thiocyanates, and to a lesser extent, iodides slightly raise the cloud point. These results, to be discussed in more detail elsewhere, resemble those reported for the comb polymethacrylates[20] and are qualitatively similar to the behavior found in salt solutions of polymers or nonionic surfactants that are known to solubilize in water by hydrogen bonding, e.g., polymers with oxyethylene moieties.[27–29]

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Surface and Bulk Phase Separation in Block Copolymers and Their Blends. Polysulfone/Polysiloxane

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ABSTRACT: The relationship between bulk phase separation and surface segregation was elucidated in a series of polysulfone/polysiloxane alternating block copolymers and their blends with polysulfone. X-ray photoelectron spectroscopy (XPS) with angular dependence was used to obtain the compositional information from the top ~6 nm of the surfaces, and transmission electron microscopy (TEM) was used to characterize the bulk morphologies. In general, solvent-cast neat block copolymers had a layer (>6 nm) at the surface enriched in siloxane and the bulk had 10–50-nm microphase-separated domain structures. In the case of blends, siloxane surface enrichment was relatively high, even at bulk concentrations as low as 0.05% w/w siloxane. The surface siloxane concentration showed a rapid increase between 1 and 10% w/w bulk siloxane concentration, corresponding to the appearance of 0.1–10-μm diameter *macro*phases of block copolymer in the bulk. The blend surfaces attained surface compositions equivalent to pure copolymer at bulk concentrations above 10% siloxane, where phase inversion occurred in the bulk. XPS results indicated that the polysiloxane block length controlled the level of surface enrichment of siloxane, while the polysulfone block length influenced the *gradient* of surface composition, or the degree of phase mixing.

Introduction

Block or segmented copolymers have long sequences (blocks) of one chemical structure type of repeat unit, A, joined at one or both ends to long sequences of an another type, B. The dissimilar nature of the two blocks combined with the fact that they are chemically linked to each other manifests in a variety of surface and bulk properties quite different from those of the corresponding homopolymeric systems.[1] An attractive feature of these copolymers is their flexible molecular design parameters that can be controlled to tailor systems for specific applications. Some of those parameters are the chemical nature of the blocks, the architecture of the copolymer, diblock, triblock, or multi-

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block, and the length (molecular weight) of the blocks—individually and in relation to one another. The surface properties of block copolymers originate from the difference in the surface free energies of the components blocks. Gibbs[2] showed that in a multicomponent system, components of lower surface free energy would tend to enrich the surface of a condensed phase. Thus in a phase-separated block copolymer, segments of lower surface free energy preferentially segregate to the air or vacuum surface. The unique bulk properties of block copolymers also arise from their microphase-separated morphology. Due to incompatibility (above a critical block size) each block tends to generate separate domains that are restricted to submicroscopic sizes (5–100 nm) by the chemical link between the blocks. The morphological configuration depends on the parameters mentioned above; many unique microphase structures are possible, giving rise to a variety of properties. Kraton[3] is one of the earliest and most successful commercial products to exploit block copolymer multiphase behavior.

The amphipathic nature of block copolymers can also be utilized by blending them with homopolymers to obtain numerous desirable properties.[4] When added in small amounts to a blend of two incompatible homopolymers corresponding to the blocks, the copolymer can provide stability between the separated phases.[5] On the other hand, small amounts of homopolymers can diffuse into the respective microphases of the original block copolymer.[6] The addition of an adequate amount of a block copolymer to a homopolymer is known to be capable of increasing the toughness of the latter.[7,8] Surface segregation occurs at very low concentrations, thereby changing the surface properties without significant change in the bulk. This has been found to be useful in such practical applications as improvement of adhesive properties,[9] enhancement of soil release capabilities in modern textiles,[10] stabilization of urethane foams,[11] and reduction of the friction coefficient.[12]

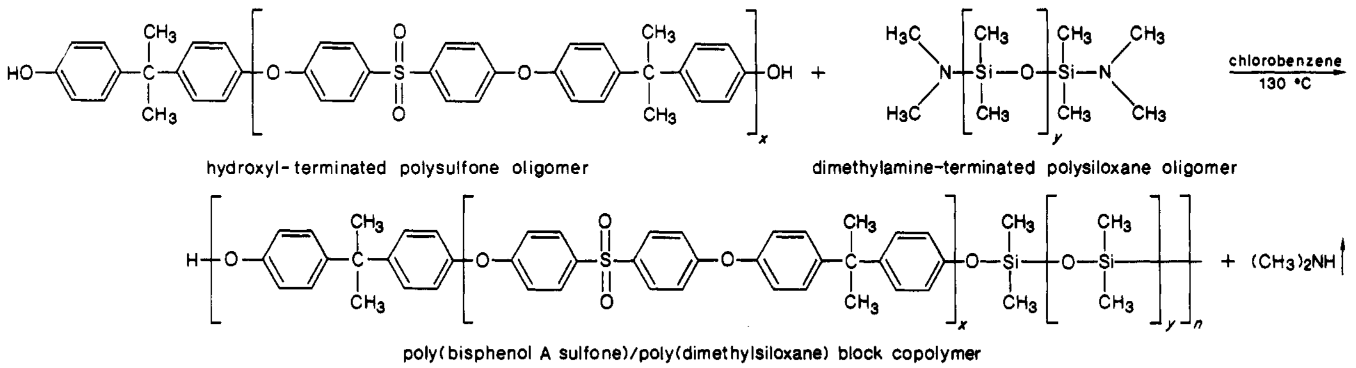
Much attention has been given in the last 15 years or so to the study of microphase separation in block copolymers,[1] since it is one of the most important factors imparting the physical and mechanical properties unique to those systems. More recently, a greater interest has been generated in morphological studies of binary or ternary systems containing block copolymers with corresponding homopolymers[6,13-21]—mainly due to their applications in toughening of glassy polymers without adversely affecting the modulus and the softening temperature. The phenomenon of microscopic heterogeneity in block copolymers is reasonably well understood experimentally, and it continues to be clarified by thermodynamic and statistical calculations.[22] The situation in the blends is more complex: the microstructure can range from highly miscible, one-phase systems to a simple microheterogeneous structure persisting throughout the sample, to a variety of isolated or bicontinuous supramolecular features which may themselves have microphases.

