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Surface and Bulk Structure of Segmented Poly(ether urethanes) with Perfluoro Chain Extenders. 3. Effects of Annealing, Casting Solvent, and Casting Conditions

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ABSTRACT: Segmented fluorine-containing poly(ether urethanes) were synthesized from 4,4'-methylenebis(phenylene isocyanate) (MDI), poly(tetramethylene glycol) (PTMO) of molecular weight 1000 or 2000, and 2,2,3,3-tetrafluoro-1,4-butanediol or 2,2,3,3,4,4-hexafluoro-1,5-pentanediol chain extender. The effects of annealing, casting conditions, and casting solvents were examined by using Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The XPS analysis for samples annealed at ~130 °C showed that the lower surface energy polyether component preferentially migrates to the surface region upon annealing. For samples cast from a range of solvents, a linear correlation between the surface fluorine content and the ratio of hydrogen-bonded to free urethane carbonyls was found, suggesting that the surface structure originates from the bulk structure. The results also indicate that even the higher surface energy component can be enriched at the surface with some casting solvents.

Introduction

Processing variables such as annealing[1,2] and casting solvent[3] are known to affect the phase separation of block copolymers. X-ray photoelectron spectroscopy (XPS) can be used to study the effects of these variables on the surfaces of block copolymers. In our previous XPS study of polyurethanes,[4] we labeled the hard-segment moiety with fluorine atoms by using various perfluoro chain extenders. The fluorine labeling simplified the analysis of the XPS spectra of polyurethanes in three ways: by reducing the dependency on the N_{1s} signal when localizing the hard segment, by providing a signal of high intensity for the hard segment, and by improving the ability to accurately resolve the C_{1s} spectrum. With these simplifications in the analysis, the hard segments at the polyurethane surface can be traced more quantitatively and precisely.

The purpose of this study is to examine the surface and bulk structural changes caused by annealing and casting treatments. We synthesized a series of segmented polyurethanes based on 4,4'-methylenebis(phenylene isocyanate) (MDI) and poly(tetramethylene glycol) (PTMO) of molecular weight 1000 or 2000 and chain-extended with 2,2,3,3-tetrafluoro-1,4-butanediol (FB) or 2,2,3,3,4,4-hexafluoro-1,5-pentanediol (FP). By using XPS and FTIR, we analyzed these polymers for effects induced by annealing, casting condition, and casting solvent.

Experimental Section

Materials. Details of the preparation, purification, and characterization of the fluorine-labeled segmented poly(ether urethanes) based on MDI and PTMO can be found in a previous paper.[4] All polymers were prepared by using a two-step solution polymerization technique. The composition data for the polymers under consideration in this study are shown in Table I. An example of the polymer nomenclature used is as follows: PEU-2000-FB-19 consists of a PTMO 2000 soft-segment unit and a tetrafluorobutanediol (FB) chain extender whose feed fraction was 19% by weight.

Polymer Characterization. A. Fourier Transform Infrared Spectroscopy (FTIR). Each sample for infrared analysis was prepared by casting a thin film onto a sodium chloride (NaCl) window from a 1% (w/v) polymer solution in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) or tetrahydrofuran (THF). The solvent was slowly evaporated under rough vacuum, and the sample was further dried under high vacuum at room temperature for 1 week to completely remove the solvent. Infrared spectra were obtained by using an Analect FX-6200 Fourier transform infrared spectrometer in the high-resolution mode (resolution, 1.6 cm^{-1}). Fifty scans or more were averaged for each sample.

Table I
Compositions of Fluorodiol Chain-Extended Segmented Polyurethanes

samples[a]	molar ratio MDI/chain extender/PTMO	hard seg, wt %	feed chain extender, wt %
PEU-2000-FB-6	2:1:1	24.9	6.1
PEU-2000-FB-19	6:5:1	53.6	18.8
PEU-1000-FB-20	4:3:1	59.8	19.5
PEU-2000-FP-8	2:1:1	26.3	7.8
PEU-2000-FP-23	6:5:1	56.2	23.2
PEU-1000-FP-24	4:3:1	62.1	24.1

[a] FB = tetrafluorobutanediol chain extender. FB = hexafluoropentanediol chain extender.

