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commercial sources.[2-4] Although the synthetic copolyesters are highly crystalline, they are not optically active and the low yield of stereoregular material (<25 wt % of the total polymer) is a drawback. Given the improvements in degree of tacticity of poly(α-olefins) that were forthcoming from advances in Ziegler–Natta catalysis, it is reasonable to expect that the same improvements in stereoregulation may be forthcoming for P(HB-*co*-HV) synthesis.

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Registry No. AlEt$_3$, 97-93-8; H$_2$O, 7732-18-5; (($\pm$)-β-butyrolactone)(($\pm$)-β-valerolactone) (copolymer), 110774-30-6.

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Anomalous Association Behavior of an Ethylene Oxide/Propylene Oxide ABA Block Copolymer in Water

In analogy to conventional, low molecular weight surfactants, one of the characteristic properties of ABA (or AB)-type block copolymers in solution is that they form micelles[1] in selective solvents which are thermodynamically good solvents for one block and precipitants for the other block. It is now well accepted that the micelles formed are composed of a relatively compact core of "insoluble" blocks and a highly swollen shell of "soluble" blocks. In most cases, block copolymer micelles are spherical in shape in dilute solution and have a narrow distriubtion of both mass and size. Micellization of block copolymers obeys the closed association model,[1] resembling thus the behavior of conventional detergents. However, a peculiar phenomenon has been reported by a number of research groups[2-10] on the micellization process of some block polymers in selective solvents. The so-called anomalous behavior manifests itself essentially in strong angular asymmetry of scattered light. In general, such an anomaly in micellization is absent in common detergents.

The aim of this paper is to try to elucidate the cause of the anomalous association behavior observed in ABA block copolymers in the transition region between molecular and micellar solutions. By designing and carrying out a filtration experiment in the anomalous region for aqueous solutions of poly(oxyethylene–oxypropylene–oxyethylene) (PEO–PPO–PEO) block copolymer, poloxamer 184, we have succeeded in eliminating the anomalous behavior, as evidenced by light-scattering intensity and line-width measurements. Based on these results we have reached a tentative conclusion that composition heterogeneity could be one possible cause to explain the anomaly in micellization behavior of (PEO–PPO–PEO) block copolymers in selective solvents. A more detailed study is under way.

Two commercial poloxamer 184 (also called Pluronic L64) samples, obtained from Fluka Co. and Polysciences Co. were used in this study without further purification. Poloxamer 184 is a PEO–PPO–PEO block copolymer containing approximately 40% oxyethylene with a nominal molecular weight of 2900 and a hydrophilic–lyophilic balance (HLB) value of 15. For light-scattering measurements, aqueous solutions were first centrifuged at 12 000 rpm ($\sim$17000*g*) and then filtered through Millipore filter GS (nominal pore size 0.22 μm) into 17-mm-o.d. cells, which were then sealed under vacuum. We used a standard, laboratory-built light-scattering spectrometer[11] capable of both absolute integrated scattered intensity and photon correlation measurements at different scattering angles. A Spectra-Physics argon ion laser (Model 165) was operated at 488 nm with an output power in the range of 200–400 mW, depending on the scattered light intensity level of the sample solution. The photoelectron count time correlation function was measured with a Brookhaven BI-2030 64-channel correlator. The temperature was controlled within 0.02 °C and data were analyzed by using either the cumulants method[12] or a double-exponential fitting method.[13]

The association process of poloxamer 184 in water has been studied via the temperature dependence of either the scattered light intensity (I) or the effective hydrodynamic radius (R_h) of the particles. Figure 1 shows the scattered intensity results obtained on an aqueous solution of poloxamer 184 (Fluka product, c = 10.0 mg/mL) before and after filtration. Similar results could be observed by using the Polysciences product. There are three distinct regions

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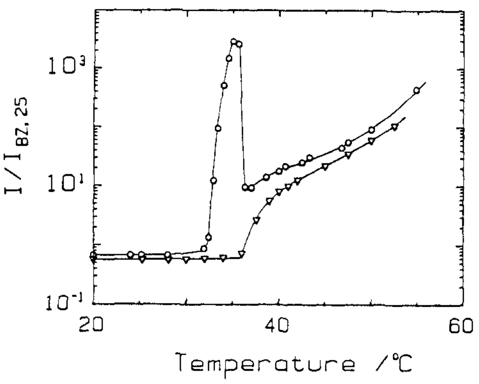

Figure 1. Effect of filtration on the temperature dependence of scattered light intensity relative to that of benzene at 25 °C for Fluka poloxamer 184 in water: circles denote before filtration with solution concentration c = 10.0 mg/mL; inverted triangles denote after filtration with solution concentration c = 9.65 mg/mL.

