Characterization of polyurethane elastomers by ^{13}C n.m.r. spectroscopy

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A ^{13}C n.m.r. study of a series of polyurethanes and selected model compounds is reported. Comparison of the observed chemical shifts with values predicted by the Grant and Paul additive theory shows reasonable agreement. The latter approach, therefore, is a useful method for the assignment of carbon resonances in these systems. The positions of carbonyl peaks are more difficult to predict, but model compound studies allow their unambiguous assignment. These peak positions are very useful for qualitative and quantitative measurements. Nuclear Overhauser Enhancement (NOE) factors have been measured for typical copolymers, and it is possible to obtain quantitative estimates of the compositions of unknown polymers and prepolymers.

INTRODUCTION

The potential of ^{13}C n.m.r. as an anlytical technique has been recognized by polymer scientists in recent years[1-3]. To obtain useful quantitative data on a given polymer system, it is necessary to assign peaks in the spectra to specific carbon atoms in the macromolecular structure, and secondly to obtain a precise knowledge of the relationship between the amount of the particular species present and the line intensity. Because of the involvement of relaxation and NOE effects, the latter consideration is usually more complicated for ^{13}C n.m.r. than, for instance, ^{1}H n.m.r. In this paper, an investigation is described of the ^{13}C n.m.r. spectra of a series of model compounds, prepolymers and polymers with sequence structures typical of diphenylmethane 4,4'-diisocyanate (MDI)-ester polyurethanes[4-6]. The results, which show that ^{13}C n.m.r. can provide a great deal of useful qualitative and quantitative information on these systems, may be considered generally applicable to polyurethane systems.

EXPERIMENTAL

Proton noise decoupled ^{13}C n.m.r. spectra were recorded at 25.15 MHz on JEOL PFT-100 and Varian XL-100 spectrometers. The model compounds were studied as 25% w/v solutions in deutero-chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (DMSO). Polymers were recorded as solutions in DMSO. Typically, 2500 transients were accumulated to provide adequate sensitivity. It was observed that, if $CDCl_3$ was used as solvent, only partial swelling of the materials occurred, involving only the soft polyester blocks. The spectrum only showed peaks from the polyester blocks, these being sufficiently mobile to produce high resolution spectra. The relatively immobile isocyanate hard blocks are not observed in this solvent.

Polyurethanes were prepared by mixing the preheated and degassed prepolymer with an appropriate curing agent at ~353K, the temperature being maintained constant for ~2 h. The material first gels, then cures to a solid mass, the properties of which depend upon the ratio of MDI to polyester. In all cases the polymer was soluble in DMSO. For low isocyanate polyurethanes, special care was required to dry the reagents, the diol chain extender being dried overnight with $CaCl_2$ and then vacuum distilled prior to use. Side reactions in the cure, e.g. to produce allophonate groups, are likely to be unimportant at the relatively low cure temperature[7].

RESULTS AND DISCUSSION

Polyurethanes may be prepared by the reaction of a diisocynate with either a hydroxy terminated polyether or polyester to produce a prepolymer, followed by reaction of the prepolymer with a diamine or diol chain extender. This stepwise formation is particularly convenient for the assignment of ^{13}C resonances since it is possible to study the individual stages separately and follow the formation of the final product. The ^{13}C n.m.r. spectrum of the eventual polymer may be considered as consisting of peaks associated with the individual components, and peaks associated with bonds between these blocks. The different types of resonances can be distinguished readily by studying a range of compounds, model compounds, prepolymers and polymers. In addition to their value for assignment purposes, the spectra of the various intermediates can provide useful information relevant to the structure of the final product. The formation of the

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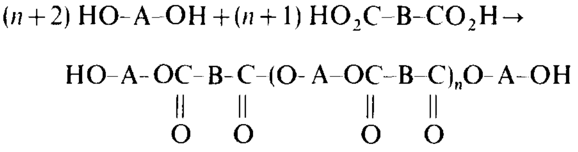
materials studied here may be represented as follows.

(i) The polyesters are linear hydroxy terminated materials prepared from the reactions of a di-acid (e.g. adipic acid) with a slight excess of a diol (e.g. ethylene glycol).



$$(n+2)\,\mathrm{HO{-}A{-}OH} + (n+1)\,\mathrm{HO_2C{-}B{-}CO_2H} \rightarrow \mathrm{HO{-}A{-}O}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}B{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}(O{-}A{-}O}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}B{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{)_nO{-}A{-}OH} \qquad (1)$$

(I)

The esters typically have molecular weights in the range 2000–4000.

