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Spectroscopic Characterization of Hydrogen Bonding in Poly(urethane−rotaxane)s

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ABSTRACT: The hydrogen-bonding interactions in a series of poly(urethane−rotaxane)s were studied by infrared spectroscopy. Spectroscopic data along with a one-dimensional mean-field model was used to calculate the enthalpy of hydrogen bond formation involving a polyurethane N-H moiety and an ether oxygen atom located in a macrocycle threaded along the polyurethane backbone. The average enthalpy of hydrogen bonding was estimated at 3.0 kcal/mol.

Introduction

Polyrotaxanes are a novel family of polymers comprising of macrocyclic rings threaded by linear molecules. These materials have shown unique behavior in terms of solubility, solid state structure, and phase transitions.[1−6] The basis for these distinct properties, we believe, originates in the enhanced molecular interactions between the macrocyclic rings and the polymeric backbone and in the molecular dynamics of the rings in their threaded state. Particularly, in the case of poly(urethane−rotaxane)s with crown ether macrocycles,[5] these interactions involve hydrogen bonding between the ether linkages of the macrocycle and the N-H group in the polyurethane backbone. Previous infrared studies have shown that poly(urethane−rotaxane)s have a higher extent of hydrogen-bonded N-H moieties than that observed in the miscible blends of the crown ethers and polyurethanes of the same composition.[2] In addition, the poly(urethane−rotaxane)s are semicrystalline with an amorphous backbone but crystallizable crown ether macrocycle.[1,2,5] Structural characterization studies indicate that polyrotaxanes form single-phase systems above the crown ether melting temperature. All samples studied here exhibit a single glass transition temperature which can be described by a composition dependent Fox equation.[1] It is interesting that in the case of larger macrocycles (60-membered rings), the crystal structure of the **threaded** crown ether macrocycle in the poly(urethane−rotaxane) is the same as that of the pure macrocycle.[7] Crystal structure studies of the ether macrocycles[7] suggest that the crown ether crystal consists of two macrocycles in a monoclinic unit cell where each macrocycle adopts a conformation consisting of two parallel 7_2 helical stems, each containing eight (or nine) ethylene oxide units, and two folds, each containing two (or one) ethylene oxide units. It seems that in order to maintain the same crystal structure in the polyrotaxane, the polyurethane chains threading the macrocycle should be located in the fold cavity of the macrocycle. Therefore, understanding the role of hydrogen bonding between the macrocycle and the polyurethane backbone is fundamental to the visualization of crystallization of macrocycles in the polyrotaxane and ultimately to the recognition of the parameters that control the material's properties.

Hydrogen bonding in polyurethanes has been the subject of numerous studies that used infrared spectroscopy.[8−17] It is now well recognized that the primary bands sensitive to hydrogen bonding are the N-H stretching mode and the amide I mode (also called a carbonyl stretching vibration). The intensity and band width of these absorptions are temperature sensitive and not only depend on the fraction of hydrogen-bonded functional groups but also reflect the distribution of hydrogen bond strengths. Furthermore, in the case of the N-H stretching mode, the absorptivity coefficient is particularly sensitive to the hydrogen bond strength and therefore is frequency dependent. Thus employing the N-H stretching region for the estimation of thermodynamic parameters associated with hydrogen bonding is usually considered nonreliable.[13,17] For such estimation, the carbonyl stretching region fares much better, since the ratio of absorptivity coefficients of the resolved bands corresponding to hydrogen-bonded and non-hydrogen-bonded carbonyl groups is believed to be close to unity.[14,17] Another type of intermolecular interaction, which is especially important in our system, involves an N-H moiety hydrogen bonding with an ether oxygen. Previous studies have demonstrated that this interaction has a strength comparable to that of the urethane N−H to C═O interaction.[13] Therefore, one would also expect that the absorption coefficients corresponding to the hydrogen-bonded N-H band involved in both of these types of interactions would be similar.

Taking into consideration these spectral interpretations, Painter and Coleman have carried out a series of studies examining the effect of hydrogen bonding on the miscibility of polymer blends.[17−22] Their work has led to the development of a theory predicting phase diagrams and miscibility windows.[17] One important conclusion arising from their work is that there may be more than one equilibrium constant necessary to describe the self-association and interassociation within a single-phase polymer blend. The polyrotaxane system has a number of possible interactions. We expect that the dominant intermolecular interaction consists of the interannular hydrogen bonding between the ether oxy-

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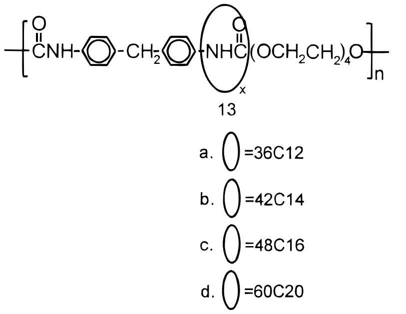

Figure 1. Chemical structure of the poly(urethane-rotaxane)s.

