

Distribution of Hydrophilic Monomer Units and Its Effect on the Property of the Water Dispersion of Polyurethaneurea Anionomer

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ABSTRACT: Water dispersion of polyurethaneurea anionomer based on polyurethane synthesized by using "one-step process" and water dispersion of polyurethaneurea anionomer based on polyurethane synthesized by using "two-step process" were prepared. Spectra of ¹³C-NMR proved that the distribution of the hydrophilic monomer units along the macromolecular chain resulted from the latter process was more uniform than that by the former

process. Uniform distribution of hydrophilic monomer units led to smaller average size and polydispersity of the polyurethaneurea particles dispersed in water, as well as higher stability of the water dispersion. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 634–640, 2007

Key words: water-borne polyurethaneurea; sequence distribution; water dispersion

INTRODUCTION

There were many reports and patents about the preparation of waterborne polyurethane or polyurethaneurea.^{1–6} To simplify the operation, most of the commercial products were based on the polyurethane prepolymer synthesized by using "one-step" process with dimethylol propionic acid (DMPA) as hydrophilic monomer, while few of them by using "two-step" process. As for the characterization of usual polyurethane or polyurethaneurea with NMR study, papers were published.^{7–10} Some NMR studies paid attention on the sequence distribution of polyurethane or polyurethaneurea,^{11–14} but the distribution of hydrophilic monomer units along the macromolecular chain and its effect on the property of the corresponding water dispersion of water-borne polyurethaneurea anionomer was not reported. It should be a very important factor in relation to property of the dispersion. The present work investigated the distribution of the hydrophilic monomer DMPA units along the macromolecular chain of polyurethane prepolymers synthesized by the different processes to determine the distinct effects of different distributions of DMPA units on the average size and polydispersity

of the polyurethaneurea particles dispersed in water, as well as the ζ electric potential of the polyurethaneurea water dispersion, which could represent the stability and quality of the dispersion.

EXPERIMENTAL

Materials

Industrial polydimethyltrimethylene glycol adipate (p756, $M_n = 2000$, functionality 2, hydroxy value 56.0 mg KOH/g) was dried at 110°C under vacuum for 1 h, and hydrophilic monomer DMPA was dried at 80°C under vacuum for 48 h before use. Diphenylmethylene diisocyanate (MDI) was also an industrial product and its content of —NCO was 33.6%. Other materials and solvents were reagent grade and used as received.

Synthesis

Water dispersion of polyurethaneurea anionomer based on the polyurethane prepolymer synthesized by using "one-step process"

The MDI melt was poured into a four-necked flask containing p756, DMPA, the catalyst dibutyltin dilaurate, and very small amount of *N*-methylpurrolidone as solvent. The reaction was carried out at 65°C under stirring and in nitrogen atmosphere, until the amount of —NCO reached theoretical value. Equivalent triethylamine, in respect to the COOH groups attached to DMPA units, was added to neutralize the system.

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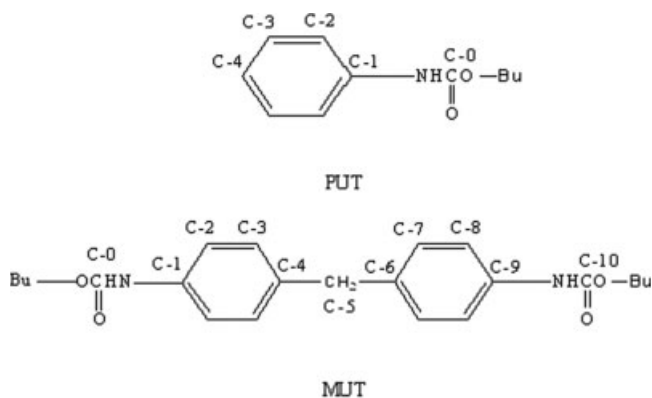


Figure 1 Urethane models according to the literature.

