

## Structure and Properties of Fatigued Segmented Poly(urethaneurea)s III. Quantitative Analyses of Hydrogen Bond

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**ABSTRACT:** Hydrogen bonds in segmented poly(urethaneurea)s (SPUU) were studied with Fourier transform infrared spectroscopy (FTIR). Absorption curves due to the urethane and urea carbonyl groups were resolved into several peaks by a peak resolving method. Evaluation of individual peak intensity enabled one to estimate the amounts of hydrogen bonds formed with urea and urethane carbonyl groups, referred to as hydrogen bond indices,  $H_{UA}$  and  $H_{UT}$ , respectively.  $H_{UA}$  and  $H_{UT}$  were defined as the ratios of absorbances of hydrogen bonded carbonyl groups to free carbonyl groups, respectively for urea (UA) and urethane (UT) carbonyl groups. It was found that the indices of hydrogen bonds of urethane and urea carbonyl groups were the parameters which represent phase mixing, *i.e.*, dispersion of hard segments in the soft segment matrix, and the cohesive force in the hard segment domain. The variation of the indices of hydrogen bonds with increasing elongation and temperature indicated progress of the phase mixing and reduction of the cohesive force of the hard segment domain.

**KEY WORDS** Segmented Poly(urethaneurea) / FTIR / Hydrogen Bond / Phase Mixing / Peak Resolving /

Structure, morphology, mechanical and thermal properties, and antithrombogenicity of segmented poly(urethaneurea)s have been studied by many workers because not only for academic interest as multicomponent polymers but also for their industrial applications such as shock absorber, clothes, and medical materials. Most of the characteristic properties of SPUUs, *e.g.*, high elasticity, durability, antithrombogenicity are due to presence of the microphase separated structure and hydrogen bonds.

In previous papers in this series,<sup>1,2</sup> the deformation mechanism of segmented poly(urethaneurea)s (SPUUs) during uniaxial stretching and fatigue process were discussed based on deformations of spherulites from the view-

points of structure and soft and hard segment orientations. The results showed that spherulites were selectively destroyed at the equatorial zone of the spherulite with respect to the stretching direction and then fragmented hard segments were dispersed in the soft segment matrix. Thus, phase mixing occurred. It was also shown that hydrogen bonds play an important role in the structural change in deformation.

In the case of SPUUs, the NH groups in the urea or urethane groups and the oxygen of the C=O groups in urea, urethane, polyether, or polyester behave as a proton donor and acceptor, respectively. Since hydrogen bonds affect the physical properties, morphology and deformation mechanism of these materials,

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it is of importance to study them in SPUUs quantitatively.

Fourier transform infrared spectroscopy (FTIR) is very useful for studying chemical bonding states of atoms or atomic groups. The difference in bonding state of atoms or atomic groups is observed as changes of absorption peak position, peak width and peak height.

Infrared absorption spectra of SPUUs were extensively studied by many investigators.<sup>3-11</sup> Especially, it was shown that the absorption peak due to hydrogen bond between NH and C=O groups decreased in intensity with increasing temperature. Similar investigations were performed in polyamides<sup>12-14</sup> which had similar chemical structures to SPUUs. These results were compared with those of SPUUs.

In this paper, we investigate the hydrogen bond which affects the physical properties of these materials to understand the deformation mechanism of SPUUs. In the forthcoming paper,<sup>15</sup> we will discuss how the hydrogen bond is influenced by stretching and increasing temperature in terms of dynamic infrared dichroism measurement.

## EXPERIMENTAL

### Samples

Table I shows the SPUU samples used in this study. These are composed of three segmental parts of poly(tetramethyleneglycol) (PTMG), 4,4'-diphenylmethane diisocyanate (MDI), and 1,2-propylene diamine (PDA) and coded as TM-1 and TM-3. They have the same molar ratios of MDI, PTMG, and PDA, whereas only the molecular weight of PTMG is different as shown in Table I. SPUU was dissolved in DMF and cast to a thin film as described in ref 1 and 2.

