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William MacKnight, *University of Massachusetts Amherst*
M. Yang

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PROPERTY-STRUCTURE RELATIONSHIPS IN POLYURETHANES: INFRARED STUDIES

W. J. MACKNIGHT and M. YANG

Chemistry Department and Polymer Science and Engineering Program, University of Massachusetts, Amherst, Massachusetts 10002

SYNOPSIS

Temperature dependent infrared studies have been carried out on three series of polyurethanes previously synthesized and characterized. The repeat units of the three series may be schematically represented as follows:

In each case n varies from 2 to 10. The H and DP series are partially crystalline while the 4M series is entirely amorphous.

It was possible to draw several conclusions concerning the hydrogen bonded NH and C=O groups in these polymers. These conclusions are: (1) The aromatic polyurethanes of the DP and 4M series are hydrogen bonded in the amorphous phase below the glass transition temperature, (T_g), to the extent of 75% or less whereas the aliphatic H series is completely hydrogen bonded below T_g . (2) Both the DP and H series are completely hydrogen bonded in the crystalline phase below the melting point, (T_m), regardless of the value of n . (3) A temperature dependent equilibrium between free and hydrogen bonded NH groups occurs in the amorphous phase above T_g in all three series. (4) The temperature dependences of the total area of the NH stretching bands exhibit transitions corresponding to T_g , T_m , and, in the case of the H series, to a first order crystal-crystal phase transition, T_t . (5) The temperature dependences of the frequencies of the hydrogen bonded NH stretching vibration also exhibit transitions corresponding to T_g and T_m .

INTRODUCTION

Previous publications from these laboratories have been concerned with

various aspects of the structures and properties of three series of polyurethanes.¹⁻⁴ Their repeat units may be represented as follows:

n varies from 2 to 10 in all three series. In what follows, each polymer will be referred to by the series name and numbers indicating the diol from which it was derived. Thus H-1,4 refers to the H series polymer with $n = 4$. The H series and DP series are partially crystalline while the 4M series is entirely amorphous.

Glass transition temperatures, (T_g), and melting points, (T_m), where applicable, have been determined for all three series by differential scanning calorimetry (DSC),¹ and the relaxation behavior associated with these transitions has also been observed.³ It was established that the T_g 's of both the H and DP series are monotonously decreasing functions of n but that the T_g 's of the 4M series do not depend on n in any regular fashion. The T_m 's of both the DP and H series show an alternating dependence on n with the even numbered members of the series possessing the higher values of T_m . An additional transition is observed in the H series which shows relatively little dependence on n . This transition occurs at a temperature intermediate between T_g and T_m and has been identified as a first order crystal-crystal phase transition, analogous to the so called "α to γ" transition which occurs in polyamides such as nylon 6.^{3,4} In what follows this transition will be designated T_t .

An important structural feature of the polyurethanes of this research is the occurrence of hydrogen bonding between the amide, (NH), and carbonyl, (C=O), functional groups. In previous studies confined to aliphatic polyurethanes of similar structures to members of the H series, the intermolecular nature of the hydrogen bonding in the crystal phase was established by x-ray crystallography.⁶ Temperature dependent infrared investigation established that hydrogen bonding was almost complete in these polymers below T_m and remained very extensive even above T_m .⁷ Later studies considered the properties of elastomeric or segmented polyurethanes.^{8,9} In these materials, the "hard" or urethane phase consists of residues analogous to the H and DP series. Although hydrogen bonding in these materials is complicated by the presence of ether linkages or ester carbonyl groups to which the NH group can hydrogen bond, the studies referred to above established the presence of considerable quantities of free NH groups at room temperature.

One of the main objectives in the earlier studies from our laboratories¹⁻⁴ was to define the role played by hydrogen bonding on the structure-property relationships in the three series of polyurethanes. This objective was only partially realized and it is the purpose of the work reported here to explore this role utilizing more fully the infrared technique. To this end we report the results of temperature dependent infrared studies, the quantitative deduction of the degree of hydrogen bonding in the three series of polyurethanes from the integrated absorbances of the free and bonded NH stretching vibrations, and the shapes and shifts of the bands in the NH stretching vibration region.

