High Internal Phase Polymeric Emulsions by Self-Assembly of Colloidal Systems

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ABSTRACT: We propose a new procedure to synthesize high internal phase polymeric emulsions (polyHIPE) that is based on the self-assembly of colloidal systems. Colloidal suspensions were used as precursors of the final polyHIPE. These were obtained by dispersing 500 nm diameter, lightly cross-linked polystyrene (PS) emulsion particles in ethanol at room temperature under continuous sonification. A polystyrene-poly(2-vinylpyridine) (PS−PVP) block copolymer with a short PS block and a long PVP block was synthesized and dissolved in the ethanol-colloidal dispersion. After solvent removal, owing to the asymmetric composition of the block copolymer and the high volume fraction of the colloid, a closely packed colloidal system was obtained, where voids were partially filled by the block copolymer discrete phase. However, under appropriate annealing, the colloidal system was shown to undergo a rearrangement in which the particles deform to polyhedrons and closely pack within a percolating phase formed by the poly(2-vinylpyridine) block of the copolymer. The volume fraction threshold for percolation of this PVP domain structure was shown to be as low as 0.10 by doping the PVP and performing conductivity measurements. We argue that the physical driving force leading to this rearrangement is the reduction of the interfacial tension of the colloidal system.

Introduction

Emulsions based on water/oil/surfactant systems have been extensively investigated during the past few decades.[1−8] High internal phase emulsions (HIPE) can be achieved in these systems, in which the dispersed phase is present in a volume fraction exceeding 0.74, i.e., the critical packing fraction of a face-centered-cubic (fcc) crystal. At these high volume fractions, it is no longer possible to closely pack monodisperse spheres, and therefore in order to maintain the high volume fraction, droplets with a narrow size distribution will rearrange into polyhedral structures. [2,6,7]

Multiple efforts have been made more recently to synthesize polymer-based HIPE, generally referred to as poly(HIPE),[9,10] owing to the potential advantages these structures may have in many practical applications, such as membranes, foams, barriers, etc. The emulsification process in such a polymer-based HIPE is analogous to that of water-in-oil emulsions. An oil, such as petroleum ether[9,11] or a low molecular weight compound phase, is generally dispersed dropwise in a solution of monomer, solvent, and surfactant so that an emulsion of up to 90% oil in the monomer bath can be obtained.[9−12] Subsequently, the continuous monomer phase is polymerized and the solvent removed. The most extensively used monomers are styrene or divinylbenzene (DVB), which can be polymerized by a free radical polymerization process,[13−19] and ionic, nonionic, and polymeric surfactants have been explored.[20−23] By following this procedure, a blend is produced in which the dispersed phase is liquidlike, and foams with very low density can be obtained by extracting this phase.[10,17−19,24−26]

Recently, we have reported a new solvent-based technique allowing the synthesis of poly(HIPE) structures in which both phases can be polymeric without the need of polymerization.[27] By following this technique, which involves appropriate selection of polymers, solvents, and block copolymer surfactant, polyHIPE structures can be produced in which a continuous minority phase is present in a volume fraction as low as 0.13. This technique was shown to be highly desirable for producing blends in which unique rheological, electrical, and barrier properties of the minority, percolating phase can be exploited. However, only poor control of mean particle size has yet to be achieved with this technique, a limitation that represents a serious drawback if optical and mechanical properties of the final blend must be uniform and controlled.

In principle, particle size can be perfectly controlled if colloidal latex particles with a narrow size distribution are used as discrete phase precursors to form polyHIPE compositions. These latex particles are readily available today, owing to the large number of applications in which they are used, ranging from coating, rubber modification, and ion-exchange technologies[28] to photonic or colloidal crystal applications.[29−31] Indeed, substantial advances have been made in the production of nearly monodisperse colloidal spheres as well as on colloidal crystallization. The main reason is that for these applications colloidal particles with a narrow size distribution are required in order to achieve well-formed crystals starting from a colloidal dispersion.[32,33] One route to self-assemble colloidal particles into dense arrays is to make use of attractive depletion interactions, induced by dispersing colloidal particles and dissolving polymer chains in the same solution.[34,35] In this way, the polymer chains, excluded from a R_g-thick corona around the colloids, where R_g is the radius of the gyration of the polymer, gain entropy on the approach of particles, whereas only a minor entropy loss

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is suffered by the colloidal particles. Other strategies to bind colloidal particles together have focused on surface interactions, by using charged particles[36] or core−shell latexes.[37] Under the influence of these forces, colloidal systems have been shown to undergo complex phase transitions, and intriguing phase diagrams have been demonstrated.[38] However, all these methods have led, in the best case, to closely packed arrays of colloidal particles in a bcc, hcp, or fcc structure. As a consequence, if polyHIPE structures without voids are to be produced by these methods, the limiting volume fraction of 0.74 for the dispersed phase cannot be overcome, and the continuous phase, formed by another polymer, has to be present at a volume fraction equal to or beyond 0.26.