### Infrared Studies

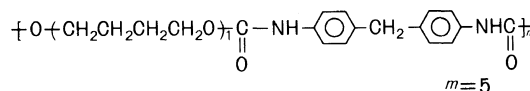
Infrared absorption spectra were obtained on FIRIS 100 Fourier transform infrared spectrometer, Fuji Electric Co., operated with a FASMIC G500/32 computer. Each spectrum

**Table I.**  
Chemical composition of the SPUU

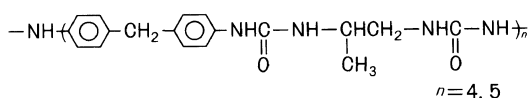
Sample	Soft segment PTMG ( $\bar{M}_n$ )	MDI:PTMG:PDA	Solvent
TM-1	856	2:1:1	DMF
TM-3	1343		

### Chemical structures of the SPUU

#### Soft segment (PTMG-MDI)



#### Hard segment (MDI-PDA)



was obtained with a deuterated triglycine sulfate (DTGS) detector under  $4\text{ cm}^{-1}$  resolution and 32 times of accumulation. The sample size used in this study was 40 mm long and 10 mm wide. The gauge length was 30 mm. Elongation and temperature dependence experiments were carried out with a temperature controlled stretching device designed for this work. The temperature was controlled with an accuracy better than  $\pm 1^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Peak Assignment

Figure 1 shows the infrared survey spectrum of TM-1 at  $20^\circ\text{C}$ . A similar spectrum was obtained for TM-3. The characteristic bands are indicated with symbols. The absorption peak  $\nu(\text{NH})_{\text{UA}}^b$  located at  $3315\text{ cm}^{-1}$  is assigned to the hydrogen bonded NH stretching. The absorption bands located at 2940 and  $2858\text{ cm}^{-1}$  are assigned to the stretching of methylene groups,  $\nu(\text{CH}_2)$ .

In the carbonyl stretching region from 1620

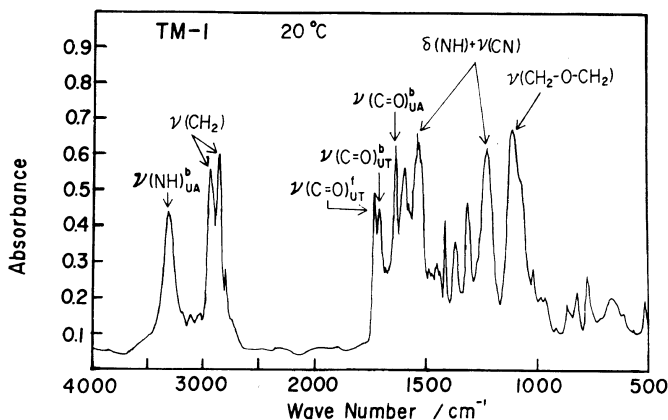


Figure 1. Infrared survey spectrum of the TM-1.

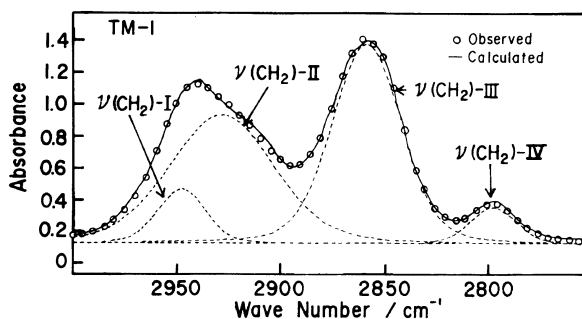


Figure 2. Curve-fitting results in the methylene stretching region of the TM-1 at 20°C. Circle, solid line and broken lines respectively denote observed and calculated spectra, and individual components of absorption bands.

to  $1750\text{ cm}^{-1}$ , the absorption peak at  $1730\text{ cm}^{-1}$ ,  $\nu(\text{C}=\text{O})_{\text{UT}}$ , is due to the free urethane carbonyl groups, and that at  $1710\text{ cm}^{-1}$ ,  $\nu(\text{C}=\text{O})_{\text{UT}}$ , is due to the hydrogen bonded urethane carbonyl groups. The absorption peak located at  $1640$ ,  $\nu(\text{C}=\text{O})_{\text{UA}}$ , corresponds to the hydrogen bonded urea carbonyl groups. The free urea carbonyl absorption peak is not observed at  $1695\text{ cm}^{-1}$  on the infrared spectrum, but its presence was recognized by peak resolving as discussed below.

