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cross-link density and so a gel with a lower value of S should exhibit a broader frequency range in which moduli are congruent.

Conclusions

The constitutive equation, eq 3, which was previously found to describe the viscoelastic properties of a PDMS network at GP, is also valid for a PU system. $G'(\omega)$ and $G''(\omega)$ have been found to be congruent and proportional to $\omega^{1/2}$ at GP, independent of the strand length between cross-links or the functionality of the cross-linker. The gel strength S strongly increases as the strand length between cross-links is decreased.

It has been shown that the crossover time of G' and G'', as measured during the cross-linking reaction, corresponds to the exact instant of gelation. However, this result remains only valid if the frequency of the experiment is sufficiently low or if the experimental temperature is sufficiently far from the temperature of vitrification of the gel.

Finally it is important to recall that the present analysis is restricted to irreversible gels formed by end-linking reaction of stoichiometrically balanced chemical species. Experiments at different stoichiometric ratios will be reported in a followup article.

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Registry No. (PPO)·(DRF) (copolymer), 102539-19-5.

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Hydrogen Bonding in Polymers. 4. Infrared Temperature Studies of a Simple Polyurethane

Michael M. Coleman,* Keun Ho Lee, Daniel J. Skrovanek, and Paul C. Painter

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received February 5, 1986*

ABSTRACT: Fourier transform infrared temperature studies of a simple linear semicrystalline aliphatic polyurethane, poly(1,4-butylene hexamethylenecarbamate), are presented. The main thrust of the work concerns the interpretation of the infrared spectral changes associated with hydrogen bonding and a comparison with our recently published studies of semicrystalline polyamides.

Introduction

We have recently published three paper pertaining to the interpretation of the infrared spectra of polyamides.[1-3] Specifically, infrared temperature studies were reported for a completely amorphous polyamide (commonly denoted nylon 6I/6T) and three semicrystalline polyamides; nylon 11, nylon 12, and a structurally irregular terpolyamide (denoted nylon 6/66/610). Three major normal modes associated with the amide group were emphasized in our studies which yield different, but complementary, information.

It is well recognized that the band envelope encompassing the N–H stretching mode is composed of two main contributions, attributed to "free" (non-hydrogen bonded) and hydrogen bonded N–H groups. The latter is primarily a reflection of the distribution of the strength of the hydrogen bonds (although there is also a degree of broadening due to anharmonicity). The mean strength of the hydrogen bonds diminishes with increasing temperature. Concurrently, there is a reduction in the area of the hydrogen bonded N–H band that is the result of two primary factors. First, a fraction of the bonded N–H groups transform to "free" N–H groups as dictated by equilibrium considerations. Second, and more importantly in the case of simple polyamides, the absorptivity coefficient is a strong function of the strength of the hydrogen bond and varies significantly as the band shifts in frequency.[1] Without a knowledge of the variation of absorptivity coefficient with hydrogen bond strength, measurements of the concentration of "free" and hydrogen bonded N–H groups are subject to large errors. As we have pointed out previously, this has serious ramifications if infrared data obtained from the N–H stretching region are to be used for the estimation of thermodynamic parameters associated with hydrogen bonding.[1-3] The hydrogen bonded N–H mode is conformationally insensitive and the presence of order ("crystallinity") is reflected only in a reduction in the relative breadth of the band, which implies a narrower distribution of hydrogen bonded strengths.[2,3]

The amide I mode (which may be considered, in simple terms, as the carbonyl stretching vibration) is, however, sensitive to order. Contributions to the amide I band envelope assigned to "free" (non-hydrogen bonded) carbonyl groups together with ordered and disordered hydrogen bonded carbonyl groups are readily discerned. This conformational sensitivity is not due principally to mechanical coupling to the main chain but rather to dipole–dipole coupling of the carbonyl groups. In addition, unlike the N–H stretching mode, the three different contributions comprising the amide I mode have absorptivity coefficients

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that do not appear to differ appreciably. This is convenient for quantitative analysis. (We should caution, however, that the relative change in the concentration of "free" carbonyl groups for the polyamides studied is rather small over the temperature range considered. Thus, variations in the absorptivity coefficients may be masked by the experimental errors involved.)

The amide II mode (which for our purposes can be considered to be the N–H in-plane bending vibration) is a mixed vibration that is sensitive to conformation via mechanical coupling and hydrogen bonding. It therefore has some characteristics of both the N–H stretching and amide I modes. In fact, this mode is sensitive to polymorphism in cases where there is a significant difference in chain conformation between the two polymorphs.[3]

In our previous papers concerning polyamides,[1-3] we intimated that the general conclusions reached should also be applicable to polyurethanes. This was based upon the similarity of hydrogen bonding occurring in both classes of polymers. In particular, the methods employed to estimate thermodynamic parameters from area measurements in the N–H region of the infrared spectrum as a function of temperature were questioned. There are, nonetheless, significant differences in the chemistry of polyurethanes compared to polyamides and we considered it important to test whether our general conclusions reached regarding the interpretation of the infrared spectra of polyamides are also applicable to polyurethanes.

There is a rather intimidating number of previously published in-depth infrared studies of hydrogen bonding in polyurethanes.[4-14] Most of these studies have focused on the effect of temperature upon hydrogen bonding in the complex, but industrially important, segmented polyurethanes.[8,10,12,13] Many report thermodynamic parameters derived from these temperature studies.[9,12,13] However, in the light of the information gained from our studies of the polyamides, we have to question the validity of these previous studies. The infrared results, per se, are not in question but rather the interpretation of the infrared changes with temperature. Accordingly, we decided to "go back to square one" and initially perform infrared temperature studies on a simple semicrystalline aliphatic polyurethane (analogous to the semicrystalline polyamides mentioned above).

Experimental Section

The polymer, poly(1,4-butylene hexamethylenecarbamate) (PU64), was synthesized from hexamethylene diisocyanate and 1,4-butanediol (both acquired from Aldrich Chemical Co.) by a solution polymerization procedure described elsewhere.[15,16] The chemical repeating unit of the polymer is as follows:

$$[CONH(CH_2)_6NHCOO(CH_2)_4O]_n$$

The polymer exhibits a crystalline melting point of 182 °C as determined by differential scanning calorimetry.

Samples for infrared analysis were prepared by casting films from a 1% (w/v) solution of the polymer in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) onto potassium bromide windows at room temperature. Following the evaporation of the majority of the solvent, the samples were placed in a vacuum oven at 100 °C for 12 h to remove residual solvent and moisture and then immediately transferred to the temperature cell contained in the spectrometer.

