Preparation of Polymerizable Hybrid Miniemulsions by Transitional Phase Inversion Emulsification

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ABSTRACT: Hybrid submicron emulsions were prepared using an energy-efficient phase inversion emulsification technique. Polyisobutene was dissolved in a vinyl monomer (styrene or methyl methacrylate), and a transitional phase inversion was induced by using a combination of hydrophilic and hydrophobic polyoxyethylene nonylphenyl ether surfactants. An important result was that the minimum size of drops was obtained in the vicinity of a locus of transitional inversion, but prior to that inversion. Increasing the monomer content in the polymer solution increased the hydrophilic−lipophilic balance at phase inversion until eventually no inversion could occur for the higher monomer content. The emulsions with average diameter of about 500 nm were subjected to polymerization. The miniemulsions prepared with a high concentration of monomer produced formulations close to those of optimum formulation, at which the interfacial tension is very low, and underwent massive coagulation during polymerizations. Miniemulsions prepared with low monomer content were sufficiently distant from the corresponding phase inversion locus and showed a good stability in the course of polymerization, leading to formation of hybrid polymer particles.

1. Introduction

Submicron emulsions, including miniemulsions, have attracted considerable attention in recent years for application in cosmetics, agrochemicals, pharmaceuticals, and surface coatings. Because of their small drop size, they enhance penetration and spreading and give uniform distribution on the substrate on which they are applied. Uglestad et al.[1] were the first who produced nanodroplets, or so-called miniemulsions, by using a cosurfactant in a method whereby mixing of the ingredients could lead to formation of miniemulsions. They intended to prove the possibility of nucleation in monomer droplets in emulsion polymerization reactions if the size of droplets was small. The proof of concept indicated a new method to produce hybrid polymer particles which is useful because conventional emulsion polymerization is restricted to monomers that can be polymerized via a free-radical mechanism (vinyl monomers). Polymers that have been made by condensation polymerization or by ionic polymerization can be dissolved in a vinyl monomer and then emulsified. Then the resulting miniemulsions can be used to polymerize the vinyl monomer and form hybrid polymer particles. Hybrid polymer particles of alkyd,[2,3] polyester,[4] and polyurethane[5−7] have been produced by using miniemulsion polymerization. Artificial polymer latexes were also made by emulsification of a polymer solution in a volatile organic solvent, and then the solvent was evaporated and polymer latex was formed.[8] It came as no surprise that scientists working on emulsion polymerization pioneered investigations of miniemulsions for polymerization purposes. Many aspects of miniemulsions, including drop stability during emulsification and polymerization and kinetics of miniemulsion polymerization, were investigated by many research groups as described in recent reviews.[9,10]

Miniemulsions found attractive applications in other fields, and the preparations of minimemulsions by other techniques were considered. Miniemulsions and submicron emulsions have been made by using high-pressure homogenizers or ultrasound. An alternative way to produce those emulsions is phase inversion emulsification.[11,12] A phase inversion emulsification technique is usually cheaper and consumes less energy than high-pressure emulsification. There are two types of phase inversion: catastrophic and transitional phase inversion.[13] In catastrophic phase inversion (CPI), increasing the coalescence rate of drops will eventually cause the dispersed phase to become the continuous phase. This may occur by addition of dispersed phase or by a change in any variable that enhances the rate of drop coalescence.[14] This type of inversion usually does not produce fine emulsions.[15,16]

On the other hand, in transitional phase inversion (TPI) the hydrophilicity of the surfactant is altered, and phase inversion occurs as the micelle-containing phase changes from oil to water or vice versa. In the vicinity of TPI the curvature of the oil−water interface gradually changes from positive to negative, passing through a zero curvature at the inversion point. The variation in the curvature of the interface is associated with changes in interfacial tension which decreases to ultralow values.[17−22] Miniemulsions can be produced as a result of phase transition during the emulsification process by a combination of interfacial tension lowering and the formation of surfactant crystals.[13,23]

TPI can be brought about by any method that can affect the affinity of surfactant or the surfactant mixture toward the phases. Shinoda and Saito,[24] who were first to report this phenomenon, used temperature changes to alter the surfactant affinity toward phases and thus induce phase inversion. Increasing the temperature decreases the hydrophilicity of the surfactant and favors the oil phase to be the continuous phase. When the temperature is lowered, the water phase becomes the preferred continuous phase. In isothermal mode, the hydrophilic−lipophilic balance

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(HLB) of the surfactant mixture can be continuously altered by the addition of a surfactant with desired properties.

In this article, we show how hybrid polymer nanoparticles can be produced by combined phase-inversion emulsification and polymerization. Low molecular weight polyisobutene (PIB), which is produced by cationic polymerization, was selected as the model polymer to be dissolved in the monomer phase. Styrene and methyl methacrylate were employed as model monomers. A mixture of polyoxyethylene nonylphenyl ethers with different HLB values was used as nonionic surfactant.

2. Experimental Section

2.1. Chemicals. Styrene (St) and methyl methacrylate (MMA), from Aldrich, were distilled under reduced pressure before use. Lauroyl peroxide (LPO), from Aldrich, and polyisobutene (PIB), supplied by British Petroleum with trade name Indopol H-7, having a number-average molecular weight of 440, a density of 871 kg/m^3 (at 15 °C), and a viscosity of 13 cSt at 100 °C, were used as received. Distilled water was used as the aqueous phase. In all experiments the water phase contained 0.5 wt % KCl (from Aldrich). Two different grades of polyoxyethylene nonylphenyl ether, with polyoxyethylene chain length of 12 (NPE12, trade name Igepal CO720, HLB = 14.2) and 5 (NPE5, trade name Igepal CO520, HLB = 10), both from Aldrich, were used as received. NPE5 was an oil-soluble grade, but NPE12 was a water-soluble grade. Sodium lauryl sulfate (SLS) was obtained from Aldrich.

