Surface and bulk structure of segmented poly(ether urethanes) with perfluoro chain extenders. V. Incorporation of poly(dimethylsiloxane) and polyisobutylene macroglycols

4 AUTHORS:

Sung Chul Yoon
Gyeongsang National University
101 PUBLICATIONS   **1,679** CITATIONS

SEE PROFILE

Buddy D Ratner
University of Washington Seattle
427 PUBLICATIONS   **18,277** CITATIONS

SEE PROFILE

Bela Iván
Institute of Materials and Environmental Che…
133 PUBLICATIONS   **2,412** CITATIONS

SEE PROFILE

Joseph P Kennedy
University of Akron
579 PUBLICATIONS   **7,948** CITATIONS

SEE PROFILE

Surface and Bulk Structure of Segmented Poly(ether urethanes) with Perfluoro Chain Extenders. 5. Incorporation of Poly(dimethylsiloxane) and Polyisobutylene Macroglycols

Sung Chul Yoon

Department of Microbiology, Gyeongsang National University, Chinju 660-701, Republic of Korea

Buddy D. Ratner*

Department of Chemical Engineering and Center for Bioengineering, BF-10, University of Washington, Seattle, Washington 98195

Béla Iván

Central Research Institute for Chemistry, Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary

Joseph P. Kennedy

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909

Received January 14, 1993; Revised Manuscript Received November 2, 1993•

ABSTRACT: Nonpolar hydrophobic soft segments were synthetically incorporated into polyurethanes based on 4,4'-methylenebis(phenyl isocyanate) (MDI)/hexafluoro-1,5-pentanediol (FP)/poly(tetramethylene glycol) (PTMO). The soft segments incorporated were dihydroxy-terminated poly(dimethylsiloxane) (PDMS) and polyisobutylene (PIB). All soft segments have similar molecular weights ($M_n \approx \sim 2000$). All polymers prepared also have similar levels of hard segment (~55 wt %), and they are soluble in common organic solvents. The solvent-cast polymers were studied by Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry, electron spectroscopy for chemical analysis (ESCA), and static secondary-ion mass spectrometry (SSIMS). The FTIR analysis showed that the absorption band at 3295 cm^{-1} is important for the interpretation of soft-segment mixing behavior in segmented poly(ether urethanes). The surface analysis data revealed that the incorporation of 20 wt % or less of PIB or PDMS in the soft segment may be sufficient to completely cover the polymer surface with each corresponding soft segment. The PDMS polyurethanes exhibited a pronounced casting solvent dependence on the surface and bulk structure, while the PIB polyurethanes showed less dependence on casting solvent.

Introduction

Segmented poly(ether urethanes) (PEUs) are attractive as engineering polymers and for biomedical applications because of their elasticity, strength, and durability.[1] These desirable bulk properties derive from the two-phase structure of hard and soft domains that is influenced by the type, chemical structure, and chain length of raw materials used in their synthesis. A PEU hard block is usually composed of a diisocyanate coupled with diamine or diol chain extenders. The soft block is typically poly(tetramethylene glycol) (PTMO), poly(propylene glycol) (PPO), or poly(ethylene glycol) (PEO). It is well established that in PEUs the extent of phase separation in the bulk is reflected in the surface structure.[2-6] Accordingly, PEU surface structures with desired properties can be tailored by changing the monomers and methods used for synthesis and fabrication of the PEU.

Studies have attempted to incorporate different types of soft segments e.g., poly(dimethylsiloxane) (PDMS),[7-12] polyisobutylene (PIB),[13] and polybutadiene,[14,15] into the polymer chains to modify the bulk properties of PEUs. The PEUs made with these soft segments have several drawbacks compared to conventional ones. The PDMS polyurethanes have poor mechanical properties.[9] Hydrocarbon soft-segment polyurethanes chain-extended with toluenediyl diisocyanate have low solubility in organic

solvents.[13] This can limit use for some practical applications. However, a partial incorporation of unique soft segments may be interesting with overall bulk properties unchanged and new surface properties noted. The partial incorporation of PDMS may lower the surface energy of polyurethanes because the surface tension of PDMS homopolymer (19.9 dyn/cm)[16] is low compared to that of PTMO (31.9 dyn/cm). The use of PIB as a soft segment is also interesting in light of its nonpolar nature. The alternate polar and nonpolar blocks in the same chain may lead to useful surface structures.

In previous studies of fluorine-containing polyurethanes,[3-5] it was found that the polyurethanes based on 4,4'-methylenebis(phenyl isocyanate) (MDI), polyether, and 2,2,3,3,4,4-hexafluoro-1,5-pentanediol (FP) chain extender were less phase segregated than when tetrafluoro-1,4-butanediol (FB) chain extender was used. The FP chain-extended polyurethanes were soluble in a wide range of solvents, permitting control of the degree of microphase segregation. Therefore, they were better model systems for studying hydrogen bonding and its influence on relationships between the surface and bulk structure. The incorporation of PDMS and PIB into polyurethanes is of interest for hydrogen-bonding studies since the two soft segments will not form hydrogen bonds with hard segments.

In this study, two series of polyurethanes incorporating PDMS and PIB were prepared based on MDI/FP/PTMO. All polymers prepared, including a 44% PIB polymer, were soluble in common solvents such as *N,N*-dimethylacet-

Table 1. Compositions and Molecular Weights of α,ω-Dihydroxy-Terminated Poly(dimethylsiloxane) (PDMS) or Polyisobutylene (PIB) Incorporated Polyurethanes Chain-Extended with Hexafluoro-1,5-pentanediol

sample	molar ratio MDI/FP/soft segment	PDMS or PIB wt % in soft segment	FP wt %	hard segment wt %	% yield	M_w (×10⁻⁴)	M_n (×10⁻⁴)	M_w/M_n	C	H	N	F	O	Si
									bulk elemental anal. (wt %)					
PTMO100–PEU	6:5:1	0	23	56	90	2.78	1.20	2.3						
PDMS20–PEU	6:5:1	20	23	56	93	10.1	3.06	3.3	56.4	6.9	3.7	12.2	18.1	2.7
PDMS50–PEU	6:5:1	50	23	55	86	2.82	1.11	2.5	52.8	6.7	3.7	12.0	16.9	7.9
PDMS100–PU	6:5:1	100	22	53	83	1.65	0.748	2.2	45.2	6.1	3.7	11.7	16.7	16.7
									(43.8	5.8	3.4	11.6	17.6	17.7)ᵃ
PIB20–PEU	6:5:1	20	23	56	86	2.33	0.896	2.6	61.1	7.5	3.8	11.9	15.8	
PIB50–PEU	6:5:1	50	23	56	86	1.48	0.704	2.1	63.5	7.8	3.7	11.7	13.3	
PIB100–PU	6:5:1	100	23	55	76	0.945	0.500	1.9	68.7	8.9	4.2	9.7	8.5	
									(67.4	8.3	3.6	12.3	8.3)ᵃ	