Relatively few systematic studies have been done on block copolymer surfaces. Several earlier efforts involved measurements of surface tensions in solutions or melts[23-28] and contact angles on solids[12,26-35] to understand the chemical nature of the surfaces. Unambiguous quantitative interpretations from such measurements are rather difficult, especially when lateral inhomogeneities and roughness are present. Also the information comes only from the first atom layer of the surface. X-ray photoelectron spectroscopy (XPS) or ESCA (electron spectroscopy for chemical analysis) made it possible to obtain direct chemical information on the top few molecular layers of polymeric[36] surfaces. Studies on pure block copolymers have shown that the surface may differ from the bulk in chemical composition and morphology. Clark, Peeling, and O'Malley[37] studied polystyrene (PS)/poly(dimethylsiloxane) (PDMS) diblock copolymers with the help of XPS and contact angles. They showed that the surfaces of those polymers consisted of essentially pure siloxane overlayer of thickness varying from 13 to 40 Å in films cast from cyclohexane (preferential to PDMS) and styrene (preferential to PS), respectively. This siloxane overlayer surface morphology differed considerably from the spherical microdomain structure of the bulk as observed by Saam et al.[38] in the same polymers. O'Malley and Thomas used angular-dependent XPS to determine surface compositions and topographies of poly(ethylene oxide) (PEO)/PS diblock[39] and triblock[40] copolymers. Studies on a number of copolymers having different compositions determined that the PS concentration at the air–polymer interface was substantially higher than that in the bulk. From the angular-dependent data, they were able to deduce that the surface morphology consisted of cylindrical PS domains slightly elevated above PEO domains. McGrath et al.[41] studied polysulfone (PSF)/poly(bisphenol A carbonate) (PBAC) and PBAC/PDMS block copolymers. XPS results in each case showed that the lower surface energy component dominated the surface, i.e., PBAC in PSF/PBAC and PDMS in PBAC/PDMS copolymers. Riffle's[42] study on a series of PBAC/PDMS block copolymers indicated that the block length of the siloxane was an important factor in determining the extent of surface segregation. Kugo and co-workers[43,44] combined contact angle measurements, XPS, and replication electron microscopy (REM) to elucidate the surface composition and morphology of triblock copolymers of poly(ϵ-*N*-(benzylcarbonyl)-L-lysine)/polybutadiene (PBD) and poly(α-methyl-D,L-glutamate)/PBD. The lower surface energy component PBD was found to dominate the surface in both systems. With the help of contact angle measurements and REM, they proposed a surface model consisting of elevated, lens-shaped PBD domains. More recently, Schmitt et al.[45] have showed surface enrichment by PDMS in PBAC/PDMS block copolymers with varying compositions. Using XPS and ion scattering spectroscopy (ISS), they concluded that the morphology of the top 50 Å of the surface consisted of discrete regions of PDMS and PBAC oriented perpendicular to the surface.

Clearly, there is no general agreement about either the topography or separated microdomain structure of block copolymer surfaces. So far, the experimental means used to draw conclusions about these important morphological aspects each have deficiencies. The few copolymers studied vary in chemistry. The conditions and kinetics of the formation of the film surfaces usually have not been specified adequately. Our preliminary studies of the kinetics of surface segregation lead us to believe that most work to date has involved nonequilibrium surfaces (days to weeks in the presence of solvent are required for equilibrium). In this work a fixed time was selected for the specimen preparation steps, so that kinetic factors were constant.

Almost no work of this kind has been reported on blends of copolymers with homopolymers. Our previous XPS studies of blends of block copolymers with homopolymers (corresponding to the higher surface energy block) indicate the presence of a "critical" concentration. In blends of PBAC/PDMS in PBAC,[42,46] a definite break was observed at about 1% siloxane by weight in bulk; the surface com-

Scheme I



position of siloxane "jumped" to a value typical of the pure block copolymer. Similar behavior was observed by Sha'aban et al.[47] in the system polyurethane/PDMS blended with Estane, a commercial polyurethane. XPS analysis of solvent-cast films revealed a transition concentration at a bulk siloxane of about 1% where the surface siloxane concentration increased rapidly, eventually to level off as the surface characteristics of the neat block copolymer were approached.

In order for the surface phenomenon in multicomponent, multiphase systems to be understood, a important question is how do the surface composition and morphology relate to their counterparts in the bulk? In the present work, we have studied the surface and bulk phase separation in several polysulfone/polysiloxane block copolymers of different molecular weights, as well as their blends with homopolysulfone. In an attempt to gain further insight, XPS(θ) was used to obtain the chemical composition gradients at the surfaces. Transmission electron microscopy (TEM) was used to elucidate the microstructural features of the bulk.

