Investigation of interactions in polyether–polyurethanes and their mixtures with other polyurethanes by high resolution n.m.r.

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The hydrogen bonds in polyether–polyurethanes based on 4,4′-diphenylmethane diisocyanate, *N*-methyldiethanolamine (MDEA) and poly(tetramethylene oxide) glycol (PTMG) and their zwitterionomers were investigated by high resolution ^1H n.m.r. in deuterated dimethyl formamide. There are four NH peaks in each of the ^1H n.m.r. spectra resulting from four kinds of hydrogen bonds. The NH groups in the hard segments may form hydrogen bonds with the C=O groups of the hard segments, the N atoms of the MDEA portions, the S=O groups of γ-propanesulfonates and the O atoms of PTMG. The relative amounts and chemical shifts of the NH peaks do not change with polyurethane concentration. Mixtures of polyether–polyurethanes with a polysiloxane–polyurea and a polyester–polyurethane were also studied by ^1H n.m.r. There are no hydrogen-bonding interactions between the hard segments of the two different polyurethanes in these mixtures. The hard segments of the two different polyurethanes cannot be mixed at the molecular level. This is proven by nuclear Overhauser effect spectroscopy (NOESY) for a mixture of a polyether–polyurethane with a polysiloxane–polyurea. The NOESY spectrum indicates that the soft segments of the two different polyurethanes can be mixed at the molecular level. Most of the hard segments form microdomains in concentrated solution. Neither the solvent nor water can invade the microdomains rich in hard segments. Thus we can study hydrogen-bonding interactions in concentrated solution and deduce those interactions in the solid state.

(Keywords: hydrogen bonds; high resolution n.m.r.; polyurethane)

INTRODUCTION

Polyurethanes are well known segmental thermoplastic elastomers with a wide range of mechanical properties depending on the ratio of the soft to the hard segments. Ionic interactions in polyurethanes improve the morphology and physical properties[1]. There are several kinds of hydrogen bonds in polyurethanes, most of which are formed by NH groups. N.m.r. and i.r.[2,3] are effective methods for studying hydrogen bonds in polyurethanes and polyamides. In the n.m.r. spectra, the chemical shifts of the NH groups are very sensitive to hydrogen bonding[4–6]. Hydrogen bonds in polyurethanes strongly affect the phase separation and physical properties (tensile strength and strength at a given elongation)[4,5]. The high elasticity of polyurethanes comes from the hard domain stabilized by hydrogen bonds between the hard segments[7]. It is of both practical and theoretical importance to study hydrogen bonds in polyurethanes.

We have studied the hydrogen bonds in polyester–polyurethanes and polysiloxane–polyurea by high resolution ^1H n.m.r. in concentrated solution[5,6]. Four NH peaks for polyester–polyurethanes and five NH peaks for polysiloxane–polyurea exist in the ^1H n.m.r. spectra. The chemical shifts and the relative amounts of the NH peaks for different hydrogen bonds are independent of concentration. The half-widths and the relative amounts of the NH peaks do not change with temperature[2,3]. The hydrogen bonds of NH groups do not dissociate or exchange with increasing temperature. The solvent effects can be ignored. The conformation of the polyurethanes in concentrated solution is similar to that in the solid state as shown by two-dimensional nuclear Overhauser effect spectroscopy (2D NOESY). The strong hydrogen bonds between NH groups and groups of the hard segments mean that the hard segments of polyurethanes are also regularly aligned in concentrated solution.

In this article, we study hydrogen bonds in polyether–polyurethanes with different hard segment contents and different degrees of ionization. The NH groups in the hard segments may form hydrogen bonds with the C=O groups of the hard segments[2,4–6], the N atoms of the chain extender, the O atoms of the soft segment polyether[2,8,9], etc. The effects of polyurethane concentration, hard segment content and degree of ionization on hydrogen bonding are reported. We also study mixtures of polyether–polyurethanes with a polysiloxane–polyurea and a polyester–polyurethane.

