Miniemulsion Polymerization of Vinyl Acetate with Nonionic Surfactant

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SYNOPSIS

The stability of vinyl acetate miniemulsions employing polyvinyl alcohol (PVOH) as the surfactant, and hexadecane and/or various polymers as the cosurfactant, were studied. Shelf lives (to phase separation) and monomer droplet sizes were measured. The results indicate that it is possible to prepare stable miniemulsions using a nonionic surfactant (PVOH) and hexadecane as the cosurfactant. Polymeric cosurfactants do not create stable miniemulsions but retard Ostwald ripening to an extent that allows predominant droplet nucleation. The polymerization behavior of these miniemulsion systems was investigated using on-line conductance measurements to differentiate droplet versus micellar/homogeneous nucleation. The effect of cosurfactant concentration on the reaction rate was compared for hexadecane and polymeric cosurfactants. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The mechanisms of conventional emulsion and miniemulsion polymerizations are in some ways significantly different. A conventional 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 takes 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-swollen polymer particles with monomer supplied by diffusion from the droplets. Interval III begins when the droplets disappear and continues to the end of the reaction. In this study, for the purpose of clearly distinguishing between conventional 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.

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. In order to create an emulsion of very small droplets, the droplets must be stabilized against coalescence and diffusional instability. Diffusional instability is caused by a phenomenon known as *Ostwald ripening*. If the disperse (oil) phase is even slightly soluble in the continuous (aqueous) phase, oil will diffuse from the smaller droplets, across the aqueous phase, and into the larger droplets. The net

effect is a reduction in total interfacial area, and consequently, in interfacial energy. This process is known as 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% wt/wt based on monomer) of a highly monomer-soluble, water-insoluble *cosurfactant*. Both long-chain alkanes such as hexadecane (HD) and long-chain alcohols such as cetyl alcohol have been used as stability agents in miniemulsions.[3–8] Although referred to as cosurfactants, these additives may play no surfactant role whatsoever.

Lack et al.[9] examined the interfacial aspects of miniemulsion stability and concluded that the overall droplet stability is not comprised solely of diffusional stability. The presence of liquid crystals at the oil–water interface were cited as the cause of the increase in droplet shear stability. Choi et al.[10] and Ugelstad et al.[11] studied various cosurfactants, recipes, and methods of preparation. Cosurfactants are usually water insoluble, monomer soluble, and operate on the principle of reducing the thermodynamic driving force for diffusion of monomer out of the small droplets. The studies of Choi and Ugelstad indicate that long-chain hydrocarbons and alcohols are favored as cosurfactants. El-Aasser[12,13] has reported on the formation and stability of miniemulsions. The process of forming a miniemulsion is dependent upon the efficiency of obtaining the initial distribution of monomer droplets and on the effectiveness of maintaining the distribution during the reaction. The most important factors in meeting these criteria are the ratio between the surfactant and cosurfactant and the means by which these substances are mixed. Delgado et al.[14] found that for the miniemulsion copolymerization of vinyl acetate and butyl acrylate, 80% of the cosurfactant (hexadecane) appeared in the polymer particles at the end of the reaction even though only 20% of the initial droplets became latex particles. They attributed the transport of hexadecane to collision between droplets and particles.

Several authors[11,15,16] have studied the use of water-soluble initiators in batch miniemulsion polymerizations of styrene. In these studies, bimodal polymer particle size distributions were obtained for various surfactant–cosurfactant ratios. The large

particles were about the same size as the initial droplets and were attributed to droplet nucleation. The small particles that were observed were thought to arise from aqueous-phase nucleation phenomena. In an early work, Ugelstad and Hansen[15] reported changes in reaction kinetics for various droplet sizes. They reported reaction kinetics varying from Smith-Ewart case III to case II kinetics as the droplet size is reduced. Gilbert et al.[17] have also studied the kinetics of the batch miniemulsion polymerization reaction. Shifts between aqueous phase nucleation and droplet nucleation were observed for various recipes and processing conditions. Their kinetic data show a rate of polymerization that is lower for the case of droplet nucleation. This fact is attributed to a reduced rate of radical entry into the particles.

