Predominant Droplet Nucleation in Emulsion Polymerization

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SYNOPSIS

Emulsions stabilized against diffusional degradation by incorporating a polymeric cosurfactant have been produced and polymerized. The presence of large numbers of small droplets shifts the nucleation mechanism from micellar or homogeneous nucleation, to droplet nucleation. When an efficient cosurfactant is used, this process is referred to as miniemulsion polymerization. Polymer, however, is known to be a poor cosurfactant. Its advantage is that, unlike most cosurfactants, it is innocuous in the recipe. Results indicate that even a poor cosurfactant (polymer) is adequate to stabilize small droplets against diffusional degradation long enough to nucleate them into polymer particles. The dependence of the concentration and molecular weight of the cosurfactant on the droplet size and distribution is investigated. Droplet diameters range from 19.5 to 141.2 nm with polydispersities of about 1.023. The polymeric cosurfactant is found to affect the mechanism of nucleation. On-line conductance measurements are used to successfully differentiate between nucleation mechanisms. The observed reaction rates are dependent on the amount of polymeric cosurfactant present. In addition, the latexes prepared with the polymeric cosurfactant have lower polydispersities (1.006) than either latexes prepared from classical emulsions (1.049) or from alkane-stabilized miniemulsions (1.037). © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The mechanisms of conventional emulsion and miniemulsion polymerizations are in some ways significantly different. A conventional unseeded (i.e., no small particles added at the beginning) batch emulsion polymerization reaction can be divided into three intervals. Particle nucleation occurs during Interval I and is usually completed at low monomer conversion (2–10%) when most of the monomer is located in relatively large (1–10 μm) droplets. Particle nucleation is believed to take place when radicals formed in the aqueous phase grow via propagation and then enter into micelles or become large enough in the continuous phase to precipitate and form primary particles that may undergo limited flocculation until a stable particle population is obtained. Significant nucleation of particles from monomer droplets is discounted because of the small total surface area of the large droplets. Interval II involves polymerization within the monomer-swol-

len polymer particles with monomer supplied by diffusion from the droplets. Interval III begins when the droplets disappear, or at least reach a polymer fraction similar to that of the particles, and continues to the end of the reaction. Because nucleation of particles can be irreproducible, commercial emulsion polymerizations are often "seeded" with polymer particles of known size and concentration, manufactured specifically for use as seed particles. In this paper, for the purpose of clearly distinguishing between convention emulsions and miniemulsions, the term *macroemulsion* will be used for the former. In addition, a *latex* will be defined as a polymerized monomeric emulsion, while the term *emulsion* will refer to an unpolymerized monomeric emulsion.

Miniemulsion polymerization involves the use of an effective surfactant/cosurfactant system to produce very small (0.01–0.5 μm) monomer droplets. The droplet surface area in these systems is very large, and most of the surfactant is adsorbed at the droplet surfaces. Particle nucleation is primarily via radical (primary or oligomeric) entry into monomer droplets, since little surfactant is present in the form of micelles, or as free surfactant available to stabilize

particles formed in the continuous phase. The reaction then proceeds by polymerization of the monomer in these small droplets; hence there may be no true Interval II.

The size of the monomer droplets plays the key role in determining the locus of particle nucleation in emulsion and miniemulsion polymerizations. The competitive position of monomer droplets for capture of free radicals during miniemulsion polymerization is enhanced by both the increase in total droplet surface area and the decrease in the available surfactant for micelle formation or stabilization of precursors in homogeneous nucleation.

When an oil-in-water emulsion is created by the application of shear force to a heterogeneous fluid containing surfactants, a distribution of droplet sizes results. To create an emulsion of very small droplets, the droplets must be stabilized against coalescence and diffusional instability (Ostwald ripening). Stabilization against coalescence is effected by adding an appropriate surfactant. If the small droplets are not stabilized against diffusional degradation, they will disappear,[1] increasing the average droplet size, and reducing the total interfacial area. Jansson[2] has shown that this disappearance can be very fast for small droplets. In creating a miniemulsion, diffusional stabilization is achieved by adding a small quantity (1–2% w/w based on monomer) of a highly monomer-soluble, water-insoluble stability agent. Both long chain alkanes such as hexadecane (HD) and long chain alcohols such as cetyl alcohol have been used as stability agents in miniemulsions.[3–5] These traditionally have been referred to as cosurfactants, although they may not actually play a surfactant role.

Current research[6,7] indicates that miniemulsion polymerization can provide benefits over the current process technology of conventional emulsion polymerization. Among these are a process that is much more robust to contamination and operating errors, a more uniform copolymer composition when used for copolymerization, and a final product that is far more shear-stable than the product of conventional emulsion polymerization. For these reasons, miniemulsion polymerization may offer an alternative to the current industrial practice of seeded emulsion polymerization, at substantial savings in operating costs. The drawback to current miniemulsion technology is the need for a volatile organic cosurfactant that must be removed from the latex after polymerization.

The use of polymer as a cosurfactant has been reported recently,[8,9] and is the primary focus of the work reported here. Conventional thinking has been that effective cosurfactants must be highly water-insoluble, highly monomer-soluble, and of low molecular weight. Polymer made from the monomer of which the miniemulsion is to be made will be highly water-insoluble, and most polymers are quite soluble in their own monomers. The requirement that the cosurfactant must be of low molecular weight is based on reported swelling experiments and theoretical swelling calculations.[10] Data reported herein demonstrate that it is possible to create miniemulsion latexes with a poor cosurfactant (polymer). The polymeric cosurfactant is thought to delay Ostwald ripening sufficiently to allow nucleation of the monomer droplets by water-phase radicals (primary or oligomeric). Once the droplets are nucleated, the polymer produced adds additional diffusional stability. It should be noted that the monomeric miniemulsions formed are not true miniemulsions in the sense that they are not stable over a period of months. However, Ostwald ripening can be reduced to permit the polymerization to be carried out. The latexes produced from polymer-stabilized emulsions have all the characteristics of miniemulsion latexes, and derive from droplet nucleation. Therefore, while we will refrain from referring to polymer-stabilized monomeric emulsions as *miniemulsions,* we feel justified in referring to the products of such polymerizations as *miniemulsion latexes.* Polymer, when used to stabilize droplets against diffusion, will be referred to as the *hydrophobe* rather than the cosurfactant, since it is not a good cosurfactant in the currently used sense, and since cosurfactant is probably a misnomer, even when the "cosurfactant" is hexadecane. Polymer has been shown to perform as well as hexadecane in stabilizing the droplets for the short periods necessary to ensure nucleation. It has the added advantages of being totally innocuous in the final product, very soluble in the monomer, and very water insoluble. This paper reports the successful use of polymethyl methacrylate as a hydrophobe for the miniemulsion polymerization of methyl methacrylate monomer.

