

POLY(METHYL METHACRYLATE) STERICALLY STABILIZED BY SILICONE

To Hans-Georg

POLY(METHYL METHACRYLATE) STERICALLY STABILIZED BY SILICONE

By

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## ABSTRACT

Nonaqueous poly(methyl methacrylate) latices were prepared by nonaqueous dispersion polymerization of poly(methyl methacrylate) in heptane in the presence of either trimethylsilyl terminated or vinyl terminated polydimethylsiloxane stabilizer. Poly(methyl methacrylate) particles stabilized by vinyl terminated polydimethylsiloxane showed smaller particle sizes than did those stabilized by trimethylsilyl terminated polydimethylsiloxane. Diameters of the various latex preparations ranged from 1.4 to 0.8  $\mu\text{m}$  and silicone content was around 2 mole percent in each case. Differences between the two types of latex were explained in terms of the nucleation mechanism operating during the preparation of the latices and in terms of the type of attachment of the stabilizer chain to the poly(methyl methacrylate) core.

The effect of the silicone concentration present during particle formation was investigated. Vinyl terminated polydimethylsiloxane stabilized latex gave better stabilized particles than did methyl terminated polydimethylsiloxane stabilized latex. The results of varying the concentration and type of initiator were consistent with the conclusions about differences in nucleation and grafting mechanisms.

The stability of polydimethylsiloxane stabilized poly(methyl methacrylate) particles was investigated in n-heptane. Acidified montmorillonite clay was determined as the optimum catalyst for this latex system. Flocculation set in at 70% of the original silicone content when the siloxane on the particle surface was degraded with montmorillonite clay in a good solvent. Flocculation was irreversible and occurred abruptly. The point of flocculation was reproducible and the rate of flocculation was identical for two different types of silicone stabilized poly(methyl methacrylate) latex.

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## CHAPTER 1

### INTRODUCTION

Polymer colloids are an important group of products with industrial applications ranging from paint formulations and inks to coatings and household products. To be useful for most applications, the colloids are generally from 1 nm to 1 $\mu$ m in diameter. They can be composed of any type of polymeric or solid substance which is insoluble in the continuous phase. The continuous phase is usually water or a hydrocarbon medium. A suspension made up of a polymeric colloid, a continuous phase and other agents is called a latex.

The present work is a fundamental study of one type of latex system and deals exclusively with poly(methyl methacrylate) [PMMA] latices containing polydimethylsiloxane [PDMS] stabilizer on the particle surface. The particles can be envisioned as follows:

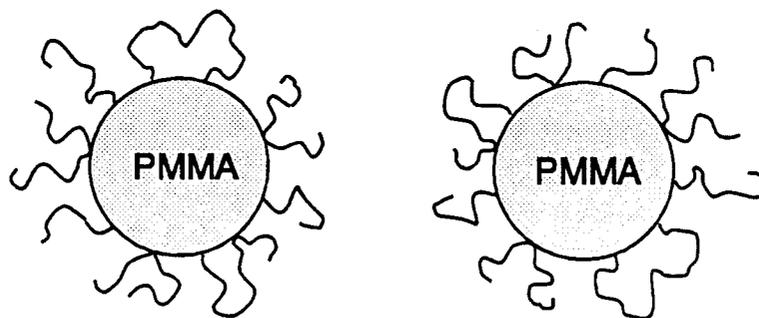


Figure 1.1: Two polydimethylsiloxane coated PMMA particles.

The hairs on the particle surface are the PDMS polymer chains which extend into the surrounding medium, n-heptane. The particle cores are composed of PMMA to which the PDMS is covalently grafted. The studies carried out on these colloids are of two kinds; the initial investigations involved the preparation and characterization of silicone stabilized PMMA latices and the second study dealt with investigating the limit of stability of these latices.

## 1.1. Characterization of PDMS stabilized PMMA Latices

The first set of studies was performed to optimize preparation and characterization methods to obtain the largest possible amount of information about the system under study. This process included determination of synthesis parameters such as type and molecular weight of stabilizer, type of initiator, concentration of all reagents and optimal preparation conditions for latex particle formation. Final latices were analyzed with respect to their stability and particle size.

### 1.1.1. Colloid Stability

In the absence of any stabilizer, two colloidal particles in a continuous phase will flocculate. In this case, the only forces acting upon each particle are the force of gravity which is negligible and the London-van der Waals force of attraction. As a result of Brownian motion, particles may approach each other at distances over which van der Waals forces operate, and any collision will result in flocculation. Floccs or aggregates are made up of more or less loose agglomerations of two or more colloidal particles.

Aggregation may be prevented or slowed down by the addition of certain stabilizer moieties. The stabilizer may be a neutral or charged polymer, monomer or an electrolyte which must be soluble in the continuous phase. Stabilization is brought about when the stabilizer moiety forms a shell around each colloid particle. As two shells on different particles approach each other, a repulsive force results. Interaction of the stabilizer with the solvent is more favourable than with another stabilizer molecule. In any system, the relative magnitude of the attractive and repulsive forces between the particles govern their stability with respect to flocculation.

### 1.1.2. DLVO Theory

The classical theory which best describes interaction of colloidal particles is the DLVO theory which was arrived at independently by Dutch and Soviet scientists (Deryaguin and

Landau, 1941, and Verwey and Overbeek, 1948). This theory serves as the framework for discussing charge stabilization. It is proposed that the interaction between colloid particles is governed by electrostatic repulsion and van der Waals attraction (Lyklema, 1968). Polymer adsorption is not accounted for by this early theory and is assumed not to be involved.

For the DLVO theory, a double layer model is invoked by which the surface charge of a particle must be neutralized by an equal but opposite countercharge in the medium. These two layers make up the double layer.

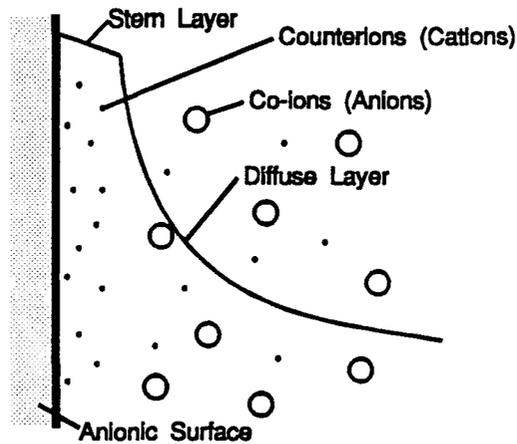


Figure 1.2: Diagram representing the structure of the double layer.

The extent of the diffuseness of the double layer is estimated by the Debye-Hückel reciprocal length  $\kappa$  defined as

$$\kappa = \left( \frac{4\pi e^2 \sum n_i z_i^2}{\epsilon_0 \epsilon_r kT} \right) = \left( \frac{8\pi e^2 n z^2}{\epsilon_0 \epsilon_r kT} \right) \quad (1.1)$$

where  $n$  is the number of ions/ $m^3$ ,  $z$  is the charge on a species and  $\epsilon_0 \epsilon_r$  is the permittivity of free space and the medium. In a medium with large dielectric constant, the double layer is very thin. In media of low dielectric constant, the double layer becomes very diffuse and the surface potential decays slowly as a function of distance from the particle surface.

### 1.1.2.1. Electrostatic Repulsion

When two particles with equivalent double layers approach each other, some overlap occurs in the double layer region. Repulsion results because work is necessary to bring the particles closer together.

The force of repulsion can be found from the work involved in bringing the particles from infinity to an interparticle distance  $d$ . The repulsive force at a distance  $d$  is given by

$$U_R = \left( \frac{\epsilon_0 \epsilon_r a \Psi_0^2}{2} \right) \ln (1 + e^{-\kappa H}) \quad (1.2)$$

for two spheres whose distance of closest approach is given by  $H=R-2a$  where  $R$  is the distance between the centres of the two particles and  $a$  is the particle radius.  $\epsilon_0 \epsilon_r$  is the permittivity of free space and the medium and  $\Psi_0$  is the potential at the particle surface. Figure 1.3 shows the energy of repulsion as a function of distance of closest approach.

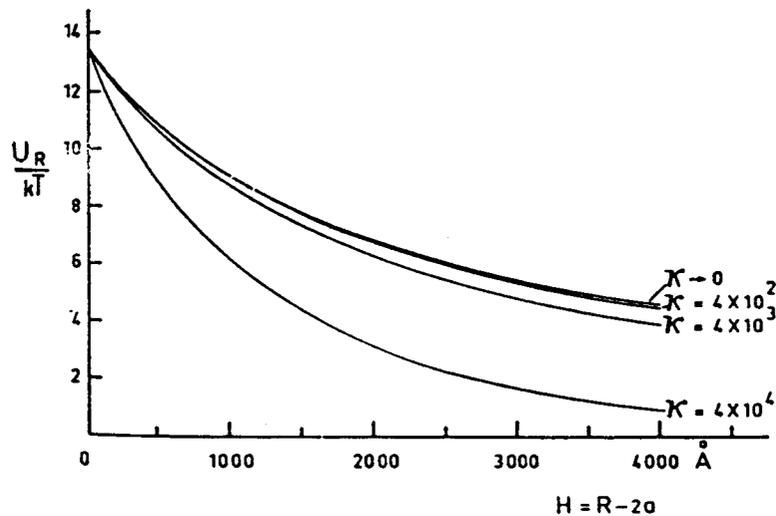


Figure 1.3: Electrostatic repulsion between two spherical particles expressed as units of  $\kappa T$  for  $a=1000\text{Å}$  for four different values of  $\kappa$ . Figure taken from J. Lyklema, *Adv. Coll. Int. Sci.*, 2, 91, (1968).

It should be noted that similar equations may be derived for the interaction of two flat plates or a flat plate and a sphere.

### 1.1.2.2. Van der Waals Attraction

Previous work by Smoluchowski was concerned with the attractive forces between particles and Hamaker was the first person to show that these forces were large enough to counteract some of the repulsive forces (Lyklema, 1968). The attractive forces were calculated under the assumption that London forces are additive. The total attractive energy between two spheres in medium 1 is given by

$$U_A = \left(\frac{-A_{12}}{6}\right) \left(\frac{2}{s^2-4} + \frac{2}{s^2} + \ln \frac{s^2-4}{s^2}\right) \quad (1.3)$$

where  $A_{12}$  is the Hamaker constant for solid 2 in medium 1 and  $s$  is the reduced distance between the particles such that  $s=R/a$ . For short distances, Equation 1.3 reduces to

$$U_A = \left(\frac{-A_{12}}{12}\right) \left(\frac{a}{H}\right) \quad (1.4)$$

The equations for attractive energies are identical for the aqueous and nonaqueous case. The difference between Equation 1.3 and 1.4 is illustrated in Figure 1.4.  $U_A$  dies away quickly but more so for the general case (solid line and Equation 1.3) than if the interparticle distance is small (dashed line and Equation 1.4). This is mainly due to a small value of  $\kappa$ . Again, the equivalent equations for attraction can be derived for two flat plates and a flat plate and a sphere.

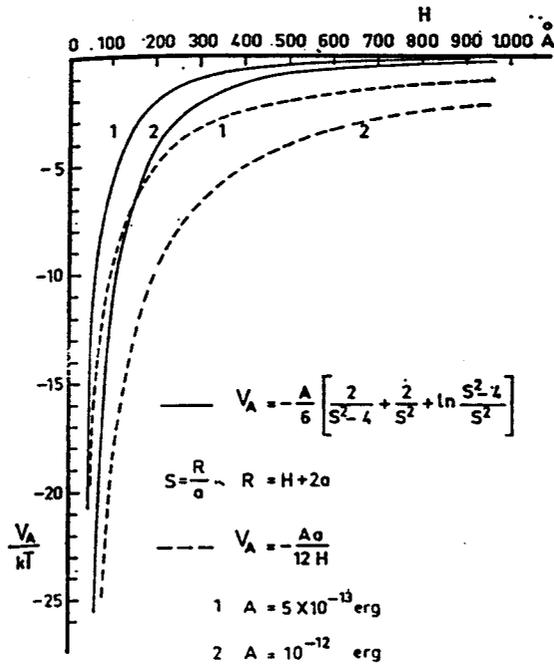


Figure 1.4: Van der Waals attraction between two spherical particles using the exact and approximated energy equation for two values of the Hamaker constant  $A$ .  $a = 1000\text{\AA}$ . Figure taken from J. Lyklema, *Adv. Coll. Int. Sci.*, 2, 93, (1968).<sup>1</sup>

### 1.1.2.3. Total Interaction Between Two Particles

If the repulsive and attractive forces are added, one can obtain the total energy between two particles. A graph of the interaction energy is illustrated in Figure 1.5 at low  $\kappa$  using equations for the general cases of attraction and repulsion.

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<sup>1</sup> It should be noted that  $U_A$  and  $V_A$  are equivalent.

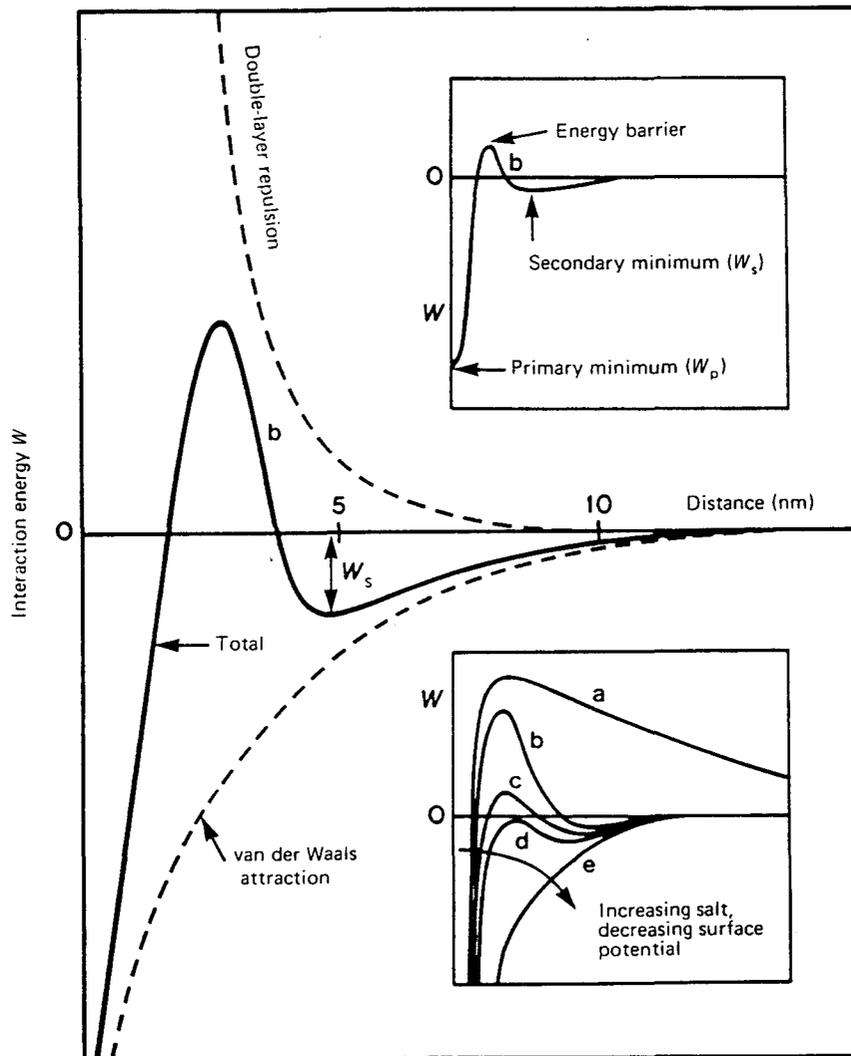


Figure 1.5: Total interaction between two spherical particles of radius  $a=1000\text{\AA}$  for two values of  $\kappa$  and the Hamaker constant  $A$ . Figure taken from J. Israelachvili, "Intermolecular and Surface Forces", Academic Press, London, (1985).