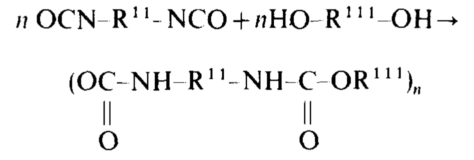
(ii) The polyester I, which may be written formally as HO–R–OH is then reacted with a dissocyanate to produce a diisocyanate prepolymer.

$$\mathrm{HO{-}R{-}OH + 2OCN{-}R^1{-}NCO} \rightarrow \mathrm{OCN{-}R^1{-}\ NHCO_2RO_2CNH{-}R^1{-}NCO} \qquad (2)$$

(II)

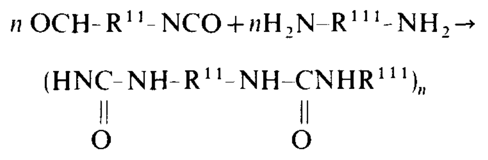
As written, simple end capping of the diisocyanate is assumed, but in principle there is a finite probability that reaction will occur at both ends of the diisocyanate, to produce some chain extensions.

(iii) The final cure stage involves the reaction of the diisocyanate prepolymer with a diol or diamine, to produce chain extension to a moderately high molecular weight polymer, which will be linear in the absence of side reactions. Writing II in the form OCB–R^{11}–NCO this may be represented by:



$$n\,\mathrm{OCN{-}R^{11}{-}NCO} + n\mathrm{HO{-}R^{111}{-}OH} \rightarrow (\underset{\underset{\mathrm{O}}{\|}}{\mathrm{O}}\mathrm{C{-}NH{-}R^{11}{-}NH{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}OR^{111}})_n \qquad (3)$$

(III)



$$n\,\mathrm{OCH{-}R^{11}{-}NCO} + n\mathrm{H_2N{-}R^{111}{-}NH_2} \rightarrow (\mathrm{H}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{N}}\mathrm{C{-}NH{-}R^{11}{-}NH{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NHR^{111}})_n \qquad (4)$$

(IV)

Since the prepolymer contains a relatively long flexible polyester or polyether block, the materials formally contain soft, rubbery polyester blocks and hard aromatic polyurethane or polyurea/polyurethane segments. The incompatibility of these two types of segment frequently leads to a two-phase polymer structure[8–10]. The favourable mechanical properties of these linear, segmented polyurethanes is partly a consequence of their phase separated nature, the elasticity arising from the mobile polyester units and the urethane segments forming a hard phase which adds strength to the polymer. This situation is illustrated by the different behaviour of the samples in $CDCl_3$ and DMSO solvents. Whereas the polymers completely dissolve in DMSO, $CDCl_3$ only swells the soft blocks, but does not effect the hard blocks sufficiently to produce high resolution ^{13}C n.m.r. spectra of the urethane moieties under these conditions.

Polyesters and chain extenders

We initially considered a series of components frequently encountered in polyurethane systems[5,7]. Their chemical shift values are shown in *Table 1*. The chemical shifts of the polyesters are characteristic of the particular material, so that ^{13}C n.m.r. provides a simple method of identification. The observed chemical shifts may be predicted using an additive scheme which is an extension of Grant and Paul's[11,12] approach for alkanes, to take account of the ether, alcohol and ester groups present.

The chemical shifts of alkanes can be expressed in the form of an additive relationship:

