Novel Interconnected Network Morphology in an Immiscible Polyblend Emulsified by a Block Copolymer

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Introduction. Molecular aspects of the morphological behavior of immiscible blends emulsified by block copolymers have recently been discussed by several authors.[1–3] Studies of immiscible blends of poly(methyl methacrylate) (PMMA) with polystyrene (PS) emulsified by a poly[(methyl methacrylate)-*b*-styrene] (PMMA-*b*-PS) copolymer were discussed by Lowenhaupt and Hellmann,[1] using transmission electron microscopy (TEM). The degree of macrophase versus microphase separation was shown to depend strongly on the block copolymer content and on the molecular weight of the block copolymer relative to those of the homopolymers. Investigations of blends containing polystyrene and poly(styrene-*b*-isoprene) or poly(styrene-*b*-butadiene) by Kinning et al.,[2] using TEM and small-angle X-ray scattering (SAXS), demonstrated that a block copolymer is a better emulsifier when the block segment is of equal or higher molecular weight compared to that of the homopolymer of like chemistry. The role of short-range monomer attractions (*exothermic mixing*) and repulsions (*endothermic mixing*) between block copolymer segments and the homopolymer matrices was explored by Akiyama and Jamieson[3] in blends containing styrene–acrylonitrile random copolymers (SAN) as the major component and PS as the minor component with PMMA-*b*-PS as the emulsifier. In these blends, exothermic mixing occurs between the PMMA copolymer segment and the continuous SAN matrix, while the PS copolymer is repelled toward the interior of the dispersed phase. Keeping the relative molecular weights of all components approximately constant, the enthalpic interactions were systematically varied by varying the acrylonitrile (AN) content of the SAN. Morphological changes were observed which were interpreted as indicating that decreasing the AN content, which increases the exothermic mixing between SAN and PMMA and decreases the repulsion between SAN and PS, leads to improved performance of the block copolymer as an emulsifier.

In this investigation, we are concerned with the well-understood concept that the minor component of an immiscible polyblend, emulsified by a block copolymer, typically forms a discrete phase in the continuous matrix of the major component. However, generally, in blends or emulsions, as the concentration of the minor component is increased, there is a range of concentration, within which the dispersed phase becomes the continuous matrix and vice versa.[4] This process is described as phase inversion. An emulsifier reduces the phase inversion concentration in water/oil emulsions. For example, in commercial emulsions the dispersed phase is frequently described as constituting over 90% of the total volume.[4] The role of emulsifier has, however, been considered relatively insignificant in immiscible organic mixtures.[4] Furthermore, to our knowledge, no observation of the phase inversion concentration in emulsified blends of two immiscible polymers has been reported, although the dependence of phase inversion of two immiscible polymers on their relative viscosities has been discussed.[5]

Here we describe an experiment in the SAN/PMMA-*b*-PS/PS system where we utilize the knowledge that a decrease in molecular weight of the PS homopolymer relative to the PS block segment, coupled with increased exothermic mixing of the PMMA block segment with SAN, enhances the emulsifying power of the block copolymer so that we can generate novel morphological structures where a minor SAN component (~10%) forms the continuous phase and the major PS component forms discrete domains. These features appear analogous to those found in commercial water/oil emulsions. We further demonstrate that we can systematically modulate this morphology by varying the degree of SAN/PMMA exothermic mixing and SAN/PS repulsion through changes in the AN content.

Experimental Section. Polymers utilized in this study were 680Kd PMMA-*b*-PS (220Kd:460Kd; $M_w/M_n = 1.10$), from Polysciences Inc., PS (90Kd; $M_w/M_n = 1.04$), from Pressure Chemical Co., and SAN with 15, 26, 29, or 33% AN content (163-, 153-, 151-, 130Kd; $M_w/M_n = 2.12, 2.16, 2.23, 1.95$),[6] supplied by Mitsui Toatsu Chemicals Inc. Stock solutions of these polymers were made up in methyl ethyl ketone (MEK) at a concentration of 1 g/100 mL. Each blend contains 77.5 v/v % of the PS solution, 15 v/v % of the PMMA-*b*-PS, and 7.5 v/v % of one SAN. The SANs will be referred to, henceforth, as SAN15, SAN26, SAN29, and SAN33 where the last two digits indicate the percentage of AN content. Note that the ratio of matrix polymer molecular weight to compatible block copolymer segment is 0.2 on the PS side and decreases slightly from 0.74 to 0.59 on the SAN side. Thus, when comparing the effect of AN content on the emulsifying power of the block copolymer in this and our earlier study,[3] the dominant effect is due to the change in enthalpic interactions.

