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Hydrogen bonding between urethane and urea: band assignment for the carbonyl region of *FT*i.r. spectrum*

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A model urethane compound and a model urea compound as viscous liquids at room temperature were synthesized. Mixtures of the two model compounds were used as the model systems of poly(urethane urea). The C=O absorption bands of the mixtures were assigned by using several infra-red techniques such as spectrum addition, spectrum subtraction and second derivative spectroscopy. Infra-red spectra of the mixtures showed the band of the free urethane carbonyl at 1732 cm^{-1}, the band of disordered urea carbonyl at 1666 cm^{-1} and a new band at 1698 cm^{-1} in the carbonyl region. The band at 1698 cm^{-1} between that from hydrogen-bonded urethane C=O (1710 cm^{-1}) and the band of free urea C=O (1694 cm^{-1}) was assigned to hydrogen bonding between the urethane carbonyl and the urea N-H. Copyright © 1996 Elsevier Science Ltd.

(Keywords: hydrogen bonding; poly(urethane urea); Fourier transform infra-red spectroscopy)

INTRODUCTION

Band assignments have been studied extensively for the carbonyl region in Fourier transform infra-red (*FT*i.r.) spectra of polyurethane[1,2], poly(urethane urea)[3–8] and polyurea[9]. The absorption band of free and hydrogen-bonded carbonyls in polyurethane are located at about 1730 and 1710 cm^{-1} [1,2,9], while free and hydrogen-bonded urea carbonyls occur at about 1695 and 1643 cm^{-1}, respectively[3–9]. The quantity of the C=O groups participating in hydrogen bonding is a measurement of the phase separation in these materials[2]. Some time ago, we followed the reaction injection moulding (RIM) process of poly(urethane urea) with a *FT*i.r. spectrometer[10]. Phase separation behaviour of the process can be studied by analysing the absorption bands assigned to carbonyls of the poly(urethane urea) in the *FT*i.r. spectra.

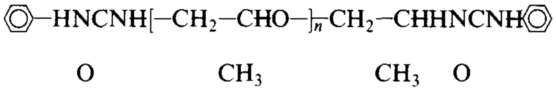
In this work, we synthesized a model urethane compound and a model urea as viscous liquids at room temperature. The band assignment for the C=O regions of the mixtures of the two model compounds, as model systems of poly(urethane urea), was discussed by using several *FT*i.r. techniques.

EXPERIMENTAL

Materials

The model urethane compound was prepared by reacting an ethylene oxide capped polyoxypropylene diol (ZS-2185®, JINLING Petrochemical Industry Corp.; content of ethylene oxide is 15%, $\overline{M}_n = 2000$) with phenyl isocyanate, PhNCO ($M_w = 119.3$, purity >98%, $d = 1.090$–1.096, $n_D = 1.535$–1.537). The model urea compound was synthesized by reacting a polyoxypropylene diamine (Jeffamine D2000, $\overline{M}_n = 2000$, functionality = 2, Texaco Chemical Company) with PhNCO. PhNCO (1.2 mol) was added slowly to the 50% solution of the polyether ZS-2185 or D2000 in dry ethyl ether. The reactions were allowed to proceed for 3 h at 40°C. The excess PhNCO and ethyl ether were removed by vacuum distillation until the NCO absorption band completely disappeared in the *FT*i.r. spectra of the products. The two types of model compounds were designated as UT2000 and UA2000, where UT denotes urethane, and UA urea. Their structures are sketched as follows:

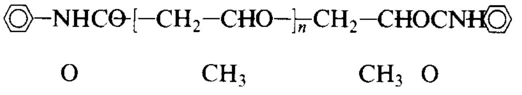
UT2000



$$\text{⌬}-\text{HN}\underset{\text{O}}{\text{C}}\text{NH}[-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}\text{O}-]_n\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}\text{HN}\underset{\text{O}}{\text{C}}\text{NH}\text{⌬}$$

$\bar{n} = 34$

UA2000



$$\text{⌬}-\text{NH}\underset{\text{O}}{\text{C}}\text{O}[-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}\text{O}-]_n\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}\text{O}\underset{\text{O}}{\text{C}}\text{NH}\text{⌬}$$

$\bar{n} = 34$

They are both viscous liquids, miscible in each other at room temperature.

