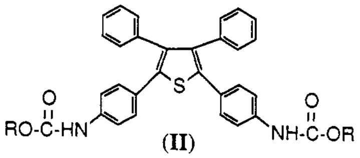

(II)

R = CH_3, IIa;

CH_2-CH_3, IIb.

Figure 2. Structure of II.

Urethane Polymers. Although a general synthetic route to urethane polymers is known,[4] the polyurethanes prepared in this study are novel and are obtained in quantitative yields. These polymers are of great interest since highly phenylated thiophene rings are incorporated in them. Because of this backbone the physical properties of these polyurethanes should differ substantially from those containing aliphatic chains and one or two aromatic ring(s) as in 4,4′-methylenebis(phenylisocyanate) (MDI) and tolylene diisocyanate (TDI). The polymerization of I at 115 °C in different solvents such as *N*,*N*-dimethylacetamide (DMAC), dimethyl sulfoxide (Me_2SO), and 2-methylpentanone (MIBK) has also been investigated and the results are given in Table I. Although the polymerization of I occurred in all three solvents, a 1/1 mixture of Me_2SO and MIBK was found to be the most ideal solvent to optimize the polymer synthesis. However, the reaction in MIBK produced low molecular weight polyurethanes. This is probably due to a limited solubility of the resulting polymer during the initial stage of the polymerization. The rate of polymerization in terms of inherent viscosity was measured during the polymerization of I with 1,4-butanediol, and the results are shown in Table I. The polymerization appeared to be complete within 5 min at 115 °C in the ideal solvent (1/1 mixture of Me_2SO and MIBK) since there was little or no change in the inherent viscosity values of the polymers between the periods of 2.0 and 7.0 h. Therefore, we conclude that the polymerization of I with aliphatic diols in an ideal solvent mixture, at 115 °C, could be completed within the first 2.0-h period.

The infrared spectrum of each polymer shows several characteristic stretching modes of vibrations due to N—H, C=O, and C—H bonds in the regions, 3390, 1710, and 2900 cm^{-1}, respectively. However, the most significant feature in the IR spectra of these polymers is the disappearance of $\nu N{=}C{=}O$ near 2300 cm^{-1}, which indicates the complete utility of this moiety in I during the polymerization. The inherent viscosity measurements and molecular weight determinations (see Table I) showed that the polyurethanes are low molecular weight species. Perhaps, the lower reactivity of I is responsible for the low molecular weights of the polyurethanes. However, our results are comparable to those of polyurethanes derived from sterically crowded diisocyanates.[4] All the polyurethanes prepared in this study melt to form a brownish mass in the temperature range around 200–220 °C. With the exception of broad resonances, the ^1H and ^{13}C NMR spectra of poly-EG, poly-DEG, and poly-BG are identical with those of model compounds IIa and IIb (see Experimental Section).

The solubility tests in various organic solvents have been conducted and the results are given in Table II. At room temperature, all the polyurethanes are highly soluble in DMAC, DMF, and THF. However, only two polymers, poly-DEG and poly-BG, are soluble in Me_2SO at elevated temperatures, and only poly-BG is highly soluble in chloroform. The urethane polymers prepared in our study are low molecular weight species and are highly phenylated. Considering these facts, it is not at all surprising that the polymers are highly soluble in many organic solvents. However, none of these polymers either dissolve or swell in benzene and acetone.

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Registry No. I, 107711-78-4; **I9**, 92996-46-8; **II9**, 107711-79-5; **IIb**, 105854-91-9; poly-EG (copolymer), 107711-85-3; poly-EG (SRU), 107711-80-8; poly-DEG (copolymer), 107711-86-4; poly-DEG (SRU), 107711-81-9; poly-BG (SRU), 107711-82-0; $COCl_2$, 75-44-5.