The blend solutions were cast on a clean mercury surface, in hollow test tubes, and the solvent was slowly removed at room temperature over 7 days. Final traces of the solvent were removed by annealing at 70 °C for 1 day at atmosphere pressure and then for 1 day under vacuum. Central portions of the cast films (~0.2–0.4 mm thick) were sectioned, using a diamond knife, with a RMC Inc. MT-7000 ultramicrotome machine in a direction normal to the surface to obtain thin films (70–90 nm thick) which were subsequently exposed to RuO_4 vapor for 1 h in an enclosed chamber containing about 1.5% aqueous solution of RuO_4. Bright-field images were obtained by mass-thickness contrast on a JEOL JEM-100SX transmission electron microscope, at 100 kV.

Results and Discussion. Transmission electron micrographs of the SAN/PMMA-*b*-PS/PS blends are displayed in Figures 1–4, in order of decreasing AN content. The darker background is the PS component which is stained by RuO_4, and the lighter regions indicate the areas occupied by SAN and PMMA. There is clearly a systematic change in blend morphology with increasing AN content of SAN, indicating an increased tendency of the SAN minor phase to form interconnected networks, i.e., to become the continuous phase, as the SAN/PMMA exothermic mixing increases and the SAN/PS repulsion decreases.

In Figure 1, the exothermic mixing between SAN33 and PMMA is minimal while the SAN/PS repulsion is maximal (see ref 3 for numerical values of their Flory–Huggins χ parameters). The minor phase predominantly forms vesicles of various sizes. The majority appear spherical, but many are not. Several, indicated by arrows, appear to be kinetically trapped in the process of vesicle coalescence and growth (coarsening). Note that their relative

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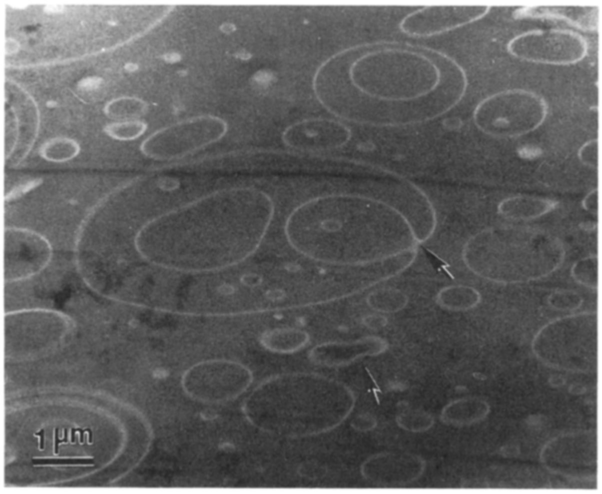

Figure 1. Vesicular structures in SAN33/PMMA-*b*-PS/PS.

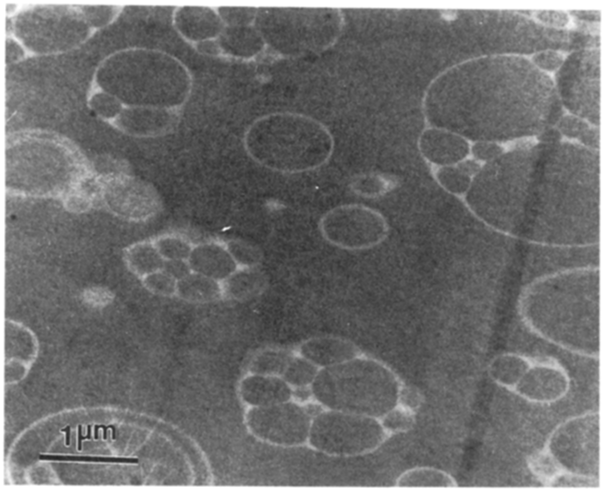

Figure 2. Short-range association of vesicles in SAN29/PMMA-*b*-PS/PS.

