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In Situ Preparation of Impact-Resistant Polystyrene

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ABSTRACT

Our research intends to prepare an "in situ" impact-resistant polystyrene with improved mechanical properties by bulk and suspension polymerization of styrene in the presence of dissolved rubber. Two specimens of three block copolymers of the styrene-butadiene-styrene type, having different polystyrene content and different molecular weight, have been used as dissolved materials. From our experiments it follows that the polymerization rate is strongly influenced by the amount of rubber contained in the original solution; it is possible to obtain materials containing up to 20 wt% of polybutadiene; it is reasonable to foresee that this value could be increased by changing the molecular weight of the copolymer and/or the chain block length; the Young modulus decreases and the impact strength increases with the rubber content of the in situ prepared blends, independently of the polymerization technique; polyvinyl alcohol has been found as the most effective

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suspending agent; the morphology of our materials is strongly different from that of commercial high impact polystyrene. Instead of a random and discontinuous distribution of large domains of the elastic component in the rigid matrix, we have a regular polybutadiene network. In conclusion, our results show that impact-resistant polystyrene can be prepared by the polymerization of styrene containing in-solution block copolymers with the outside blocks sufficiently compatible with the monomer to give an homogeneous distribution of the rubbery component. A good balance between modulus and strength can be obtained, and it can be foreseen that results of practical interest could be achieved when copolymer with appropriate molecular weight and block length are used.

INTRODUCTION

Impact resistant polystyrene can be obtained by incorporation of fine particles of rubber into a rigid matrix. This result can be achieved in several ways, and the properties of the final products are highly dependent on the method of preparation as well as on the number and size of the dispersed particles [1-3].

Many papers are available in the literature [4] describing polymerization of styrene in the presence of dissolved rubber, and a phase-inversion usually takes place during the reaction.

The present paper intends to prepare an "in situ" impact resistant polystyrene (PS) with improved mechanical properties by bulk and suspension polymerization. Two copolymers with different PS content and different molecular weight were used. The results show that a large amount of rubbery phase can be regularly dispersed in the polystyrene matrix with a good balance between modulus and strength. It seems to be possible to improve the final characteristics using block copolymers with different block and total molecular weights.

EXPERIMENTAL

Materials

A commercial grade styrene, purified and dried over $CaCl_2$ as described in the literature [5, 6], has been used as monomer.

Initiator (benzoyl peroxide) and suspending agent (polyvinyl alcohol, PVA) were high purity commercial products, added directly to the system without any further physical treatment.

Styrene (S)-butadiene (B) block copolymers, having a symmetrical starlike molecular structure in which four S-B blocks are coordinated on a silicium atom, were used as elastomers. S forms the external part of each tail; for this reason, large amounts of these products can be dissolved rather easily in the monomer at room temperature, particularly when the percent of the polystyrene in the copolymer molecule is quite high. Two commercial samples, kindly supplied by Enoxy Chimica S.p.A. and labeled Europrene Sol T 161 and T 162, were employed; they have weight average molecular weights of 2.50×10^5 and 1.50×10^5 (with $\overline{M}_w/\overline{M}_n$ equal to 1.3 and 1.5) and polystyrene contents of 30 and 40 wt%, respectively [7, 8].

Polymerization

Selected amounts of rubber have been dissolved at room temperature in the monomer, which has been polymerized both in bulk and in suspension at 85 ± 0.5°C.

The bulk polymerization has been performed following the well-established technique for pure styrene [5], and both elastomers have been used as dissolved materials.

As far as the suspension polymerization is concerned, 500 mL of distilled water, containing the suspending agent and the initiator (1.5 and 1.0 wt%, respectively, referred to the monomer, if not differently quoted), were stirred in a three-necked flask; the styrene solution, prepared at room temperature by mixing a selected amount of copolymer to 70 g of monomer, was added dropwise under stirring in order to help the formation of the suspending beads. In these experiments only the Europrene Sol T 162 copolymer has been used.