It was obvious from the size of the bulk domains that the resolution of an ordinary SEM is insufficient by 1 or 2 orders of magnitude to resolve such domains at the surface. We have made preliminary attempts at direct resolution of surface topography with ultrahigh resolution SEM in the scanning transmission electron microscope (STEM). This field is itself a suitable subject for extensive, basic research. Our data base is still small and not adequately reproducible at this time. However, representative specimens from the XPS studies reported herein were examined at an independent laboratory. All films were found to "appear essentially featureless at the maximum magnification of our instrument (200000×)".[48]

Experimental Section

Materials. Perfectly alternating poly(bisphenol A sulfone)/poly(dimethylsiloxane) was prepared in dry refluxing chlorobenzene, as originally described by Noshay,[8a] by using the silylamine–hydroxyl condensation reaction depicted in Scheme I. Both oligomers used in this reaction were also synthesized in our laboratories. The hydroxyl-terminated poly(bisphenol A sulfone) oligomers were prepared by reaction of excess bisphenol A with bis(4-chlorophenyl)sulfone by using *N*-methylpyrrolidone/toluene as solvent and potassium carbonate as the base. The dimethylamino-terminated poly(dimethylsiloxane) oligomers were prepared by the tetramethylammonium siloxanolate base catalyzed equilibration of (dimethylamino)disiloxane with the cyclic siloxane tetramer. Number-average molecular weights of the resulting oligomers were characterized by potentiometric titration of their respective end groups. The composition of the block copolymers was easily controlled since the two preformed oligomers can only condense with each other. Hence, the overall ratio of sulfone and siloxane incorporated in the block copolymer was essentially the same as that of the molecular weights of the oligomers charged in the reaction, and this was confirmed by NMR. The copolymers were coagulated in stirred methanol followed by filtration and reprecipitation from chloroform and vacuum drying at 70 °C to a constant weight. Table I summarizes the relevant characterization data of the copolymers, all of which formed clear, tough films when cast from chloroform. An obvious concern was to check for any oligomeric contamination, which would be critical for the subsequent surface analysis. For this, gel permeation chromatography was utilized. This technique showed unimodal distributions, clearly indicating the absence of any unreacted oligomeric species. More detailed synthetic and characterization information can be obtained elsewhere.[49]

Table I
Characterization Data

polym	polysulfone block length *M*, g/mol	polysiloxane lock length *M*, g/mol	wt % siloxane	$CHCl_3$ [η], dL/g (25 °C)
PSFPSX-1	4900	12800	72	0.55
PSFPSX-2	9700	12800	57	1.27
PSFPSX-3	4900	4400	47	0.55

The homopolysulfone was Udel from Amoco Performance Products, Bound Brook, NJ, and had a molar mass of about 25 000 daltons. A poly(dimethylsiloxane) gum elastomer network reference material was obtained from Thoratec Laboratories Corporation, Berkeley, CA, in the form of silicone rubber sheets.

Methods. Sample Preparation. The samples of the neat copolymers and their blends with homopolysulfone (0.1–50% w/w) were prepared by casting from dilute (~0.05 g/mL) chloroform solutions. For XPS, films of approximately 0.5-mm thickness were cast on scrupulously cleaned stainless steel strips of dimensions suitable for direct attachment to the spectrometer probe. Atmospheric solvent evaporation for 2 h was followed by vacuum drying for 30 min. The samples were analyzed immediately to minimize atmospheric contamination. Absence of chlorine peaks in the spectra was considered to be an indicator of complete evaporation of the solvent.

For TEM, thin films (~0.1 μm) were prepared by spreading a drop of the solution onto a water surface with subsequent solvent evaporation. The dried films were then lifted off onto TEM grids.

Instrumentation. A KRATOS XSAM 800 X-ray photoelectron spectrometer equipped with a hemispherical electron energy analyzer and a Mg Kα X-ray source operated at 15 kV and 20 mA was used for the surface chemical analyses. The pressure in the sample chamber was maintained at $\sim 10^{-9}$ Torr during spectra collection. The analyzer was operated in the fixed retarding ratio (FRR) mode. Angle-dependent studies were done by rotating the circular probe rod. The depth of analysis decreases with the angle between the analyzer slit and the sample plane.[50] Angles ranging from 10° to 90° were used corresponding approximately to sampling depths ranging from 10 to 60 Å.

A JEOL Model-100C electron microscope was used at 80 kV for the TEM work.

XPS Line-Shape Analysis. For quantitative interpretation of XPS, the signal intensities were converted to weight percentage of the two components, i.e., siloxane and sulfone, using the following steps. First, the atomic ratio of carbon to silicon was calculated from the experimental C_{1s} and Si_{2s} signal intensities, from the basic principles of XPS[51] using published values of photoelectron cross-sections[52] and mean free paths.[53] With the

