Poly(methyl methacrylate) prepared with Lewis acid catalysts (at all temperatures) contains approximately twice as many syndiotactic as heterotactic sequences. This contrasts with the 1:1 syndiotactic:heterotactic ratio observed with bifluoride catalyst at ambient temperature but approximates the tacticity observed with bifluoride catalyst at −78 °C.[2] Poly(ethyl acrylate) prepared by GTP with anionic or Lewis acid catalysts has random tacticity.

Lewis acid catalyzed GTP of simple alkyl acrylates provides a powerful means for control of polymer architecture that far exceeds the results obtained with anionic polymerization.[1]

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(4) In a typical procedure, zinc iodide (6.48 g, 20 mmol) was heated in a 100-mL three-necked flask to 300 °C in vacuo for 30 min and then allowed to cool under argon. Then dichloromethane (50 mL) was added followed by 1-(trimethylsiloxy)-1-(2-(trimethylsiloxy)ethoxy)isobutene[8] (1.4 mL, 4.71 mmol). After the mixture was cooled to −78 °C, ethyl acrylate (10 mL, 92.22 mmol) was added. The reaction was allowed to warm to −15 °C, whereupon the temperature rose very quickly to +38 °C over 3 min. The temperature was allowed to fall to +20 °C. When more ethyl acrylate (1.0 mL, 0.92 mmol) was added, no further reaction occurred. The solvent was evaporated, and the residue was dissolved in ethyl acetate (100 mL) and washed three times with 100-mL portions of water. The organic layer was dried over $MgSO_4$, filtered, and evaporated to give 9.91 g of poly(ethyl acrylate). GPC: $\bar{M}_n = 2200$, $\bar{M}_w = 2300$, $D = 1.05$ (theoretical molecular weight 2160).

(5) In a typical procedure, a solution of 0.87 g (1 mL, 5 mmol) of 1-methoxy-1-(trimethylsiloxy)isobutene in 20 mL of anhydrous methylene chloride was cooled to −78 °C under an argon atmosphere and treated with 0.28 mL (0.5 mmol) of 1.8 M diethylaluminum chloride/toluene. Then 10 g (10.8 mL, 100 mmol) of ethyl acrylate (purified by passage over a short column of neutral alumina under an argon atmosphere) was added at such a rate that the temperature of the reaction mixture did not exceed −70 °C. After 15 min at −78 °C, 5 mL of methanol was added, and the mixture was allowed to warm to room temperature. Evaporation under reduced pressure gave 10.7 g of poly(ethyl acrylate) as a viscous liquid. GPC: $\bar{M}_n = 2130$, $\bar{M}_w = 2580$, $D = 1.21$ (theoretical molecular weight 2100).

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(9) Contribution No. 3480.

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Depression of Glass Transition Temperature in Aramid–Polybutadiene Multiblock Copolymers

A number of studies on two-phase polymer systems have shown that the properties of a finely dispersed microphase are not the same as those of the polymer in bulk. The relation between glass transition temperature (T_g) and two-phase morphology is still unsolved.[1] Two-phase polymers that segregate into distinct large domains usually exhibit two T_g's identical with those of the component polymers. When the domains are very small, say less than a few hundred angstroms, the T_g's of the individual components are shifted: elevation of the temperature of the low T_g and depression of the high T_g. This inward shift of both T_g's has been observed by Meyer et al.[2] on styrene–isoprene–styrene block copolymers and by Gaur et al.[3] on high molecular weight block copolymers of α-methylstyrene and styrene. The depression of the high T_g of hard-component microphases dispersed in a soft matrix has been observed by many authors.[4] Bares[5] interpreted the high-T_g depression as the effect of an interfacial zone that increases the average free volume available to the glassy microphase. Couchman et al.[6] argued that even in the absence of the finite interfacial zone, the effect of interfacial tension on the equilibrium pressure within the microphase will cause the high-T_g depression.

On the other hand, the *depression* of the *low* Tg has been observed in rubber-toughened plastics such as ABS (acrylonitrile–butadiene–styrene copolymer), HIPS (high-impact polystyrene), and blends of styrene–butadiene block copolymer with the corresponding homopolymers.[7-9] These systems consist of microspherical inclusions of a rubber in a rigid plastic matrix. Depression of the rubber T_g has been explained on the basis of negative pressure resulting from differential contraction due to the thermal expansion mismatch upon cooling from the liquid state.[7-9]

Here we report another T_g shift phenomenon: the depression of the low T_g of a rubber matrix in aramid–polybutadiene multiblock copolymers.