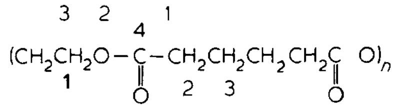
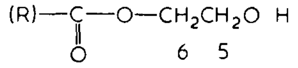
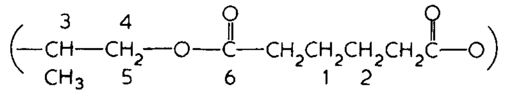
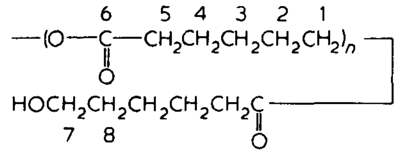
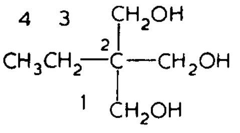
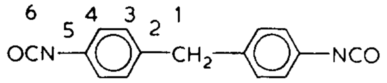
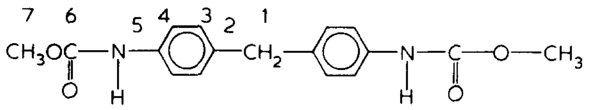
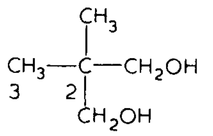
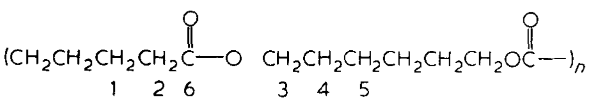
$$\delta_c^i = \mathrm{B} + \sum_j A_j n_{ij} \qquad (5)$$

δ_c^i is the chemical shift of the ith carbon in an alkane chain, and B is a constant approximately equal to the chemical shift of methane. The summation over j refers to carbon nuclei around the carbon atom C_i under consideration, the coefficient A_j depending on the number of bonds between the adjacent carbon atom and C_i and n_{ij} being the number of carbon atoms of type j around C_i. Thus, A_j has characteristic values of α, β, γ, δ and ε carbons (that is, carbons from one to five bonds removed from C_i). Values are given in *Table 2*. The δ and ε values are small, and are usually smaller than the error in the overall scheme when comparing absolute shift values. Thus, they may usually be neglected, but they are not entirely useless as they do indicate the range over which effects are likely to be observed in ^{13}C n.m.r. Peaks separated by 0.1 ppm should be resolved readily with standard instrumentation, so we may expect that otherwise identical carbon atoms, which differ in the type and number of atoms, four or five bonds removed, may in general be expected to be distinguishable. When branching occurs, additional terms have to be introduced to take account of this[11,12].

To extend this scheme, we have taken substituent values from the appropriate mono-substituted alkanes[2,13–15]. Thus, by considering the chemical shifts of the normal alcohols[13], ethers[14] and esters[15], suitable additive parameters are obtained which can be used to predict the chemical shift of diols, polyols and polyester and polyether diols (*Table 1*). The agreement is usually better than ±2 ppm, the values being adequate for assignment purposes. Better agreement could be obtained by adjusting the parameters to fit the present data, particularly since the data used is frequently for solvents other than DMSO, but this has not been done since the object is to provide a rough treatment to describe the overall features of the spectra.

Assignment of the peak positions of MDI is less straightforward. We may distinguish two groups of resonance, those associated with the diisocyanate MDI itself, and those associated with the diurethane derivative of MDI, which is the form in which MDI will occur in a fully cured polyurethane. The chemical shifts for the latter are, in fact, easier to assign. As a model compound we consider the dimethyl urethane, prepared by reaction of MDI with methanol, for which the chemical shifts are expected to be similar to those in a polyurethane with the exception of the carbonyl and methyl peaks. These shifts

Table 1 ^{13}C n.m.r. spectra of components and model compounds for polyurethanes

Compound	Structure	^{13}C Shifts ppm Predicted		Observed
1,4 butanediol	$HOCH_2CH_2CH_2CH_2OH$ 1 2	C_1	62.0	60.9
		C_2	29.4	29.1
Polytetramethylene ether glycol	$HOCH_2CH_2CH_2CH_2(OCH_2CH_2CH_2CH\ )_n—O(CH_2)_4OH$ 4 3 1 2	C_1	71.5	69.8
		C_2	27.7	26.1
		C_3	30.3	29.4
		C_4	60.5	62.7
Polyethylene glycol	$HOCH_2CH_2O(CH_2CH_2O)_n(CH_2)_2OH$ 3 2 1	C_1	72.2	69.9
		C_2	62.8	60.3
		C_3	74.4	72.5
Polyethylene adipate		C_1	63.6	61.9
		C_2	34.3	33.0
End group		C_3	25.0	23.9
		C_4	–	173.0
		C_5	61.3	59.1
		C_6	67.3	65.6
Polypropylene adipate		C_1	34.4	33.2
		C_2	25.2	23.8
		C_3	66.7	65.3
		C_4	69.2	67.7
		C_5	15.9	16.0
		C_6	–	172.8
Poly(caprolactone)		C_1	64.8	63.6
		C_2	29.9	28.0
		C_3	26.9	25.0
		C_4	25.0	24.1
		C_5	33.8	33.5
		C_6	–	172.8
		C_7	62.5	60.7
		C_8	33.8	32.3
Trimethylol propane		C_1	61.7	62.0
		C_2	40.2	43.2
		C_3	19.2	21.3
		C_4	9.3	7.4
Diphenylmethane 4,4′ diisocyanate (MDI)		C_1	43.3	40.69
		C_2	141.1	138.2
		C_3	128.9	129.8
		C_4	124.5	124.7
		C_5	130.8	131.5
		C_6	–	124.7
MDI dimethyl urethane		C_1	43.3	41.9
		C_2	138.5	137.10
		C_3	136.5	135.5
		C_4	127.9	128.7
		C_5	117.9	118.3
		C_6	–	153.6
		C_7	–	51.6
2,2 dimethyl 1,3 propanediol		C_1	70.0	70.0
		C_2	45.8	43.7
		C_3	19.7	20.7
Hexamethylene adipate		C_1	25.2	25.0
		C_2	34.4	34.2
		C_3	64.6	64.3
		C_4	29.8	28.6
		C_5	27.6	25.7
		C_6	–	173.5