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EXPERIMENTAL

Samples

The polyether–polyurethanes were prepared by condensation reactions from poly(tetramethylene oxide) glycol (PTMG, average $M_w = 1000\,\mathrm{g\,mol^{-1}}$), 4,4′-diphenylmethane diisocyanate (MDI) and *N*-methyldiethanolamine (MDEA)[1]. The zwitterionomers were prepared by quaternization of the tertiary amine MDEA with γ-propanesulfonate[10]. The polyether–polyurethane chemical structure is shown in *Scheme 1*. The codes for the polyether–polyurethanes take the form ET-*A*-*B*, where ET denotes polyether–polyurethane, *A* gives the weight percentage of the hard segment and *B* gives the theoretical degree of ionization on the N atom of the chain extender MDEA.

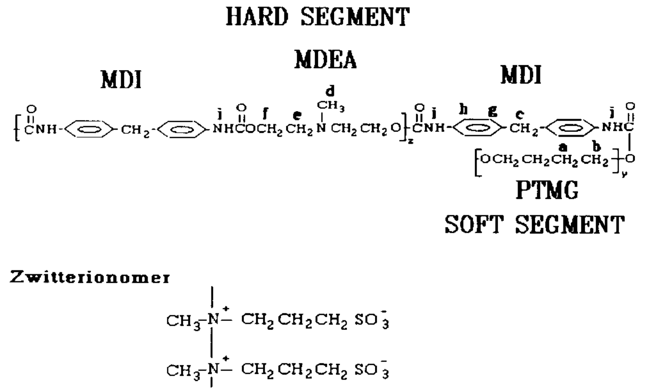
The polysiloxane–polyurea used in this study has been described in an earlier paper[6]. The weight fraction of the hard segment is 16.8%, and the molecular weight of the soft segment, α,ω-diaminopropyl-terminated poly(cyanopropylmethylsiloxane), is $3674\,\mathrm{g\,mol^{-1}}$. The hard segment consists of MDI and ethylenediamine. The abbreviation for the polysiloxane–polyurea is PCS-PU-3-15.

The polyester–polyurethane used in this study was prepared by a two-step polycondensation reaction from poly(ethylene–propylene) adipate (PEPA, average $M_w = 1972\,\mathrm{g\,mol^{-1}}$), MDI and MDEA[4,11]. The weight fraction of the hard segment is 41%. The degree of ionization on the N atom of the chain extender MDEA is 30%. The abbreviation for the polyester–polyurethane is ES-41-30.

N.m.r. experiments

All n.m.r. experiments were carried out on a Bruker AM-300 spectrometer operating at 300 MHz for ^{1}H at room temperature. The polyether–polyurethanes, ES-41-30 and PCS-PU-3-15 were dissolved in 99% deuterated dimethyl formamide (DMF-d_7) after membrane formation. The chemical shifts were measured relative to the aldehyde proton of DMF at 8.0 ppm. The samples for one-dimensional and two-dimensional ^{1}H n.m.r. were contained in 5 mm tubes. The polyurethane concentration was about 25% (w/v).

Two-dimensional NOESY spectra were acquired using the 90°–t_1–90°–t_m–90°–t_2 pulse sequence[12,13]. A total of 256 × 1024 data points were acquired with a sweep width of 3425 Hz in both dimensions. The data matrix was zero filled to 512 × 1024 points and multiplied by a sine bell window function in both dimensions before Fourier transformation. The 2D NOESY spectra are presented in absolute form.



Scheme 1 The chemical structure of the polyether–polyurethanes and the assignments of the ^{1}H n.m.r. peaks

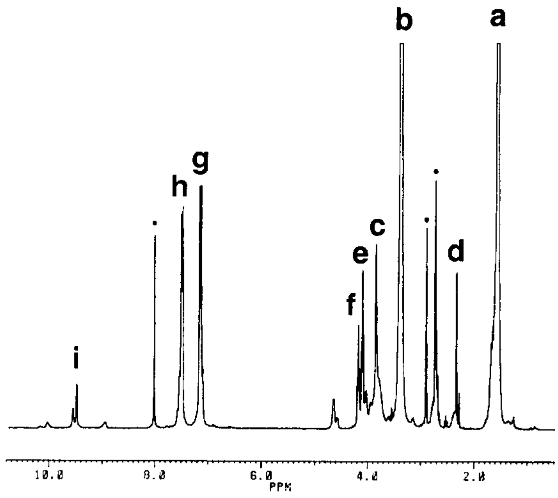


Figure 1 The ^{1}H n.m.r. spectrum of polyether–polyurethane ET-37-35 in DMF-d_7 at room temperature (● indicates a solvent peak): (a) 1.56 ppm; (b) 3.37 ppm; (c) 3.84 ppm; (d) 2.32 ppm; (e) 4.09 ppm; (f) 4.17 ppm; (g) 7.14 ppm; (h) 7.49 ppm; (i) 8.5–10.5 ppm. See *Scheme 1* for assignments (a) to (i)

