Infrared Studies of Hydrogen Bonding in Toluene Diisocyanate Based Polyurethanes

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ABSTRACT: Infrared analysis was applied to obtain quantitative estimates of the extent of microphase segregation in two series of toluene diisocyanate polyurethanes based on the individual 2,4- and 2,6-TDI isomers, a polyether soft segment and butanediol. Almost all the NH groups are hydrogen bonded. In the 2,6-TDI polyurethanes, 80% of the carbonyl groups are hydrogen bonded to urethane NH groups but in the comparable 2,4-TDI only 50% of the carbonyl groups are hydrogen bonded. Assuming that the only other proton acceptor is the ether oxygen of the soft segment, the results provide a quantitative measure of hard segment and soft segment interactions. However, the ir analysis of copolymer analogs of the hard segment indicate a significant participation of the urethane alkoxyl oxygen which introduces some uncertainty into the above estimates. Prior thermal transition data showed a steep increase in T_g with urethane concentration in the 2,4-TDI polyurethanes. To account for this behavior in terms of the ir results two models were invoked. It was found that the copolymer equation severely overestimates the hard segment concentration mixed with soft segment phase. A cross-linking model provides a reasonable fit to the ir results and establishes the basis for a useful relation between the soft segment glass transition and the degree of microphase segregation.

A previous paper reported studies of the thermal transition behavior in two series of polyurethanes, one based on 2,4-TDI and the other on 2,6-TDI. From the differences in the thermal transition behavior and the properties of these samples it was concluded that a greater degree of phase segregation, with well-ordered and in some cases microcrystalline domain structure, occurred in the 2,6-TDI polyurethanes.[2a] However, it was not possible to obtain a quantitative estimate of the relative degree of microphase segregation in these samples based on the techniques which had been used.

One method for evaluating the degree of phase segregation relies on the analysis of ir spectra to estimate the degree of hydrogen bonding between urethane NH protons and possible proton acceptors. Tanaka, *et al.* [2b] estimated that 85% of the NH groups were hydrogen bonded in a solid polyurethane based on TDI (80:20 mixture of 2,4 and 2,6 isomers). Judging by these results and the weight of the other evidence reported[3,4] it can be assumed that almost all NH groups in different polyurethanes examined thus far are hydrogen bonded. However, it appears that only a portion of the urethane carbonyls are involved in hydrogen bonding as the proton acceptor and it has been postulated that the remaining NH groups are bonded to the ether oxygen of the polyether.[5,6] There is indirect evidence that NH bonding to the ester oxygen of the polyester soft segment is greater than hydrogen bonding to polyether.[7] The degree of hydrogen-bonded carbonyl represents the extent of hard-hard segment bonding, the ether bonding obtained by difference shows the extent of hard-soft segment bonding and by inference the extent of mixing of hard segments with the soft segment phase. We have attempted to apply this approach to the two series of TDI based polyurethanes and to several model compounds and polyurethane copolymers.

Experimental Section

Model Compounds. *n*-Butyldiurethanes of both 2,4-TDI and 2,6-TDI were prepared by reacting TDI with excess 1-butanol at 118° for 2 hr. The melting point (81–82°) of the *n*-butyldiurethane of 2,4-TDI was consistent with the reported values.[8,9] Even though the *n*-butyldiurethane of 2,6-TDI exhibited a melting point of 125°, which is much higher than the reported value of 75°,[10] the elemental analysis of this compound indicates the correct composition.

Polymers. The polymers used in this study were the two series of polyether polyurethanes, one based on 2,4-TDI and the other series based on 2,6-TDI which were described previously.[2a] The molar ratio of TDI–butanediol–poly(tetramethylene oxide) (mol wt 1000) was varied in five equal steps from 2.1:1:1 to 6.3:5:1. Copolymers of 2,4-TDI, 2,6-TDI and MDI with butanediol were prepared by conventional bulk polymerization as models of the respective polyurethane hard segment units. Owing to the difficulty in dissolving the 2,6-TDI–butanediol copolymer this sample was prepared by solution polymerization in 50:50 mixture of dimethyl sulfoxide and methylisobutyl ketone following Lyman's procedure.[11]

Ir Measurement. A Beckman-12 infrared spectrophotometer was used to record absorption spectra at room temperature. Polymers and hard segment copolymer analogs in DMF solution were cast directly on NaCl or KBr plates and dried in a vacuum oven. The ir spectra did not show any evidence of residual solvent. Model compounds were studied in chloroform solution at various concentrations. For the examination of the ether region (1300–1000 cm^{-1}), a reference cell of the same path length as the sample cell and containing chloroform was used to minimize solvent interference over the region of interest. The DuPont 310 curve resolver was used in all cases to obtain the relative ratios of areas of ir absorption peaks by assuming a Lorentzian curve for a single chromophore absorption band.