The two absorption peaks at  $1538$  and  $1223\text{ cm}^{-1}$  are due to coupling of NH deformation and CN stretching,  $\delta(\text{NH}) + \nu(\text{CN})$ . The absorption peak located at  $1112\text{ cm}^{-1}$  is assigned to the ether C-O stretching of PTMG,  $\nu(\text{C}-\text{O}-\text{C})$ .

We focused attention on the carbonyl stretching and methylene stretching bands and decomposed these bands into individual absorption peaks with a peak resolving method. We assumed that each absorption band was given by a linear combination of Gaussian and Lorentzian functions. It is useful to focus on the  $\text{CH}_2$  groups as well as the carbonyl groups because they are used for the estimation of soft segment orientation which will be discussed in the forthcoming paper.<sup>15</sup> Figure 2 shows the results of the peak resolving in the methylene stretching region from  $2750$  to  $3000\text{ cm}^{-1}$  for the TM-1 at  $20^\circ\text{C}$ . In this case the fraction of the Gaussian component was  $0.8$ . In this region the spectrum was resolved into four peaks designated by I to IV. The

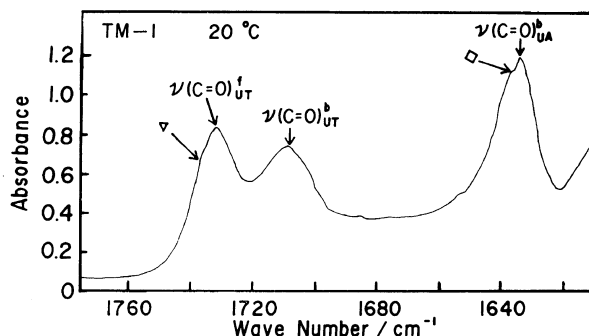


Figure 3. Infrared spectrum of the TM-1 in the carbonyl region from 1610 to 1775  $\text{cm}^{-1}$ .

absorption peaks of I and III were respectively due to antisymmetric and symmetric stretching as reported by Schroeder *et al.*<sup>12</sup> However, those of II and IV have not been assigned exactly.

This can be explained in terms of differences in vibrational modes like symmetric and anti-symmetric stretching and in the positions where the methylene units are located, *i.e.*, in a PTMG sequence or in an MDI. These differences induce changes in the vibrational force constant due to interaction from other atoms.

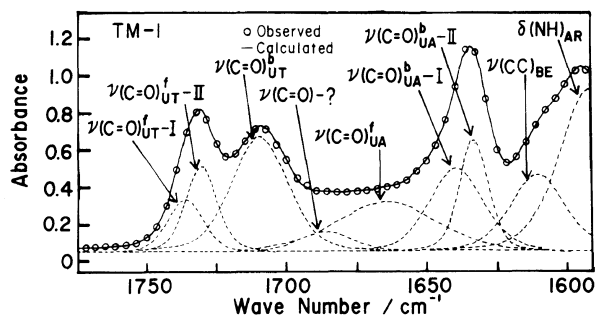
Figure 3 shows an infrared spectrum in the carbonyl stretching region from 1600 to 1750  $\text{cm}^{-1}$ . Obviously, three distinct peaks are observed in this region. When observing this spectrum carefully, shoulders are observed on the high-wave number side of the peaks at 1730 and 1640  $\text{cm}^{-1}$ , as marked by  $\nabla$  and  $\diamond$ , respectively. As discussed below, we cannot ignore these shoulders in the peak resolving process since they increased with temperature, and were judged to be significantly different from noise. In fact, by taking the second-derivative on the spectrum, minimum values were detected at the wave number corresponding to the shoulders. Thus, the presence of the absorption peaks was confirmed. If one takes into consideration peak symmetry, the absorbance plateau region from 1660 to 1700  $\text{cm}^{-1}$  cannot be explained as a result of superposition of the absorption peaks at 1709 and 1640  $\text{cm}^{-1}$ . Therefore, it should be regarded