may be predicted approximately from those of urethane derivatives of phenyl isocyanate (e.g. methyl phenyl carbamate) and ethyl benzene from simple additive considerations. Thus ethyl group substitution in an aromatic ring produces chemical shifts of +15.4, −0.6, −0.2 and −2.8 ppm at the directly bonded ,*ortho*, *meta* and *para* positions, respectively[16], relative to benzene whereas substitution by the NHCOR group produces analogous shifts of +10.6, −10.6, −0.2 and −5.6 ppm[17]. A combination of these effects produces the calculated values shown in *Table 1*, which agree well with the observed shifts. The carbonyl peaks appear at approximately 154 ppm, a typical value for an aromatic urethane, and the central methylene unit occurs at about 40 ppm.

The chemical shifts for MDI itself are very different. Assignment is complicated by the fact that the isocyanate carbon is very different from most carbonyl groups and

Table 2(a) Aliphatic shift parameters used in the prediction of the spectra of model compounds

	Position relative to predicted carbon				
Series	α	β	γ	δ	ε
Alkane–R	+ 9.1	+ 9.4	–2.5	+0.3	+0.1
Alcohols–OH Primary	+48.3	+10.2	–5.8	+0.3	+0.1
Secondary	+44.5	+ 9.7* + 7.4†	–3.3	+0.2	+0.1
Others	+40.8	+ 7.7	–3.7	+0.3	+0.3
Ethers —OR	+57.7	+ 8.0	–4.9	+1.0	
Esters $\text{—O}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—R}$	+50.6	+ 6.5	–5.0	+0.6	+0.3
$\underset{\underset{\text{O}}{\|}}{\text{—C}}\text{—OR}$	+19.8	+ 2.5	–2.5	+1.1	+0.5

* Carbon atom forming part of hydrocarbon chain
† Terminal carbon atom in β position

Table 2(b) Chemical shift parameters for the calculation of aromatic carbon chemical shifts of MDI and MDI diurethanes. The values are the chemical shift increment of the substituent, relative to benzene, for the appropriate monosubstituted benzene

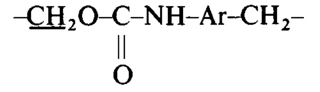
	Chemical shift increment (ppm)			
Substituent	C_1	*ortho*	*meta*	*para*
–NCO	+ 4.9	– 4.0	+0.8	–3.0
$-NHCO_2R$	+10.6	–10.6	–0.2	–5.6
$-CH_2-C$ (ethyl benzene)	+15.4	– 0.6	–0.2	–2.8

resonates in a region typical of aromatic carbons between 120 and 130 ppm[18]. From the spectrum of phenyl isocyanate[17], the isocyanate group produces chemical shifts of +4.9, +4.0, +0.8 and −3.0 ppm at the directly bimodal, *ortho*, *meta* and *para* carbons respectively. Using a simple additive scheme with the chemical shifts for ethyl benzene[16], the calculated values for MDI are in reasonable agreement with the experimental values, as shown in *Table 1*. It is seen that all the carbon atoms from the diurethane are completely resolved from those of the diisocyanate, so that the ^{13}C n.m.r. spectrum offers a simple means of determining the amount of reacted and unreacted MDI in a prepolymer. None of the observed peaks in the ^{13}C spectrum of MDI (in chloroform) can be assigned to the isocyanate group. From the value in phenyl isocyanate, we expect this peak to occur at about 125 ppm and it appears to coincide exactly with one of the ring carbons.