In general, this work addresses the effects of hydrophobe levels and molecular weight of the hydrophobe on the droplet size and droplet size distribution. Emulsion stability is inferred from these results. It also addresses the effects of surfactant levels on the droplet sizes and distributions. The effects of these recipe variations on the rate of polymerization and mechanism of nucleation are presented. To aid in this, conductance measurements are used as a diagnostic tool. Finally, the impact of the hydrophobe and surfactant levels on the final latex characteristics is evaluated in terms of average particle size, polydispersity of particle size distribution, and latex stability.

EXPERIMENTAL

Emulsion Preparation

Forty-eight emulsions were prepared using the following reagents:

- Methyl methacrylate (MMA) monomer, supplied by Rohm and Haas Company, inhibited with 10 ppm methylethyl hydroquinone
- Sodium lauryl sulfate (SLS), supplied by BDH Limited, Poole, England (available in the U.S. through Gallard Schlesinger Chemicals Manufacturing Company, Carle Place, NY)
- Deionized (DI) water
- Polymeric cosurfactant

Polymeric hydrophobes were obtained through solution polymerizations with varied amounts of chain transfer agent (carbon tetrachloride) and initiator (AIBN) to adjust molecular weight. Viscometry was used to measure the molecular weight of the polymethyl methacrylate hydrophobe. Polymer-stabilized emulsions were prepared by varying soap concentration, hydrophobe concentration, and molecular weight of the hydrophobe as follows:

- 500 g H_2O
- 200 g MMA
- 1, 2, or 3 g of SLS
- 2, 4, 6, or 8 g of PMMA with viscosity average molecular weights of 33,000, 94,000, 350,000, or 1,050,000 g/gmol
- 5 min of sonication at 60% full output

The desired amount of polymeric hydrophobe was added to the appropriate amount of monomer, then mixed with a stirring bar at room temperature until the polymer was dissolved. This solution was then added to the previously prepared surfactant solution. The entire contents were then sonicated with a Fisher 300W Sonic dismembrator for 5 min at 60% output (180 W), with bulk mixing provided by the stirring bar.

Conductance

After sonication, approximately 30 mL of the emulsion was drawn off into a small test tube and a conductance probe was inserted, making sure it was free from the tube wall. The test tube was chosen to minimize monomer loss by evaporation. The conductance meter was calibrated using data from *The Handbook of Chemistry and Physics,*[12] for standard anhydrous sodium sulfate solutions. The conductances of SLS solutions were measured to ascertain the free surfactant concentration as a function of conductance. All data were corrected for temperature deviations.

Droplet Size

Droplet sizes were measured by the Malvern Autosizer IIc. Using a quartz cuvette, the emulsions were diluted with a saturated solution of monomer and DI water to about 50 : 1. The diluent, being saturated with monomer, was not found to be a "sink" for the monomer, which would affect the droplet size. Measurements were made at 5 min intervals. The Autosizer provides average diameters, standard deviations, and distributions based on mass, intensity and number.

Shelf-Life Stability

Shelf-life was measured by placing approximately 30 mL of an emulsion in a capped glass vial and observing the time necessary for a visible creaming line to appear.

Latex Preparation

A standard recipe for latex preparation is as follows:

- 500 g DI water
- 200 g MMA
- 1, 2, or 3 g SLS
- 2, 4, 6, or 8 g of polymeric hydrophobe (MW = 350,000 g/gmol)
- 0.675 g $K_2(SO_4)_2$
- 5 min of sonication at 60% full output

The inhibited monomer was washed with 40 mL of a 5% NaOH solution, then subsequently with a saturated NaCl solution to remove the methyl ethyl hydroquinone. The monomer was then transferred to a covered vessel. Preweighed polymeric hydrophobe was then allowed to dissolve in the monomer with gentle agitation. The molecular weight of the polymeric hydrophobe chosen was based on the emulsion stability data.

After the polymer was totally dissolved, it was added to the desired SLS solution, and then sonicated for 5 min. The emulsion was then transferred to a reaction flask and submerged in a water bath at 60°C. A condenser was added and the entire system was purged with nitrogen for 5 min. Agitation was provided by a Propeller stirrer with a rpm of

700 ± 100. To continuously measure conductance, a recycle loop containing the conductance cell was then attached. After the nitrogen purge, the initiator was injected through a syringe. Every 5 min, for the first 30 min after initiation, samples (approximately 10 mL) were drawn for gravimetric conversion analysis. Samples were then taken every 10 min for the duration of the polymerization. These drawn samples were added to a 0.5 wt % solution of hydroquinone and placed in a refrigerator.

Conductance

The conductance cell was fed the reaction mixture via a positive-displacement pump. All tubing to and from the pump was submerged in the water bath to ensure that the effluent from the cell was at a temperature of no less than 57°C. This was facilitated by the high flow rate through the line, whose total volume was kept at a nominal 50 mL. Readings from the cell were taken every 2 min for the entire length of the reaction.

Particle Size

The final latexes were diluted 100 : 1 with a 0.02 wt % solution of SLS. Particles sizes and particle size distributions were then measured on the Malvern Autosizer.

Shear Stability

To ascertain the latexes' shear stability, they were sonicated again at 60% output for 5 min. The particle sizes and distributions were then measured again. Any change in particle size or distribution was noted, especially those accompanying coagulation.

Freeze/Thaw Characteristics

The latexes were frozen at −12°C for 8 h, then left to thaw at room temperature for 8 h. This constituted one cycle. The number of cycles a latex could undergo before coagulating was noted.

RESULTS AND DISCUSSION

Monomeric Emulsions

Shelf-Life

The shelf-life of the emulsions ranged from 2 min to 6 h. The variables affecting the shelf-life were the surfactant concentration, the hydrophobe concentration, and the molecular weight of the hydrophobe.