ᵃ Theoretical value calculated from feed molar ratio.

amide, 2-butanone (MEK), and tetrahydrofuran (THF). The solvent-cast polymers were studied by IR spectroscopy, differential scanning calorimetry (DSC), electron spectroscopy for chemical analysis (ESCA), and static secondary-ion mass spectrometry (SSIMS).

Methods

Polymer Synthesis and Purification. Fluorine-containing polymers were prepared by a two-step solution polymerization method published elsewhere.[2] The soft-segment oligomers were dihydroxy-terminated PDMS (M_n = 2300, Mercor Inc., Berkeley, CA), PTMO (M_n = 2000, DuPont, Wilmington, DE), and PIB (M_n = 2060, M_w/M_n = 1.12). The narrow molecular weight distribution hydroxyl telechelic PIB was prepared using living carbocationic polymerization techniques.[17] This process yielded tertiary chloro telechelic polyisobutylene. Quantitative regioselective dehydrochlorination of this product by *t*-BuOK[18] followed by hydroboration/oxidation[19] led to ditelechelic PIB with primary hydroxyl end groups. FP and MDI were obtained from Columbia Organic Chemical Co. and The Upjohn Co. (Kalamazoo, MI), respectively.

A typical reaction procedure for synthesizing segmented polyurethanes incorporating PDMS soft segments follows. PTMO (4.00 g) and PDMS (1.00 g) were dissolved in 30 mL of dry THF. MDI (3.66 g) was dissolved in 20 mL of THF. The MDI solution was added to the PTMO/PDMS solution. Tin octoate catalyst (0.2 wt % of the reactants) was added to the reaction solution at room temperature. The prepolymerization was carried out at 50 °C for 1 h. FP (2.58 g) was subsequently added to this solution. The chain extension reaction proceeded for 1 h at 60–65 °C under reflux. The resulting viscous solution was diluted to a concentration of 5% w/v or less in THF. The solution was precipitated into methanol, exhaustively washed with methanol, and then vacuum-dried. The polymer recovered was labeled as PDMS20–PEU since it contained 20 wt % of PDMS and 80 wt % of PTMO in the soft segment (Table 1).

The polyurethanes with PIB incorporated in their structure were prepared similarly. The reaction solvent was replaced with a cosolvent of *N,N*-dimethylacetamide (DMAc) and toluene (3: 2) because of its good solvent property for both the PIB oligomer and the polymer product. The prepolymerization and chain extension were carried out at 80–90 °C for 1 and 2 h, respectively, and then the reaction solution was allowed to stand overnight at room temperature. It was then precipitated in methanol. The molar ratio of MDI/FP/soft segment for all polymers in this study was 6:5:1.

PDMS polyurethanes were readily soluble in solvents such as DMAc, acetone, THF, and MEK but were less soluble in hexafluoro-2-propanol (HFIP) (> ~3–4% w/v). The PIB polyurethanes have a narrow range of solubility. They were soluble in DMAc and MEK up to ~20% w/v, while the solubility in acetone and HFIP decreased significantly with PIB content in the polymer.

Polymer Characterization. The stoichiometric incorporation of PDMS or PIB oligomers was confirmed by bulk elemental analysis (Huffman Laboratories, Golden, CO) and IR spectroscopy. The bulk oxygen content in the polymer samples was calculated as the fraction to give 100% total when considering
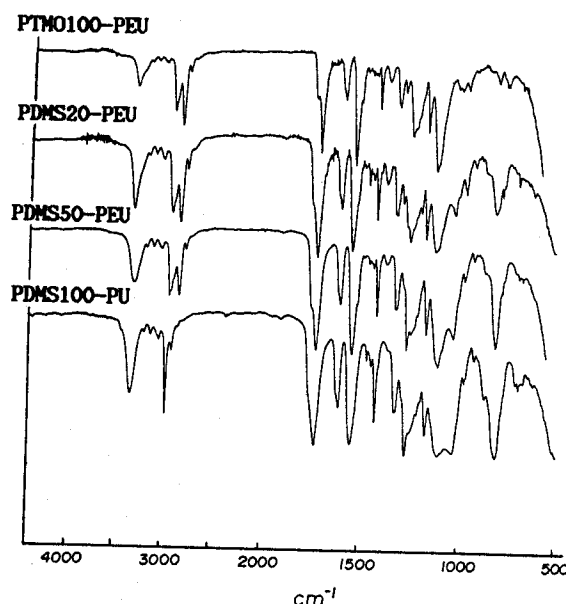

Figure 1. IR transmission spectra of polyurethanes incorporating PDMS.

all elements other than oxygen (Table 1). This assumption was made because of the interfering effect of fluorine on the oxygen determination.[2]

Table 1 shows good agreement between the theoretically calculated and experimentally determined values for the PDMS100–PU and PIB100–PU polymers. Similar PDMS or PIB incorporation in the polymers as in the feeds was also supported by the IR data for the two series of polyurethanes (Figures 1 and 2).