Spectra were acquired on a Digilab Model FTS-15E Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm^{-1}. A minimum of 64 scans were signal averaged, and the spectra were stored on a magnetic disc system. The frequency scale is internally calibrated with a reference helium–neon laser to an accuracy of 0.2 cm^{-1}. The films used in this study were sufficiently thin to be within an absorbance range where the Beer–Lambert law is obeyed. Spectra recorded at elevated temperatures were obtained with a Micristar heat controller. This device has a reported accuracy of ±0.1 °C.

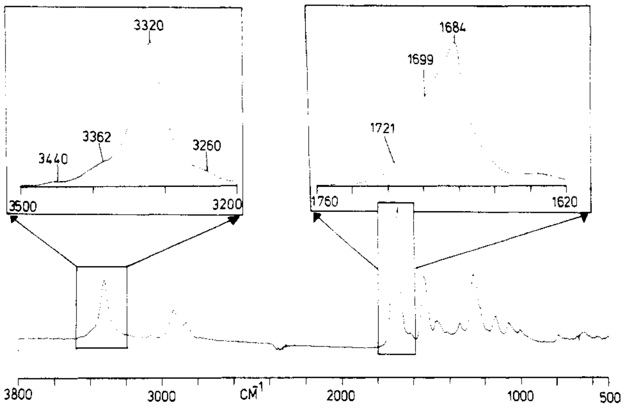

Figure 1. Room temperature infrared spectrum, in the range 500–3800 cm^{-1}, of a film of PU64 cast from HFIP. Inserts: scale-expanded spectra between 3200–3500 and 1620–1760 cm^{-1}.

Thermal analysis was performed on a Perkin-Elmer 7 Series differential scanning calorimeter. A heating rate of 20 °C/min was used, with a sample size of approximately 2.5 mg.

Results and Discussion

The infrared spectrum of a sample of PU64 recorded at room temperature is shown in the region from 500 to 3800 cm^{-1} in Figure 1. Also included in this figure are inserts containing expanded spectral regions of particular interest; the N–H stretching from 3200 to 3500 cm^{-1} and the carbonyl stretching from 1620 to 1760 cm^{-1} (analogous to the amide I mode of polyamides and polypeptides). Before we become immersed in the details of the spectral changes with temperature, certain other infrared bands should be mentioned. The bands occurring between 2800 and 3000 cm^{-1} are associated with the symmetric and asymmetric C–H stretching vibrations of the aliphatic CH_2 groups. The area of these bands may be monitored to ensure that there is no loss of the sample during the temperature studies. The moderately intense band observed at about 1540 cm^{-1} is similar in form to the amide II mode in polyamides in that it involves a significant contribution to the potential energy distribution from the in-plane N–H bending vibration. In the forthcoming discussion we will initially present the results obtained in the N–H stretching region and then turn our attention to the carbonyl stretching region. This will be followed by brief remarks on other regions of the spectra.

N–H Stretching Region. Examination of the N–H stretching region of the infrared spectrum of PU64 recorded at room temperature (see insert in Figure 1) leads one to conclude that the band envelope is composed of *at least* four contributing bands. The infrared bands at 3440 and 3320 cm^{-1} are assigned to the N–H stretching modes of the "free" and hydrogen bonded N–H groups of the polyurethane, respectively. The frequencies of these two bands are remarkably similar to those observed for the analogous aliphatic polyamides.[2,3] The other two bands at about 3362 and 3260 cm^{-1} are attributed to two phonon vibrations involving the intense carbonyl vibrations in Fermi resonance with the N–H stretching fundamental vibration. Two phonon bands also complicate the N–H stretching region of polyamides. The 3362-cm^{-1} band in the polyurethane has no counterpart in the aliphatic polyamides, however, and it is germane that the fundamental carbonyl stretching vibration of the former occurs at a higher frequency by some 45 cm^{-1}. (A probable assignment of the 3362-cm^{-1} band would be the overtone of the fundamental at 1684 cm^{-1}).

Table I
Curve-Fitting Results of the N–H Stretching Region

	"free" N–H			hydrogen bonded N–H			overtone			
temp, °C	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_F	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_{HB}	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A	A_{CH_2}
210	3444	52	50	3347	87	210	3396	75	112	589
190	3442	54	47	3344	86	220	3392	75	109	560
170	3442	55	44	3343	85	237	3393	77	117	552
155	3442	54	37	3343	86	276	3396	76	107	552
145	3438	52	31	3341	83	249	3390	77	114	548
135	3442	54	32	3342	84	294	3397	72	95	552
125	3439	55	31	3337	76	308	3394	69	111	552
110	(3440)[a]	(50)[a]	19	3329	52	377	3386	69	141	552
90	(3440)	(50)	11	3327	46	418	3376	73	181	552
70	(3440)	(50)	10	3324	43	433	3366	82	237	560
50	(3440)	(50)	15	3323	43	477	3365	79	240	563
30	(3440)	(50)	13	3321	41	521	3362	79	270	588

[a] Assumed values in parenthesis—not refined.

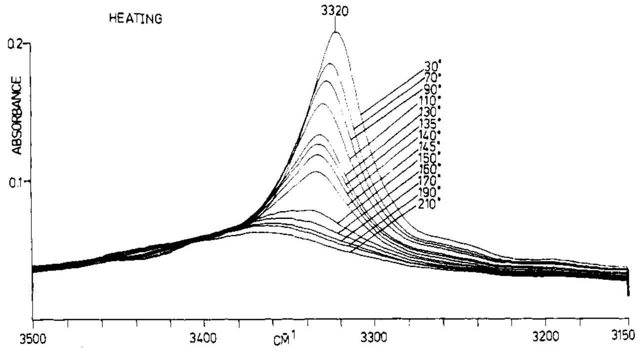

Figure 2. Infrared spectra, in the range 3150–3500 cm^{-1}, of the same sample of PU64 recorded as a function of *increasing* temperature from 30 to 210 °C. Note that the spectra are presented on an absolute absorbance scale.

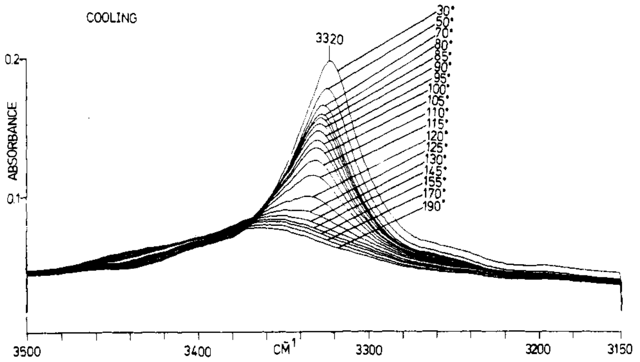

Figure 3. As in Figure 2 except the spectra were recorded as a function of *decreasing* temperature from 210 °C.

