

# Molecular interactions in polyurea by 1-D and 2-D n.m.r.

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(Received 22 July 1991; revised 17 December 1991)

$\alpha,\omega$ -Diaminopropyl terminated polycyanopropyl methylsiloxane-polyurea is studied by high resolution  $^1\text{H}$  n.m.r. in concentrated dimethylformamide (DMF) solution, there are no hydrogen bonds between polyurea and DMF, and between polyurea and water. Hence, solvent effects can be ignored. There are several NH resonances in the  $^1\text{H}$  n.m.r. spectra. The different chemical shifts are due to different types of hydrogen bonds. At higher temperatures, hydrogen bonding of the NH groups is not dissociated, and the relative amounts of each NH peak remain the same in the temperature range 23–82°C. The chemical shift changes of the NH group forming hydrogen bonds are greater than those of free NH with increasing temperature. The morphology of the polyurea chain in concentrated DMF solution appears to be similar to that in the solid state from the two-dimensional NOESY spectrum.

(Keywords: molecular interactions; hydrogen bonding; polyurea; high resolution n.m.r.; two-dimensional n.m.r.)

## INTRODUCTION

Polyurethanes are a class of well-known segmented thermoplastic elastomers. There are several kinds of hydrogen bonds between the hard and the hard segments, and the hard and the soft segments<sup>1</sup>, where most of the hydrogen bonds are formed by the NH group. Hydrogen bonds have a significant effect on physical properties (for example, on tensile strength and on strength at definite elongation) and on phase separation<sup>1</sup>. It is of both practical and theoretical interest to study hydrogen bonding of the NH group in polyurethanes. Both n.m.r. and i.r.<sup>2,3</sup> are effective methods for studying hydrogen bonding in polyurethanes and polyamides. Numerous authors<sup>4–11</sup> have performed extensive research on hydrogen bonding in polyamides and polyurethanes using i.r. Trifan *et al.*<sup>4</sup> using i.r. spectroscopy concluded that at room temperature there is essentially 100% hydrogen bonding in linear, aliphatic homopolyamides. Lu *et al.*<sup>1</sup> using high resolution n.m.r. considered that all NH groups in polyesterpolyurethanes and their zwitterionomers form hydrogen bonds in DMSO- $d_6$ . In n.m.r., different chemical shifts result from different kinds of hydrogen bonds. However, the resolution of solid state  $^1\text{H}$  n.m.r. is unable to discriminate between different NH peaks. Polyurethanes in concentrated solution were studied by high resolution n.m.r. in order to benefit from the increased resolution.

Chen *et al.*<sup>12</sup> studied  $\alpha,\omega$ -diaminopropyl terminated polycyanopropyl methylsiloxane-polyurea using FT i.r. spectroscopy, dynamic mechanical analysis, wide-angle X-ray diffraction, d.s.c. and mechanical properties. They found that the solubility of polyurea decreases

after membrane formation and considered that strong hydrogen bonds were formed between the hard segments in polyurea.

We found a linear correlation between the tensile strength and the number of hydrogen bonds, and between the definite strength and the number of hydrogen bonds<sup>1</sup>. The hydrogen bonding interactions were studied by high resolution n.m.r. in concentrated solution, but the physical properties were studied in the solid state. We also studied the relationship between hydrogen bonding interactions and the phase separation in polyester-polyurethanes. The hydrogen bonding interactions in concentrated polyesterpolyurethane solution are similar to those in the solid state.

Mirau and Bovey<sup>13</sup> used two-dimensional n.m.r. (NOESY) to study the interactions between polymer chains of polystyrene/poly(vinyl methyl ether) mixtures in concentrated toluene solutions. The results parallel those obtained for solid polystyrene/poly(vinyl methyl ether) blends.