IR spectra were obtained on a Perkin-Elmer 1600 FTIR with 64 scans averaged for each sample at a resolution of 4 cm⁻¹ in the weak apodization mode. Samples for IR analysis were solvent-cast thin films on sodium chloride windows. The gradual increase of PDMS content in the polymers leads to a gradual increase of absorption at 2963, 1020, and 800 cm⁻¹ due to the C–H stretching of the methyl group, Si–O–Si bending, and CH_3 rocking in the PDMS chains,[8] respectively (Figure 1). When PTMO was increasingly replaced with PIB, the absorption at 1100 cm⁻¹ due to the C–O–C bending gradually disappeared.[2]

Molecular weight estimation was made on a gel permeation chromatograph (GPC) with a Waters 410 detector and 590 pump using two Alltech Nucleosil C18 coated silica gel columns (1000 and 80 Å). Molecular weights were reported based upon polystyrene retention times. Apparent number-average molecular weights of PDMS polyurethanes were in the range 30 000–7500, while those of PIB polyurethanes were 9000–5000.

Thermal transition data were obtained with a Mettler TA 3000 DSC. Samples for DSC were prepared by casting the polymer into aluminum pans from a ~5% w/v solution in HFIP and MEK. The heating rate was 20 °C/min. In low-temperature DSC runs, as-cast samples were quenched from room temperature to –130 °C and heated to room temperature at 20 °C/min. Glass transition temperatures (T_g) are reported for the midpoint of the T_g process. High-temperature DSC runs were carried out from
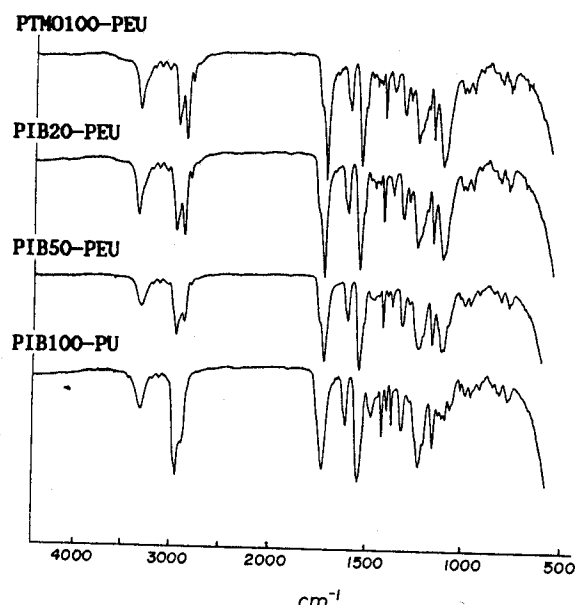
Figure 2. IR transmission spectra of polyurethane incorporating PIB.

room temperature to 250 °C to characterize the hard-segment melting of as-cast samples. The reported apparent melting transition temperatures (T_m) are peak temperatures.

ESCA and SIMS Experiments. ESCA 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.[2]

In the SIMS experiments,[6] samples were bombarded with 9.5-keV Xe[+] with a current density of ~1 nA cm^{-2} (3.6-mm spot size). The total ion dose during setup and spectral acquisition was <10[13] ions cm^{-2}, corresponding to static SIMS conditions. Charge neutralization was effected by a flood of 30–60-eV electrons with a current density of the same order as the primary ion beam.

Results and Discussion

Table 2 shows the effect of casting solvent on the IR absorption and thermal transitions of PDMS or PIB co-soft-segment polyurethanes based on PTMO/FP/MDI. The stretching band of N–H groups H-bonded to carbonyl oxygen appears at ~3332 cm^{-1}.[5] The free and bonded carbonyls absorb at 1748 and 1720 cm^{-1},[5] respectively (Table 2 and Figure 3a). There is little casting solvent effect on the carbonyl absorption shift, whereas a significant shift of the N–H stretching band is observed for the PDMS50–PEU and PIB50–PEU polymers cast from MEK (Table 2). As seen in Figure 3a, the relative free carbonyl absorption at 1748 cm^{-1} is enhanced when PDMS20–PEU is cast from MEK. The enhancement is accompanied by an increase in the 3295-cm[-1] absorption that is ascribed to the absorption band of N–H groups H-bonded to ether oxygen in polyether.[20,21]

For the PDMS50–PEU, the maximum absorption frequency of MEK-cast polymer is shifted down to 3316 cm^{-1} (Table 2 and Figure 3b). The free carbonyl content also increases. The increase of free carbonyl and the absorption band shift to lower frequency may be related to the solubilization of hard segment into the soft PDMS and PTMO domains. However, the absorption shift reflects only the mixing between hard segment and polyether segment since the siloxane oxygen may not H-bond with the N–H group on the hard segment because of steric crowding of two methyl groups near the oxygen.

Direct evidence for the inability to form H-bonds between urethane N–H's and siloxane oxygens can be found in the analysis of the IR spectrum of the PDMS100–

PU polymer (Figure 3c). The absorption of the bonded N–H and C=O for the polyether-free polymer occurs at 3331 and 1720 cm^{-1}, respectively. Though not fully resolved, the carbonyl absorption band shows a discernible shoulder around 1748 cm^{-1}. In contrast, the N–H absorption exhibits a symmetric band centered at 3331 cm^{-1}. The symmetric absorption band may indicate only one type of hydrogen bond, an interurethane bond. The carbonyl band also reveals that the PDMS100–PU cast from HFIP is microscopically almost completely phase segregated. The inability to form hydrogen bonds between the PDMS unit and hard segment may enhance the degree of phase segregation.

In this respect, it is interesting to consider the polyurethanes with nonpolar hydrocarbon soft-segment chains. Figure 3d shows the N–H and C=O stretching bands of the PIB100–PU cast from HFIP and MEK, respectively, and the PTMO100–PEU cast from HFIP. The absorption frequencies corresponding to each characteristic band are nearly the same except those of the PIB100–PU cast from MEK at 3314 and 1723 cm^{-1}. The symmetric N–H absorption bands may confirm the absence of different types of hydrogen acceptors for H-bond formation, other than urethane carbonyls. However, the N–H absorption band of PTMO100–PEU clearly illustrates the existence of two types of acceptors, polyether and carbonyl oxygens. The carbonyl absorption data show that the HFIP-cast PIB100–PU is microscopically almost completely phase segregated compared to the MEK-cast polymer. The interpretation, of course, is based on the assumption that the free carbonyls originate mostly from the urethanes dissolved in soft domains as has been observed in the PEUs.[5] The cause of the shifts of both the N–H and the C=O absorption in the MEK-cast PIB100–PU polymer is unclear. This may be a matrix effect[22] derived from the solubilization of self-associating hard segments into the soft domains. However, this explanation is not completely consistent with the thermal transition data presented later.