Results and Discussion

Analysis of Ir Spectra. Table I reviews the characteristic properties and composition of the polymers which were studied. Figure 1 shows the ir spectra for 2,4-TDI polymers in the three principal regions of interest while analogous spectra are represented in Figure 2 for 2,6-TDI polymers. The stretching frequencies and the intensities observed for the NH, carbonyl, and ether bands are summarized in Table II.

It is well known that a band near 3300 cm^{-1} is caused by the H-bonded NH group while the non-H-bonded NH group appears near 3460 cm^{-1}. MacKnight and Yang[12] have reported an integrated extinction coefficient E_f = 3.44 × 10^3 l./(mol cm^2) for the free NH group and E_b = 1.19 × 10^4 l./(mol cm^2) for the H-bonded NH groups from measurement on the *n*-butyldiurethane of 2,4-TDI. These values for the extinction coefficient were used to calculate the fraction of H-bonded NH groups from the curve-resolved peaks obtained for the 2,4-TDI and 2,6-TDI polyurethanes. The results indicate that 95% of all NH groups

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Table I
Polyurethane Sample Composition and Properties

Sample no.	Wt % urethane[a]	TDI–BD–PTMO	$M_n \times 10^{-3}$	Properties
2,4-TDI-2	31	2.10 : 1 : 1	16	Soft, tacky rubber
2,4-TDI-3	42	3.15 : 2 : 1	14	Tough, live rubber
2,4-TDI-4	49	4.20 : 3 : 1	13	Elastic, not snappy
2,4-TDI-5	55	5.25 : 4 : 1	25	Flexible, but boardy
2,4-TDI-6	60	6.30 : 5 : 1	14	Almost plastic
2,6-TDI-2	31	2.10 : 1 : 1		Transparent, waxy
2,6-TDI-3	42	3.15 : 2 : 1	13	Opaque, hard and tough; thin sections are elastic
2,6-TDI-4	49	4.20 : 3 : 1	14	
2,6-TDI-5	55	5.25 : 4 : 1	7	
2,6-TDI-6	60	6.30 : 5 : 1	13	

[a] Calculated as weight percentage of TDI and BD per total polymer weight.

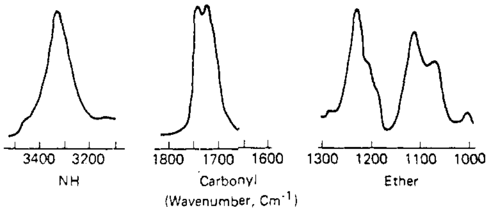

Figure 1. Ir spectra showing the NH, carbonyl, and ether regions of the 2,4-TDI polyurethane.

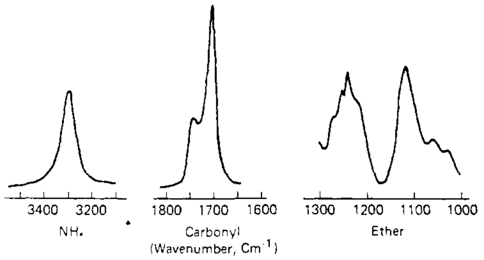

Figure 2. Ir spectra showing the NH, carbonyl, and ether regions of the 2,6-TDI polyurethane.

