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Fourier Transform Infrared Spectroscopy Study on Effects of Temperature on Hydrogen Bonding in Amine-Containing Polyurethanes and Poly(urethane−urea)s

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ABSTRACT: Three types of amine-containing polyurethanes and poly(urethane−ureas), *N*-methyldiethanolamine (MDEA) and/or tetraethylenepentamine (TEPA) as the chain extender and poly(ethylene glycol) of MW 400 as the soft-segment component, have been studied by FTIR. The hydrogen bonding in hard and soft segments was examined for the extent of phase separation, and the microstructure was evidenced by differential scanning calorimetry (DSC). The temperature effects on the hydrogen bonding were also investigated. They show a significant amount of hydrogen bonding between the hard and soft segments. It indicates that there exists a large amount of partial phase mixing of hard and soft segments compared to the conventional polyurethanes. The bulky CH_3 groups of MDEA in hard segments restrict the hydrogen bonding within the hard segments, while the TEPA-containing urethane−urea polymers have more distinct phase separation. However, all of the polymers studied are amorphous materials such that the dissolved soft segments in the hard-segment domains may interfere with molecular packing in the domains. It shows that the hydrogen bonding in these polymers persists up to 200 °C. The hydrogen bonding of NH to the ether oxygen decreases significantly at $T > 50$ °C.

Introduction

Polyurethanes are usually composed of a polyether or polyester soft segment and a diisocyanate-based hard segment. From the viewpoint of the chemical structures of the hard segments, polyurethanes may be classified into urethane polymers (PU) which are formed by extending a diisocyanate with a low-molecular-weight diol such as 1,4-butanediol and urethane−urea polymers (PUU) which are formed by extending a diisocyanate with a low-molecular-weight diamine such as ethylenediamine. Because of the immiscibility between the hard segment and the soft segment, polyurethanes undergo microphase separation resulting in a hard-segment domain, soft-segment matrix, and poorly characterized interphase. The hard-segment domains act as physical cross-links as well as filler particles for the soft-segment matrix. The primary driving force for domain formation is the strong intermolecular interaction of hydrogen bonding between the hard−hard segments of urethane and/or urea linkages. It has also been shown that some hard segments are dissolved in the soft-segment matrix phase.[1−6]

Hydrogen bondings in polyurethanes have been extensively studied using infrared spectroscopy,[3−24] which has been demonstrated as a particularly useful tool in characterizing the hydrogen-bonding characteristics in the domain. The hydrogen bonding is evidenced by a frequency shift to values lower than those observed when these groups are free (i.e., not hydrogen bonded). The magnitude of the frequency shift is a measure of hydrogen-bonding strength. In the polyether-based polyurethanes, the fraction of the hydrogen-bonded carbonyls, which is characterized by a hard−hard segment hydrogen bond (NH- - -O═C bond), was used as a measure of the extent of phase separation. The NH group could also form a hard−soft segment hydrogen bond with the ether oxygen (NH- - -O-bond), which represents the extent of phase mixing between hard and soft segments. It is also known that the MDI- and TDI-based polyether PUUs show the presence of three-dimensional hydrogen bonding between the hard segments where each urea carbonyl was bonded to two NH groups.[3,10,11] The various studies of effects of temperature on H bonding indicate that the absorption coefficient of a particular band is a strong function of frequency. That is, as the temperature is increased, the average strength of the hydrogen bonds decreases, which is observed as an infrared absorbance peak shifted to a higher frequency. Meanwhile, the absorption coefficient decreases, leading to a reduction in the intensity of the band.[13,19,25,26]

In this work, infrared spectra of three types of amine-containing polyurethanes and poly(urethane−urea)s were obtained by using Fourier transform infrared spectrophotometry (FTIR). The effects of the hard segments on the hydrogen bonding and the extent of phase separation in these polymers are studied. Variation of hydrogen bonds in the polyurethanes with temperature was also examined.

Experimental Section

Polymers. The polymers studied were a series of amine-containing polyurethanes and poly(urethane−urea)s with a nominal hard-segment content of 60%. Poly(ethylene glycol) (PEG) of MW 400 was used as the soft-segment component. The hard segment was composed of 4,4′-diphenylmethane diisocyanate (MDI) chain-extended with *N*-methyldiethanolamine (MDEA) and/or tetraethylenepentamine (TEPA). The polymers were prepared by a two-step process in *N,N*-dimethylformamide (DMF) as done elsewhere.[3,27] Details of the polymerization procedures have been described previously.[28] There are MDEA-extended polyurethane and TEPA-extended poly(urethane−urea) which are denoted 4MPU and 4TPUU, respectively, whereas 4MTPUU is composed of MDEA and TEPA with mol ratio of 1/1 as chain extender.

