Study of hydrogen bonds in polyester–polyurethanes by solution n.m.r.

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High resolution ^1H n.m.r. spectra are used to investigate the hydrogen bonds in polyester–polyurethanes based on 4,4′-diphenylmethane diisocyanate, *N*-methyldiethanolamine and poly(ethylene–propylene) adipate and their zwitterionomers. There are several NH peaks in the ^1H n.m.r. spectra resulting from different kinds of hydrogen bonds. In concentrated dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) solutions, there are few hydrogen bonds between the polyurethanes and the solvent or water. The solvent effect can be ignored for hydrogen bonds. The relative amounts and the half-widths of each NH peak remain the same in the temperature range 23–82°C. The chemical shifts of the NH peaks move to lower frequency at higher temperature. The strong hydrogen bonds between groups of the hard segments make the hard segments align in a very orderly fashion. The percentage of NH groups forming hydrogen bonds with C=O groups of the hard segment is large (>45%). Neither the solvent nor H_2O can destroy the strong hydrogen bonds of the hard segment groups in concentrated solution. We deduce the conformation of the hard segments from two-dimensional nuclear Overhauser effect spectroscopy. There is no exchange between NH groups. The conformation of the polyester–polyurethanes in concentrated solution is similar to that in the solid state. Thus we can study the hydrogen-bonding interactions in concentrated solution and deduce those interactions in the solid state.

(Keywords: hydrogen bonds; molecular interactions; polyurethane)

INTRODUCTION

There are several kinds of hydrogen bonds in polyurethanes of which most are formed by NH groups. N.m.r. and i.r.[1,2] are significant methods of studying hydrogen bonds in polyamides and polyurethanes. Many authors[3–10] have performed extensive research on hydrogen bonds in polyamides and polyurethanes using i.r. Hydrogen bonds have significant effects on the phase separation and physical properties of polyurethanes. We have studied polyester–polyurethanes and their zwitterionomers with high resolution n.m.r. and found that different types of hydrogen bonds have different effects on physical properties (tensile strength, strength at a given elongation)[11]. It is important to study the hydrogen bonding of NH groups in polyurethanes. In high resolution n.m.r. spectra, it is known that the different chemical shifts of the NH peaks is from different kinds of hydrogen bonds[11–13]

A dynamic study of polyester–polyurethanes was performed through proton spin-lattice relaxation times for 30% (w/v) polyester–polyurethane solutions using high resolution n.m.r. at various temperatures[14]. The molecular reorientations are not on the same timescale for the hard and soft segments. The molecular reorientations of the soft segments are much faster than those of the hard segments. Strong hydrogen bonds between the hard segment groups mean that the molecular reorientations of the hard segment groups have similar correlation times. The interactions between the hard and soft segments can be studied by comparison of the apparent activation energies of the NH lines.

The conformation of polysiloxane–polyurea in concentrated dimethyl formamide (DMF) solution is similar to that in the solid state, as shown by one-dimensional ^1H n.m.r.[13]. Two-dimensional nuclear Overhauser effect spectroscopy (2D NOESY) shows that there are strong cross-peaks between the NH lines of NH groups forming hydrogen bonds and free NH groups. This indicates that the distance between NH groups forming hydrogen bonds and free NH groups is very small. The strong hydrogen bonds between the hard segments mean that the hard segments of polysiloxane–polyurea are regularly aligned; there are no hydrogen bonds between the soft segments or between the soft segments and the hard segments. The hydrogen bonds of the NH groups do not dissociate and show no exchange with increasing temperature or varying concentration.

Mirau and Bovey[15] have successfully 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.

