Macromolecules 1988, 21, 2950–2959

SIMS and XPS Studies of Polyurethane Surfaces. 1. Preliminary Studies[†]

Martin J. Hearn,[‡] Buddy D. Ratner,* and David Briggs[‡]

Center for Bioengineering and Department of Chemical Engineering, BF-10, University of Washington, Seattle, Washington 98195. *Received October 26, 1987*

ABSTRACT: Segmented poly(ether urethanes) (PEU's) and model polymers were examined by using static secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS). The PEU's were composed of a polyether (either poly(propylene glycol) (PPG) or poly(tetramethylene glycol) (PTMG)) capped with methylenebis(phenylene isocyanate) (MDI) and chain-extended with ethylenediamine. Model soft segments included poly(ethylene glycol), PTMG, and PPG of various molecular weights. Hard-segment models for the PTMG PEU's were based on MDI and butanediol, whereas ones for the PPG PEU's were based on MDI and dipropylene glycol or tripropylene glycol. Molecular fragmentation patterns from SIMS analysis were established for the soft- and hard-segment models and used to identify these components in the PEU's. Combining the surface sensitivity and the molecular fingerprinting ability of SIMS with the chemical composition specificity of XPS provided a refined characterization of these polymer surfaces. Specifically, this study confirmed the enrichment in polyether at the PEU surface but suggested that this layer is interspersed with small quantities of hard-segment components.

Introduction

Segmented poly(ether urethanes) (PEU's) have assumed considerable importance in biomedical applications, and the surfaces of these materials have been extensively studied in order to understand the interdependence of surface structure and biological response (e.g., blood compatibility).[1-7] In addition, the surfaces of PEU's have been studied with regard to the application of these materials as adhesives and coatings.[8,9]

X-ray photoelectron spectroscopy (XPS) has proved to be the most valuable tool for characterizing PEU surfaces. A number of studies have shown that the surface of these materials can exhibit an enrichment of polyether compared to the bulk.[10-14] This polyether component (soft segment) and the urethane component (hard segment) have generally been found to separate into two discrete phases with a domain size of 100–200 Å. The factors that control the extent of phase separation include the molecular weight of the soft segment,[15] the size of the chain extender,[16-18] and the thermal and solvent history of the sample.[19-21] Although much is known about the bulk phase separation of PEU's, surface phase separation is less well understood.

Recently, the use of angular dependent XPS for nondestructive depth profiling of cast PEU films has further highlighted that several compositional gradients exist within the surface region and that there may be little or no hard segment present at the uppermost surface.[22,23] However, depth profile models generated from XPS data must be treated with caution because certain assumptions are made concerning inelastic mean free path values, surface smoothness, and surface lateral heterogeneity. Clearly, the accuracy of such models could be better assessed if more specific information were available regarding the composition of the uppermost molecular layer and the degree of lateral and vertical heterogeneity.

In this respect, secondary ion mass spectrometry (SIMS) has the potential for providing much additional information about the surface chemical structure of PEU's. Relative to XPS, SIMS data provide more specific molecular information with greater sensitivity. Furthermore, SIMS analysis can also be carried out with much higher spatial resolution and in an imaging mode.[24]

Static SIMS studies on a range of simple polymers have demonstrated the fingerprint capacity of both positive and negative ion SIMS.[24-27] Usually, the spectra can be rationalized on the basis of backbone/side-chain fragmentation processes, and they often contain prominent secondary ions that are closely related to the original polymer structure (e.g., multiple repeat unit fragments).[27] In particular, recent studies on polymethacrylates[27,28] and Nylons[26] have illustrated the sensitivity of SIMS to monomer structure and have also established a basis for quantifying SIMS intensity data from polymers. The sampling depth for static SIMS in polymeric systems has been estimated at 8–12 Å.[25]

In this paper, we explore the potential of SIMS as a tool for the surface characterization of polyurethanes, examining in detail its capability for providing both qualitative and quantitative surface compositional information. When both XPS and SIMS are applied, the complementary aspects of the two techniques are exploited to provide surface compositional information necessary for establishing the true extent of surface heterogeneity. Also, the high surface sensitivity of SIMS and its ability to unambiguously identify hard- or soft-segment components justify using SIMS together with XPS to study phase separation. However, only a preliminary application of SIMS to this problem will be made in this paper. A more detailed SIMS study describing surface phase separation for PEU's prepared with fluorinated chain extenders has been published.[25]

Experimental Section

1. **Materials.** Three types of model poly(ether diol)s were employed in this study: poly(ethylene glycol) (PEG MW 2000) (Fluka AG); poly(propylene glycol) (PPG MW 425, 775, and 2000) (Reichold); and poly(tetramethylene glycol) (PTMG MW 625, 1000, and 2000) (Du Pont). Polyethers were typically dried at 50–60 °C for 24 h at pressures of ~1 Torr.

The diisocyanate used in these polymers, 4,4′-methylenebis(phenylene isocyanate) (MDI, Isonate 2340, Upjohn), was vacuum distilled and refrigerated before use. *N*,*N*-dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO) (Burdick and Jackson; high purity) were dried over molecular sieves and distilled. Ethylenediamine was distilled over molecular sieves. Dipropylene glycol (Kodak) and tripropylene glycol (Alfa Chemical) were distilled under vacuum.

---

* Author to whom correspondence should be addressed.

[†] Considered to be part 8 of the series "Analysis of Polymer Surfaces by SIMS".

[‡] ICI PLC, Wilton Materials Centre, P.O. Box 90, Wilton, Middlesbrough, Cleveland TS6 8JE, U.K.

0024-9297/88/2221-2950$01.50/0

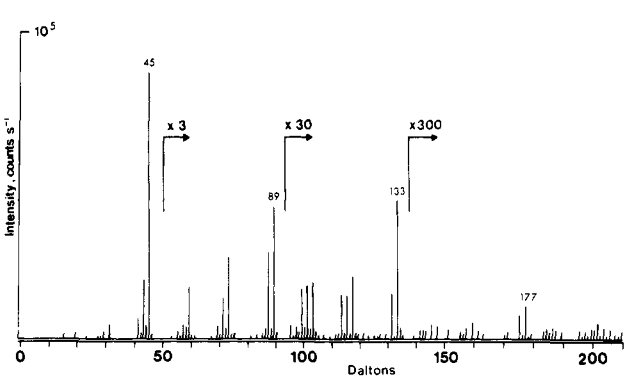


Figure 1. Positive ion SIMS spectrum of PEG 2000.

2. Synthesis of Hard-Segment Model Polymers. As illustrated in Chart I, polyurethanes serving as models for the hard-segment units were prepared by capping the terminal hydroxyl groups of butanediol (BD), dipropylene glycol (DPG) and tripropylene glycol (TPG) with MDI and then chain-extending the resulting compounds with ethylenediamine (ED). A typical reaction procedure for synthesizing hard-segment model polymers follows. MDI (50 g) was dissolved in 75 mL of 4-methyl-2-pentanone. DPG (13.9 g) was dissolved in 75 mL of DMSO and degassed under vacuum for 1 h. The DPG solution was slowly added to the MDI solution for 2 h at 105 °C. The solution was cooled to 25 °C and added to 500 mL of dimethylformamide (DMF). Ethylenediamine (6 g) in 50 mL of DMF was slowly added to this solution. The reaction was allowed to proceed 10 min, and then the product was precipitated into water and exhaustively washed in water/methanol mixtures. Most of the polymers were further extracted in a Soxhlet extractor with methanol/acetone (1:1). The polymers were then dried, redissolved in hexafluoro-2-propanol (HFIP) or DMAc, filtered, and centrifugally cast at 4000 rpm on acid-cleaned glass disks.

3. Synthesis of Segmented Polyurethane Polymers. The poly(ether urethane) (PEU) polymers examined in this study were composed of a low molecular weight polyether capped with MDI and chain-extended with ED as shown in the generalized sequence in Chart I. The procedure for the preparation of these polymers is a modification of the method described by Brash et al.[29] and is basically the same as outlined in the previous section. Minor variations in solvents, concentrations, reaction times, and temperatures were used to synthesize the many polymers described in this study.

4. ESCA and SIMS Experiments. ESCA analysis was performed on an SSX-100 instrument (Surface Science Instruments, Inc.) using a monochromatized Al Kα X-ray source and a low-energy electron flood gun to control sample charging.