for the upper curve (before filtration) in Figure 1: (1) At room temperatures where low scattered intensity is seen, essentially unimers are present, as indicated by the weight-average molecular weight value ($M_w = 3.15 \times 10^3$) at 25 °C, obtained by extrapolating intensity data to zero concentration. (2) The high-temperature region (above 36 °C) corresponds to systems containing practically only micelles. The micellar weight measured is of the order of 10^5–10^6, and the aggregation number becomes larger with increasing temperature. (3) In the transition region where a typical anomalous micellization behavior is observed, the maximum scattered intensity is about 10^3 times more than that of the unimer and the dissymmetry ratio reaches a high value of about 7.6 instead of being unity in both unimer and micelle regions, indicating the existence of large particles with dimensions of the same order as the optical wavelength. Composition heterogeneity may be the reason for the existence of the peak region in Figure 1. Some model calculations[14] show that even in the case of a copolymer with a narrow distribution of molecular weight, the chemical heterogeneity could be appreciable.

We cannot exclude, however, the possibility that the anomalous behavior might be an inherent property of block copolymers, in contrast to the association behavior of homopolymeric PEO in water.[15] In order to distinguish those two possible mechanisms, we have designed a filtration experiment which is performed in close vinicity to the peak temperature. If the large angular dissymmetry is due to local concentration fluctuations, filtration cannot separate the local temporal inhomogeneities in concentration and equilibrium would be reestablished on standing after filtration so that the anomalous behavior actually could not be eliminated. On the contrary, if the composition heterogeneity mechanism is correct, i.e., large particles are formed, then after an effective filtration a normal micellization behavior should be observed on the temperature curve. The filtration was carried out at 34 °C (near the peak position) by using Millipore filter VM with a nominal pore size of 500 Å. Results of the corresponding apparent hydrodynamic radius obtained under the same conditions are shown in Figure 2. Figures 1 and 2 both clearly indicate that after effective filtration the anomalous region has disappeared completely. Instead, as in the case of conventional nonionic amphiphiles, a normal association behavior is observed.

An inflection point, known as the critical micelle temperature (cmt), exists on the temperature curve. Above cmt, micelle formation becomes appreciable so that some properties of the system, such as light-scattering intensity and line width in our case, change more or less abruptly.

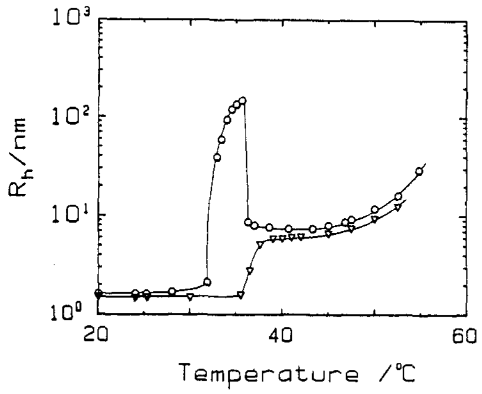

Figure 2. Effect of filtration on the temperature dependence of apparent hydrodynamic radius for Fluka poloxamer 184 in water. Same symbols as in Figure 1.

With increasing temperature the equilibrium unimers $\rightleftharpoons$ micelles shifts toward micelles and finally micelles become the predominant form in the system. Our filtration results strongly suggest that the anomaly in micellization is due to some composition heterogeneity of the block copolymer. Furthermore, from Figures 1 and 2 we have noticed that (1) all the peak regions end at the onset of the normal micellization and (2) the removal of the anomalous region is accompanied by only a minor change in solution concentration, namely, the filtrate concentration is 9.65 mg/mL as compared to the original value of 10.0 mg/mL before filtration. Therefore, on the basis of these experimental facts, we suggest that the minor components with lower oxyethylene contents, i.e., with larger hydrophobicity, may form large "polymer vesicles", not far from the phase separation temperature (T_p < cmt) of the minor components. Upon raising the temperature, we first meet the phase separation of the minor components, which leads to the formation of a dilute emulsion of "polymer vesicles". As soon as the critical micelle temperature of the major component is reached, the insoluble minor components can either be incorporated into the cores of micelles or form mixed micelles, depending on their molecular characteristics. Consequently, the temperature dependence of the scattered light intensity and the particle size would go through a maximum, as experimentally evidenced in our light-scattering measurements. The peak region would then disappear after the removal of those insoluble minor components, as strongly evidenced in our filtration experiment.

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Registry No. (EO)(PO) (block copolymer), 106392-12-5.