The IR absorption for the PIB20–PEU polymers cast from HFIP and MEK showed little casting solvent effect (Table 2, spectra not shown). In contrast to PIB20–PEU, PIB50–PEU showed a significant casting solvent effect on the IR absorption (Figure 3e). The free to bonded carbonyl ratio is higher in the MEK-cast polymer than in the HFIP counterpart. The MEK solvent also shifted the bonded N–H absorption from 3333 to 3312 cm^{-1}. The shift may be caused by increased mixing of hard segments and polyether segments. A similar shift to 3310 cm^{-1} was also observed for the well phase-mixed polymer based on MDI/FP/poly(propylene glycol) (PPO; M_w = 400) (molar ratio = 1.5:0.5:1; 55 wt % of hard segment) in our previous study.[5]

The mixing behavior of hard and soft segments can be explained in terms of thermal transition properties such as soft-segment T_g and hard-segment melting point depression. As can be seen in Table 2, for both the PDMS- and PIB-containing polymers, the HFIP-cast polymers show lower T_g's than the corresponding MEK-cast polymers, exclusive of the polyether-free PDMS100–PU polymer. The glass transitions parallel the IR absorptions, depending on the casting solvent. The sample that has a higher fraction of hydrogen-bonded carbonyl exhibits a lower T_g, meaning better phase segregation in soft domains. All co-soft-segment polymers showed a single soft-segment glass transition. Therefore, each two oligomer pair (e.g., PIB/PTMO and PDMS/PTMO) might be randomly incorporated during polymerization, and not forming blocks of pure components. This is reasonable since the mixed soft-segment oligomers (1 mol) were end-capped in the presence of excess MDI (6 mol) and then chain

Table 2. Casting Solvent Effect on the Degree of Hydrogen Bonding and the Thermal Transition Properties of PDMS or PIB Incorporated Polyurethanes Chain-Extended with Hexafluoro-1,5-pentanediol

sample	N–H stretching band (cm⁻¹)		bonded C=O absorption (cm⁻¹)		free C=O absorption (cm⁻¹)		fraction of H-bonded carbonyl		T_g (°C) of soft segment			T_m (°C) of hard segment		ΔH (J/g) of hard segment	
	HFIP	MEK	HFIP	MEK	HFIP	MEK	HFIP	MEK	Fox[a]	HFIP	MEK	HFIP	MEK	HFIP	MEK
PDMS20–PEU	3334	3331	1720	1721	1748	1748	0.81	0.66	−89	−60	−47	169	173	32	21
PDMS50–PEU	3331	3316	1719	1721	1748	1748	0.77	0.65	−102	−86	−66	169	174	28	29
PDMS100–PU	3329	3331	1719	1720						−114	−115	178	180	35	25
PIB20–PEU	3333	3331	1720	1720	1747	1746	0.74	0.71	−78	−41	−39	170, 197	165, 192	34	28
PIB50–PEU	3333	3312	1720	1721	1747	1747	0.74	0.67	−76	−38	−33	173	172	26	28
PIB100–PU	3333	3314	1720	1723						−39	−36	165	169	22	19
PTMO100–PEU	3331	3331	1719	1720	1746	1747	0.77	0.71		−37[b]		153[b]			
MDI/FP copolymer												190, 215[c]			
pure PDMS[d]										−120					
pure PIB[e]										−72					
pure PTMO[f]										−79					

[a] Calculated from the Fox relation. [b] Data for the sample cast from *N,N*-dimethylacetamide (DMAc), taken from ref 3. [c] Data for the as-precipitated MDI/FP copolymer, taken from ref 3. [d] Data taken from refs 8, 10, and 12. [e] Data taken from ref 13. [f] Data taken from ref 3.
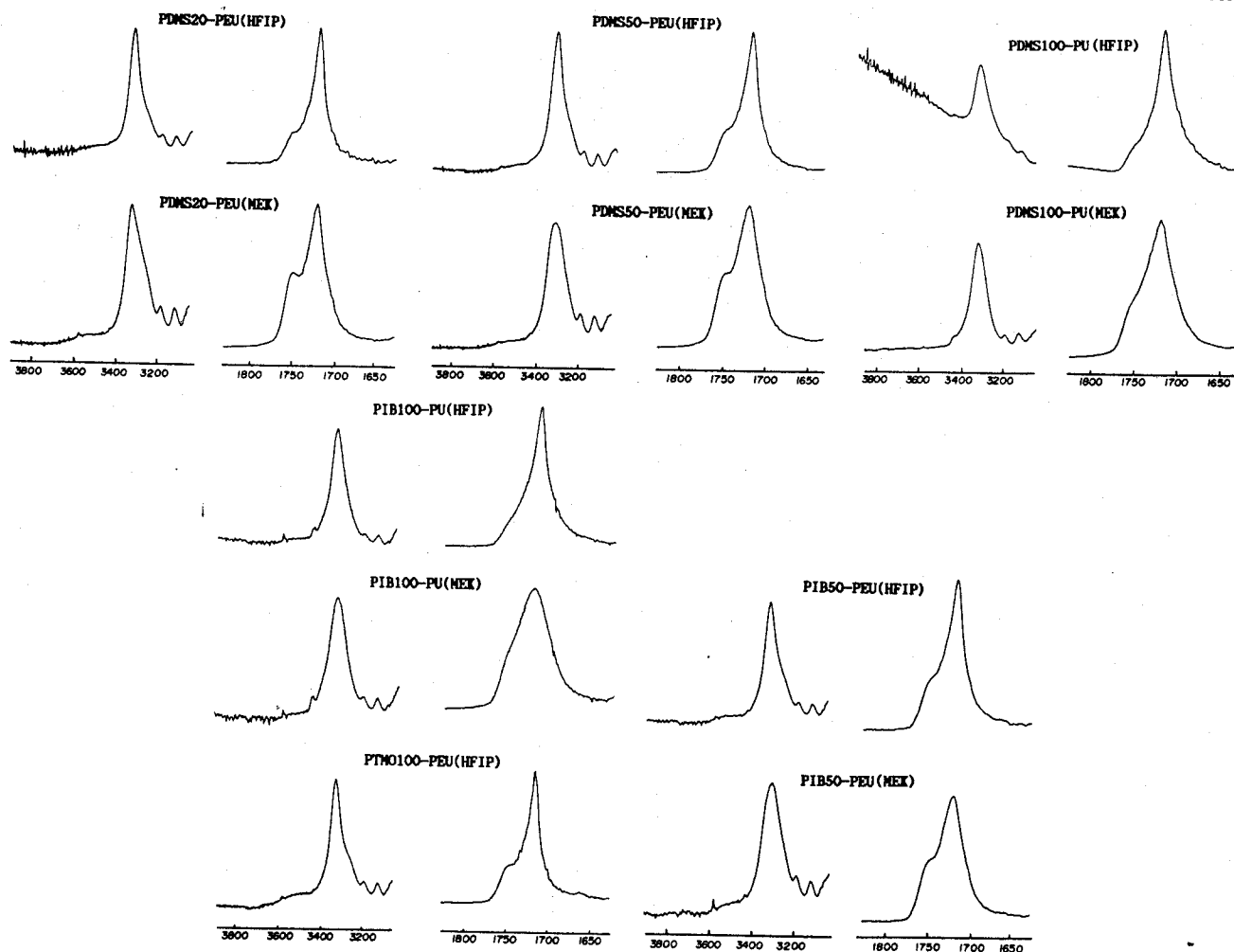

