emulsions. Thus the aim of this chapter is to mimic the emulsion oil/water interfaces and attempt to measure relevant parameters that will further indicate how the particle behaviour changes as a function of pH.

It is anticipated that the data obtained when investigating interfacial tension and particle contact angle at 2D oil-water interfaces in conditions replicating those investigated in the cases of the emulsions studied in previous chapters may give some insights as to the particle behaviour leading to the different emulsion behaviours.

In order to understand the interfacial behaviour of novel types of particulate emulsifiers, it is vital to first introduce similar studies published in the academic literature first. In this regard, various recently developed responsive particles and used for emulsion stabilisation can be focused on to draw comparisons with the particles synthesised in this work. For example, (aqueous dispersed) microgel particles are a system where changes in temperature or pH allow for swelling and de-swelling as well as very different interfacial behaviour (Ngai et al., 2006; Ngai et al., 2005; Brugger et al., 2008; Destribats et al., 2011b). A brief literature review of relevant interfacial behaviours (evaluated on planar oil-water interface and on 2-Dimensional curved interfaces) of microgels and their influence on emulsion properties is given in Chapter 2 (Section 2.3.3, respectively).

In addition to this previous review of the literature, it is worth mentioning the possibility of monitoring an adsorption coefficient of Pickering emulsifiers to the oil-water interface, which is crucial to understand the ability of those materials to adsorb onto the interface (Li et al., 2013; Ward and Tordai, 1946; Monteux et al., 2010; Brugger et al., 2009; Brugger et al., 2008; Brugger and Richtering, 2008). Recently for example, Li et al. evolved the derivation of the diffusion-controlled model equation of Ward and Tordai (Ward and Tordai, 1946) into another expression to calculate the diffusion coefficient of irreversibly adsorbed microgels. In their work, they used the term of interfacial diffusion coefficient to quantify the particle interfacial adsorbing speed. However, not every contact between particle and interface will result in an adsorption event. Thus, we used the term of adsorption kinetic instead. They used their derived equation (Equation 6-1 below) to fit dynamic interfacial tension data under different external conditions(Li et al., 2013).

$$k_i = 2RT\sqrt{\frac{D_{interface}}{\pi}}C_0$$

Equation 6-1(Li et al., 2013)

Where $\boldsymbol{C_0}$ is the particle concentration, $\boldsymbol{R}$ represents the ideal gas constant, $\boldsymbol{T}$ is the temperature, and $\boldsymbol{k_i}$ represents the slope of surface tension vs time illustrating in Figure 6-1. The slope $\boldsymbol{k_i}$ can be derived according to the linear fitting of normalized interfacial tension data.

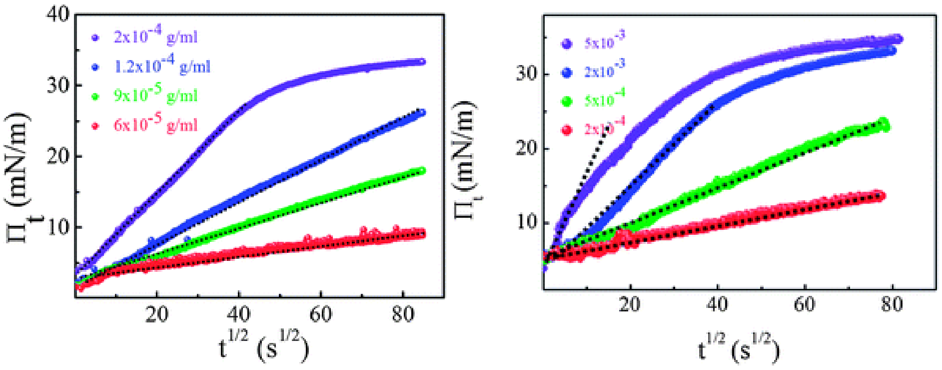


Figure 6-1 Normalized interfacial tension data is showing the influence of particle concentrations on the relation between dynamic surface pressures (Π_t) *vs.* $t^{1/2}$ at 298 K (left) and 317 K (right). (taken from (Li et al., 2013))

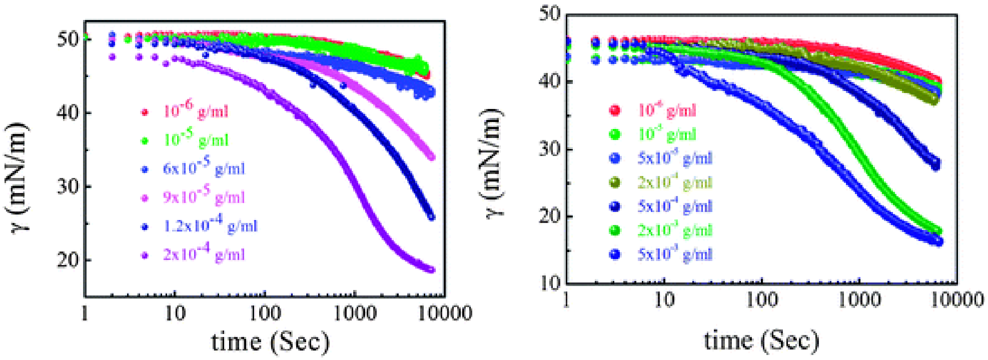


Figure 6-2: Interfacial tension of heptane-water interface as a function of time at 298K (left) and 317K (above the volume phase transition temperature VPTT) (right) in the presence of varied concentrations of 3.2%BA PNIPAM microgels. (Taken from (Li et al., 2013))

Practically, these authors first measured the interfacial tension of heptane-water interface at different temperature in the presence of varied microgel concentrations (Figure 6-1). Secondly, they obtained the slope k_i of normalized interfacial tension data (Figure 6-2), which were evolved from the relationship between surface tension and time. The surface tension illustrated the differences of measured interfacial tension in the presence of microgel particles and pure n-heptane –water interfacial tension (Li et al., 2013) . The relation between k_i and C_0 were then replotted and linear fitted by extracting another slope $\frac{k_i}{C_0}$. Eventually, the 'adsorption coefficient' of the particles to the interface, $D_{interface}$ was calculated from the expression shown below:

$$\boldsymbol{D_{interface} = (\frac{k_i}{C_0 2RT})^2 \pi} \qquad \text{Equation 6-2}$$

According to their derivation, the final unit of $D_{interface}$ is $\frac{m^2}{s} \cdot (\frac{g}{mol})^{-2}$. The molar mass M ($\frac{g}{mol}$) of synthesised polymeric particle is difficult to estimate at this stage. Li compared the interfacial diffusion coefficient of the same temperature-responsive microgels while varying the temperature (Figure 6-2). As a result, in these authors' case, molar mass remained constant and played no role in the differences seen in $D_{interface}$. However in our case, we aim to compare the $D_{interface}$ of varied oil-dispersed particles at different pHs, where the diameter and molar mass of these various particles needs to be taken into consideration. Thus, C_0 can be expressed as:

$$\boldsymbol{C_0 \sim \frac{wt\%}{\left[\frac{4}{3}\pi\left(\frac{d}{2}\right)^3 \times \rho_{particle}\right]}} \qquad \text{Equation 6-3}$$

here $wt\%$ is the concentration of measured particle suspension, d is the diameter of particle, N_A represents Avogadro's number. The particle concentration C_0 can be converted into particle quantity of per volume unit.

Thus, the $D_{interface}$ for a range of concentrations and particle samples can be estimated in our systems.