The main feature of this graph is that attractive forces only modify the interaction energy at close approach. The highest point of the curve,  $U_{\max}$ , is the energy barrier to be overcome for flocculation to take place. The higher  $U_{\max}$ , the more stable a system is to flocculation.

Flocculation kinetics also depend on these energy maxima. Depending on the height of the barrier, the system can be unstable, coagulating slowly, or infinitely stable. Verwey and Overbeek use  $15\text{ kT}$  as a value to predict stable systems, but in current practice,  $10\text{ kT}$  for non-aqueous systems is usually accepted (Napper, 1983).

### 1.1.3. Steric Stabilization

Steric stabilization of colloidal particles occurs as a result of a polymer which forms a stabilizer layer around the particles. The stabilizer is anchored in one of two ways. A polymer may be attached by adsorption which occurs when part or all of the stabilizing moiety adheres reversibly to the colloid surface (a). Stabilizers which do not adsorb spontaneously are anchored by forming one or more covalent bonds to the colloid surface (b). Variations of these two anchoring mechanisms are achieved by the use of AB block copolymers of which one block may adsorb reversibly and spontaneously, and the other block may interact with the continuous phase (c). Alternatively, one block may contain sites to form grafts to the colloid and the other block will protrude into the continuous phase (d). Colloidal stability may also be achieved by the use of random copolymers which may adsorb or graft along one or more sections (d). Any of the above types of attachments may leave loops or tails which extend into the continuous phase forming a stabilizer layer around the colloid.

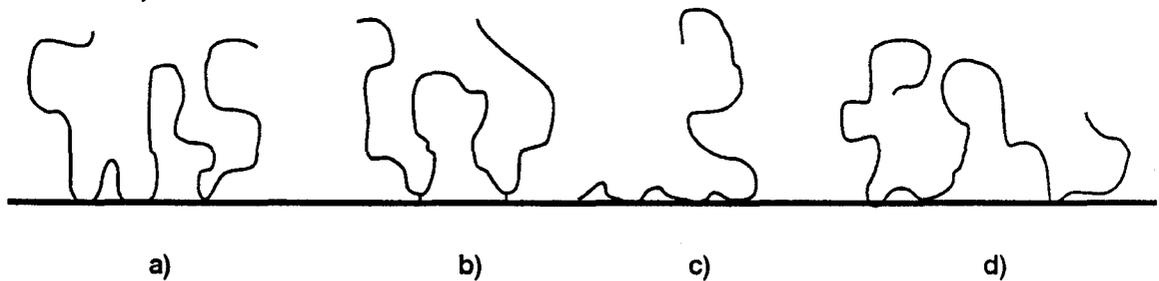


Figure 1.6: Various methods of polymer adsorption and anchoring on the surface of a colloidal particle.

When two sterically stabilized particles approach each other, the equation governing the force of attraction is the same as for charge stabilized systems. However, the force of repulsion changes to the general formula first derived by Fischer and later modified by Napper and others (Napper, 1983). In general, the interaction energy between two spheres of equal radius is given by

$$\Delta G_M = 2\pi a k T \omega^2 \left( \frac{V_2^2}{V_1} \right) N_A \left( \frac{1}{2} - \chi_1 \right) S_M \quad (1.5)$$

where  $\omega$  is the weight of stabilizer moieties attached per unit surface area,  $v_2$  is the partial specific volume of the attached polymer chains,  $V_1$  is the partial molar volume of the continuous phase,  $\chi_1$  is the Flory-Huggins Chi parameter of the attached polymer chain and the continuous phase, and  $S_M$  is a distance dependent parameter.

As two sterically stabilized particles approach, their stabilizer moieties begin to "see" each other and eventually start to interpenetrate, as illustrated in Figure 1.7.

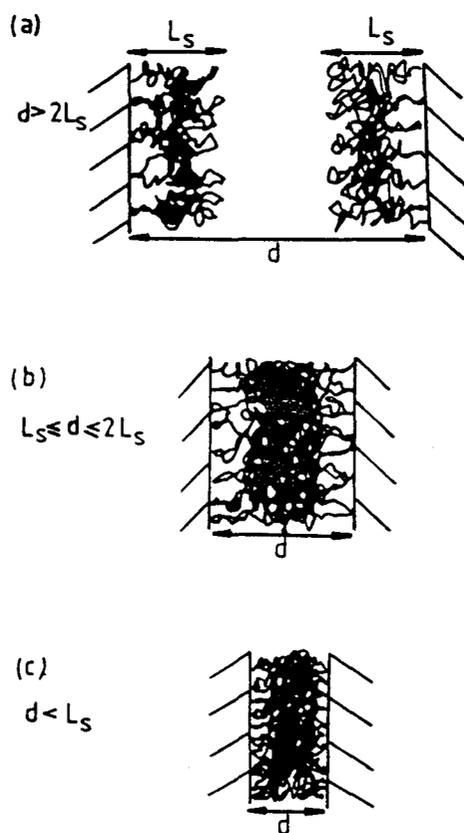


Figure 1.7: Diagram of the interpenetrational domain (b) and the compressional domain (c) when two particles approach each other. (a) Represents the equilibrium thickness of the stabilizer layers. Figure taken from D.H. Napper, "Polymeric Stabilization of Colloidal Dispersions", Academic Press, San Diego, (1983).

When the separation between the surfaces of the two particles becomes less than twice the thickness of the stabilizer layer, the stabilizer chains touch and subsequently intermix and the interpenetrational domain is reached. As the particles continue to approach and the distance between the surfaces becomes less than a single thickness of the stabilizer chains, the

compressional domain is reached. To accommodate the polymeric stabilizer, the chains are compressed.

When two particles are far apart, the distance dependent parameter  $S_M$  is zero. As the particles approach,  $S_M$  changes. In the interpenetrational domain, chain interactions are incorporated into  $S_M$  which becomes

$$S_{M(i)} = \left(1 - \frac{H_o}{2L_s}\right)^2 \quad (1.6)$$

$S_M$  changes further in the interpenetrational and compressional domain and becomes equal to

$$S_{M(i+c)} = 3 \ln \left(\frac{L_s}{H_o}\right) + 2 \left(\frac{H_o}{L_s}\right) - 1.5 \quad (1.7)$$

The Flory-Huggins parameter  $\chi_1$  in Equation 1.5 deserves special mention. In the case of nonaqueous dispersions,  $\chi$  and  $(1/2 - \chi)$  is found to vary parabolically with temperature over a broad temperature range. At the upper and lower temperature extremes,  $\chi$  is 1/2 and decreases between these two extremes.  $\chi$  values below 1/2 indicate that the solvency conditions for the polymer are favourable. The lower the  $\chi$  value, the better the solvency conditions for the polymer. Croucher and Hair's experimental determinations (Croucher and Hair, 1978, and Napper, 1983) of enthalpy and entropy between the two extreme temperature points have shown that the two temperatures at which  $\chi$  is 1/2 correspond to the upper and lower critical flocculation temperatures (UCFT and LCFT, respectively) for nonaqueous latices. Latices are stable at temperatures and pressures between these two points but flocculate readily as one of these extremes is reached.

Colloidal dispersions stabilized by silicone polymers were first reported by Dow Corning in the early 1970's (Dow Corning, 1973). The Dow Corning group were awarded a patent in 1973 for "any and all stable dispersions" of synthetic polymers with dispersed silicone block or graft copolymers in organic media. In this claim, special significance was given to stabilizers of AB block copolymers with the A moiety being a hydrocarbon chain and the B moiety being PDMS. The A block of the copolymer which would be similar in structure to the core polymer, adheres to the surface of the particle allowing the B block to act as the stabilizer chain. Stable particles

were obtained using a variety of these polymers when the degree of polymerization (DP) of the stabilizer was a minimum of about 10 to 20 repeat units. The limit of stability was dependent on the substituents. Particle sizes spanned a large range from 0.005 to 50  $\mu\text{m}$ .

Saam and Tsai, also from Dow Corning, reported preparations of poly(methyl methacrylate) stabilized by PDMS containing mercaptoalkyl groups (Saam and Tsai, 1974). Their work placed a special emphasis on the nucleation mechanism. Of interest is their finding that the minimum degree of polymerization of the silicone for formation of stable particles was around 15 repeat units with 150 to 200 units being most effective. Their experimental results of studies on nucleation mechanisms and particle growth showed two stages which were both characterized by particle size distribution, number of particles and amount of silicone incorporated. Initially, a large number of small particles with a "fairly broad" distribution was observed which contained about 40 to 50% silicone. With increased conversion, the silicone incorporated into the particles decreased to 5% but the particle size increased to more than four times the initial diameter from 30 to 160 nm. Saam and Tsai attributed these changes to a change in growth from an initial stage of graft copolymer formation followed by an agglomeration stage. During this stage, a number of small precursor particles would come together to form larger particles which would further increase in size upon polymerizing monomer in the core of the particle.

Everett and Stageman reported the preparation of similar PMMA colloidal particles with the stabilizer being an AB block copolymer made up of PDMS and polystyrene (PS), respectively (Everett and Stageman, 1977). It was believed that grafting to the PMMA core particle occurred along the PS segments. Particle sizes were narrowly distributed around 0.2  $\mu\text{m}$  diameter. Everett and Stageman characterized their latices by measuring upper and lower critical flocculation temperatures in low molecular weight hydrocarbon media. The critical flocculation temperatures define the boundaries of the stable regime for certain types of suspensions as described before. The UCFT was shown to correlate well with the theta temperature of the surrounding medium, as previously reported by Napper and Croucher and Hair (Croucher and

Hair, 1978, Napper, 1983). The theta temperature is the temperature at which  $\chi = 1/2$  and at which phase separation of a dispersion occurs.

## 1.2. Determination of the Critical Limit of Steric Stability in PMMA-PDMS Latices

The second set of experiments in the present study deals with the limit of stability. In this part, the PDMS stabilized PMMA latex is destabilized by degrading the "hairs" on the particle surface until flocculation sets in. Degradation of the siloxane chain is brought about with a catalyst in a characteristic reaction for siloxane called the equilibration reaction.

### 1.2.1. Siloxane Equilibration Chemistry

PDMS has the general structure shown in Figure 1.8 and may be terminated in a number of ways. In this case, a "normal" trimethylsilyl terminus is shown as is another common type, the vinyl terminus.

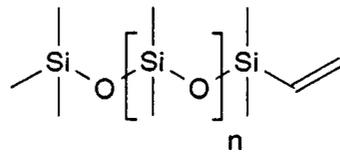


Figure 1.8: Polydimethylsiloxane having a trimethylsilyl terminated end (LHS) and a vinyl terminated end (RHS).

In siloxanes, the partial ionic character of the Si-O bond renders it suitable to both acid and base catalyzed cleavage.

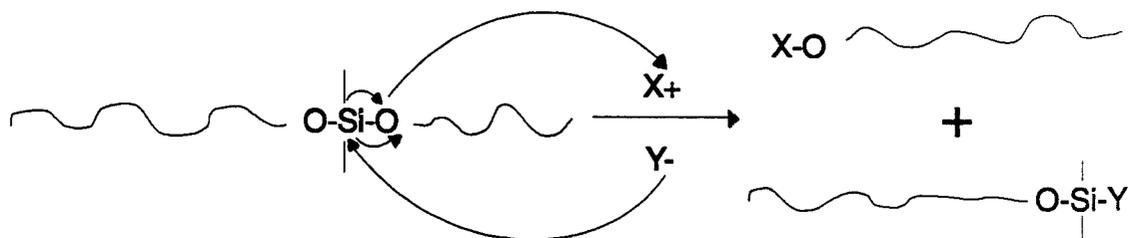


Figure 1.9: Mechanism and products formed during a typical equilibration reaction.

During the reaction of a PDMS moiety, for example, the catalyst may cleave any Si-O bond along the PDMS backbone to form shorter chain intermediates. In addition, any short chain reaction products may act as catalysts themselves, attacking other protonated siloxane moieties. This reaction takes place both intra- and intermolecularly. In the intramolecular case, a backbiting reaction takes place and the products formed will be cyclic.

