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LETTER TO THE EDITOR

Structures in Styrene-Butadiene Block Copolymers

Styrene/butadiene/styrene terblock polymers (SBS) are examples of a type of thermoplastic elastomer which can be processed above the softening temperature of the glassy (or crystalline) block and which at ambient temperatures exhibits elastomeric properties. The unique properties of block polymers are attributed to microscale phase separation due to incompatibility of the blocks [1, 2]. With the aid of electron microscopy and an osmium tetroxide staining technique [3] first Hendus [2] and then Beecher [4] showed that in styrene/butadiene/styrene terpolymers the polystyrene domains are of colloidal dimensions and are randomly dispersed in the polybutadiene matrix. Occasionally the blocks form ribbon-like structures similar to those observed by Vanzo [5] and Bradford and Vanzo [6] in two-block polymers. Experiments have shown [4] that the sizes, shapes, and the dispersion of the domains, as well as the method of specimen preparation [1], have a marked influence on the mechanical properties of the block polymers.

In this communication we would like to report about a regular arrangement of the polystyrene regions which has not been observed previously.

The polymer was a styrene-butadiene-styrene block copolymer which was prepared in this laboratory. The total styrene content was 38 wt. %, and intrinsic viscosity measurements gave an estimated molecular weight of 125, 000. A pressed film of the polymer had a tensile strength of 254 kg/cm^2 and an elongation at break of 860% when tested by an Instron tester at a strain rate of 50 cm/min at 25°C. The strength and elongation of the block polymer compares well with that of filled vulcanizates. Block polymers of the BSB type, on the other hand, are nonelastomeric and have negligible strength.

For the purpose of phase studies with the electron microscope a very thin film of approximately 300 Å was prepared by casting from a 0. 05% toluene solution on mercury. After a slow evaporation of the solvent at room temperature, the film was further dried in a vacuum oven at 40°C for 24 hr. Small pieces of the film were placed on electron microscope support screens and stained with osmium tetroxide and examined under the electron microscope (Fig. 1). Since osmium reacts with the double bond of polybutadiene but not with polystyrene, only the rubbery phase becomes stained.

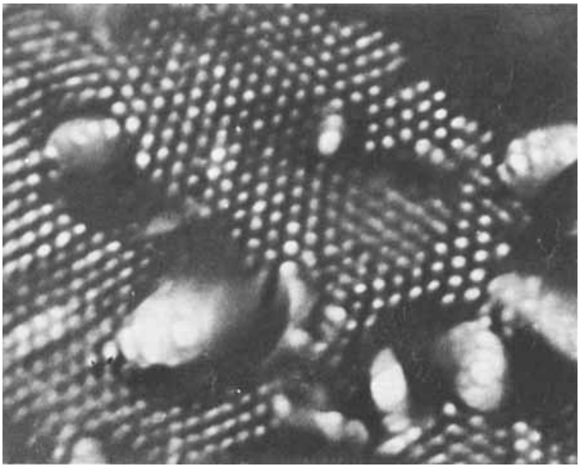

Fig. 1. Electron micrograph of a styrene-butadiene block copolymer containing 38 wt.% styrene.

The white of the micrograph represents regions of polystyrene and the black regions of polybutadiene. (The few large white areas, seen on the micrograph, are regions of high styrene content, which probably contain low molecular weight polystyrene blocks and possibly also some two-block material.)

Of particular interest is the uniformity in shape and size and the regular spacing of the polystyrene domains. The polystyrene spheres are arranged in a hexagonal pattern forming a honeycomb structure. It should be emphasized that these polymers are not stereoregular and shown no traces of crystallinity by any method of test applied so far. The polystyrene spheres have a diameter of approximately 300 Å and a center-to-center distance of about 500 Å. Low-angle X-ray diffraction revealed a periodicity of 530 Å, which agrees well with the electron microscope observations. From composition and the sizes of the blocks it was estimated that the spheres contain approximately 400 polystyrene end blocks.

Since the films were prepared from very dilute solutions and under slow drying conditions, the observed structures and the regular arrangement of the phases are probably determined by thermodynamic conditions. Somewhat similar arrangement of phases was suggested by Skoulios and Finaz [7] for concentrated solution of two-block polymers of styrene and ethylene oxide on the basis of their low-angle X-ray scattering studies.