In this chapter, we examine the oil-dispersed core-shell p(MMA-2-VP)-PDMS pH-responsive particles' dynamic adsorption behaviour at the dodecane-water interface. In previous chapters, such particles are clearly showing a different behaviour at the interface resulting in a range of emulsion types and stability, particularly when the pH of the aqueous phase is varied. In order to provide some further insights in the behaviour of the particles at the oil-water interface under these different conditions, we study here the adsorption kinetics of these pH responsive particles. A pendant drop tensiometer is employed to record the evolution of the dodecane-water interfacial tension as function of time in the presence of three different kinds of oil-dispersed core-shell p(MMA-2-VP)-PDMS pH responsive particles (MV62, MV90 and MV90-5mol%). According to the results in previous chapters, MV62 particle contains 62% polymerized 2-VP in its core while MV90 has 90% by the estimation from Proton-NMR. MV90-5mol% were synthesized and expected to be cross-linked by 5mol% DVB, but copolymerized with 10% MMA and 90% 2-VP in accordance with MV90 on its copolymer ratios. These particles were chosen in particular to highlight behaviour differences for cases where drastically different emulsion characteristics were observed and also to explore potential differences between cross-linked and uncross-linked particles. In addition to monitoring adsorption kinetics, we are using the derivation from Li et al. described above to quantify this kinetics and draw comparisons between the different samples.

6.2 Experimental Methodology

In this section, involved materials and their briefly purpose are introduced initially. In this part of work, the main effort was spending on the measurement of dynamic interfacial tension by a typical pendant drop tensiometer. Since that, its principle is shown in follow. In the prior of the interfacial tension measurement, the calibration of equipment, cleaning and the preparation of the oil and aqueous phases need to be taken into considerations. A detailed measuring procedure of interfacial tension and the obtained data analysis is explained in the final section with the examples of pure dodecane-water interfacial tension upon two pH.

6.2.1 Materials

Table 6-1: Chemicals involved in this Chapter's experiments.

Entry	Materials	Standard	Supplier
1.	Water	Milli-Q water	Milli-Q reagent water system
2.	Dodecane	Reagent Plus®, ≥99%	Sigma-Aldrich
3.	Sodium hydroxide (NaOH)	reagent grade, ≥98%, pellets (anhydrous)	Sigma-Aldrich
4.	Hydrogen chloride (HCl)	ACS reagent, 37%	Sigma-Aldrich
5.	Decon		
6.	Ethanol	ACS reagent, absolute ≥99.8%	Sigma-Aldrich
7.	Acetone	CHROMASOLV® Plus, for HPLC, ≥99.9%	Sigma-Aldrich
8.	Isopropanol (2-Propanol)	ACS reagent, ≥99.5%	Sigma-Aldrich

Involved chemicals are listed in Table 6-1. All chemicals are used as received. Milliq water and dodecane are employed as aqueous phase and oil phase, respectively. Sodium hydroxide and hydrogen chloride are dissolved in water to adjust the pH of aqueous phase. Decon, ethanol, Acetone and milli-q water are cleaning agent and solvents.

6.2.2 Interfacial tension measurement

6.2.2.1 Pendant drop Tensiometry

The definition of interfacial tension and its basic measurement methods have been introduced and reviewed in chapter 2. The so-called pendant drop tensiometer has been employed as the main methodology to study oil-dispersed pH responsive particle adsorption behaviour at dodecane-water interface. Figure 6-3 demonstrates the involved tensiometer and setup in this work. The equipment is made up of two main parts: a computer controlled Attension Theta Optical tensiometer and an automatic liquid dispenser (It has been calibrated in factory, no calibration is necessarily required before use). The detailed elements of such equipment are shown in Figure 6-3 (from 1-7).

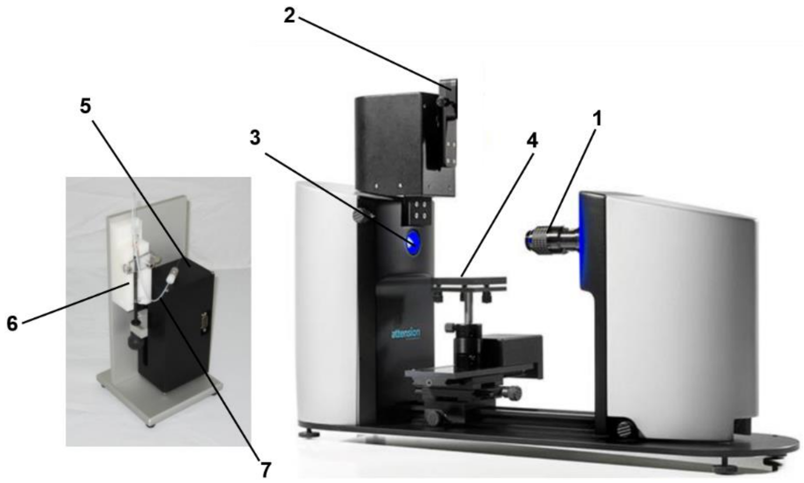


Figure 6-3 The Computer controlled Attension Theta Optical Tensiometer (right) comprises of: 1) camera lens and lens focus; 2) liquid dispenser holder and adjustment; 3) LED light source; 4) sample stage. Automatic dispenser setup (left) consists of: 5) automatic single liquid dispenser; 6) Syringe, syringe holder and piston; 7) tubing and connected needle (hooked).

The interfacial tension measurements were based on the analysis of pendant drop shape. The droplet shape of a less dense liquid holding on the hooked needle is affected by the interfacial tension of between such liquid and the bulk aqueous phase. The interfacial tension related with the droplet shape can be expressed by the following equation:

$$\gamma = \Delta\rho g \frac{R_o^2}{\beta} \qquad \text{Equation 6-4}$$

where γ represents the interfacial tension, $\Delta\rho$ represents the difference between two liquids, g is the gravitational constant, R_o represents the radius of drop curvature, and β represents a shape factor.

And the shape factor β is defined through the Young-Laplace equation expressed as the equations shown below:

$$\frac{dx}{ds} = \cos\theta$$

$$\frac{dz}{ds} = \sin\theta$$

$$\frac{d\theta}{ds} = 2 + \beta z - \frac{(\sin\theta)}{x}$$

Equation 6-5

Where involved variables are illustrating in Figure 6-4 below.

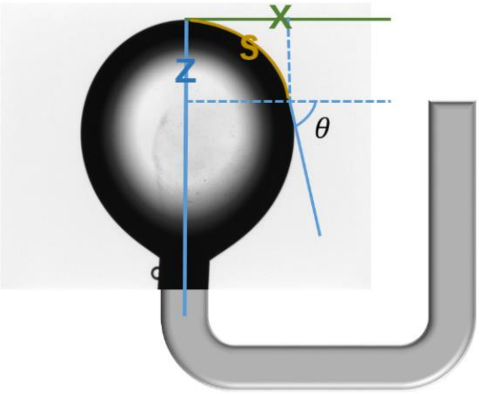


Figure 6-4 A schematic example of reversed pendant drop on a hooked needle and relevant variables which can define the shape factor β.

Thus, the surface tension γ can be obtained basing on Young-Laplace equation and the estimation of the shape factor β from repeated approximations of software and equipment. The biggest advantage of pendant drop method is to be able gain the surface tension γ from very small amount of sample (especially suits for lab scale). Besides that, the very low interfacial tension value differences can be told by such method as well. However, such method requires a suitable pendant droplet shape to obtain the reliable data as the required shape of droplet is influenced by the density difference and interfacial tension of both phases.

6.2.2.2 Particle dilution and bulk phase preparation

The interfacial tension of dodecane-water interface was examined in the presence of varied concentrations of the oil-dispersed core-shell p(MMA-2-VP)-PDMS particle suspension (MV62, MV90 and MV90-5mol%). The purified original particle suspensions were initially ultrasonicated in an ultrasonic bath at 25℃ for 30 minutes. Following that, particle suspensions were diluted with pure dodecane into different concentrations (from 1wt% to 10^{-4} wt%). Before measurement, the particle dilution samples were needed to be ultrasonicated for 10 minutes in 22 ℃ water bath. The obtained samples were ready to use.

As known, particles were dispersed in dodecane directly after synthesis. The diluted particle suspensions were used as oil phase directly. Experiments were carried out upon pH 6 and pH 2. Preliminarily prepared acid solution (1mol/L HCl) and base solution (1mol/L NaOH) were employed to adjust the pH of milliq water. The pH determined solution was then used as aqueous phase for further interfacial tension measurement.