that some absorption peaks, which do not appear on the infrared absorption spectrum, exist in this region.

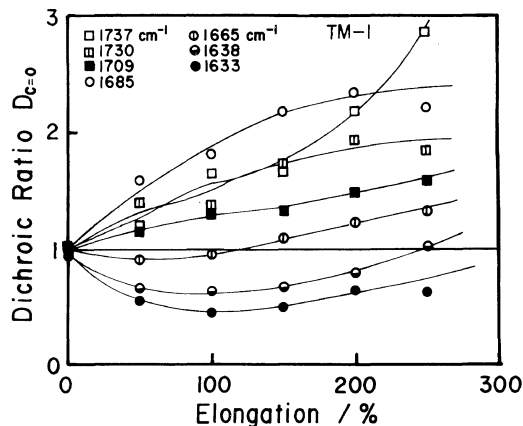
In this respect, Ishihara *et al.*<sup>5</sup> observed an absorption peak due to free urea carbonyl groups at 1695  $\text{cm}^{-1}$  by measuring a spectrum for a dimethylsulfoxide (DMSO) solution of the SPUU. We also confirmed the appearance of an absorption peak around 1660  $\text{cm}^{-1}$  for TM-1 and TM-3 dipped in a mixture of DMF and water. Furthermore, these absorbances increased by elevating temperature. Therefore it is regarded that all of these peaks are due to free urea carbonyl groups.

Coleman *et al.*<sup>10</sup> and Skrovanek *et al.*<sup>14</sup> reported that from detailed studies on polyurethane and polyamide there existed a disordered hydrogen bonded carbonyl group besides the free and completely hydrogen bonded carbonyl groups. Taking these into consideration, we resolved the peaks in the carbonyl stretching region from 1590 to 1750  $\text{cm}^{-1}$  as shown in Figure 4. When the fraction of the Gaussian component was 0.7, the difference between the observed and calculated spectra was minimized. The absorption peaks at 1610 and 1592  $\text{cm}^{-1}$  are introduced in order to resolve the hydrogen bonded urea carbonyl peak exactly, and are assigned to CC stretching of the benzene ring,  $\nu(\text{CC})_{\text{BE}}$ , and the NH deformation bonded to aryl group,  $\delta(\text{NH})_{\text{AR}}$  as shown in ref 5, respectively.

We examined the elongation dependence of



**Figure 4.** Curve-fitting results in the carbonyl stretching region of the TM-1 at 20°C. Circle, solid line and broken lines respectively denote observed and calculated spectra, and individual components of absorption bands.



**Figure 5.** Elongation dependence of dichroic ratio of each carbonyl band for TM-1.

the dichroic ratio in order to clarify the assignment of the carbonyl stretching bands. Figure 5 shows the results obtained for TM-1. Here, the dichroic ratio,  $D$ , is defined as  $D = A_{\perp} / A_{\parallel}$  using perpendicular and parallel absorbances with respect to the strain direction. Since these transition moments are roughly perpendicular to the molecular axis,  $D > 1$  and  $D < 1$  mean positive and negative orientations of the segment, respectively. As shown in the figure, the bands at 1737, 1730, 1709, and 1685  $\text{cm}^{-1}$  orient positively. As it is known that the soft segment generally orients positively by stretching, it seems that these bands are due to urethane carbonyl groups in the soft segment.