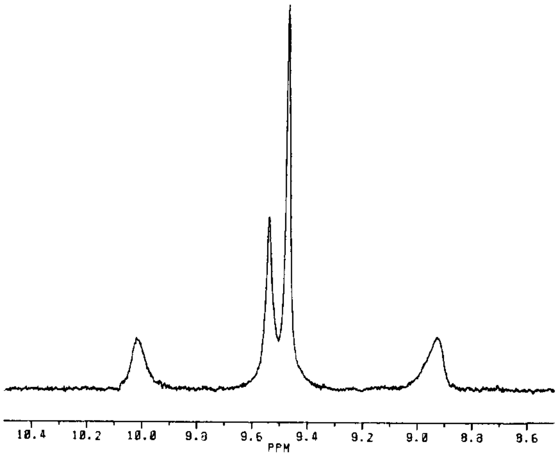


Figure 2 Typical pattern of NH peaks in the ^{1}H n.m.r. spectrum of ET-37-35 at room temperature in DMF-d_7

RESULTS AND DISCUSSION

^{1}H n.m.r. spectra of polyether–polyurethanes

The ^{1}H n.m.r. spectra were assigned according to earlier results[4,6]. The assignments for the ^{1}H n.m.r. spectra are shown in *Scheme 1* and *Figure 1*. The line at 3.78 ppm belongs to trace amounts of water in the DMF-d_7, and the intensity of this line varies with the polyether–polyurethane concentration. There are several NH peaks in the range 8.5–10.5 ppm as there are for the polyester–polyurethane[4] and polysiloxane–polyurea[5,6]. The NH peaks will be discussed in more detail later.

NH peaks in the ^{1}H n.m.r. spectra

There are four NH peaks in the ^{1}H n.m.r. spectra of certain samples (*Figure 2*), and their chemical shifts are 10.00 ppm (α), 9.53 ppm (β), 9.47 ppm (γ) and 8.94 ppm (δ). The relative amounts of the NH peaks vary with the hard segment content and the degree of ionization. The percentages of the four NH peaks are listed in *Table 1*;

Table 1 The percentages of the NH peaks obtained by computer decomposition of the ^1H n.m.r. spectra

Sample	α peak	β peak	γ peak	δ peak
ET-23-0	–	–	77	23
ET-23-25	–	–	81	19
ET-23-65	–	–	82	18
ET-23-100	–	–	82	18
ET-37-0	–	26	52	22
ET-37-35	15	28	40	17
ET-37-65	32	12	39	17
ET-37-100	35	11	37	17

they were obtained from a computer decomposition of the ^1H n.m.r. spectra with a non-linear least-squares routine.

The assignments of the NH peaks are as follows.

1. The peak at 10.00 ppm comes from the NH groups forming hydrogen bonds with the S=O groups of γ-propanesulfonates.
2. The β peak at 9.53 ppm comes from the NH groups forming hydrogen bonds with the N atoms of the chain extender MDEA portions.
3. The γ peak at 9.47 ppm comes from the NH groups forming hydrogen bonds with the O atoms of the soft segment PTMG. The mobility of the soft segment PTMG is much larger than that of the hard segment in solution, and thus the half-width of the γ peak is smaller than the half-widths of the α, β and δ peaks. The fraction of the γ peak decreases with increasing hard segment content, as can be seen by comparison of ET-23-0 and ET-37-0 (*Table 1*).
4. The δ peak at 8.94 ppm comes from the NH groups forming hydrogen bonds with the C=O groups of the hard segments. The C=O, N and phenyl of MDI form a hybrid π bond, and the shielding effect of the C=O is large.

