# A Study of Electrostatically Stabilized Poly(methyl methacrylate) Latex

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## SYNOPSIS

Poly(methy methacrylate) latex with various solid contents, stabilized electrostatically, was studied. The hydrodynamic layer (H.L.) extends rapidly at volume fraction larger than 0.35. The agglomeration of particles was found. When the reduced thickness ($\delta/r$) of H.L. exceeds 3.0, particle agglomeration becomes more serious and the gel-like product forms. In comparison, the value of ($\delta/r$) is much smaller than 3.0 when the H.L. begins to contact each other. Using a higher amount of emulsifier, the thickness of H.L. decreases. This is attributed to the fact that more free emulsifier presenting in the aqueous phase leads to more depletion stabilization. Meanwhile, in the presence of unreacted monomer, the use of the monomer-swollen volume fraction is suggested to replace the unswollen volume fraction. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

In emulsion polymerization, some methacrylates such as methyl methacrylate (MMA)[1] and cyclohexyl methacrylate (CHMA),[2] were found to form a gel-like product easily, especially when recipes were prepared to have higher solid contents. Another report[3] mentioned that the gel-like product was formed in high solids latices stabilized electrostatically. The gel-like product was recognized as a result of the interactions between the double layers surrounding each particle.[3]

Sometimes, the electrostatic stabilization may not be efficient enough in certain applications, such as in high solids nonaqueous dispersions,[4,5] where the spatial extension ("thickness") of the double layer is so great that little repulsion acts between the double layers and the particles coagulate.

MMA has a high water-solubility[6] of 1.50% wt, and nucleation occurs predominantly in the aqueous phase.[7] The presence of free polymer or free emulsifier in the aqueous phase is possible and has a great effect. Therefore, the depletion flocculation[3] or

bridging flocculation[8] becomes important and the latex is easier to form aggregates.

Since the precise structure of the flocs formed by aggregation is rarely known or even determined, it is difficult to distinguish flocculation from coagulation,[3] and these two terms are sometimes interchangeable with each other.

Reversible flocculation has been found in latex,[3] for instance, the creaming of a natural rubber latex by adding sodium alginate (0.15%).[9] The type of flocculation was reversed by dilution and the latex could be taken through the aggregation–redispersion–aggregation cycle many times. There also exist many electrostatically stabilized dispersions that undergo reversible coagulation (e.g., clays, Carey Lea silver sols).[3] This was attributed[10] thermodynamically to a redispersion from a shallow minimum in the potential energy curve, rather than from a deep primary minimum.

To obtain the data for the thickness of the hydrodynamic layer, viscosities of latices have been decided in this study. In the literature, a number of studies[11-21] have been performed on the viscosity–concentration relationship for latex. An extensive survey of the viscosity–concentration literature has also been made by Rutgers.[22] Generally, the curve for the relationship between viscosity and concen-

tration of latex has a rapid increase at high concentration. A typical curve can be seen in Ref. 11. Therefore, the purpose is not aimed here to obtain the viscosity–concentration equation for the PMMA latex.

Rudimentary study of the gel formation in MMA emulsion polymerization with high initial monomer content revealed that the gel is redispersible. The use of a higher concentration of electrostatic stabilizer was helpful in delaying the gel formation. The spatial extension of hydrodynamic layer was determined in this study. The extension changed substantially when the solid contents varied from low to high. Both the particle size and spatial extension of hydrodynamic layer were found to be smaller for the recipe with higher stabilizer concentrations.

Totally clarifying the mechanism of gel formation in emulsion polymerization seems impossible here. However, the study provides some insights for the understanding of the mechanism of gel formation and the colloidal stability.

## EXPERIMENTAL

### Materials

MMA was purified by prewashing and vacuum-distillation. Water was doubly distilled. Others were used as received.

### Polymerization

A typical recipe is shown in Table I. Recipes vary in the amount of monomer, $H_2O$, or emulsifier. Polymerizations were conducted in a 250 mL four-neck round-bottom flask at 50°C in a constant temperature water bath. The mechanical agitation was set at 240 rpm for the beginning 5 min and then reduced to 120 rpm.

