

Silicone-Stabilized Nonaqueous Emulsion Polymerization

JOHN C. SAAM and CHUNG H. TSAI,* *Research Department,
Dow Corning Corporation, Midland, Michigan 48640*

Synopsis

Stable dispersions are prepared by free-radical polymerization of methyl methacrylate in aliphatic hydrocarbons containing poly(dimethylsiloxane) modified with mercaptoalkyl side groups. The particles are pictured as being stabilized by a protective layer of solvated poly(dimethylsiloxane). Some important features of the polymerization are described.

INTRODUCTION

Poly(dimethylsiloxane), showing a solubility parameter significantly lower than the lyophilic elements of stabilizers typically used for nonaqueous dispersions,¹ might be expected to stabilize a variety of colloidal polymeric particles in nonsolvents for the polymer but good solvents for poly(dimethylsiloxane). The present effort describes how poly(dimethylsiloxane) may be incorporated as a protective layer around colloidal polymeric particles formed during free-radical polymerization in aliphatic hydrocarbons. The approach is to provide sufficiently reactive sites at the ends or along poly(dimethylsiloxane) chains to permit grafting by chain transfer with a growing free radical during the course of the polymerization. The ensuing grafts can anchor the lyophilic siloxane elements to the surface of the forming colloidal homopolymer particles to provide a steric stabilization mechanism.¹ Mercaptoalkylsilyl groups, showing a chain transfer constant orders of magnitude greater than the silylmethyl groups in siloxanes,² were incorporated as the reactive group in the siloxane stabilizer precursor. The effort emphasized primarily polymerization of methyl methacrylate, but examples of other monomers are included to illustrate the scope of the method.

EXPERIMENTAL

The mercaptoalkyl-modified poly(dimethylsiloxanes)³ found useful as stabilizer precursors were of a minimum number-average molecular weight of about 1500. The most effective were in the molecular weight range of

* Present address: Copolymer Corporation, Baton Rouge, Louisiana.

about 15,000 to 20,000 and contained an average of at least two mercaptoalkyl groups per chain.

Poly(methyl Methacrylate). In a typical procedure, a mixture of 15 g methyl methacrylate, 5.0 g of a mercaptoalkyl-ended poly(dimethylsiloxane), ($\bar{M}_n = 21,000$), 0.015 g azobisisobutyronitrile, and 100 g hexane was heated to reflux in a nitrogen atmosphere. After about 20 min, the emulsion nucleated and an additional 10.0 g MMA and 0.020 g initiator were added in increments to the refluxing dispersion over a period of 8 hr. By this procedure, a 78% conversion of monomer was obtained as a stable emulsion of very uniform particles of poly(methyl methacrylate). Particle sizes were in the range of 1100–1300 Å. Isolated particles contained 4.5% silicone. These were separated prior to analysis by centrifugation, redispersed to give a stable emulsion in hexane, again separated by centrifugation, and dried.

Polystyrene. A hexane solution which contained 60.0 ml styrene, 10 g $\text{Me}(\text{Me}_2\text{SiO})_n[\text{Me}(\text{HSCH}_2\text{CH}_2\text{CH}_2)\text{SiO}]_m\text{SiMe}_3$ ($n/m = 15/1$, $\bar{M}_w = 12,000$), and 340 ml hexane was flushed with N_2 for 30 min. Benzoyl peroxide, 1 g, was then added to the solution to initiate the polymerization.

The reaction was carried out at $55 \pm 2^\circ\text{C}$ with continuous stirring under N_2 atmosphere. A milky-white, stable emulsion was obtained after 8 hr.

Poly(methacrylic Acid). A solution containing 21 g $\text{Me}(\text{Me}_2\text{SiO})_{150}$ $[\text{Me}(\text{HSCH}_2\text{CH}_2\text{CH}_2)\text{SiO}]_{10}\text{SiMe}_3$, 15 g methacrylic acid, and 104 g hexane was deaired by boiling the solution under nitrogen purge. Then, 0.20 g benzoyl peroxide was added to initiate the polymerization. The polymerization was then carried out at refluxing temperature under N_2 atmosphere with continuous stirring. A very stable organosol was obtained after 3 hr. The organosol contained 25% polymer (40% PMA and 60% dimethylsiloxane), and its viscosity was essentially that of hexane. The conversion was 81.8%.

