

Investigation of interaction of polyester–polyurethanes and their zwitterionomers by solid-state nuclear magnetic resonance

Xingjun Lu*, Yuanshen Wang and Xuewen Wu

Magnetic Resonance Laboratory, Analytical Center, East China Normal University, Shanghai 200062, PR China

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High-resolution ^1H and ^{13}C nuclear magnetic resonance spectra are used to investigate the intermolecular interaction of polyester–polyurethanes with different contents of hard segments and different degrees of ionization. Because there are several kinds of hydrogen bonds, the hydrogen bonds play an important role in phase separation and physical properties. The higher the percentage of intermolecular hydrogen bonds, the greater are the tensile strength and strength at definite elongation. The interaction between 4,4'-methylene diphenyl diisocyanate and *N*-methyl-diethanolamine is weak for the ES-33.4 series. Ionization does not change the percentage of intermolecular hydrogen bonds for the ES-33.4 series and ES-41 series, and ionization does not improve the physical properties and phase separation.

(Keywords: hydrogen bond; polyester–polyurethane; nuclear magnetic resonance; intermolecular interaction; physical properties)

INTRODUCTION

Polyurethanes are a class of well known segmented thermoplastic elastomers, the hard phase of which is regarded as physical crosslinks and plays an important role in physical properties. How do the molecular chains interact? In this paper the interaction between the soft and hard phases, and the effect of interaction on phase separation and physical properties, have been investigated.

The authors have studied polyurethanes with different contents of hard segments and different degrees of ionization^{1–3}. The effects of the hard segment and degree of ionization on microphase separation have been studied qualitatively with infra-red (i.r.) spectroscopy, differential scanning calorimetry (d.s.c.), dynamic mechanical spectroscopy, dielectric measurements and stress–strain analysis. Ionization does not affect the glass transition temperature T_g of the soft phase, but the higher the degree of ionization, the higher is the T_g of the hard phase observed when the hard-segment content is low. The investigation of polyester–polyurethanes by solid-state n.m.r.⁴ shows that the extender, *N*-methyl-diethanolamine (MDEA), exists in the soft phase by comparison of the content of protons from decomposition of free induction decay (FID) with chemical structure, when the hard-segment content is low.

In polyurethanes, especially in the polyester–polyurethanes, the NH group can form hydrogen bonds with the carbonyl group in both the soft and hard segments and with the nitrogen atom in the extender MDEA. In this paper, various hydrogen bonds are studied quantitatively and interpreted.

EXPERIMENTAL

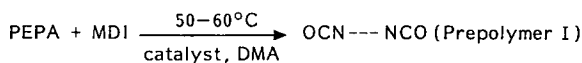
Synthesis of samples

The polyurethanes used in this study were prepared by a two-step polycondensation reaction² from poly(ethylene–propylene adipate) (PEPA; average $MW = 1972$), 4,4'-methylene diphenyl diisocyanate (MDI) and *N*-methyl-diethanolamine (MDEA) in anhydrous *N,N*-dimethylacetamide (DMA)¹.

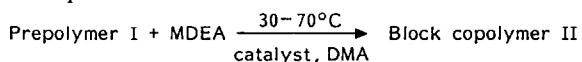
The prepolymer was prepared as follows: MDI was dissolved in DMA at a concentration of about 20% by weight. This solution was added to a solution of DMA, PEPA (20% by weight) and stannous octoate (0.1% by weight). The synthesis of the urethane prepolymer was carried out at 65°C for 3 h. The chain extender MDEA was added in an appropriate quantity to maintain an NCO:OH ratio of 1:1, and the reaction was continued for 4 h. Then the polyurethane was precipitated with distilled water and dried under vacuum at 80°C for 1 week.