2.2. Apparatus. The experiments were performed using a standard baffled 0.5 L jacketed glass vessel and a conventional four-flat-blade turbine agitator connected to a digital variable speed motor. The reaction temperature was kept constant within ±0.5 °C of the desired temperature by passing water with appropriate temperature through the vessel jacket.

2.3. Measurements. The size of oil drops in oil-in-water (O/W) emulsions was measured using a laser diffraction particle sizer (CoulterLS130). Samples taken from the emulsion were directly injected into the particle sizer. In cases with a substantial amount of submicron drops, drop size was also measured by photon correlation spectroscopy (Malvern Zetasizer 3000 HSA). A relative electrical conductivity meter was used to detect the inversion point.

The morphology of polymer particles was studied using a transmission electron microscope (TEM) (JEOL JEM100CX). Latex samples were embedded in an epoxy resin and cut with a microtome. Ruthenium tetroxide (RuO$_4$) was used as a stain to distinguish between polystyrene (darker part) and PIB (brighter part) in the TEM images.

2.4. Procedure. Experiments were started with about 30 cm^3 of the desired solution/emulsion. Additions were carried out at the rate of ∼5 cm^3/min. The surfactant concentration of 5.0 wt % in each phase was used, unless otherwise stated. All experiments were carried out at an agitation speed of 500 rpm.

Transitional phase inversion points were obtained using methods a and b as described below.

(a) A normal O/W emulsion with both phases containing the same quantity of the high HLB surfactant was formed. Then oil and water phases containing the low HLB surfactant were added separately to the emulsion at the same ratio, to ensure a constant water volume fraction (f_w), until phase inversion to W/O morphology occurred. The process was then reversed by addition of the phases containing high HLB surfactant to the emulsion at the constant f_w until reinversion to initial O/W emulsion occurred.

(b) The oil phase containing the oil-soluble surfactant was added to a water phase containing the water-soluble surfactant until phase inversion from O/W to W/O morphology occurred. The concentration of the surfactants in both phases was the same.

In both procedures a and b, the addition of second phase(s) was associated with a change in the emulsion HLB. The weight-average HLB was used to indicate the HLB of emulsion. Note that the average HLB of the mixed surfactant layer at the interface will be different from the emulsion HLB due to favored solubility of the surfactants in the oil phase.

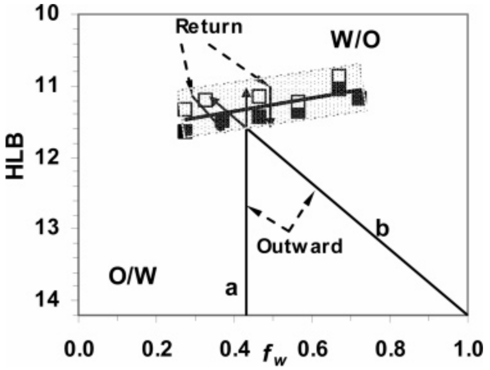

Figure 1. Emulsification paths and locus of transitional phase inversion for the (PIB−St)/W/NPE system, PIB/St = 90/10, T = 60 °C, 5 wt % surfactant (based on each phase). Outward and return inversions are shown by open and closed symbols, respectively. The three-phase microemulsion region is shown by the shaded area.

In experiments which were followed by polymerization of monomer in the polymer/monomer drops, the initiator (LPO) was added to the oil phase prior to the experiment. Then, after TPI, the emulsion was purged by nitrogen. No conversion of monomer was detected during phase inversion because oxygen (in the air) acts as an inhibitor. An inhibition effect of a few minutes was observed after purging with nitrogen. The time "zero" for polymerization was considered when polymer was detected in the samples.

3. Results and Discussion

3.1. Emulsification by Phase Inversion. 3.1.1. Locus of Transitional Phase Inversion, Reversibility, Stability, and Evolution of Drop Size. TPI requires the surfactant to be soluble in the oil phase, but the presence of a high molecular weight polymer may prevent that. We previously reported phase behavior of polyisobutene/water in the presence of a mixture of nonionic surfactants.[25] We showed that when the oil phase is a relatively low molecular weight polymer (or a polymer solution in an inert solvent), transitional inversion may be induced. There are also some reports in the literature of phase inversion emulsification of other polymers such as epoxy resins,[26] alkyd resins,[27] and polyurethane ionomers[28] or solutions of polymer−monomer, for example polyurethane−fluoroacrylic monomers,[29] with subsequent polymerization of vinyl monomer. However, all these reports referred to catastrophic phase inversion in which the size of droplets is mainly determined by the mechanical energy supplied to the system.

Figure 1 shows the locus of transitional phase inversion for a typical PIB−St/W/NPE system at 60 °C when the PIB/St weight ratio was kept constant at 90/10. Transitional phase inversion is the transformation of a normal emulsion of one type to the normal emulsion of the opposite type. Transitional phase inversion is normally reversible, so that the initial emulsion morphology is regained when the change in the variable (that provoked the inversion) is reversed. Such reversibility does not exist in CPI because there is a hysterisis effect. To ensure the type of inversion involved is the transitional one, the following procedure was adopted for the two emulsification paths described in the Experimental Section. Each path is identified by two data points: one for the outward inversion and the other for the return inversion. The outward inversion from an O/W emulsion to a water-in-oil (W/O) emulsion was induced by adding phase(s) containing oil-soluble surfactant. The return transition was marked where the inverted W/O emulsion was subjected to addition of phase(s) containing the

