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Dispersion Polymerization in Non-Polar Solvent: Evolution Toward Emerging Applications

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ABSTRACT

Currently, there is a resurgence of interest in the preparation of monodisperse, size-controlled latex particles in non-polar solvents by the dispersion polymerization technique. This technique has great potential for manufacturing bespoke latex particles for emerging applications such as the use of latex particles in electrophoretic displays, where one of the numerous requirements is that the particle systems be suspended in low dielectric constant, non-polar solvents. This article reviews the academic literature around the typical monomers used in non-polar dispersion polymerization. It briefly introduces the origin of the technique and the initial seminal work carried out in this area. It also describes how such particles have been used in the past as model colloids for academic purposes and provide recent examples where dispersion polymerization is used to create novel functional particles. Subsequently, the article provides a thorough knowledge basis for each monomer used in non-polar dispersion polymerization, with a focus on the evolution of the technique, including progress in controlling the final particle characteristics and in designing novel effective stabilizers. Finally, a brief review on the use of the technique to prepare well-controlled latex particles in supercritical fluids is also presented.

CONTENTS

1. INTRODUCTION

The preparation of well-controlled monodisperse latex particles has been the subject of several decades of academic and industrial research and this has led to the development of different methods of polymerization. During the development of these methods, the emphasis has been primarily on the production of such lattices in an aqueous phase or a mixture of polar phases involving water or short-chain alcohols. Comparatively, the academic literature contains far less examples of synthesis of such well-controlled latex particles in non-polar solvents. However, it remains a fact that there are a great many industrial applications for these latex dispersions in non-polar media.

In this review our distinction between polar and non-polar solvents is based on two commonly used parameters to describe the polarity of solvents, viz. (i) the dielectric constant, and (ii) the dipole moment. [1] The dielectric constant (ε) of a solvent characterizes the tendency of an ion dispersed in the solvent to dissociate: High tendency for ion dissociation is observed in a solvent with high dielectric constant. Here, we consider solvents as non-polar when $\varepsilon < 15$ (i.e. ionic species will strongly associate), and polar when $\varepsilon > 15$. [1] Typical examples of non-polar solvents (i.e. with low dielectric constants) are hexane and dioxane. The dipole moment (μ) is an indication of the arrangement of charge within the solvent molecule. [1] Non-polar solvents are typically molecules where charge is symmetrically distributed around the molecule. Examples include carbon tetrachloride, benzene and hexane.

Hence, a solvent is characterized as non-polar when (i) it does not support ion dissociation easily (i.e. low dielectric constant) and (ii) it has symmetrical charge distribution around the solvent molecule (i.e. small dipole moment).

In this review, the non-polar solvents used for dispersion polymerization are generally alkanes or mixture of different alkanes (with exceptions mainly in the patent literature – see Section 2.1). This is primarily due to the fact that the solvent has to meet other requirements for a successful dispersion polymerization reaction, such as a high solvency for the monomer (mostly methacrylate, acrylate and styrene) and a poor solvency for the resulting polymer as well as a relatively high boiling point (as most reactions are thermally initiated). Finally, although supercritical carbon dioxide can be considered as a non-polar solvent, it will not be included in the main body of the review since it has been extensively reviewed elsewhere (see Section 6).

Thus, the patent literature abounds in examples of synthesis of latex particles in such solvents. This has mainly been driven by the coatings industry, for which monodisperse lattices were initially developed in the mid-1960s. However in the last 30 years or so, such systems have increasingly been applied to other areas such as chromatography column packing materials and as fillers for modification of composite materials strength, porosity or rheological properties. Aside from these 'historical' applications, this method is currently being revisited due to the expansion of the use of small particles of controlled properties in inkjet printing or electronic displays for example. Revived interest from academia has been driven by these new applications, as additional properties are sought for the lattices in order to design innovative particulate systems. Thus, it is timely that a fresh review of the academic literature on dispersion polymerization in non-polar solvents be available.

A significant part of the dispersion polymerization development in non-polar solvents is reported in the patent literature and despite on occasions referring to some of this work here, our intention is to mainly review the published academic literature. Thus, in order to focus the article on the specific academic interest linked with this method, the first section will provide the reader with background understanding of the academic drivers for developing this polymerization route. This first section will describe the evolution of academic interest in this area and the motivations associated with it, including renewed interest driven by the use of particles in electrophoretic displays. The subsequent sections will introduce a comprehensive review of the syntheses carried out by dispersion polymerization in non-polar solvents, focusing on the two main monomers, methyl methacrylate (MMA) and styrene. In these sections, the reader will find extensive information on the type of stabilizers, continuous phases and reaction types that have been used in non-polar dispersion polymerization. Two other sections will subsequently consider less commonly used monomers and the use of supercritical fluids as the continuous phase for dispersion polymerizations.

2. FIVE DECADES OF DISPERSION POLYMERIZATION

Heterogeneous polymerization techniques that result in the precipitation of polymer chains into particulates within the reaction continuous phase have significantly progressed over the last 50 years. In parallel, improvements in synthesizing suitable stabilizers for the latex dispersions have enabled researchers to control size, size distribution and composition of the particles prepared via these processes. Amongst these synthesis routes, the most commonly used is emulsion polymerization [2], where the monomer and the continuous phase are immiscible. Variants of emulsion polymerization leading to the preparation of particles in suspension include miniemulsion and suspension polymerization; all of these are processes primarily used with polar continuous phases.

The dispersion polymerization process, introduced above, has been used extensively to produce well-controlled latex particles in non-polar solvents. This process consists of an initially homogeneous system where the monomer, initiator and stabilizer are all soluble in the continuous phase.[3] Here, once the polymer chain grows in the continuous phase, it reaches a solubility limit and precipitates into particle seeds, which continue to grow until all the monomer is consumed. Historically, this process was developed from precipitation polymerization, where a similar process of precipitation for a growing polymer chain within a continuous phase, that initially dissolves the monomer, led to macroscopic polymeric particles of uncontrollable size. When precipitation polymerization was carried out in the presence of suitable stabilizers, well-controlled and colloidally stable polymer latex particles were then prepared.[3] Initial experiments were carried out in organic solvents for the reasons mentioned above but this method has since been adapted to polar solvents with great success. In particular, the possibility of mixing different solvents to adjust the solvency conditions in which the polymer precipitates to form particles has been extensively investigated. However, synthesis in non-polar solvents has remained of interest to academics for its potential in creating standard particle dispersions. Such particles have been used to study fundamentals of colloidal dispersions and their stabilization. Recently, this interest has expanded to the synthesis of bespoke particles for use in high technology applications, electrophoretic displays for example.

2.1. INITIAL PATENTS FROM THE COATINGS INDUSTRY

As mentioned above, dispersion polymerization was originally derived from precipitation polymerization when it was found that the addition of a suitable polymer to the system could efficiently stabilize the latex particles produced. One of the main aims for developing this technique was to enable industry to significantly increase the polymer content in surface coating formulations without significantly increasing the viscosity of the systems. Specifically, in the mid-1960s, producing well-controlled stable particles of the required polymers in non-polar solvents was initiated by companies involved in the coatings industry.

Two main companies were involved in the initial development of dispersion polymerization, mainly as a consequence of their implication in the coatings industry; a British company, Imperial Chemical Industries (ICI) and a North American company, Rohm & Haas. The first report of the dispersion polymerization process (where named as such) was made by ICI in 1962 and explains in details the necessary conditions for which successful synthesis of stable latex in both organic/non-polar and polar solvents can be achieved.[4] However, most of the examples given in this patent and indeed subsequent ICI reports of this technique all made use of organic, non-polar phases as the continuous phase. Throughout the next few years, ICI extended this work and patented the use of graft and/or block copolymers as stabilizers [5], the use of mixtures of monomers of varying polarity for building particles with different polymer ratios across their radius [6], and the use of cross-linkers for the polymer particles [7].

In parallel, Rohm & Haas developed essentially the same procedure to form latex particles in organic solvents. One of their main interests was to investigate a range of hydrocarbon oils as the continuous phase and the monomers that could be used in combination with the oils. The aim was to extend their range of formulated coatings for potential use at different temperatures (e.g. paints applied in cold climates or coatings applied in drying ovens) and pressures. This is explained in details in their initial patent.[8] Another advantage that justified the interest of this company in the technique was the possibility of synthesizing water-soluble polymers in a particulate form that enabled fewer and shorter purification steps.[9]

Most of the examples of dispersion polymerization in these patents were based on the use of methyl methacrylate as the monomer with the occasional addition of other acrylates as co-monomers, such as 2-ethoxy ethyl methacrylate (2EMA) or ethyl acrylate (EA). Initially the stabilizer originated from the processing of natural rubbers before a clear intent of moving towards more controlled structures was noticeable. Several examples utilized copolymers combining the polymer used for the particle core (or one that mixes well with the core) together with a polymer well solvated in the continuous phase. In addition, the reaction phase, in which the dispersion polymerization syntheses were conducted, had, in most cases, a direct relevance to the specific coating application for the dispersion. Hence, non-polar solvents such as octane, benzene, hexane or refined oils were regularly used. Since then, hexane has been the non-polar solvent of choice for dispersion polymerization processes, particularly in academic studies.

2.2. ACADEMIC INTEREST FOR THE PREPARATION OF MODEL COLLOIDAL SYSTEMS

It was realized early in the academic community that the dispersion polymerization process could be used as a way of preparing model colloidal systems to enable fundamental studies. This led to significant progress in understanding steric stabilization of particle systems [10,11,12], rheology and flow properties of such particle dispersions [10,13,14] and adsorption (or non-adsorption) of polymers to solid surfaces [15,16]. Indeed, the technique gave the opportunity to synthesize and study monodisperse latex particles suspended in experimental fluids of low Hamaker constant and where electrostatic forces originating from ionization of surface groups (as commonly found in polar continuous phases) are negligible due to the low dielectric constants of these dispersing media. Accordingly, the possibility of creating these model colloids in non-polar solvents has been the key academic driver for the development of the dispersion polymerization technique beyond the initial commercial examples described above. In the next paragraphs, we focus (in chronological order) on three areas to which dispersion polymerization has extensively contributed since its development. The latex particles prepared to enable these studies are characteristic of the progress of the technique over the last five decades, which are themselves discussed in Sections 3 to 6 of this article.

2.2.1. STERIC STABILIZATION

The stability of dispersed systems is of high importance. In the case of non-polar solvents with typically low dielectric constants, ionic dissociation of surface groups is unlikely, which means that colloidal stability through electrical double layer forces is generally unachievable. As a consequence, stability is generally controlled by the presence of an adsorbed solvated polymer layer creating a steric barrier around the colloidal particles (i.e. a dense polymer layer which is soluble in the dispersing media). [**Error! Bookmark not defined.**] This mechanism is called "steric stabilization" and several topical review articles have been published by Vincent [17], Napper [18], Tadros [19]. We provide only a brief introduction in the following paragraphs, those interested in more detail should refer to these earlier review articles.

Steric barrier layers are formed by polymer chains that are either freely adsorbed or chemically grafted onto the colloid particle surfaces. In order to obtain efficient steric stabilization some requirements are considered essential: [20]

- High surface coverage for the polymeric stabilizer, Γ (to prevent bridging),
- Strong adsorption of the polymeric stabilizer,
- Good solvent for stabilizing chains (Flory-Huggins parameter $\chi < 0.5$),
- Low free polymer concentration (to avoid depletion interaction effects).

In practice, copolymers are mostly used for steric stabilization of dispersions, while homopolymers are only efficient in a limited number of cases. Different polymeric architectures are generally considered as defined below where A is the block anchoring onto the particle surface and B the block soluble in the solvent:[20]

- Random copolymer: A-*co*-B,
- A-*b*-B / A-*b*-B-*b*-A block copolymers,
- A-*g*-B graft copolymers,
- Reactive B homopolymers,

For polymer chains homogenously coated on the particle surface, two distinct stabilization mechanisms have been identified. As the particles approach each other (less than twice the thickness of the stabilizing polymer layer), the extended polymer chains can either interpenetrate or be compressed resulting in a local increase of the polymer concentration (Figure 1).[20] The latter generates a steric repulsive force between the colloidal particles due to an increase of the osmotic pressure and free energy (reduction of the configurational entropy) in the system[19], which compensates for the attractive van der Waals forces.[20] In practice, steric stabilization is possibly a combination of the two phenomena described above.[19]

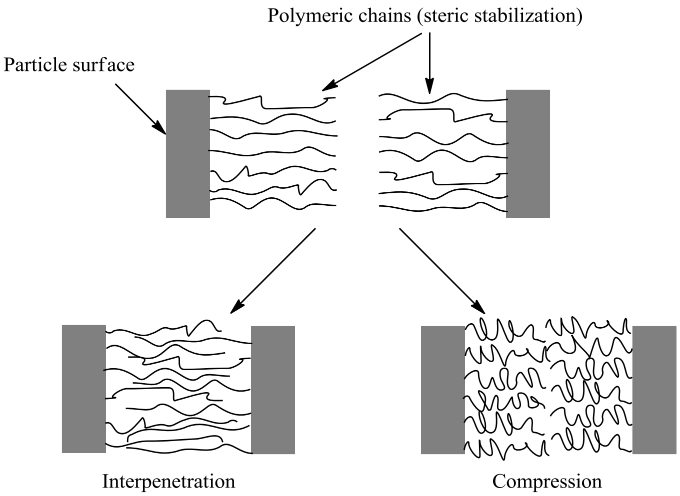


Figure 1: Steric stabilization mechanism: interpenetration or compression (adapted from [20]).

Fischer mathematically described this steric repulsive energy (V_S) between two polymer-stabilized-particles (radius r) by the following equation:[21]

$$\frac{V_s}{k_B T} = 4\pi r \Gamma^2 N_A \frac{\bar{v}_2^2}{\bar{V}_1}\left(\frac{1}{2} - \chi\right)\left(1 - \frac{D}{2L_0}\right)^2$$

where $\overline{v_2}$ is the specific volume of the polymer chains, $\bar{V}_1$ is the molar volume of the solvent molecules, Γ is the surface coverage, L_0 is the unperturbed polymeric layer thickness and D is the distance between the two particle surfaces. For steric stabilization (i.e repulsive interactions), V_s has to be positive.

Lastly, one should note that instability can also be driven in these systems through other processes such as bridging and depletion. Bridging occurs through the adsorption of a polymer chain onto two or more particles (due to stabilizing polymer with several adsorbable blocks and low particle surface coverage), which eventually leads to dispersion destabilization via bridging flocculation.[22] Another destabilization mechanism which is caused by non-adsorbing free polymer chains in the dispersing medium is referred to as depletion flocculation. Here, due to conformation restriction of the free polymer chains in solution, polymer coils become excluded from interparticle areas when the particles are in close proximity (closer than the polymer coil diameter). The free polymer chains generate attractive forces between the particles called depletion attraction and this leads to dispersion destabilization.[23]

Through the understanding of these different mechanisms, one can design appropriate polymeric stabilizers according to the desired properties of the specific colloidal system. This article reviews such colloidal systems dispersed in non-polar solvents.

One of the first academic report of the synthesis of latex particles via dispersion polymerization by Walbridge and Walters (from ICI) in 1966 described the preparation in mixtures of cyclohexane and decane of 400 nm to 4.5 μm poly (methyl methacrylate) (PMMA) latex stabilized by a copolymer of PMMA and poly (12-hydrostearic acid) (PHSA).[10] From rheological measurements on the particle suspensions, the authors estimated that the stabilizer thickness was well in excess of the necessary barrier thickness to prevent aggregation as a result of van der Waals forces. Other reports within the same decade studied the efficiency of steric forces in stabilizing latex particles. For example, Napper showed that instability of sterically-stabilized latex could be induced by decreasing the solvency of the continuous phase for the stabilizer.[11] This was achieved by either addition of a non-solvent to the continuous phase or by cooling.

The dispersion polymerization process continued to be used to manufacture monodisperse latex particles in non-polar solvents over the next two decades for the purpose of developing the steric stabilization theory. Several other publications reported measurements of stabilizing layer thickness [24] and interparticle forces [12,25] and/or studied latex flocculation as a function of temperature [26], stabilizer properties such as molecular weight and composition [27,28], particle size [11,27] and presence of free polymer in the continuous phase [16,29].

When studying such phenomena (for instance, depletion flocculation in the latter case), model particles were used both in polar and non-polar phases to perform complementary parallel studies. When studies were carried out in non-polar phases, dispersion polymerization was the method of choice to prepare monodisperse latex particles with a steric layer of controlled composition and thickness.

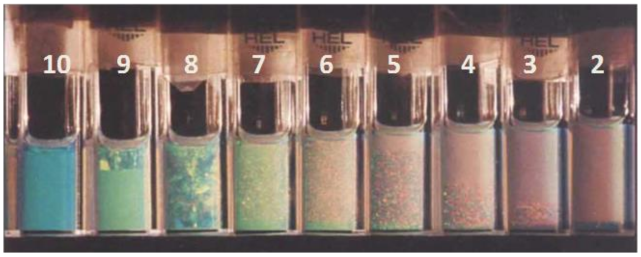


Figure 2. Suspensions of PHSA-stabilized PMMA latex particles increasing concentrations from the right (effective particle volume fraction from 0.39, sample 2 to 0.53, sample 10) showing some clear crystallization phases increasing in volume from sample 3 to sample 8 and some amorphous glassy regions in samples 9 and 10. (Reproduced from reference [30])

2.2.2. RHEOLOGY STUDIES

As mentioned above, and in combination with the previously described interests, the particles produced by this method have also been used in rheology to study the structure and flow properties of model suspensions. Again, a key driver for this work was the particular relevance to the coatings industry. Strivens studied the viscoelastic properties of concentrated latex suspensions using a specially developed shear stress rheometer.[14] Ten to fifteen years later, a series of articles built on this initial study and used optical techniques [30,31,32,33], such as dynamic light scattering [31] or photon correlation spectroscopy [32], and ‘mechanical’ rheometers [33,34,35,36,37] to gain more information on the viscosity and shear-stress behavior (such as shear-thinning and shear-thickening properties) of sterically-stabilized particles. For example, the research group of Mewis carried out several studies using PMMA latex particles stabilized with poly (12-hydroxystearic acid) chains, which the authors synthesized using the procedure described by Antl *et al.*[38] In one specific example, they systematically investigated the effect of the ratio between large and small particles on the viscosity and storage modulus of a bimodal suspension of PMMA latex (Figure 3).[37]

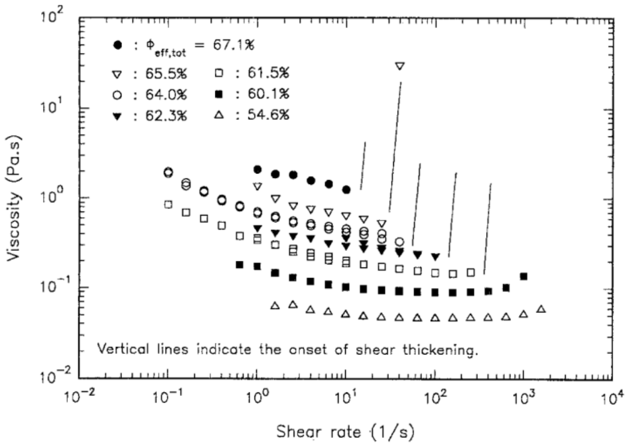


Figure 3. Dependence of viscosity on shear rate for a bimodal dispersion of small particles (129 nm) and coarse particles (823 nm) with a respective ratio of 1:10 at different total effective volume fractions (indicated in the inset). (Reproduced from reference [37])

2.2.3. FLUORESCENT LATEX FOR CONFOCAL MICROSCOPY STUDIES

In the first part of the last decade, several studies investigated the possibility of producing fluorescent monodisperse particles in non-polar solvents. Such systems were sought to enable confocal microscopy studies in which the precise position of particles in three dimensions could be determined with high accuracy. Model colloidal systems in index matched solvents were required in this case to study crystal nucleation and growth in concentrated particle suspensions around the glass transition region. Therefore, core-shell particles, where the fluorescent dye is incorporated within the particle core, facilitated the precise imaging of single particles in real time within colloidal crystals. In this case, the dispersion polymerization process was considered advantageous over other methods as the fluorescent dyes could be incorporated directly during the synthesis and no potentially damaging processes such as swelling of pre-prepared particles was involved. Using dispersion polymerization, the fluorescent dyes were encapsulated within the latex particle cores in two different ways. The particle design is described in details in the Section 3.

In one case, the dispersion polymerization process was carried out in the presence of a non-polymerizable dye.[39,40] For example, Hu and Larson incorporated a lipophilic dye, initially dissolved in the polymerization medium, into the core of PMMA latex particles stabilized by a PHSA-graft PMMA copolymer.[40]

In a second case, fluorescent monomers were prepared in a first instance and copolymerized in the dispersion polymerization process with MMA and methacrylic acid (MA). [41,42,43,44,45] Here the fluorescent monomers were added in the reaction medium and were covalently bound to the particle core. In a particular case, the cross-linked core was subsequently used as a seed to grow the particles further in the absence of the dye to obtain a fluorescent core-nonfluorescent shell structure allowing for better particle visualization using confocal microscopy.[43,44] For instance, such particles have been used for efficiently tracking single particles in colloidal crystals (Figure 4) [41-44,46], and more recently in clusters of controlled number of particles [45] and in structures assembled upon applying an electric field.[47]

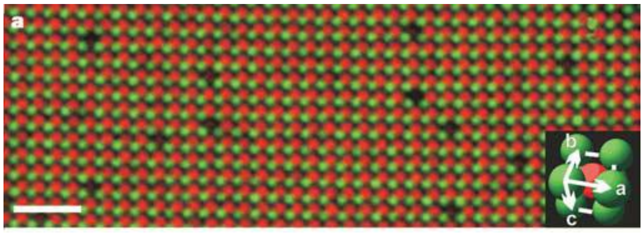


Figure 4. Confocal microscopy image of a colloidal crystal constituted of fluorescent PMMA particles stabilized by PHSA and synthesized through dispersion polymerization (scale bar, 10 μm). Oppositely charged particles (1.08 μm, loaded with rhodamine isothiocyanate; and 0.99 μm, loaded with 7-nitrobenzo-2-oxa-1,3-diazol) irreversibly assemble at high concentrations into a cubic lattice. (Reproduced from reference [46])

2.2.4. NEW APPLICATIONS DRIVING CURRENT AND FUTURE DEVELOPMENTS

As mentioned previously, the development of new technologies has recently increased the interest in latex particles prepared by the dispersion polymerization technique. This is because some of these applications require the preparation of smart, bespoke particles in a range of solvents depending on the application. Particulate systems prepared from this technique are thus being used or considered for inkjet printing, lubricant additives or electronic displays, for instance. The use of such particles in electronic displays is exemplified in the next paragraphs since it is of particular relevance as the particles are suspended in non-polar solvents within the display pixels.