Figures 1 and 2 show the dependence of shelf life on these variables. It can be seen that there is a range of hydrophobe molecular weights for which the emulsions are stable. This range, which depends on the concentrations of both the surfactant and hydrophobe, is from about 350,000 to 750,000 g/gmol. It can be seen further that within this range, the stability can be further enhanced by low surfactant levels and high hydrophobe levels.

Low surfactant level increases stability by decreasing the solubility of the monomer and hydrophobe in the aqueous phase. High hydrophobe levels, in contrast, impart diffusional stability. The Gibbs free energy of forming a droplet i can be expressed by the Morton equation[12]:

$$\frac{\Delta G_i}{RT} = \ln \Phi_m + (1 - m_{mp})\Phi_p + \chi_{mp}\Phi_p^2 + \frac{2\gamma V_m}{r_i RT} \quad (1)$$

where Φ_m and Φ_p are the volume fractions of monomer and polymer, respectively, m_{mp} is the molar volume ratio of monomer to polymer, χ_{mp} is the interaction parameter between the two, γ is the interfacial tension between the continuous and dispersed phases, r_i is the droplet radius, and V_m is the molar volume of the monomer. Increasing Φ_p (and therefore, decreasing Φ_m) reduces the Gibbs free energy of forming the droplet and diffusional stability is imparted to the emulsion. Diffusional stability allows the continued existence of small droplets, which are less susceptible to creaming (phase separation) than the large droplets resulting from Ostwald rip-
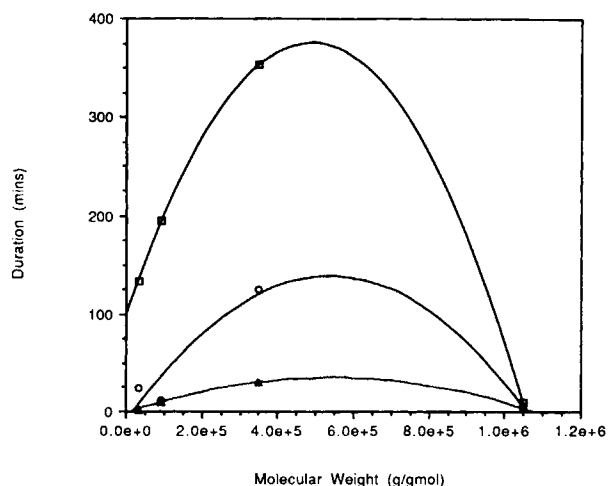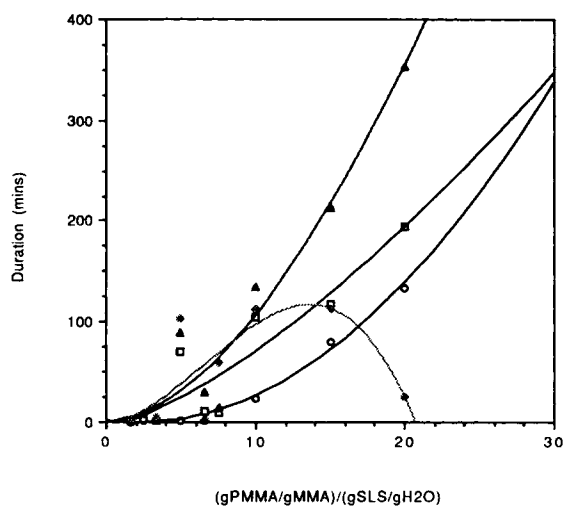

Figure 1   Duration of emulsions versus molecular weight of the hydrophobe for different surfactant concentrations: (O) 0.00693; (□) 0.0139; (▲) 0.0208 gmol SLS/L aq. The hydrophobe concentration is 0.04 g PMMA/g MMA. The curves connecting the data points are intended only to indicate trends.
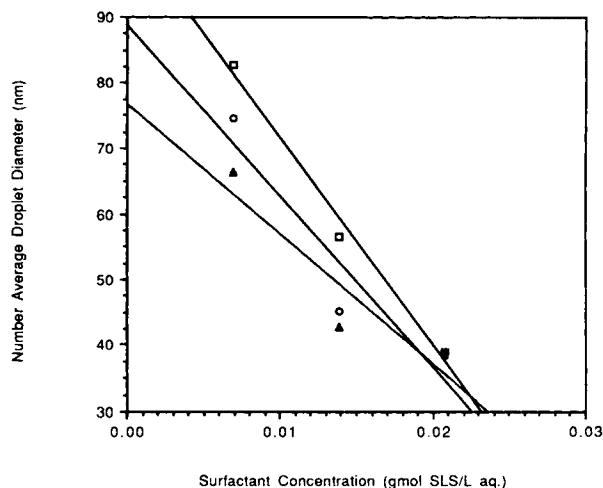
ening. A simpler way of expressing this is to note that as a small droplet shrinks due to diffusion of monomer out of the droplet (Ostwald ripening), the concentration of polymer (which is highly water-insoluble, and cannot diffuse out of the droplet) must increase. This is thermodynamically unfavorable. It should be noted that the polymer-stabilized emulsions in this work are not thermodynamically stable, since calculations from the Morton equation indicate that true stability at the droplet sizes reported requires at least three times the highest level of hydrophobe used here. This is manifest in creaming times of up to 6 h as compared to 3 weeks to 3 months for equivalent emulsions stabilized with HD.[8] Rather, it is believed that the partial stability induced by the hydrophobe retards diffusional degradation sufficiently to allow initiation of the droplets before extensive degradation occurs.

Droplet Size

The droplet sizes for the miniemulsions ranged from 19.5 to 141.2 nm. These values are close to those reported by Rodriguez[13] for MMA miniemulsions employing HD as the cosurfactant. Rodriguez also showed that the droplet size decreased with increasing hydrophobe concentration. This appears to be true for polymeric hydrophobe as well. Figure 3 shows the droplet size decreasing for both increases in the hydrophobe and increases in the surfactant concentration. (The lines were chosen by best fit and are intended only to show trends.) The effect of the hydrophobe can be justified from the Morton

Figure 3   Droplet diameter versus surfactant concentration for different hydrophobe concentrations: (□) 0.01; (○) 0.02; (▲) 0.03 g PMMA/g MMA. The molecular weight of the hydrophobe is 1,050,000 g/gmol.

equation. At equilibrium the surface energy term and the mixing term are equal, and eq. (1) becomes

$$-\frac{2\gamma V_m}{r_i RT} = \ln \Phi_m + (1 - m_{mp})\Phi_p + \chi_{mp}\Phi_p^2 \quad (2)$$

As the polymer concentration increases, the right-hand side of the equation becomes more negative. Therefore, the radius these emulsions can accommodate becomes smaller.