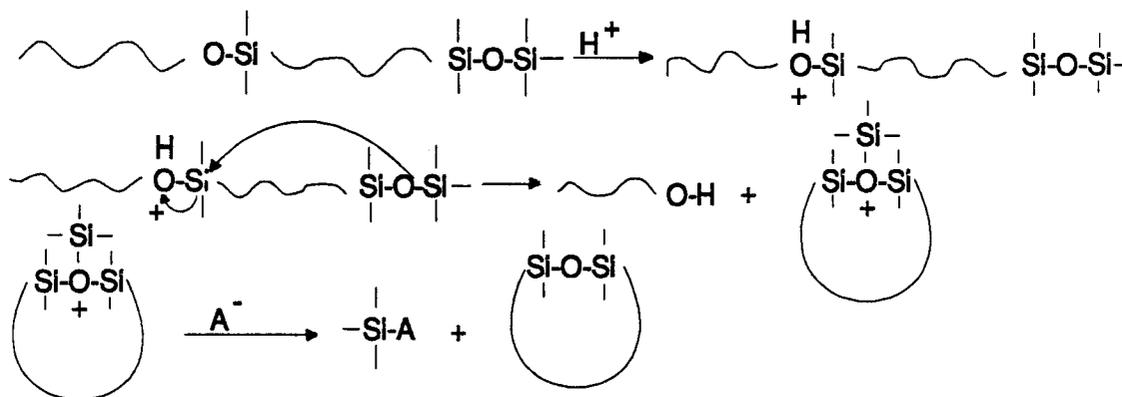
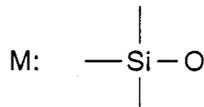
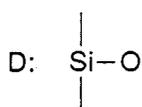


Figure 1.10: Schematic of an intramolecular equilibration reaction and products.

The final reaction products under equilibration conditions for long chains tend toward  $D_3$  and  $D_4^2$  rings containing 3 or 4 Si-O moieties respectively.  $D_3$  and  $D_4$  are 6 and 8 membered rings, respectively, which are the energetically most stable reaction products. The equilibrium can be forced toward linear products if an "end blocker" for the PDMS ions is included in the reaction. This end blocker is usually hexamethyldisiloxane or  $M_2$  which upon cleavage of its Si-O bond forms two molecules which are able to terminate siloxane intermediates rendering them unreactive and linear.

<sup>2</sup> In silicone chemistry, dimethylsiloxane units are known as D units and trimethylsiloxane units as M units, as illustrated below.



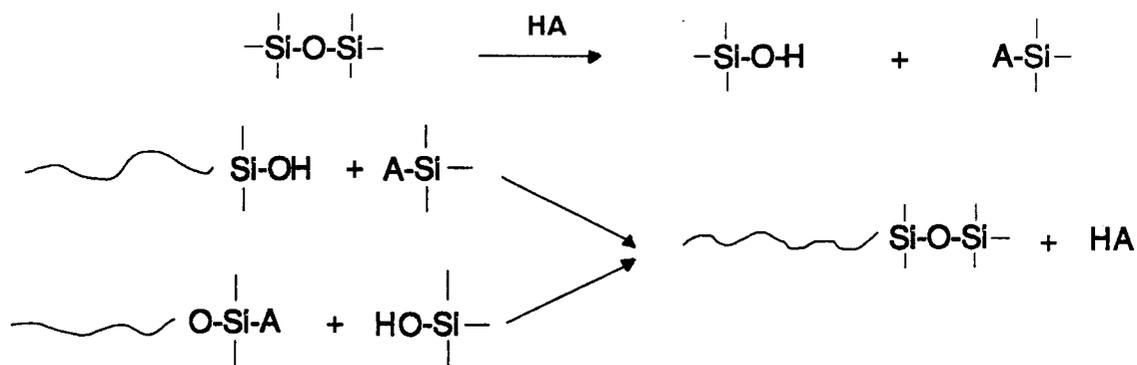


Figure 1.11: Dissociation of hexamethyldisiloxane and subsequent reaction with siloxane intermediates formed during the equilibration reaction to form linear reaction products.

Catalysts for the equilibration reaction include almost any reactant which can attack the polarized Si-O bond. Reaction conditions dictate the optimum type of catalyst. Usually a soluble catalyst is preferred. Salts such as potassium trimethyl silanolate are often used under polar conditions. Soluble acids or bases are often chosen in hydrocarbon media.

Silicone equilibration chemistry has been explored experimentally since the 1940's and 50's. Of interest is a solid acid catalyst called "Wofatit" used by German researchers since the late 1970's (Riederer, 1986). "Wofatit" is an acidic cation exchange resin catalytically similar to sulfuric acid in both rate and mechanism. However, "Wofatit" columns were very moisture sensitive and reaction rates were dependent on the drying time of the catalyst and the drying temperature. Equilibration reactions of polysiloxanes were usually complete in 4 to 5 hours at 50 to 80°C. This catalyst is a viable alternative in a system in which soluble catalysts are inappropriate.

Gilbert and Kantor have reviewed base catalysts which are usually salts that may catalyze equilibration reactions under a variety of conditions (Gilbert and Kantor, 1959). More recently, however, Spinu and McGrath described how cyclic siloxane polymers were equilibrated using tetramethylammonium hydroxide pentahydrate at 80°C for 24 hours (Spinu and McGrath,

1988). The catalyst was eventually decomposed by heating the mixture to 140 or 145°C for 15 minutes after which time no catalyst was left in solution.

In 1972, Carl Litteral was assigned a patent which used macroreticular sulfonic acid resin beads to equilibrate organosiloxanes (Litteral, 1972). Columns of 5 different resins were investigated at 90°C, each with a different pore volume. Resins with a pore volume above 0.01 mL/g showed increased rates of catalysis with those above 0.03 mL/g giving the highest reaction rates and shortest reaction times at this temperature. The larger the pore volume, the greater was the degree of siloxane rearrangement as measured by a change in viscosity. No viscosity changes were reported in pore volumes of less than 0.005 mL/g.

In the case of a solid colloid with PDMS polymers attached to the surface, a solid catalyst may be employed. This type of catalyst will not penetrate into the colloid core and react with any occluded PDMS if such is present. Solids of the same dimensions or larger than the colloid would selectively react with surface PDMS only. The above-mentioned resins would be a valid choice as would montmorillonite clay.

Montmorillonite refers to a group of clays of similar structure derived from either the mineral pyrophyllite or talc (van Olphen, 1977). Both minerals have the same three-layer structure made up of one octahedral sheet containing aluminum, oxygen and hydroxyl groups sandwiched between two tetrahedral sheets made up of silicon, oxygen and hydroxyl groups. The three layers are held together by van der Waals forces which arise from the sharing of oxygen atoms between the metals in the two layers.

When atomic substitutions are introduced into either pyrophyllite or talc, montmorillonite clay results. Typically, in the tetrahedral sheet, silicon is replaced by trivalent aluminum and in the octahedral sheet, trivalent aluminum may be replaced by magnesium, iron, chromium, zinc, lithium and other atoms. As an atom of lower positive valency replaces one of higher valency, an excess of negative charge results. The excess charge is neutralized by adsorbed cations which can easily be exchanged by other available cations in solution. Therefore, montmorillonite clay may be easily acidified with hydrochloric acid.

The earliest reported reactions of PDMS with acidified clay have been carried out in the Ukraine and Czechoslovakia in the mid 1960's. The only available early English literature is of the use of soil samples containing montmorillonite clay to catalyze the breakdown (equilibration) of PDMS (Buch, 1979). Both acidified and non-acidified soils catalyze the formation of low molecular weight silicone oils. Most recently, Shiseido Cosmetics in Japan have applied for a patent in which the use of various clays with siloxanes of 3 to 6 D units is described (Shiseido, 1986).

## CHAPTER 2

### EXPERIMENTAL

#### 2.1. Preparation of PDMS and PDMS-V Stabilized Latices

Prior to reaction, the inhibitor hydroquinone was removed from methyl methacrylate monomer by washing it twice with an equal volume of 10% potassium hydroxide for 5 minutes. The aqueous layer was removed and the methyl methacrylate dried over sodium sulfate, filtered and shaken with 5Å molecular sieves for 8 hours. The sieves were filtered off and the monomer was distilled under vacuum in the presence of sulfur and then stored at 4°C before use. The methyl methacrylate was stable over 4 months at 4°C. Azobis(isobutyronitrile) [2,2'-azobis(2-methyl-propionitrile), AIBN] was recrystallized three times from hot methanol before use to remove its inhibitor.

For the preparation of trimethylsilyl terminated or vinyl terminated PDMS stabilized latex, 20 g of PDMS were dissolved in 375 mL (0.256 kg) of n-heptane. The stirred solution was transferred to a one litre glass reaction kettle and warmed to 70°C for 30 minutes while bubbling ultra high purity [UHP] nitrogen gas through the mixture. After 30 minutes, 2.5 g of benzoyl peroxide [BPO] or 1.1 g of AIBN (both  $2.4 \times 10^{-2}$  molal [m]) and 40 mL (1.48 m) of MMA were added under stirring. The final mixture was allowed to react at 70°C for 7 hours in the presence of nitrogen. An opaque white latex resulted.

To remove unreacted PDMS, MMA and the initiator, the final latex was centrifuged at 7 000 rpm for 10 minutes and the clear supernatant decanted. Fresh n-heptane was added to the solid and the procedure repeated twice more.

The amount of silicone associated with the latex particles was determined by nuclear magnetic resonance spectroscopy (NMR). The dispersions were dried using a rotary evaporator under mild heating. The dried latex powder was dissolved in deuterated chloroform and a proton

spectrum was recorded using a Varian AC200 spectrometer. There was no sign of residual heptane in the NMR spectra. The ratio of PMMA to PDMS was determined by comparing the areas of the PMMA methyl ester protons (3.9 ppm) and the silicone methyl protons (0.2 ppm). Replicated analyses showed that the NMR results were reproducible to within 3%.

The particle sizes for the PDMS and PDMS-V stabilized latices were determined using a Nicomp Model 370 Dynamic Light Scattering apparatus. The theory is discussed in the Appendix. Because an organic solvent was employed, the Nicomp was used with a glass cuvette in the chamber. Standard deviations were generally no larger than 30% using dynamic light scattering. The measurements obtained on the Nicomp 370 were verified using transmission electron microscopy and agreed well with those generated by the light scattering device.

## 2.2. Preparation and Reaction of PMMA Latices with Functionalized PDMS

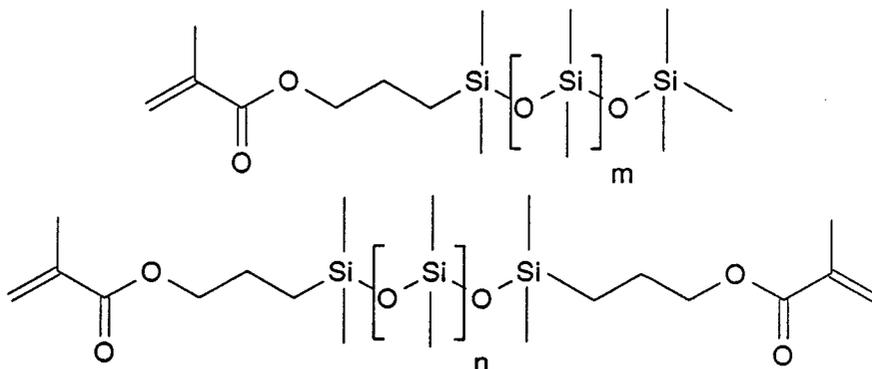


Figure 2.1: PDMS functionalized with methacryloxypropyl groups on one and two ends respectively.

In the case of the functionalized siloxanes shown in Figure 2.1, 3 g ( $3.9 \times 10^{-4}$  *m*) of PDMS was dissolved in 375 mL (0.256 kg) of *n*-heptane. The stirred solution was transferred to a one litre reaction kettle and warmed to 70°C for 30 minutes while bubbling UHP nitrogen through the mixture. After 30 minutes, 1.1 g AIBN ( $2.4 \times 10^{-2}$  *m*) and 40 mL of MMA (1.48 *m*) were added while stirring. The final mixture was allowed to react for 7 hours under a nitrogen blanket.

Suspensions were cleaned and the amount of silicone associated with the particles obtained in a manner identical to that for the above latices.

To prepare the catalyst for the equilibration reaction, montmorillonite clay was stirred in 1N hydrochloric acid for 4 hours at room temperature. The suspension was then centrifuged at 1000 rpm for 5 minutes and the clear supernatant decanted, fresh water added and the clay resuspended. This procedure was repeated until the washings were neutral in pH, usually 4 more times. The moist clay was dried overnight at 105°C and kept at 105°C until use.

For equilibration reactions, the cleaned latices were diluted to 4% solids by weight in n-heptane and sonicated for 15 seconds before reacting. The equilibration mixture consisted of 3 mL of the dilute latex and 5 mL of n-heptane in the presence of 10 mg of acidified montmorillonite clay. The closed equilibration vessels were stirred and maintained at 70°C for the entire reaction. Samples were removed at specific intervals and analyzed for particle size distribution and silicone content. The particle size distributions were determined using a Horiba CAPA -700 Particle Size Distribution Analyzer. The centrifugal particle size analysis is based on the principle of liquid phase sedimentation. The measurements are made using optical transmission and combining Stokes' sedimentation equation with the absorbance and concentration of the particle suspension.

Particles in a gravitational field will settle at a constant velocity according to Stokes' law. In a polydisperse suspension, particles will settle according to their diameter with the large ones settling first followed by successively smaller ones. Since smaller particles may require considerable time to settle in a gravitational field, and some may never settle, the measuring time can be accelerated by using a centrifugal field. A photodiode is used to measure the degree of particle sedimentation by measuring the amount of light transmitted from a light source. The change in concentration is expressed in units of absorbance. The relationship between absorbance and size and number of particles can be expressed as follows

$$\log I_0 - \log I_t = K \sum_i^n k(D_i) N_i D_i^2 \quad (2.1)$$

where  $I_0$  is the incident light intensity,  $I_t$  is the transmitted light intensity,  $K$  is the optical coefficient of the cell including the form factor of the sample,  $k$  is the absorption coefficient of the particle  $D_i$ , and  $N$  is the number of particles of diameter  $D$ . The measurements are obtained in an area weighted mode as illustrated by the dependence on  $ND^2$  and can be converted into other weightings such as volume, length and intensity.

For the latices containing functionalized PDMS stabilizer, the gradient or accelerated analysis mode was chosen at a volume weighting, since results in this weighting mode corresponded to the best agreement with a polystyrene latex standard. The acceleration was 960 RPM/minute in every case.

## CHAPTER 3

### PREPARATION AND CHARACTERIZATION

The results presented and discussed in this chapter are restricted to studies on latices stabilized by trimethylsilyl terminated and vinyl terminated PDMS. Latices with functionalized silicone stabilizers will be discussed in the next chapter.

#### 3.1. Trimethylsilyl Terminated PDMS Stabilizer

The first series of latices was prepared using a constant quantity of poly(methyl methacrylate) in the presence of trimethylsilyl terminated PDMS of varying chain lengths. The PDMS ranged in molecular weight from 1 250 to 308 000 corresponding to a degree of polymerization (DP) of 17 to 4 162. The weight concentration of PDMS added was held constant at 20 g (6 weight percent with respect to MMA) during the synthesis of these latices.