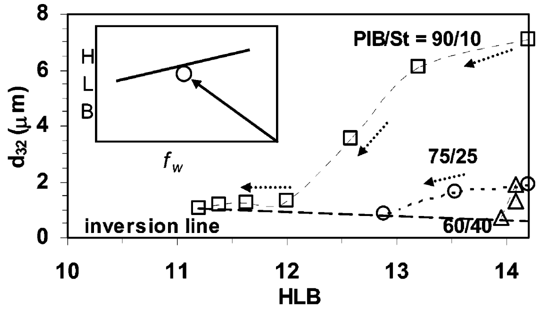

Figure 2. Variation in Sauter mean diameter of oil drops across the emulsification path b (shown in the inset) for three PIB/St ratios with $f_w = 0.47$, $T = 60$ °C, and 5 wt % surfactant.

water-soluble surfactant. The difference in the methods is that in method b only one phase is added to an emulsion at any one time so that the volume fraction of water (f_w) is changing with time, but in method a an appropriate proportion of both phases is added to the emulsion to keep f_w constant. There are two data points for the HLB at the inversion point or optimum HLB (HLB_{op}) for any given path. The outward and return inversions are shown by open and closed symbols, respectively, in Figure 1 and in some other figures in the article. The gap between the two points represents the locus of the three-phase microemulsion region. This zone was represented by the best line passing through the data points. The phase inversion line thus defines the domains of emulsion morphology. Above the line, W/O emulsion morphology tends to be dominant. Below the line, O/W emulsion morphology is predominant. As Figure 1 shows, a full reversibility of the inversion was achieved. The interfacial tensions of some selected samples in the vicinity of inversion points were estimated using a Du Nouy tensiometer and found to be less than 0.1 mN/m. (The Du Nouy tensiometer cannot measure values smaller than 0.1 mN/m.) This, together with reversibility of inversions, indicates that the inversion was transitional.

It is known that for common oil−water systems the transitional lines, in plots of HLB against f_w (as shown in Figure 1), are negatively slanted due to favored partitioning of nonionic surfactants in the oil phase.[30] The higher the concentration of the oil phase, the more of the oil-soluble surfactant is dissolved in the oil phase and less remains at the interface. Therefore, to induce phase inversion at lower f_w, the concentration of the oil-soluble component should be increased, leading to a lower apparent HLB value for the surfactant mixture. The transitional lines obtained in this research, however, appear to be positively slanted, opposite to what was described above; TPI occurs at lower HLB values with increasing f_w. One possible reason for this is the increased relative solubility of the water-soluble surfactant in the monomer phase so that most of the water-soluble surfactant is dissolved in the oil phase. Therefore, more water-soluble surfactant is required to induce phase inversion with increasing oil volume fraction.

Figure 2 illustrates the variations in drop Sauter mean diameter (d_{32}) across the emulsification path b (see Figure 1) for typical O/W emulsions prepared with three PIB/St ratios of 90/10, 60/40, and 75/25. The experiments were conducted by addition of the oil phase containing the low HLB surfactant to the water phase containing the high HLB surfactant until phase inversion to W/O emulsion occurred. This means that across emulsification path b the increase in oil phase fraction was accompanied by a decrease in the emulsion HLB. As shown in Figure 2, drop size initially decreased rapidly and then more slowly in the vicinity of phase inversion. The minimum drop size was achieved just before phase inversion from O/W emulsion to W/O morphology. The minimum drop size was shifted toward the higher values of HLB as the polymer solution became richer in the styrene monomer. Interestingly, drop size was quite small for PIB/St = 60/40 right from beginning and only slightly decreased with addition of oil.

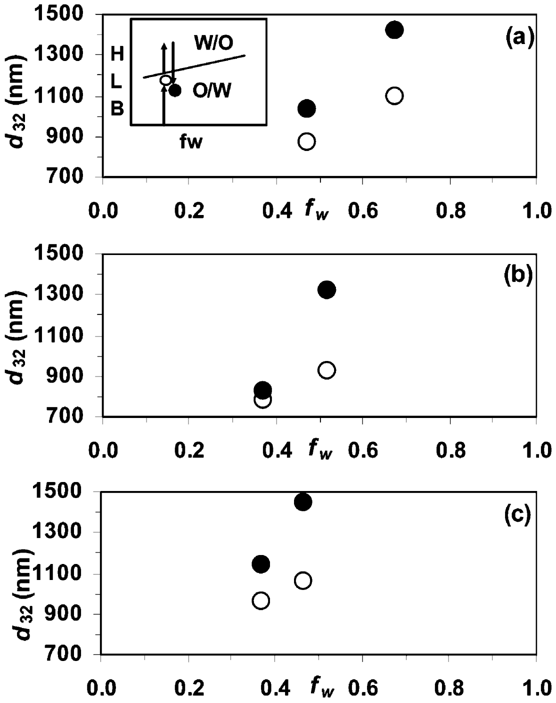

Figure 3. Variations in d_{32} in O/W emulsions just before inversion to W/O emulsion (open symbol) and after a second phase inversion from W/O to O/W emulsion (closed symbol) at different values of f_w for PIB/St = (a) 60/40, (b) 75/25, and (c) 90/10. The inset in (a) shows the paths schematically.