Table II
Stretching Frequency and Intensity of NH, C=O, and C–O–C Band in Polyurethanes[a]

Group/band	Wave number, cm^{-1} 2,4-TDI polyurethane	Wave number, cm^{-1} 2,6-TDI polyurethane
NH H bonded	3320 strong	3300 strong
Non-H bonded	3460 weak	3460 weak
C=O H bonded	1720 strong	1700 strong
Non-H bonded	1740 strong	1740 medium
C–O–C bond	1230 strong	1275 medium
	1210 medium	1260 medium
	1190 medium	1240 medium
	1120 strong	1120 strong
	1070 strong	1060 medium
	1000 weak	1030 medium

[a] Variation in wave number of stretching vibrations with composition within each series of TDI polyurethanes was negligible.

are hydrogen bonded in the solid state at room temperature. The error due to the curve-fitting procedure is estimated as ±5%. This conclusion is in accord with reported values of greater than 85% H-bonded NH groups for MDI and TDI based polyurethanes.[2b,6]

The carbonyl region shows splitting of the absorption band into two peaks at 1740 and 1720 cm^{-1} for 2,4-TDI polymers and at 1740 and 1700 cm^{-1} for 2,6-TDI polymers. MDI based polyurethanes show similar carbonyl splitting. Cooper and coworkers[6] interpreted a band at 1703 cm^{-1} as caused by H-bonded carbonyl while a band at 1733 cm^{-1} was attributed to the free carbonyl group.

Model compounds of the *n*-butyldiurethane of 2,4-TDI and 2,6-TDI were used to confirm the assignment for the carbonyl absorption peaks. Figure 3 shows that the absorption peak for the *n*-butyldiurethane of 2,4-TDI in dilute solution occurs at 1740 cm^{-1}. As the concentration of the model compound increases, a shoulder develops at 1720 cm^{-1}. In analogy to the behavior of this model compound, we assigned the band at 1720 cm^{-1} to bonded carbonyl and the band at 1740 cm^{-1} to free carbonyl for 2,4-TDI polyurethanes.

For the *n*-butyldiurethane of 2,6-TDI, a single narrow band occurs at 1740 cm^{-1} in dilute chloroform solution. In this case no clear splitting of the carbonyl peak is obtained with increasing concentration up to 0.6 *M*. As shown in Figure 4, the narrow dilute solution peak broadens progressively. It was noted that the solution also becomes viscous with increasing concentration of the model compound, suggesting the reversible formation of aggregated polymers presumably through progressive intermolecular hydrogen bonding between urethane groups. This phenomenon might be the cause for the blurring of the carbonyl peaks. Since 2,6-TDI is symmetrical in a manner which resembles MDI and the nonbonded peak occurs at the same frequency in the two, we have assumed that the bonded carbonyl peak in 2,6-TDI polymers occurs at 1700 cm^{-1}, the value assigned in MDI.

No values of the extinction coefficient of H-bonded and free carbonyl have been reported for model urethane compounds. But studies with other compounds indicated that the increase in the extinction coefficient due to H-bonded carbonyl is not greater than 20%.[13] As an approximation, it was generally assumed that the extinction coefficients for both bonded and free carbonyl bands were the same. The values for the fraction of H-bonded carbonyl calculated directly as the ratio of the areas for the two curve-resolved carbonyl absorption bands are reported in Table III.

These results indicate that approximately 50% of the urethane carbonyl group for 2,4-TDI polyurethane samples and 80% for 2,6-TDI samples are bonded to the urethane NH group. The remainder of NH groups are necessarily bonded with other proton acceptors. It has been commonly assumed that the only other proton acceptor is the ether oxygen of the soft segment. Therefore, such data would provide a simple indication of hard segment–soft segment

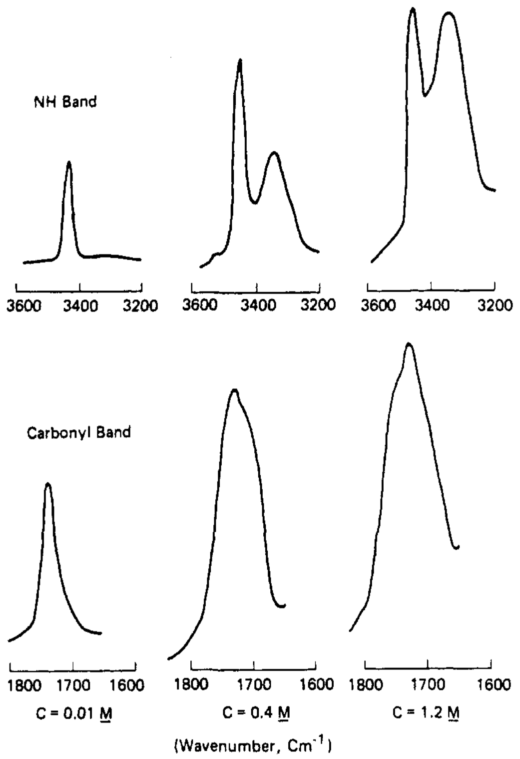

Figure 3. Ir spectra of the *n*-butyldiurethane of 2,4-TDI in chloroform.