There are no free NH groups in polyether–polyurethanes. All NH groups participate in hydrogen bonding. There are also no hydrogen-bonding interactions between the NH groups and DMF or H_2O.

For the ET-23 series, there are only two NH peaks in the ^1H n.m.r. spectra. The percentages of the NH peaks are not altered after ionization. There are no hydrogen-bonding interactions between the NH group of MDI and the N atom of MDEA or between the NH group of MDI and the S=O group of γ-propanesulfonate for the ET-23 series. The molecular motions of the chain extender MDEA are greater for the ET-23 series[4].

For ET-37-0, there are three NH peaks in the ^1H n.m.r. spectrum. After ionization the percentage of the α peak increases, and the percentages of the β, γ and δ peaks decrease as expected. The fraction of NH groups forming hydrogen bonds with groups of the hard segment is larger than 60% for ET-37-35, ET-37-65 and ET-37-100.

The fraction of the γ peak is greater than that of the other NH peaks in *Table 1*, but the fraction of O atoms from PTMG forming hydrogen bonds with NH groups is much smaller than the fraction of groups of the hard segment forming hydrogen bonds with NH groups, in accordance with the chemical structure.

Variation in NH peaks with concentration

The percentages and half-widths of the NH peaks as obtained from a computer decomposition of the ^1H n.m.r. spectra do not change with concentration. The spectra in *Figure 3* were obtained under the same acquisition conditions except for the polyether–polyurethane concentration. Concentration has little effect on the hydrogen-bonding behaviour of the NH groups. This is in accordance with earlier results[5,6]. It is concluded that the solvent cannot destroy the hydrogen bonds in polyether–polyurethanes.

Mixture with polysiloxane–polyurea

In polysiloxane–polyurea PCS-PU-3-15 solution there are free NH groups. In polyether–polyurethane ET-37-65 solution there are many groups which can form hydrogen bonds with NH groups. If the hard segments of these two polyurethanes can be mixed at the molecular level, the relative amount of each NH peak will be changed and the number of free NH groups in polysiloxane–polyurea will decrease. For PCS-PU-3-15, the line at 6.18 ppm belongs to free NH groups, while the lines at 8.43 ppm and 8.65 ppm belong to NH groups forming hydrogen bonds with groups of the hard segments. *Figure 4* shows that the line for the free NH groups in polysiloxane–polyurea is present for the mixture. The ratios of the NH peak percentages for each polyurethane before mixing are close to those after mixing (*Table 2*). The percentages, chemical shifts and half-widths of the NH peaks are independent of time, and the relative amounts of the NH peaks show few changes, within experimental error, as shown by the computer decomposition results in *Table 2*. The chemical shifts of the NH peaks of PCS-PU-3-15 show a few changes after mixing with polyether–polyurethane ET-37-65. The δ peak of ET-37-65 and the NH peak of PCS-PU-3-15, of which

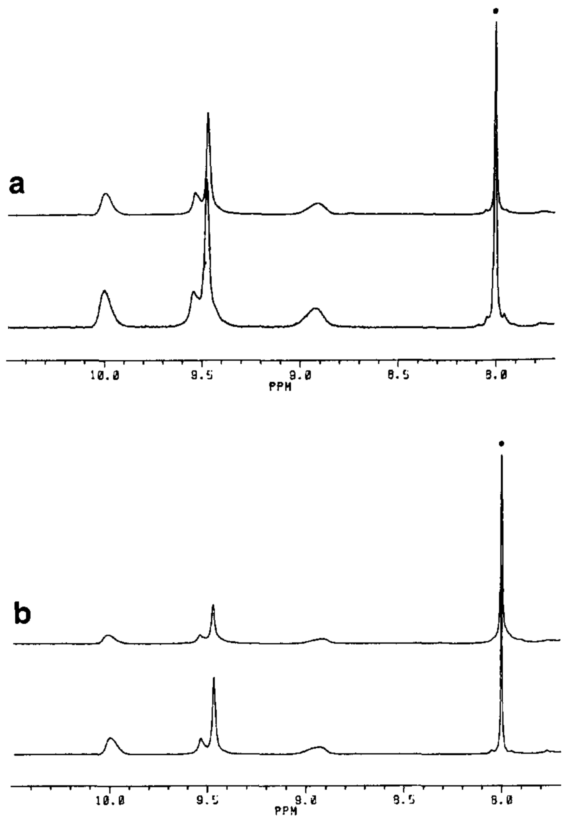


Figure 3 Variation in NH peaks with concentration at room temperature in DMF-d_7 (● indicates a solvent peak): (a) ET-37-65; (b) ET-37-100

the chemical shift is 8.65 ppm, are merged into one peak. The chemical shift of the NH peak is sensitive to the polyurethane. We think that there are no hydrogen-bonding interactions between the hard segments of these two polyurethanes and that the hard segments of these two polyurethanes cannot be mixed at the molecular level.