We prepared a series of aramid–polybutadiene multiblock copolymers having various lengths of aramid and a constant length of polybutadiene. Direct polycondensation of isophthalic acid with excess 4,4′-diaminodiphenyl ether was carried out in *N*-methylpyrrolidone/LiCl with triphenyl phosphite/pyridine as the condensing agent. Block copolymerization of the oligoaramid with α,ω-dicarboxylatopolybutadiene ($\bar{M}_n = 5200$) was performed in the same way. The multiblock copolymer is poly(4,4′-oxydi-*p*-phenyleneisophthalamide)-*b*-polybutadiene (Figure 1). Details of the polymer synthesis will be presented elsewhere.[10] The block copolymer was dissolved in DMAc (*N,N′*-dimethylacetamide) and the solution was cast onto a flat dish. The solvent was evaporated at room temperature under reduced pressure for 60 h.[11] Prior to further drying, the cast film was washed with methanol in a Soxhlet extractor for 0.5 h to exchange any residual solvent in the film with methanol. Finally, the film was dried under a vacuum of 10^{-4} mmHg at 80 °C for 1 day. The film thus prepared was used for differential scanning calorimetry (DSC) and electron microscopy.

DSC thermograms were obtained at a constant heating rate of 20 °C/min. For transmission electron microscopy, osmium tetraoxide staining and fixation were employed. Electron micrographs of ultrathin sections cut normal to the film surface are shown in Figure 2.

The dark portions in the micrographs are the polybutadiene phase stained selectively by osmium tetraoxide. The domains are extremely small. Short rodlike domains

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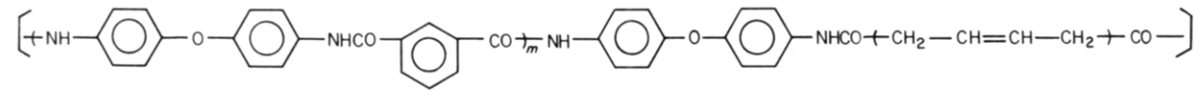
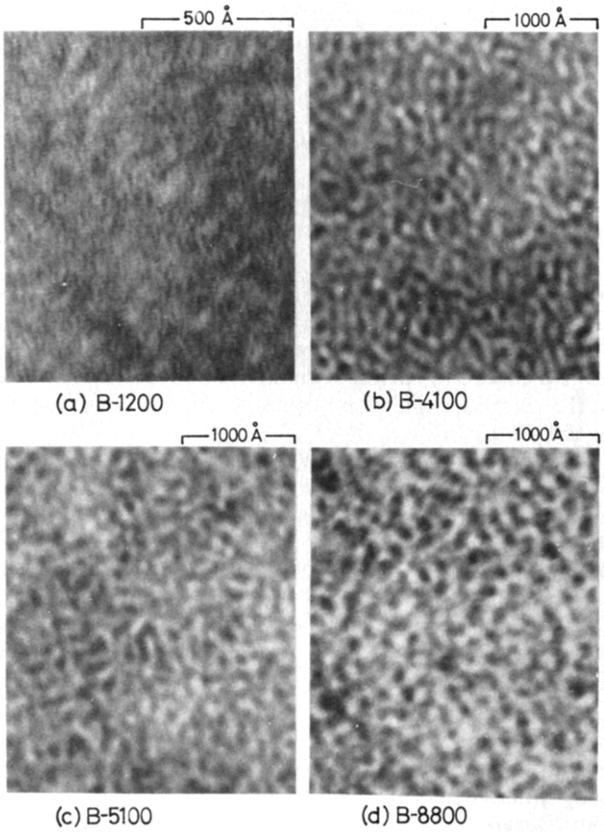


Figure 1.

Table I
Molecular Characteristics, Morphologies, and Glass Transition Temperatures of Block Copolymers

sample code	$\bar{M}_n$ of aramid block[a]	η_{inh}[b]	domain size[c] D/Å	domain size[c] T/Å	T_g/K
B-1200	1200	0.31	18	35	196.5
B-4100	4100	0.61	65	162	194.0
B-5100	5100	0.60	67	170	192.0
B-8800	8800	0.78	97	208	187.5
PB[d]		(0.70)[d]			197.5

[a] Stoichiometricals. [b] Inherent viscosity; 0.5 dL/g in DMAc at 30 °C. [c] Estimated from electron micrographs. [d] Homopolybutadiene prepared by chain extension of α,ω-dicarboxylatopolybutadiene (M_n = 5200) through polycondensation with *p*-phenylenediamine. η_{inh} = 0.70 (0.5 dL/g in benzene at 30 °C).