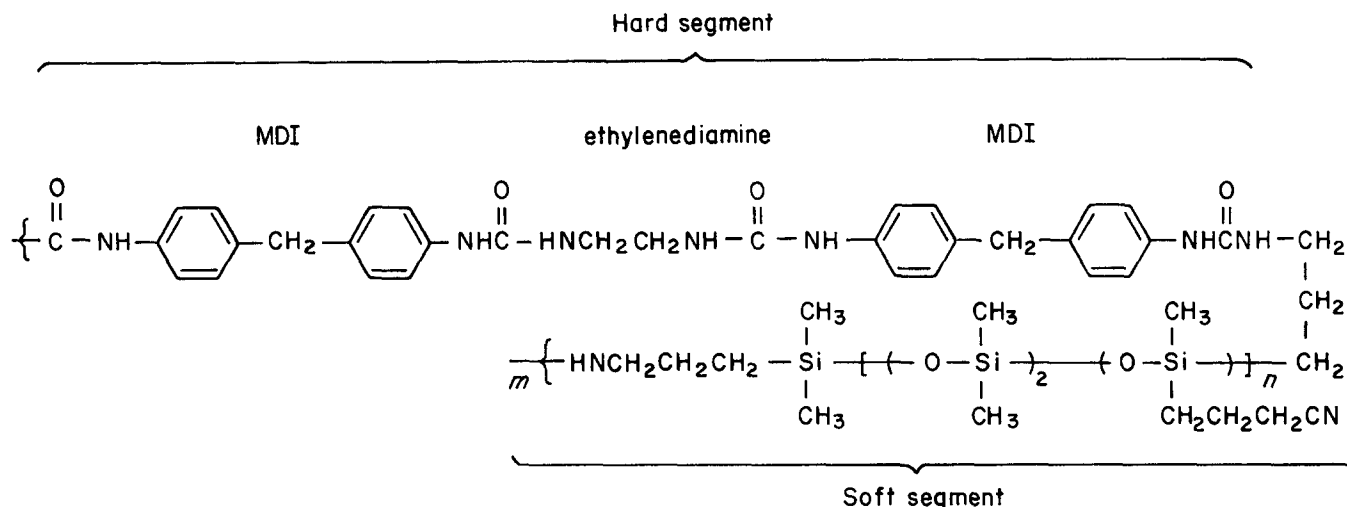
In this paper, molecular interactions, particularly hydrogen bonding, are investigated using one-dimensional (1-D) and two-dimensional (2-D)  $^1\text{H}$  n.m.r.

## EXPERIMENTAL

### Materials

The samples of  $\alpha,\omega$ -diaminopropyl terminated polycyanopropyl methylsiloxane-polyurea (PCS-PU) and  $\alpha,\omega$ -diaminopropyl terminated polydimethylsiloxane-polyurea (PS-PU) were prepared by condensation polymerization in dimethylacetamide<sup>12,14</sup>. The chemical structure of polyurea is shown in *Scheme 1* (where MDI is 4,4'-methylene diphenylene diisocyanate) and *Table 1* gives the sample compositions.

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Scheme 1

Table 1 Sample compositions

Sample	Soft segment $M_n$	Hard segment content (%)	$C_3H_6CN/CH_3$ (molar ratios)
PS-PU-2-11	2045	10.9	0
PS-PU-3-15	3437	14.2	0
PCS-PU-3-7	3674	6.8	1/5
PCS-PU-3-15	3674	16.8	1/5
PCS-PU-3-28	3674	28.1	1/5
PCS-PU-6-28	6276	27.7	1/5
PCS-PU-9-28	9033	27.5	1/5

### N.m.r. experiments

$^1H$  n.m.r. experiments were performed on a Bruker MSL-300 spectrometer operating at a frequency of 300.13 MHz. The temperature range was 23–82°C and the temperature controlling unit used was a Bruker B-VT 100. The 1-D and 2-D  $^1H$  n.m.r. spectra were observed in a 5 mm tube at a concentration of 30% (w/v) in deuterated *N,N*-dimethylformamide (DMF- $d_7$ ).  $^1H$  chemical shifts were measured relative to the aldehyde proton of DMF at 8.00 ppm. DMF- $d_7$  (99% deuterated) was obtained from Aldrich Chemical Company.