The effect of the molecular weight of the hydrophobe has a slight influence on the droplet diameter. This affects the value of m_{mp} in the above equation—higher molecular weights decrease its value. This will tend to increase the droplet diameter, though the effects are not pronounced.
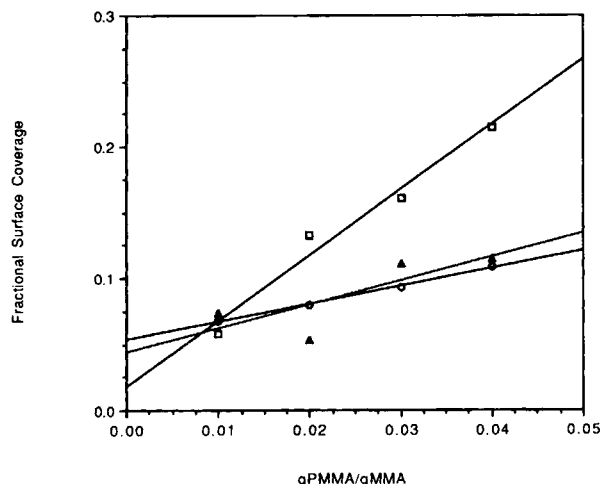
The droplet diameter dependence on surfactant is what is typically seen in emulsions. As more surfactant is added more surface area can be stabilized, thereby reducing the droplet size. This effect, although present, was not dramatic in this case. This implies that thermodynamic stability is more important than surface stabilization.

Droplet Size Distributions

Miniemulsions stabilized with polymeric hydrophobe had polydispersity indexes of between 1.008 and 1.039. This is in line with measurements by Fontenot and Schork[6,7,14,15] for miniemulsions of methyl methacrylate with HD as cosurfactant.

Surfactant Coverage

Coverage of the droplet surface by the surfactant molecules was calculated from the conductance of

Figure 2   Duration of emulsions versus the ratio of hydrophobe to surfactant concentrations for different molecular weights of the hydrophobe: (○) 33,000; (□) 94,000; (▲) 350,000; (♦) 1,050,000 g/gmol.

Figure 4 Fractional surface coverage by surfactant molecules versus the hydrophobe concentration for different molecular weights of the hydrophobe: (O) 33,000; (□) 350,000; (▲) 1,050,000 g/gmol. The surfactant concentration is 0.0139 gmol SLS/L aq.

the miniemulsion. The conductance of standard surfactant solutions was used to assess the amount of free surfactant. This was then used to find the amount of surfactant adsorbed on the droplets by difference from the total recipe surfactant. The area occupied by a surfactant molecule was estimated from Vijayendran's work[16] as 0.79 nm^2. This value is based on pure MMA droplets. It should decrease slightly as the polymer content increases. Figure 4 shows the dependence of surface coverage on the concentration and molecular weight of the hydrophobe. Coverage is seen to increase with increasing polymer concentration and molecular weight. An optimal molecular weight is seen as 350,000 g/gmol. Since increased hydrophobe results in smaller particles, and smaller particles have a larger aggregate interfacial area, one would expect (at constant total surfactant concentration) surface coverage to go down with increased hydrophobe concentration.

A rise in surface coverage with the presence of polymer can be explained in part by the difference in polarity between the monomer and polymer. Vijayendran[16] has shown that the area occupied by a surfactant molecule increases with increasing polarity of the interfacial phase. Since the monomer is more polar than the polymer, as the polymer concentration increases and more is present at the surface, the area occupied by a surfactant molecule must decrease. The result is more total surface coverage. This surface coverage may affect radical absorption, because of columbic interactions between the anionic surfactant head and the free radical. In addition, if the hydrophobe were polymerized with a wa-

ter-soluble initiator, then a hydrophilic substituent would reside on one end of the polymer chain. This would make the chain prefer the polymer/water interface as opposed to residing inside the particle. This would crowd the surfactant molecules and reduce the overall surface coverage. In this work the hydrophobe was produced through solution polymerization with AIBN as the initiator. This resulted in a hydrophobic chain end that preferred the particle phase, and should not have interfered with the surface coverage on a columbic basis.

Hydrophobe Molecular Weight

Based primarily on the emulsion shelf-life data, an optimal molecular weight of the hydrophobe was chosen. The molecular weight of the polymer that was found to contribute most to the stability was 350,000 g/gmol. All subsequent work on latex preparation and polymerizations used this molecular weight for the hydrophobe.

Some speculation must be offered as to why lower and higher molecular weights were less successful at stabilizing the emulsions. Low molecular weights (33,000 g/gmol) produced small droplets (as shown in Fig. 5). These droplets were small enough to be strongly influenced by Brownian motion. This, in turn, can lead to flocculation and coalescence. Figure 5 also shows that as the molecular weight increases from 350,000 to 750,000 g/gmol, the droplet size is maximized for a given hydrophobe level. Past this upper molecular weight, the droplet size drops off
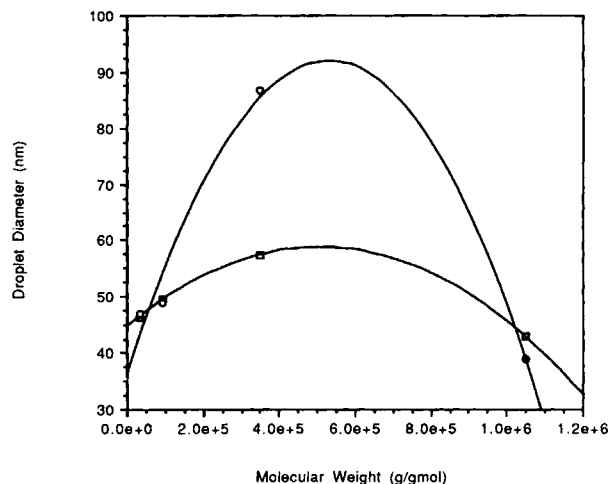
Figure 5 Droplet diameter versus the molecular weight of the hydrophobe for different surfactant concentrations: (O) 0.00693; (□) 0.0139 gmol SLS/L aq. The hydrophobe concentration is 0.02 g PMMA/g MMA. The curves connecting the data points are intended only to indicate trends.

again, and Brownian motion induced coalescence is again a possibility. In addition, large molecular weights can produce elastic energies that tend to reduce the equilibrium droplet size.[9]

Latexes

Monomer Conversion

Conversion versus time data were collected for 12 miniemulsion polymerizations, varying over four different hydrophobe concentrations and three different surfactant concentrations. Three reference macroemulsions were also run, varying the surfactant level. Figures 6 and 7 show the effects of surfactant and hydrophobe concentrations on the rate of polymerization.

