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Fourier Transform Infrared Thermal Analysis of a Segmented Polyurethane

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ABSTRACT: Fourier transform infrared spectroscopy (FTIR) has been used to study the extent of hydrogen bonding and its temperature dependence in a segmented polyurethane elastomer synthesized from 2,6-toluene diisocyanate, 1,4-butanediol, and poly(tetramethylene oxide) of 2060 number average molecular weight. It is found that the ratio of the molar extinction coefficient for the hydrogen bonded to the free amine stretching vibration is 4.6 and that this ratio is 1.05 for the hydrogen bonded to the free carbonyl stretching vibration. The temperature dependence of the concentration of hydrogen bonded groups is without any discontinuity at the hard segment glass transition temperature, and the enthalpy and entropy of hydrogen bond dissociation are 29 kJ mol^{-1} and 64 J mol^{-1} K^{-1}, respectively. An additional absorption band in the carbonyl stretching region at 1726 cm^{-1} is attributed to an oxidation product of the polyether segment formed during initial sample preparation and subsequent thermal treatment.

Segmented polyurethanes are generally composed of a polyether or polyester soft segment and a polyurethane hard segment. The composition of the latter varies, but it frequently involves the reaction product of an aromatic diisocyanate and an aliphatic diol. Such polyurethanes are capable of forming several kinds of hydrogen bonds. In all cases, the hydrogen atom of the N-H group in the urethane linkage is the donated proton, while the acceptor groups may include the carbonyl and adjacent oxygen atom in the urethane linkage as well as those of the ester linkage when a polyester soft segment is present or the ether oxygen when a polyether soft segment is present. Hydrogen bonding in polyurethanes has been the subject of numerous investigations using infrared spectroscopy. It is manifested by shifts in the N—H and C═O stretching frequencies to lower values than those observed when these groups are not hydrogen bonded.[1] The temperature dependence of hydrogen bonding is also amenable to examination by the infrared technique. In a previous study from these laboratories,[2] a series of model hard segment polyurethanes based on the reaction products of 2,4-toluene diisocyanate (TDI) or *p,p'*-diphenylmethane diisocyanate (MDI) with α,ω diols were examined. It was found that these polyurethanes are hydrogen bonded to the extent of 75% or less below their glass transition temperatures (T_g) and that the integrated absorbances of the N-H stretching vibration showed discontinuities at temperatures corresponding to the T_g or melting point (T_m) of the polymers.

The relationship between hydrogen bonding and thermal transitions in segmented polyurethanes is not clear. In a study of polyether-TDI segmented polyurethanes, Paik Sung and Schneider[3] concluded that the temperature dependence of hydrogen bonding is not correlated to T_g or T_m. They found that measurable dissociation of hydrogen bonded N—H and C═O groups began at about 65 °C for 2,6-TDI polyurethanes independent of hard segment content. In the case of 2,4-TDI polyurethanes, hydrogen bonded N-H began to dissociate between 40 and 60 °C, while hydrogen bonded C═O underwent little change to temperatures in excess of 150 °C.

Segmented polyurethanes are generally considered to exhibit microphase separation due to incompatibility between the hard segment and the soft segment. The degree of interurethane hydrogen bonding and the enthalpy of hydrogen bond dissociation have been used as indicators of phase separation in MDI polyurethane segmented elastomers.[4] In this study it was found that the extent of interurethane hydrogen bonding and the enthalpy of hydrogen bond dissociation increase as phase separation becomes pronounced.

