Surface and Bulk Structure of Segmented Poly(ether urethanes) with Perfluoro Chain Extenders. 4. Role of Hydrogen Bonding on Thermal Transitions

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ABSTRACT: Segmented poly(ether urethanes) were synthesized from 4,4'-methylenebis(phenylene isocyanate) (MDI), poly(propylene glycol) (PPO) of molecular weight 400, 2000, and 4000, and 2,2,3,3,4,4-hexafluoro-1,5-pentanediol (FP) and 1,5-pentanediol (PD) chain extender. The samples, with various degrees of microphase segregation, were prepared by using a variety of solvents for each polymer. Infrared and differential scanning calorimetry analyses were applied to the solvent-cast polymers to study the effect of hydrogen bonding on thermal transitions in the poorly phase-segregated polyurethanes. 1,1,1,3,3,3-Hexafluoro-2-propanol was found to be the strongest "structure-enhancing" solvent for all polymers under consideration. The symmetric fluorine substitution in the chain-extender region generally enhances the mixing of hard and soft segments. The fluorine substitution has little effect on the absorption frequency shifts $\Delta\nu$ of the hydrogen-bonded to free carbonyl, which is indicative of the similar strength of hydrogen bonding between N–H and O=C groups in the fluorinated and nonfluorinated systems. The shift value is in the range 18–22 cm^{-1} for both PD and FP chain-extended polymers. This indicates that the enhanced mixing by fluorine substitution is not due to any hydrogen-bond strength difference. However, for the same polymer samples cast from various solvents, the sample having the highest fraction of hydrogen-bonded carbonyl at room temperature shows the highest hard-segment melting point and/or the lowest soft-segment glass transition temperature (T_g).

Introduction

Hydrogen bonding is an important aspect of the chemical structure of polymers because it may provide physical cross-links between polymer chains, thereby influencing the various physical properties of polymers.[1] It has therefore been the subject of numerous investigations using infrared (IR) spectroscopy to study the role of hydrogen bonding on phase separation and mechanical properties in segmented polyurethanes.[2-11] However, no satisfactory theory has yet been developed for this relationship since, in many cases, hydrogen bonding plays only a secondary role in determining overall polymer properties.

In our previous study of segmented poly(ether urethanes) with perfluoro chain extenders,[12] we found a linear correlation between X-ray photoelectron spectroscopic (XPS) surface composition data and IR band ratios of hydrogen-bonded to nonbonded urethane carbonyls for the poorly phase-segregated 2,2,3,3,4,4-hexafluoro-1,5-pentanediol (FP) chain-extended polymers. The correlation provided direct evidence for our suggestion that, in segmented polyurethanes, the surface structure originates from the bulk structure. This interpretation was based on the assumption that the degree of carbonyl hydrogen bonding is proportional to the degree of hard- and soft-segment mixing.[11] The assumption may be applicable to poorly phase-segregated polymers in which hard–hard and soft–hard interactions are balanced so that phase segregation is easily perturbed by a processing variable such as casting solvent. These poorly phase-

segregated polymers, which probably have "small" domains, may show a relationship between "short-range order" structure from IR data and rather "longer range order" structure from thermal transition data. The XPS and thermal transition data showed that FP chain-extended polyurethanes (where the FP chain extender contains an odd number of carbons) cast from *N,N*-dimethylacetamide (DMAc) have small hard and soft domains compared to polymers containing an even number of carbons in their chain extenders.[11] A previous study also showed that, in contrast to conventional polyurethanes, the FP polymers have a variety of good solvents.[12] With these casting solvents, the degree of phase segregation at room temperature of the cast polymers can be controlled. Furthermore, the linear correlation strongly implies that in the odd-diol FP chain-extended polymers composed of high-conformation-energy hard segment, the degree of O=C hydrogen bonding may serve as a key parameter in the determination of surface and bulk structure when cast from various solvents. In these respects, the FP chain-extended polymers are considered to be good model systems for studying hydrogen bonding relating to thermal transitions.

