for 24 h to afford 0.862 g (96%) of **22a** as a coarse, yellow powder: $[\eta]$ = 5.25 dL/g (25 °C; di-*m*-cresyl phosphate/*m*-cresol, 0.5 mol % ratio). Anal. Calcd for $C_{66}H_{42}N_2O_2$: C, 88.57; H, 4.73; N, 3.13. Found: C, 88.67; H, 4.74; N, 3.10.

Poly[2,2′-(*p*,*p*′-biphenylene)-6,6′-bi[4-(4-(4-phenylphenoxy)phenyl)quinoline]] (22b). The above procedure was followed except 0.7288 g (1.000 mmol) of 3,3′-bis[4-(4-phenylphenoxy)benzoyl]benzidine (**15**) and 0.2383 g (1.000 mmol) of 4,4′-diacetylbiphenyl (**21**) were used as the monomer reagents. The monomers were polymerized, precipitated, and purified as above to afford 0.985 (110%) of **22b** as hard granules, which were contaminated with occluded *m*-cresol: $[\eta]$ = 5.26 dL/g (25 °C; di-*m*-cresyl phosphate/*m*-cresol, 0.5 mol % ratio). Anal. Calcd for $C_{66}H_{42}N_2O_2$: C, 88.57; H, 4.73; N, 3.13. Found: C, 84.81; H, 4.62; N, 3.06.

Poly[2,2′-(*p*,*p*′-biphenylene)-6,6′-bi[4-(4-(4-phenoxyphenoxy)phenyl)quinoline]] (22c). The above procedure was followed except 0.7608 g (1.000 mmol) of 3,3′-bis[4-(4-phenoxyphenoxy)benzoyl]benzidine (**18**) and 0.2383 g (1.000 mmol) of 4,4′-diacetylbiphenyl (**21**) were used as the monomer reagents. The monomers were polymerized, precipitated, and purified as above to afford 0.904 g (98%) of **22c** as a coarse, bright-yellow powder: $[\eta]$ = 26.0 dL/g (25 °C; di-*m*-cresyl phosphate/*m*-cresol 0.5 mol % ratio). Anal. Calcd for $C_{66}H_{42}N_2O_4$: C, 85.51; H, 4.57; N, 3.02. Found: C, 85.58; H, 4.61; N, 3.00.

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Study of Surface Composition and Morphology of Block Copolymers of Bisphenol A Polycarbonate and Poly(dimethylsiloxane) by X-ray Photoelectron Spectroscopy and Ion Scattering Spectroscopy

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ABSTRACT: X-ray photoelectron spectroscopy and ion scattering spectroscopy results are presented for block copolymers of bisphenol A polycarbonate (BPAC)/poly(dimethylsiloxane) (DMS). Analysis of these results shows surface enrichment in the copolymer of the lower surface energy DMS segments over the range 25–65% DMS. Models are presented for the morphology of the top 50 Å of the sample surface consisting of discrete regions of DMS and BPAC oriented perpendicular to the surface.

Introduction

Previous work[1,2] has shown that composition at the surface of AB block copolymers can differ greatly from that of the bulk. Since many of a polymer's properties depend on its surface bonding and composition (weathering,[3] adhesion,[4] biocompatibility,[5] etc.), the ability to predict the extent of surface speciation of one component should add greatly to the development of structure-specific polymers.

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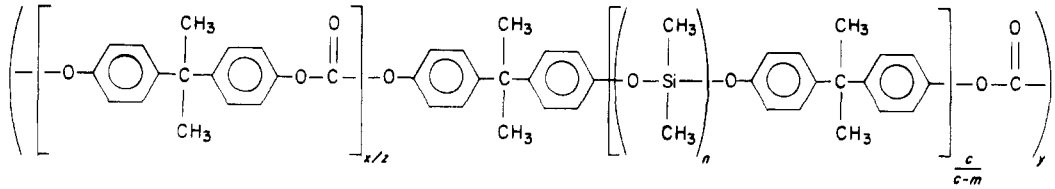

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X-ray photoelectron spectroscopy (XPS or ESCA), over the past 15 years, has emerged as an important method for studying polymer surfaces.[6] Much of this success can be attributed to the rich information provided by ESCA. The core-level photoemission lines provided multielement determinations as well as chemical-state identification.[7]