In the SIMS experiments, samples were bombarded with 4 KeV Xe^+ with a current density of $\sim$1 nA cm^{-2} (irradiated area $\sim$0.3 cm^2). The total ion dose during setup and spectral acquisition was $<10^{13}$ ions cm^{-2}, corresponding to static SIMS conditions.[30] Charge neutralization was effected by a flood of 700-eV electrons with a current density of the same order as the primary ion beam. The apparatus has been described previously.[31]

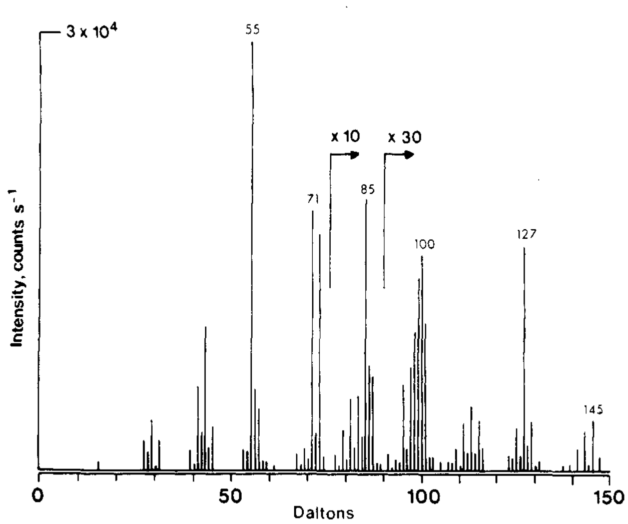


Figure 2. Positive ion SIMS spectrum of PTMG 2000.

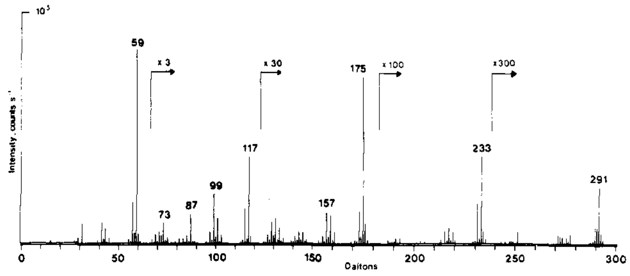
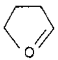
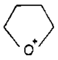
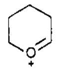


Figure 3. Positive ion SIMS spectrum of PPG 425.

Table I
Possible Structures of Characteristic Positive Secondary Ions from Poly(tetramethylene glycol)

mass	ion structure	relative intensity MW 1000	relative intensity MW 2000
55	$C_3H_3O^+$, $C_4H_7^+$	80	100
71	$CH_2{=}CHCH_2CH{=}OH^+$, 	57	62
73	$CH_3CH_2CH_2CH{=}OH^+$, 	100	53
85	$CH_3CH_2CH_2O^+{=}CH_2$ $CH_3CH{=}O^+CH_2CH_3$ $OCHCH{=}CHCH{=}OH^+$ $CH_3CH_2CH{=}CHO^+{=}CH_2$ $CH_3CH_2O^+{=}CH{-}CH{=}CH_2$ 	7.5	6.5
87	$CH_3CH_2CH_2CH_2O^+{=}CH_2$ $CH_3CH_2CH{=}O^+CH_2CH_3$	3.2	2.3
101	$CH_3CH_2CH_2CH_2O^+{=}CH{-}CH_3$	2.1	0.9
127	$CH_3CH_2CH_2CH_2O^+{=}CHCH_2CH{=}CH_2$	3.3	1.5
145	$CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_2{=}O^+H$	2.7	0.4

Results and Discussion

1. Soft-Segment Models. 1.1. Poly(ethylene glycol) (PEG). The positive ion spectrum of PEG (MW 2000) shown in Figure 1 is in good quantitative agreement with results reported previously.[24,32] The spectrum contains clusters due to ions derived directly from the repeat unit with the general formula $[(CH_2CH_2{-}O)_nH]^+$. Thus, the peaks at 45, 89, 133 and 177 D correspond to n = 1–4, respectively. To complete the fingerprint series, another series of ions having one or two additional $-CH_2-$ groups is also observed at 59, 73, 103, and 117 D.

1.2. Poly(tetramethylene glycol) (PTMG). As shown in Figure 2, the base peak of the positive ion SIMS spectrum from PTMG (MW 2000) occurs at 55 D and probably results from both $C_3H_3O^+$ and $C_4H_7^+$, whereas the peak at 73 D is from the protonated polymer repeat unit $[(-CH_2CH_2CH_2CH_2{-}O){-}H^+]$. Only a weak peak at 145 D is found from the dimeric unit $[(-CH_2CH_2CH_2CH_2{-}O)_2{-}H^+]$. Ions with more than two repeat units were not observed.

Other prominent peaks that complete the SIMS fingerprint for PTMG are found at 71, 85, 99–101, and 127 D. In Table I, some possible structures for these ions are given, along with the relative peak intensities for PTMG 1000 and PTMG 2000. With the possibility of chain cleavage in the α- or β-position on either side of the oxygen, a number of different linear or cyclic ion structures could be proposed as is shown for masses 73 and 85 D.

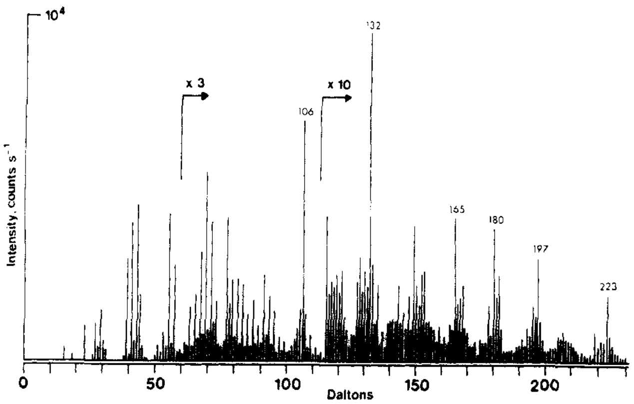
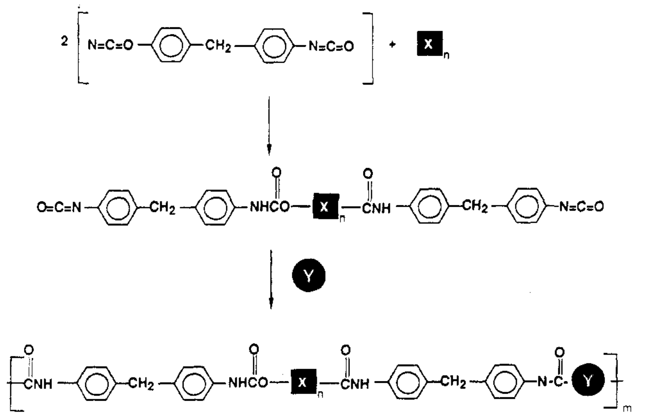


Figure 4. Positive ion SIMS spectrum of a butanediol hard-segment model polyurethane.

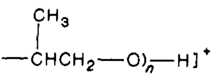
Chart I
Polyetherurethane Synthesis



X	Abbreviation	n	MW
$-(\text{-}CH_2CH_2\text{-}O\text{-})_n$	PEG	45.5	2000
$-(\text{-}CH_2\overset{CH_3}{CH}\text{-}O\text{-})_n$	PPG	7.3 13.4 34.4	425 775 2000
	DPG	2.0	116
	TPG	3.0	174
$-(\text{-}CH_2CH_2CH_2CH_2O\text{-})_n$	PTMG	8.7 13.9 27.8	625 1000 2000
	BD unit	1.0	72

Y	Abbreviation	MW
$NH_2CH_2CH_2NH2$	ED	60
$OHCH_2CH_2CH_2CH_2OH$	BD	90

1.3. Poly(propylene glycol) (PPG). The most prominent peak in the positive ion spectrum of PPG (MW 425) shown in Figure 3 occurs at 59 D and is assigned to the protonated polymer repeat unit



$$[(\overset{CH_3}{\overset{|}{C}}HCH_2{-}O)_n{-}H]^+$$

where $n = 1$. In addition, peaks at 117, 175, 233, and 291 D correspond to $n = 2$–5, respectively. Two other sets of peaks observed at 73, 87, 99 D and 131, 143, 157 D also correspond to simple fragments of the polymer chain. Some probable ion structures for the most intense ions are presented in Table II, along with the relative ion peak intensities in PPG 775 and PPG 2000.

2. Hard-Segment Models. Positive ion SIMS spectra were obtained for two types of hard-segment models which aim to reproduce the characteristic urethane and urea structural units of some typical polyurethane types.

