

NMR Studies of Water-Borne Polyurethanes

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ABSTRACT: A series of water-borne polyurethanes were prepared by prepolymerization process. Isophorone diisocyanate, polyester diol, and dimethylol propionic acid were used to conduct the reaction. ¹H- and ¹³C-NMR spectra of the raw materials and products thereof were measured with a high-resolution spectrometer, and their chemical shifts were assigned. ¹H- and ¹³C-NMR spectra of urethane group and urea group were compared. The chemical shifts of side

products from the reaction between water and the isocyanate group were also analyzed. Much useful information may be obtained from the NMR analysis of this kind of polyurethanes. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 257–260, 2003

Key words: ionomers; polyurethanes; isophorone diisocyanate; polyester diol; hydrophilic polymers

INTRODUCTION

The introduction of small amounts of ionic groups into polymer chains forms a series of interesting ionomers. When these ionomers are dispersed in water, water-borne polymers are produced. Water-borne polyurethanes are representative of this kind of polymers. Water-borne polyurethanes have been given great importance because of environmental and legislative pressures.^{1,2} Among polyurethane ionomers, anionic polyurethane dispersions have been most frequently used in many applications. The preparation and properties of anionic polyurethane dispersions have been fully researched.^{3–8} However, their structures may not be well characterized, such as by NMR. NMR has been widely used to elucidate the structure of some polymers. To study NMR characteristics of water-borne polyurethanes, we prepared a series of polyurethanes based on isophorone diisocyanate (IPDI), polyethylene–butylene adipate glycol (PE–BA), polyhexane–neopentyl adipate glycol (HNA), dimethylol propanoic acid (DMPA), triethyl amine (TEA), and ethylene diamine (EDA). High-resolution NMR spectrometry was used to perform the NMR measurement.

EXPERIMENTAL

Synthesis of water-borne polyurethanes

HNA and PE–BA (MW = 1500 and 2000, respectively) were dehydrated for 2 h at 80°C and under 1 mmHg pressure before use. IPDI was obtained from Bayer

and used without further purification. NMP, EDA, and TEA were of analytical purity.

HNA or PE–BA, DMPA, IPDI, and *N*-methyl pyrrolidone (NMP) were charged into a four-neck flask. The prepolymerization was carried out in NMP for 5 h at 80°C in a dry nitrogen atmosphere. TEA was added to neutralize the prepolymer at the same temperature. The reaction mixture was cooled to 50°C. Distilled water was dropped into the flask in 5 min under stirring. Chain extension was immediately carried out at 50°C. A well-dispersed mixture was obtained. The product was dried at 60°C under vacuum pressure for 24 h to ensure any trace water was excluded.

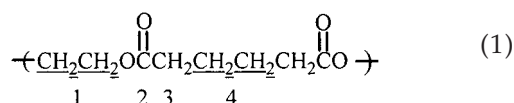
Measurement of NMR spectra

¹H and proton noise decoupled ¹³C-NMR spectra were recorded on a Varian 400 spectrometer (Varian Associates, Palo Alto, CA). Samples submitted to measurement were dissolved in deuterated DMSO solutions.

RESULTS AND DISCUSSION

NMR analysis of raw materials

The polyesters with molecular weights of 1000–4000 are linear hydroxyl-terminated materials prepared from adipic acid and diols. The diols used in this study include ethylene glycol, 1,4-butanediol, 1,6-hexanediol, and 2,2'-dimethyl-1,3-propanediol. PE–BA is composed of structure (1) and structure (2) at random. The structures and assignment of chemical shifts (Table I) are as follows.



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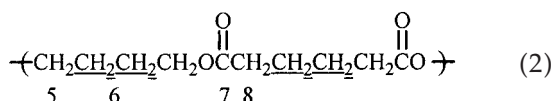


TABLE I
¹H and ¹³C Chemical Shifts of PE-BA

H and C species	Chemical shift (ppm)
1H	4.213
3H	2.306
4H	1.598
5H	4.036
6H	1.653
8H	2.306
1C	62.99
2C	171.76
3C	33.04
4C	23.67
5C	61.47
6C	24.84
7C	171.68
8C	32.89

The chemical shifts of 2C and 7C, 3C and 8C are slightly different, attributed to the result of slightly different chemical environments as (OCH₂CH₂) and (OCH₂CH₂CH₂CH₂) connected to the carbonyl group, respectively. The chemical shifts of end groups are also available. They are shown as structure (3) and structure (4) and are assigned in Table II.