Some preliminary measurements have shown that the reaction rate decreases with an increase in the amount of dissolved rubber. This phenomenon is more relevant when T 162 copolymer is present. In our experiments satisfactory yields (higher than 90%) have been reached with reaction times of 12 and 7 h for bulk and suspension polymerization, respectively.

The as-polymerized material was washed with methyl alcohol in order to remove unreacted monomer, and dried at 50°C under vacuum.

Polymer Characterization

Impact strength measurements have been performed according to the Izod method at room temperature on notched specimens (bending radius: 0.25 mm; notch depth: 0.25 ± 0.02 mm) obtained by milling from plates 3.0 ± 0.1 mm thick. These plates were prepared in a Carver hydraulic press by compression molding of the polymer at 210 ± 10°C (5 min at normal pressure and 5 min at 270 ± 20 atm), followed by cooling to room temperature in 10 min.

The stress-strain behavior has been followed at 20°C with an automatic Instron 1122 machine on specimens 200 μm thick, prepared by the same technique. In this case the temperature was about 150°C and the pressure about 250 atm.

The as-polymerized materials have been preliminarily submitted to a thorough mixing treatment in a Reocord EC apparatus (T = 190 ± 5°C; 3 min at 4 rpm and 3 min at 8 rpm).

The morphology of the samples has been studied in a Siemens Elmiscope 102 transmission electromicroscope. Sections about 500 Å thick have been cut by ultramicrotomy using a Reichert Om U_2 Ultratome apparatus with a Shandon FC 150 device to reach low temperatures (specimen at -90°C; blade at -60°C) [9].

The staining has been obtained by submitting sections to the absorption of OsO_4 vapors, fixed by the residual double bonds of the butadiene molecules. Therefore, in the following pictures the butadiene phase will appear dark and the polystyrene phase bright [10].

RESULTS AND DISCUSSION

Tables 1 and 2 summarize the experimental results of both bulk and suspension polymerization together with the more relevant mechanical properties of the resultant polymers.

In both series of experiments the conversion yields decrease on increasing the rubber content. This result reflects the influence on the polymerization rate of the amount of rubber contained in the original solution, as far as the reaction time is fixed (12 and 7 h for bulk and suspension polymerization, respectively). Actually the system is able to produce more polymer if it is allowed to react for a longer time; for example, the mixture leading to sample L_3 reaches a conversion of 96.3% after 8 h of polymerization.

The conversion yield of L_6 has been purposely reduced to a quite low value in order to prepare an alloy containing a relevant amount of elastomer. This result is otherwise hindered by the difficult dissolution of the rubber in the monomer when the system reaches high viscosity.

Polymers containing only up to about 15% of polybutadiene can be obtained from styrene solutions of T 161. This value can be accounted for by considering the lower solubility in the monomer of this copolymer owing to the higher value of its molecular weight together with a smaller amount of styrene in the starlike molecule.

From our experiments it follows that it is possible to obtain materials containing up to 20 wt% polybutadiene; it is reasonable to foresee that this value could be increased by changing the molecular weight of the copolymer and/or the chain block length.

Beside this, on increasing the percent of the suspending agent, the polymerization rate decreases (Table 3) and the morphology of the as-polymerized material changes macroscopically.

Actually, by adding 1.5 wt% PVA the product consists of well-defined beads only when the monomer to rubber ratio is up to 10:1 by weight; for higher values pearls collapse together in the final part of the polymerization and a rather compact polymer is obtained. This

TABLE 1. In Situ Preparation of Polystyrene-$(SB)_4Si$ Blends: Bulk Polymerization

Sample	LM_1	LM_2	LM_3	LM_4	LM_5	LM_6	LM_7	PS[b]	HIPS
Elastomer	T 161	T 161	T 161	T 162	T 162	T 162	T 162	-	-
Yield, %	98.2	97.0	95.5	95.2	95.1	91.2	91.1	-	-
% PB	5.8	10.8	15.3	10.8	16.2	18.2	21.6	0	14.5
Young's modulus, GPa	-	2.97	1.85	2.9	-	1.2	1.2	3.5	1.7
Impact strength, kJ/m^2	-	-	-	2	3	7[a]-12	-	2.4	8.6

[a] Before thorough mixing.