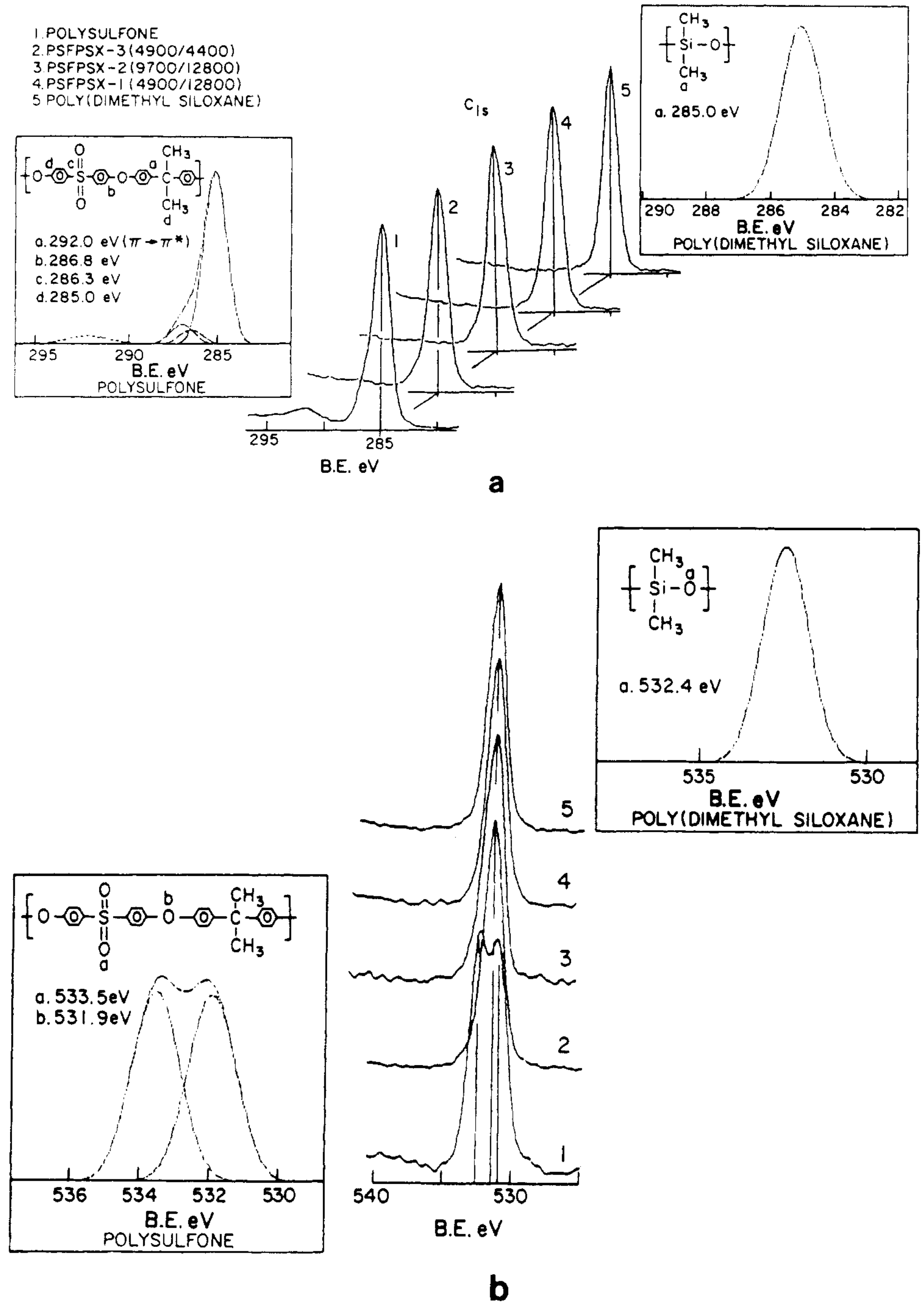


Figure 1. XPS spectra from the block copolymers as compared to homopolymers: (a) carbon 1s spectra and (b) oxygen 1s spectra.

knowledge of the C/Si ratio in a siloxane repeating unit (2.0 from reference standard material), the number of carbon atoms, and the molecular weight of each of the siloxane and sulfone repeating units, the observed C/Si ratio was then converted into weight percent siloxane at the surface. Replicate specimens always were reproducible to better than 5%. Repeat measurement on the same specimen were even more precise. This can be appreciated visually from the consistency of the resulting plots, each of which is comprised of two dozen independent measurements.

Results and Discussion

Neat Block Copolymers. Figure 1 shows the C_{1s} and the O_{1s} spectra collected at normal exit angle from the two homopolymers and each block copolymer. The boxes in Figure 1 depict the curve-fit C_{1s} and the O_{1s} peaks of the homopolymers. Assignments of the component peaks are labeled on the polymer structure. Full width at half-maximum (FWHM) of 1.5 and 1.6 eV were used for curve-fitting the C_{1s} and O_{1s}, respectively. The C_{1s} spectrum of homopolysulfone is composed of four components located at 285.0 eV, due to C–C; 286.3 eV, due to C–S; 286.8 eV, due to C–O; and 292.0 eV, due to $\pi \rightarrow \pi^*$ transitions. On the other hand, the C_{1s} spectrum from pure poly(dimethylsiloxane) is a single, symmetrical C–C peak (FWHM of 1.5 eV) at 285.0 eV. The O_{1s} spectrum from homopolysulfone is comprised of two overlapping peaks of equal intensity, one at 531.9 eV due to S═O═S and the other at 533.5 eV due to C–O. The O_{1s} spectrum from poly(dimethylsiloxane) is a single Si–O–Si peak (FWHM of 1.6 eV) at 532.4 eV.