EXPERIMENTAL

Materials

The synthesis and characterization of the polyurethanes has been described previously.¹⁻⁴ In summary, solution polymerization techniques were used. The H series was based on 1,6 hexane diisocyanate and the appropriate α, ω diol; the DP series was based on 4, 4' methylene diphenyl diisocyanate and the appropriate α, ω diol, and the 4M series was based on 4 methyl-metaphenylene diisocyanate and the appropriate α, ω diol. Number average molecular weights were found to be in the region of 20,000–50,000 and elemental analysis yielded a very close correspondence to the theoretical structure, indicating that possible side reactions occurring during polymerization are not of importance.

Films of thicknesses of the order of 10^{-4} cm were prepared by solvent casting or compression molding. Films of 4M-1,5 to 4M-1,10 were compression molded between steel plates at 80°C above their T_g 's and at 35,000 to 45,000 psi. All other samples were prepared by solvent casting the polymers from trifluoro-acetic acid directly onto salt plates. Samples prepared in this manner were vacuum dried to constant weight and until the solvent became undetectable in the infrared spectrum.

Three model compounds were synthesized from *n*-butanol and the corresponding diisocyanate according to a method described by Tanaka, Yokoyami, and Yamaguchi.⁸ Melting points, elemental analysis, and infrared spectra determined the structures of these compounds as shown below.

Measurements

All infrared spectra were obtained using a Perkin-Elmer double beam infrared spectrophotometer, model 257. The frequency range covered was from 4000 to 625 cm^{-1} . Normal slit width and medium scanning speed were employed. A specially constructed chamber¹⁰ was used for the temperature variation studies. Temperature was monitored by means of an iron-constantan thermocouple maintained in contact with the sample. Dry nitrogen gas cooled by passage through liquid nitrogen was used for temperatures in the range below room temperature and temperature control was achieved by regulating the flow of the gas. Electric heaters installed in the chamber were used for temperatures above room temperature and control in this range was achieved by means of variacs. Dry nitrogen was continuously flushed through the chamber to avoid the presence of moisture and to prevent oxidation of the sample at the higher temperatures. The temperature range was from -60 to 250°C and temperatures were maintained to $\pm 1^\circ$.

Film thicknesses were measured by using a suitable infrared band as an internal standard. The CH_2 stretching vibration at 2857 cm^{-1} was used for the

H series and the out of plane, (C=O), bending vibrations were used for the DP and 4M series. In the DP series this band occurs at 768 cm^{-1} and in the 4M series it occurs at 780 cm^{-1} . Calibration curves were obtained by plotting the peak absorbances of the internal standard bands against thickness for films of known thickness. The resulting plots were straight lines which extrapolated through the origin in all cases. Thicknesses were obtained at each temperature for all the samples. With the exception of the thickness measurements just described, all analyses were carried out on the basis of areas of absorption bands rather than peak absorptions. The procedure is described in detail by Wilson and Wells.¹¹

The model compounds were used to estimate the apparent molar extinction coefficients of the free NH stretching vibrations in all three series. Chloroform solutions of the model compounds of different concentrations were prepared and a pair of spacer variable liquid cells were used for the solution spectra measurements. Cell path lengths were obtained from the calibration of interference patterns. The free NH stretching band occurs at 3440 cm^{-1} in these model compounds. Its integrated absorbance was plotted against concentration for each of the model compounds. These plots were straight lines which were extrapolated to zero concentration to yield the apparent molar extinction coefficients of the free NH groups. The assumptions were made that the model compound extinction coefficients thus obtained were identical

to the corresponding polymer extinction coefficients and that their values did not depend on the values of n in the repeat units of the polymers.

The free and hydrogen bonded NH stretching bands occur in the region from 3300 to 3540 cm^{-1} in these polymers. Considerable overlapping of these bands exists and in order to use them to quantitatively assess the degree of hydrogen bonding, a separation procedure must be adopted. Any such procedure is necessarily arbitrary, at least to some extent, inasmuch as particular band shapes must be assumed. The method used in this work was based on a least squares procedure assuming bands of a Gaussian shape which has been described previously.^{10,12} Densities were measured in absolute ethanol at 20°C using the displacement method.