B. X-ray Photoelectron Spectroscopy (XPS). A Surface Science Laboratories SSX-100 ESCA spectrometer was used to analyze all surfaces. An electron flood gun was used to neutralize surface charging. The quantitation of data and the sample mounting geometry for angular dependent studies are described in a previous paper.[4] Because of the low intensity of the N_{1s} signal from the samples, the number of scans was increased to 40–60 scans in the angular dependent experiments to increase the precision and accuracy of the nitrogen content data. In the angular dependent experiment which uses a small aperture (6° solid angle), it took 10–12 h to complete the data collection for each sample at five angles. During the experiment, no carbon contamination or sample degradation was observed.

Each sample for the XPS study was prepared by centrifugally casting the polymer onto a clean glass disk from a 1% (w/v) solution in one of the following solvents: HFIP, THF, 1-methyl-2-pyrrolidone (MPY), acetone, 2-butanone (MEK), cyclopentanone, dioxane, or *N,N*-dimethylacetamide (DMAc). All polymer samples used in the XPS study were purified by reprecipitating twice in methanol to remove low molecular weight materials that could potentially dominate the surface structure.[4]

Results and Discussion

Effect of Annealing. At room temperature, only the soft segments are above their glass transition temperatures, whereas the hard segments are generally glassy and their mobility is low. Therefore, a polymer might require several months to reach equilibrium morphology at room tem-

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Table II
Effect of Annealing on the XPS Surface Compositions of Fluorinated Segmented Polyurethanes

		N, atom %	F, atom %	reduced N (%) after anneal	reduced F (%) after anneal
PEU-2000-FB-19	control	2.22	2.81		
	annealed	1.93	2.02	13.1	28.1
PEU-2000-FP-23	control	2.77	6.28		
	annealed	2.39	4.10	13.7	34.7
PEU-1000-FB-20	control	3.85	5.54		
	annealed	3.40	3.60	11.7	35.0
PEU-1000-FP-24	control	3.80	8.42		
	annealed	3.43	5.58	9.7	33.7
PEU-2000-FB-6	control	1.16	0.71		
	annealed	1.21	0.41	-4.3	42.2
PEU-2000-FP-8	control	0.91	1.01		
	annealed	1.15	0.47	-26.4	53.5

perature, depending on its hard-segment content.[5] However, annealing above the hard-segment T_g is expected to increase the mobility of the rigid hard blocks and to permit the reordering of the hard domains to minimize system energy. Accordingly, an annealing-induced morphological change would be expected to result in a reorganization of the surface structure.

To observe the surface structural changes with annealing, we annealed the solvent (DMAc)-cast surfaces of several selected polymers at 120–130 °C under an argon atmosphere for 10 days and then slowly cooled them to room temperature. The control samples were stored under high vacuum for 1 week until XPS measurements were made. The data were collected normal to the surface ($\theta = 0°$) at a 100-eV pass energy. As shown in Table II, the XPS fluorine content changed more under the above annealing conditions than the nitrogen content did. Analysis of the XPS data also suggested that annealing above the hard-segment T_g enhances phase separation in the surface region—the fluorine-substituted hard segment migrates into the bulk phase and the soft segment comes out to the surface region. In the case of polymers which have a lower hard-segment content, the nitrogen fraction near the surface is relatively constant under the above annealing conditions. Thus, the short MDI unit that can couple two soft-segment units is not phase separated.