This particular application has, for example, driven an increased interest in the research studying charge in non-polar liquids, with some academic studies utilizing latex particles prepared from dispersion polymerization as model colloids[48]. Charge dissociation at the particle surface in non-polar solvents in most of these cases is achieved by the use of inverse micelles that are able to carry the counterions away from the particle surface. However, this method suffers from drawbacks as the surfactants can desorb from the particle surfaces and the presence of excess micelles in the continuous phase drives electrohydrodynamic instabilities that reduce the lifetime of a display. Therefore, there is great interest in using dispersion polymerization to prepare particles that are inherently charged in non-polar dispersants. A first example from Sànchez and Bartlett has recently used this technique to produce latex particles with oleophilic ionic groups covalently linked to the particle core.[49] In addition, dispersion polymerization also offers the possibility of encapsulating pigment particles or organic dyes within the particle core, which provide the reflective properties of the displays.[50,51,52] Developments driven by such fast-moving applications will stem from the current knowledge of the non-polar dispersion polymerization particle synthesis route, which we provide a thorough review of in the subsequent chapters.

3. DISPERSION POLYMERIZATION OF METHACRYLATE-BASED MONOMER IN NON-POLAR SOLVENT

Herein, radical dispersion polymerizations of MMA and MMA-based monomers are discussed. As in a polar solvent (water, alcohol, etc.), radical dispersion polymerization in a non-polar solvent (Figure 5) follows five stages.[53] Initially, the reaction medium is a single homogeneous phase (stage 1). Stage 2 is characterized by the initiation and early stages of reaction propagation (soluble oligomers). Then, stage 3 is the precipitation of oligomer chains upon reaching a critical length at which they are not soluble anymore, and the coagulation of these oligomer chains into particle nuclei. Coagulation of these oligomer chains continues until steric stabilization of the latex particles starts. The particle stabilization phase is started when enough stabilizer chains cover the particle surface (stage 4). At this stage no further coagulation of oligomers occurs. Finally, the sterically stabilized latex particles keep growing until nearly complete monomer consumption (stage 5).

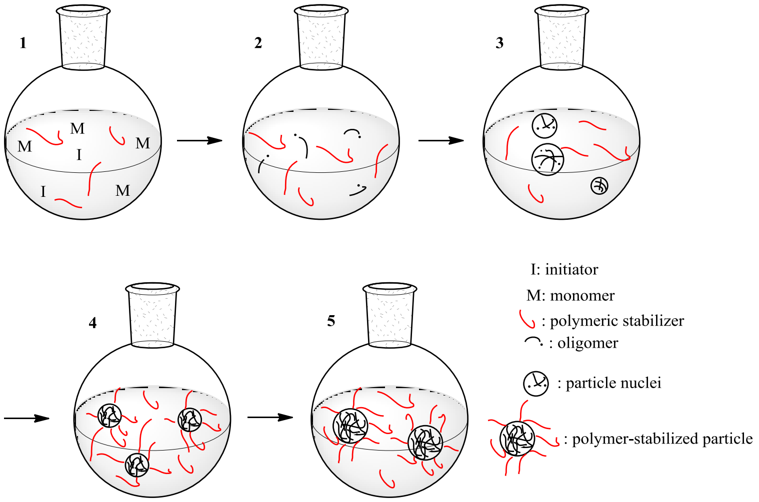


Figure 5: Dispersion polymerization mechanism in non-polar solvent: (1) initial homogeneous phase, (2) polymerization initiation (soluble oligomers), (3) oligomer precipitation and oligomer coagulation into particle nuclei, (4) particle stabilization by polymer adsorption, (5) particle growth (adapted from Barrett [3]).

Initially considered as a complex system due to the lack of appropriate characterization techniques, MMA dispersion polymerizations in non-polar solvent have been more extensively studied over the years thanks to the emergence of improved characterization techniques (particle sizing, electron microscopy, etc.). In addition, progress in the chemistry of the synthetic approach (silicone chemistry, controlled polymerization, etc.) and the emergence of a range of new applications (inkjet printing, electrophoretic displays...) has also driven a renewed interest. The chemistry of the non-polar dispersant medium has also developed further in recent years; initially mostly based on dodecane and hexane solvent, dispersion polymerizations have recently been performed in more "exotic" solvents such as supercritical carbon dioxide ($scCO_2$) (see Section 6.).

In this section, the discussion will focus on methacrylate-based (essentially MMA) monomer dispersion polymerization in non-polar solvents using various stabilizers. Initially, the discussion is centered around poly (12-hydroxystearic acid) (PHSA)-based polymers, as they were the first successful class of stabilizers used. Section 3.2 will focus on the stabilizers developed as a result of the emergence of silicon chemistry, such as methacryloxypropyl terminated polydimethylsiloxane. Section 3.3 will subsequently discuss new stabilizers developed through the use of new controlled radical polymerization approaches (RAFT, ATRP, NMP).

3.1. USING POLY(12-HYDROXYSTEARIC ACID)-BASED STABILIZER

The first widely reported stabilizers for the synthesis of PMMA latex particles in non-aqueous solvents were based upon poly (12-hydroxystearic acid) (PHSA). Despite being a non-commercial material, PHSA-based copolymers have been widely studied over many years. It is important to note here that PHSA has never been used as a homopolymer but rather as the major component (soluble part) of various copolymers. PHSA-based stabilizers are always synthesized using multi-step methodologies. Three PHSA-based stabilizers can be found in the academic literature: PHSA-graft-PMMA-poly(glycidyl methacrylate) (PHSA-g-PMMA-PGMA), PHSA-g-PMMA and cross-linker PHSA-based stabilizer. The cross-linker PHSA-based stabilizer (difunctional stabilizer) was studied in only one specific case; hence it will be discussed separately in Section 3.1.6.

3.1.1. STABILIZER SYNTHESIS

PHSA-g-PMMA-PGMA stabilizer is covalently bonded to the latex particles after completion of the dispersion polymerization. It is the most widely utilized PHSA-based stabilizer for MMA dispersion polymerization in non-polar solvents. The preparation of the PHSA-g-PMMA-PGMA was reported as a three-stage synthesis for which all the various authors described a common procedure. Although the original report was found in the patent literature, the work by Antl *et al.* [38] has been taken as reference in most of the academic publications.[39,41,42,57,58] Using this approach, PHSA homopolymer (Figure 6) was firstly prepared by polycondensation of 12-hydroxy stearic acid in toluene, usually in the presence of a sulphonic acid catalyst, such as methane sulfonic acid. To achieve sufficient conversion and avoid hydrolysis (i.e. PHSA decomposition), the water was continuously removed by azeotropic distillation (an azeotrope forms between water and toluene at about 85°C). The PHSA homopolymer synthesis was stopped when an acid value of around 30-32 mg KOH per gram of polymer was found by titration which required at least 75% esterification. This first reaction step usually led to short polymeric chains of about 5-6 units. In the second step, a PHSA macromonomer (Figure 6) was formed in an aliphatic medium by reaction between the acidic end-group of PHSA homopolymer and the glycidyl group of glycidyl methacrylate (GMA). The reaction was performed in the presence of a ring opening catalyst, typically an amine and a free radical inhibitor in order to prevent polymerization of the glycidyl methacrylate monomer. After reaction, the acid value of the synthesized polymer decreased from that of the homopolymer due to the disappearance of the acid group. Extra alkane was usually added to maintain a low viscosity.

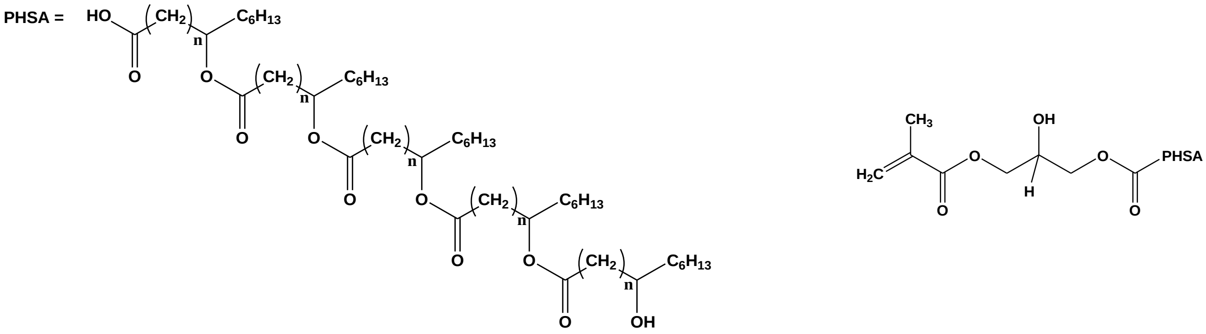


Figure 6. Chemical structure of PHSA homopolymer (left) and PHSA macromonomer (right)

Finally, the comb-stabilizer was obtained by conventional radical copolymerization of the PHSA macromonomer with methyl methacrylate and glycidyl methacrylate (MMA/GMA at 90:10 w/w) in a mixture of ethyl and butyl acetate. The final stabilizer generally possessed a broad polydispersity index (PDI) (around 4-5). Because of its limited solubility in alkanes, the final stabilizer was typically kept in solution at 40 wt% in a mixture of ethyl and butyl acetate.

Although the various authors cited earlier did not mention any particular synthesis issue, Elsesser and Hollingsworth [54] recently revealed a reproducibility problem, which explained the lack of commercial availability for this stabilizer. They revisited in detail each step of the PHSA-g-PMMA-PGMA synthesis [54] and showed clearly that during the first step of the synthesis (i.e. PHSA homopolymerization), azeotropic distillation was essential to achieve a suitable yield of esterification and that a minimum of 15% toluene with respect to the total volume was required to efficiently remove the water produced. They also reported that a higher 12-hydroxystearic acid purity can lead to a higher esterification rate and a longer PHSA chain of approximately 13 ester linkages. Concerning the second step, only the possible rival oxirane-ring-opening reaction of GMA with residual water was discussed. For the final step of the PHSA-g-PMMA-PGMA stabilizer synthesis, they revealed that the solids content of the final solution should stay below 40 wt% to avoid stabilizer precipitation and irreversible aggregation, as mentioned by Kargupta *et al.*[55]

The second stabilizer type in this class is PHSA-g-PMMA. This polymer, which only interacts via weak physical interactions with the latex particle surface, has been extensively studied by Barrett *et al.* [56] and Hu *et al.* [59]. It was also used by Hu *et al.* [40], Jardine *et al.* [42] and Bosma *et al.* [41] for syntheses involving the incorporation of a fluorescent dye into the resultant latex. Its synthesis is very similar to the PHSA-g-PMMA-PGMA discussed above and only the final step (i.e. copolymerization stage) differs. In this case, PHSA macromonomer (Figure 4) is copolymerized with a mixture of MMA/MA at 98:2 (w/w) rather than a mixture MMA/GMA.

In consequence, the main difference between both stabilizers is that PHSA-g-PMMA-PGMA can be attached to the latex particle surface by covalent bonding (see Section 3.2.2) while PHSA-g-PMMA only forms weak physical interactions with the same latex particle surface. However, Hu *et al.* claimed that PHSA-g-PMMA has the advantage of preventing coagulum due to shorter reaction time.[40]

3.1.2. STABILIZATION MECHANISM

In a non-polar solvent, repulsion forces from electrostatic interaction are not likely to be present and colloid stability is provided by a short-range steric stabilization mechanism. In such systems, the stabilizer must adsorb strongly to the latex particle surface with a sufficient surface coverage and project away from the surface into the solvent to provide stability.

3.1.2.1. USING PHSA-G-PMMA-PGMA

PHSA-g-PMMA-PGMA has been the most widely used PHSA-based stabilizer for the dispersion polymerization of MMA-based monomers in non-polar solvents. A typical MMA radical dispersion polymerization using PHSA-g-PMMA-PGMA as stabilizer involves three steps: particle preparation; chemical bonding of the stabilizer to the particle surface; and final purification of the reaction mixture (removal of excess monomer and stabilizer). The first step can be considered as standard radical dispersion polymerization in which the different components (monomer, initiator, solvent, stabilizer and chain transfer agent) of the reaction are mixed together in a common solvent. The polymerization is thermically initiated (80°C) and kept under an inert atmosphere at all times, following the procedure of Antl *et al.* [38] and subsequent research reports. [39,41,42,58] Cairns *et al*. [57] also reported a seeded polymerization which involves the early formation of seeded latex and a subsequent slow continuous introduction of a feed solution. After the latex formation is complete (typically 2 hours), and in order to prevent possible desorption of stabilizer from the latex particle surface, the PHSA-g-PMMA-PGMA copolymer is chemically reacted to the particle surface (second step). To achieve this, a low concentration of methacrylic acid (MA) monomer is copolymerized with the MMA monomer (1-2 wt% MA with respect to MMA) and the acidic groups reacted with the pendant glycidyl groups on the stabilizer. This reaction is generally performed at high temperature (around 130-140°C) for at least 24 hours in the presence of an amine used as a reaction catalyst. However, this relatively high temperature can lead to the formation of coagulum in the dispersion medium if not carefully controlled. [40]

A final purification step through centrifugation [38] or natural sedimentation cycles [58] is generally done. Analysis of the supernatant via Fourier transform infrared spectrometry (FTIR) (carbonyl stretching band) allowed determination if free residual stabilizer chains remained in the dispersion. [38]

3.1.2.2. USING PHSA-G-PMMA

Hu *et al.* used PHSA-g-PMMA for preparing a wide range of PMMA latex particles of different sizes (2 to 10 μm) [59] and analogous fluorescent PMMA latex particles (0.55 to 1.40 μm). [40] In their approach, a standard radical dispersion polymerization was performed with no subsequent grafting or purification steps. Solvent ratio and/or monomer concentration were finely tuned to achieve bespoke final particles with a well-controlled size. In these cases, the PHSA-g-PMMA adsorbed to the particle surface through purely physical interactions between the common PMMA polymer chains on both the stabilizer and particle cores. The fact that this procedure does not require a grafting reaction (with the associated high temperatures and long reaction time) was found beneficial as formation of coagulum was avoided.

3.1.3. KINETIC STUDIES

Several reports [38,57,58] have focused on controlling size and polydispersity by varying monomer and/or stabilizer concentrations. However, Barrett *et al*. and Kargupta *et al.* also provided interesting kinetic data as a function of different monomer and/or stabilizer concentrations.[55,56,57] Both groups also worked with PHSA-g-PMMA copolymers that provided stability by adsorption on the surface via physical interactions.

Barrett *et al.* [56] investigated the MMA free radical dispersion polymerization in dodecane stabilized by PHSA-g-PMMA copolymers and initiated with azobisisobutyronitrile (AIBN). They estimated the effect of changing different reaction parameters on the rate of polymerization. They found that the rate was higher in a dispersion polymerization than a solution polymerization or a precipitation polymerization, which they attributed to lower termination rate due to either diffusion control or isolation.[56] The termination was generally slow in the polymer particles due to the viscosity increase during dispersion polymerization. In addition, if changing the stabilizer concentration did not affect the polymerization rate (in the range where the stabilizer was efficient), the latter was higher when increasing initiator concentration. In parallel, lower monomer concentration shifted the maximum rate to lower conversion. A decrease of reaction temperature led to a faster polymerization than expected due to the viscosity increase at lower temperature. Finally, Barrett *et al*. [56] showed that adding a plasticizing solvent to the system slowed down the polymerization reaction, thus decreasing viscosity and increasing termination rate.

On the other hand, Kargupta *et al.* [55] ran MMA dispersion polymerization using PHSA-based stabilizer of different length in petrol (mixture of alkane chains with solubility characteristics between heptane and toluene). In their study, they decided to work with benzoyl peroxide initiator rather than AIBN which led to higher polymer formation.[55] They showed that the stabilizer concentration affected the molecular weight of the polymer and polymerization rate. Because PHSA-based stabilizer does not dissolve totally in petrol, there molecules formed micelles where the MMA polymerization starts. Increasing stabilizer concentration led to higher polymerization rate and PMMA molecular weight. However, too high stabilizer concentration induced chain entanglement between micelles reducing the monomer access and then the rate of polymerization. Barrett *et al*. also found that a reduced termination rate led to higher polymerization rate and longer polymer chains.[56]

3.1.4. SOLVENT CONSIDERATION

In dispersion polymerization, the dispersing medium must solubilize all the initial reaction components (initiator, monomer, chain transfer agent and stabilizer) but not the resulting polymer chains so that they can precipitate into the desired latex particle. Several examples used a mixture of solvents as the dispersing medium: hexane/high boiling hydrocarbon fraction [38], petroleum ether/dodecane (40/60) [57] or hexane/dodecane [39,42,58,59]. No noticeable difference was found between these reaction mixtures, possibly because the solvency of the polymer formed did not vary significantly across this range of solvent mixtures. However, it is important to note that the solvency of the initial reaction mixture was also dependant on the concentration of monomer and stabilizer. For example, because MMA is a relatively good solvent for its own polymer, for two reactions run at two different initial monomer concentrations, the initial reaction mixture solvency for the polymer produced is drastically different. This reaction medium solvency affects the polymer chain length at which the oligomers precipitate out from the solvent mixture as well as colloidal stabilizer configuration. This was shown to impact the final particle size and polydispersity (see Section 3.1.5.).

Varying the PHSA-based stabilizer concentration is likely to have a similar effect than a variation of the monomer concentration. In the case of the stabilizer however, the change in solvency for the polymer comes from the fact that the stabilizer is generally used in solution (40 wt%) in a mixture of ethyl and butyl acetate, which are good (polar) solvents for PMMA. Consequently, changing the stabilizer concentration and hence the amount of ethyl/butyl acetate present in the reaction mixture is likely to affect particle size as well as latex particle polydispersity (see Section 3.1.5).

3.1.5. PARTICLE SIZE AND POLYDISPERSITY

The size and size distribution of particles obtained from MMA dispersion polymerizations are very sensitive to a range of parameters, such as monomer concentration, stabilizer concentration, solvent composition, concentration and type of initiator (peroxide or diazo compound) and reaction temperature. Each has been shown to strongly influence the size and polydispersity of the final particles produced. Through careful control of these factors, monodisperse PMMA latex particles from a few tens of nanometers to around ten microns are accessible.[38,58,59] Amongst the tuneable parameters, stabilizer and monomer concentration along with solvent composition are considered the most critical factors and, in consequence the most studied . Table 1 summarizes the characteristics of particles obtained from non-polar dispersion polymerization when using PHSA-based stabilizers.

Table 1. Properties of particles obtained with PHSA-based stabilizers in various non-polar mediums

Monomer concentration (wt%)	Stabilizer concentration (wt% vs. M)	Size (nm)	PDI (%)	Reference
5 to 60	5	85 to 2,586[1]	3.9 to 10.3	38
50	5 to 20	2,590 to 200-850[1]	Monodisperse to very polydisperse	
10 to 15	13	155 + 87 (7%)	Two populations	57
5 to 30	28	40 to 72[2]	Monodisperse	58
32 to 36	15	51 to 107[2]	Monodisperse	
42 to 44	15	400 to 900[2]	Polydisperse	
35	10	81[2]	Monodisperse	
Up to 50-56	-	2,000 to 10,000[1]	Around 1	59
50	5	200 to 581[1]	2.5 to 6.7	41
54 to 58	5	1,080 to 2,400[2]	3 to 21	39
46 to 50	5	120 to 306[3]	7 to 13	42
48	-	550 to 1430[1]	3.2 to 4.1	40

1: Estimated with scanning electron microscopy (SEM); 2: Measured with Static Light Scattering (SLS); 3: Measured using Dynamic Light Scattering (DLS).

- **Monomer concentration and comonomer incorporation**

Antl *et al.* [38] and Pathmamanoharan *et al.* [58] studied particle size variation as a function of monomer concentration. Antl *et al.* [38] identified three distinctive monomer concentration ranges for which the particle size and stability varied significantly. The monomer concentration ranges were: < 8.5%; from 8.5% to 34%; and from 35% to 50%. The reported data, for dispersion polymerizations with 5 wt% stabilizer, showed that the smallest particles were found at < 8.5% monomer (75 to 85 nm) and the largest at ~ 50% (2.6 µm) monomer. Interestingly, they also observed a domain (8.5% to 34%) in which flocculation and/or coagulation occurred.[38] However, by correctly tuning the stabilizer concentration to the monomer concentration, Pathmamanoharan *et al.* were able to obtain stable particles across the entire monomer concentration range.[58] With increasing monomer concentration, it was shown, as expected, that the particle size was increasing. For the highest monomer concentrations (35% to 50%), because MMA is a good solvent for its own polymer (like most monomers), particle size was affected by the reaction medium solvency. In this case, the MMA present in the dispersion medium allows longer polymer chains to be soluble, which in turns reduces the number of particle nuclei. However, at low monomer concentration, Antl *et al.* [38] could not clearly identify the particle formation mechanism and suggested that the particles were formed from initial micelle-like aggregates made of stabilizer and monomer (or oligomers). Subsequently, Pathmamanoharan *et al*. [58] suggested that particle formation at low monomer concentration (5%) was only possible using a large amount of stabilizer (28 wt% with respect to monomer), which increases the availability of the stabilizer for the precipitating polymer surface. In the case of PHSA-based stabilizers, increasing stabilizer concentration also increases ethyl/butyl acetate content in the system. This has a drastic effect on the dispersing medium polarity and its overall solvency for both PMMA chains and stabilizer. As a consequence, Pathmamanoharan *et al.* obtained stable particles for monomer concentrations in the range from 5% to 44%.[58]

Campbell and Bartlett [39], Hu Larson [40], Bosma *et al.*[41] and Jardine and Bartlett [42] reported MMA dispersion polymerizations incorporating fluorescent dyes (reactive or non-reactive molecules). Generally, non-reactive dyes are unmodified and consequently have well characterized fluorescent properties but can show relatively high rates of leaching. Using reactive dyes covalently binds the fluorophores to the particle core and consequently avoids potential leakage during storage. However, the modified dyes may display different fluorescent properties as a result, particularly undesired high rates of bleaching. (see Section 1.2.3). Both non-polymerizable dyes such as [9-diethylamino-5H-benzo[α]phenoxazine-5-one (Nile Red), 3,6-bis(dimethylamino) acridine hydrochloride (Acridine Orange)] [39], [1,1'-dioctadecyl-3,3,3',3'-tetramethylindocarbocyanine perchlorate (DilC18), 3,3'-dioctadecyloxacarbocyanine perchlorate (DiOC18)] [40] and such as [4-chloro-7-nitrobenzo-2-oxa-1,3-diazaol] [41] and polymerizable dyes such as [(rhodamine isothiocyanate)-amino styrene (RAS) [42] and 4-methylaminoethyle methacrylate-7-nitrobenzo-2-oxa-1,3-diazol (NBD-MAEM)] [41] were used (Figure 7). Significant size changes were seen with relatively small changes in monomer concentration (between 43% and 58%) in each of these reports, as shown in Table 2.