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Phase-Mixing Effect in Styrene–Butadiene Block Copolymers

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For a number of years, workers in this laboratory have studied the decrease in the glass transition temperatures of low molecular weight styrene microphases in phase-separated block copolymers below those of polystyrene homopolymers of comparable molecular weight both in styrene–dimethylsiloxane[1,2] and in styrene–butadiene block copolymers.[3,4] The glass transition temperature, T_g, of the styrene microphases in styrene–dimethylsiloxane block copolymers became equal to that of comparable molecular weight polystyrene homopolymers at a block molecular weight of about 1.8×10^4;[1,2] no effect of dimethylsiloxane block molecular weight on styrene (S) microphase T_g was found. In the case of styrene microphases in styrene–butadiene block copolymers, the T_g of the styrene microphases remained below that of polystyrene homopolymers of comparable molecular weight up to the highest molecular weight styrene block investigated, $M_n^s = 1.2 \times 10^5$;[4] the butadiene block molecular weight did not affect the

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styrene microphase T_g in these block copolymers. Data were obtained in all cases using both differential scanning calorimetry (DSC)[1,3,4] and either refractive index vs. temperature measurements[2,3] or dilatometry.[4] Studies of the heat capacity change at the glass transition of the styrene microphases indicated that many microphases with depressed T_g values had elevated values of the heat capacity change at the glass transition; this indicated that segments of the rubbery blocks, dimethylsiloxane in one case and butadiene in the other, were dissolved in the styrene microphases.[1,3] As already mentioned, neither the percent composition nor the number of blocks in the diblock and triblock copolymers investigated had any effect on the data observed. In the present work, we have found the approximate value of styrene block molecular weight in styrene–butadiene block copolymers at which the microphase T_g becomes equal to that of polystyrene homopolymer of comparable molecular weight.

Experimental Section

Materials. Eight high molecular weight styrene–butadiene diblock copolymers were examined in this work. Five samples, with M_n^s ranging from 8.8×10^4 to 1.86×10^5, M_w/M_n between 1.03 and 1.11, and 66–90 wt % styrene, were kindly supplied to us by J. DiCorleto and R. E. Cohen of the Massachusetts Institute of Technology. One of us (L.J.F.) synthesized three samples: $M_n^s = 3.5 \times 10^5$ to 7.1×10^5, $M_w/M_n = 1.05$–1.1, 74–77 wt % styrene. All styrene contents were obtained with high-resolution ^{1}H nuclear magnetic resonance, and the molecular weights and molecular weight distributions of the five lower molecular weight samples were obtained with size exclusion chromatography. The methods used have been described previously;[3,4] the block copolymer size-exclusion chromatography (SEC) data were analyzed with proper regard for the compositions of the copolymers.[4] The analysis of the three highest molecular weight segments was facilitated by the removal from the reactor of the first segment polymerized and its subsequent characterization via SEC.

Thermal Analysis. The DSC data were collected on a Perkin-Elmer DSC-4, at a heating rate of 10 K min^{-1} after cooling from 450 to 300 K at 10 K min^{-1} to erase previous thermal history effects. Details of the instrument calibration and data evaluation have been described previously.[4] Glass transition temperatures are defined as the points on the heat capacity–temperature curve at which half of the heat capacity change at the glass transition has taken place; the heat capacity change at the glass transition is measured between extrapolated base lines above and below the glass transition. If a tangent is drawn to the heat capacity–temperature curve at the glass transition tempreature, then the width of the glass transition region is defined as the temperature interval between the point at which this tangent intersects the high-temperature base line and the point at which this tangent intersects the low-temperature base line. The reasons for this definition have been discussed previously.[1] The dilatometry experiment[4] and the refractive index–temperature method[2] have also been described previously; in the present work, data were collected only on cooling.

Results and Discussion

Figure 1 shows the T_g vs. M_n^s data obtained with DSC. This figure includes previous data[4] for completeness; the previous data included samples with a weight percent of styrene as low as 27. The vertical lines in Figure 1 indicate the width of each glass transition. Two points on a single vertical line represent T_gs of two different samples that had the same M_n^s. This figure indicates that the S microphase T_g becomes equal to that of high molecular weight polystyrene when $M_n^s = 3.5 \times 10^5$ to 7.1×10^5. The width of the glass transition region remains greater than that of the homopolymers even at the highest M_n^s studied; the same phenomenon was observed in styrene–dimethylsiloxane block copolymers.[1]

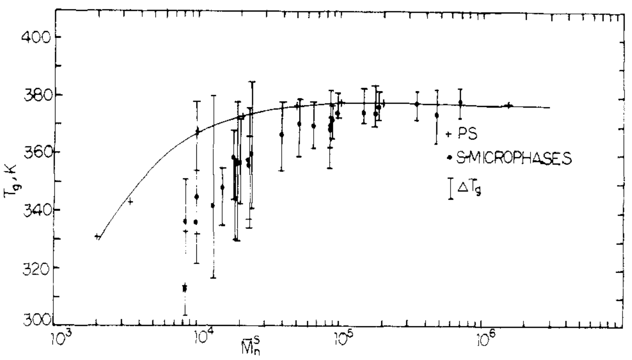

Figure 1. Glass transition temperature vs. number-average molecular weight of polystyrene homopolymer or styrene block in styrene–butadiene block copolymers as determined by DSC. The width of the glass transition range is shown by vertical lines.