It can be seen that the spectra from the block copolymers resemble closely those from pure poly(dimethylsiloxane). The narrow main C_{1s} peaks and the absence of $\pi \rightarrow \pi^*$ shake-up satellites at 292.0 eV indicate the dominance of siloxane at the surface. In the case of the O_{1s} level, the block copolymer peak position and width are the same as those from the poly(dimethylsiloxane). The

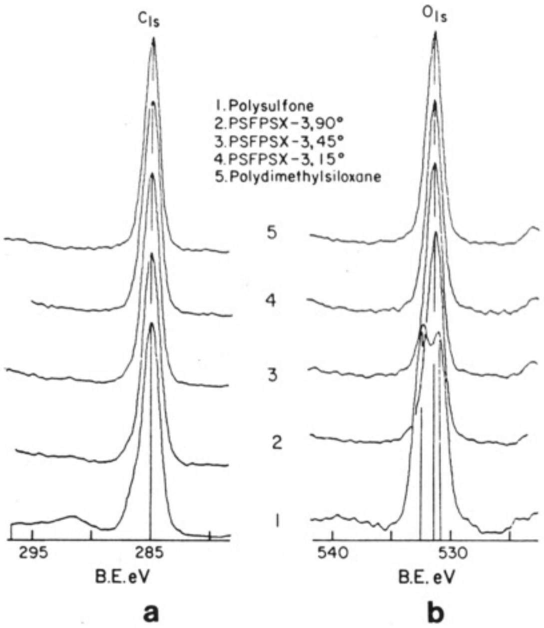


Figure 2. XPS spectra illustrating angle-dependent behavior of PSFPSX-3 as compared with that of homopolymers: (a) carbon 1s spectra and (b) oxygen 1s spectra.

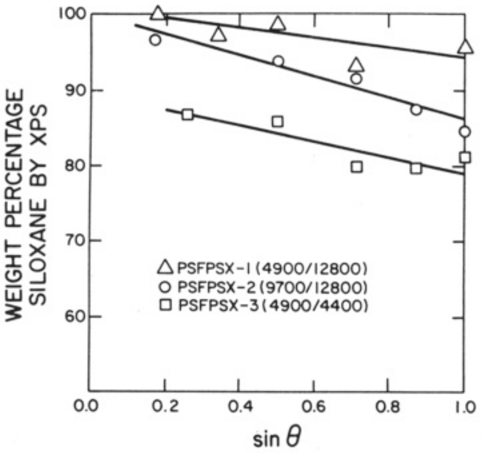


Figure 3. Angle-dependent surface behavior of block copolymers.

polysulfone peaks at 531.9 and 533.5 eV are not visible. A more quantitative analysis can be made by comparison of the FWHM's. For example, the FWHM of the polysulfone O_{1s} peak is 3.1 eV, while all peaks from the block copolymers were found to be 1.6 eV, illustrating that the signals came predominantly from the siloxane component. Figure 2 shows the angle-dependent C_{1s} and O_{1s} spectra from PSFPSX-3. The O_{1s} peaks are very similar to that from poly(dimethylsiloxane), each at 532.4 eV with FWHM of 1.6 eV, regardless of the electron exit angle. A slight variation can be observed in the C_{1s} peak as the angle is changed. At $\theta = 90°$, a small shake-up satellite and asymmetry on the left side of the main peak signify some mixing of polysulfone, while at $\theta = 10°$, both effects vanish completely.

Figure 3 depicts the surface concentration gradient in each block copolymer. The higher siloxane content in a copolymer always gives a higher surface siloxane composition. Extrapolation of the lines to zero depth indicates that the higher siloxane molecular weight (12 800) produces one complete monolayer coverage. The subsurfaces consist of a siloxane-rich layer of decreasing siloxane content with depth, but the siloxane concentration is at least 30% higher in the top, ca. 6 nm, than in the bulk. The siloxane block size has a secondary effect upon the degree of segregation and the subsurface gradient. There may be separated microphases at the surface of the PSFPSX-3 and in the subsurface of PSFPSX-1 and PSFPSX-2. However, we are unable to obtain reproducible evidence for this by scanning transmission electron microscopy.

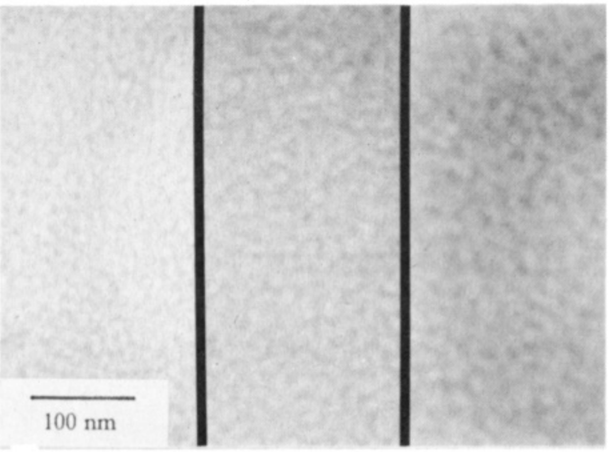


Figure 4. TEM photomicrographs of neat block copolymers (left) PSFPSX-3, (middle) PSFPSX-1, and (right) PSFPSX-2.

The slope of the curves is a measure of the change in compositional heterogeneity versus depth, and provides an another level of information. The relatively small gradients for all neat copolymers show that each has a siloxane-rich overlayer that is thick with respect to the XPS analysis depth. Curves 1 and 3 have nearly identical gradients, whereas the slope of curve 2 is higher. This can be interpreted in terms of the block lengths of the copolymers. PSFPSX-1 and PSFPSX-3 have the same sulfone block lengths, while PSFPSX-2 has a longer sulfone block. This implies that the length of the sulfone block plays a role in controlling the compositional gradient of the surface layer.

Figure 4 shows TEM photomicrographs of the three copolymers, depicting their bulk morphology. Although no staining was used, there appear spherical microdomain structures ranging between 100 and 500 Å in diameter. Note that the size of the domains increases with increasing block length.