### Determinations of Conversion, Particle Size, Viscosity, and Hydrodynamic Properties

Samples were withdrawn using a hypodermic needle and syringe. Monomer conversion was determined gravimetrically. Particle size was determined with a Photal DLS-3000/3100 dynamic light-scattering

**Table I  A Typical Recipe for the Emulsion Polymerization**

| | |
|---|---|
| MMA (monomer) | 80 g |
| $H_2O$ | 120 g |
| $K_2S_2O_8$ (initiator) | 0.188 g |
| SDS (surfactant) | 0.6 g |

spectrophotometer. The residual monomer in the samples was removed by letting the diluted sample open to air overnight. Monodisperse latex was chosen for the viscosity determination. Viscosity was measured with a Brookfield viscometer, Model DV-II, with a UL adapter; most of the measurements were carried out at 100 rpm.

The specific viscosity [ $\eta_s = [\eta/\eta_0) - 1$] is related to the thickness ($\delta$) of the hydrodynamic layer[23–25] of the latex with respect to Einstein's law according to

$$\eta_s = 2.5\phi(1 + \delta/r)^3 \qquad (1)$$

where $\eta$ and $\eta_0$ are viscosities of latex and water, respectively; $r$, the particle radius; and $\phi$, the volume fraction of the polymer phase (i.e., dispersed phase).

The computation of the number-average diameter ($D_n$), volume-average diameter ($D_v$), and weight-average diameter ($D_w$) followed the same formulas as those in Ref. 26.

The $N$ value, defined as the total particle number per $cm^3$ of aqueous solution, was computed as follows:

$$N = [6(M/W)(\% \text{ conversion})\rho_w]/$$
$$[100\pi(\rho_p)(D_v)^3(10^{-24})] \qquad (2)$$

where $M/W$ is the initial monomer to water weight ratio; $\rho_w$, the density of water = 1.00 $g/cm^3$; and $\rho_p$, the density of PMMA = 1.175 $g/cm^3$; and $D_v$ is in Å, and $N$, in $cm^{-3}$.

### Solubilities of "MMA in Water" and "Water in MMA"

Ten grams of MMA with 60 ppm of hydroquinone (inhibitor) was added to 100 g of water. The components were mixed using end-over-end agitation at 50°C for 2 h. The water phase and MMA phase were separated through use of a fractionation funnel.

The solubility of water in the MMA phase was determined by converting MMA into a polymer via polymerization and deciding the residual water content. The solubility of MMA in the water phase was determined by the ultraviolet technique, using the absorbance at a wavelength of 200 nm.

### Solubility of PMMA in Water

Ten grams of PMMA was mixed with 100 g of water, using end-over-end agitation at 50°C for 2 h. Then, the mixture was filtered. The filtrate was dried to determine the solid content, and, therefore, the dissolved PMMA.

**Figure 1** Relative viscosity vs. polymer volume fraction for PMMA latex.



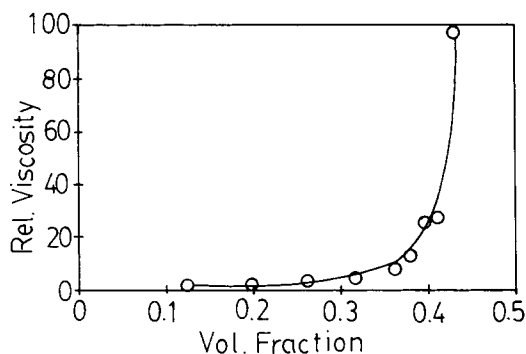**Figure 3** Volume-average particle diameter $(D_v)$ vs. polymer volume fraction for PMMA latex.