Effect of Casting Solvent. It has been shown that the casting solvent has profound influence on the surface and bulk structures of polystyrene–poly(ethylene oxide) diblock copolymers.[6] In a "long" diblock copolymer containing well-defined domains, the content of a specific polymer component increases at the copolymer surface as the casting solvent becomes more preferential for that polymer. A similar solvent effect can be anticipated to occur in the multiblock system studied here, but the relative magnitude of the effect might be smaller than in the "long" diblock system as a result of the wide distribution of block lengths, the multiplicity of blocks, and the polar nature of both hard and soft segments in polyurethanes.

For solvent effect studies, two polymers, PEU-2000-FP-23 and PEU-1000-FP-24, were chosen because there are a variety of good solvents available for these polymers. Among these solvents are a proton donor solvent (HFIP), highly polar amide-type solvents (DMAc and MPY), keto-type solvents (acetone, MEK, and cyclopentanone), and cyclic ethers (THF and 1,4-dioxane). The solubility of the FP chain-extended polymers in the ketones and cyclic ethers is a function of the fluorine-substituted hard-segment content. But the pure hard-segment polymer, poly[oxycarbonylamino-1,4-phenylenemethylene-1,4-phenyleneaminocarbonyloxy(2,2,3,3,4,4-hexafluoropentane-1,5-diyl)] (polyurethane B),[4] has a limited solubility (~1% w/v or less) in this type of solvent, and the solution eventually becomes a gel. It seems likely that the exceptional ease with which the FP polymers can be solubilized arises from the perturbation of highly polar hard-segment units by fluorine substitution and from the extensive mixing of hard and soft phases. The more highly phase-separated FB chain-extended polymers are not soluble in such a range of solvents.

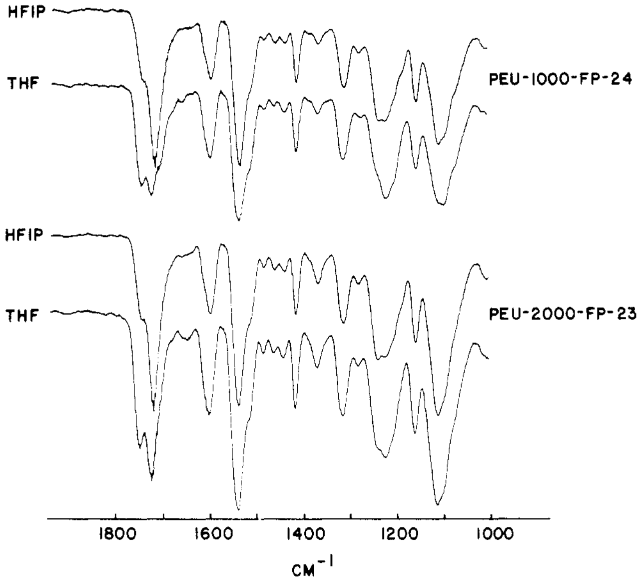

Figure 1. Infrared spectra of PEU-1000-FP-24 and PEU-2000-FP-23 cast from HFIP and THF.

Figure 1 shows the FTIR spectra for the films of PEU-1000-FP-24 and PEU-2000-FP-23 cast from HFIP and THF. Each polymer was cast as a film onto a NaCl window from a single drop of 1% (w/v) polymer solution. After evaporation of the majority of the solvent, the film was further dried under vacuum at room temperature for at least 1 week. The spectra for each polymer show significant differences in the carbonyl region depending on the casting solvent employed. If the degree of hydrogen bonding determined from the peak ratio is proportional to the degree of hard- and soft-segment mixing, as assumed in the IR analysis, the extent of phase separation in the solvent-cast polymers should strongly depend on the solvent from which the films were cast.