The purpose of this study was to examine in the poorly phase-segregated FP chain-extended polymer system how hydrogen bonding affects thermal transitions such as the glass transition temperature (T_g) of the soft segment and the melting transition temperature (T_m) of the hard segment as a function of the extent of phase segregation. Several segmented polyurethanes were prepared using 4,4'-methylenebis(phenylene isocyanate) (MDI) and poly-

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Table I
Compositions of Segmented Poly(ether urethanes) Chain Extended with 1,5-Pentanediol (PD) and Hexafluoro-1,5-pentanediol (FP)

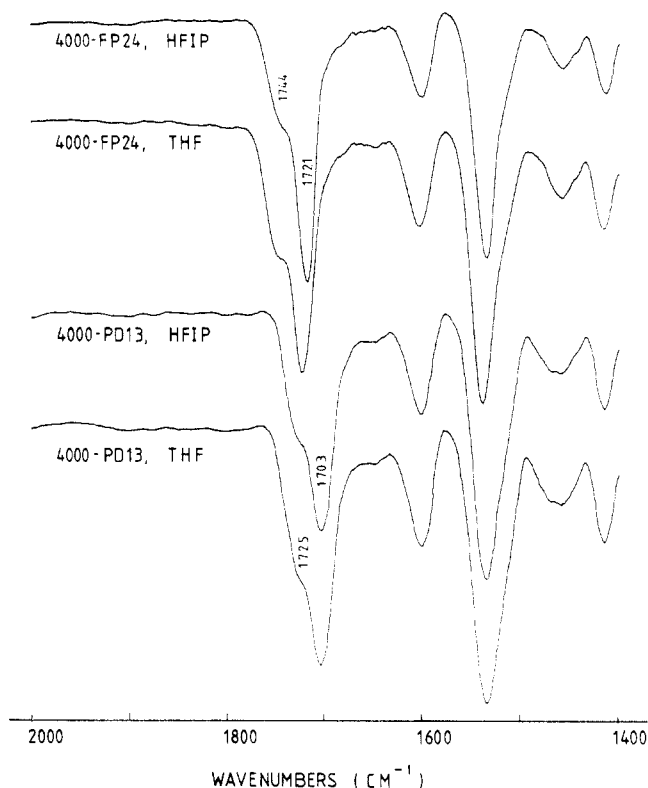| sample	molar ratio MDI/chain extender/PPO	chain extender	mol wt of PPO	hard segment, wt %	chain extender, wt %
4000-FP16	6:5:1	FP	4000	39.0	16.2
4000-FP24	11:10:1	FP	4000	54.9	23.9
2000-FP23	6:5:1	FP	2000	56.2	23.2
400-FP12	1.5:0.5:1	FP	400	54.6	12.1
400-FP36	6:5:1	FP	400	86.5	35.8
4000-PD13	11:10:1	PD	4000	48.7	13.3
2000-PD13	6:5:1	PD	2000	50.3	12.9
400-PD6	1.5:0.5:1	PD	400	51.6	6.3
MDI-PD	1:1:0	PD		100	29.4

Figure 1. Casting solvent effect on the carbonyl absorption bands of 4000-FP24 and 4000-PD13 polymers.

(propylene glycol) (PPO) of molecular weight 400, 2000, and 4000 and chain extended with FP (Table I). Another series of polyurethanes chain extended with the hydrocarbon analogue chain extender 1,5-pentanediol (PD) was also synthesized to compare the effect of symmetric fluorine substitution in the chain-extender region on the hydrogen-bonding properties of segmented polyurethanes.

Experimental Section

All polymers were prepared by using a two-step solution polymerization technique. Details of the preparation, purification, and characterization of the fluorodiol chain-extended segmented poly(ether urethanes) based on MDI and polyether glycol are contained in a previous paper.[13] The 1,5-pentanediol chain-extended polymers were also prepared in a similar manner, but the chain extension was carried out at a higher temperature (100 °C) for 1 h. The compositions of the polymers based upon the stoichiometry of the components used in this synthesis in this study are shown in Table I. The notation used for the synthesized polymers is as follows: 4000-FP16 consists of a PPO4000 soft-segment unit and a hexafluoropentanediol (FP) chain extender with a feed fraction of 16% by weight. Each sample for infrared analysis was prepared by casting a thin film on a sodium chloride (NaCl) window from a 2% (w/v) polymer solution in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), acetone (ACE), cyclohexanone (CYC), 2-butanone (MEK), dioxane (DIO), tetrahydrofuran (THF), N,N-dimethylacetamide (DMAc), and N,N-dimethyl-