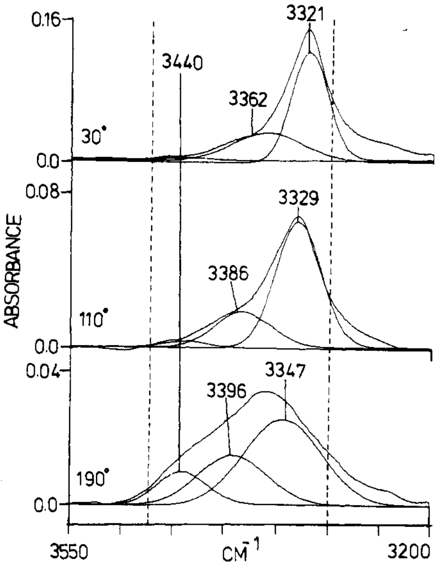

Figure 4. Curve-fitting results in the N–H stretching region of the PU64 spectra recorded at 190, 110, and 30 °C during cooling of the sample from 210 °C. Note that the absorbance scales differ. The broken lines represent the limits of the frequency range used in the curve-fitting procedure.

Spectra of the N–H stretching region of the same sample of PU64, displayed on an absolute absorbance scale and recorded as a function of both increasing and decreasing temperature, are shown in Figures 2 and 3, respectively. The dramatic change in band area with temperature is immediately apparent. In fact, if one only recorded the spectra throughout the heating run (Figure 2), one might suspect significant loss of sample through degradation, depolymerization, or flow out of the infrared cell. Recovery of the area (Figure 3) upon cooling the same sample and an essentially constant absorption of the CH_2 bands throughout the temperature study (Table I) eliminates this possibility. In common with the infrared spectral changes observed in the temperature studies of the polyamides, the hydrogen bonded N–H stretching mode of PU64 broadens and shifts to higher frequency as the temperature increases. With the exception of the presence of the high-frequency two-phonon band in PU64, the trends observed in the N–H stretching region are much the same for the semicrystalline polyamides[2,3] and PU64.

Curve fitting of the N–H stretching region was performed on the spectra recorded as the sample was cooled from 210 °C, in much the same manner as described previously.[1,2] A linear base line was drawn from 3800 to 2500 cm^{-1}. The individual spectra were of excellent quality and there were no detectable absorptions at these frequencies (see Figure 1). The careful selection of a logical and consistent base line cannot be overemphasized for studies such as these. Setting the limits of the curve-fitting procedure to between 3300 and 3475 cm^{-1} obviated the necessity to account for the lower frequency two-phonon band (at about 3260 cm^{-1}; see Figure 1). Three Gaussian bands, corresponding to the "free" and hydrogen bonded N–H groups together with the higher frequency two-phonon vibration, were employed in the curve-fitting procedure. An iterative least-squares computer program was used to obtain the best fit of the experimental data by varying the frequency (ν), width at half-height ($W_{1/2}$), and intensity of three bands. (An exception to this procedure was made for the "free" N–H band when its contribution approached the noise level of the spectral data; in this case the frequency and breadth of the band was fixed.) Representative examples of the spectral components obtained from the curve-fitting procedure for the PU64 sample as it is cooled from 210 °C are shown in Figure 4. The three examples are displayed on different absorbance scales reflecting the overall increase in area with decreasing temperature and corresponds to a twofold anf fourfold attenuation as we progress from 190 to 110 to 30 °C.

The curve-fitting results for the N–H stretching region of the PU64 sample as it is cooled to room temperature from 210 °C are given in Table I. The individual results and overall trends are intuitively pleasing. First we see that the hydrogen bonded N–H band shifts systematically in frequency from 3347 to 3321 cm^{-1} over the temperature range of 210 to 30 °C: a trend similar to that reported for the polyamides.[2,3] This we interpret as an increase in the *average* strength of the hydrogen bonds. The $W_{1/2}$ of the band is essentially constant from 210 to 135 °C (~85 cm^{-1}), whereupon a marked reduction occurs as the sample cools to room temperature (41 cm^{-1}). Again, this result is similar to that seen in semicrystalline polyamides.[2,3] This we interpret as a narrowing of the *distribution* of the hydrogen bond strengths as the sample crystallizes. The area of the hydrogen bonded N–H stretching band (A_{HB}) increases by a factor of approximately 2.5 as the temperature decreases from 210 to 30 °C. This increase in area is due not only to the transformation of "free" to hydrogen bonded N–H groups as the temperature is reduced but also to an increase in the absorption coefficient as the average strength of the hydrogen bonds increases. We will return to this subject later.

The "free" N–H stretching band occurs at approximately 3440 cm^{-1} and has a $W_{1/2}$ of about 50 cm^{-1}. The area of this band is difficult to measure accurately, especially below 125 °C, but the trend is clear. The area of the "free" band approximately halves as the temperature decreases from 210 to 120 °C and then halves again as we approach room temperature. The assumption that the absorptivity coefficient does not vary with *temperature*, (a reasonable assumption over the temperature range considered) allows this change in area to be a *direct* measure of those "free" groups that transform to hydrogen bonded groups. If one knew the total number of urethane groups in the infrared beam and the absolute absorption coefficient of the "free" N–H band, quantitative analysis would appear possible. The errors inherent in such measurements, however, lead us to conclude that quantitative measurements in the N–H stretching region are unlikely to be rewarding.

The spectral contribution of the high-frequency two-phonon band is also presented in Table I. The frequency of the two-phonon band decreases from 3396 to 3362 cm^{-1} ($W_{1/2}$ = 75 ± 6 cm^{-1}) as the temperature is reduced from 210 to 30 °C. This is to be expected as the two-phonon-band frequency depends upon the frequencies of the fundamental modes in the carbonyl stretching region, which also shift with temperature in the corresponding direction (see later). The area of the two-phonon band remains reasonably constant from 210 to 125 °C but then increases significantly as the sample is further cooled to room temperature. It is difficult to predict the intensity of two-phonon bands, especially if the possibility of Fermi resonance exists. Qualitatively, however, we might anticipate an increase in the two-phonon-band intensity as the sample is cooled and crystallizes because there are differences in the absorption coefficients of the "free" and hydrogen bonded carbonyl stretching vibrations. In itself, the two-phonon band is more of a nuisance than anything else for studies of hydrogen bonding. We must emphasize, nonetheless, that its presence cannot be ignored. Simple area measurements in the N–H stretching region that assume only "free" and hydrogen bonded N–H contributions will be subject to additional errors associated with changes in the frequency and intensity of the two-phonon band.

