and decay times, a poorer solvent has to be used in which the coils are smaller.

Toluene as the theta solvent at 37 °C[14] was chosen for such a study despite the poorer optical quality of glasses formed at 77 K. The results, which will be published elsewhere, show that the general spectroscopic behavior is rather similar in both solvents. Intramolecular triplet–triplet annihilation is therefore likely to be the cause of delayed fluorescence of PVCA in these solvents. The process is favored by the slow first-order triplet decay in carbazole derivatives. In 10^{-3} M solutions in MTHF at 77 K we measured τ_P = 8.2 s (PVCA VI) and τ_P = 7.8 s (*N*-isopropylcarbazole). Neglecting second-order decay, we roughly estimate that on the average we have one triplet/macromolecule if the molecular weight is 2×10^4. At higher molecular weights the chance to meet two or more triplets together at the same molecule increases and delayed fluorescence can occur (Figure 4), competing with phosphorescence. Delayed fluorescence decays much faster than phosphorescence ($\tau_{DF} \approx$ 3–4 ms in toluene), which indicates that the triplets whose decay is observed in phosphorescence are not the mobile triplets causing delayed fluorescence.

Similar conclusions have been drawn by Yokoyama et al.[16] in a recent study of the phosphorescence of PVCA in which strong evidence from quenching experiments is presented for a trap (probably carbazole end groups) as origin of the phosphorescence.

Recently, delayed fluorescence due to photoionization and recombination has been observed in carbazole/ether at 77 K.[15] Using the monomeric model *N*-isopropylcarbazole in MTHF we did not detect any delayed fluorescence. In the case of the polymer, the molecular weight dependence seems to exclude photoionization as a major cause of delayed fluorescence. A final decision about the mechanism, however, can only be made after a kinetic analysis of the quantitative study now under way.

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References and Notes

(1) Paper presented in part at the 3rd European Symposium on Polymer Spectroscopy in Uxbridge, London, April 1974.
(2) (a) R. F. Cozzens and R. B. Fox, *J. Chem. Phys.*, **50**, 1532 (1969); (b) C. Hélène and J. W. Longworth, *ibid.*, **57**, 389 (1972).
(3) W. Klöpffer and D. Fischer, *J. Polym. Sci., Polym. Symp.*, **No. 40**, 43 (1973).
(4) M. Yokoyama, T. Nakamo, T. Tamamura, and M. Mikawa, *Chem. Lett.*, 509 (1973).
(5) A. C. Somersall and J. E. Guillet, *Macromolecules*, **6**, 218 (1973).
(6) G. E. Johnson, *J. Chem. Phys.*, **62**, 4697 (1975).
(7) M. Bazin, R. Santus, and C. Hélène, *Chem. Phys.*, **2**, 119 (1973).
(8) P. Avakian, R. P. Groff, A. Suna, and H. N. Cripps, *Chem. Phys. Lett.*, **32**, 466 (1975).
(9) W. Klöpffer and H. Bauser, *Z. Phys. Chem. (Frankfurt am Main)*, **100**, 25 (1976).
(10) R. D. Burkhart, *Macromolecules*, **9**, 234 (1976).
(11) D. Fischer, *J. Appl. Phys.*, **44**, 1977 (1973).
(12) W. Klöpffer, *J. Chem. Phys.*, **50**, 2337 (1969).
(13) G. Sitaramaiah and D. Jacobs, *Polymer*, **11**, 165 (1970).
(14) N. Kuwahara, S. Higashida, M. Nakata, and M. Kaneko, *J. Polym. Sci., Part A-2*, **7**, 285 (1969).
(15) D. Muller, M. Ewald, and G. Durocher, *Can. J. Chem.*, **52**, 3707 (1974).
(16) M. Yokoyama, T. Tamamura, T. Nakano, and H. Mikawa, *J. Chem. Phys.*, **65**, 272 (1976).

Temperature Dependence of Hydrogen Bonding in Toluene Diisocyanate Based Polyurethanes

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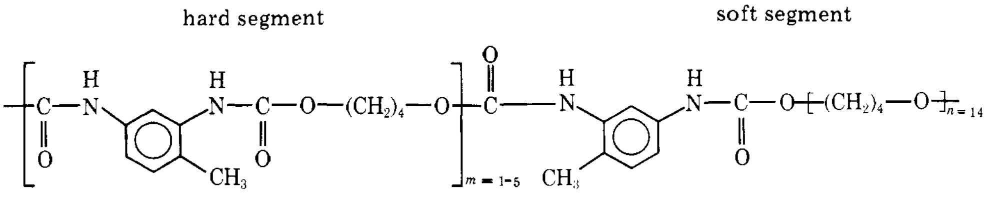
ABSTRACT: The temperature dependence of hydrogen bonding in 2,4-TDI and 2,6-TDI based polyurethanes was investigated using simple procedures to resolve hydrogen bonded and nonbonded NH and carbonyl. The fraction of hydrogen bonded carbonyl was used as a measure of the extent of interurethane hydrogen bonding. The onset temperature for dissociation of both hydrogen bonded NH and carbonyl in 2,6-TDI polymers occurs at 65 °C, independent of urethane content and well below the melting temperature of crystalline hard segment structure (130 to 170 °C). For 2,4-TDI polyurethanes the onset temperature for dissociation of hydrogen bonded NH occurs at 40 to 60 °C, close to the transition temperature for amorphous domain structure, but there is little change in hydrogen bonded carbonyl up to the highest temperature studied (150 °C). Heats of dissociation were about 4 kcal/mol in both series. The 2,4-TDI results demonstrate the preferential dissociation of urethane to soft segment bonding and, by contrast with the lower stability of interurethane bonding in 2,6-TDI samples, suggest that hydrogen bonding to the 4 position of the TDI ring is stronger than the 2 position. The structural implications of the 2,6-TDI and 2,4-TDI results are discussed. Overall, the behavior indicates that the cause of hydrogen bond dissociation bears little relation to the state of structural organization.