RESULTS

Figures 1 through 3 show infrared spectra for representative members of each of the three series of polyurethanes. Band assignments for some of the more prominent absorptions are collected in Table I.^{6,8,13} Hydrogen bonding in these polyurethanes is conveniently studied by an examination of the NH

FIG. 1. (a) Infrared spectrum of 4M-1, 10 in the region 4000 to 625 cm^{-1} at -52°C . (b) Same as (a) except at 121°C .

stretching bands. These are suitable for this purpose both because they possess an appropriate intensity and are free from interference from other strong bands as shown in Figures 1 through 3. The shapes and intensities of the bands

FIG. 2. (a) Infrared spectrum of DP-1, 10 in the region 4000 to 625 cm^{-1} at -44°C . (b) Same as (a) except at 142°C . (c) Same as (b) except at 158°C .

in the NH stretching region are temperature dependent. For the 4M-1, 10 polymer in Figure 1 at -52°C , below T_g , the bonded NH stretching band at 3300 cm^{-1} is prominent and there is a small shoulder representing the free NH stretching band at 3430 cm^{-1} . In going to 121°C , considerably above T_g , the free NH band becomes much more prominent and the overall intensity of the NH stretching band decreases. Similar trends are noted in the DP-1, 10 polymer depicted in Figure 2. In this case, three temperatures are chosen. In Figure 2a the spectrum is representative of behavior below T_g , in Figure 2b it is representative of behavior between T_g and T_m ; and in figure 2c it is representative of behavior above T_m . In this case, the bonded NH stretching vibration noticeably broadens above T_m , becoming comparable to the bonded NH stretching band in 4M-1, 10 above T_g . Three temperatures were chosen for H 1, 10 in a similar fashion to those chosen for DP-1, 10. Figure 3a shows that, below T_g , there is no evidence of a free NH band. In Figure 3b, between

FIG. 3. (a) Infrared spectrum of H-1, 10 in the region 4000 to 625 cm^{-1} at -47°C . (b) Same as (a) except at 137°C . (c) Same as (b) except at 155°C .

T_g and T_m , the free NH vibration appears as a shoulder on the bonded NH band and, in Figure 3c, the NH stretching region becomes similar in appearance to the DP and 4M samples above T_m and T_g , respectively.

The quantitative assessment of hydrogen bonding in the polyurethanes was accomplished in the following manner. The area of the free NH stretching band is given by

$$S_f = \int_{\text{band}} \ln(I_0/I) \, d\nu = a_f l b c_f$$

where S_f is the area of the free NH stretching vibration obtained from the least squares separation procedure alluded to in the experimental section, a_f is the integrated molar extinction coefficient of the model compound, b is the sample thickness obtained from the internal standard, and c_f is the concentration of free NH groups in the sample. The total concentration of NH groups in the polymer is given by

TABLE I
Infrared Band Assignments for Polyurethanes^a

Band Location (cm ⁻¹)	Assignment	Occurrence
3430	free NH stretching	H, DP, 4M
3300	hydrogen bonded NH stretching	H, DP, 4M
2925	asymmetric CH ₂ stretching	H, DP, 4M
2857	symmetric CH ₂ stretching	H, DP, 4M
1700-1740	free and hydrogen bonded carbonyl stretching	H, DP, 4M
1600	C-C multiple bond stretching in the aromatic groups	DP, 4M
1530	"amide II band"	H, DP, 4M
1420	C-C stretching in aromatic groups	DP, 4M
1250	"amide III band"	H, DP, 4M
1080	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}-\text{C} \end{array}$ asymmetric stretching ^b	DP, 4M

^aOnly strong bands and those used in analysis are reported here. For a more complete listing see ref. 10, Tables IV-1-IV-3.

^bThis band also appears in the H series at 1050 cm⁻¹, but is weak.

$$c_{\text{NH}} = \frac{2000\rho}{M_u} \quad (2)$$

where c_{NH} is the total concentration of NH groups, in moles/liter ρ is the density, and M_u is the molecular weight of the polymer repeat unit. c_f is obtained from eq. (1) as the only unknown quantity in the relationship. The difference between c_{NH} and c_f then yields c_b , the concentration of hydrogen bonded NH groups in the polymer. The integrated molar extinction coefficient for the hydrogen bonded stretching vibration is then obtained from a relationship identical to eq. (1), namely

$$S_b = \int_{\text{band}} \ln(I_0/I) dv = a_b^{-1} bc_b \quad (3)$$

where S_b is the area of the hydrogen bonded NH stretching band and the other symbols have the same significance as in eq. (1) except that they refer to the hydrogen bonded instead of the free NH groups.