Table 1. Summary of Physical Data of Poly(urethane−rotaxane)s

sample	crown	x/n	T_g	T_m	M_n (GPC)	M_w (GPC)
1	60C20	0.89	233.2	320.2	8.03	13.3
2	60C20	0.58	246.2	318.2	7.5	13.4
3	60C20	0.34	269	315.2		
4	42C14	0.29	274.5	N.A.	19.3	37.5
5	36C12	0.16	288.2	N.A.	7.24	10.8
6	NA	0	324.2	328.2	12.1	27

gen atoms in the macrocycle and the N-H moiety in the polyurethane backbone. Unlike in a polymer blend, where a “chemical” theory may be appropriate to account for deviations from nonrandom mixing due to specific directional interactions,[19] in the case of a polyrotaxane, the location of the macrocycles along the backbone may be assumed to be unidirectionally random, since the presence of a macrocycle around one repeat unit does not influence the nature of the interactions between an adjacent urethane repeat unit and another macrocyclic ring. Consequently, a one-dimensional mean-field model may be quite appropriate in the calculation of equilibrium constants associated with this type of interaction. Another specific interaction may involve hydrogen bonding between the ether oxygen of the threaded macrocyclic ring with an N-H group situated on an adjacent polyurethane chain, forming a cross-intermolecular hydrogen bond. The “chemical theory” approach may be useful here. Furthermore, there are also possible interactions between the polyurethane chains, themselves, involving N-H groups and the carbonyl oxygens or the ether atoms in the chain extender. From these considerations, it is quite clear that more than one hydrogen-bonding mechanism may be necessary to describe the association in this type of a system. However, in this particular study, we shall primarily focus on the dominant interaction, namely, the one involving the polyurethane N-H group and the ether oxygen atoms in the macrocyclic ring.

Experimental Section

The various polyrotaxanes (Figure 1) were synthesized via the statistical threading method using 4,4′-methylenebis(phenylisocyanate) (MDI), tetraethylene glycol (TEG), and various crown ethers as solvents. The details of the synthesis and the purification process are outlined in ref 2. Table 1 summarizes the sizes of the macrocyclic crown ethers and their compositions in the poly(urethane−rotaxane)s utilized in this study, as well as other relevant physical data. The label 60C20, for example, means a 60-membered ring with 20 ether linkages. The label x/n designates the ratio of the number of macrocycles to the number of repeat units along the polyrotaxane. Model (i.e., unthreaded) polyurethanes were also synthesized by the same method but with diglyme as solvent.

Infrared spectra were collected with a 4 cm^{-1} resolution on a Digilab 40A FTIR spectrometer, equipped with a MCT-A detector. Samples for the infrared studies were prepared by dissolving the polyrotaxanes in acetone and casting films from solution onto KBr plates followed by drying in a vacuum oven at room temperature for several days. Infrared studies at elevated temperatures were conducted using a heating cell from Harrick Scientific, controlled by an Omega programmable temperature controller, with ±0.5 °C precision.

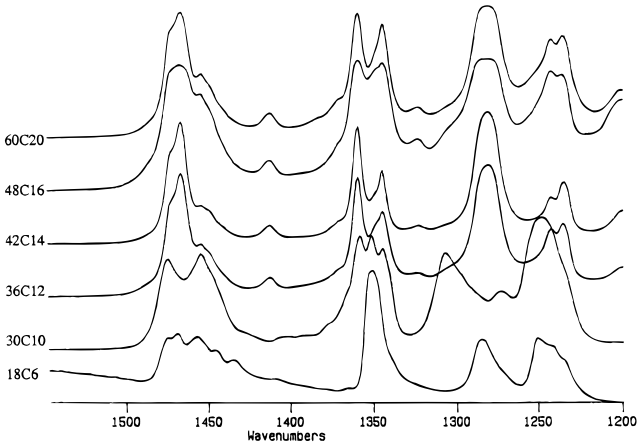

Figure 2. Infrared spectra of pure crown ethers as a function of ring size.

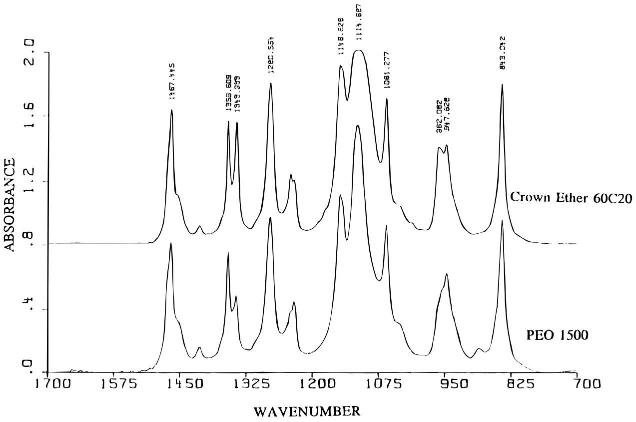

Figure 3. Comparison of infrared spectra of 60C20 crown ether and poly(ethelene oxide).

Results and Discussion

Spectral Assignments. Before we embark on the analysis of the poly(urethane−rotaxane) spectra, we first need to discuss the infrared spectra of the pure crown ether macrocycles. This will be essential to the interpretation of the poly(urethane−rotaxane) infrared spectra later because the structure of the crown ether ring may influence the nature of the specific interactions between the ether ring and the polyurethane backbone. Figure 2 shows the infrared spectra of crown ethers of various sizes in a region where the absorption bands are most sensitive to conformational changes. In our previous work,[7] we have postulated that the 60-crown-20 macrocycle assumes the same helical crystal structure as poly(ethylene oxide) (PEO), namely, a loosely turned helix with seven repeating units and two helical turns per period. Comparison of the various crown ether spectra suggests that the four largest macrocycles crystallize in the same crystal structure as PEO (Figure 3) because the infrared bands appear at identical frequency positions.[23−25] In particular, we note the CH_2 wagging doublet located at 1359 and 1343 cm^{-1}, the quasi-symmetric and quasi-antisymmetric twisting modes of the CH_2CH_2 groups at 1244 and 1283 cm^{-1}, and the rocking modes at 947 and 963 cm^{-1}.[20] The two smallest