formamide (DMF). The solvent was slowly evaporated in a laminar flow hood, and the sample was further dried under high vacuum at room temperature for 1 week or more to completely remove the solvent. Infrared spectra were obtained by using a Nicolet MX-S Fourier transform infrared spectrometer. Fifty scans or more were averaged for each sample under a dry nitrogen purge. Thermal transition data were obtained with a Perkin-Elmer differential scanning calorimeter (DSC-4) equipped with a data station. The instrument was calibrated with indium and n-octane. Samples for DSC study were prepared by casting the polymer into aluminum pans from a 10–20% (w/v) solution in one of the solvents used for IR study. The specimens were subjected to further drying under vacuum at room temperature for 2 weeks or more. Sample size was in the range 10–15 mg. Experiments were carried out at a heating rate of 20 °C/min under a dry helium purge. In low-temperature DSC runs, as-cast samples were quenched from room temperature to –100 °C and heated at 20 °C/min. Glass transition temperatures (T_g) are reported for the midpoint of the glass transition process. High-temperature DSC runs were started from 40 °C in order to characterize the hard-segment melting of as-cast samples. The reported apparent melting transition temperatures (T_m) are peak temperatures.

Results and Discussion

N–H stretching and the amide I vibrations of segmented polyurethanes have been studied by using infrared absorption to characterize the molecular-level mixing of hard and soft segments.[2-11] Analysis of the N–H stretching absorption data is complicated due to the presence of two types of hydrogen bonds, N–H- - -O=C (urethane carbonyl) and N–H- - -O= (ether in soft segment). Furthermore, there is disagreement over the frequency and absorptivity coefficient of the N–H stretching vibration for an N–H group hydrogen bonded to an ether oxygen.[5,7-9] For the amide I vibration, two discernible peaks assignable to free and hydrogen-bonded carbonyls are generally observed.[2-12] The hydrogen-bonded carbonyls are formed by interurethane hydrogen bonding resulting from self-association, while most free carbonyls are formed when hard- and soft-segment mixing occurs, thereby giving rise to hydrogen bonding between urethane and ether groups. The difference in the absorptivity coefficient of free and bonded carbonyls is not large (the ratio is approximately 1–1.7).[3,5,6,8,10] Therefore, the mixing behavior of hard and soft segments will be discussed based on a simple analysis of the carbonyl band.[2,7,10-12,14] The fraction of free and bonded carbonyls can be comparatively determined by the peak height method assuming the same spectral distribution function.[10-12] In the kinetic study of phase separation for a quenched polyurethane material, Lee et al. observed that the overall integral intensity of free and bonded carbonyls is independent of time at a given temperature, showing that the inherent extinction coefficient of the C=O stretching vibration remains relatively constant.[10] In that study they assumed that peak height measurements can be used to represent the changing band intensity as a function of time without significant error. This also

Table II
Effect of Casting Solvents on the Hydrogen Bonding in Segmented Poly(ether urethanes) Chain Extended with
1,5-Pentanediol (PD) and Hexafluoro-1,5-pentanediol (FP)

sample	fraction of H-bonded carbonyl[a]						
	HFIP	ACE	CYC	MEK	DIO	THF	DMAc
4000-FP16	0.65	0.61	0.58	0.60	0.61	0.60	0.58
4000-FP24	0.71	0.66	0.67	0.65	0.65	0.65	0.64
4000-PD13	0.63	c	c	c	e	0.62	0.60
2000-FP23	0.70	0.48	0.47	0.48	0.47	0.48	0.47
2000-PD13	0.60	c	c	c	e	0.57	0.56
2000-FP23[b]	0.70	0.58	e	0.58	0.59	0.55	0.60
400-FP12	d	0.47	0.47	0.48	0.46	0.47	0.47
400-PD6	d	0.49	e	0.48	e	0.49	0.48
400-FP36	0.72	0.54	0.52	0.54	0.51	0.54	e