Peak intensities can also be used for semiquantitative analysis of the surface region.[2] Sensitivity to the near-surface region of a solid derives from the electron mean free path in the sample matrix and on the angle of the sample surface with respect to the electron kinetic energy analyzer.[2]

Thomas and O'Malley[1] have used angle-resolved ESCA to study both block copolymers and blends of Polystyrene (PS) and Poly(ethylene oxide) (PEO). This work showed that lower surface energy PS is present in higher concentrations at the surface than in the bulk for both the block copolymers and the blends. Through careful analysis of angle-resolved results, they proposed a model for the copolymer topography consisting of isolated domains of each component at the surface that appear thick on the ESCA scale.

Clark et al.[8] used ESCA in conjunction with contact-angle measurements to study AB block copolymers of poly(dimethylsiloxane) (DMS) and PS. Contact-angle results showed the topmost atomic layers to be pure DMS for all samples. The ESCA results indicate that the surface region is comprised of an overlayer of DMS ranging from approximately 13 to greater than 40 Å, depending on the solvents used to cast the film. Dwight and McGrath[2,9] have also shown surface speciation for the lower surface energy component in block copolymers of bisphenol A polycarbonate (BPAC) and DMS. When low siloxane concentrations (0.01–10 wt %) were examined, a "critical" siloxane concentration of 1% bulk was found to cause the surface to be siloxane-dominated.[9] Also, over a narrow concentration range near 50% siloxane, the surface was found to be nearly pure siloxane.[2] However, detailed quantitative data were not presented for either study.

Unlike ESCA, ion scattering spectroscopy (ISS) has not seen much use in the study of polymer surfaces. The biggest advantage in using ISS to study polymers is the fact that it samples only the top 3–5 Å of a solid surface.[10] Earlier work by Gardella and Hercules[11] comparing ESCA and ISS analysis of polymethacrylates found ISS added no information regarding surface composition to that obtained from ESCA. However, since polymethacrylate homopolymers are very glassy and amorphous, one would not expect a surface structure differing greatly from the bulk structure. Both techniques demonstrated a homogeneous surface structure.[7] Thomas et al.[12] have published ISS spectra for a collection of hydrocarbon homopolymers that show the carbon to oxygen (C/O) peak intensity ratio to be characteristic for a given sample but not directly related to the stoichiometry of the sample. Since impurities were detected in a number of samples in this study, any quantitative conclusions would be somewhat suspect.

In the present work we give data from combined ESCA and ISS measurements of the surface of block copolymers of DMS and BPAC. The ESCA results yield a quantitative analysis to a depth of approximately 50 Å,[6] while ISS measurements are limited to the top 3–5 Å of the sample.[10] Depth information intermediate between these two was obtained by angle-resolved ESCA. The sampling depth was reduced by sin 30°[13] by using an escape angle of 30°. This gives a sampling depth of approximately 25 Å. Therefore, we can present a "nondestructive" depth profile for the copolymers, using these measurements.

The choice of the BPAC/DMS block copolymer system was made for several reasons. First, a wide range of compositions can be prepared (samples used ranged from 65 to 25% DMS). Second, the two components have very different surface energies (24 dyn/cm for DMS and 34.5 dyn/cm for BPAC[14]), which should favor surface enrichment of DMS.[1] Third, they can be obtained in pure form, showing no contamination. Last, as mentioned above,[2,9] previous work has shown DMS does indeed show a surface preference in BPAC/DMS block copolymers. However, earlier work was limited to a narrow range of concentrations and did not present quantitative results.

Table I
Composition of BPAC/DMS Copolymer Samples

sample	wt % BPAC[a]	wt % DMS[a]	av DMS block length
I	35 (37.2)	65 (62.8)	20
II	75 (78.1)	25 (21.9)	20
III	50 (52.2)	50 (47.8)	20

[a] Later characterization of these samples[15] indicated that the values in parentheses are more accurate. The rounded numbers are retained here to facilitate comparison with earlier literature.