In the present work we propose a new procedure to synthesize polyHIPE based on self-assembly and collapse of colloidal dispersions. We show that properly designed block copolymers added as surfactant to the colloidal dispersion can be used to pack colloidal systems beyond the volume fraction of 0.74 and maintain the dispersed phase embedded in a continuous percolating phase whose volume fraction can be as low as 0.10. Thus, compared to the other procedures available to synthesize polyHIPE, this technique should allow a greater control of the morphology of both the continuous and dispersed phases.

Experimental Section

Materials. Polystyrene (PS) and poly(2-vinylpyridine) (PVP) were selected to produce polyHIPEs in which the PVP phase was maintained as continuous structure. Carboxyl-functionalized PS emulsion particles, having an average diameter of 514 nm and narrow size distribution, were received from the Dow Chemical Co. Swelling experiments in tetrahydrofuran (THF) and differential scanning calorimetry (DSC) experiments indicated that the PS particles were slightly cross-linked. Indeed, the particles, whose glass transition temperature was measured at 108 °C, were observed to be swollen without dissolving in THF for a period of 30 days. Two different PS−PVP diblock copolymers were selected for the study. The first, PS−PVP_1, synthesized as described elsewhere,[39] had an overall M_w = 70 000 g/mol with a PVP volume fraction, f_{PVP}, of 0.84, determined from the nitrogen content obtained by elemental analysis.[40] The second similar diblock copolymer was used as received from Polymer Source, Inc., and is referred in the present work as PS−PVP_2. It had an overall M_w = 60 000 g/mol, with f_{PVP} = 0.78. Finally, PVP homopolymers of M_w = 8000 g/mol and M_w = 160 000 g/mol were synthesized by anionic polymerization, following the procedure described elsewhere.[39] For all polymers used, the polydispersity index was lower than 1.1. Camphorsulfonic acid (CSA) (Fluka) was used as a doping agent for the PVP phase, when required by conductivity measurements.

Procedures. *Blend Preparation.* Ethanol was chosen as a selective solvent for PVP and a nonsolvent for PS. Colloidal dispersions of PS microbeads and PS−PVP block copolymer in ethanol were prepared as follows: PS−PVP block copolymer was added to 5 g of ethanol in various concentrations and dissolved by continuous stirring and gentle heating (60 °C). After cooling the solution down to room temperature, microbeads were added and finely dispersed by continuous sonification for 60 min. To explore PVP volume ratios between 0.04 and 0.16, the total weight of the dry colloidal system was fixed at 0.1 g, with the block copolymer amount varying between 0.005 and 0.02 g. To slowly evaporate the solvent without inducing boiling of the solution, the temperature was raised to 70 °C (ethanol boiling point 78 °C) at atmospheric pressure. Maintaining these conditions for 24 h allowed all the solvent to be removed. Samples were finally annealed under vacuum at 140 °C, i.e., above the glass transition temperature of both PS microbeads and block copolymer (100 °C) for durations of 3, 7, and 24 h.

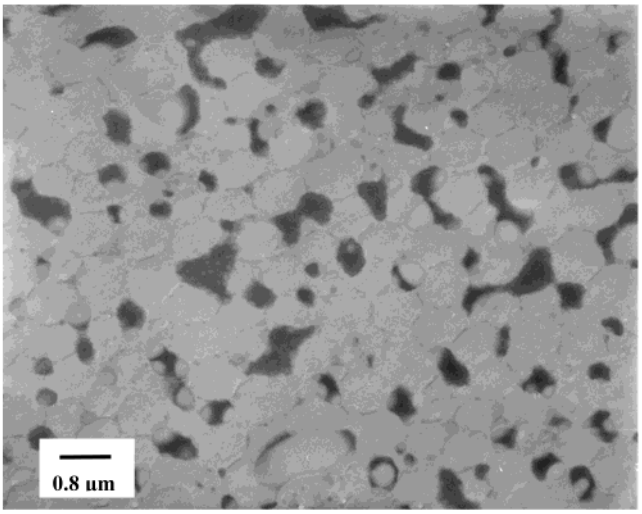

Figure 1. TEM micrograph showing the disordered structure observed for the colloidal system formed by PS microbeads and a volume fraction of 0.15 PS−PVP_1 block copolymer after solvent removal and prior to annealing. The dark phase represents the PVP block stained by I_2 while the white phase includes unstained 514 nm PS microbeads, PS from the PS−PVP_1 block copolymer, and voids.