6.2.2.3 Cleaning procedure and calibrations

- *Cleaning*

The cuvettes were cleaned by sonication in 2wt% Decon solution (anionic solution) for 10 min and then rinsed with Milli-Q water and acetone before drying using nitrogen. However, the syringe, connection tube and the hooked needle tip were cleaned by pushing through isopropanol and milliq water each three times. Eventually, the connected syringe, tubing and needle was filled up with milliq water before installation. The setup was then ready to use.

- *Pendant drop calibrations*

As known, the estimation of interfacial tension is based on the fitting of a pendant drop image. Therefore, the quality of the image taken by the tensiometer is vital for the accuracy of the results. A calibration must be made before the measurement, and it is necessary of every time the magnification of camera has been altered. Technically, there are two calibration ways: calibration with ball and needle. In current experimental work, all work has been done based on the calibration of the 22 gauge hooked needle, which has a Nominal outer diameter of 0.7176 mm.

Initially, such needle was placed by hanging on top of sample stage and in front of the camera. The position of needle can be adjusted to bring the needle into the image on-screen. Secondly, the needle image must be zoomed appropriately to ensure both most magnified needle image and the seeing of entire image. The larger drop can be investigated on screen; the greater accuracy will be. Following that, the focus of image can also be adjusted to make sure the high and sharp as possible of the needle edge. At the same time, the optimal contrast was tuned by using 'Adjust camera parameters' dialog to optimize the image quality.

Once the needle was in centre and focused with a good quality of background, the calibration of needle started. By entering the diameter of the needle and ticking the calibration with needle option, the equipment was calibrated. The calibration performed successfully only if by showing a green line along with the edge of the needle and a calibration factor. After the calibration, the equipment is ready for further actions.

6.2.2.4 Interfacial tension measurement and analysis

After the cleaning and calibration, the equipment setup is ready to use. A cuvette must be placed on the sample stage. Differ from other responsive particle/microgel system, the studied p(MMA-2-VP)-PDMS core-shell pH responsive particle system is dodecane based. Therefore, the oil-water interfacial tension measurement in such system has to be done with a hooked needle by holding an inversed droplet in aqueous phase (pH 2 and 6) (Figure 6-5). The experiment started with pushing out a less dense liquid drop (14ul) and recording image of the drop as function of time by the system (2 images per second). To remain the droplet volume constantly while time escape, which is vital for fitting and calculation later, an ‘evaporation compensation’ option must be ticked. Thus, automatic dispenser will work on to keep droplet size in consistency during the measurement. The recorded images were eventually analysed by the software (The OneAttension software) by following the principle of pendant drop tensiometer (6.2.2.1). The outcome data was then plotted by using OriginPro 2015.

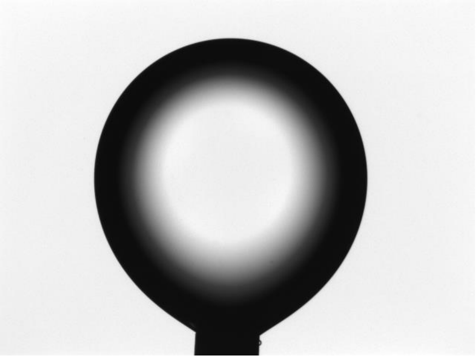


Figure 6-5 The reversed pendant drop of dodecane in water phase.

The dodecane-water interfaces are chosen as a model system in this part of work due to two reasons: first, particles were synthesized and dispersed in dodecane initially; second, all the investigation of emulsion stabilisation work were carried on at dodecane-water system, the obtained results can be compared with previous emulsion properties. Before the measurement of interfacial tension of oil-water interface in the presence of particles, the pure dodecane-water interfacial tension need to be examined as function of time at different pH. Figure 6-6 illustrates the preliminary measurement of dodecane-water interfacial tension. The analysed and replotted time-dependant dodecane-water interfacial tension show a constant value in accordance with literature data (approximately 53 mN/m at 22℃) (Goebel and Lunkenheimer, 1997; Zeppieri et al., 2001). The measured dodecane-water interfacial tension illustrates a stability regardless of pH and time changing, indicating the reliability and steadiness of the system and instrument. Thus, the equipment and experimental setup are ready for dynamic particle suspension-aqueous phase interfacial tension measurement.

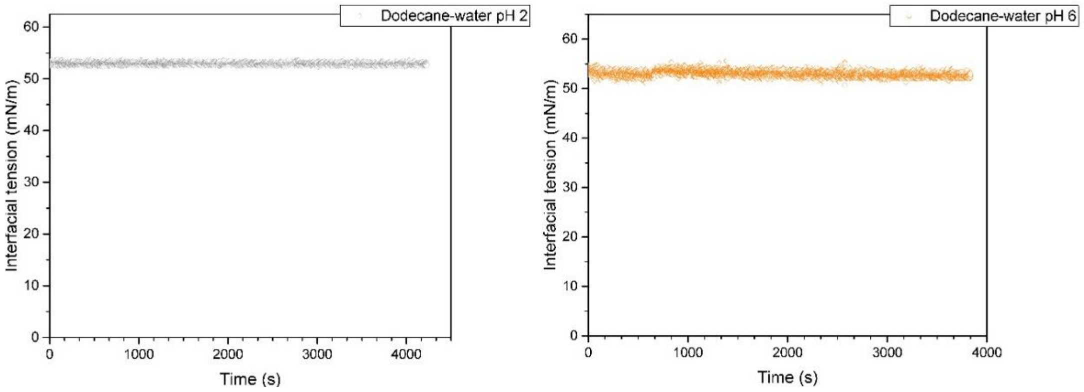


Figure 6-6 Pure dodecane-water interfacial tension measurement as a function of time at two different pHs (grey: pH 2; orange pH 6) at 22°C.

6.3 Result and discussion

In this part of study, the dynamic interfacial tension of dodecane-water interface was measured in the presence of three different types of oil-dispersed pH-responsive core-shell p(MMA-2-VP)-PDMS particles at two pHs. The influence of particle concentration on the adsorption kinetics was first investigated at both pHs. Secondly, the equilibrium interfacial tension of each concentration was estimated from the dynamic interfacial tension value after 6000s. The influence of pH and concentrations on interfacial tension of three types of particles are then demonstrated. Thirdly, the influence of particle core content and the effect of cross-linker on the interfacial tension data at different pHs are also investigated. Eventually, the particle adsorption coefficients are estimated according to dynamic interfacial tension measurement indicating the influence of pH on particle adsorption kinetics at dodecane-water interface.

6.3.1 Results

6.3.1.1 Effect of particle concentrations

Figure 6-7, Figure 6-8 and Figure 6-9 (graphs on the left) show the typical dynamic interfacial tension (γ_t) of the dodecane-water interface in the presence of MV62, MV90 and MV90-5mol% with different concentrations at pH 6. The graphs on the right of Figure 6-7, Figure 6-8 and Figure 6-9 illustrate the evolution of interfacial tension of the dodecane-water interface in the presence of MV62, MV90 and MV90-5mol% with various concentrations at pH 2.