Stable dispersions were only obtained with trimethylsilyl terminated PDMS stabilizer of molecular weight 62 700 or larger. The resulting particle diameters are given in Table 3.1 as measured using a Nicomp 370 dynamic light scattering apparatus in the number weighted mode. Transmission electron micrographs were carried out randomly on some of the latices and confirmed the DLS sizes to within 15%.

Viscosity (m <sup>2</sup> /s)	Molecular Weight	DP	Diameter (nm)	Silicone Content	
				Weight %	Molecules/m <sup>2</sup>
10 <sup>-3</sup>	1250	16	*		
10 <sup>-2</sup>	1970	26	*		
10 <sup>-1</sup>	28000	378	*		
1	62700	847	1289	1.98	4.87x10 <sup>16</sup>
10	139000	1878	1255	2.08	1.28x10 <sup>16</sup>
100	308000	4162	899	17.4	6.05x10 <sup>16</sup>

Table 3.1: Correspondence of stabilizer molecular weight to latex particle size and silicone content for PDMS stabilized latex in n-heptane. (\* = flocculated)

The surface concentration of grafted PDMS was calculated from the amount of grafted silicone, as determined by NMR, and the silicone molecular weight. The determinations are considered accurate since the PDMS has a narrow molecular weight distribution. However, it was assumed that all PDMS was located on the particle surface and that the particles were hard spheres.

Dispersions stabilized by PDMS of molecular weight less than 62 700 (DP = 847) flocculated during synthesis. In this case, the van der Waals attractive forces between two colloidal particles is large enough to overcome the repulsive forces between the stabilizing moieties. If the stabilizer is of high molecular weight or long chain length, the van der Waals attraction forces between the core particles is too small to induce flocculation and repulsion dominates (Napper, 1983).

In order to discuss the various reasons for the formation of stable and unstable latex, it is important that the events which occur during the particle formation stage or nucleation are discussed first. The two classical models for nucleation are self-nucleation and aggregative nucleation. During self-nucleation, a growing oligomer chain collapses into a small precursor particle when its limit of solubility in the continuous phase is reached. Therefore, every chain initiated should form one particle. In the process of aggregative nucleation, some of the growing oligomer chains associate with each other as their molecular weight and concentration increases. The formation of new particles is inhibited since most newly formed oligomers are captured before they can form a new nucleus.

As is usually the case, the most likely mechanism operating in non-aqueous dispersions is a combination of the two models proposed. According to a model by Fitch and Tsai, most oligomers are probably irreversibly captured before they reach the critical size required for self-nucleation, but those which grow rapidly, especially during the initial stages of polymerization when a high monomer concentration is present, may form nuclei which consist of one long oligomer chain (Fitch and Tsai, 1971). Self nucleated precursor particles may adsorb shorter chain oligomers to increase their internal radical concentration which is required for further particle growth.

The presence of stabilizer during nucleation increases the rate of nucleation. In the self-nucleation process, growing oligomers which associate with stabilizer moieties reach a molecular weight at or near the critical limit of solubility faster than in the absence of stabilizer. In addition, by association with stabilizer, the polarity of the oligomer is changed and the rate of oligomer aggregation decreased. During aggregative nucleation, stabilizer moieties associate with oligomers and reduce the surface tension between the precursor particle and the solvent and decrease the rate of capture of new oligomers. In both cases, particles continue to grow to their final size by polymerizing monomer which partitions itself between the solvent and the growing particle as is evidenced by swelling studies (Barrett, 1975). These particle formation theories have recently been qualitatively verified by Saam and Tsai with respect to the PMMA-PDMS system used in this work as reported earlier (Saam and Tsai, 1974).

Factors contributing to the flocculation for the PMMA latices in this work which are stabilized by shorter chain siloxanes may include incomplete surface coverage, a thin steric layer or a large particle size. As the particle size increases, the London-van der Waals attraction also increases and therefore latices having larger particle sizes would be easier to flocculate even in a good solvent for the stabilizing moiety.

The PMMA-PDMS particles in this study increase in size with decreasing stabilizer chain length. This trend can be extrapolated to the flocculated latices where particle sizes could not be determined, but are believed to be increasing with decreasing stabilizer chain length. Everett and Stageman have found similar results when measuring critical flocculation temperatures for PMMA particles with stabilizer chains of different molecular weights (Everett and Stageman, 1977). Larger particles flocculated at lower temperatures than smaller particles under the identical conditions.

Incomplete surface coverage may be a possible contributor to flocculation in these latices when shorter chain graft stabilizer is employed. During the nucleation stage, as the oligomers grow from a soluble to an insoluble chain, the graft precursor polymer chains aggregate into precursor particles. During this process, the free radicals present are incorporated into the

precursor particles and the free monomer distributes itself between the solvent and the precursor particle according to its solubility and polarity. The polymer chains in the precursor particle which contain radicals will continue to polymerize with fresh monomer and the particle size will increase until the monomer is depleted, the radicals terminate or a combination of these two events occurs. During the growth stage, the surface area of the particle may increase to a size larger than one which can effectively be stabilized by the amount of graft stabilizer which has been incorporated into the growing particles. If this event occurs, the growing particles which can no longer be dispersed adequately will aggregate. Due to the covalent grafting of the stabilizer chains onto the polymer, the stabilizer cannot redistribute itself within the flocculated particles and produce stabilized aggregates as may be the case with more loosely held stabilizer moieties in other systems (Barrett, 1975).

Multiple attachments of the stabilizer chains to the particle surface could occur and thereby decrease the thickness of the effective stabilizer layer on the particle surface. Direct evidence for the number of attachments cannot be obtained since the total amount of silicone incorporated into the particle is less than 10 percent. No method currently available can determine the difference between one or more attachments in a polymer of degree of polymerization in the thousands or higher. Longer chains are more likely to exhibit multiple attachments than shorter chains. However, flocculation occurs at chain lengths shorter than a DP of 847. Therefore, multiple attachments are unlikely to be occurring in the PMMA-PDMS system.

Flocculation is sometimes thought to occur as a result of a stabilizer segment bridging two core particles (Napper, 1983). Longer stabilizer chains should be able to bridge larger distance and the particles need not approach one another nearly as closely as when a short chain stabilizer is employed. Flocculation in this system occurs as shorter chain stabilizers are employed. Due to these contradictory criteria, flocculation due to bridging is believed to be an unlikely reason for the instability of PMMA core particles as evidenced in this study.

Hence the most likely contributing factor to unstable particles is the short chain length of the stabilizer moieties. The repulsion between two short chain stabilizing segments would be insufficient to overcome the London-van der Waals attraction between the cores of two fairly large particles.

Barrett and coworkers at ICI have found that as the proportion of reactive groups in the stabilizer is raised, or if the type of reactive group is replaced with one which has a higher reactivity to grafting, smaller particles are obtained (Barrett, 1975). The parallel results are seen in this study where the particle size decreases in the presence of longer graft stabilizer chains. Since all methyl groups on the siloxane backbone have similar reactivities to hydrogen abstraction by the peroxide radical, longer stabilizer chains with more silylmethyl groups present during nucleation will produce smaller particles.

### 3.2. Vinyl Terminated PDMS Stabilizer

A second stabilizer type which was systematically investigated was vinyl terminated PDMS. As in the trimethylsilyl terminated PDMS, the concentration of the silicone, the methyl methacrylate monomer and the initiator were held constant in all cases. The only variable was the chain length or molecular weight of the stabilizer moieties.

Viscosity (m <sup>2</sup> /s)	Molecular Weight	DP	Diameter (nm)	Silicone Content	
				Weight %	Molecules/m <sup>2</sup>
5x10 <sup>-4</sup>	770	10	*		
10 <sup>-2</sup>	5970	80	1390	1.09	3.02x10 <sup>17</sup>
10 <sup>-1</sup>	28000	378	1360	1.49	8.62x10 <sup>16</sup>
1	62700	847	1150	1.55	3.39x10 <sup>16</sup>
10	139000	1878	1060	2.86	2.60x10 <sup>16</sup>
100	308000	4162	830	10.2	3.26x10 <sup>16</sup>

Table 3.2: Correspondence of stabilizer molecular weight to latex particles size and silicone content for PDMS-V stabilized latex in n-heptane. (\* = flocculated)

Table 3.3 shows the same trend as that seen for PDMS stabilized latices. The limit for stable particles, however occurs at a degree of polymerization of 81 versus that of 847 for PDMS. The degree of polymerization of PDMS-V at the point of flocculation is one tenth that of the

trimethylsilyl stabilizer indicating that the vinyl terminated stabilizer is more effective in preventing aggregation between two particles with small stabilizer layer thickness. Intuitively, this suggests that a higher concentration of chains must be present to prevent flocculation of the larger particles, and this is indeed found. In addition, it is believed that the vinyl terminated PDMS is grafted onto the PMMA mainly by the terminal vinyl groups as they are more reactive to radical initiation as compared to the methyl groups on the siloxane backbone (Saam and Gordon, 1970). Therefore, the average tail length of the grafted vinyl stabilizer extending into the surrounding medium if one end of the molecule is attached is that of the entire PDMS-V chain. In the case of PDMS, the grafting site to PMMA could be any of the methyl groups along the backbone. In PDMS, the average length of the tails extending from the PMMA core would be half of that of the entire PDMS chain (Pelton, Osterroth and Brook, 1990).

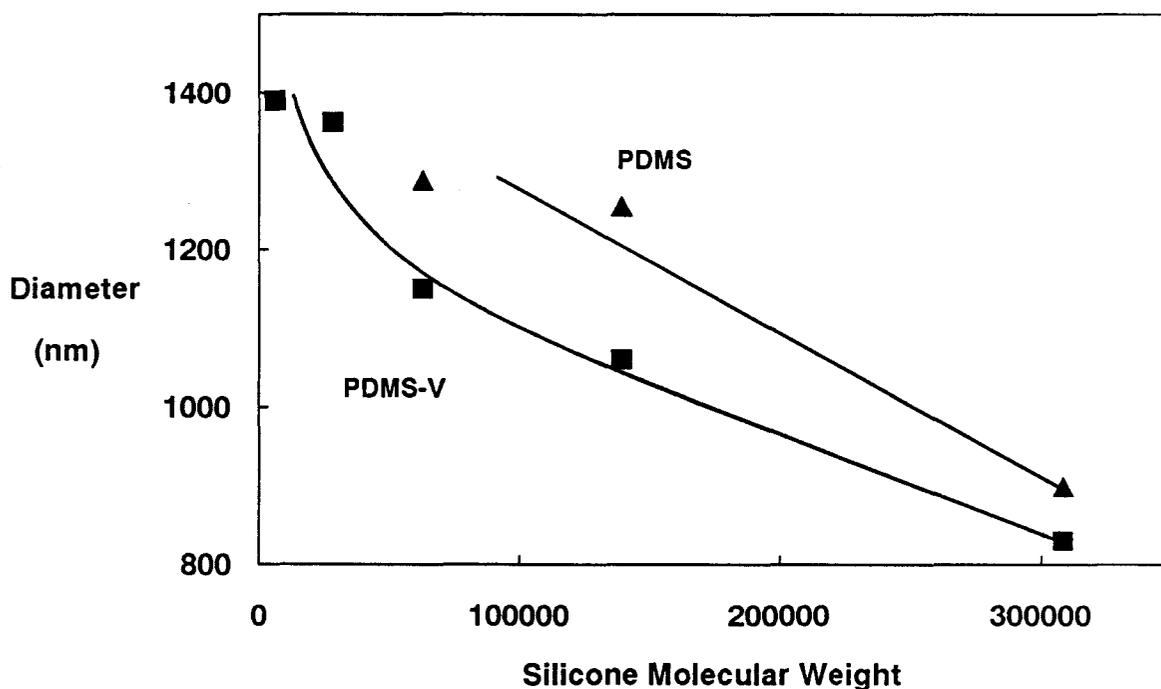


Figure 3.1: Comparison between particle diameter and silicone stabilizer molecular weight for PDMS and PDMS-V stabilized latices.

If the data from Table 3.1 and 3.2 are plotted on the same graph, the PDMS-V stabilized particles generally have a lower particle diameter. As explained previously, if the reactive group of the stabilizer is replaced by one which is more reactive to grafting or initiation, smaller particles result (Barrett, 1975). The results of this study are in full support of this theory since vinyl groups have a higher reactivity toward a radical species than a methyl proton has toward abstraction by a radical group.

### 3.3. Influence of Stabilizer Concentration

The influence of varying the stabilizer concentration on the resulting latices was investigated systematically. The results for PDMS stabilized latices are summarized in Table 3.3. Silicone oil was of a constant molecular weight of 139 000 (DP 1 878).

PDMS Concentration (molal)	Diameter (nm)	Silicone Content	
		Weight %	Molecules/m <sup>2</sup>
6.20x10 <sup>-5</sup>	*		
1.24x10 <sup>-4</sup>	*		
2.48x10 <sup>-4</sup>	1850	0.39	6.25x10 <sup>15</sup>
4.96x10 <sup>-4</sup>	1260	1.18	1.28x10 <sup>16</sup>
7.44x10 <sup>-4</sup>	1100	11.64	1.10x10 <sup>17</sup>
9.92x10 <sup>-4</sup>	848	8.63	8.44x10 <sup>16</sup>

Table 3.3: Correlation between PDMS concentration, latex particle size and silicone content. (\* = flocculated)

Stable latices were only obtained at 2.48x10<sup>-4</sup> m and above. The observation that less than 10% of the added silicone is incorporated into the final particles supports the view that the methyl groups on the siloxane chains are slow to react to form grafts to PMMA during the nucleation stage. Particle size is again observed to decrease with increasing PDMS concentration which reflects the increase in available methyl groups for grafting to the PMMA core polymer generating a higher number of graft precursor molecules during nucleation.