Under the assumption that a_f^{-1} and a_b^{-1} do not vary with temperature, c_f and c_b may be conveniently obtained at any temperature from the relationship

$$\frac{S_{\text{total}}}{b} = a_b^{-1} c_b + a_f^{-1} c_f \quad (4)$$

where S_{total} is the total area of the NH stretching band, and the other symbols have been previously defined.

The equilibrium constant defining the relationship between free and bonded NH groups is immediately obtainable from these data.

$$K = \frac{c_f}{c_b} \quad (5)$$

The results of the calculations summarized above are collected in Table II. The free NH groups present are expressed as a percentage of the whole. That is,

$$\text{percent free NH} = (c_f/c_{\text{NH}}) \times 100. \quad (6)$$

TABLE II

Spectroscopic Data for Polyurethanes Obtained from the NH Stretching Vibration

Polymer	a_f^1 (liter/mole cm^{-2}) ^a	percent free NH ^b	a_b^1 (liter/mole cm^{-2})	ΔH (kcal/mole) ^c
4M 1-10	3.44×10^3	28	1.32×10^4	5.0
4M 1-9	3.44×10^3	29	1.10×10^4	5.0
4M 1-7	3.44×10^3	25	1.06×10^4	5.0
4M 1-6	3.44×10^3	32	1.06×10^4	4.6
4M 1-5	3.44×10^3	22	1.07×10^4	5.5
4M 1-4	3.44×10^3	21	1.19×10^4	
DP 1-10	6.3×10^3	26	1.49×10^4	
DP 1-9	6.3×10^3	28	1.59×10^4	
DP 1-8	6.3×10^3	28	1.52×10^4	
DP 1-7	6.3×10^3	27	1.50×10^4	
DP 1-6	6.3×10^3	28	1.70×10^4	
DP 1-5	6.3×10^3	26	1.62×10^4	
DP 1-4	6.3×10^3	26	1.65×10^4	
DP 1-3	6.3×10^3	28	1.40×10^4	
DP 1-2	6.3×10^3			
H 1-10	4.47×10^3	0	1.20×10^4	10.5
H 1-9	4.47×10^3	0	1.19×10^4	
H 1-8	4.47×10^3	0	1.21×10^4	9.6
H 1-7	4.47×10^3	0	1.39×10^4	
H 1-6	4.47×10^3	0	1.36×10^4	10.4
H 1-5	4.47×10^3	0	1.41×10^4	
H 1-4	4.47×10^3	0	1.41×10^4	
H 1-3	4.47×10^3	0	1.27×10^4	8.5
H 1-2	4.47×10^3	0	1.30×10^4	

^aObtained from the model compounds and assumed constant throughout each series.

^bBelow T_g .

^cAbove T_g , for 4M; above T_m for H.

Also included in Table II are values of the enthalpy of dissociation for the hydrogen bonds obtained from plots of $\log K$ against $(1/T)$. Such plots are meaningful only above T_g for the 4M series and only above T_m for the H and DP series as will be discussed below. Due to decomposition reliable values of ΔH were not obtainable for the DP series.

In view of the many approximations inherent in the data treatment it is difficult to assign error limits to the quantities listed in Table II. However, it is estimated that a_f^1 and a_b^1 are reliable to within ± 15 liter/mole cm^2 , that the

percent free NH are reliable to within $\pm 1.5\%$, and that ΔH 's are reliable to within ± 1.5 kcal mole $^{-1}$.

It is apparent from Table II that values of a_b^1 are about three times larger than corresponding values of a_f^1 . This situation is common to many intermolecularly hydrogen bonded materials.¹⁴ From this fact and eq. (4), it follows that the total area of the NH stretching band will decrease with a decrease in c_B . Therefore a plot of S_{total} against temperature will reflect the temperature c_B and this will be independent of any scheme used to separate the hydrogen bonded and free NH stretching bands. Figures 4 through 6 show such plots

FIG. 4. Total area of NH absorption band (arbitrary units) as a function of temperature for 4M-1, 10 and 4m-1, 9.

for typical members of all three series. In the case of the 4M series, Figure 4 shows that the S_{total} remain constant below a temperature designated T_1 , and decrease linearly above this temperature. A similar phenomenon is noted in the case of the DP series, in Figure 5. In addition there is a further marked decrease in S_{total} at a temperature designated T_2 in Figure 5. The exact location of T_2 is obtained by extrapolation and is taken as the onset of the slope decrease. The same trends appear in the H series shown in Figure 6. An additional transition, occurring at temperature T_3 , appears between T_1 and T_2 .