Mixture with polyester–polyurethane

Polyether–polyurethane and polyester–polyurethane in this study have the same chemical structure except for the soft segment. In these two polyurethanes there are the same kinds of hydrogen bonds except for the hydrogen bonds between NH groups and the soft segment. For ES-41-30, the lines at 10.00 ppm, 9.61 ppm, 9.55 ppm and 8.79 ppm belong to NH groups forming hydrogen bonds with the S=O groups of γ-propanesulfonates, the C=O groups of the soft segments (PEPA), the N atoms of the chain extenders (MDEA) and the C=O groups of the hard segments, respectively. *Figure 5* shows the ^{1}H n.m.r. spectra before and after mixing. The NH peaks reflecting the same kinds of hydrogen bonds in these two polyurethanes are merged into one peak after mixing. The chemical shifts of some peaks show a few changes after mixing (*Table 3*). The chemical shifts of some NH peaks are sensitive to the polyurethane. The half-widths of the NH peaks reflecting the same kinds of hydrogen bonds in the polyurethanes have similar values in *Figure 5*. The percentages, chemical shifts and half-widths of the NH peaks are also independent of time in the mixture.

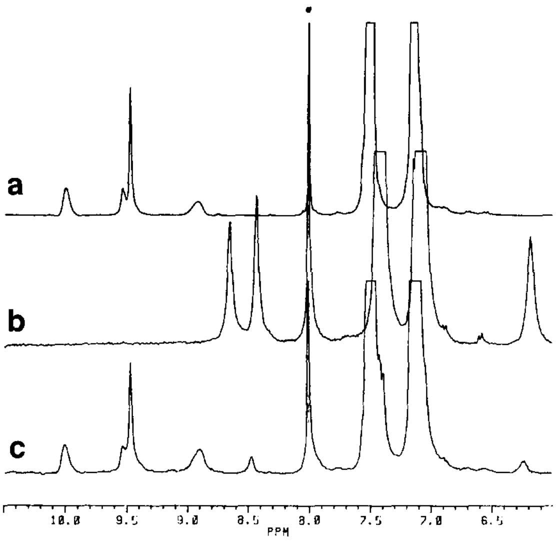


Figure 4 Comparison of NH peaks before and after mixing at 22°C in DMF-d_7 (● indicates a solvent peak): (a) ET-37-65; (b) PCS-PU-3-15 (c) mixture

If the hard segments of these two polyurethanes can be mixed at the molecular level, the ratios of the NH peak percentages reflecting the hydrogen bonds of NH groups with groups of the hard segments will be altered. On the other hand, if the hard segments of the polyurethanes cannot be mixed at the molecular level, the ratios of the NH peak percentages will remain the same and the linear equations derived from the data in *Table 3* will have only one solution. The linear equations are as follows:

$11x+35y=23$ for hydrogen bonds between NH groups and S=O groups (γ-propanesulfonate),

$20x+11y=15$ for hydrogen bonds between NH groups and N atoms (MDEA) and

$45x+17y=30$ for hydrogen bonds between NH groups and C=O groups (MDI).

The only solution to these equations is $x=0.47$ and $y=0.51$. Thus the ratios of the NH peak percentages reflecting hydrogen bonds of NH groups with groups of the hard segments in each polyurethane remain the same after mixing. The hard segments of these two polyurethanes cannot be mixed at the molecular level.