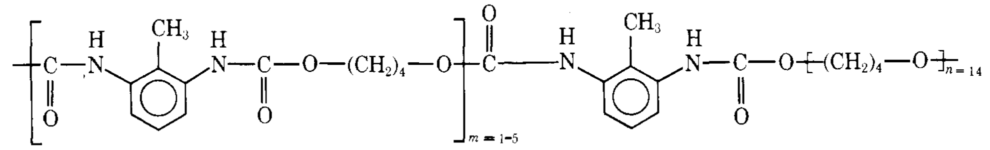
In previous work, two series of segmented polyurethanes, one based on 2,4-toluene diisocyanate (TDI), the second on 2,6-TDI, were investigated to determine the effect of asymmetric placement of the isocyanate groups on domain structure, microphase segregation, and polyurethane properties.[2a] Quantitative infrared analysis of the urethane NH and carbonyl bands was carried out as a means of assessing the degree of phase segregation,[2b] under the assumption that the fraction of NH involved in interurethane bonding was a direct measure of phase segregation. The infrared results showed that extensive mixing of hard and soft segment occurred in the 2,4-TDI polymers and provided a basis for explaining the rapid increase in the soft segment T_g which occurs with increasing urethane content in these samples.

In the present work, we have attempted to examine the relation between hydrogen bonding and the higher thermal transitions. The first such studies were carried out by Seymour and Cooper[3] to determine the relation between hydrogen bonding and domain morphology in MDI based polyurethanes. They showed that the transitions observed by DSC

Chart I



2,4-TDI polyurethanes



2,6-TDI polyurethanes

could be moved to higher temperatures whereas the onset temperature for hydrogen bonding dissociation, obtained from infrared analysis of the NH absorbance, remained unchanged at 70 to 80 °C. These results lead to the conclusion that hydrogen bonding, in fact, played only a secondary role in the structure and properties of the hard segment domains. In the 2,4-TDI based polyurethanes only weak domain related transitions below 100 °C are observed, due to the amorphous nature of the domain structure, and these transitions are insensitive to annealing. In the 2,6-TDI samples the domain structure is crystalline. Therefore it is of interest to determine whether the relation between hydrogen bonding and domain transitions for these samples is consistent with that observed by Seymour and Cooper. Since the urethane groups are distributed between the domain structure and the soft segment phase, we looked at the behavior of both NH and carbonyl groups as a function of temperature using simple procedures for resolving hydrogen bonded and nonbonded components of the two absorption bands. The changes in the carbonyl band monitor the interurethane hydrogen bonding and, therefore, the process occurring mainly in hard segment domains. Despite difficulties in the data analysis, the results lead to conclusions which in part are consistent with Seymour and Cooper's work but also represent behavior and problems not previously observed.

Experimental Section

Polymers. The polymers investigated 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 as shown in Chart I. The soft segment is poly(tetramethylene oxide) of molecular weight 1000. The detailed synthesis of these polymers was described previously.[2a] The molar ratio of TDI:butanediol:polyether was varied in five equal steps from 2:1:1 to 6:5:1. In sample designation, the number of moles of diisocyanate per mole of polyether is indicated by the integer which follows the specified TDI isomer.

Infrared Temperature Studies. A Beckman-12 infrared spectrophotometer was used with a variable temperature unit (Wilks Model No. 19) connected to the temperature controller (Wilks Model No. 37). Subambient temperature was obtained by passing a stream of liquid nitrogen through ¼ in. copper tubing soldered to a copper plate which was attached to the salt plate holder. The temperature range was from −20 to 160 °C and the temperature was controlled within ±1 °C. The chamber containing the cell was flushed with dry nitrogen to avoid the condensation of moisture on the salt plate. All the samples were prepared by casting from DMF solution (~2% by weight) and drying in a vacuum oven until there was no evidence of residual solvent.

Small-Angle X-Ray Scattering. A Kratky camera was used to obtain the angular dependence of scattered intensity for 2,4-TDI polyurethanes. Radiation was supplied by a graphite monochromated Norelco copper fine-focus tube operated at 50 kV and 30 mA. The Kratky camera was equipped with automatic step scanning, counting, and printing devices.