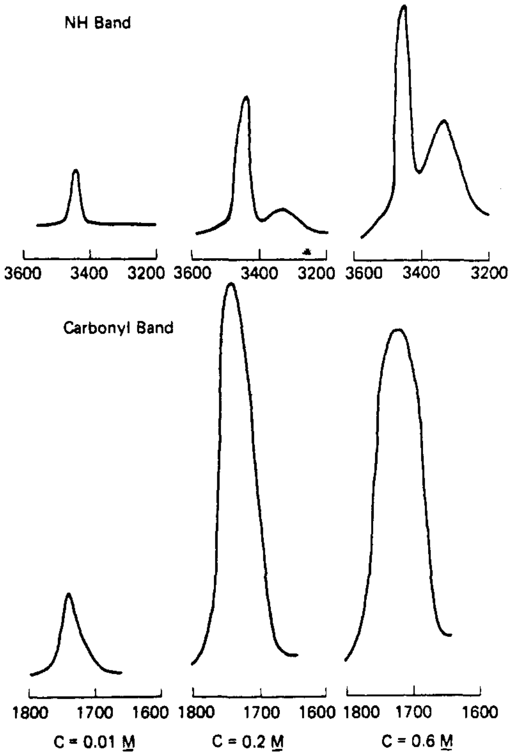

Figure 4. Ir spectra of the *n*-butyldiurethane of 2,6-TDI in chloroform.

Table III
Fraction of H-Bonded Carbonyl in Polyurethanes and Diisocyanate–Butanediol Copolymers

Sample	% H-bonded[a] carbonyl	Maximum[b] % H-bonded ether
	Polyurethanes	
2,4-TDI-2	46	19
2,4-TDI-3	47	28
2,4-TDI-3	48	36
2,4-TDI-5	50	44
2,4-TDI-6	52	50
2,6-TDI-3	78	12
2,6-TDI-4	78	15
2,6-TDI-5	80	18
2,6-TDI-6	77	24
	Copolymers	
2,4-TDI–BD (1:1)	73 (69)	
2,6-TDI–BD (1:1)	90 (88)	
2,6-MDI–BD (1:1)	82 (79)	

[a] Values assuming $E_b = E_f$, values in parentheses assuming $E_b = 1.2E_f$. [b] Represents fraction of soft segment repeat units which are hydrogen bonded.

interactions and, by implication, the degree of hard segment–soft segment mixing. However, in examining other model systems, it has been found that, unfortunately, the situation can be more complicated. The ir spectra were determined for three copolymers which contained only the appropriate diisocyanate (2,4-TDI, 2,6-TDI, or MDI) and butanediol. The ir spectra (shown in Figure 5) indicate that the NH groups are essentially completely hydrogen bonded but it is evident that a significant fraction of the carbonyl groups remain in the non-H-bonded state. The calculated values are summarized in Table III. The hard segment analog of 2,6-TDI–butanediol when cast from DMF solution produced a transparent film. The film could be reversibly crystallized by annealing or quenched to the transparent state which showed a lower amount of hydrogen-bonded carbonyl than the crystalline form. The value in Table III corresponds to the sample in the crystalline form which is considered more representative of the state of the hard segment in the corresponding polyurethanes.

The only additional proton acceptor in these copolymers is the urethane alkoxyl oxygen. Even though the possibility of hydrogen bond formation between the urethane NH group and urethane alkoxyl group had been postulated by Boyarchuk,[5] it has not been observed before. If the conclusion that the urethane alkoxyl oxygen is involved in hydrogen bonding is correct, then the measured fraction of the H-bonded carbonyl group underestimates the degree of hard–hard segment bonding and the values calculated from the difference do not provide an accurate representation of the amount of hydrogen bonding or intermixing of hard with soft segments. In view of the uncertainty introduced by the NH bonding to the urethane alkoxyl oxygen, a careful investigation of the ether region (1000–1300 cm^{-1}) was made to determine whether useful information concerning hydrogen bonding for urethane alkoxyl ether or for soft segment polyether could be obtained directly. It was found that no conclusive results could be obtained due to complexities introduced by amide III and the asymmetric ester stretching bands. This situation leaves the analysis of the carbonyl splitting as the only means of estimating the degree of hydrogen bonding between the urethane groups and the soft segment.

