(3) H. Gilbert and F. F. Miller, U. S. Patent 2,745,814 (1956); *Chem. Abstr.*, **51**, 10922a (1957).
(4) M. Hirooka, *Kobunshi*, **16**, 1172 (1967).
(5) A. B. Conciatori, L. E. Trapasso, and R. W. Stackman, "Encyclopedia of Polymer Science and Technology," Vol. 14, N. M. Bikales, Ed., Interscience, New York, N. Y., 1971, p 587.
(6) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972.
(7) J. Schaefer, *Macromolecules*, **4**, 107 (1971).
(8) J. K. Stille and D. Chung, *Macromolecules*, submitted for publication.

## The Morphology of Polystyrene–Polybutadiene–Polystyrene Three-Block Copolymers

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It has been reported[1] recently that polystyrene–polybutadiene–polystyrene (SBS) three-block copolymers with constant composition ($\simeq$30% by weight of polystyrene) and overall molecular weights $M_n$ ranging from $4.9 \times 10^4$ to $9.0 \times 10^5$ g mol$^{-1}$ show morphologies characterized by spherical domains of polystyrene arranged on a simple face centered cubic lattice. The study involved low-angle X-ray scattering using films cast from a 10:90 mixture of methyl ethyl ketone and tetrahydrofuran. The conclusions were found to be in good agreement with the theory of Meier.[2]

We have some experimental results which are in disagreement with these conclusions.

A well-characterized SBS copolymer,[3] having a polystyrene content of about 33% by weight, molecular weight $M_w$ of $1.02 \times 10^5$, and a rather low heterogeneity ($M_w/M_n \simeq 1.2$) was used to prepare thin films by casting dilute solutions ($\simeq$1% w/v). The evaporation rate was controlled and was rather slow (0.5 cm$^3$/hr) at the temperature of 50 ± 0.5°; this operation was performed on a mercury surface in order to obtain uniformly thin films (0.2–0.4 mm) suitable for testing in a stress–strain dynamometer. The films were completely dried under vacuum at 50°. The solvents used to prepare the solutions were different mixtures of methyl ethyl ketone and tetrahydrofuran (90:10, 50:50, and 10:90).

The morphological study was performed on ultrathin sections (about 500 Å thick) obtained by low-temperature microtomy[4] after inclusion of the specimens in an epoxy resin.[5] The sections were cut perpendicular to the surface of the films and were stained with osmium tetroxide.[5] Therefore, in the following pictures the polystyrene phase appears bright and the rubbery matrix dark.

Figure 1 shows the electron micrographs of samples obtained both from pure methyl ethyl ketone and from its mixtures with tetrahydrofuran. Clearly, the morphology of our specimens is always characterized by lamellae, roughly parallel to the surface of the films. The thickness of the polystyrene lamellae does not seem to change systematically with the solvent composition and it is about 120–150 Å. The distance between two consecutive lamellae is about 300 Å. These values correspond to the regions where the lamellae seem to be perpendicular to the section plane. We have not been able to find regions where the observed structure could be correlated with a face centered cubic arrangement of spherical polystyrene domains.[6]

Obviously our results are completely in disagreement with earlier studies by Campos-Lopez and coworkers.[1] We do not have any definitive explanation for this.

Actually small differences in the polystyrene content of the copolymer cannot produce such different morphologies. By solution casting from methyl ethyl ketone we obtained a lamellar structure like that of Figure 1a using a copolymer having a lower polystyrene content, *i.e.*, 26% by weight.[7]