Shinoda[31] developed a technique in which an O/W emulsion was heated to a temperature 4 °C below its transitional phase inversion temperature and then was suddenly cooled to room temperature. This method produced a much finer emulsion than that which was obtained when an emulsion was heated to a temperature above the inversion temperature and then cooled to the room temperature. By analogy with that work, we studied sizes of drops that were formed close to the transitional phase inversion boundary, but our changes were achieved by crossing the inversion boundary twice. Figure 3 compares the Sauter mean diameter of drops in typical O/W emulsions just before inversion to W/O emulsion and after reinversion of the resulting W/O emulsion to an O/W emulsion using emulsification path a. The water and oil phases containing the low HLB surfactant were added in a prefixed phase ratio to an O/W emulsion containing high HLB surfactant with the same phase ratio. The results shown in Figure 3 indicate that smaller oil drops are formed if the locus of phase inversion is approached but not crossed (the two paths are schematically shown in the inset of Figure 3a). The reinversion of resulting W/O emulsions to O/W emulsions produced drops which were larger than those in the emulsion just before inversion. The difference seems to increase with f_w independent of oil composition. It should be noted that, at any given value of f_w, the HLBs of the emulsions corresponding to the points shown in Figure 3 are different; they are slightly higher for the reinversion (see also Figure 1). The results extended the finding of Shinoda[31] for temperature-induced phase inversion to isothermal phase inversion.

3.1.2. Effect of Monomer Content. Solutions of PIB and styrene with different monomer concentrations (10, 25, and

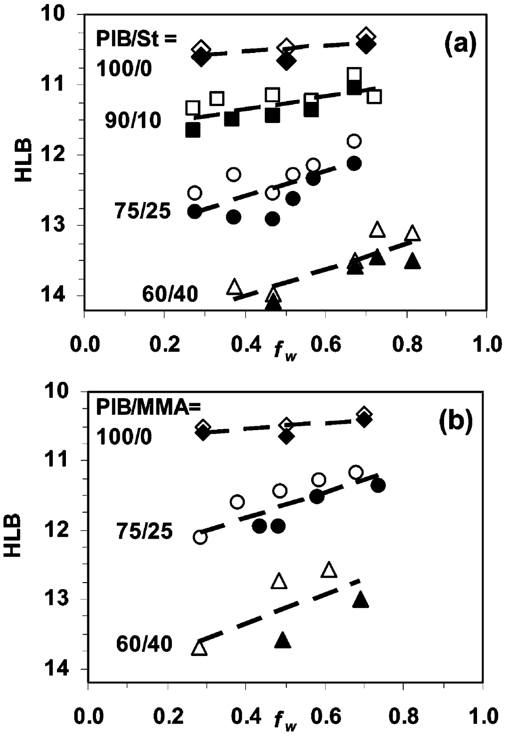

Figure 4. Transitional phase inversion boundaries for (a) (PIB−St)/W/NPE and (b) (PIB−MMA)/W/NPE systems with different PIB/monomer ratios, $T = 60$ °C, and 5 wt % surfactant. Outward and return inversions are shown by open and closed symbols, respectively.

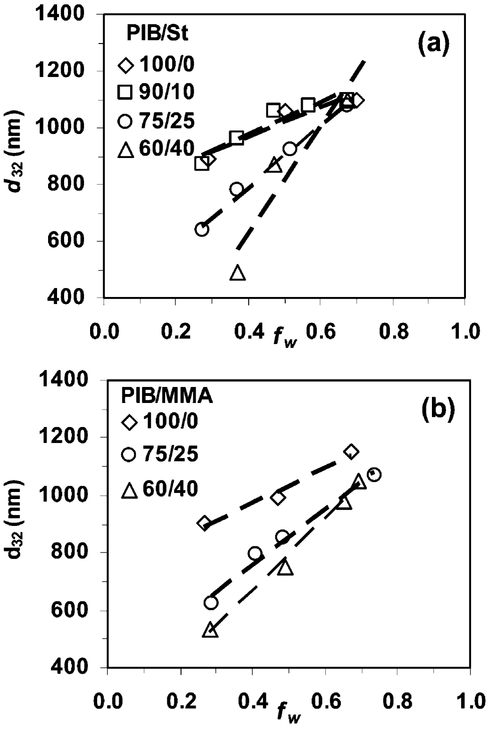

Figure 5. Variation in Sauter mean diameter with f_w just before phase inversion to O/W emulsion for (a) (PIB−St)/W/NPE and (b) (PIB−MMA)/W/NPE systems, with $T = 60$ °C and 5 wt % surfactant.

40 wt % for St and 25 and 40 wt % for MMA) were used as the oil phase. Figure 4 shows the phase inversion lines for the PIB−monomer/W/NPE systems at 60 °C.

The TPI line for the pure polymer (PIB) at the same conditions has been shown in this figure for comparison. It is clear from Figure 4 that addition of monomer increased the value of the HLB at which phase inversion occurred (HLB_{op}). For both monomers, the transitional lines shifted toward higher values of HLB with increasing monomer fraction in the polymer solution. This seems to be caused by favored dissolution of the high HLB surfactant in the monomer phase, so that more of high HLB surfactant is required in order to raise the surfactant HLB at the interface and induce phase inversion. The slope of the lines seems to slightly increase with monomer concentration in the oil phase.

Figure 5 shows the Sauter mean diameter (d_{32}) of oil drops just before TPI for different PIB to monomer ratios. Drops with a Sauter mean diameter as small as 500 nm were obtained. According to Figure 5, the size of drops practically converged at higher water volume fractions and showed more variations at low values of f_w.

Figure 5 also reveals that monomer incorporation into the oil phase decreased the drop size at the phase inversion. The size of droplets in an emulsification process with a constant input of mechanical energy is mainly governed by the interfacial tension and viscosity. With increasing viscosity of the dispersed phase in a liquid−liquid dispersion, the rate of drop breakup decreases because resistant forces are higher.[32,33] Thus, for a high polymer content in the oil phase, drop viscosity affects the size of drops at the locus of transitional inversion.