Upon careful examination of the spectra for the PEU-1000-FP-24 sample cast from THF, we found that the carbonyl band has a slight, broad hump (at ~1713 cm^{-1}) on the main hydrogen-bonded carbonyl peak. All PEU-1000-FP-24 films cast from the ketone and the other ether solvents exhibited this additional absorption in the carbonyl band. On the other hand, none of the PEU-2000-FP-23 samples showed the additional absorption band. The appearance of the additional band indicates that in the PTMO 1000 samples, the solvent-induced enhanced mixing of soft and hard segments is accompanied by strong structural perturbations in the hard domains. The exact assignment of the additional split bands is difficult. Since the amide I mode is conformationally sensitive through dipole–dipole interactions,[7] the multiple splitting of the carbonyl band is anticipated in some condensed phases, depending on the population of various oriented states and the degree of association.[7-9] Furthermore, the matrix effect[10] should also be considered in nonhomopolymer systems. Therefore, although the mechanism for the solvent effect is not clear, HFIP is considered to be a "structure enhancing" solvent for these two polymers compared to THF on the basis of the results presented in Figure 1 and

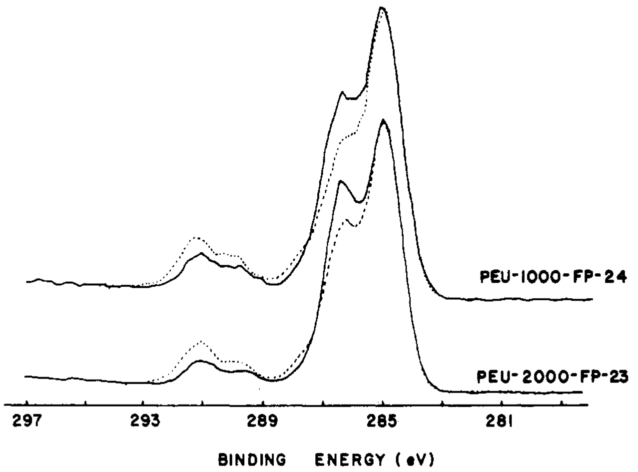

Figure 2. XPS C_{1s} core level spectra for PEU-1000-FP-24 and PEU-2000-FP-23 cast from different solvents: (—) cast from HFIP; (- - -) cast from acetone.

Table III
Effect of Casting Solvents on the Surface Compositions of Fluorine-Containing Segmented Polyurethanes As Measured by XPS

	PEU-1000-FP-24		PEU-2000-FP-23	
	F, atom %	N, atom %	F, atom %	N, atom %
HFIP	7.4	3.3	4.8	2.3
MPY	7.2	3.7	6.2	3.1
DMAc	8.7	3.8	6.5	2.6
THF	8.7 (8.6)	3.8 (3.7)[a]	7.3 (7.0)	3.0 (3.2)
acetone	(11.4)	(4.5)[b]	8.1 (10.4)	3.4 (3.8)
MEK	8.5	3.6	6.8	2.9
cyclopentanone	8.9	3.8	7.3	2.9
dioxane	8.9	3.7	7.0	3.1
in bulk	8.5	4.4	7.4	3.7

[a] All values in parentheses are for the surfaces prepared by evaporation without spinning. [b] Uniformly coated surfaces could not be obtained by spin coating for this polymer.

the previously mentioned assumption about the relationship between hydrogen bonding and phase mixing.[11]

Figure 2 shows the effect of casting solvent on the XPS C_{1s} core level spectra of PEU-2000-FP-23 and PEU-1000-FP-24. The polymers cast from the "structure perturbing" solvent (e.g., acetone) have more hard segments at the surface than those cast from a "structure enhancing" solvent (HFIP). In order to study this relationship more closely, the surface fluorine content is plotted in Figure 3 as a function of the fraction of hydrogen-bonded carbonyl calculated by the peak height method.[11] The surface composition data are also shown in Table III. The plot shows a very good linear correlation for PEU-2000-FP-23, but the correlation for PEU-1000-FP-24 is rather poor as expected from the analysis of the FTIR data. The PEU-2000-FP-23 correlation line exhibits a higher slope and a greater difference in fluorine content between the bulk and the HFIP cast surface (Table III) than its PTMO 1000 counterpart. These differences must be due to the lower configurational constraint of the longer soft and hard segments in PEU-2000-FP-23, leading to increased microphase separation in the bulk. The structure-enhancing capability of solvents follows the order of HFIP > amides > cyclic ethers, ketones. It seems likely that the solvent hydrogen-bonding capability and polarity are important factors influencing metastable structures at the surface and in the bulk. However, the solubility parameters for the solvents (not including HFIP) are relatively close [20.7 ± 1.6 × 10^{-3} $(J/m^3)^{1/2}$].