PDMS-V Concentration (molal)	Diameter (nm)	Silicone Content	
		Weight %	Molecules/m <sup>2</sup>
6.20x10 <sup>-5</sup>	*		
1.24x10 <sup>-4</sup>	1330	0.81	9.45x10 <sup>15</sup>
2.48x10 <sup>-4</sup>	1010	2.97	1.08x10 <sup>16</sup>
4.96x10 <sup>-4</sup>	1060	2.86	2.40x10 <sup>16</sup>
7.44x10 <sup>-4</sup>	853	6.67	1.14x10 <sup>17</sup>
9.92x10 <sup>-4</sup>	841	10.9	2.08x10 <sup>17</sup>

Table 3.4: Correlation between PDMS-V concentration, latex particle size and silicone content. (\* = flocculated)

In comparison, vinyl terminated PDMS gives stable latices at a slightly lower PDMS concentration of  $1.24 \times 10^{-4} m$ . This result reflects the type of grafting operating. The tails on the surface of these colloids have different lengths. For PDMS, the average tail length is 939 repeat units, half of that of the entire PDMS molecule of DP 1 878. In the case of PDMS-V grafted at the terminal vinyl groups, the tail length is twice that of PDMS because the molecule can extend to the full length of the polymer chain. The results agree with this prediction. Table 3.4 also supports the assumption that vinyl groups are more reactive to radical initiation than the methyl groups in PDMS are to hydrogen abstraction since the weight percent of silicone in the final PDMS-V particle is approximately twice that of the PDMS stabilized ones. Higher reactivity of the stabilizer produces more grafts to PMMA oligomers during nucleation and will in turn result in more stabilizer found in the final latex particle (Fitch and Tsai, 1970, Barrett, 1975). Although all conditions were identical for the two types of latex, vinyl stabilized latices gave consistently lower diameters than PDMS stabilized ones for the same reason as discussed in the previous section.

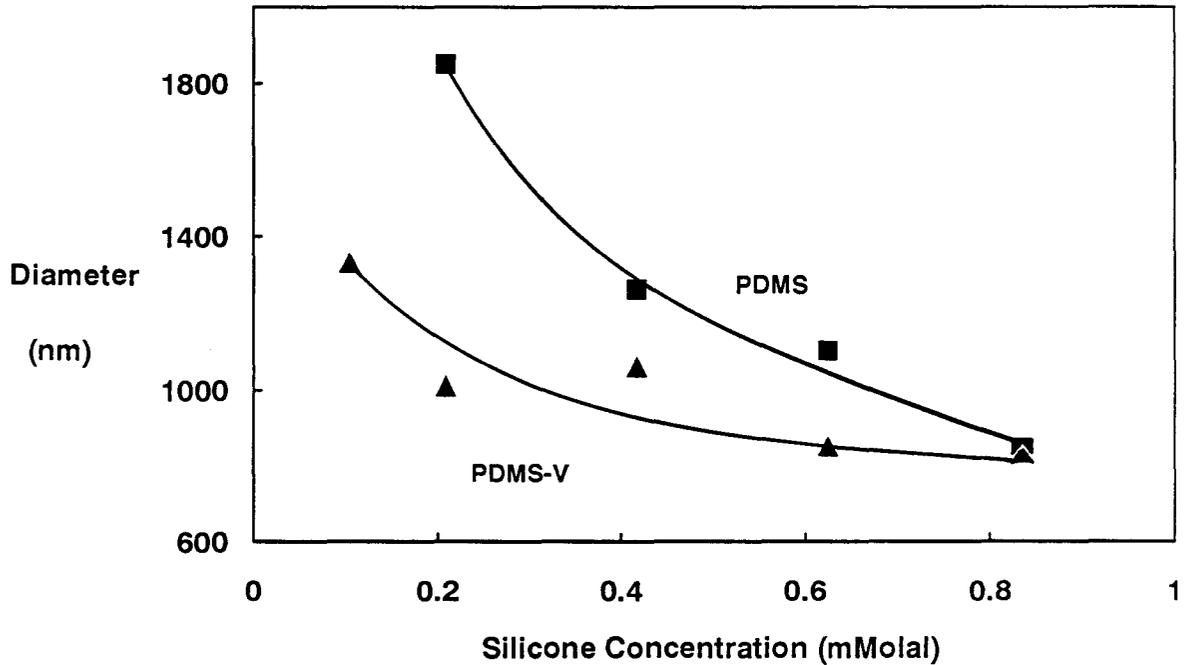


Figure 3.2: Comparison between particle diameter and silicone stabilizer concentration for PDMS and PDMS-V stabilized latices.

#### 3.4. Effect of Initiator Concentration

The effect of benzoyl peroxide concentration on the resulting latex was investigated for both PDMS and PDMS-V stabilized latices. PDMS stabilized latices were unstable at a concentration of  $1.42 \times 10^{-2} m$  of BPO whereas the limit of instability was found to be at  $3.56 \times 10^{-3} m$  for PDMS-V stabilized latex. The fact that PMMA in the presence of PDMS-V will form a stable latex at a concentration of one order of magnitude less than that necessary for PDMS further illustrates the fact that the vinyl groups are more reactive than the methyl hydrogens are to hydrogen abstraction.

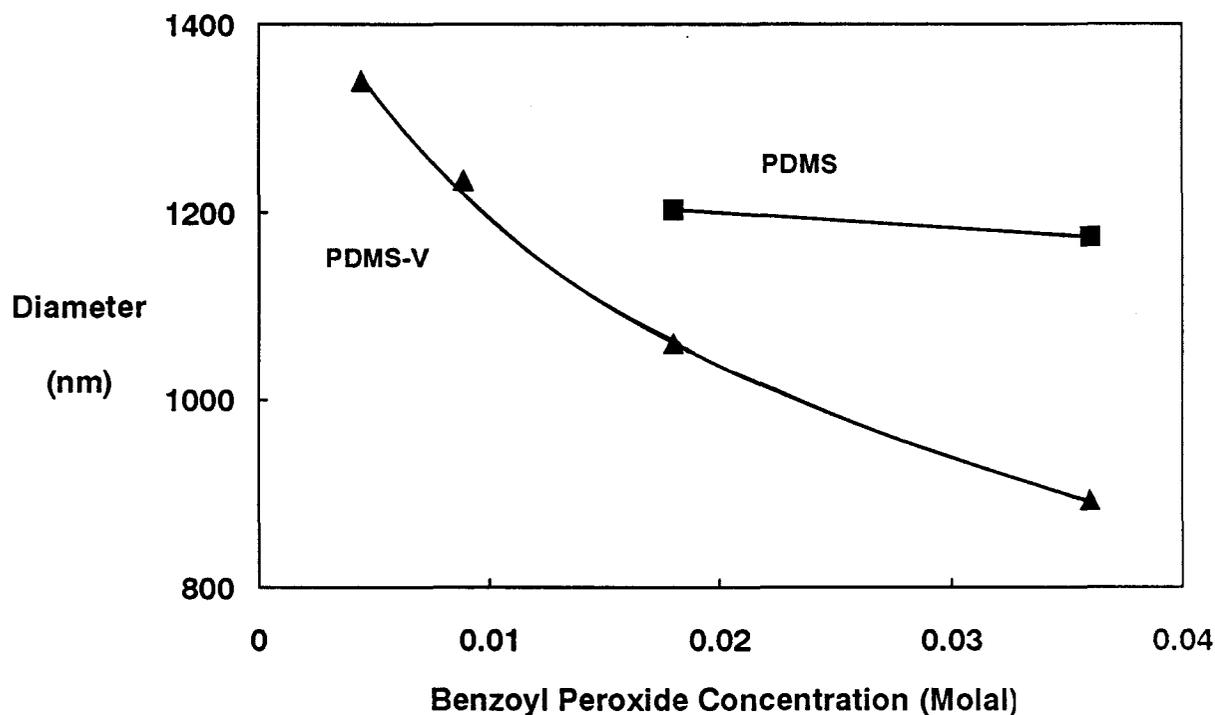


Figure 3.3: Comparison between particle size and benzoyl peroxide concentration for PDMS and PDMS-V stabilized latices in n-heptane.

More evidence to support this theory arose when AIBN was used to initiate the identical reaction mixtures as were previously initiated with BPO. AIBN cannot successfully abstract hydrogens from the methyl groups on polydimethylsiloxane (Saam and Gordon, 1970). Stable latex was not obtained when AIBN was used to initiate grafting of high molecular weight PDMS to PMMA. In the case of PDMS-V, however, stable latex of similar diameter to those initiated with BPO resulted when AIBN was used. In each case, the same initiator concentrations were used and all other conditions were identical to the preparations illustrated in Tables 3.1 and 3.3.

	Molecular Weight	Diameter (nm)	
		BPO	AIBN
PDMS	139000	1255	*
PDMS	308000	899	*
PDMS-V	5970	1360	1671
PDMS-V	139000	1060	854

Table 3.5: Comparison of BPO and AIBN for PDMS and PDMS-V under identical reaction conditions.

### 3.5. Latex Morphology

In the presence of limiting amounts of stabilizer during particle growth, flocculation of the particles results. However, under certain circumstances, especially with very soft polymers, controlled flocculation may take place. During this process, smaller particles associate to form fewer and larger particles with a smaller overall surface area.

When PMMA is polymerized in the presence of vinyl terminated PDMS, smooth particles result as is expected for nonaqueous dispersion polymerization in the presence of adequate stabilizer. Smooth spherical particles are formed when particle growth occurs from monomer swollen particles (Barrett, 1975). However, particles which result from the agglomeration of smaller primary particles can exhibit a rough surface morphology. PMMA polymerized in the presence of trimethylsilyl terminated PDMS exhibits a much rougher surface than seen in the case of PDMS-V stabilized particles. The electron micrographs in Figure 3.4 illustrate the difference between the two types of latex.

The agglomeration of smaller primary particles in the case of PDMS stabilized latex can arise for two different reasons. Either the preparation does not contain sufficient stabilizer with respect to the amount of monomer and initiator present, or the grafting process of stabilizer to PMMA oligomers is inadequate. Since in all preparations with trimethylsilyl terminated stabilizer, the final latex contains large quantities of unreacted silicones, the first case can be excluded and aggregation of primary particles is most likely due to insufficient grafting of stabilizer in the case of PDMS. This explanation supports earlier conclusions which invoked the fact that PDMS-V is more reactive to radical initiation than PDMS is to proton abstraction. The conclusions with

respect to group reactivities toward radical attack and the resulting particle morphologies are in full support of earlier findings (Barrett, 1975).

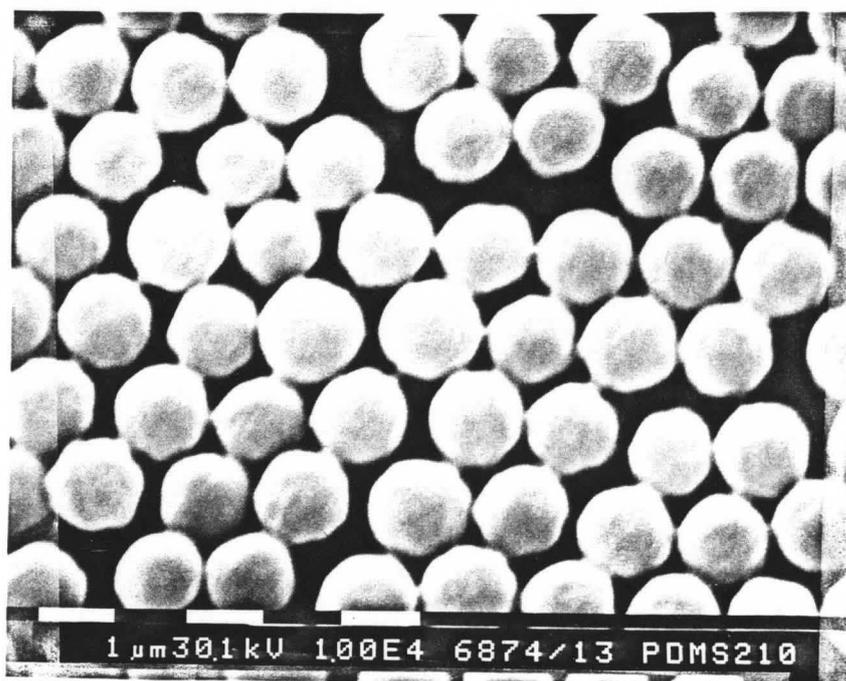
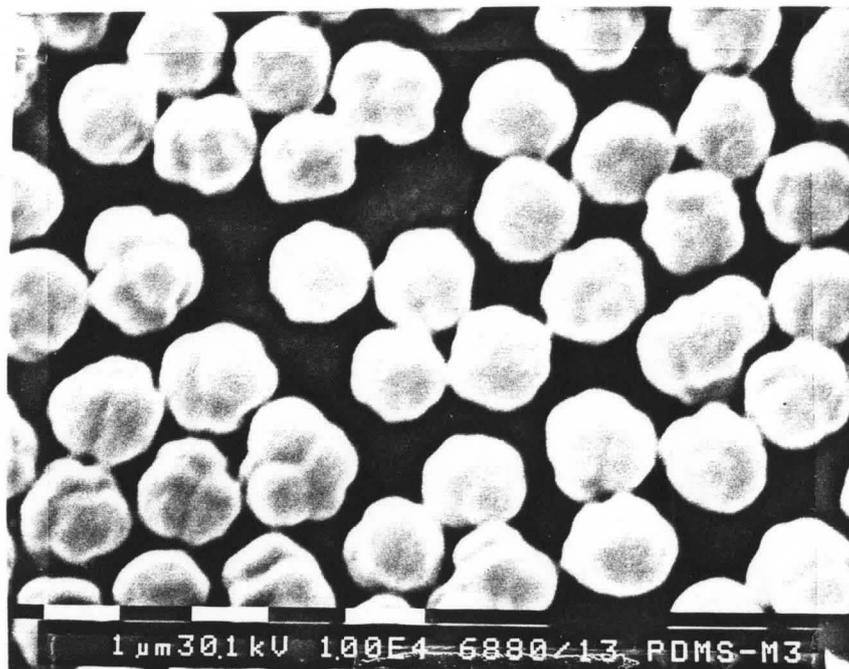


Figure 3.4: Scanning electron micrographs of PDMS (above) and PDMS-V (below) stabilized PMMA particles.

## CHAPTER 4

### FLOCCULATION OF PMMA-PDMS LATICES

In this chapter, the results of studies on silicone stabilized PMMA in the presence of a catalyst which degrades the steric stabilizer layer will be discussed. The silicone stabilizing polymers contain methacryloxypropyl functional groups which will ensure that grafting occurs at well-defined points on the polymer chain. Because the methacryloxy groups are identical in structure to the methyl methacrylate monomer, it is believed that grafting will occur through the vinyl group and not through a methyl group on the siloxane backbone. Hence, the graft points can be defined more easily and the type of tails extending into the surrounding medium is better known. The stabilizer moieties are of two types. One consists of a PDMS chain of DP 415 with both ends containing a methacryloxypropyl functional group. The other consists of a PDMS chain with DP 289 having one end functionalized with the methacryloxypropyl group and the other end having a trimethylsilyl group. The former will be considered first.