As seen in Figure 6, the reaction rate is comparable for polymer concentrations of 0.01 and 0.02 g PMMA/g MMA, increases for a concentration of 0.03 g PMMA/g MMA, and then decreases slightly for a value of 0.04 g PMMA/g MMA. A dramatic increase is seen between the macro- and miniemulsion polymerizations. The macroemulsion requires 90 min to achieve 90% conversion, while the miniemulsion requires only 35 min for the same conversion. In the miniemulsions, the size of the droplets can be of the order of the size of the micelles. Micelles are typically 10 nm and the droplets sizes ranged down to 24.2 nm. On a surface area basis, these droplets can effectively compete with micelles for radicals. In addition, in miniemulsions, the free surfactant (dissolved in the aqueous phase) concen-
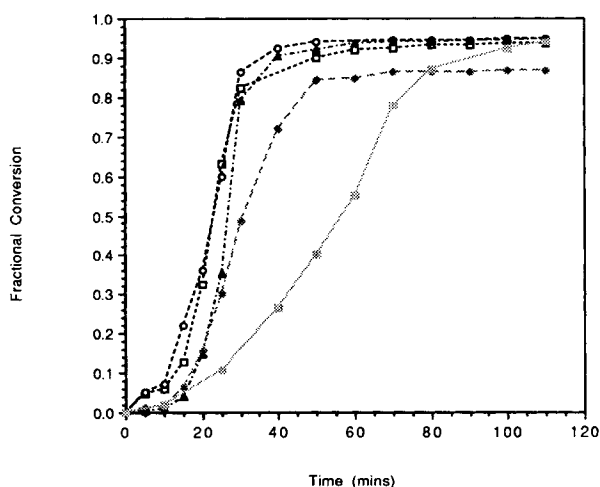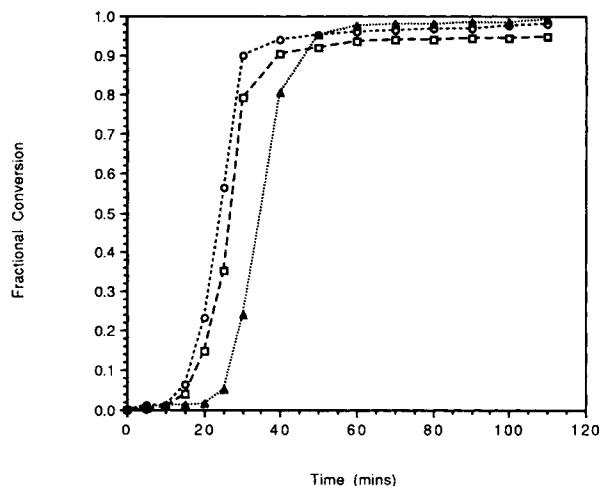
Figure 7   Fractional conversion versus time for miniemulsion polymerizations for different surfactant concentrations: (□) 0.00693; (○) 0.0139; (▲) 0.0208 gmol SLS/L aq. The hydrophobe level is 0.03 g PMMA/g MMA.

tration is often well below the critical micelle concentration (CMC).[6] The total surfactant concentrations chosen for these experiments were 0.77, 1.66, and 2.3 times the CMC value. Possibly, reaction rates resulting from droplet nucleation (miniemulsions) are faster because they do not depend on diffusional mass transfer of the monomer across the aqueous phase. The particle numbers are similar for these cases, $1.788(10)^{17} \pm 1.609(10)^{16}$ particles. The mass transfer, calculated from Frossling's equation, to a 10-nm micelle with negligible forced convection is on the order of 10^{-21} gmol/s. The rate of polymerization per particle is also on the order of 10^{-21} gmol/s. Therefore, the reaction may be mass transfer limited, and mechanisms that do not depend on limiting mass transfer should yield faster reaction rates. Figure 7 demonstrates this concept.

The curves in Figure 7 represent polymerizations with surfactant levels of 0.00693, 0.0139, and 0.0208 gmol/L, all with a hydrophobe level of 0.03 g PMMA/g MMA. No micelles are present in the first case. In the second case both micelles and droplets are present in comparable numbers—both competing for initiator radicals. These two polymerizations have similar rates. However, when the surfactant level is increased, micellar nucleation dominates and the reaction exhibits an induction period. From conductance data, the amount of micellar soap can be calculated. This, along with droplet size measurements, can afford a ratio of the number of micelles to the number of droplets. For the polymerizations depicted in Figure 7 these were 0, $10^2 : 1$, and $10^3 : 1$, respectively. The droplet numbers were $1.81(10)^{17}$, $1.93(10)^{17}$, and $2.63(10)^{17}$, respectively. In

Figure 6   Fractional conversion versus time for emulsion polymerizations for different hydrophobe concentrations: (□) 0.01; (○) 0.02; (▲) 0.03; (◆) 0.04; (■) 0.0 g PMMA/g MMA (macroemulsion). The surfactant concentration is 0.00693 gmol SLS/L aq.

contrast the particle numbers are $2.02(10)^{17}$, $2.42(10)^{17}$, and $2.45(10)^{17}$, respectively. This dramatizes the preferred mechanism of droplet nucleation. The assumption that the droplet number remains constant can be justified through the thermodynamic stability, and the probability that all the droplets can be nucleated. Further proof can be offered by the analysis of the latex particle size distributions and the conductance during polymerization.