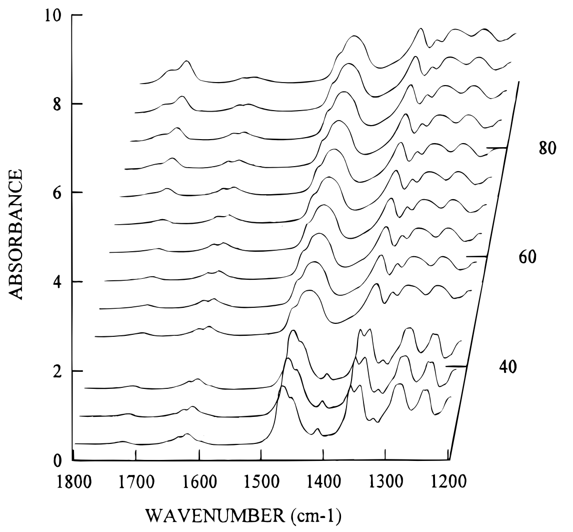

Figure 4. Low-frequency IR spectrum of 48C16 crown ether as a function of temperature.

macrocycles, i.e., 30-crown-10 and 18-crown-6, however, do not match those frequencies. These results are also consistent with recent X-ray diffraction studies of the anhydrous 30-crown-10 macrocycle, which suggest that the crystalline structure is orthorhombic.[7]

Furthermore, the doublet crystalline bands found in the largest macrocycles are replaced by an amorphous band upon heating (Figure 4). These transitions in the spectra, occurring at about 40 °C, are also consistent with the melting temperatures as determined by DSC. It should also be pointed out that the low molecular weight macrocycles tend to degrade during heating, as demonstrated by the increasing presence of an aldehyde peak (Figure 4), although in the polyrotaxanes, this does not appear to be a problem. In addition, the carbonyl band of the polyrotaxane may also contain a small aldehyde contribution from a glycol impurity generated during synthesis.

Infrared spectra of various poly(urethane−rotaxane)s, including the model polyurethane, were collected at temperatures ranging from 30 to 90 °C in 5° intervals. These runs were reversible when enough time (ca. 60 min) was given between temperature changes for samples to reach "equilibrium". Figure 5 shows the N-H stretching region of a series of polyrotaxanes whose composition ratio (x/n) of the macrocycle to the polyurethane repeat unit varies from 0.87 to 0.0 (0.0 corresponding to the pure polyurethane). As expected, the primary absorption band corresponding to associated N-H moieties is centered at 3310 cm^{-1}, and the so-called "free" or nonassociated N-H stretch appears as a very weak band near 3400 cm^{-1}. On the other hand, the appearance of several additional lower frequency N-H stretching bands at 3220 and 3270 cm^{-1}, whose intensity increases with increasing macrocycle concentration, becomes very striking. These bands are totally absent in the spectrum of the model polyurethane and the spectra of the pure macrocyclic rings. Furthermore, these bands decrease in intensity with increasing temperature. Due to these simultaneous dependencies and the amorphous nature of the polyurethane component, it is highly unlikely that these bands correspond to overtones or phonon bands. However, the small peaks located at 3190, 3050, and 3110 cm^{-1} can indeed be attributed to combination bands or overtones of the C−N−H stretching−bending band at 1530 cm^{-1} because