The zwitterionomers were prepared by quaternization of the tertiary amine with γ -propanesultone for 3 h at 65°C in DMA (30%). The components and their relative molecular weights are listed in Table 1. The reaction scheme is outlined below:

Step 1

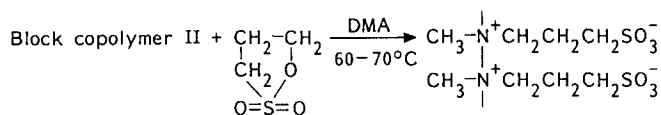


Step 2



* To whom correspondence should be addressed

Ionization



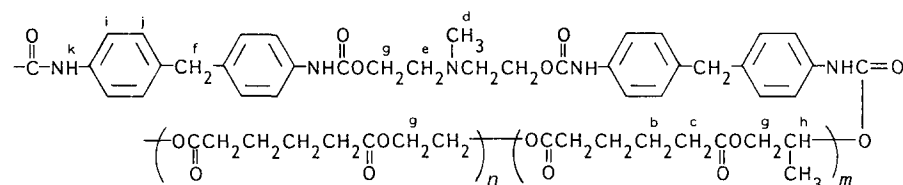
N.m.r. experiments

All n.m.r. experiments were carried out on a Bruker MSL-300 spectrometer at room temperature, the resonance frequencies being 300.13 MHz for ^1H and 75.47 MHz for ^{13}C . The ^1H n.m.r. and ^{13}C n.m.r. spectra were obtained on approximately 30% solutions in deuterated dimethylsulphoxide (DMSO- d_6 , 99.5% deuterated). ^{13}C n.m.r. spectral editing was carried out on an approximately 30% solution in deuterated dimethylformamide (DMF, 99% deuterated). All chemical shifts were referenced to DMSO- d_6 (39.5 ppm for ^{13}C , 2.61 ppm for ^1H).

RESULTS AND DISCUSSION

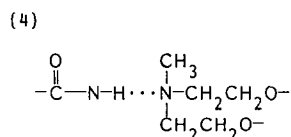
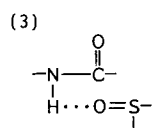
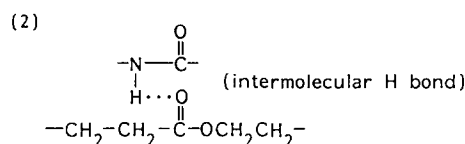
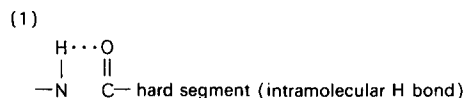
 ^1H n.m.r. spectra and hydrogen bonds

The proton n.m.r. spectrum of polyester-polyurethane in DMSO- d_6 (99.5%) is shown in Figure 1. The assignments are made according to Wang⁵ and Eisenberg³, and are shown in Figure 1 and Scheme 1.



Scheme 1

In polyurethane, the NH groups participate in hydrogen bonding in the solid state⁶. In polyester-polyurethane, the NH groups can form four kinds of H bonds as follows:



The ^1H chemical shift of NH reflects information about the H bonds. The NH peaks of the proton n.m.r. spectra are shown in Figure 2. The resonance assignments of the NH peaks are as follows: α (9.95 ppm) is a peak of NH forming H bonds with S=O (including solvent

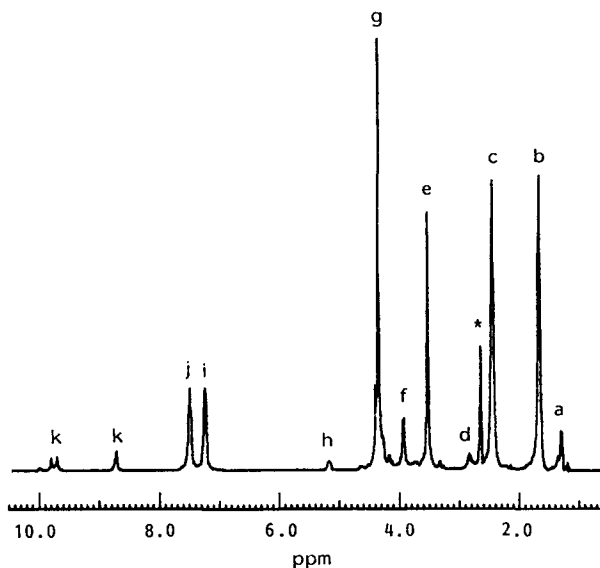


Figure 1 The ^1H n.m.r. spectrum of polyester-polyurethane in DMSO- d_6 (asterisk indicates the peak of DMSO): a, 1.27 ppm; b, 1.63 ppm; c, 2.41 ppm; d, 2.80 ppm; e, 3.70 ppm; f, 3.90 ppm; g, 4.24 ppm; h, 5.15 ppm; i, 7.16 ppm; j, 7.49 ppm; k, 8.6–10.0 ppm