Fontenot and Schork[7,8,18–20] studied the batch polymerization of methyl methacrylate with sodium lauryl sulfate (SLS) as the surfactant and hexadecane as the cosurfactant. Particle nucleation was shown to follow two distinguishable mechanisms (micellar and droplet). Conductance during polymerization was used to substantiate the difference. This difference in nucleation mechanism was shown to lead to a difference in the importance of initiator and surfactant on the formation of new particles. Droplet nucleation was shown to induce a limit on the number of particles in the reactor. Particles nucleated from droplets were observed to have higher radical numbers than the macroemulsion particles. Cosurfactant (HD) was shown to greatly enhance the stability of small droplets and therefore increase particle numbers. No "ideal" ratio between HD and SLS was found. Miniemulsion polymerization was found to produce latexes that are more shear-stable than those produced by macroemulsion polymerization.

This work treats two issues in miniemulsion polymerization: The use of polymeric cosurfactants, and the creation of miniemulsions using nonionic surfactant [in this case, polyvinyl alcohol (PVOH)]. The use of polymer as a cosurfactant has been reported recently.[21] 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. However, due to their high molecular weights, polymers are generally rather poor cosurfactants. Data reported herein demonstrate that it is possible to create miniemulsion latexes with a poor cosurfactant (polymer). The poly-

meric 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 thermodynamically stable. 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 study reports the results of miniemulsion polymerization of vinyl acetate (VA) using a nonionic surfactant (PVOH) and hexadecane or various polymers as a cosurfactant.

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. It should be noted that the monomeric emulsions stabilized against diffusion with a polymeric hydrophobe are not true miniemulsions in the sense that they are not stable on the time scale of weeks or months, as are true miniemulsions created with HD. 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*.

Most previously reported miniemulsions have been formed using low-molecular-weight anionic surfactants. There are applications in which nonionic surfactants provide benefits in the end-use properties. This work also treats the formation and polymerization of miniemulsions formed with high-molecular-weight nonionic surfactant (PVOH).

EXPERIMENTAL

Materials

Vinol 205, polyvinyl alcohol supplied by Air Products and Chemicals Inc., was dissolved at 10% (wt/wt) concentration at 90°C for 9 h in deionized (DI) water. Its molecular weight and degree of hydrolysis were 11,000–31,000 and 87–89%, respectively. Vinyl

acetate (Fisher) was distilled under vacuum and stored at 0–5°C until use. Hexadecane (Fisher), hydroquinone (Fisher), polymethyl methacrylate (MW 100,000, Polyscience), and polystyrene (MW 100,000–165,000, Polyscience) were used as supplied. The polyvinyl acetate used as cosurfactant was synthesized in this laboratory by emulsion and solution polymerization. The weight-average molecular weighs were 90,000 for the emulsion polymer and 2800 for the solution polymer. All water used was deionized.

Emulsion Preparation and Polymerization

Miniemulsions were prepared according to the following recipe: 600 g water; 250 g vinyl acetate (VAc); 0, 2.5, 5, or 7.5 g polymeric cosurfactant or hexadecane; and 15, 25, or 35 g Vinol 205 (PVOH).

The desired amount of cosurfactant/hydrophobe was dissolved in the appropriate quantity of monomer. The PVOH was dissolved in water by mixing at room temperature. An emulsion was created by dispersing the monomer solution into the water solution. The emulsion was then sonicated with a Fisher 300 W sonic dismembrator for 5 min at 60% output (180 W), during which time the vessel containing the emulsion was immersed in a cool water bath to prevent heat-up.