The 2-D NOESY spectroscopy was performed in a frequency range of 3311 Hz in both dimensions at room temperature. The time domain data were collected in a data matrix of  $256 \times 1024$  points using the pulse sequence  $90^\circ-t_1-90^\circ-t_m-90^\circ-acq(t_2)$  proposed by Ernst *et al.*<sup>15,16</sup>, with a mixing time  $t_m$  of 600 ms and a recycle time of 1.8 s. For each  $t_1$  value, 128 transients were accumulated. The data matrix was zero-filled to  $512 \times 1024$  points and multiplied by sine-bell window functions in both dimensions before Fourier transformation. The 2-D NOESY spectrum is presented in absolute values.

## RESULTS AND DISCUSSION

### N.m.r. studies of NH groups of polyurea in DMF

Figure 1 shows the  $^1H$  n.m.r. spectrum of PCS-PU in DMF- $d_7$ . The line at 0.155 ppm can be assigned to the methyl groups of the soft segment. The lines at 0.58, 1.60 and 3.21 ppm are due to the three methylene  $CH_2$  groups of the main chain at the end of the soft segment. The lines at 0.74, 1.73 and 2.56 ppm belong to the three

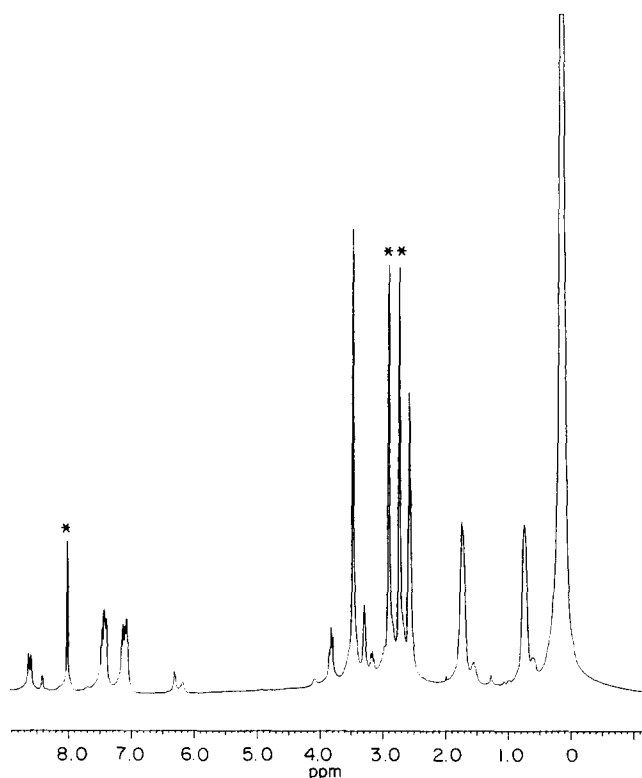
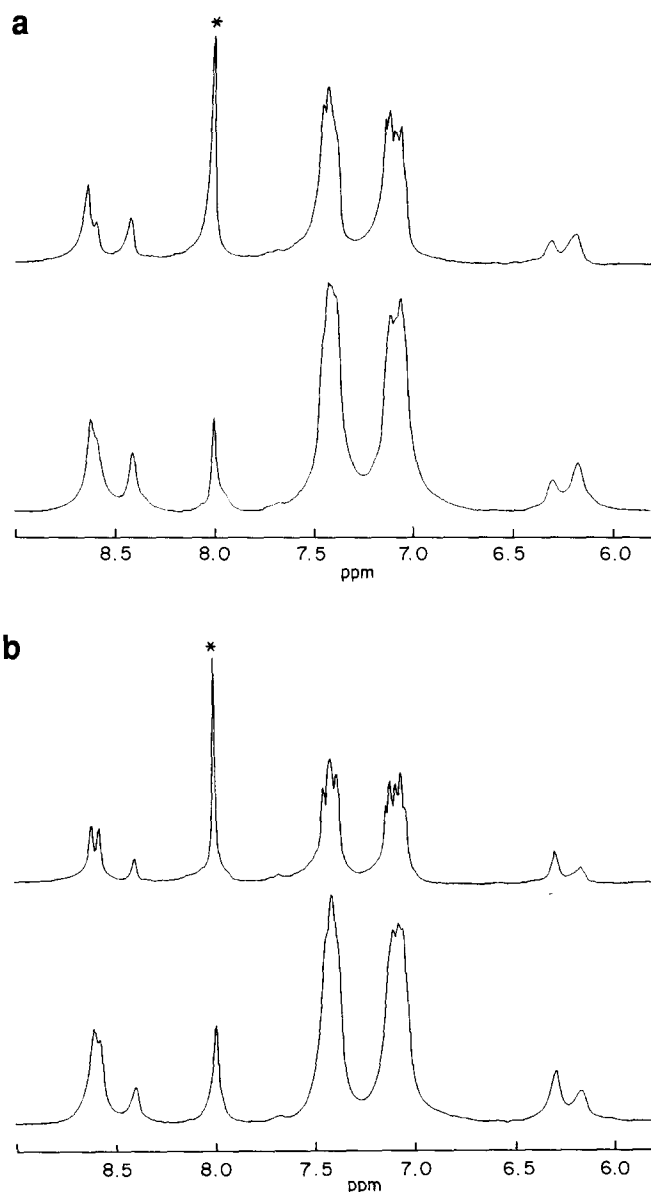