Figure 3. (a) Casting solvent effect on N–H and C=O stretching absorption bands of PDMS20–PEU. (b) Casting solvent effect on N–H and C=O stretching absorption bands of PDMS50–PEU. (c) Casting solvent effect on N–H and C=O stretching absorption bands of PDMS100–PU (d) N–H and C=O stretching absorption bands of PIB100–PU and PDMS100–PEU. (e) Casting solvent effect on N–H and C=O stretching absorption bands of PIB50–PEU.

extended by the diol FP (5 mol).

For the PDMS series polymers, increasing the PDMS content decreased the soft-segment T_g. The T_g of PDMS100–PU is comparable to that of the pure PDMS oligomers, indicating that the hard segments are almost completely excluded from the PDMS soft domains. But the T_g's of PIB100–PU and PTMO100–PEU are significantly higher than those of their corresponding pure oligomers. We anticipated that the hydrocarbon soft-segment polymer of PIB100–PU would be completely

phase segregated into the hard and soft domains due to the large polarity difference between the hard and soft segments. Surprisingly, the PTMO and PIB polyurethanes exhibited similar hard segment solubilization into soft domains, estimated from the change of T_g of each soft segment. The similar surface tension of PTMO (31.9 dyn/cm) and PIB (33.6 dyn/cm)[16] may contribute to the similar miscibility. The invariability of the soft-segment T_g with increase of PIB content in the PIB series polymers is interesting. Considering the similar T_g of pure PIB (−72
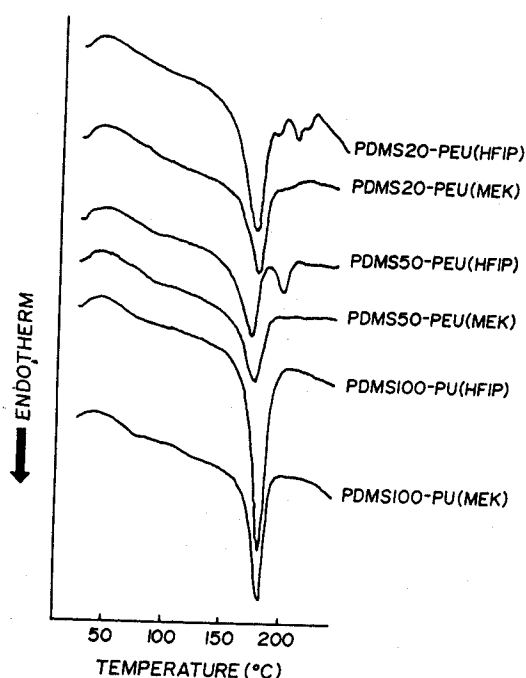
Figure 4. Hard-segment melting endotherms for polyurethanes incorporating PDMS.

Figure 5. Hard-segment melting endotherms for polyurethanes incorporating PIB.

°C) and PTMO (−79 °C), the constant T_g suggests a similar level of hard-segment content in soft domains for the PIB-containing polymers. The theoretical T_g's calculated from the Fox relation are shown in Table 2 assuming the complete exclusion of hard segments from the soft domains in which PTMO units are completely randomly mixed with PDMS or PIB units. A smaller deviation of experimental T_g from the value by the Fox relation was observed with increasing PDMS content for the PDMS polymers. The increase of PDMS content results in an enhanced phase segregation in soft domains. For the PIB polymers, the deviation is insensitive to the PIB content increase, as expected.