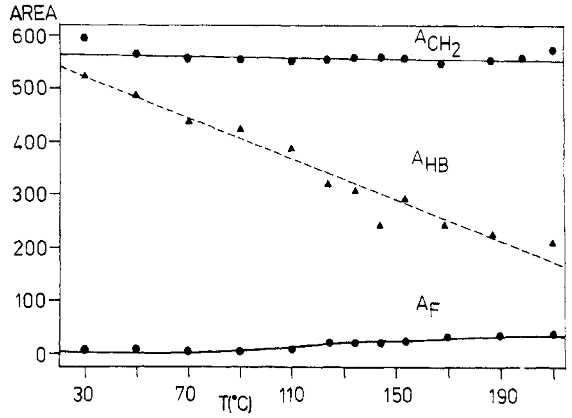

Figure 5. Plot of the *areas* attributed to the CH stretching bands (A_{CH_2}) and the hydrogen bonded (A_{HB}) and "free" (A_F) N–H stretching bands of PU64 obtained from curve fitting the infrared spectra recorded upon cooling from 210 °C.

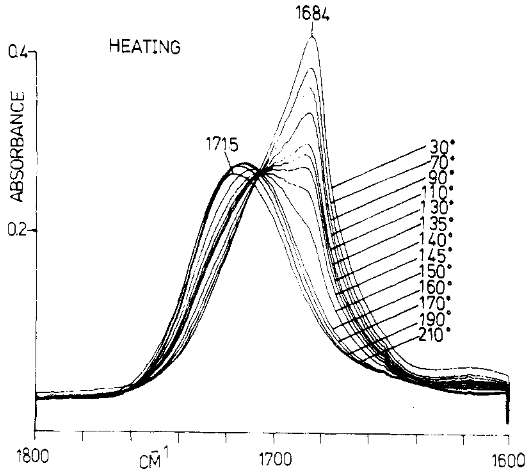

Figure 6. Infrared spectra, in the range 1600–1800 cm^{-1}, of the same sample of PU64 recorded as a function of *increasing* temperature from 30 to 210 °C. Note the spectra are recorded on an absolute absorbance scale.

The area changes with temperatures of the "free" (A_F) and hydrogen bonded (A_{HB}) N–H stretching bands are displayed graphically in Figure 5. The broken line drawn through the hydrogen bonded data is for illustrative purposes only. Although the data appears to fit a straight line reasonably well, we do not believe, given the number of variables involved, that is necessarily has any significance. The area of the CH stretching band envelope is also given in Figure 5. As mentioned previously, the essentially constant area with temperature is satisfying in that it indicates no loss of sample through degradation, etc.

Carbonyl Stretching Region. We return to Figure 1; the insert showing the carbonyl stretching region of the spectrum of PU64 recorded at room temperature suggests the presence of at least three bands, at about 1684, 1699, and 1721 cm^{-1}. From our previous studies of semicrystalline polyamides[2,3] we thought it likely that we would see bands that could be attributed to ordered and disordered hydrogen bonded carbonyl groups and "free" (non-hydrogen bonded) carbonyl groups, respectively. However, there is no evidence for a splitting of the ordered carbonyl peak due to dipole/dipole interactions. Examination of the spectra in the 1600–1800-cm^{-1} region recorded as a function of increasing (Figure 6) and decreasing (Figure 7) temperature supports this contention. These spectra

Table II
Curve-Fitting Results of the C=O Stretching Region

	"free" C=O			hydrogen bonded C=O											
				ordered				disordered							
temp, °C	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_F	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_O	A_O'[a]	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_D	A_D'[b]	A_T[c]	A_T'[d]	A_F/A_T'	A_O/A_T'
210	1724	34	345					1707	48	840	491	1185	836	0.41	
190	1723	34	326					1705	48	841	492	1167	818	0.40	
170	1723	34	316					1705	47	842	492	1158	808	0.39	
155	1723	34	308					1704	46	848	496	1156	804	0.38	
145	1723	34	306					1703	46	861	504	1167	810	0.38	
135	1723	34	306					1703	46	875	512	1181	818	0.37	
125	1722	34	293					1701	47	919	537	1212	830	0.35	
110	1723	34	137	1684	22	212	124	1704	44	894	523	1243	784	0.18	0.16
90	1723	34	115	1684	19	244	143	1702	45	947	554	1306	812	0.14	0.18
70	1721	34	95	1684	19	260	152	1700	45	966	565	1321	812	0.12	0.19
50	1721	34	85	1684	18	269	157	1700	44	957	560	1311	802	0.11	0.20
30	1721	34	93	1684	18	298	174	1699	43	994	581	1385	848	0.11	0.21

[a] $A_O' = A_O/1.71$. [b] $A_D' = A_D/1.71$. [c] $A_T = A_F + A_O + A_D$. [d] $A_T' = A_F + A_O' + A_D'$

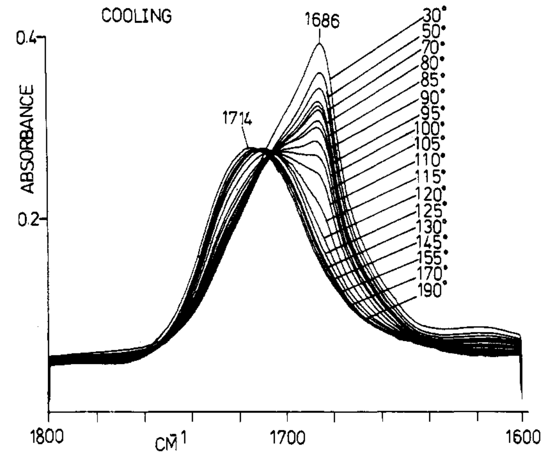

Figure 7. As in Figure 6 except that the spectra are recorded as a function of decreasing temperature from 210 °C.

are all recorded from the same sample and are displayed in absolute absorbance units. Qualitatively, the spectrum recorded at 30 °C (Figure 6) is dominated by a relatively sharp contribution at 1684 cm^{-1} with a second component apparent at about 1700 cm^{-1}. As the temperature is raised, the contribution from the component near 1684 cm^{-1} decreases and is replaced by spectral contributions at about 1700 and 1715 cm^{-1}. Between 150 and 160 °C the contribution from the ordered hydrogen bonded carbonyl band vanishes and a very broad band is observed that is composed of the disordered hydrogen bonded and "free" carbonyl bands. Thermal analysis performed at 20 °C/min reveals that the onset of melting occurs at about 165 °C. As the sample cools from 210 °C the trends are reversed (Figure 7) except that the first signs of an ordered hydrogen bonded component occurs at about 115 °C. Recrystallization of PU64 appears complete at about 125 °C in the thermal analysis experiment.