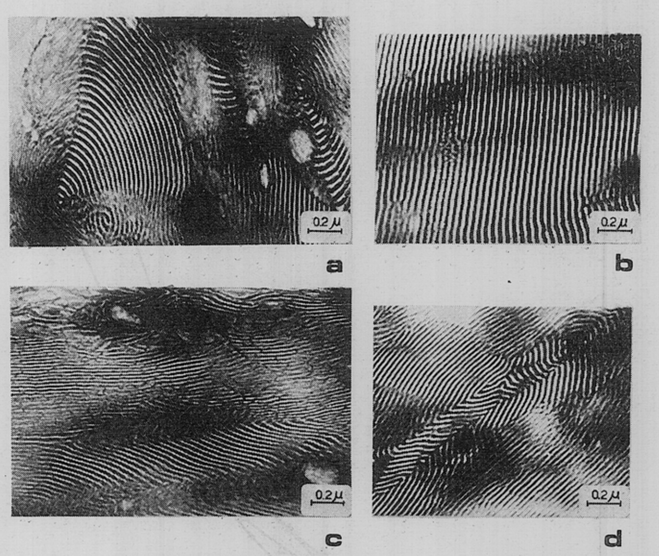

**Figure 1.** Electron micrograph of osmium-stained ultrathin sections of SBS copolymer films cast from dilute solutions: (a) methyl ethyl ketone; (b) methyl ethyl ketone–tetrahydrofuran mixture, 90:10; (c) methyl ethyl ketone–tetrahydrofuran mixture, 50:50; (d) methyl ethyl ketone–tetrahydrofuran mixture, 10:90

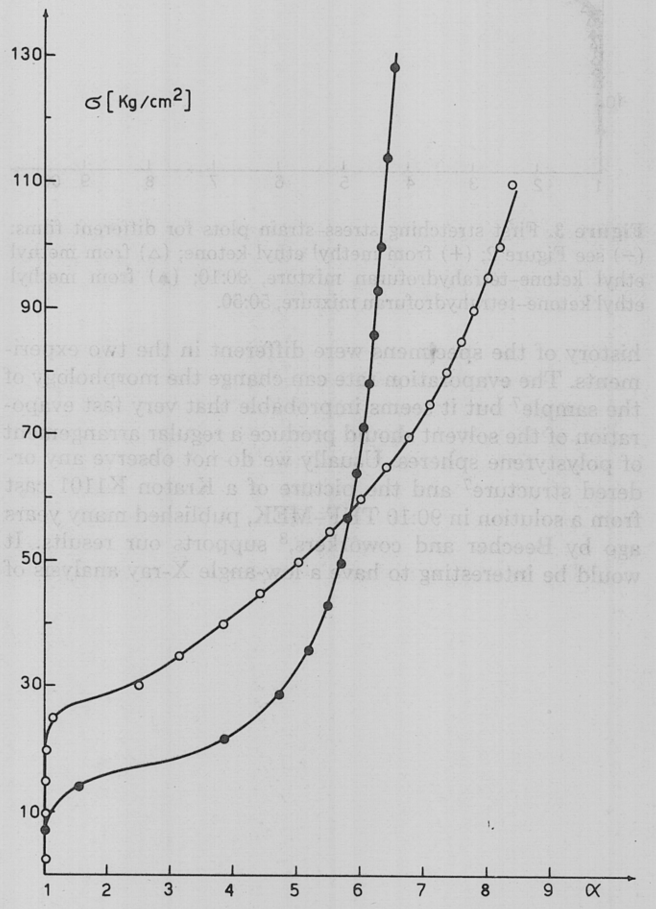

**Figure 2.** Stress–strain plot for the 10:90 methyl ethyl ketone–tetrahydrofuran film: (○) first stretching; (●) second stretching after relaxation of 10 min at zero load.

The molecular weight brings us to the same conclusions. Campos-Lopez and coworkers[1] found the same structure for very different $M_n$ values, as stated at the outset.