Deionized water was poured into the obtained water-dispersible polyurethane prepolymer, and the solution of the chain extender ethyldiamine in water was then added. At last, the terminal —NCO groups were capped with diethanolamine. For synthesis of the polyurethane prepolymer, the ratio of —NCO /total —OH groups equaled 1.8 (mol). The amount of DMPA was 6% (by weight) in respect of the total amount of MDI, p756, and DMPA itself. The dosage of the catalyst dibutyltin dilaurate was 1‰ of the total raw materials. The amount of diethanolamine was 2/3 (mol) of the terminal —NCO groups of the polyurethane prepolymer. The solid content of the end water dispersion of polyurethaneurea was 30%.

Water dispersion of polyurethaneurea anionomer based on the polyurethane prepolymer synthesized by using “two-step process”

The MDI melt was poured into a four-necked flask containing only p756, the catalyst, and *N*-methylpyrrolidone. The reaction was carried out until theoretical content of —NCO was reached. DMPA was then added. The following process and the amount of each reagent was just the same as preparation of the water dispersion of polyurethaneurea anionomer, based on polyurethane prepolymer synthesized by using “one-step process.”

Characterization

^{13}C -NMR

Proton noise decoupling and inversion gate decoupling (for minimizing NOE) ^{13}C -NMR spectra was recorded

TABLE I
 ^{13}C -NMR Chemical Shifts for Urethane Model Compounds

Urethane	C-0	C-1	C-2	C-3	C-4
PUT	153.9	139.6 (M-1), (M-9)	118.4 (M-2), (M-8)	128.7 (M-3), (M7)	122.3 (M-4), (M6)
MUT	153.6	137.1	118.4	128.7	135.3

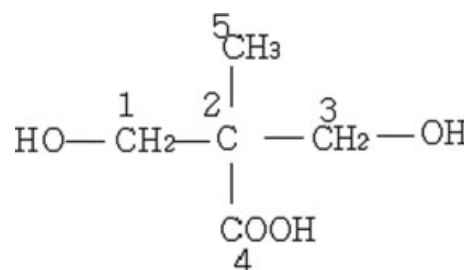


Figure 2 Structure of DMPA.

on a DRX500 spectrometer at 293.0 K, 125.7 MHz of frequency, and 37.95 kHz of spectrum width. Polyurethane prepolymer before water dispersion was dissolved in deuterated (99.9%) sulfoxide (DMSO). 32,000 transients were accumulated. The relaxation time T_1 was 30 s to avoid accumulated errors. For all spectra, chemical shifts were quoted with reference TMS as standard.

Average size of dispersed polymer particles

Measure of the average size of polyurethaneurea particles dispersed in water was carried out by using AutosizerIIC Light-scattering instrument.

Zeta electric potential of water dispersion

A JS94F microelectrophoresis instrument was used to determine the ζ electric potential of the water dispersion of polyurethaneurea anionomers.

RESULTS AND DISCUSSION

Attribution of the peaks of the ^{13}C -NMR spectra

Atsushi Kali and Masao recorded the ^{13}C -NMR spectra¹¹ of urethane models (Fig. 1) as shown in Table I. In the present work, the structure and ^{13}C -NMR spectrum of DMPA is shown in Figures 2 and 3 (The letter D represents the carbon of DMPA in Fig. 2), respectively. According to the empirical equation for

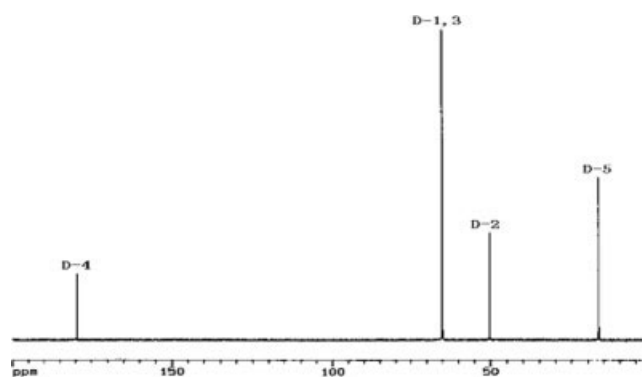


Figure 3 ^{13}C -NMR spectrum of DMPA. (The letter D represents the carbon of DMPA in Fig. 2.)