[a] The values were averaged over a minimum of two measurements and are reproducible within a maximum error of mean deviation ±4%. [b] Data for the PTMO2000-FP23 polymer taken from: Yoon, S. C.; Ratner, B. D. *Macromolecules* 1988, *21*, 2401. [c] Insoluble. [d] Not calculated due to the interference of trapped residual solvent. [e] Not determined.
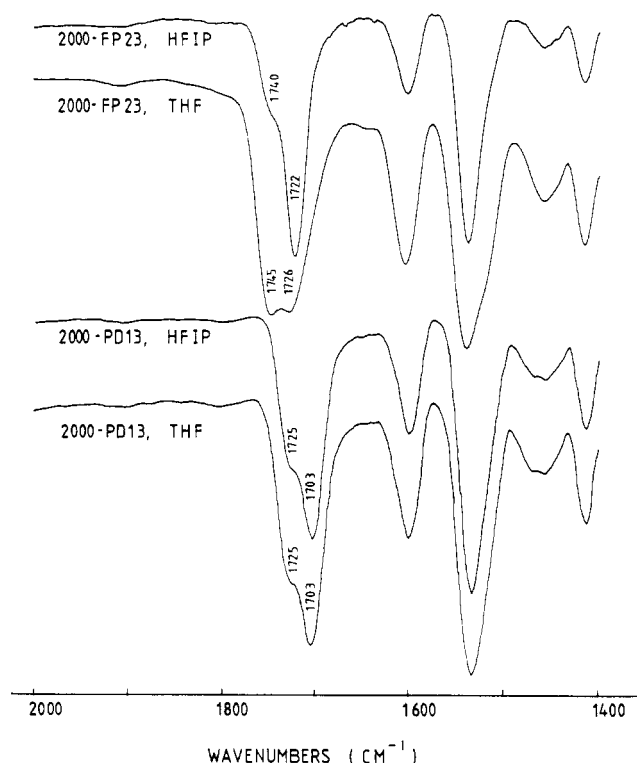

Figure 2. Casting solvent effect on the carbonyl absorption bands of 2000-FP23 and 2000-PD13 polymers.

Figure 3. Carbonyl absorption bands of short soft- and hard-segment polymers (400-PD6 and 400-FP12).

suggests that the C=O stretching vibration is a suitable band for estimating the extent of phase segregation of segmented polyurethanes. This was confirmed in our previous report.[11,12]

The spectra of FP and PD chain-extended polyurethanes are almost identical except for an additional CF_2 stretching band at 1155 cm^{-1}. The absorption for the hydrogen-bonded N–H stretching vibration of the long hard-segment polymer (MDI/FP/PPO4000 = 11:10:1), 4000-FP24, occurs at 3332 cm^{-1}. The short hard-segment polymers, 400-FP12 and 400-PD6 (MDI/chain extender/ PPO400 = 1.5:0.5:1), show slightly shifted absorption bands centered at 3310 cm^{-1}. The fluorine substitution in the chain extender does not shift the N–H stretching absorption band. Significant differences can be seen in the carbonyl stretching region of the infrared spectra (Figures 1–3). The free C=O stretching band is well separated from that of the "disordered" hydrogen-bonded C=O stretching band.

