Composite Polymer Nanoparticles via Transitional Phase Inversion Emulsification and Polymerisation

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Summary: A new route was employed to produce composite polymer nanoparticles. First, a model polymer (a low molecular-weight polyisobutene) was dissolved in a model monomer (styrene) and then the solution was emulsified in water containing a pair of nonionic surfactants via a transitional phase inversion route. After phase inversion, which produced an oil-in-water miniemulsion, polymerisation of the vinyl monomer gave composite polymer particles. Low temperature emulsification was not practical because the inverted oil-in-water emulsions reinverted to water-in-oil emulsions upon raising the temperature to the reaction temperature. Miniemulsions prepared at the reaction temperature with low monomer content in the oil phase showed good stabilty in the course of polymerisation and produced latexes with a particle size similar to the size of drops in the initial miniemulsions.

Keywords: miniemulsions; nanoparticles; non-ionic surfactants; polymerisation; transitional phase inversion

Introduction

Composite polymer particles can contain a polymer that has been produced by a polymerisation process which does not have a free-radical mechanism (e.g., condensation or ionic polymerisation). Those hybrid polymer particles, which can be used to modify the properties of other polymers, have been recently made by miniemulsion polymerisation. Examples include hybrid particles of alkyds,[1] polyesters[2] or polyurethanes[3] with acrylic (or styrenic) polymers.

In miniemulsion polymerisation fine emulsions, with drop sizes below 500 nm, are often prepared by using energy-intensive techniques (via high-pressure or ultrasound).[4,5] An alternative way to produce fine emulsions is by phase inversion emulsification. A phase inversion technique is usually cheaper, and consumes less energy, than those techniques mentioned above. There are two types of phase inversion, catastrophic and transitional. In catastrophic phase inversion, increasing the coalescence rate of drops eventually causes the dispersed phase to become the continuous phase. That may be provoked by increasing the dispersed phase ratio or by changing other variables that boost the rate of drop coalescence.[6] Although this type of inversion can produce fine emulsions, it cannot form submicron drops.[7,8] On the other hand, transitional phase inversion (TPI) can be brought about by any method that can affect the affinity of the surfactant, or the surfactant mixture, toward the phases. In transitional phase inversion the hydrophilicity of the surfactant(s) is altered and phase inversion occurs as the micelle-containing phase changes from oil to water or vice versa. This is accompanied by a change in the curvature of the oil-water interface from positive to negative passing through a zero curvature at the inversion point, corresponding to an ultra-low interfacial tension.[9–12] Changing the temperature[9] alters the surfactant affinity toward

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phases and thus can induce phase inversion. When the temperature is raised the hydrophilicity of the surfactant is decreased and thus the oil phase becomes the preferred continuous phase. The formation of ultrafine droplets via transitional phase inversion was first reported and documented by Shinoda and co-workers.[9] They used a temperature change in order to alter the HLB of a surfactant. In isothermal mode, the hydrophilic-lipophilic balance (HLB) of the surfactant mixture can be continuously altered by the addition of a surfactant with desired properties. Transitional phase inversion emulsification has been widely studied for the preparation of ultra fine emulsions.[13–15]

In this article we show that hybrid polymer nanoparticles can be produced via phase inversion miniemulsification and polymerisation. A low molecular weight polyisobutene (PIB), which is produced by cationic polymerisation, was selected as the model polymer to be dissolved in a vinyl monomer, styrene. Free-radical polymerisation of the styrene produced the second polymer. A pair of polyoxyethylene nonylphenylether non-ionic surfactants with different HLB values was used.

Experimental Part

All chemicals were provided by Aldrich, unless otherwise stated. Styrene (St) was distilled under reduced pressure before use. Lauroyl peroxide (LPO) and polyisobutene (PIB), supplied by British Petroleum with trade name Indopol H-7, having a number average molecular weight of 440 g/mol, a density of 0.871 g/cm^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 (to increase electrical conductivity). Two different grades of polyoxyethylene nonylphenylether (NPE), with polyoxyethylene chain lengths of 12 (NPE12, trade name Igepal CO720, HLB = 14.2) and 5 (NPE5, trade name Igepal CO520, HLB = 10) were used as received. NPE5 was an oil-soluble grade, but NPE12 was a water-soluble grade.

The experiments were performed using a standard baffled 0.5-litre jacketed glass vessel, and a conventional 4 flat-blade turbine agitator connected to a digital variable speed motor. The temperature was kept constant within ±0.5 °C of the desired temperature by passing water with appropriate temperature through the vessel jacket. All experiments were carried out at an agitation speed of 500 rpm.

The mean size of oil drops (Sauter mean diameter, d_{32}) 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. A relative electrical conductivity meter was used to detect the inversion point.