Prepolymers and polyurethanes

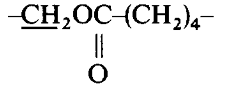
The assignment of peaks in the prepolymer and cured polymers can be obtained either by the application of the additive parameters (Model I) or by comparison with the values from the model compounds (Model II). Values for typical prepolymers and polyurethanes are given in *Table 3*.

^{13}C n.m.r. provides useful information on the composition of the prepolymers. Consider, for example, the MDI/polyethylene adipate polyester prepolymer. The characteristic polyethylene adipate and MDI absorptions can be used to identify the major components. Also, the aromatic MDI absorptions give a good measure of the proportion of MDI which has reacted. As mentioned previously, the chemical shifts for the ring carbons of species with isocyanate and urethane substituents are completely different. Thus the ratio of the carbon atoms *meta* to isocyanate to those *ortho* or *meta* to urethane can be used to give a good quantitative estimate of the fraction of MDI rings which have reacted. The spectrum does not show any hydroxyl end groups for the polymer, which give characteristic peaks in the unreacted polyester diol, and if it is assumed that all the reacted MDI units have reacted with polyester, the latter amount may be used to provide an estimate the original hydroxyl content of the polyester, and hence an estimate of the number of average molecular weights of the polyester block. As far as the terminal ethylene glycol unit of the ethylene adipate polyester is concerned, the effect of the adjacent MDI urethane group in the prepolymer is to produce chemical shifts very similar to those of the ester group. Thus, the



$$-\underline{C}H_2O-\underset{\underset{O}{\|}}{C}-NH-Ar-CH_2-$$

–group occurs in the ^{13}C spectrum close to that of the

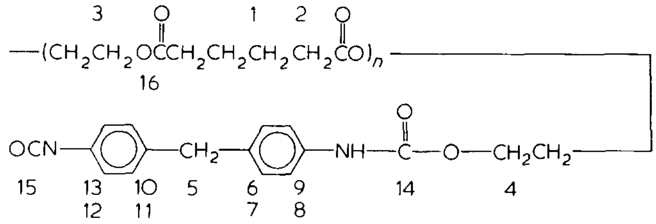
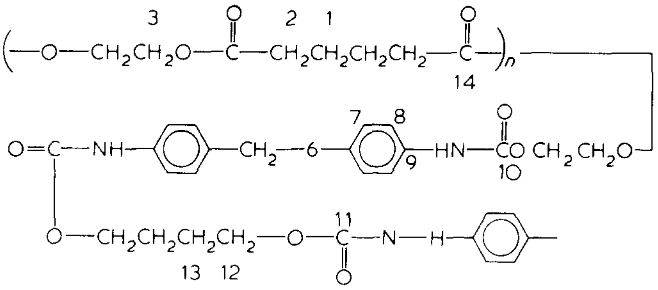
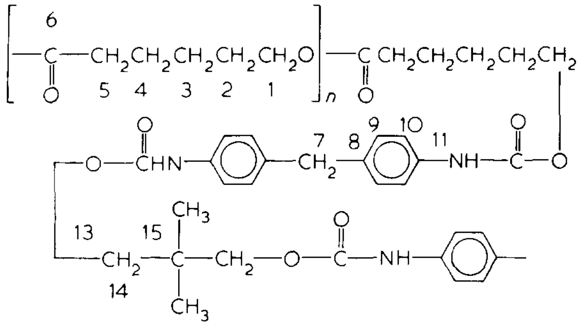


$$-\underline{C}H_2O\underset{\underset{O}{\|}}{C}-(CH_2)_4-$$

—group of the main polyester chain. However, this peak can be readily resolved as a small peak near the base of, and slightly to low field of the main polyester peak. In the absence of unreacted hydroxyl end groups in the prepolymer, this peak gives a direct estimate of the number average molecular weight of the polyester block. If hydroxyl end groups are present, these can readily be estimated.

