If the distance associated with this peak is calculated by means of Bragg's law,

$$\lambda = 2d \sin \theta/2$$

one ends up with $d \simeq 1.095$ nm.

This distance is close to that found for the 110 plane in semicrystalline isotactic polystyrene.[7] However, this would imply two consequences that do not seem realistic: (i) gelation would then be due to isotactic sequences, in contradiction with recent results[8] and rather surprising in view of their low content; (ii) since the 110 plane does not involve first but second neighboring stems, this would entail that the physical junctions would arise from the creation of long-range order, a property which should have manifested itself in the bulk state.

This peak does not correspond either to the halo observed in amorphous polystyrenes[7] ($d \simeq 0.93$ nm) and is also much more narrow ($\Delta d/d \simeq 9\%$, Δd = width at half-height, compared to 43%). Incidentally, it is almost as narrow as certain crystalline peaks ($\Delta d/d \simeq 6\%$ in the best cases).

Highly syndiotactic polystyrene has been recently synthesized.[9] Data on the crystalline order are thus now available, yet no similar peak corresponds to the one reported here (strictly speaking there is one peak at 0.114 nm which is so weak for the pure polymer that it does not seem worthy of consideration).

If now we consider the peak to be associated with the distance between first neighboring stems, the discrepancy with classical packing in either iPS or sPS is very large, since close packing gives distances of 0.7–0.8 nm (note that in the case of parallel stems the distance corresponding to the peak should be calculated with $1.15\lambda = 2d \sin \theta/2$). This large gap between adjacent stems can be accounted for through the formation of a polymer–solvent compound, a conclusion already drawn from thermodynamic studies.[6] For solvent incorporation leads inevitably to polymer stem separation.

Further studies are in progress to provide these conclusions with further support.

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Registry No. aPS, 9003-53-6; CS_2, 75-15-0; neutron, 12586-31-1.

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Self-Diffusion of Polymers in Block Copolymer Solution

There seems to have been considerable progress in the understanding of the effect of the intermolecular interaction on the slow diffusive motion of a polymer chain at finite concentration. From recent studies on semidilute polymer solutions, for example, we may expect that a probe chain in a polymer matrix behaves as the nondraining chain, the free-draining chain, and subsequently as the reptating chain with an increase in the ratio of molecular weight of the matrix polymer to the diffusing chain.[1,2] The solutions are believed to be molecularly mixed, i.e., on a spatial scale of the monomeric unit order. If a solution is inhomogeneous on the order of the polymer coil size or on a larger scale, then how does such an inhomogeneity affect the diffusion motion of a test chain dissolved in the solution? An experimental study to answer the question may be worth trying, if it is regarded as the first step for elucidation of the complicated mass transport process occurring in inhomogeneous polymeric industrial products.

For this purpose, microdomain structure of block copolymers formed in solutions is quite suitable as a new type of matrix. In the strong segregation limit, block copolymers undergo microphase separation in the size of molecules and form the various ordered structures, i.e., spherical, cylindrical, and lamellar structures, which are determined by temperature, concentration, fraction of blocks, and so on.[3,4] By dissolving a homopolymer, being one component of the block copolymer, in the solution as a test chain, we can investigate the effect of various microphase-separated structures on the diffusion of the test chain.

In this study, homopolystyrene (HPS) and styrene–ethylene/butylene–styrene triblock copolymer (SEBS; KRATON G-1650, Shell Development Co., Houston, TX; $M_w = 1.04 \times 10^5$, $M_w/M_n = 1.16$, PS wt % = 28.9)[5] were used as the diffusing and the matrix polymer, respectively. Dibutyl phthalate (DBP) was used as solvent, which is highly selective, good for PS block chains and poor for poly(ethylenebutylene) (PEB) block chains. Since static as well as dynamic properties of the SEBS–DBP system itself are not well-known, we first characterized the system using small-angle X-ray scattering (SAXS) and forced Rayleigh scattering (FRS).[6] The FRS apparatus and the method of labeling of the polymers have been described in detail elsewhere.[7,8]