The miniemulsion was then transferred to a 2000-mL four-neck flask that was equipped with nitrogen inlet–outlet tube, condenser, conductance cell, and mechanical stirrer. The system was purged with nitrogen for 20 min and heated to 60°C. Agitation was provided by a paddle wheel stirrer at 500 rpm. The polymerization was begun by injecting 20 mL of 0.5% (wt/wt based on monomer) aqueous sodium persulfate solution. The reaction was followed by continuous conductance measurement and gravimetric monomer conversion analysis. For gravimetric conversion analysis, samples of 5–7 g were taken by syringe at intervals and injected into a weighing dish containing 1 g of 1% (wt/wt) aqueous hydroquinone solution. The samples were kept in an oven at 70°C for 24 h. The conversion was calculated from the polymer content. Macroemulsions were prepared by the same procedure with the exceptions that no cosurfactant (or hydrophobe) was added, and the emulsion was not sonicated.

Conductance

The conductances of water, PVOH solutions, and emulsions were measured directly at room temper-

ature. The conductance changes during polymerization were read every minute at polymerization temperature from a probe inserted into the reactor, and characterized with relative conductance, i.e., normalized against the initial conductance.
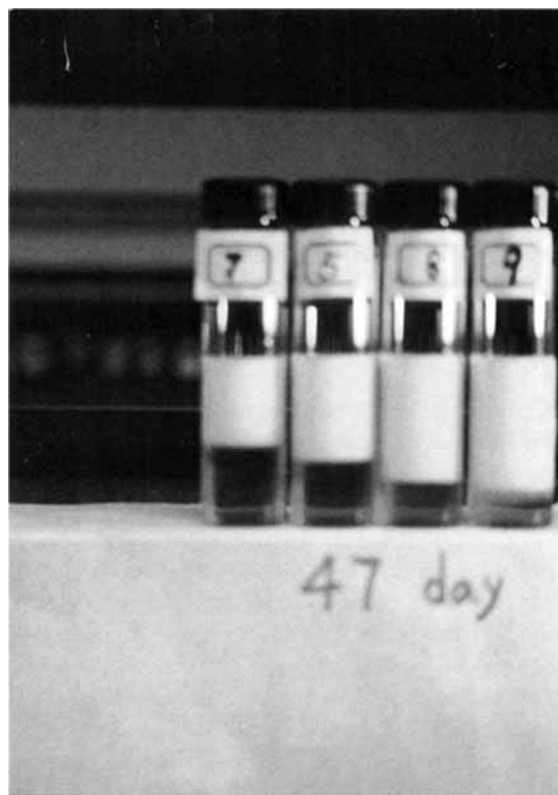
Droplet and Particle Size

Droplet and particle size distributions were measured by dynamic light scanting using the Malvern Autosizer IIc. For monomer droplets, the emulsion was first diluted with a monomer-saturated water solution of 0.1% (wt/wt) PVOH to about 50 : 1. Then 2 mL of this diluted emulsion was put into a quartz cuvette and the droplet size distribution was measured. Polymer particle size was measured by a similar process, with the exception that the dilution was 100 : 1 with 0.1% (wt/wt) PVOH solution containing no monomer.

Shelf Life Stability

Emulsion shelf life were measured by placing approximately 30 mL of sample in a capped glass vial and observing the time necessary for a visible creaming line to appear. In order to observe the interface easily, two drops water-soluble red pigment solution were added.
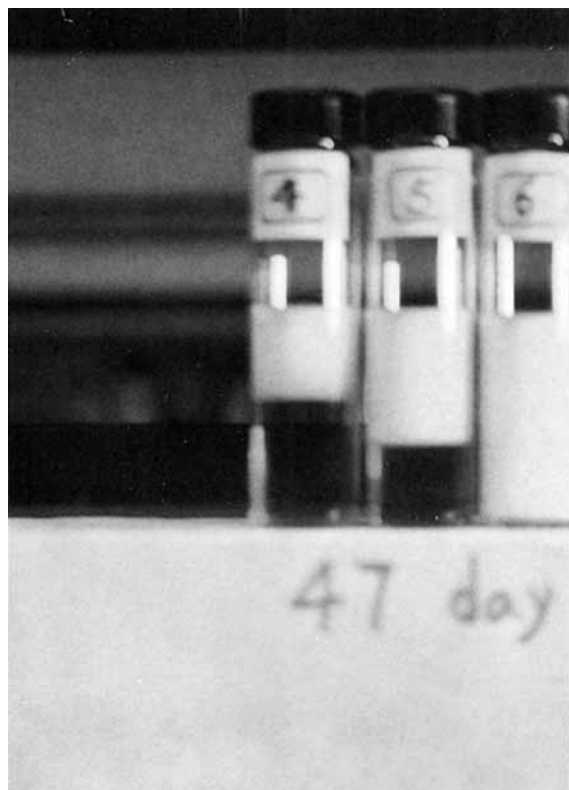