Previous studies of the temperature variation of the hydrogen bonding equilibrium in segmented polyurethanes have required curve-resolving techniques for the separation of overlapping absorption bands, a method which entails the assumption of a Gaussian or Lorentzian shape for the contributing absorptions. Several symmetric absorption

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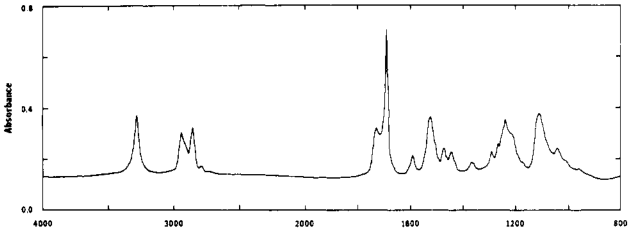

Figure 1. Infrared spectrum of 2,6-T-2P-43 at 25 °C.

maxima may be required to fit a single asymmetric band. The powerful spectral subtraction and data manipulation capabilities of the Fourier transform infrared spectrometer (FTIR) can be useful in circumventing some of these difficulties. The advantages of FTIR spectroscopic methods have been discussed in several reviews.[5,6] This study describes the application of FTIR spectroscopy to the quantitative assessment of the temperature variation of hydrogen bonding in a polyether–TDI segmented polyurethane.

Experimental Section

A linear segmented polyurethane with 43 wt % hard segments composed of the reaction product of 2,6-TDI and 1,4-butanediol and 2060 number average molecular weight poly(tetramethylene oxide) soft segments was supplied through the courtesy of Dr. N. S. Schneider of the Army Materials and Mechanics Research Center, Watertown, MA. This polyurethane corresponds to 2,6-T-2P-43 employed in a dynamic mechanical study of phase segregation in segmented polyurethanes.[7] The polymer was cast from *N*,*N*-dimethylformamide solution onto a 25-mm diameter NaCl plate. The resulting film, about 3 μm in thickness, was subjected to a thermal treatment similar to that described in ref 7, except that the film was cooled slowly under vacuum.

A room temperature survey spectrum of the polyurethane film was recorded on a Perkin-Elmer Model 283 infrared spectrometer between 4000 and 800 cm^{-1}. For the temperature scans, the sample was placed in an aluminum block containing two resistance heaters and heated to the desired temperature. The film temperature was maintained to within 1 °C with a Versatherm temperature controller and monitored by a copper–constantan thermocouple junction placed directly on the sample. The temperature was held constant for about 5 min before the collection of spectra was initiated. Infrared spectra were recorded with a Digilab FTS-15 Fourier transform spectrometer by averaging 256 scans at a resolution of 2 cm^{-1}. A dry nitrogen flow was maintained over the film throughout the measurements.

Results and Discussion

A survey IR spectrum of 2,6-T-2P-43 at room temperature is shown in Figure 1. A strong band, assigned to the hydrogen bonded N–H stretching vibration, is present at 3283 cm^{-1}. The free N–H stretch appears as a shoulder on the high-frequency side of this band. Several C–H stretching vibrations occur between 3100 and 2600 cm^{-1}. The asymmetric CH_2 stretch at 2942 cm^{-1} is used as an internal standard, as will be discussed later. Two very strong carbonyl stretching bands are apparent. The band at 1733 cm^{-1} is assigned to the free C=O stretch, while that at 1691 cm^{-1} is assigned to the hydrogen bonded C=O stretch. The C=C stretching vibration in the aromatic ring at 1595 cm^{-1} is also used as an internal standard. Assignments for many polyurethane absorption bands are given in several publications.[2,8,9] IR spectra of 2,6-T-2P-43 at 29 and 98 °C in the N—H and C=O stretching regions are shown in Figure 2. The hydrogen bonded N-H peak absorbance decreases at the higher temperature with a corresponding increase in the free N-H peak absorbance. The hydrogen bonded N-H band maximum also shifts from 3283 to 3290 cm^{-1} between 29 and 98 °C. The peak absorbances of the free and bonded C=O stretching bands show similar trends, but their maximum positions are independent of temperature.