As Figure 4 suggests, with the surfactants used here, we were not able to induce transitional phase inversion for PIB−monomer solutions that contained more than 40% monomer. In a recent report, Esquena et al.[34] had to use a large proportion (>50%) of a hydrophobe, tetradecane, to produce submicron styrene droplets. When nonionic surfactants were used alone, TPI of emulsions containing water and vinyl monomers, such as MMA and St, did not occur at temperatures that are high enough for free-radical polymerization using oil-soluble initiators such as LPO. Lade et al.[35] reported TPI for MMA/W, using an alkyl poly(ethylene glycol), C_iE_j, surfactant ($C_{10}E_6$), at about 9 °C. Esquena et al. reported that the phase inversion temperatures for a solution of styrene−tetradecane, using $C_{16}E_6$ as the surfactant, decreased from about 50 to 0 °C when the percentage of styrene in the oil phase increased from 0 to 50%. They estimated the TPI for pure styrene to be about −57.5 °C by extrapolating their data.

Figure 6 shows that an increase in the surfactant concentration from 5.0 to 15 wt % leads to a decrease in the required HLB for inversion at low f_w values and produced emulsions of smaller droplet size. This policy, however, is not suitable for production purposes because it has associated costs with increased surfactant concentration and the adverse effects of surfactant on the final properties of the emulsions.

3.1.3. Effect of Temperature on TPI. Polymerization reactions are usually carried out at temperatures above 50 °C, which is the operating region for most free radical initiators. Therefore, it is quite important that the O/W emulsions, produced via TPI, remain stable at the reaction temperature. For this reason, we carried out the emulsification stage at the same temperature as that of reaction. However, it is essential to evaluate the size of droplets obtained by emulsification at lower temperatures.

TPI was carried out at different temperatures for (PIB−styrene)/W/NPE systems with constant f_w (=0.47) but with different PIB−St ratios. Figure 7 shows that the transitional lines became more slanted with increasing temperature, in accordance with the data published for simple oil/water emulsions.[36] This behavior can be attributed to increasing hydrophobicity of the water-soluble surfactant with temperature. Therefore, more water-soluble surfactant should be used in order to compensate

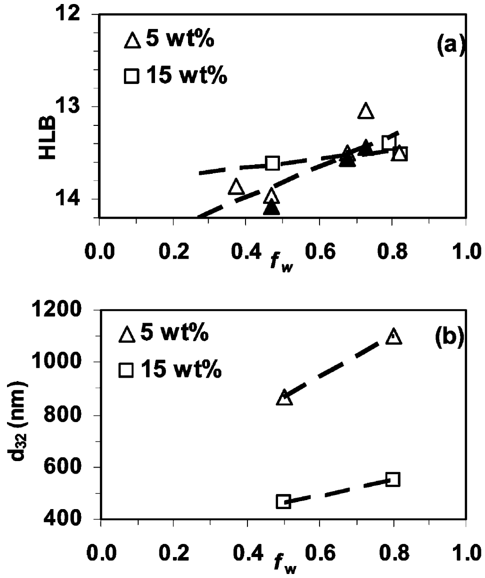

Figure 6. Variations in (a) phase inversion HLB and (b) Sauter mean diameter of oil droplets with f_w for two surfactant concentrations (PIB/St = 60/40). Outward and return inversions are shown by open and closed symbols, respectively.

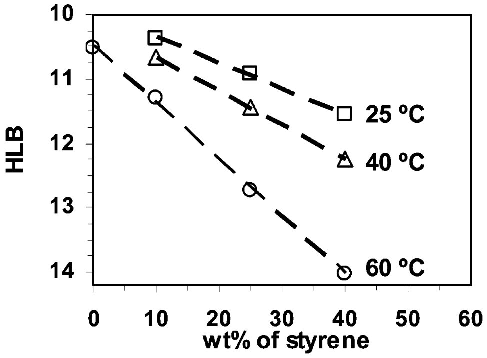

Figure 7. Variation in HLB_{op} with styrene weight % in the oil phase at different temperatures (f_w = 0.47, 5 wt % surfactant).

that effect, leading to higher emulsion HLB at the inversion point for the higher temperature. Figure 7 also shows that decreasing the emulsification temperature increases the probability of phase inversion for solutions with higher monomer contents (in the range of HLB of the surfactants used here, i.e., 10−14.2). This is an important result which may indicate that it is more feasible to produce hybrid particles from these drops at lower temperatures. The reinversion of the resulting O/W emulsion to a W/O emulsion at reaction temperature, however, is the main obstacle to using low-temperature phase-inversion emulsification.

Figure 8 shows the variation in d_{32} at inversion point with temperature for the same system while f_w was kept constant at 0.47. The size of oil drops did not significantly change with temperature, indicating that phase inversion emulsification can be carried out at the same temperatures as polymerization with no significant effect on the size of resulting drops.

3.2. Polymerization. From the phase inversion study, it became clear that miniemulsions of PIB/monomer systems using NPE surfactants with Sauter mean drop diameter of about 500 nm can be obtained if the PIB content in the oil phase is kept below 75% and emulsion phase inversion is conducted at a water volume fraction of 35% or smaller. Note that the number-average diameter for a broad distribution is significantly smaller than the Sauter mean diameter.

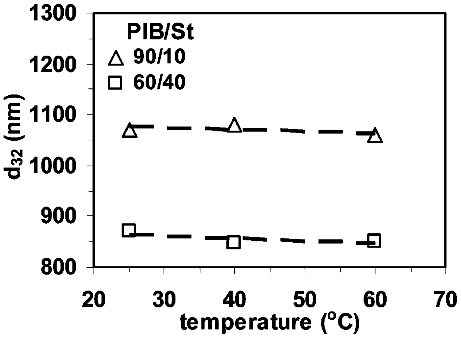

Figure 8. Variation in Sauter mean diameter with temperature for two different PIB−St weight ratios (f_w = 0.47, 5 wt % surfactant).