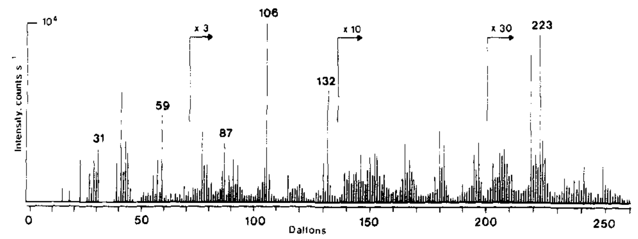
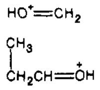
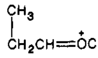
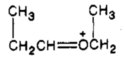
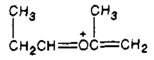
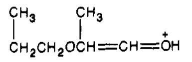
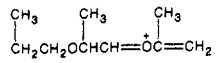
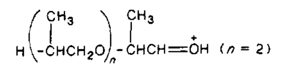
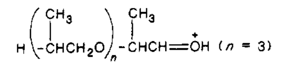
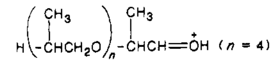


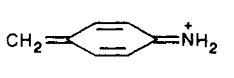
Figure 5. Positive ion SIMS spectrum of a dipropylene glycol hard-segment model polyurethane.

Table II
Possible Structures of Characteristic Positive Secondary Ions from Poly(propylene glycol)

		relative intensity (% of base peak at 59 D)		
mass	structure	MW 425	MW 775	MW 2000
31	$HO^+{=}CH_2$	11.8	17.4	11.4
59	 $\overset{CH_3}{CH_2}CH{=}\overset{+}{O}H$	100	100	100
73	 $\overset{CH_3}{CH_2}CH{=}\overset{+}{O}CH_3$	3.3	6.7	4.9
87	 $\overset{CH_3}{CH_2}CH{=}\overset{+}{O}\overset{CH_3}{CH_2}$	4.9	15.0	12.7
99	 $\overset{CH_3}{CH_2}CH{=}\overset{+}{O}\overset{CH_3}{C}{=}CH_2$	8.8	15.0	10.3
117	 $\overset{CH_3}{CH_2}CH_2O\overset{CH_3}{CH}{=}CH{=}\overset{+}{O}H$	13.7	16.5	7.3
157	 $\overset{CH_3}{CH_2}CH_2O\overset{CH_3}{CH}CH{=}\overset{+}{O}\overset{CH_3}{C}{=}CH_2$	0.5	1.2	0.5
175	 $H\left(\overset{CH_3}{CH}CH_2O\right)_n\text{-}\overset{CH_3}{CH}CH{=}\overset{+}{O}H\ (n = 2)$	3.7	2.3	0.7
233	 $H\left(\overset{CH_3}{CH}CH_2O\right)_n\text{-}\overset{CH_3}{CH}CH{=}\overset{+}{O}H\ (n = 3)$	0.5	0.3	0.1
291	 $H\left(\overset{CH_3}{CH}CH_2O\right)_n\text{-}\overset{CH_3}{CH}CH{=}\overset{+}{O}H\ (n = 4)$	0.1	0.1	

The spectrum of a butanediol PEU is shown in Figure 4. In this hard-segment model for the PTMG/MDI/ED-type polymers, a butanediol has been substituted for the PTMG soft segment. The SIMS spectrum of a polymer based on dipropylene glycol is given in Figure 5 as a hard-segment model for PPG/MDI/ED polyurethanes.

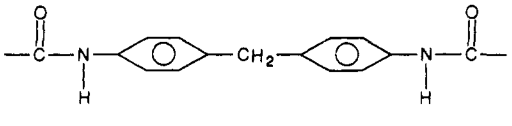
Qualitatively, these spectra show very similar features. In each case, the low mass region (<100 D) is completely dominated by the often observed $C_nH_m^+$ fragments (e.g., 29, 41, 55, 57, 69, 77, 79), whereas between 100 and 250 D, the spectra exhibit a highly characteristic cluster pattern with prominent peaks at 106 and 132 D. The following ion structures can be proposed for these two peaks:



132 D

106 D

These higher mass clusters originate from the MDI part of the hard-segment unit, i.e.



which is common to all three polymers. Other less intense

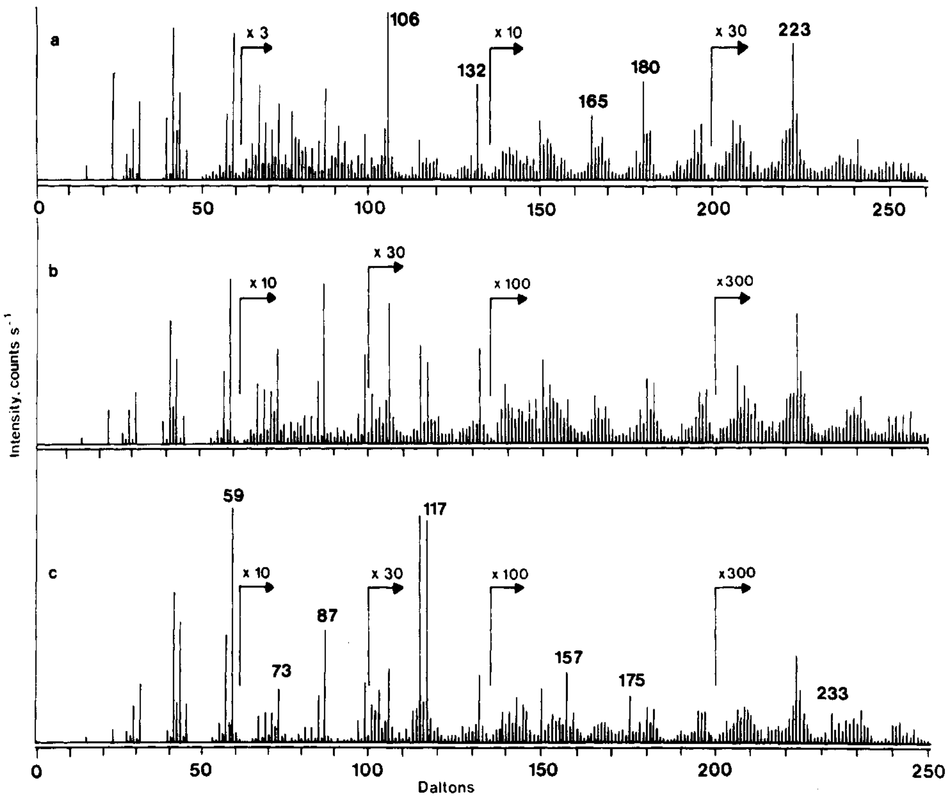


Figure 6. Positive ion SIMS spectra of PPG/MDI/ED PEU's prepared with (a) PPG 425, (b) PPG 775, and (c) PPG 2000.

Table III
Ion Structures Corresponding to the Major Peaks of the MDI Hard-Segment Unit

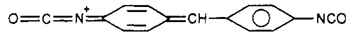
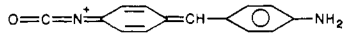
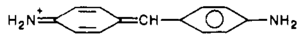
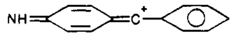
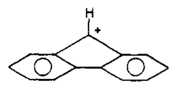
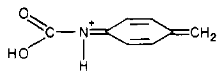
mass	structure
249	
223	
197	
180	
165	
150	
132	
106	

Table IV
Positive Secondary Ion Relative Intensities for PPG/MDI PEU's

	secondary ion peaks from SS (PPG)						
polymer	59	73	87	99	117	157	175
DPG PEU	100	5.0	20.0	3.0	3.0	0.10	
TPG PEU	100	5.5	16.6	2.8	2.8		
PPG 425 PEU	100	4.5	5.7	2.5	1.0	0.14	
PPG 775 PEU	100	5.4	8.9	5.1	1.4	0.15	
PPG 2000 PEU	100	7.5	16.1	8.6	3.1	0.28	0.20
PPG 775 PEU + 5% PPG 2000	100	5.9	12.9	10.6	5.9	0.47	0.69
PPG 775 PEU + 10% PPG 2000	100	6.0	13.0	11.0	7.2	0.70	0.90

	secondary peaks from HS							
polymer	106	132	150	165	180	197	223	249
DPG PEU	67.0	41.0	5.0	6.7	7.8	6.7	6.3	1.3
TPG PEU	44.4	29.6	3.9	4.4	5.6	4.4	4.3	0.90
PPG 425 PEU	9.5	6.0	1.2	1.2	1.7	1.1	0.8	0.15
PPG 775 PEU	2.7	1.9	0.50	0.27	0.36	0.36	0.26	
PPG 2000 PEU	1.0	0.90	0.20	0.10	0.15	0.15	0.10	
PPG 775 PEU + 5% PPG 2000	1.3	0.90	0.20	0.10	0.15	0.20	0.10	
PPG 775 PEU + 10% PPG 2000	1.0	0.70	0.20	0.10	0.15	0.15	0.10	

peaks found at 150, 165, 180, 197, 223, and 249 D can also be assigned to fragments arising from the diisocyanate function. The small peak at 249 D represents an MDI unit, $(M - H)^+$, and the ion at 223 D corresponds to an MDI molecule with one isocyanate group replaced by an amino group. The assignments of probable structures for these ions are summarized in Table III. Together they represent a unique fingerprint for the MDI hard-segment unit.