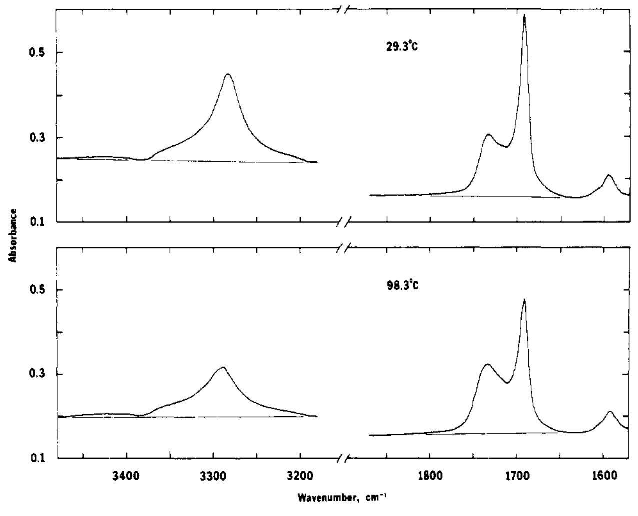

Figure 2. Infrared spectra of 2,6-T-2P-43 in the N—H and C=O stretching region at 29 and 98 °C.

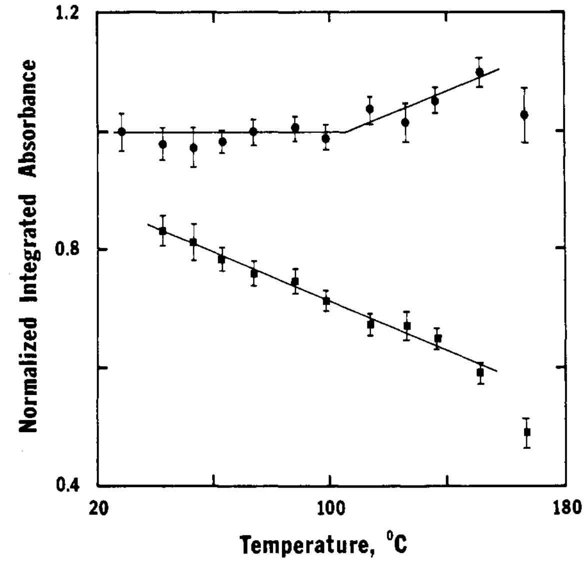

Figure 3. Normalized integrated absorbances as a function of temperature (circles, C=O stretch; squares, N—H stretch).

The integrated absorbances of the N–H stretch over the range 3180–3470 cm^{-1} and the C=O stretch at 1830–1630 cm^{-1} are determined by integration at each temperature. Figure 3 illustrates the temperature dependence of the normalized integrated absorbances, obtained by dividing the integrated absorbances by their corresponding values at 29 °C. It is noted that the C=O band absorbance is independent of temperature until temperatures in excess of 100 °C are reached, while the N–H band absorbance shows a linear decrease with increasing temperature. The 167 °C integrated absorbances for both C=O and N—H show an anomalous decrease. This could be caused by a change in film thickness at this temperature due to the flow of the vertically mounted sample, since the polymer is near its T_m, determined to be 177 °C.[7] The decrease could also be attributed to sample degradation. Evidence for degradation is provided by the appearance of two bands in the 167 °C spectrum at 2170 and 2340 cm^{-1}, which may arise from carbon dioxide and free isocyanate, respectively. Carbon dioxide and an amine are thought to form during the thermal degradation of the TDI urethane linkage,[10,11] and the evolution of carbon dioxide on high temperature