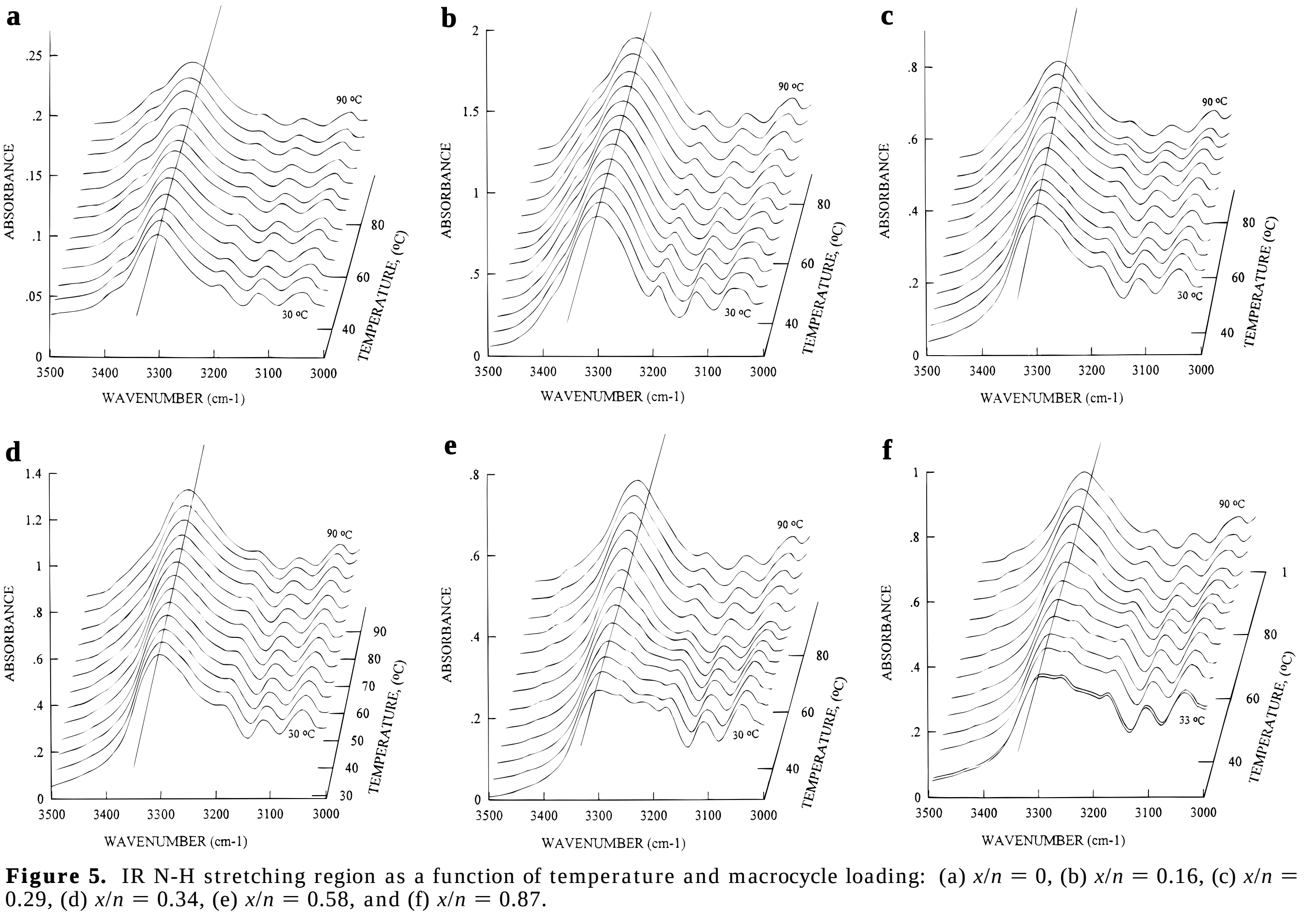

Figure 5. IR N-H stretching region as a function of temperature and macrocycle loading: (a) x/n = 0, (b) x/n = 0.16, (c) x/n = 0.29, (d) x/n = 0.34, (e) x/n = 0.58, and (f) x/n = 0.87.

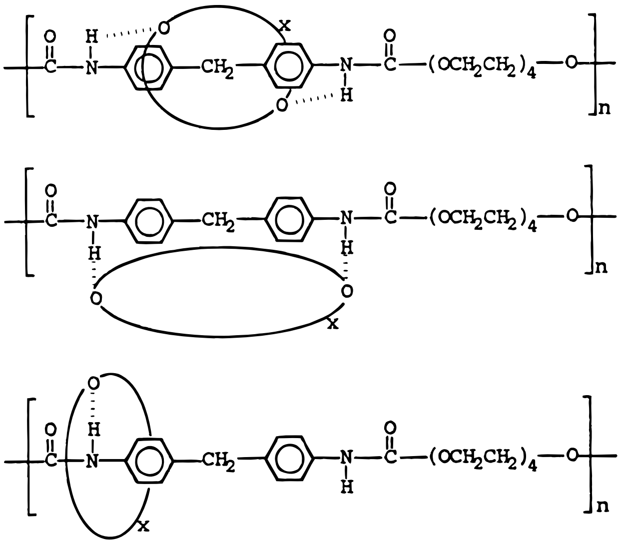

Figure 6. Summary of possible hydrogen-bonding interactions.

they are independent of the macrocycle loading in the polyrotaxanes. On the other hand, we believe that the bands at 3220 and 3270 cm^{-1} are associated with the N-H stretch, hydrogen bonded to an ether oxygen in the macrocycle. One possibility is that the appearance of such multiple peaks reflects the formation of different types of hydrogen-bonded complexes, as has been found in the case of hydrated 18-crown-6 crown ether.[26] In that particular study, the number, position, and width of the OH stretching band (3800−3200 cm^{-1}) indicated the presence of two forms of bound water, one with the H_2O molecule attached by a single hydrogen bond and the other with the H_2O molecule attached by two hydrogen bonds in a bidentate fashion.[26] Similarly, one can envision the simultaneous hydrogen bonding of two N-H moieties in one urethane repeat unit to a threaded macrocycle as illustrated in Figure 6. Other types of possible interactions are also depicted in Figure 6.

Furthermore, although in some cases the N-H stretching vibration corresponding to the N−H···O complex with ether oxygens may lie in the same frequency range as the carbonyl-associated N-H stretch,[13] there is also evidence (particularly in cases of lower molecular weight materials) that the stretching vibration of the hydrogen-bonded complex is shifted to even lower frequencies.[17] This observation lends further support to our assignment of the multiple peaks, as associated with the N-H group hydrogen bonded to an ether oxygen of the macrocycle. It is interesting that these multiple bands are still detectable above the melting point of the macrocycle, although they have much lower intensity. The melting point varies from 42 to 47 °C in the polyrotaxanes, depending on the composition. Hence the bands cannot be specifically assigned to the hydrogen-bonding interaction between a backbone N-H group and an ether atom in a crystalline macrocycle. It seems that because of the "threading" constraint, the macrocycles are coerced to interact with the backbone urethane groups, even above the melting point of the macrocycles. Once melted, however, the rings are free to diffuse along the backbone or to rotate about it, diminishing the number of hydrogen-bonded macrocycles.

Figure 7 shows the carbonyl region at different temperatures for the same series of polyrotaxanes.