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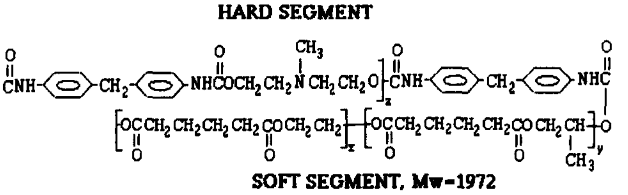
Table 1 Components and their proportions for the polyester–polyurethanes[16]

Sample[a]	PEPA:MDEA:MDI	Viscosity (ml g^{-1})	Fraction of SO_3^- (wt%)
ES-33.4-0	1:2:3	47.6	0
ES-33.4-30			1.6
ES-33.4-70			3.7
ES-33.4-100			4.9
ES-41-0	1:3:4	48.5	0
ES-41-30			2.1
ES-41-60			4.1
ES-41-100			6.5
ES-60-0	1:7.3:8.3	36.9	0

[a] Codes for samples are as follows, e.g. ES-41-60: ES, polyester–polyurethane; 41, fraction of hard segments (MDI + MDEA) by weight; 60, degree of ionization of the N atom of the chain extender (MDEA)



Scheme 1 The polyester–polyurethane chemical structure

For polyester–polyurethanes there are four NH peaks in the ^1H n.m.r. spectra. In this paper, the hydrogen bonds are precisely investigated using high resolution one-dimensional and two-dimensional ^1H n.m.r. We found that the conformations of polyester–polyurethane chains in concentrated dimethyl sulfoxide (DMSO) and DMF solutions are similar to those in the solid state.

EXPERIMENTAL

Materials

The polyester–polyurethanes in this study were prepared by a two-step condensation reaction from poly(ethylene–propylene) adipate (PEPA) (average $M_w = 1972\ g\ mol^{-1}$), 4,4′-diphenylmethane diisocyanate (MDI) and *N*-methyldiethanolamine (MDEA)[16]. The zwitterionomers were prepared by quaternization of the tertiary amine of MDEA with γ-propane sultone. The polyester–polyurethanes were reacted with γ-propane sultone for 3 h at 65°C in anhydrous *N,N*-dimethyl acetamide[11,16].

The components and their proportions for the polyester–polyurethanes are listed in *Table 1*. The polyester–polyurethane structure is shown in *Scheme 1*.

N.m.r. experiments

N.m.r. experiments were carried out on Bruker MSL-300 and AM-300 spectrometers operating at a frequency of 300.13 MHz. The temperature range studied was 23–82°C and the temperature-controlling unit used was a Bruker B-VT 100. The polyester–polyurethanes were dissolved in DMSO-d_6 (99.5% deuterated) or DMF-d_7 (99% deuterated) after membrane formation. The samples for 1D and 2D ^1H n.m.r. study were contained in a 5 mm tube at a concentration of 30% (w/v). ^1H chemical shifts were measured relative to the methyl protons of DMSO at 2.51 ppm and the aldehyde proton of DMF at 8.00 ppm. DMSO-d_6 was obtained from the Beijing Chemical Factory and DMF-d_7 was obtained from Aldrich.

The 2D NOESY spectra were measured over a frequency range of 2800 Hz in both dimensions at room temperature. The time domain data were collected in a data matrix of 256 × 1024 points using the pulse sequence $90°–t_1–90°–t_m–90°–t_2$ proposed by Ernst *et al.*[17,18] with a recycle time of 2.0 s. The mixing time was varied randomly to within ±8% to suppress zero quantum *J* cross-peaks. For each t_1 value 64 transients were accumulated. The data matrix was zero filled to 512 × 1024 points and multiplied by sine bell window functions in both dimensions before Fourier transformation. The 2D NOESY spectra are presented in absolute form.

RESULTS AND DISCUSSION

^1H n.m.r. spectra and hydrogen bonds

The ^1H chemical shifts of the NH peaks give information about the hydrogen bonds. The expanded proton n.m.r. spectra of the ES-41 series are shown in *Figure 1* in the chemical shift range 8.4–10.4 ppm. The assignments of the NH peaks have been made in earlier papers[11,14]. The assignments of the NH peaks are as follows.

1. The α peak (9.95 ppm) belongs to NH groups forming hydrogen bonds with S=O groups (including solvent DMSO-d_6 and γ-propane sultone).