#### 4.1. Difunctional PDMS Stabilizer

Particles synthesized in the presence of difunctional PDMS have an average diameter of 840 nm with a standard deviation of 40%. The surface morphology is envisioned as follows.

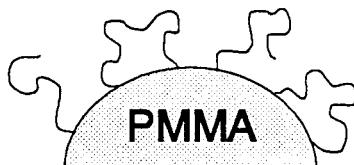


Figure 4.1: Grafting of difunctional PDMS to the particle surface.

Some PDMS chains could also act as interparticle bridges due to their dual functionalization.

Attachment via the siloxymethyl groups is rarely if ever found because of the initiator being AIBN.

The reason can be found in the previous chapter and Saam and Gordon's work (Saam and Gordon, 1970).

The particle size is smaller than that obtained with both vinyl and trimethylsilyl terminated PDMS. The main reason for this result is the higher reactivity of the methacryl groups to the AIBN initiator. There should be little difference in reactivity between a methyl methacrylate monomer unit and the terminal methacryl group on PDMS during polymerization. It is believed that the attached PDMS chain will decrease the mobility of the methyl methacrylate group, and diffusion of the prepolymer will be slowed with respect to methyl methacrylate monomer.

Particles are still slightly larger than those obtained by Saam and Tsai who used mercaptosilicone graft precursors (Saam and Tsai, 1974). Their particle sizes were 0.12  $\mu\text{m}$  and reflect the radical initiator used to abstract protons from the highly reactive mercapto groups (Saam and Gordon, 1970). Silicone incorporation was 3.5% with respect to Saam and Tsai's 4.5% (Saam and Tsai, 1974). Again Saam and Tsai's results reflect the use of a stabilizer with a higher reactivity (Barrett, 1975).

The amount of silicone incorporated into the particles is 3.9 mole percent which is higher than that incorporated with both PDMS and PDMS-V although more silicone was available during the nucleation stage for PDMS and PDMS-V. The increase in incorporated silicone is evidence for the higher reactivity of the methacryl groups to AIBN as compared to the vinyl groups or methyl hydrogens to BPO. It also supports the notion that more PDMS graft precursor particles were generated during the nucleation period just prior to particle formation. Given a higher reactivity of methacryl groups of PDMS to the AIBN initiator, the graft precursor particles which form during the initial polymerization stage should contain relatively short segments of PMMA homopolymer. If the reactivity of the PDMS molecule is lower, PMMA can form longer homopolymer chains before a PDMS moiety is successfully attached to the growing chain.

This PMMA latex stabilized by monofunctional PDMS is one of two which were studied to determine the minimum or critical silicone concentration on the surface necessary for stable PMMA particles. The particles were reacted with a catalytic amount of montmorillonite clay to

bring about equilibration of the siloxane groups as outlined in the Introduction. In this study as compared to earlier ones (Napper, 1970, Dawkins and Taylor, 1980), the solvent remained unchanged from that present during synthesis, hence the solvation conditions for the silicone polymer remained the same during the entire equilibration reaction. The particle size distribution and silicone content were monitored throughout the equilibration. Table 4.1 summarizes the results for difunctional PDMS stabilizer.

Time (h)	Diameter ( $\mu\text{m}$ )	Percent Silicone
0	0.84	3.9
3	0.67	3.9
6	1.23	3.9
20	1.11	3.6
24	1.00	3.6
28	0.96	3.4
44	1.20	3.2
48	0.83	3.2
52	0.84	3.2
56	0.81	3.1
58	30.1	3.0
60	32.2	3.0

Table 4.1: Particle size and silicone content during equilibration for PMMA latex stabilized by difunctional PDMS.

The critical flocculation behaviour is illustrated in Figure 4.2. The silicone concentration on the surface decreases steadily but the particle size distribution remains unchanged until the critical silicone concentration is reached and flocculation occurs. For this particular latex, a decrease in silicone of 23% results in flocculation.

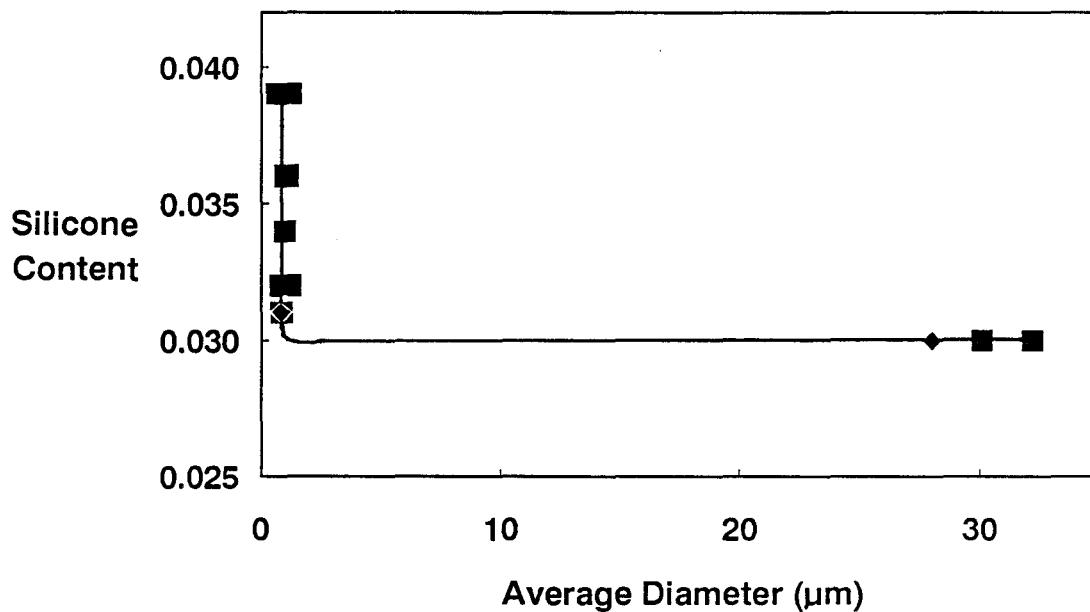


Figure 4.2: Equilibration of PMMA latex stabilized by difunctionalized PDMS in n-heptane. Diamonds represent replicated analyses.

It is believed that during the reaction, the surface silicone undergoes equilibration to generate both linear and cyclic short chain oligomers as chains continually break and reform. The steady decrease of PDMS attached to the particle surface is illustrated in Figure 4.3.

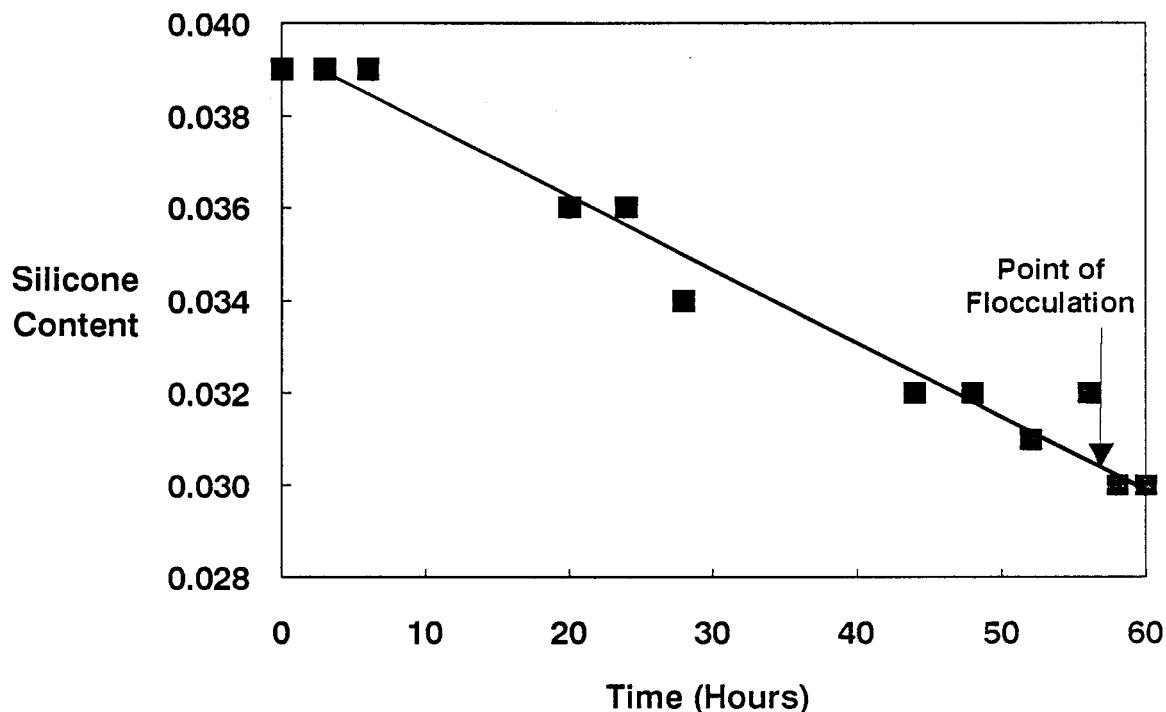


Figure 4.3: Silicone content of the latex particles stabilized by difunctionalized PDMS over time during equilibration.

Flocculation of the latex occurs at 3.0 mole percent silicone with respect to PMMA. At this silicone concentration, the steric repulsive forces between any two PMMA particles are no longer strong enough to overcome the interparticle attraction. Since the surface coverage remains constant at  $9.72 \times 10^{16}$  molecules/m<sup>2</sup> and the solvation conditions have not changed, the flocculation is simply due to the thinner steric layer which is unable to stabilize the particles.

Theoretically, flocculation of the latices under study may occur as a result of two distinct events. The most likely occurrence during silicone equilibration is that all surface chains are degraded simultaneously and at the same rate so that the number of chains remains constant but the chain length decreases. In this case, flocculation is a result of the steric layer becoming too thin to generate repulsive forces large enough to overcome interparticle attraction.

The other event possible during silicone equilibration is that the particle will adhere to the clay particle and the area in close proximity to the catalyst will be degraded exclusively. In the event that two particles with areas devoid of stabilizer come in close proximity, flocculation will occur. The criticality of the point of flocculation does not support the latter theory consistently. If

adhesion of the latex to the clay particle occurs, degradation should be a relatively fast process because of the close contact of the two entities. This is not seen. Flocculation occurs after 56 hours. In addition, flocculation should not be a critical phenomenon which exhibits an increase in particle size of one order of magnitude. The concentration of montmorillonite clay was relatively low with respect to the latex particles, so that it is unlikely that one latex particle adheres to more than one clay particle. Therefore, flocs should be made up of a maximum of 3 or 4 particles and the particle size distribution should shift gradually to an increasing diameter. What is found, however, is that the particle size distribution upon flocculation shifts spontaneously from 1  $\mu\text{m}$  to 30  $\mu\text{m}$  with few flocs of intermediate size as shown in Figure 4.4. Therefore, formation of areas without PDMS on the latex particle surface is thought to be unlikely.

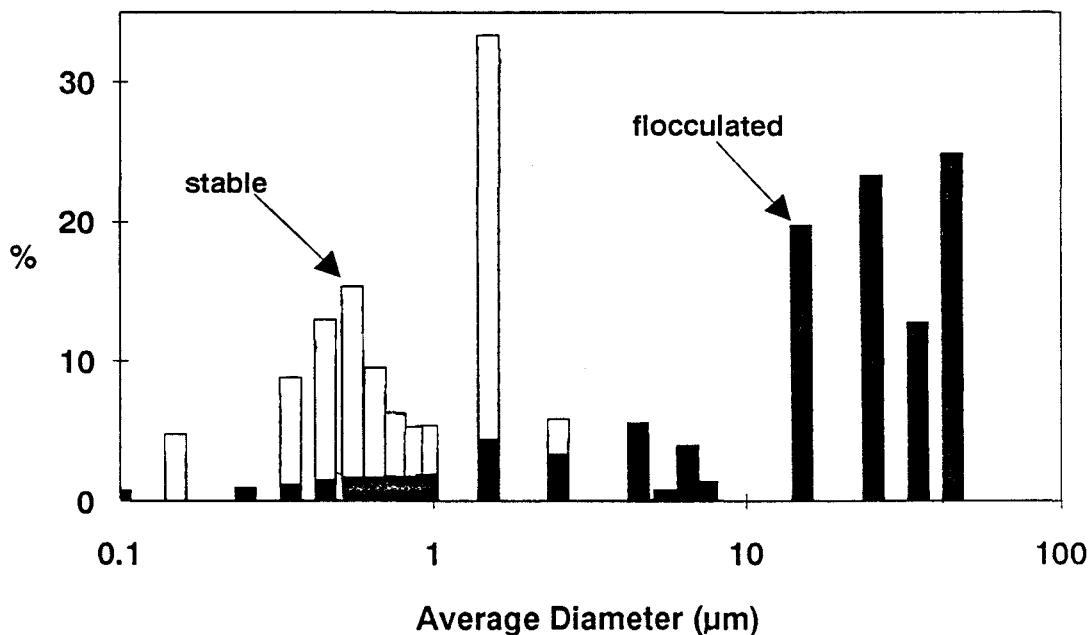


Figure 4.4: Particle size distribution for latex stabilized with difunctional PDMS before and after equilibration.

#### 4.2. Monofunctional PDMS Stabilizer

In this part of the study, particles were synthesized in the presence of PDMS which was terminated with a methacryloxypropyl group on one chain end only, the other being trimethylsilyl functionalized. All reaction conditions remained unchanged from the previous study which

employed difunctionalized siloxane. The diameter of the particles was 1.3  $\mu\text{m}$  and the standard deviation was 45%. The larger size in this case is a reflection of the shorter stabilizer chains used (21 500 versus 31 000) and the single graft point available for attachment. Compared to the previous latex, the number of sites on PDMS available for grafting to PMMA has been reduced by half. Therefore, during the precursor particle formation stage, PMMA homopolymer formation is significantly increased. The PMMA chains grafted to PDMS during the precursor particle formation stage can grow twice as long in the presence of monofunctionalized PDMS than difunctionalized PDMS before grafting to a silicone chain. The silicone concentration confirms this hypothesis, since only 3.3 mole percent PDMS is grafted to the PMMA particles. The surface coverage is comparable at  $1.82 \times 10^{17}$  molecules/ $\text{m}^2$ . The slight increase may be due to the shorter PDMS chains when compared to the difunctional PDMS.