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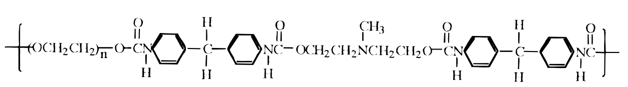
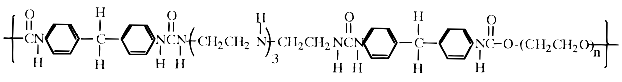
The chemical structures are shown as follows:

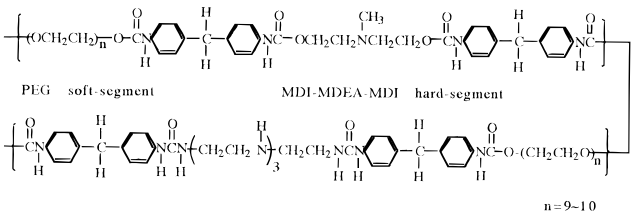
(1) MDEA-extended polyurethane (4MPU)



(2) TEPA-extended polyurethane-urea (4TPUU)



(3) MDEA/TEPA (1/1 by mole)-extended polyurethane-urea (4MTPUU)



Thermogravimetric Analysis (TGA). TGA was measured by a DuPont-951 thermal analysis system. The sample was scanned at a rate of 20 °C/min under nitrogen purging. All the samples were prepared as films and employed a range in mass of about 10 mg.

Thermal Analysis. Thermal transition data were obtained by a DuPont DSC 2910 differential scanning calorimeter linked to a TA Instrument Thermal Analysis 2000 system for data acquisition. The samples were scanned from −40° to +250 °C at a rate of 10 °C/min under nitrogen purging. The sample films were approximately 20 mg in mass. Glass transition temperatures (T_g) are reported for the midpoint of the glass transition process.

Infrared Analysis. The samples for infrared analysis were prepared by solution casting of 1% (w/v) polymer in DMF directly onto KBr pellets and dried at 80 °C. Following evaporation of most of the solvent, the samples were placed in vacuum at 50 °C for about 3 days to remove the residual solvent. The films used in this study were sufficiently thin to be within the absorbance range where the Beer−Lambert law is valid.

Infrared spectra were obtained with a Fourier transform IR spectrophotometer (Bio-Rad FTS-40A) and recorded by averaging 64 scans at a resolution of 2 cm^{-1}. For the temperature scans, the sample was placed in a variable-temperature cell (Graseby Specac Limited, P/N 21500) connected to a temperature controller (Graseby Specac Limited, P/N 20120 series). The temperature was held constant for about 45−60 min before collection of spectra was initiated. Correction to raw spectra data was normalization of absorbances for sample thickness. Further, the thickness of a given sample usually changed during heating as a result of thermal expansion. To correct for sample thickness, the CH_2 stretch near 2905 cm^{-1} was used as the normalizing factor. Therefore, all reported areas have been normalized to the integrated area of the CH_2 stretching vibration.

Results and Discussion

Table 1 shows the characteristics of the three polymers studied. It shows that the polymers have an onset decomposition temperature (T_d) around 340 °C, and the residue is 6.9−10.3%. As compared to conventional polyurethane,[27] the polymers studied have a higher thermal stability property. This indicates that no weight loss would occur for these polymers within the temperature range 30−200 °C in the FTIR study. Figure 1 shows the DSC thermogram of these polymers. It shows that there was no crystallinity observed up to 250 °C. It indicates that the polymers studied are amorphous polymers. The T_g data are summarized in Table 1. For these polymers studied a soft-segment T_g of −4 to +28 °C was observed, which is substantially higher than that of pure PEG (ca. −40 °C).[29] This indicates that the polymers have a certain degree of hard- and soft-segment mixing. The soft-segment T_g decreases in the order 4MPU > 4MTPUU > 4TPUU. Thus the phase separation increases in the order 4MPU > 4MTPUU > 4TPUU. The hard-segment T_g's of 4MTPUU and 4TPUU are observed in the range 54−68 °C, however; the hard-segment T_g of 4MPU is not detected. Seymour and Cooper[30−32] have studied the thermal transition behavior of MDI-based polyurethanes using DSC analysis. Three characteristic endotherm transitions were observed at temperatures of 60−80, 120−190, and 200 °C. These endotherms were correlated respectively with the short range, long range, and microcrystalline ordering of hard-segment domains. Therefore, the observed hard-segment T_g may be attributed to phase-segregated structures of the shorter hard-segment unit. Further, it is consistent with the soft-segment T_g so that the TEPA-containing polymers exhibit more distinct phase separation.

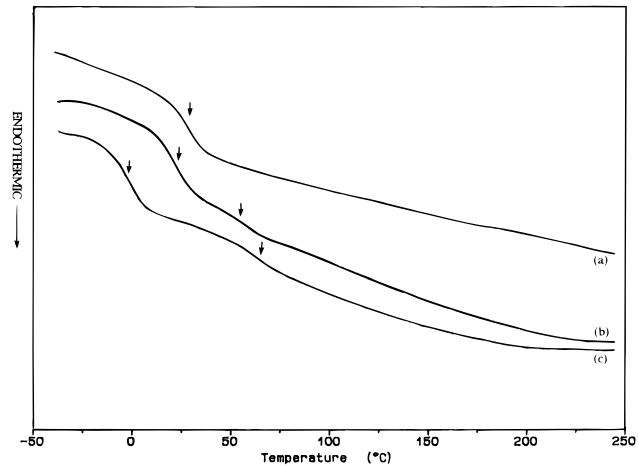


Figure 1. DSC thermogram of the polyurethanes: (a) 4MPU; (b) 4MTPUU; (c) 4TPUU.