Gaines[54] suggested that the thermodynamic criterion of liquid spreading should apply in block copolymer systems to explain their surface morphologies. The surface free energy of poly(dimethylsiloxane) is at least 10 dyn/cm lower than for most other polymers, and the interfacial tensions between polymers rarely exceed this value.[55,56] Thus, Gaines pointed out that siloxane would almost always form an overlayer in a block copolymer where it is one of the components, which is what has been observed by Clark et al.[37] Gaines showed that a criterion based on differences in surface energy applied to other cases such as poly(propylene oxide)/poly(ethylene oxide), for the observed overlayer type of morphology,[25] and poly(ethylene oxide)/poly(styrene), for the isolated domain type of morphology.[39,40] In our system the difference in solubility parameters is about 3.0, so Gaines' overlayer model should apply. However, the XPS(θ) results indicate that both relative and absolute block sizes determine the extent of siloxane enrichment of the overlayer. For siloxane block MW 12 800, the overlayer is 100% siloxane but still is only one monolayer thick. The top monolayer contains at least 10% sulfone in the copolymer with MW 4400 siloxane blocks.

Blends of Block Copolymers with Homopolymers. The quantitative results in Figure 5 on blends of

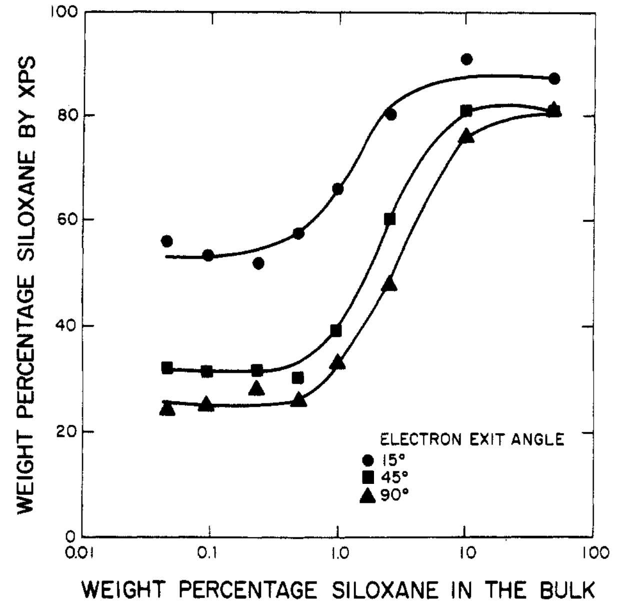


Figure 5. Surface behavior of PSFPSX-3/homopolysulfone blends.

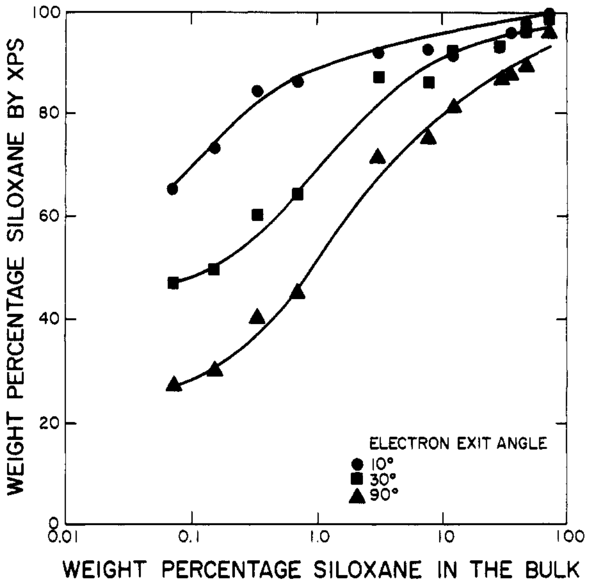


Figure 6. Surface behavior of PSFPSX-1/homopolysulfone blends.

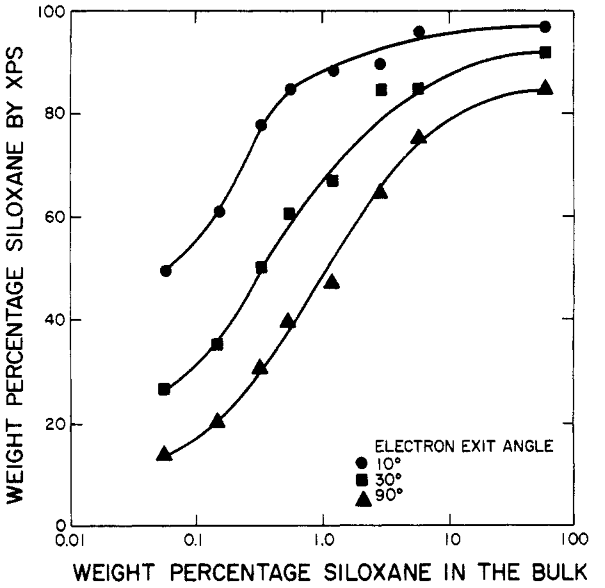


Figure 7. Surface behavior of PSFPSX-2/homopolysulfone blends.