Table 1 Components and relative molecular weights of polyester-polyurethanes¹

Samples ^a	PEPA:MDEA:MDI	$[\eta]$ (ml g ⁻¹)	Fraction of SO ₃ ⁻ (wt%)
ES-33.4-0			0
ES-33.4-30	1:2:3	47.6	1.6
ES-33.4-70			3.7
ES-33.4-100			4.9
ES-41-0			0
ES-41-30	1:3:4	48.5	2.1
ES-41-60			4.1
ES-41-100			6.5
ES-60-0	1:7.3:8.3	36.9	0

^a ES-41-60: ES, polyester-polyurethane; 41, fraction of hard segments by weight; 60, degree of ionization of N atom in MDEA

DMSO and γ -propanesultone); β (9.76 ppm) is a peak of NH forming H bonds with C=O of the soft segments; γ (9.68 ppm) is a peak of NH forming H bonds with the N atom of extender MDEA; δ (8.66 ppm) is a peak of NH forming intermolecular H bonds with C=O of the hard segments.

The results of decomposition of the NH peaks and tensile strengths at definite elongation of samples are listed in Table 2.

From Table 2 and Figure 2, the percentage of H bonds between NH and the N atom of MDEA is smaller for ES-33.4-0 than for ES-41-0 and ES-60-0. The interaction between MDI and MDEA is very weak for ES-33.4-0.