Interpretation of Glass Transition Temperature Behavior. One of the principle differences in the transition temperature behavior of 2,4-TDI and 2,6-TDI polyurethanes is the pronounced increase in the glass transition temperature of the PTMO soft segment in the 2,4-TDI samples and the progressive change in properties with increasing urethane hard block concentration. In contrast,

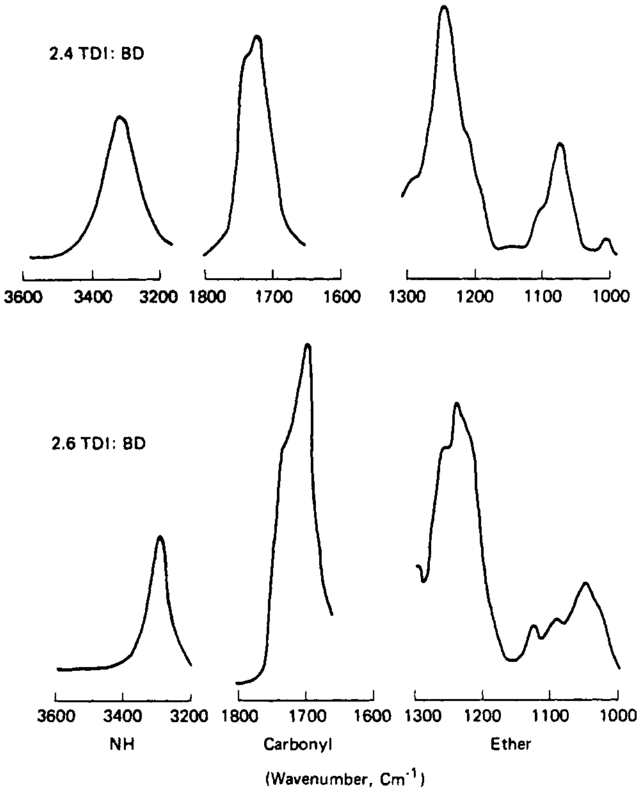

Figure 5. Ir spectra of the NH, carbonyl, and ether regions of films of copolymer analogs of hard segments.

Table IV
Determination of Extent of Hard–Soft Segment Mixing Using the Copolymer Equation

Sample no.	T_g, °K	$W_2{}^a$	$W_2{}'^b$
2,4-TDI-2	233	0.38	0.18
2,4-TDI-3	257	0.53	0.27
2,4-TDI-4	285	0.67	0.33
2,4-TDI-5	296	0.72	0.38
2,4-TDI-6	310	0.78	0.43
2,6-TDI-3	213	0.26	0.13
2,6-TDI-4	213	0.24	0.16
2,6-TDI-5	210	0.21	0.20
2,6-TDI-6	212	0.23	0.23

[a] Values calculated from the elevation of the glass transition using eq 1. [b] W_2' corresponds to the maximum value of the weight fraction of hard segment dispersed in soft segment phase calculated from ir analysis.

the glass transition of the 2,6-TDI polyurethanes and the properties were essentially independent of composition. It might be suggested that the increased glass transition temperatures are due to the influence of the domain structure acting as reactive filler particles. However, studies of carbon black reinforcement in elastomers show that while the modulus is increased with carbon black loading the glass transition temperature is unaltered.[14] An alternative explanation which appears more compelling is that the glass transition behavior, along with other differences in properties, is the result of greater intermixing of hard and soft segment regions in the 2,4-TDI samples. It then appears useful to inquire to what degree the ir evidence on hard segment–soft segment interactions can be used to account for the glass transition behavior.

Two simple models can be invoked to calculate the effect of hard segment–soft segment interactions. The first assumes that the elevation of T_g is merely due to the additive effect of the mixed composition as described by the copolymer equation; the second model assumes that the hydrogen bonding which accompanies intermixing is equivalent to cross-linking of the soft segment.