The melting point depression may be a criterion for the miscibility of hard and soft segments.[3,5] However, the appearance of multiple endothermic peaks could hamper the analysis.[5] The DSC endotherms of co-soft-segmented polyurethanes with PDMS and PIB are shown in Figures 4 and 5, respectively. Little casting solvent effect on the hard-segment T_m was observed, except for PIB20–PEU (Table 2 and Figures 4 and 5). In PIB20–PEU, at least two endothermic peaks appeared. The temperatures of the two endotherms are considerably lower than those for the as-precipitated MDI/FP polymer. The T_m's of all other polymers are also lower (by a minimum of 20 °C) than those of hard-segment polymer, suggesting appreciable soft segment in the hard-segment domains. It was observed that the T_m of PIB100–PU is lower than that of PDMS100–PU. A poly(propylene oxide)-containing PEU, PPO100–PEU, has a T_m of 204 °C when cast from HFIP,[5] suggesting good phase separation. Thus, it may be concluded that the large polarity difference alone between soft and hard segments cannot be a major factor for the enhancement of phase segregation in hard domains. Other thermodynamic driving forces (e.g., entropic effects) should be considered to explain the unusual miscibility in PIB100–PU. The enhanced phase segregation in hard domains of the PDMS polyurethane over that of the PIB100–PU can also be rationalized from the higher fusion enthalpy of the former than that of the latter. The lowered enthalpy of hard domains in PIB100–PU may be due to weak van der Waals interaction between the polar and nonpolar chains resulting from the increased mixing.
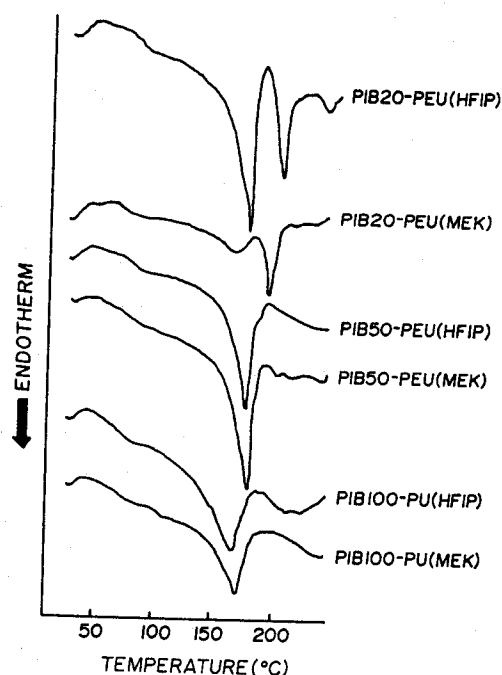
Table 3. ESCA (at 55° Take-off Angle) and Bulk Composition Data of PDMS or PIB Incorporated Polyurethanes

sample	casting solvent	elemental composition (atom %)				
		C	N	O	F	Si
PDMS20–PEU	HFIP	62.8	2.0	19.3	4.3	11.7
PDMS20–PEU	MEK	61.3	1.8	19.9	3.7	13.4
	MEK (at θ = 80°)	52.4	0.4	21.4	0.9	24.9
PDMS20–PEU	bulk composition	68.7	3.9	16.6	9.4	1.4
PDMS50–PEU	HFIP	60.9	2.1	20.1	3.8	13.2
PDMS50–PEU	MEK	57.0	1.6	20.6	3.0	17.7
PDMS50–PEU	bulk composition	66.3	4.0	15.8	9.6	4.3
PDMS100–PU	MEK	54.1	1.8	21.6	3.6	19.0
PDMS100–PU	bulk composition	60.0	4.2	16.6	9.8	9.5
PIB20–PEU	HFIP	85.4	2.1	9.2	3.2	
PIB20–PEU	MEK	86.0	2.0	8.3	3.7	
PIB20–PEU	bulk composition	72.9	3.9	14.2	9.0	
PIB50–PEU	HFIP	87.9	2.0	6.7	3.5	
PIB50–PEU	MEK	87.5	2.1	6.6	3.9	
PIB50–PEU	bulk composition	75.5	3.8	11.9	8.8	
PIB100–PU	HFIP	89.2	2.2	4.5	4.1	
PIB100–PU	bulk composition	79.8	3.7	7.4	9.2	
PTMO100–PEU	HFIP	76.3	2.4	16.7	4.6	
PTMO100–PEU	MEK	75.0	2.6	15.9	6.6	

Surface composition data within the uppermost ∼100 Å of surface can indirectly give useful information on the bulk morphology.[2,3] Table 3 presents ESCA data (55° take-off angle, ∼80-Å sampling depth) and bulk composition data for the polyurethanes incorporating PDMS or PIB. Comparison of the surface and bulk composition data suggests that solvent-cast films have surfaces enriched with PDMS or PIB. The extent of enrichment depends on the ratio of mixed soft segments and the casting solvent used.

For the PIB and PDMS polyurethanes, the dependence on casting solvent is reduced compared to previously examined systems. HFIP was found to be a "structure-enhancing" solvent for the PTMO/MDI/FP[4] and PPO/MDI/FP[5] polyurethanes. The polymers cast from HFIP have less surface hard segment than those cast from a "structure-perturbing" solvent (MEK). This was confirmed in control experiments in this study for PTMO100–PEU, whose ESCA data were in good agreement with those previously published[4] (Table 3). For the PDMS poly-
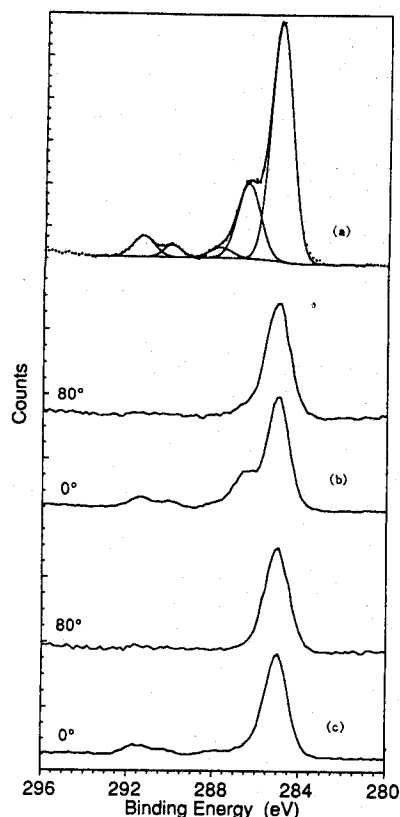
Figure 6. High-resolution C_{1s} ESCA spectra of polyurethanes incorporating PDMS: (a) Curve resolution of the spectrum obtained at 55° take-off angle for PDMS20–PEU; (b) the spectra obtained at 0° and 80° take-off angles for PDMS20–PEU; (c) the spectra obtained at 0° and 80° take-off angles for PDMS100–PU.

Figure 7. High-resolution C_{1s} ESCA spectra of polyurethanes incorporating PIB: (a) curve resolution of the spectrum obtained at 55° take-off angle for PIB20–PEU; (b) the spectra obtained at 0° and 80° take-off angles for PIB20–PEU; (c) the spectra obtained at 0° and 80° take-off angles for PIB100–PU.

urethanes, this solvent effect is reduced and, surprisingly, MEK enriches the PDMS soft segments more effectively than HFIP.