Table 2. Particle properties for fluorescently-labeled PMMA particles synthesized by non-polar dispersion polymerization

Dye choice	Monomer concentration (wt%)	Particle size range (nm)	Reference
DilC$_{18}$ & DiOC$_{18}$	43.3 – 47.0	550 - 1430	40
NBD-MAEM	43.3 – 45.0	224 - 615	41

Nile Red & Acridine Orange	54.0 – 58.0	1080 - 2400	39
RAS	46.5 – 49.5	160 - 306	42

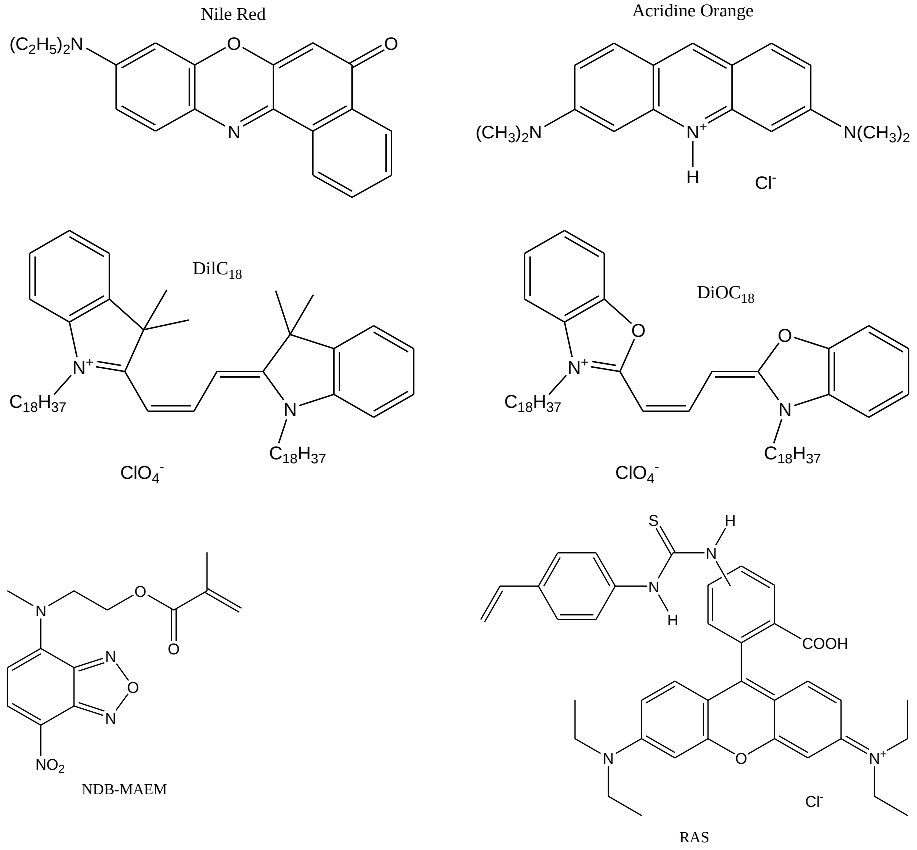


Figure 7. Example of non-polymerizable (4 molecules at the top) and polymerizable (two structures at the bottom) dyes used in MMA dispersion polymerization (structures reproduced from references [39] and [41])

- **Stabilizer concentration**

Antl *et al.*[38] showed significant effect of the stabilizer concentration on particle size by varying the stabilizer concentration between 5 and 20 wt% with respect to monomer. Increasing stabilizer concentration led to smaller particles but with an associated increase in polydispersity: monodisperse particles at < 5 wt%, moderately monodisperse between 7.5 and 10 wt% and very polydisperse > 15.0 wt%. In addition, Kargupta *et al.* mentioned that the polymer molecular weight prepared was increased by increasing the stabilizer concentration.[55] Finally, Pathmamanoharan *et al.* showed that the preparation of a stable colloidal dispersion using a PHSA-based stabilizer was stabilizer and monomer concentration dependant: at low monomer concentration (5 wt%) a high stabilizer concentration (28 wt%) is required while at high monomer concentration (35 wt%) a lower stabilizer concentration is sufficient (10 wt%).[58]

- **Solvency of dispersing medium**

The solvency of reaction mixture was not explicitly investigated. Its effect was only observed indirectly through other parameter changes, particularly monomer and stabilizer concentration. By varying monomer concentration in the dispersion polymerization mixture, Antl *et al.*[38] and Pathmamanoharan *et al.*[58] found that an increase in the solvency for both PMMA and stabilizer led to larger latex particles. As explained above, the critical polymer chain length at which the PMMA chains became insoluble was in direct dependence to the reaction mixture composition. For the same reason, increasing stabilizer concentration led to the increase of solvency for the PMMA chains. In this case, the better PMMA solvency in the reaction mixture was due to the increase in the amount of ethyl and butyl acetate present in the medium. Pathmamanoharan *et al.* [58] ran two reactions in two different solvent mixtures; one in a mixture of hexane and high boiling hydrocarbon fraction, and the other in Exxsol D-100, which was also a mixture of hydrocarbons. For otherwise identical conditions, a significant change in particle size (89 nm vs. 112 nm) was observed.

3.1.6. SPECIAL CASE: DIFUNCTIONAL PHSA-BASED STABILIZER

Only one example of a difunctional PHSA-based stabilizer (Figure 8) has been reported.[60] This stabilizer includes two reactive vinyl groups and was explicitly designed to produce latex particle dispersions for improved coatings in automotive applications (better gloss appearance, for example).

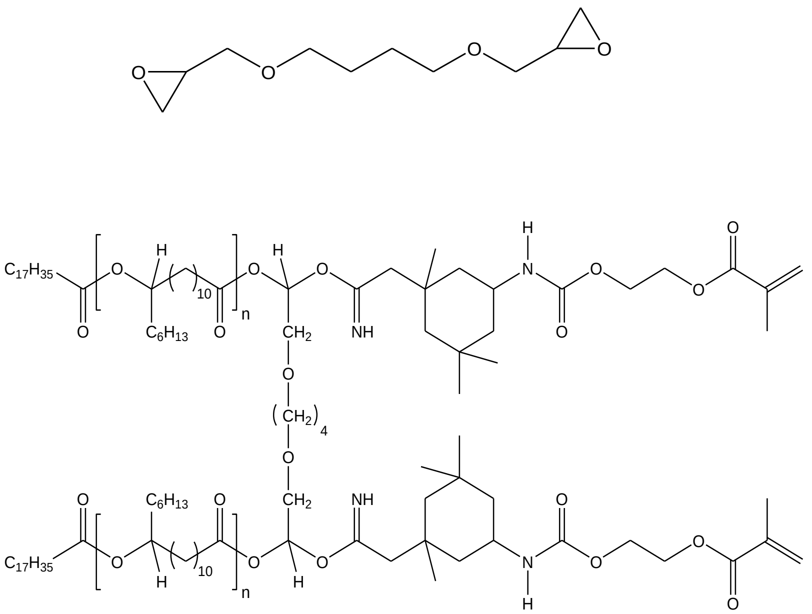


Figure 8. Chemical structure of diepoxy-1,4-butanediol diglycidylether (top) and “cross-linker” PHSA-based stabilizer (bottom)[60]

This difunctional PHSA-based stabilizer was synthesized in a four-step process: the first step was the 12-hydroxystearic acid polycondensation in presence of tetraisopropyl titanate (reaction catalyst); the second step is the combination of two PHSA homopolymer chains into a single molecule using a diepoxy-1,4-butanediol diglycidyl ether (Figure 8); the third step is the introduction of an isocyanate group using the isophore diisocyanate molecule (primary isocyanate reacted before the secondary ones); the final step was using the remaining isocyanate group to introduce two double bonds to the stabilizer (Figure 8).

Using this stabilizer, a dispersion polymerization was carried out by dissolving monomer (MMA + HEMA), initiator (AIBN), stabilizer, methoxymethyl melamine and phenyl acid phosphate (catalyst) in naphta under reflux.[60] During the dispersion polymerization, a double cross-linking reaction allowed the formation of reticulated PMMA latex particles. The first cross-linking reaction stemmed from the polymerization of the two vinyl groups of the stabilizer with the monomers. The second cross-linking reaction took place between the HEMA and methoxy melamine; this second mechanism was slower than the standard radical polymerization. The second process allowed for an increasing level of cross-linking throughout the polymer particles. As with the other stabilizers, Chattha *et al.*[60] found that changing parameters such as stabilizer or acid catalyst concentrations had an effect on the particle size and polydispersity. Decreasing the stabilizer concentration and/or increasing the amount of acid catalyst led to larger particles, while the level of HEMA/methoxymethyl melamine did not affect the final particle size.

3.2. POLYDIMETHYLSILOXANE-BASED (PDMS) STABILIZERS

As a colorless, odorless viscous liquid, PDMS-based stabilizers are easily soluble in various non-polar solvents. Different molecular weight PDMS and end-group functionality are commercially available. Methacryloxypropyl-terminated polydimethylsiloxane (PDMS-MA) emerged a few years after PHSA-based stabilizers due to the progress in silicone chemistry and have been used as an efficient alternative since.

3.2.1. PDMS-BASED STABILIZERS

PDMS polymers with various molecular weights (200 to 155,000 g/mol), reactivities (mono-, di- or tri-functional), end-group functionalities (vinyl group, methacrylate/acrylate group, amine, hydride, silanol, epoxy group, etc.), branching (linear, T-shape) are commercially available (Figure 9). These polymers do represent a suitable alternative (enhanced by the extensive options that synthetic silicone chemistry offers) to the non-commercial PHSA-based stabilizers, which have reproducibility issues (see Section 3.1.1). Despite the commercialization of this wide range of PDMS polymers and their good solubility in non-polar solvents, their use as stabilizers for radical dispersion polymerization in non-polar solvent is limited. Non-reactive PDMS and methacryloxypropyl-terminated polydimethylsiloxane mono- or di-functional (PDMS-MA or MA-PDMS-MA) have been the only PDMS polymers chains used in non-polar radical dispersion polymerization. In addition, in the last two decades, PDMS-MA has been mostly used as stabilizer in supercritical carbon dioxide ($scCO_2$), which will be discussed in Section 6. Block copolymers containing PDMS have also been used (PDMS-co-PMMA, PDMS-co-PS) in MMA dispersion polymerization in non-polar solvent.

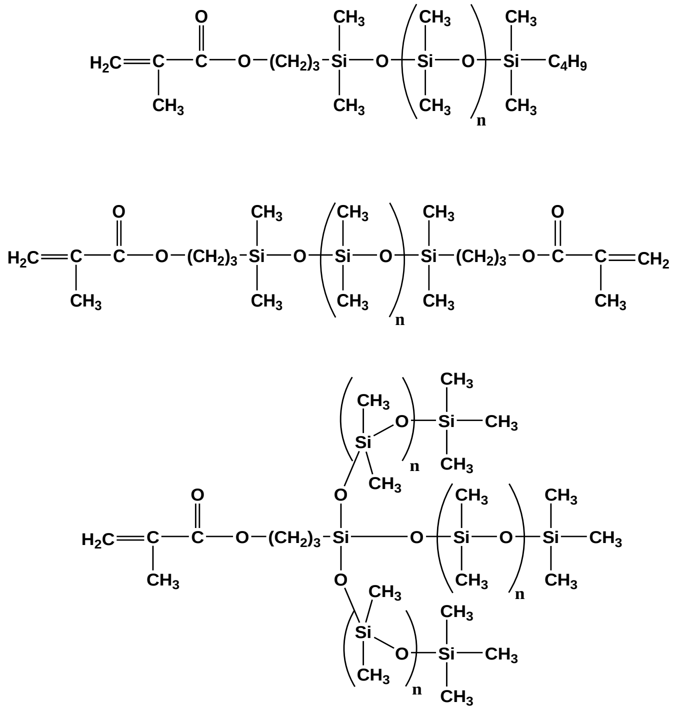


Figure 9 Chemical structure of methacryloxypropyl terminated (mono- (top) or di-functional (middle)) polydimethylsiloxane and branched methacryloxypropyl terminated polydimethylsiloxane (bottom)

In the next few paragraphs, we discuss the importance of PDMS-based stabilizer molecular weight and reactivity.[28,61,62,63]

3.2.1.1. STABILIZATION MECHANISM

PDMS stabilizer chains are highly soluble in non-polar solvents like hexane, heptane and dodecane. However, through different studies it was shown that the PMMA latex particles stabilization was a function of parameters such as stabilizer molecular weight (chain length for steric stabilization) and stabilizer reactivity (stabilizer grafting onto the PMMA latex particles). Non-reactive PDMS stabilizers [61] as well as PDMS stabilizers terminated at one [28,61,62] or both [28,63] ends by a reactive group (vinyl or methacryloyl group) were investigated. As a result, these studies have built an understanding of the stabilization mechanism offered by such polymers.

Pelton *et al.* were the first to investigate the efficiency of a PDMS homopolymer as stabilizer for radical dispersion polymerization of MMA in heptane.[28,61] They studied the effect of stabilizer molecular weight, stabilizer concentration as well as the importance of reactive end-group of the stabilizer (no reactive group, vinyl group or methacryloyl group). Their study focused on stabilization mechanism, particle formation and the importance of the stabilizing silicone layer in order to understand how particle size and stability were affected. First, they compared a trimethylsilyl-terminated PDMS (PDMS-Si) with a vinyldimethylsilyl-terminated PDMS (PDMS-V), as summarized in Table 3.

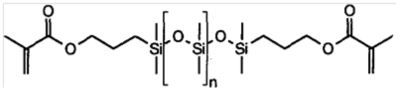
Table 3. Effect of stabilizer choice and concentration on particle properties as synthesized by Pelton *et al.* [61]

Stabilizer type	Stabilizer MW (g/mol)	Stabilizer concentration (g/kg)	Grafting mechanism	Particle size (nm)
PDMS-Si	63,000 – 308,000	59	Hydrogen abstraction by peroxide	900 – 1290
PDMS-V	6,000 – 308,000	59	Copolymerization with MMA	830 - 1390

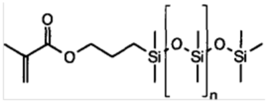
With PDMS-Si stabilizer (grafting to growing PMMA polymer particles via hydrogen abstraction by peroxide), they showed that stable latex particles could be obtained for a wide range of stabilizer molecular weights (Table 3). As stabilizer grafting *via* H abstraction was an inefficient process (only 2 to 4% PDMS-Si was incorporated), high molecular weight stabilizer were required to form stable latex particles.[61] In comparison, lower PDMS-V Mw (grafting by copolymerization with MMA) was sufficient to stabilize PMMA latex particles (Table 3). Subsequently, they investigated the influence of silicone concentration on the particle size with 308,000 g/mol stabilizers. They showed that for PDMS-Si stabilizer, a minimum concentration (2.48×10^{-4} g/mol) of about an order of magnitude higher was required compared to PDMS-V (1.2×10^{-5} g/mol).

This was attributed to the slow incorporation of the PDMS-Si stabilizer. Once again, the particles obtained with PDMS-Si led to larger PMMA latex particles. The particle size was shown to increase with decreasing stabilizer concentration. It was also demonstrated that the more stabilizer present during the nucleation stage, the more particles were produced.

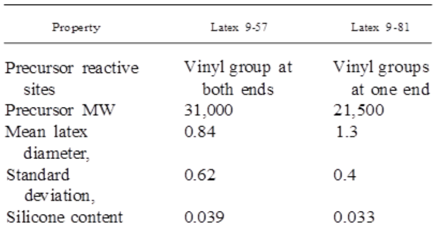
Finally, the influence of initiator type and concentration was studied. Both AIBN and benzyl peroxide led to similar size, except when AIBN and PDMS-Si were associated because hydrogen abstraction along the PDMS chains using AIBN is impossible. As a consequence, PDMS-Si could not be grafted to the PMMA polymer chains and could not provide efficient steric stabilization. As expected, the particle size increased with decreasing initiator concentration.



Used in Latex 9-57



Used in Latex 9-81



Property	Latex 9-57	Latex 9-81
Precursor reactive sites	Vinyl group at both ends	Vinyl groups at one end
Precursor MW	31,000	21,500
Mean latex diameter,	0.84	1.3
Standard deviation,	0.62	0.4
Silicone content	0.039	0.033

Figure 10. Chemical structures of the silicone macromonomers used by Pelton *et al.* (top) and properties of latex particles obtained by dispersion polymerization in n-heptane (bottom) (reproduced from reference [28])

In a separate study, Pelton *et al.* [28] compared the efficiency of mono- and di-functionalised methacryloxypropyl-terminated polydimethylsiloxane (PDMS-MA and MA-PDMS-MA) in order to determine the minimum stabilizer concentration required to prepare stable latex PMMA particles in heptane. (Figure 10) To evaluate the minimum stabilizer grafting density on the latex particle surface, a degradation technique was used to progressively remove the PDMS backbone chains. A critical chain length for efficient stabilization was defined and this was calculated for each stabilizer from the amount of PDMS detected at the flocculation point. However, because a reasonable amount of stabilizer was trapped (about 66%) in the latex particles, only approximate values were determined and this differed from theoretical values.

Separately, Srinivasan *et al.* prepared PMMA latex particles which were thermally labile, in order to design porous materials.[62] They combined a dispersion polymerization in non-polar solvent (hexane) with the use of a cobalt-based chain transfer agent. This reduced the final molecular weight of PMMA produced and created unsaturations which induced polymer thermal instability. In order to bring more thermal instability along the PMMA chains, dimethylmaleic anhydride was also used as co-monomer. This co-monomer led to head-to-head defect by termination via recombination. PDMS stabilizers at 1,200 and 25,000 g/mol were used to investigate the thermal stability of the particles formed. Thermal gravimetric analysis (TGA) showed that PMMA prepared in presence of cobalt chain transfer agent (CTA) degraded below 300˚C due to depolymerization, while PMMA prepared without CTA degraded above 300˚C.[62] Once again, the addition of cobalt-based transfer agent resulted in lower molecular weight and higher thermal sensibility. The amount of transfer agent introduced into the dispersion medium was a critical parameter as high concentrations led to soluble PMMA chains, whereas low concentrations resulted in PMMA chains of similar thermal sensitivity.

Finally, Klein *et al*. studied the influence of monomer and stabilizer concentration on particle size and polydispersity.[63] In their work, a PDMS polymer terminated at both ends with a methacryloxypropyl group (MA-PDMS-MA) with different MW (5,000 to 55,000 g/mol) was used. A minimum stabilizer MW 10,000 g/mol was required to form stable PMMA latex dispersions. The stabilizer to monomer weight ratio was required to be in the range 0.02 to 0.1 to obtain monodisperse particles (Figure 11). By varying the stabilizer and/or monomer concentrations, these authors successfully prepared monodisperse latex particles in the size range 0.4 to 1.5 μm. [63]

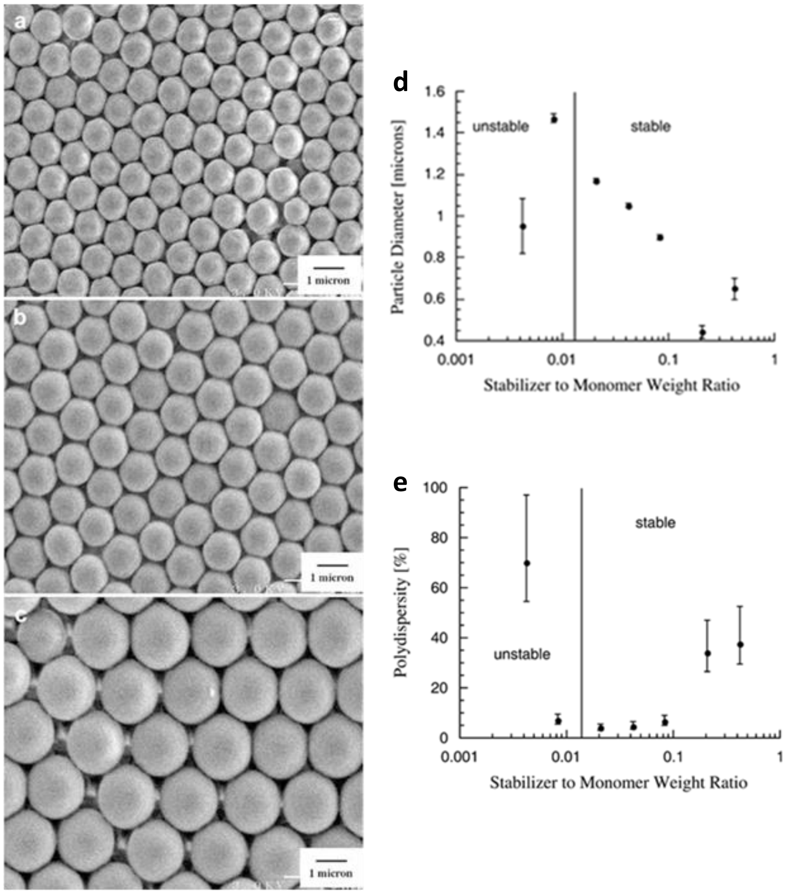


Figure 11. SEM images (left) of PMMA latex particles obtained from dispersion polymerization in hexane at different monomer concentration: 15.2 % w/w (a), 26.3 % w/w (b) and 47.2 % w/w (c), and particle size (d) and polydispersity (e) for different stabilizer concentrations (reproduced from the reference [63])

Table 4. Latex particle properties obtained in radical dispersion polymerization in non-polar solvents using PDMS-based stabilizers

Monomer concentration (wt%)	Stabilizer concentration (wt%)	Stabilizer MW (g/mol)	Size (nm)	PDI (%)	Reference
PDMS-Si					
10	5	62,000 to 308,000	1289 to 899	-	61
PDMS-V					
10	5	5,790 to 308,000	1390 to 830	-	61
PDMS-MA					
10	8	21,500	1300	Monodisperse	28
8	10	1,200 and 25,000	1000 to 1300	-	62
MA-PDMS-MA					
-	-	5,000 to 55,000	800 to 1000	3.84 to 40.79	63
15.2 to 47.2	-	-	1000 to 1800	3.41 to 4.73	
10	8	31,000	840	Polydisperse	28

3.2.1.2. PARTICLE SIZE AND POLYDISPERSITY ACCESSIBLE

In this section, the key parameters governing the latex particle size and polydispersity are summarized.