(a) B-1200 (b) B-4100

(c) B-5100 (d) B-8800

Figure 2. Transmission electron micrographs of aramid–polybutadiene multiblock copolymers cast from DMAc solution and stained with osmium tetraoxide.

of aramid dispersed in a matrix of polybutadiene are seen in the block copolymer with a short aramid block (Figure 2a). In block copolymers with longer aramid blocks, we see the rodlike domains partly interconnected (Figure 2b,c), resulting in a network structure (Figure 2d). The domain structure in Figure 2d is still far from that of a perfect inclusion of a rubber microphase in a rigid matrix as in ABS and HIPS. That is, the polybutadiene phase is still continuous even in the block copolymer with the longest aramid block. The diameters of the rodlike domains D and the interdomain distance T perpendicular to the rod axis were estimated from the micrographs (Table I). The longer the aramid block, the larger the D and T, as shown in Fig. 3.

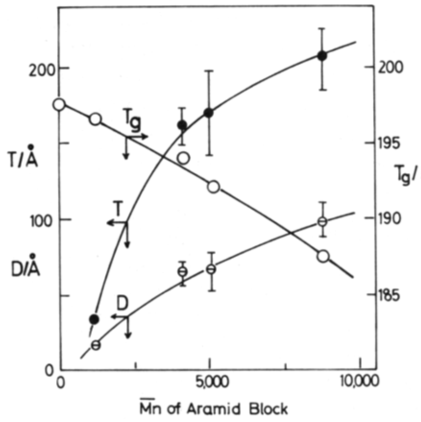


Figure 3. Diameter of rodlike domains of aramid D, interdomain distance T, and glass transition temperature T_g of the polybutadiene phase as a function of molecular weight of the aramid block $\bar{M}_n$.

From Table I we see that the glass transition temperatures of the polybutadiene phase are lower than that of bulk polybutadiene. Thus it is the matrix (continuous) phase that exhibits the low-T_g depression.

Although we cannot give a definite interpretation of these observations, a plausible one may be based on the negative pressure concept for ABS and HIPS.[7,8] That is, the low-T_g depression may be due to the negative pressure resulting from differential contraction due to the thermal expansion mismatch. The mismatch is expected to be greater for our combination of aramid and polybutadiene than for that of polystyrene and polybutadiene (HIPS). On the other hand, the polybutadiene chains are expected to be seriously constrained during microphase separation because the chains are connected at both ends to the rigid aramid chains that form the microdomains. The longer the rigid chains, the stronger the constraints on the flexible chains. Upon cooling, the constraints suppress normal contraction of the polybutadiene matrix as in bulk homopolybutadiene. Hence a situation similar to that of the occluded rubber phase in ABS and HIPS may occur in the matrix phase of the aramid–polybutadiene block copolymers.

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(11) A 20–30 mmHg for 10 h and at 1 mmHg for 50 h.

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Triphase Equilibrium in Aqueous Solutions of the Rodlike Polysaccharide Schizophyllan

It is well established experimentally[1-5] and theoretically[6-9] that a solution of a rodlike polymer separates into two phases, isotropic and anisotropic, above some critical concentration. The solution becomes completely anisotropic above another critical concentration. From the pioneering theories on this phenomenon of Onsager[6] and of Flory,[7] who treated monodisperse solutes, we can draw one common conclusion that the long asymmetric shape of the molecule is of primary importance for the formation of the anisotropic phase; no specific intermolecular interaction needs to be involved.

Subsequently Flory and Abe[8] extended the original Flory theory to polymers polydisperse in molecular weight neglecting polymer–solvent interactions. As the simplest case of polydisperse polymers, Abe and Flory[9] treated mixtures of two monodisperse polymers of different axial ratios, paying particular attention to phase behavior for different combinations of polymer molecular weights. We here quote two important predictions from their theory: (1) Phase separation of such a ternary mixture is accompanied by pronounced fractionation according to molecular weight; the higher molecular weight species is almost excluded from the isotropic phase, especially when the mixture contains the lower molecular weight species in excess. (2) When the difference in axial ratio between the two polymers is large, the binodal contains a relatively wide region in which two anisotropic phases and an isotropic phase coexist at triphase equilibrium. Figure 1 shows a ternary phase diagram calculated according to Abe and Flory for the system containing two polymers with axial ratios x of 18.3 and 223, where ξ stands for the weight fraction of the smaller x component in the polymer mixture and ϕ_i (i = 1, 2) for the volume fraction of polymer component i. The hatched triangle IA_1A_2 indicates the region for the three-phase separation. So far no experimental evidence for these important predictions, especially prediction 2, has been reported in the literature.[10]