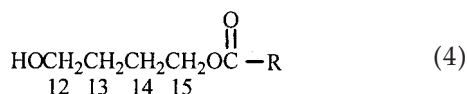
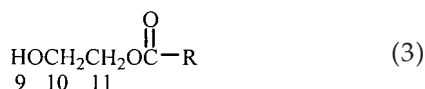


TABLE II
 End-Group ¹H and ¹³C Chemical Shifts of PE-BA

H and C species	Chemical shift (ppm)
9H	4.382
10H	3.574
11H	4.213
12H	2.952
13H	1.431
14H	1.485
15H	3.431
10C	59.03
11C	65.22
12C	60.23
13C	28.92
15C	63.25

HNA is composed of structure (5) and structure (6) at random. The structures and assignment of chemical shift (Table III) are as follows.

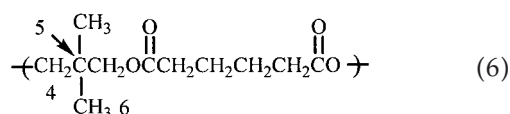
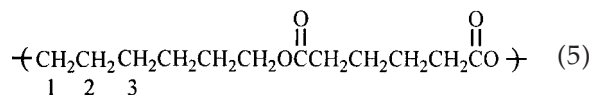


TABLE III
¹H and ¹³C Chemical Shifts of HNA

H and C species	Chemical shift (ppm)
1H	3.882
2H	1.661
3H	1.384
4H	4.063
6H	0.917
1C	64.17
2C	28.50
3C	25.56
4C	68.96
5C	Not observed
6C	21.74

¹H and ¹³C chemical shifts of HNA are similar to those of PE-BA, except the atoms marked with numbers. They are assigned in Table III.

The diisocyanate used here is IPDI, shown in structure (7). Although IPDI is commonly used to prepare waterborne polyurethane, its NMR spectra is not always recorded. Its chemical shifts are assigned in Table IV.

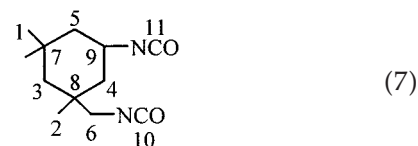


TABLE IV
¹H and ¹³C Chemical Shifts of IPDI

H and C species	Chemical shift (ppm)
1H-2H	0.9-1.3
3H-5H	1.4-1.9
6H	3.083
9H	3.2-3.8
1C-2C	22-27
3C-5C	29-36
6C	49.95
7C-8C	42-48
9C	55.94
10C	121.50
11C	122.23

We know commonly used IPDI consists of *cis* and *trans* isomers, so ^1H and ^{13}C spectra of IPDI are very complicated. For some instances, we can only assign them with a range of peaks, such as 1H–2H with 0.9–1.3.

NMR analysis of water-borne polyurethane from PE-BA

PE-BA is a very common raw material for preparing water-borne polyurethanes. Raw materials used here also include IPDI, DMPA, EDA, and TEA. The water-borne polyurethane prepared from the above raw materials was studied by NMR. Structures (8)–(10) represent the main parts of the polymer, and chemical shifts are assigned in Table V. It is well known that isocyanate connected to carbon 1 is more reactive than the one bonded to carbon 2, attributed to steric hindrance of the six-member ring. [In structure (8) the isocyanate bonded to carbon 1 has reacted with the soft component.] It is thus easy to understand that in prepolymerization, structure (8) and structure (9) are produced more easily and quickly. Then the soft component and DMPA may react with either structure (8) or structure (9) to give the other four structures, although only structure (10) is presented as an example.