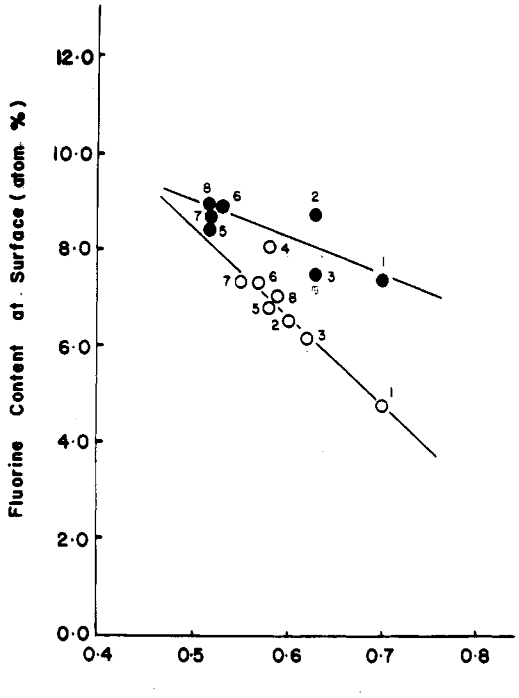

Figure 3. Correlation between the fluorine content at the surface and the hydrogen-bonded carbonyl fraction for PEU-1000-FP-24 and PEU-2000-FP-23 cast from various solvents. The darkened circles are for PEU-1000-FP-24; the open circles, for PEU-2000-FP-23; (1) HFIP; (2) DMAc; (3) 1-methyl-2-pyrrolidone; (4) acetone; (5) 2-butanone; (6) cyclopentanone; (7) THF; (8) 1,4-dioxane.

One additional factor to be considered is the solvent evaporation rate. The surface fluorine content of the films cast from THF (bp = 67 °C) is independent of the two casting conditions (high-speed spin-casting with rapid evaporation and slow evaporation) (Table III). On the other hand, the polymer cast from acetone (bp = 56 °C) with slow evaporation shows an increase in fluorine content at the surface by ~25% compared to the spin-cast thin films. This difference suggests that acetone has a high affinity for the fluorine-containing hard segment. Thus, slow evaporation of the solvent fractionates more hard-segment-rich chains toward the surface region. The high affinity for acetone to the hard segments is supported by the significant deviation of data point 4 from the correlation line in Figure 3.

The casting solvent effect on the surface structure of PEU-1000-FP-24 is shown in Figure 4. The fluorine content of the HFIP-cast sample exhibits a relatively sharp XPS angular dependence at the top surface, but remains below the bulk value of 8.5%, suggesting an enhanced phase separation. Interestingly, a negative gradient in surface fluorine content with sampling depth is observed for the sample cast from the "structure perturbing" solvent, THF. The samples cast from the other perturbing solvents show no angular dependence, though the surface fluorine content is a little higher than the bulk value. These results indicate that the hard segment, with a surface energy higher than that of the soft segment, can be enriched at the air–polymer interface depending on the properties of the casting solvent used.