Emulsion Seed Particles. A poly(methyl methacrylate) dispersion was prepared as described above from 15.0 g stabilizer, 100 g methyl methacrylate, 460 g hexane, and 0.03 g azobisisobutyronitrile. The polymer was separated from the dispersion by refrigerated centrifugation at 12,000 rpm for 1 hr. The precipitate was comprised of two distinctly different layers, the upper layer being more clear than the lower layer. The layers were separated, and each was redispersed in hexane and again separated by centrifugation three times. The particles from the upper layer were of an average diameter of 1500 Å while those from the lower layer were 2300 Å according to electron microscopy. These were used in the rate study.

Particle Growth Study. A solution containing 5.0 g $\text{Me}(\text{Me}_2\text{SiO})_n[\text{Me}(\text{HSCH}_2\text{CH}_2\text{CH}_2)\text{SiO}]_m\text{SiMe}_3$ ($\bar{M}_n \sim 21,000$, $n/m = 17/1$), 20.0 g methyl methacrylate, and 75.0 g hexane was deaired by flushing N_2 at refluxing temperature for 30 min. A 0.015-g portion of azobisisobutyronitrile in 0.3 ml acetone was then added to the above solution. The polymerization was carried out at reflux and samples were removed at various intervals. The first sample, 20 ml, was taken 3 min after the reaction became cloudy.

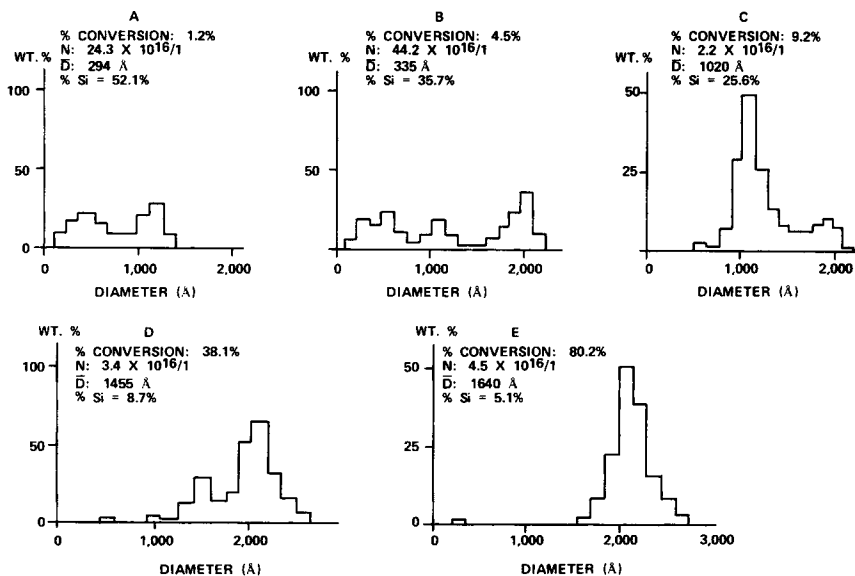


Fig. 1. Particle growth at various stages of a nonaqueous emulsion polymerization of 20 g MMA in 70 g refluxing hexane with 5.0 g mercaptosilicone stabilizer and 0.015 g azobisisobutyronitrile. Particle number N and weight-average diameter \bar{D} were determined by electron microscopy using platinum-shadowed specimens to which a standard polystyrene latex was added as internal reference. Weight-% silicone at each conversion is also shown.

The sample was added to 20 ml hexane containing 100 ppm hydroquinone monomethyl ether. A small drop of the above sample solution was quickly taken and applied to an electron microscope grid. The rest of the sample was dried in a rotary vacuum evaporator, and the conversion of monomer was determined gravimetrically. The second to fourth samples were taken successively after 10 min to 3 hr, and were prepared and analyzed in the manner described above. After $3\frac{1}{2}$ hr of reaction, an additional 10 mg initiator (in 0.2 ml acetone) was added to the reaction. A fifth sample was taken after 18 hr. The resulting reaction mixture was a very stable dispersion. The data are summarized in Figure 1.