PDMS20–PEU displayed the highest PDMS enrichment, nearly 10 times the bulk value. The Si atom % at grazing angles ($\theta = 80°$, sampling depth = $\sim$20 Å) reached 25%. This is the theoretical maximum, equivalent to the Si atom % in pure PDMS [C (50%), O (25%), and Si (25%)]. Thus, the uppermost surface region was overlaid with only PDMS soft segment. During solvent evaporation in film casting, the low surface energy PDMS-rich chains preferentially and rapidly migrate to the air–polymer solution interface. In the present two-component soft-segment system, the large surface energy difference between the hard and soft segments probably drives formation of such layered structures. This is in contrast to our previous suggestion that the surface structure originates from the bulk structure in the segmented polyurethanes with a single soft segment.[2,3]

The surface composition of PDMS100–PU determined at $\theta = 80°$ also nearly approached the elemental composition of pure PDMS, indicating strong surface phase segregation. This correlates well with the soft-segment T_g data for the PDMS100–PU polymer with a T_g (–115 °C) close to that of the PDMS homopolymer. The comparable T_g's indicate the complete phase segregation of soft domains within the bulk. Thus, the phase segregation in the bulk may influence the surface phase segregation.

The PIB-segmented polyurethanes show little casting solvent effect on the surface composition, as in the thermal transition properties described previously. In comparison with the bulk composition, the hard-segment content of the three polymers at the surface is significantly reduced.
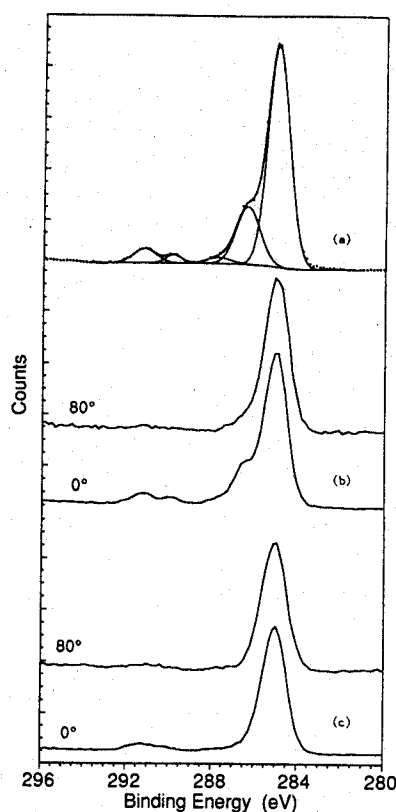
Approaching the top $\sim$20 Å surface region (80° take-off angle), the carbon content increases to $\sim$95 atom %, i.e., the uppermost surface is covered with pure soft-segment hydrocarbon. However, PIB and PTMO are reported in the literature to have similar surface energies of 33.8 and 32.0 dyn/cm,[16] respectively. This surface energy difference cannot explain the degree of phase segregation at the surface. However, it is well known that the tension of small-molecule hydrocarbon liquids is low (e.g., 18 dyn/cm for n-hexane[16]). An analogy between the surface tension of low molecular weight organic molecules and the surface energy of chemically related polymers has often been made. Hence, the literature value for the surface energy of PIB may be artifactual.

The C_{1s} ESCA spectrum of polymers gives detailed structural information about chemical groups present in the surface region.[23] The angle-resolved C_{1s} spectra[2,23] for PDMS20–PEU and PDMS100–PU are shown in Figure 6. The C_{1s} spectrum is composed of five subpeaks. Detailed assignment of the binding energies corresponding to each of the chemical groups was made in the previous study.[2] The maximum of the main peak at the lowest binding energy, associated with the unsubstituted hydrocarbon and PDMS carbon, was shifted to 285.0 eV, the expected value for these species. The other four peaks at 286.4, 287.8, 290.1, and 291.2 eV are associated with the carbon singly bonded to oxygen in the PTMO unit, the ether carbon in the fluorine-containing chain-extender unit, the urethane carbonyl carbon, and the fluorine-substituted carbon, respectively. In PDMS20–PEU, as the topmost surface is approached, the intensities of the 286.4-eV peak as well as the three peaks at higher binding energy significantly decrease. This indicates the decrease of both hard segment and polyether soft segment with depth into the surface. As expected for the PDMS100–
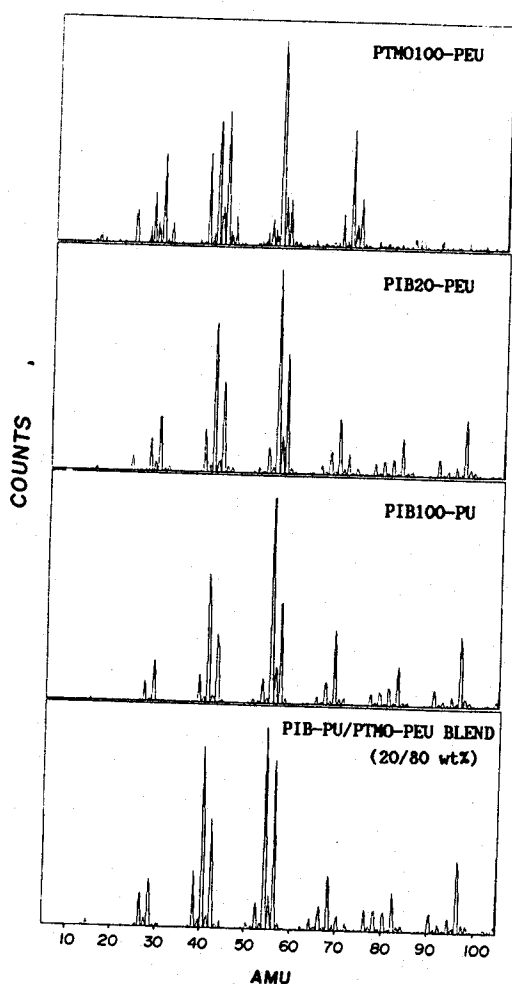
Figure 8. Positive ion SIMS spectra of PTMO100–PEU, PIB20–PEU, PIB100–PU, and PIB100–PU/PTMO100–PEU blend (mixing ratio: 20:80 wt %).