Polymerization of monomer in the oil drops will not be feasible unless the emulsions are stable at least during the major part of reaction. The two main causes of emulsions instability are drop coalescence and Ostwald ripening. The rate of increase in the mean radius of drops (r) via the ripening process is given by

$$\frac{d}{dt}(r)^3 = \frac{8\gamma D C V_m}{RT} \tag{1}$$

where D is the diffusivity, C is the solubility of the dispersed phase in the continuous phase, V_m is the molar volume of the dispersed phase, γ is the interfacial tension, R is the universal gas constant, and T is the absolute temperature.[37] The above equation suggests that very small drops are quite unstable and will disappear because their contents will migrate to large drops via the continuous phase unless there exists in the drops a component insoluble in the continuous phase.

The use of a costabilizer, to retard the Ostwald ripening effect in miniemulsions and to stabilize small drops, is often necessary. In this work, we did not use a costabilizer. It has been shown in the literature, however, that the addition of polymer into miniemulsions improves radical capture by monomer droplets.[38,39] Reimers and co-workers[40,41] showed that the presence of polymer in the monomer droplets, even without using a costabilizer, can significantly increase the stability of monomer droplets to a degree where the droplet size is preserved long enough for droplet nucleation to occur. The presence of an oil-soluble initiator can also serve to stabilize nanodroplets.[42−44] In the present work, the PIB content of the initial polymer droplets, as well as the LPO used as initiator, both acted as costabilizers to stabilize the droplets. Furthermore, miniemulsions prepared at conditions close to inversion points have ultralow interfacial tension and thus may seem to be stable to ripening, according to eq 1. However, they are unstable to drop coalescence in the vicinity of the locus of transitional inversion as a result of equal affinity of the surfactant mixture toward both phases. These emulsions separated into three phases within an hour of cessation of mixing. The phase separation is associated with the thermodynamic instability of emulsions at the optimum point.[45,46] For this reason, we improved the stability of the miniemulsions by addition of water containing the water-soluble NPE surfactant. This placed the final formulation of the miniemulsions far from the locus of inversion. No significant rise in the size of drops was observed with this dilution of the miniemulsions.

In a recent paper, Xie and Brooks[47] polymerized hybrid O/W emulsions prepared by phase inversion at room temperature. The polymerization reaction was carried out at a higher temperature. In order to prevent phase reinversion to W/O

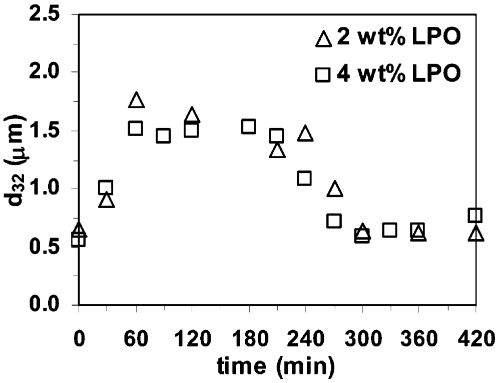

Figure 9. Particle size variations during the polymerization ($f_w = 0.70$, PIB/St = 60/40, HLB = 14, $T = 60$ °C, 5 wt % surfactant).

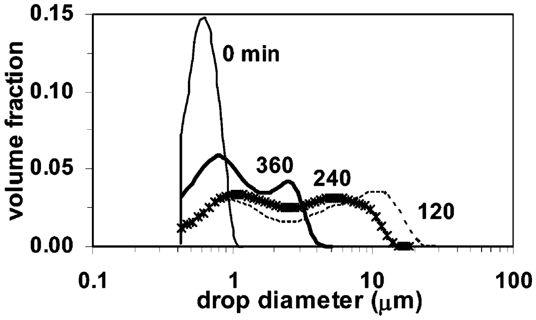

Figure 10. Particle size distributions during the polymerization ($f_w = 0.70$, PIB/St = 60/40, HLB = 14, $T = 60$ °C, LPO = 4 wt %, 5 wt % surfactant).

emulsion at the reaction temperature, they added anionic surfactants to the emulsion. That led to formation of a large number of secondary particles. In the current research, the transitional nature of the inversion was first ascertained as explained before. All O/W miniemulsions used for polymerization were obtained via method a. In order not to disturb the stability of emulsions by raising the temperature, the polymerization reactions were carried out at the same temperature as that used to create the emulsions. The results are presented for two categories of high concentration and low concentration of styrene.

3.2.1. Miniemulsions with High Monomer Content in the Oil Phase. Phase inversion emulsification of the PIB−monomer/water systems produced drops with size decreasing with increasing styrene content and increasing with water volume fraction (f_w). The highest styrene content in the oil phase examined in this research was 40% (PIB/St = 60/40, see Figure 4). Free-radical polymerizations were carried out with the inverted O/W emulsions with 40 wt % styrene in the oil phase. The inclusion of LPO into the oil phase did not significantly affect the size of droplets in the miniemulsions, but it improved the stability of droplets with time. The emulsion formed at the inversion point (HLB = 13.8, $f_w = 0.35$) was further diluted with water containing 5.0 wt % NPE12 to give a final emulsion at (HLB = 14.0, $f_w = 0.70$). This procedure of phase inversion emulsification−dilution ensured that the emulsion formulation is away from the optimum formulation as much as possible, and the phase inversion emulsification was conducted at the appropriate condition to produce small drops. The Sauter mean diameter of drops was about 500 nm after phase inversion and remained so during dilution. Then the emulsion was purged by nitrogen. The reaction temperature was 60 °C.