It has been found from analysis of SAXS profiles that SEBS molecules form disordered micelles consisting of the PEB core and the PS shell below a polymer concentration C of 20 wt %, and also above C = 25 wt %, the SEBS micelles form an ordered micelle suspension on the face-centered cubic lattice. FRS measurements on DBP solutions of labeled but otherwise the same SEBS[9] have shown

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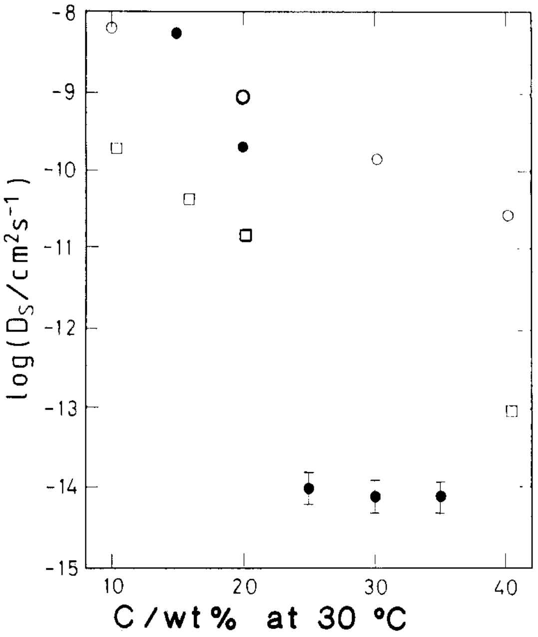

Figure 1. D_s of SEBS in DBP solution is plotted against the concentration of SEBS (●). For comparison, D_s of PS in a DBP solution is also plotted against the concentration of PS: (○) M_w = 43 900; (□) M_w = 355 000.

that the self-diffusion coefficient D_s of SEBS sharply decreases at aroung $C \simeq 20$ wt %, as is shown in Figure 1. Here typical D_s behavior of unentangled and entangled PS solutions is shown for comparison.[10] The value of D_s at $C = 15$ wt %, 7×10^{-9} cm^2/s, can be identified as the D_s value of the micelle which is making the Brownian motion in the solution. The concentration region where the decrease in D_s by about 5 orders of magnitude was observed corresponds to the C region where the microdomain structure of the face-centered cubic lattice is formed. Hashimoto et al. have concluded from rheological measurements on solutions of a similar block copolymer–solvent pair that the lattice is mainly stabilized by the repulsive force between the micelles.[11] Thus no micelle can migrate in the solution unless a vacant lattice point is found at neighboring sites. This may explain a very small D_s value of an order of 10^{-14} cm^2/s being almost independent of concentration above $C \geq 25$ wt %. It may be noticed that a dramatic decrease in D_s due to the formation of the macrolattice in the micelle suspension of block copolymer has been first found in this study.

Thus, in the range $C \geq 25$ wt %, SEBS solutions form the ordered structure in which spherical particles composed of PEB chains are dispersed in the PS phase in the form of a face-centered cubic lattice. To study the topological interaction between the SEBS matrix and HPS solubilized, D_{tr} of labeled narrow molecular weight distribution HPS with seven molecular weights in the range 6000–355 000 was measured. The concentration of SEBS (C_{SEBS}) was fixed at 30 wt % and that of HPS (C_{PS}) at 1 wt %. At this particular SEBS concentration of 30 wt %, estimated sizes of the micelle and the lattice are 16 and 63 nm, respectively. The former value is close to that of the radius of gyration of a diffusing PS chain with M_w = 355 000 in the Θ state.[12] Decay curves of light intensity $I_d(t)$ diffracted from the solutions could be analyzed by the single-exponential type of decay function for HPS molecular weight less than 102 000[8]