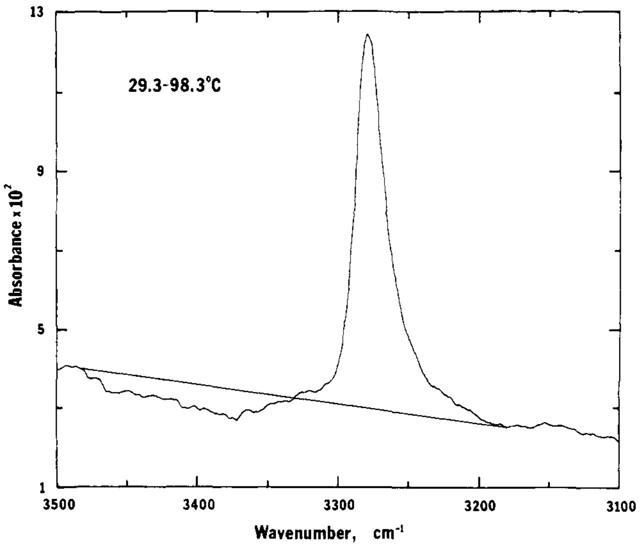

Figure 4. Difference between 29 and 98 °C spectra in the N-H stretching region.

aging has previously been observed.[12,13] For these reasons, the 167 °C values are excluded from further consideration. The decrease in integrated N-H absorbance can be understood as arising from the fact that the extinction coefficient of the hydrogen bonded N-H is three to four times greater than that of the free N-H.[2,9] The affect of a decrease in hydrogen bonded N-H with increasing temperature controls the over-all temperature dependence of the integrated N-H absorbance. No discontinuity or change of slope occurs in the N-H absorbance at the T_g of the hard segment, which is about 60 °C.[7] The relative insensitivity of the total carbonyl absorbance to temperature at low temperatures reflects the fact that both the free and bonded C=O stretching vibrations have about the same extinction coefficient. The upturn observed above 100 °C is attributed to the increasing contribution of a new band in the C=O region, arising from thermal oxidation. This will be discussed in more detail later.

The infrared spectra at various temperatures were used to assess quantitatively the temperature variation of hydrogen bonding in 2,6-T-2P-43. The procedure is to first subtract the high-temperature spectra from the 29 °C spectrum, chosen as the reference. Detailed subtraction procedures have been reviewed by several authors,[5,6] and the methods outlined therein were generally followed in this work. Figure 4 shows a typical result obtained for the N-H stretching region by subtracting the 98 °C N-H spectrum from the 29 °C spectrum of Figure 2. The subtraction was carried out by adjusting the multiplication factor for the high-temperature spectrum while maintaining unit weighting of the reference spectrum until the asymmetric C-H stretching band at 2942 cm^{-1} was eliminated in the difference spectrum. Multiplication factors ranged from 1.11 to 1.06 over the temperature range examined. A similar procedure was employed to determine difference spectra in the C=O stretching region. Figure 5 shows a difference spectrum obtained by subtracting the 98 °C C=O spectrum in Figure 2 from the 29 °C reference spectrum. In the carbonyl region, elimination of the 1595-cm^{-1} band was used as a criterion for subtraction, and the scaling factors ranged from 1.05 to 0.95. A shoulder appears in the negative part of the difference spectrum at 1726 cm^{-1}. This shoulder is thought to be a real spectral feature rather than an artifact produced by subtracting bands of differing frequency since its position remained constant while the subtraction scaling parameter varied over a wide range of values. The contribution of this shoulder was excluded from the determinations of integrated absorbance described below.

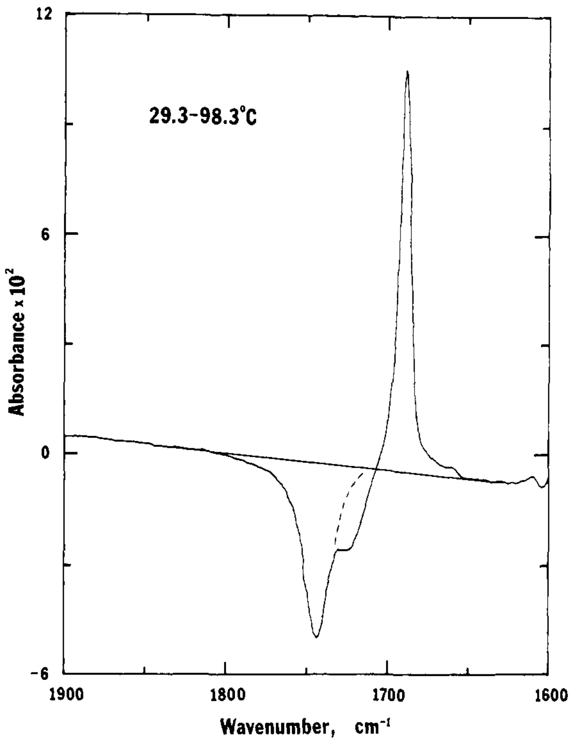

Figure 5. Difference between the 29 and 98 °C spectra in the C=O stretching region.

