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Surface Properties of Styrene-Tetrahydrofuran Block Copolymers

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ABSTRACT

Surface properties of styrene-tetrahydrofuran (St-THF) block copolymers (AB and ABA type) were studied. Morphology observed by electron micrography showed the formation of fibrils of poly-THF covered with poly-St for THF-rich block copolymers and the accumulation of poly-THF segments for St-rich block copolymers. The poly-THF segment was found to have a surface of activity 3 dyne/cm lower than the poly-St segment. Modification of the poly-St surface by adding St-THF block copolymers was examined by measuring the surface tension drop during heating. Inverse gas chromatography of the block copolymers revealed that the surface of St-rich block copolymer changes from poly-St to poly-THF on baking. The contact angle of water droplets was a linear function of surface composition, and water wettability of St-rich block copolymers by accumulation of surface active poly-THF segment was indicated.

INTRODUCTION

Significant advances have been made in the synthesis, characterization, and utilization of block and graft copolymers over the last twenty years. A major contribution to these developments has been the "living polymer" technique pioneered by Szwarc. The preparation by this technique of polymers with well defined structure made it possible to clarify fundamental characteristics of block and graft copolymers, such as domain formation and thermoplastic elasticity. The "living" tendency frequently observed in ring-opening polymerization can provide novel methods for the preparation of tailor-made polymers with specific properties.

New development in the synthesis of block and graft copolymers has been made by the cationic polymerization of tetrahydrofuran (THF). We are interested in the synthesis of a well-defined block copolymer by ion coupling of anionic and cationic living polymers [1]. A recommended procedure is the use of super acid derivatives as initiators for the polymerization of THF and carboxylation of the polystyrene anion to improve the block efficiency by ion coupling [2].

Besides phase separation and domain formation resulting from incompatibility of block chains, these block copolymers are characterized by crystallization and surface activity of the poly-THF segment [3]. A change in morphology caused by crystallization of the crystalline block chain is expected. A surface-active block segment is expected to modify the surface of the bulk polymer. This paper describes the surface chemical studies of this block copolymer carried out by inverse gas chromatography [4], surface tension measurements [3], and contact angle measurements [5].

EXPERIMENTAL

Materials

An AB block copolymer of St and THF (ST) and an ABA block copolymer of St-THF-St (STS) were synthesized by the ion-coupling reaction between the living ends of poly-St anions and poly-THF cations. The initiators for the polymerization of THF were prepared by the reaction of silver perchlorate with 2-bromoethyl acetate or bis-2-bromoethyl sebacate in nitromethane. Bulk polymerization of THF was carried out at 0°C. Poly-St anion was prepared by the polymerization of St with cumylpotassium in THF at 0°C followed by end-capping with carbon dioxide. The ion-coupling reaction of equimolar amounts of cationic and anionic living polymers was carried out in THF at room temperature. The precipitated block

TABLE 1. Observed Molecular Weights and Compositions of St and STS Block Copolymers

	$\overline{M}_n \times 10^{-3}$			
Polymer	PS Block	PTHF Block	Block copolymer	PSt, mole %
ST-1	9	60.5	70	12.1
2	30.1	60.5	103	26.9
3	84.6	60.5	134	44.2
4	137	60.5	224	57.8
5	342	60.5	(456)	91.1
STS-1	9	72.0	103	14.3
2	30.1	72.0	-	34.7
3	84.6	72.0	287	42.2
4	137	72.0	260	57.6
5	342	72.0	500	87.6

copolymers were fractionated with THF-isopropyl alcohol mixed solvents to remove homopolymers. The block copolymers were characterized by $\overline{M}_n$ from high speed membrane osmometer, by St mole fraction from ^{1}H-NMR and by sedimentation patterns. Results of characterization of the samples are shown in Table 1.