[b] BDH atactic polystyrene $\overline{M}_w = 1.0 \times 10^5$.

TABLE 2. In Situ Preparation of Polystyrene-$(SB)_4Si$ Blends: Suspension Polymerization

Sample	L_1	L_2	L_3	L_5	PS[b]	HIPS
Yield, %	99.8	91.5	89	56.7	-	-
% PB	5.5	10.7	18.6	24.7	0	14.5
% PVA	1.5	1.5	1.5	1.5	-	-
Young's modulus, GPa	-	2.2	1.3	0.9	3.5	1.7
Impact strength, kJ/m^2	-	2.4	7[a]-11	11	2.4	8.6

[a] Before thorough mixing.
[b] BDH atactic polystyrene $\overline{M}_w = 1.0 \times 10^5$.

TABLE 3. Suspension Polymerization: Effect of the Suspending Agent

Sample	L_3	L_6	L_7
Yield, %	89	62.7	94.7
% PB	18.6	23.1	18
% PVA	1.5	2.3	2.3
Reaction time, h	7	7	14
Young's modulus, GPa	1.3	0.9	1.35
Impact strength, kJ/m^2	7[a]-11	19	-

[a] Before thorough mixing.

can be accounted for by assuming that the increasing amount of polystyrene, which develops inside each drop, progressively reduce the solubility of the inner polybutadienic blocks of the copolymer, and segregation on the bead's surface occurs. Obviously, the aggregation process can be avoided if a larger percent of suspending agent is used; beads obtained with 2.3% of PVA are rather small and show a particularly sharp size distribution.

PVA has been found to be the most effective suspending agent; sodium dodecylsulfate and other products depress the conversion yields dramatically.

As far as the mechanical properties are concerned, Tables 1 and 2 show that Young's modulus decreases and the impact strength increases

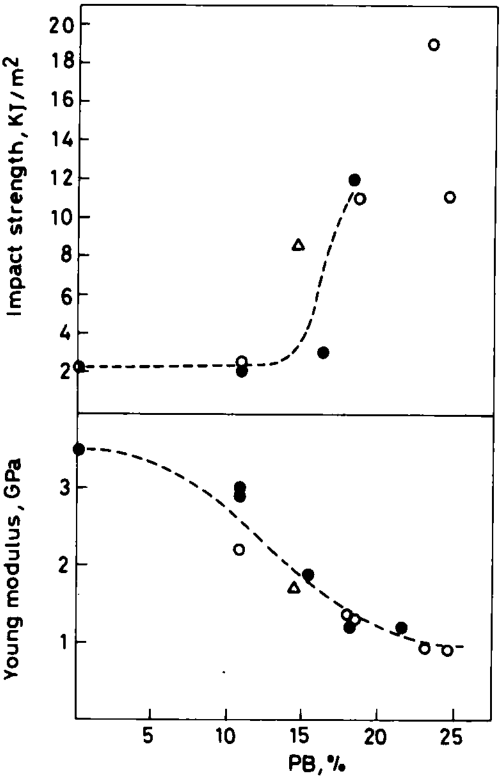

FIG. 1. Impact strength and Young's modulus behavior vs polybutadiene content for in situ prepared high impact polystyrene. (●) Bulk polymerization, (○) suspension polymerization, (◑) atactic polystyrene ($\overline{M}_w$ 1.0 × 10^5), (△) commercial HIPS.

with the rubber content of the in situ prepared blends, independent of the polymerization technique (Fig. 1). These results are in agreement with those observed with blends prepared in more traditional ways [11, 12].

Blends with a rubber content up to 10% polybutadiene have about the same properties as the pure polystyrene. On the other hand, Blends LM_6 and L_3 approximate the physical characteristics of high impact commercial polystyrene; in our materials a smaller value of the modulus is balanced by a higher impact strength, and these characteristics fit with a slightly larger amount of polybutadiene. Finally, Blend L_6 allows us to improve the strength well over the HIPS value.