The presence of three major spectral components in the carbonyl stretching region is confirmed by second-derivative spectroscopy. An example, obtained from the sample cooled to 110 °C which is in the transition zone before significant crystallization has taken place, is shown in Figure 8. Second-derivative spectroscopy performed on the spectral data obtained throughout the temperature range yielded consistent evidence supporting only two or three bands contributing to the band envelope for the amorphous and semicrystalline materials, respectively.

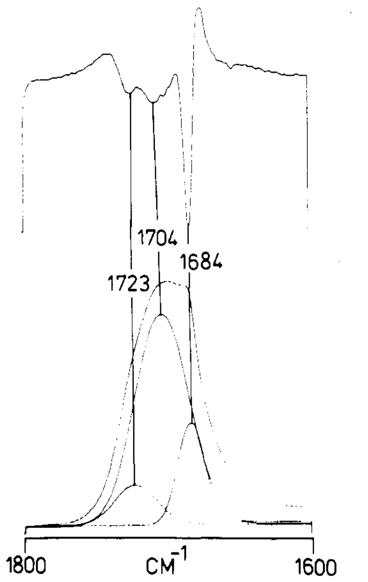

Figure 8. Infrared spectrum, in the range 1600–1800 cm^{-1}, of PU64 recorded at 110 °C upon cooling, together with the second derivative and the individual components comprising the band envelope.

Curve fitting of the carbonyl stretching region was performed in a manner similar to that described previously for the polyamides.[2,3] A linear base line was drawn between 2000 and 600 cm^{-1} through minima in the spectral data where there were no detectable absorptions. The limits of the curve-fitting procedure were set to between 1675 and 1740 cm^{-1}, which minimizes the effect of any absorptions in the wings of the band envelope. Three Gaussian bands, corresponding to "free" and hydrogen bonded disordered and ordered carbonyl groups, were employed in the curve-fitting procedure. At the higher temperatures no contribution from the ordered hydrogen bonded carbonyl band was necessary and only two bands were used in curve fitting. An iterative least-squares computer program was used to obtain the best fit of the experimental data by varying the frequency (ν), width at half-height ($W_{1/2}$), and intensity of the three bands. Representative examples of the spectral components obtained from the curve-fitting procedure for the PU64 sample as it is cooled from 210 °C are shown in Figure 9.

The complete curve-fitting analysis of the carbonyl stretching region of PU64 as a function of decreasing temperature is given in Table II. The results are immediately gratifying and consistent with our spectroscopic prejudices. First, the "free" carbonyl band shifts slightly to lower frequency with decreasing temperature (3 cm^{-1} from 210 to 30 °C) and remains at constant breadth ($W_{1/2}$ = 34 cm^{-1}). The area of the "free" band (A_F) decreases

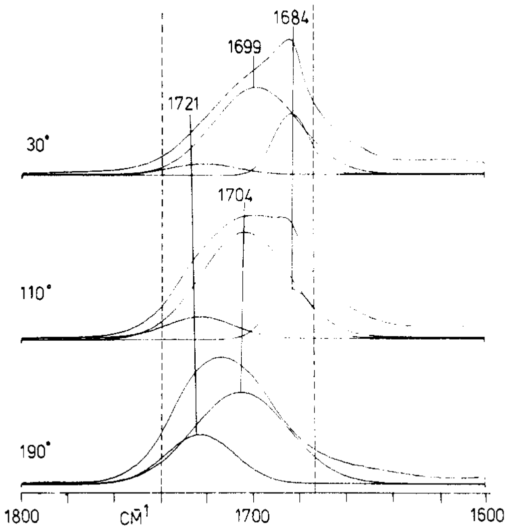

Figure 9. Curve-fitting results in the carbonyl stretching region of the PU64 spectra recorded at 190, 110, and 30 °C during cooling of the sample from 210 °C. The broken lines represent the limits of the frequency range used in the curve-fitting procedure.

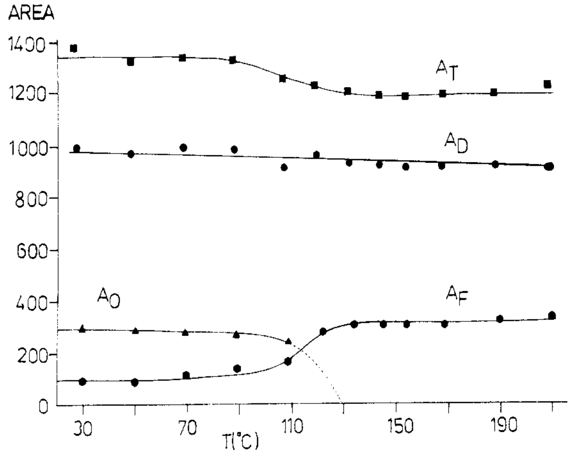

Figure 10. Plot of the *areas* attributed to "free" (A_F) and hydrogen bonded ordered (A_O) and disordered (A_D) carbonyl stretching bands of PU64 obtained from curve fitting the infrared spectra recorded upon cooling from 210 °C. A_T is the total area.

gradually from 210 to 125 °C, whereupon there is a jump to about one-third of the area as the sample crystallizes at temperatures below 120 °C. This is illustrated graphically in Figure 10. The ordered hydrogen bonded carbonyl band does not contribute until the temperature is below 125 °C and the sample has crystallized to some extent. As we would expect the band is narrower ($W_{1/2} = \sim 20$ cm^{-1}) than either the "free" or disordered hydrogen bonded carbonyl bands. The area of the ordered hydrogen bonded carbonyl band (A_O) increases with decreasing temperature (and time?), reflecting an increase in the degree of order. The disordered hydrogen bonded carbonyl band is at least twice as broad ($W_{1/2} = 46 \pm 2$ cm^{-1}) as its ordered counterpart, again a predictable result. The frequency varies from 1707 to 1699 cm^{-1} systematically over the complete temperature range. The areas of the disordered hydrogen bonded carbonyl band (A_D) and the total area of the three bands comprising the carbonyl region ($A_T = A_F + A_O + A_D$) as a function of temperature are also shown in Figure 10.