Measurements

Thin films of block copolymers were cast from cyclohexane solutions at 20°C, and the films were observed under a polarizing microscope. Ultrathin films were cast onto mesh sheets and stained by osmium tetroxide vapor and observed under electron microscope. Melting temperatures of the poly-THF block and the glass transition temperature of the poly-St block were determined by dilatometry. The degree of the crystallinity of the films was measured by differential scanning calorimetry.

For the characterization of the block copolymers by inverse gas chromatography, polymers were coated from chloroform solutions onto an inert support (Chromosorb G, 60-80 mesh) by slowly evaporating the solvent under reduced pressure. The polymer-coated support was packed into a stainless column of 1 m length. Specific retention volume for n-dodecane was calculated from the retention time, polymer loading weight, and a carrier gas flow rate by using corrections for pressure drop, water vapor pressure and gas holdup [4].

Surface tensions of the melt polymers were measured in argon by the pendant drop method [3]. Contact angles of water droplets against cast films were measured by microscopy [5].

RESULTS AND DISCUSSION

Morphology

An electron micrograph of the block copolymers cast from cyclohexane is shown in Fig. 1. The poly-THF segment was stained with osmium tetroxide. For THF-rich block copolymers such as ST-1 and STS-1, a fibril structure was observed which corresponds to the spherulite under polarizing microscope. The crystallization of poly-THF segment prevailed over microphase separation during casting. The white appearance of the fibrils shows that the surface of the crystalline fibrils is covered by amorphous poly-St segments. Close inspection reveals that besides fibrils, spherical domains are also observed in STS-1.

A change in the morphology with increasing poly-St content is observed (Fig. 1). For ST-3,4 and STS-3,4, rodlike domains or lamellae appear and fibrils disappear, the continuous phase changes from poly-THF to poly-St. Although spherulites could not be observed for these films, they are definitely crystalline as evidenced by the DSC measurements, and crystallization of the poly-THF segment proceeds in the spherical domains after phase separation.

For the case of St-rich block copolymers, such as ST-5 and STS-5, considerable accumulation of poly-THF segments is noticeable, contrary to the decrease of poly-THF content. This might be explained by the surface activity of the poly-THF segment.

St surface fractions of the cast films were measured from the electron micrograph by planimetry. The relationship between St surface fraction and the block copolymer composition is shown in Fig. 2. It is apparent that the surface fraction does not depend on the bulk composition; rather, an inverse relationship was observed. For poly-THF rich block copolymers, crystallization segregation occurs during film formation, and amorphous poly-St covers the surface of the crystalline fibrils of poly-THF. Such a phenomenon was reported by O'Malley et al. for St-ethylene oxide block copolymers [6]. For poly-St-rich block copolymers, diffusion of the surface active poly-THF