Table 1. Characteristic of the Amine-Containing Polyurethane and Poly(urethane−urea)

		TGA		DSC T_g (°C)	
sample designation	PEG (wt %)	T_d (°C)	residue (%)	soft segment	hard segment
4MPU	39.2	330	6.9	27.7	
4MTPUU	37.2	344	7.7	23.1	53.5
4TPUU	36.7	346	10.3	−3.6	67.6

Infrared Analysis. The FTIR spectra of the three polymers at 30 °C are shown in Figure 2. The CH_{asym} and CH_{sym} stretching vibration peaks of the PEG soft segments are located at 2905 and 2870 cm^{-1}, respectively. Two main spectra regions in this study are of main interest: the NH stretching vibration from 3150 to 3500 cm^{-1} as well as the carbonyl stretching vibration from 1600 to 1800 cm^{-1}. The experiments were designed to follow the infrared absorption of the two spectral regions as a function of temperature in order to directly study the extent and strength of both hard−hard and hard−soft segment hydrogen bonding.

NH Stretching Region. Figure 3 shows the IR spectra of the NH stretching region heating from 30 to 200 °C for each of the three polymers. In each spectrum

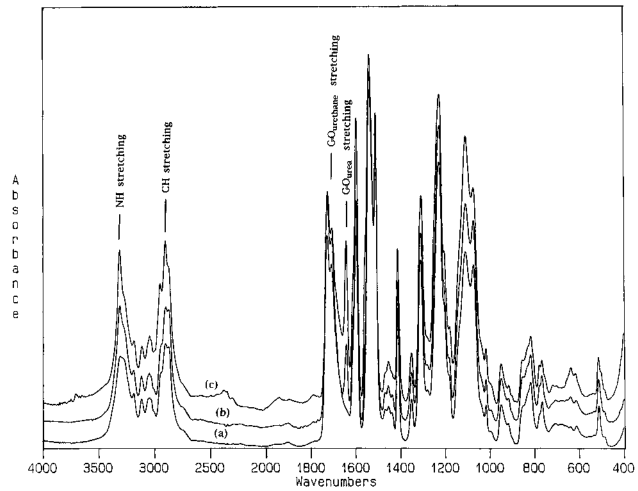


Figure 2. FTIR spectra of the polyurethanes at 30 °C : (a) 4MPU; (b) 4MTPUU; (c) 4TPUU.

at 30 °C, the NH stretching vibration exhibits a strong absorption peak centered at around 3315 cm^{-1} arising from the hydrogen bonding of NH to carbonyl groups, while the free NH stretching vibration appears as a weak shoulder at about 3445 cm^{-1}. Note that there appears another obvious shoulder or peak at 3268 cm^{-1}. This is different from some previous reports,[5-7,9,11] which show only a strong absorption peak or broader peak for the hydrogen-bonded NH stretching mode in conventional polyurethanes. Lee et al. show that the stretching vibration of the NH- - -O– hydrogen bond at 3295 cm^{-1} is only observed in the quenched polyurethane sample maintained below the soft-segment T_g and thus represents the phase-mixed state.[15] Further evidence for the NH- - -O- hydrogen bond is obtained from the frequency of the NH stretching vibration at 3258–3265 cm^{-1}.[14] The present work indicates that there is a large number of hard–soft segment hydrogen bonds in the polymers studied. It is consistent with the DSC data that these polymers have a certain degree of hard- and soft-segment mixing.

The spectra of the NH stretching region recorded as a function of decreasing temperature are shown in Figure 4. An "Initial" spectrum at 30 °C prior to heating is included for comparison. In fact, the weight loss of the sample was due to degradation at elevated temperatures. However, the TGA analysis indicated that the polymers studied are highly thermally stable. One observed that the spectra of samples upon heating closely match those obtained during cooling at all temperatures. This indicates that reproducibility of the results was observed throughout the temperature study.