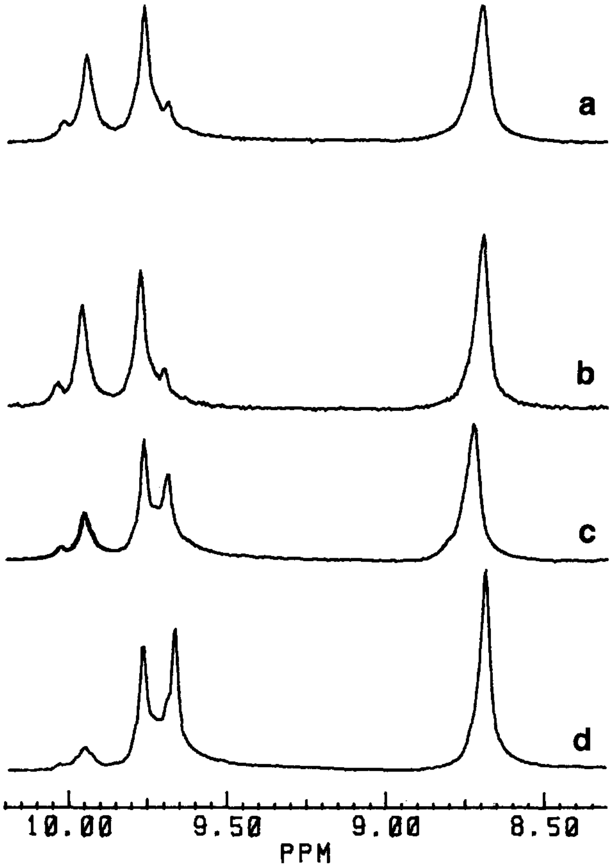


Figure 1 The ^1H n.m.r. spectra of the NH groups of (a) ES-41-100, (b) ES-41-60, (c) ES-41-30 and (d) ES-41-0 in DMSO-d_6 at a concentration of about 30% (w/v) at room temperature

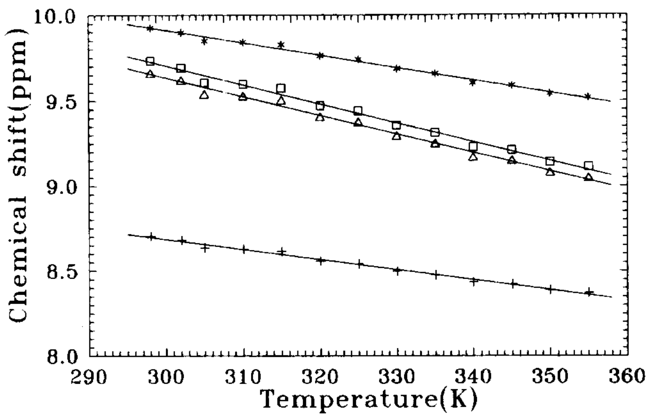


Figure 2 Variation in the chemical shifts of the NH peaks of ES-41-30 with temperature at a concentration of 30% (w/v) in DMSO-d_6: (+) α peak; (△) β peak; (□) γ peak; (∗) δ peak

2. The β peak (9.76 ppm) belongs to NH groups forming hydrogen bonds with the C=O groups of the soft segments (PEPA).
3. The γ peak (9.68 ppm) belongs to NH groups forming hydrogen bonds with the N atoms of the chain extenders (MDEA).
4. The δ peak (8.66 ppm) belongs to NH groups forming hydrogen bonds with the C=O groups of the hard segments.

In polyester–polyurethanes, the number of donors for hydrogen bonds is much greater than the number of acceptors (i.e. NH groups). All NH groups participate in hydrogen bonding and the half-widths of the NH lines are approximate. This is different from the case of polysiloxane–polyureas, in which there are no donors for hydrogen bonds in the soft segments, and not all NH groups participate in hydrogen bonding[12,13].