Results

2,6-TDI Based Polyurethanes. In our previous publication,[2a] we reported that segmented polyurethanes based on symmetric 2,6-toluene diisocyanate were semicrystalline and opaque. IR analysis on these polymers showed that 80% of NH groups are bonded to carbonyl groups in the urethane linkage. This implies that almost all the urethane segments reside in hard segment domains, while the remaining 20% of NH groups are bonded either to soft segment ether groups or to urethane alkoxyl groups.[2b]

Figure 1 shows the effect of temperature on the NH region of IR spectra for a representative 2,6-TDI polyurethane, 2,6-TDI-3. At 0 °C, all the 2,6-TDI polymers exhibit NH absorption bands, which are almost completely hydrogen bonded, centered at 3300 cm^{-1}. As the temperature is raised, the hydrogen bonded NH absorption decreases while a free NH absorption shoulder develops which is centered at 3460 cm^{-1}. Since the extinction coefficient of free NH groups is about one third of that for hydrogen bonded NH groups,[4] the increase in free NH absorption is not as great as the decrease in bonded NH absorption. At 0 °C, curve resolving using the Du Pont 310 curve resolver indicated that 95–97% of NH are

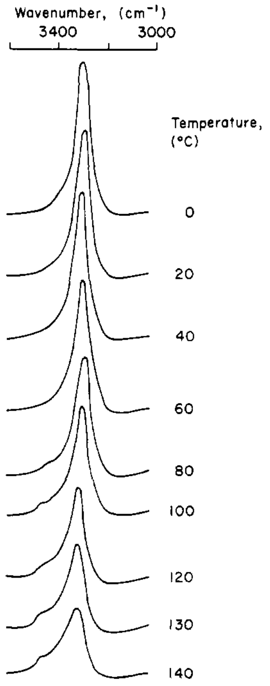


Figure 1. Temperature dependence of the NH region in the IR spectrum for 2,6-TDI-3.

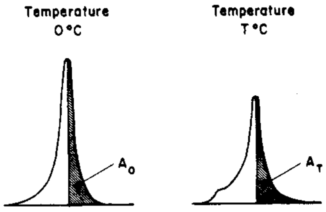


Figure 2. Estimation of fraction of bonded NH in 2,6-TDI polyurethanes (fraction of bonded NH = $(A_T/A_0) \times 0.95$).

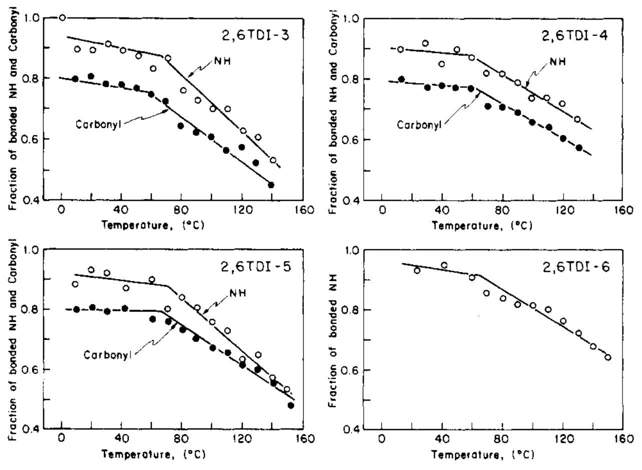


Figure 3. Fraction of bonded NH groups and carbonyl in 2,6-TDI polymers as a function of temperature.

hydrogen bonded. The fraction of bonded NH at higher temperatures was then calculated by comparing one-half of the total bonded area, as shown in Figure 2, with that of the reference spectra at 0 °C. Figure 3 illustrates the results of this analysis as a function of temperature for the various 2,6-TDI polymers. The onset of the dissociation of hydrogen bonded NH groups appears to occur around 60 to 70 °C for all of 2,6-TDI based polyurethanes.

The dissociation of hydrogen bonded NH groups for these polymers follows an equilibrium process governed by the following equation above the onset temperature;

$$\mathrm{d} \ln k/\mathrm{d}(1/T) = -\Delta H/R$$

where k, the equilibrium dissociation constant, is equal to $[C_f]^2/[C_b]$ with C_f the fraction of free NH and C_b the fraction of bonded NH. Figure 4 shows a typical plot of ln k vs. $1/T$, whose slope gives $\Delta H/R$, where ΔH is the dissociation energy of hydrogen bonded NH groups. It should be noted that when plotted in this form the data show a clearly defined transition in behavior for the values above $1/T = 3.0 \times 10^{-3}$ despite the scatter. Some care must be exercised in interpreting the discontinuity in NH absorbance or in the fraction of bonded NH as an indication of a transition. For certain values of the heat and entropy of dissociation, an apparent transition will occur in the absorbance or fraction of bonded NH even when equilibrium behavior is followed over the temperature range of interest (see Appendix).

The results from the analysis of the data in Figure 3 are summarized in Table I, where it can be seen that ΔH values of 4–5 kcal/mol of hydrogen bond are obtained. The values seem to be independent of urethane concentration and are reasonable for the dissociation of hydrogen bonded NH groups.[4] The small variation in ΔH values within the 2,6-TDI polymer series, in part, reflects the error in estimating the initial bonded fraction at 0 °C. For example, a 5% decrease in the bonded fraction at the reference temperature would lower ΔH values by as much as 1 kcal/mol of hydrogen bond.

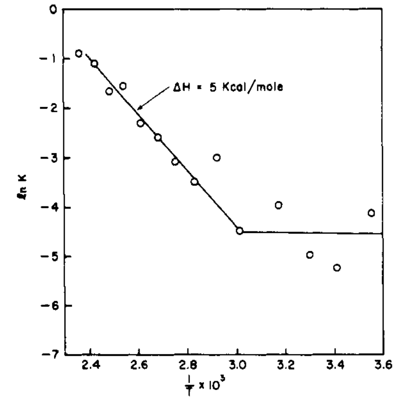


Figure 4. Gibbs–Helmholtz plot of ln k vs. $1/T$ for the dissociation of bonded NH groups for 2,6-TDI-5.