Deconvolution of the NH stretching region was done using the Bandfit software. The best fits were obtained using a Gaussian–Lorentzian sum. The maximum frequency (v) and area of each band were determined using the Nelder–Mead optimization method. The root mean square (RMS) deviations were smaller than 0.001 for all three polymers at all temperatures. The smaller the RMS deviation is, the better the fit. This shows excellent analytical fits were obtained. The wavenumber of the free NH stretching vibration for all samples remained essentially constant at all temperatures, with the values between 3445 ± 2 cm^{-1}. While the v of hydrogen bonding of NH to carbonyls in 4MPU, 4MTPUU, and 4TPUU shift from 3317 to 3320, 3314 to 3320, and 3314 to 3319 cm^{-1}, respectively, the v of hydrogen bonding of NH groups to ether oxygens of the PEG soft segment in 4MPU, 4MTPUU, and 4TPUU shift from 3264 to 3267, 3269 to 3278, and 3270 to 3280 cm^{-1}, respectively. The shift of v to lower values in the hard–hard segments of 4TPUU and 4MTPUU, as well as those in hard–soft segments of 4MPU were obtained at room temperature. It implies that the introduction of TEPA in 4TPUU and 4MTPUU gives a strong hydrogen bond in the hard segments. In contrast, the average strength of the hydrogen bond of 4MPU in hard–soft segments is greater than that of 4MTPUU and 4TPUU. Pimentel and Sederholm[33] have found a linear relationship between the bond distance (R) of NH- - -O=C and the frequency shift (Δv) of the NH absorption band caused by hydrogen bonding, expressed as follows:

$$\Delta\nu = 0.548 \times 10^3 \,(3.21 - R) \qquad (1)$$

Accordingly, the values of R of these polymers were estimated to be 3.15–3.16 Å. These are higher than that reported by Brunette et al.[12] in a crystalline model urethane based on MDI-BD, the R varies between 2.90 and 3.02 Å. This provides evidence that the hard-segment domains are packed in a less ordered arrangement.

Figure 5 shows the plot of the normalized area of the NH stretching region vs temperature. The areas of the free NH groups increase over the ranges of temperature studied. The areas of the NH hydrogen-bonded to carbonyls decrease with increasing temperature. However, the polymers exhibit a transition in the slope for the NH bonded to ether oxygen at about 50 °C. The literature[1,21] report that the dissociation of hard–hard segment hydrogen bonding occurs at 80–100 °C. Notably, below 50 °C the slopes do not change as significantly as above 50 °C. This implies that the strength of hydrogen bonds is weakened at $T > 50$ °C where the segment mobility of the polymer chains becomes more significant at its rubbery state. When $T > 50$ °C, the areas of the NH hydrogen-bonded to ether oxygens decrease with increasing temperature. The area of the NH hydrogen-bonded to ether oxygens decreases more significantly than that of the NH hydrogen-bonded to carbonyl groups. It indicates that the hard–soft segments are more weakly hydrogen-bonded than the hard–hard segments. Although the intensity of hydrogen bonding of hard–hard segments was found to decrease with increasing temperature, a significant concentration of these bands remained intact even at 200 °C. The dissociation of the hard–hard segment hydrogen bonds of polyurethanes have been reported to be at about 140–170 °C.[1,21] Thus, the polymers have stabilized hydrogen-bonded hard segment domains which may be the reason for the higher thermal stability property (Table 1).

C=O Stretching Region. Figure 6 shows the IR spectra of the carbonyl stretching region heating from 30 to 200 °C for each of the three polymers. All spectra appear to be composed of two bands at the urethane carbonyl stretching region, although there is considerable overlap at higher temperatures. The narrower band centered at around 1729 cm^{-1} is assigned to stretching of free urethane carbonyl groups, while the band at 1710 cm^{-1} is attributed to hydrogen-bonded urethane carbonyl groups. Furthermore, 4TPUU and 4MTPUU show an additional band centered at 1643 cm^{-1} due to hydrogen-bonded urea carbonyl. Previous investigators[8,17] have attributed the urethane carbonyl stretch at roughly 1707 cm^{-1} to hydrogen bonding in

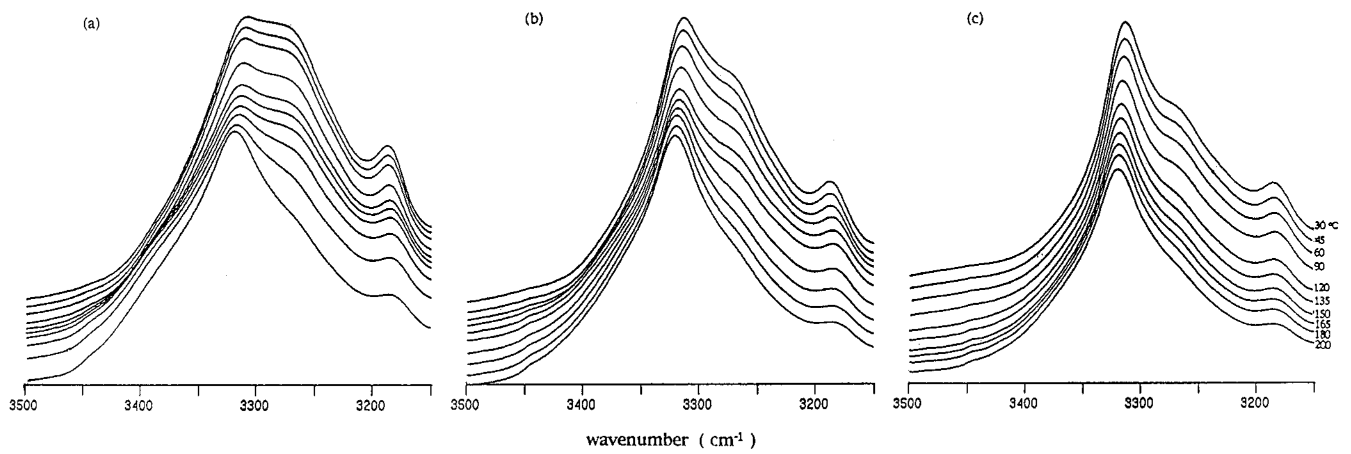


Figure 3. Temperature dependence of FTIR spectra in the NH stretching region: (a) 4MPU; (b) 4MTPUU; (c) 4TPUU.