First we consider the result of applying the copolymer equation (eq 1) where T_{g1} is the glass transition temperature of the PTMO soft segment (188°K), T_{g2} = 380°K for the 2,4-TDI–BD copolymer, and T_{g2} = 374°K for the 2,6-TDI–BD copolymer.

$$1/T_g = (W_1/T_{g1}) + (W_2/T_{g2}) \tag{1}$$

Here W_2 represents the amount of hard segment, expressed as the weight fraction of the mixed hard segment–soft segment phase, which increases the glass transition to the observed value. The calculated values shown in Table IV indicate that W_2 for the 2,4-TDI polyurethanes varies between 0.38 and 0.78 and is approximately 0.24 for the 2,6-TDI polyurethanes. These values can be compared with the maximum hard segment–soft segment mixing W_2' permitted by ir analysis. With the assumption that H-bonded carbonyl exists only in hard segment domains, the following equation can be used to calculate W_2'

$$W_2' = (1 - a)f/[(1 - a)f + (1 - f)] \tag{2}$$

where a is the fraction of H-bonded carbonyl obtained from column II of Table III and f is the overall weight fraction of urethane from column II of Table I. Comparison of the values of W_2 required by the copolymer equation with the maximum values W_2' permitted by ir analysis in the adjacent column of Table IV indicates how seriously the copolymer equation overestimates hard segment–soft segment mixing. Furthermore, the values of W_2 are even greater than the overall weight fraction of hard segment actually present (column II of Table I) which in effect represents the limiting case with all the hard segment dissolved in the soft segment phase. It can be concluded that the effect of simple mixing described by the copolymer equation does not explain the glass transition behavior.

To describe the effect of the hydrogen bonding between hard and soft segment as cross-linking, we use eq 3 developed by DiBenedetto[15] and DiMarzio[16] where T_g is the glass transition temperature of the polyurethane, T_{g1} is the transition temperature of polyether, X_c is the mole fraction of ether units hydrogen bonded to urethane NH groups, and k is a constant between 1.2 and 1.5

$$\frac{T_g - T_{g1}}{T_{g1}} = kX_c/(1 - X_c) \tag{3}$$

As shown in Table V, the extent of hard and soft segment bonding for all polyurethane samples (column III) is now within the limit established from ir analysis (column IV). The difference between column IV and column III in turn provides a crude estimate of the extent of the hydrogen bonded urethane alkoxyl oxygen which is consistent with the ir data obtained with the hard segment analogs (Table III). These results lend further support to the utility of the cross-linking model.

Lastly we have considered the result obtained by combining the copolymer and cross-linking effects. We have used the following relations to convert eq 1 from weight fraction units to X_c

$$W_1 + W_2 = 1 \tag{4}$$

$$W_2 = M_1X_c/(M_1X_c + M_2) \tag{5}$$

where M_1 is half the molecular weight of the repeat unit of

Table V
Distribution of H-Bonded NH Group between Urethane Carbonyl, Ether Oxygen, and Urethane Alkoxyl Oxygen Groups

Sample no.	Fraction of H-bonded ether (X_c)[a]	Fraction of NH bonded to ether[b]	Fraction of NH not bonded to carbonyl[c]	Fraction of NH bonded to alkoxyl
2,4-TDI-2	0.14	0.47	0.54	0.07
2,4-TDI-3	0.20	0.44	0.53	0.09
2,4-TDI-4	0.26	0.43	0.52	0.09
2,4-TDI-5	0.28	0.37	0.50	0.13
2,4-TDI-6	0.30	0.33	0.48	0.14
2,6-TDI-3	0.08	0.17	0.22	0.05
2,6-TDI-4	0.08	0.13	0.22	0.09
2,6-TDI-5	0.09	0.12	0.20	0.08
2,6-TDI-6	0.08	0.09	0.23	0.14

[a] Values calculated from the elevation of the glass transition using eq 3 with $k = 1.5$. [b] Values calculated from column II. [c] Values directly from ir analysis assuming $E_b = E_f$.

hard segment (=133) and M_2 is the molecular weight of the repeat unit of soft segment (=72). The following equation is obtained for the copolymer effect alone by substituting eq 4 and 5 into eq 1.

$$\Delta T_g'/T_{g1} \simeq X_c/(1.1 + X_c) \tag{6}$$

If we assume that copolymer and cross-linking effects on the glass transition temperature can simply be added, then eq 7 results. The maximum error in using the approximate

$$\frac{\Delta T_{\text{total}}}{T_{g1}} \simeq \frac{1.5X_c}{1 - X_c} + \frac{X_c}{1.1 + X_c} \simeq \frac{2.6X_c}{1.1 - 0.1X_c} \tag{7}$$

form of eq 7 is 8%. Table VI illustrates the values obtained using eq 7 for hard and soft segment mixing (X_c). The combined effect, as expected, lowers the calculated extent of hard segment and soft segment mixing as indicated by the values in column II. The estimated fraction of NH bonded to urethane alkoxyl groups, obtained as the difference between the values in column IV and III, is now in better agreement with the values set by ir analysis on the copolymers in Table III.