Proton conductive polyHIPE were produced by doping the PVP block of the block copolymer with CSA by dissolving both the PS−PVP block copolymer and CSA in ethanol. A 1:1 molar ratio of the sulfonic groups to the nitrogen atoms of the PVP was used when preparing the solution. After forming the PVP:CSA complex in the ethanol solution, PS microbeads were added in the required weight fraction and dispersed by continuous sonification for 60 min. Similarly, the same conditions described previously were used for solvent removal and sample annealing.

Transmission Electron Microscopy (TEM). The 100 nm thick films of the final blends were microtomed with a Leica Ultra Cut microtome. The PVP phase was stained for 6 h at room temperature in saturated I_2 vapor above solid I_2. Micrographs of the final morphologies were taken using a JEOL 2000FX transmission electron microscope operated at 200 kV.

Electrical Conductivity. Electrical conductivity measurements were performed on polymer films of thickness ranging between 1 and 60 μm. Films were cast above a glass substrate with a four-probe gold pattern that was used to measure the resistance. The final specific conductivity was calculated from the measured resistance and thickness of the film. Following the procedure described above, the lowest conductivity, which was possible to be measured for a film of 60 μm in thickness, was of the order of 10^{-9} S/cm. The thickness of the thinnest films was measured by scratching the film with a razor blade and performing atomic force microscopy on the film. The thickness of the thickest films was determined by peeling the film off the substrate and measuring it with optical microscopy.

Dynamic Light Scattering. To measure the size of the block copolymer micelles in solution in ethanol, dynamic light scattering experiments (DLS) were performed using a Brookhaven Instruments system. Solutions of 0.5% PS−PVP by weight in ethanol were prepared and analyzed. Successively, to form the PS−PVP:CSA complex, CSA was added to the solution in the needed concentration, and continuous stirring was maintained for 30 min, after which measurements were performed at room temperature.

Results and Discussion

Figure 1 shows an electron micrograph of the colloidal system formed by blending PS latex particles with PS−PVP_1 block copolymer (to a nominal copolymer volume

fraction of 0.15) after solvent removal and prior to annealing. A disordered structure is obtained, where the block copolymer forms a discrete phase (the dark stained phase is the PVP block of the PS−PVP). The clear phase in Figure 1 includes both the unstained PS colloidal particles and voids. Indeed, since the solvent is removed at room temperature, which is below the glass transition temperature of both PS and PVP, the colloidal spheres will pack similarly to hard spheres in a box, leaving some empty space in between. Owing to the low volume fraction of the block copolymer phase (lower than 0.26), these voids will be only partially filled by the block copolymer phase. Thus, although an interface between PVP and PS is generated, the free surface of the PS particles can only be partially wet by the diblock copolymer. Therefore, both surface (against air) and interface energy will contribute to the energetic status of the dry colloidal system. It can be then expected that, if the system is annealed under appropriate conditions, this should rearrange into a lower free energy configuration.

Figure 2 shows TEM micrographs of the structure observed after annealing. The system considered is the same as that shown in Figure 1, with the difference that annealing times of 3, 7, and 24 h at 140 °C have been applied (Figure 2, a, b, and c, respectively). Although some refinement in the block copolymer distribution can be observed during the 24 h, Figure 2 indicates that (i) the final morphology is achieved in a relatively short time and (ii) the final structure is stable enough to maintain the same morphology at 140 °C. By comparison with Figure 1, it is clear that, upon annealing, the colloidal particles undergo a strong rearrangement, deforming to polyhedrons wet by a continuous PVP phase. During this process, the block copolymers redistribute, segregating to the surface of the particles and coating them more or less uniformly to decrease the excess free energy associated with the PS−PVP interfacial area in the micelles and between the PS colloids and the PVP coronae of the micelles. Concurrently, the PS colloidal spheres deform into polyhedral shapes to eliminate remaining voids. In the case considered, the resulting geometric polyHIPE obtained has an approximate volume composition of 0.87 PS and 0.13 PVP, which is comparable with the compositions previously reported in the literature for polyHIPE foams and blends. However, besides the simplicity of the present technique, the unique features characteristic of the present polyHIPE composition are that (i) the particles are uniform in size and (ii) the dispersed majority phase is not interpenetrating as reported in other polyHIPE foams.[12] This allows, in principle, the use of these polyHIPEs as barrier materials, where an expensive polymer having barrier properties could be used in very low volume fraction and still provide the blend with needed barrier properties.