## Solubility of PMMA in MMA

Fifty grams of MMA with 60 ppm of hydroquinone was mixed with different amounts of PMMA (i.e., 10, 20, 30, 40 and 50 g). Each mixture was contained in a 4 oz bottle and agitated end-over-end at 50°C for 2 h to determine if the PMMA was dissolved.

## Solubility of PMMA in Water in the Presence of MMA

Ten grams of PMMA was dissolved in 10 g of MMA in the presence of 60 ppm of hydroquinone. The mixture was then mixed with 80 g of water, using end-over-end agitation at 50°C for 2 h. After filtration, the filtrate was dried to determine the solid content and, therefore, the dissolved PMMA.

## RESULTS AND DISCUSSION

### Effect of Solid Content

A series of PMMA latices with different solid contents were prepared. The viscosity–volume fraction relationship of PMMA latex follows the general re-
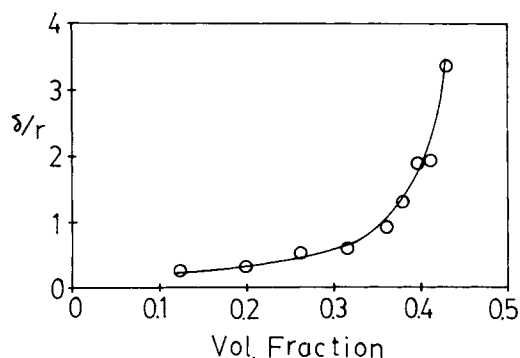
lationship found for the latex, such as shown in Ref. 11. Figures 1–3 and Table II show increasing trends in the relative viscosity, reduced thickness $(\delta/r)$ of the hydrodynamic layer (H.L.), and volume-average particle diameter $(D_v)$ with increase in the volume fraction. The curves increase rapidly with the volume fraction larger than 0.35.

It was found that the higher solid the latex has, the greater thickness the hydrodynamic layer has. Obviously, the higher solid latex particles have a greater interaction between hydrodynamic layers and particles tend to agglomerate together. Therefore, $(\delta/r)$ and $D_v$ increase simultaneously at higher solids, as shown in Figures 2 and 3.

A theoretical computation[27] of the interparticle distance $(d_i)$ has been suggested as follows:

$$(d_i/2r) + 1 = (0.74/\phi)^{1/3} \qquad (3)$$



**Figure 2** Reduced thickness $(\delta/r)$ of the H.L. vs. polymer volume fraction for PMMA latex.

**Table II** Relative Viscosity $(\eta_r)$, Volume-average Particle Diameter $(D_v)$, and Reduced Thickness $(\delta/r)$ of the Hydrodynamic Layer (H.L.) for PMMA Latex with Various Polymer Volume Fractions $(\phi)$, as Shown in Figures 1–3

| $\phi$ | $\eta_r$ | $D_v$ [Å] | $(\delta/r)$ | Initial Content[a] | | |
|--------|----------|-----------|--------------|--------|--------|--------|
| | | | | $M$(g) | $W$(g) | $E$(g) |
| 0.124 | 1.6 | 730 | 0.27 | 20 | 120 | 0.88 |
| 0.199 | 2.2 | 781 | 0.32 | 35 | 120 | 1.53 |
| 0.262 | 3.4 | 830 | 0.53 | 50 | 120 | 2.20 |
| 0.316 | 4.4 | 813 | 0.62 | 65 | 120 | 2.90 |
| 0.362 | 7.6 | 879 | 0.94 | 80 | 120 | 3.50 |
| 0.380 | 13 | 1100 | 1.31 | 80 | 108 | 0.60 |
| 0.397 | 26 | 1160 | 1.91 | 80 | 98 | 0.60 |
| 0.412 | 27 | 1180 | 1.95 | 80 | 88 | 0.60 |
| 0.431 | 97 | 1440 | 3.37 | 80 | 80 | 0.60 |