Conclusions

The studies of hydrogen bonding were undertaken to provide a quantitative estimate of hard segment–soft segment mixing in the 2,4-TDI and 2,6-TDI polyurethanes as a means of explaining the steep increase in soft segment glass transition which occurs in the first but not in the second series of polyurethanes. Analysis of the urethane NH and carbonyl absorption bands has clearly shown that interurethane hydrogen bonding is far greater in 2,6-TDI samples, and correspondingly, that the intermixing of hard and soft segment is much greater in the 2,4-TDI samples and increases with increasing urethane concentration. The failure of the copolymer equation to account for the change in T_g of the 2,4-TDI samples, treated as due simply to the mixing of hard and soft segments, indicates that the hydrogen bonding between urethane and ether oxygen groups must be considered. When the hydrogen bonding is treated as an effective cross-link the predicted degree of hard segment–soft segment mixing is in good agreement with infrared results. This approach for the first time presents a clear explanation of the increase in T_g with urethane concentration which is observed in certain polyurethanes.

Table VI
Distribution of Hydrogen Bonding Based on Combined Copolymer and Cross-Linking Effects

Sample no.	Fraction of H-bonded ether (X_c)[a]	Fraction of NH bonded to ether[b]	Fraction of NH not bonded to carbonyl[c]	Fraction of NH bonded to alkoxyl
2,4-TDI-2	0.10	0.33	0.54	0.21
2,4-TDI-3	0.15	0.33	0.53	0.20
2,4-TDI-4	0.21	0.36	0.52	0.20
2,4-TDI-5	0.24	0.32	0.50	0.18
2,4-TDI-6	0.27	0.30	0.48	0.18
2,6-TDI-3	0.06	0.13	0.22	0.09
2,6-TDI-4	0.06	0.10	0.22	0.12
2,6-TDI-5	0.06	0.08	0.20	0.12
2,6-TDI-6	0.06	0.07	0.23	0.16

[a] Values calculated from the elevation of the glass transition using eq 7 with $k = 1.5$. [b] Values calculated from column II. [c] Values directly from ir analysis assuming $E_b = E_f$.

Despite the success achieved in accounting for the change in glass transition temperature in terms of the infrared analysis, the levels of hard segment–soft segment mixing determined in this way must be viewed with caution. There are two factors which affect the accuracy of these estimates. First, the calculated values assume that the only proton acceptors are urethane carbonyl and soft segment ether oxygen. The observation that NH hydrogen bonding also can occur with urethane alkoxyl oxygen implies that interurethane bonding is somewhat higher than customarily estimated. Second, it has been assumed that all hydrogen bonded carbonyl resides in hard segment domains. In effect, this neglects the possibility that small aggregates of hard segments are also mixed with the soft segment phase. There is indirect evidence that this could be a serious oversimplification for the 2,4-TDI polyurethanes. Values for the fraction of hydrogen bonded carbonyl in Table III show that only a small increase in interurethane hydrogen bonding occurs over the full range of 2,4-TDI concentration. An explanation for this behavior can be provided based on the occurrence of small aggregates of hard segments in the soft segment phase. The build up in domain structure with increasing urethane concentration, indicated by the low angle X-ray behavior, can take place accompanied by a decrease in the proportion of distributed hard segment aggregates without requiring a change in the extent of interurethane hydrogen bonding.

The explanation of the increase in soft segment T_g discussed above appears to be well established despite the difficulties in obtaining a quantitative estimate of the extent of phase mixing from the infrared data. The semiquantitative treatment, which combines the copolymer and cross-linking effects, should be helpful in estimating the extent of urethane bonding to soft segment carbonyl from the T_g behavior of polyester type polyurethanes, where it is not possible to determine the extent of NH bonding to urethane carbonyl directly by infrared. Finally, it might be stated that while it is correct that hydrogen bonding plays only a secondary role in determining transitions of the domain structure, it is apparent that in certain cases hydrogen bonding can exercise a profound role in determining overall polymer properties through its effect on the soft segment glass transition.