The driving forces leading to the rearrangement of the morphology of the colloidal system under annealing deserve some discussion. Keddie et al. have investigated the deformation of colloidal systems under annealing.[41] After drying colloidal dispersions with procedures similar to that used in the present work, and annealing the system at temperatures above the glass transition temperature of the latex, they showed that the colloidal particles deform, leading to a consolidation of the system and closure of the voids left after solvent evaporation. The driving force for this rearrangement was shown to be the reduction of surface energy associated with the free surfaces of the colloidal particles. A similar explanation can be used to explain the rearrangement in morphology observed by other groups upon annealing core/shell hydrophobic latex films[42] or by solution casting of dispersions formed by poly(divinylbenzene) colloidal particles with polystyrene chains grafted on their surface.[43] In those cases, the colloidal systems reorganized into a two-phase morphology that is very similar to the polyHIPE reported in the present work, i.e.,

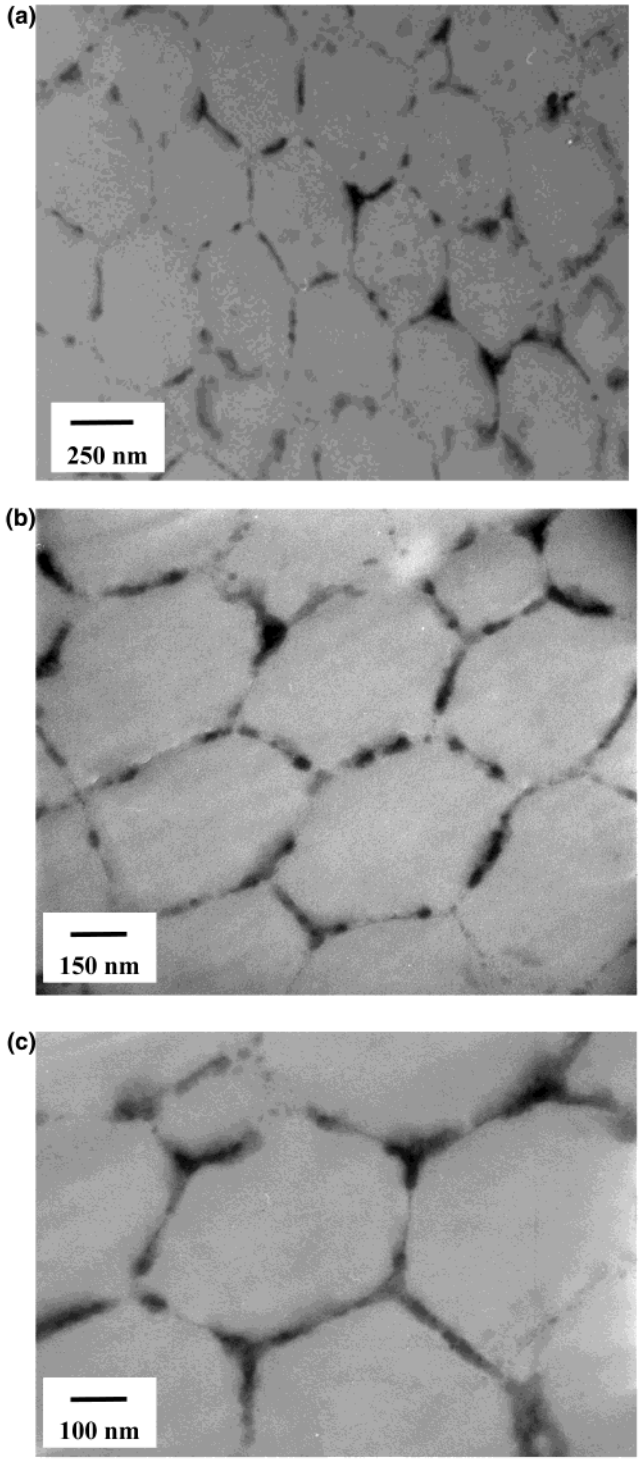

Figure 2. TEM micrographs at the different annealing times of 3 (a), 7 (b) and 24 h (c) of the structures observed for the colloidal system formed by PS microbeads and 0.15 volume fraction of PS−PVP_1 block copolymer after solvent removal and annealing at a temperature of 140 °C.