- Monomer concentration

All studies on modifying monomer concentration showed that increasing monomer concentration produced larger particles. This was due to the fact that more monomer was available for polymerization and to the fact that the critical chain length was greatly affected by the presence of MMA monomer in the dispersion mixture. Again, because MMA is a good solvent for PMMA, high concentrations of MMA allowed the PMMA chains to precipitate at higher chain lengths and induced the precipitation of fewer nuclei, thus forming larger particles.

- Stabilizer concentration

Higher stabilizer concentration produced smaller PMMA latex particles. Because the polymerization was initiated in the stabilizer micelles, more stabilizers allowed the formation of more micelles and thus, more particles. Subsequently, the monomer was distributed between more particles and thus, smaller latex particles were obtained.

- Stabilizer functionality

In the case of PDMS-Si (no reactive moiety), the links with the latex particles are created via H-abstraction due to the use of a peroxide. Because this mechanism is very limited, a higher stabilizer concentration is required. A more efficient stabilization is generally obtained with reactive PDMS stabilizers (PDMS-V or PDMS-MA). In this case, the reactive group is a monomer unit and can then take part in the polymerization, generally leading to very efficient stabilization.

3.2.2. BLOCK COPOLYMER STABILIZER WITH A PDMS BLOCK

PDMS-based block copolymers were also investigated as stabilizers for MMA free radical dispersion polymerization in non-polar solvents. In these cases, the insoluble copolymer block should offer sufficient affinity to the particle surface in order to provide good surface coverage and efficient stabilizer adsorption. This is because there are no chemical bonds created between the stabilizer molecules and the latex particles. Meanwhile, the role of the soluble PDMS block is to extend into the continuous phase and to provide a steric barrier against aggregation.

- Block copolymer of polydimethylsiloxane (PDMS) / polystyrene (PS)

Two examples of MMA free radical dispersion polymerization in hexane using PDMS-block-PS stabilizers were published by Everett *et al*. and Dawkins *et al*.[64,65] . Dawkins *et al*. [64] used a PDMS-b-PS diblock copolymer while Everett *et al*. [65] used a PDMS-b-PS-b-PDMS triblock copolymer. In both cases, the copolymer stabilizers were synthesized by sequential anionic polymerization. Everett *et al*. studied latex stability in a range of solvents, while Dawkins *et al.* investigated the effect of reaction parameters on the properties of final particles.

Everett *et al*. investigated the stability of 123 nm PMMA latex particles in low molecular weight solvents: from propane to hexane (stable PMMA dispersions were not obtained from ethane downwards). Depending on the dispersing medium, they identified a thermal stability domain delineated by both an upper and lower flocculation temperature (respectively at 56 and -82°C for dispersion in propane).[65] The study showed that this thermal stability domain became narrower when the solvent changed from hexane to propane.

Dawkins *et al.*[64] studied the mechanism behind free radical dispersion polymerization (figure 12). Using a range of PDMS-b-PS block copolymer stabilizers (2,400 < $\overline{M}$n (PDMS) < 48,000 g/mol and 8,800 < $\overline{M}$n (PS) < 44,000 g/mol, with the PS to PDMS weight block ratio from 0.5 to 4.0), they notably showed a linear relationship ($D \propto c^{-0.77}$) between particle diameter (D) and stabilizer concentration (c).[64] They also pointed out the importance of stabilizer molecular weight. They demonstrated that smaller latex particles were obtained when using PDMS-b-PS of higher molecular weight because of the ability of longer stabilizer chains to stabilize larger particle surface area.

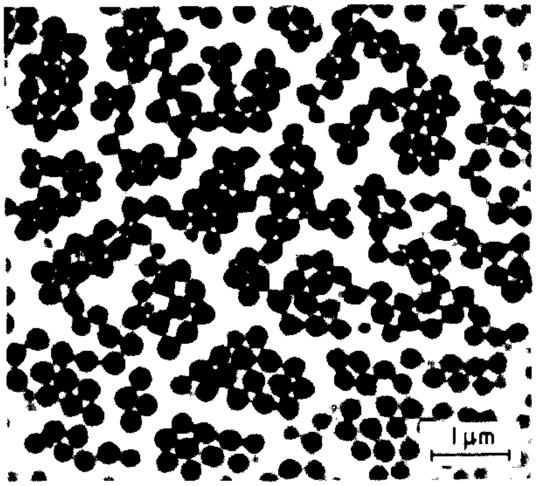


Figure 12. TEM image of PMMA latex particles (around 250 nm) produced by radical dispersion polymerization in n-hexane (reproduced from reference [62])

It was also shown that the surface covered by the stabilizer was independent of the particle size, and independent of the PS molecular weight (due to its limited extension in hexane). As a consequence, the anchoring efficiency was not improved by increasing the PS molecular weight. However, the high stability of PMMA latex particles proved that the PS block was indeed an efficient anchor block for stabilizing PMMA latex particles in non-polar solvents.

- Block copolymer of PDMS and PMMA

Saam and Tsai also reported the use of mercaptoalkyl-ended PDMS stabilizers for MMA dispersion polymerization in hexane.[66] In this example, the PMMA-b-PDMS block copolymer is generated in situ during the dispersion polymerization and the monomer/initiator mixture is continuously added over 8 hours. The final

PMMA colloidal particle size was in the range of 110 – 130 nm for a monomer conversion of 78 %. Finally, they estimated the silicone content around 4.5 %.

- Grafted copolymer of PDMS and PMMA

Croucher *et al.* produced PMMA latex particles (700 to 900 nm) stabilized by a PMMA-g-PDMS polymer in heptane and investigated the shear viscosity of such particles in n-hexadecane.[13] The PMMA-g-PDMS was prepared by hydrogen abstraction by peroxide along the PDMS chain allowing the grafting of growing PMMA polymer chains (similar to the process discussed by Pelton *et al.*[61] in Section 3.2.1.1). These authors showed temperature dependence of the latex suspension; at low particle volume fractions, the viscosity decreased when temperature was increased (an effect of the continuous n-hexadecane phase), and at high particle volume fractions, the viscosity increased when increasing temperature (an effect of particle interactions in the system).[13]

3.3. RECENT PROGRESS IN STABILIZER DESIGN

Recent developments in polymer chemistry, particularly in free radical controlled polymerization, have allowed the preparation of bespoke stabilizers (of chosen functionality, chain length, morphology, etc.). For example, various stabilizers have recently been synthesized using Atom Transfer Radical Polymerization (ATRP) or Reversible Addition-Fragmentation chain Transfer (RAFT) polymerizations. In this section, several representative examples of such stabilizers are discussed; starting from simple polyethylene macromonomers to complex stabilizers designed via controlled free radical polymerization techniques.

- MMA dispersion polymerization in dodecane using polyethylene macromonomer as stabilizer

Kawaguchi *et al.* synthesised PMMA-g-polyethylene (PMMA-g-PE) and investigated their efficiency as steric stabilizer for MMA free radical dispersion in dodecane.[67] Using this macromonomer, they successfully produced submicron monodisperse PMMA latex particles.

- MMA dispersion polymerization in *n*-decane using PS-block-poly(ethylene-co-propylene) as stabilizer

PS-block-poly(ethylene-co-propylene) (PS-b-(PE-co-PP)) was used for dispersion polymerizations of MMA-based monomers in n-alkane.[68,69] Both Hirzinger *et al*. [68] and Hölderle *et al.* [69] used commercial PS-b-(PE-co-PP) stabilizer that form micelles in n-decane. For this reason, the stabilization mechanism was expected to be different from that of a dispersion polymerization performed with a macromonomer as the stabilizer.

Hirzinger *et al.* investigated the micellization of the stabilizer in the oil phase in order to draw a correlation between colloidal dispersion properties and stabilizer micelle characteristics.[70] They also investigated MMA free radical dispersion polymerization in n-decane. [68,71,72] From their studies, they found that the PS block of Kraton 1701 acted as an anchor to link the stabilizer to the PMMA particles (the PS chains were entangled with the core-forming PMMA chains). Therefore, Hirzinger *et al.*[68] found that a colloidal particle grew from a micelle for a shell-to-core mass ratio > 0.25, while smaller amount of colloidal latex particles were produced at lower shell-to-core mass ratio. As found with macromonomers, an increase of stabilizer concentration led to smaller latex particles.

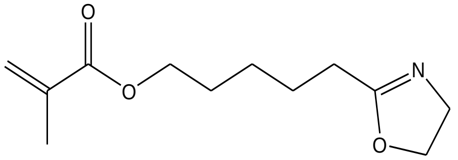


Figure 13. Chemical structure of 2-(5-methacryloyl-pentyl)-1,3-oxazoline monomer

Later, Hölderle *et al.* used the same stabilizer (Kraton 1701) at different concentrations to control the size of particles obtained from dispersion copolymerization of MMA and oxalinefunctional methacrylate (Figure 13) in n-heptane.[69]

These authors found that oxazoline monomer content and cross-linking density had a minor effect on the particle size, but affected the particle polydispersity. Increasing the oxazoline content led to narrower particle size distributions, while increasing the grafting density had an opposite effect. Oxazoline monomer incorporation also led to lower glass transition temperature (T_g). In comparison, stabilizer and monomer concentrations had a major impact on the final particle produced. When the stabilizer concentration varied from 1.3 to 15 wt%, the particle size decreased from 520 to 110 nm, while a change in monomer concentration from 11.3 to 23.5 wt% led to an increase in particle size from 80 to 270 nm.

- MMA dispersion polymerization in CCl_4/2,2,4-trimetylpentane using polyisobutylene as stabilizer

Williamson *et al*. used a polyisobutylene polymer as steric stabilizer for MMA free radical dispersion polymerization in 2,2,4-trimethylpentane and introduced various amounts of carbon tetrachloride (CCl_4) in order to study the effect of dispersing medium solvency.[73] The main observation was that particle size was dramatically increased by adding CCl_4; from 1 µm in pure 2,2,4-trimethylpentane to 8 µm in a mixture of 2:1 (by volume) CCl_4:2,2,4-trimethylpentane (a maximum particle size of 13 µm had even been observed). Another effect of CCl_4 addition was a decrease in polymerization rate. At high ratios of CCl_4, competing polymerization processes took place; classical growth of colloidal particles and solution polymerization due to high solvency of dispersing medium. The coexistence of these two processes led to lower polymer molecular weight and slower polymerization rate.

- MMA dispersion polymerization in iso-octane using polyisobutylene as stabilizer

Winnik *et al.* have been very interested in dispersion polymerization in non-polar solvent.[74,75,76] Their research was driven by industrial potential application that they identified as colored inks for electrostatic imaging system. However, not like all the other research groups, they have been interested in investigating the morphology of the final particle, i.e. how the stabilizer chains and the polymer of the core are organized and / or segregated on the particle surface as well as within the colloidal particles. To locate the interfaces between stabilizer chains and polymer chains Winnik *et al.* used fluorescence quenching between two fluorescent groups. The colloidal particles are made of PMMA and sterically stabilized by PIB chains in iso-octane. However, after purification (centrifugation / redispersion cycles) the particles were transferred in cyclohexane. For the fluorescence quenching experiments, particles were fluorescently labeled on the PMMA chains and on the stabilizer chains (PIB) by different dyes which allow fluorescent transfer. Fluorescent dyes usually used as comonomer were 1-naphtylmethyl methacrylate or 9-anthrylmethyl methacrylate.[74] The quenching is observed when fluorescent dyes are in very close proximity. Their experiment of fluorescence transfer allowed them to make several observations. First of all they showed by fluorescence decay measurements that labeled stabilizer where located within the core of the particles. They also showed that after swelling of the particles (due to temperature increase) more fluorescent decay could be observed. Because the swelling of the core was due to the presence of PIB chains, the core-shell model usually identified for such particles was incoherent. Winnik *et al.* suggested a new model called "microphase" model (Figure 14).

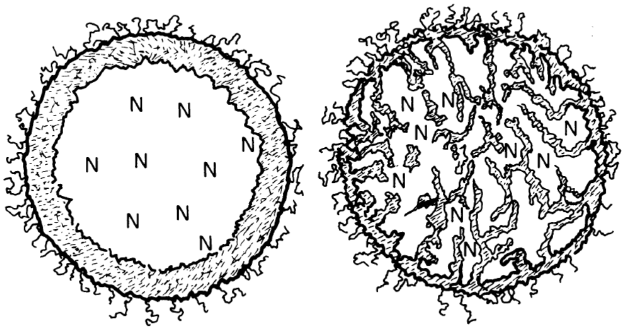


Figure 14. "Core-shell" structure (left) vs. "microphase" model (right) (reproduced from reference [74])

- MA dispersion polymerization in isododecane using poly(2-ethylhexyl acrylate) as macroRAFT agent / stabilizer

Recently, Houillot *et al.* used controlled free radical polymerization by RAFT to design a macroRAFT agent which efficiently stabilised poly(methyl acrylate) (PMA) latex particles prepared via dispersion polymerization in iso-dodecane.[77,78] They designed poly(2-ethylhexyl acrylate) (P2EHA) stabilizers by bulk free radical polymerization controlled using dithiobenzoate (DTB) or trithiocarbonate (TTC) RAFT agents (Figure 15).

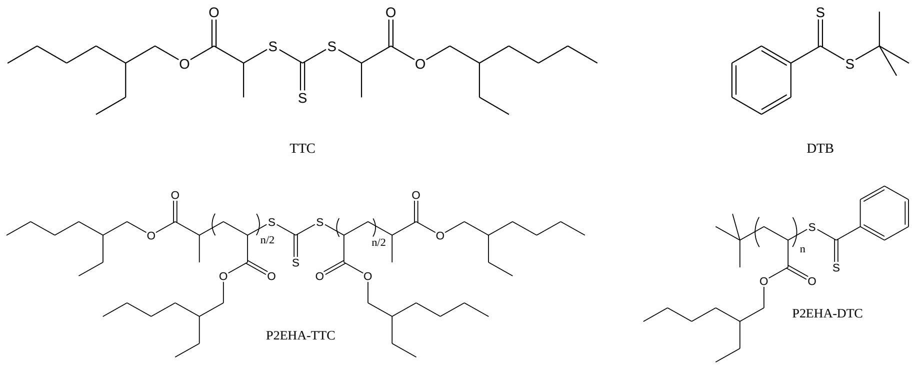


Figure 15 Different structure of RAFT agent used in the macro-RAFT agent design

Subsequently, they performed free radical dispersion polymerization of methyl acrylate (MA) in iso-dodecane using three different stabilizers; a non-reactive P2EHA, a P2EHA terminated with DTB (one reactive site) (P2EHA-DTB) and a P2EHA incorporating TTC (two reactive sites) (P2EHA-TTC). These authors demonstrated that presence of the RAFT agent on the stabilizer chain was crucial to allow for covalent grafting and thus efficient colloidal particle stabilization; the non-reactive P2EHA was unable to absorb onto the particle surface.[78] In addition, a kinetic study of the free radical polymerization in the presence of P2EHA-TTC and P2EHA-DTB showed that only the P2EHA-TTC stabilizer was able to control the polymerization leading to well-defined triblock copolymers forming small monodisperse core-shell colloidal particles (120 to 320 nm).[77,78] The use of P2EHA-DTB macro-RAFT agent as stabilizer at the lowest concentration did not provide control over the polymer structure (PDI =18) but led to the formation of small monodisperse particles (39 to 93 nm). However, the monomer conversion stayed low compared to the other macro-RAFT agent and an important retardation phenomenon was observed. When the P2EHA stabilizer concentration was increased, a better control of the polymerization was achieved but the colloidal particle polydispersity increased.

- MMA dispersion polymerization in hexane/dodecane using PMMA-poly(octadecyl acrylate) (block or random) as stabilizer

ATRP was used by Harris *et al.* to design a new stabilizer for MMA dispersion polymerizations in a mixture of hexane and dodecane.[79] Harris *et al.* prepared three random PMMA-co-poly(octadecyl acrylate) (PMMA-co-PODA) and three block copolymers (PMMA-b-PODA) of methyl methacrylate (MMA) and octadecyl acrylate (ODA) (at different monomer ratios) in toluene.[79] On the contrary to stabilizers prepared via RAFT polymerization, these polymers did not possess a reactive group and, as a result, could not be covalently linked to the particle surface. For this reason, block copolymers with long PODA blocks were expected to be more efficient stabilizers than the random copolymers.

The authors showed that all stabilizers were able to form stable colloidal particles in the range of 400 to 2730 nm but that drastic variations in particle characteristics (size, polydispersity) existed depending on the stabilizers properties (random or block, monomer ratio). However, no apparent correlations between the stabilizer parameters and the colloidal particles properties were drawn. In addition, the fact that random copolymers were able to stabilize MMA dispersion polymerization in hexane/dodecane mixture were unexpected. This was probably due to the difference between the MMA and ODA compositions which led to PODA segments that were long enough to provide stabilization. This assumption was supported by the fact that the best random copolymer stabilizer was the one incorporating the highest ODA fraction.

4. DISPERSION POLYMERIZATION OF STYRENE-BASED MONOMERS IN NON-POLAR SOLVENTS

This section reviews the dispersion polymerization of styrene in “standard” non-polar hydrocarbon solvents. The discussion is structured around the two main polymerization techniques; anionic dispersion polymerization (ADP) and free radical polymerization (FRP). Dispersion polymerization of styrene in alternate mediums, such as supercritical fluids, will be briefly discussed in Section 6, as the research in this area, albeit relatively recent, has already been reviewed by various other authors.
Table 5 provides a summary of the stabilizers used in the syntheses of polystyrene particles in the non-polar solvents considered here.

Table 5. Summary of stabilizers used in dispersion polymerization of styrene in various non-polar solvents

Medium	Stabilizer	Particle size range	Reference
Butane	Polystyrene-*block*-polybutadiene (PS-b-PB)	2 – 5 μm	87
Pentane	Polystyrene-*block*-polybutadiene (PS-b-PB)	1 – 2 μm	87
Hexane	Mercaptoalkyl-modified poly(dimethylsiloxane) (MCTA-PDMS)	-	66
	Poly(isoprene)-*block*-polystyrene) (PIP-b-PS)	50 – 150 nm	16,80
	Polystyrene-*block*-poly(4-trimethylsilylstyrene) (PS-*b*-PTMSS)	0.5 – 3.8 μm	82
	Polystyrene-*block*-polybutadiene (PS-*b*-PB)	1.4 – 7.1 μm	83,84
	Polystyrene-*block*-polyisobutylene (PS-*b*-PIB)	0.4 – 2.0 μm	86
	Poly(tert-butylstyrene)-*block*-polystyrene (PtBS-*b*-PS)	0.05 – 6.4 μm	80,85
	Polystyrene-*block*-polybutadiene-*block*-polystyrene		83

	(PS-*b*-PB-*b*-PS)	1.8 μm	
Heptane	Poly(vinyl ethyl ether) (PVEE)	-	81
	Polystyrene-*block*-poly(dimethylsiloxane) (PS-*b*-PDMS)	0.6 – 12.5 μm	88
Decane	Polystyrene-*block*-poly(ethene-*alt*-propene) (PS-*b*-P(E-*alt*-P))	0.05 – 10 μm	90
Isopar	Poly(butadiene)-*block*-poly(isoprene) (PB-*b*-PIP)	2.5 μm	89

4.1. ANIONIC DISPERSION POLYMERIZATION

The uniqueness of anionic dispersion polymerization (ADP), also known as living dispersion polymerization (LDP), lies in the "living" character of the polymer anions. This allows a high degree of control on the molecular weight and distribution of the polymer anions, in turn producing monodisperse particles. ADP also allows ease of chain-end/surface functionalization, thus allowing application potentials in biomedicine, catalysts, surface coatings, etc. It also facilitates polymerization at low temperatures and viscosities, while maintaining high solids content. However, ADP does have its limitations. The "living" character of the polymerization requires extra care in experiment preparation in order to have a truly living synthesis. Any impurities, such as water, alcohol, molecular oxygen, etc., as well as changes in the composition will affect the polymerization control. Generally, all reaction vessels must be dried extensively. The reactants and solvent are extensively purified and used immediately for synthesis, with the reaction kept under ultra-high purity nitrogen throughout.

Once the reactants (monomer, copolymer stabilizer and solvent) are homogenously mixed, the initiator is added in stages; dropwise initially to deactivate any impurities (i.e. when the pale red color of the styryl anion persists) and subsequently in quick addition turning the solution ruby red. The polystyrene chains then grow to a critical chain length, at which the chains precipitate and aggregate, allowing the copolymer stabilizer to adsorb onto the nuclei. The dispersion is orange-yellow in appearance at this point. Coalescence and flocculation persists until sufficient stabilizer is adsorbed. As polymerization progresses, monomer diffuses into the particles allowing continuous growth. At the end, polymerization is terminated by quenching with methanol or passing dry air into the dispersion. The particles can be redispersed if required. In some cases, 5 wt% paraffin wax has also been added to improve redispersion of cross-linked polystyrene particles [80].

4.2. STABILIZER SELECTION

For stable polystyrene particle dispersions in a non-polar medium, it is essential to have an amphipathic stabilizer, which is typically a block copolymer comprising an anchoring organophobic polystyrene and a stabilizing organophilic moiety. The balance between the anchoring and steric stabilizing moieties of the stabilizer governs the adsorption efficiency of the stabilizer to the newly precipitated particles. This in turn contributes to the particle size and polydispersity. The polymeric stabilizer can either be preformed prior to particle synthesis, or made in situ via anionic polymerization with a polymeric organolithium compound [80].

- Homopolymer

In the last 40 years, a range of polymeric stabilizers were investigated, consisting of homopolymer, diblock and triblock copolymers. Stampa performed the first ADP of α-methylstyrene in heptane in 1970 with poly(vinyl ethyl ether) (PVEE) as a stabilizer [81]. PVEE adsorbed to the particles through coordination with the polar reaction site, while remaining soluble in heptane. A minimum of 0.1 wt% (with respect to monomer) PVEE was necessary to produce stable particles. The stabilizer should possess a minimum MW 1,000,000 in order to form a sufficient steric barrier. Unfortunately, there was no report on the particle size and size distribution for the poly(α-methylstyrene) particles produced in this case.

