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¹³-Nuclear Magnetic Resonance Studies of Polyetherurethaneureas

Alok R. Ray[a]; Ashis Bhowmick[a]
[a] Centre for Biomedical Engineering Indian Institute of Technology Delhi All India Institute of Medical Sciences Hauz Khas, New Delhi, India

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^{13}C-NUCLEAR MAGNETIC RESONANCE STUDIES OF POLYETHERURETHANEUREAS

ALOK R. RAY* and ASHIS BHOWMICK

Centre for Biomedical Engineering
Indian Institute of Technology Delhi

All India Institute of Medical Sciences
Hauz Khas New Delhi 110016, India

ABSTRACT

A series of linear polyurethaneureas was prepared by a two-step solution polymerization method. The prepolymer formed by the reaction of 4,4′-diphenyl methane diisocyanate with polyethylene glycol/polypropylene glycol was further chain extended with ethylene diamine/propane diamine/hexane diamine. The chemical shift values of various carbon species of the block copolymer were analyzed and assigned. The products formed due to the presence of water at different stages of polymerization were also characterized.

INTRODUCTION

^{13}C-NMR has been widely used [1–4] to elucidate the structure of polymers. Similar studies [5] of polyurethaneureas are very limited. Therefore, it was difficult to establish the structures of the polymer and its side products. In order to overcome these difficulties, we have prepared and characterized ^{13}C-NMR spectra of a series of polyurethaneureas based on 4,4′-diphenyl methane diisocyanate, polyethylene glycol (PEG)/polypropylene glycol (PPG), and ethylene diamine (EDA)/propane diamine (PDA)/hexane diamine (HDA). Because the presence of water in either the starting materials and/or the solvents leads to the formation of several side products, an attempt was made to identify them by separately synthesizing these products and subsequently characterizing their spectra. This approach enabled us to follow the reaction path and to determine the structure of the final product.

EXPERIMENTAL

Polypropylene glycol (Polysciences) and polyethylene glycol (Sigma Chemicals) of molecular weights 400, 600, and 1000 were degassed for 3 h at 60°C at 0.01 mmHg pressure before use.

4,4′-Diphenyl methane diisocyanate (MDI), obtained from TMI, Japan, was distilled under reduced pressure (0.01 mmHg) at 140°C in a jacketed Vigreux column and used immediately. The isocyanate content was determined by using the ASTM D1638-74 method. Dimethylformamide (DMF) and dimethylsulfoxide (DMSO), obtained from Fisher Scientific, were double distilled over calcium hydride under 0.01 mmHg pressure. 1,6-Hexane diamine and 1,3-propane diamine were obtained from Fisher Scientific and were used without further purification.

All reactions were carried out in flame-dried glassware. The prepolymerization was carried out in a mixed solvent of DMF and DMSO (2:3 by volume) at 80°C for 2 h in a dry nitrogen atmosphere. The chain extension reactions were carried out at 0°C in a 10% w/v solution containing a mixture of DMF and DMSO in a 2:3 volume ratio. All model compounds were synthesized following the methods described by Pethrick et al. [6, 7]. The chemical compositions of all the synthesized materials are given in Table 1.

Proton noise decoupled ^{13}C-NMR spectra were recorded on a Jeol PFT-100 spectrometer. Both polymers and intermediates were studied in deuterated DMSO solutions at ambient temperature. Usually 5000–8000 scans were collected for each spectrum.

RESULTS AND DISCUSSION

We followed Paul and Grant's [5] additive relationship in assigning chemical shift values for different carbon species. Chemical shifts are expressed in the following way in this approach.

$$j_i = B + \Sigma A_j n_{ij} \tag{1}$$

TABLE 1. Compositions and Abbreviations of Synthesized Linear Polyetherurethanureas