Change in chemical shift with temperature

The chemical shifts of the NH peaks move to lower frequency at higher temperature, as shown in *Figures 2* and *3*. The change in chemical shift of each NH peak varies with the kind of hydrogen bond. The order of chemical shift change for the NH peaks in the temperature range studied is β peak > γ peak > α peak > δ peak. In an earlier paper[14], we investigated the dynamics of polyester–polyurethanes in DMSO-d_6 using high resolution n.m.r. The apparent activation energies of the four NH peaks are in the order β peak > γ peak > α peak > δ peak. The change in chemical shift of each NH peak is therefore in accordance with the dynamics: the greater the apparent activation energy, the greater is the change in chemical shift.

The relative amounts and half-widths of the NH lines remain the same in the temperature range 23–82°C, as shown through computer decomposition of the ^{1}H n.m.r. spectra using a non-linear least-squares regression routine.

The chemical shift of water undergoes a large change with temperature, and also the line shape becomes broader. It is therefore deduced that proton exchange is faster at a higher temperature. Since the relative amounts and half-widths of the NH lines of the polyester–polyurethanes remain unchanged, it is clear that the NH groups do not form hydrogen bonds with water. There is no proton exchange between the NH

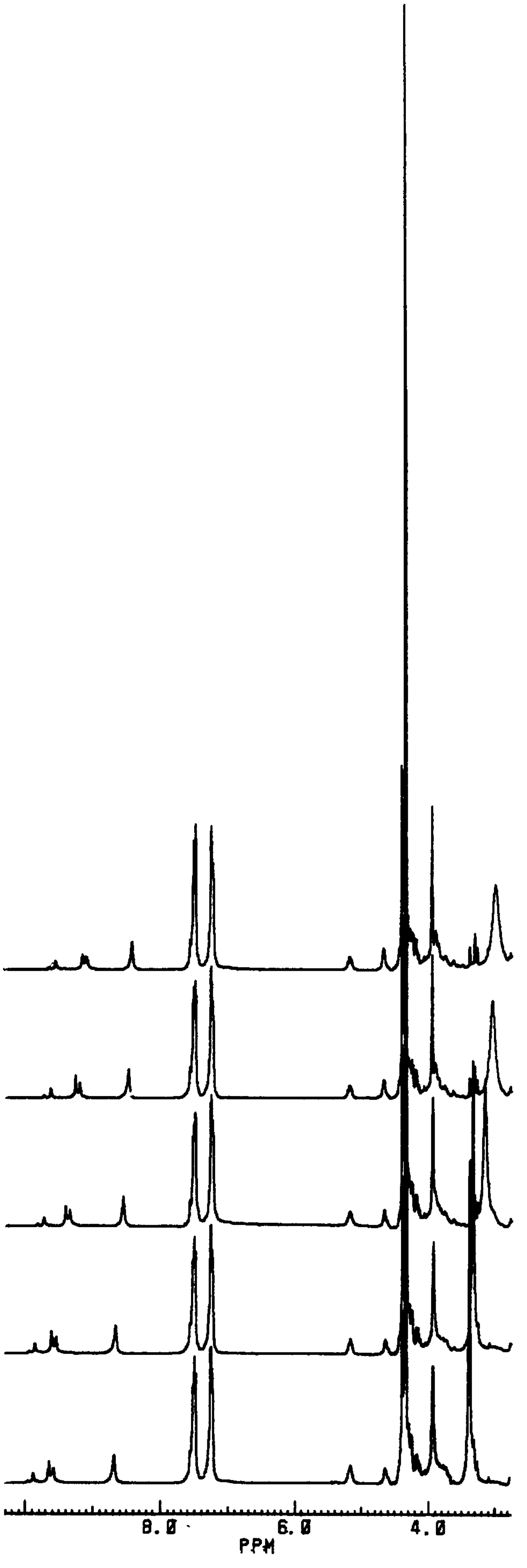


Figure 3 ^{1}H n.m.r. spectra of ES-41-30 with increasing temperature (bottom to top) at a concentration of 30% (w/v) in DMSO-d_6