[a] $M$(g), monomer amount in grams; $W$(g), water amount in grams; $E$(g), SDS amount in grams.
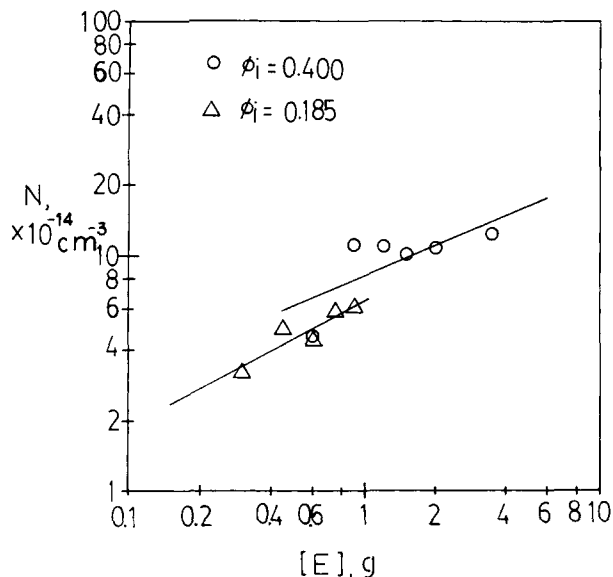
**Figure 4** Order dependence of particle number per cm³ of the aqueous phase ($N$) on the emulsifier content ($[E]$, g) for PMMA latices of two levels of solid contents.

where $\phi$ is the volume fraction of the polymer. It is possible to predict the volume fraction at which the boundaries of the H.L. begin to contact each other. By letting $(\delta/r)$ equal to $(d_i/2r)$, eq. (3) becomes

$$(\delta/r)_c + 1 = (0.74/\phi)^{1/3} \qquad (4)$$

where subscript $c$ denotes the incipient contact between boundaries of the hydrodynamic layers. Actually, at this volume fraction, the interaction between the hydrodynamic layers is not great. Instead, the interaction will not be determinant until $(\delta/r)$ > 3.0, as shown in the later section.

To characterize the stabilizing effect of the emulsifier in the emulsion polymerization of MMA, the
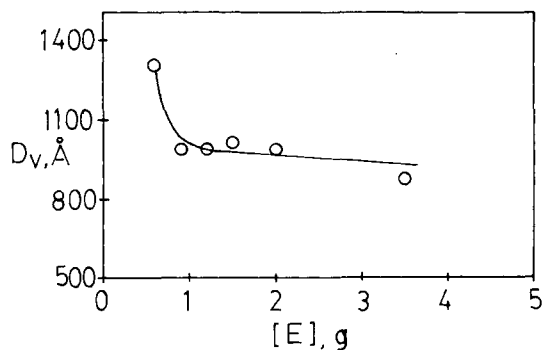


**Figure 5** Volume-average particle diameter decreases with increasing the emulsifier content for PMMA latex with polymer volume fraction of about 0.36.
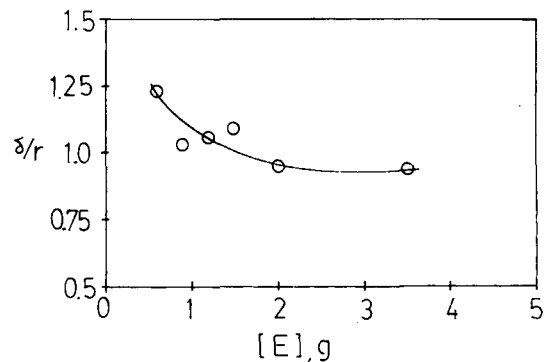


**Figure 6** Reduced thickness ($\delta/r$) of the H.L. decreases with increasing the emulsifier content for PMMA latex with polymer volume fraction of about 0.36.

order dependence of the particle number per cm³ of the aqueous phase, $N$, on the emulsifier amount, $[E]$, was carried out at two levels of solid content. The order dependence varies from 0.53 to 0.43 as the initial monomer content of emulsion changes from 18.5 to 40.0% wt. The correlation is shown in Figure 4. Note that the stabilizing efficiency of the emulsifier increases at a lower rate at a higher solid.