Figure 1  $^1H$  n.m.r. spectrum of PCS-PU in DMF- $d_7$  at a concentration of 30% (w/v) at room temperature. The asterisks indicate the peaks of the solvent DMF

methylene peaks on the side chain of the soft segment. The line at 3.35 ppm is due to the extender ethylenediamine. The line at 3.459 ppm belongs to water; the intensity of this line varies with the concentration of polyurea. The chemical shift of methylene in MDI is 3.81 ppm<sup>1</sup>. The lines at 7.09 and 7.42 ppm can be assigned to the aromatic proton of MDI. The chemical shifts of the NH groups are in the range of 6.0–6.5 ppm and 8.2–8.9 ppm. These are discussed in more detail later.

Figure 2 shows the expanded spectrum of NH peaks in the region of 6–9 ppm. Apparently there are five NH resonances. The NH resonances are partially overlapped and can be resolved through curve decomposition. The values are listed in Table 2. There are only two NH



**Figure 2** Dependence of NH peaks on concentration: (a) PCS-PU-3-28; (b) PCS-PU-6-28. The asterisk indicates the aldehydic proton of DMF

**Table 2** Relative amounts (%) of NH lines

Chemical shift (ppm)	$\alpha$ , 8.62	$\beta$ , 8.59	$\nu$ , 8.41	$\delta$ , 6.30	$\epsilon$ , 6.17
PS-PU-2-11	—	—	45	—	55
PCS-PU-3-7	—	—	48	—	52
PS-PU-3-15	31	—	26	—	43
PCS-PU-3-15	33	—	31	—	36
PCS-PU-3-28	27	17	20	12	24
PCS-PU-6-28	29	20	12	23	16
PCS-PU-9-28	45	13	13	16	13

lines for samples PCS-PU-3-7 and PS-PU-2-11, which were made without the extender ethylenediamine, and there are three NH lines for samples PCS-PU-3-15 and PS-PU-3-15. From Table 2, the relative amount of NH lines of sample PCS-PU-3-7 is close to those of PS-PU-2-11, and that of PCS-PU-3-15 is close to that of PS-PU-3-15. When the hard segment content is higher, there are five NH lines. The NH peaks of amide adjacent to aliphatic hydrocarbon disappear in the

1-D  $^1\text{H}$  n.m.r. spectrum (Figure 1) because of fast exchange<sup>17</sup>. However, the rate of exchange of NH adjacent to aromatic hydrocarbon is very slow. Hydrogen bonds of NH adjacent to aromatic hydrocarbon can be investigated in the  $^1\text{H}$  n.m.r. spectrum without interference.