Transitional phase inversion points were approached using either addition of one phase to the other phase or addition of both phases to an initial emulsion so that a constant volume fraction of water was maintained. Additions were carried out at the rate of approximately 5 cm^3/min. The surfactant concentration of 5.0 wt% in each phase was used.

In polymerisation experiments, the initiator, LPO, was added to the oil phase (at 4 wt% based on monomer) prior to the phase inversion. Then, after TPI, the emulsion was purged with nitrogen. No conversion of monomer was detected during phase inversion because oxygen (in the air) acts as an inhibitor. An inhibition period of a few minutes was observed after purging with nitrogen. The time ‘‘zero’’ for polymerisation was taken when polystyrene was detected in the samples. Monomer conversion was measured gravimetrically.

Results and Discussion

Low-Temperature Emulsification and High-Temperature Polymerisation

In the first part of this work the transitional phase inversion of a PIB-St/water/NPE system was conducted at temperatures of

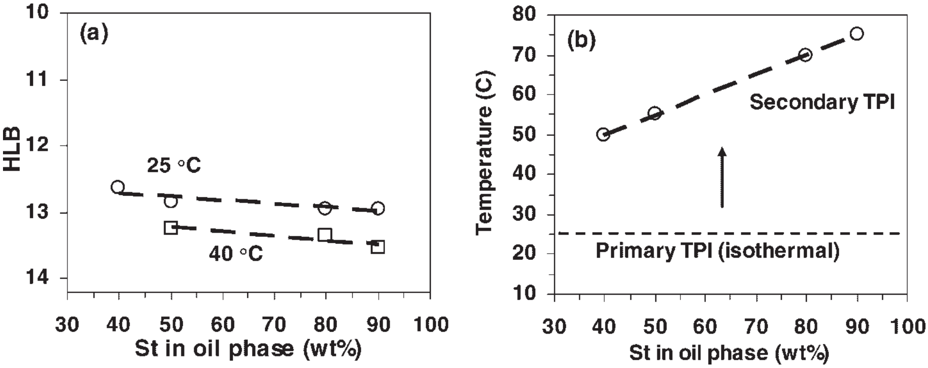

Figure 1.

(a) Optimum HLB vs styrene wt% in oil phase at different temperatures, and (b) temperature at the second TPI vs styrene wt% in oil phase, after the first TPI at 25 °C.

25 °C or 40 °C. Oils with different PIB/St ratios were used. The water phase containing 5 wt% NPE12 was added to the oil phase containing 5 wt% NPE5 until phase inversion to an O/W emulsion occurred. Figure 1a shows how the HLB at which phase inversion occurred, the optimum HLB, changed with the St weight percentage in the oil phase. It should be noted that the water volume fraction (f_w) at the inversion point was not constant and in fact increased with St percentage in the oil phase, as shown in Figure 1a. This is because the water-soluble surfactant was contained in the water phase and a high HLB is obtained at a high f_w.

The O/W emulsions formed under isothermal conditions had an average drop diameter of around one micron. In order to carry out polymerisation using thermal initiators such as lauroyl peroxide, the temperature of O/W emulsions formed by inversion was increased. However, an excessive rise in emulsion temperature eventually led to a phase inversion and restoration of the initial water-in-oil (W/O) emulsion morphology. That re-inversion could be the result of increased hydrophobicity of the surfactants with increasing temperature, as described above. After emulsions had been formed at 25 °C, the temperature at which the re-inversion, or secondary TPI, occurred depended on the weight percentage of St in the oil phase. That is shown in Figure 1b. The re-inversion to original W/O emulsion morphology occurred at lower temperatures with decreasing styrene content in the oil phase. The re-inversion occurred in the range of 50–75 °C, which is a suitable temperature range for polymerisation reactions, when the oil phase contains 40–90 wt% St. The emulsification temperature of 25 °C thus was found to be impractical for polymerisation purposes.

For the inverted O/W emulsions formed at 40 °C, however, no secondary phase inversion occurred when the temperature was increased to 70 °C. This is because primary phase inversion occurred at a higher HLB, as shown in Figure 1a, indicating that the surfactant mixture had a more hydrophilic nature. Therefore, a higher temperature would be required to render hydrophobicity to the surfactant mixture. The results indicated that polymerisation could be carried out at a temperature of 70 °C. However, drops underwent massive growth during polymerisation. The difference between drop diameter in the inverted O/W emulsion at an emulsification temperature of 40 °C and the final particle size from polymerisation at 70 °C, as shown in Figure 2, clearly indicates that drop coalescence was significant during polymerisation.