Figure 7 is a plot of the frequency of the hydrogen bonded NH band as a function of temperature for typical members of all three series. It is seen that there is a general tendency for the frequency to increase with increasing tem-

FIG. 5. Total area of NH absorption band (arbitrary units) as a function of temperature for DP-1, 10 and DP-1, 9.

FIG. 6. Total area of NH absorption band (arbitrary units) as a function of temperature for H-1, 10 and H-1, 9.

FIG. 7. Temperature dependence of the frequency (cm^{-1}) of the hydrogen bonded NH stretching band for 4M-1, 10; DP-1, 10; and H-1, 10.

perature and that transitions occur corresponding to the T_1 's and T_2 's discussed above.

DISCUSSION

An examination of Table II reveals that the percentage of free NH groups below T_g is quite comparable for all members of the DP and 4M series at values around 25–30%, and there are no free NH groups present in the H series below T_g . This result for the H series is consistent with those obtained previously for comparable aliphatic polyurethanes and polyamides. By analogy with structural studies made on polyamides,⁵ it is probable that the urethane group is planar due to the partial double bond character of the carbon to nitrogen bond. In the case of the 4M and DP series it is to be expected that this resonance effect will extend to the aromatic ring making the entire structure planar as illustrated schematically below.

The bulkiness of the aromatic ring is taken to result in considerable steric hindrance to hydrogen bond formation, thus accounting for the relatively

large proportion of free NH groups in the 4M and DP series below T_g . Effects analogous to this have been commented on previously^{15,16}. The comparison between the values of the percentages of free NH groups in the 4M and DP series is somewhat misleading inasmuch as the DP series is partially crystalline and the 4M series completely amorphous. The concentration of free and hydrogen bonded NH groups in the crystalline phase of the DP series is unknown in the absence of detailed information about the crystal structure. It has been suggested that the chains are present in the all *trans*, planar conformation in the crystal and that complete hydrogen bonding of the NH groups occurs in the even numbered members of the series and only one half of the NH groups are hydrogen bonded in the odd numbered members of the series.¹⁷ Since there is no reason to expect much change in the values of the percentage of free NH in the amorphous phase between even and odd numbered members of the series, it is apparent that differences in hydrogen bonding in the crystal phase should be reflected in the values of percent free NH given in Table II with the values for the odd numbered members being the higher. Inasmuch as no such alternation exists, it is reasonable to conclude that the chain conformations of the odd numbered series members in the crystalline phase must depart from the transform in order to allow complete hydrogen bonding to occur. This conclusion is reinforced by the data for the H series in which all members show complete hydrogen bonding below T_g whether or not their values of n are even or odd. Since the crystallinities of the DP series are in the neighborhood of 30%,⁴ the percent free NH groups in the amorphous phase will generally be 1.4 times greater than the values reported in Table II. Thus the concentration of free NH groups in the DP series compared to the completely amorphous 4M series is considerably greater.

It is also to be noted from Table II that ΔH , the enthalpy of dissociation for hydrogen bonded NH groups, is almost twice as great for the H series as it is for the 4M series. This result again reinforces the suggestion that steric hindrance plays a role in the hydrogen bonding occurring in aromatic polyurethanes. Presumably the hydrogen bonds in the 4M series are "weaker" than those in the H series because the aromatic rings in the former prevent the NH and C=O groups from approaching each other as closely as is the case with the aliphatic H series.

The temperature dependence of the infrared spectra of the three series of polyurethanes in the NH stretching region is in accord with qualitative concepts previously developed to explain the mechanical properties of semicrystalline polymers and their temperature dependence. Below T_g , the polymer molecules are capable of localized motions only so that whatever degree of hydrogen bonding obtains at T_g is maintained unchanged to lower temperatures. Above T_g micro-Brownian segmental motion occurs in the amorphous phase allowing a temperature dependent equilibrium to be established between free and hydrogen bonded NH groups in this phase. No such equilibrium is established in the crystal phase which remains unchanged with hydrogen bonding essentially complete for all series members as discussed above. At the melting point, with the collapse of the crystal lattice equilibrium between free and hydrogen bonded NH groups is established

throughout the polymer. From this discussion it is apparent that the T_1 's and T_2 's of Figures 4-6 should correlate with the corresponding T_g 's and T_m 's, respectively. Table III provides such a comparison, and it is readily seen that