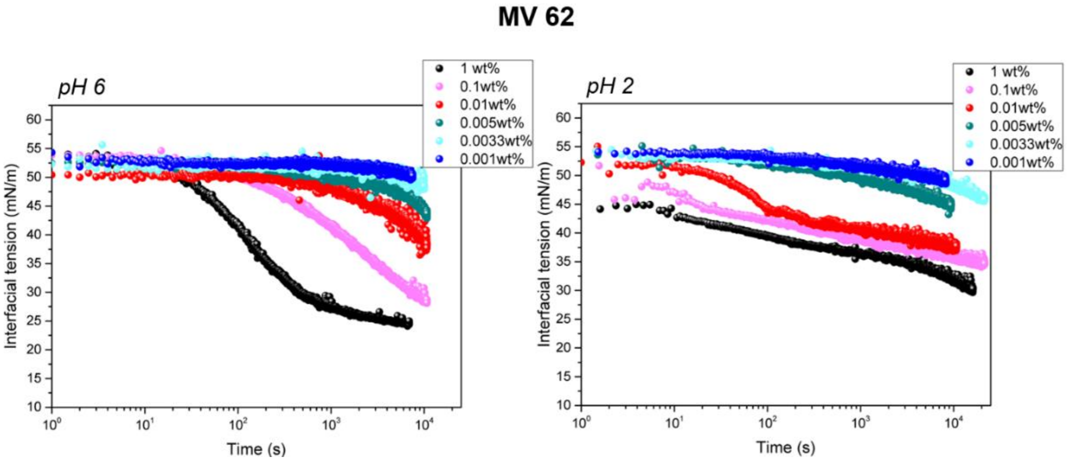


Figure 6-7: At both pH 6 and pH 2, Oil-dispersed pH responsive particle concentration dependence of interfacial tension γ_t (mN/m) as function of time (s) at dodecane-water interface and 22 ℃, in which the used particles are MV62.

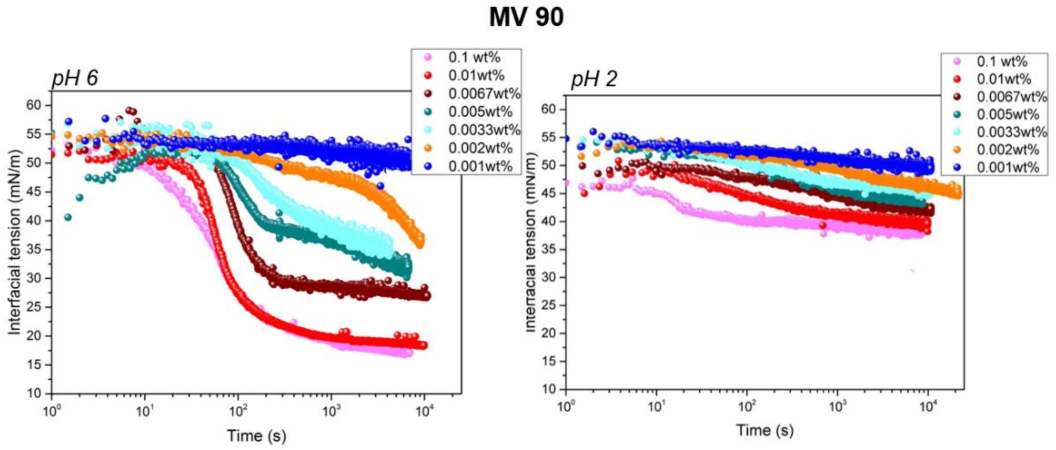


Figure 6-8: At both pH 6 and pH 2, Oil-dispersed pH responsive particle concentration dependence of interfacial tension γ_t (mN/m) as function of time (s) at dodecane-water interface and 22 ℃, in which the used particles are MV90.

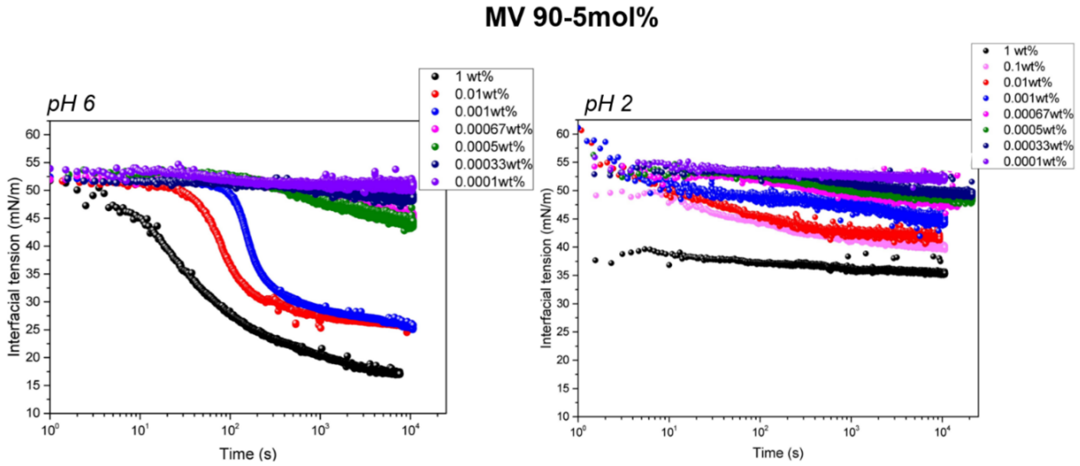


Figure 6-9: At both pH 6 and pH 2, Oil-dispersed pH responsive particle concentration dependence of interfacial tension γ_t (mN/m) as function of time (s) at dodecane-water interface and 22 ℃, in which the used particles are MV90-5mol%.

At all concentrations, the interfacial tension decreases with time as expected for all three kinds of particles. This observation indicates the spontaneous adsorption of particles to the dodecane-water interface regardless of particle conformation, which indicates that these particles have a strong affinity for the interface at pH6, in agreement to observations made of the stability of emulsions produced under the same conditions for the same particles.

The interfacial tension also decreases as a function of time at pH 2 in all cases. According to the results and discussion in previous chapters, such oil-dispersed pH responsive particles are charged at pH 2 and uncharged at pH 6. It indicates that such particles are still interfacially active even when their final interfacial configuration involves a charged core. However, one can notice a marked difference in the values of the interfacial tensions recorded when comparing the same particles at pH 6 and pH 2. However, in both cases the dependence of interfacial tension on the particle concentration appears to show the same trend with very small effects seen for low particle concentrations (e.g. at 0.001w%), and much larger decrease at higher particle concentrations. From this observation, one can conclude that it is likely that the diffusion and adsorption events leading to particles adsorbing at the interface are occurring with similar kinetics at both pHs tested here. However, these data also imply that when the particle core is protonating in contact with the water phase, the particles' ability to reduce the interfacial tension is lower. This could be due to several reasons, including fewer particles adsorbed at the interface due to lateral repulsion between particles at the interface as a result of electrostatic interactions, although little evidence for this has been found in observing emulsion droplets via CryoTEM.

6.3.1.2 Effect of pH

The dynamic interfacial tension value obtained at t=6000s were averaged and used as the equilibrium interfacial tension for varied particle concentrations and pH (Li et al., 2013). Figure 6-10, Figure 6-11 and Figure 6-12 show the data of estimated equilibrium interfacial tension with increased particle concentrations at the two pHs.

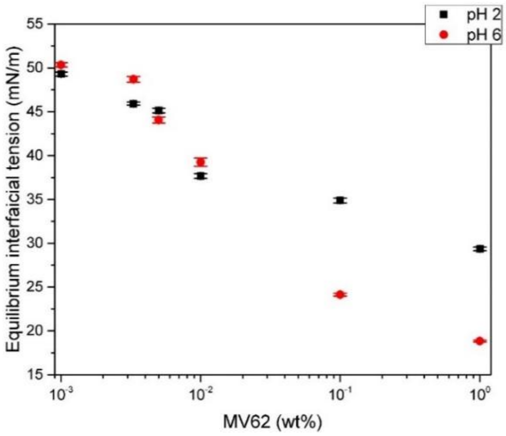


Figure 6-10: The equilibrium interfacial tension γ_m (mN/m) of the dodecane -water interface in the presence of varied concentrations of MV62 particles at both pH 2 and pH 6.