DISCUSSION

Emulsion Polymerization

Particle formation and growth were found to take place in two principal stages. This was demonstrated by characterization of a nonaqueous emulsion polymerization of methyl methacrylate at various stages of conversion. Observed were weight-average particle size distribution, particle number, and amount of silicone stabilizer incorporated into the particles. During the initial stage, a large number of very small particles of broad size distribution formed which contained a relatively high amount of silicone

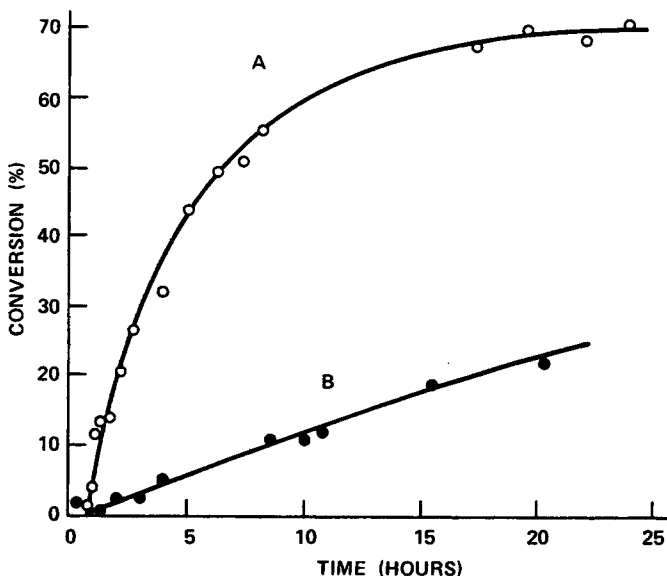


Fig. 2. Rates of polymerization of 20 g MMA, 2.7 g mercaptoalkylsilicone, and 0.015 g azobisisobutyronitrile at 65° in (A) 288 ml hexane, and (B) equivalent amount of benzene. Curve A, initial rate = 0.26%/min, $[\eta]_0$ (benzene) = 0.258; curve B, initial rate = 0.02%/min, $[\eta]_0$ (benzene) = 0.087.

stabilizer in the form of graft copolymer, (Figs. 1A and 1B). At this stage, the majority of the graft polymer is pictured as forming along with some homopolymer. As the relative amount of homopolymer increased, the particles tended to agglomerate to give some larger particles and a broad size distribution (Fig. 1B).

At a critical point between 5% and 10% conversion, the smaller particles were absorbed on the larger particles present in the system, as indicated by a decrease in particle number and the narrowing of the size distribution (Fig. 1C). From this point onward, fewer new particles formed and polymerization evidently occurred within the particles swollen with monomer. This is evidenced by steady particle growth (Figs. 1D and 1E), to give finally a narrow size distribution.

The rates of polymerization and the molecular weights of the product were significantly higher than those obtained by comparable solution polymerization as might be expected of a typical nonaqueous emulsion polymerization (Fig. 2). This is consistent with a reduced rate of termination relative to the rate of propagation and implies that polymerization occurs within the monomer-swollen polymer particles.⁴

An important factor determining the rate in the particle growth stage was found to be the total area of the colloidal particles. This was demonstrated by redispersing colloidal particles of poly(methyl methacrylate) isolated from previously prepared silicone-stabilized dispersion. The new medium was hexane containing methyl methacrylate. The particle size

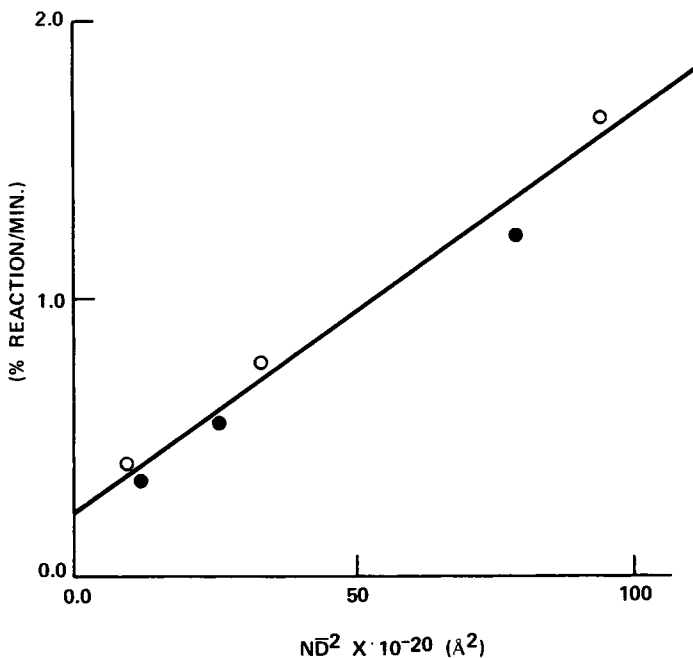


Fig. 3. Effect of particle surface area. Initial rates for the first 10% of polymerization, at 65°C, of 8.3 g MMA with 0.015 g azobisisobutyronitrile in the presence of various amounts of redispersed seed particles in 20 ml hexane: (○) $\bar{D} = 1500 \text{ \AA}$; (●) $\bar{D} = 2300 \text{ \AA}$.

and particle number of each of the specially prepared dispersions were characterized by electron microscopy. The dispersions of known particle concentration and particle size were then polymerized each with the same amount of initiator, and initial rates of polymerization were determined. The rates increased linearly with the product of the particle number N and the square of the weight-average particle diameter \bar{D} (Fig. 3), which is directly proportional to the total particle area. Attempts to correlate total particle volume or particle number failed to give linear relationships with rate.