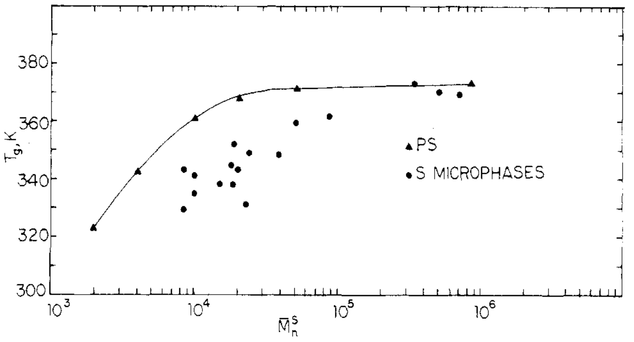

Figure 2. Glass transition temperature vs. number-average molecular weight of polystyrene homopolymer or styrene block in styrene–butadiene block copolymers as determined by dilatometry and by refractive index vs. temperature measurements.

Figure 2 shows the T_g vs. M_n^s collected for all present and previous samples both by refractive index–temperature measurements and by dilatometry. All glass transition regions were very small with these measurement techniques, as found in previous work.[2-4] Figure 2 indicates that the S microphase T_g may become equal to that of high molecular weight polystyrene at a molecular weight slightly above the highest molecular weight styrene block microphase investigated, 7.1×10^5.

Since the depression of the T_gs of styrene microphases made up of the lower molecular weight blocks in both styrene–dimethylsiloxane and styrene–butadiene block copolymers has been attributed to the mixing in of some rubbery segments and since butadiene segments mix in up to $M_n^s = (3.5\text{–}7.1) \times 10^5$ or even higher while dimethylsiloxane segments mix in only up to about $M_n^s \sim 1.8 \times 10^4$, this difference in M_n^s has been attributed to the difference in compatibility between polystyrene and polybutadiene vs. poly(dimethylsiloxane). The interaction parameter, χ, between polystyrene and polybutadiene is approximately 0.08,[5] while that between polystyrene and poly(dimethylsiloxane) is approximately 0.5.[6]

Let us note that all the styrene–butadiene block copolymers investigated, both in this work and in our earlier work,[4] were microphase separated and exhibited two T_gs, one of the styrene microphases and one of the butadiene microphases. Thus, the results on the styrene microphage T_g discussed here concern a change in phase mixing *within* the styrene microphases, not the onset of microphase separation.

In discussions of the onset of microphase separation in block copolymers, without consideration of phase mixing and its possible mechanism, the variable of prime importance appears to be χN, where N is the degree of polymerization of the block copolymer.[7] Krause[8] has argued that the mechanism of phase mixing involves the dissolution of whole block copolymer molecules into one or both of the microphases; a simple thermodynamic feasibility study of this process[8] also involved the variable χN, thus leading to the prediction that the values of $M_n{}^s$ at which the phase mixing should stop for two different rubbery segments into styrene microphases should be in the inverse ratio of the corresponding interaction parameters. The ratio of the interaction parameters for polystyrene with polybutadiene to that with poly(dimethylsiloxane) is 0.16, leading to the expectation that the $M_n{}^s$ at which phase mixing should stop in styrene–butadiene block copolymers is about 1.1×10^5. This does not happen, even within the large experimental error of these measurements. We would like to suggest that phase mixing is actually a different effect with respect to microphase separation and that its controlling variable may be $\chi^2 N$. If so, the expected values of $M_n{}^s$ at which phase mixing should stop will be the inverse ratio of the square of the ratio of the corresponding interaction parameters. In that case, the predicted value of $M_n{}^s$ at which phase mixing should cease in butadiene–styrene block copolymers is 7.0×10^5, in agreement with our observations.

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Registry No. (Styrene)(butadiene) (block copolymer), 106107-54-4.