The presence of different diol units in the PEU hard-segment model polymer chain accounts for the differences between the spectra in Figures 4 and 5. An important distinguishing feature in the spectrum from the PPG/MDI/ED model (Figure 5) is the presence of intense peaks at 31, 59, and 87 D. These peaks were identified earlier in Figure 3 and Table II as major fragments from PPG itself. Because these peaks are of negligible intensity in the butanediol PEU spectrum (Figure 4), these ions originate only from the propylene glycol unit of the PEU and not from the hard-segment unit. The SIMS spectra from the PPG/MDI/ED hard-segment models made with DPG and TPG were similar. Data are presented in Table IV.

3. Segmented Poly(ether urethanes). 3.1. PPG/MDI/ED Polymers. Figure 6 compares the positive ion SIMS spectra for a series of PPG/MDI/ED PEU's prepared with 425, 775, and 2000 molecular weight PPG segments. In the low mass region (<100 D), these spectra show a series of intense clusters at 59, 73, 87, and 99 D, which are undoubtedly due to ions derived directly from the PPG soft segment. At higher masses, the familiar key peaks associated with the hard segment are found (e.g., 106, 132, 223 D). These PPG/MDI/ED spectra are virtually identical in simple fingerprint terms; however, clear

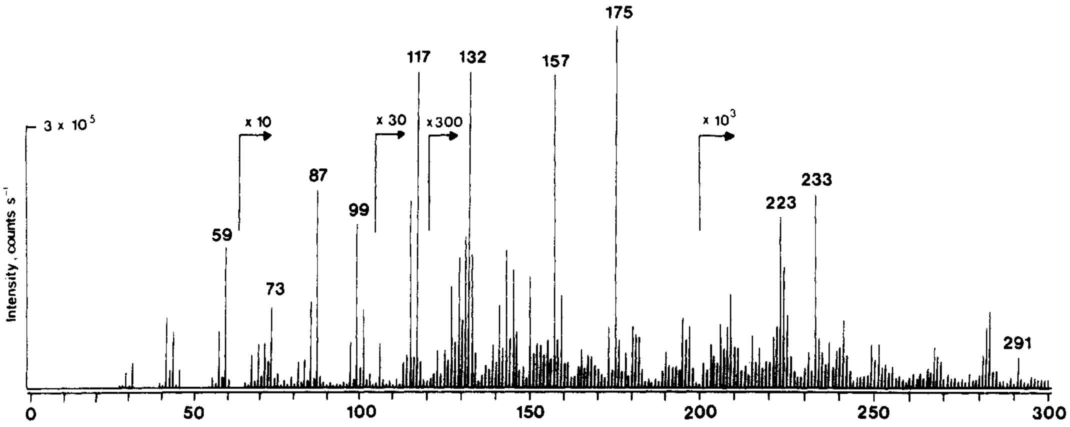


Figure 7. Positive ion SIMS spectrum of a PPG 775 /MDI/ED PEU prepared with a 10% PPG 2000 additive.

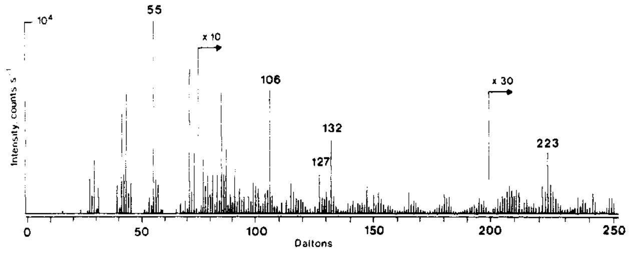


Figure 8. Positive ion SIMS spectrum of PTMG 625/MDI/ED PEU.

differences between the three materials emerge when the pattern of relative intensities are compared for certain peaks. The significance of these intensities will be discussed in section 5.1.

In Figure 7, the SIMS spectrum of a PPG 775 PEU doped with 10% PPG (MW 2000) is shown. When this spectrum is compared with those in Figure 6, a large difference in the relative abundance of the soft-segment peaks (e.g., 157, 175, 233 D) can be noted. Relative peak intensity data taken from spectra in Figures 5–7 are collected and compared in Table IV. In each case normalization is to the 59 D peak, and relative intensities of less than 0.1 have not been included.

3.2. PTMG/MDI/ED Polyurethanes. Positive ion SIMS spectra were obtained for a series of PTMG/MDI/ED poly(ether urethanes) prepared with 625, 1000, and 2000 molecular weight PTMG blocks. The spectrum for the PTMG 625 PEU shown in Figure 8 is typical, containing peaks characteristic of both the hard and soft segments. The series of low mass clusters appearing at 55, 71, 73, 85, and 127 D can be attributed directly to fragments of the polyether PTMG units. Above 100 D, the weaker, but nonetheless still distinct, series of ions at 106, 132, and 223 D are observed that originate from the diisocyanate. Subtle differences in relative peak intensities were apparent within the series of PEU's with different soft-segment molecular weights, especially when contrasting the 100–150 D region as is shown in Figure 9.

4. General Considerations. The model polyethers have yielded unequivocal positive ion fingerprints that are easily interpretable in terms of the original polymer structures. A straightforward distinction can be made between the PEG, PTMG, and PPG soft-segment types in a PEU polymer. Generally, the polyether spectra show a rational series of ions corresponding to the successive additions of carbon atoms and an oxygen atom to a single repeat unit. The most prominent secondary ions observed for each polyether provide fingerprints that can subsequently be used to establish the presence of that soft-segment species at the surface of a PEU polymer.

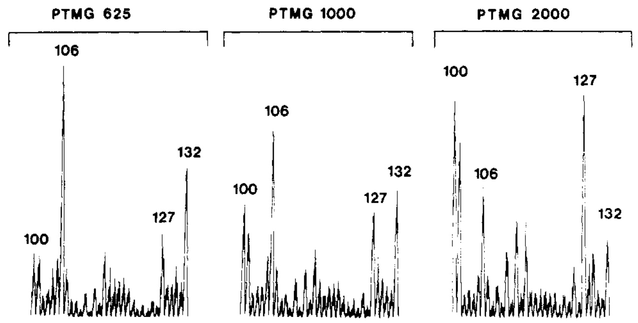


Figure 9. Positive ion SIMS spectra of PEU's prepared with PTMG 625, 1000, and 2000.

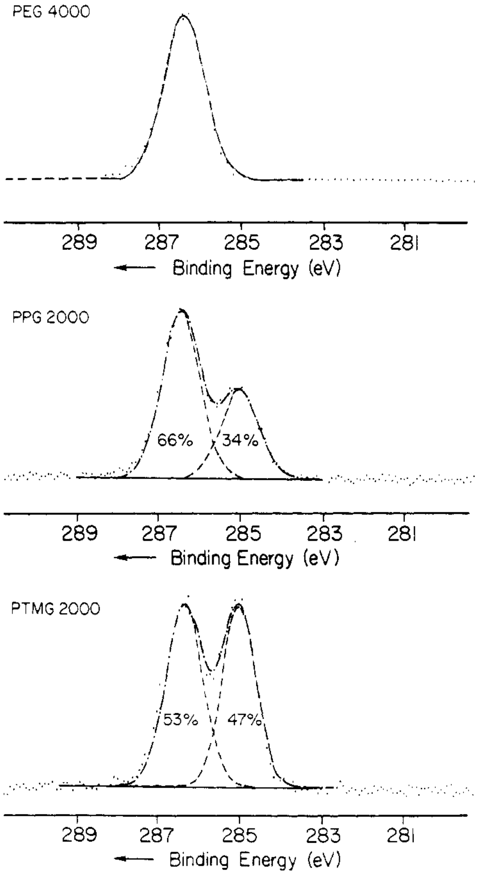


Figure 10. C1s XPS spectra of pure polyethers (a) PEG 4000, (b) PPG 2000, and (c) PTMG 2000.