Experimental Section

Sample Preparation. Poly(dimethylsiloxane), methyl-terminated gum was obtained from Polysciences, Inc. Homopolymer BPAC and copolymers of BPAC/DMS, with a DMS block length of approximately 20 units, were provided by Dr. Roger Kambour of General Electric Co., Schenectady, NY. The chemical structure of the copolymer is shown in structure 1, while the sample compositions are listed in Table I. All samples, except the BPAC homopolymer, were cast as films from 1% solution in chloroform and analyzed without any other preparation. The BPAC homopolymer was cast from 1 wt % solution in chloroform and then cleaned by ultrasonic solvent extraction in hexane to remove residual siloxane-type impurities to below the level of ESCA detectability. Surface segregation of contaminants of this type has been reported previously by Clark et al.[16]

Instrumentation. ESCA spectra were recorded by a Physical Electronics Model 560 ESCA/SAM using a cylindrical mirror analyzer with an angle-resolved drum. Mg Kα X-rays were used as the source, operated at 300 W, 15.0 kV, and 20 mA. Base pressure was maintained at 5×10^{-9} torr, and a pass energy of 25 eV was employed for all spectra. These conditions give a gold 4f $^7/_2$ peak at 83.8-eV binding energy for calibration and a full width at half-maximum (FWHM) of 1.1 eV at a count rate of 1 000 000 counts/s. No radiation damage was observed during 1.5 times the data collection time. Charge correction in the binding energy scale was accomplished by setting the CH_x peak of the carbon 1s envelope to 285.0 eV. Spectra for all samples were recorded at both integrated and 30° angles. This leads to a sampling depth of approximately 50 and 25 Å, respectively.[6,13]

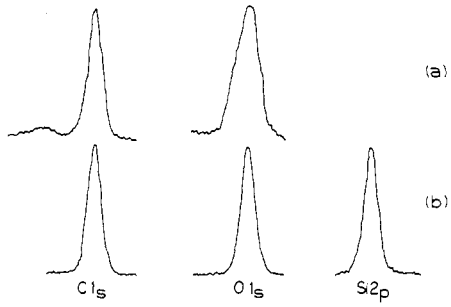

Figure 1. ESCA spectra for (a) DMS homopolymer and (b) BPAC homopolymer.

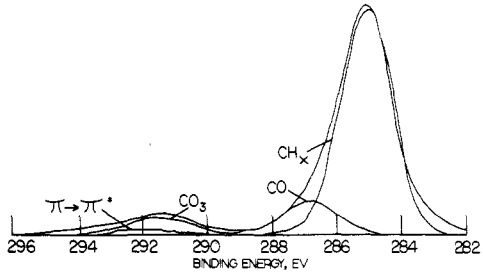

Figure 2. Curve resolution analysis of the carbon 1s region from pure BPAC, used to calibrate quantitative analysis.

Table II
Binding Energies for the C 1s Region in BPAC/DMS Homopolymers

carbon environment	binding energy, eV	carbon environment	binding energy, eV
CH_2	285.0	CO_3	291.0
CO	286.5	$\pi \rightarrow \pi^*$	292.0

ISS spectra were recorded on a Physical Electronics Model 560 ESCA/SAM with ISS modification. A 2-kV beam of $^3He^+$ ions was utilized with a scattering angle of 144°. Current densities were 3–5 nA/cm^2. A tungsten-filament electron emitter was used for charge neutralization, set at 2-mA emission current and 0-eV acceleration.

All data manipulation was accomplished with the standard MACS (Version 6) software of the Model 560.

Results

ESCA. Homopolymers. In order to understand the BPAC/DMS copolymers, it was first necessary to analyze the homopolymer constituents. The ESCA core-level spectra for BPAC and DMS homopolymers are shown in Figure 1.