Conclusions

The XPS analysis of the samples annealed at ~130 °C for 10 days showed that annealing induces the migration of the soft segment to the surface region, thus improving the phase separation of polymers. This migration also

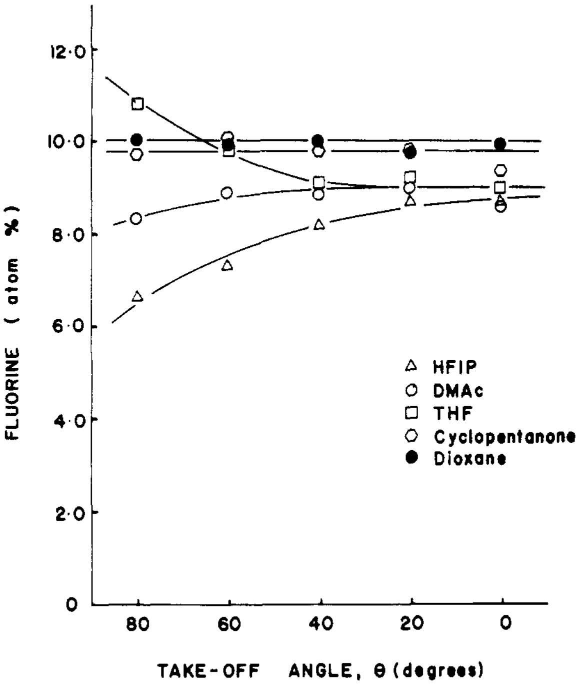

Figure 4. Casting solvent effect on the fluorine depth profile of PEU-1000-FP-24.

suggests that the soft segment has a lower surface energy than the hard segment.

The effect of casting solvent on the surface and bulk structure was studied for the PEU-2000-FP-23 and PEU-1000-FP-24 polymers, which can be prepared with a variety of good solvents. A remarkable linear correlation between the XPS composition data and the IR band ratios of bonded to nonbonded urethane carbonyls was obtained. This correlation provides direct evidence for the suggestion that the surface structure originates from the bulk structure. Also, when a very strong bulk-structure-perturbing solvent is used as a casting solvent, even the hard segment with a high surface energy can be enriched at the surface.

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Registry No. (FB)(MDI)(PTMG) (block copolymer), 112666-66-7; (FP)(MDI)(PTMG) (block copolymer), 112666-67-8.

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Infrared Dichroism Study of the Relaxation of Selected Segments along a Stretched Polymer Chain and Comparison with Theoretical Models

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ABSTRACT: The differences in chain relaxation as a function of segmental position along a deformed chain have been elucidated by studying linear isotopically labeled block polystyrenes. Films from three different copolymers have been stretched at constant strain rate and various temperatures. The orientation of the different blocks has been measured by infrared dichroism. End blocks appear to relax faster than the overall chain, the relaxation of which is still more rapid than that of the central block. The kinetics of the relaxation are sensitive to the length of the end block and the total molecular weight of the copolymer. The relative relaxation of chain ends with respect to the average orientation has been compared to the predictions of the Doi-Edwards model of chain relaxation. Good agreement has been obtained, without any adjustable parameter, when retraction, chain length fluctuations, and reptation processes have been considered.

I. Introduction

Recent molecular theories on the motion and the relaxation of polymer melts[1-4] have stimulated various experimental studies in order to test their validity. Many of them have been devoted to the viscoelastic behavior of entangled amorphous polymers in both the linear[5-9] and nonlinear domain.[10-14] Spectroscopic techniques like small-angle neutron scattering,[15-17] fluorescence polarization,[15,18,19] or infrared dichroism[20-24] have been used to directly study the behavior or relaxing deformed polymer chains on a molecular scale.

Molecular weight effects[21,23] or matrix influences[19,24] have already been studied and considered in the light of the Doi-Edwards (DE) molecular theory. A deeper testing of the basic processes of this model can be achieved by studying the relaxation of chain segments as a function of their location along the backbone by using isotopically labeled block copolymers. Indeed, the relaxation at long times is predicted to be nonuniform since two relaxation processes, the equilibration or retraction of the deformed

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