TABLE II
Calculated ^{13}C -NMR Chemical Shifts for DMPA

Carbon	δ
C-1	64.4 (D-1)
C-2	55.3 (D-2)
C-3	64.4 (D-3)
C-4	180 (D-4)
C-5	17.5 (D-5)

the chemical shift of aliphatic compound,¹⁵ the calculated ^{13}C -NMR chemical shifts of DMPA are indicated in Table II. The structure, ^{13}C -NMR spectrum, and Dept spectrum of p756 are expressed in Figures 4–6. (C 7, 8, 9 were the carbons along the molecular chain except the carbons nearest to the terminal —OH groups with the code 7', 8', 9'; the letter P represents the carbon of p756 in Fig. 4.).

The five negative peaks at δ 69.70, 69.95, 68.80, 34.42, and 24.98 in Figure 6 are attributed to —CH₂ groups. The positive peaks at δ 22.35 (P-10, 11) should be in relation to C-10 and C-11 in Figure 5, because there is not any —CH group in the structure of p756. The peaks at δ 35.29, 36.95, and 173.71 exist only in Figure 5, do not in Figure 6. This phenomenon means that these peaks are resulted from quaternary carbon atoms, i.e., the peak at δ 173.71 (P-1, 6) from the carbonyl carbon atoms C-1 and C-6, the peak at δ 35.29 (P-8) from C-8 and the peak at δ 36.95 (P-8') from the C8' near to the terminal OH group in Figure 4. The ^{13}C -NMR chemical shifts of C-2 (ca δ 36.2), C-3 (ca δ 24.8), C-4 (ca δ 24.8), and C-5 (ca δ 36.2) in Figure 5 were also calculated by empirical equation.¹⁵ On the basis of the earlier results, it could be derived that the peak of C-7 and C-9 should be located at δ 69.70 (P-7, 9) in Figure 5. In addition, Figure 4 reveals that the electronegativity of the atom around C-7' is stronger than that around C-9'. For this reason, the peak of C-7' should located at δ 69.95 (P-7') and C-9' at δ 68.80 (P-9'). According to the earlier discussion, the ^{13}C -NMR chemical shifts for p756 are gathered in Table III. Figures 7 and 8 show the ^{13}C -NMR spectrum of the MDI/DMPA/p756 copolymer synthesized by two-step process and by one-step process, respectively.

The code of the peaks in Figure 8 is the same as in Figure 7. In these two figures, two peaks in relation to —NHCOO could be found, one at δ 152.5 and the other at δ 153.4. To determine the attribution of these two

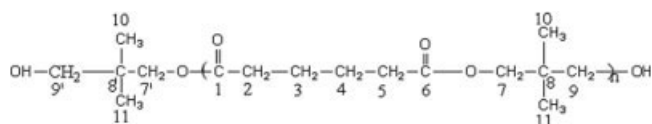


Figure 4 Structure of p756. (C 7, 8, 9 were the carbons along the molecular chain except the carbons nearest to the terminal —OH groups with the code 7', 8', 9'.)

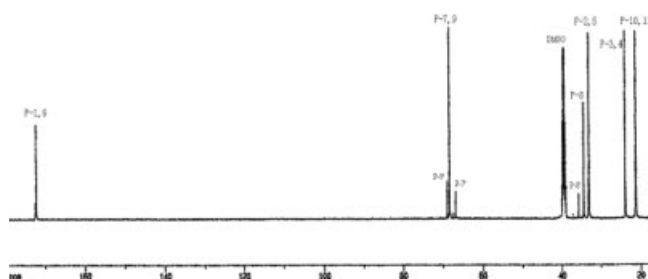


Figure 5 ^{13}C -NMR spectrum of p756. (The letter P represents the carbon of p756 in Fig. 4.).