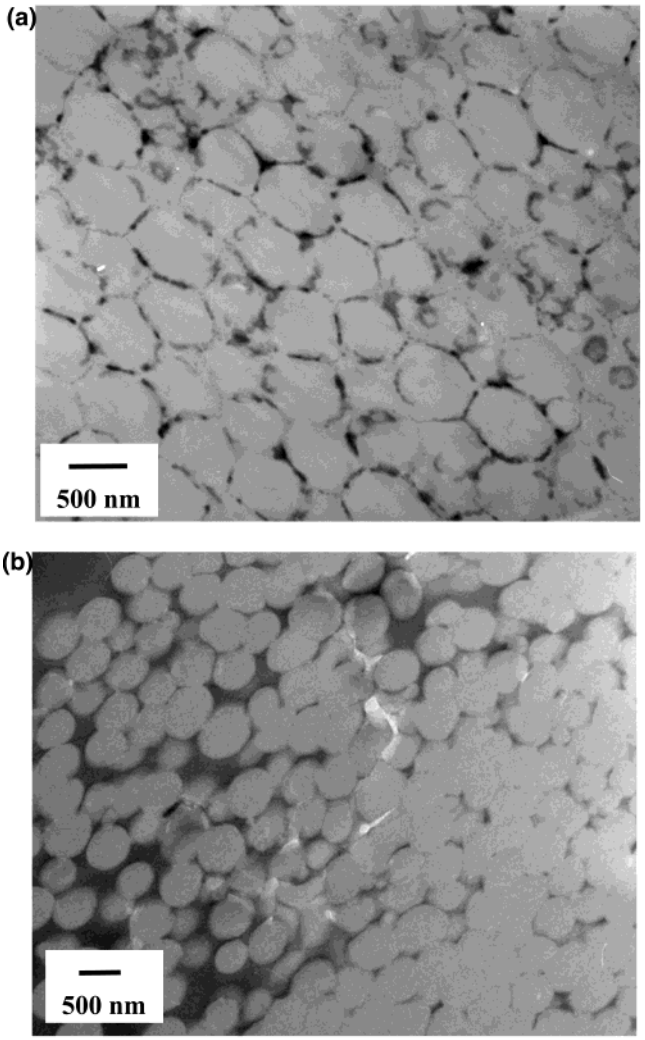

Figure 3. TEM micrographs of the polyHIPE obtained from the colloidal dispersion formed by PS microbeads, PS−PVP_1 block copolymer, and PVP homopolymer in volume fractions of 0.85, 0.08, and 0.07, respectively, after solvent removal and 7 h annealing at 140 °C. **(**a**)** The PVP homopolymer has a molecular weight of 8000 g/mol, providing wet brush conditions on the PVP block of the PS−PVP_1 block copolymer. **(**b**)** PVP homopolymer has a molecular weight of 160 000 g/mol, providing dry brush conditions on the PVP block of the PS−PVP_1 block copolymer side.

where the core of the particles was maintained as a dispersed phase embedded in a continuous phase obtained by the consolidation of the shells of the latex particles. Therefore, in both the previous and present cases, the energy gained by reducing the total free surface of the system leads to the observed change in morphology. However, in the present work, the rearrangement of the morphology is also driven by the reduction of the interfacial free energy associated with the PS−PVP interface. Indeed, if the only driving force were the reduction in PS surface energy, the colloid would close the voids by entrapping the block copolymer into a dispersed phase, leading to a final morphology similar to that observed prior to annealing. On the contrary, the block copolymers segregate rapidly to the free particle surfaces, evidently because chains transferred from a bulk mesophase to the surface of a PS particle can relieve both stretching energy and PS−PVP interfacial energy. Simultaneous with this wetting by copolymers, the particles deform into polyhedral structures.