PU polymer, the 286.4-eV peak is not seen in the C_{1s} spectra (Figure 6c). The component peaks due to the hard segment gradually diasppear moving closer to the top surface ($\theta = 80°$).

From the chemical structure of PIB, similar C_{1s} spectra for PIB20–PEU and PDMS20–PEU are expected (Figure 7). A similar pattern with take-off angle was observed and can be interpreted in an analogous fashion to that of the PDMS series polymers.

Static SIMS spectra of PIB-containing polyurethanes are shown in Figure 8. Static SIMS analyzes polymer surfaces to a depth of 10–20 Å, similar to the surface zone examined by ESCA at high glancing angles.[6] The surface zone for the PIB polyurethanes is seen to be dominated by the PIB component. The positive ion SIMS spectrum for the PTMO100–PEU shows peaks such as $CH_2=CHCO^+$ (m/z 55), $CH_2=CHCH_2CH^+OH$ (m/z 71), and $CH_3CH_2CH_2CH^+OH$ (m/z 73) that are characteristic of PTMO. It has been often observed that PTMO-containing PEUs are enriched at their surfaces with the PTMO component.[6] For all the PIB–PEUs, a characteristic hydrocarbon series is observed dominated by $C_2H_5^+$ (m/z 29), $C_3H_5^+$ (m/z 41), $C_4H_7^+$ (m/z 55), $C_5H_9^+$ (m/z 69), $C_6H_{11}^+$ (m/z 83), and $C_7H_{13}^+$ (m/z 97). The almost complete absence of the m/z 71 peak in the positive ion SIMS spectra of PIB-containing polyurethanes is striking and suggestive of surface domination by the PIB phase.

The PIB100–PEU blended at 20% concentration in the PTMO100–PEU also shows this strong surface dominance of the PIB component.

Conclusions

PEUs containing PIB soft segments or PDMS soft segments show strong surface enrichment of these components, even in the presence of PTMO, a soft segment that ordinarily dominates PEU surfaces. The solvent, during casting, probably provides the needed chain mobility through plasticization, permitting the air–polymer interface to reach its lowest interfacial energy, *i.e.*, with PIB or PDMS concentrated at the surface. Such hydrocarbon- or siloxane-enriched surfaces may offer advantages for chemical stability, resistance to calcification *in vivo*, lubricity, and blood compatibility.[24]

References and Notes

(1) Lelah, M. D.; Cooper, S. L. *Polyurethanes in Medicine*; CRC Press: Boca Raton, FL, 1986.
(2) Yoon, S. C.; Ratner, B. D. *Macromolecules* 1986, *19*, 1068.
(3) Yoon, S. C.; Ratner, B. D. *Macromolecules* 1988, *21*, 2392.
(4) Yoon, S. C.; Ratner, B. D. *Macromolecules* 1988, *21*, 2401.
(5) Yoon, S. C.; Sung, Y. K.; Ratner, B. D. *Macromolecules* 1990, *23*, 4351.
(6) Hearn, M. J.; Briggs, D.; Yoon, S. C.; Ratner, B. D. *Surf. Interface Anal.* 1987, *10*, 384.
(7) Shaában, A. K.; McCartney, S.; Patel, N.; Yilgör, I.; Riffle, J. S.; Dwight, D. W.; McGrath, J. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1983, *24* (2), 130.
(8) Yilgör, I.; Shaában, A. K.; Steckle, W. P., Jr.; Tyagi, D.; Wilkes, G. L.; McGrath, J. E. *Polymer* 1984, *25*, 1800.
(9) Tyagi, D.; Yilgör, I.; McGrath, J. E.; Wilkes, G. L. *Polymer* 1984, *25*, 1807.
(10) Okkema, A. Z.; Fabrizius, D. J.; Grasel, T. G.; Cooper, S. L.; Zdrahala, R. J. *Biomaterials* 1989, *10*, 23.
(11) Shibayama, M.; Inoue, M.; Yamamoto, T.; Nomura, S. *Polymer* 1990, *31*, 749.
(12) Kajiyama, M.; Kakimoto, M.; Imai, Y. *Macromolecules* 1990, *23*, 1244.
(13) Kennedy, J. P.; Iván, B.; Chang, V. S. C. In *Urethane Chemistry and Application*; Edwards, K. N., Ed.; ACS Symposium Series 172; American Chemical Society: Washington, DC, 1981; p 383.
(14) Chen-Tsai, C. H. Y.; Thomas, E. L.; MacKnight, W. J.; Schneider, N. S. *Polymer* 1986, *27*, 659.
(15) Li, C.; Goodman, S. L.; Albrecht. R. M.; Cooper, S. L. *Macromolecules* 1988, *21*, 2367.
(16) Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982.
(17) Kennedy, J. P.; Iván, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*; Hanser Publishers: Munich, 1991.
(18) Kennedy, J. P.; Chang, V. S. C.; Smith, R. A.; Iván, B. *Polym. Bull.* 1979, *1*, 575.
(19) Iván, B.; Kennedy, J. P.; Chang, V. S. C. *J. Polym. Sci., Polym, Chem. Ed.* 1980, *18*, 3177.
(20) Lee, H. S.; Wang, Y. K.; MacKnight, W. J.; Hsu, S. L. *Macromolecules* 1988, *21*, 270.
(21) Lee, H. S.; Wang, Y. K.; Hsu, S. L. *Macromolecules* 1987, *20*, 2089.
(22) Schrems, O.; Oberhoffer, H. M.; Luck, W. A. P. *J. Phys. Chem.* 1984, *88*, 4335.
(23) Dilks, A. In *Electron Spectroscopy: Theory, Techniques, and Applications*; Baker, A. D., Brundle, C. R., Eds.; Academic Press: London, 1981; Vol. 4, pp 277–359.
(24) Hanson, S. R.; Harker, L. A.; Ratner, B. D.; Hoffman, A. S. *J. Lab. Clin. Med.* 1980, *95*, 289.