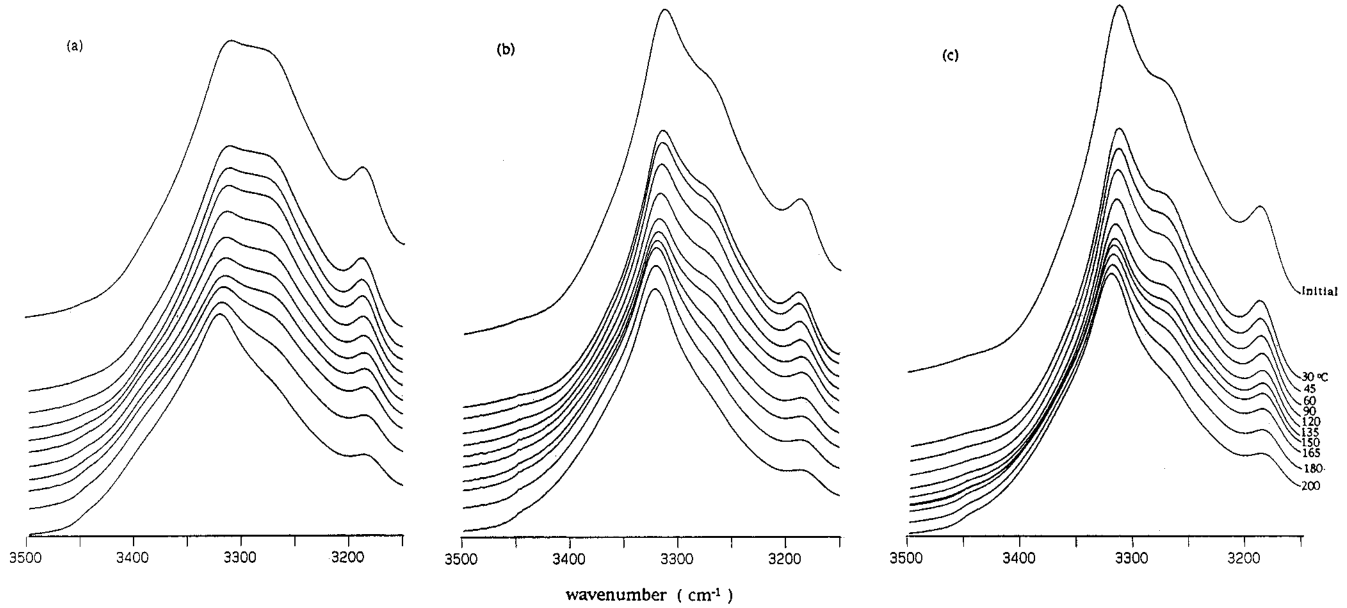


Figure 4. FTIR spectra in the NH stretching region recorded as decreasing temperature. An “Initial” spectrum at 30 °C prior heating is included for comparison: (a) 4MPU; (b) 4MTPUU; (c) 4TPUU.

disordered regions, that is, urethane linkages of interfacial regions or “dissolved” in the soft phase. For the stronger hydrogen bonds in ordered or crystalline regions, the stretching absorbance occurs at a lower frequency ranging from 1684 to 1702 cm^{-1}. Wang and Cooper[3] suggested a frequency shift of the urea carbonyl band of polyether PUU’s from 1645 to 1635 cm^{-1} upon going from samples containing 36 wt % hard segment to 25 wt % and attributed it to some soft-segments apparently dissolved in the hard-segment domains. Thus, these polymers show dissolved soft segments dispersed in the hard-segment domains, and an ordered hydrogen bonding carbonyl bond is not observed. It provides further evidence that the polymers studied are amorphous polymers.