TABLE III
Comparison of T_g 's and T_m 's Obtained by DSC with those Obtained Spectroscopically for the Polyurethanes

Polymer	$T_g(\text{DSC})^a$	T_1	$T_m(\text{DSC})^a$	T_2
4M 1-10	40	42		
4M 1-9	65	35		
4M 1-7	63	43		
4M 1-6	43	28		
4M 1-5	66	55		
4M 1-4	58	45		
DP 1-10	64	50	192	142
DP 1-9	64	46	190	128
DP 1-8	64	66	197	158
DP 1-7	81	64	191	158
DP 1-6	68	85	197	182
DP 1-5	85	91	189	178
DP 1-4	108	74	242	187
DP 1-3	119	95	234	178
DP 1-2	139	112	243	
H 1-10	6	0	154	134
H 1-9	6	2	147	130
H 1-8	10	8	157	146
H 1-7	12		146	
H 1-6	16	10	165	152
H 1-5	20	12	155	130
H 1-4	25	25	180	162
H 1-3	31	17	161	140
H 1-2	42	32	167	148

^aRef. 1 and 4.

such a correlation exists. It is seen that the T_1 values are generally somewhat lower than the corresponding T_g 's and the same is true for the T_2 's and the comparable T_m 's. It is, of course, well known that T_g 's and T_m 's in polymers do not occur as sharp transitions, but are somewhat diffuse. The results summarized in Table III tend to suggest that hydrogen bond breaking starts to occur as a result of somewhat shorter range segmental motions than those accompanying the thermal transition observed at T_g . The differences between the T_2 's and the T_m 's can largely be accounted for, at least in the case of the H series, by the fact that T_2 was taken as the onset of the transition and the DSC T_m was taken as the temperature at which the melting endotherm returned to the base line. This explanation may also apply to the DP series. An additional point may bear in this case which is that a mechanical relaxation in

the crystal phase occurs in the DP series at about 50°C below T_m ³. If this relaxation results in hydrogen bond breaking, T_2 may reflect this process in the DP series to some extent.

The presence of a crystal-crystal phase transition occurring at T_i in the H series has been alluded to in the introduction. It has been postulated that conformational rearrangements of the chains in the crystal phase accompany this transition.³ These changes are presumed to occur in such a way as to allow complete hydrogen bonding to take place in the crystal phase. The experimental results of the present study indicate that complete hydrogen bonding does occur in the crystal phase for all members of both the H and DP series. The additional transition occurring between T_1 and T_2 in the H series and labeled T_3 in Figure 6 is consistent in location with T_i and is therefore assigned to this transition.

The temperature dependences of the frequency of the bonded NH stretching band summarized in Figure 7 indicate a single transition for the 4M series and two transitions for the H and DP series. The temperature locations of those transitions also correlate with T_g and T_m . The general trend of the band to shift towards higher frequencies may be explained on the basis of thermal expansion. Thermal expansion acts to increase the average distance between the NH and C=O groups, thus weakening the hydrogen bonds. The transitions in the plots in Figure 7 occur because of the discontinuity in the coefficient of thermal expansion which occurs at T_g and because of the discontinuity in volume which occurs at T_m .

CONCLUSIONS

The following conclusions may be drawn from the infrared evidence presented in this paper.

- (1) The aromatic polyurethanes of the DP and 4M series are hydrogen bonded in the amorphous phase below T_g to the extent of 75% or less whereas the aliphatic H series is completely hydrogen bonded below T_g .
- (2) Both the DP and H series are completely hydrogen bonded in the crystal phase below T_m , regardless of the value of n .
- (3) A temperature dependent equilibrium between free and hydrogen bonded NH and C=O groups occurs in the amorphous phase in all three series above T_g .
- (4) The temperature dependence of the total area of the NH stretching band exhibits transitions corresponding to T_g , T_m , and, in the case of the H series, to T_i .
- (5) The temperature dependence of the frequency of the hydrogen bonded NH stretching vibration also exhibits transitions corresponding to T_g and T_m .

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