Figure 1 shows the carbonyl absorption band region of the FTIR spectra for the 4000-FP24 and 4000-PD13 films cast from HFIP and THF. For the FP chain-extended
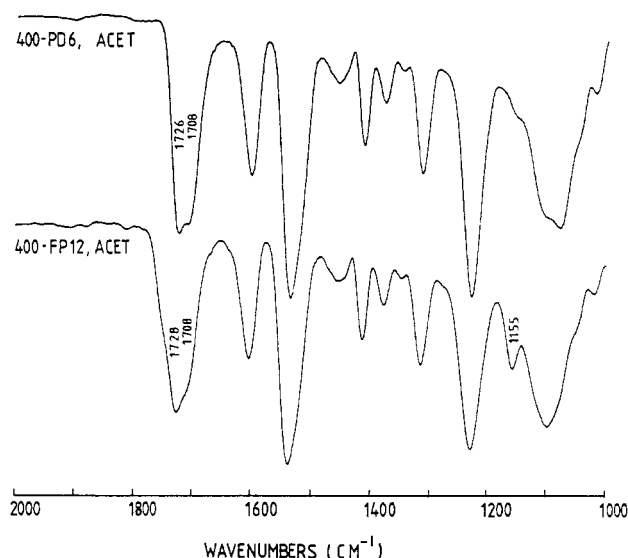
polymers, the 1744-cm^{-1} component is assignable to the carbonyls free of hydrogen bonding, and the lower frequency component at 1721 cm^{-1} is associated with hydrogen-bonded carbonyls. In the case of the hydrocarbon analogous polymer, 4000-PD13, the absorption of free and bonded carbonyl occurs at 1725 and 1703 cm^{-1}, respectively, each frequency shifting by ca. 20 cm^{-1} compared to the 4000-FP24 polymer. It is also seen that the absorption frequency does not change with casting solvents in the same polymer system. It is interesting to note that the shifts $\Delta\nu$ of the free to hydrogen-bonded carbonyl frequency are in the same range (18–22 cm^{-1}) for both PD and FP chain-extended polymer systems. The magnitude of frequency shift $\Delta\nu$ is a measure of hydrogen-bond strength.[15] The constancy of the frequency shifts, therefore, may indicate that the symmetric fluorine substitution in the chain extender with an odd number of carbons has little effect on the hydrogen-bonding strength between the N–H and C=O groups. A similar shift trend was also observed in the tetrafluorobutane-diol chain-extended polyurethanes[11] when compared to the butanediol chain-extended polyurethanes.

As seen in Figure 2, the spectra for 2000-FP23 show significant differences in the carbonyl stretching region, depending on the casting solvent employed, whereas for the PD chain-extended counterpart, 2000-PD13, only a small difference is observed.

The calculated values for the fraction of hydrogen-bonded carbonyl are shown in Table II. The PD chain-

Table III
Effect of Casting Solvents on the Soft-Segment Glass Transition Temperature (T_g) of Segmented Poly(ether urethanes) Chain Extended with 1,5-Pentanediol (PD) and Hexafluoro-1,5-pentanediol (FP)

	T_g, °C								
sample	HFIP	ACE	CYC	MEK	DIO	THF	DMAc	DMF	from Fox relation
4000-FP16	-41	-38	-39	-37	-37	-38	-39	-41	-24
4000-FP24	a	-39	-36	-38	-38	-38	-40	-37	-2
4000-PD13	-53	a	a	a	c	-54	-52	c	c
2000-FP23	-24	-5	-9	-9	-11	-10	-13	-15	-2
2000-PD13	-38	a	a	a	c	-35	-35	c	c
400-FP12	6	12	3	7	0	-2	5	8	-2
400-PD6	5	c	c	8	c	3	-2	c	c
PPO400 (-65)[b]									
PPO4000 (-63)[b]									

[a] Slightly soluble or insoluble. [b] The determined value for pure PPO. [c] Not determined.

extended polymers 4000-PD13, 2000-PD13, and 400-PD6 exhibit little casting solvent effect on the ratio of free to hydrogen-bonded carbonyls. However, the effect is large in the FP chain-extended polymers 400-FP36 (Figure 4), 2000-FP23, and 4000-FP24. Of the solvents used, HFIP is generally the strongest "structure-enhancing" solvent.[12] Similarly to the PTMO/FP/MDI polymer system[12] (see footnote b in Table II), all solvents except HFIP show a leveling effect on the ratio of free to bonded carbonyls in the PPO/FP/MDI polymers. Table II also shows that the PTMO2000-FP23 polymer, which contains a crystallizable linear soft segment, is more phase segregated than PPO2000-FP23. As indicated in Tables I and II, the polymers 4000-FP24 and 4000-PD13, which have longer soft- and hard-segment blocks, have higher fractions of hydrogen-bonded carbonyl, as expected. The 2000-FP23 films cast from THF and DMAc have lower fractions of hydrogen-bonded carbonyl compared to the 2000-PD13 samples cast from the same solvents. The effect of fluorine substitution on O=C hydrogen bonding is most significant in the PPO2000 samples. The 4000-FP24 and 4000-PD13 polymers cast from THF and DMAc display a reversed effect of fluorine substitution on the hydrogen-bonded carbonyl fraction in comparison to the PPO2000 polymers. This may be ascribed to the probable increase of free carbonyl content in hard domains resulting from the increased chain stiffness and/or the change of thermodynamic mixing parameters with increasing chain length. The analysis of the carbonyl band for the 400-FP12 polymer is complicated by overlapping of the bonded carbonyl band (1722 cm⁻¹) from the MDI unit linked to the FP unit and the free carbonyl band (1725 cm⁻¹) from the MDI unit linked to the PPO unit (Figure 3). Considering 33% FP-linked and 66% PPO-linked MDI units of the 400-FP12, the calculated values from the peak height method may be erroneous, but the overall trends with casting solvent are internally consistent in the same polymer system.