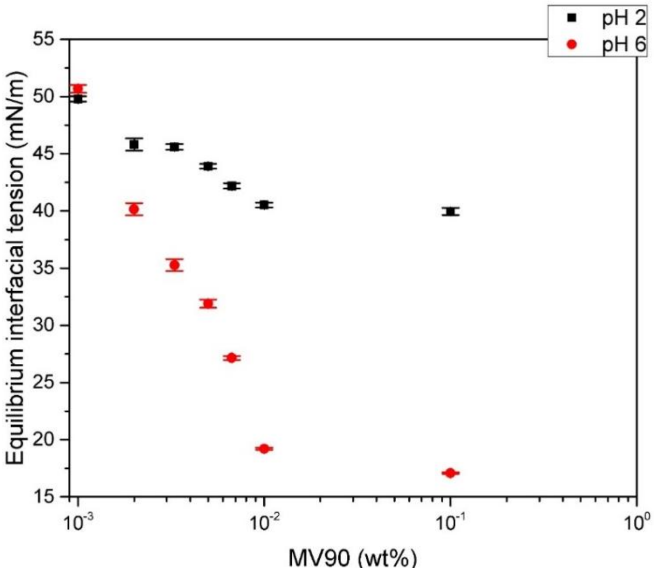


Figure 6-11: The equilibrium interfacial tension γ_m (mN/m) of the dodecane -water interface in the presence of varied concentrations of MV90 particles at both pH 2 and pH 6.

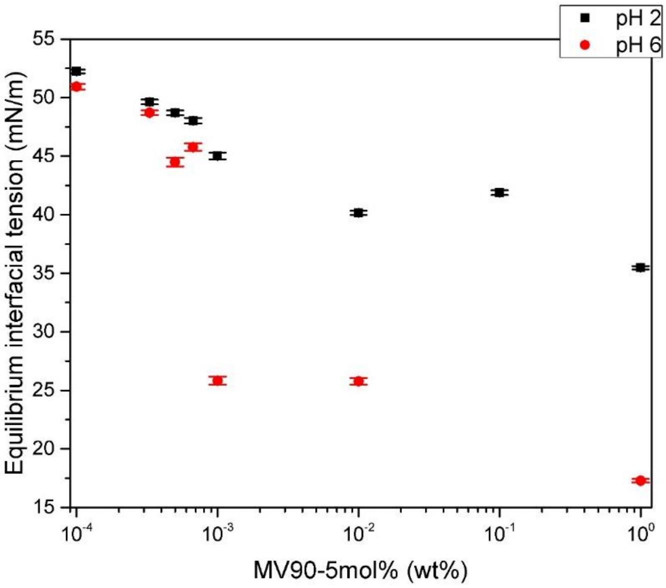


Figure 6-12: Equilibrium interfacial tensions γ_m (mN/m) of the dodecane -water interface in the presence of increasing concentrations of MV90-5mol% particles at both pH 2 and pH 6.

These equilibrium interfacial tension values decrease as a function of increasing particle concentration for both charged (pH 2) and uncharged (pH 6) particle cores. The interfacial tension of dodecane –water at pH 6 dropt until approximately 18.85 ± 0.1 mN/m, 17.08 ± 0.1 mN/m and 17.28 ± 0.15 mN/m in the presence of MV62, MV90 and MV90-5mol% oil-dispersed particles, respectively, with increased particle concentrations. Thus, the interfacial tension at pH 6 has been reduced around 30 mN/m. However, at pH 2, the interfacial tension decreased to 29.36 ± 0.2 mN/m (MV62), 39.95 ± 0.31 mN/m (MV90) and 35.47 ± 0.15 mN/m (MV90-5mol%) as a function of particle concentration of each particle type. Therefore, the reduction of interfacial tension value is less (around 13 ~20 mN/m) at pH 2 than pH 6 (30 mN/m). Such difference of equilibrium interfacial tension at two pH indicates that less particles adsorbed at interface under pH 2 than pH 6, which also imply the pH-responsiveness of such oil-dispersed particles at oil-water interface. This is due to the charge-charge lateral repulsion interactions, then the maximum surface coverage by charged particles (pH 2) would be lower than that of uncharged particles (pH 6)(Binks and Horozov, 2006; Rhodes, 2008).

6.3.1.3 Effect of core cross-linking on the particles ability to interact at the interface.

As further study, we collected dynamic interfacial tension data in the presence of 0.01wt% particle concentrations (MV62, MV90 and MV90-5mol%) at both pHs. Additionally, all examined particles’ contact angle changes in favour of lower angles for pH2, which drives a different interface curvature leading to the formation of oil/water emulsions. MV62 shows evidence of deformation on o/w emulsion droplet surface at pH 2, and such emulsions have been shown to be stable for long periods of time. No evidence of deformation was seen for

MV90 and MV90-5mol% particles, which were seen to stabilise o/w emulsion droplets. However, in MV90-5mol% stabilised emulsion systems, stable w/o and o/w droplets were observed at pH 6 and pH 2, respectively, as well as the o/w HIPE emulsion gels at pH 2 with 70 vol% oil phase.

Figure 6-13 shows the interfacial tension change of dodecane-water as a function of time at pH 6 and pH 2 in the presence of 0.01wt% MV62 and MV90 particles. At pH 6, MV62 particles adsorbing at the interface lead to a final interfacial tension value of around 18 mN/m within 1000 seconds while MV90 only decrease the interfacial tension to 28 mN/m even after 10000 seconds at the same pH. At pH 2, both sets of particles are seen to decrease the interfacial tension gradually to reach a similar value after 10000s, indicating that both MV90 and MV62 have similar interfacial activity at pH 2.

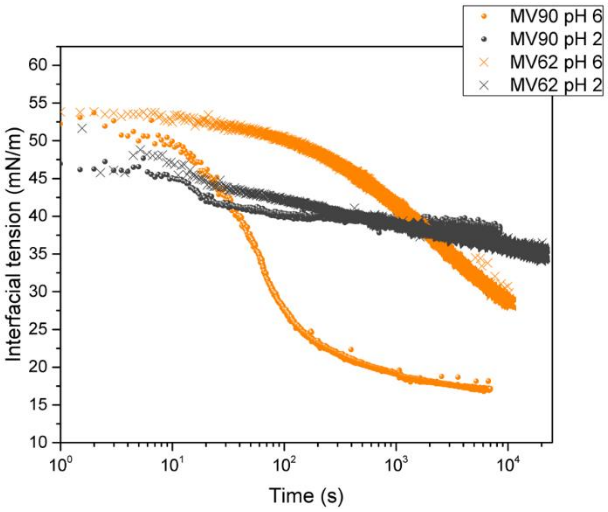


Figure 6-13: Influence of 2-VP content in oil-dispersed (non-crosslinked) particles on interfacial tension γ_t (mN/m) at dodecane-water interface for both pHs. MV62 and MV90 particle concentration is fixed at 0.01 wt%. (Cross: MV62; sphere: MV90; Dark grey: pH 2 and Orange: pH 6)

The dodecane-water interfacial tension was also examined with (cross-linked) MV90-5mol% particles and particles of the same composition without the cross-linker (MV90). These experiments were run with a particle suspension at a concentration of 0.01wt% for both pHs, as seen in Figure 6-14. Again, MV90 and MV90-5mol% have similar interfacial activity when the p2-VP part of the core is protonated (pH 2), but it appears that the cross-linked particles display a longer induction period (i.e. slower kinetics). At pH 6 in contrast, the cross-linked particles are seen to be less interfacially active at than the non-cross-linked particles.