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Observation of Cluster Formation in an Ionomer

Ionomers exhibit unique mechanical and rheological properties as a consequence of strong associations between the ionic species. Although the spatial arrangement of the ionic groups in ionomers is still an unresolved question, it is now generally agreed that in most ionomers microphase-separated ion-rich aggregates, termed clusters,[1] are the dominant morphological feature. The primary evidence for ionic clusters comes from small-angle X-ray (SAXS) and neutron scattering (SANS) experiments where a maximum corresponding to a distance of 2–4.5 nm is observed for most ionomers.[2,3]

We have been studying the effects of thermal history and low molecular weight diluents on the structure–property relationships of ionomers, particularly lightly sulfonated atactic polystyrene (SPS). In several recent publications[4-6] we showed by electron spin resonance spectroscopy and SAXS experiments that polar solvents, such as alcohols or water, can preferentially solvate the ionic interactions in SPS ionomers in solution or in the solid state. This result suggested that solvent history might be used for controlling the structure and properties of ionomers. In fact, when films of an SPS ionomer were cast from different solvents, very different morphologies occurred, as is demonstrated by the SAXS data for a Mn(II) salt of 7.6 mol % SPS shown in Figure 1. Similar results were obtained for other metal salts of SPS.

The most striking observation in Figure 1 is the absence of the SAXS maximum for the sample cast from a mixture of 90% tetrahydrofuran (THF) and 10% water. This result suggests the absence of ionic clusters in this sample. We should point out, however, that an alternative interpretation might be that the characteristic size for the cluster morphology is sufficiently large that the scattering maximum is positioned too close to the beam stop for adequate resolution. Such a conclusion might be based on the fact that a high degree of zero angle scattering was observed for this sample (as it was for most ionomer samples studied by us as well as other laboratories) and that the addition of water to a compression-molded SPS ionomer tends to shift the SAXS peak to lower scattering angle.[7,8] It should be emphasized, however, that no water could be detected in the sample used to generate the data in Figure 1 by either gravimetric techniques or infrared spectroscopy. Although this does not exclude the possibility of trace amounts of water, we have found that detectable water concentrations of several percent cannot account for the disappearance of the SAXS maximum in this SPS ionomer.

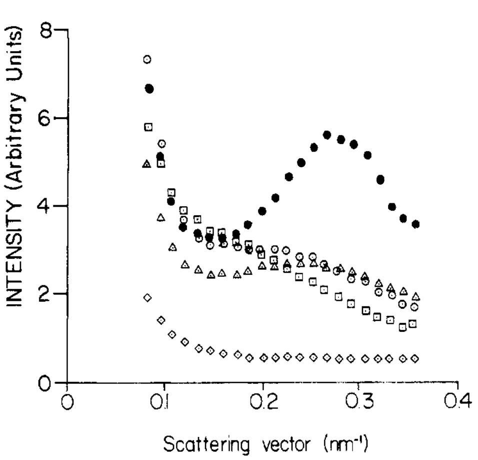

Figure 1. Scattered X-ray intensity versus scattering vector for 7.6 mol % MnSPS samples prepared by (●) compression molding: (○) casting from THF solution; (□) casting from DMF solution; (△) casting from 90% toluene/10% methanol; and (◇) casting from 90% THF/10% water. (Reprinted with permission from ref 5.)

In this paper, we report recent results of an experiment in which an ionomer with a microstructure characterized by the absence of a SAXS maximum (herein interpreted as being void of ionic clusters) is heated to elevated temperatures. By use of the high flux afforded by a synchrotron radiation source the formation of the cluster morphology in this material was observed during heating at a controlled rate. To our knowledge, this represents the first time that the development and growth of microphase separation in an ionomer has been reported.

Experimental Section. SPS containing 7.6 mol % sulfonic acid groups was prepared by the homogeneous sulfonation of polystyrene (M_n = 100 000 and M_w = 260 000) in dichloroethane solution with acetyl sulfate.[9] This was neutralized with an equivalent amount of manganese acetate. A 25-μm film was prepared by casting a 10% solution of the ionomer in a mixed solvent of 90% THF and 10% deionized water onto glass. The solvent was evaporated in air and the film was dried under vacuum for 5 days at 60 °C.

The X-ray scattering experiments were performed at Beam Line I-4 of the Stanford Synchrotron Radiation Laboratory (SSRL), Stanford, CA. The ionomer film was placed in an aluminum sample cell that was fashioned from a conventional DSC pan. The pan contained thin Kapton windows in the top and the bottom so as to maximize the transmission of X-rays. The sample assembly was placed in a Mettler FP82 Hot Stage that controlled the heating of the sample at a rate of 10 °C/min between 40 and 240 °C. SAXS curves were collected every 26 s and reflect the scattering integrated over a temperature interval of ca. 4 °C.

The sample-to-detector distance was 35 cm. The wavelength of the incident radiation was 0.143 nm and the detector covered a range of scattering angles, 2θ, from 0.6° to 3.3°. This corresponded to long periods of 13–2.5 nm. Beam monitors placed before and after the sample cell allowed for correction for specimen adsorption effects and normalization of the reported intensities by the sample thickness and incident beam intensity. Additional information on the experimental setup can be found elsewhere.[10]

Results and Discussion. The corrected SAXS data collected during the heating cycle at controlled heating rate are given in Figure 2. A scattering maximum is not de-

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