These results reflect a different morphology between our samples and commercial high impact polystyrene. Instead of a random and

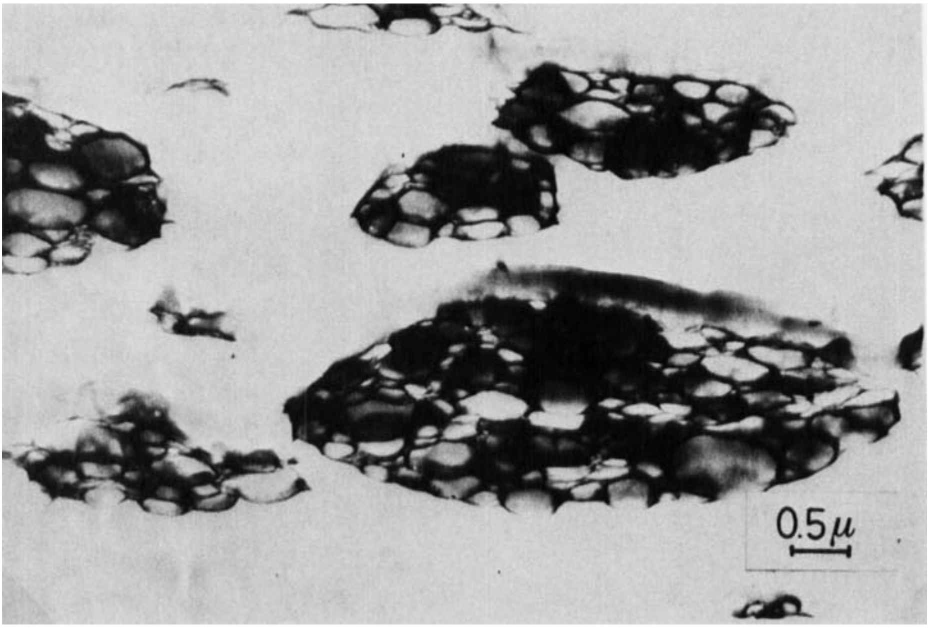

FIG. 2. Morphology of commercial HIPS.

discontinuous distribution of large domains of the elastic component in the rigid matrix (Fig. 2), we have a regular polybutadiene network (Figs. 3-5); this macrostructure is nearer to that of the original copolymer (Fig. 6).

The technique used for the preparation of the material accounts for the formation of this peculiar morphology; the segregation of the copolymer molecules is also avoided by the grafting of polystyrene chains on polybutadiene molecules, as solubility tests on the resultant material suggest.

The bulk polymerization leads to a nonuniform morphology. Lamellar structures (Fig. 3a) are joined to large regions with a higher concentration of polystyrene (Fig. 3b).

Mats of lamellae are obtained by suspension polymerization (Fig. 5); the polybutadienic phase is always about 200 Å thick and the polystyrene phase has a different thickness according to the final composition of the material. From one point to another the mats of lamellae have different orientations, and therefore the whole sample looks like a macrocrystalline material: regions about 1 μm large having a rather ordered structure are joined by irregular boundaries in which