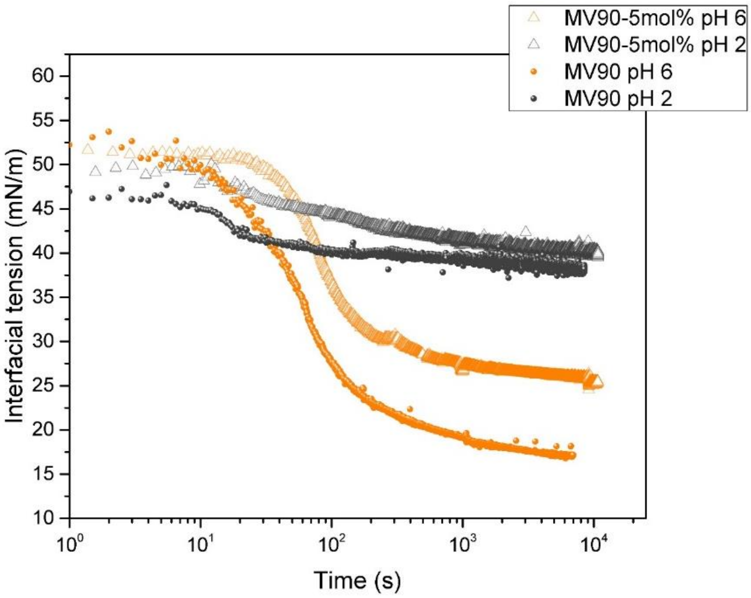


Figure 6-14: Influence of cross-linking particle cores on interfacial tension γ_t (mN/m) at dodecane-water interface for both pHs. In these experiments, particle concentration was fixed at 0.01 wt% for both MV90-5mol% (Open triangles) and MV90 (Circles) particles.

6.3.1.4 Particle adsorption kinetics

As known, spherical colloidal particles (over 0.5 nm in radius)can be considered as irreversibly adsorbed at the oil-water interface(Binks, 2002;

Binks and Horozov, 2006), for example: inorganic particles (silica, clay)(Binks and Whitby, 2004; Binks and Lumsdon, 2000; Ashby and Binks, 2000; Bon and Colver, 2007), organic particles (polystyrene)(Binks and Lumsdon, 2001), tailored responsive particles (shell responsive latex, pNIPAM microgels) (Li et al., 2013; Li et al., 2014; Ngai et al., 2006; Brugger et al., 2009; Richtering, 2012; Amalvy et al., 2003; Binks et al., 2007). Our oil-dispersed pH responsive p(MMA-2-VP)-PDMS particles have a diameter range of 500 nm to 750nm, which is one of the irreversibly adsorbed colloidal particles. Once colloidal particle adsorb at interface, the required energy to detach a particle is far too large (10^5 kT for a 200 nm diameter particle). Thus, no desorption of particle from interface can be taken into consideration. Therefore, the change in interfacial tension is directly related to the adsorption kinetics. As the theory we used here, the adsorption kinetics can be calculated basing on the time depended interfacial tension of varied particle concentrations, which also rely on Equation 6-2 and Equation 6-3 mentioned in Section 6.1.

The eventual calculated interfacial adsorption coefficients of MV62 and MV90-5mol% particles at pH 2 and pH 6 are illustrated in Table 6-2. Evidently, the diffusion coefficient values are far larger in the presence of pH 2 in aqueous phase than pH 6, which indicates a highly rapider adsorption of particles to interface at charged state than uncharged state regardless of particle configurations. Nevertheless, both MV62 and MV90-5mol% particles reduce interfacial tension very slowly and moderately at pH 2 than pH 6 (Figure 6-7and Figure 6-9). On the other hand, uncross-linked and less 2-VP copolymerised MV62 particles have neither rapider adsorption behaviours at pH 2 and pH 6 than cross-linked MV90-5mol% particles according to the calculated coefficient values. Especially at pH 2, the diffusion of MV90-5mol% particles from bulk to adsorb on interface is approximately 30 times quicker than MV62 particles. It is worth pointing out that MV90-5mol% particles can stabilise most stable emulsions (both w/o and o/w) at two pH among all our tailored particle stabilised emulsion systems, but MV90-5mol% reduces less interfacial tension comparing with its uncross-linked one (MV90) (Figure 6-8 and Figure 6-9).

Table 6-2: The calculated diffusion coefficients of when MV62 and MV90-5mol% particles are adsorbing from bulk to interface at pH 2 and pH 6. The calculation was based on the measured interfacial tension, Equation 6-2 and Equation 6-3.

$D_{interface}$	Particle	pH
0.42	MV62	6
12.5	MV62	2
5	MV90-5mol%	6
400.83	MV90-5mol%	2

6.3.2 Discussions

In this part of work, we present some initial measurement of interfacial tension as a function of time in the presence of three types oil-dispersed pH responsive particles (MV62, MV90 and MV90-5mol%) at two pHs. The ability of the particles to reduce the interfacial tension is investigated first here, that comparisons are drawn between different particle cores, including cross-linked (MV90-5mol%)vs noncross-linked particles (MV90), and varied 2-VP content (MV62 vs MV90).

As well as that, the initial interfacial tension data in the presence of oil-dispersed pH responsive particles is potentially linking to the behaviour of the emulsions they stabilise. Note, the measurement of interfacial tension with oil-dispersed particles and the process of getting the particles at the interface in an emulsification procedure are quite different. These interfacial tension value gained were based on the spontaneous adsorption of particles to the dodecane-water interface, while there are lots of energy input during the homogenisation to stabilise emulsions. But, nevertheless, some initial links can be draw.

First of all, all examined particles show their interfacial activity at both pH, which is similar to all other interfacial active materials, for example surfactants, polymers, microgels and other colloidal particles(Li et al., 2013; Li et al., 2014; Monteux et al., 2010; Brugger et al., 2009; Brugger and Richtering, 2008; Brugger et al., 2008; Ward and Tordai, 1946; Das and Chattoraj, 1980). They diffuse from oil bulk to spontaneously adsorb to the dodecane-water interface, such process was evidently controlled by particle concentrations(Li et al., 2013). This is also similar to microgel particles and other majority colloidal materials(Li et al., 2013; Ward and Tordai, 1946; Das and Chattoraj, 1980).

Secondly, these oil-dispersed particles have copolymeric p(MMA-2-VP) particle cores which can respond to environmental pH change while particles adsorb at oil-water interface. Our oil-dispersed pH responsive particles reduce interfacial tension in different extent at pH 2 and 6. Thus, the charged particles are less interfacially active than uncharged particles in a contrast with pNIPAM microgel particles, which have similar extent interfacial activity at heptane-water interface regardless of environment triggers change(Li et al., 2013; Li et al., 2014). Li et al. stated that pNIPAM microgels have a larger “interfacial diffusion coefficient” value at lower temperature (298K) than higher temperature (317K), indicating a more rapid adsorption of swelled microgels (298K) to the interface than collapsed microgels (317K) (Li et al., 2013; Li et al., 2014). In our case, both MV62 and MV90-5mol% evidently illustrate a rapid adsorbing behaviour to the oil-water interface at charged state (pH 2) than pH 6. It is vital to note that lowering temperature induces the swelling of microgels, even they are diffusing from bulk to adsorb at interface, which highlight the fact that lowering temperature accelerate both diffusion and adsorption process. However, our particles are not charged until they are in (close) proximity to the interface, thus the diffusion to the interface is probably not affected by the pH of the water phase, but the affinity of the particles for the interface and the resulting adsorption process most certainly is.

Nevertheless, o/w emulsions formed at pH 2 are relatively more stable than w/o emulsion at pH 6. As well as that, o/w emulsion droplets are much smaller than w/o emulsions. The key aspects induced such transitional phase inversion from o/w to w/o can be concluded as the contact angle shifting and particle deformation at oil-water interface by responding to the environmental trigger. The interfacial tension measurements were carried on basing on same pHs (pH 2 and pH 6), which can be summarized that the final thermodynamic equilibrium reached after the particles have adsorbed at the interface does not seem to influence the final emulsion characteristics. However, the calculated adsorption coefficient of two example types of oil-dispersed particles at pH 2 and pH 6, respectively implies that the particle adsorption kinetics appear to have a more drastic influence on emulsion characteristics. Evidently, o/w emulsion can be stabilised with a small mean diameter at pH 2 generally, which may be because of faster adsorption kinetics. Thus, it seems that kinetics have a larger role to play in deciding of the characteristics of such oil-dispersed pH responsive particle stabilised emulsions.