## Effect of Emulsifier Concentration

The increase in emulsifier concentration will reduce the average particle size since higher stabilizing efficiency is imparted and, therefore, the particle number is increased. See Figures 4 and 5.

Consider that the average number of emulsifier molecule per particle increases with the increase of total emulsifier used. If the extra emulsifier did not adsorb onto the surface of particles, then the concentration of free emulsifier will be increased.

It was found that the reduced hydrodynamic layer ($\delta/r$) for PMMA latex (40% wt) decreases with increasing emulsifier content, as shown in Figure 6 and Table III. This may be because there is more free emulsifier existing in the aqueous phase and more depletion stabilization is actuating. Therefore, the spatial extension ("thickness") of the H.L. of latex particles is reduced.

## Effect of the Presence of Unreacted Monomer

The solubility data determined in this study are shown in Table IV. The solubility of MMA in water is 1.69% wt (compared to 1.50% wt measured by Lindemann[6]), which is comparatively larger than that of styrene (3.6 × 10⁻²% wt). Meanwhile, the solubility of water in MMA is considerably high (31.6% wt).

**Table III   Reduced Thickness ($\delta/r$) of the Hydrodynamic Layer (H.L.) (Fig. 6), Volume-average Particle Diameter ($D_v$) (Fig. 5), and Relative Viscosity ($\eta_r$) vs. Emulsifier Content [$E$ (g)] for PMMA Latex with the Same Level of Polymer Volume Fraction ($\phi$)**

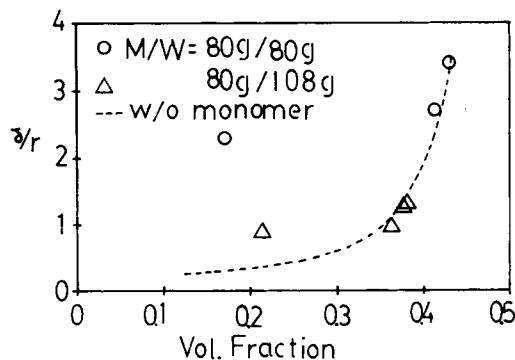| $\phi$ | $E$ (g) | ($\delta/r$) | $D_v$ (Å) | $\eta_r$ |
|--------|---------|--------------|-----------|----------|
| 0.349 | 0.60 | 1.23 | 1310 | 11 |
| 0.360 | 0.90 | 1.03 | 991 | 8.6 |
| 0.355 | 1.2 | 1.06 | 992 | 8.9 |
| 0.359 | 1.5 | 1.09 | 1020 | 9.3 |
| 0.354 | 2.0 | 0.95 | 992 | 7.7 |
| 0.354 | 3.5 | 0.94 | 879 | 7.6 |



**Figure 7**   Reduced thickness ($\delta/r$) of hydrodynamic layer vs. unswollen polymer volume fraction for PMMA latex in the presence of monomer. ($M/W$) denotes the initial content of monomer to that of water in the recipe.

The solubility of PMMA in water is low whether in the presence of MMA or not, in spite of the solubility of 100 times found when the MMA was present. The presence of emulsifier may also increase the solubility of PMMA. However, it is still limited. Therefore, the effect of free polymers in the aqueous phase can be minute. However, it is known that MMA can be nucleated easily in the aqueous phase,[7] and there may be some precipitated polymers in the latex.

It is generally accepted that the monomer droplets disappear and the polymer particles are swollen by the monomer at conversion higher than about 35%. It is difficult to evaluate the swollen particle volume fraction. Figure 7 shows that in the presence of unreacted monomer the value of ($\delta/r$) is much higher than that without monomer. But if the swollen particle volume fraction is used, the data points will move closer to the dashed line and the use of swollen particle volume fraction instead of the unswollen one is appropriate.