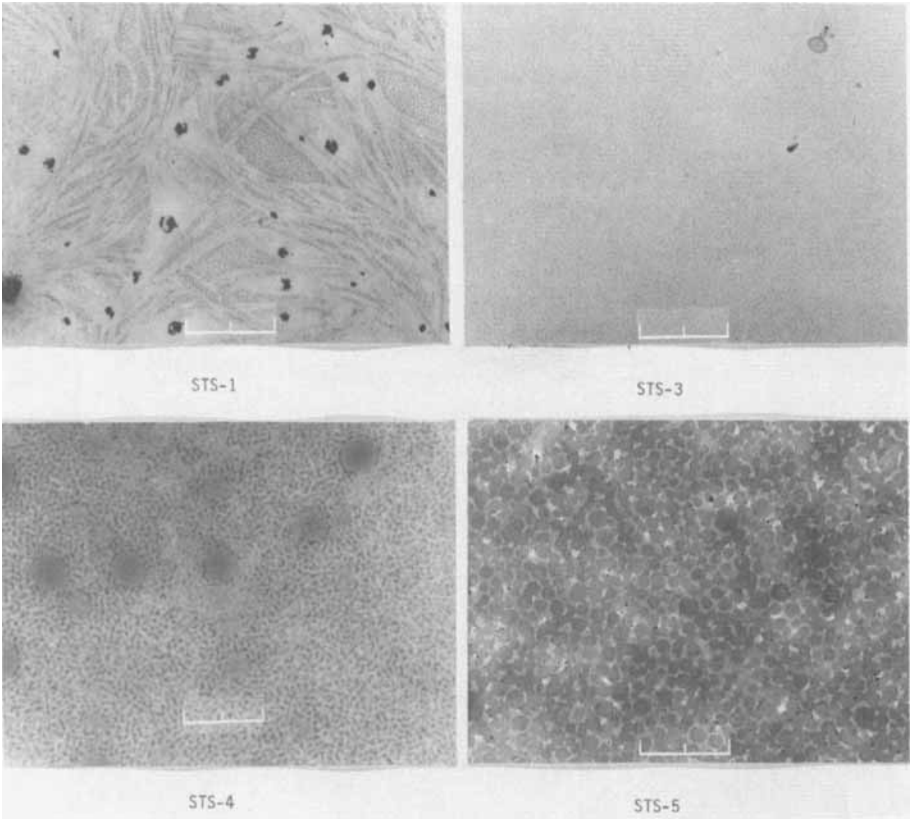

FIG. 1. Electron micrographs of STS-1, STS-3, STS-4, and STS-5 copolymer films cast from cyclohexane at 20°C (stain O_sO_4; bar = 1 μm).

segment proceeds during film formation and the poly-THF covers the surface of the cast film.

Surface Activity

Adsorption of a surface-active segment of a block copolymer on the surface is of interest for modification of the surface properties. Surface tension vs. temperature for poly-St and poly-THF are shown in Fig. 3. The data agree well with the literature values [7]. The

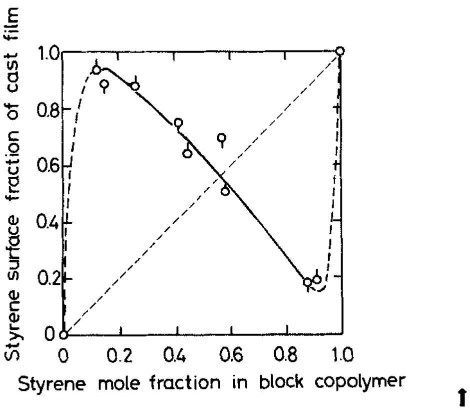

FIG. 2. Styrene surface fraction of cast films plotted against composition of block copolymers: (●) poly-THF; (○) poly-St; (ȯ) ST; (⚲) STS.

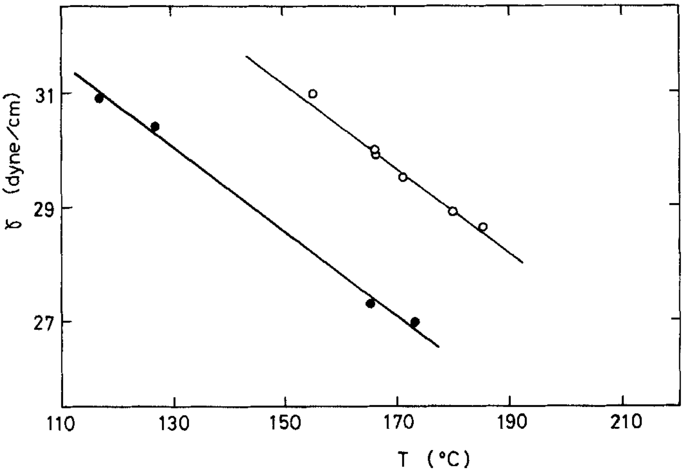

FIG. 3. Surface tension vs. temperature plots for (○) poly-St and (●) poly-THF.