Materials	Abbreviation	Composition
Polyethylene glycol, MW 400: 4,4′-diphenyl methane diisocyanate: 1,3-propane diamine	PEUU(400)PDA	1:2:1
Polyethylene glycol, MW 600: 4,4′-diphenyl methane diisocyanate: 1,3-propane diamine	PEUU(600)PDA	1:2:1
Polyethylene glycol, MW 1000: 4,4′-diphenyl methane diisocyanate: 1,3-propane diamine	PEUU(1000)PDA	1:2:1
Polyethylene glycol, MW 600: 4,4′-diphenyl methane diisocyanate: 1,2-ethylene diamine	PEUU(600)EDA	1:2:1
Polyethylene glycol, MW 600: 4,4′-diphenyl methane diisocyanate: 1,6-hexane diamine	PEUU(600)HDA	1:2:1
Polypropylene glycol, MW 1000: 4,4′-diphenyl methane diisocyanate: 1,3-propane diamine	PPUU(1000)PDA	1:2:1
Polypropylene glycol, MW 1000: 4,4′-diphenyl methane diisocyanate: 1,6-hexane diamine	PPUU(1000)HDA	1:2:1

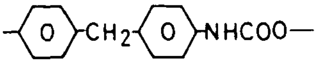
where j_i = chemical shift of ith C atom
B = a constant given by the ^{13}C-NMR chemical shift of methane (−2.3 ppm)
n_{ij} = number of C atoms in position j with respect to C_i
A_j = additive shift parameter of C atom j

Additives parameters (A_j) for alkanes, esters, and ethers are available [7]. By using these values, chemical shifts for polymers containing these functional groups can be predicted with an accuracy of ±2 ppm. Additive parameters for urethane and urea groups are not available, but by the model compound method the chemical shifts for carbon species in the urethane and urea groups have already been assigned. By taking

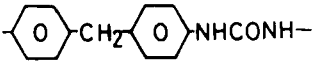
TABLE 2. Additive Parameters (A_j)

Chemical structure code	α	β	γ	δ	ϵ
A	49.02	4.95	−6.19		
B	24.45	7.18	−3.45	−1.65	
C[a]	57.70	8.00	−4.90	1.00	0.30
D[a]	9.10	9.40	−2.50	0.30	0.10

[a] Data taken from Ref. 7.



A



B

$-CH_2CH_2O-$

C

$-CH_2CH_2-$

D

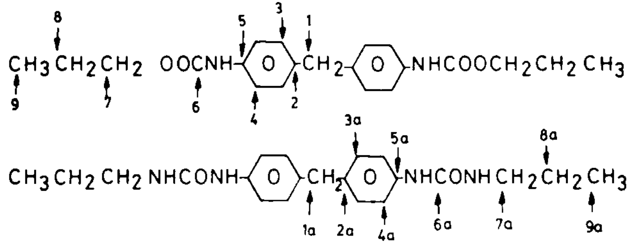
these values into consideration, a linear multiple regression analysis of chemical shift values for urethane and urea groups was made by using Eq. (1). The values obtained for these additive parameters are given in Table 2. These additive parameters were used in calculating the chemical shift values of the alkane skeletons from which these molecules are derived. Chemical shift values for propanol-based urethane and propylamine-based urea compounds were also calculated (Table 3). When these

TABLE 3. ^{13}C Chemical Shift of Dipropyldicarbamate and Dipropyldiurea

Chemical structure code	Chemical shift (ppm)	Carbon species								
		1	2	3	4	5	6	7	8	9
E	Predicted	40.3	138.5	127.9	117.9	136.5	153.6	65.2	23.0	10.0
	Observed	39.8	135.6	129.0	118.6	137.6	154.0	65.8	22.0	10.0
		1a	2a	3a	4a	5a	6a	7a	8a	9a
F	Predicted	39.8	134.8	129.0	118.0	138.7	155.6	40.6	23.0	12.7
	Observed	39.8	134.6	129.0	118.0	138.7	155.6	40.8	23.0	11.2

E

F

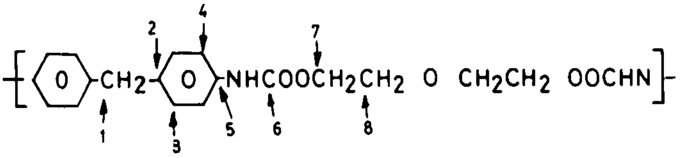


chemical shift values were compared with those observed experimentally, the difference was within ±2 ppm. This approach was further extended to diethylglycol-based urethane and polypropylene glycol and polyethylene glycol-based urethaneureas (Tables 4, 5, and 6).