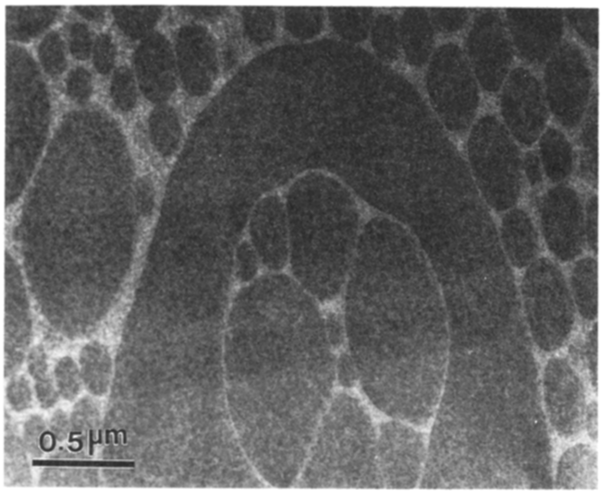

Figure 3. Minor phase as the continuous matrix and major phase as the discrete domains in SAN26/PMMA-*b*-PS/PS.

population is small. These two characteristics indicate that the structures that are displayed in the figures are near equilibrium.

As the AN content is reduced to 29%, the SAN/PMMA exothermic mixing increases and the SAN/PS repulsion decreases. In the SAN29/PMMA-*b*-PS/PS blend (Figure 2), there are still many isolated vesicles but extensive aggregation of the vesicles is clearly occurring. Note that the association of the vesicles means that, locally, the SAN/PMMA minor phase becomes the continuous phase.

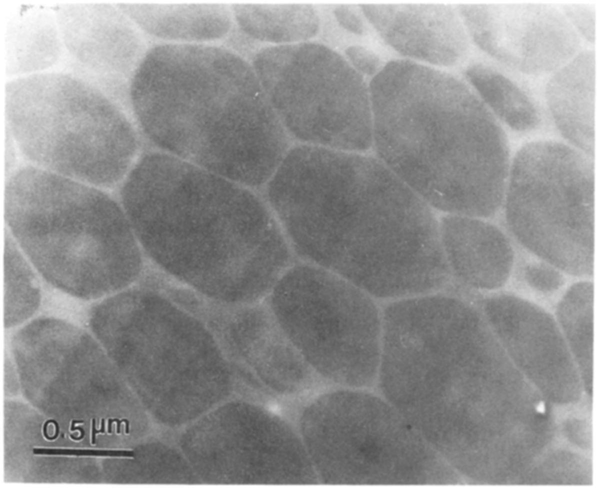

Figure 4. Interconnected polygonal structures formed in SAN15/PMMA-*b*-PS/PS.

Further reduction of the AN content leads to a more extensive interconnection of the minor phase so that the major component PS forms discrete domains in a continuous matrix of the minor component SAN/PMMA (Figure 3). Some inclusions of PS contain associated vesicles similar to those in Figure 2.

Finally, at maximal SAN/PMMA exothermic mixing and lowest SAN/PS repulsion, a fully interconnected polygonal network was observed as displayed in Figure 4. Identical morphological features were obtained on sectioning this specimen in directions normal, diagonal, and parallel to the film surface, indicating that the polygonal structure formed by the minor component is three-dimensionally connected. It is evident that this structure is equilibrated from the lack of curvature of the SAN domains between the PS inclusions. These experiments demonstrate that by enhancing the exothermic character of the interaction between a block copolymer segment and the minor component in an immiscible blend one can produce phase inversion at low volume fractions.

Conclusions. We have demonstrated that novel interconnected morphological structures can be generated in immiscible polymer blends by manipulating the attraction and the repulsion between the polymer matrices and the segments of an emulsifying block copolymer. By systematically increasing the exothermic interaction of one segment with the minor phase and decreasing the repulsion of that segment with the major phase, a gradual morphological transformation is induced which generates structures where the minor component forms the continuous matrix while the major component forms the discrete domains. Our results further confirm that a block copolymer will be a better emulsifier if there is exothermic mixing between its segments and the matrix polymers.

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References and Notes

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