PSFPSX-3 with homopolysulfone show the weight percent surface siloxane as detected by XPS plotted against the known weight percent siloxane in the bulk. Spectra were collected at three electron exit angles, and the differences between the curves obtained from each angle signify the extent to which concentration changes occur in the top 60 Å or so. Above 10% siloxane in the bulk, the three curves are close to each other, implying that the surface region is a relatively homogeneous overlayer, enriched in siloxane by a factor of about 1.8 relative to the block copolymer composition. In other words, the XPS(θ) results on blends of greater than 10% bulk siloxane are very similar to those obtained on the pure copolymer. At concentrations below about 0.5% bulk siloxane, the surface composition seems to be independent of the bulk value, although there is still a considerable extent of surface segregation (55% siloxane in the top 15 Å). The variation of surface percent siloxane with angle shows that the siloxane-rich layer has a pronounced compositional gradient within the XPS sampling depth. At bulk concentrations between 1 and 10% siloxane, there is a transition between the two types of overlayers, with an accompanying rapid rise in surface siloxane concentration.

The results of XPS(θ) analysis on PSFPSX-1 copolymer blended with polysulfone are shown in Figure 6. By comparison of Figures 5 and 6, it is clear that the extent of surface segregation of siloxane at any given bulk concentration is much greater for PSFPSX-1—a manifestation of the longer siloxane blocks. Also, the segregating copolymer molecule is of higher siloxane percentage. A low-concentration plateau is not evident even at 0.05% siloxane in the bulk. The XPS results from blends of PSFPSX-2 with the homopolysulfone are depicted on the Figure 7. The curves show the same general shape as for the other two copolymers. Comparison of Figures 6 and 7 reveals that at any fixed bulk composition, the surface siloxane concentration is lower in the latter. This correlates with the increased length of the sulfone blocks (siloxane blocks remaining the same) combined with the effect of lower siloxane content in the segregating species. Considering all three copolymer blends, it is clear that all surfaces are preferentially enriched by siloxane. At low bulk concentrations, siloxane surface concentrations are enhanced by orders of magnitude. Although the three plots are generally "S"-shaped, the slope and position of each curve is characteristic of the respective copolymer. This "signature" appears to related to block sizes in a reasonable manner.

Figure 8 displays the XPS data from the PSFPSX-1 blends as a function of electron take-off angle. At bulk siloxane concentrations of 0.7% or lower, the curves are slightly convex, which is characteristic of thin (<3 nm) siloxane-rich overlayers. Also, the values of surface and subsurface siloxane concentration are indicative of considerable phase mixing with sulfone. At bulk siloxane concentrations of 3% and greater, the curves are slightly concave. A thicker siloxane-rich overlayer or separate siloxane microphases in the subsurface could explain this change in the shape of the curves. Above 12% siloxane in the bulk, there is less than 10% phase mixing within the XPS sampling depth. Between 3% and 12% bulk siloxane, 10% phase mixing appears in the surface and more than 20% in the subsurface.

A variety of structures were observed by TEM on thin, solvent-cast films of the blends. Five cases were selected, from which generalizations can be made. Two repre-

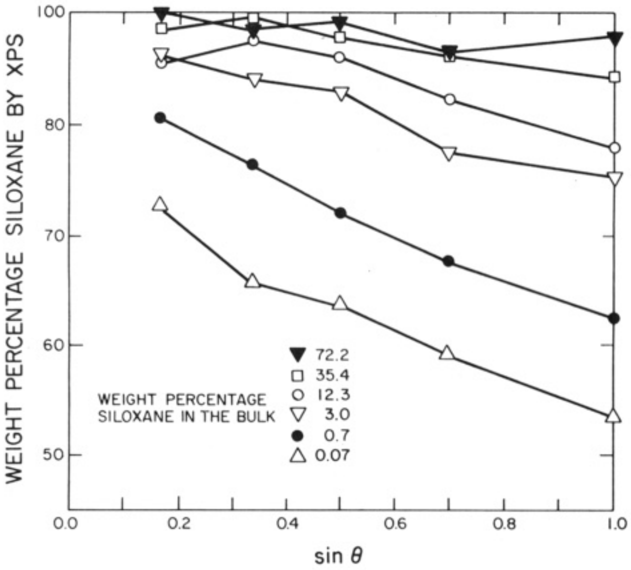


Figure 8. Angle-dependent surface behavior of PSFPSX-1/homopolysulfone blends.

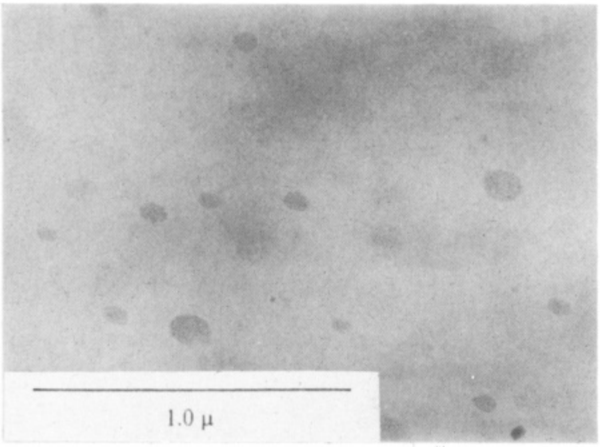


Figure 9. TEM photomicrograph of 4.5% bulk siloxane blend of PSFPSX-3 with homopolysulfone.

sentative PSFPSX-3 samples, 0.05% and 4.5% bulk siloxane, were characterized. At 0.05% siloxane, the blend was found to be homogeneous, signifying that the two components are miscible at that concentration. Figure 9 shows the photomicrograph of the bulk at 4.5% siloxane, a composition at which the surface siloxane concentration measured by XPS rapidly increases with small increase in bulk siloxane. Here, the block copolymer forms domains, about 0.1 μm in diameter, in a matrix of homopolymer. These structures are *macro*phases, and they contain the inherent microdomain structure characteristic of neat copolymer. TEM analysis of three PSFPSX-1 blends completes the characterization of the phase behavior. Figure 10 shows a blend of 3% siloxane, where a few *macro*phases of block copolymer are visible. Figure 11 shows the phases in a 7.5% blend, demonstrating the simultaneous existence of continuous and microheterogeneous copolymer phases (a hint that this is a nonequilibrium film). At higher copolymer concentrations, there is a phase inversion. PSFPSX-1 copolymer is the continuous phase and homopolysulfone forms large, dispersed phases. Figure 12 is the photomicrograph of a 45.5% siloxane blend. Now the block copolymer is the continuous phase with homopolymer macrophases dispersed in it. Each macrodomain contains smaller domains of block copolymer, which in turn, are composed of microdomains of siloxane and sulfone.