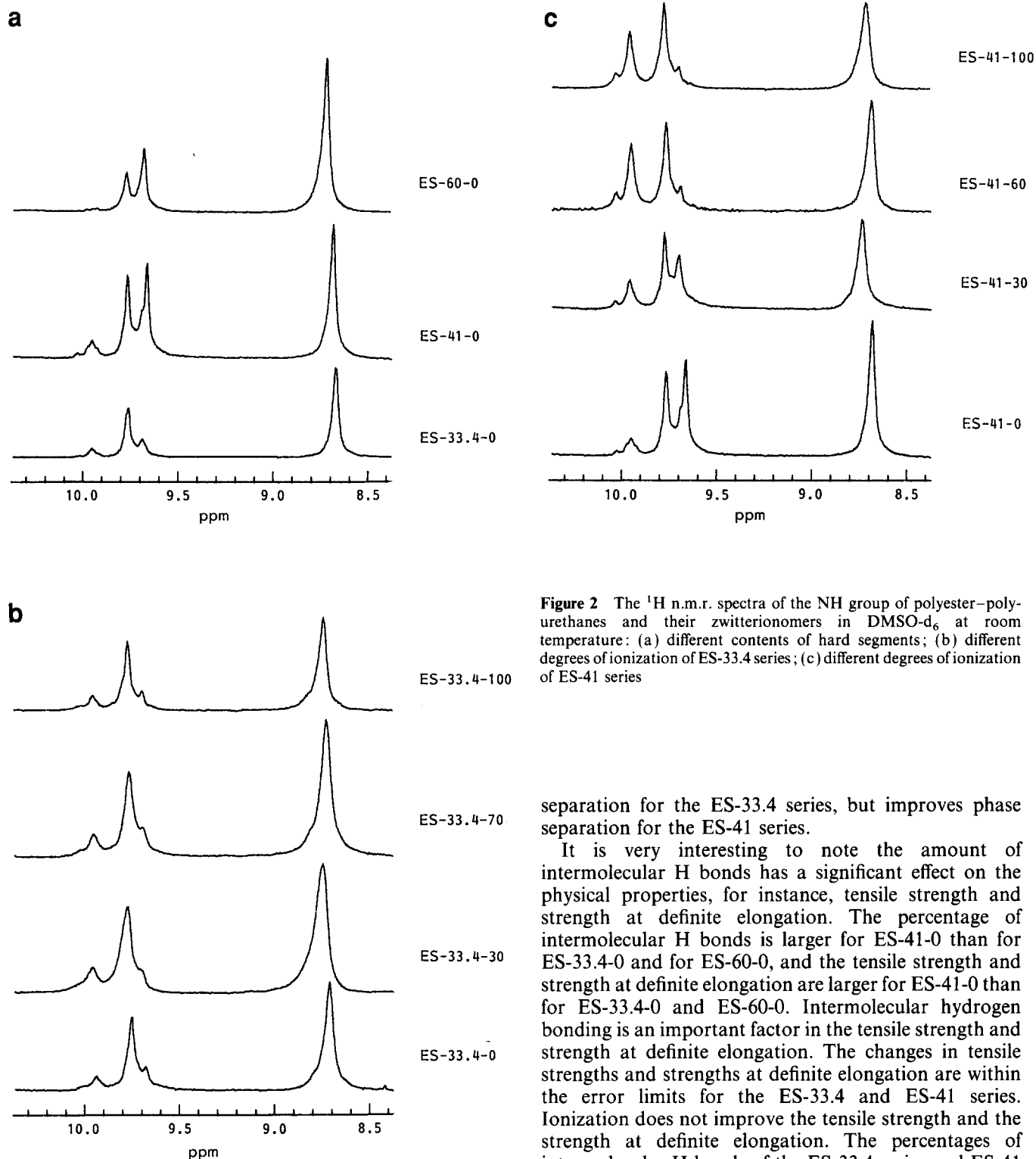


Figure 2 The ^1H n.m.r. spectra of the NH group of polyester-polyurethanes and their zwitterionomers in DMSO-d_6 at room temperature: (a) different contents of hard segments; (b) different degrees of ionization of ES-33.4 series; (c) different degrees of ionization of ES-41 series

separation for the ES-33.4 series, but improves phase separation for the ES-41 series.

It is very interesting to note the amount of intermolecular H bonds has a significant effect on the physical properties, for instance, tensile strength and strength at definite elongation. The percentage of intermolecular H bonds is larger for ES-41-0 than for ES-33.4-0 and for ES-60-0, and the tensile strength and strength at definite elongation are larger for ES-41-0 than for ES-33.4-0 and ES-60-0. Intermolecular hydrogen bonding is an important factor in the tensile strength and strength at definite elongation. The changes in tensile strengths and strengths at definite elongation are within the error limits for the ES-33.4 and ES-41 series. Ionization does not improve the tensile strength and the strength at definite elongation. The percentages of intermolecular H bonds of the ES-33.4 series and ES-41 series remain the same with degree of ionization.

For ES-33.4-0, ES-41-0 and ES-60-0, the percentage of H bonds between NH and S=O of solvent DMSO is very small. The relative amounts of various H bonds change in a small range with concentration (*Table 3*). Thus the situation is similar for a bulk sample and a concentrated solution.

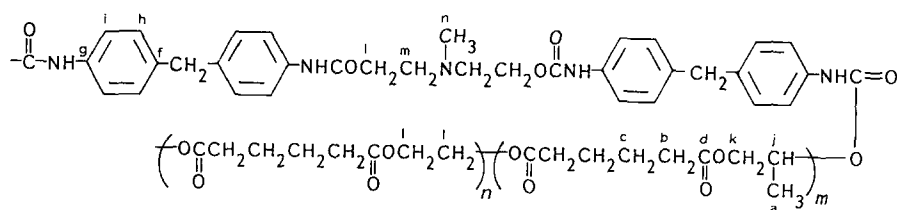
^{13}C n.m.r. spectra

Figure 3 shows the ^1H noise-decoupled ^{13}C spectrum of polyester-polyurethane in DMSO-d_6 , and *Figure 4* shows the editing of the ^{13}C spectra in DMF-d_7 . The assignments of the ^{13}C spectrum of polyester-polyurethane are listed in *Figure 3* and *Scheme 2*.