All observed ^{13}C-NMR chemical shift values of the synthesized material could not be assigned by using this approach. All side products were analyzed in order to identify them. The most significant side reaction is the interaction of isocyanate with water and with solvents. DMF and DMSO were the two solvents used. DMSO does not react with isocyanate. Aromatic isocyanate reacts with DMF as shown in Fig. 1 [8]. However, when an isocyanate and DMF were heated up to 100°C, which was the reaction temperature for polymerization, this type of product (Product 1) could not be isolated.

TABLE 4. ^{13}C Chemical Shift of Polydiethylene Ether Urethane

Chemical structure code	Carbon species	Chemical shift Predicted, ppm	 Observed, ppm
G	1	40.3	40.0
	2	138.5	135.6
	3	127.9	129.0
	4	117.9	118.6
	5	136.5	138.5
	6	153.6	153.6
	7	63.8	65.2
	8	69.4	69.7

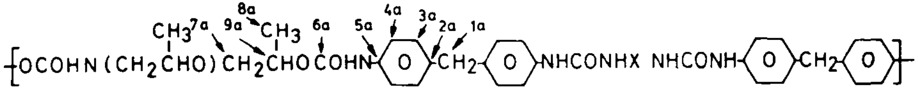


G

TABLE 5. ^{13}C Chemical Shifts of Synthesized Polypropoxy Urethaneureas

Chemical structure code	Chemical shift, ppm	Carbon species									
		1	2	3	4	5	6	7	8	9	10
	Predicted	43.3	138.7	127.9	118.0	136.5	153.6				
PPUU(1000)PDA	Observed	41.7	138.2	128.8		135.7	153.6	16.9	17.2	72.9–71.5	70.1–71.0
PPUU(1000)HDA	Observed	40.9	138.4	129.5	118.3	135.5	153.6	17.1	17.7	72.4–75.4	70.0–72.0
		1a	2a	3a	4a	5a	6a	7a	8a	9a	
	Predicted	39.8	134.6	129.0	118.0	138.5	155.6	37.2	30.2		
PPUU(1000)PDA	Observed	40.8	135.1	129.2		137.6	153.0	38.3	30.0		
PPUU(1000)HDA	Observed	40.7	134.1	128.6	118.8	137.6	155.5	38.3[a]	30.2[b]	27.3[c]	

[a] Predicted value 38.4.
[b] Predicted value 30.3.
[c] Predicted value 27.1.



$X = CH_2CH_2CH_2$ in PPUU (1000) PDA

$X = CH_2CH_2CH_2CH_2CH_2CH_2$ in PPUU (1000) HDA

TABLE 6. ^{13}C Chemical Shifts of Synthesized Polyetherurethaneureas

Chemical structure code	Chemical shift, ppm	Carbon species									
		1	2	3	4	5	6	7	8	9	10
	Predicted	43.3	138.5	138.5	127.9	117.9	136.5	153.6	63.8	69.4	72.5
PEUU(400)PDA	Observed	41.7	137.6	137.6	129.4	118.6	136.2	154.1	64.1	69.3	70.4
PEUU(600)PDA	Observed	41.4	137.6	137.6	128.6	118.3	135.4	153.6	63.5	68.8	70.0
PEUU(1000)PDA	Observed	41.5	137.8	137.8	128.7	118.4	135.1	153.6	63.6	68.9	70.0
PEUU(600)HDA	Observed	40.8	137.6	137.6	129.4	119.0	136.1	154.1	64.1	70.0	70.9
PEUU(600)EDA	Observed	40.9	137.5	137.5	128.6	118.5	136.3	153.4	63.6	68.9	70.2
		1b	2b	3b	4b	5b	6b	7b	8b		
	Predicted	39.8	134.8	129.0	118.0	138.7	155.6	37.2	30.2		
PEUU(400)PDA	Observed	40.8	134.7	130.1	119.0	138.9	156.1	37.3	30.1		
PEUU(600)PDA	Observed	40.9	134.1	128.6	118.8	138.4	155.6	37.2	30.1		
PEUU(1000)PDA	Observed	40.7	134.7	128.7	118.9	138.5	155.6	37.0	30.2		
PEUU(600)HDA	Observed	40.7	134.7	129.4	118.0	138.8	156.0	38.3[a]	30.9[c]		
PEUU(600)EDA	Observed	40.8	134.5	128.5	118.8	138.6	155.3	38.5[b]	26.9[d]		