When this latex is equilibrated with montmorillonite under identical conditions as previously, the following results are obtained.

Time (h)	Diameter ( $\mu\text{m}$ )	Percent Silicone
0	1.3	3.3
5	1.5	3.3
20	1.3	3.5
30	1.2	2.6
40	1.4	2.8
48	1.1	2.4
58	1.2	2.3
72	1.3	2.2
76	24.0	2.1

Table 4.2: Particle size and silicone content during equilibration of PMMA latex stabilized by monofunctionalized PDMS.

Once again, flocculation can be seen to be a very critical phenomenon as is illustrated below in

Figure 4.5.

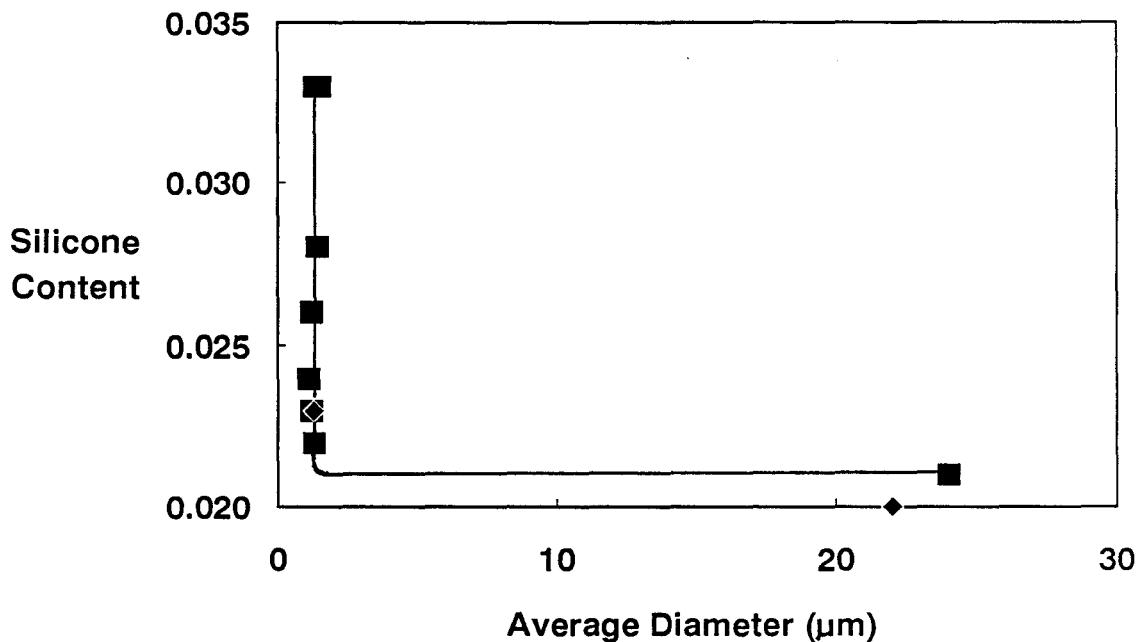


Figure 4.5: Equilibration of PMMA latex stabilized by monofunctionalized PDMS. Diamonds represent replicated analyses.

At a silicone concentration of 2.1 mole percent, the latex flocculates. The decrease in silicone concentration corresponds to a reduction of molecular weight by 36%. The final concentration of silicone on the particle surface is lower than that in the previous study. The difference in final silicone may be explained by the slightly higher surface coverage in the case of the monofunctionalized PDMS. Assuming the attraction between two particles is identical for both types of latex when corrected for particle size and molecular weight effects, the steric repulsion between two more densely coated particles is larger than that of two less densely covered spheres. The steric stability is therefore higher and a larger decrease in steric stabilizer concentration must occur to destabilize more densely covered spheres.

The observation that flocculation is dependent on surface coverage is supported by results of Napper and others who determined upper and lower critical flocculation temperatures and found no correlation between flocculation temperatures and particle size or the nature of the anchor polymer (Napper, 1970, Dawkins and Taylor, 1980).

Once again, a steady decrease in silicone concentration is observed as illustrated in

Figure 4.6.

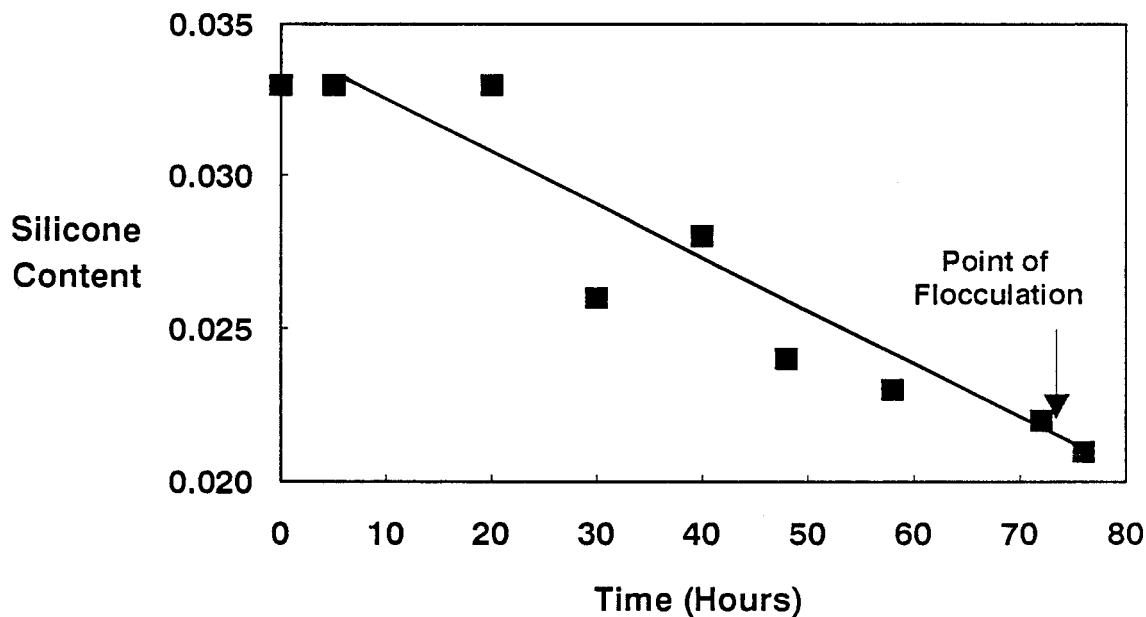


Figure 4.6: Silicone content of the latex particles stabilized by monofunctional PDMS over time during equilibration.

As seen in the previous study with difunctional PDMS, the particle size distribution of the latex upon flocculation shifts from 1  $\mu\text{m}$  to 30  $\mu\text{m}$ . During the equilibration reaction, the distribution remains that of the original latex until the point of flocculation is reached when the distribution shown in Figure 4.7 is obtained.

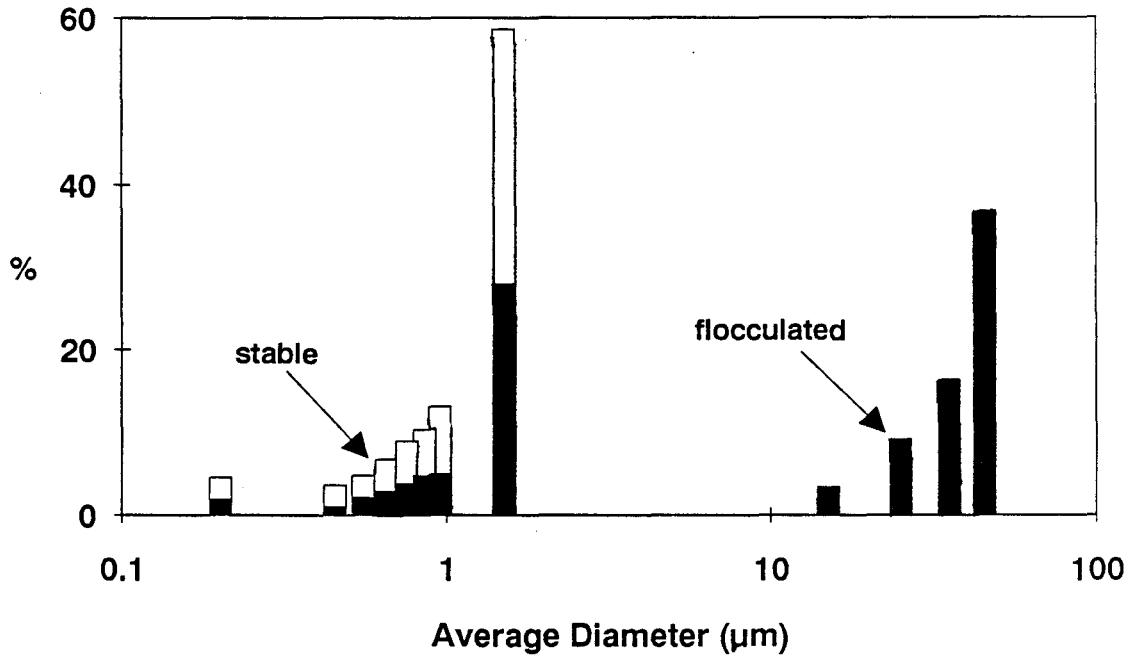


Figure 4.7: Particle size distribution of latex stabilized with monofunctional PDMS before and after flocculation.

It is interesting to note that the slope of the silicone decay curve is identical for both types of stabilizer employed. In the case of difunctional PDMS, the graph has a slope of 0.0163 mole percent/hour. That of the monofunctional PDMS graph is 0.0166 mole percent/hour which can be considered identical within experimental error.

Since the silicone concentration and amount of catalyst were identical in the two different latex equilibrations, and since it was ensured that all other reaction and analysis conditions were identical, this observation combined with the reproducibility of the point of flocculation is evidence for a very well behaved system which undergoes equilibration at the same rate in both cases. In addition, the point of flocculation for both systems was reproducible to within one hour.

The onset of flocculation differed from one type of latex to another. In the case of the monofunctional PDMS, the critical point occurred at 76 hours whereas in the difunctional PDMS, it occurred at 58 hours. Since previous work established that flocculation is not dependent on the size of the particle, its size distribution and the anchor polymer, the only explanation which would account for the discrepancy of the point of flocculation is the surface coverage (Napper, 1969,

Dawkins and Taylor, 1980). The density of chains varies by 23% from one type of latex to another and the onset of flocculation also varies by exactly 23%.

To determine how much silicone could be removed from the particle surface even after flocculation had set in, experiments were carried out for 120 hours and the amount of silicone on the particle surface measured. It was found that for both types of functionalized PDMS, the associated silicone does not change significantly from the amount associated with the particle at the onset of flocculation.

The lack of further removal of silicone from the latex particles could be for two reasons. Either a true equilibration in the reaction mixture is achieved where the amount of silicone on the particle surface is in equilibration with that in the solvent, or, more likely, the remaining silicone is buried below the surface of the particles and thus inaccessible to the solid catalyst. A large amount of indirect evidence points toward the latter case. The latex exhibits no transition temperature characteristic of pure or nearly pure PMMA and therefore the particle core may be a mixture of PDMS and PMMA. When subjected to an electron beam, such as that used in low level electron microscopy, the particles "evaporate", a phenomenon characteristic of soft particle matrices.

To further address the problem of how much silicone is buried within the particle core, equilibrations may be carried out under conditions where the free siloxane is removed during the course of the reaction or the solvent is diluted successively to prevent the onset of flocculation. Alternatively, particles can be prepared using crosslinker or other conditions which prevent silicone incorporation into the particle core.

## CHAPTER 5

### CONCLUSIONS

Poly(methyl methacrylate) latex can be stabilized by trimethylsilyl terminated PDMS as short as 62700 which corresponds to a degree of polymerization of 847. If the stabilizer molecular weight is increased, the particle diameter decreases owing to the formation of increasingly better stabilized precursor particles during the nucleation period.

When PMMA latex is stabilized with vinyl terminated PDMS, particles can still be formed when the stabilizer DP is 81 repeat units. The formation of stable particles with short chain stabilizer is attributed to terminal grafting of the vinyl groups to PMMA versus internal methyl groups in the case of trimethylsilyl terminated PDMS.

Particle size is again observed to decrease with increasing stabilizer molecular weight because of increasing rate of precursor particle formation during the nucleation stage. Latex silicone content and surface coverage for both types of stabilizers are comparable to previous work by Dow Corning.

Varying the concentration of the type of stabilizer showed a similar decrease of particle size with increasing silicone concentration supporting the theory of increasing graft precursor particle generation during nucleation. Changing initiator concentration had similar effects. Using AIBN, no stable particles were formed with PDMS, whereas stable particles of comparable size to those formed in the presence of BPO were generated. This evidence is in support of the formation of terminal grafts for PDMS-V and internal grafts for PDMS.

PDMS stabilized PMMA particles can be flocculated using acidified montmorillonite clay in a good solvent for the stabilizer moiety. The critical silicone concentration is 3 mole percent with respect to PMMA at a stabilizer molecular weight of 28 000. Destabilization occurs by the successive cleavage and shortening of PDMS stabilizer chains on the particle surface. The rate of degradation is constant for two different types of stabilizer.

Some promising areas for future research are:

- i) The synthesis of PDMS stabilized particles in the presence of ethylene glycol dimethacrylate [EGDMA]. EGDMA will crosslink PMMA chains and prevent or reduce the incorporation of silicone in the particle core. It is believed that some PDMS may be incorporated into the particle core of all particles synthesized in this study.
- ii) Acidifying montmorillonite clay at an elevated temperature. Evidence points toward an increase in strength of the montmorillonite catalyst if the clay is acidified above 50°C (Buch and Ingebrigtson, 1979). The rate of equilibration of PDMS should then be accelerated.
- iii) Using acidified carbon black as a catalyst. Carbon black possesses all the advantages which make montmorillonite clay an excellent catalyst for this system. In addition, carbon black is easier to disperse in nonaqueous systems because of its smaller size.

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## APPENDIX

### A.1. Dynamic Light Scattering and the NICOMP 370

Particles in a vacuum or in a solvent interact with light as it strikes them. Some of the light is deflected in a direction away from the original direction of the light beam. The deflected light is also known as "scattered light" and it is this light upon which the optical phenomenon of light scattering is based.