The ratios of the NH peak percentages reflecting hydrogen bonds of NH groups with groups of the soft

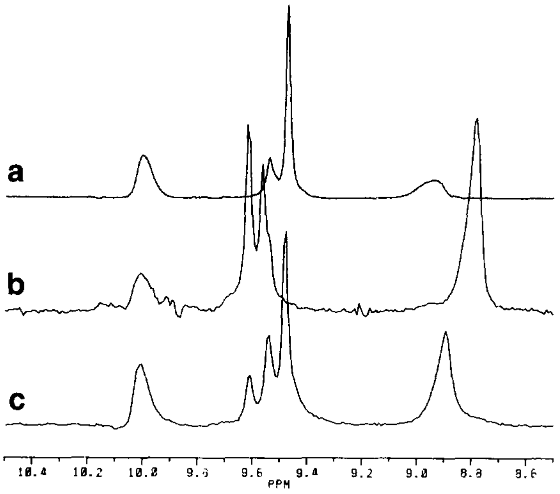


Figure 5 Comparison of NH peaks before and after mixing at 22°C in DMF-d_7: (a) ET-37-100; (b) ES-41-30; (c) mixture

Table 3 The percentages of the NH peaks before and after mixing

Chemical shift (ppm)	10.0	9.61	9.55	8.79	9.47	8.94	8.90
ES-41-30	11	24	20	45	–	–	–
ET-37-100	35	–	11	–	37	17	–
Mixture	23	6	15	–	26	–	30

Table 2 The percentages of the NH peaks before and after mixing

Chemical shift (ppm)	8.65	8.43	6.18	10.00	9.53	9.47	8.94	8.47	6.23
PCS-PU-3-15	33	31	36	–	–	–	–	–	–
ET-37-65	–	–	–	32	12	39	17	–	–
Mixture (at 2 min after mixing)	–	–	–	23	9	29	26	6	7
Mixture (at 40 days after mixing)	–	–	–	22	9	28	23	9	9

segments show changes after mixing. The NH peak percentage for hydrogen bonds between NH groups and polyester PEPA C=O groups is increased by about 7%, while the NH peak percentage for hydrogen bonds with polyether PTMG O atoms is decreased by about 5% in the mixture, because the hydrogen-bonding abilities of C=O groups (PEPA) and O atoms (PTMG) are different. It is concluded that the soft segments of these two polyurethanes are mixed at the molecular level.

2D NOESY spectrum of the mixture of polyether–polyurethane with polysiloxane–polyurea

NOESY can be used to investigate the interactions between protons. If polyether–polyurethane and polysiloxane–polyurea can be mixed at the molecular level, there will be cross-peaks between the peaks of these two polyurethanes. *Figure 6* shows the NOESY spectrum of the mixture with a mixing time of 500 ms at 22°C. The peak at 0.16 ppm belongs to the CH_3 of α,ω-diaminopropyl-terminated poly(cyanopropylmethylsiloxane). There are strong cross-peaks between the peaks of the soft segments for these two polyurethanes, i.e. cross-peaks between 0.16 ppm and 1.56 ppm and between 0.16 ppm and 3.37 ppm. These cross-peaks indicate that the soft segments of these two polyurethanes can be mixed at the molecular level. On the other hand, there are no cross-peaks between the NH peaks except for the cross-peak between 6.17 ppm and 8.41 ppm in *Figure 7*. The cross-peak between 6.17 ppm and 8.41 ppm has been explained in an earlier paper[6]. It is concluded that the hard segments of these two polyurethanes cannot be mixed at the molecular level.

The molecular polarity of the hard segments is greater than that of the soft segments and the solvent. We think that the strong hydrogen bonds between NH groups and groups of the hard segments effect a regular alignment of the hard segments of the polyurethanes in concentrated solution. Study of the 2D NOESY spectrum and the hydrogen-bonding interactions in the mixture indicates that the hard segments of two polyurethanes cannot be mixed at the molecular level. The regularly aligned hard segments construct a microdomain in concentrated solution, so that the hard segments cannot be mixed at the molecular level between two kinds of polyurethanes. The solvent does not destroy the hydrogen bonds in polyurethanes. There are no hydrogen bonds between water and the NH groups, or between the solvent and the NH groups. We can therefore study the hydrogen-bonding interactions in polyurethanes in concentrated solution and deduce those interactions in the solid state.