XPS spectra can also readily differentiate the pure polyethers (see Figure 10). However, when these polyethers are incorporated into polyurethanes, it becomes considerably more difficult to differentiate them. Still,

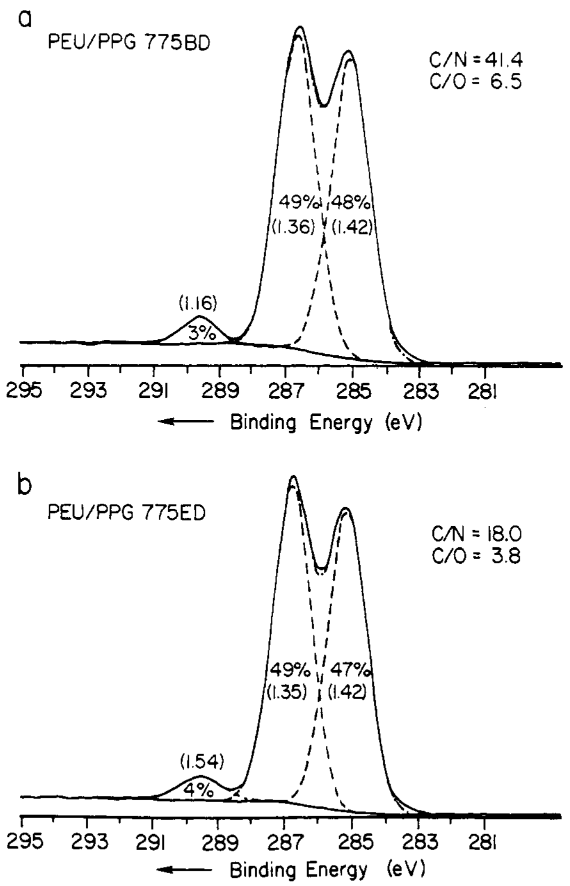
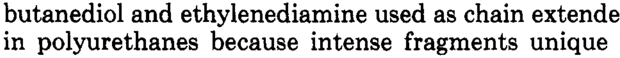


Figure 11. C1s XPS spectra of (a) PPG 775/MDI/BD and (b) PPG 775/MDI/ED. Peak fwhm values are indicated in parentheses.

some information can be derived from the XPS spectra to suggest which polyether might have been used in a polyurethane (see XPS results in section 5.2).

SIMS spectra from the hard-segment models have revealed that fragment ions characteristic of the original diisocyanate will identify the PEU hard-segment surface functionality. However, SIMS has been relatively ineffective in distinguishing the small differences in the hard-segment-rich model polyurethanes prepared with DPG and TPG.

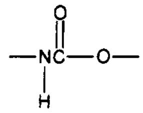
For the segmented polyurethanes, the fragmentation of the polymer chain leads to positive ion SIMS spectra that show the characteristic fragments of the original diisocyanate and diol components. These fragments are also common features in the pyrolysis mass spectra of similar types of PEU materials,[33-35] and it is generally accepted that the principal thermal degradation processes are as follows:



$$R{-}NH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}R' \nearrow R{-}N{=}C{=}O + HO{-}R' \qquad \searrow RNH_2 + CO_2 + \text{olefinic products}$$

Cleavage of the PEU polymer chains in this manner would explain the overall appearance of the positive ion SIMS spectra described above. The close similarity between SIMS and high-temperature pyrolysis mass spectra was previously noted in a recent study of Nylon polymers.[26]

It is doubtful that SIMS could distinguish between butanediol and ethylenediamine used as chain extenders in polyurethanes because intense fragments unique to these components could not be identified in the hard-segment models. The positive ion SIMS spectrum from PPG 775/MDI/BD is identical with that of Figure 6(b) from PPG 775/MDI/ED. However, a distinction can be surmised from the XPS spectra. The C1s spectra for these two poly(ether urethanes) prepared with different chain extenders are shown in Figure 11. These high-resolution spectra have been resolved into three component peaks: a hydrocarbon environment (C–C, 285.0 eV), a carbon singly bound to oxygen environment (C–O, 286.5 eV), and a carbon in a carbamate environment (~289.4 eV). Although the full widths at half-maximum (fwhm) are similar for the hydrocarbon and C–O peaks in both spectra, the fwhm for the carbamate peak differs significantly between the two polymers. We ascribe the broader carbamate peak (fwhm = 1.54 eV) observed for the ED chain-extended PEU to contributions from the carbamate and urea linkages.[36] The narrow (fwhm = 1.16 eV) carbamate peak seen for the BD chain-extended polymer is representative of only one molecular species



$$-\underset{\displaystyle H}{\underset{|}{N}}\overset{\displaystyle O}{\overset{\|}{C}}-O-$$

Thus, by using the high-resolution C1s spectra, we can extract information consistent with relatively subtle variations in the expected structure.

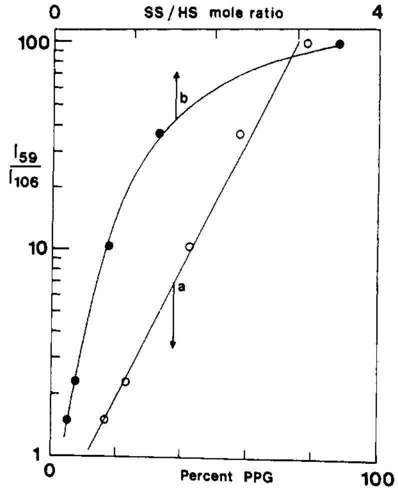


Figure 12. log (I_{59}/I_{106}) peak intensity ratios plotted as a function of bulk concentration expressed in terms of (a) % PPG content and (b) SS/HS ratio.

5. Quantitative Surface Composition. 5.1. SIMS Results. Intense secondary ions which are uniquely associated with only one structural component of the PEU polymer might provide quantifiable SIMS signals useful for correlation with PEU surface composition. Suitably intense ions for monitoring the level of soft segment (SS) at the surface can be chosen from the appropriate fingerprint series given in Figures 1–3 (e.g., 59 D for PPG). For the hard-segment (HS) case, because the spectra from the SS polymers PEG, PTMG, and PPG contain no peaks at masses 106 and 132 D, the intensity of these ions from an MDI-type PEU matrix will reflect the HS surface concentration. On this basis, it is reasonable to consider that a peak intensity ratio of the type I_{SS}/I_{HS} (e.g., I_{59}/I_{106} for a PPG/MDI PEU) is representative of the relative concentrations of HS and SS within the uppermost surface layer and can be adopted as a measure of surface composition.

To test this hypothesis, plots of several I_{SS}/I_{HS} peak ratios as a function of bulk composition were made. For the PPG PEU series (including the PPG hard-segment models), the best plot was obtained by using the I_{59}/I_{106} ion ratios (as presented in Table V). In Figure 12, the log

Table V
Theoretical Average Bulk Compositions and SIMS Ratios of Peak Intensities for the PPG PEU Series

	bulk composition		I_{SS}/I_{HS} secondary ion intensity ratios				
polymer	% SS	SS/HS	59/106	117/106	99/132	157/132	117/223
DPG/MDI PEU	16.7	0.2	1.5	0.05	0.05		0.48
TPG/MDI PEU	23.1	0.3	2.3	0.06	0.06		0.65
PPG 425/MDI PEU	42.4	0.7	10.5	0.11	0.42	0.023	1.25
PPG 775/MDI PEU	57.3	1.3	37.0	0.50	2.7	0.079	5.4
PPG 2000/MDI PEU	77.6	3.5	99.0	3.10	9.6	0.31	31.0
PPG 775/MDI PEU + 5% PPG 2000	59.3	1.5	77.0	4.50	11.8	0.52	59.0
PPG 775/MDI PEU + 10% PPG 2000	61.2	1.6	100	7.20	15.7	100	72.0

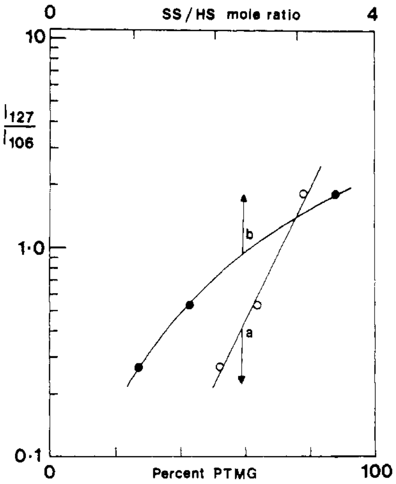


Figure 13. log (I_{127}/I_{106}) peak intensity ratios plotted as a function of bulk concentration expressed in terms of (a) % PTMG content and (b) SS/HS ratio.

of this ratio is plotted as a function of bulk composition expressed both as a percent PPG content (curve a) and as a SS/HS ratio (curve b). Similar plots were made for the PTMG/MDI/ED polymers by using I_{127}/I_{106} as shown in Figure 13. The correlations shown by the (a) curves in Figures 12 and 13 provide a relationship between SIMS data and polymer composition for comparing various PEU polymers of the PPG/MDI/ED and PTMG/MDI/ED types. In the (b) curves in Figures 12 and 13, the departure from linearity may result from a simple matrix effect, but it more likely represents a genuine effect arising from differences between the surface and bulk compositions.