Method

*FT*i.r. spectra were recorded on a Nicolet 5DXC

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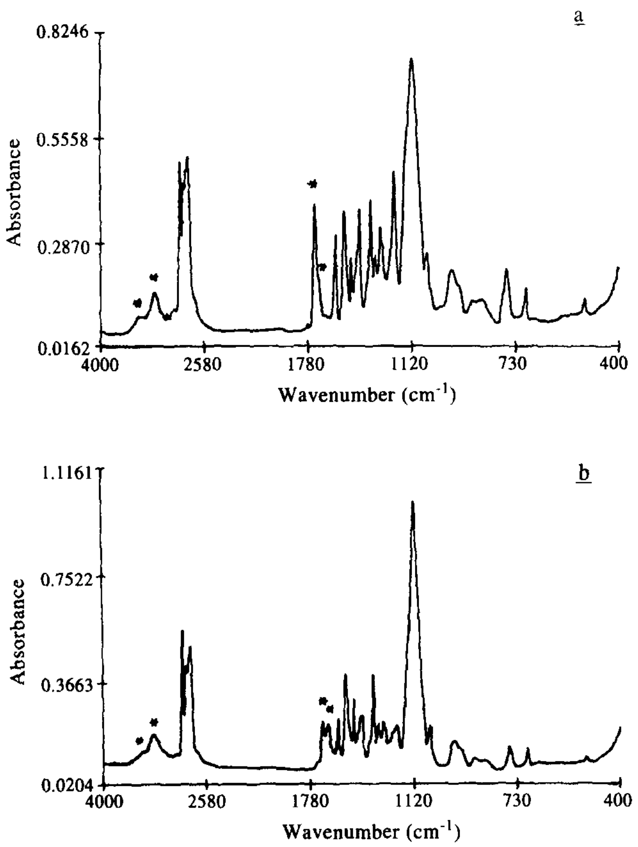

Figure 1 I.r. spectra of (a) UT2000 and (b) UA2000

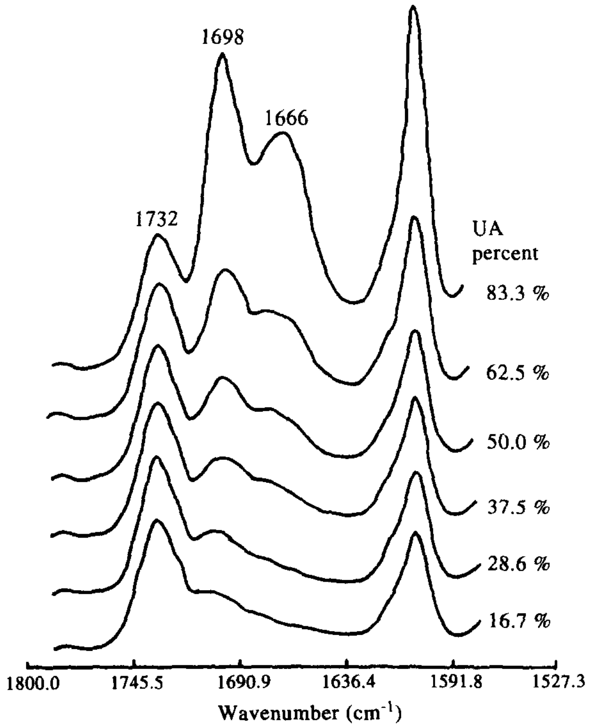

Figure 2 The C=O region of mixtures of UT2000 and UA2000 as a function of urea percent

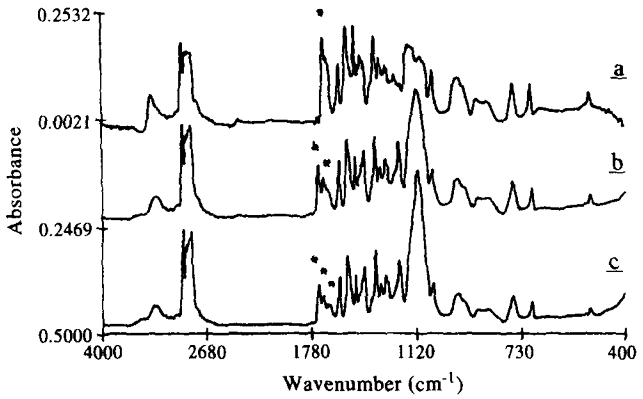

Figure 3 (a) Subtraction spectrum, (b) survey spectrum and (c) addition spectrum of mixture of 50% UT2000 and 50% UA2000