In our previous studies of polyamides we made the assumption that the absorption coefficients of the three carbonyl bands making up the amide I band envelope (i.e., "free" and ordered and disordered hydrogen bonded) were not radically different. (An assumption that, incidentally, cannot be reasonably applied to the N–H stretching mode.) A constant total area as the three bands vary in intensity with temperature is good evidence for the validity of this assumption. Indeed in the case of the polyamides studied there was only a relatively small change in total area.[2,3] However, there was also little change in the area of the "free" vs. hydrogen bonded (ordered plus disordered) bands with temperature. Accordingly, if the fraction of "free" carbonyl groups is small and does not vary significantly with temperature, the total area will appear to be reasonably constant. In other systems, it is well-known that the absorption coefficient of carbonyl bands attributed to hydrogen bonded groups is greater than the corresponding "free" groups. In fact, in our own work of ethylene/vinyl acetate copolymer blends with poly(vinylphenol) we estimated a value of 1.5 for the ratio of the absorptivity coefficients of the hydrogen bonded to the "free" carbonyl bands.[17] A similar conclusion was reached by Garton for phenoxy blends with poly(caprolactone).[18]

We return to Figure 10; it is evident that the total area A_T is not constant over the temperature range explored and that the area of the "free" band (A_F) is not just a minor fraction of the total area. As we are confident from our measurements of the CH stretching region (see Figure 5) that we have not lost any of the sample through degradation or flow out of the infrared cell, it seems reasonable to assume that the changes in total area in the carbonyl stretching region primarily reflect the differences in the absorptivity coefficients of the "free" and hydrogen bonded bands. We are tacitly assuming that the absorptivity coefficients of the ordered and disordered hydrogen bonded carbonyl bands are identical. This is plainly simplistic given the data obtained and the arguments presented in our previous studies of the N–H stretching region of polyamides[1-3] and the polyurethane discussed here. The differences between the absorptivity coefficients of hydrogen bonded carbonyl bands, however, is much less than their N–H stretching counterparts. In truth, we are assuming that the difference in absorptivity coefficients between "free" and hydrogen bonded (both ordered and disordered) carbonyl bands is much greater than that between ordered and disordered hydrogen bonded carbonyl bands. Thus we can combine the latter into an *average* absorptivity coefficient. We are under no illusions that this is anything but a first-order approximation.

In order to "correct" the data shown in Table II to account for the difference in the absorptivity coefficients of the "free" (a_F) and hydrogen bonded (a_{HB}) carbonyl bands, the areas corresponding to the hydrogen bonded bands (A_O and A_D) were divided by a constant, k, the value of which was varied until the total area $A_T' = A_F + A_O' + A_D'$ was constant within error over the total temperature range. The constant, k, is the ratio of the absorptivity coefficients, as the following argument demonstrates:

$$A_{HB}^{Ti} = A_O^{Ti} + A_D^{Ti}$$

$$A_T^{T1} = A_F^{T1} + A_{HB}^{T1} \quad \text{at temperature } T1$$

$$A_T^{T2} = A_F^{T2} + A_{HB}^{T2} \quad \text{at temperature } T2$$

Dividing A_{HB} by k such that $A_T^{T1} = A_T^{T2} = A_T'$ yields

$$k = (A_{HB}^{T2} - A_{HB}^{T1})/(A_F^{T1} - A_F^{T2})$$

Now $A_{HB}^{Ti} = a_{HB}x^{Ti}$; where x_{HB} is the fraction of carbonyl groups that are hydrogen bonded. Thus $A_F^{Ti} = a_F(1 - x^{Ti})$ and

$$k = a_{HB}(x^{T2} - x^{T1})/a^F[(1 - x^{T1}) - (1 - x^{T2})]$$

$$k = a_{HB}/a_F$$

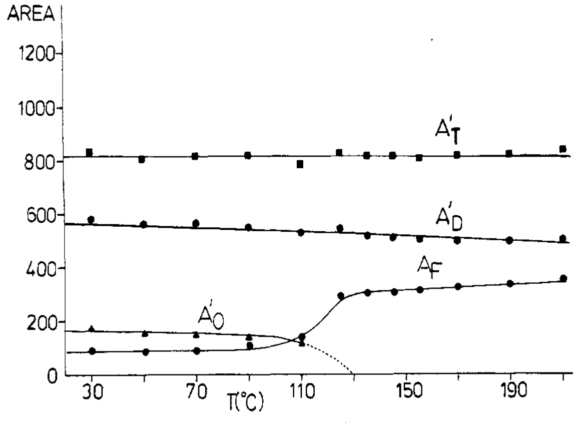

Figure 11. Plot of the areas corrected for variations in the absorptivity coefficients of "free" and hydrogen bonded carbonyl bands (see text).

A simple computer program was written to determine the value of the absorptivity ratio, k, using all the data in an iterative least-squares minimization of the differences in calculated total area. A value of $k = 1.71$ was determined and the "adjusted" values of the ordered (A_{O}'), disordered (A_{D}') and total (A_{T}') areas are included in Table II and displayed graphically in Figure 11. The adjusted total area (A_{T}') appears constant within error over the full temperature range considered. If our assumptions are valid, then the data presented in Figure 11 represent a quantitative measure of the fraction of "free" and hydrogen bonded carbonyl groups present in PU64 as it is cooled from 210 to 30 °C under our specific experimental conditions.

The fraction of "free" carbonyl groups is simply $A_{\mathrm{F}}/A_{\mathrm{T}}'$. At 210 °C we estimated that roughly 40% of the total carbonyl groups are not hydrogen bonded. Upon cooling to 125 °C, while the sample is still in the amorphous state, the concentration of "free" groups decreases gradually to about 35%. There is a marked decrease in the concentration of "free" carbonyls as crystallization takes place below 125 °C, and a steady decrease from 18 to 11% occurs with further cooling to room temperature. Meanwhile, the concentration of ordered hydrogen bonded carbonyl groups increases from about 16 to 21% over the same temperature range.

N–H Stretching Region (Revisited). Assuming that the values of the concentration of "free" carbonyl groups as a function of temperature ($A_{\mathrm{F}}/A_{\mathrm{T}}'$ in Table II) are correct, it should now be possible to return to the N–H stretching region and estimate the absorptivity ratio between the infrared bands attributed to "free" and hydrogen bonded N–H groups at a particular temperature. In addition, an indication of how the absorptivity ratio varies with the average strength of the hydrogen bonds may be gained from a comparison of the estimates obtained at the different temperatures. For example, at 210 °C, the fraction of "free" carbonyl groups is 0.41 (table II) while the areas determined for the "free" (A_{F}) and hydrogen bonded (A_{HB}) N–H stretching bands are 50 and 210 units, respectively (Table I). A simple calculation reveals that an absorptivity ratio of $a_{\mathrm{HB}}/a_{\mathrm{F}} = 2.9$ is required to yield a "free" fraction of 0.41. Please note that a_{HB} is an *average* value representing the mean value of the strengths of the hydrogen bonds at this temperature.[2] Furthermore, this calculated ratio should not be taken too literally because of the possible errors introduced by Fermi resonance. Similar calculations reveal that the absorptivity ratio increases from about 2.9 to 5.4 over the range from 210 to 125 °C. In other words, as the average strength of the hydrogen bonds increases upon cooling and as the hydrogen bonded N–H stretching band shifts to lower frequency by approximately 10 cm^{-1} (Table I), the absorptivity coefficient nearly doubles. This is in pleasing agreement with the findings we published concerning the amorphous polyamide system.[1] We do not have sufficient confidence in the values obtained for the "free" N–H band areas below 125 °C to warrant further calculations. We anticipate, however, that the value of the absorptivity ratio continues to increase sharply as the frequency of the hydrogen bonded N–H band shifts to lower frequency. This, of course, reemphasizes the inherent difficulties in employing the N–H stretching region for quantitative measurements of "free" and hydrogen bonded groups in polyamides and polyurethanes.