Detailed analysis of the PEU SIMS spectra in terms of the relative intensity of the major fragments revealed several significant differences that might be related to variations in the PEU surface structure. For the PPG/MDI/ED polymers, when the chain length of the PPG is increased, one observes an increase in the intensities of the characteristic soft-segment peaks relative to those from the hard segment. As an illustration, compare parts a and c of Figure 6, where changing the molecular weight from 425 to 2000 dramatically increases certain I_{SS}/I_{HS} secondary ion intensity ratios as shown in Table V. These spectral changes suggest that the surface composition of these segmented polyurethanes progressively changes from domination by hard segment to domination by the polyether as the soft-segment molecular weight is increased.

A similar picture is revealed in a comparison of the spectra from the PTMG/MDI/ED PEU series: An increase in the relative spectral contribution from the PTMG soft segment occurs with increased polyether molecular weight. In particular, this trend can be seen from the changes in the I_{127}/I_{106} ratios as shown in Figure 13 and Table VI.

Table VI
Theoretical Average Bulk Compositions and Secondary Ion Intensity Ratios for the PTMG PEU Series

	bulk composition		I_{SS}/I_{HS} secondary ion intensity ratios
polymer	% SS	SS/HS	127/106
PTMG 625 PEU	52.0	1.1	0.27
PTMG 1000 PEU	63.4	1.7	0.53
PTMG 2000 PEU	77.6	3.5	1.80

Two explanations can account for the observation that the surface composition depends on the polyether molecular weight. First, a simple concentration effect accounts for an increased weight fraction of soft segment in these polyurethanes with increased polyether chain length. Theoretical average bulk compositions are given in Tables V and VI. Second, these changes in surface composition would also be expected to result from differences in the extent of surface phase segregation and the migration tendency of the soft segment, especially since it is well-known that such behavior is strongly influenced by the chain length of the polyether. [The effect of low MW oligomeric components can be ruled out since spectra of PEU's are identical before and after MeOH extraction.] From the results obtained in this study, it is not possible to separate these two effects. This would require studying PEU's containing different soft-segment MW's but having the same hard-segment content. Such a requirement was realized to a large extent in a recently completed XPS/SIMS study of fluorinated PEU's in which the soft-segment concentration and chain length effects were examined independently.[25]

5.2. XPS Results. The XPS data are completely consistent with the results obtained by SIMS. In addition, absolute and relative quantitative comparisons can be made with a higher degree of certainty since the factors influencing quantitation are better understood in XPS. The C1s spectra and elemental ratios for the PPG/MDI/ED series of polymers are shown in Figure 14. Comparable data for the PTMG/MDI/ED series are given in Figure 15. A striking increase in the C–O peak area of the C1s spectra for the PPG series is observed as the polyether molecular weight is increased. Also, as the polyether MW increases in this series, the C/N atomic ratio decreases. These same trends are echoed in the data for the PTMG/MDI/ED series (Figure 15), although the magnitude of the change in the C1s spectra is not as dramatic as exhibited by the PPG series. Since the PPG soft segment has a higher C–O/C–C ratio than PTMG, the shape of the C1s spectrum would be expected to be more sensitive to PPG concentration in the surface zone.

A comparison between the XPS-derived elemental ratios and those expected based upon the stoichiometry of the polymers (Table VII) is of interest. For the DPG and TPG hard-segment model polymers, generally good agreement was found between expected and observed stoichiometries.

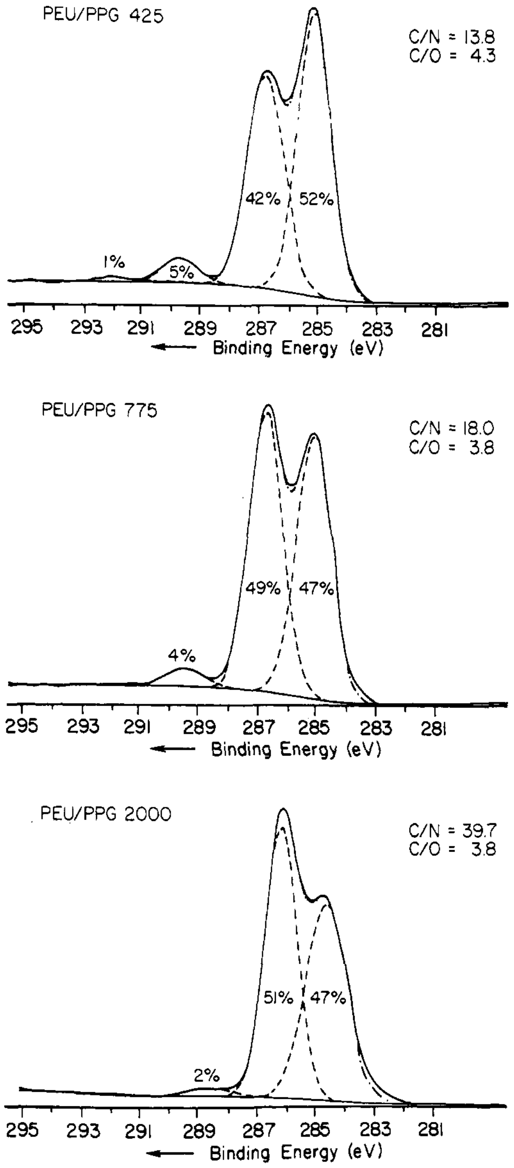


Figure 14. XPS C1s spectra and elemental ratios for (a) PPG 425 PEU, (b) PPG 775 PEU, and (c) PPG 2000 PEU.

Table VII
Stoichiometric and XPS-Derived Elemental Ratios

	stoichiometry		XPS	
	C/O	C/N	C/O	C/N
DPG PEU	5.4	6.3	5.5	8.6
TPG PEU	5.1	6.8	5.1	7.7
PPG 425 PEU	4.4	9.0	4.3	13.8
PPG 775 PEU	3.9	12.0	3.8	18.0
PPG 2000 PEU	3.4	22.5	3.8	39.7
PTMG 625 PEU	4.9	11.1	4.4	20.3
PTMG 1000 PEU	4.6	14.6	4.2	31.0
PTMG 2000 PEU	5.2	23.9	5.0	65.2

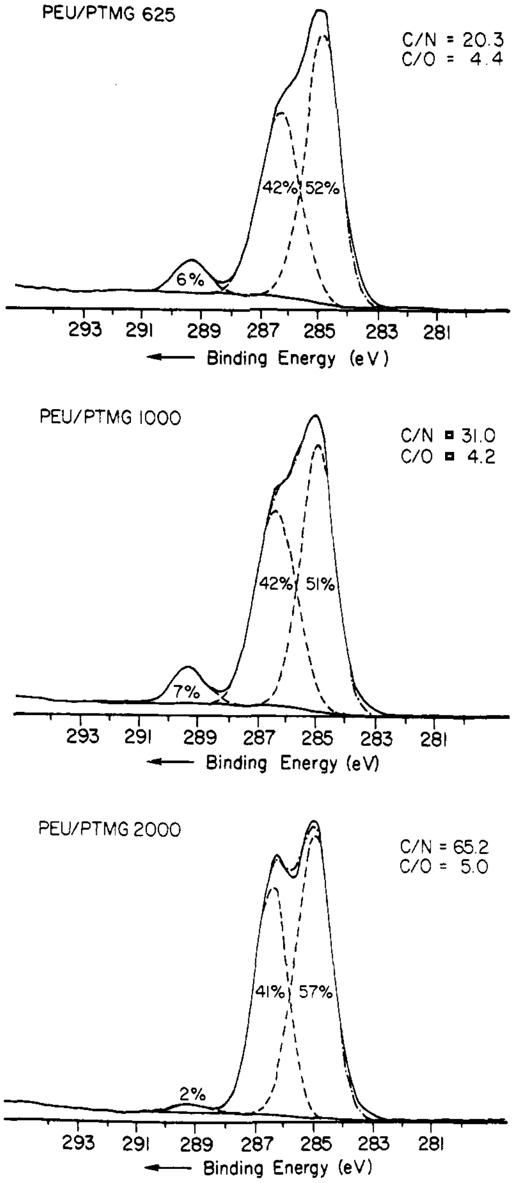


Figure 15. XPS C1s spectra and elemental ratios for (a) PTMG 625 PEU, (b) PTMG 1000 PEU, and (c) PTMG 2000 PEU.