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Oriented Polymer Growth in Thermotropic Mesophases

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ABSTRACT: Long-range order in polymers obtained through polymerization within mesomorphic and potentially mesomorphic media has been studied. Three representative monomers have been polymerized in mesomorphic and isotropic media and the properties of the polymers were investigated by means of X-ray and polarizing diffraction microscopy. *N*-*p*-Methacryloyloxybenzylidene-*p*-aminobenzoic acid (MBABA) was polymerized in its nematic state and in solution in DMF. In both cases a "locked in" nematic superstructure was observed. *N*-*p*-Butoxybenzylidene-*p*-aminostyrene (BBAS) was polymerized in bulk, in the nematic and isotropic states. Here again in both cases a "locked in" nematic superstructure was observed by X-ray diffraction. *p*-Methacryloyloxybenzoic acid (MBA) was polymerized in the isotropic bulk, in a nematic solvent, and in isotropic solvents. When polymerized in bulk, the polymer displayed pronounced crystallinity. A mesomorphic smectic superstructure appeared in films of the polymer cast from DMF, regardless of the method of polymerization, although none of the PMBA's studied are stereoregular. The results show on three examples that neither the presence of a mesomorphic matrix nor large amounts of cross-linking agent are necessary for the development and locking in of mesomorphic superstructure in polymers.

It was in 1963 that Herz, *et al.*,[1] succeeded in "locking in" the organization of the neat phase of the 11-sodium styrylundecanoate–water system through free radical polymerization. The reaction was carried out in the presence of a small amount of divinylbenzene used to cross-link the structure. A polymer was obtained with a molecular organization of a neat soap phase permanently locked in through cross-linking. Shortly thereafter, the locking in of the quasi-smectic organization of monolayers of polar monomer molecules adsorbed on montmorillonite was described by Blumstein, *et al.*[2] Here again a cross-linking agent (tetraethyleneglycol dimethacrylate) was used to stabilize the two-dimensional arrangement of monomer molecules. More recently Liebert and Strzelecki[3] obtained a number of anisotropic glasses by locking in the organization of different mesomorphic monomers. Polymeric glasses of nematic, smectic, and cholesteric symmetry were obtained. The authors stressed the necessity of using important quantities of cross-linking agents to avoid backcoiling of macromolecular chains with subsequent loss of order. Either bifunctional mesomorphic monomers were used, or mixtures of monofunctional mesomorphic monomers with at least 30 wt % of bifunctional monomers.

The locking in of mesomorphic superstructures through polymerization is analogous to locking in of molecular orientation through cooling. Such experiments have been described for different mesomorphic compounds by Chistyakov, *et al.*,[4] and more recently by Kessler and Lydon.[5] In both cases the long-range order in the glass was introduced through the quick depression of molecular motions, either through increase of the T_g (cross-linking) or direct freezing of the mesomorphic compound below its T_g. These facts suggest that the presence of a cross-linking agent may not always be necessary, provided the thermal motion of segments of the polymer, developing in the mesomorphic medium, is sufficiently depressed and that the polymer does not separate abruptly from the medium.

Polymerization within mesomorphic media has also been found to influence the degree of crystallinity of the resulting polymers. Such effects have been reported by Amerik and Krentsel[6] for poly(vinyloleate), by Hardy, *et al.*,[7] for cetyl vinyl ether, and by Perplies, Ringsdorf, and Wendorff[8] for a number of acrylic and methacrylic derivatives of Schiff bases.

The origin of the differences in supramolecular organization between polymers prepared in isotropic and mesomorphic media is unclear. There appears to be an interplay of three factors: (a) influence of the organization of the initial monomeric matrix (topotactic control); (b) strong interactions between side groups of the polymer, that is, the polymer's intrinsic tendency to organize; (c) possible influence of the matrix on the configuration of the polymer (topochemical control), which would in turn influence the supermolecular organization. We are attempting to discuss these questions on three representative examples. We would like to show evidence that anisotropic superstructures can be produced not only from systems displaying mesomorphism, but also from systems in which neither the polymer seg-