The integrated absorbances above and below the base line in Figures 4 and 5, ΔA, refer to the hydrogen bonded and free N—H and C=O groups, respectively. They may be used to assess the temperature dependence of the concentrations of these species as follows. In general, the difference in the integrated absorbance of a band at two temperatures may be represented by Beer's law as

$$\frac{\Delta A}{l} = \frac{A(T_2) - A(T_1)}{l} = \epsilon(T_2)C(T_2) - \epsilon(T_1)C(T_1) \quad (1)$$

where l is the path length of the radiation (assumed independent of temperature since the subtraction procedure automatically compensates for the thickness variation), $\epsilon(T)$ is the extinction coefficient at a given temperature, and $C(T)$ is the concentration of the species at a given temperature.

The temperature dependence of the extinction coefficient is generally represented by

$$\epsilon = \epsilon(T_0) + \alpha(T - T_0) \quad (2)$$

where α is usually negative, and T_0 is a reference temperature.[14] Combining eq 1 and 2 and choosing the reference temperature equal to T_1 yields

$$\Delta A/l = \epsilon(T_1)\Delta C + \alpha(T_2 - T_1)C(T_2) \quad (3)$$

Thus the concentration of the species at any temperature may only be arrived at from integrated absorbance difference measurements if $\epsilon(T_1)$, α, and $C(T_1)$ are known. Since no values of α are available for the N—H and C=O bands in the polyurethanes, it is necessary to neglect the temperature dependence of ϵ in order to proceed further. This is probably justified over the temperature range of this study, since many experimental values of α have been reported to be in the range of $0.003\epsilon(T_1)$ K^{-1} or less.[15]

The ΔA values are plotted as a function of temperature in Figure 6 for the free and hydrogen bonded N—H and

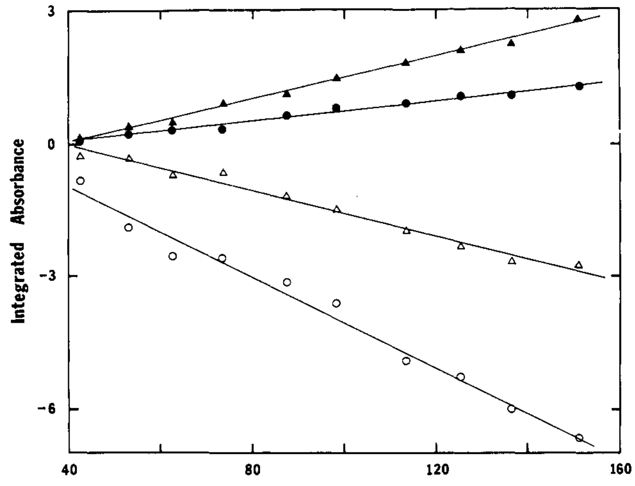

Figure 6. Integrated absorbance (arbitrary units) of the difference spectra in four spectral regions vs. temperature (reference temperature 29 °C; filled points, free absorption; open points, hydrogen bonded absorption; triangles, C=O stretch; circles, N—H stretch).