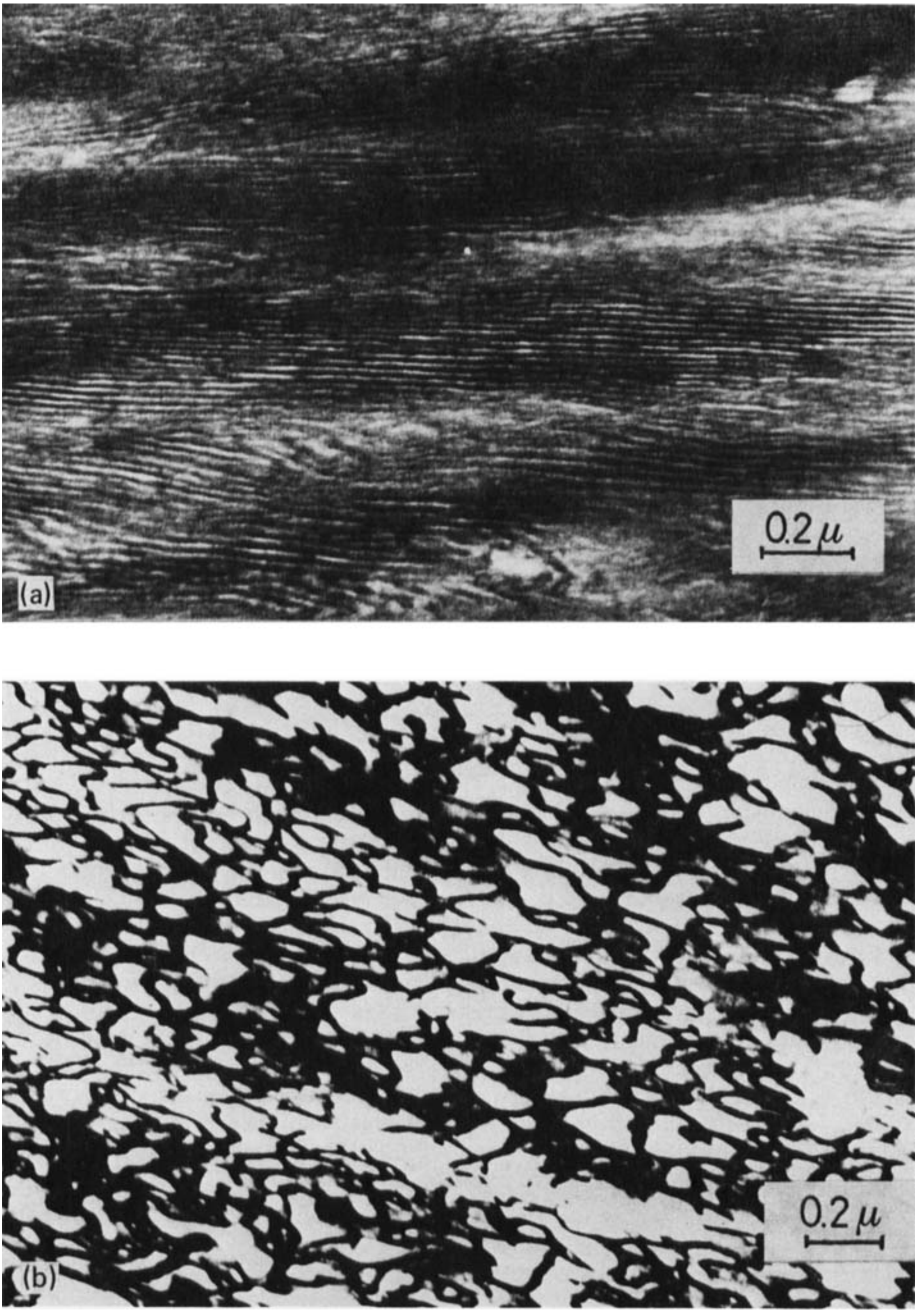

FIG. 3. Morphology of in situ prepared impact-resistant polystyrene. Bulk polymerization LM_7 sample: (a) rubber reach region, (b) polystyrene reach region.

