

NMR STUDIES ON POLYETHER-POLYURETHANE ZWITTERIONOMERS—CHAIN STRUCTURE AND PHASE SEPARATION

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ABSTRACT

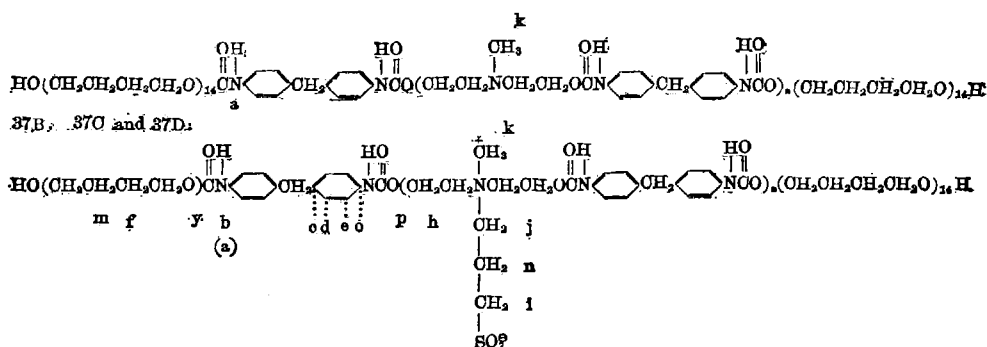
The ^1H and ^{13}C NMR spectra of polyether-polyurethanes (A) based on 4,4'-diphenylmethane diisocyanate (MDI), N-methyl diethanolamine (MDEA), and polytetramethyleneoxide (PTMO) and the zwitterionomers derived from A with various degree of ionization was assigned by comparing with model compounds.

Phase separation of the samples was visualized through pulsed NMR investigations. The FID signals of these multiphase elastomers were recorded and decomposed by non-linear least squares regression into fast Gaussian and slow exponential components associated with the hard, the soft and the interface respectively. Thus pulsed NMR gives both qualitative and quantitative information about the existence of multiphases and the relative amounts of materials in each phase.

Polyether-polyurethanes (A) based on polytetramethylene oxide (PTMO), 4,4'-diphenylmethane diisocyanate (MDI) and N-methyl diethanolamine (MDEA) and zwitterionomers (B, C and D) containing quaternary ammonium sulfonate obtained by sulfonation of A with γ -propane sultone have been synthesized by Yang, Hwang and Cooper^[1].

The formulae of the polymers are as follows:

37A:



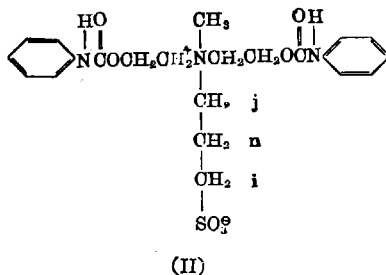
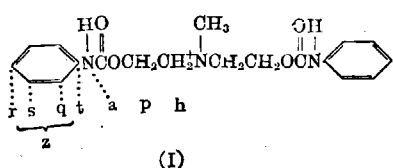
It is readily seen from the above formulae that the NMR spectra of these condensation

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polymers would be rather complex and difficult in the assignment of some overlapping and small peaks is expected, therefore, two model compounds (I & II) were synthesized to compare with these polymers.



The ^{13}C chemical shifts of MDEA, $\text{C}_6\text{H}_5\text{NHCOCH}_3$ ^[2], $\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ ^[3], tertiary amines^[4] and quaternary alkyl amines^[5] and the ^1H chemical shifts of γ -propane sultone and *N*-methyl diethylamine are known. Thus the spectra of 37A and 37 B, C, D can readily be assigned.

Pulsed NMR measurements on solid samples were made to investigate the different degree of phase separation of the polyurethanes^[6] and zwitterionomers. The FID signals were decomposed by means of nonlinear least squares regression into fast Gaussian and slow exponential components associated with the rigid and the mobile phases respectively. It was found that both qualitative and quantitative information of phase separation can be obtained by this simple and rapid method.

EXPERIMENTAL

1. Synthesis

Model compound I was synthesized by dropping slowly 26.2 g (0.22 mole) phenylisocyanate to 11.9 g (0.10 mole) ice-cooled MDEA, the temperature was kept below 65°C and the mixture further maintained at that temperature for 2 h^[7].

I and an equimolar amount of γ -propane sultone were dissolved in THF and the mixture refluxed for 2–3 h until a white powder separated which is hitherto unreported compound II.

2. Samples

The code 23A, 31A, 37A represent the polyurethanes in which the ratio of MDI, MDEA and PTMO are 3:1:2, 2:1:1, 3:2:1 respectively, and 37B, 37C and 37D the polyurethanes.

with 35%, 65% and 95% conversion of $-\text{N}-\text{CH}_3$ in 37A to $-\overset{\text{e}}{\underset{|}{\text{N}}}-\text{CH}_3$ respectively.