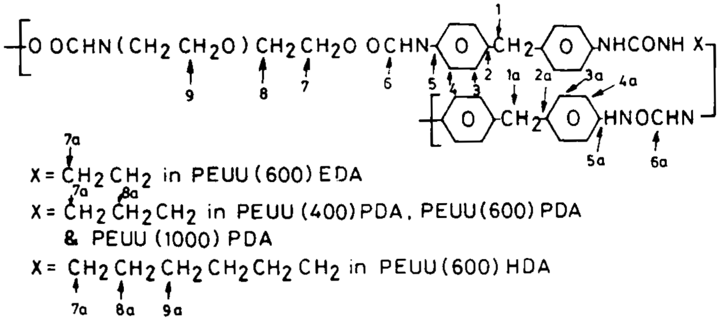
[a] Predicted value 38.5.

[b] Predicted value 38.4.

[c] Predicted value 30.3.

[d] Predicted value 27.1.

TABLE 6. Continued.



$X = CH_2CH_2$ in PEUU(600)EDA

$X = CH_2CH_2CH_2$ in PEUU(400)PDA, PEUU(600)PDA & PEUU(1000)PDA

$X = CH_2CH_2CH_2CH_2CH_2CH_2$ in PEUU(600)HDA

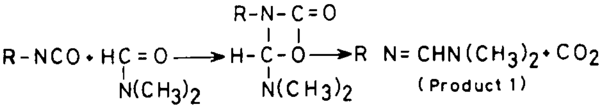


FIG. 1.

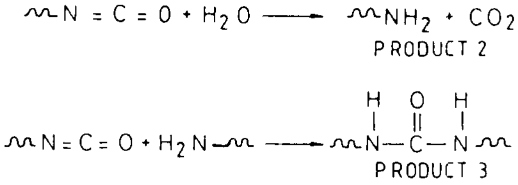


FIG. 2.

TABLE 7. ^{13}C Chemical Shift of 4,4′-Diphenyl Methane Diamine and Polydiphenyl Methane Urea

	Carbon species	Chemical shift, ppm
Product 2	1b	40.3
	2b	136.0
	3b	129.2
	4b	114.0
	5b	146.5
Product 3	1c	40.3
	2c	135.2
	3c	128.9
	4c	118.3
	5c	138.0
	6c	153.0

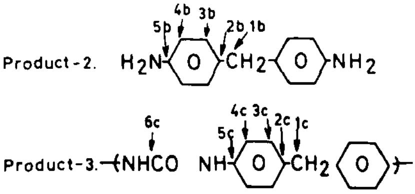
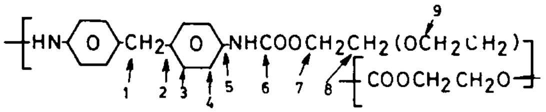


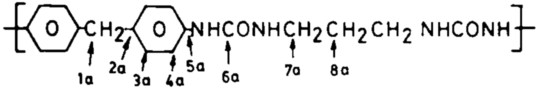
TABLE 8. ^{13}C Chemical Shift of Copolyurethaneureas Synthesized in the Presence of Water in the Prepolymerization Step

Chemical structure code		Carbon species								
		1	2	3	4	5	6	7	8	9
H	Chemical shift (ppm)	40.8	135.7	128.7	118.9	138.5	153.6	63.6	68.9	70.0
		1a	2a	3a	4a	5a	6a	7a	8a	
I	Chemical shift (ppm)	40.7	135.2	128.7	118.9	137.1	156.6	37.1	30.0	
		1c	2c	3c	4c	5c	6c			
J	Chemical shift (ppm)	40.6	135.5	128.7	118.9	137.8	152.7			