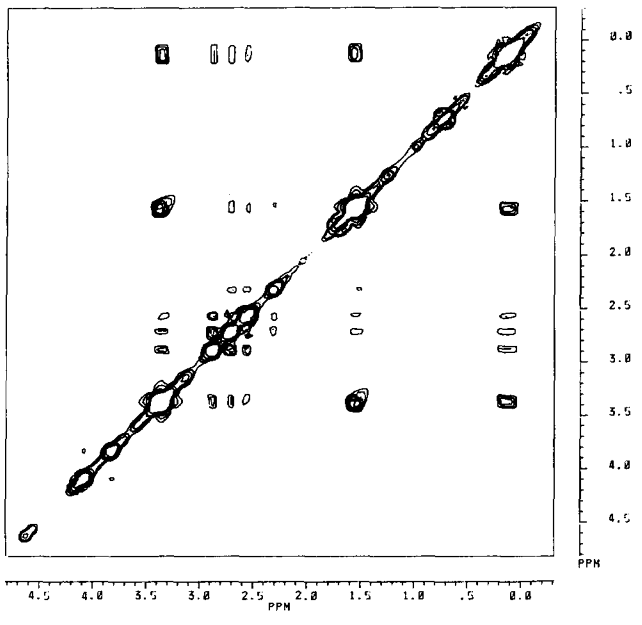


Figure 6 The NOESY spectrum of the mixture of ET-37-65 with PCS-PU-3-15 in the soft segment region (mixing time of 500 ms) at room temperature in DMF-d_7

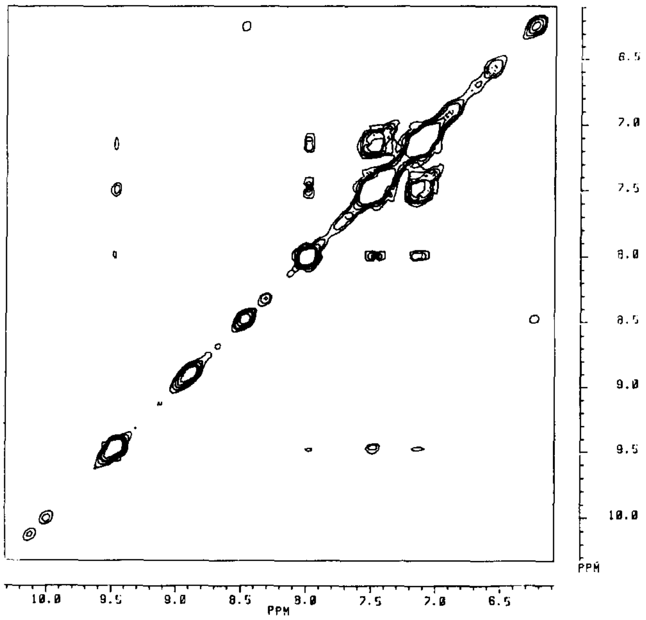


Figure 7 The NOESY spectrum of the mixture of ET-37-65 with PCS-PU-3-15 in the range 6.0–10.5 ppm (mixing time of 500 ms) at room temperature in DMF-d_7

CONCLUSIONS

From the above discussion, the hard segments of polyether–polyurethanes in concentrated solution are aligned in a very orderly fashion. The hard segments of polyether–polyurethanes form microdomains in concentrated solution, and neither the solvent nor water can destroy the hydrogen bonds which are formed by the NH groups. Changes in concentration do not affect the relative amounts and chemical shifts of the NH peaks. The solvent effects on the NH peaks can be ignored. The fraction of C=O groups forming hydrogen bonds with NH groups is greater than the fraction of O atoms forming hydrogen bonds with NH groups.

The soft segments of polyether–polyurethanes and polysiloxane–polyurea can be mixed at the molecular level, as shown by the NOESY spectrum of the mixture of a polyether–polyurethane with a polysiloxane–polyurea. But the hard segments of these polyurethanes cannot be mixed at the molecular level, and there are no cross-peaks between the NH peaks of polyether–polyurethane and polysiloxane–polyurea in the NOESY spectrum. There are no hydrogen-bonding interactions between the hard segments of polyether–polyurethane and polysiloxane–polyurea or between the hard segments of polyether–polyurethane and polyester–polyurethane in the mixtures.

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