Figure 1 Miniemulsions at different hexadecane levels after 47 days: vial 7, 1% HD; vial 5, 2% HD; vial 8, 3% HD; vial 9, 4% HD. All contain 2.5% (wt/wt monomer) PVOH as surfactant.

RESULTS AND DISCUSSION

Macroemulsions and Miniemulsions

Table I shows the droplet diameters and shelf lives for various macroemulsions and miniemulsions. The macroemulsions of VAc with PVOH surfactant were not stable. Their shelf lives were short (1.5–4.1 h), and their diameters were larger than 2000 nm. Stability was increased somewhat by the use of additional surfactant, although the effect is not great. With the addition of hexadecane as a cosurfactant, true miniemulsions were formed (Table I). Droplets were formed with average diameters of 304 nm and less. The shelf lives varied in the range from 24 to 576 h. This is adequate to allow droplet nucleation before significant degradation of the droplet distribution due to Ostwald ripening. Table I also shows a decrease in droplet diameter with increases in surfactant and cosurfactant levels. The associated creaming results are shown in Figures 1 and 2, and follow the expected trend. (Emulsions with smaller droplets cream at slower rates.)

Table I Shelf Life and Monomer Droplet Diameter with Hexadecane Cosurfactant

Monomer (g)	HD (g)	10% PVOH (g)	Water (g)	Droplet Diameter (nm)	Shelf Life (h)
		Recipe			
			Macroemulsion		
25	0	15	60	2678	1.5
25	0	25	50	2469	3.2
25	0	35	40	2304	4.1
			Miniemulsion		
25	0.5	15	60	148	240
25	0.5	25	50	130	408
25	0.5	35	40	57	576
25	0.25	25	50	304	24
25	1.0	25	50	217	504
25	1.5	25	50	247	504

Figure 2 Miniemulsions at different polyvinylalcohol levels after 47 days: vial 4, 1.5% PVOH (wt/wt monomer); vial 5, 2.5% PVOH; vial 6, 3.5% PVOH. All three contain 2% (wt/wt monomer) HD as cosurfactant.

Polymethyl methacrylate (PMMA) is a moderately good hydrophobe for methyl methacrylate (MMA) emulsions.[21] Based on this fact, polyvinyl acetate (PVAc) was selected as a hydrophobe to make vinyl acetate emulsions. Results are shown in Table II. Results indicate that the emulsions made with PVAc (MW 2800), are quite unstable, with shelf lives of less than one hour. In retrospect this is not surprising, since solution of the Morton equation[22] indicates that PVAc is almost totally ineffective at retarding Ostwald ripening in VAc emulsions. Based on these results, PMMA and polystyrene (PS) were tried as hydrophobes for VAc monomer. Table II shows the results. Using PMMA as the hydrophobe, marginal miniemulsions were obtained. The monomer droplet diameters decreased from 420 to 262 nm when the PMMA concentration was changed from 1 to 4% (wt/wt based on monomer). Shelf life reached to 7.5 h. Although the VAc/PMMA emulsions are not true miniemulsions (with long-term stability), the presence of the PMMA seems to retard Ostwald ripening to the point were nucleation of

monomer droplets becomes dominant, as was found by Reimers and Schork for the MMA–PMMA system stabilized with SLS.[21] Similar results were obtained for a single experiment using the VAc–PS–PVOH system.