The assignment of NH lines is as follows:  $\epsilon$ (6.17 ppm) and  $\nu$ (8.41 ppm) are NH lines of amides adjacent to the soft segment. The line at 6.17 ppm can be assigned to free NH, but 8.41 ppm is due to the NH forming hydrogen bonds with carbonyl C=O. The relative amounts of these two peaks decrease in the order of PCS-PU-3-7, PCS-PU-3-15, PCS-PU-3-28. The line at 6.29 ppm belongs to free NH of amides adjacent to the extender ethylenediamine and does not form hydrogen bonding. This line appears after addition of ethylenediamine.  $\alpha$ (8.62 ppm) is due to the NH line of amide adjacent to ethyldiamine and forms hydrogen bonding with carbonyl C=O. The relative amount increases with the length of the soft segment (Table 2). The chance of forming hydrogen bonding increases in the order of PCS-PU-3-28, PCS-PU-6-28, PCS-PU-9-28.  $\beta$ (8.59 ppm) is due to NH forming hydrogen bonding as the following, N-H...N. The fraction of hydrogen-bonded NH groups is >60% when the content of the hard segment is high (>15%) (Table 2).

#### Dependence of NH peaks on concentration

Concentration has little effect on the relative amount of NH peaks as shown in Figure 2. The relative amounts and the line shape of each NH peak, except for the aldehyde proton of DMF, change slightly through computer decomposition after increasing the concentration. The chemical shifts of the NH group are unaffected. This is in accordance with previous results for polyester-polyurethanes<sup>1</sup>.

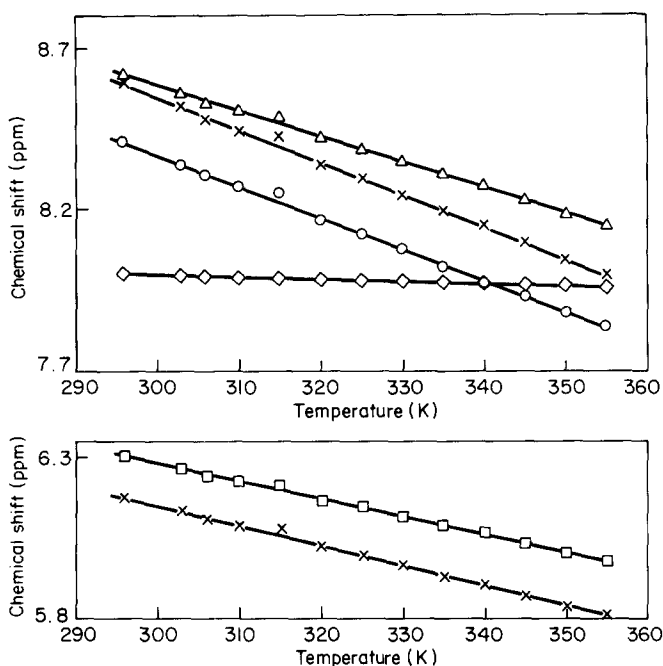
#### Change of chemical shifts with temperature

Figure 3 shows the changes of NH chemical shifts and aldehyde proton of DMF with temperature. The following results are obtained:

1. The chemical shift of the aldehyde proton of the solvent DMF moves slightly to lower frequency with increasing temperature. The aldehyde proton does not form hydrogen bonding with polyurea.
2. The relative amounts and half-widths of the NH lines remain the same in the temperature range 23–82°C through computer decomposition of the  $^1\text{H}$  n.m.r. spectrum. The chemical shifts of NH of polyurea move significantly to lower frequency as shown in Figures 3 and 4. The chemical shift changes of NH forming hydrogen bonding are greater than those of free NH. The line shapes of NH groups are unchanged as shown in Figure 4.
3. The chemical shift of water undergoes a large change with temperature, also the line shape becomes broader (Figure 4). It is deduced that the hydrogen bonding of water has dissociated at higher temperature. Since the relative amounts and line shape of the NH peaks of polyurea are unchanged, polyurea does not form hydrogen bonding with water.

#### 2-D NOESY spectrum of polyurea

Cross signals in a NOESY spectrum rely on the cross relaxation of longitudinal magnetization during the



**Figure 3** Chemical shifts of each NH (including the solvent line): ( $\Delta$ )  $\alpha$  peak; ( $\times$ )  $\beta$  peak; ( $\circ$ )  $\gamma$  peak; ( $\square$ )  $\delta$  peak; ( $\times$ )  $\varepsilon$  peak; ( $\diamond$ ) solvent aldehyde H

The aldehyde proton (8.00 ppm) of solvent DMF has no cross peaks with other peaks. The peak at 3.46 ppm of water has a cross peak with the peak at 6.17 ppm.

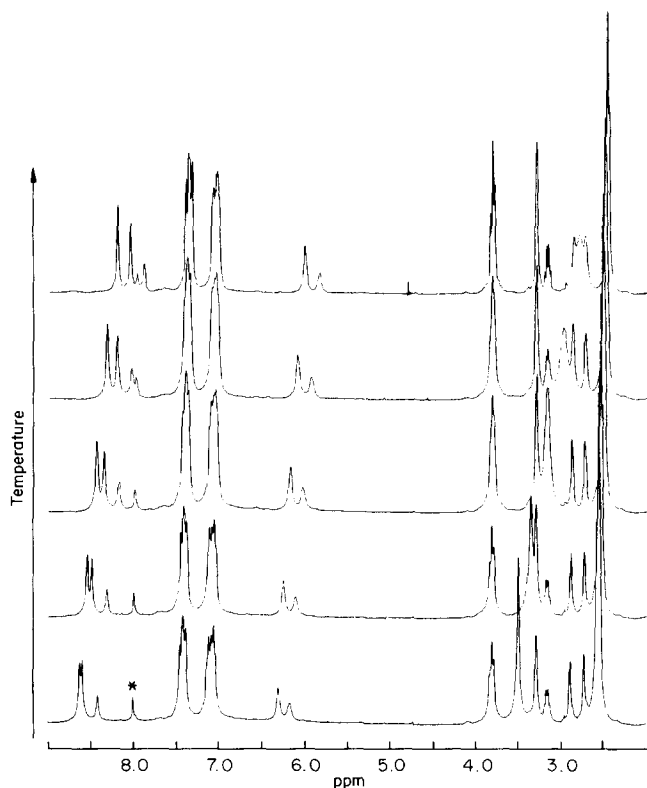
Further interesting results can be obtained from other cross peaks in *Figure 5*. The peak of free NH (6.17 ppm) has a cross peak with the peak of NH (8.41 ppm) forming hydrogen bonding, and the peak of free NH (6.30 ppm) has a cross peak with the peak of NH (8.62 ppm) forming hydrogen bonding. There are no other cross peaks between NH peaks. There exists no exchange between NH groups. This indicates that the distance between NH groups forming hydrogen bonds and free NH groups is very small.