$$I_d(t) = A \exp(-2\Gamma t) + B \tag{1}$$

$$\Gamma = Dq^2 \tag{2}$$

where, q is the wave vector related to the grating spacing d as $q = 2\pi/d$ and A and B are constants determined by experiment. On the other hand, unusual relaxation curves such that they first decay, then rise, and after a maximum decay once again were obtained for the solutions with M_w = 102 000, 186 000, and 355 000. Such a relaxation curve is usually attributed to the complicated photochemical reaction of the photochromic dye used.[13] In our experiment, such an anomalous decay curve was not observed to the labeled SEBS solutions. This indicates that the above complicated behavior cannot be related to the photochemical reaction of the dye. According to Rhee et al.[14] and Zang et al.,[15] this curve shape may arise from diffusive relaxation of the two sets of refractive index modulation. Hence we analyzed data following their method assuming heterogeneity of the matrix and obtained two decay rates, Γ_1 and Γ_2 ($\Gamma_1 > \Gamma_2$). Γ_1 and Γ_2 had large experimental errors (about 50%), but they are roughly proportional to q^2. Therefore we estimated two apparent diffusion coefficients, D_1 and D_2 ($D_1 > D_2$), from eq 2.

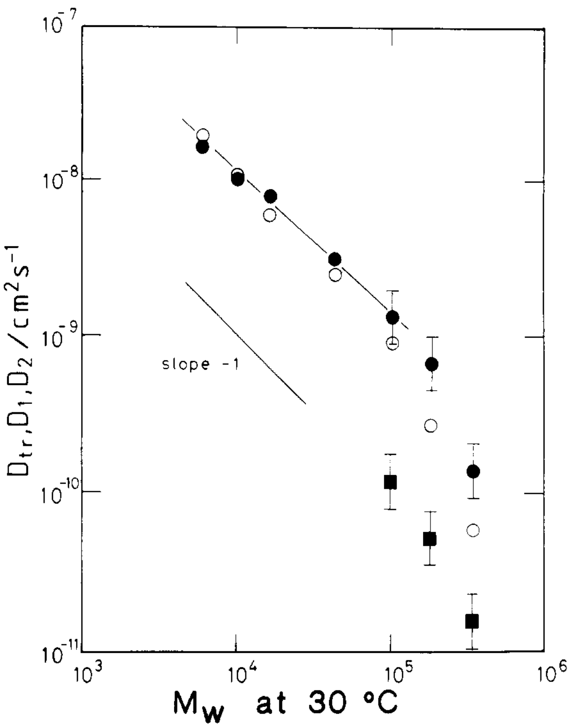

Figure 2. D_{tr}, D_1, and D_2 of HPS in SEBS–DBP solution is plotted against the molecular weight of HPS: (●) D_{tr}, D_1; (■) D_2. Concentrations of SEBS and PS are 30 wt % and 1 wt %, respectively. For comparison, the tracer diffusion coefficient, $D_{tr,e}$, of PS (○) in entanglement network is also plotted.

In Figure 2, D_{tr}, D_1, and D_2 of HPSs in SEBS solutions with C_{SEBS} = 30 wt % are plotted against the molecular weight of HPSs. If we restrict our discussion in the low molecular weight range of M_w < 100 000, values of D_{tr} of HPS are much larger than D_s of SEBS, which is on the order of 10^{-14} cm^2/s at this concentration. This means that PS can diffuse fairly fast in the structure of SEBS, which is nearly fixed in the space. Furthermore, it should be mentioned that values of D_{tr} of HPS in the SEBS solution are larger, by an order of magnitude, than D_s values of HPS in corresponding binary HPS–DBP solutions with the same molecular weight and polymer concentration. The difference may be interpreted in terms of two structural effects associated with the lattice formation in the solution. First, the HPS molecules only diffuse through the PS chains which are anchored to the PEB core. Thus comparison should be made with D_{tr} data in an entanglement network in which entanglement points are fixed in space during the characteristic diffusion time of the test chain. Second, the concentration of the PS phase of the microdomain is surely lower than the total concentration, because DBP is distributed selectively in the PS phase. We define the effective concentration of PS in the PS phase C_{eff} by

$$C_{\mathrm{eff}} = \frac{C_{\mathrm{SEBS}} w_{\mathrm{PS}} + C_{\mathrm{PS}}}{1 - C_{\mathrm{SEBS}} w_{\mathrm{EB}}} \qquad (3)$$