Conductance

Profound differences in the conductance versus time curves were observed for mini- versus macroemulsion polymerizations. These measurements were used to probe the nucleation and polymerization processes. The effects of the levels of polymeric hydrophobe and surfactant on the polymerizations are shown in Figures 8 and 9. A general description of these profiles can be developed. Consider a macroemulsion. Initiator is charged at around 5 min into the reading. There is a corresponding rise in conductance since the initiator is an electrolyte. This is followed by a reduction in the conductance as particles are initiated and absorb surfactant. Then at around 30 min (30% conversion), there is a sharp rise in conductance. It is thought that this is the point at which the monomer droplets disappear (end of Interval II). The aqueous phase becomes desaturated with monomer, causing the conductance to rise. As the hydrophobe concentration is increased from zero (macroemulsion), to 0.04 g PMMA/g
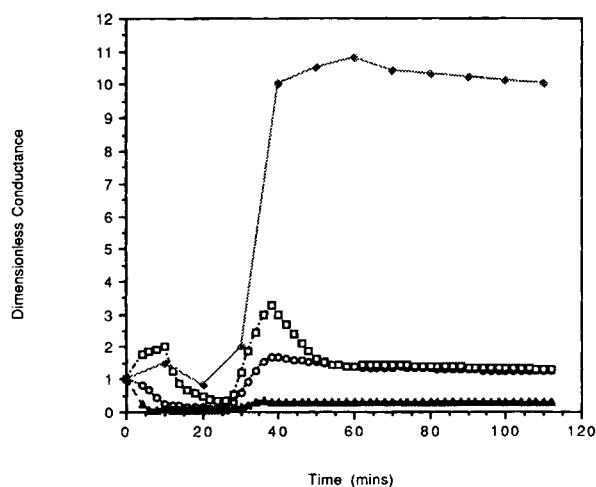
Figure 8   Dimensionless conductance (mhos/cm/mhos/cm_0) versus time during polymerizations for different hydrophobe levels: (O) 0.01; (□) 0.02; (▲) 0.03; (◆) 0.0 g PMMA/g MMA (macroemulsion). The surfactant level is 0.0139 gmol SLS/L aq.
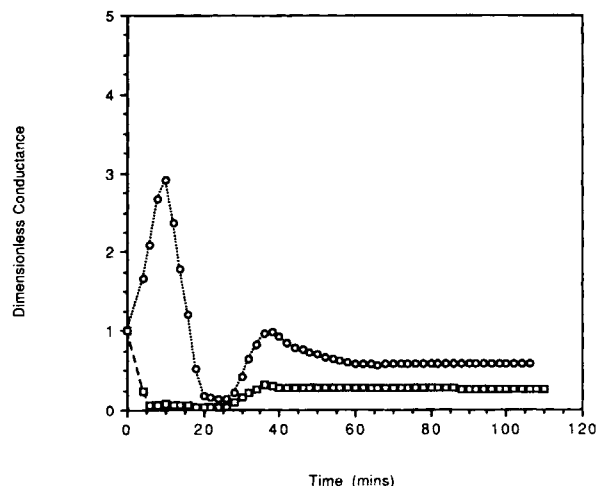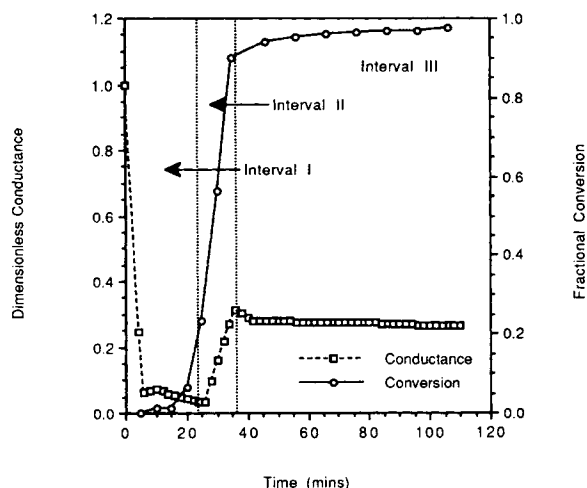

Figure 9   Dimensionless conductance (mhos/cm/mhos/cm_0) versus time during polymerization for different surfactant levels: (□) 0.00693; (O) 0.0139 gmol SLS/L aq. The hydrophobe concentration is 0.03 g PMMA/g MMA.

MMA (miniemulsion), this phenomena becomes less pronounced. This implies that miniemulsion polymerizations occur with very little change in surface characteristics, and supports the mechanism of droplet nucleation. Since miniemulsion droplets transfer only a minimal amount of monomer to micelles (and other droplets or particles), any existing micelles must be starved for monomer. Hence it is a good assumption that the bulk of the polymerization takes place in the droplets. These conductance results are in agreement with those of Fontenot and Schork[6] for MMA miniemulsions made with HD as the cosurfactant. It is not known why some polymerizations do not show a rise in conductance upon addition of the initiator.

Figure 9 indicates that increasing the surfactant concentration in a miniemulsion polymerization has the same effect on the conductance profile as decreasing the hydrophobe concentration. Both increasing surfactant and decreasing hydrophobe decrease the miniemulsion "character" of the system.

These conductance profiles were found to be a useful tool in describing the various intervals in miniemulsion polymerization. Figure 10 shows a direct correlation between the intervals and the numerous inflections in the conductance versus time curve. The end of Interval I (not present in true miniemulsion polymerizations when the aqueous phase is below the CMC from time zero), corresponding to the desaturation of the aqueous phase with surfactant, can be seen by an initial minimum in the conductance curve. This occurs at about 25% conversion. The Smith–Ewart model predicts it should happen between 2 and 20% conversion.[16] The

Figure 10 Dimensionless conductance (mhos/cm/ mhos/cm$_0$) and fractional conversion versus time during polymerization of miniemulsion.

conductance then rises to a maximum, as monomer droplets are depleted. The maximum of this rise is the end of Interval II. This accounts for 75% of the conversion. The conductance then levels off as there is little interfacial area during Interval III. This results in the final 10% of the conversion. The presence of these three intervals probably indicates that there is some micellar nucleation taking place, and that not all of the monomer droplets are being nucleated. However, it should be noted by comparison with Figure 8 that these characteristics of the conductance curve of the miniemulsion are almost insignificant in comparison with the same characteristics of the macroemulsion polymerization, indicating predominant droplet nucleation in the miniemulsion.

Particle Size

The particle sizes for the fully converted miniemulsion latexes ranged from 90.5 to 126.5 nm. These are on the low end of the range for miniemulsions. (Typically miniemulsion particles are from 50 to 200 nm.) These final diameters were found to be dependent on both the hydrophobe and surfactant levels. Figure 11 shows the above dependence.