- Diblock copolymer

Over a decade on, Murray and Schwab produced cross-linked polystyrene particles (50 – 150 nm) in hexane [80]. These particles were used as organic fillers in styrene-butadiene rubber (SBR), replacing the more common carbon blacks. Murray and Schwab illustrated that by changing the type and concentration of the polymeric stabilizer used, it was possible to make either isolated particles or “structured” agglomerates. The selected stabilizers are 80:20 wt% tert-butylstyrene/styrene for the isolated particles and 80:20 wt% isoprene/styrene for the agglomerates. These stabilizers were formed in situ by using a polymeric co-initiator of polyisoprenyl lithium, giving the advantage of a one-step one-pot synthesis. Murray and Schwab used 1 – 5 wt% copolymer stabilizers in their syntheses. Nonetheless, a recommendation was proposed for a minimum MW 20,000 and 30,000 for tert-butylstyrene/styrene and isoprene/styrene respectively. Vincent *et al.* also synthesized 100 nm polystyrene particles in n-hexane, which were stabilized with poly(styrene-block-isoprene) (PS-b-PIP) (MW 1,300) [16]. Limited information was available regarding the synthesis of the particles, which were used to study depletion flocculation mechanisms.

In 1990s, the understanding of synthesis of polystyrene particles in non-polar media was greatly improved. Various parameters were investigated, including stabilizer concentration, size of anchoring and stabilizing blocks, monomer concentration, monomer addition procedure, initiator concentration, promoter addition and reaction temperature.

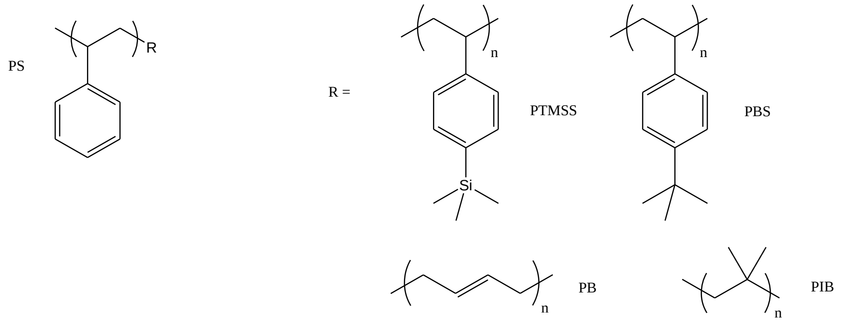


Figure 16. Chemical structure of PS-b-PTMSS, PS-b-PB, PS-b-PBS and PS-b-PIB

These studies were performed in hexane for polystyrene particles stabilized with either polystyrene-block-poly(4-trimethylsilylstyrene) (PS-b-PTMSS) [82], polystyrene-block-polybutadiene (PS-b-PB) (Stereon 721A or 730A) [83,84], polystyrene-block-poly(t-butylstyrene) (PS-b-PBS) [85] or polystyrene-block-polyisobutylene (PS-b-PIB) [86]. (Figure 16)

The characteristics of the stabilizers used, including the particle size obtained, are listed in Table 6. For PS-b-PTMSS, a minimum of 5 wt% stabilizer was required, which produced polydisperse 600 nm polystyrene particles. Further increase in stabilizer concentration did not improve the particle size distribution [82]. Awan *et al.* [83] found that Stereon 730A was more efficient in producing monodisperse micron-sized particles compared to Stereon 721A (Figure 17). Stereon 721A was less effective because of its short polystyrene anchoring block, resulting in particle flocculation as the stabilizers desorbed easily. The larger solubilizing block in Stereon 721A also delayed the adsorption process, resulting in higher polydispersity. Schneider and Mülhaupt [82] and Kéki *et al.* [86] also observed an inverse relationship between particle size and molecular weight of polystyrene anchoring block. Although with a larger polystyrene block, particle dispersions displayed narrower size distributions [83,86]. Kim *et al.* deduced their observations based on the size of the poly(t-butylstyrene) stabilizing block [85]. They found that a minimum MW 17,600 as required for PBS block for synthesis of stable particles, albeit a broader size distribution was obtained. This polydispersity was caused by differences in the local concentration of active species within each particle, leading to different reaction rates.

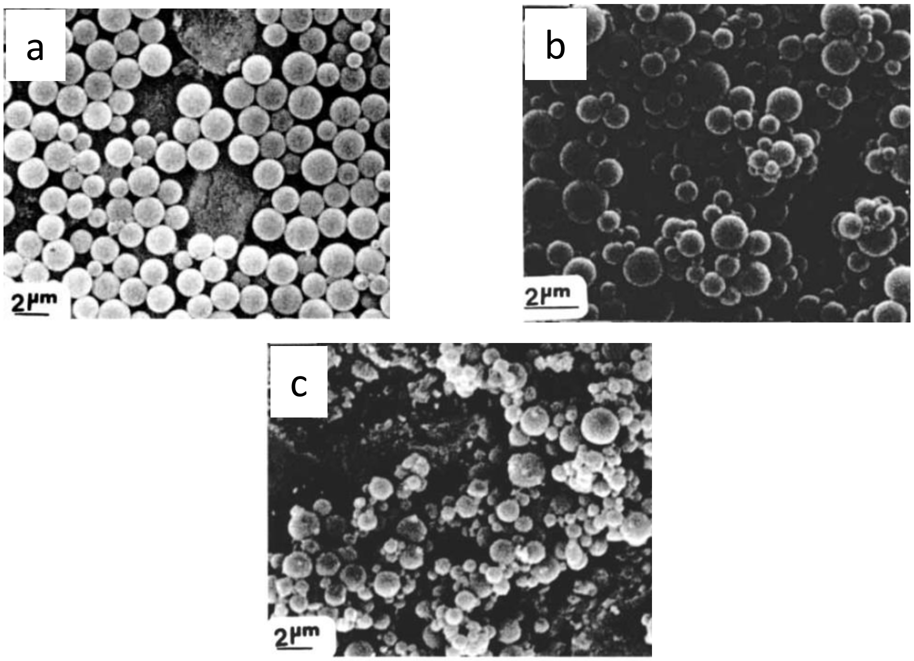


Figure 17. SEM images of polystyrene particles prepared in the presence of diblock polymeric stabilizers (a) Stereon 730A, (b) Stereon 721A (larger solubilizing block), and triblock stabilizer (c) Stereon 840A (Reproduced from reference [83]**)**

Table 6. Diblock polymeric stabilizers used for systematic study of synthesis of polystyrene particles in hexane

Authors	Stabilizer	Molecular weight (g/mol)	Size of PS block (wt%)	Amount of stabilizer (wt%)	Particle size (μm)
Schneider & Mülhaupt [82]	PS-*b*-PTMSS	110,000 – 180,000	50 – 75	5 – 10	0.5 – 3.8
Awan *et al.* [83, 84]	PS-*b*-PB	125,000 – 150,000	7 – 23	0.8 – 7	1.4 – 7.1
Kim *et al.* [85]	PS-*b*-PBS	35,000 – 140,000	20 – 57	1 – 5	0.06 – 6.4
Kéki *et al.* [86]	PS-*b*-PBS	15,000 – 140,000	28 - 54	4.4	0.4 – 2.0

Kéki *et al.* revealed PS-b-PIB with 54% polystyrene block as the most efficient stabilizer [86]. The large anchoring block possessed high adsorption energy, minimizing any stabilizer desorption during the polymerization, thus giving more monodisperse dispersions.

Recently, Tausendfreund *et al*. further developed ADP in butane and pentane to produce micron-sized copolymer particles of poly(styrene-b-butadiene) and poly(styrene-b-butadiene-b-styrene) [87]. The PS-b-PB stabilizer (with total MW 63,000 and 32% polystyrene block) was used. It was found that polybutadiene, with MW 30,000 – 40,000, and polystyrene, MW > 17,300, was optimum for particle stabilization. Further increase in PB block dramatically swelled the particles, causing severe aggregation. Tausendfreund *et al*. also demonstrated that the active chain centers were well distributed throughout the particle volume, by sequentially copolymerizing styrene and butadiene and selectively staining polybutadiene for TEM observations [87]. This was in contradiction to Kim *et al*. who proposed the location of active centers to be on the surface of their synthesized polystyrene particles [85].

- Triblock copolymer

Awan *et al*. investigated the efficiency of the triblock copolymer, polystyrene-polybutadiene-polystyrene (Stereon 840A), in the synthesis of polystyrene particles in hexane [83]. Stereon 840A, with MW 94,000 and 43% polystyrene block, yielded 1.8 µm particles with relatively broad size distribution (Figure 16). The ineffectiveness of Stereon 840A was due to (i) the triblock configuration causing entropic strain on the particle surface, (ii) the small polybutadiene block producing a thin steric layer and (iii) the tendency of adsorption of shorter stabilizer chains due to the broad molecular weight distribution of Stereon 840A. Murray and Schwab made a similar observation with the triblock copolymer, 'Kraton' rubber, which was showed to be less effective than a diblock stabilizer [80].

4.3. POLYMER MOLECULAR WEIGHT AND PARTICLE SIZE ACCESSIBLE

The key factors to synthesizing polystyrene particles in non-polar solvents include the chemical composition and adsorption rate of stabilizer, as well as the rate of initiation and growth of particle-forming chains. It is the balance between these parameters that governs the uniformity of particle dispersion, both in terms of particle size and polymer molecular weight distribution. Generally, the particle size was measured using TEM or SEM, while the molecular weight of polymer chains was determined via gel permeation chromatography (GPC), calibrated with polystyrene standards.

- Effect of stabilizer concentration

Decreasing stabilizer concentration led to an increase in particle size, with no effect on polydispersity [83,85]. This was due to the lower induced stabilizer adsorption rate, which allowed higher monomer conversion, resulting in longer chains and hence, larger particles. Awan *et al.* confirmed this by performing ellipsometry studies on polystyrene substrates, showing a reduction in copolymer adsorption rate at lower stabilizer concentrations [84]. They also demonstrated the dependence of polymerization rate on stabilizer content when monomer conversion was between 25 to 70% [83]. In this region, presence of more stabilizers produced smaller particles. This enhanced monomer transport to growing anions resulted in faster polymerization rate. Below 25% conversion, the polymerization kinetics was governed by concentration of growing anions. Whilst above 70%, most monomer was found inside the particles, rendering the effect of stabilizer concentration insignificant.

- Effect of monomer concentration

Awan *et al.* and Schneider and Mülhaupt observed a decrease in particle size when monomer concentration increased to 20 wt% [82,83]. This was caused by changes in medium solvency and strong association of stabilizer micelles at low monomer concentration. Stabilizer micelles are formed when the solvent preferentially solvates one of the blocks in a linear diblock copolymer. As the monomer concentration increases, the medium solvency for both polymer blocks improves, thus reducing the association of stabilizer micelles. Once the optimum concentration is achieved (~ 25 wt%) [83], further monomer increase results in the steady growth of polystyrene chains, producing larger particles. The increase in monomer concentration also increased the molecular weight of polystyrene chains steadily, without affecting polydispersity.

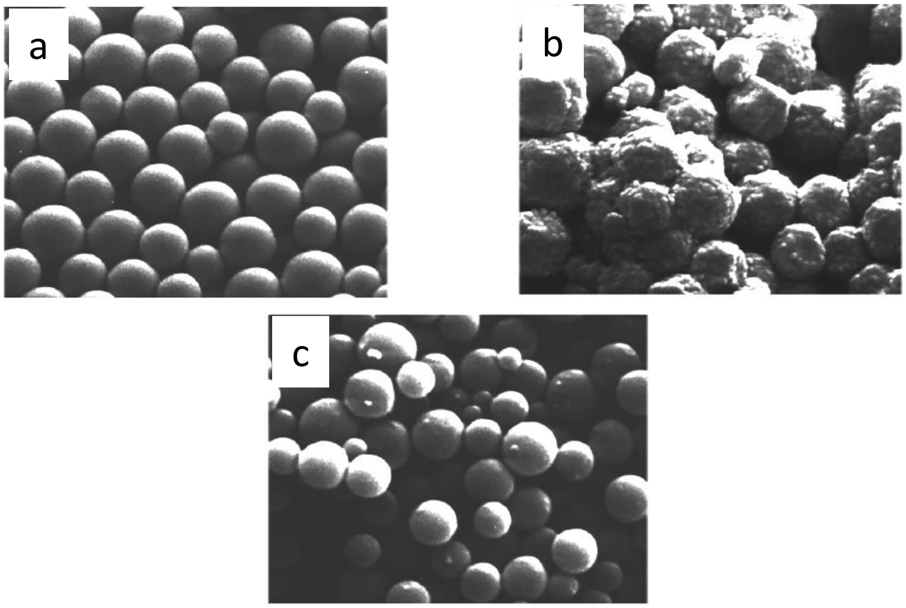


Figure 18. Reflection electron micrographs of (a) polystyrene, (b) poly(styrene-b-butadiene) and (c) poly(styrene-b-butadiene-b-styrene) particles respectively, as synthesized by ADP (Reproduced from reference [87])

Tausendfreund *et al.* [87] copolymerized monomers styrene and butadiene to investigate the effects of monomer in non-polar dispersion polymerization. They observed a smooth surface for poly(styrene) and poly(styrene-b-butadiene-b-styrene) particles, while (polystyrene-b-polybutadiene) particles possessed a rough surface with multiple notches (Figure 18). This was attributed to the favorable interaction of PB with alkane, thus swelling the PB layer to give an uneven surface. The PB chains also preferentially grew into the continuous phase, inducing particle aggregation. To prevent this, it was found that the molecular weight of PB should be kept below 8,000 g/mol.

- Effect of monomer addition

The advantages of sequential monomer addition include: (i) preparation of high solids content latex samples; (ii) prevention of nucleation of new particles; and (iii) independent control of particle size and molecular weight. Awan *et al.* introduced four monomer addition steps and observed a gradual and uniform increase in particle size and molecular weight of polystyrene chains. As all initiator was consumed within 1 – 2% of conversion during first addition, all subsequent added monomer was consumed by the existing growing anions [84]. However, this was only true if a highly efficient stabilizer was used (e.g. Stereon 730A) [83,84]. Less effective stabilizers (such as Stereon 840A [83]) showed a broadening in size distribution after the third addition.

- Effect of initiator concentration

Increasing initiator concentration (up to 0.24 wt% with respect to monomer) led to synthesis of larger particles with shorter polystyrene chains [81,84]. This was due to higher initiation and polymerization rates [80,83], thus producing lower molecular weight chains. Together with a decrease in medium solvency, this encouraged more chain aggregation, producing larger particles at lower count. Further initiator increase had little impact on the particle size. Both particle size and polymer molecular weight distributions remained narrow for all initiator concentrations. Murray and Schwab observed an increase in particle agglomeration with decreasing initiator concentration [80]. However, no explanation was provided for the observation made. As for in-situ formation of stabilizer with polymeric organolithium initiator [85], it was shown that a reduction in the molar ratio of simple to polymeric organolithium produced less stabilizers. This led to particle aggregation and hence, an increase in particle size.

- Effect of promoter addition

The alkyl lithium initiator and growing anions exist as associated complexes in non-polar media. This causes a reduction in reaction rate. Addition of a promoting agent was shown to facilitate the solvation of initiator and active ions, thus allowing an increase in polymerization rate [80,81,82,83]. Stampa added equimolar of hexamethyl phosphoramide (Figure 19) to initiator, allowing synthesis completion in an hour at 0°C [81].

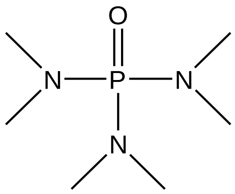


Figure 19. Chemical structure of the hexamethyl phosphoramide initiator

Unfortunately, the particle size and polydispersity were not discussed. However, Murray and Schwab found the addition of ether gave a broader size distribution [80]. This was attributed to the lower stabilizer adsorption to the precipitated nuclei, thus leading to flocculation in the system. Similar results were also observed after the addition of tetrahydrofuran as a promoting agent [82,83].

- Effect of solvent type

Most of the above syntheses of polystyrene particles were conducted in hexane. Other non-polar media in which polystyrene particles were successfully prepared included butane [87], pentane [87] and heptane [81]. It is worth pointing out that the effect of solvent type on particle synthesis is ultimately determined by the choice of polymeric stabilizer. Therefore, the consideration here is case-specific to PS-b-PB stabilizer in butane and pentane [87]. It was found that styrene monomer was required as a co-solvent for the solubilization of PS-b-PB stabilizers in butane and pentane. It was determined that a minimum styrene concentration of 21 and 7 wt%, for butane and pentane respectively, was needed. Uniform individual particles were successfully formed in pentane, whereas particle aggregation was observed in butane. The high amount of co-solvent styrene in butane had a more dramatic effect as polymerization progressed. The medium solvency decreased extensively until the PB block became insoluble and entangled. This led to inefficient steric stabilization and hence, particle aggregation.

- Effect of crosslinker concentration

Murray and Schwab found that by increasing the concentration of divinylbenzene (DVB), the polymerization rate was greatly reduced [80]. This allowed more time for particle aggregation, thereby increasing the extent of agglomeration. DVB concentration beyond 10% resulted in incomplete conversion.

- Effect of temperature

Temperature affects the viscosity of dispersing medium. At low polymerization temperatures (12 – 39°C), cluster formation of diblock copolymer was greatly enhanced. Coupled with slower diffusion due to the increase in viscosity, the stabilizers adsorbed more slowly onto the newly formed nuclei. This allowed more time for chain aggregation and agglomeration of precursor particles. In this case, larger but monodisperse particles were synthesized [82,84]. The molecular weight and its distribution were unaffected at these temperatures. However, if the temperature was too low, such as below 12°C [84], a broad molecular weight distribution with larger polymer chains was obtained. This was due to the lower polymerization rates as a result of the associate complexes of initiator in hexane.

4.4. FREE RADICAL POLYMERIZATION

An alternative for synthesizing polystyrene particles in non-polar solvents is via free radical polymerization (FRP). FRP is a versatile technique, applicable in emulsion, suspension and dispersion polymerization protocols. It is highly robust, thus it is relatively insensitive to impurities, solvent type and atmospheric conditions. However, its limitation lies in a broader particle size distribution due to the reduced control over polymerization kinetics. A typical FRP includes initially dissolving the stabilizer and monomer into the dispersing medium, which is generally purged with nitrogen for 30 mins. Next, a thermal initiator is added and the temperature is raised to 50 – 70°C. The initiator decomposes to form free radicals, initiating the polymerization process. This is carried out in a nitrogen atmosphere for 8 – 50 hrs. At the end, a milky-white stable dispersion is obtained and the particles can be centrifuged and redispersed into their original medium, or alternatively in solvents such as n-hexane, n-decane, n-dodecane, cyclohexane and Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane). [88]

4.4.1. STABILIZER SELECTION

Saam and Tsai were the first to explore the synthesis of polystyrene particles in hexane with homopolymeric mercaptoalkyl-modified poly(dimethylsiloxane) (PDMS-MCTA) in the 1970s [66]. They proposed a minimum MW 1,500 for stable dispersion, but the most effective stabilizer was found to be MW 15,000 – 20,000 with at least two mercaptoalkyl groups per chain. Information on the particle size and polydispersity were not reported.

Around the same time, Dawkins and Taylor reported the synthesis of polystyrene particles in n-heptane with a preformed block copolymer stabilizer, polystyrene-b-poly(dimethylsiloxane) (PS-b-PDMS) [88]. They found the polymerization kinetics to be extremely slow, where only 50% conversion was obtained despite leaving the synthesis for 50 hrs. This was due to the absence of "gel" effect, which typically accelerates the polymerization process. The "gel" effect is an auto-acceleration process that occurs when the localized viscosity in the polymerizing system increases causing a reduction in the termination reaction rate. The absence of "gel" effect was supported by the low MW 5,000 – 18,000 polystyrene chains formed in the latex, which was attributed to the immediate termination of chains by combination upon reaching the critical molecular weight. The high medium solvency also affected the diffusion of oligomeric radicals into existing particles, resulting in a broad size range of 600 nm to 12.5 μm.

Since then, no reports of synthesis of polystyrene particles via FRP have been made until recently, when Tauer and Ahmad synthesized relatively monodisperse 2.5 μm polystyrene particles in isopar [89]. The stabilizer was poly(butadiene)-b-poly(isoprene) (PB-b-PIP) and the particles were obtained after 24 hrs at 70°C. It was believed that the stabilizer had a stabilizing block of at least 20 carbon atoms in length, but unfortunately the exact details were not reported. Tauer and Ahmad also found that the same diblock copolymer was not an efficient stabilizer for dispersion polymerization of styrene in hexane.

4.4.2. POLYMER MOLECULAR WEIGHT AND PARTICLE SIZE ACCESSIBLE

With this synthesis route, the particle size was typically determined by light microscopy, TEM or DLS techniques. Polymer molecular weight was measured using Size Exclusion Chromatography (SEC), calibrated against polystyrene standards. Two main experimental parameters have been investigated; initiator type and stabilizer concentration. First, various thermal initiators were tested, including AIBN [88,89], benzoyl peroxide [66,88] and bis(4-tert-butylcyclohexyl)peroxydicarbonate (Perkadox 16) (Figure 20). [88]

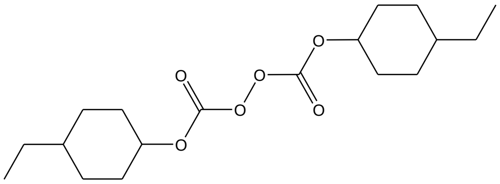


Figure 20. Chemical structure of bis(4-tert-butylcyclohexyl)peroxydicarbonate (Perkadox 16) initiator

Polystyrene particles were successfully synthesized using all initiators, with Perkadox 16 showing a higher monomer conversion at lower temperature.

When studying the effect of stabilizer concentration, it was observed that a higher stabilizer concentration led to smaller particles [88,89]. Tauer and Ahmad discovered that it was only possible to synthesized polystyrene particles larger than 1 µm, even with 1:1 (by weight) of PB-b-PIP stabilizers to monomer [89]. However, the polydispersity improved with increasing stabilizer concentration due to the reduction in particle aggregation at higher stabilizer concentration. Further increase in stabilizer concentration led to coagulum formation. This was attributed to enhance bridging as the stabilizers associated more strongly at high concentrations.