For the ES-41 series, the higher the degree of ionization, the smaller is the percentage of H bonds between NH and the N atom of MDEA, and the higher is the percentage of H bonds between NH and O=S. But for the ES-33.4 series, ionization does not change the percentage of H bonds between NH and the N atom of MDEA, nor the percentage of H bonds between NH and S=O. On the other hand, the percentage of H bonds between NH and the N atom of MDEA and between NH and S=O is small. Thus the interaction between MDI and MDEA is very weak for the ES-33.4 series. It is possible that ionization does not improve phase

Table 2 The results of peak resolution^a and physical properties

Samples	α (%)	β (%)	γ (%)	δ (%)	a (%)	b (MPa)	c (MPa)	
							100%	300%
ES-33.4-0	8	33	4	55	45	26.1	5.3	12.9
ES-33.4-30	6	32	5	57	43	26.1	5.2	13.1
ES-33.5-70	7	32	7	54	46	25.5	4.9	10.9
ES-33.4-100	8	35	5	54	46	25.0	5.0	11.1
ES-41-0	5	22	29	44	56	35.2	6.6	17.1
ES-41-30	11	24	20	45	55	35.3	7.1	17.7
ES-41-60	22	28	8	42	58	33.8	6.9	16.1
ES-41-100	24	30	3	43	57	30.3	6.2	14.5
ES-60-0	2	14	21	63	37	15.6	6.6	11.7

 a = percentage of intermolecular H bonds b = tensile strength c = strength at definite elongation

Scheme 2

Table 3 The results of peak resolution for ES-41-0

Concentration (% w/v)	α (%)	β (%)	γ (%)	δ (%)
30	5	22	29	44
10	7	26	26	41
4	7	27	23	43

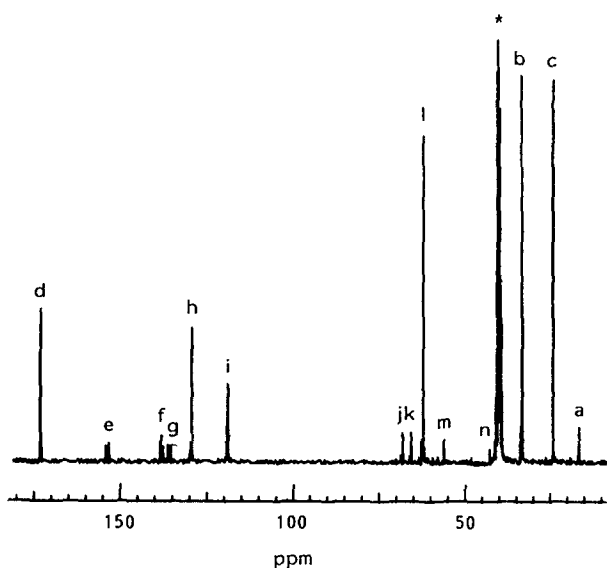


Figure 3 The ^1H noise-decoupled ^{13}C n.m.r. spectrum of polyester-polyurethane in DMSO-d_6 at room temperature (asterisk indicates the peak of solvent DMSO): a, 16.5 ppm; b, 34.2 ppm; c, 24.7 ppm; d, 173.4 ppm; e, 154.0 ppm; f, 138.6 ppm; g, 136.3 ppm; h, 129.6 ppm; i, 119.1 ppm; j, 68.7 ppm; k, 66.2 ppm; l, 62.8 ppm; m, 56.7 ppm; n, 43.0 ppm;