At a constant hydrophobe level the particle diameter decreases with increasing surfactant. This is the usual response to increases in surfactant. There is an increase in the total surface area as more surfactant is present to stabilize it. This argument and its justification are identical to the one given for the droplet stability. In contrast, the particle diameter is seen to rise on the introduction of polymeric hydrophobes. However, none of these vari-

ables has a significant overall effect on the particle size.

The coefficient of variation (COV) for the distribution of the particles was provided by the Malvern Autosizer. The COV and the polydispersity index (PDI) are related by the formula[17]

$$PDI = \left[1 + \frac{\sigma^2}{\mu^2}\right]^{1/2} = \left[1 + \frac{(COV)^2}{100^2}\right]^{1/2} \quad (3)$$

where σ is the variance of the PSD, and μ is the number average diameter. These coefficients ranged from 10.9, a polydispersity index (PDI) of 1.006, to 24.7. Latex with a COV of less than 10.0 is generally considered to be monodisperse.[17] Hence, the feasibility of manufacturing monodispersed latexes with polymeric hydrophobe appears to be quite positive. Previous work[6] with alkane cosurfactants produced latexes with COVs ranging from 27.4 to 39.4, and a typical macroemulsion has a COV of about 31.7.[6] Thus polymeric hydrophobes appear to produce much narrower particle size distributions.

Figure 12 shows the effects of the surfactant and hydrophobe concentration on the COV of the final product. The lowest COV corresponds to a latex made with a low surfactant concentration (0.00693 gmol/L), and a low hydrophobe concentration (0.01 g PMMA/g MMA). Low surfactant concentration ensures that droplet nucleation is dominant in these experiments, because polymerization took place entirely below the CMC. When droplet nucleation is dominant, particles may be formed over a short nucleation period, and a large percentage of the potential nucleation sites (droplets plus micelles) are nucleated. By contrast, micellar nucleation can take
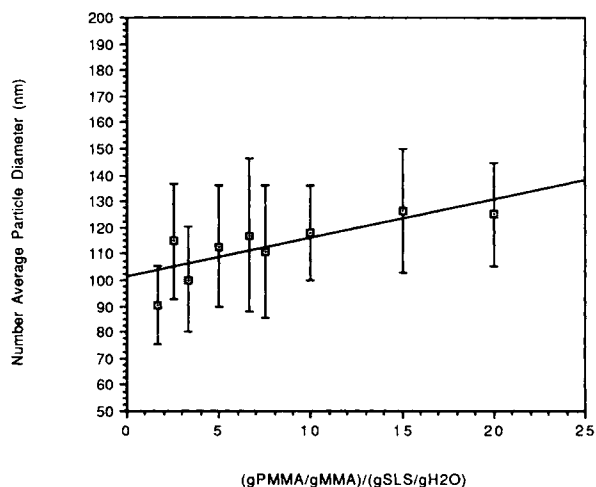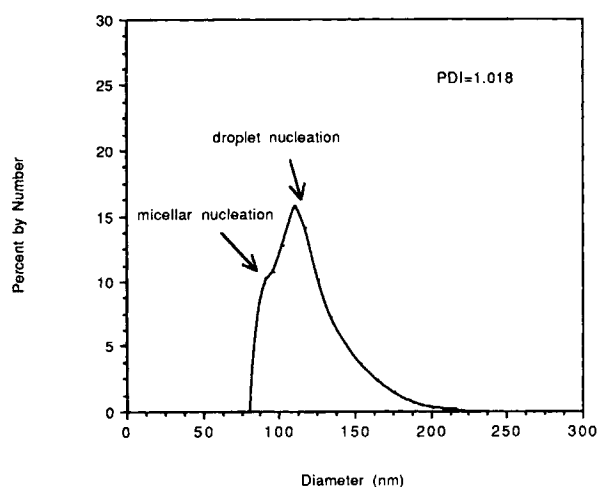

Figure 11 Number average diameter of miniemulsion latexes as a function of the ratio of hydrophobe concentration to surfactant concentration.
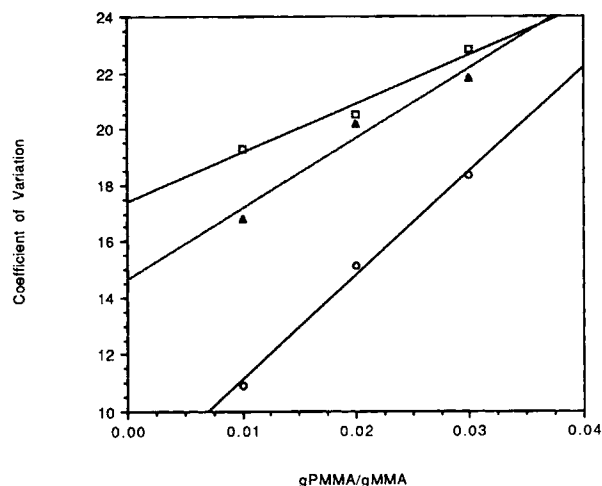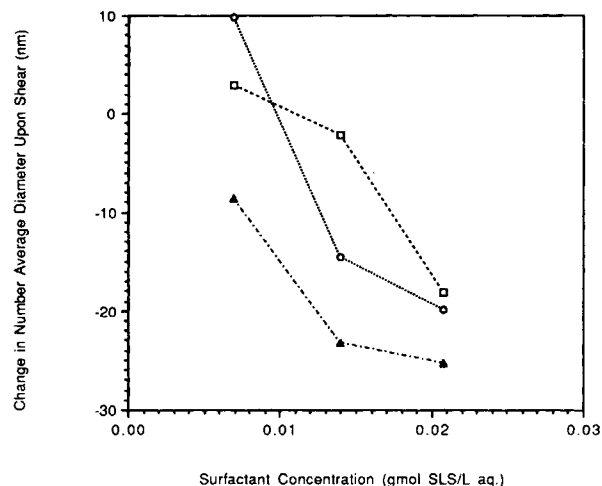
Figure 12 Coefficient of variation (*COV*) of the particle distribution versus the hydrophobe concentration for different surfactant concentrations: (O) 0.00693; (□) 0.0139; (▲) 0.0208 gmol SLS/L aq.