The soft-segment T_g data for the FP or PD chain-extended polyurethanes are given in Table III. For samples prepared with the same chain extender, the T_g of FP and PD polymers increases gradually with decreasing soft- and hard-segment length, as expected. The PD polymers have considerably lower T_g's than the corresponding FP polymers. The overall trends of T_g with fluorine substitution can be correlated to the IR data except for PPO4000 polymers. In the short soft-segment polymers, 400-FP12 and 400-PD6, the T_g approaches the value (-2 °C) estimated from the Fox relation, which assumes complete molecular-level mixing of hard and soft segments.[11] This is the expected result for short soft and hard segments (Table I). The T_g's of 2000-FP23 samples are slightly lower than the theoretical value, assuming random molecular-
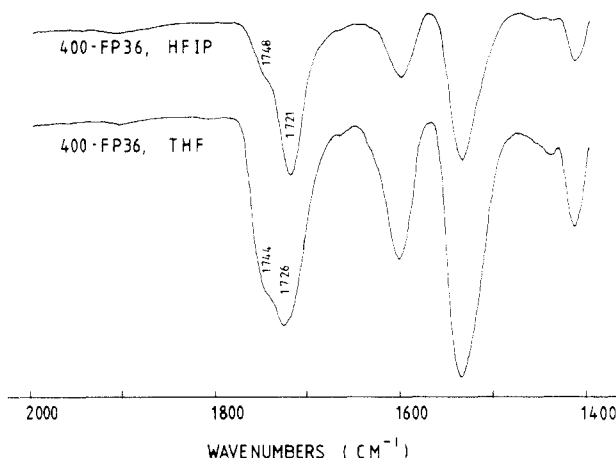

Figure 4. Casting solvent effect on the carbonyl absorption band of 400-FP36 polymer.
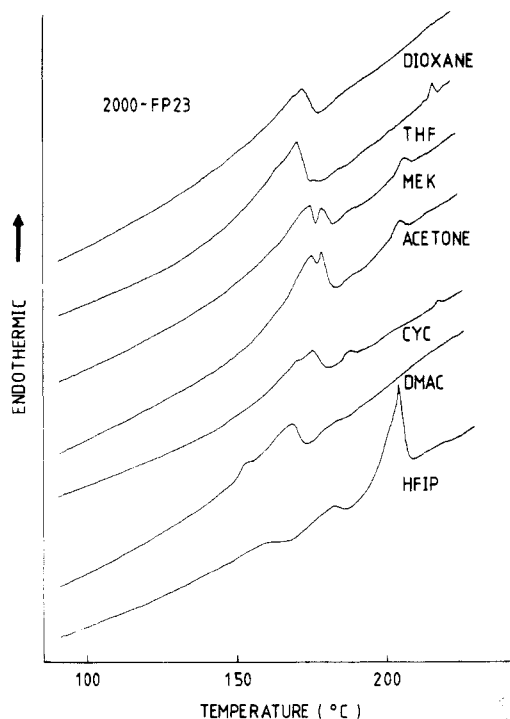

Figure 5. Casting solvent effect on the hard-segment melting transition of 2000-FP23.

level mixing, except for the sample cast from HFIP. For the 2000-FP23 polymer, it is interesting to note that the T_g of the HFIP-cast sample is lowest, indicative of the best phase separation in the soft domains. This is consistent with the IR data shown in Table II and fully supports the idea that in this polymer system, the most carbonyl hydrogen-bonded sample is best phase separated. This