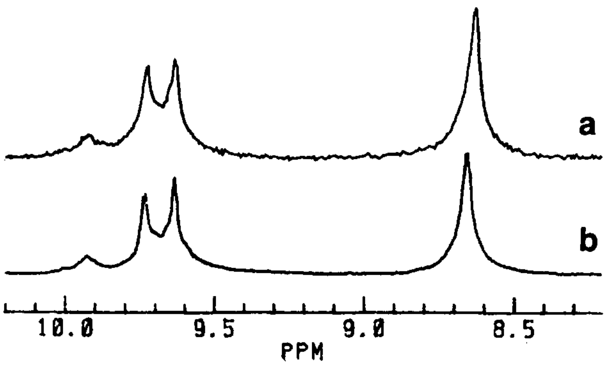


Figure 4 Variation in the NH peaks of ES-41-0 with concentration in DMSO-d_6 at room temperature: (a) about 10% (w/v); (b) about 30% (w/v)

Table 2 The fractions (%) of the NH lines in each of two solvents, obtained through computer decomposition of the ^1H n.m.r. spectra

Sample		α peak	β peak	γ peak	δ peak
ES-41-100	DMSO-d_6	24	30	3	43
	DMF-d_7	23	26	3	48
ES-60-0	DMSO-d_6	2	14	21	63
	DMF-d_7	0	14	19	67

groups and H_2O or between NH groups involved in different kinds of hydrogen bond. This is verified in the NOESY spectra: there are no cross-peaks between the water and NH peaks or between NH peaks corresponding to different kinds of hydrogen bond, as shown in *Figure 5*.

Variation in NH peaks with concentration and solvent

Concentration has little effect on the relative amounts and half-widths of the NH peaks, as shown in *Figure 4*. The spectra of ES-41-0 in *Figure 4* were obtained under the same conditions except for concentration. The chemical shifts of the NH peaks do not change and the half-widths show little change with changes in concentration. It is concluded that the NH groups in polyester–polyurethanes show little interaction with the solvent DMSO-d_6. If there were interactions between the NH groups in polyester–polyurethanes and the solvent, the chemical shifts, relative amounts and half-widths of the NH lines would show large changes if the concentration was decreased.

The relative amounts of the NH peaks in DMF-d_7 are close to those in DMSO-d_6 (*Table 2*). The chemical shifts of the NH peaks in DMF-d_7 are 9.98 ppm (α), 9.60 ppm (β), 9.56 ppm (γ) and 8.77 ppm (δ). Therefore, the chemical shifts of the NH peaks show little change with solvent. We can also conclude that the NH groups form few hydrogen bonds with the solvent. If there were large numbers of hydrogen bonds, the relative amounts of the NH peaks would show large changes upon changing the solvent. This is in accordance with earlier results[11] which show that fewer than 8% of the NH groups form hydrogen bonds with the solvent S=O groups. The relative amount of the α peak is decreased for ES-33.4-0, ES-41-0 and ES-60-0. The percentages for the α peak are 8% for ES-33.4-0, 5% for ES-41-0 and 2% for ES-60-0.

2D NOESY

Cross-signals in the NOESY spectrum rely on internuclear distance and the cross-relaxation of longitudinal magnetization during the mixing period. The intensity of the cross-signal contains valuable information about the internuclear distance. There are no cross-peaks between the water peak (3.70 ppm) and the NH peaks in NOESY spectra, because there is no exchange between water and the NH groups. There are also no cross-peaks between NH peaks, presumably because the NH groups are very inactive and the distances between NH groups forming different kinds of hydrogen bond are large. In the 2D NOESY spectrum, the cross-peak between the phenyl proton at 7.35 ppm (H2 in *Scheme 2*) and the δ peak at 8.66 ppm (H1 in *Scheme 2*) is strong, but the cross-peak