4.5. OTHER DEVELOPMENTS IN FREE RADICAL POLYMERIZATION

4.5.1. SEEDED POLYMERIZATION

Early attempts to develop one-step synthesis of polystyrene particles in *n*-heptane produced broad particle size distributions ranging from 600 nm to 12.5 µm. As a result, Dawkins and Taylor proposed seeded polymerization to improve polydispersity [88], as this method allows the solvency of the growing polystyrene chains to be controlled more effectively. Seeding required initial polymerization of around 10% styrene with the corresponding amount of stabilizer and initiator for 2 hrs. Subsequently, the remaining monomer, stabilizer and initiator were added incrementally over 9 to 12 hrs. Narrower particle size distributions from 400 to 1600 nm were obtained [88]. However, the constituent polystyrene chains were of even lower molecular weight, compared to the non-seeded FRP. This was due to the decrease in medium solvency, which encouraged earlier chain precipitation. Dawkins and Taylor also discovered that seeding was only effective when the PDMS block constituted at least 19% of the total molecular weight of the polymeric stabilizer [88]. With lower MW PDMS block, the stabilizers formed irreversibly associated micelles, which acted as polymerization seeds. Addition of more such stabilizers only formed new nuclei, resulting in an even broader size distribution.

4.5.2. CONTROLLED RADICAL POLYMERIZATION

In 1990s, Hölderle *et al.* proposed controlled radical polymerization (CRP) to improve polystyrene particle size distribution in non-polar medium [90]. This involved fast initiation by BPO, followed by propagating chain control using radical scavengers, such as 2,2,6,6-tetramethyl-1-piperidyloxy radical (TEMPO). The reversible coupling of stable nitroxy free radicals with polystyrl chains allowed spontaneous reversible termination, resulting in a living polymerization process. The polymerization rate was controlled by the balance between dormant and active chains within the dispersing medium.

50 nm to 10 μm polystyrene particles were produced in decane, stabilized with polystyrene-b-poly(ethene-alt-propene) (Kraton G1701). The polymerization took place under argon at 135°C for 70 hrs. It was observed that polymerization started slowly and accelerated after 30 hrs. At this point, particles began to form, indicated by the onset of turbidity in the dispersion. The acceleration was probably due to higher local styrene concentration within monomer-swollen particles, resulting in faster reaction rates. However, the difference in TEMPO concentrations within the particles and in the medium affected the equilibrium of reversible termination. This allowed simultaneous chain propagation in the particles and in decane. As a result, the size distribution deteriorated with increasing monomer conversion.

In addition, particle formation was also observed upon cooling. The partial solubility of low molecular weight polystyrene chains, coupled with high reaction temperature and styrene content at the end of synthesis, encouraged the remaining chains to precipitate as cooling began. This thus created new particles, which broadened the size distribution. The long reaction times also led to the possibility of unwanted side reactions, contributing to high polydispersity. Unfortunately, this method was unsuccessful in producing monodisperse particles despite a promise of living polymerization with reversible termination for steady chain growth.

5. OTHER MONOMERS

5.1. DIVINYLBENZENE

The examples of non-polar dispersion polymerization of divinylbenzene (DVB) in the academic literature relate to the production of sterically-stabilized DVB microgel particles in heptane or benzene by anionic dispersion polymerization (ADP) [91,92,93]. The aim of these studies was to demonstrate the possibility of preparing stable microgel particles in non-polar solvents. For this purpose, polymerization of monomer 1,4-divinylbenzene (1,4-DVB) was initiated by living stabilizer chains, comprising of either poly(t-butylstyrene) (PtBS) [91,92] or polystyrene (PS) [93]. In ADP, the reactivity of double bonds in DVB is significantly more active than the pendant double bonds. Therefore, poly(4-vinylstyrene) (PVS) chains are more likely to be formed during polymerization. As the PVS and PtBS blocks are highly incompatible in heptane, the PtBS-PVS chains aggregate as micelles with PVS as the cores. As polymerization continues, the PVS chains precipitate to form nuclei. At this point, DVB continues to diffuse into the core, resulting in rapid polymerization and crosslinking reactions. This produces highly cross-linked nuclei that are vitrified and less swellable by the remaining DVB monomer. At this stage, the reactions stop (generally within 17 to 30 mins of reaction initiation) [92]. Polymerization then occurs at the living ends on the nuclei surface for any remaining monomer and this forms interparticle bridges, causing particle aggregation.

Three factors governed the successful synthesis of DVB microgel; (i) length ratio of soluble (PtBS or PS) to insoluble PVS blocks, (ii) initial degree of swelling of PVS blocks by monomer and (iii) overall concentration of reaction medium, which determines the CMC value. These factors were controlled by monomer (DVB) concentration as well as the concentration of initiator (*sec*-butyllithium) used in the synthesis of living polymeric stabilizers.

- Effect of monomer concentration

With increasing concentration of DVB monomer, the molecular weight of PVS increased slowly initially. Upon reaching a critical concentration of DVB (ccr) (around 30 to 35% based on ratio of monomer to stabilizer) [91], the molecular weight increased dramatically. Subsequent increase in DVB concentration produced stable particle dispersion. The ccr represented the transition from microgel to macrogel, which occurs due to particle agglomeration driven by inter-particle cross-linking of the double bonds located on the particle surface. It was found that longer living polymeric chains supported more DVB molecules, thus increasing the DVB concentration required [91,93]. However, the length ratio of PtBS to PVS remained constant at the transition region for a given temperature and polymer concentration.

The hydrodynamic diameter of microgel and the intrinsic dispersion viscosity behaved similarly to the molecular weight of PVS, with an initial slow increment followed by an abrupt growth with increasing monomer concentration. The sub-50 nm microgels dominated initially, but as conversion progressed, the number of sub-50 nm particles decreased by up to 35% with a corresponding rise in 50 to 100 nm microgels [91,92]. The growth of these larger particles contributed to the sudden increase in molecular weight and intrinsic viscosity at the transition region.

- Effect of initiator concentration on living stabilizer

Initiator *sec*-butyl lithium (*sec*-BuLi) was used to grow the living stabilizer chains, which were subsequently employed as the polymeric initiator for microgel synthesis. Okay and Funke [94] illustrated a dependence of the final product (linear polymer, branched polymer, microgel or macrogel) on the concentration of *sec*-BuLi, which governed the balance between the crosslinking reaction rate and the length of living stabilizer chains. For a high initiator concentration, shorter stabilizer chains were obtained despite acceleration in the polymerization and crosslinking reactions. The shorter chains reduced the crosslinking density, thus affecting the microgel-macrogel transition. Therefore, as the initiator concentration decreased, longer stabilizer chains were formed, allowing more cross-linking sites and thus induced the microgel-macrogel transition. However, if the initiator concentration was too low initially, the reactions then became too slow and in this case, the microgel-macrogel transition was not reached. Hence, increasing *sec*-BuLi concentration at this point would accelerate the reactions and induce the transition region. Therefore, the competing effects between the length of living stabilizer chains and the rate of crosslinking reactions governed the final dispersion.

- Effect of overall concentration of reaction medium

The overall concentration of reaction medium, which takes into account the amount of monomer and living polymeric stabilizer, determined the rate of nuclei growth as well as the swelling capacity of the nuclei itself. If the overall concentration was too low, there was a high possibility of accidental deactivation of the living polymeric chains. However, if the overall concentration was too high, the reaction medium became too viscous, leading to macro-gelation. It was found that the microgel consisted of a maximum of 60 – 70% of the added DVB monomer [91,93]. Incorporation of DVB beyond this level induced a high likelihood of dispersion gelation. However, it was still possible to increase the DVB content within the nuclei further by either diluting the DVB with styrene to increase the swelling capacity of the nuclei or decreasing the monomer concentration to induce faster nuclei growth.

5.2. ACRYLONITRILE

Polyacrylonitrile (PAN) is generally used in the production of synthetic fibers. These fibers are made into outdoor products (e.g. tents, sails, *etc*.), hot gas filtration systems and knitted clothing. However, the traditional fabrication method for PAN is costly and damaging to the environment. Hence, there is an interest for a cost-effective greener alternative for PAN production. Dispersion polymerization of PAN offers an alternative to current methods of production. However, it is more difficult compared to other monomers due to the limited solubility of PAN in its own monomer. Consequently, only few studies have investigated the synthesis of PAN particles via dispersion polymerization.

Early synthesis work concentrated primarily on producing PAN particles for flocculation studies [16,65]. Everett and Stageman [65] and Vincent *et al*. [16] employed seeded free radical dispersion polymerization to synthesize 100 – 220 nm PAN particles in hexane. These particles were stabilized with a PDMS-b-PS-b-PDMS triblock copolymer, which was synthesized via sequential anionic polymerization. The copolymer possessed a total MW 20,000 – 80,000, with the solubilizing PDMS blocks constituting between 42.0 and 49.0 wt% of the polymer. The synthesized particles were subsequently cleaned by repeated centrifugation and redispersed in ethane, propane, butane, pentane, xenon and liquid PDMS [65] and exhibited weak flocculation in ethyl acetate [16].

Applying a similar technique, Ansarifar and Luckham investigated the synthesis of PAN particles in cyclohexane using a diblock copolymer of poly(2-vinylpyridine)-block-poly(tert-butylstyrene) (P2VP-b-PtBS) (MW 5,000 – 30,000, with stabilizing PtBS block between 26.0 and 78.0 wt%) [95]. 40 to 60 nm seed particles were grown to 140 nm by sequential feed addition (up to a maximum of 16 – 20% monomer). The particles were then centrifuged and redispersed in cyclohexane or toluene. Particle flocculation occurred when the copolymer possessed more than 74 wt% P2VP block. This was due to the insolubility of copolymer in the dispersing medium and the incompatibility between PAN and P2VP. This prevented the migration of PAN chains into the micelles, leading to severe flocculation.

The subsequent example of synthesis of PAN particles was only reported recently by Penfold *et al.*, who employed new stabilizers of diblock copolymer poly(octadecyl acrylate)-block-poly(methyl methacrylate) (PODA-b-PMMA) synthesized by ATRP [96]. Two types of stabilizer were made; gradient copolymer synthesized from copper (I) salt and block copolymer from PMMA macroinitiator. Using these stabilizers, the authors successfully carried out dispersion polymerization of acrylonitrile and obtained PAN particles in a hexane/dodecane mixture. It was found that using the block PODA-b-PMMA stabilizer led to smaller PAN particles between 80 to 120 nm, while using the gradient copolymer produced 350 to 480 nm particles (Figure 21). A minimum of 60 mol% solubilising PODA block was required to produce stable particle dispersions.

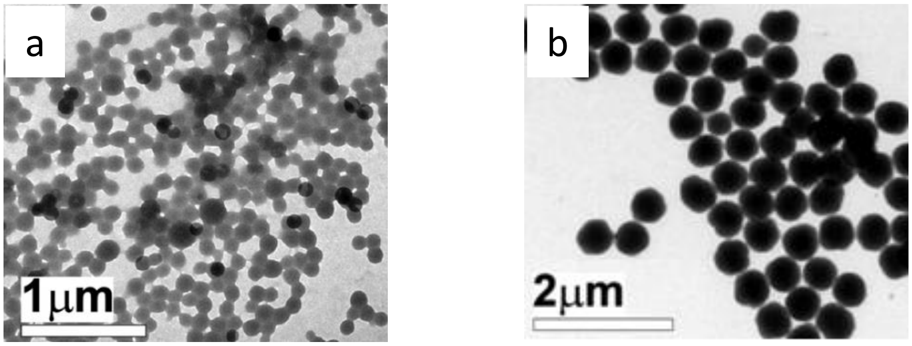


Figure 21. TEM images of PAN particles stabilized by (a) block and (b) gradient PODA/PMMA stabilizers respectively (Reproduced from reference [96])

Generally, it was observed that with increasing stabilizer concentration, smaller PAN particles were obtained [16,95,96]. With the PDMS-b-PS-b-PDMS stabilizer, increasing stabilizer coverage encouraged more exposed tails, leading to greater particle stability. However, for sufficiently large stabilizers, the effect of molecular weight became insignificant as the solubilising blocks appeared to create enough stabilizing effect [16,95]. Meanwhile, varying the initiator concentration did not seem to affect the particle size [95].

5.3. VINYLPYRROLIDONE

Dispersion polymerization of hydrophilic monomers in non-polar media is relatively limited. An example of such monomer is 1-vinyl-2-pyrrolidone (VP), which in its polymerized form, poly(1-vinyl-2-pyrrolidone) (PVP), is a highly hydrophilic biocompatible polymer. It is commonly used in a range of industries, such as drug and detergent formulations, adhesives, photographic coatings, pigments and textile dyes, contact lenses and others. Dispersion polymerization of VP was first successfully attempted by Horák *et al.* to produce submicron cross-linked particles (250 nm to 1.3 μm) in cyclohexane [97]. Free radical polymerization was performed with azoinitiators producing narrower size distribution than dibenzoyl peroxide. Various copolymer stabilizers were investigated, including polystyrene-b-hydrogenated polybutadiene-*b*-polystyrene (Kraton G1650), polystyrene-b-hydrogenated polyisoprene (Shellvis 40 or 50) as well as diblock, triblock and pentablock copolymers of styrene-butadiene. The copolymers had MW 74,000 – 180,000 with 25 – 44 wt% anchoring PS block. All stabilizers were effective in producing stable PVP particles, with larger particles achieved by lowering stabilizer concentration or using stabilizers with smaller stabilizing block. Kraton G1650 (up to 3 wt%) and Shellvis stabilizers produced lower PDIs than the styrene-butadiene copolymers. The latter styrene-butadiene copolymers showed more adverse effects on PDI with increasing number of blocks in the copolymer. PVP particles were also synthesized in toluene, producing broader distribution with larger sizes (~ 4.5 μm) due to the improved solubility of PVP in toluene [97].

5.4. CAPROLACTONE / LACTIDE

Caprolactone and Lactide monomers have rarely been used in dispersion polymerization. However, a few examples can be found in the literature where the aim of the synthesis of biodegradable latex particles from such monomers lies in their potential use for medical applications, particularly as drug carriers. Ring opening dispersion polymerization has been the method of choice for the preparation of such particles in non-polar solvents with only a few research groups leading these studies.[98,99] In particular, Slomkowski *et al.* have investigated a series of stabilizers for this polymerization type in a mixture of 1,4-dioxane and heptane. Most of their work and that of others has already been reviewed in an article that interested readers can access for further details.[98] More recently, such biodegradable latexes have also been synthesized in non-polar solvents by anionic dispersion polymerization route. [100,101]

5.5. URETHANE

Polycondensation of monomers in non-polar solvents has mainly been used by the coatings industry for its ease of use in preparing latex particles of diameter above 1 μm. Only a few examples can be found in the academic literature, which are limited to a small number of monomers. In the case of non-polar continuous phases, mostly urethane has been used for preparation of latex particles via polycondensation. Such particles can find applications as adhesives and coatings for textiles, wood and metals. Polyurethane particle show specific advantages with respect to adhesion and resistance to corrosion and chemicals when used in metal coating formulations. They are highly used in the automotive, aircraft and industrial maintenance industries.[102] In this case, dispersion polymerization for the preparation of polyurethane latex was investigated in order to improve the control over particle size and polydispersity lacking in the standard methods of production such as suspension polymerization and cryogenic grinding of thermoplastic polyurethanes.[103] In all the examples, the precipitating polymer chains are formed by reacting the two 'monomers', ethylene glycol (EG) with tolylene-2,4-diisocyanate (TDI), in the presence of the catalyst dibutyl tin dilaurate. EG is insoluble in the non-polar solvents used in these cases and is thus present in the form of droplets in the reaction medium. Consequently, there is a necessity in this process to transport EG to the site of reaction (particle nuclei/micelles), as in the case of emulsion polymerization. As described later, a simple mechanism has been proposed for this process. However, further studies are required to fully exemplify it.

Sivaram *et al.* reported the synthesis of polyurethane microspheres via dispersion polymerization (or polycondensation) in paraffin oil using different stabilizers; a polycondensable macromonomer based on dihydroxy-terminated poly(dodecylmethacrylate) and two diblock copolymers, poly(butadiene-b-ethylene oxide)[104] and poly(1,4-isoprene-b-ethylene oxide),[103] whereby the insoluble PEO block acted as the anchor into the particle core. These authors generally synthesized particles between 1 and 10 μm, with some exceptions in the submicron region when increasing the stabilizer concentration to above 10 wt% of the monomer.

In another series of articles, Cramail *et al.* systematically investigated the dispersion polycondensation of urethane in cyclohexane [105] and supercritical CO_2 [106] in the presence of a range of stabilizers. They showed that the rate of addition of monomer played a crucial role in the final particle size and polydispersity.[105] In a later example, they compared the use of two PDMS stabilizers, either monohydroxy-terminated (PDMS-OH) or isocyanate-terminated (PDMS-NCO), for the same dispersion polycondensation reaction.[107] They investigated reaction yield and final particle size as a function of stabilizer type, molar mass and concentration. The authors proposed that the affinity of the stabilizer for the growing polyurethane chains greatly influenced the particle size on the basis of difference in particle size when using PDMS-OH instead of PDMS-NCO. They also proposed a mechanism of particle formation that involved both the formation of particle nuclei comprising of oligourethane chains and the copolymerization of PDMS-PUR (formed in-situ by reaction between the stabilizer and TDI), as well as the subsequent swelling by EG leading to polycondensation with TDI within the nuclei.

5.6. VINYL ACETATE

Dispersion polymerization of vinyl acetate using poly(ethylhexyl methacrylate (PEHMA) as steric stabilizer in non-polar solvent has been investigated by Winnik *et al.*[108,109] Rather than studying the dispersion polymerization mechanism in depth, their work focused on using fluorescence quenching (by oxygen) to determine the morphology of the poly(vinyl acetate) (PVAc) particles (similar work had been done with PIB-stabilized PMMA particles and is presented Section 3.3). For this purpose, they prepared fluorescently-labeled PVAc colloidal particles made by dispersion polymerization in iso-octane. As for other monomers, by running different sets of reactions they noticed that the particle size were decreasing by increasing the stabilizer content as well as that the formation of wider particles resulted in a broader particle size distribution. In their work different methacrylate-based dyes (phenanthrene (Phe), anthracene (Ant), naphthalene (Nap) and pyrene (Py)) were incorporated to either the core of the particles (CLP) or to the steric stabilizer (SLP) of the particles (Figure 22).

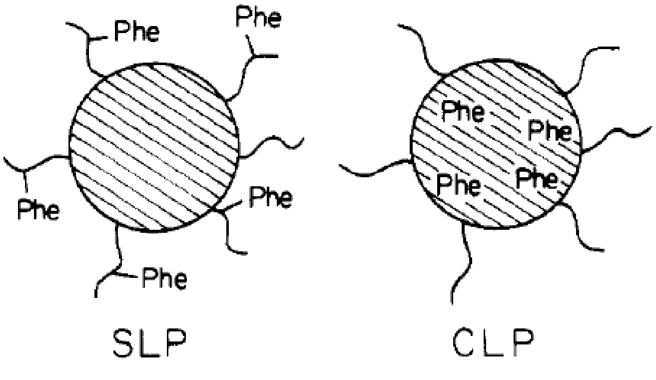


Figure 22. Morphology of the PVAc particles designed by Winnik *et al.*: core labeled particles (CLP) or stabilizer labeled particles (SLP) (Reproduced from reference [109])

For the fluorescence studies the samples were systematically transferred from iso-octane to cyclohexane.

Winnik *et al.* showed that the incorporation of dye in the core of the particles was difficult due to unfavorable reactivity ratios. However, fine conditions tuning (lower methacrylate dye concentration, increase in initiator content…) allowed the formation of particles with much higher PVAc content. They also noticed that the addition of fluorescent monomer was promoting particles with broader size distribution.[108] On the other hand, due to very similar reactivity ratios, the design of labeled stabilizers was much easier and led to random polymer chain structure.

To facilitate result interpretations, references (such as dyed stabilizer in cyclohexane solution or dried powders of SLP and CLP) had been considered. Phenanthrene was chosen as the best oxygen quencher because it does not form excimers which are known to bring a component in the fluorescence decay curves. Fluorescence quenching by oxygen is a powerful tool to elucidate particle morphology within the labeled regions. Exposing fluorescently dyed samples to oxygen saturated solution leads to increase in the rate of fluorescence decay (when oxygen can reach the fluorescent dyes). This fluorescent experiment helps in estimating the "availability" of the dye: total when the dye is on the stabilizer chains and limited when the dye is located in the core.

After reaction, different dispersions of SLP were exposed (or not) to oxygen and compared. The fluorescence decay curves are presented Figure 23.

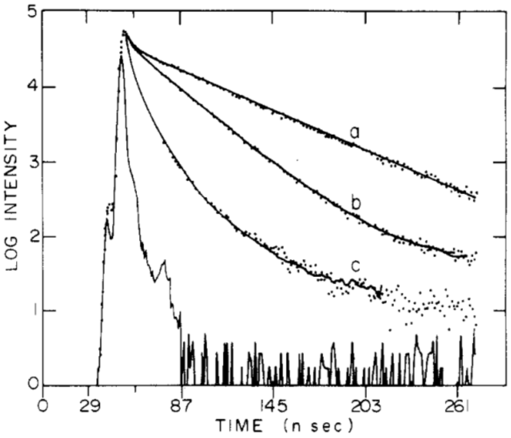


Figure 23. Fluorescence decay curves (λ_{ex} = 295 nm and λ_{em} = 345-395 nm) of SLP dispersions in cyclohexane in presence of different oxygen concentrations: 0M (a), 2.08 × 10^{-3} (b), and 10.8 × 10^{-3} (c) (Reproduced from reference [109])

Winnik *et al.* noticed a strong fluorescence quenching and that the PEHMA stabilizer phase was swollen even for stabilizer chains trapped within the particle core.

The same study was done using CLP dispersions. As the dye was supposed to be totally trapped within the PVAc core of the particles, no quenching was expected. However, clear and intense oxygen quenching happened revealing that oxygen could partially get to dye-rich regions *via* solvent-swollen domains created by the presence of the stabilizer chains inside the particles. 50% of the Phe groups could be directly accessible by the oxygen and the remaining 50% were made accessible by addition of methanol (particle swelling). Finally, based on their fluorescence study Winnik *et al.* defined a new model (called "microdomain") for such particles made *via* dispersion polymerization in non-polar solvent (Figure 24).