Table IV
Effect of Casting Solvents on the Hard-Segment Melting Transition Temperature (T_m) of Segmented Poly(ether urethanes)
Chain Extended with 1,5-Pentanediol (PD) and Hexafluoro-1,5-pentanediol (FP)

sample	T_m,[a] °C						
	HFIP	ACE	CYC	MEK	DIO	THF	DMAc
4000-FP24	b	(176, 191, 208)	(175, 190, 207)	(174, 189, 208)	(177, 192, 209)	176	(172, 180)
4000-PD13	161	b	b	b	c	161	157
2000-FP23	204	174	174	173	170	169	166
2000-PD13	164	b	b	b	c	168	156
400-FP36	198	175	172	170	171	170	c
MDI-PD		(170)[d]					
MDI-FP		(190, 215)[e]					

[a] The 4000-FP16, 400-FP12, and 400-PD6 polymers do not show definite hard-segment melting endotherms. [b] Insoluble or slightly soluble. [c] Not determined. [d] The value for the as-precipitated material. [e] Data taken from: Yoon, S. C.; Ratner, B. D. *Macromolecules* **1988**, *21*, 2392.

Figure 6. Casting solvent effect on the hard-segment melting transition of 4000-FP24.
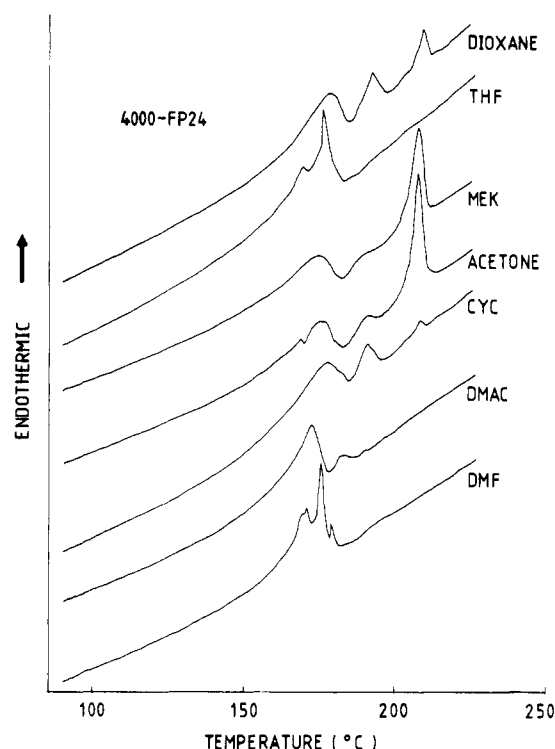

Figure 7. Casting solvent effect on the hard-segment melting transition of 400-FP36.

suggestion is also strongly supported by the highest hard-segment T_m, as seen in Figure 5 and Table IV. This is reasonable because the melting point depression is another criterion for phase mixing.[16]