3. NMR spectra

The ^1H and ^{13}C spectra in solution were recorded on a Varian FT-80A NMR spectrometer at a concentration of 15% w/w at 31°C for ^1H and 50°C for ^{13}C . The solvent used was $\text{DMSO}-d_6$ except for the ^{13}C spectra of 37A and 37D where it was $\text{DMF}-d_7$. The number of

accumulation for I and 37A was 4,000 and that for II and 37D was 40,000.

The FID measurements of the solid samples were conducted on a Bruker SXP 4-100 spectrometer at 90MHz and 293K in the phase sensitive detection mode. The transverse magnetization of the samples was produced with 90° pulses of 2 μ s length. The pulses were spaced 1 sec apart and the total dead time from the initiation of a pulse was 10 μ s. The number of accumulation was 10 times.

RESULTS AND DISCUSSION

1. The ^1H and ^{13}C spectra of model compounds I and II and polyurethanes 37A and 37D are compared and assigned. Chemical shifts of the peaks are listed in Table 1 and Table 2. The alphabetic letters denoting the peaks are signed under the formulae of the corresponding H or C atom.
2. There are two kinds of NH peaks marked as "a" in compound II and "b" in compound I; a (9.83 ppm) corresponds to the NH which is hydrogen-bonded to the S=O oxygen of the ammonium sulfonate ion, while b (9.52 ppm) corresponds to the NH which is hydrogen-bonded to C=O. Since the quantities of the reactants were equimolar during the synthesis of compounds I and II, it can be reasonably concluded that the NH peak in 37A is bonded to C=O and assigned as "b" (9.50 ppm).

Table 1 ^1H Chemical shifts of I, II, 37A and 37D

Peak Sample	a	b	z	p	h	k	j	n	i	m	f
Compound. I		9.52	7.14	4.12	2.64	2.12					
Compound. II	9.80		7.50— 7.10 7.47	4.44	3.70	3.22	3.14	2.42	2.01		
γ -Propane sultone							4.38	2.43	3.30		
MDEA				3.69	2.60	2.28					
37A		9.50		4.05	2.42	2.02				1.43	3.25
37D	9.83	9.50		4.42	3.73			2.45	2.02	1.43	3.16

Table 2 ^{13}C Chemical shifts of I, II, 37A and 37D

Peak Sample	y	o(t)	c(r)	d(s)	e(q)	f	g
Compound I	153.57	139.22	128.58	122.32	118.45		
Compound II	152.58	138.83	128.67	122.67	118.53		
37A	153.61	137.14	135.42	128.53	118.24	69.85	63.83
37D	152.59	137.29	135.46	128.57	118.29	69.88	63.90
References [2—5]	153.6	137.1	135.5	128.7	118.3	69.8	

Table 2 ^{13}C Chemical shifts of I, II, 37A and 37D

(cont'd)

Peak Sample	p	h	i	j	k	l	m	n
Compound I	62.04	55.86			42.33			
Compound II	62.19	60.56	57.66	49.05	47.88			18.67
37A	62.80	55.73			40.02	39.79	26.12	
37D	61.49	60.86	57.69	48.88	47.76	39.86	26.15	18.04
References [2-5]						41.9	26.1	

Letters in parenthesis are peaks of model compounds

3. In 37D two kinds of NH peaks a and b are present together in ratio relating to the degree of ionization of the polyurethanes (Fig. 1).

The percentage of one of the peaks may be obtained by comparing the integrated values of the spectra with the theoretical values assuming "x" hydrogen-bonds between NH and S=O per mole. It is shown in Table 3 that when $x=2$ the theoretical and experimental results coincide with each other.

Table 3 Degree of ionization

Stoichichemical (%)	Theoretical			Experimental (%)
	$x=1$	$x=2$	$x=3$	
35	11.7	23.3	35.0	26.7
65	21.7	43.3	65.0	43.5
95	31.7	63.3	95.0	61.9

4. Decomposition of the FID signal shows that there are apparently two phases within the polyurethanes investigated. A nonlinear least square fit of the form

$$M(t) = M_f \exp(-t/T_{2f}) + M_s \exp(-t/T_{2s}) = M_f \exp(-t^2 M_2/2) + M_s \exp(-t/T_{2s})$$

is then applied to the data, where $M(t)$ is the magnetization of the fast and slow components, T_{2f} and T_{2s} the spin-spin relaxation times of the fast and slow components, and M_2 the second moment of the Gaussian time decay (Figs. 2-5).

Since the initial magnetization is proportional to the number of protons in the samples, the relative amounts of protons in the hard and the soft phases can be obtained by extrapolation of the experimental curves (Figs. 2 & 3). It is noted that when the degree of ionization increased, M_s decreased and M_f increased. The ratio of protons in the two phases is also changed as can be seen from Table 4.