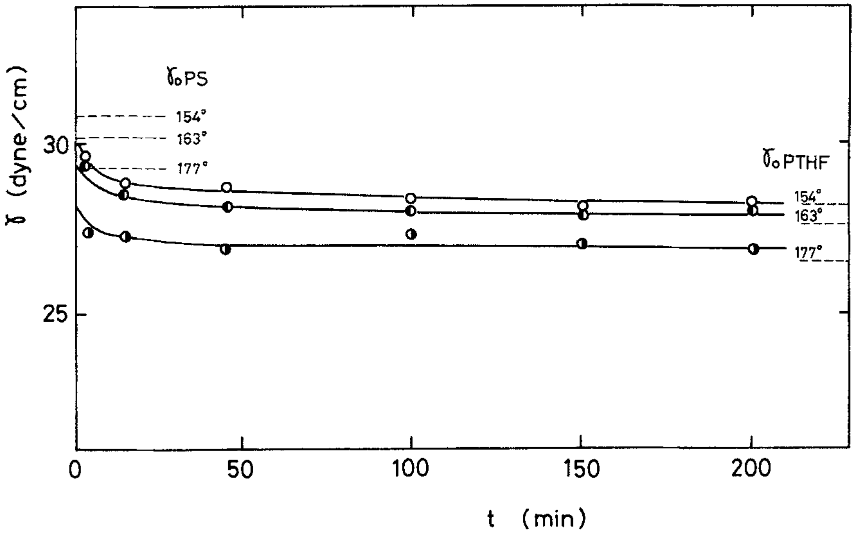

FIG. 4. Surface tension vs. time for St-1 copolymer-poly-St blend (ST-1, concn = 1 wt %).

surface tension of poly-THF is 3 dynes/cm lower than that of poly-St. Modification of surface properties of a homopolymer by incorporating a small proportion of block copolymer was studied. The surface tension-time curves obtained by blending a block copolymer with poly-St are shown in Fig. 4. Small amounts (0.3-1 wt %) of the block copolymer were added to poly-St and the mixture was dissolved in benzene and freeze-dried. The surface tensions of the blends fall rapidly and then approach that of molten poly-THF. Thus poly-THF blocks are adsorbed at the surface of the molten blends. Comparison of ST-1, ST-2, and ST-3 shows that the rate of decrease of surface tension decreases with increasing poly-St content. This is caused by the effect of the molecular weight of the block copolymer.

The surface tension of various polymer blends was studied. The blend of poly-THF and poly-St showed only a small lowering of surface tension. Although the surface tensions of both St-poly-THF and poly-St-poly-THF blends decrease with time, the initial surface tensions approach that of molten poly-THF and never that of molten poly-St.

From these results, it is concluded that for the St-poly-St blend, both the surface tension difference and the incompatibility between poly-THF segment and homopoly-St assist in the adsorption of the poly-THF segment, which has a lower surface tension than molten poly-St. On the contrary, it is clear that incompatibility alone is not sufficient to force the poly-St segment to the surface of the ST-poly-THF blend against the increase of surface free energy. Therefore, quite an important conclusion has been reached from these studies: an AB block copolymer, in which the surface tension difference between the two blocks is as small as 3 dynes/cm, is still sufficiently surface-active when it is added in low concentration to a homopolymer corresponding to block A as long as B is more surface-active.

Comparison of the poly-THF-poly-St and the ST-poly-St blends indicates the critical importance of block structure. Thus adsorption of the poly-THF block at the homopoly-St surface may represent the surface analog of domain formation in the bulk. Electron micrographs of cast films of ST-5 and STS-5 shown in Fig. 1, in which the concentration of poly-THF segment is ca. 10%, seem to support this idea.

Surface adsorption of more surface-active segment of a block copolymer incorporated in small amounts in homopolymer has been reported in case of polydimethylsiloxane [7-10]. The present investigation indicates that diffusion of spherical domain of poly-THF occurs from the bulk phase to the surface promoted by the decrease of the surface energy.