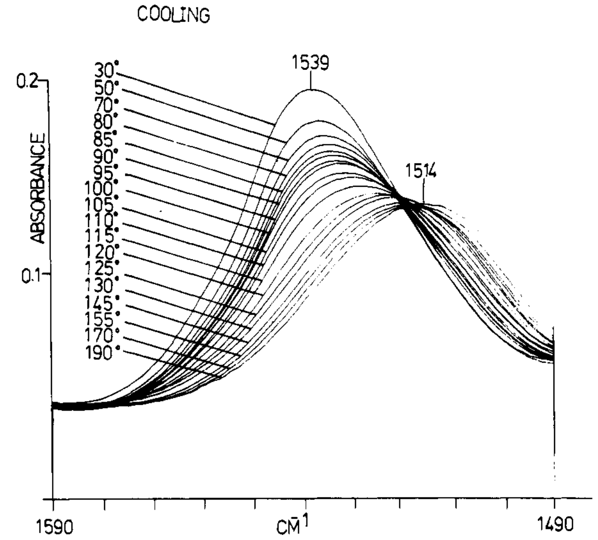

Figure 12. Infrared spectra, in the range 1490–1590 cm^{-1}, of the same sample of PU64 recorded as a function of decreasing temperature from 210 °C. Note the spectra are presented on an absolute absorbance scale.

Region below 1600 cm^{-1}. We will limit ourselves to relatively brief comments on the spectral changes that are observed with temperature in the region between 1600 and 450 cm^{-1}. Normal vibrations in this region of the infrared spectrum are generally highly mixed and coupled; i.e., they contain appreciable contributions to the potential energy distribution from a number of different motions. For example, in simple highly ordered polyamides the amide II vibration is composed of about 40% N–H in-plane bend, 25% C–N stretch, 20% C–C$^{\alpha}$ stretch and 10% N–C$^{\alpha}$ stretch.[19] This type of normal vibration is sensitive to conformation and intermolecular hydrogen bonding, which in turn are functions of temperature, thermal history, degree of order, etc., and which leads to a complexity that defies simple interpretation. In other words, it is not a straightforward task to differentiate between conformational and interactional effects that occur in the infrared temperature studies from these highly mixed modes. With the above reservations in mind there are nonetheless some interesting infrared spectral changes occurring with temperature that warrant at least qualitative description.

The infrared band of medium intensity centered at about 1540 cm^{-1} (Figure 1) is akin to the amide II mode found in polyamides and polypeptides. As indicated above, the amide II mode contains a major contribution from the N–H in-plane bending vibration and it is sensitive to both chain conformation and intermolecular hydrogen bonding.[2,3] Figure 12 shows the effect of temperature upon this mode in PU64 as it is cooled from the melt. The band shifts to higher frequency (from 1514 to 1539 cm^{-1}) and

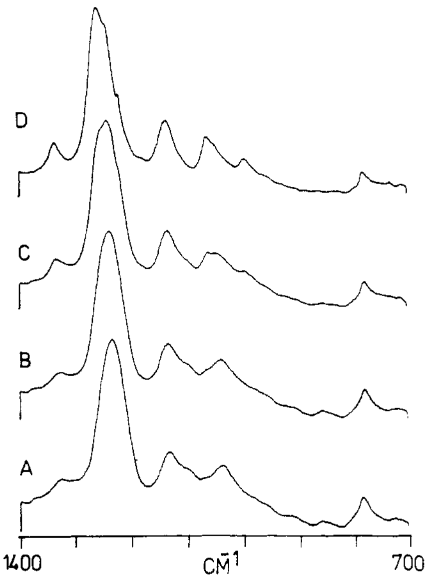

Figure 13. Infrared spectra, in the range 700–1400 cm^{-1}, of the same sample of PU64, recorded upon cooling at (A) 190, (B) 125, (C) 110, and (D) 30 °C.

gains intensity as the temperature is reduced from 190 to 30 °C. The trend is identical with that observed for the polyamides previously studied.[2,3] The overall character of this mode is similar to that of the N–H stretching vibration in that there are no obvious separate contributions from ordered and disordered hydrogen bonded domains. Additionally, there is no evidence for a distinct "free" band in the envelope. In essence, the "amide II" mode in polyurethanes reflects the distribution of hydrogen bond strengths similar to that of the N–H stretching vibration.

Representative spectra in the 700–1400-cm^{-1} region, obtained as the sample was cooled from the melt, are shown in Figure 13. A precise description of the potential energy distribution of the normal modes observed in the region between 1300 and 1000 cm^{-1} is not available even for the preferred crystalline infinite chain conformation. However, we know that the vibrations are highly mixed and are composed of motions associated with numerous stretching and bending vibrations, including the C–O stretch. Accordingly, the spectral differences with temperature seen in Figure 13, especially those in the 1200–1300-cm^{-1} and 1000–1100-cm^{-1} region, are attributable to both conformational (ordered, preferred conformation, and disordered, amorphous conformations) and interactional (strength and degree of intermolecular hydrogen bonding) contributions.

Spectral subtraction of one infrared spectrum from another acquired at a different temperature has not been widely applied to polymers that are strongly self-associated or to polymer blends where there are strong intermolecular interactions between the components.[20] This is because the frequency shifts of bands containing contributions from motions affected by hydrogen bonding lead to derivative type features that are difficult to interpret. On the other hand, difference spectroscopy applied to infrared spectra of PU64 samples of different morphologies recorded at the *same temperature* are pleasingly "clean" and do not exhibit significant distortions to the band shapes. Figure 14 shows a typical example. (For illustrative purposes the individual spectra are scale expanded in the three spectral regions and cannot be directly compared with respect to intensity.) Spectrum B was recorded at 130 °C from the PU64 sample during the heating cycle while the sample was still semicrystalline. Spectrum A is of the same sample recorded at the same temperature during the cooling cycle before any appreciable crystallization had taken place. The difference spectrum (B – A) was obtained by trial and error using different values of a subtraction parameter until a maximum amount of spectrum A was removed without distortion to the band shapes. A value for the subtraction parameter of 0.8 was determined. As the amount of sample in the infrared beam is constant, this is directly related to the fraction of the amorphous spectrum removed. This is very gratifying, as it corresponds to a degree of order of 1 – 0.8 = 0.2, which is consistent with the results obtained from curve resolving the carbonyl stretching region (Table II).