On chain extension with butanediol, additional peaks arise from the butanediol derived urethane units. Thus the $\underline{C}H_2O-CONH-$ and $\underline{C}H_2CH_2O-CONH-$ peaks at 63.8 and 25.5 ppm are well separated from the polyethylene adipate derived peaks, and can be used immediately to provide a quantitative estimate of the amount of butanediol chain extender. The urethane carbonyl peak is also sensitive to the type or urethane linkage, so that the peaks for the butanediol/MDI and polyethylene adipate/MDI linkages are readily resolved. Provided, therefore, that reliable intensity measurements can be made, the spectra provide estimates of the amounts

Table 3 ^{13}C Chemical shift data for prepolymers and polyurethanes

		^{13}C Shifts ppm		
		Predicted		Observed
		Model I	Model II	
Poly(ethylene adipate)/MDI prepolymer 	C_1	25.3	23.9	23.5
	C_2	35.3	33.0	32.7
	C_3	64.2	61.9	61.5
	C_4			61.9
	C_5	43.3	41.0	40.6
	C_6	138.5	137.1	137.1
	C_7	127.9	128.7	128.7
	C_8	117.9	118.3	118.6
	C_9	136.5	135.5	135.5
	C_{10}	141.1	138.2	138.4
	C_{11}	128.9	129.8	129.6
	C_{12}	124.5	124.7	124.6
	C_{13}	130.8	131.5	131.3
	C_{14}	–	153.6	153.2
	C_{15}	–		124.6
	C_{16}	–	173.0	173.3
Poly(ethylene adipate)/MDI/ Butanediol polymer 	C_1	25.3	23.9	23.5
	C_2	35.3	33.0	32.7
	C_3	64.2	61.9	61.5
	C_4			61.9
	C_5	43.3	41.0	40.6
	C_6	138.5	137.1	137.1
	C_7	127.9	128.7	128.7
	C_8	117.9	118.3	118.5
	C_9	136.5	135.5	135.4
	C_{10}	–	153.6	153.3
	C_{11}	–	153.6	153.6
	C_{12}	64.3	63.8	63.8
	C_{13}	25.8	25.4	25.5
	C_{14}	–	173.0	173.0
Poly(caprolactone)/MDI/ 2,2′ dimethyl propane-diol 	C_1	64.8	63.6	63.6
	C_2	29.9	27.9	27.9
	C_3	26.8	25.0	25.0
	C_4	25.0	24.1	24.1
	C_5	23.8	33.5	33.4
	C_6	–	172.8	172.7
	C_7	43.3	41.0	40.6
	C_8	138.5	137.1	137.1
	C_9	127.9	128.7	129.4
	C_{10}	117.9	118.3	120.3
	C_{11}	136.5	135.6	135.7
	C_{12}	–	153.6	154.0
	C_{13}	70.0	70.0	67.0
	C_{14}	19.7	20.7	21.3
	C_{15}	40.2	43.2	42.8

of MDI, polyethylene adipate and butanediol chain extender, as well as the number average molecular weight of the polyester block.

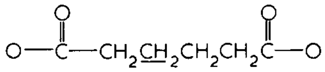
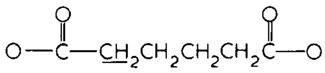
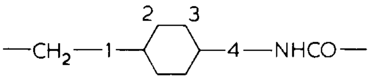
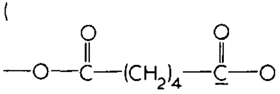
Similar considerations apply to the poly-caprolactone based polymers. The 2,2′dimethyl propanediol chain extender shows characteristic peaks at 67.0 and 21.3 ppm due to the CH_2 adjacent to urethane and methyl peaks respectively. The quaternary carbon is expected to occur at about 41 ppm and is therefore obscured by the D_6DMSO solvent peak.

In many cases, it is possible to separate the resonances associated with the polyester-urethane linkages from the in chain ester groups, thus providing a direct measure of the polyester block end groups and hence an estimate of the polyester block average molecular weight. However, in cases where the samples give relatively broad ^{13}C n.m.r. spectra, this may not be possible. In these cases, it is in principle possible to estimate these quantities by comparison of the relative intensities of other carbons in the system. For example, the relative intensities of the adipic acid and ethylene glycol derived peaks in the ethyl adipate polymers may provide an estimate of the polyester block lengths. However, because of the difficulties in obtaining accurate quantitative ^{13}C data, this is likely to be subject to large uncertainties except for very short blocks. Quantitative data is particularly difficult for carbonyl groups because of their long T_1's and small Overhauser effects.