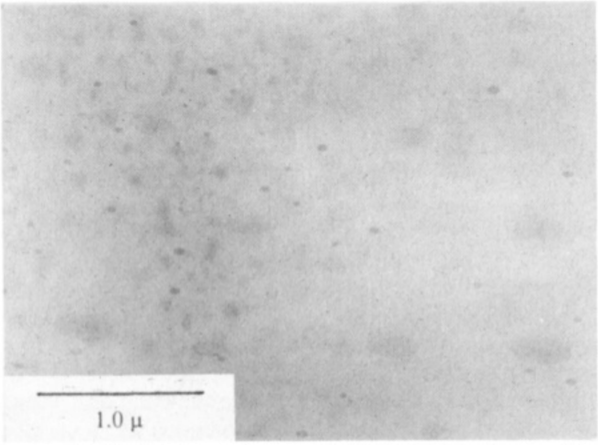


Figure 10. TEM photomicrograph of 3.0% bulk siloxane blend of PSFPSX-1 with homopolysulfone.

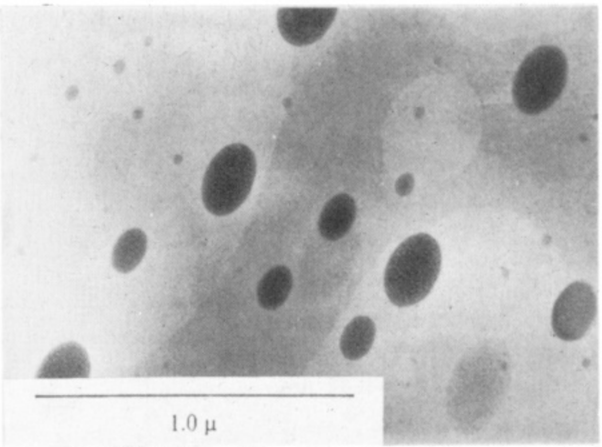


Figure 11. TEM photomicrograph of 7.5% bulk siloxane blend of PSFPSX-1 with homopolysulfone.

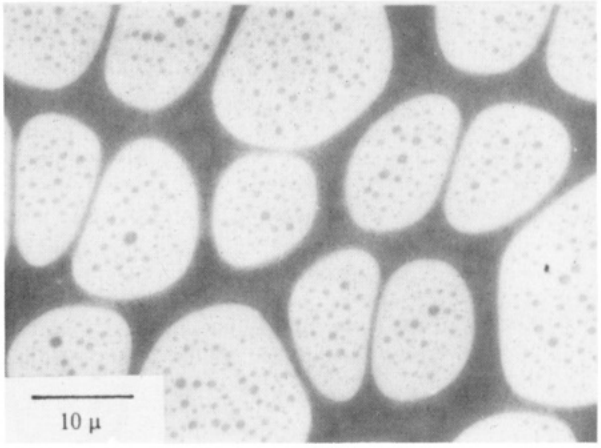


Figure 12. TEM photomicrograph of 45.5% bulk siloxane blend of PSFPSX-1 with homopolysulfone.

Summary and Conclusions

Relationships have been elucidated between microphase separation in the bulk and siloxane surface segregation in a series of alternating sulfone/siloxane block copolymers and blends with polysulfone. The neat copolymers form spherical domains in the bulk. Microphase size ranges from ca. 10 to 40 nm and varies according to block size. The surfaces of the neat copolymers are an essentially homogeneous, ca. 5-nm-thick overlayers enriched in siloxane. The slight gradients of overlayer composition (or degree of phase mixing) depend on the block lengths. A siloxane MW between 4400 and 12800 is required to form a complete siloxane monolayer.

For blends of copolymers with polysulfone, very high levels of surface segregation of siloxane (>50%) are displayed even at bulk concentrations below 0.1%. Upon increasing the bulk siloxane content to about 1%, surface siloxane concentration shows a sudden, rapid increase to values typical of the pure block copolymers. At equivalent siloxane content in the bulk, longer siloxane blocks result in enhancement of surface segregation. Macrophase separation of the block copolymer from the homopolymer is first observable by TEM at concentrations corresponding to the rapid rise in surface siloxane content. The copolymer macrophases are composed of microdomain structures similar to the pure block copolymers. Diffusion of these macrophases to the surface could explain the rapid increase in surface siloxane composition to the level of pure copolymer. Phase inversion occurs between 15 and 30% bulk siloxane; the block copolymer becomes the continuous phase. Very large, dispersed homopolymer phases contain macrophases with microphase-separated copolymer within them.

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Registry No. Udel, 54847-90-4; (bis(4-chlorophenyl)sulfone)(bisphenol A)(octylmethylcyclotetrasiloxane) (block copolymer), 114838-45-8.

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