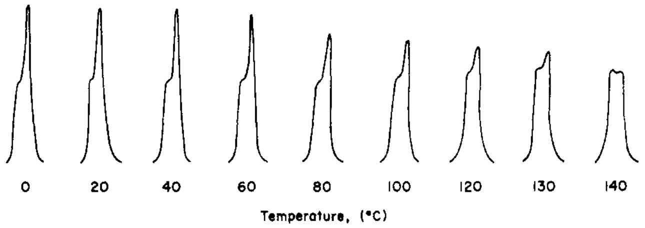


Figure 5. Temperature dependence of the carbonyl region in the IR spectrum for 2,6-TDI-3.

Table I
The Onset Temperature and ΔH of Dissociation of Hydrogen Bonded NH Groups in 2,6-TDI Polyurethanes

Polymer	Onset temp, °C	ΔH/mol of hydrogen bond, kcal
2,6-TDI		
-3	66	4
-4	60	4
-5	72	5
-6	64	4

Since 80% of NH groups in 2,6-TDI polyurethanes are bonded to urethane carbonyl, the dissociation of NH groups must reflect a process occurring almost exclusively within the hard segment domain. However, it is complicated with a small contribution from dissociation of NH groups bonded to soft segment ether which cannot be distinguished on the basis of the results of Figure 3. Therefore, we investigated the temperature dependence of hydrogen bonded carbonyl groups to obtain information which is more sensitive to the changes in the hard segment domains. The behavior of the carbonyl absorption is illustrated in Figure 5 for a representative 2,6-TDI polymer, 2,6-TDI-3. As the temperature is raised, hydrogen bonded carbonyl absorption at 1700 cm^{-1} decreases and free carbonyl absorption at 1740 cm^{-1} increases. In several samples it was apparent that both bonded and nonbonded regions of the carbonyl band consisted of a number of severely overlapping peaks. The fraction of bonded carbonyl was calculated based on peak height at 1700 cm^{-1} for bonded carbonyl and at 1740 cm^{-1} for free carbonyl rather than peak area because of the difficulty of resolving these closely overlapping peaks and the results are plotted in Figure 3. Since the bonded peak

Table II
The Onset Temperature and ΔH of Dissociation of Hydrogen Bonded Carbonyl Groups in 2,6-TDI Polyurethanes

Polymer	Onset temp, °C	ΔH/mol of hydrogen bond, kcal
2,6-TDI		
-3	60	3
-4	60	3
-5	68	4

is broader than the nonbonded carbonyl, this will tend to overestimate the fraction of free carbonyl groups. As in earlier calculations, it was assumed that the extinction coefficients for free and bonded carbonyl are equal.

The onset temperature for the dissociation of the bonded carbonyl is between 60 and 65 °C which is in the same temperature range for the analogous process involving NH groups. The dissociation energy, ΔH, was calculated for 2,6-TDI polymers by assuming 80% bonded carbonyl at 0 °C, which was obtained by curve resolving. As summarized in Table II, ΔH values of 3–4 kcal/mol are obtained for the dissociation energy of carbonyl groups. The values are somewhat smaller than those obtained from analysis of the NH band but again are independent of urethane concentration. The smaller values of ΔH for the dissociation of carbonyl groups might be due to underestimation of the initial 0 °C value for bonded carbonyl or to discrepancies in the estimation of free carbonyl based on the relative peak height changes. These results support the conclusion that dissociation of hydrogen bonds in the 2,6-TDI samples occurs mainly in hard segment domains above the onset temperature. Some insight concerning the behavior of the urethane to ether hydrogen bonding can be gained from a comparison of the results for bonded NH and for bonded carbonyl in Figure 3 when plotted together as a function of temperature. It then becomes apparent that the two sets of data are nearly parallel and separated by a constant interval below the onset temperature for all three samples where the comparison can be made. Above the onset temperature, the behavior is somewhat variable. The results for the fraction of bonded NH and carbonyl continue on a parallel course in 2,6-TDI-4 but converge at higher temperature in 2,6-TDI-5. The behavior below the onset temperature indicates that urethane bonding to proton acceptors other than carbonyl in all cases is stable up to the onset temperature. This may be contrasted with results on 2,4-TDI, to be discussed in the following section, where a decrease of about 10% in bonded NH occurs below the onset temperature without any change in the carbonyl distribution. If only urethane to ether bonding is considered, this would imply that such bonding is stronger in 2,6-TDI than in 2,4-TDI polyurethanes, a difference which is difficult to explain on the basis of the structure of the isomers.