by assuming that DBP is exclusively present in the PS phase. Here w_{PS} and w_{EB} are weight fractions of PS and PEB blocks of SEBS, respectively. Equation 3 gives C_{eff} = 13 wt % for C = 30 wt %. D_{tr} of HPS in DBP solutions of HPS at C = 13 wt % ($D_{\mathrm{tr,e}}$) was measured under the condition that the M_{w} of diffusing HPS is about six times smaller than the M_{w} of matrix HPS and is plotted in Figure 2. The molecular weight between entanglements M_{e} was estimated as about 120000 at C = 13 wt %.[16]

For diffusion in the entanglement network, we reported that in the region with $M \leq 0.1M_{\mathrm{e}}$, the topological interaction was very small and Rouse-like behavior $D_{\mathrm{tr}} \propto M^{-1}$ could be observed.[2] Such a molecular weight dependence is also observed in the case of HPS diffusion in the SEBS solution. Moreover, it should be noticed that in the low molecular weight region, values of D_{tr} and $D_{\mathrm{tr,e}}$ agree very well with each other. This shows that if the molecular weight of PS is small, the effect of the SEBS matrix on the diffusing chain is very similar to that of entanglement network.

In the higher molecular region $M_{\mathrm{w}} \geq 102000$, two D_{tr} values (D_1 and D_2), different by about 1 order of magnitude, indicate that two diffusion processes are present. In order to characterize these processes, more detailed FRS as well as SAXS measurements on SEBS systems with different molecular weight and concentration are in progress.

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Direct Measurement of Radical Termination in an Acrylic Copolymer by ESR and Application to Kinetic Studies

Semicontinuous emulsion polymerization is an important commercial process for the preparation of polymers by free-radical polymerization. Elucidation of the kinetics of semicontinuous emulsion polymerization is important for both fundamental understanding and practical application. ESR has previously been shown to be extremely valuable for determining the concentration of propagating free radicals and the propagation rate constant k_{p} for both semicontinuous emulsion polymerization[1] and batch emulsion polymerization.[2] Another parameter which is very important for understanding the polymerization kinetics is the termination rate constant k_{t} for the propagating free radicals. The termination rate constant directly influences the concentration of the propagating radicals in the polymer particles as expressed by

$$\mathrm{d}[\mathrm{R}^{\bullet}]/\mathrm{d}t = \text{entry rate} - k_{\mathrm{t}}[\mathrm{R}^{\bullet}]^2 - \text{exit rate} \qquad (1)$$

where $[\mathrm{R}^{\bullet}]$ is the concentration of propagating free radicals in the polymer particles, entry rate is the rate of entry of free radicals generated in the aqueous phase into the polymer particles, and exit rate is the rate at which free radicals are desorbed from the polymer particles. If it is assumed that monomer diffusion is not rate limiting and that the bulk of the polymerization occurs in the polymer particles, then the propagating radical concentration governs the rate of polymerization according to[1]

$$\text{rate of polymerization} = k_{\mathrm{p}}[\mathrm{R}^{\bullet}][\mathrm{M}] \qquad (2)$$

where [M] is the concentration of monomer in the polymer particles.

Despite its importance, the termination process is not well understood, and the reported rate constants are often derived from indirect measurements, which could possibly introduce significant error. The situation is especially difficult when the polymerization is in a state of high conversion such as in semicontinuous emulsion polymerization.

We have previously described[1] the use of ESR to directly measure the concentration of propagating free radicals in a semicontinuous emulsion polymerization of 8 BA/91 MMA/1 MAA. The polymerization was carried out by using a redox initiator system at temperatures between 50 and 65 °C. Samples were extracted from the reactor, and the propagating free radicals were stabilized by rapid freezing of the latices at −80 °C. Radical concentrations measured for particle sizes of ~50 and ~500 nm showed that the average number of radicals per particle varies greatly with particle size in this system. By use of the concentrations of the propagating free radicals measured by ESR, the propagation rate constants were calculated