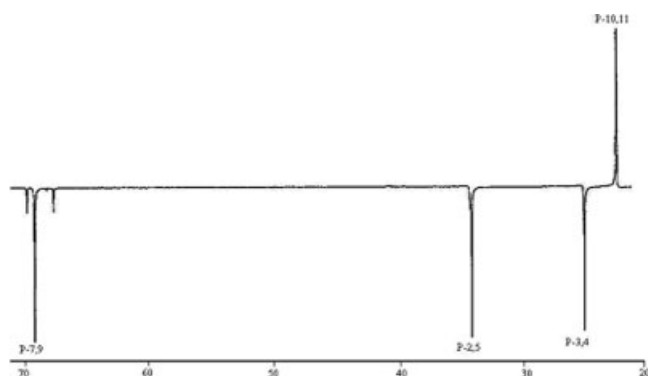


Figure 6 Dept spectrum of p756.

TABLE III
 ^{13}C -NMR Chemical Shifts for p756

δ	Carbon atom
22.35 (p10,11)	C-10, C-11
34.42 (P2, 5)	C-2, C-5
36.95 (P8')	C-8'
69.95 (P7')	C-7'
173.71 (P1, 6)	C-1, C-6
24.98 (P3, 4)	C-3, C-4
35.29 (P8)	C-8
69.70 (P7, 9)	C-7, C-9
68.80 (P9')	C-9'

peaks, the ^{13}C -NMR spectrum of copolymer consisting of MDI and p756 (mol ratio of 1 : 2) was recorded (Fig. 9). According to Figure 9, the peak of the —NHCOO formed by reactions of MDI with p756 is located at δ 153.4. The peak at δ 152.5 and 153.4 in Figures 7 and 8 should thus be attributed to the NHCOO formed by reaction of MDI with DMPA and to the NHCOO formed by reaction of MDI with p756, respectively. The peak at δ 124.21 should be due to unreacted —NCO.^{16,17}

By referring the chemical shifts of the above three compounds and of the —NHCOO groups, the attribution of peaks in the ^{13}C -NMR spectra (Figs. 7 or 8) of the MDI/DMPA/p756 copolymer could be inferred and listed in Table IV (In Table IV, "D" "P" "M" were used instead of "C"). In Table IV, it could be discovered that the peaks of the original symmetrical carbon atoms contained in MDI (C-1, C-9 and C-2, C-4