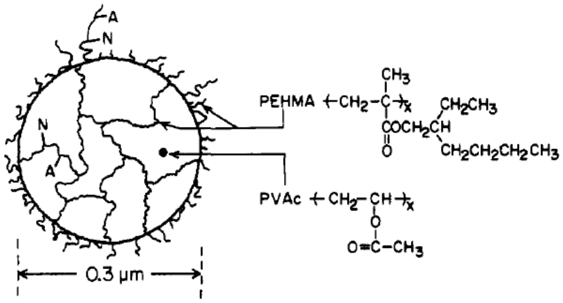


Figure 24. "Microdomain" model proposed by Winnik *et al.* (Reproduced from reference [109])

6. DISPERSION POLYMERIZATION IN SUPERCRITICAL FLUIDS

Supercritical fluids (scFs) are unusual solvents. They possess both properties of liquids (solvency) and gases (low density). Typical examples are supercritical carbon dioxide ($scCO_2$) and supercritical water (scH_2O). $ScCO_2$ is a non-polar solvent which has been used as a dispersion polymerization medium in the last few decades. We briefly describe in this chapter dispersion polymerization in $scCO_2$ in order to give a general introduction for interested readers. It is not the aim of this paper to review this topic in detail as recent progress for these reactions have been extensively reviewed elsewhere. [106,107,110,111,112,113,114,115]

The emergence of $scCO_2$ in dispersion polymerization is due to the increasing environmental awareness associated with the use of volatile organic solvents. $ScCO_2$ attracts significant attention as a green alternative solvent due to its non-toxic and non-flammable properties, as well as its tuneable solvating properties (controlled by varying pressure and/or temperature). It is also worth mentioning that contrary to "standard" FRP in non-polar solvents (such as hexane/dodecane), $scCO_2$ is only a reaction medium and the final particles are recovered in the form of free-flowing powders. Finally, due to the high mass transfer properties of $scCO_2$ (plasticization), controlled FRP can be easily run in $scCO_2$. [116,117]

Over the last two decades, because of its unique properties, two main challenges remained of interest for the dispersion polymerization in $scCO_2$. The first one was to develop new stabilizers to replace the commonly used but extremely expensive, fluorinated and silicone-based stabilizers. Because the stabilizer is a key component to achieve efficient dispersion polymerization, extensive work on stabilizer design has been done since dispersion polymerization merge in the late 90s. The second challenge was (as for every new reaction mixture), to investigate the range of monomer that can be polymerized in $scCO_2$.

Fluorinated and silicone-based polymers are the most soluble polymers in $scCO_2$. As a consequence, these polymers are the best candidates to stabilize dispersion polymerization in such medium. For this reason, fluorinated polymers [118,119,120,121] and silicone-based polymers [122,123,124] are the most studied stabilizers for FRP in $scCO_2$. For example, the use of PDMS-based stabilizer in FRP is much more extensive in $scCO_2$ than in typical non-polar solvents like hexane or dodecane. Shaffer *et al*. [125] were the first group to report dispersion polymerisation in $scCO_2$ using methacryloxypropyl-terminated PDMS macromonomer (PDMS-MA). Since then, PDMS-based stabilizers with various end-group functionality (such as aminopropyl-terminated PDMS [126], mercaptopropyl-terminated PDMS [127], PDMS-based azoinitiator [128], etc) or/and morphology (block copolymer [129] grafted copolymer [130]) have been successfully investigated.

Additionally, new hydrocarbon-based stabilizers have been developed. For example, Beckman *et al*. and Cooper *et al.* have successfully demonstrated that fully hydrocarbon stabilizers can be used as efficient stabilizers for dispersion polymerization in $scCO_2$.[131,132,133] A few other research groups have also recently shown interest in understanding the solubility of such hydrocarbon stabilizers in $scCO_2$.[134,135]

Regarding the range of monomer that can be polymerized in $scCO_2$, to date a wide range of monomer have successfully been used for this purpose; namely MMA, styrene, carbonate, (N-vinyl pyrrolidone), lactide, ε-caprolactone, etc.[135,136,137] Like in conventional non-polar solvents, different types of polymerization techniques have been used in $scCO_2$ such as free radical dispersion polymerization [138], ring-opening dispersion polymerization [136] and dispersion polycondensation [137].

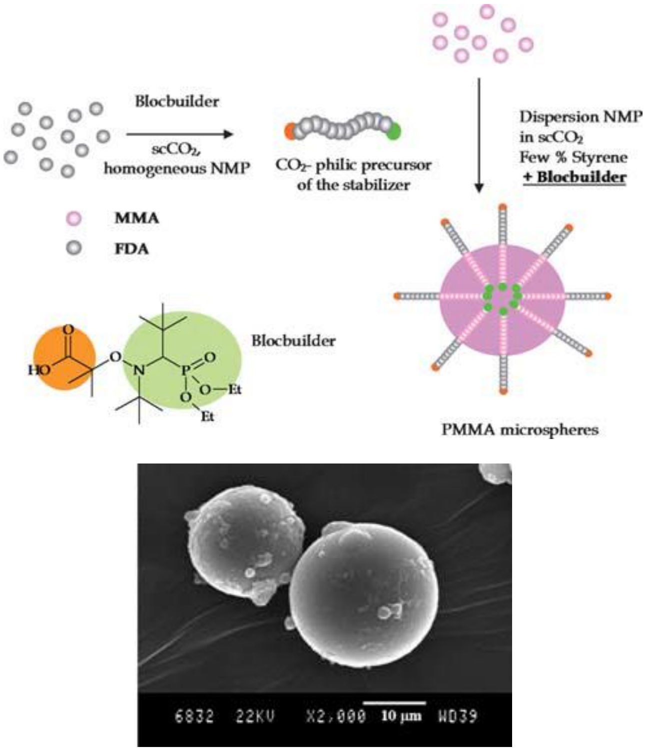


Figure 25. Schematic diagram of the polymerization mechanism (left) and SEM picture of PMMA particles (Reproduced from reference [139])

In addition, due its efficient plasticizing properties, $scCO_2$ has also been used as a reaction medium to perform controlled radical dispersion polymerization (ATRP, NMP, RAFT). For instance, Detrembleur *et al*. successfully performed ATRP dispersion polymerization of MMA and styrene in $scCO_2$ using aminated fluoropolymers acting as both steric stabilizers and macro-ligand. They also investigated MMA dispersion polymerization controlled via atom transfer radical polymerization with activators generated by electron transfer (AGET ATRP). [138] Detrembleur *et al*. also investigated MMA dispersion polymerization in $scCO_2$ controlled via NMP. [139] In their system, they combine an SG1-based alkoxiamine (to initiate and control the polymerization) with SG1-terminated perfluorinated poly(acrylate) chains which acts as the steric stabilizer (Figure 25).

RAFT radical controlled polymerization of MMA has been intensively studied by Howdle *et al.*[116] In their system, PDMS-MA steric stabilizer is used and different free RAFT agents are introduced to control the polymerization: R-cyanobenzyl dithionaphtalate, R-cyanobenzyl dithiobenzoate, 2-cyanoprop-2-yl dithiobenzoate or 4-cyano-1-hydroxypent-4-yl dithiobenzoate.

Finally, new polymer morphologies (such as block copolymer) designed from dispersion in $scCO_2$ have also been developed. Block copolymer morphologies are obtained by successive monomer addition. By association of two incompatible monomers, Jennings *et al*. showed the formation of PMMA particles with phase segregation (presence of domains of each polymer within the particle core) which can be tune by varying the different monomer contents (Figure 26).[140]

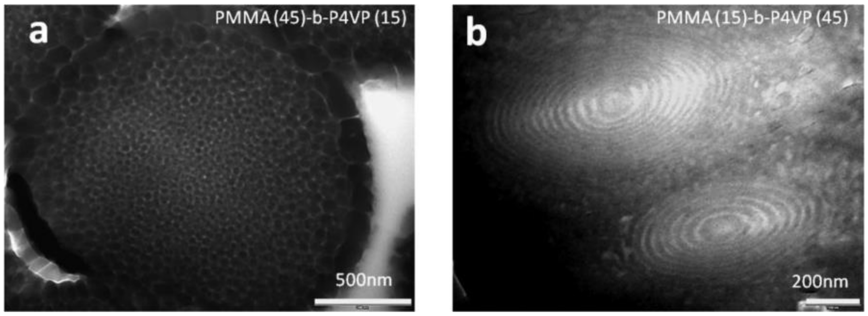


Figure 26. TEM images of PMMA-*b*-P4VP block copolymer particles designed via dispersion polymerization in $scCO_2$. Influence of the monomer ratio on the phase segregation (Reproduced from reference [140])

7. CONCLUSIONS

This article presents a detailed review of the academic literature addressing non-polar dispersion polymerization. The discussion is based on the preparation of latex particles from different monomers, MMA and Styrene being the most commonly used. In our discussion, we compare the efficiency of particle synthesis for these different monomers with respect to particle diameter, size distribution and stability. This involves the description of optimized experimental conditions and choice of stabilizers, including recent developments in the synthesis of bespoke stabilizers using modern living-radical polymerization methods such as ATRP or RAFT. In addition, throughout the chapters we explore the differences between different polymerization methods for the dispersion polymerization process itself (e.g. radical or ionic polymerization), particularly when reviewing less commonly used monomers.

Dispersion polymerization in non-polar solvents has been used for decades both in the coatings industry and as a way to provide model colloid particles for academic studies. However, some applications (e.g. electrophoretic displays, ink-jet printing, lubricants) have recently explored the possibility of using bespoke particle systems to improve existing products or develop new ones. Consequently, the use of non-polar dispersion polymerization for the purpose of providing ways to control and vary the properties/functionalities of latex particles in this context will play an important role in both academic understanding and product development in these areas. Particularly, the emergence of the use of particle technologies in electrophoretic displays is driving a specific interest for non-polar dispersion polymerization techniques in this area.

Examples of challenges in this specific area are: - encapsulating pigments within the latex particles, - more efficient packing of particles at electrodes, which are driven by the particle polydispersity and surface properties and consequently may require new stabilizer designs, providing sufficient charge density to the particles (within the core or at the surface) to allow for rapid switching of particles upon current reversal between electrodes. Some academic publications (and industrial efforts), as mentioned in Section 1.2.4, are starting to use non-polar dispersion polymerization for addressing some of these issues.

The present review article is designed to provide specific information on the type of particle systems (including size, size distribution, surface properties) that can be achieved through non-polar dispersion polymerization; and it is expected that readers will use this article as a basis for developing bespoke particle systems such as those that will be used in future electrophoretic displays generations and other emerging applications.

ABBREVIATIONS

ADP	Anionic Dispersion Polymerization
AIBN	AzobisIsoButyroNitrile
ATRP	Atom Transfer Radical Polymerization
C	Stabilizer concentration
CCl_4	Carbon tetrachloride
CRP	Control Radical Polymerization
CTA	Chain Transfer Agent
D	Particle diameter

DLS	Dynamic Light Scattering
DTB	DiThioBenzoate
DVB	DiVinylBenzene
1,4-DVB	1,4-divinylbenzene
EA	Ethyl Acrylate
EG	Ethylene Glycol
2-EMA	2-Ethoxy ethyl MethAcrylate
FTIR	Fourier Transform Infrared Spectrometry
FRP	Free Radical Polymerization
GPC	Gel Permeation Chromatography
GMA	Glycidyl MethAcrylate
HEMA	HydroxyEthyl MethAcrylate
ICI	Imperial Chemical Industries
LCP	Living Dispersion polymerization
$\overline{\mathrm{M}_\mathrm{n}}$	Number average molecular weight
MA	Methacrylic Acid
MMA	Methyl MethAcrylate
MW	Molecular Weight
NMP	Nitroxide-Mediated Polymerization
ODA	OctaDecyl Acrylate
PAN	PolyAcryloNitrile
PB-*b*-PIP	Poly(Butadiene)-block-Poly(IsoPrene)
PDI	Polydispersity index
PDMS	PolyDiMethylSiloxane
PDMS-MCTA	MerCapToAlkyl-modified Poly(DiMethylSiloxane)
PDMS-*b*-PS	PolyDiMethylSiloxane-block-PolyStyrene
PDMS-*b*-PS-*b*-PDMS	PolyDiMethylSiloxane-block-PolyStyrene-block-PolyDiMethylSiloxane
PDMS-MA	Mono-functionalised MethAcryloxypropyl-terminated PolyDiMethylSiloxane
MA-PDMS-MA	Di-functionalised MethAcryloxypropyl-terminated PolyDiMethylSiloxane
PDMS-NCO	Isocyanate-terminated PolyDiMethylSiloxane
PDMS-OH	Monohydroxy-terminated PolyDiMethylSiloxane
P2EHA	Poly(2-EthylHexyl Acrylate)
PB	PolyButadiene
PDMS-Si	Trimethylsilyl-terminated PolyDiMethylSiloxane
PDMS-V	Vinyldimethylsilyl-terminated PolyDiMethylSiloxane
PEHMA	Poly(EthylHexyl MethAcrylate)

PHSA	Poly (12-HydroStearic Acid)
PHSA-*g*-PMMA	Poly (12-HydroStearic Acid)-graft-Poly (Methyl MethAcrylate)
PHSA-*g*-PMMA-PGMA	Poly (12-HydroStearic Acid)-graft-Poly (Methyl MethAcrylate)-co-Poly (Glycidyl MethAcrylate)
PMA	Poly(Methyl Acrylate)
PMMA	Poly (Methyl MethAcrylate)
PMMA-*g*-PE	Poly(Methyl Methacryalte)-grafted-Poly(Ethylene)
PMMA-*co*-PODA	Poly(Methyl MethAcrylate)-co-poly(octadecyl acrylate)
PODA-*b*-PMMA	Poly(OctaDecyl Acrylate)-block-Poly(Methyl MethAcrylate)
PS	PolyStyrene
PS-*b*-PB	PolyStyrene-b-PolyButadiene
PS-*b*-PBS	PolyStyrene-b-Poly(t-ButylStyrene
PS-*b*-(PE-*co*-PP)	PolyStyrene-block-poly(ethylene-co-propylene)
PS-*b*-PIB	PolyStyrene-b-PolyIsoButylene
PS-*b*-PIP	PolyStyrene-b-Poly(Isoprene)
PS-*b*-PTMSS	PolyStyrene-b-poly(4-TriMethylSilylStyrene)
PtBS	Poly(t-ButylStyrene)
PVAc	Poly(Vinyl Acetate)
PVEE	Poly(Vinyl Ethyl Ether)
P2VP-*b*-PtBS	Poly(2-VinylPyridine)-block-Poly(tert-ButylStyrene)
PVP	Poly(1-Vinyl-2-Pyrrolidone)
PVS	Poly(4-VinylStyrene)
RAFT	Reversible Addition Fragmentation Transfer
SBR	Styrene-Butadiene Rubber
ScCO$_2$	SuperCritical Carbon Dioxide
scFs	SuperCritical Fluids
scH$_2$O	Supercritical water
SEC	Size Exclusion Chromatography
sec-BuLi	sec-Butyl Lithium
SEM	Scanning electron Microscopy
SLS	Static Light Scattering
TDI	Tolylene-2,4-DiIsocyanate
TEM	Transmission Electron Microscopy
TEMPO	2,2,6,6-tetramethyl-1-piperidyloxy radical
T$_g$	Glass transition temperature
TGA	Thermal Gravimetric Analysis
TTC	TriThioCarbonate

VAc	Vinyl Acetate
VP	1-Vinyl-2-Pyrrolidone

REFERENCES

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[1] T.H. Lowry K. Schueller Richardson, Mechanism and Theory in Organic Chemistry, third edition, Harper International Edition, 1987.

[2] P.A. Lovell, M.S. El-Aasser, Emulsion Polymerization and Emulsion Polymers, John Wiley & Sons, 1997.

[3] K.E.J. Barrett, Dispersion Polymerization in Organic Media, John Wiley & Sons, 1975.

4] D.W.J. Osmond , Dispersion Polymerisation, Imperial Chemical Industries, 1962, GB Patent: 893429.

[5] D.W.J. Osmond , Polymer Dispersion, Imperial Chemical Industries, 1963, GB Patent: 941305.

[6] D.W.J. Osmond , Copolymer Dispersions, Imperial Chemical Industries, 1964, GB Patent: 958023.

[7] R.J. Carter, R.H. Cousens, D.W.J. Osmond , Modified Organosols, Imperial Chemical Industries, 1964, GB Patent: 971885.

[8] Polymer Dispersions in Organic Liquid Media and Methods of Preparation, Rohm & Haas Company, 1963, GB Patent: 934038.

[9] Preparation of Particulate Polymers, Rohm & Haas Company, 1964, GB Patent: 956453.

[10] D.J. Walbridge, J.A. Waters, Rheology of sterically stabilized dispersions of poly(methylmethacrylate) in aliphatic hydrocarbons, Disc. Faraday Soc. 42 (1966) 294-300.

[11] D.H. Napper, Flocculation studies of non-aqueous sterically stabilized dispersions of polymers, Trans. Faraday Soc. 64 (1968) 1701-1711.

[12] R.J.R. Cairns, R.H. Ottewill, D.W. Osmond, I. Wagstaff, Studies on the Preparation and Properties of Latices in Nonpolar Media, J. Colloid Interface Sci. 54 (1976) 45-51.

[13] M.D. Croucher, T.H. Milkie, Temperature dependence of the shear viscosity of sterically stabilised polymer colloids, Faraday Discuss. Chem. Soc. 76 (1983) 261-276.

[14] T.A. Strivens, The viscoelastic properties of concentrated suspensions, Colloid Polym. Sci. 261 (1983) 74-81.

[15] D.W.J. Osmond, D.J. Walbridge, Steric stabilization of polymer suspensions in hydrocarbon media by adsorbed layers of graft copolymers, J. Polym. Sci. Part C: Polym. Lett. 30 (1970) 381-391.

[16] B. Vincent, J. Clarke, K.G. Barnett, The flocculation of non-aqueous sterically-stabilised latex dispersions in the presence of free polymer, Colloids Surf. 17 (1986) 51-65.

[17] B. Vincent, The effect of adsorbed polymers on dispersion stability, Adv. Colloid Interface Sci., 4 (1974) 193-297.

[18] D.H. Napper, Polymeric stabilisation of colloid dispersions, London: Academic Press, 1983.

[19] T. Tadros, Polymeric surfactants in disperse systems, Adv. Colloid Interface Sci., 147-148 (2009) 281-299.

[20] T. Cosgrove, Colloid Science, Principle, Methods and Applications, Wiley, 2010.

[21] E.W. Fischer, Elektronenmikroskopische untersuchungen zur stabilität von suspensionen in makromolekularen lösungen, Kolloid Z., 160 (1958) 120-141.

[22] M.J. Rosen, Surfactants and interfacial phenomena, John Wiley & Sons Inc., New York, 1978.

[23] P. Jenkins, M. Snowden, Depletion flocculation in colloidal dispersions, Adv. Colloid Interface Sci., 68 (1996) 57-96.

[24] S.J. Barsted, L.J. Nowakowska, I. Wagstaff, D.J. Walbridge, Measurement of steric stabilizer barrier thickness in dispersions of poly(methyl methacrylate) in aliphatic hydrocarbon, Trans. Faraday Soc. 67 (1971) 3598-3603.

[25] I. Marković, R.H. Ottewill, S.M. Underwood, T.F. Tadros, Interactions in concentrated polymer lattices, Langmuir 2 (1986) 625-630.

[26] D.H. Everett, J.F. Stageman, Stability studies on polymer colloids in simple liquids, Colloid Polym. Sci. 255 (1977) 293-294.

[27] J.V. Dawkins, G. Taylor, Flocculation studies of non-aqueous poly(methyl methacrylate) dispersions stabilized by AB block copolymers of polystyrene and poly(dimethyl siloxane), Colloid Polym. Sci. 258 (1980) 79-84.

[28] R. Pelton, A. Osterroth, M.A. Brook, Silicone stabilized poly(methyl methacrylate) nonaqueous latex 2.Flocculation by degradation of the steric layer, J. Colloid Interface Sci. 147 (1991) 523-530.

[29] P.A. Reynolds, C.A. Reid, Effect of nonadsorbing polymers on the rheology of a concentrated nonaqueous dispersion, Langmuir 7 (1991) 89-94.

[30] P.N. Pusey, W. van Megen, Phase behavior of concentrated suspensions of nearly hard colloidal spheres, Nature 320 (1986) 340-342.

[31] W. van Megen, S.M. Underwood, R.H. Ottewill, N.St.J. Williams, P.N. Pusey, Particle diffusion in concentrated dispersions, Faraday Discuss. Chem. Soc. 83 (1987) 47-57.

[32] R.H. Ottewill, N.St.J. Williams, Study of particle motion in concentrated dispersions by tracer diffusion, Nature 325 (1987) 232-234.

[33] P. d'Haene, J. Mewis, G.G. Fuller, Scattering dichroism measurements of flow-induced structure of a shear thickening suspension, J. Colloid Interface Sci. 156 (1993) 350-358.

[34] J. Mewis, W.J. Frith, T.A. Strivens, W.B. Russel, The rheology of suspsensions containing polymerically stabilized particles, AIChE J. 35 (1989) 415-422.

[35] W.J. Frith, T.A. Strivens, J. Mewis, Dynamic mechanical properties of polymerically stabilized dispersions, J. Colloid Interface Sci. 139 (1990) 55-62.

[36] W.J. Frith, P. d'Haene, R. Buscall, J. Mewis, Shear thickening in model suspensions of sterically stabilized particles, J. Rheol. 40 (1996) 531-548.

[37] P. d'Haene, J. Mewis, Rheological characterization of bimodal colloidal dispersions, Rheol. Acta 33 (1994) 165-174.

[38] L. Antl, R.D. Goodwin, R.H. Ottewill, S.M. Owens, S. Papworth, J.A. Waters, The preparation of poly(methyl methacrylate) lattices in non-aqueous media, Colloids Surf. 17 (1986) 67-78.

[39] A.I. Campbell, P. Bartlett, Fluorescent hard-sphere polymer colloids for confocal microscopy, J. Colloid Interface Sci. 256 (2002) 325-330.

[40] H. Hu, R.G. Larson, Preparation of fluorescent particles with long excitation and emission wavelength dispersible in organic solvents, Langmuir 20 (2004) 7436-7443.

[41] G. Bosma, C. Pathmamanoharan, E.H.A. de Hoog, W.K. Kegel, A. van Blaaderen, H.N.W. Lekkerkerker, Preparation of monodisperse, fluorescent PMMA-latex colloids by dispersion polymerization, J. Colloid Interface Sci. 245 (2002) 292-300.

[42] R.S. Jardine, P. Bartlett, Synthesis of non-aqueous fluorescent hard-sphere polymer colloid, Colloids Surf. A 211 (2002) 127-132.

[43] R.P.A. Dullens, M. Claesson, D. Derks, A. van Blaaderen, W.K. Kegel, Monodisperse core-shell poly(methyl methacrylate) latex colloids, Langmuir 19 (2003) 5963-5966.

[44] R.P.A. Dullens, E.M. Claesson, W.K. Kegel, Preparation and properties of cross-linked fluorescent poly(methyl methacrylate) latex colloids, Langmuir 20 (2004) 658-664.