Inverse Gas Chromatography

The retention data of n-dodecane were examined as a function of column temperature by using inverse gas chromatography which uses the block copolymers as the stationary phase. The results are shown in Fig. 5, which plot the logarithm of specific retention volume against reciprocal column temperature. The plot should be linear for a retention mechanism which does not change over the temperature range applied. This was found to be the case not only for poly-THF above its melting temperature (42°C), but also for a block copolymer ST-2, whose glass transition around 90°C due to poly-St block could scarcely be detected in the diagram. Since the result was independent of the polymer loading weight, the retention is clearly determined by the bulk sorption mechanism. That is, the solute molecule penetrates into the bulk polymer phase and interacts with the whole polymer segments, regardless of the presence of poly-St segments, a result which is caused presumably by the melt phase of poly-THF segments at these temperatures.

A similar result was obtained (Fig. 5) with a block copolymer St-5 with a St content of 88 mole %, though an inflection is apparent in the retention diagram around T_g due to poly-St block. In contrast, poly-St showed a typical Z-shaped diagram with a minimum around its T_g [11]. The linear region below T_g is characterized by the

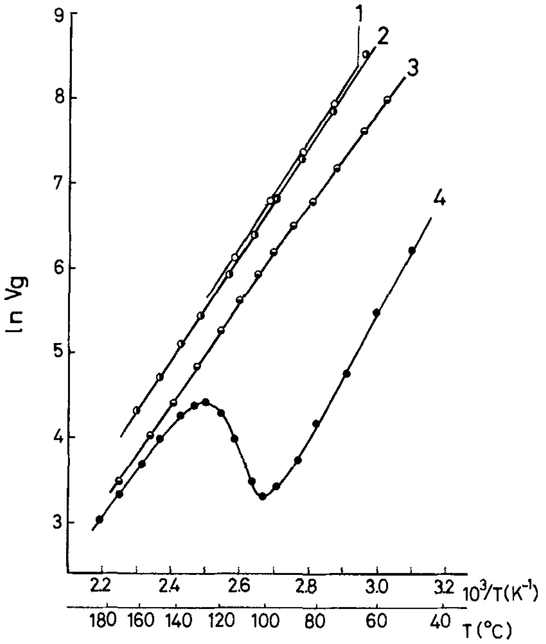

FIG. 5. Retention diagrams of n-dodecane on packed columns: (1) poly-THF; (2) ST-2; (3) ST-5; (4) poly-St.

surface adsorption mechanism, and the other linear region much higher than T_g by the equilibrium bulk sorption mechanism; the intermediate curved region just above T_g is related to diffusion-controlled sorption of the solute to bulk polymer phase.

Inverse gas chromatography technique of homopolymers has been explored by Guillet [11]. We found most interesting effects of thermal history for the case of ST-5. Retention data were collected twice on each column, first by using the column originally prepared from chloroform solution at room temperature, and second by using the column which had been baked at 180°C for 6 hr after the first measurement and then allowed to stand at room temperature for more than 3 days. The results in Fig. 5 were obtained with the columns after baking. While no substantial change in the retention diagram was observed on baking the column of poly-THF, poly-St, and St-2, a striking change was apparent with the column of ST-5 in Fig. 6. That is, a Z-shaped diagram before baking, characteristic of poly-St,

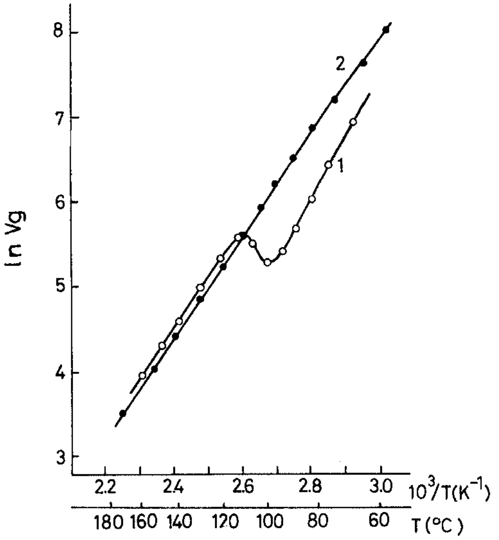

FIG. 6. Effect of baking on retention diagram of n-dodecane for a block copolymer ST-5: (1) before baking; (2) after baking.