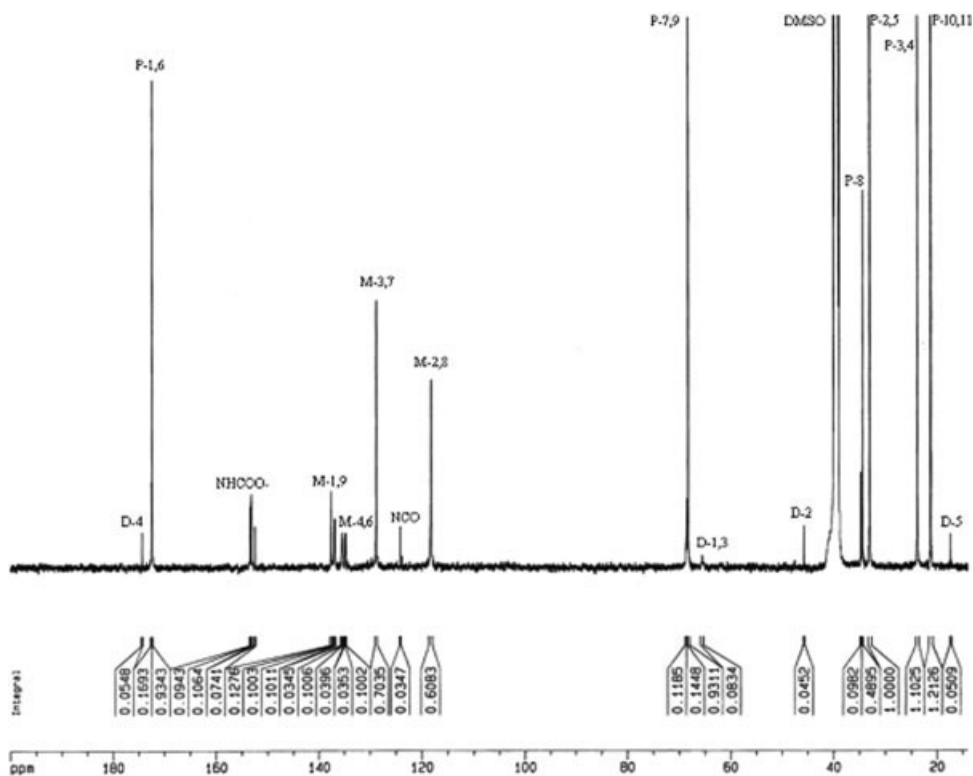


Figure 7 ¹³C-NMR spectrum of the MDI/DMPA/p756 copolymer synthesized by two-step process. (The letter M represents the carbon of MDI in Fig. 1.)

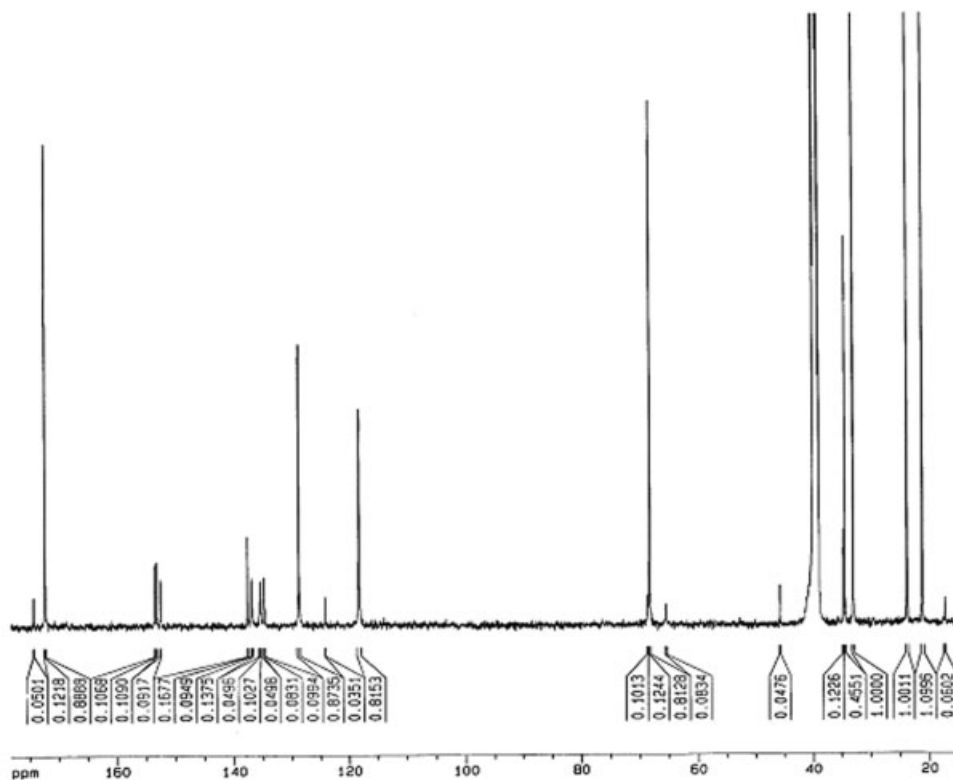


Figure 8 ¹³C-NMR spectrum of the MDI/DMPA/p756 copolymer synthesized by one-step process.