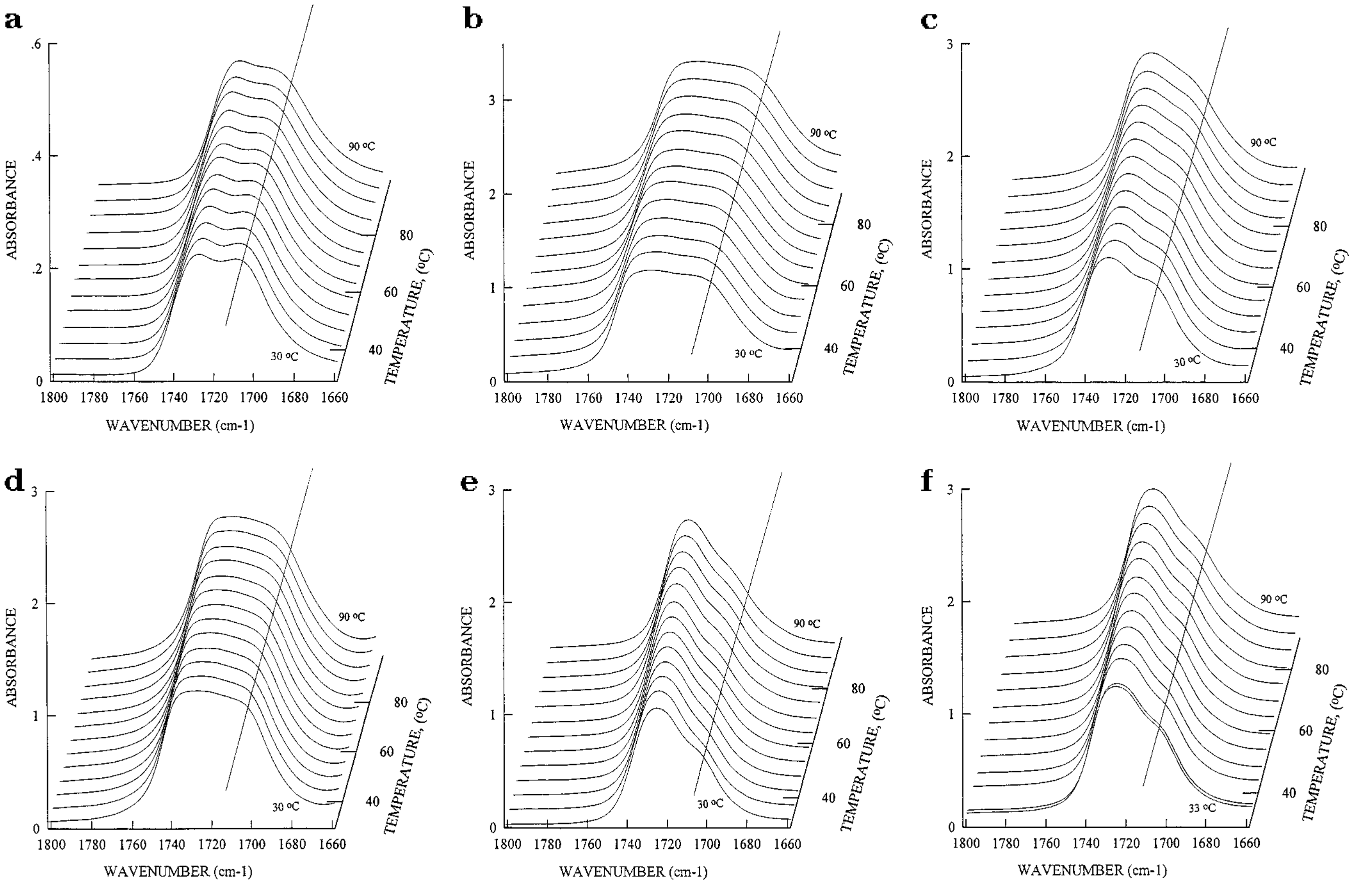

Figure 7. IR carbonyl region as a function of temperature and macrocycle loading: (a) $x/n = 0.0$, (b) $x/n = 0.16$, (c) $x/n = 0.29$, (d) $x/n = 0.34$, (e) $x/n = 0.58$, and (f) $x/n = 0.87$.

Table 2. Ratio of Hydrogen-Bonded to Free Carbonyl Absorbances

sample	ratio
1	0.66
2	0.58
3	0.90
4	0.77
5	0.89
6	0.94

Comparison of spectra of the various samples at room temperature shows large differences in peak widths and relative intensities, reflecting the variations in hydrogen bonding from sample to sample. As mentioned earlier, the carbonyl band may also have some contribution from impurities generated during synthesis, thus making detailed analysis of the carbonyl region difficult. However, if we focus on the relative intensities of the so-called "free" carbonyl band near 1730 cm^{-1} and the "associated" carbonyl band at 1705 cm^{-1}, especially in samples 1−4, we see that compared to the model polyurethane (sample 6), these polyrotaxanes exhibit a much lower degree of self-association of the polyurethane backbone. This observation is summarized in Table 2. This is reasonable, since the presence of macrocycles along the backbone should disrupt such intermolecular interactions due to steric hindrance. Due to this effect, the intensity of the "associated" carbonyl bands appears to decrease with macrocycle loading. Furthermore, the relative intensities of the "free" and "associated" carbonyl bands corresponding to the polyrotaxanes do not change with temperature, although small shifts in peak positions to higher frequencies are quite visible. On the other hand, the relative intensity of the same bands in the model polyurethane does change with increasing temperature, reflecting a decrease in the number of hydrogen-bonded carbonyl groups. Again, this suggests that over the narrow temperature range studied, the intermolecular hydrogen bonding between the polyurethane backbones of the polyrotaxanes is largely unaffected by temperature, thereby implying that the majority of the interactions of the urethane N-H groups must be with the ether atoms of the constrained macrocycles.

One-Dimensional Mean-Field Model. As a first approximation, let us assume that the predominant interaction in the polyrotaxane is the intra-annular hydrogen-bonding association between the macrocycle and the polyurethane backbone. Due to the geometric constraints, we cannot calculate the equilibrium constant of association simply from concentration ratios.[12] Therefore, we will employ a "necklace" model for association. Let us imagine that we have a necklace of length R (polyurethane chain). On this necklace we have N beads (macrocycles) of length a each. We also have L stickers (N-H groups) which are frozen on the necklace. If a bead sticks on a sticker, it cannot move anymore and contributes a quantity, b, to the partition function. In the mean-field approximation, the partition function is

$$Z_{N,M} = \frac{L!N![R - Na]^{N-M}b^{M}}{(L - M)![M!(N - M)!]^{2}} \qquad (1)$$

where M is the number of "stuck" beads (hydrogen-bonded macrocycles). Instead of the length R, it is easier to use the maximal number of beads which the necklace can contain:

$$N_{\max} = \frac{R}{a} \qquad (2)$$

Introducing

$$K = \frac{b}{a} \qquad (3)$$

we see that

$$Z_{N,M} = \frac{L!N![N_{\max} - N]^{N-M}K^{M}a^{N}}{(L - M)![M!(N - M)!]^{2}} \qquad (4)$$

Now we want to know the degree of hydrogen bonding. It is the ratio of "stuck" beads (M) to the whole number of beads (N). It is easy to show that it is

$$p = \frac{\langle M\rangle}{N} = \frac{1}{KN}\frac{\partial}{\partial K}\ln Z_{N} \qquad (5)$$

where

$$Z_{N} = \sum_{M=0}^{\min(l,N)} Z_{N,M} \qquad (6)$$

For small N (≤ 10), we can use summation and differentiation to obtain p. For larger N (as is the case here), we must use a different approach.