The root-mean-square end-to-end distance of a polybutadiene chain of 70,000 molecular weight was calculated [8] as 250 Å, which is in satisfactory agreement with the observed distance between the polystyrene domains. It appears, therefore, that the regu-

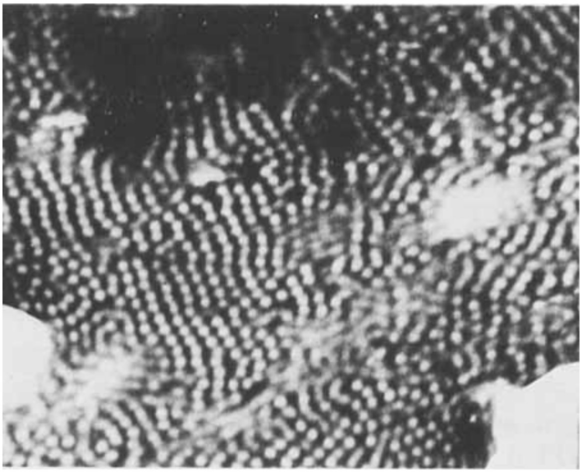

Fig. 2. Electron micrograph of the polymer shown in Fig. 1, stretched about 50% (stretching direction horizontal).

larity of arrangement of the polystyrene domains in the polybutadiene matrix is related to the uniformity of molecular weights of the individual blocks.

Figure 2 shows an electron micrograph of the same polymer which, prior to staining, was stretched about 50% and then placed on

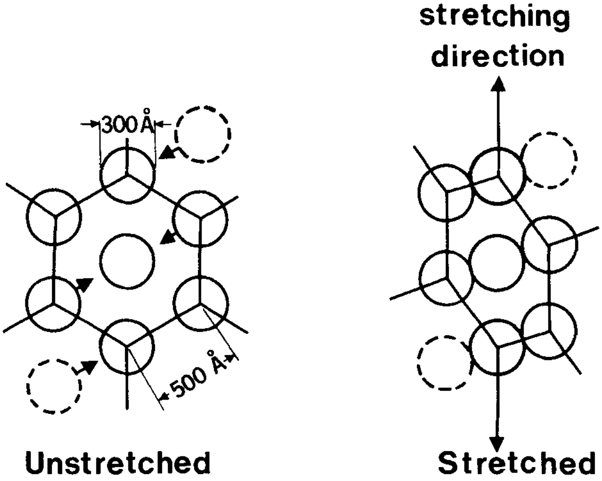

Fig. 3. Schematic diagram showing the rearrangement of the polystyrene regions from a hexagonal to a pseudohexagonal packing due to stretching.

the support screen. The initial step of stretching caused a change in the arrangement of the polystyrene spheres from a hexagonal to a pseudohexagonal packing, as shown schematically in Fig. 3. This change in packing pattern accounts for the formation of rows, or ribbon-like structures, of polystyrene which are inclined about 70° to the stretching direction. This arrangement of the polystyrene domains leads also to the formation of "V-shaped" patterns, as reported by Beecher et al. [4].

The results of these experiments have shown that long-range supermolecular order can also exist in polymer systems which are not stereoregular. The structural regularity appears to be related to uniformity of composition and individual block sizes.

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REFERENCES

[1] J. F. Henderson, K. H. Grundy, and E. Fischer, paper presented at the International Symposium on Macromolecular Chemistry, Prague, 1965; *J. Polymer Sci.*, **C16**, 3121 (1968).

[2] H. Hendus, K. H. Illers, and E. Ropte, *Kolloid-Z.*, **216-217** (1967).

[3] K. Kato, *J. Polymer Sci.*, **4**, 35 (1966); *Polymer Eng. Sci.*, **1**, 38 (1967).

[4] J. F. Beecher, L. Marker, R. D. Bradford, and S. L. Aggarwal, *Polymer Preprints*, **8**, 1532 (1967).

[5] E. Vanzo, *J. Polvmer Sci.*, **(A-1)4**, 1727 (1966).

[6] E. B. Bradford and E. Vanzo, paper presented at the Symposium on Block Copolymers in Pasadina, Calif., June 1967.

[7] A. Skoulios and G. Finaz, *Compt. Rend.*, **252**, 3467 (1961).

[8] L. R. G. Treloar, *The Physics of Rubber Elasticity*, Oxford, New York, 1958.

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