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Depletion Layer of a Lyotropic Polymer Liquid Crystal at the Air–Solution Interface

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Scaling analyses have proved to be useful in understanding the statistical physics of solutions of nematically or otherwise confined semiflexible polymers.[1–4] Sometimes scaling theories are merely highly simplified versions of theories that are more quantitative and detailed (for a review see ref 3; in addition compare ref 1 with ref 5, 6, and 7, and ref 2 with ref 8 and 9, ref 4 with ref 14). Often scaling ideas are the only ones available because it seems difficult to make headway in some complicated problem. For instance, it is not hard to derive the asymptotic concentration dependence of the elastic constants of polymer nematics,[4,13,14] but a precise theory is still lacking. In a similar vein this note addresses the depletion of nematic polymer chains near an interface by scaling methods only.

First, we look at a nematic solution of slender, hard rods of a bulk density ρ_r, diameter D, and length L in the second virial approximation.[10] For scaling purposes, it is enough to approximate the orientational distribution function of a test rod by a Gaussian ($\alpha \gg 1$)

$$f(\theta) \sim \tfrac{1}{2}\alpha e^{-(1/2)\alpha\theta^2} \qquad (0 \leq \theta \leq \tfrac{1}{2}\pi)$$

$$f(\theta) \sim \tfrac{1}{2}\alpha e^{-(1/2)\alpha(\pi-\theta)^2} \qquad (\tfrac{1}{2}\pi \leq \theta < \pi) \tag{1}$$

with $\int_0^\pi f(\theta) \sin \theta \, d\theta = 1$ to leading order. The angle θ is specified with respect to the director. Then, one can derive the relation[10] between the sharpness of the distribution and the scaled number density $c_r \equiv b\rho_r$ with the rod–rod excluded volume $b = (\pi/4)L^2D$

$$\alpha \simeq c_r{}^2 \simeq L^4D^2\rho_r{}^2 \tag{2}$$

Here and further on we omit numerical coefficients, all of which are of order unity.

Let us assume the director is oriented parallel to the air–solution interface. In solution each rod is allowed orientational freedom only within a cone of approximate angle $\alpha^{-1/2}$ as can be seen from eq 1, but its freedom becomes yet more severely restricted once its center of mass M approaches the interface. Auvray has discussed this effect for a variety of problems.[11] When M is a distance d from the surface, the cone's angle is reduced to dL^{-1} provided d is small enough. Hence, the decrease in confinement entropy per rod is given by[18]

$$\Delta S \simeq -k_B \ln \left(\frac{L}{d\alpha^{1/2}} \right) \tag{3}$$

where k_B is the Boltzmann constant. Similarly, there is a decrease in the free energy per rod because the excluded volume is diminished[18]

$$\Delta F_b \simeq k_B T \bar{c}_r(d) \left(\frac{d^2\alpha^{1/2}}{L^2} - \alpha^{-1/2} \right) \tag{4}$$

where T is the temperature and $\bar{c}_r(d)$ is a representative scaled number density for layer thickness d.

Equations 3 and 4 determine the depletion $\rho_r(d)$ of rods near the surface

$$\rho_r(d) \simeq \rho_r \exp\left(-\frac{\Delta F_b}{k_B T} + \frac{\Delta S}{k_B} \right) \tag{5}$$

Note that $\rho_r(0) \rightarrow 0$ as it must and $\rho_r(d) \ll \rho_r$ for $d = \eta L \alpha^{-1/2}$, with η a number somewhat smaller than unity.[19] Accordingly, the thickness d_r of the depletion layer for nematic rods is

$$d_r \simeq L\alpha^{-1/2} \tag{6}$$

Thus, eq 2 and 6 yield the increase in the surface tension

$$\Delta\tau \simeq k_B T d_r \rho_r \simeq \frac{k_B T}{LD} \tag{7}$$

This result, correct to the leading order, does not depend on the concentration, and is in agreement with detailed calculations by Doi and Kuzuu.[12]

The extension of this result to the case of long semiflexible polymers is straightforward. Another length scale, the deflection length λ, enters the description.[1,2] The nematic field exerted by the surrounding macromolecules on a test chain causes it to be deflected toward the director on a scale λ on the average. It is connected to the persistence length P via[2,3]

$$\lambda = P/\alpha \tag{8}$$

A scaling analysis is fruitful when the chains are long enough—the contour length L is much longer than λ. As long as the connectedness of the chains is unimportant we