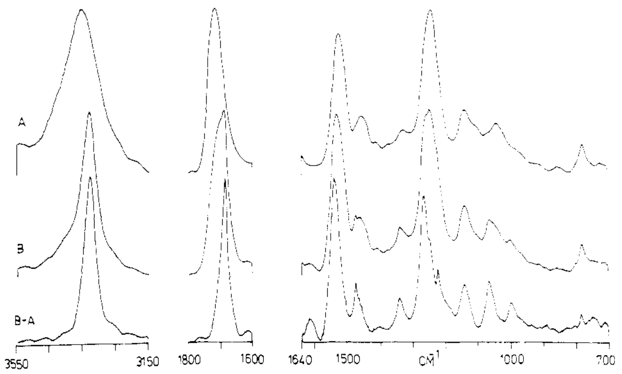

Figure 14. Scale-expanded infrared spectra of PU64 recorded at the *same* temperature, 130 °C: (A) spectrum recorded upon cooling from 210 °C; (B) spectrum recorded upon heating from 30 °C and (B – A) difference spectrum.

The difference spectrum represents the infrared spectrum of PU64 in the ordered state at 130 °C. To be more accurate, the spectrum reflects that of a single chain in a preferred conformation that is perturbed by the presence of intermolecular hydrogen bonding at 130 °C. As one would expect the N–H stretching (3341 cm^{-1}), the C=O stretching (1684 cm^{-1}) and the predominantly N–H in-plane (1540 cm^{-1}) bands of the ordered material are relatively sharp, reflecting narrow distributions of both chain conformations and intermolecular hydrogen bonded distances and geometries. Other relatively sharp bands at 1000, 1069, 1223, 1250, 1270, 1340, and 1475 cm^{-1} can readily be attributed to the ordered state.

Conclusions

In general, our interpretation of the infrared spectral changes observed with temperature for a linear, aliphatic, semicrystalline polyurethane has much in common with our previous studies of analogous semicrystalline polyamides.

The N–H stretching region contains separate infrared bands attributed to "free" and hydrogen bonded N–H groups. The latter primarily reflects the distribution of the strength of the hydrogen bonds. An important two-phonon band also contributes to the N–H stretching band envelope in PU64 and must be taken into account. In common with polyamides, the intensity (area) of the hydrogen bonded N–H stretching band of PU64 varies dramatically with temperature. This is not simply the result of hydrogen bonded N–H groups transforming to "free" groups but is primarily a consequence of the strong dependence of the absorptivity coefficient with the strength of the hydrogen bond, which, in turn, varies with temperature. Even if it were possible to accurately measure the area contributions from "free" and hydrogen bonded N–H groups as a function of temperature—a dubious assumption at best given the problems of measuring the area of the "free" band—a function describing the variation of

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absorptivity coefficient with frequency would be required for quantitative analysis. To add to the misery, the validity of the van't Hoff procedure to determine the enthalpy of hydrogen bond formation must be questioned when we have direct evidence that the average strength of the hydrogen bond is not constant with temperature. We reluctantly conclude that we cannot simply describe the average strength of the intermolecular hydrogen bond in polyurethanes and polyamides in terms of a single ΔH.

The carbonyl stretching region of the infrared spectrum of PU64, which is analogous to the amide I region of polyamides, contains contributions attributed to ordered and disordered hydrogen bonded carbonyl groups together with "free" groups. Distinction between ordered and disordered hydrogen bonded carbonyl groups is a consequence of dipole/dipole interactions. The difference between the absorptivity coefficients of the "free" and hydrogen bonded carbonyl bands is significant but not radical as in the case of the N–H stretching mode. Accordingly, quantitative analysis is feasible with a procedure that accounts for the variation of absorptivity coefficients of the different carbonyl bands. Approximately 40% of the carbonyl groups in PU64 are "free" at 200 °C in the amorphous state.

The infrared band observed in the spectrum of PU64 at approximately 1540 cm^{-1} is akin to the amide II band in polyamides and contains an appreciable contribution from the N–H in-plane bending vibration. The striking shift to lower frequency with temperature is again an indication of the weakening of the hydrogen bonds. Significant changes in the spectra recorded at different temperatures are also seen in the region below 1500 cm^{-1}. An undistorted difference spectrum, representing the preferred polymer chain conformation perturbed by intermolecular hydrogen bonding, was successfully obtained by subtracting the amorphous spectrum from that of a semicrystalline spectrum, both recorded at the same temperature. The degree of order suggested by the subtraction procedure was in agreement with that determined independently from curve fitting the carbonyl region of the spectrum.

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Registry No. (Hexamethylene diisocyanate)·(1,4-butanediol) (homopolymer), 25748-74-7; poly(1,4-butylene hexamethylenecarbamate), 25035-42-1.

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Mass Spectrometric Analysis of the Thermal Degradation Products of Poly(*o*-, *m*-, and *p*-phenylene sulfide) and of the Oligomers Produced in the Synthesis of These Polymers

G. Montaudo,*† C. Puglisi,‡ E. Scamporrino,† and D. Vitalini‡

Dipartimento di Scienze Chimiche, Università di Catania, and Istituto per la Chimica e la Tecnologia dei Materiali Polimerici, CNR, 95125 Catania, Italy. *Received February 20, 1986*

ABSTRACT: Gel permeation chromatography and mass spectrometry have been used to detect and identify the oligomers formed in the polymerization reactions leading to poly(*o*-phenylene sulfide) (*o*-PPS), poly(*m*-phenylene sulfide) (*m*-PPS), and poly(*p*-phenylene sulfide) (*p*-PPS). The thermal degradation of *o*-PPS, *m*-PPS, and *p*-PPS was investigated by direct pyrolysis in the ion source of a mass spectrometer. The results indicate that *o*-PPS, *m*-PPS, and *p*-PPS decompose, producing cyclic oligomers. The distribution of the pyrolysis products is different in the three cases and is dependent on the structure of each isomeric polymer.

Introduction

The formation of cyclic oligomers in polycondensation reactions is a phenomenon frequently observed.[1-5]

Current methods of detecting oligomers contained in polymer samples are based on gas, liquid, and size-exclusion chromatography, followed by a suitable method of structural identification. These techniques are indeed powerful, but sometimes low volatility of samples, low solubility, and low resolution problems in gel permeation chromatogtraphy (GPC) make alternative and rapid methods of detection and identification for mixtures of low molecular weight compounds highly desirable.

Mass spectrometry (MS) is particularly suitable to the detection of these materials since they are volatile under

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† Università di Catania.

‡ Istituto per la Chimica e la Technologia dei Materiali Polimerici.

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