changed to an almost linear diagram after baking, characteristic of poly-THF, suggesting that a phase inversion occurred during baking of the column. This is caused by the diffusion of the surface-active poly-THF segment to cover the surface. Thus, the solute molecule, which could not enter into the bulk phase because of the original poly-St-rich surface below its T_g, became free to pass through the poly-THF-rich surface of the melt after baking the column, to be forced to interact with the whole polymer segments in bulk. Similar results were obtained with STS-5 triblock copolymers, and with other solutes such as n-octane or n-hexanol.

Wettability

Contact angles θ of water droplets against cast film were measured, and cos θ was plotted against copolymer composition. The results in Fig. 7 show that wettability is not a linear function of copolymer composition. Poly-THF is wettable to water because it contains hydrophilic ether linkage. The wettability of THF-rich block copolymers such as ST-1 and STS-1 is similar to that of poly-St, and the wettability

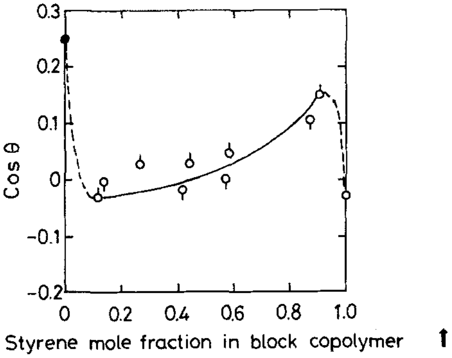

FIG. 7. Relationship between composition and wettability of block copolymers: (●) poly-THF; (○) poly-St; (♂) ST; (♀) STS.

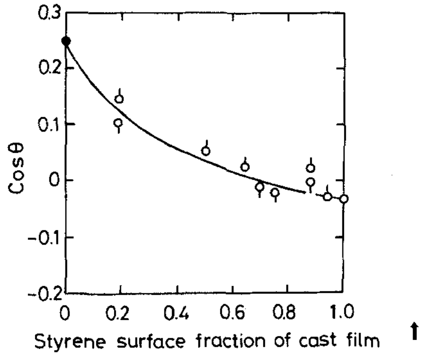

FIG. 8. Relationship between wettability and styrene surface fraction of cast films: (●) poly-THF; (○) poly-St; (♂) ST; (♀) STS.

of St-rich block copolymers such as St-5 and STS-5 is similar to that of poly-THF. This is explained by the facts that wettability is the reflection of the surface composition and that the surface composition of the block copolymer is different from the bulk composition as shown in Fig. 2.

A linear plot is obtained in Fig. 8, where contact angles are plotted against St surface fraction shown in Fig. 2. Thus wettability is determined by surface composition irrespective of the type of block copolymers, such as AB or ABA, and of morphologies such as fibril, sphere or lamellae. Surface composition is determined by the ease of crystallization, by phase separation, and by diffusion to the surface The size and structure of the domains is not important, because macroscopic surface properties such as wettability depend on the average surface composition and not on the small domain size which lies between 40 and 200 nm, as shown in Fig. 1.

The poly-THF segment is useful for hydrophilic modification of the polymers because it is surface-active and because it is hydrophilic. Surface modification by hydrophilic block copolymers is also reported by Litt [12]. The importance of block copolymer is claimed because domain structure seems necessary for the diffusion of surface-active segments. Further studies on surface modification of polymer A by using an AB block copolymer, where B is surface-active and also contains functional groups, are in progress.

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