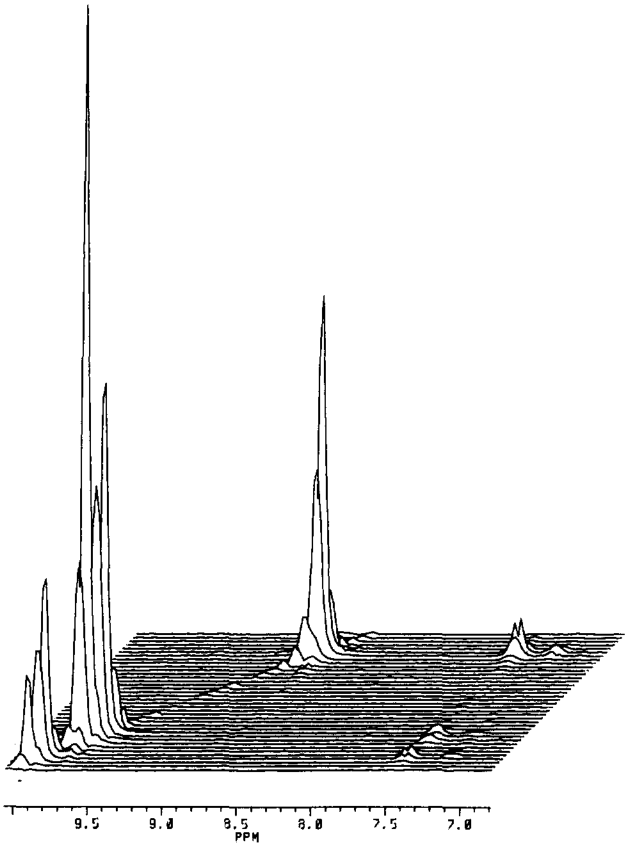
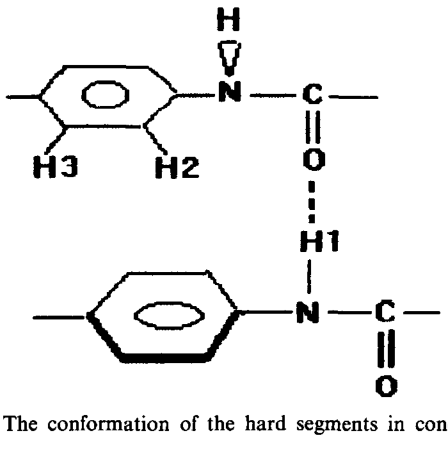


Figure 5 The stacked plots of the NOESY spectrum of ES-41-30 with a mixing time of 200 ms



Scheme 2 The conformation of the hard segments in concentrated solution

between the phenyl proton at 7.16 ppm (H3 in *Scheme 2*) and the δ peak is weak. *Figure 6* shows how the NOE values vary with mixing time. The NOE value has a maximum at about 200 ms for the cross-peak between the δ peak and the phenyl proton at 7.35 ppm (H2 in *Scheme 2*). The NOE value has no maximum for the cross-peak between the δ peak and the peak at 7.16 ppm (H3 in *Scheme 2*) in our experiments. This indicates that the distance between H1 and H2 is small, and so the cross-peak between H1 and H2 is strong in the NOESY spectrum. The cross-peaks are weak between the phenyl proton at 7.35 ppm and the other NH peaks apart from the δ peak. The polyester–polyurethane hard segment conformation in concentrated solution is shown in *Scheme 2*, in which the distance between H1 and H2 is smaller than that between H1 and H3. The C=O, N atom and phenyl of MDI are in a plane in *Scheme 2*.

Discussion of the conformation

After computer decomposition of the NH peaks (*Figure 1*), the percentage of each group forming hydrogen bonds with NH groups can be calculated according to the chemical structure (*Scheme 1*) and the components in *Table 1*. The percentages of groups forming hydrogen bonds with NH groups in the polyester–polyurethanes are shown in *Table 3*.