In this approach we can substitute the sum in eq 6 by its maximal element. It gives for p the following equation:

$$\left(\frac{L}{N} - p\right)(1 - p)^{2}K = p^{2}\left(\frac{N_{\max}}{N} - 1\right) \qquad (7)$$

Equation 7 depends only on the ratios of the extensive variables L, N, and $N_{\max}$ and can be written in the following form, more suitable for comparison with the experiment:

$$\left(\frac{l}{z} - p\right)(l - p)^{2}K = p^{2}\left(\frac{m}{z} - 1\right) \qquad (8)$$

where l is the number of H-bonding groups per repeat unit, z is the number of rings per backbone repeat unit ($z = x/n$), m is the maximal number of rings per repeat unit which can be packed in the backbone, and K is the equilibrium constant. We have assigned the value of 2 to both l and m because there are two N-H groups per backbone repeat unit. Presently no experimental or theoretical data is available which could give us the maximal number of rings that can be packed in the backbone. However, the actual value of m does not affect the final calculated enthalpy, since enthalpy depends only on the slope of ln K vs $1/T$ and not the absolute numbers. The conversion factor p varies with K as shown in Figure 8. As described below, we used eq 8 to determine the values of the equilibrium constant K from the experimental data on p. It can be seen from Figure 8 that the sensitivity of K to $z = x/n$ (in our particular experimental range) is very small.

Quantitative Analysis of the N-H Stretching Region. Although in the past quantitative analysis of the N-H stretching region has been considered with skepticism due to the large variations in the absorption coefficient with frequency,[13−15,17] we believe that, at least in this case, semiquantitative analysis is feasible because the amount of "free" N-H formed with increas-

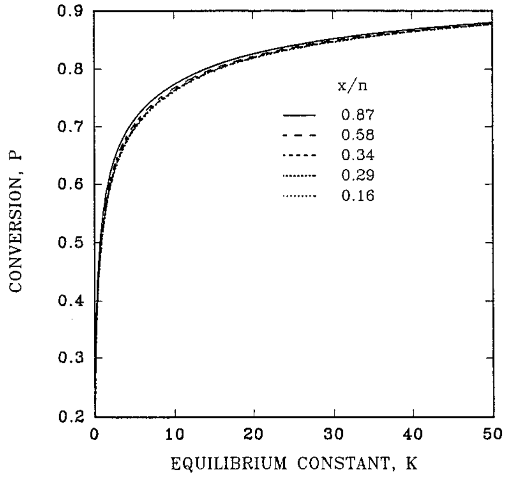

Figure 8. Theoretical conversion as a function of equilibrium constant and macrocycle loading.

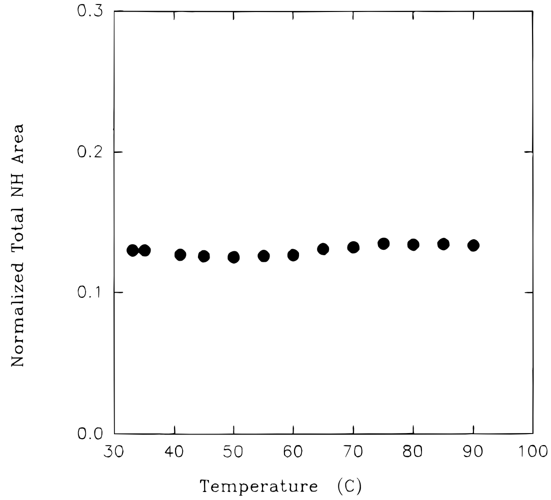

Figure 9. Total N-H stretch area (normalized for thickness changes) as a function of temperature.

ing temperature is virtually negligible. In fact, the total N-H area remains constant as a function of temperature, as shown in Figure 9. Total N-H stretch area was corrected for thickness variations from sample to sample by dividing through by the corresponding integrated C-H stretch band. This suggests that the observed changes in the N-H stretching region primarily reflect the transformation of one type of hydrogen-bonded species to another, i.e., from a strongly associated complex to a weaker hydrogen-bonding interaction. Furthermore, because the carbonyl region is unaffected by temperature changes, it seems that the change involves only the association of the N-H group of the polyurethane backbone with ether atom(s) of the macrocycle. For the quantitative analysis to be possible, we will further assume that the absorption coefficients for the different hydrogen-bonded species are the same and do not vary with temperature. Again, due to the fact that the total N-H absorption area remains constant, this initial assumption seems quite reasonable. Finally, we would like to point out that these experiments have been carried out over a relatively small temperature range (30−90 °C), as compared to previous studies of polyurethanes, which typically take the sample above 200 °C, greatly disrupting the hydrogen bonding between molecular chains.