H



I



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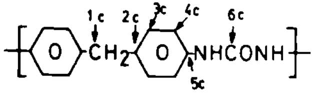

TABLE 9. ^{13}C Chemical Shift of Block Copolymers Synthesized in the Presence of Water in the Chain Extension Step

Chemical structure code		Carbon species								
		1	2	3	4	5	6	7	8	9
K	Chemical shift (ppm)	40.7	135.0	128.7	118.4	138.7	153.6	63.6	68.9	70.0
		1a	2a	3a	4a	5a	6a	7a	8a	
L	Chemical shift (ppm)	40.7	135.1	128.7	118.9	137.8	155.6	38.3	37.0	
		1b	2b	3b	4b	5b	6b	7b	8b	
M	Chemical shift (ppm)	41.5	135.1	128.1	118.9	137.8	155.6	38.3	30.0	
		1c	2c	3c	4c	5c				
N	Chemical shift (ppm)	41.0	135.0	128.0	114.0	—				
		1d	2d	3d	4d	5d	6d			
O	Chemical shift (ppm)	40.7	135.0	128.7	118.4	137.8	152.7			

TABLE 9. Continued.

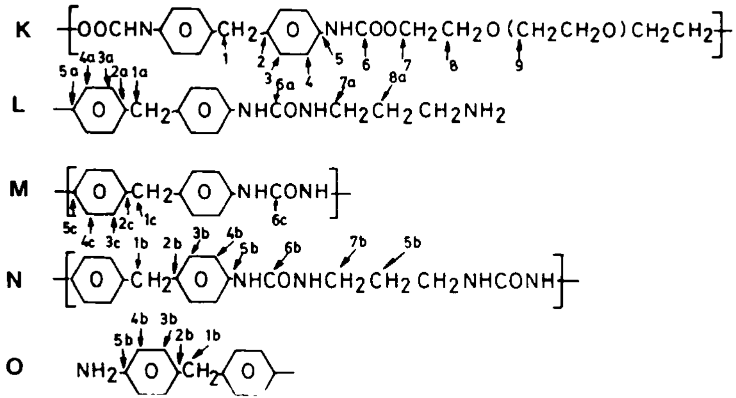

Figure 2 shows the reaction of water with isocyanate. 4,4′-Diphenyl methane diamine (Product 2) and polyurea (Product 3) are two stable products. We prepared these two products separately and assigned chemical shift values to the carbon species (Table 7). We could not identify either of these products in the final compound when trace amounts of water were present in the reactants and solvents.

The polymerization was carried out in two steps. In the first step (prepolymerization), polyol was reacted with isocyanate in the solvent medium at high temperature (100°C). In the second step (chain extension), a chain extender was added at low temperature (0°C). In the preparation of these polymers, we deliberately added trace amounts of water in the prepolymerization step and used an absolutely water-free chain extender. The structure of the product is shown in Table 8.

In the next preparation, a trace amount of water was deliberately added with the chain extender. Table 9 shows the structure of the product. It was observed that, in addition to the main product, when water is present in the prepolymerization stage, material containing randomly distributed urethane, urea derived from amine, and urea derived from water were also generated. However, when water was added with the chain extender, the main impurity was polymer with amine groups at the chain end. This was possibly due to the smaller availability of free isocyanate at the chain extension stage. Further, since the temperature is low at this stage, the reaction leading to the formation of urea and diamine (Products 2 and 3 in Fig. 2) is very slow. Our results indicate that it is possible to identify the reactions products with the help of ^{13}C spectra due to the presence water at the different reaction stages.

CONCLUSION

The chemical shift values for various carbon species of block copolyurethaneurea are assigned by using the Paul and Grant approach. The presence of water either in the starting materials and/or in the solvents leads to the formation of several side products during the preparation of polyurethaneurea. The presence of water at the prepolymerization stage leads to the formation of randomly distributed urethane and urea groups. Polymers with amine groups at the chain ends are one of the impurities when water is present at the chain extension stage.

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