The additional evidence from the melting point depression may be applicable only to the relatively poorly phase-segregated polymers. For example, in the better phase-segregated polymer with longer hard and soft blocks, 4000-FP24, the T_g and IR hydrogen-bonding data are consistent with each other, while the hard-segment T_m data are not. The 4000-FP24 samples show multiple endotherms in an unsystematic way depending on the casting solvent (Figure 6). The multiple melting endotherms, which are usually observed in well phase-separated polymers, may be attributed to polymorphism[17] and/or the disruption of long-range order of an unspecified nature.[18,19] There is no clear explanation for the fact that, considering the anisotropic nature of the hydrogen bond, the IR free-to-bonded carbonyl ratios representing "short-range" ordering are independent of casting solvent used in spite of the significant structural dissimilarity between the solvent-cast 4000-FP24 polymers. The 400-FP36 polymer is another example showing a close relationship between the degree of C=O hydrogen bonding and hard-segment T_m. The HFIP-cast 400-FP36 polymer has the
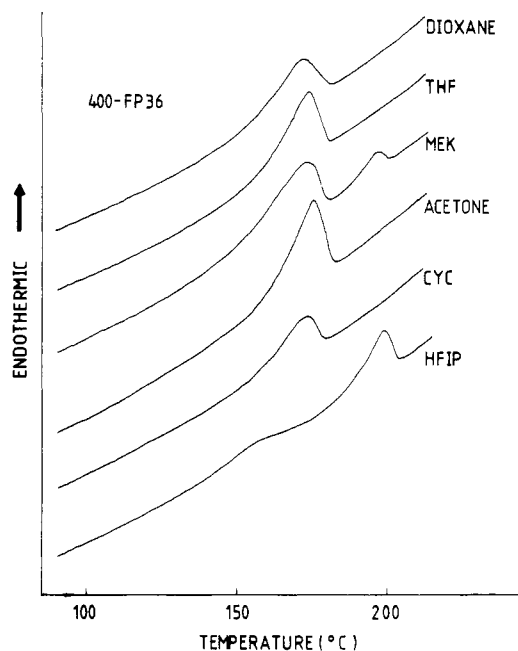
highest T_m and fraction of hydrogen-bonded carbonyls for these polymer systems (Figure 7 and Table II). As noted in Table I, 400-FP36 has 87 wt % hard segment. The soft segments, therefore, are expected to dissolve into the hard domains. The soft-segment glass transition is not observed for the 400-FP36 samples. Therefore, appreciable free carbonyl may be derived from the "disordered" structure in hard domains. This was demonstrated in wide-angle X-ray diffraction and infrared studies of MDI–butanediol urethane model compounds. The results showed that the degrees of segmental ordering and O=C hydrogen bonding decrease with increasing segment length.[6] In high hard-segment polymers such as 400-FP36 and long hard-block polymers such as 4000-FP24, therefore, the T_m data do not reflect the degree of phase segregation. Figure 8 shows the hard-segment melting endotherm behavior of the PD chain-extended polymers as a function of casting solvents. As in the IR and T_g data for the PD polymers, their hard-segment melting transitions show little effect of casting solvent. As seen in Table IV, the fluorine substitution elevates the T_m of hard segment by ca. 40 °C while in the better phase-segregated butanediol chain-extended polymers, it has no effect on the T_m.

Conclusions

For the poorly phase-segregated FP chain-extended polyurethanes the following conclusions may be drawn:

1. Symmetric fluorine substitution in the chain-extender region has little effect on the N–H---O=C
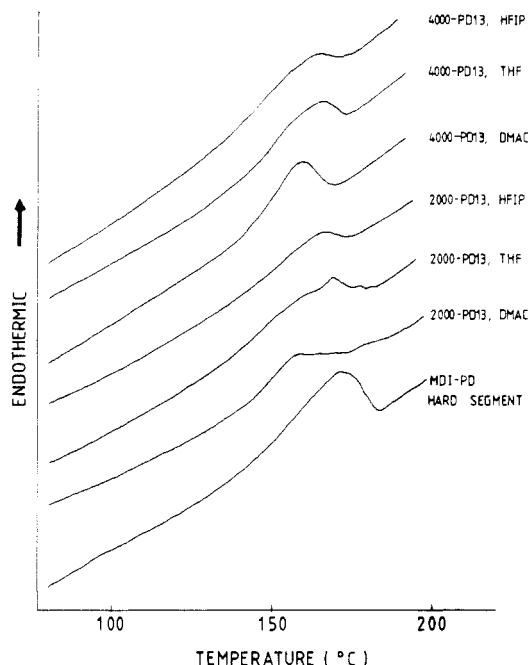
Figure 8. Casting solvent effect on the hard-segment melting endotherms of the PD chain-extended polyurethanes.

hydrogen bond.

2. For the moderately long hard-block polymers (MDI/FP/PPO = 6:5:1 molar ratio), the degree of O=C hydrogen bonding represents the degree of phase segregation, which is strongly reflected in thermal transitions such as hard-segment melting and soft-segment glass transition. This is new direct evidence identifying the correlation between spectroscopic and thermal transition data.

3. An increase of hard-block length as in 4000-FP24 (MDI/FP/PPO = 11:10:1) reduces the extent of correlation, in spite of the increased degree of phase segregation. Thus, the poor correlation between O=C hydrogen bonding and hard-segment melting transition in the better phase-segregated polymer may be due to the polymorphic nature of phase-segregated hard domains resulting from the increased chain stiffness.

4. The assumption of proportionality between the degree of O=C hydrogen bonding and the degree of hard- and soft-segment mixing might be applicable only to relatively poorly phase-segregated or molecular-level mixed systems.

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