One possible way out of this dilemma is to invoke the contribution of urethane to alkoxy bonding which can occur within the highly ordered domain structure of 2,6-TDI polyurethanes. The persistence of this bonding in some degree well beyond the onset temperature indicates that it is comparable in strength to the urethane to carbonyl bonding. Urethane to alkoxy bonding would be present to only a minor extent in the 2,4-TDI samples since a large fraction of the urethane segments are distributed in the soft segment phase. This explanation implies that the infrared values for the fraction of nonbonded carbonyl overestimate the amount of urethane soft segment mixing. In fact, this conclusion is consistent with the observation that values for the soft segment glass transition calculated from the infrared results using the Fox copolymer equation are equal to or higher than the experimental values in the 2,6-TDI polyurethanes, but the calculated values fall well below the experimental values for 2,4-TDI samples.[2b]

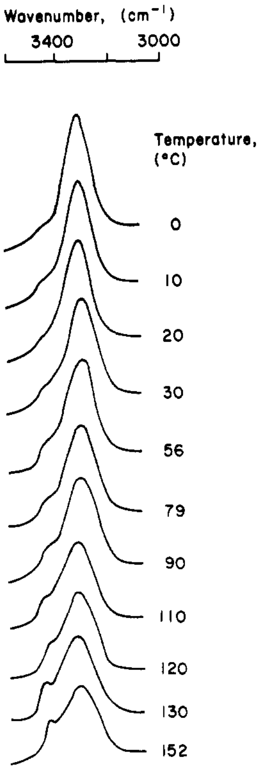


Figure 6. Temperature dependence of the NH region in the IR spectrum of 2,4-TDI-2.

2,4-TDI Based Polyurethanes. We reported that segmented polyurethanes based on asymmetric 2,4-toluene diisocyanate were transparent and amorphous and that their properties changed progressively from rubbery to plastic with increasing urethane concentration.[2a] IR analysis on these polymers revealed that 50% of NH groups are bonded to carbonyl presumably with the rest hydrogen bonded to the soft segment, thereby indicating extensive intermixing of hard and soft segment.

Figure 6 shows the effect of temperature on the NH region of the IR spectrum for a representative 2,4-TDI polyurethane, 2,4-TDI-2. At 0 °C, NH groups show up to 95% hydrogen bonding with an absorption peak at 3320 cm^{-1}, while free NH groups (5%) exhibit a small shoulder at 3460 cm^{-1}. With increasing temperature, the hydrogen bonded peak decreases while the free NH peak develops. The fraction of bonded NH groups was obtained by the same procedure used for 2,6-TDI polymers. Figures 7a and 7b illustrate the results obtained as a function of temperature for all the 2,4-TDI polyurethanes. At higher temperatures, the method of taking a half of the bonded NH peak tends to overestimate the fraction of the bonded NH and the flattening of the curve in Figure 7b for 2,4-TDI-4 in the range of 80–140 °C may reflect this effect. In Figure 7, the discontinuity in the curves as drawn occurs at about 40 °C for the first three samples and at 60 to 70 °C for the two samples of highest urethane content. The values for all samples are summarized in Table III together with other pertinent data. In all cases the onset temperatures are well above the glass transition temperature of the soft segment phase and, in fact, fall in closer line with the T_2 transition of hard segment domains (see Table III) although the correlation is not exact. The dissociation energy ΔH is about 3–4 kcal/mol of hydrogen bonds for all 2,4-TDI polymers above the onset

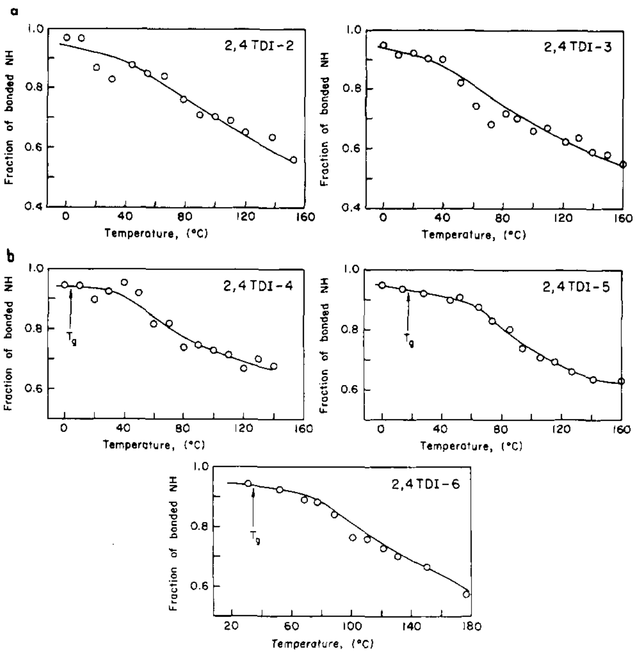


Figure 7. (a) Fraction of bonded NH groups in 2,4-TDI-2 and 2,4-TDI-3 as a function of temperature. (b) Fraction of bonded NH groups in 2,4-TDI-4, 2,4-TDI-5, and 2,4-TDI-6 as a function of temperature.

Table III
The Onset Temperature and ΔH of Dissociation of Hydrogen Bonded NH Groups in 2,4-TDI Polyurethanes

Polymer	T_g,[a] °C	T_2,[b] °C	Onset temp, °C	ΔH, kcal/mol of hydrogen bond
2,4-TDI				
-2	−36	18	38	4
-3	−14	33	35	3
-4	1	60	38	3
-5	11	70	55	4
-6	23	80	65	4

[a] For samples compression molded at 180 °C. [b] Intermediate thermal transition observed as additional softening in penetrometer runs.[2a]

temperature. It is also interesting to note that the soft segment glass transition temperature for 2,4-TDI-5 and -6 falls in the temperature range under study but the data in Figure 7b show that the NH hydrogen bonding is almost unaffected as the sample goes through the glass transition. This is a necessary condition for the treatment of hydrogen bonding between hard and soft segment as equivalent to cross-linking in elevating the soft segment glass transition temperature in these polymers.[2b]