Polymerization and Latex Stability

The miniemulsions obtained with HD and PMMA as cosurfactants–hydrophobes were polymerized, and the final latex particle size distribution was measured. The conductance changes during polymerization were followed and compared with that for an equivalent macroemulsion polymerization. Figure 3 shows the conversion versus reaction time for miniemulsion polymerizations with HD cosurfactant at various PVOH concentrations. A slight increase in polymerization was noted with increasing PVOH concentration. This can be accounted for by noting (Table II) that increased PVOH concentration results in smaller droplets, and hence more droplets that can be nucleated. Figure 4 shows the results of polymerizations with different amounts of hexadecane cosurfactant. No significant change in polymerization rate with HD concentration was observed. This is in agreement with the results in Table I where the change in monomer droplet diameter with HD level is not great.

Conductance changes during selected VAc miniemulsion polymerizations are shown in Figure 5. Results at other surfactant and cosurfactant levels were similar. These should be compared with the same data for the equivalent macroemulsion (Fig.
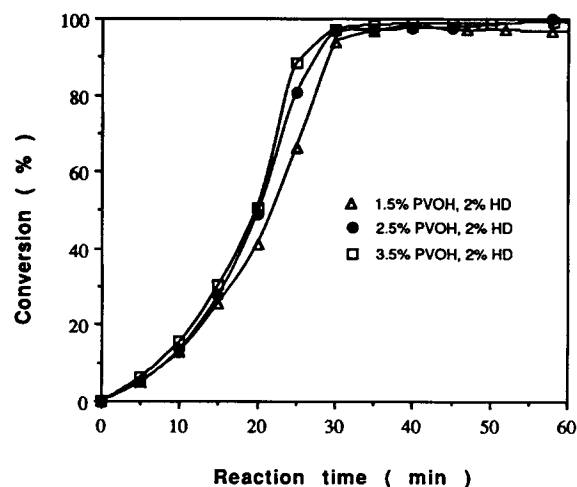
Figure 3 Conversion vs. time for miniemulsion polymerizations at different surfactant (PVOH) levels.

Table II Shelf Life and Monomer Droplet Diameter with Polymeric Cosurfactants
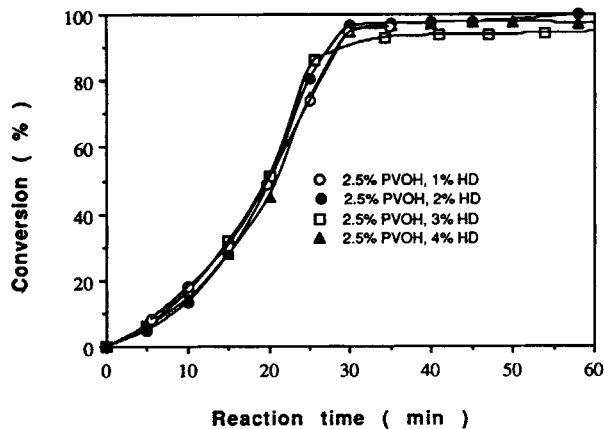
Monomer (g)	Cosurfactant (g)	10% PVOH (g)	Water (g)	Droplet Diameter (nm)	Shelf Life (h)
		No Cosurfactant			
25	0	25	50	2469	3.2
		Polymethyl Methacrylate			
25	0.25	25	50	420	4.5
25	0.50	25	50	313	7.0
25	1.0	25	50	255	7.5
25	2	25	50	262	7.0
		Hexadecane			
25	0.25	25	50	304	24
25	0.5	25	50	130	408
		Polystyrene			
25	0.5	25	50	849	6.0
		Polyvinyl Acetate			
25	0.25	25	50	816	0.8
25	0.5	25	50	878	0.75
25	1.0	25	50	967	0.75