Only the evaporation rate of the solvent and the thermal

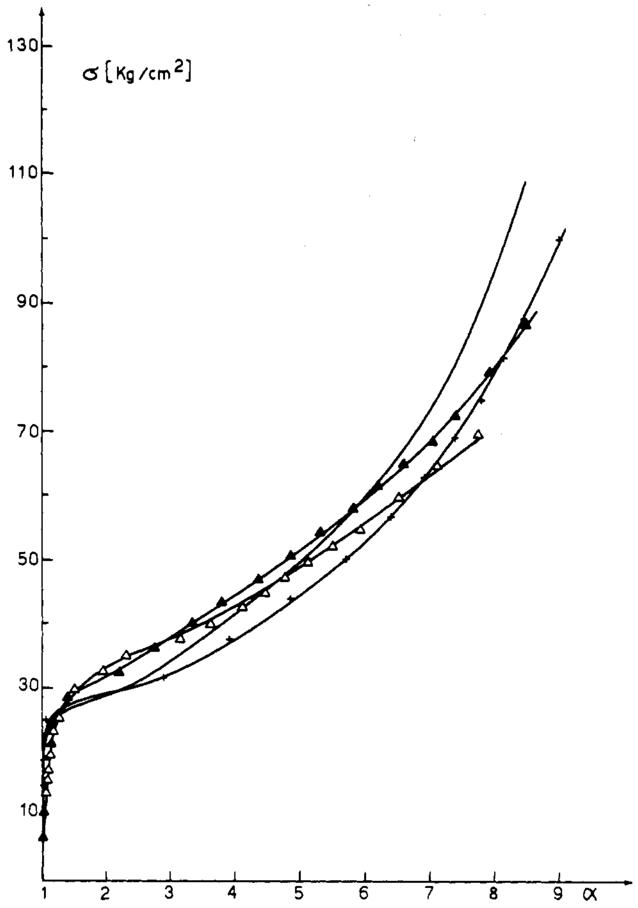

**Figure 3.** First stretching stress-strain plots for different films: (−) see Figure 2; (+) from methyl ethyl ketone; (Δ) from methyl ethyl ketone–tetrahydrofuran mixture, 90:10; (▲) from methyl ethyl ketone–tetrahydrofuran mixture, 50:50.

history of the specimens were different in the two experiments. The evaporation rate can change the morphology of the sample[7] but it seems improbable that very fast evaporation of the solvent should produce a regular arrangement of polystyrene spheres. Usually we do not observe any ordered structure[7] and the picture of a Kraton K1101 cast from a solution in 90:10 THF–MEK, published many years ago by Beecher and coworkers,[8] supports our results. It would be interesting to have a low-angle X-ray analysis of specimens prepared at a different solvent evaporation rate.

As far as the thermal history of the specimen is concerned, we do not believe that the experimental conditions used by Campos-Lopez and coworkers[1] could transform a lamellar into a cubic structure. Our previous experiments[3,6,9,10] have shown, that very high temperatures (150–170°) and very long annealing time (up to 1 month) are necessary to reach some structural modifications. Anyhow, it does not involve any variation in the morphology but removes only the distortion of the lattice, due to the preparation of the specimens, so that a more ordered structure is obtained.

On the other hand the stress–strain measurements, obtained with a commercial dynamometer at a deformation rate of about 3 cm/min at room temperature, support the existence of a polystyrene continuous phase inside our specimens. Actually the Young's modulus is rather high (Figures 2 and 3) and we observe the stress-softening effect between the first and the second stretching cycles for low values of the deformation ratio. Both of these phenomena have been attributed to the presence of a continuous polystyrene phase and to its breakdown[11] and contradict an assembly of separated polystyrene spheres.

The differences between the plots are more logical in the rubbery region but are not relevant here. We discuss this point in more detail in another paper.[12]

## References and Notes

(1) E. Campos-Lopez, D. McIntyre, and L. J. Fetters, *Macromolecules*, **6**, 415 (1973).

(2) D. J. Meier, *J. Polym. Sci., Part C*, **26**, 81 (1969).

(3) E. Pedemonte, S. Cartasegna, P. Devetta, and A. Turturro, *Chim. Ind. (Milan)*, **55**, 861 (1973).

(4) G. Dondero, L. Olivero, P. Devetta, S. Cartasegna, and E. Pedemonte, *Nuova Chim.*, **48**, 1 (1973).

(5) D. Kay, "Techniques for Electron Microscopy," Blackwell, Oxford, 1961.

(6) E. Pedemonte, A. Turturro, U. Bianchi, and P. Devetta, *Polymer*, **14**, 145 (1973).

(7) E. Pedemonte, S. Cartasegna, and A. Turturro, *Chim. Ind. (Milan)*, **56**, 3 (1974).

(8) J. F. Beecher, L. Marker, R. D. Bradford, and S. L. Aggarwal, *J. Polym. Sci., Part C*, **26**, 117 (1969).

(9) A. Keller, E. Pedemonte, and F. M. Willmouth, *Kolloid-Z. Z. Polym.*, **238**, 385 (1970).

(10) J. Dlugosz, A. Keller, and E. Pedemonte, *Kolloid-Z. Z. Polym.*, **242**, 1125 (1970).

(11) E. Pedemonte, A. Turturro, and G. Dondero, *Brit. Polym. J.*, submitted for publication.

(12) E. Pedemonte, G. C. Alfonso, and G. Dondero, *Brit. Polym. J.*, to be submitted for publication.