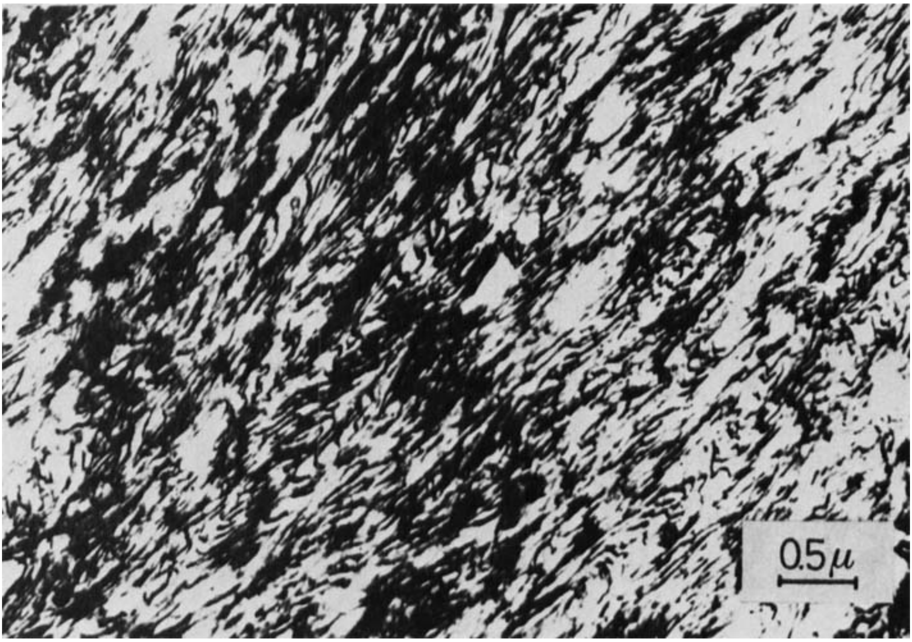

FIG. 4. Morphology of LM_7 sample after thorough mixing.

small particles of pure polystyrene are observed. Besides this, large domains of polystyrene are regularly dispersed in the structure.

The morphological observations account for the thorough mixing treatment; it does not substantially affect the distribution of the rubbery phase (Fig. 4) but nevertheless the mechanical properties are largely improved (Tables 1 and 2; Samples LM_6 and L_3).

In conclusion, our results show that impact-resistant polystyrene can be prepared by the polymerization of styrene containing in solution block copolymers, with the outside blocks sufficiently compatible with the monomer in order to give an homogeneous distribution of the rubbery component. A good balance between modulus and strength can be obtained, and it can be foreseen that results of practical interest could be achieved when copolymers with appropriate molecular weights and block lengths are used.