The deconvolution of the carbonyl region was also performed, and a Gaussian function was used. Excellent analytical fits were also obtained with the RMS deviation smaller than 0.001 for all three polymers at all temperatures. 4MPU shows the stretching vibration band of hydrogen-bonded urethane carbonyl at 1710 cm^{-1} at 30 °C, nearly independent of temperature. While both 4TPUU and 4MTPUU show the v of the hydrogen-bonded urethane carbonyl shift from 1711 to 1716 cm^{-1} as the temperature increased from 30 to 200 °C. The last two polymers also show that the v of the hydrogen-bonded urea carbonyl band is nearly constant (1643 ± 2 cm^{-1}), while the free urea carbonyl band at 1965 cm^{-1} was not detected.[10] It implies that most of the urea carbonyl groups are associated in hydrogen bonding, while urethane carbonyls are not as much. Several reports in the literature[3,10,11] suggest that there exists a three-dimensional hydrogen bonding between the hard-segments in polyether PUUs. However, the former NH stretching region shows some soft segment dispersed in the hard-segment domains. This disrupts the ordering of the hard segments and also allows the polyether oxygens to compete with urea carbonyls for the urea NH groups. Thereby, there may exist a mixed state with three-dimensional as well as conventional interurea bonds (one urea carbonyl is bonded to one NH group) in 4TPUU and 4MTPUU.

Figure 7 shows the plot of the normalized area of the carbonyl stretching region vs temperature. The area of the free urethane carbonyl groups increases but that of the hydrogen-bonded one decreases with increasing temperature. However, the total area of the carbonyl groups (free and bonded) is nearly constant. As compared to the NH stretching region, the frequencies of the vibrations in the carbonyl stretching region do not shift as much with temperature, and the absorption coefficient (ϵ) is not as strong a function of frequency.

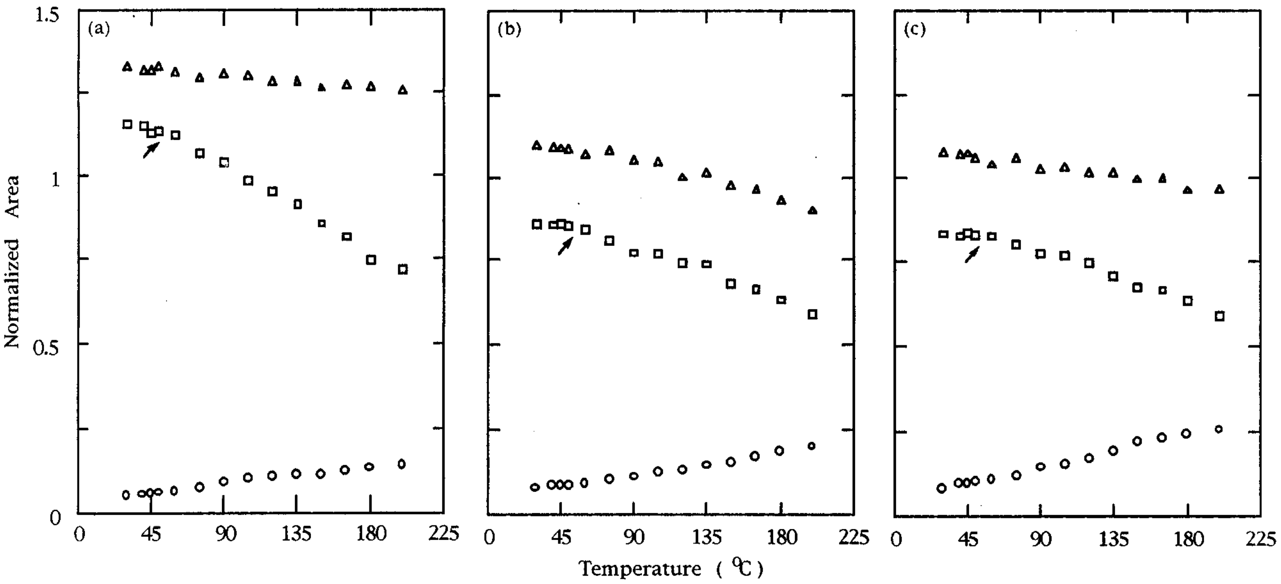


Figure 5. Normalized areas of assigned bands in the NH stretching region as a function of temperature: (a) 4MPU; (b) 4MTPUU; (c) 4TPUU. Key (△) NH bonded to carbonyl; (□) NH bonded to ether oxygen; (○) free NH groups.