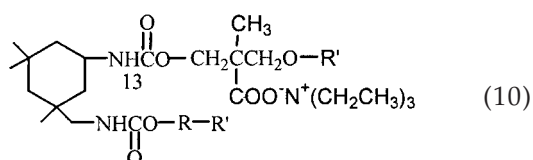
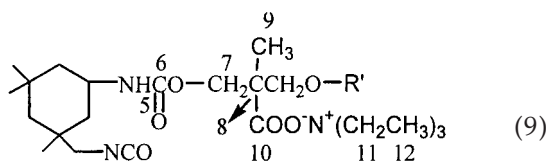
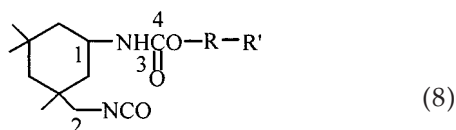


TABLE V
 ^1H and ^{13}C Chemical Shifts of Polyurethane Segments

H and C species	Chemical shift (ppm)
3H	6.881
5H	6.825
7H	4.128
9H	1.088
11H	2.498
12H	0.784
13H	7.240
1C	58.87
2C	53.32
4C	158.20
6C	157.35
7C	62.25
8C	54.21
9C	22.96
10C	174.42
11C	46.62
12C	Not observed

where R denotes the soft segment and R' denotes the IPDI segment in all structures unless otherwise indicated.

The chemical circumstances of 3H in structure (8), 5H in structure (9), and 13H in structure (10) are slightly different, so their chemical shifts are different. The chemical shifts of 4C and 6C are also slightly different, but 14C is similar to 6C.

During the extension step ethylene diamine reacts with the residual isocyanate group to connect different prepolymer structures to form polymer molecules. Two representative structures are shown below as formulas (11) and (12). Table VI reveals that the chemical shifts of H and C in the urea group both occur at a higher magnetic field compared to those in the urethane group. This result conforms to a previous report of MDI-type polyurethane.⁹

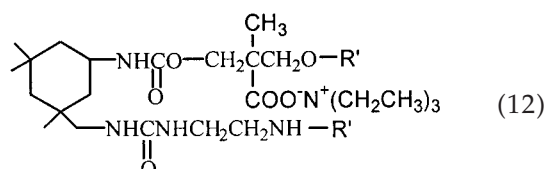
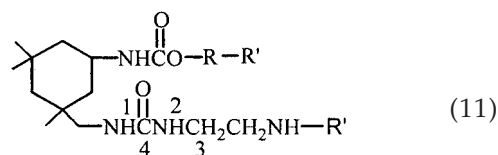


TABLE VI
 ^1H and ^{13}C Chemical Shifts of Urea Segments from Ethylene Diamine

H and C species	Chemical shift (ppm)
1H	5.860
2H	5.682
3H	2.750
3C	41.20
4C	154.60

The trace water present in raw materials and the process of dispersion make it possible to produce structure (13). Here we present structure (13) only as an example; other similar structures may exist in the polymer.

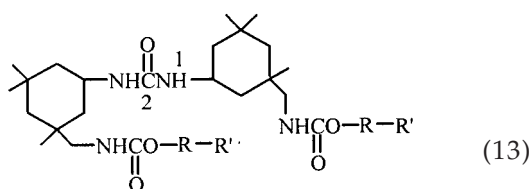


TABLE VII
 ^1H and ^{13}C Chemical Shifts of Urea Segments from Water

H and C species	Chemical shift (ppm)
1H	7.661
4C	156.30

Table VII indicates that chemical shifts of the urea group are distinct from those of the urethane group or the urea group from amine extension. This may be used to detect a side product from water.

NMR analysis of water-borne polyurethane from HNA

In general, the NMR spectra of water-borne polyurethane from HNA is similar to that from PE-BA, so no details about the chemical shifts are given. We must keep in mind, however, that CH_3 is present in both the

soft segments and the hard segments, which makes it difficult to distinguish them. Because we have the data of raw materials, it is easier to elucidate.

CONCLUSIONS

The above discussion indicates that a considerable amount of information can be obtained from ^1H - and ^{13}C -NMR spectra of water-borne polyurethanes. If NMR spectra are measured under high-resolution conditions, small chemical-shift differences can be observed that differentiate between similar structures.

Related to IPDI-type water-borne polyurethanes the following conclusions are put forward.

1. The chemical shifts of H and C in urethane groups from acyclic NCO and alicyclic NCO are slightly different.
2. ^1H - and ^{13}C -NMR spectra of IPDI are very complex, attributed to *cis* and *trans* isomers present together.
3. The chemical shifts of H and C from the urea group, produced using ethylene diamine, occur at a higher magnetic field compared to those from the urethane group.
4. It is straightforward to detect the side product from the reaction between water and the isocyanate group.

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