However, since the wave number of absorption peaks at 1685  $\text{cm}^{-1}$  is close to that of free urea carbonyl groups, this band can also be considered due to free urea carbonyl groups. Therefore, it is very difficult to assert this band at this stage. Tentatively, we named this band  $\nu(\text{C}=\text{O})-?$ . Coleman *et al.*<sup>10</sup> assigned the absorption peaks at 1737, 1730, and 1790  $\text{cm}^{-1}$  to the free, disordered, and hydrogen bonded urethane carbonyl groups, respectively. Although we tried to assign the individual peaks which appeared by peak resolving based on the elongation dependence of dichroic ratios of these peaks, it was found that further investigation would be required. Because the absorption peak at 1730  $\text{cm}^{-1}$  was close to that of the free urethane carbonyl group among these, we classified it roughly as due to free urethane carbonyl groups. Hence we named each band at 1737, 1730, and 1709  $\text{cm}^{-1}$  as  $\nu(\text{C}=\text{O})_{\text{UT}}^{\text{f-I}}$ ,  $\nu(\text{C}=\text{O})_{\text{UT}}^{\text{f-II}}$ , and  $\nu(\text{C}=\text{O})_{\text{UT}}^{\text{b}}$ , respectively.

The absorption bands at 1665, 1638, and 1633  $\text{cm}^{-1}$  orient negatively at low elongation region, so these are assigned to the urea carbonyl groups in the hard segment. The peaks at 1665, 1638, 1633  $\text{cm}^{-1}$  are due to free, incompletely hydrogen bonded, and completely hydrogen bonded urea carbonyl groups, and are named  $\nu(\text{C}=\text{O})_{\text{UA}}^{\text{f}}$ ,  $\nu(\text{C}=\text{O})_{\text{UA}}^{\text{b-I}}$ , and  $\nu(\text{C}=\text{O})_{\text{UA}}^{\text{b-II}}$ , respectively. Because the absorption peak at 1638  $\text{cm}^{-1}$  is close to that

of the hydrogen bonded urea carbonyl group, it was roughly classified as due to hydrogen bonded urea carbonyl groups. No other atomic groups besides the carbonyl groups are expected in this range for SPUU.

Since the infrared absorption spectra give information on bonding states, the above results indicate that the states of the hydrogen bonds cannot be described only in the two states, *i.e.*, the free and hydrogen bonded states. There exist hydrogen bonds at various strengths between the free to completely bonded states.

If both NH and carbonyl groups exist in the hard segment domain, hydrogen bonds may be formed between hard segments. If it is not so, they are formed between hard and soft segments or between soft segments. Therefore, it is expected that the strength among these hydrogen bonds differs from each other. However, complete assignment of these bands has not been reported in the literature and requires further investigation.

Regarding the NH stretching band, it is expected that the broad absorption around  $3315\text{ cm}^{-1}$  is due to superposition of several peaks of the hydrogen bonded NH groups different in strength. Only the hydrogen bonded NH peak, however, was observed in spite of the presence of free carbonyl groups. In this respect, MacKnight *et al.*<sup>4</sup> estimated the molar extinction coefficient of the free NH group to be  $3.44\text{--}6.3 \times 10^3\text{ l mol}^{-1}\text{ cm}^{-2}$  and that of the hydrogen bonded NH group being  $1.06\text{--}1.7 \times 10^4\text{ l mol}^{-1}\text{ cm}^{-2}$ . Recently, Skrovanek *et al.*<sup>13</sup> indicated that the molar extinction coefficient of the hydrogen bonded NH group decreased with increasing wave number. The difference in the molar extinction coefficients between the free and hydrogen bonded states and wave number dependence of that are explained in terms of remarkable increase in dipole moment due to the formation of a charge transfer complex.<sup>16</sup>

The absorption peak due to the free NH group cannot be observed in the spectra be-

cause the molar extinction coefficient is very small compared with the hydrogen bonded NH group. Since only the absorption peak due to the hydrogen bonded NH group was observed, it has been believed that all the NH groups form a hydrogen bond. However, this is questionable.