6). To understand these trends, the conductance was measured at the following points during miniemulsion preparation: (i) before PVOH addition (DI water only), (ii) after PVOH addition, (iii) after monomer addition and stirring, and (iv) after sonication. The results are shown in Table III in which conductance is shown as relative conductance with the conductance of DI water taken as unity. It can be seen that the addition of both PVOH and VAc increases the conductance. Thus the decrease in con-
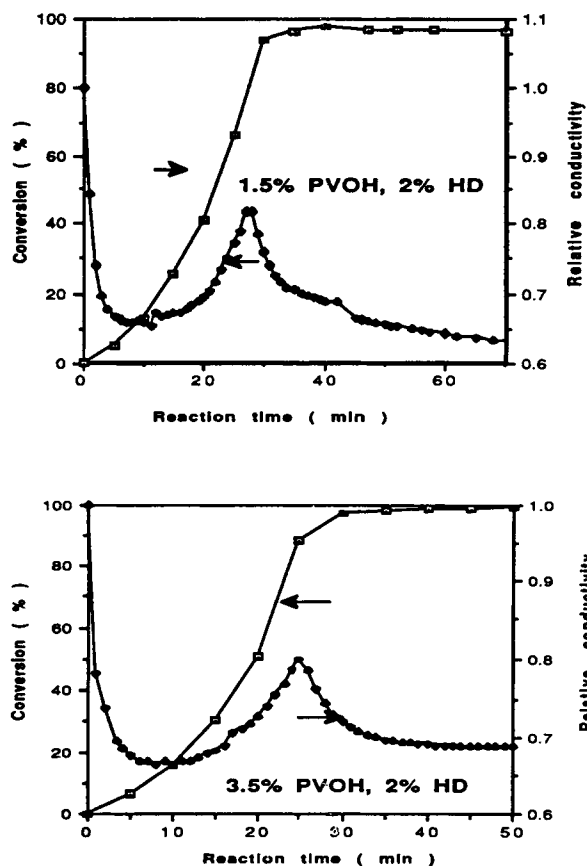

Figure 4 Conversion vs. time for miniemulsion polymerizations at varying hexadecane concentrations.

ductance during macroemulsion polymerization can be attributed to depletion of both initiator ($K_2S_2O_8$) and VAc from the aqueous phase. As reported previously,[7,21] the conductance change in miniemulsion polymerization is substantially less than that in the equivalent macroemulsion. This is indicative of the relative lack of change in interfacial area during miniemulsion polymerization.

Figure 7 shows conversion and conductance versus reaction time for VAc polymerization with 2.5% PVOH and PMMA at 1 and 4%. The inhibitor in monomer was not removed prior to polymerization when polymeric hydrophobe was used in order to avoid any polymerization during the interval necessary to dissolve the polymeric hydrophobes in the monomer. This explains the inhibition period at the beginning of the conversion-time curves. Both the conversion and conductance curves are similar to those of miniemulsions made with HD. Thus it would appear that PMMA can serve as a hydrophobe to the point of retarding Ostwald ripening long enough to allow nucleation of monomer droplets.

Table IV lists the particle diameter (weight average) and polydispersity of latexes obtained with macro- or miniemulsion polymerization. All are in the normal emulsion polymerization range, and all nearly monodisperse.