C=O bands. Over the temperature range studied, all are linear functions of temperature. The temperature dependence of the hydrogen bonded N-H ΔA is much greater than that of the free N-H ΔA, while that of both C=O integrated absorbances is about the same. On the assumption that the extinction coefficients are independent of temperature, the ratio of the ΔA values for a given free and hydrogen bonded species should be a measure of the ratio of the extinction coefficients. From the data of Figure 6, the ratio of $\epsilon_{\text{bonded}}/\epsilon_{\text{free}}$ for N-H was determined to be 4.6 ± 25%. This result may be compared with values of 3.1–3.8 previously obtained for a series of model hard segment polyurethanes.[2] The ratio $\epsilon_{\text{bonded}}/\epsilon_{\text{free}}$ for C=O was found to be 1.05 ± 15%, in good agreement with other values for hydrogen bonded carbonyl groups which range between 1.0 and 1.3.[16-18]

The hydrogen bonded N-H stretching band maximum shifts from 3283 to 3296 cm^{-1} over the temperature range investigated, as noted earlier. This shift may cause difficulties with a subtraction procedure which assumes a constant peak position. In order to check the validity of these subtraction results, the hydrogen bonded and free N-H bands were resolved, and their elevated temperature integrated absorbances were subtracted from the corresponding values at the 29 °C reference temperature to produce plots similar to the N-H data shown in Figure 6. The ratio of extinction coefficients obtained by this method agrees within experimental error with that obtained by direct subtraction.

In order to evaluate $C(T_1)$ in eq 1, it is necessary to resolve the 29 °C N—H and C=O bands into their free and hydrogen bonded components. This was carried out according to the method of Paik Sung and Schneider[3] in the N-H region. By this procedure it was found that 88% of the N-H groups are hydrogen bonded at 29 °C, a result that is comparable to determinations of 75–95% reported for other polyurethanes.[3,4,8,19,20] In the case of the C=O band, the overlapping absorbances shown at 29 °C in Figure 2 were resolved by fitting two Gaussians to the band. From this it was estimated that 60% of the C=O groups were hydrogen bonded at 29 °C. Values of hydrogen bonded N—H and C=O fractions at the temperatures studied are collected in Table I. The fact that a greater fraction of N-H groups are hydrogen bonded than are carbonyl groups is a reflection of incomplete phase separation in this segmented polyurethane. It is consistent with the elevation of the T_g of the soft phase above that of a model soft phase polymer.[7]

Table I
Changes in the Degree of Hydrogen Bonding with Temperature

temp, °C	fraction bonded N—H, %	fraction bonded C=O, %
29	0.875 ± 2	0.600 ± 2
42	0.845 ± 2	0.585 ± 2
53	0.790 ± 2	0.570 ± 2
63	0.770 ± 2	0.560 ± 2
74	0.760 ± 2	0.545 ± 2
88	0.695 ± 2	0.520 ± 2
98	0.650 ± 2	0.500 ± 2
114	0.605 ± 2	0.470 ± 2
126	0.565 ± 2	0.450 ± 2
136	0.550 ± 2	0.430 ± 2
151	0.500 ± 2	0.410 ± 2

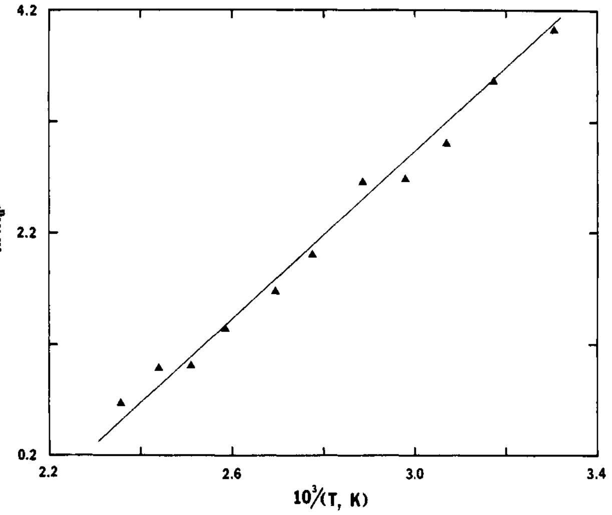

Figure 7. Temperature variation of the hydrogen bonding equilibrium constant in 2,6-T-2P-43.