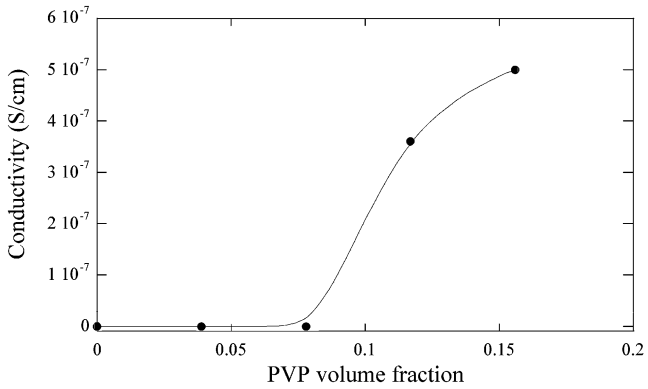

Figure 4. Specific (proton) conductivity of the polyHIPE blend measured vs the volume fraction of the percolating PVP phase. Conductivity onset is measured at PVP volume fractions between 0.08 and 0.12, indicating the percolation threshold at a volume fraction as low as 0.10.

Figure 3 shows the structures of polyHIPEs obtained by including PVP homopolymers in the percolating phase. The blends were obtained with the usual procedure, with the difference that PVP homopolymer was dissolved together with PS−PVP block copolymer in the ethanol solution. Solvent was then removed as described previously, and samples were annealed under vacuum for 7 h at 140 °C. To have dry and wet brush conditions on the PVP block side of the interface, both low and high molecular weight PVP homopolymers were considered. The wet brush condition was obtained by swelling the PVP block side of the interface with a 8000 g/mol PVP homopolymer, and the corresponding morphology is shown in Figure 3a. Figure 3b shows the morphology obtained for the dry brush condition, realized by adding 160 000 g/mol homopolymer PVP. In both cases the composition of the dry blends was maintained at 0.85 PS colloid, 0.08 PS−PVP_1 block copolymer, and 0.07 PVP homopolymer by volume. The most ordered structure was obtained by using low molecular weight PVP. This result can be attributed to the higher interpenetration of the low molecular weight homopolymer into the PVP block, characteristic of wet brush conditions, and is in agreement with results reported previously for polyHIPE obtained by an emulsion process.[27]

The continuous phase of the polyHIPE realized with the present technique can be utilized for specific mechanical, rheological, or transport applications, for example to conduct electrons or protons. Proton conductivity proves to be a straightforward way to detect the threshold for percolation of the PVP phase. In the present work, to explore percolation, we first dope the continuous phase with CSA and then measure the ionic conductivity of the final blend. A similar P4VP−methanesulfonic acid (MSA) system has already been shown in the literature to be proton conducting.[44] As anticipated in the Experimental Section, the colloidal dispersion is prepared as usual in ethanol, but CSA is added and dissolved in the solution at a concentration corresponding 1:1 molar ratio of the sulfonic groups to the nitrogen atoms of the PVP. Thus, if the PVP and CSA form a strong complex already in solution, the surfactant used to create the percolating structure will no longer be the block copolymer but the PS−PVP_2:CSA complex. Owing to the overlapping of sulfonic and aromatic groups in Fourier transform infrared spectroscopy, dynamic light scattering is preferred to demonstrate the formation of the PS−PVP_2:CSA complex. The