The DMS spectrum is comprised of three strong peaks at approximately 530, 285, and 101 eV that result from direct photoionization from the O 1s, C 1s, and Si 2p core levels, respectively. No shake-up peaks were observed in the DMS spectrum, and the results are in agreement with those previously published by Clark et al.[8]

The BPAC spectrum is more complicated than the DMS spectrum. Figure 2 shows a least-squares computer fit for the C is region of BPAC, while Table II lists the binding energies for these peaks. Analysis of relative peak intensities yields the proper stoichiometry of 13/2/1 with the shake up from the $\pi \rightarrow \pi^*$ transition equal to 2.92% of the peak at 285.0 eV (CH_x and C–O).[17] All peak assignments are in agreement with Clark's previously published results.[4] The O 1s peak was also resolved into C–*O* and $O_2C{=}O$ contributions. The relative peak areas lead to the expected 2/1 ratio.

Quantitation. From areas obtained from the computer fit shown in Figure 2, the higher binding energy peak at 291.5 eV (CO_3 plus shake up) is 8.9% of the main peak at 285.0 eV for the homopolymer of BPAC. In the copolymers, DMS contributes only to the peak at 285.0 eV. Therefore, the peak at 291.5 is proportional to the contribution of BPAC in the main peak. The remaining contribution is from DMS. This allows calculation of the relative peak areas contributed from each component. The relative peak areas are then converted to weight percent values by correcting for the number of carbons and the molecular weight of the monomer units. This method of quantitation eliminates the need to consider cross sections for photoionization, since only carbon is being considered. Also, because all emitted electrons being considered are of approximately the same kinetic energy, it is not necessary to correct for differences in mean free paths as it is when quantitating with electrons emitted from different atoms. This approach allows calibration for quantitative analysis of the block copolymers given below.

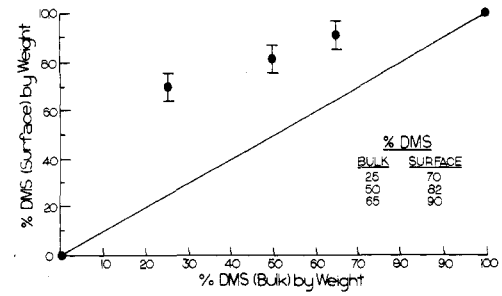

Figure 3. Surface vs. bulk composition for copolymers, taken from ESCA.

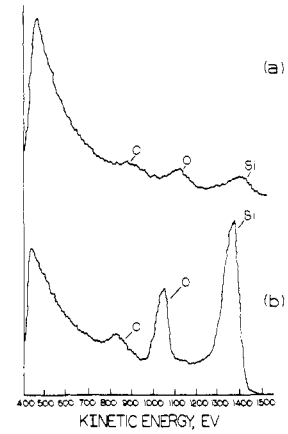

Figure 4. ISS spectra for (a) DMS homopolymer and (b) BPAC homopolymer.

Copolymers. ESCA of the copolymer samples again yielded peaks for carbon, oxygen, and silicon. By the quantitative approach derived above, the data given in Figure 3 show the degree of surface enrichment of the DMS component in the copolymers. All samples showed preferential speciation of the lower surface energy DMS, with the 25/75 sample showing the greatest deviation from the bulk concentration.

For each sample, results from angle-resolved ESCA showed no difference (within experimental error) from those at integrated angle.

ISS. Homopolymers. Figure 4 shows the ISS spectrum for the DMS homopolymer, which is comprised of peaks for carbon, oxygen, and silicon centered at 793-, 1006-, and 1357-eV kinetic energy respectively corresponding to calculated energy ratios of 0.396, 0.503, and 0.679, expected from 2-kV $^3He^+$ scattering at 144°.[10]

The ISS spectrum of the BPAC homopolymer is also given in Figure 4. This spectrum contains the characteristic carbon and oxygen peaks centered at 793 and 1000

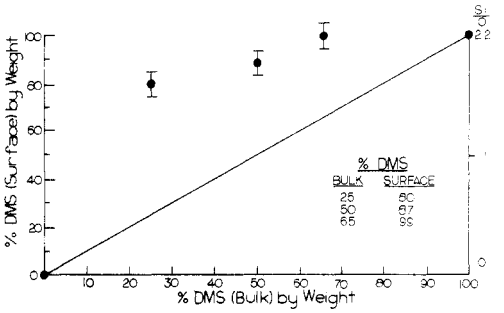

Figure 5. Surface vs. bulk composition for copolymers, taken from ISS analysis.

eV, respectively, as well as a third peak at 1357 eV that can be assigned to silicon. This disagrees with a previous assignment of this peak by Thomas et al.[12] as a sodium contamination. The silicon assignment, however, is supported by comparison to the DMS spectrum, by the growth of this peak with increasing DMS concentration in the copolymers, and by the observation of silicon in the ESCA spectrum for BPAC homopolymer before solvent washing. While solvent extraction lowered the silicon contamination below the ESCA detectability level, it could not remove its presence in the ISS results. For simplicity, the silicon contribution from BPAC in the copolymers is taken as 0 and the bulk concentration for BPAC homopolymers is assumed to be 100% BPAC.