#### Elongation Dependence

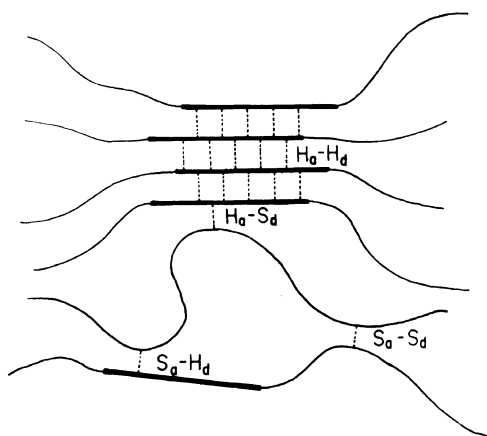
We estimate the amount of the hydrogen bonds by the indices of hydrogen bonds as defined by the following equations,

$$H_{\text{UT}} = \frac{A^{\text{l}}(1709)}{A^{\text{l}}(1737) + A^{\text{l}}(1730) + A^{\text{l}}(1709)} \quad (1)$$

$$H_{\text{UA}} = \frac{A^{\text{l}}(1638) + A^{\text{l}}(1633)}{A^{\text{l}}(1665) + A^{\text{l}}(1638) + A^{\text{l}}(1633)} \quad (2)$$

where  $A^{\text{l}}(x)$  represents integrated absorbance having a maximum at  $x$  ( $\text{cm}^{-1}$ ), and  $H_{\text{UT}}$  and  $H_{\text{UA}}$  denote the indices of hydrogen bonds of urethane and urea groups, respectively. It should be noted that these indices do not mean exact fractions of hydrogen bonds because the extinction coefficient of neither free or hydrogen bonded carbonyl groups has been precisely evaluated.

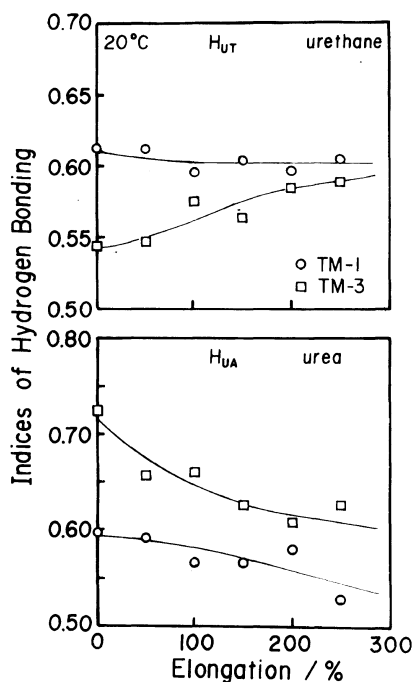
Since the proton acceptors, *i.e.*, urea carbonyl group and urethane carbonyl groups, locate on hard segments and soft segments, respectively, it is interesting to estimate the strength of hydrogen bond with eq 1 and 2. However, the major proton donors, in this case, urea protons or urethane protons, locate on both hard and soft segments. Therefore, there are at least four types of hydrogen bonds as shown in Figure 6. Figure 6 schematically shows the type of hydrogen bond expected in segmented poly(urethaneurea)s. The thick solid lines, thin curved lines, and dashed lines denote the hard segments, soft segments, and hydrogen bonds, respectively. The capitals H and S and subscripts a and d denote the hard segment, soft segment, proton acceptor ( $\text{C}=\text{O}$ ), and proton donor (NH). As shown in the figure, there are four types of hydrogen