Since the bonded NH groups are equally distributed among hard segment and soft segment, it is important to determine which type of hydrogen bond is responsible for the observed NH dissociation. In order to answer this question, the temperature dependence of carbonyl groups for these polymers was investigated and Figure 8 illustrates the behavior of carbonyl groups for a representative 2,4-TDI. At 0 °C, free carbonyl at 1740 cm^{-1} is about equal to the bonded carbonyl peak at 1720 cm^{-1}. As the temperature is raised, the free carbonyl peak increases to a small extent, accompanied by a decrease in bonded carbonyl peak. There is also a distinct reduction in the contribution of side bands occurring mainly near 1700 cm^{-1}. However, quantitative analysis in the carbonyl region as a function of temperature was not carried out since it was impossible to resolve the free and bonded carbonyl groups accurately, especially in view of the small total change, at most 20% dissociation, in the temperature range studied. Since NH groups show about 50% dissociation in the same temperature range, as indicated in Figure 8, the dissociation of carbonyl groups alone cannot account for the dissociation observed in the NH region. In fact, the data imply that the greater part of NH dissociation must involve NH to ether bonding. This suggests that only a small amount of NH to urethane alkoxyl is present in 2,4-TDI polymers. The carbonyl data also show that the remaining interurethane bonding, accounting for about 50% of the NH, is almost unaffected up to the temperature limit of the experiment which is far above the temperature at which any domain structure remains.

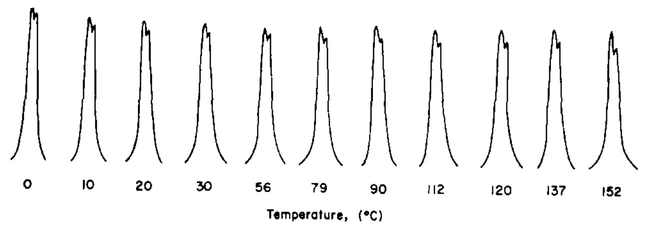


Figure 8. Temperature dependence of the carbonyl region in the IR spectrum for 2,4-TDI-2.

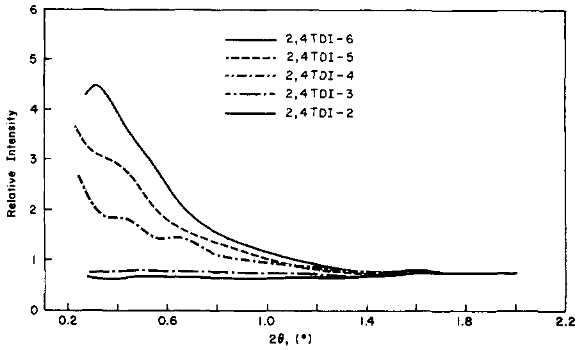


Figure 9. Angular dependence of SAXS intensity in 2,4-TDI based polyurethanes.

We have previously referred to the results of low-angle x-ray scattering on the 2,4-TDI polyurethanes[2a] without displaying the data. In view of the weak nature of the transition behavior and the importance attached to phase segregation it was believed worthwhile to present the scattering curves. The angular dependence of intensity obtained at room temperature is shown in Figure 9. As can be seen clearly, the three polymers with longer hard segment exhibit the type of angular dependence which implies the presence of domain structure. It is also to be noted that total area under the curve is strongly dependent on the urethane content, implying that the organization of domains is the best for 2,4-TDI-4, 2,4-TDI-5, and 2,4-TDI-6 in increasing order. For the two samples 2,4-TDI-2 and 2,4-TDI-3, no angular dependence is observed. This may imply that the domain structure is not present at room temperature but, in view of the closeness of the T_2 transition to room temperature for these two polymers, this conclusion should be viewed with caution.

Discussion and Conclusion

The contrast in the stability of the interurethane hydrogen bonding in the 2,6-TDI and 2,4-TDI polyurethanes is paradoxical. It was expected that very little dissociation of in-

interurethane hydrogen bonds would be detected in the 2,6-TDI samples below the crystalline melting point of hard segment domain structure whereas the dissociation of interurethane hydrogen bonding in the 2,4-TDI samples would begin at low temperatures related to the hard segment transitions and reflecting the incomplete and amorphous nature of the domain organization. Thus, it is necessary to understand the implications of these two observations; the relatively low temperature which marks the onset of dissociation of the interurethane hydrogen bonding in the 2,6-TDI samples and the unusual stability of the interurethane hydrogen bonding in the 2,4-TDI samples.

Previous thermal studies[2a] showed that the melting temperature of hard segment domains in the 2,6-TDI samples occurs at about 130 °C in 2,6-TDI-3 and increases to about 170 °C in 2,6-TDI-6, indicating an improvement in crystalline order or stability with increasing hard segment length. Not only does the onset of the interurethane hydrogen bond dissociation occur well below the melting temperature but both the onset temperature and the dissociation energy are essentially constant with increasing urethane content. Thus, the thermal lability of the interurethane hydrogen bonds are insensitive to the improving degree of crystalline order. The situation is analogous to that observed by Seymour and Cooper[3] in their study of the annealing behavior of MDI based polyurethanes. Although DSC measurements showed that annealing moved the transition connected with the disruption of hard segment domains to progressively higher temperatures the onset of hydrogen bonding dissociation at 70 to 80 °C was unaffected. They concluded that the onset temperature was controlled by the glass transition temperature of the hard segments.