The observations are consistent with the initiation of polymerization in the medium to give oligomeric free radicals which become insoluble with further chain growth. These will tend to agglomerate into particles early in the polymerization or, at later stages, to be absorbed on or through the surface of already existing colloidal particles swollen with monomer. This is similar in concept to the proposals of Barrett and Thomas for nonaqueous emulsions stabilized with organic polymers.⁴ The active free radicals will thus concentrate in the particles where polymerization is postulated to occur. The overall radical concentration in the particles would therefore be dependent on the rate of diffusion of the oligomeric radicals into the particles. This process would be rate limiting and give the observed de-

pendence of rate on total particle area. The polymeric free radicals located in the highly viscous particles are restricted in movement, resulting in a retarded rate of termination and a greater radical concentration than found in solution polymerization. The consequence is the observed enhanced rates of polymerization and molecular weights over those observed in solution polymerization.

The high degree of insolubility of poly(dimethylsiloxane) in the PMMA particles which are the locus of the polymerization renders the polymeric radicals inaccessible to the reactive sites on the dissolved stabilizer precursor during the later stages of the polymerization. Formation of graft copolymer is therefore pictured as occurring primarily in the brief preliminary stage, and any remaining stabilizer precursor is not utilized. Thus, it was observed that the stabilizer precursor was incompletely incorporated in the particles and free siloxane was generally present in the emulsion medium.

Emulsion Properties

The particles could be separated from emulsion by centrifugation at about 10,000 rpm to give hydrophobic powders. Similar powders but containing some free siloxane are obtained by simple evaporation of the media. These powders are readily redispersed in alkanes upon vigorous agitation. Inclusion of limited amounts of plasticizers gives films upon evaporation of the media. Coagulation was effected by adding polar materials such as acetone which are poor solvents for poly(dimethylsiloxane) and presumably "collapse" the stabilizing elements through desolvation. Alcohols were more commonly used to coagulate the emulsions.

Emulsion viscosity is in the range of 1–10 cstks up to 40% dispersed polymer. The overall polymer concentration shows little effect on viscosity below 40 wt-% polymer, but significant increases in viscosity are seen when the polymer concentration is in excess of 50 wt-%.

The extremely low θ -temperatures of poly(dimethylsiloxane) in alkanes⁵ leads to the prediction that silicone stabilized emulsions should show stability at very low temperature.⁶ Thus, dispersions of poly(methyl methacrylate) prepared herein were stable for several months at -20°C . A similar dispersion of poly(ethyl acrylate) was stable to -80°C . In contrast, critical flocculation temperatures are reported in the range of -20°C for nonaqueous dispersions in heptane where the stabilizing element is poly(12-hydroxystearic acid) hexamer, and emulsions stabilized with poly(lauryl methacrylate) are reported to flocculate at -58°C .

The surface area covered by a stabilizing element was estimated on particles isolated from emulsions sampled from a polymerization. Data were taken from Figures 1C, 1D, and 1E, and surface area coverages are given in Table I. The results show significantly fewer stabilizing elements per unit area than reported for particles of PMMA comparably stabilized with poly(12-hydroxystearic acid) hexamer.⁷ While this can be due to the

TABLE I
Surface Area of Poly(methyl Methacrylate) Particles Covered by
Poly(dimethylsiloxane) Stabilizer

% Conversion	Weight-average particle size, Å	Area per stabilizer molecule, Å ²	Weight of stabilizer per unit area, (g/Å ²) × 10 ²³
9.2	1020	667	5.20
38.1	1455	1401	2.49
80.2	1640	2085	1.67

greater molecular weight of the silicone, another important factor must be a high degree of extension of the solvated stabilizing elements.

Other monomers were polymerized by essentially the same procedure described here for methyl methacrylate to give stable emulsions. These included poly(methacrylic acid), poly(ethyl acrylate),⁸ and polystyrene.

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