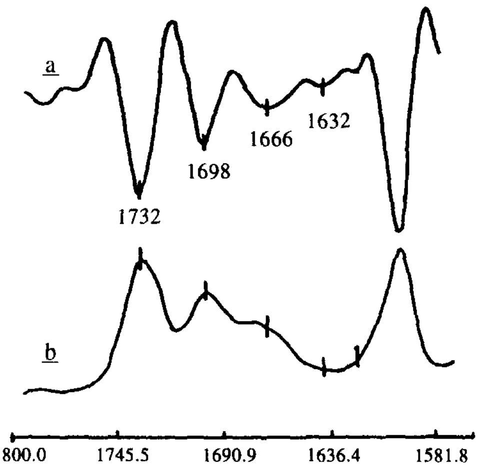

Figure 4 C=O region of second derivative spectrum (a) and survey spectrum (b) of the blend containing 50% UA2000 and 50% UT2000

*FT*i.r. spectrometer equipped with a TGS detector. Two hundred scans at 4 cm^{-1} resolution were signal averaged.

RESULTS AND DISCUSSION

In the C=O region of the *FT*i.r. spectrum of UT2000 (*Figure 1a*) there appears a free urethane carbonyl band at 1732 cm^{-1} and a hydrogen-bonded urethane carbonyl shoulder at 1709 cm^{-1}. The spectrum of UA2000 (*Figure 1b*) shows two bands at 1694 and 1666 cm^{-1} in the carbonyl region. The feature at 1694 cm^{-1} was assigned to the free urea carbonyl[9]. More recently, we have shown that the band at 1666 cm^{-1} could be attributed to the stretching vibration of disordered urea carbonyl[10]. *Figure 1* indicates that a considerable amount of free carbonyl exists in the two model compounds.

If UT2000 and UA2000 are mixed, hydrogen bonds should be formed between them, predominately between the urethane C=O and the urea N-H groups for the stronger acidity of urea N-H than that of urethane N-H. A new band at 1698 cm^{-1} is revealed in the spectra of the mixtures (*Figure 2*). For investigating the assignment of this band, a subtraction spectrum (*Figure 3a*) was obtained by subtracting the spectrum of UT2000 (*Figure 1a*) from the survey spectrum (*Figure 3b*). The subtraction spectrum should be the same as the spectrum of UA2000 (*Figure 1b*) if no interaction took place between the two mixed model compounds. An obvious difference in spectral characterization, however, can be found between the subtraction spectrum and that of UA2000. By comparing the addition spectrum (*Figure 3c*) with the survey spectrum (*Figure 3b*), one can also discern considerable differences in the carbonyl region. Thus, *Figure 3* indicates a strong interaction between UT2000 and UA2000 in their mixtures. The results suggest that the band at 1698 cm^{-1} is related to hydrogen bonding between the urethane and urea groups.

The nature of the band near 1698 cm^{-1} band can be investigated further. The second derivative spectrum of the mixture of 50% UT2000 and 50% UA2000 (*Figure 4a*) reveals that the band near 1698 cm^{-1} is a single absorption. It is presumed that the 1698 cm^{-1} band results from a simple addition of the bonded urethane C=O band (1710 cm^{-1}) with free urea C=O band (1694 cm^{-1}), which means no interactions exist between the two compounds. Analysis of *Figure 4b* using Chen's criterion[11] gives $\Delta X = 0.73 W_{1/2} = 10.4$, where ΔX is a critical interval by which a second derivative spectrum can be resolved and $W_{1/2}$ is the half width of a sharp band in the carbonyl region. The half width of the band at 1709 cm^{-1} is 36.0 cm^{-1} and that at 1694 cm^{-1} is 17.5 cm^{-1}. The interval between the two peaks is large enough (the calculated critical interval, 10.4 cm^{-1}), that two bands (1710 and 1694 cm^{-1}) should be resolved in the second derivative spectrum if the above assumption was correct. The experimental result (*Figure 4*), however, only shows a single band at 1698 cm^{-1} and hence the feature should not be considered as a simple overlapping of the two bands.

According to the above analysis, we suggest that the band at 1698 cm^{-1} is due to hydrogen bonding between an urethane carbonyl and an urea N-H. The frequency of the band is just slightly lower than the inter-urethane band (1709 cm^{-1}) suggesting the interaction between an urethane C=O and an urea N-H is stronger than that between urethane C=O and urethane N-H.

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