The equilibrium constant for the dissociation of hydrogen bonded N-H may be written as

$$K_d = \frac{[\mathrm{B}][\mathrm{N\text{-}H}]}{[\mathrm{B}\cdots\mathrm{H\text{-}N}]} = \frac{(1-X_b)^2}{X_b} \tag{4}$$

where B is the proton acceptor and X_b is the fraction of hydrogen bonded N-H.

The temperature dependence of the equilibrium constant is:

$$K_d = \exp(-\Delta H/RT + \Delta S/R) \tag{5}$$

where ΔH and ΔS are the enthalpy and entropy for hydrogen bond dissociation.

Figure 7 is a plot of -ln (K_d) vs. T^{-1}, constructed from the data in Table I. The data were fitted to eq 5 by a least-squares procedure which gave a value of ΔH of 29.3 kJ mol^{-1} and a value of ΔS of 64.0 J mol^{-1} K^{-1}. Corresponding values for an MDI polyurethane of similar composition have been determined to be ΔH = 32.6 kJ mol^{-1} and ΔS = 70.7 J mol^{-1} K^{-1}.[4]

An additional carbonyl band amounting to about 5% of the total carbonyl absorbance is present in the 29 °C spectrum between the bonded and free carbonyl. It was evident as a residual from the two-peak fit in the carbonyl region discussed previously. This carbonyl is thought to arise from degradation of the polyether soft segments occurring during drying by heating to 180 °C under vacuum. Oxidation could introduce a ketone or internal ester into the polyether chain; these groups have absorption maxima at 1715–1750 and 1735–1750 cm^{-1}, respectively.[21] Polyether urethanes are known to suffer from thermal instability if suitable protective additives are not incorporated.[22] An internal ester carbonyl formed by oxidation would be indistinguishable from the free urethane carbonyl; however, a ketone absorbance would appear at a position between the free and bonded urethane carbonyl. The shoulder at 1726 cm^{-1} in Figure 5 can be attributed to a ketone group formed from oxidation, shifted toward higher wavenumber by the dominant free urethane carbonyl absorption. Slight oxidation begins at 74 °C upon heating, as indicated by the 1726-cm^{-1} shoulder in the subtraction results, and increases continually to 151 °C, where the 1726-cm^{-1} band amounts to 15% of the total carbonyl absorption area. Sample degradation was observed for a series of MDI polyether polyurethanes[4] as an increase in the normalized carbonyl area beginning at 120 to 160 °C in each of the materials studied. The total carbonyl area at 190 °C increased 30–75% over the room-temperature value, indicating that oxidation is occurring at elevated temperatures in these materials.

Conclusions

Infrared thermal analysis of a block polyurethane by Fourier transform infrared spectroscopy has proven to be a useful method for the study of hydrogen bonding equilibria. The ratio of hydrogen bonded to free extinction coefficients is determined to be 4.6 for the N–H stretch and 1.05 for the carbonyl stretching absorptions. No discontinuities in the extent of hydrogen bonding are found at the hard segment T_g. Resolution of hydrogen bonded and free N—H and C═O stretching absorptions in the 29 °C reference spectrum indicates that 88% of the N—H groups and 60% of the C═O groups are hydrogen bonded. The fraction of hydrogen bonded N—H and C═O groups at temperatures up to 151 °C is determined without further curve resolving methods. The enthalpy and entropy for hydrogen bond dissociation in this polyurethane are found to be 29 kJ mol^{-1} and 64 J mol^{-1} K^{-1}, respectively, based on the N–H concentration. Oxidation of the soft segment polyether to form a ketone group absorbing at 1726 cm^{-1} occurred to the extent of about 5% during the initial thermal treatment and began to take place to a measurable extent above 74 °C as the temperature was raised, reaching a level of 15% of the total carbonyl area at 151 °C.

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