The intensity of the scattered light depends on the wavelength of the incident beam, the size and shape of the scattering object, its properties, and the angle of observation. The scattering object may be analyzed if the relationship between the intensity and the scattering variables is known. Light of any region of the electromagnetic spectrum has common properties and characteristics. Electromagnetic radiation consists of oscillating electric and magnetic fields which are perpendicular to each other and mutually perpendicular to the direction of propagation of the light wave. Light scattering centers on the oscillations of the electric field. When a beam of radiation (or light) strikes a molecule or particle, a certain amount of the incident light is scattered. Any incident light not scattered will continue to travel past the molecule in its original path. Unscattered light is also known as transmitted light. The transmitted light will be attenuated when compared to the incident beam. Since conservation of energy holds true, the sum of the transmitted light and the light scattered over all possible angles must be equal to the incident light, when light energies are used and compared.

Since light intensity is defined as the radiation energy per unit area per unit time, the ratio of light intensities is equal to the ratio of light energies at a given location (Hiemenz, 1986). Light intensity is equal to the square of the amplitude of the electric field.

### A.1.1. Classical Light Scattering

In the Rayleigh scattering region, the particle diameter is much smaller than the wavelength of the incident beam. Scattered light results when an alternating electric field strikes a particle and causes all polarizable electrons within that particle to oscillate at the same frequency resulting in a new oscillating electric field radiating in all directions from the particle. In the Rayleigh region, all polar electrons oscillate in phase and at the same frequency as the incident electric field since they all experience the same initial beam. Thus, the amplitude or intensity of the scattered electric field is proportional to the number of polarizable electrons multiplied by the incident amplitude (or intensity) of the electric field. The number of polarizable electrons is related to the molecular weight or volume of the particle by the index of refraction of the solvent and the particle (Nicoli, 1984). In the Rayleigh region, the angular dependence on the scattering intensity is negligible.

When particle size becomes comparable to the wavelength of the incident beam, the Rayleigh equation must be modified. G. Mie developed the relevant theories in 1908 and hence the region of application for his equations is known as the Mie scattering region. In Mie's equations, intraparticle interferences are taken into consideration. The polarizable oscillating electrons no longer oscillate in phase and therefore discrete scattered waves originate from different regions of the particle. These discrete scattered waves interfere at the detector and the total intensity measured is diminished compared to the Rayleigh regime. Rayleigh's equations can be multiplied by a "form factor" which has the value of 1 in the Rayleigh regime and decreases non-linearly as the particle size increases. In this classical method of light scattering, the molecular weight or volume of a particle can be determined from the scattered light intensity using calibration standards and the indices of refraction of solvent and solute.

### A.1.2. Dynamic Light Scattering [DLS]

In dynamic light scattering, the fluctuations of the scattered light intensity over time are evaluated. The light intensity at the detector fluctuates because the final intensity is the result of

the addition of interfering light waves from different particles within the scattering volume. However, each individual wave at the detector has a phase relationship to the incident beam. The phase relationship depends on the location of the scattering particle within the scattering volume. All particles within the scattering volume diffuse due to Brownian motion. This motion randomly affects the phase of the scattering wave and results in an interfering wave at the detector. The net intensity of the interfering wave then fluctuates randomly in time. The net scattering intensity is dependent on the angle of the detector which, in the Nicomp 370, is located at 90° to the incident beam.

Since the light source in the Nicomp 370 is a monochromatic unpolarized He-Ne laser of wavelength about 0.6  $\mu\text{m}$ , even small particle displacements can cause significant phase changes and produce large fluctuations in the measured intensity. The amplitude of the final intensity may fluctuate from a minimum of net intensity zero corresponding to total destructive interference of the waves at the detector, to a maximum corresponding to total constructive interference of all waves arriving at the detector in phase (Nicoli, 1984). Over time, the intensity can take on any value between these two extremes and the resulting intensity signal looks like a random noise signal.

How can one relate this signal to particle dimensions? The time scale of the fluctuations of the intensity signal depends on the size of the particles which cause the scattering. Small particles diffuse much faster than larger ones and will result in a more rapidly "varying" intensity signal whereas larger ones result in slower variations in time.

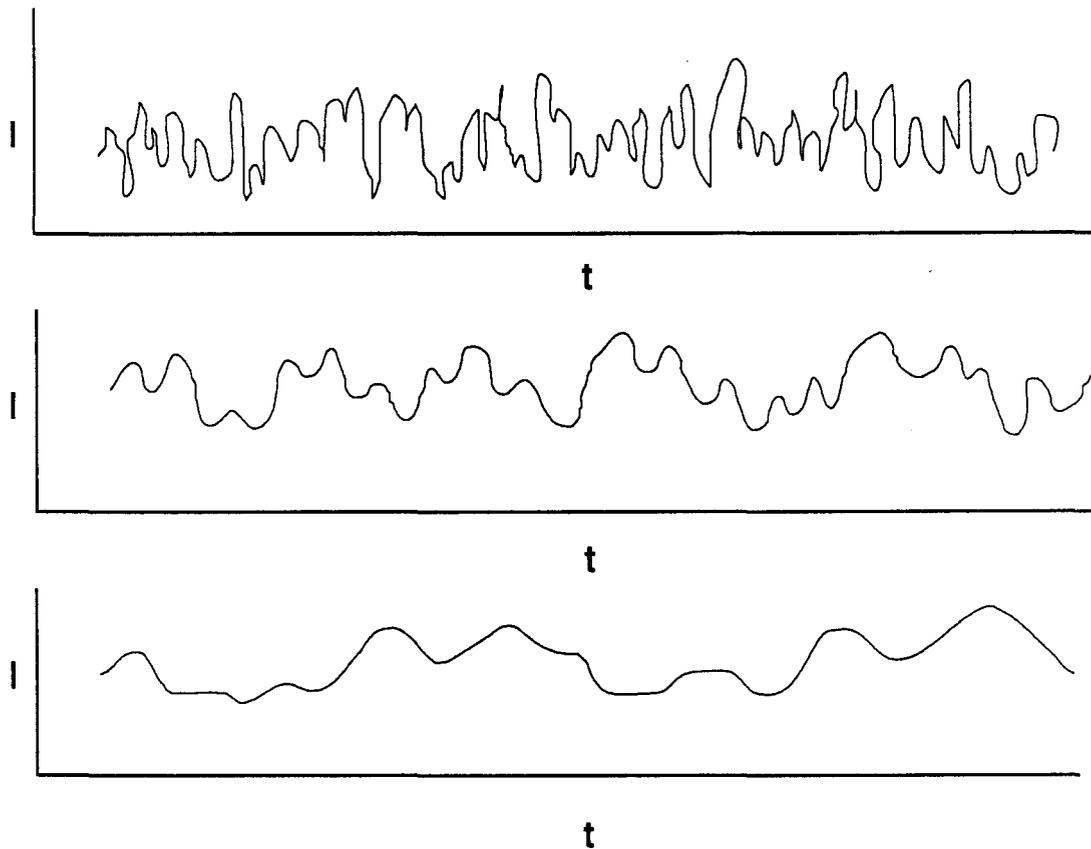


Figure A.1: Light intensity over time for small, intermediate and large particles, respectively.

The final signal varies around some average intensity which is proportional to the number of particles in the illuminated scattering volume and their individual scattering powers. The time scale of the fluctuations depends on the particle diffusivity which is proportional to its size. The intensity fluctuations give rise to a diffusion coefficient  $D$  for the particle within the scattering volume. Using the Stokes-Einstein equation

$$D = \frac{kT}{6\pi\eta R} \quad (\text{A.1})$$

the particle radius,  $R$ , can be determined using the shear viscosity,  $\eta$ , of the solvent. Equation A.1 shows that the diffusion coefficient of particles with a given size increases with temperature due to the temperature dependence of the solvent viscosity. With increasing temperature, the solvent becomes less viscous and particle diffusion becomes more rapid giving more swiftly fluctuating intensities. Therefore, the temperature for DLS measurements should be well

controlled and accurately known because intensity fluctuations due to temperature are indistinguishable from those due to particle radius. A fluctuating intensity signal may be translated to give a diffusion coefficient using the phenomenon known as autocorrelation.

### A.1.3. Autocorrelation

The autocorrelation function will give an indication of the lifetime, length or duration of the width of a "hump" in the scattered light intensity signal. Another way to express the significance of the autocorrelation function is that it sheds light on the similarity between the net light intensity at a time  $t$  and the intensity at a time  $t - \Delta t$ . Intensity comparisons are carried out at different values of  $\Delta t$  with a constant value of  $t$  to obtain a meaningful statistical average for the intensity autocorrelated function  $A$ .  $A$  is obtained by

$$A = \sum_{t=1}^x [I_s(t)] \times [I_s(t - \Delta t)] \quad (A.2)$$

At small values of  $\Delta t$ , the function  $A$  is said to be highly correlated and as the limit when  $\Delta t$  goes to zero, the product is equal to the square of the intensity at time  $t$ . The large value of the autocorrelation function verifies that the scattered light intensities are essentially the same and little change in intensity has occurred during a very short time interval.

At larger values of  $\Delta t$ , the function becomes less well correlated reflecting changes in light intensity over time. In the extreme case as  $t$  goes to infinity, the function and the signal are said to be uncorrelated because any number of changes could have occurred over long time periods resulting in the final intensity. An example of the type of the comparisons at different values of  $\Delta t$  to one value of  $t$  are seen below.

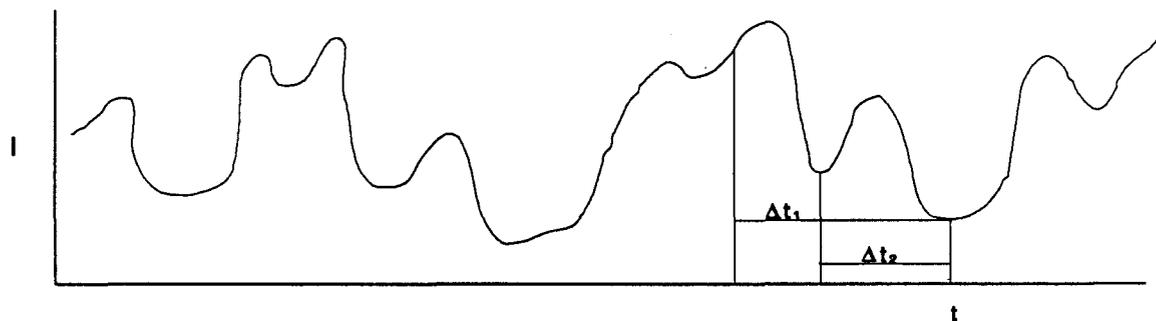


Figure A.2: Illustration of the principle of autocorrelation in DLS.

To obtain a full picture of the correlation of the fluctuating signal intensity, many values of  $t$  must be chosen. At each value for  $t$ , many values of  $\Delta t$  are used and correlations calculated. In the Nicomp 370 during a 5 minute measurement of particles of diameter  $0.2 \mu\text{m}$ , 15 million values of  $\Delta t$  are used and compared for each value of  $t$ . In total, 643 different values of  $\Delta t$  are investigated simultaneously (Nicoli, 1984).

As may be apparent from the earlier discussion, the autocorrelation function has two limits. The upper limit of the function occurs at low or zero  $\Delta t$  and approaches the sum of the square of the intensities at time  $t$ . The lower limit occurs when  $t$  approaches infinity and the correlation approaches zero. The product at this limit is equal to the square of the average intensity. The location of the upper and lower extremes is verified by the fact that the sum of the square of a fluctuating quantity is always larger than the square of the average quantity of the fluctuations. The shape of the decay curve depends on the particle size and the concentration of the particles in the continuous phase, assuming it is a sphere. For randomly diffusing, non-interacting particles of uniform size, the autocorrelation function decays exponentially over time and may be described simply by

$$A = B \exp\left(\frac{-\Delta t}{\tau}\right) + C \quad (\text{A.3})$$

where  $B$  is the difference between the two extreme loci at  $t = 0$  and  $t = \infty$ , and  $C$  is the squared sum of the average intensity or baseline value.  $\tau$  is the decay time constant of the exponential function and characterizes the speed of decay of the function  $A$  to the limiting baseline value  $C$ . In reality,  $\tau$  describes the average lifetime of a major fluctuation in the intensity signal.

The diffusion coefficient is related to the decay constant via

$$\frac{1}{\tau} = 2DK^2 \quad (\text{A.4})$$

K is the scattering wave vector and depends on the wavelength of the light beam, the angle at which the scattered light is detected and the index of refraction of the solvent. The radius of the scattering object is found from the Stokes-Einstein equation as discussed earlier.

In summary, by measuring the fluctuating scattered light intensity of a suspended particle over time, the autocorrelation function of the fluctuating intensity is obtained. From the exponentially decaying autocorrelation function, the decay time constant may be determined. Since the decay constant is inversely proportional to the diffusivity of the particles, the radius may be obtained by using the Stokes-Einstein equation.

#### A.2. Sample Calculation of Surface Coverage

To determine the number of chains or number of attachments per unit area on the particle surface, the following quantities must be established first. All results will be given on a per gram of latex basis. The weight of PMMA and PDMS is obtained from the total number of moles as follows:

$$\text{Mol} = \frac{1}{M_D * x_D + [(1-x_D) * M_{\text{MMA}}]} \quad (\text{A.5})$$

where  $M_D$  and  $M_{\text{MMA}}$  are the molecular weight of a D unit and methyl methacrylate respectively and  $x_D$  is the mole fraction of D units.

The mass of PMMA is calculated from the molecular weight, mole fraction and total number of moles

$$W_{\text{PMMA}} = \text{Mol} * M_{\text{MMA}} * (1-x_D) \quad (\text{A.6})$$

The mass of PDMS is simply

$$W_{\text{PDMS}} = 1 - W_{\text{PMMA}} \quad (\text{A.7})$$

The specific surface area in m<sup>2</sup> per gram is found from

$$SSA = \frac{3}{a * \rho_{PMMA} * 1000000} \quad (A.8)$$

where  $a$  is the particle radius and  $\rho_{PMMA}$  is the density of PMMA.

Finally, the surface coverage is obtained by dividing the number of chains per molecule by the total surface area.

$$Cov = \frac{\frac{W_{PDMS} * N_{Av}}{M_{PDMS}}}{SSA * W_{MMA}} \quad (A.9)$$

where  $N_{Av}$  is Avogadro's number and  $W_{MMA}$  is the mass of PMMA.