Quantitation. Silicon to oxygen (Si/O) peak height ratios were used uncorrected for the quantitation of the ISS results. A homogeneous mixture of DMS and BPAC in bulk concentration was assumed between 0 and 100% DMS, and this would yield a linear increase in Si/O ISS ratios. Surface enrichment of DMS is then interpreted as a positive deviation from this line (in Figure 5).

Copolymers. The ISS spectra for the copolymers are comprised of peaks from carbon, oxygen, and silicon at approximately 800, 1000, and 1350 eV, respectively, as in the homopolymer DMS. Figure 5 is the plot of the Si/O peak height ratios found by ISS vs. those expcted by assuming the homogeneous mixture model of the bulk as described above. All samples show a surface enrichment of the lower surface energy DMS. The degree of enrichment is much greater in the top 3–5 Å (ISS region) than in the top 50 Å (ESCA region) in each case. For example the surface weight percent DMS in the 25/75 DMS/BPAC sample found by ISS was 82% while the percent DMS found by ESCA was 70%.

Discussion

It has been well established that BPAC/DMS block copolymers exist in a domain structure on the scale of 100 Å.[18,19] Kambour[18] has shown with electron microscopy and thermal analysis that at low BPAC concentration discrete particles composed largely of BPAC blocks exist in a DMS continuum, at intermediate BPAC concentrations, both polycarbonate and siloxane continua exist, and at high BPAC concentrations, discrete siloxane particles exist in a polycarbonate continuum. The question to be answered by this study is whether this or some other microstructure also exists in the near-surface region of the solution-cast film samples.

While the samples clearly show an excess of DMS in the surface region, it is readily apparent from the ESCA results that this is not due to a thin (10–20 Å) overlayer of DMS residing at the surface, as was found by Clark[8] for AB block copolymers of DMS and polystyrene. If this were the case, one would expect the DMS concentration (i.e., the ESCA silicon signal) to increase exponentially when going from

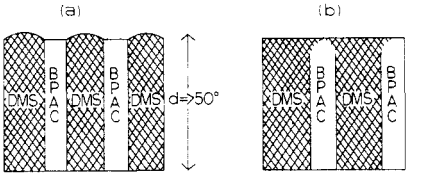

Figure 6. Models for the surface morphology of BPAC/DMS block copolymers: (a) showing DMS regions raised above the BPAC regions and (b) showing a distorted surface region.

integrated-angle to 30°-angle ESCA measurements, since the sampling depth is effectively halved. The fact that the results of the angle-resolved experiment are equivalent to the angle-integrated experiments can be interpreted as the sample being uniform over the ESCA sampling range. This can best be explained by a model similar to that put forth by Thomas and O'Malley[1] and Magill,[20] where domains of both components are arranged perpendicular to the surface and extend into the sample to a depth greater than the ESCA sampling depth.

Although the results obtained with angle-integrated ESCA show a uniform concentration over the range of approximately 50 Å, the results obtained with ISS show a much larger surface enrichment of the DMS component in the uppermost atomic layers. There are two possible explanations for this high DMS concentration found at the surface by ISS that are consistent with the model presented above. First, the ISS experiment can show "shadowing effects",[21,22] where one component is effectively screened by atoms residing above it. If the DMS regions are raised above the BPAC regions, then "shadowing" would lead to an increase in the DMS signal. This type of description was included in the structural model presented by Thomas and O'Malley[1] derived completely from angular-dependent ESCA for the surface morphology of PS/PEO block copolymers. Second, previous studies on BPAC/DMS[18,19] have shown the DMS regions to be quite mobile. Mobility of DMS can be related to the fact that DMS has a low glass transition temperature ($T_g < -120$ °C) and a low surface energy and there is a large difference in surface energies between BPAC and DMS. However, the important aspect to be stressed is the exaggeration of the segregation in the near-surface regions by a concentration gradient that can be developed because the DMS segments of the copolymer distort the topmost layers in order to further lower the surface energy. Figure 6 gives a representation of each of these two possible models.[19] It should be noted that while Figure 6b has an overlayer of DMS at the surface, it would be too shallow to be determined by ESCA. Thus the ISS measurements become crucial in exactly describing the outermost layers.