For the C=O groups of the hard segments, the average fractions forming hydrogen bonds with NH groups are 55% for the ES-33.4 series, ~44% for the ES-41 series and 63% for ES-60-0. Ionization does not alter the fractions for the ES-33.4 and ES-41 series (*Table 3*). On the other hand, the C=O groups of the soft segments can also form strong hydrogen bonds with NH groups, but the fraction of the soft segment C=O groups forming hydrogen bonds with NH groups is only about 10%. We think that the hard segments are regularly aligned and the NH groups contact incompletely with the C=O groups of the soft segments. The hard segments cannot move freely in the presence of strong hydrogen bonds between the groups of the hard segments. It is possible that C=O groups of the soft segments form hydrogen bonds with NH groups at the interface. Neither the solvent nor water can invade the microdomain of the hard segments.

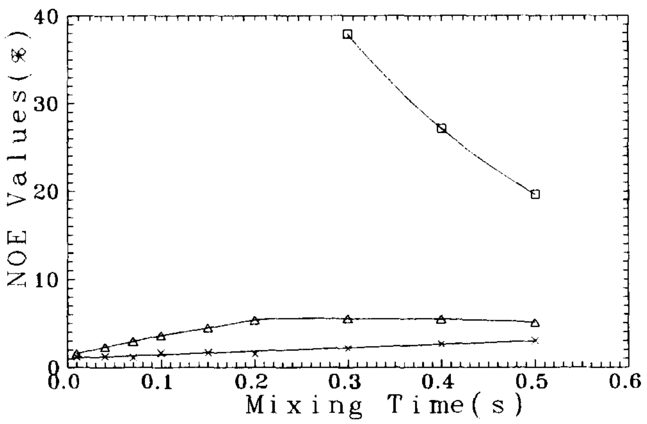


Figure 6 Dependence of the NOE values of ES-41-30 on mixing time at room temperature in DMSO-d_6: (□) diagonal peak of H1; (△) cross-peak between H1 and H2; (×) cross-peak between H1 and H3. H1, H2 and H3 are defined in *Scheme 2*

For the MDEA N atoms in the ES-33.4 series, the average fraction forming hydrogen bonds with NH groups is about 8%. This indicates that the activity of MDEA in the ES-33.4 series is high, in accordance with earlier solid-state results[19]. However, for ES-41-0 and ES-60-0 the fractions of N atoms forming hydrogen bonds with NH groups are very high.

The molecular polarity of the hard segments is greater than that of the soft segments. The strong hydrogen bonds make the hard segments align in an orderly fashion. The hard segments of polyester–polyurethanes construct a microdomain in concentrated solution. The hard segments of polyester–polyurethanes cannot move freely in concentrated solution. The correlation times of molecular reorientation are similar for the hard segment groups[14].

CONCLUSIONS

From the above discussion, we can conclude that the hard segments of polyester–polyurethanes in concentrated solution are aligned in a very orderly fashion. Neither the solvent nor water can invade the microdomain of the hard segments. Concentration has little effect on the chemical shifts and relative amounts of the NH lines. Concentration changes do not alter the size of the hard segment microdomain in DMSO-d_6 solution. There is no proton exchange between NH groups, and the half-widths of the NH lines are not increased at higher temperature. The water peak in the ^1H n.m.r. spectrum becomes broader at higher temperature. It is concluded from the 2D NOESY spectra that the hard segments are aligned in an orderly fashion. Finally, we can say

Table 3 Percentages of groups forming hydrogen bonds with NH groups in polyester–polyurethanes at a concentration of approximately 30% (w/v) at room temperature

Sample	γ-Propane sultone S=O groups	Soft segment C=O groups	MDEA N atoms	Hard segment C=O groups
ES-33.4-0	–	9	6	55
ES-33.4-30	30	9	8	57
ES-33.4-70	15	9	11	54
ES-33.4-100	12	10	8	54
ES-41-0	–	8	39	44
ES-41-30	49	9	27	45
ES-41-60	49	10	11	42
ES-41-100	32	11	4	43
ES-60-0	–	10	24	63

that the hydrogen-bonding interactions in a bulk polyurethane are similar to those in a concentrated solution.

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