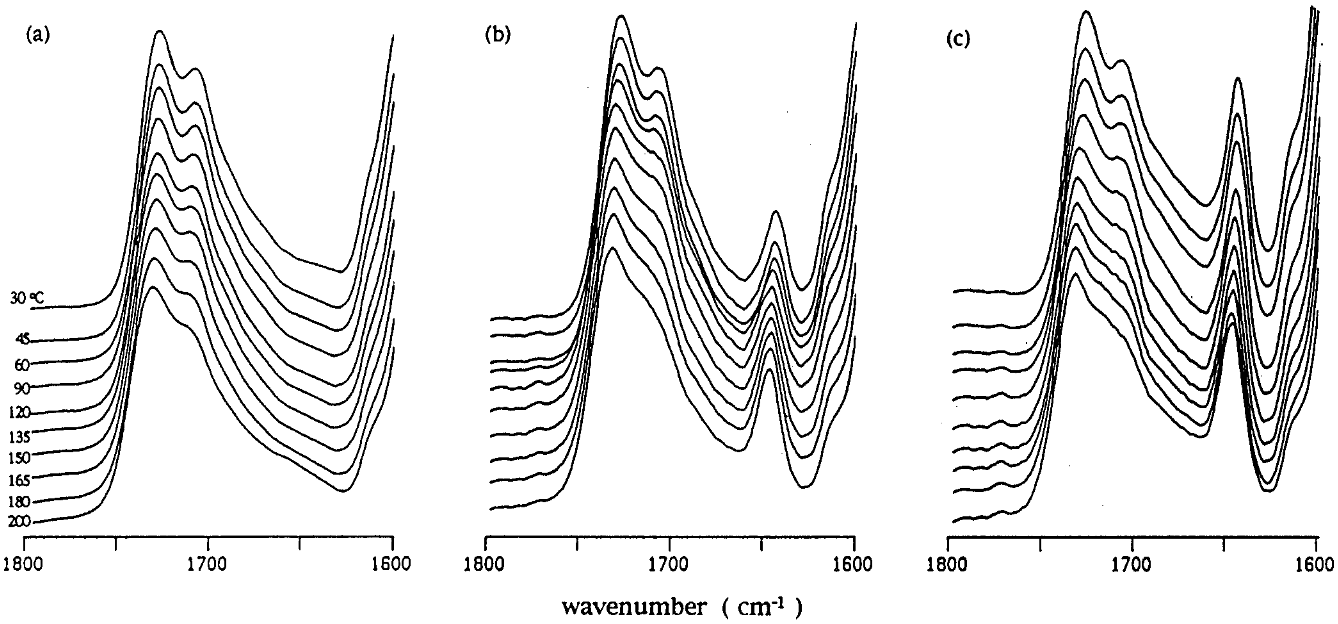


Figure 6. Temperature dependence of FTIR spectra in the carbonyl stretching region: (a) 4MPU; (b) 4MTPUU; (c) 4TPUU.

The band area changes of the urethane carbonyl region are therefore directly related to a decrease in the fraction of hydrogen-bonded urethane carbonyls (X_B) with increasing temperature. This trend is similar to that of previous studies on polyurethane.[5,8,9,13,17] The fraction of free and hydrogen-bonded urethane carbonyl groups can be approximated by the following analysis. The total concentration of carbonyl groups is given by[5]

$$C_{\mathrm{T}} = C_{\mathrm{F}} + C_{\mathrm{B}} \tag{2}$$

where C_F and C_B are the concentration of free and hydrogen-bonded urethane carbonyl groups, respectively. The fraction of hydrogen-bonded urethane carbonyl is given by

$$X_{\mathrm{B}} = C_{\mathrm{B}}/C_{\mathrm{T}} \tag{3}$$

Substituting the Beer–Lambert law for the integrated area of the free (A_F) and bonded (A_B) absorbance peaks as a function of temperature T is given by

$$A_F(T) = C_{\mathrm{T}} L \epsilon_{\mathrm{F}}(T)[1 - X_{\mathrm{B}}(T)] \tag{4}$$

and

$$A_B(T) = C_{\mathrm{T}} L \epsilon_{\mathrm{B}}(T) X_{\mathrm{B}}(T) \tag{5}$$

respectively, where L is the path length. Since the results have already been normalized such that the product $C_T L$ is a constant. If it is assumed that ϵ_{F} and ϵ_{B} are constant with temperature, rearrangement of eqs 4 and 5 gives

$$X_B = \frac{1}{1 + r\dfrac{A_{\mathrm{F}}(T)}{A_{\mathrm{B}}(T)}} \tag{6}$$

where the ratio $r = \epsilon_{\mathrm{B}}/\epsilon_{\mathrm{F}}$ is constant and could be determined experimentally.

In this work, one finds that the total areas of the urethane carbonyls is nearly constant (Figure 7). The