For the DPG-containing polyurethane, the elemental ratios calculated were C/O = 5.4 and C/N = 6.3, compared with the actual measured values of C/O = 5.5 and C/N = 8.6. Similarly, for the TPG/MDI polymers, calculated elemental ratios were C/O = 5.1 and C/N = 6.8, whereas XPS-derived values were C/O = 5.1 and C/N = 7.7. However, for the segmented PEU's, large differences were noted between expected and XPS-measured elemental ratios, particularly the C/N ratio. For example, PTMG 2000/MDI/ED was expected to have a C/N ratio of 23.9, whereas the value actually measured was 65.2. In all cases, the segmented PEU's had actual surface C/N ratios higher than that expected based upon the stoichiometry. This difference is a reflection of the polyether localization at the surface of these polymers. The overlayering effect of this polyether attenuates the N signal, leading to the high XPS C/N values.

6. Combining SIMS and XPS Results. To summarize, XPS results indicated that there was a surface excess of polyether in the segmented PEU's and provided a quantitative measurement of the magnitude of this excess. Angular dependent XPS would permit further confirmation of this polyether surface excess.[22] In addition, increasing polyether levels at the surface were observed as the molecular weight of the polyether increased. SIMS confirmed this latter observation but could not quantitatively indicate the overall surface excess of polyether.

Even with the complications associated with quantitative interpretation of SIMS spectra, certain phenomenological observations concerning the polyether component can be exploited to yield new information about PEU's. A significant spectral feature apparent only amongst the PPG/MDI/ED polymers is highlighted by comparing the SIMS relative intensity data in Tables IV and V. Although the characteristic fragments expected from PPG units appear in the PEU spectra, their relative intensities vary considerably and are quite different from those measured for the pure PPG's. Relative to the base peak at 59 D, the intensities of the other clusters derived from the PPG segments increase as the molecular weight of the PPG units in the PEU increases (Table IV). This is contrary to the general trend shown by the pure polyethers where the highest cluster intensities are exhibited by the lower molecular weight PPG's (Table II). Moreover, the relative intensities of the higher mass clusters from the PPG units are especially low when compared with the original PPG polyether data. This trend is best illustrated by comparing the relative intensity changes for the ion series at 59, 117, and 175 D, corresponding to $[(CH_2CHO)_nH^+]$ for $n = 1–3$.

For a polyurethane matrix, we suggest that the relative yields of ion fragments from the soft segment can be influenced by the surface morphology (i.e., microdomain structure). Indeed, if the polyether chain ends are being effectively "anchored" by their connection with the rigid hard-segment units, the mobility of the soft-segment block molecular chains would be constrained, affecting their conformation/orientation at the outermost surface. This explanation is supported by the fact that an addition of 5% or 10% of a PPG 2000 to the base polymer PPG 775 PEU casting solution creates a PEU surface which gives rise to enhanced polyether peak intensities (Table IV) similar to those for pure PPG 2000. This behavior is consistent with the presence of a surface layer of free PPG. Accordingly, one observes the type of cluster intensities expected for pure PPG 2000.

Another important point is that for a relatively small amount of free PPG added to the casting solution (i.e., a small total increase in the PPG content of the final PEU film), one observes a dramatic increase in I_{SS}/I_{HS} ratios. Together with the above observations, this suggests that the added PPG migrates directly to the PEU surface to form a surface layer enriched with the polyether. This preferential migration of the soft segment conforms to the thermodynamic requirement of lowest surface free energy. Angular dependent XPS data generally indicate that a significant excess of polyether soft segment is commonly present within 20 Å of the surface, and the hard-segment domains are largely, if not completely, excluded.[14,22] In contrast, SIMS, which has a higher analytical sensitivity for hard segment than XPS, clearly reveals the presence of some hard segment in the outermost surface region.

There is no systematic variation in the relative intensities of the characteristic PTMG soft-segment peaks from a PTMG/MDI/ED-type PEU matrix, perhaps a reflection of the strong surface-concentrating tendency of the PTMG related to its better phase separation.[22] However, in this case, the relative intensities of the larger fragment ions from PTMG units of the PEU ($[-(CH_2)_4O]_n-H^+$, where $n > 1$) were significantly weaker than for the PPG equivalent and could not be followed accurately. For PPG PEU's, one would not expect as large a degree of phase separation as for PTMG PEU's. Thus, the PPG surface should have more hard segment mixed or distributed within it than an equivalent molecular weight PTMG/PEU surface, and this hard segment may be affecting the ion yield of the PPG soft segment.

Conclusions

By using model polymers and purified polyurethanes of defined structure, we have established a basis for the static SIMS analysis of segmented polyurethanes. XPS has also been used to provide corroborative information on PEU surface structure and to contribute certain specific data that would be difficult to obtain from SIMS alone. It is worthwhile to compare the two techniques directly in light of these studies. SIMS has been shown to provide much higher detection sensitivity than XPS and also to be more surface-sensitive. SIMS has, in some cases, also provided specific structural information that is not available from XPS (e.g., distinguishing between the three types of polyether soft segments in PEU's). XPS, on the other hand, has also provided structural information that SIMS was incapable of resolving (e.g., distinguishing poly(ether urethanes) from poly(ether urethane ureas)). XPS data are also more specific as to the chemical species present. With SIMS, one must infer which elements or functional groups are present on the basis of the molecular weight of each ion. XPS probes to a sample depth of 50–100 Å, considerably deeper than SIMS. However, XPS at a glancing angle from the sample surface will permit sampling to ~10 Å (similar to the depth studied by static SIMS, see ref 25), but the signal-to-noise ratio will decrease. The angular dependent XPS methods allow the nondestructive depth profiling of materials which is not possible with SIMS. Finally, quantification is better understood in XPS, but internally consistent, relative quantitative comparisons can be made by using static SIMS, as shown here and in previous papers.[25,28] In summary, both SIMS and XPS have strong and weak points, but when used together, a more highly refined surface characterization can be performed.

This study has also yielded new information about the nature of PEU surfaces. The enrichment in polyether at the PEU surface seen by others has been confirmed. However, new evidence has been obtained indicating that this surface layer of polyether is not pure but is interspersed (in the uppermost 10–15 Å) with small quantities of hard-segment components. On the basis of the fragmentation patterns observed for the SIMS peaks associated with the soft segment, we suggest that SIMS may provide valuable information about surface morphology as well as chemistry. However, at this point, it is difficult to interpret these data precisely.

A framework for understanding molecular fragmentation patterns obtained with static SIMS on polyurethanes has been provided. Future studies will deal with commercial polyurethanes and will expand upon our preliminary observations on the relationship between PEU surface morphology and SIMS spectra. Also, there is significant concern that the surface structure of polyurethanes may rearrange in contact with aqueous solution. This phenomenon has been observed with other polymer systems[37] and may have far-reaching consequences for understanding the biological interactions of polyurethanes. We will perform studies on hydrated (frozen) polyurethane surfaces and compare the results obtained to those reported here. There should be an energetic driving force leading to surface rearrangement (i.e. hard segment migrating to the surface). However, the rearrangement may not be observed if molecular mobility in the polyurethanes is impeded by the rigid, crystalline hard segments.

Acknowledgment. Generous support was received from NIH Grants RR01296 and HL25951 for portions of this work. The assistance of David G. Castner and Robert McElhaney with some of the ESCA spectra is appreciated, as are Nancy B. Mateo's editorial contributions to this work.

Registry No. (DPG)(MDI) (copolymer), 59952-43-1; (TPG)(MDI) (copolymer), 52747-01-0; (PPG)(MDI) (block copolymer), 115383-48-7; (PPG)(MDI) (SRU), 55973-42-7; (PTMG)(MDI) (block copolymer), 109211-47-4; (PTMG)(MDI) (SRU), 65086-54-6; (MDI)(BD) (copolymer), 25805-16-7; (PPG)(MDI)(ED) (block copolymer), 106102-96-9; PEG (SRU), *Macromolecules* 1988, *21*, 2959-2963

25322-68-3; PTMG (SRU), 25190-06-1; (PPG)(MDI)(BD) (block copolymer), 106208-51-9.