Figure 14 Change in the number average particle diameter upon high shear versus surfactant concentration for different hydrophobe concentrations: (O) 0.01; (□) 0.02; (▲) 0.03 g PMMA/g MMA.

place over a longer period, and a minute fraction (i.e., one thousandth) of the potential nucleation sites are actually nucleated. At any time during nucleation in a macroemulsion, a great number of unnucleated micelles exist, waiting to be nucleated at a later time, or to be consumed in supporting surface coverage of existing particles. Low hydrophobe concentration allows more monomer to freely transport between droplets to ensure a uniform size, based on equilibrium swelling. By a similar argument the highest *COV* corresponds to the polymerization with the highest hydrophobe and surfactant concentra-

Figure 13 Particle size distribution of miniemulsion latex showing micellar nucleated particles and droplet nucleated particles. The surfactant concentration is 0.0139 gmol SLS/L aq. and the hydrophobe concentration is 0.02 g PMMA/g MMA.

tions (0.0208 gmol/L and 0.04 g PMMA/g MMA), respectively. This is due to dominating micellar nucleation and poor interdroplet transport. Thus, it would appear that highest monodispersity is achieved at low surfactant concentration, and intermediate hydrophobe concentration.

If these extreme cases represent droplet and micellar nucleation, respectively, then a mixture of the two mechanism must be present in an intermediate recipe of hydrophobe and surfactant. This shown in Figure 13, where a bimodal distribution is seen. The surfactant concentration was 0.0139 gmol/L and the hydrophobe concentration was 0.02 g PMMA/g MMA. The smaller particles result from micellar nucleation, and the larger ones from droplet nucleation. This is justified by viewing the nucleated micelles leading to macroemulsion sized particles, 10 to 1000 nm, while the nucleated droplets lead to miniemulsion sized particles, 100 to 10,000 nm.

Shear Stability

In general the average particle size of the miniemulsion latexes was lowered by shearing the latex. This is indicative of some reversible flocculation. As seen in Figure 14, the average change in the particle diameter was −11.49%. This corresponds to aggregates existing in the latex having an average of 1.5 particles each. Therefore this flocculation cannot be seen as dramatic. No coagulation was observed in any of the miniemulsion latexes. They showed an increased shear stability, presumably due to their low polydispersities. By contrast the macroemulsion latexes coagulated almost immediately upon shear-

ing. Presumably this due to the presence of large nucleated droplets that become sites of coagulation or flocculation for the smaller particles. The average change in the polydispersity after shearing was −0.54%. This resulted in a general narrowing of the particle size distribution upon shearing. This is also indicative of some reversible flocculation.

Freeze/Thaw Characteristics

All the latexes survived only one cycle of freezing and thawing before coagulating. This was to be expected. The latexes were stabilized with an anionic surfactant, so their Debye length, a measure of electrostatic repulsion, is reduced upon cooling. A nonionic polymer can be introduced into aqueous phase to provide stearic stabilization, which is only weakly affected by temperature. This would improved impart freeze/thaw stability.

SUMMARY AND CONCLUSIONS

Polymer makes an ideal hydrophobe for numerous reasons. Primarily, it is able to fulfill the two major requirements of any hydrophobe: water insolubility and monomer compatibility. The effects of insolubility can be profound. If the hydrophobe is to stabilize the droplets, it should remain in the droplets. This demands that the hydrophobe be *very* hydrophobic. In this case the saturation concentration of polymer in water is insignificant. Secondly, since the hydrophobe is residing in the droplets it should be soluble in the monomer. Most polymers are infinitely soluble in their monomers. For the PMMA/ MMA system, this is evident in the solubility parameters. PMMA has a solubility parameter of 19.3 $MPa^{1/2}$ and that of the MMA is 18.9 $MPa^{1/2}$.[18] It has been thought, based on data on limited swelling,[10] that effective hydrophobes must be of low molecular weight. This appears to be true for equilibrium swelling that produces stable miniemulsions. Present data show that stability is not necessary to cause predominantly droplet nucleation.

Water insolubility and monomer solubility are essential, but additional favorable properties exist for polymeric hydrophobes. Certain processing advantages arise when using polymeric hydrophobe. One is a reduction in the vapor pressure of the monomer upon addition of the polymer. The extent of this reduction can be calculated from Henry's law. A decrease in vapor pressure helps reduce monomer loss as well improving the health environment, both of which are engineering concerns. Another advantage is that polymer, for obvious reasons, does not

have to be removed after the polymerization. Presently used cosurfactants, if left in the latex, will slowly evaporate (causing high VOC) in the case of alkanes, or cause water swell in the case of alcohols. Therefore these hydrophobes, if used in a commercial process, would require removal, probably by steam stripping. This is a costly processing step, and, as shown by this work, unnecessary.

These processing concerns are augmented by the ability to control the particle size distribution. As it was shown, particle size distributions were obtainable at both ends of the range: narrow, broad, or even bimodal. By varying the surfactant and polymeric hydrophobe levels, a reproducible particle size distribution is possible. At the low end these particles are almost monodispersed. There is little doubt that further experiments, lowering both the surfactant and hydrophobe concentrations, can lead to monodisperse particles. This control over the distributions is attributed to the crude control over the droplet and the micellar nucleation. Droplet nucleation tends to lead to narrow particle size distributions and micellar nucleation tends to broader ones. A mixture of the two mechanisms gives distributions that lie somewhere in between. Controlling the two mechanisms is therefore paramount to controlling the resulting product's characteristics. This can be achieved through manipulation of the aforementioned variables. It should be noted that if droplet nucleation is to occur at all, the emulsion and subsequently the droplets must be stable.

Since the stability of the emulsion is dependent on the droplet size, it is desirable to correlate the size of emulsion droplets to their composition, which can be controlled. Insight into this can be obtained using the Morton equation. This thermodynamic relationship shows the direct dependence of the composition on the droplet size. Furthermore, assuming that all the droplets have the same composition, it shows that an equilibrium droplet size must exist, although it may not be reachable with polymeric hydrophobes at low hydrophobe concentrations. When the droplet size is decreased, droplets compete with micelles for surfactant and free radicals, and become the predominant sight for nucleation. Since polymerizations resulting from this nucleation do not depend on monomer transfer, they may precede faster, particularly with monomers that are only very slightly water soluble.

Polymer has proven to be an excellent hydrophobe for the system of methyl methacrylate/polymethyl methacrylate. This could easily be extended to other systems as well. Systems such as styrene/ polystyrene and styrene/polybutadiene could be attempted. As long as the polymer meets the afore-

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mentioned criteria, any system is a candidate. In general polymeric hydrophobes should be seen as the preferred alternative to presently used materials.

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