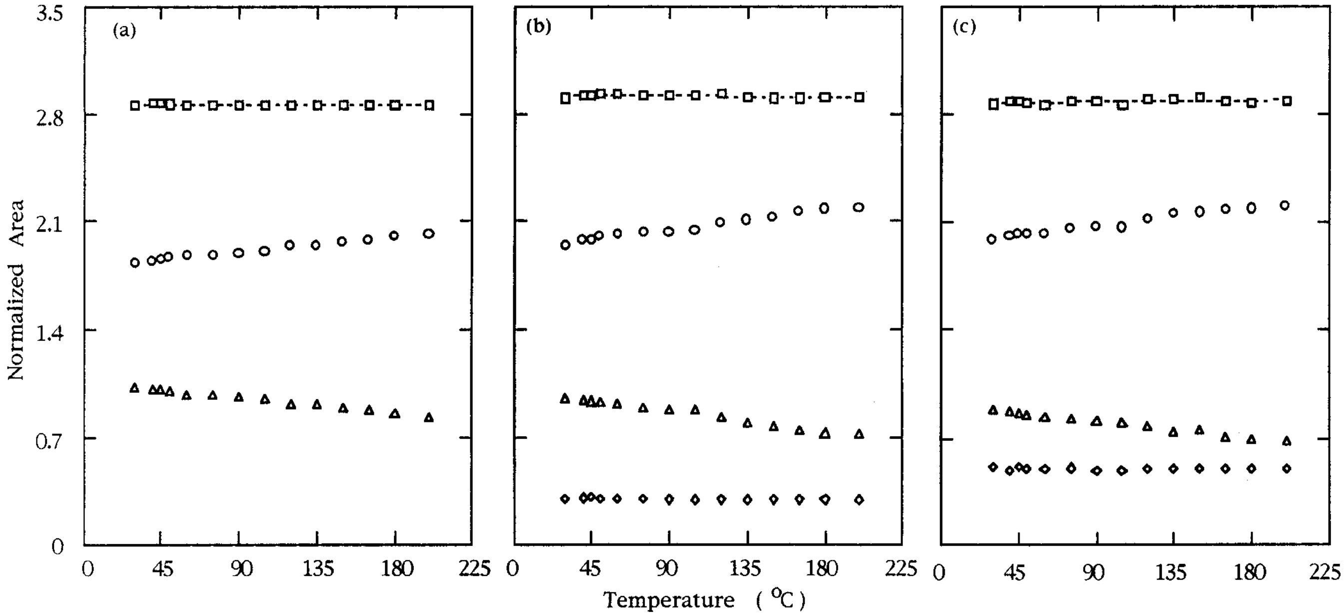


Figure 7. Normalized areas of assigned bands in the carbonyl stretching region as a function of temperature: (a) 4MPU; (b) 4MTPUU; (c) 4TPUU. Key (◇) bonded urea carbonyls; (△) bonded urethane carbonyls; (□) total urethane carbonyls; (○) free urethane carbonyls.

equation of the total absorbance area is given by

$$A(T) = C_T L\{\epsilon_F[1 - X_B(T)] + \epsilon_B X_B(T)\} \quad (7)$$

which is constant only if $\epsilon_B = \epsilon_F$.

Thus, r is taken to be 1.0, whereas previously reported values of r are in the range 1.0–1.3.[5,9,16,17,19] The results of X_B at 30 °C are 0.36 for 4MPU, 0.33 for 4MTPUU, and 0.31 for 4TPUU. One finds that X_B steadily decreases with increasing temperature for all three polymers. The X_B at 200 °C is thus determined to be 0.28 for 4MPU, 0.23 for 4MTPUU, and 0.20 for 4TPUU. And 4TPUU and 4MTPUU polymers show that the area of the hydrogen-bonded urea carbonyls is nearly constant over the ranges of temperature studied. It suggests that the strength of this hydrogen-bonded urea carbonyl is not much affected by temperature. Consequently, a fraction of hard–hard segments persists at a higher temperature of 200 °C. This is consistent with the trend of the NH stretching region.

For 4MPU polymer, the distribution of various hydrogen bonds was obtained using the calculated fractions of free and hydrogen-bonded urethane carbonyl groups, as the total number of NH groups equal to that of C=O groups. This can be written as

$$C{=}O_{free} + C{=}O_{bonded} = NH_{free} + NH_{C=O} + NH_{ether} + NH_{others} \quad (8)$$

Results from previous studies on various polyurethanes[8,13,24] suggest that NH_{others} is on the order of 10%, which includes hydrogen bonding of NH groups to urethane alkoxy oxygens and π orbitals of aromatic rings. Therefore, one estimates that 54% of NH groups are either free or bonded to ethers at 30 °C. However, the peak of the free NH groups shows a weak shoulder that the intensity of the free NH groups are much smaller than hydrogen-bonded NH to ether oxygens (Figure 3a). This implies that a substantial fraction of NH groups in 4MPU are hydrogen-bonded to ethers of the PEG soft segment. It may be attributed to steric hindrance of the bulky CH_3 groups in the hard segments, which reduce the effectiveness of hydrogen bonding within the NH and urethane carbonyl groups.

Conclusion

In this work, amine functional groups of TEPA and/or MDEA as chain extenders were introduced into the hard segments of polyurethane and poly(urethane–urea). The polymers so obtained contain nearly equal weight compositions of soft and hard segments. These polymers show obviously partial phase mixing which is evidenced by soft segments dissolved in the hard-segment domains and by hard segments dissolved in the soft-segment domains. It shows that some PEG soft segments dissolved within the hard-segment domains might interfere with the microstructural ordering of hard segments such that these polymers are amorphous. However, the MDEA-containing 4MPU polymer shows a large fraction of hard–soft segments hydrogen bonding such that the bulky CH_3 groups of MDEA retard the formation of hydrogen bonds among the hard segments, whereas the TEPA-containing polymers exhibit a strong hard–hard segment hydrogen bonding with a mixed state of three-dimensional as well as conventional interurea bonds. Thus, they exhibit more distinct phase separation. The extent of phase separation increases in the order 4MPU < 4MTPUU < 4TPUU. The hydrogen bonding of these polymers was found to persist up to 200 °C. In addition, the hard–soft segments are more weakly hydrogen-bonded than the hard–hard segments.

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