[45] M.T. Elesser, A.D. Hollingsworth, K.V. Edmond, D.J. Pine, Large core-shell poly(methyl methacrylate) colloidal clusters: synthesis, characterization and tracking, Langmuir 27 (2011) 917-927.

[46] M.E. Leunissen, C.G. Christova, A.-P. Hynninen, C.P. Royall, A.I. Campbell, A. Imhof, M. Dijkstra, R. van Roij, A. van Blaaderen, Ionic colloidal crystals of oppositely charged particles, Nature 437 (2005) 235-240.

[47] T. Vissers, A. Wysocki, M. Rex, H. Löwen, C.P. Royall, A. Imhof, A. van Blaaderen, Lane formation in driven mixtures of oppositely charged colloids, Soft Matter 7 (2011) 2352-2356.

[48] M.F. Hsu, E.R. Dufresne, D.A. Weitz, Charge stabilization in nonpolar solvents, Langmuir 21 (2005) 4881-4887.

[49] R. Sanchez, P. Bartlett, Synthesis of charged particles in an ultra-low dielectric solvent, Soft Matter 7 (2011) 887-890.

[50] B.J. Park, J.H. Sung, K.S. Kim, I. Chin, H.J. Choi, Preparation and characterization of poly(methyl methacrylate) coated TiO_2 nanoparticles, J. Macromol. Sci. 45 (2006) 53-60.

[51] M.A. Lee, Y.H. Kim, B.J. Park, H.J. Choi, Synthesis and electrophoretic properties of poly(acrylamide-co-methylmethacrylate) coated organic pigments, Mol. Cryst. Liq. Cryst. 499 (2009) 627-632.

[52] M. Badila, A. Hébraud, C. Brochon, G. Hadziioannou, Design of colored multilayered electrophoretic particles for electronic inks, ACS Appl. Mater. Interfaces. 3 (2011) 3602-3610.

[53] S. Kawaguchi, K. Ito, Dispersion Polymerization, Adv. Polym. Sci. 175 (2005) 299-328.

[54] M.T. Elsesser, A.D. Hollingsworth, Revisiting the Synthesis of a well-known comb-graft copolymer stabilizer and its application to the dispersion polymerization of poly(methyl methacrylate) in organic media, Langmuir 26 (2010) 17989-17996.

[55] K. Kargupta, P. Rai, A. Kumar, Effect of graft chain length of the stabilizer on dispersion polymerization of methyl methacrylate in petrol, J. Appl. Polym. Sci. 49 (1993) 1309-1329.

[56] K.E.J. Barrett, H.R. Thomas, Kinetics of dispersion polymerization of soluble monomers. I. Methyl methacrylate, J. Polym. Sci., Part A: Polym. Chem. 7 (1969) 2621-2650.

[57] R.J.R. Cairns, R.H. Ottewill, D.W.J. Osmond, I. Wagstaff, Studies on the preparation and properties of latices in nonpolar media, J. Colloid Interface Sci. 1 (1976) 45-51.

[58] C. Pathmamanoharan, C. Slob, H.N.W. Lekkerkerker, Preparation of polymethacrylate latices in non-polar media, Colloid Polym. Sci. 267 (1989) 448-450.

[59] H. Hu, G. Larson, One –step preparation of highly monodisperse micron-size particles in organic solvents, J. Am. Chem. Soc. 126 (2004) 13894-13895.

[60] M.S. Chattha, J.C. Cassatta, A new preparation of nonaqueous dispersions, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 453-456.

[61] R.H. Pelton, A. Osterroth, M.A. Brook, Silicone stabilized poly(methyl methacrylate) nonaqueous latexes I. Preparation and characterization, J. Colloid Interface Sci. 137 (1990) 120-127.

[62] S.A. Srinivasan, J.L. Hedrick, D.R. McKean, R.D. Miller, J.G. Hilbom, Preparation of thermally labile PMMA particles by combined non-aqueous dispersion polymerization and polymer chain transfer, Polymer 39 (1998) 1497-1501.

[63] S.M. Klein, V.N. Manoharan, D.J. Pine , F.F. Lange, Preparation of monodisperse PMMA microsphere in nonpolar solvents by dispersion polymerisation with a macromonomeric stabilizer, Colloid Polym. Sci. 282 (2003) 7-13.

[64] J.V. Dawkins, G. Taylor, Nonaqueous poly(methyl methacrylate) dispersions: radical dispersion polymerization in the presence of AB block copolymers of polystyrene and poly(dimethyl siloxane), Polymer 20 (1979) 599-604.

[65] D.H. Everett, J.F. Stageman, Preparation and stability of novel polymer colloids in a range of simple liquids, Faraday Discuss. Chem. Soc. 65 (1978) 230-241.

[66] J.C. Saam, C.H. Tsai, Silicone-stabilised nonaqueous emulsion polymerisation, J. Appl. Polym. Sci. 18 (1974) 2279-2285

[67] S. Kawaguchi, T. Okada, K. Tano, K. Ito, Synthesis of polyethylene macromonomers and their radical copolymerizations with methyl methacrylate in homogeneous and oligoehtylene melts media, Des. Monomers Polym. 3 (2000) 263-277.

[68] B. Hirzinger, M. Helmstedt, J. Stejskal, Light scattering studies on core-shell systems: determination of size parameters of sterically stabilized poly(methylmethacrylate) dispersions, Polymer 41 (2000) 2883-2891.

[69] M. Hölderle, G. Bar, R. Mülhaupt, Synthesis and characterization of oxazoline-functional polymer particles by free radical nonaqueous dispersion polymerization, J. Polym. Sci., Part A: Polym. Chem. 35 (1997) 2539-2548.

[70] J. Stejskal, D. Hlavatá, A. Sikora, Č. Koňák, J. Pleštil, P. Kratochvil, Equilibrium and non-equilibrium copolymer micelles: polystyrene-block-poly(ethylene-co-propylene) in decane and in diisopropyether, Polymer 33 (1992) 3675-3685.

[71] J. Stejskal, P. Kratochvil, P. Koubik, Z. Tuzar, J. Urban, M. Helmstedt, A.D. Jenkins, Light scattering characterization of spherical particles prepared by the dispersion polymerization of methyl methacrylate in a non-aqueous medium, Polymer 31 (1990) 1816-1822.

[72] M. Helmstedt, H. Schäfer, Determination of sizes of spherical particles, prepared by dispersion polymerization of methyl methacrylate in non-aqueous medium, by analysis of the particle scattering and autocorrelation functions, Polymer 35 (1994) 3377-3383.

[73] B. Williamson, R. Lukas, M.A. Winnik, M.D. Croucher, The preparation of micron-size polymer particles in nonpolar media, J. Colloid Interface Sci. 119 (1987) 559-564.

[74] M.A. Winnik, Fluorescence in structured media: a look at polymer colloids, Pure & Appl. Chem. 9 (1984) 1281-1288.

[75] M.A. Winnik, B. Williamson, T. Russell, Small-angle X-ray scattering studies of polymer colloids: nonaqueous dispersions of poly(isobutylene)-stabilized poly(methyl methacrylate) particles, Macromolecules 20 (1987) 899-901.

[76] M.A. Winnik, B. Disanayaka, O. Pekcan, M.D. Croucher, Fluorescence quenching studies of core and stabilizer-labeled non-aqueous dispersions: the nature of the core-stabilizer interface, J. Colloid Interface Sci. 139 (1990) 251-259.

[77] L. Houillot, C. Bui, M. Save, B. Charleux, C. Farcet, C. Moire, J.-A. Raust, I. Rodriguez, Synthesis of well-defined polyacrylate particle dispersion in organic medium using simultaneous RAFT polymerization and self-assembly of block copolymers. A strong influence of the selected thiocarbonylthio chain transfer agent, Macromolecules 40 (2007) 6500-6509.

[78] L. Houillot, C. Bui, C. Farcet, C. Moire, J.-A. Raust, H. Pasch, M. Save, B. Charleux, Dispersion polymerization of methyl acrylate in nonpolar solvent stabilized by block copolymers formed in situ via the RAFT process, ACS Appl. Mater. Interfaces 2 (2010) 434-442.

[79] H.V. Harris, S.J. Holder, Octadecyl acrylate based block and random copolymers prepared by ATRP as comb-like stabilizers for colloidal micro-particle one-step synthesis in organic solvents, Polymer 47 (2006) 5701-5706.

[80] J.G. Murray, F.C. Schwab, Organic fillers by anionic dispersion polymerisation, Ind. Eng. Chem. Proc. 21 (1982) 93-96.

[81] G.B. Stampa, The anionic dispersion of polymerization of α-methylstyrene, J. Appl. Polym. Sci. 14 (1970) 1227-1233.

[82] M. Schneider, R. Mülhaupt, Living dispersion polymerization of styrene in the presence of polystyrene-block-poly(4-trimethylsilylstyrene), Polym. Bull. 32 (1994) 545-550.

[83] M.A. Awan, V.L. Dimonie, M.S. El-Aasser, Anionic dispersion polymerization of styrene. I. Investigation of parameters for preparation of uniform micron-size polystyrene particles with narrow molecular weight distribution, J. Polym. Sci. Part A: Polym. Chem. 34 (1996) 2633-2649.

[84] M.A. Awan, V.L. Dimonie, M.S. El-Aasser, Anionic dispersion polymerization of styrene. II. Mechanism of particle formation, J. Polym. Sci. Part A: Polym. Chem. 1996; 34: 2651-2664.

[85] J. Kim, S.Y. Jeong, K.U. Kim, Y.H. Ahn, R.P. Quirk, Anionic disperison polymerization. I. Control of particle size, J. Polym. Sci. Part A: Polym. Chem. 34 (1996) 3277-3288.

[86] S. Kéki, G. Deák, L. Daróczi, A. Kuki, M. Zsuga, Star-shaped nanomicelles of polyisobutylene-polystyrene diblock copolymers. New stabilizer for living dispersion polymerization of styrene, Macromol. Symp. 157 (2000) 217-224.

[87] I. Tausendfreund, F. Bandermann, H.W. Siesler, M. Kleimann, Anionic dispersion copolymerisation of styrene and 1, 3-butadiene, Polymer 43 (2002) 7085-7091.

[88] J.V. Dawkins, G. Taylor, Nonaqueous polystyrene dispersions: Radical dispersion polymerization in the presence of AB block copolymers of polystyrene and poly(dimethyl siloxane), Eur. Polym. J. 15 (1978) 453-457.

[89] K. Tauer, H. Ahmad, Study on the preparation and stabilization of pyrene labeled polymer particles in non-polar media, Polym. React. Eng. 11 (2003) 305 – 318.

[90] M. Hölderle, M. Baumert, R. Mülhaupt, Comparison of controlled radical styrene polymerizations in bulk and nonaqueous dispersion, Macromolecules 30 (1997) 3420-3422.

[91] O. Okay, W. Funke, Anionic dispersion polymerisation of 1,4-divinylbenzene, Macromolecules 23 (1990) 2623 – 2628.

[92] O. Okay, W. Funke, Steric stabilization of reactive microgels from 1,4-Dinvinylbenzene, Makromol. Chem.-Rapid 11 (1990) 583 – 587.

[93] F.A. Taromi, P. Rempp, “Porcupine” polymers and double-star polymers, Makromol. Chem. 190 (1989) 1791 – 1798.

[94] O. Okay, W. Funke, Conditions of microgel formation in homogeneous anionic polymerization of 1,4-Divinylbenzene, Makromol. Chem. 191 (1990) 1565 – 1573.

[95] M.A. Ansarifar, P.F. Luckham, The preparation of monodisperse polyacrylonitrile particles in the presence of AB block copolymers of poly-2-vinylpyridine/poly(tertbutylstyrene), Colloid Polym. Sci. 266 (1988) 1020 – 1023.

[96] H.V. Penfold, S.J. Holder, B.E. McKensie, Octadecyl acrylate – methyl methacrylate block and gradient copolymers from ATRP: Comb-like stabilizers for the preparation of micro- and nano-particles of poly(methyl methacrylate) and poly(acrylonitrile) by non-aqueous dispersion polymerization, Polymer 51 (2010) 1904 – 1913.

[97] D. Horák, M. Kryštůfek, J. Spěváček, Effect of reaction parameters on the dispersion polymerization of 1-Vinyl-2-Pyrrolidone, J. Polym. Sci. Part A: Polym. Chem. 38 (2000) 653 – 663.

[98] S. Sosnowski, M. Gadzinowski, S. Slomkowski, S. Penczek, Synthesis of bioerodible poly(ε-caprolactone) latexes and poly(D, L-lactide) microspheres by ring-opening polymerization, J. Bioact. Compat. Pol. 9 (1994) 345-366.

[99] W. Jajubowski, J.-F. Lutz, S. Slomkowski, K. Matyjaszewski, Block and random copolymers as surfactants for dispersion polymerization. I. Synthesis via atom transfer radical polymerization and ring-opening polymerization, J. Polym. Sci. Part A: Polym. Chem. 43 (2005) 1498-1510.

[100] M. Muranaka, Y. Kitamura, H. Yoshizawa, Preparation of biodegradable microspheres by anionic dispersion polymerization with PLA copolymeric dispersion stabilizer, Colloid Polym. Sci. 285 (2007) 1441-1448.

[101] M. Muranaka, H. Yoshizawa, T. Ono., Design of polylactide-grafted copolymeric stabilizer for dispersion polymerization of D,L-lactide, Colloid Polym. Sci. 287 (2009) 525-532.

[102] A.T. Chen, R.T. Wojcik, Polyurethane coatings for metal and plastics substrates, Met. Finish. 108 (2010) 108-121.

[103] L.S. Ramanathan, D. Baskaran, P.G. Shukla, S. Sivaram, Preparation of polyurethane microspheres via dispersion polycondensation using poly(1,4-isoprene)-block-poly(ethylene oxide) as steric stabilizer, Macromol. Chem. Phys. 203 (2002) 998-1002.

[104] L.S. Ramanathan, P.G. Shukla, S. Sivaram, Synthesis and characterization of polyurethane microspheres, Pure Appl. Chem. 70 (1998) 1295-1299.

[105] B. Radhakrishnan, E. Cloutet, H. Cramail, Synthesis of uniform polyurethane particles by step growth polymerization in a dispersed medium, Colloid Polym. Sci. 280 (2002) 1122-1130.

[106] P. Chambon, E. Cloutet, H. Cramail, Synthesis of core-shell polyurethane-poly(dimethylsiloxane) particles in supercritical carbon, Macromolecules 37 (2004) 5856-5859.

[107] P. Chambon, E. Cloutet, H. Cramail, Synthesis of core-shell polyurethane-polydimethylsiloxane particles by polyaddition in organic dispersant media: mechanism of particle formation, Macromol. Symp. 226 (2005) 227-238.

[108] L.S. Egan, M.A. Winnik, Synthesis and characterization of fluorescently labelled poly(vinyl acetate) particles, J. Polym. Sci. Part A: Polym. Chem. 24 (1986) 1895-1913.

[109] L.S. Egan, M.A. Winnik, Oxygen quenching studies of nonaqueous dispersions of poly(vinyl acetate) labeled with phenanthrene groups, Langmuir 4 (1988) 438-445.

[110] E.J. Beckman, Supercritical and near-critical CO_2 in green chemical synthesis and processing, J. Supercrit. Fluid 28 (2004) 121-191.

[111] C.D. Wood, A.I. Cooper, J. M. DeSimone, Green synthesis of polymers using supercritical carbon dioxide, Curr. Opin. Solid St. M. 8 (2004) 325-331.

[112] P.B. Zetterlund, Y. Kagawa, M. Okubo, Controlled living radical polymerization in dispersed systems, Chem. Rev. 108 (2008) 3747-3794.

[113] A.I. Cooper, Polymer synthesis and processing using supercritical carbon dioxide, J. Mater. Chem 10 (2000) 207-234.

[114] J.L. Kendall, D.A. Canelas, J.L. Young, J.M. DeSimone, Chem. Rev. 99 (1999) 543-563.

[115] D.A. Canelas, J.M. DeSimone, Adv. Polym. Sci. 133 (1997) 103-140.

[116] A.M. Gregory, K.J. Thurecht, S.M. Howdle, Controlled dispersion polymerization of methyl methacrylate in supercritical carbon dioxide via RAFT, Macromolecules 41 (2008) 1215-1222.

[117] K.J. Thurecht, A.M. Gregory, W. Wang, S.M. Howdle, "Living" polymer beads in supercritical CO_2, Macromolecules 40 (2007) 2965-2967.

[118] H.S. Hwang, H. Yuvaraj, W.S. Kim, W.K. Lee, Y.S. Gal, K.T. Lim, Dispersion polymerization of MMA in supercritical CO_2 stabilized by random copolymers of 1H,1H-perfluorooctyl methacrylate and 2-(dimethylaminoethyl methacrylate), J. Polym. Sci. Part A: Polym. Chem. 46 (2008) 1365-1375.

[119] C. Lepilleur, E.J. Beckman, Dispersion polymerization in supercritical CO_2, Macromolecules 30 (1997) 745-756.

[120] J. Shin, W. Bae, H. Kim, Synthesis of cross-linked poly(methyl methacrylate) via dispersion polymerization in supercritical carbon dioxide, Colloid Polym. Sci. 288 (2010) 271-282.

[121] Y.L. Hsiao, E.E. Maury, J.M. DeSimone, S. Mawson, K.P. Johnston, Dispersion polymerization of methyl methacrylate stabilized with poly(1,1-dihydroperfluorooctyl acrylate) in supercritical carbon-dioxide, Macromolecules 28 (1995) 8159-8166.

[122] M.R. Gilles, J.N. Hay, S.M. Howdle, R.J. Winder, Macromonomer surfactants for the polymerization of the methyl methacrylate in supercritical CO_2, Polymer 41 (2000) 6715-6721.

[123] S.H. Han, K.K. Park, S.M. Lee, GMA-functionalized reactive stabilizer for polymerization of methyl methacrylate in supercritical CO2: Effect of stabilizer, initiator and monomer concentrations, Macromol. Res. 16 (2008) 120-127.

[124] H. Yuvaraj, H.S. Hwang, W.S. Kim, H.G. Kim, E.D. Jeong, K.T. Lim, Dispersion polymerization of methyl methacrylate in supercritical CO_2 in the presence of non-fluorous random copolymers, Eur. Polym. J. 44 (2008) 2253-2261.

[125] K.A. Shaffer, T.A. Jones, D.A. Canelas, J. M. DeSimone, S.P. Wilkinson, Dispersion polymerisations in carbon dioxide using siloxane-based stabilisers, Macromolecules 29 (1996) 2704-2706.

[126] M. Okubo, S. Fujii, H. Minami, Production of poly(methyl methacrylate) particles by dispersion polymerization with aminopropyl-terminated poly(dimethylsiloxane) stabilizer in supercritical carbon dioxide, Progr. Colloid Polym. Sci. 124 (2004) 121-125.

[127] S. Fujii, H. Minami, M. Okubo, Production of poly(methyl methacrylate) particles by dispersion polymerization with mercaptopropyl terminated poly(dimethylsiloxane) stabilizer in supercritical carbon dioxide, Colloid Polym. Sci. 282 (2004) 569-574.

[128] M. Okubo, S. Fujii, H. Maenaka, H. Minami, Production of submicron-sized poly(methyl methacrylate) particles by dispersion polymerization with a poly(dimethylsiloxane)-based azoinitiator in supercritical carbon dioxide, Colloid Polym. Sci. 280 (2002) 183-187.

[129] L-Q. Cao, L-P. Chen, P-Y Cui, J-D. Wang, Synthesis of PNIPA/PDMS-g-PAA core-shell composites in supercritical carbon dioxide, J. Appl. Polym. Sci. 108 (2008) 3843-3850.

[130] G. Li, M.Z. Yates, K.P. Johnston, Trifunctional ambidextrous surfactants for latexes in supercritical CO_2 and water, Macromolecules 33 (2000) 1606-1612.

[131] B. Tan, H.M. Woods, P. Licence, S.M. Howdle, A.I. Cooper, Synthesis and CO_2 solubility studies of poly(ether carbonate)s and poly(ether ester)s produced by step growth polymerization, Macromolecules 38 (2005) 1691-1698.

[132] C. Drohmann, E.J. Beckman, Phase behavior of polymers containing ether groups in carbon dioxide, J. Supercrit. Fluid 22 (2002) 103-110.

[133] T. Sarbu, T.J. Styranec, E.J. Beckman, Design and synthesis of low cost, sustainable CO_2-philes, Ind. Eng. Chem. Res. 39 (2000) 4678-4683.

[134] M.J. Hollamby, K. Trickett, A. Mohamed, S. Cummings, R.F. Tabor, O. Myakonkaya, S. Gold, S. Rogers, R.K. Heenan, J. Eastoe, Tri-chain hydrocarbon surfactants as designed micellar modifiers for supercritical CO_2, Angew. Chem. Int. Ed. 48 (2009) 4993-4995.

[135] N.A. Birkin, N.J. Arrowsmith, E.J. Park, A.P. Richez, S.M. Howdle, Synthesis and application of new CO_2-soluble vinyl pivalate hydrocarbon stabilisers via RAFT polymerisation, Polym. Chem. 2 (2011) 1293-1299.

[136] I. Blakey, A.G. Yu, S.M. Howdle, A.K. Whittaker, K.J. Thurecht, Controlled polymerisation of lactide using an organo-catalyst in supercritical carbon dioxide, Green Chem. 13 (2011) 2032-2037.

[137] J.Y. Lee, C.H. Song, J.I. Kim, J.H. Kim, Preparation of aromatic polycarbonate nanoparticles using supercritical carbon dioxide, J. Nanopart. Res. 4 (2002) 53-59.

[138] B. Grignard, C. Jerome, C. Calberg, R. Jerome, W.X. Wang, S.M. Howdle, C. Detrembleur, Dispersion atom transfer radical polymerization of vinyl monomers in supercritical carbon dioxide, Macromolecules 41 (2008) 8575-8583.

[139] B. Grignard, T. Phan, D. Bertin, D. Gigmes, C. Jerome, C. Detrembleur, Dispersion nitroxide mediated polymerization of methyl methacrylate in supercritical carbon dioxide using in situ formed stabilizers, Polym. Chem. 1 (2010) 837-840.

[140] J. Jennings, M. Beija, A. Richez, S. Cooper, P. Mignot, K. Thurecht, K. Jack, S. Howdle, One-pot synthesis of block copolymers in supercritical carbon dioxide: A simple versatile route to nonastructured microparticles, J. Am. Chem. Soc. 134 (2012) 4772-4781.