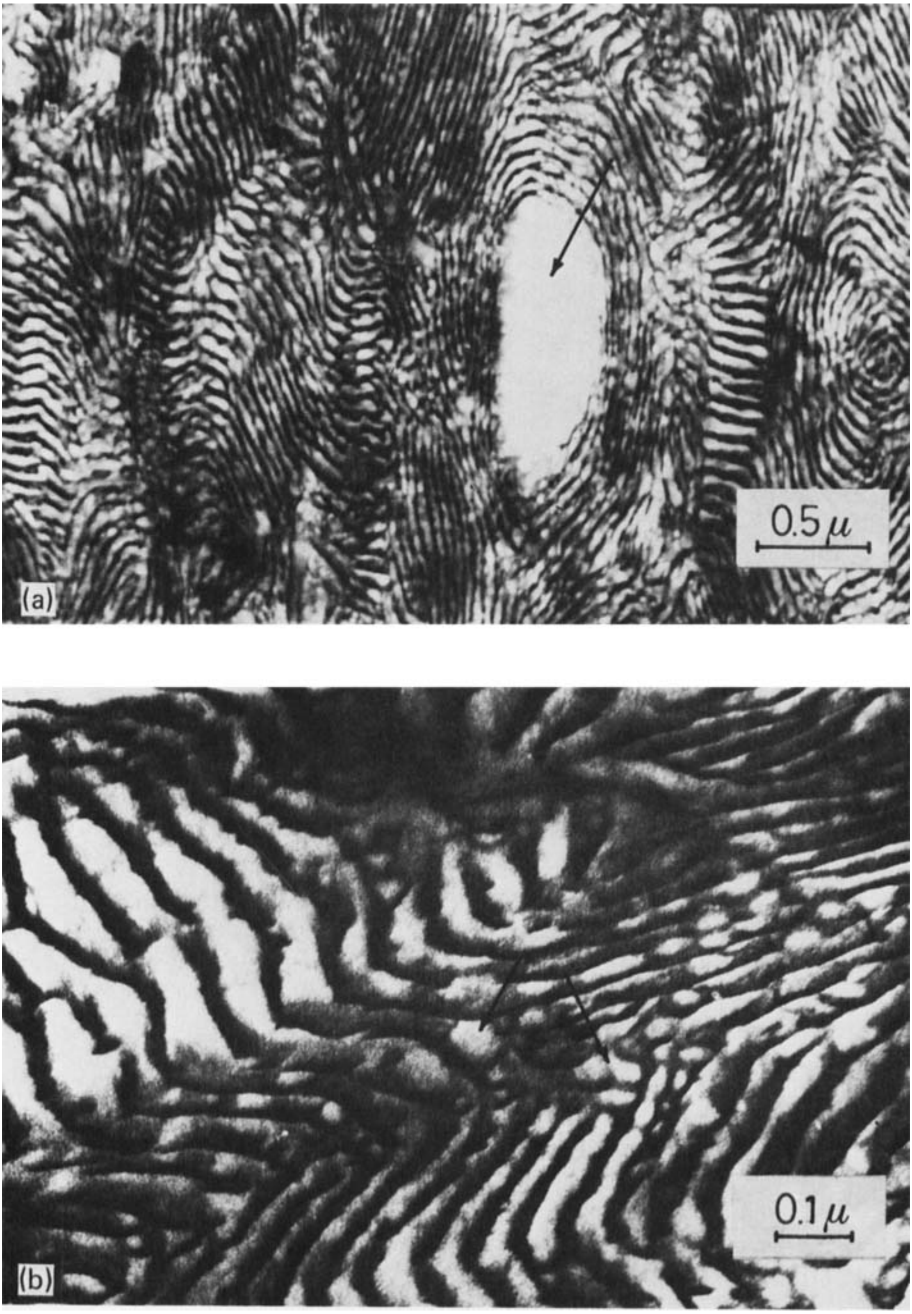

FIG. 5. Morphology of in situ prepared impact-resistant polystyrene. Suspension polymerization, L_7 sample: (a) expanded area with a large domain of polystyrene; (b) detail, with small particles of pure polystyrene (see arrows).

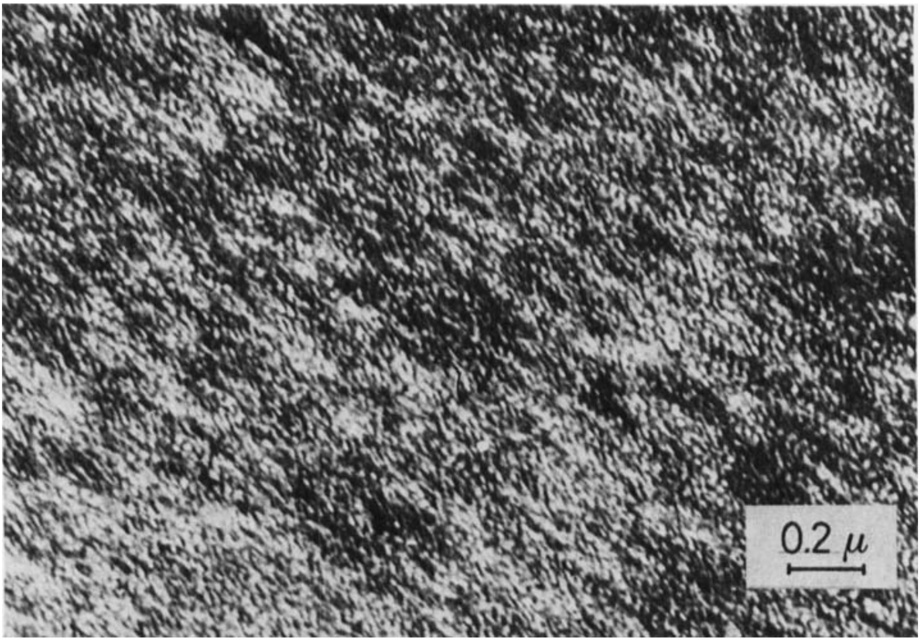

FIG. 6. Morphology of T 162 block copolymer.

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