Thus, one interpretation of the present results is that the onset of interurethane hydrogen bond dissociation marks the glass transition temperature of urethane segments in 2,6-TDI crystalline regions. It seems reasonable that the loss of segmental mobility at the glass transition temperature will also result in a freezing of the hydrogen bonding equilibrium as first argued by Wolkenstein and Ptitsyn.[5] However, in these 2,6-TDI samples, no hard segment T_g was observed either by DSC or penetrometer techniques. Thus, accepting the connection between the onset temperature and hard segment mobility implies that there are amorphous hard segment regions of the crystalline domains which are below detectable limits. Furthermore, since the dissociation of interurethane bonding occurs to levels of 50% or more at temperatures which are still below the melting point, the results indicate that extensive disruption of hydrogen bonding occurs within the crystalline structure. Perhaps the disruption is restricted to crystal defect regions. These defects could present a continuous distribution of order including at one extreme amorphous segments. However, the possibility that hydrogen bond dissociation can occur within well organized crystalline regions cannot be excluded at the present time.

It is worth noting that there are comparable difficulties in understanding Seymour and Cooper's results. The glass transition temperature can no longer be detected by DSC at 70 or 80 °C in the annealed samples, but the onset temperature for hydrogen bond dissociation still occurs at 70 to 80 °C. Moreover, the entire course of hydrogen bond dissociation is unaffected by the improved order that results from annealing. This indicates that hydrogen bond dissociation can occur within MDI hard segment regions which appear paracrystalline or crystalline to DSC.

The behavior of the onset of dissociation of NH bonding in the 2,4-TDI polyurethanes, which is clearly related to the dissociation of urethane to ether bonding, is puzzling. Except for a small amount of hydrogen bond dissociation which occurs at lower temperature, the rapid decrease in NH bonding occurs well above the soft segment glass transition temperature and appears to be related to the domain transition. Such an effect could result from soft segment mixing in hard segment regions, a possibility considered by Bonart[6,7] in attempts to analyze the absolute intensity of small-angle x-ray scattering. This model implies that hard segment domains are actually mixed regions in which soft segment is present but the hard segment concentration is high enough to give rise to a distinct transition. The large change in 2,4-TDI hard segment transition temperature with urethane content could be due to the effect of such soft segment mixing in combination with the increasing hard segment length. In fact, droplet like morphology has been observed in certain noncrystalline MDI and TDI polyurethanes, where the dimensions of the droplets require mixing of hard and soft segment regions.[8] However, this model is not without its problems, not the least of which is the difficulty in explaining how the limited mixing can control the overall hydrogen bonding behavior with the soft segment.

The second half of the problem is concerned with the large difference in the inherent stability of the interurethane bonds in the 2,6-TDI and 2,4-TDI samples. It appears reasonable to attribute this difference to steric hindrance from the methyl group which interferes with the formation of urethane NH to carbonyl hydrogen bonds in the most stable configuration in 2,6-TDI samples. The survival of the interurethane bonding in the 2,4-TDI samples at higher temperatures would then be due to the greater stability of bonds with the urethane at the 4 position on the TDI ring. If the foregoing statements are correct then the measured ΔH values in the 2,4-TDI samples determined from the change in NH bonding (Table III) are those of the weakly bonded urethane groups at the 2 position on the TDI ring.

The principle lesson which can be distilled from the present results is that the thermal behavior of the hydrogen bonding is essentially independent of the structural organization. There is extensive evidence, both for 2,6-TDI and for MDI samples, that hydrogen bond dissociation occurs within ordered domain structure at temperatures well below the domain transition temperature and with little regard for improvement in the degree of order. Finally, in all cases a significant degree of hydrogen bonding persists to the highest temperatures measured in this study (150 °C) and as high as 200 °C in Seymour and Cooper's work on MDI polyurethanes. However, as Seymour and Cooper have pointed out, the rate of hydrogen bond interchange is sufficiently rapid that hydrogen bonding has little effect on melt flow or long time mechanical properties.

The ability to answer many of the questions raised by these results is limited by the error and uncertainties inherent in recording the spectra and by the curve resolving procedures. However, recent advances provided by Fourier Transform IR Spectrometry might enable one to obtain the necessary detail for a more reliable analysis through the use of signal averaging and the capability of obtaining difference spectra of unusual sensitivity.