In our analysis, we are primarily concerned with estimating the relative decrease of the 3220 and 3270 cm^{-1} bands, which we believe represent hydrogen-bonded complexes of one or more N-H groups with ether atoms of a macrocyclic ring. Curve fitting of the entire N-H region proved to be very difficult to accomplish with reasonable accuracy due to the presence of a large number of bands in the N-H band contour. These bands also shifted in frequency with temperature. Hence, subtraction of the model polyurethane spectra from the polyrotaxane spectra at each corresponding temperature seemed to be the only way to obtain the contribution of the two desired stretching vibrations. This was accomplished by multiplying the model polyurethane spectrum by a factor, such that the polyrotaxane and the model polyurethane spectra coincided at 3310 cm^{-1} which is the primary absorption band corresponding to N-H moieties associated with carbonyl groups in the polymer. Once this contribution was cancelled out, what remained was the negative area, associated with the excess free N-H groups present in the model polyurethane, and a positive area, associated with the 3270 and 3220 cm^{-1} stretching vibration in the polyrotaxane. This area was evaluated as shown in Figure 10. This approach generated area values which steadily decreased with increasing temperature, which was consistent with our qualitative observations.

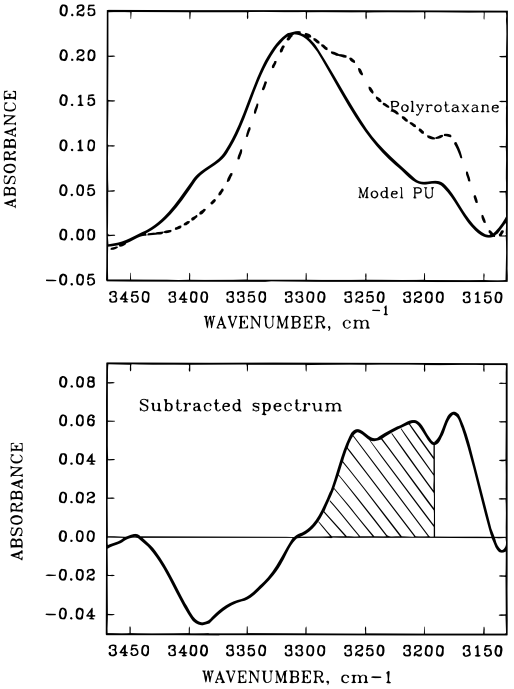

Figure 10. Subtracted spectrum of the model polyurethane from the polyrotaxane, $x/n = 0.87$ at 50 °C.

Since the spectra of the model polyurethane were scaled to match the polyrotaxane spectra at 3310 cm^{-1}, any excess intensity present in the 3220−3270 cm^{-1} range was assumed to be associated with the N-H groups hydrogen bonded with the macrocyclic rings. The fractional decrease of these two bands, as compared to the total N-H stretch area, is tabulated in Table 3 for two samples having the highest macrocycle loading. Polyrotaxane samples with lower macrocycle concentrations were difficult to analyze because the subtracted areas were of the same magnitude as the measurement error. Unfortunately, as we shall see later, the subtraction approach tends to overestimate the total area contributing to the N-H/macrocycle hydrogen-bonding interaction because the number of hydrogen-bonded N-H groups observed in the model polyurethane de-

Table 3. Fractional Decrease of Hydrogen-Bonded N-H Groups as Compared to Total N-H Stretching Region

x/*n*		
0.87	0.58	*T* (°C)
0.399		30
0.395	0.293	35
0.380	0.290	40
0.378	0.281	45
0.365	0.255	50
0.352	0.238	55
0.334	0.225	60
0.311	0.189	65
0.284	0.192	70
0.284	0.174	75
0.264	0.194	80
0.247	0.163	85
0.22	0.145	90

Table 4. Change in the Peak Height of the 3270 cm^{-1} Band with Temperature

x/*n*		
0.87	0.58	*T* (°C)
	0.270	30
0.342	0.261	35
0.331	0.257	40
0.326	0.251	45
0.318	0.248	50
0.311	0.242	55
0.305	0.235	60
0.300	0.229	65
0.292	0.225	70
0.285	0.218	75
0.273	0.216	80
0.263	0.208	85
0.254	0.198	90

creases faster with temperature than in the polyrotaxane. Again, this is quite evident in the carbonyl region as well. In order to understand just how much of a deviation we have in our analysis, we have also measured the peak height of the 3370 cm^{-1} band relative to a base line drawn from 3607 to 2650 wavenumbers as a function of temperature. This data is summarized in Table 4.

Using the "necklace" model, we can now calculate the equilibrium constant of backbone/macrocycle complex formation as a function of temperature. The variable *p*, representing the ratio of hydrogen-bonded macrocycles to whole number of macrocycles, can be calculated indirectly be determining the fraction of N-H groups actually complexed with the macrocycles compared with the maximum possible fraction of N-H groups that can be complexed with the macrocycles, given the (*x*/*n*) ratio. Therefore,

$$p = \frac{\text{subtracted(N-H) area}}{\text{total(N−H) area}} \cdot \frac{1}{x/n} \qquad (9)$$