Fourth, Figure 6-13 and Figure 6-14 demonstrate that the composition of the particle core has a strong influence on their interfacial activity for pH 6. MV62 appears to reduce less interfacial tension than MV90 particle, while cross-linked MV90-5mol% particle was lowering interfacial tension more slowly than uncross-linked MV90 particle. However, this appears to be less significant when measuring interfacial tension variations over time at pH 2. This is because the presence of 2-VP monomer in the copolymer infers a larger affinity to the interface generally at pH 6. If this monomer is protonated (pH 2), this affinity becomes large anyway, independently of how much VP is in the polymer (say for VP> a ratio of 60%). Thus, the behaviour of charged particle becomes very similar on reducing interfacial tension and stabilising o/w emulsion droplets. However, when the polymer is not protonated (pH 6), the more VP there is in the system the more drastic the change in affinity for the interface will be and thus the more differences in behaviour may observe.

Be aware of highly cross-linked MV90-5mol% particles, they can stabilise most stable w/o and o/w emulsion droplets and also spontaneously adsorb at dodecane-water interface rapidly at both pHs in our system, which is in line with highly cross-linked pNIPAM microgels(Li et al., 2013). It is necessary to highlight the fact that our oil-dispersed pH responsive particle system and aqueous based pNIPAM microgel particles respond to changes in the aqueous phase conditions differently - i.e. our particles only respond when in contact with the interface. There is no evidence showing that the influence of higher cross-linker density in our particle cores is lowering their emulsion stability and adsorption behaviours at this stage, which is different from Destribats et al.'s work(Destribats et al., 2012). In their opinion, the less density of cross-linked particle is, the more stable emulsion they can stabilise(Destribats et al., 2012). Additionally, microgel stabilised emulsion systems have evidently shown that the stability is mainly governed by relevant rheological properties (viscoelasticity) of microgel particles when they adsorbed at oil-water interface (Liu et al., 2012; Brugger et al., 2010; Brugger et al., 2009; Brugger et al., 2008; Brugger and Richtering, 2008; Richtering, 2012; Geisel et al., 2012; Li et al., 2013). Senff and Richtering also indicated the correlations of cross-linking density in particle cores and particle rheological properties(Senff and Richtering, 2000). Thus, the comparable good stability of MV90-5mol% particle stabilised o/w emulsions (no oil resolved after 10 months preparation) and the formation of HIPE emulsion gels (70vol%, pH 2) (no cream and coalescence investigated) may be due to the good rheological properties of such particles, which is necessary to exam in future. Besides that, the charged MV62 particles show evidence of deformation at o/w droplet surface, but less effectively on decreasing the interfacial tension at both pH comparing to other particles. The concept of PNIPAM microgels softness is not applicable to our system(Li et al., 2013; Dickinson, 1999).

6.4 Conclusions

To conclude, the interfacial behaviours of MV62, MV90 and MV90-5mol% particles as a function of particle concentrations at pH 2 and pH 6 have been investigated on measuring the dynamic interfacial tension in the presence of such particles. Oil-dispersed pH responsive particles are more interfacially active at pH 6 than pH 2. The reduction of interfacial tension of such particles at pH 6 and pH 2 seem not appear strong relationship with the stability of emulsions they stabilised under same conditions. However, examined particles adsorb to the interface more rapidly at pH 2 than pH 6, which can stabilise smaller o/w emulsions at pH 2 and w/o at pH 6. Thus, such particle stabilised emulsion properties are governed mainly by their adsorption kinetics. Results show that the adsorption behaviour of our particles are different from pNIPAM microgel. The influence of particle configuration is more obvious on particle interfacial activity at pH 6 (uncharged state) rather than charged states. No obvious evidence shows that the influence of higher cross-linker density in oil-dispersed particle cores is lowering their emulsion stability and adsorption behaviours at this stage, which is different from literature.

However, the well-defined basic mechanism of our oil-dispersed particle adsorption at interface and their potential adsorbing schematics haven't clearly draw out based on those studies. This part of work still provides strong evidences of their attractive interfacial behaviours and also questioned the differences of oil and water based systems.

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Chapter 7. Conclusion and future work

7.1 Conclusion

Oil-dispersed p(MMA-2-VP)-PDMS Particle synthesis

Non-polar solvent dispersion polymerization has been employed to synthesize the oil-dispersed p(MMA-2-VP)-PDMS core-shell particles. The synthesised polymeric particles can be divided into two groups. In the first group, particles are un-crosslinked. The systematically increased 2-VP ratio in particle core can be obtained by varying the initial monomers (MMA and 2-VP) ratio during the synthesis. Due to the reactivity ratio differences between MMA and 2-VP, the synthesised copolymer particle cores contained higher actual 2-VP ratio than the initial input. In the second group, particles are cross-linked with DVB. The spherical and smooth cross-linked particle with different DVB densities were synthesized successfully by later adding cross-linker during the dispersion polymerization. Such particles were designed to have a fixed MMA and 2-VP ratio in their particle cores, which lead to similar particle sizes though they were theoretically controlled to have different cross-linking densities.

Oil-dispersed p(MMA-2-VP)-PDMS Particle stabilised Pickering emulsions at varied pH

The as-synthesized well-tailored oil-dispersed polymeric particle with varied core contents (i.e. un-crosslinked and cross-linked copolymers with different MMA/2-VP ratios) have been demonstrated to be effective Pickering emulsifiers to stabilise w/o or o/w emulsion droplets in the presence of a range of particle concentrations. The properties and type of emulsions exhibited responsiveness to the pH trigger. For instance, even with the 2-VP content in the particle core being as few as 30% (i.e. the particle MV30), the stabilized w/o emulsion droplets became flocculated when the pH was reduced to pH2 regardless of the particle concentration, which undoubtedly indicate the pH-sensitivity of such particles at oil-water interface. Furthermore, as the 2-VP content in the particle core was increased to 62% and 90%(that is, the oil-dispersed MV62 and MV90 particles), transitional phase inversion from w/o to o/w emulsions can be readily induced by only tuning the pH in the aqueous phase from pH6 to pH2. To our knowledge, this is the first and the only case ever reported of pH induced transitional phase inversion occurred in Pickering emulsions stabilized using core-responsive Pickering emulsifiers, which are particularly dispersing in oil and copolymerised with an unresponsive monomer. Hence, there is no doubt the pH responsiveness of such particular emulsifiers are thus proven. From another point of view, the phase inversion from w/o to o/w can also be realized in such oil-dispersed particle stabilised emulsion system at pH 2 by increasing 2-VP ratio in particle cores.

On the other hand, similar to Pickering emulsions stabilised by typical aqueous-dispersed particles, the w/o emulsion droplets stabilised by the oil dispersed Pickering emulsifiers show a general trend of an increase in mean droplet size with decreased particle concentrations under pH 6, regardless of particle core content. Moreover, with increased cross-linker density in the particle core, the stability of the emulsion systems, not matter the w/o or the o/w type, are greatly enhanced. For example, the o/w emulsions stabilised at pH2 by MV90-5mol% are ultra-stable, lasting for more than 10 months without any evident oil release. Meanwhile, the mean droplet size of such inversed o/w emulsions remains almost constant, being not a function of particle concentrations, core content and cross-linking density. All of the findings imply that the underlying stabilisation mechanisms behind such pH responsive Pickering emulsion are greatly related to the p2-VP content and the cross-linking density in the particle cores, which control the particle configurations at both uncharged and charged states and thereof the corresponding interfacial behaviour at oil/water interface.

As anticipated, the emulsion stabilisation mechanisms in the w/o system at pH6 and in the o/w system at pH2 are different given that the particles can be uncharged with a deswelling configuration at neutral condition whilst charged with a swelling configuration at extreme acid conditions. In particular, the MV62 particles were observed to deform on the surface of o/w droplets at pH 2 though this was not observed under same conditions in the MV90 particles which however remained spherical. This abnormality in the case of MV90 with particles un-deformed at pH2 but the o/w emulsion capable to be stabilized is likely to be a consequence of fast contact angle decrement of the particle upon protonation when the pH was switched from 6 to 2. It is worthy of highlighting that the pH-triggered deformation of core-responsive particles is firstly discovered in the current study in an oil-dispersed pH responsive particular emulsifier system. Even so, more explicit work is still needed to further reveal in an exact way the potential interfacial particle behaviour and emulsion stabilisation mechanisms.