Figure 5 Conversion and conductance during vinyl acetate miniemulsion polymerization with different surfactant (PVOH) and cosurfactant (HD) levels.
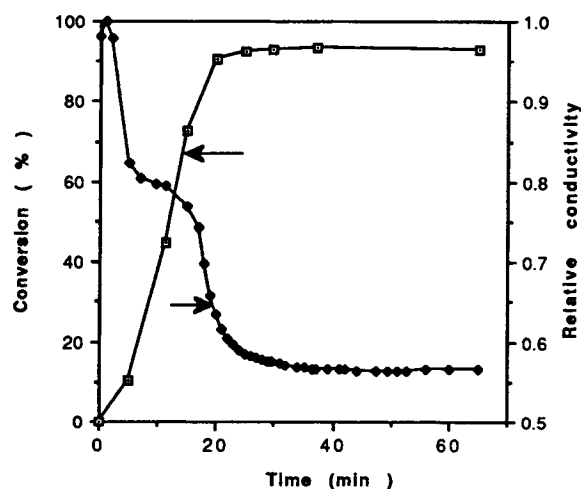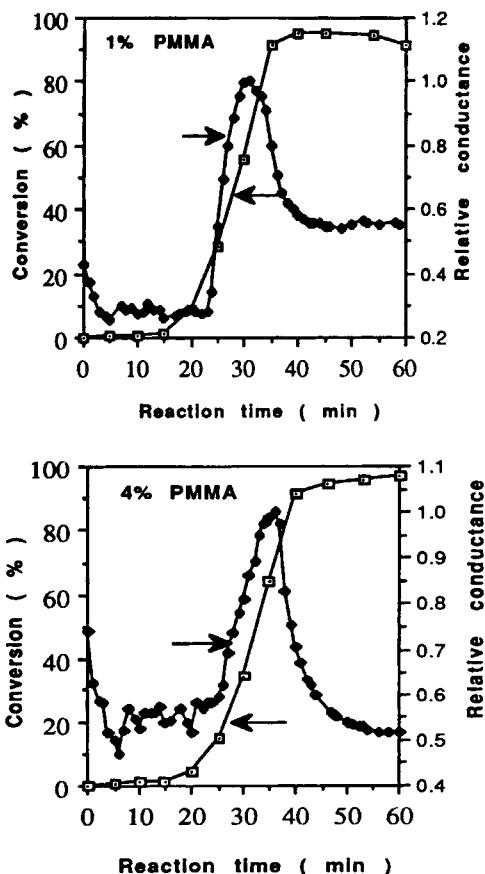

Figure 6 Conversion and conductance during vinyl acetate macroemulsion polymerization with 1.5% polyvinyl alcohol and no cosurfactant.

Table III   Relative Conductance During Miniemulsion Preparation

Cosurfactant (wt/wt mono.)	PVOH (% wt/wt mono.)	Relative Conductance
Water		
0	1.5	1.0
0	2.5	1.0
1	2.5	1.0
2	2.5	1.0
3	2.5	1.0
Polyvinyl Alcohol Solution		
0	1.5	2.0
0	2.5	2.2
1	2.5	2.2
2	2.5	2.0
3	2.5	2.1
After Addition of Monomer and Stirring		
0	1.5	2.4
0	2.5	2.7
1	2.5	2.8
2	2.5	2.6
3	2.5	2.5
After Sonication		
0	1.5	3.3
0	2.5	3.6
1	2.5	3.5
2	2.5	3.3
3	2.5	2.6

Table IV   Particle Size Distributions

System			
PVOH% (wt/wt mono.)	HD% (wt/wt mono.)	Diameter (nm)	Polydispersity
1.5	0	222	1.002
2.5	0	130	1.002
3.5	0	131	1.002
2.5	1	278	1.011
2.5	2	275	1.011
2.5	3	262	1.010
2.5	4	252	1.007
1.5	2	309	1.013
2.5	2	275	1.011
3.5	2	276	1.011

Figure 7 Conversion and conductance during vinyl acetate miniemulsion polymerization with 2.5% PVOH (wt/wt monomer) and PMMA cosurfactant at 1 and 4% (wt/wt monomer).

SUMMARY AND CONCLUSIONS

It is possible to create miniemulsions with a nonionic, polymeric surfactant (PVOH). When PVOH is used for VAc miniemulsion formulation, with HD as a cosurfactant, true, stable miniemulsions result. This is confirmed by shelf lives of 10 or more days. When PVAc is used as a hydrophobe, miniemulsions are not formed due to the poor diffusional stabilization effect of PVAc. When PMMA is used as the hydrophobe, marginal miniemulsions are formed. The presence of the polymeric hydrophobe does, however, retard Ostwald ripening sufficiently to allow predominant droplet nucleation. Thus, latexes can be prepared by the miniemulsion process using nonionic surfactant and polymeric hydrophobe. The polymeric hydrophobe has the advantage of being innocuous in the product. This is not the case with much better cosurfactants such as HD, which must be removed from the product before use.

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