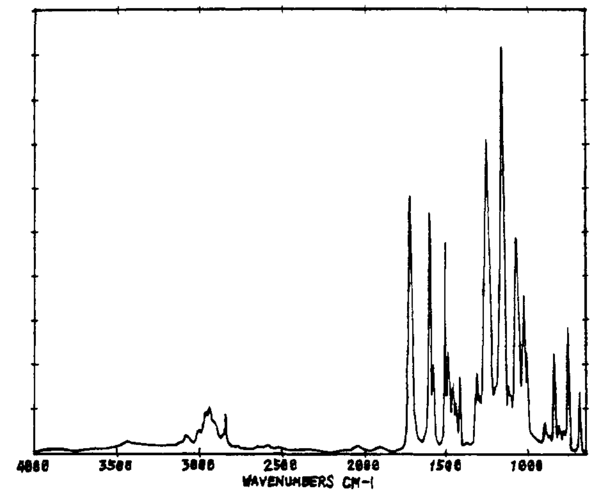

Figure 7. IR spectrum of the polymer.

bands between the two spectra. For example, the carbonyl stretching mode is at 1728 cm^{-1} for the monomer but is at 1730 cm^{-1} with an increased width for the polymer. The benzene C=C stretchings at 1608 (m), 1581 (m), 1512 (m), and 1486 (m) cm^{-1} of the monomer have shifted respectively to 1606 (s), 1582 (m), 1511 (s), and 1489 (m) cm^{-1} of the polymer. The C–O stretchings at 1259 (vvs) and 1154 (vs) cm^{-1} of the monomer have shifted to 1253 (vs) and 1161 (vvs) cm^{-1}. These results and others not described here indicate that the chemical structure of the mesogenic unit of the monomer did not change during the thermal polymerization, but the molecular conformation of the mesogens might have changed to fulfill the spatial requirement in the polymer.

The IR studies thus suggest that the chemical structure of the mesogenic units in the monomer molecules was untouched during polymerization and that the polymer molecules were built up presumably by thermally initiated addition polymerization of the vinyl monomer. A polymer with mesogens laterally attached to the main chain via only a single covalent bond (no flexible spacer) was thus obtained.

Acknowledgment. We are grateful to the Fok Ying Tung Education Foundation and the State Education Committee of China for supporting this study.

Registry No. I, 117439-39-1; I (homopolymer), 117439-40-4.

References and Notes

(1) Finkelmann, H.; Wendorff, H. J. Structure of Nematic Side Chain Polymers. In *Polymeric Liquid Crystals*: Blumstein, A., Ed.; Plenum Press: New York, 1985; p 295.

(2) Zhou, Q. F.; Li, H. M.; Feng, X. D. *Mol. Cryst. Liq. Cryst.* 1988, *155*, 73.

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Received May 25, 1988

Evidence by Neutron Diffraction of Ordered Structures in Atactic Polystyrene/Carbon Disulfide Physical Gels

Atactic polystyrene (aPS) should be, by nature, an uncrystallizable polymer, and so far, there has been no evidence of any trace of crystallinity in the bulk state. Accordingly, the report on the propensity of this polymer to give physical gels in some solvents came as a surprise,[1] often followed by disbelief. However, different types of experiments carried out with different techniques[2-6] have all pointed to a genuine phenomenon. A thermal analysis study of the gel formation and fusion[6] revealed the presence of exotherms and endotherms, respectively, that were interpreted as resulting from the existence of three-dimensional objects, possibly possessing a nematic-like order (order in only one dimension). Here we report on a series of neutron diffraction experiments intended to give direct evidence of the appearance of order in the physical gels of this polymer.

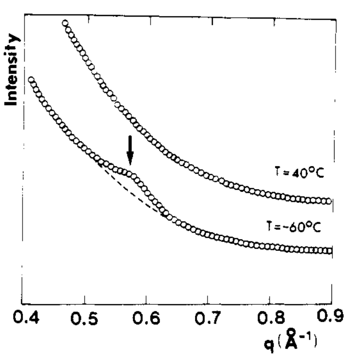

Figure 1. Intensity (in arbitrary unit) as a function of the transfer momentum $q = (4\pi/\lambda)\sin\theta/2$ in Å^{-1}. Temperatures as indicated. Arrow shows the position of the peak maximum.

Neutrons were chosen over X-rays for two essential reasons: (i) by labeling the polymer (deuteriated polystyrene), its diffraction power is significantly increased with respect to the solvent ($b_{\text{deuterium}} = 0.67 \times 10^{-12}$ cm while $b_{\text{sulfur}} = 0.285 \times 10^{-12}$ cm); (ii) as a result, while the use of X-rays would only give the diffraction by the solvent, neutrons are mainly diffracted by the polymer. Due to the low amount of physical junctions, this condition is peremptory (for we do not exactly know what this amount is[6]).

The experiments were carried out on G-6-1 (LLB, further details on request). Only one polymer concentration was investigated (40% w/w). The reasons for using such a concentration are based on the temperature–concentration phase diagram[6] that shows that physical gelation in CS_2 arises from the formation of a polymer–solvent compound whose stoichiometry is defined somewhere between $C_{\text{pol}} \simeq 40\%$ and 50%. Correspondingly, the maximum amount of physical junctions is also in this concentration range.

The solvent used was of high-purity grade. The polymer was characterized by gel permeation chromatography in tetrahydrofuran ($M_w = 1.5 \times 10^5$ and $M_w/M_n \simeq 1.26$).

The polymer–solvent mixture was introduced into an amorphous silica tube (10-mm inner diameter) which was sealed from atmosphere and held at 60 °C for a week in order to obtain a true solution. Then this system was cooled to the desired temperature. At such a concentration, gelation already occurs at room temperature.[1,6] Yet, the maximum amount of physical junctions should be obtained for $T = -60$ °C as deduced from the phase diagram.[6]

A blank sample containing only solvent was prepared under the same conditions.

The diffraction patterns at 40 and −60 °C were accordingly recorded and are drawn in Figure 1. As can be seen, a broad peak is visible at −60 °C. Since the solvent does not display any additional peak at this temperature, this result confirms without ambiguity the presence of ordered structures in this type of gel.

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.

Acknowledgment. We are indebted to G. Beinert from the ICS for synthesizing the deuteriated polymer and to G. Parette and J. P. Ambroise from the LLB for experimental assistance. We also thank referee II for helpful suggestions.

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

References and Notes

(1) Tan, H. M.; Hiltner, A.; Moet, H.; Baer, E. *Macromolecules* **1983**, *16*, 28.
(2) Guenet, J. M.; Willmott, N. F. F.; Ellsmore, P. A. *Polym. Commun.* **1983**, *24*, 230.
(3) Clark, J.; Wellinghoff, S. T.; Miller, W. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1983**, *24*(2), 86.
(4) Gan, Y. S.; François, J.; Guenet, J. M.; Allain, C.; Gautier-Manuel, G. *Makromol. Chem. Rapid Commun.* **1985**, *6*, 225.
(5) Gan, Y. S.; François, J.; Guenet, J. M. *Macromolecules* **1986**, *19*, 173.
(6) François, J.; Gan, Y. S.; Guenet, J. M. *Macromolecules* **1986**, *19*, 2755.
(7) Natta. G.; Corradini, P. *Makromol. Chem.* **1955**, *16*, 77.
(8) François, J.; Gan, Y. S.; Sarasin, D.; Guenet, J. M. *Polymer* **1988**, *29*, 898.
(9) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2465.

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Received June 8, 1988

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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