The reason for instability of drops during polymerisation is not clear, however, it is

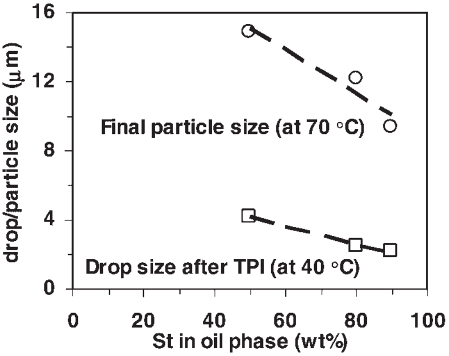

Figure 2.
Average diameter of drops in O/W emulsions after phase inversion (squares) and that of particles from polymerisation of corresonding emulsions (circles) versus styrene wt% in the oil phase.

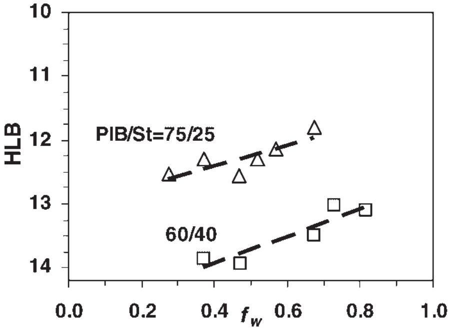

Figure 3.
Transitional phase inversion lines for the (PIB-St)/W/NPE system with different PIB/St ratios (T = 60 °C, and 5 wt% surfactant).

thought that drops become more unstable as the boundary of secondary inversion is approached. It is known that the emulsions are quite unstable in the vicinity of the locus of transitional inversion, or optimum formulation. For this reason, it was concluded that a better policy could be to conduct both phase inversion emulsification and polymerisation at the same temperature.

Isothermal Emulsification and Polymerisation

In this series of experiments phase inversion emulsifications were carried out using a different approach. In this method, an initial O/W emulsion at a predetermined phase ratio was made using the water-soluble grade surfactant. Then water and oil phases containing the low HLB surfactant were added with the same phase ratio as the O/W emulsion until phase inversion to a W/O emulsion occurred. The inverted emulsion then was reinverted to the original O/W emulsion by addition of the phases containing the high HLB surfactant with the pre-fixed phase ratio. The advantage of this approach over the one used above is that it maintains a constant f_w during phase inversion. Both stages of emulsification and polymerisation were carried out at 60 °C. Figure 3 shows the phase inversion lines for emulsions having PIB/St ratios of 75/25 and 60/40. It is clear from this figure that inclusion of monomer in PIB increased the value of the HLB at which phase inversion occurred (optimum HLB). The transitional lines shifted toward higher values of HLB with increasing monomer fraction in the polymer solution. This seems to be due to favoured dissolution of the high HLB surfactant in the monomer phase. So more high HLB surfactant is required in order to have a sufficient packing of the surfactant at the interface to induce phase inversion.[16]

Figure 4 shows the time evolution of d_{32} during polymerisation of an emulsion with PIB/St = 60/40. The average size of drops increased significantly within the first hour of reaction and then apparently remained

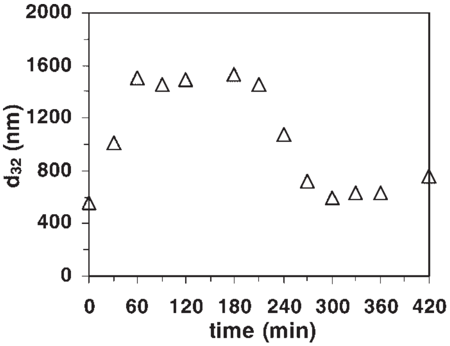

Figure 4.
Particle diameter variations during the polymerisation (f_w = 0.35, PIB/St = 60/40, HLB = 14, T = 60 °C, 5 wt% surfactant).

constant for the next two hours. In fact, the emulsion was quite unstable from the beginning of the reaction and particle coagulation occurred extensively.[16] Visual observations indicated massive coalescence of drops on the baffle and the stirrer. After this stage the size of drops showed a decrease simply because larger drops were lost via flocculation and deposition on the vessel. Only some of the droplets remained in the emulsion and all enlarged drops were lost. It appears that polymerisation of miniemulsions formed by using a PIB/St ratio of 60/40 is difficult to carry out for the current system. This is mainly because miniemulsions formed with this formulation were very close to locus of a three-phase microemulsion and thus were unstable.