Quantitative measurements

Although there are difficulties in obtainint quantitative ^{13}C n.m.r. data, these can be overcome if sufficient care is taken. Certain instrumental problems associated with early Fourier Transform spectrometers should not be important with current instrumentation. These include

Table 4 Nuclear overhauser enhancement factors in polyethylene adipate/butanediol/MDI polymers

Chemical shift (ppm)	Type of carbon		NOE
23.7	 $O-\overset{O}{\overset{\|}{C}}-CH_2\underline{CH}_2CH_2CH_2\overset{O}{\overset{\|}{C}}-O$		2.19
32.9	 $O-\overset{O}{\overset{\|}{C}}-\underline{CH}_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-O$		2.25
25.3	$-O-CH_2\underline{CH}_2CH_2CH_2O-$		2.04
61.7	$-O-\underline{CH}_2CH_2O-$		1.96
63.2	$-O-\underline{CH}_2CH_2CH_2CH_2O$		1.98
137.0		C_1	1.34
135.2		C_4	1.25
128.6		C_2	1.85
118.2		C_3	1.79
172.9	 $-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{\underline{C}}}-O$		1.24

insufficient digital resolution due to restricted computer memory, non-uniform filtering effects across the spectrum, and poor integration software. The two main considerations, therefore, are spin lattice relaxation time (T_1) effects and NOE effects.

To ensure that complete recovery of magnetization occurs between pulses so that intensities are not affected by selective saturation effects, a time of at least 5 T_1 should be left between pulses for a 90° pulse. In the present work, where the applied pulse width was either 30° or 45°, a delay of 5 T_1 should be more than adequate for quantitative data. In the systems studied, a wide range of T_1 values was encountered so that the ease with which this condition could be achieved varied considerably. In the polymers, T_1's for protonated carbons are generally less than one second. However, in the prepolymer, the in-chain protonated carbons are of the order of one second, and the end groups may have T_1's of the order if several seconds. This difference in T_1's between in-chain and end group carbons in polyester polyols is an important consideration when attempting end group analysis in these systems. T_1 values may be even longer for carbonyl groups in polyester diols and prepolymers, so extreme care should be taken in making quantitative measurements involving carbonyl groups. However, with sufficient care in considering relaxation factors, and provided sufficient sensitivity is available, it should be possible to overcome these difficulties in most cases.

The second important feature in quantitative ^{13}C n.m.r. is the NOE effect[19,20] which means that different carbon atoms have different intensity factors. To investigate this problem, we have measured the NOE factors for polyethylene adipate/butanediol/MDI polymers (*Table 4*). In common with many polymers, the NOE factors are appreciably less than the maximum value of 2.98 to be expected in the limit of extreme motional narrowing. They appear to fall into groups of values, with appreciable variation between the different groups. The larger values are observed for the aliphatic methylene groups. The values for the adipic acid carbons are close to 2.2, and are slightly larger than the ethylene glycol and butanediol carbons, which are all close to 2.0. The protonated aromatic carbons have NOE factors again slightly lower at about 1.8. The values for the quaternary aromatic and carbonyl carbons are lowest at about 1.25, the values close to unity reflecting the frelatively inefficient $^1H-^{13}C$ dipole contribution to the carbon T_1. It is clear from the appreciable variation in the measured values that these effects must be taken into account for quantitative ^{13}C measurements, either by running spectra using a pulse sequence which eliminates the Overhauser effect or by measuring the NOE and correcting for it (thus maintaining the sensitivity enhancement), although the errors are minimized if one is comparing similar types of carbon.

CONCLUSIONS

The results presented here indicate that a considerable amount of information can be obtained from the ^{13}C n.m.r. spectra of polyurethanes and related systems. An additive chemical shift scheme is useful in predicting the general features of the spectra. In addition, if spectra are measured under high resolution conditions, small chemical shift differences can be observed which differentiate between similar structures. Nuclear Overhauser Enhancement factors have been measured, and there is considerable variation between different carbons in these systems, so that this effect must be taken into account for quantitative measurements. With suitable allowance for NOE and T_1 effects, ^{13}C n.m.r. provides a useful quantitative technique for the characterization of polyurethanes.

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