**Figure 6.** Schematic diagram showing four types of hydrogen bonds expected in segmented polyurethane.

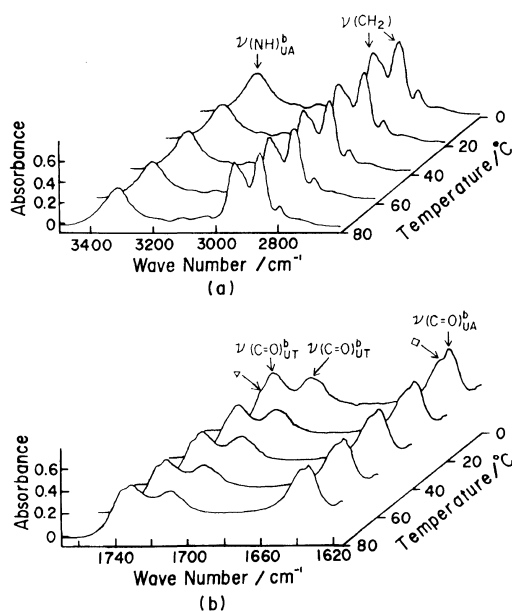
bonds,  $H_a-H_d$ ,  $H_a-S_d$ ,  $S_a-H_d$ , and  $S_a-S_d$ .  $H_a-H_d$  contributes to cohesion of the hard segment domains.  $H_a-S_d$  is located on the interface between the hard and soft segment phases. However, since the density of urea and/or urethane protons are heavily located on the hard segment domains, the hydrogen bonds of type  $H_a-S_d$  and  $S_a-S_d$  are less expected compared to  $H_a-H_d$  and  $S_a-H_d$ . Simple calculation based on chemical structures, assuming equal mass densities of the hard and soft segments, reveals that the donor proton density is about 7 times higher in hard segment domains than in soft segment domains for TM-1. Therefore, it is expected that an decrease in  $H_{UA}$  indicates lowering of the cohesive power of hard segments and/or destruction of the hard segment domains and increase in  $H_{UT}$  dose phase mixing between hard and soft segment domains.

Figure 7 shows elongation dependence of  $H_{UT}$  and  $H_{UA}$  at 20°C for TM-1 and TM-3. The  $H_{UT}$  for TM-1 hardly varies with elongation, but that for TM-3 increases with elongation. On the other hand,  $H_{UA}$  decreases. The increase in  $H_{UT}$  and decrease in  $H_{UA}$  with increasing elongation mean reduction of the cohesive force in hard segment domains and



**Figure 7.** Elongation dependence of indices of hydrogen bond of urethane (upper) and urea (lower) for the TM-1 and TM-3.

the progress of phase mixing between the hard and soft segments. This phenomenon causes the hard segment domains to be destroyed into small fragments and they begin to be dispersed in the soft segment matrix. Comparing  $H_{UT}$  and  $H_{UA}$  for unstretched TM-1 and TM-3, it is shown that  $H_{UT}$  for TM-3 is lower than that for TM-1 and  $H_{UA}$  for TM-3 is larger than that for TM-1. These indices mean that the cohesive force of the hard segment of TM-3, having a larger soft segment molecular weight, is stronger and the phase separation is much more developed in TM-3 than in TM-1. This is consistent with the results of Shibayama *et al.*<sup>1</sup> and Hartmann *et al.*,<sup>17</sup> *i.e.*, the larger the soft segment molecular weight, the better are the phases developed. Variation in  $H_{UT}$  and  $H_{UA}$  for TM-1 is smaller than that for TM-3 because phase mixing has already progressed in TM-1.

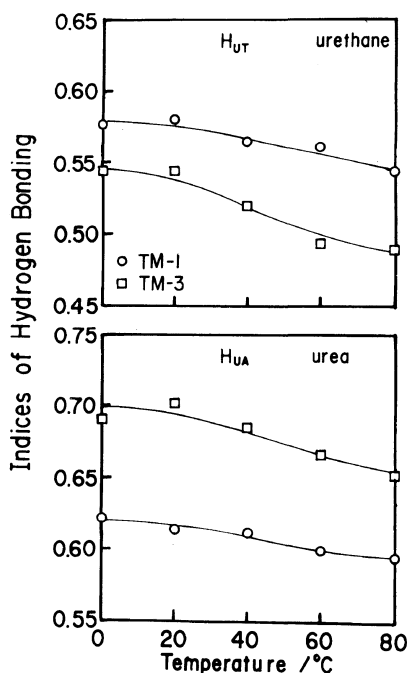


**Figure 8.** Temperature dependence of the infrared spectra of the TM-1. (a) in the region from 2600 to 3500  $\text{cm}^{-1}$ . (b) in the region from 1610 to 1775  $\text{cm}^{-1}$ .