Figure 9 shows the time evolution of d_{32} for experiments using PIB/St = 60/40 and different LPO concentrations. The size of particles significantly increased within the first hour of reaction and then apparently remained constant for the next 2 h. In fact, the latex was quite unstable from the beginning of the reaction and particle coagulation occurred extensively. Visual observations indicated massive coagulation of particles on the baffle and stirrer. After this stage the size of particles showed a decrease simply because larger particles were lost as a result of flocculation and deposition on the vessel wall. Only small particles remained in the emulsion, and all enlarged particles were lost. Conversion could not be monitored accurately due to the mass coagulation. The mass of coagulum at the end of polymerization was about 23%.

Figure 10 shows the time evolution of particle size distribution for the experiment with 4 wt % LPO. The same sequence of events can be inferred from this figure. TEM micrographs showed the presence of a number of small particles in the final latex. Those particles were probably formed by secondary nucleation. It seems that several competitive events including coagulation of the polymer particles and nucleation in the micelles occur simultaneously in the course of polymerization. The vast majority of reports in the literature regarding miniemulsion polymerization are devoted to application of anionic surfactants as stabilizers. However, there are a few reports on miniemulsion polymerization using nonionic surfactants.[48−51] The simultaneous nucleation and coagulation is consistent with the data reported in the literature. The formation of secondary particles by homogeneous nucleation is less likely in the system containing a water-insoluble initiator. While the presence of micelles in the initial miniemulsions cannot be eliminated, it is also likely that new micelles were formed during polymerization and nucleated to form new particles. Nonionic surfactants are known to partition between monomer droplets and the aqueous phase to an extent that depends on the properties of the oil phase. As more monomer is converted to polymer, the surfactants may become less soluble in the particles and migrate into the water phase to form micelles. The continuous, or two-stage, nucleation has been also reported for conventional emulsion polymerization using nonionic surfactants.[52−54]

Polymerizing drops appeared to be very unstable for the emulsions using a high concentration of monomer, and this instability was independent of water volume fraction. To verify this point, an experiment was conducted at a lower HLB (HLB = 13.4) by increasing the water volume fraction ($f_w = 0.60$) (see Figure 4a), and then the inverted O/W emulsion was further diluted with water containing 5.0 wt % NPE12 to give a final dilute emulsion at HLB = 13.8 and $f_w = 0.85$. The particles after dilution were about 900 nm in diameter. The time evolution of d_{32} and particle size distribution for the same run are shown in Figure 11. While the instability of particles became apparent from the beginning of reaction, the rate of coagulation was relatively slow, probably because of low solids content of the latex (15%), so that particle growth could be monitored and measured. Conversion measurements were also possible as the latex shows fewer tendencies for coagulation (Figure 11c).

It can be concluded from the results that polymerization of emulsions formed using PIB/St of 60/40 is difficult to carry out for the present system. This is mainly due to the fact that emulsions formed with this formulation, also using the pair of NPE5 and NPE12 surfactants, are very close to the locus of a three-phase microemulsion and thus are inherently unstable (see Figure 4a). The locus of inversion is within the HLB range 13.10−13.80 (for $f_w = 0.80−0.35$) and is very close to the HLB of the water-soluble surfactant used in this study.

In order to improve the stability of the emulsions, we added some anionic surfactant (SLS) to the emulsions prior to

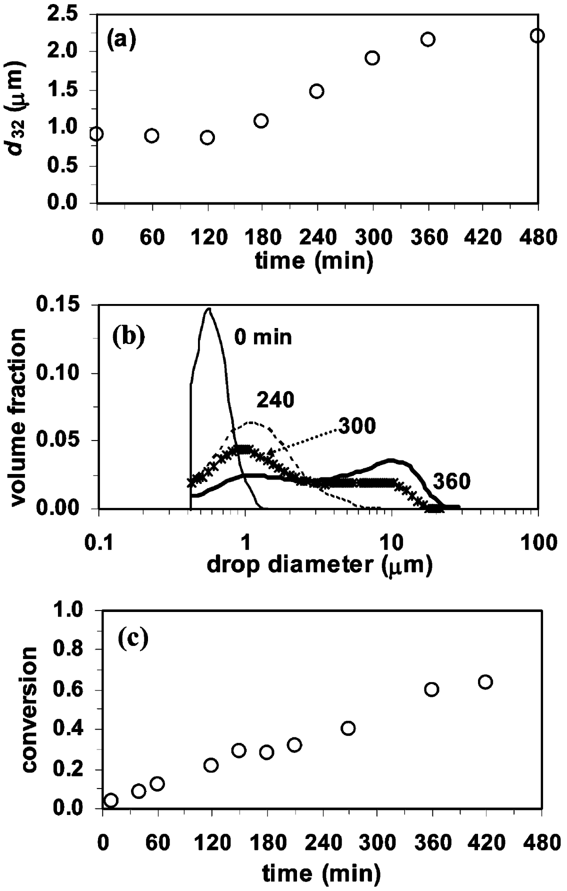

Figure 11. Variations in (a) particle size, (b) particle size distribution and (c) conversion during the polymerization ($f_w = 0.85$, PIB/St = 60/40, HLB = 13.8, $T = 60$ °C, LPO = 2 wt %, 5 wt % surfactant).