In order to improve the stability of the miniemulsions, we attempted to use an HLB for the emulsion that was not close to the HLB for inversion. That could be done by dilution of the emulsions with water containing the water-soluble grade surfactant (NPE12). It was thought that another reason for growth of drops during polymerisation was a high concentration of the oil phase ($f_w = 0.35$). To study the effect of emulsion HLB and solids content (or f_w) on the stability of drops, an experiment was conducted at a higher value of f_w ($= 0.60$) which gave a phase inversion at an HLB of 13.4 (the HLB at inversion decreases with increasing f_w as shown in Figure 3). The inverted O/W emulsion was further diluted with water containing 5.0 wt % NPE12 to give a final emulsion at HLB = 13.8 and $f_W = 0.85$. Thus, the emulsion is less concentrated (oil phase fraction reduced from 0.40 to 0.15) and it has an HLB which is as far from the inversion line as is possible with this surfactant system. The particles, after dilution, were about 900 nm in diameter. The time evolution of conversion and d_{32} for the run are shown in Figure 5. While the instability of particles became apparent during reaction, the rate of coagulation was relatively slow, probably because of low solids content of the latex, so that particle growth could be monitored and measured. Conversion measurements were also possible as the latex showed fewer tendencies for coagulation. It is clear from Figure 5 that drop size follows a trend similar to that in suspension polymerisation in which drop size increases after intermediate conversion due to a viscosity increase in the drops and/or instability of drops.[17]

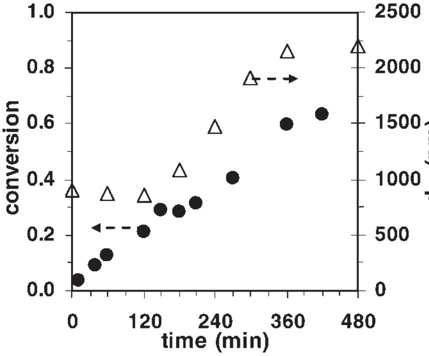

Figure 5.
Variations in conversion and particle size during the polymerisation ($f_w = 0.85$, PIB/St = 60/40, HLB = 13.8, $T = 60\,^{\circ}C$, 5 wt% surfactant).

It can be concluded that, with the surfactant system used here, it was not possible to displace the HLB of the inverted emulsion, with PIB/St = 60/40, far enough from that of the optimum formulation to maintain stability. It is inferred from the results that the main criterion for obtaining a stable miniemulsion for polymerisation is that the emulsion formulation should not be close to that of the optimum formulation.

Figure 3 shows that emulsions made with PIB/St = 75/25 undergo phase inversions at HLB values of 11.8–12.5 which are far from the HLB of the water-soluble grade of surfactant (14.2). This suggests that emulsions made with a lower content of St in the oil phase can be further stabilised by addition of water containing the water soluble surfactant. Those emulsions may remain stable during polymerisation. To verify this point, a phase inversion emulsification was carried out using an emulsion with a PIB/St ratio of 75/25 and at a constant value of $f_w = 0.30$.

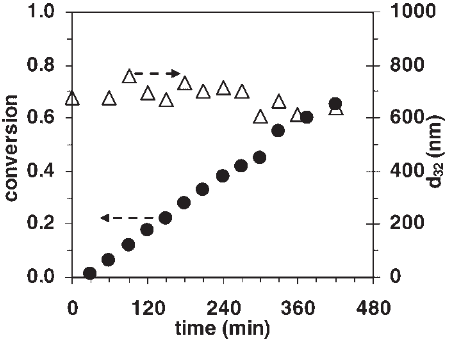

Figure 6.
Monomer conversion and particle size variations during polymerisation for PIB/St = 75/25, $f_w = 0.80$, $T = 60\,^{\circ}$C, 5wt% surfactant).

After phase inversion to an O/W emulsion at an HLB value of 12.6, additional aqueous phase was added to enhance the stability of droplets by departing from optimum formulation (final $f_w = 0.80$). Figure 6 shows the variations in monomer conversion and average polymer particle size during the polymerisation. The initial average size of drops was about 670 nm. There was no significant variation in the size of particles in the course of polymerisation indicating that polymerisation occurred mainly within the particles according to droplet nucleation mechanism. Generally the rate of polymerisation and the final conversion achieved were rather low. This could be due to the presence of impurities in the commercial grade PIB used in this research.

Conclusions

Submicron Polymer/monomer drops were produced by transitional phase inversion emulsification of PIB-St/water/NPE systems. The locus of inversion showed substantial variations with the monomer content in the oil phase. A high content of St produced miniemulsions with inversion HLB close to that of the higher HLB component in the system. These minimulsions thus could not be adequately stabilised and, as a result, underwent massive coagulation during polymerisation. A low content of St led to phase inversion at intermediate HLB values. The stability of the emulsions could then be increased significantly by addition of the high-HLB surfactant. The size of drops did not change significantly during the polymerisation when the monomer content of the oil phase was low.

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