Oil-dispersed p(MMA-2-VP)-PDMS Particle stabilised Pickering emulsions with varied oil-water volume ratio

In this chapter we have continually investigated the influences of oil-water volume ratios, particle concentrations and pH on the formation, structure and stability of the emulsion systems. In particular, the experiments were performed with four batches of particles, that is, MV90 containing the highest 2-VP ratio (90%), MV30 containing the lowest 2-VP ratio (30%), MV90-0.5mol% with the lowest cross-linker density(initial 0.5 mol% relative to monomer) and MV90-5mol% with the highest cross-linker density(initial 5 mol% relative to monomer). Specifically, the oil-water volume study regarding the emulsion properties and types is demonstrated in presence of constant particle amount of whole system

(1wt%) and particle concentration of oil phase (2wt%) while particles subjected to different charging state (pH 2, pH 2.5 and pH 3).

Firstly, within a narrow pH range(2.0 to 3.0) the critical pH point that drives the phase inversion from w/o to o/w has been found to lie between pH 2.5 and pH 3.0 based on particle MV90(2wt% in oil) at a water/oil volume ratio of 50/50. By increasing the oil/water volume ratio in the emulsions with the particle concentration fixed at 2wt% (in oil), catastrophic phase inversion from o/w to o/w/o was induced when the oil fraction is approaching 70% at pH2 and pH2.5, where the particles are supposed to be at charged state. To the best of our knowledge, this is the first time multiple emulsion is achieved by simply varying oil/water phase ratio based on the responsive particle/microgel systems. However, the w/o emulsions at pH3 show not clear phase inversion within the studied oil/water volume ratios for these un-crosslinked particles, but only the emulsion stability and the droplet size are affected. Worthy to notice, the o/w/o was not observed in the systems with 1 wt% particles in whole even at high oil/water volume ratios (fewer particle amount compared to the case of 2wt% in oil). Hence, we would conclude that the as-prepared o/w/o multiple emulsion is likely to be attributed to the coexistence of both protonated and un-protonated particles in the system which stabilize either o/w or the o/w in oil.

Secondly, in the systems of cross-linked particles (i.e. MV90-0.5mol% and MV90-5mol%), the hysteresis of catastrophic phase inversion happened with emulsion inversion from o/w to o/w/o at pH2 and 2.5 taking place at a higher oil/water volume ratio of 9/1 compared to the un-crosslinked particles. One surprising finding is that for the w/o emulsion systems stabilized at pH3, only the case of MV90-0.5mol% (with 2wt% in oil) underwent a catastrophic phase inversion from w/o to simple o/w. Moreover, for the particles with potential highest crosslinking density (initial cross-linker concentration), namely the MV90-5mol%, a remarkable emulsion system of o/w HIPE (high internal phase emulsion) was formed at pH 2.0 regardless of the studied particle concentrations. Again, this is reported for the first time based on oil-dispersed pH responsive particle/gel systems. Meanwhile, an interesting flocculated o/w/o emulsions was found with lower oil fraction in presence of 1wt% MV90-5mol% at pH 3.

Furthermore, all these phenomena concerning the phase inversions have been confirmed by the measurements of mean droplet diameter and emulsion viscosity, which both show an increment in the vicinity of the inversion point. The viscosity increase was reflected from the phase appearances such as rigid chunk, flocculated and HIPE states, etc. Besides, as revealed from the data of the resolved dispersed/continuous phase (creaming/sedimentation) after 24 hours preparation, the stability of emulsion experiences a decrease within the critical regime of phase inversion. According to our estimations, the catastrophic phase inversion is induced by the variation of oil-water volume fraction, but dominated by the proton quantity and concentrations with the corresponding particle amount in the system. As far as the crosslinking effect is concerned, the MV90-5mol% prepared emulsions have better stability regardless of emulsion types at each pH, particle concentrations and oil-water fractions than the MV90 (uncross-linked) and MV90-0.5mol% (lower cross-linker density) stabilised emulsions, indicating stronger adsorption of MV90-5mol% at oil-water interface and greater interfacial properties to against coalescence.

Oil-dispersed pH responsive particle adsorption kinetics

The interfacial behaviours of MV62, MV90 and MV90-5mol% particles as a function of particle concentrations at pH 2 and pH 6 have been investigated on measuring the dynamic interfacial tension in the presence of such particles. Oil-dispersed pH responsive particles are more interfacially active at pH 6 than pH 2. The reduction of interfacial tension of such particles at pH 6 and pH 2 seem not appear strong relationship with the stability of emulsions they stabilised under same conditions. However, examined particles adsorb to the interface more rapidly at pH 2 than pH 6, which can stabilise smaller o/w emulsions at pH 2 and w/o at pH 6. Thus, such particle stabilised emulsion properties are governed mainly by their adsorption kinetics. Results show that the adsorption behaviour of our particles are different from pNIPAM microgel. The influence of particle configuration is more obvious on particle interfacial activity at pH 6 (uncharged state) rather than charged states. No obvious evidence shows that the influence of higher cross-linker density in oil-dispersed particle cores is lowering their emulsion stability and adsorption behaviours at this stage, which is different from literature.

7.2 Future work

This work opens the door of investigation of oil-dispersed responsive particle system, which make the idea of combining oil-dispensability and responsiveness on single particle system to come true. As the initial work, there are still lots of interesting investigations and understandings that need to be continued. In light of conclusions drawn, the following actions for future work are recommended in this area:

- For the existed oil-dispersed p(MMA-2-VP)-PDMS particle system

The present work has provided a good knowledge bank about the investigation of various oil-dispersed pH responsive particles as Pickering emulsifiers. As well as that, the initial results of such oil-dispersed particles' interfacial behaviours have been drawn out by measuring the interfacial tension of dodecane-water interface as a function of time. However, there are still existing some questions which haven't been answered.

1) Such oil-dispersed pH responsive particles' configuration and pH induced interfacial deformability/swelling is not very clear, in particular the relations between particle core content and particles' interfacial configurations. Thus, the observation of particles at static planar interface is suggested to understand this part of questions, which Cryo-SEM investigation of particle interfacial behaviour at liquid-liquid interface by a Langmuir trough is in progress.
2) The stabilisation mechanism of inversed o/w emulsion at pH 2 is not very clear at this stage. The relationship between such oil-dispersed emulsion and their interfacial properties hasn't been clarified, which requires more investigations in depth. 2D curved interface study needs to be expanded as well as the interfacial rheology investigations. The particle interfacial rheology study is obtained understandings.

3) As known, aqueous based microgel spontaneous interfacial adsorption hasn’t been defined properly. Especially, their interfacial structure and adsorption mechanism attracted lots of attentions. Our oil-dispersed pH responsive particle encountered same concerns as well, which needs some strong evidences to clarify. The role of cross-linker in particle cores and influence of pH on oil-dispersed particle interfacial activity needs to be taken into considerations.

- For oil-dispersed responsive polymeric particle system

It is interesting to study particle interfacial behaviours with a range of varied polarities of oil phases in the future. As well as that the investigation of oil-dispersed responsive particle system cannot be limited by the polymeric particles mentioned in this work. The particle shell (polymer stabilisers) can be switched, which may result in varied particle interfacial configurations. For the particle itself, it is also worthy to investigate the pure 2-VP core contained particle system’s bulk and interfacial behaviours. Moving forward from 2-VP contained oil-dispersed pH responsive particle system, it is also recommended to investigate the oil-dispersed responsive particle behaviour with a replaced responsive monomer, for example: PDMAEMA.