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Appendix

Since the hydrogen bonded and nonbonded components of the NH absorption bands are difficult to resolve, the total absorbance has sometimes been used and the discontinuity in the absorbance–temperature curve has been taken as an indication of a transition occurring in the polymer. However,

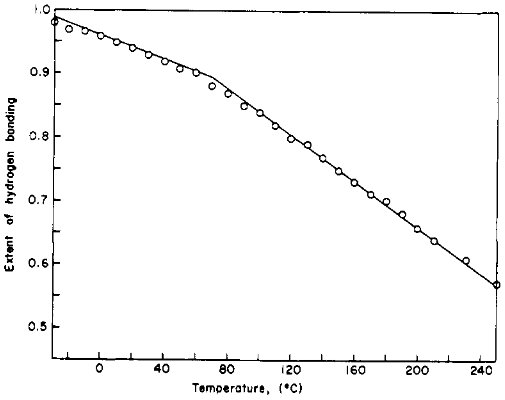

Figure 10. Extent of hydrogen bonding as a function of temperature in dilute solution when $\Delta H = 6$ kcal/mol and $\Delta S = 10$ eu.

one should be cautious in identifying the discontinuity displayed in this manner with a transition because even the equilibrium dissociation of hydrogen bonding in dilute solution can yield a similar discontinuity, depending on the values of ΔH and ΔS. For example, the dissociation of hydrogen bonding between hydroxyl and amine in dilute solution was represented by $\Delta H = 6$ kcal/mol and $\Delta S = 10$ eu.[9] When the fraction of hydrogen bonding is plotted as a function of temperature, Figure 10 is obtained, showing that an apparent discontinuity in slope occurs near 70 °C. Likewise, the discontinuity will be observed in the rubbery region of amorphous polymers if the values of ΔH and ΔS are in the range specified above. At the temperature where vitrification occurs, the hydrogen bond equilibrium is frozen in and the fraction of bonded NH should be in variance with temperature. Nonetheless, a distinct slope to the experimental data below the discontinuity is not uncommon.

One method of verifying the presence of a physical transition when evidence of a thermal transition by TMA or DSC is not applicable is to calculate the ratio $[C_B]/[C_f]^2$ from the absorption band using $\epsilon_f/\epsilon_B = 0.29^4$ to construct the normal plot of ln K vs. $1/T$ shown in Figure 4. The appearance of a discontinuity in the curve plotted in this fashion provides support for a physical transition. Furthermore, the values of ΔH and ΔS obtained for the high-temperature branch of the plot may be used to calculate the apparent absorbance so that the equilibrium and experimental data can be compared. It is of interest to note that Seymour and Cooper's data,[3] after correction for an assumed 85% bonded NH at room temperature and treated in the above fashion, lead to $\Delta H = 6.6$ kcal/mol and $\Delta S = -12.4$ eu.[10] The calculated curve for the fraction of bonded NH and the experimental data fit reasonably well above the discontinuity but separate sharply at lower temperatures confirming the physical origin of the discontinuity.

References and Notes

(1) (a) Massachusetts Institute of Technology; (b) Army Materials and Mechanics Research Center.
(2) (a) N. S. Schneider, C. S. P. Sung, R. W. Matton, and J. L. Illinger, *Macromolecules*, **8**, 62 (1975); (b) C. S. P. Sung and N. S. Schneider, *ibid.*, **8**, 68 (1975).
(3) R. W. Seymour and S. L. Cooper, *Macromolecules*, **6**, 48 (1973).
(4) W. J. MacKnight and M. Yang, *J. Polym. Sci., Part C*, **42**, 817 (1973).
(5) M. W. Wolkenstein and O. B. Ptitsyn, "Hydrogen Bonding", D. Hădzi, Ed., Pergamon Press, New York, N.Y. (1959).
(6) R. Bonart and E. H. Müller, *J. Macromol. Sci., Phys.*, **10** (1), 177 (1974).
(7) R. Bonart and E. H. Müller, *J. Macromol. Sci., Phys.*, **10** (2), 345 (1974).
(8) N. S. Schneider and A. O. King, unpublished results.
(9) R. L. Denyer, A. Gilchrist, J. A. Pegg, J. Smith, T. E. Tomlinson, and L. E. Sutton, *J. Chem. Soc.*, 3889 (1955).
(10) S. L. Cooper, private communication.

Heats of Dissociation of Mixture of Poly(γ-benzyl L- and D-glutamate)

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ABSTRACT: The heats of dissociation of stacked side-chain benzyl groups in mixtures of various proportions of poly(γ-benzyl L- and D-glutamate) have been measured by a differential scanning calorimeter. In order to obtain further information about the dissociation, the heats of solution of poly(γ-benzyl L- and D-glutamate) were also measured by a twin micro calorimeter at 303 K. The agreement between the heat of dissociation obtained by DSC and that determined by the heat of dissolution is good. The average value of the heat of dissociation of stacking estimated by both methods is about 5 kJ/(mol of pairs of residue).

Complex formation in mixtures of poly(γ-benzyl L- and D-glutamate) (PBLG + PBDG) has been confirmed by several investigators,[1,2] and the physical properties of the complex have also been reported in a few papers.[3-5]

In order to obtain further information about the complex formation, we carried out thermal analysis for solid mixtures of various proportions of poly(γ-benzyl L- and D-glutamate) (PBLG + PBDG) and poly(γ-methyl L- and D-glutamate) (PMLG + PMDG) or poly(γ-benzyl L-glutamate) (PBLG) and poly(γ-benzyl D-glutamate) (PBDG) by using a differential scanning calorimeter (DSC).

The DSC curve obtained for the (PBLG + PBDG) system had a transition peak which may be considered to correspond to the dissociation of a complex, whereas for the (PMLG + PMDG), PBLG, and PBDG systems no peak existed. From DSC curves of the former system, the heat of the transition was obtained.

To study the complex formation further and estimate the heat of dissociation, we measured the heats of dissolution of a (PBLG + PBDG) solid mixture and that of PBDG into the mixed solvents. The difference between these two heats of solution gave a value of the heat of dissociation which coin-