It is also noted that the $M(t)-t^2$ curves of the 37-series are not linear; but they can be further decomposed into two components, the faster one corresponding to the zwitterion hard segment and slower one, the interface between the hard and the soft phases. This phenomenon

Table 4 Ratio of soft and hard phases

Samples	Hard/soft	Soft phase		Hard phase	
		T_2 μs	γ^*	M_2^{-1} μs^{-2}	γ^*
23A	0.050/1.000	280.0	0.9998	275.1	0.9954
31A	0.141/1.000	218.0	0.9995	650.2	0.9954
37A	0.425/1.000	184.4	0.9998	702.8	0.9932
37B	0.343/1.000	197.8	0.9998	505.8	0.9948
37C	0.505/1.000	205.5	0.9998	444.5	0.9920
37D	0.518/1.000	194.4	0.9996	414.2	0.9977

* The coherence coefficient

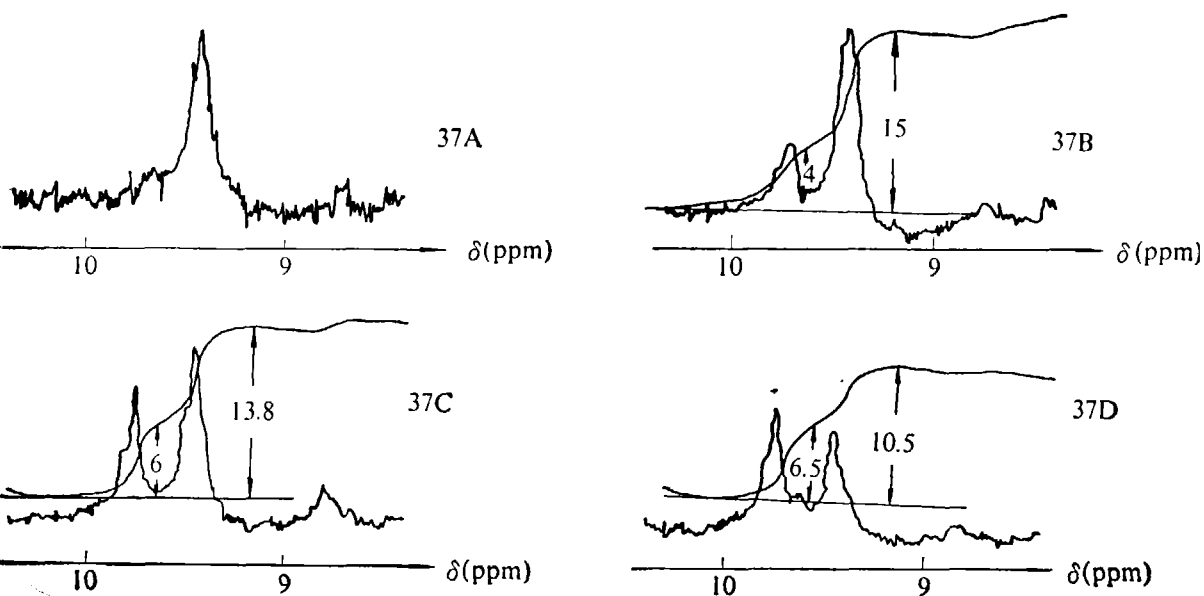


Fig. 1 Chemical shifts and integration values of NH peaks of samples 37A—D

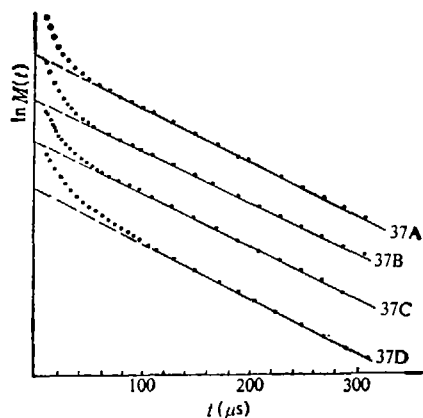


Fig. 2 FID of samples with different ratios of hard and soft segments

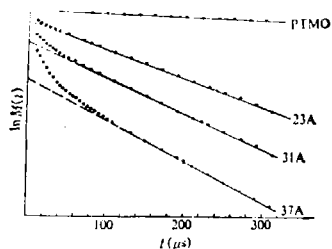


Fig. 3 FID of samples with different degree of ionization

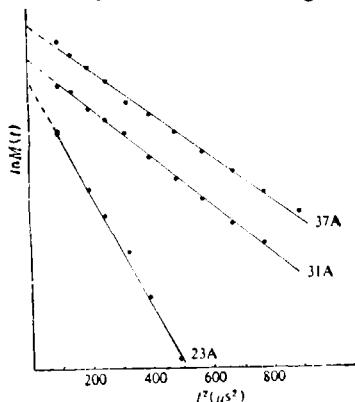


Fig. 4 Gaussian behavior of the fast component

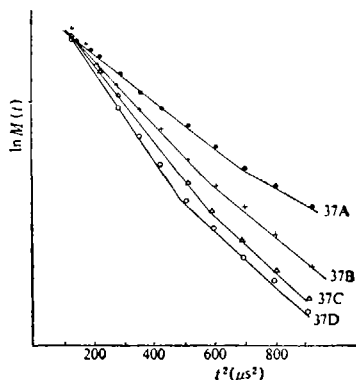


Fig. 5 Gaussian behavior of a faster and a slower component of 37A—D

is to be investigated in a following paper.

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