In our recent work,[11-14] we have been concerned with a polysaccharide called schizophyllan. This is because schizophyllan can be taken as an appropriate model polymer for investigating solution properties of rodlike polymers. In fact, schizophyllan exists in aqueous solution as a triple helix, forming a rigid cylindrical rod at low molecular weights, at least up to an axial ratio x of 100, and being essentially rodlike up to x of 250.[15,16] We found that an aqueous solution of this polysaccharide becomes birefringent at high concentrations, forming a cholesteric mesophase.[11,12] The critical concentrations for the incipience of the cholesteric phase and disappearance of the isotropic phase decrease with increasing axial ratio.[13] This is essentially the same trend found in polypeptide solutions[2,3] and naturally expected from the rodlike shape of this polysaccharide. However, the molecular weight dependence of the critical concentrations cannot be described precisely by either of the existing theories for rodlike polymers.[13]

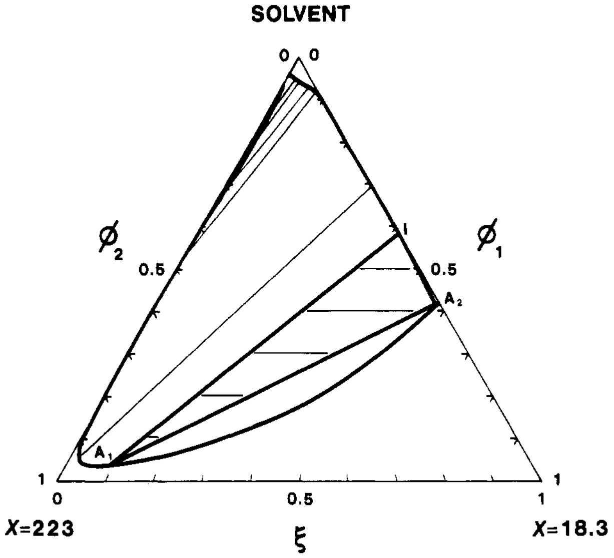

Figure 1. Theoretical phase diagram for an athermal system of two monodisperse polymers with axial ratios x of 18.3 and 223 + a single solvent calculated according to Abe and Flory.[9] The hatched triangle IA_1A_2 shows the region of three-phase separation.

This paper describes a preliminary experiment performed on the same polysaccharide in water to test the prediction by Abe and Flory[9] on the ternary mixture mentioned above.

We used two reasonably well fractionated samples of schizophyllan designated T-3 (M_w = 80.0 × 10^4, x = 223) and U-110 (M_w = 6.58 × 10^4, x = 18.3); they are characterized by M_z/M_w ratios smaller than 1.3. Appropriate amounts of the two samples and water were mixed in a calibrated stoppered tube (about 1-mL capacity), stirred by a magnetic stirrer bar at room temperature for about 2 days, kept in an air bath thermostated at 25 °C with occasional stirring, and finally kept standing for 1–2 days to attain an equilibrium state. Since no macroscopic phase separation took place within an accessible period of time less than a week, the solution was centrifuged at ca. 2100g to obtain phase separation.[17] The volume ratio of each separated phase was determined from its column height. Then an aliquot of each phase was taken to analyze for the total concentration by differential refractometry and average molecular weight by viscometry. Each phase was also analyzed by gel permeation chromatography. The weight fraction ξ of U-110 in a given polymer mixture was estimated both from the average molecular weight and from the GPC data, yielding essentially the same result.

Figure 2 shows a typical photograph of a phase-separated solution, where three different phases are clearly distinguished. Observation between crossed polars indicated that the uppermost phase was isotropic and the bottom two phases were anisotropic. Usually, the upper two phases were clear but the bottom one was more or less turbid, reflecting its very high viscosity. The results from such phase separation experiments are summarized in a ternary phase diagram in Figure 3. Here a given solution with the composition expressed by a cross separated into two or three phases indicated by circles. The solid curves connecting the circles represent the phase boundaries. As predicted by Abe and Flory (1), the biphase equilibrium accompanies pronounced molecular weight fractionation.

In any case with the three-phase separation, it was not easy to determine the composition of the smallest volume

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