In order to more fully understand the gradient and structure at the outermost atomic layers of the copolymers, several additional experiments would be useful. The use of an ESCA instrument with a rotatable sample holder (i.e., rod or stage) with a hemispherical analyzer would allow angular-dependent ESCA measurements with greater angle variation and resolution with a lower angle of as low as 10°, thus yielding a further reduction in sampling depth. This arrangement would be more sensitive to small changes taking place at the outer surface. Also, high-resolution electron microscopy of the sample would be used in determining if a raised profile of the copolymers is indeed present and on what scale these features occur. However, specific staining would be necessary to confirm segregation of the DMS. These studies are currently under way.

By combining the data obtained from ESCA and ISS, we see that the morphology of the surface region can be explained by a microdomain similar to that present in the

bulk but with a different (exaggerated) concentration profile, and we have provided quantitative data from both techniques to support the model.

Conclusions

In summary the following points can be made:

(1) Block copolymers of BPAC/DMS show a distinct surface preference for the lower surface energy DMS segments over a wide range of compositions. This segregation, while seen in previous work, is given quantitative significance.

(2) The ISS technique provides a strong complement to ESCA for the study of polymer surfaces. In this case, ISS analysis detailed a very shallow surface change not seen by ESCA.

(3) The morphology of the surface region of BPAC/DMS block copolymers can be explained as consisting of microdomains of each component oriented perpendicularly to the surface, with a depth greater than the sampling depth of ESCA. Therefore, while the composition of the surface is very different from that of the bulk, the morphology of both is similar.

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Registry No. PBAC (copolymer), 25037-45-0; BPAC (SRU), 24936-68-3.

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Polymerization of β-Lactones Initiated by Potassium Solutions

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ABSTRACT: Polymerization of β-lactones 1 by alkali metal solutions proceeds fast with a yield higher than 90%. Polyesters with a molecular mass ($\bar{M}_n$) higher than 100 000 can be obtained when the concentration of that initiator is sufficiently low. The initiation step of polymerization involves an unusual, till now unreported, scission of the C–C bond in the β-lactone ring.

Introduction

Polymerization of β-propiolactone and its derivatives constitutes the subject of intensive studies of many authors.[1-3]

However, the polymerization of β-lactones by alkali metals has not been investigated in great detail. One of the supposed reasons may be the very low yields obtained in the polymerization of these monomers by suspensions of alkali metals.[4,5] A quite different picture provides the polymerization of β-propiolactone **1a**, initiated by potassium and sodium solutions, i.e., in a homogenous system.[6] The same initiators, i.e., alkali metal solutions, were found previously to be very active in the polymerization of vinyl monomers.[7]

The aim of this work was to study the ring-opening polymerization of β-lactones 1 initiated by potassium solutions. The β-propiolactone (**1a**), α-methyl,α-ethyl-β-propiolactone (**1b**), and β-butyrolactone (**1c**) were selected as model monomers.

Experimental Section

Measurements. The ^1H NMR spectra were run in $CDCl_3$ with Me_4Si as internal standard, using a Varian Xl-100 spectrometer. The GPC experiments were conducted in CH_2Cl_2 solution at 20 °C with a Waters GPC-200 gel permation chromatograph connected to a flow-through cell equipped with a Wilks IR detector (1735 cm^{-1}). Gas chromatographic analyses were run on a 2-m-long glass column packed with OV-17, 15% Chromosorb W AW DMSC 60–80 mesh, using a Varian 2700 gas chromatograph. Number-

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