### Temperature Dependence

Figures 8(a) and (b) show the temperature dependence of the infrared absorption spectra for TM-1 in the region from 2600 to 3500  $\text{cm}^{-1}$  and from 1620 to 1750  $\text{cm}^{-1}$ , respectively. The shoulders marked by  $\nabla$  and  $\diamond$  in Figure 8(b) increase and absorbance of  $\nu(\text{C}=\text{O})_{\text{UT}}^{\text{b}}$  decreases with increasing temperature. All these results indicate reduction in the strength of the hydrogen bonds of urethane and urea carbonyl groups. The free NH band at 3445  $\text{cm}^{-1}$  is not observed in spite of the decrease in absorbance in the hydrogen bonded carbonyl groups.

Temperature dependence of the infrared spectra has been studied by many workers, and wave number shifts of the band associated with the hydrogen bonds were observed. For example, Siesler<sup>8</sup> reported that shifts of absorption maximum of the hydrogen bonded NH and methylene bands from 3331 to 3365  $\text{cm}^{-1}$  and from 2959 to 2954  $\text{cm}^{-1}$  were accompanied by temperature change from 27 to



**Figure 9.** Temperature dependence of indices of hydrogen bonds of urethane (upper) and urea (lower) for the TM-1 and TM-3.

234°C in polyester urethane. Skrovanek *et al.*<sup>13</sup> also reported a shift of the hydrogen bonded NH band from 3310 to 3332  $\text{cm}^{-1}$  in the temperature range from 30 to 210°C in amorphous polyamide. We observed a shift from 3315 to 3318  $\text{cm}^{-1}$  and an increase in the half width of the hydrogen bonded NH band as well. But no shift of the methylene band was observed in our study. Their and our results showed a decrease in strength of the hydrogen bonds with increasing temperature, indicating an increase in distance and spreading of distance distribution between hydrogen and oxygen atoms in hydrogen bonds.

Figure 9 shows temperature dependence of the indices of hydrogen bond of the urethane,  $H_{\text{UT}}$ , and urea,  $H_{\text{UA}}$ . These values obviously decrease with increasing temperature. Since  $H_{\text{UT}}$  and  $H_{\text{UA}}$  are the parameters which describe phase mixing and cohesive force in the hard segment domain, the results in Figure 9



indicate the progress of phase mixing and reduction in cohesive force in the hard segment domain. The contribution of scission of the hydrogen bond in  $H_{UT}$  has to be considered as well. As shown in Figure 9, the reduction in cohesive force for TM-3 is more remarkable than for TM-1. This may be explained by the fact that  $H_{UA}$  for TM-1 does not show drastic temperature dependence due to lower cohesive force in the hard segment.

As will be described in forthcoming paper,<sup>15</sup> the difference in self-cohesive force between TM-1 and TM-3 affects considerably deformation behavior in SPUU.

### CONCLUSIONS

The following facts are disclosed by the FTIR study on segmented poly(urethane-urea)s:

(1) There exist hydrogen bonds with various strengths in SPUUs. This results from differences in the circumstances forming the hydrogen bonds, *i.e.*, the inside of the hard and soft segment domains or the interface between the hard and soft segment domains.

(2) The hydrogen bonds formed in SPUUs decrease with increasing temperature and elongation.

(3) The indices of hydrogen bond of the urethane and urea groups were found to be parameters indicating the degree of phase mixing and cohesive force in the hard segment.

(4) TM-3 having larger soft segment molecular weight has well developed hard segment domains.

(5) The progress of phase mixing and reduction of cohesive force in the hard segment were observed by increasing temperature and elongation.

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