References and Notes

(1) Grasel, T. G.; Cooper, S. L. *Biomaterials* **1986**, *7*, 315.
(2) Hanson, S. R.; Harker, L. A.; Ratner, B. D.; Hoffman, A. S. In *Biomaterials 1980, Advances in Biomaterials*; Winter, G. D., Gibbons, D. F., Plenk, H., Jr., Eds.; Wiley: Chichester, England, 1982; Vol. 3, p 519.
(3) Lelah, M. D.; Grasel, T. G.; Pierce, J. A.; Cooper, S. L. *J. Biomed. Mater. Res.* **1986**, *20*, 433.
(4) Lyman, D. J.; Albo, D.; Jackson, R.; Knutson, K. *Trans.—Am. Soc. Artif. Intern. Organs* **1977**, *23*, 253.
(5) Sa Da Costa, V.; Brier-Russell, D.; Salzman, E. W.; Merrill, E. W. *J. Colloid Interface Sci.* **1981**, *80*, 445.
(6) Ratner, B. D.; Paynter, R. W. In *Polyurethanes in Biomedical Engineering, Progress in Biomedical Engineering*; Planck, H., Egbers, G., Syre, I., Eds.; Elsevier: Amsterdam, 1984; Vol. 1, p 41.
(7) Takahara, A.; Tashita, J.; Kajiyama, T.; Takayanagi, M.; MacKnight, W. *Polymer* **1985**, *26*, 987.
(8) Kaul, A.; Ratner, B. D.; Mateo, N. B., submitted for publication in *J. Adhes.*
(9) Crawford, D.; DiNardo, M.; Dwight, D.; Rials, T. Abstracts of the 7th Annual Meeting of the Adhesion Society, Jacksonville, FL, Feb 13–15, 1984.
(10) Graham, S. W.; Hercules, D. M. *J. Biomed. Mater. Res.* **1981**, *15*, 465.
(11) Hu, C. B.; Sung, C. S. P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1980**, *21*, 156.
(12) Knutson, K.; Lyman, D. J. In *Biomaterials: Interfacial Phenomena and Applications*; Cooper, S. L., Peppas, N. A., Eds.; Advances in Chemistry 199; American Chemical Society: Washington, DC, 1982; p 109.
(13) Lelah, M. D.; Stafford, R. J.; Lambrecht, L. K.; Young, B. R.; Cooper, S. L. *Trans.—Am. Soc. Artif. Intern. Organs* **1981**, *27*, 504.
(14) Paynter, R. W.; Ratner, B. D.; Thomas, H. R. In *Polymers as Biomaterials*; Shalaby, S. W., Hoffman, A. S., Ratner, B. D., Horbett, T. A., Eds.; Plenum: New York, 1984; p 121.
(15) Wilkes, G. L.; Abouzahr, S. *Macromolecules* **1981**, *14*, 456.
(16) Blackwell, J.; Nagarajan, M. R.; Hoitink, T. B. *Polymer* **1982**, *23*, 950.
(17) Blackwell, J.; Nagarajan, M. R. *Polymer* **1981**, *22*, 202.
(18) Blackwell, J.; Quay, J. R.; Nagarajan, M. R.; Born, L.; Hespe, H. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1247.
(19) Crystal, R. G.; Erhardt, P. F.; O'Malley, J. J. In *Block Polymers*; Aggarwal, S. L., Ed.; Plenum: New York, 1970; p 179.
(20) Leung, L. M.; Koberstein, J. T. *Macromolecules* **1986**, *19*, 706.
(21) Van Bogart, J. W. C.; Bluemke, D. A.; Cooper, S. L. *Polymer* **1981**, *22*, 1428.
(22) Yoon, S. C.; Ratner, B. D. *Macromolecules* **1986**, *19*, 1068.
(23) Yih, R. S.; Ratner, B. D. *J. Electron Spectrosc. Relat. Phenom.* **1987**, *43*, 61.
(24) Briggs, D. *Surf. Interface Anal.* **1986**, *9*, 391.
(25) Hearn, M. J.; Briggs, D.; Yoon, S. C.; Ratner, B. D. *Surf. Interface Anal.* **1987**, *10*, 384.
(26) Briggs, D. *Org. Mass Spectrom.* **1987**, *22*, 91
(27) Hearn, M. J.; Briggs, D. *Surf. Interface Anal.* **1988**, *11*, 198.
(28) Briggs, D.; Ratner, B. D. *Polym. Commun.* **1988**, *29*, 6.
(29) Brash, J. L.; Fritzinger, B. K.; Bruck, S. D. *J. Biomed. Mater. Res.* **1973**, *7*, 313.
(30) Briggs, D.; Hearn, M. J. *Vacuum* **1980**, *36*, 1005.
(31) Briggs, D.; Wootton, A. B. *Surf. Interface Anal.* **1982**, *4*, 109.
(32) Briggs, D.; Hearn, M. J. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 47.
(33) Dussel, H. J.; Wenzel, N.; Hummel, D. O. *Angew. Makromol. Chem.* **1982**, *106*, 107.
(34) Foti, S.; Giuffrida, M.; Maravigna, P.; Montaudo, G. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1583.
(35) Coleman, D. L.; Meuzelaar, H. L. C.; Kessler, T. R.; McClennen, W. H.; Richards, J. M.; Gregonis, D. E. *J. Biomed. Mater. Res.* **1986**, *20*, 417.
(36) Ratner, B. D. In *Photon, Electron, and Ion Probes of Polymer Structure and Properties*; Dwight, D. W., Fabish, T. J., Thomas, H. R., Eds.; ACS Symposium Series 162; American Chemical Society: Washington, DC, 1981; p 371.
(37) Ratner, B. D.; Weathersby, P. K.; Hoffman, A. S.; Kelly, M. A.; Scharpen, L. H. *J. Appl. Polym. Sci.* **1978**, *22*, 643.

Cross-Link Point Mobility in Swollen Polymer Networks by Phosphorus-31 Spin–Lattice Relaxation in the Rotating Frame

L. Charles Dickinson,* James C. W. Chien, and W. J. MacKnight

Department of Polymer Science and Engineering and Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003.

Received December 2, 1987

ABSTRACT: Spin–lattice relaxation of ^{31}P nuclei in the rotating frame at 50 KHz, $T_{1\rho}{}^{P}$, has been measured as a function of the linear swelling ratio ($\lambda = (V/V_0)^{1/3}$) and of M_c (molecular weight between cross-links) for a series of nearly monodisperse trifunctional α,ω-dihydroxypoly(propylene oxide) (M_c = 425, 1000, 2000, 3000) networks with tris(4-isocyanatophenyl) thiophosphate as the cross-linking agent. $T_{1\rho}{}^{P}$ is strongly dependent upon both λ and M_c and offers a direct measure of the cross-link point motion. For M_c of 2000 or less, the $T_{1\rho}{}^{P}$ versus λ plot has a minimum. Both line shapes and $T_{1\rho}{}^{P}$ reach limits near full swell, indicating molecular motion is constrained by the swollen chains. For M_c = 3000, $T_{1\rho}{}^{P}$ increases monotonically with increase of λ; the swollen chains do not appreciably restrict the motion of the cross-link. The results are entirely consistent with our previous studies on the motion of the chain by $T_{1\rho}{}^{H}$ and $T_{1\rho}{}^{C}$ in these networks where the effect of the cross-links is pronounced only for $M_c \leq 2000$.

Introduction

The level of understanding of the structure and dynamics of networks has been greatly elevated by recent improved spectroscopic and scattering techniques. Small angle neutron scattering (SANS) of labeled chains has shown the nonaffine elongation of single chains in networks.[1] Orientational dynamics has been studied by magnetic resonance relaxation and fluorescence correlation techniques. The central purpose of this work is to obtain quantitative information about the motion of the cross-link point itself in a series of cleanly synthesized model networks.

Nuclear magnetic resonance (NMR) has long been used to study rubbery materials. Nishi[2] studied T_2 of protons in carbon black filled natural rubber and was able to distinguish regions of restricted motion near the filler particles which were not affected by swelling in CCl_4. Rowland[3] and Charlesby[4] investigated the proton relaxation, $T_1{}^{H}$, in several rubbery polymers as a function of temperature and cross-link density and found that the

0024-9297/88/2221-2959$01.50/0