**Particle Agglomeration**

As shown in Figure 8, the particle agglomeration occurred during the polymerization, since the particle size increased. The dashed line in Figure 8 represents the calculated unswollen particle size for the

case of constant particle number. Obviously, the measured particle size data at low conversions are smaller than the calculated ones and, hence, the particle agglomeration occurs at high conversions. Furthermore, the higher the initial monomer content the latex has, the more serious the agglomeration is. The recipe having an initial content of (80/80
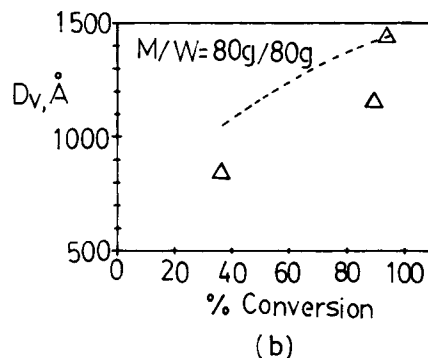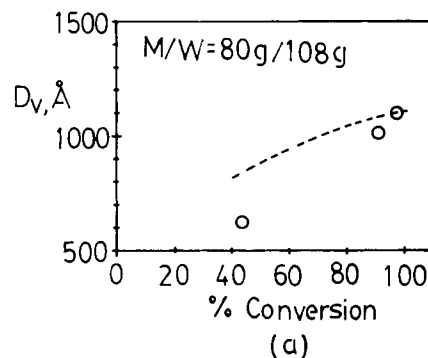


(a)



(b)

**Figure 8**   Variation of unswollen volume-average particle diameter with % conversion. Dashed line represents the predicted unswollen constant particle number line.

**Table IV   Solubility Data**

| | |
|---|---|
| MMA in water | 1.69% wt |
| Water in MMA | 31.6% wt |
| PMMA in water | $3.03 \times 10^{-4}$% wt |
| PMMA in water (in the presence of MMA) | $2.56 \times 10^{-2}$% wt |
| PMMA in MMA | > 50% wt |

g) in ($M/W$) has a greater agglomeration, as shown in Figure 8(b).

The greater interaction between H.L. is the cause for the occurrence of particle agglomeration, while this is reflected by the larger value of ($\delta/r$). The great interaction between H.L. leads to the gel-like product formation. It seems that the gel-like product forms when the reduced thickness ($\delta/r$) of the H.L. is larger than a certain value (say, 3.0). This may be considered as a criterion for the formation of gel-like product.

Note that the ($\delta/r$) value for the recipe with an initial monomer content of 50.0% was larger than 3.0 at a high level of conversion, as shown in Figure 7. This recipe formed a gel-like product before the completion of the emulsion polymerization, whereas those recipes with smaller ($\delta/r$) values did not form a gel-like product during the polymerization. Furthermore, using a larger amount of emulsifier (e.g., 2.0 g of SDS) could not prevent (but can delay) the formation of a gel-like product in the emulsion polymerization. This shows the limitation of electrostatic stabilization. The recipe using a mixture of 3.0 g of nonionic emulsifier, Emulphogene BC-840, and 0.60 g of SDS was proved to be efficient enough. This illustrates the fact[3] that the steric stabilization (i.e., the kind of stabilization that the nonionic emulsifier usually has) has an equal efficacy at both high and low solid contents.

## CONCLUSION

As the solid content of poly(methyl methacrylate) latex is increased, the reduced thickness ($\delta/r$) of the hydrodynamic layer (H.L) becomes larger, the agglomeration of particles occurs, and the average particle size increases.

The particle agglomeration and the value of ($\delta/r$) increase at even higher rates when the volume fraction is larger than 0.35. The gel-like product forms when the value of ($\delta/r$) is larger than 3.0. Usually, the value of ($\delta/r$) is much smaller than 3.0 as the H.L. begins to contact.

Using higher concentrations of emulsifier, the thickness of H.L. was found to be decreasing. This is due to that more free emulsifier is existing in the aqueous phase and more depletion stabilization is actuating.

In the presence of unreacted monomer, it is suggested that the monomer swollen volume fraction should be used to replace the unswollen volume fraction.

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