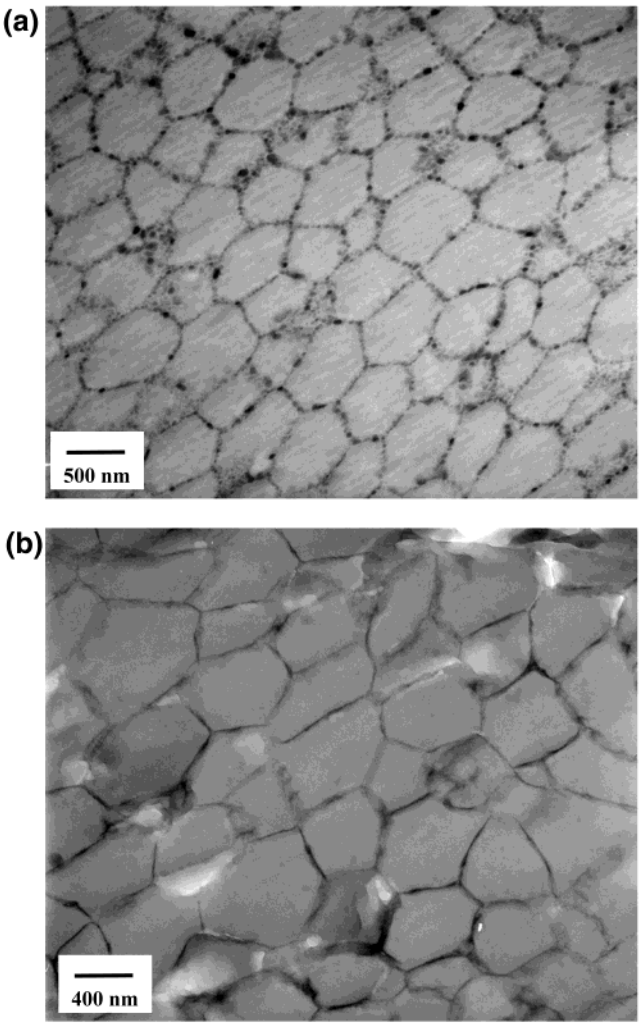

Figure 5. TEM micrographs showing the structures of the polyHIPE formed by 514 nm PS microbeads and PS−PVP_2:CSA block copolymer surfactant. (a) The structure formed at a PVP:CSA volume fraction of 0.08 is discontinuous and is not conductive. (b) The structure formed at a PVP:CSA volume fraction of 0.12 is continuous, and a conductivity of 4×10^{-7} S/cm is measured.

correlation functions obtained by DLS at room temperature for a 0.5 wt % solution of the PS−PVP_2 in ethanol and the PS−PVP_2:CSA in ethanol were measured and compared. In the former case micelles are detected whose average measured diameter is 65 nm. However, by introducing CSA, the measured diameter of the micelles increase to 102 nm. This is a consequence of the fact that the PVP_2 micelle coronae are swollen by the CSA and thus confirms that the PVP_2:CSA is formed in solution in ethanol.

This PVP_2:CSA complex was shown to be conductive by performing conductivity measurements on dried PS−PVP_2:CSA films. The specific conductivity had a measured value of 6×10^{-6} S/cm. To measure the percolation threshold of the continuous phase, conductivity measurements on the PS/PS−PVP_2:CSA blends were performed using the procedure described in the Experimental Section. Figure 4 shows the specific (proton) conductivity of the different polyHIPEs measured as a function of the volume fraction of the PVP:CSA phase. As it can be noted, conductivity starts to be measurable at a volume fraction of PVP:CSA between 0.08 and 0.12. This is consistent with the phase structure observed with the TEM at these two compositions, shown in parts a and b of Figure 5, respectively. At a volume fraction of 0.08 PVP:CSA (Figure 5a), the PVP:CSA phase is not continuous, and it is not surprising that no conductivity is measured. However, by increasing the PVP:CSA volume fraction up to 0.12 (Figure 5b), a continuous conductive phase is observed and an overall conductivity of 4×10^{-7} S/cm was measured, as shown in Figure 4. We note that the volume fraction of the continuous phase at the percolation threshold can be adjusted, for example, by changing the length of the PVP block. A longer block can be used when greater conductivity is desired.

Conclusions

We have proposed a new, simple procedure to synthesize polyHIPE blends, which allows controlling the morphologies of both the continuous and dispersed phase to an extent well beyond that possible with other currently available techniques. This procedure makes use of narrow size distribution colloidal particles as precursors of the final dispersed phase and properly designed block copolymers to build up the continuous phase. The block copolymer has to be designed in such a way to have two immiscible blocks, one of which is short and compatible with the colloid and the other of which is long and soluble in the solvent used to disperse the colloid. The system selected in the present work was polystyrene emulsion particles, polystyrene−poly(2-vinylpyridine) block copolymer, and ethanol as solvent. The final polyHIPE structure was obtained from the colloidal dispersion in a sequence of two steps only: solvent evaporation and sample annealing. During annealing, driven by the surface tension associated with trapped voids in the dried dispersion and the high chemical potential of copolymer chains in the medium surrounding the particles, the morphology of the system undergoes a reorganization where the particles deform to polyhedrons and the solvent-soluble block of the block copolymer forms a continuous, percolating structure wetting the discrete phase. The volume fraction threshold of this percolating phase can be detected by proton conductivity, after doping the poly(2-vinylpyridine) phase with camphorsulfonic acid. The percolation onset was measured at a volume fraction as low as 0.10. This highlights the potential of the proposed procedure for producing high internal phase ratio polyHIPE structures in which the continuous phase can be exploited for specific applications.

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