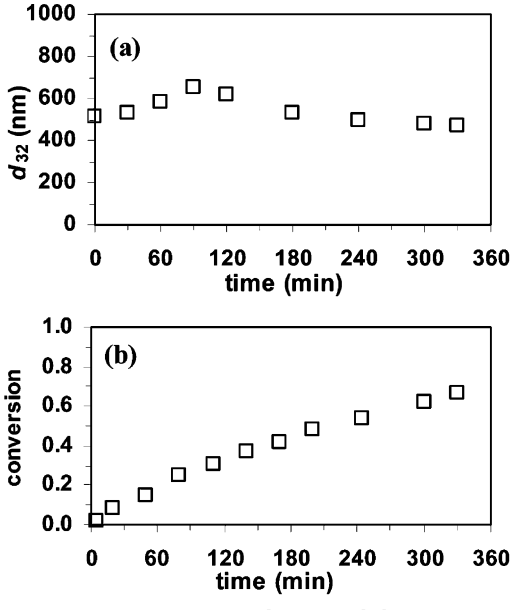

Figure 12. Variations in (a) particle size and (b) conversion during the polymerization ($f_w = 0.80$, PIB/St = 60/40, HLB = 14, $T = 60$ °C, LPO = 4 wt %, 5 wt % nonionic surfactant, 0.25 wt % SLS). The average HLB did not include that of SLS.

polymerizations. Figure 12 represents the evolution of d_{32} and conversion for the formulation explained in the caption of Figure 9. It is shown in Figures 9 and 10 that miniemulsions obtained under these conditions, but without addition of SLS, suffered coagulation during polymerization. With the addition of SLS, coagulation of particles became more controllable, and particle deposit on the reactor baffles was quite limited. Consequently, the particle size measurement could accurately reflect the size of particles in the latex. With addition of SLS, the growth of particles slowed down, but secondary particle formation occurred during polymerization. TEM measurements confirmed the formation of a large number of small particles, probably via micellar nucleation. Figure 12a indicates a combined particle coagulation and nucleation during polymerization.

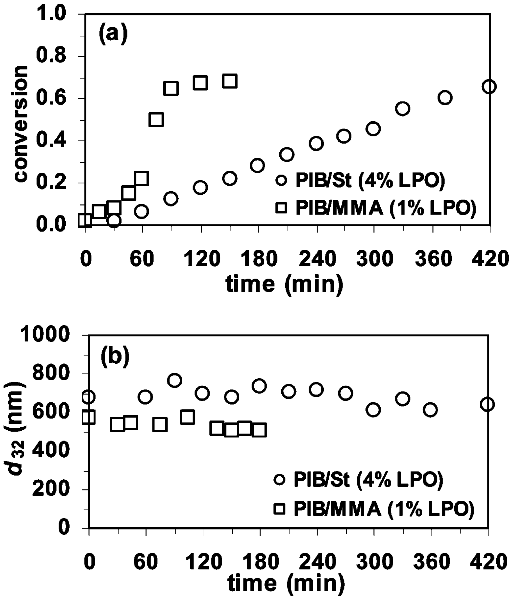

Figure 13. (a) Monomer conversion and (b) particle size variations during the polymerization (PIB/monomer = 75/25, $f_w = 0.80$, $T = 60$ °C, 5 wt % surfactant, $\mathrm{HLB}_{\mathrm{St/PIB}} = 13.7$, $\mathrm{HLB}_{\mathrm{MMA/PIB}} = 13.6$).

For MMA/PIB = 60/40, the locus of inversion was within the HLB range 13.00−13.60 (for $f_w = 0.70-0.30$). Although the locus of inversion was still close to the HLB of the water-soluble surfactant, there was some limited degree of flexibility available to depart from the optimum formulation. However, significant coagulation occurred during the polymerization.

3.2.2. Miniemulsions with Low Monomer Content in the Oil Phase. For this series of experiments, emulsions with a rather low monomer content (or a high PIB content) were used. Phase inversion emulsification of low monomer content systems produced emulsions with drops larger than those obtained with a high monomer content. The stabilization of these emulsions, however, was possible within the HLB range of the surfactant system used.

The phase inversion emulsifications were carried out with a constant value for f_w of 0.30 and with a PIB/monomer ratio of 75/25. After phase inversion to an O/W emulsion at an HLB of 12.6 and 12.1 for St and MMA monomer, respectively, additional aqueous phase was added to enhance the stability of droplets by departing from optimum formulation. The HLB ranges for inversion for PIB/monomer = 75/25 were 11.1−12.1 and 11.8−12.8 for MMA and St, respectively. This implies that the stability of O/W emulsions could be sufficiently improved by dilution with water containing the water-soluble surfactant (HLB = 14.2). The final f_w was set to 0.80. This corresponded to HLB of 13.7 and 13.6 for PIB/St and PIB/MMA, respectively.

Figure 13 shows the variations in monomer conversion and average polymer particle size during the polymerization. The initial average size of drops was about 500−670 nm. There was virtually no variation in the size of particles in the course of polymerization, indicating that polymerization occurred within the particles according to the particle nucleation mechanism. However, TEM examination of the samples showed a small number of new particles.

The study of morphology of particles was hindered by difficulties arising from the presence of PIB, with a low glass transition temperature, in the particles. Cross-linking of the particles under a UV beam, or freeze fracturing of particles at −150 °C, gave no improvement in the quality of images obtained. From the micrographs, islands of PIB could be observed in the polystyrene matrix. However, further characterization of the morphology was not possible.

4. Conclusions

The presence of a vinyl monomer, such as St and MMA, affected the transitional phase inversion line in the system (PIB−monomer)/W/surfactant using a mixture of NPE surfactants. Polymer/monomer drops with an average size as small as 500 nm were produced by transitional phase inversion. Increasing the monomer fraction in the initial PIB−monomer solution increased the HLB at phase inversion ($\mathrm{HLB}_{\mathrm{op}}$) and decreased the drop size after the inversion. Any decrease in temperature decreased $\mathrm{HLB}_{\mathrm{op}}$, as it favors water solubility of the surfactants, but did not affect the particle size significantly. It was shown that a smaller drop size is obtained by approaching TPI but not crossing it.

Free radical polymerization of the monomer, inside the polymer/monomer drops after phase inversion, was carried out using an oil-soluble initiator to form nanocomposite polymer particles. The size of droplets/particles did not change significantly during the polymerization when the monomer content was low.

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