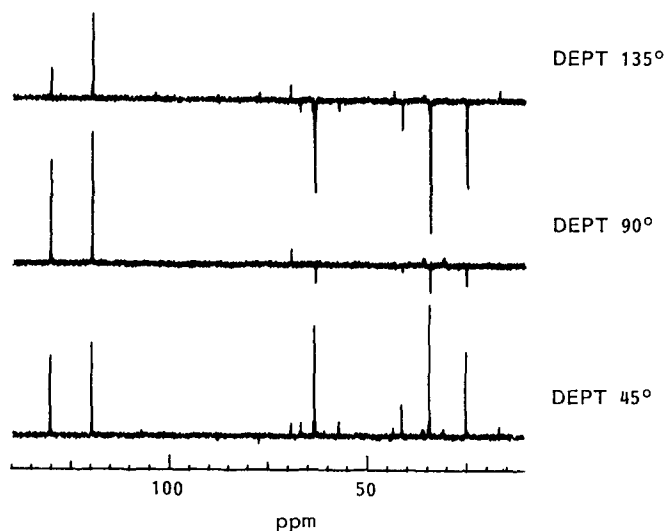


Figure 4 The spectral editing of the ^{13}C n.m.r. spectrum of polyester-polyurethane in DMF-d_7 at room temperature

Table 4 The peak integrals of amide carbonyl of ^{13}C spectra

Samples	α' (%)	β' (%)	γ' (%)	δ' (%)
ES-33.4-0	0	45	0	55
ES-41-0	30	22	5	43
ES-60-0	31	14	0	55

On the other hand, since the ^{13}C carbonyl group is affected by the formation of a H bond, further investigations on the formation of a H bond, and the results were as expected. The expansion spectra of amide carbonyl peaks are shown in *Figure 5*. The assignments of the amide carbonyl peaks are as follows:

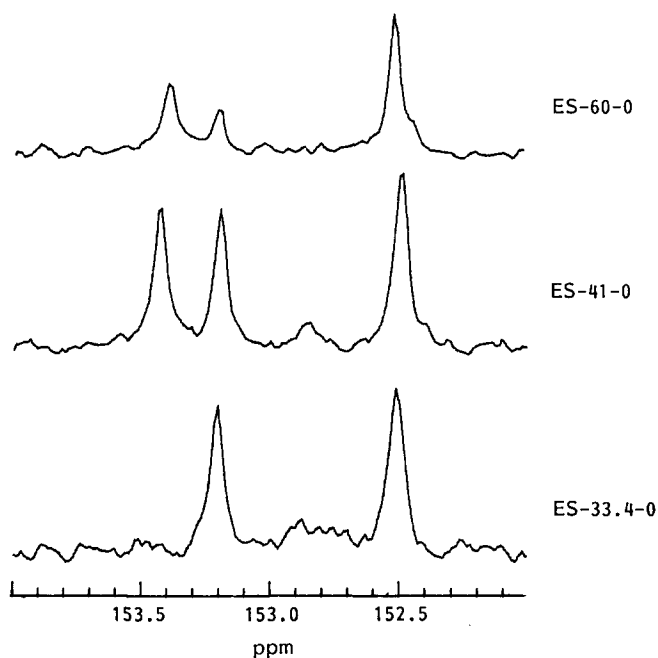


Figure 5 The expansion ^{13}C n.m.r. spectra of amide carbonyl peaks with different contents of hard segment

α' (153.42 ppm) H bonds between NH and the N atom on MDEA; β' (153.18 ppm) H bonds between NH and C=O of the soft segments; γ' (152.85 ppm) H bonds between NH and S=O (including solvent DMSO and γ -propanesultone); δ' (152.49 ppm) H bonds between NH and C=O of the hard segments.

The results of decomposition of the peaks are shown in Table 4. On comparison of the values in Tables 2 and 4, the results are close.

CONCLUSIONS

In polyester-polyurethanes, there are four kinds of H bonds: intermolecular H bonds play an important role in physical properties, for example, tensile strength and strength at definite elongation. The more intermolecular H bonds there are, the greater is the tensile strength and the strength at definite elongation. Ionization does not change the percentage of intermolecular H bonds for the ES-33.4 series and ES-41 series, and the tensile strength and the strength at definite elongation remain the same.

The interaction between MDI and MDEA is very weak for the ES-33.4 series, and it is possible that extender MDEA exists in the soft phase when the content of the hard segments is low.

Since the peak at 9.95 ppm (H bond between NH and S=O of solvent) is very low compared to the others, the effect of solvent may be ignored. The situation for a bulk sample is similar to that of a concentrated solution.

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