For example, when $x/n = 0.87$, there is 0.87 macrocycle/polyurethane repeat unit. Although each repeat unit contains two N-H moieties, both of these could, in principle, form hydrogen bonds with one macrocycle. Hence, the maximum possible fraction of N-H groups that can form intra-annular hydrogen bonds with the macrocycles is 0.87. The rest of the N-H groups form hydrogen bonds with either macrocycles not threaded along the same backbone or carbonyl or ether oxygens of neighboring polyurethane chains. As a first approximation, we assume that the number of free N-H groups is negligible in this temperature range. Once we obtain *p* as a function of temperature, we can calculate the equilibrium constant *K* from eq 8. Figure 11 shows the plots of ln(*K*) as a function of 1/*T* for the sample with the largest macrocycle loading, using the subtraction method to obtain the area of the N-H groups hydrogen bonded to the macrocyclic rings. This plot is curved, suggesting that there is a temperature dependence of the enthalpy term. Measuring the limiting slopes at either extreme, we obtain an enthalpy value of 3.9 kcal/mol at the low-temperature end and 12.9 kcal/mol at the high-temperature end. Compared to the enthalpy of hydrogen bond formation reported in literature (typically 5 kcal/mol),[17] the low-temperature value seems quite reasonable, particularly because we believe we are looking at the difference between a strongly hydrogen-bonded complex and a weaker hydrogen-bonding interaction. However, the enthalpy value obtained from the limiting slope at the higher temperature end is rather unrealistic. Again, this is due to the fact that the formation of free N-H groups in the model polyurethane occurs at a faster rate with temperature than in the corresponding polyrotaxane, and hence the calculated area is overestimated. For this reason we have used the peak height measurements, which are independent of the model polyurethane, to correct the rate of change of the N-H area reflecting the N-H groups hydrogen bonded with the ether atoms of the macrocyclic rings. Using the new area values, we have recalculated the equilibrium constant *K*. Figures 12 and 13 show the corrected plots of ln(*K*) as a function of 1/*T* for samples with $x/n = 0.87$ and 0.58, respectively. Here the data follow a straight line, giving enthalpy values of 3.5 ± 0.5 kcal/mol for sample with $x/n = 0.87$ and 2.5 ± 0.5 kcal/mol for sample with $x/n = 0.58$. The error reflects the effects of base-line choices in peak height and area measurements on the slope of the ln(*K*) vs 1/*T* curve.

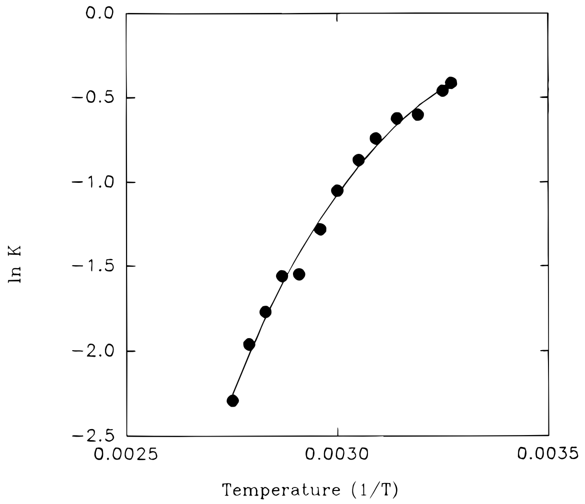

Figure 11. Logarithmic plot of the equilibrium constant *K* obtained via the subtraction method, $x/n = 0.87$.

As already mentioned, the dissociation of the hydrogen bonds between the macrocycle and the backbone is much more predominant in the temperature range studied than the dissociation of hydrogen bonding between polyurethane chains in the polyrotaxane. This latter phenomenon, which becomes significant at higher temperatures, may be better described by a different equilibrium constant.

Conclusions

Infrared spectra of the poly(urethane−rotaxane)s examined suggested the existence of an N-H stretching

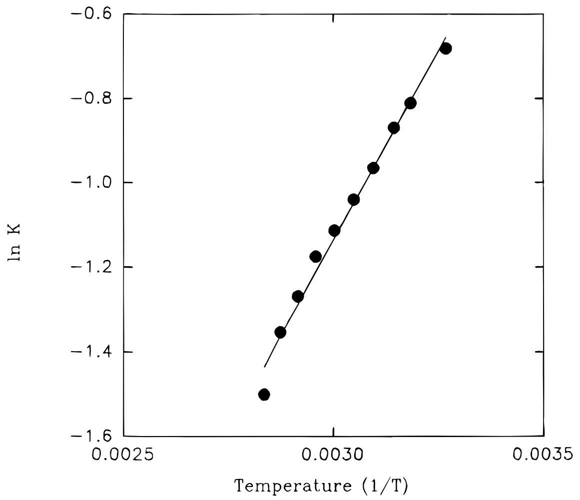

Figure 12. Logarithmic plot of the equilibrium constant *K* obtained via peak heights, $x/n = 0.87$.

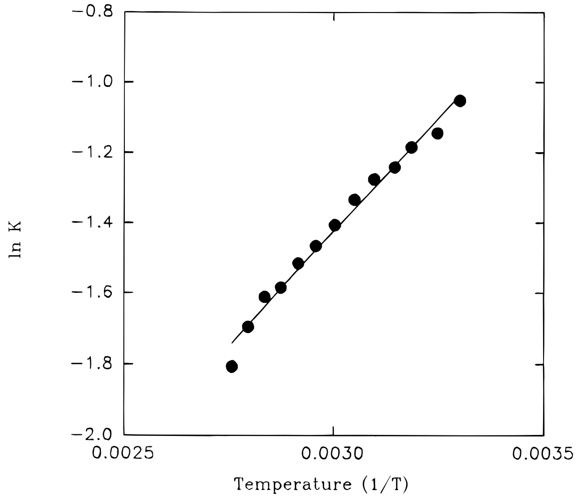

Figure 13. Logarithmic plot of the equilibrium constant *K* obtained via peak heights, $x/n = 0.58$.

vibration specifically arising as a result of a polyurethane N-H moiety hydrogen bonding to an ether oxygen atom in a macrocycle treaded along the polyurethane backbone. Temperature dependence of the intensity of this band, along with a one-dimensional mean-field model, was used to calculate the enthalpy of such a hydrogen-bonding interaction. In the case of the 60C20 macrocyclic ring, the average calculated enthalpy value was 3.0 ± 1 kcal/mol. Unfortunately, due to the precision errors associated with the spectral analysis, we were not able to obtain enthalpy values for polyrotaxanes with macrocycle loading $<x/n = 0.58$.

Knowing the strength of the hydrogen-bonding interaction between the macrocycle and the backbone is important to the prediction of threading efficiency during synthesis and in understanding the crystallization mechanism of the cyclic rings which is limited by the diffusion of the macrocycles along the polyurethane backbone.

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