From the above discussion, the hard segments of polyurea in concentrated solution are aligned in a very orderly fashion. The hard segments of polyurea construct a microdomain in concentrated solution. The conformation of the polyurea chain in concentrated DMF solution is similar to that in the solid state. The solvent does not destroy the hydrogen bondings in polyurea. There are no hydrogen bonds between water and NH groups. Thus we can study the interactions in polyurea in concentrated solution and deduce those in the solid state. Increasing temperature does not destroy the microdomain of the hard segment in concentrated DMF solution, so the relative amounts of each NH peak and the half-widths of the NH peaks remain the same.

## CONCLUSIONS

In concentrated DMF solution, there are no interactions (hydrogen bonding) between polyurea and DMF and between polyurea and water. Concentration has little effect on the chemical shifts of NH lines and the relative amounts of NH lines. The DMF solvent cannot destroy the hydrogen bonds formed by NH groups. Hence, the effect of solvent can be neglected.

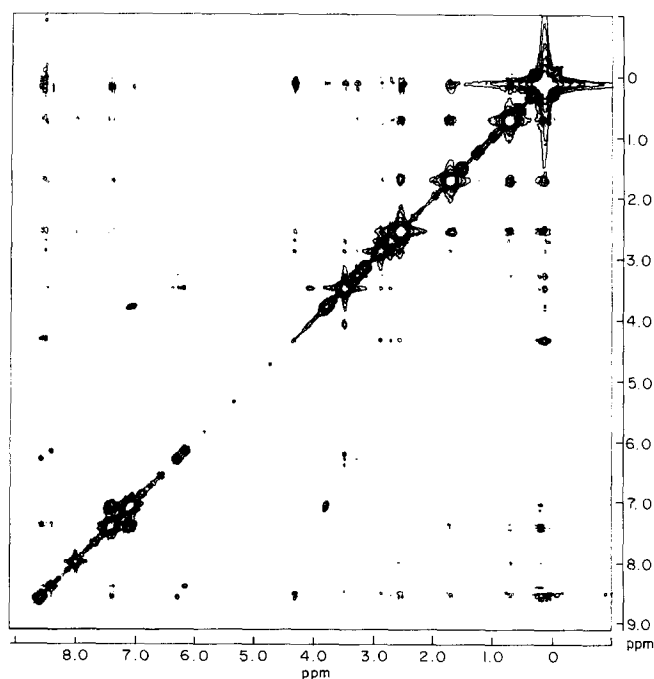
At higher temperatures, the hydrogen bonding of water is dissociated, whilst the hydrogen bonding of the NH



**Figure 4**  $^1\text{H}$  n.m.r. spectra of PCS-PU-6-28 with increasing temperature. The asterisk indicates the peak of the solvent DMF

mixing period and internuclear distance. The NOE varies as the inverse sixth power of the internuclear distance<sup>14</sup>. Hence, the intensity of the signals contains valuable information about the internuclear distances<sup>18–21</sup>.

The 2-D NOESY spectrum of PCS-PU-6-28 is shown in *Figure 5*. As DMF is not a good solvent for the soft segment  $\alpha,\omega$ -diaminopropyl terminated polycyanopropyl methylsiloxane, the soft segments stack closely and have large cross peaks as shown in *Figure 5*.



**Figure 5** 2-D NOESY spectrum of PCS-PU-6-28 at room temperature with a mixing time of 600 ms. The spectrum is given in absolute values

group of polyurea is not. The relative amounts and the half-widths of NH peaks remain the same in the temperature range 23–82°C, but the NH chemical shifts of polyurea move largely to higher field. Increasing temperature also does not destroy the hydrogen bonding. The chemical shift changes of NH forming hydrogen bonds are greater than that of free NH. The strong hydrogen bonds means the hard segments of polyurea are aligned orderly, so the conformation in concentrated DMF solution is similar to that in the solid state.

We can study the interactions of polyurea in concentrated solution and deduce those in the solid state. Further work on the NH of polyurethanes is in progress.

#### ACKNOWLEDGEMENT

The authors are grateful to Professor Xuehai Yu, Department of Chemistry, Nanjing University for providing samples.

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