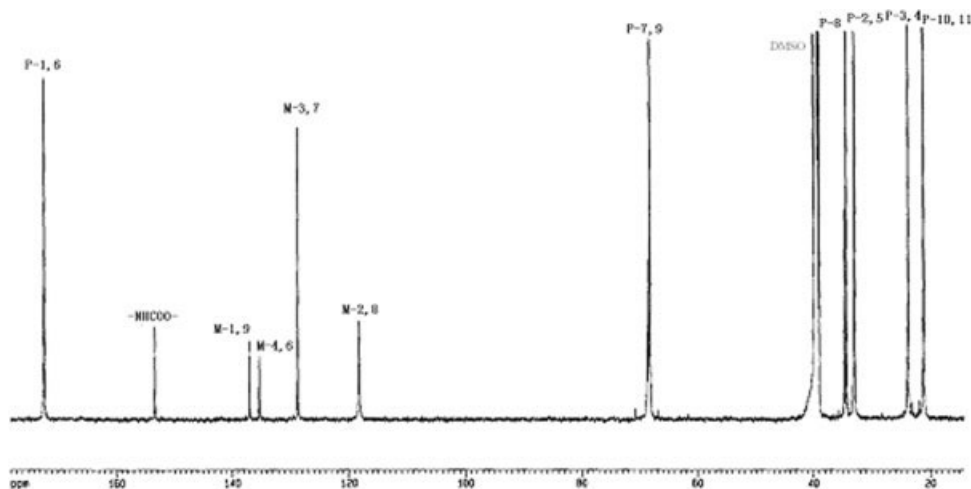


Figure 9 ^{13}C -NMR spectrum of the p756/MDI/p756 copolymer.

in Fig. 1) split and result in different peaks (M-1, M-9 and M-4, M-6 in Table IV) due to the existence of MDI-DMPA and MDI-p756 linkages. Figure 10 is the partial enlargement of Figure 7 (two-step process). By referring to Atsushi and Masao,¹¹ the range of M4–M6 (from δ 134.5 to 136.0) in Figure 7 is enlarged as Figure 10 shows.

The sum of the area of the five peaks in Figure 10 equals 0.3102, while the sum of the area of the two —NHCOO— peaks in Figure 7 is 0.2748. The difference between these two values indicates that the copolymer MDI/DMPA/p756 contained some unreacted —NCO groups, such as the terminal —NCO groups. M4 or M6 could normally split into only two peaks and generally not into three peaks, if no unreacted —NCO was present. The unreacted —NCO in the present work should thus be located at “a” or “b” or “c” (Fig. 10). The value of the area at δ 124.21 in Figure 7 is 0.0347, which is

TABLE IV
 ^{13}C -NMR Chemical Shifts for MDI/DMPA/p756 Copolymer

δ	Carbon atom
17.42	D-5
52.90	D-2
65.51	D-1, D-3
174.32	D-4
118.29	M-2, M-8
124.21	unreacted —NCO
128.80	M-3, M-7
134.7–135.6	M-4 and M-6
21.24	P-10, P-11
23.86	P-3, P-4
33.07	P-2, P-5
34.45	P-8
68.31	P-7, P-9
172.54	P-1, P-6
136.9–137.6	M-1, M-9
152.5	—NHCOO (DMPA)
153.4	—NHCOO (P756)

nearly the same of the peak “a” (0.0345) in Figure 10. It could thus be concluded that the peak “a” in Figure 10 should be due to the carbon of unreacted terminal —NCO groups. The same conclusion was obtained by treatment of Figure 8 (one-step process).

Calculation of sequence distribution¹⁵ of polyurethane anionomer before water dispersion

Polyurethane anionomer synthesized by using two-step process

According to the literature,¹¹ the calculation of sequence distribution depends mainly on the split of the peaks M-4 and M-6 in Table IV.

There are three types of linkage in the copolymer MDI/DMPA/p756:

1. DMPA-MDI-DMPA (DMD, hard segment–hard segment; Fig. 11)
2. p756-MDI-p756 (PMP, soft segment–soft segment; Fig. 12)
3. DMPA-MDI-p756 (DMP, hard segment–soft segment; Fig. 13)

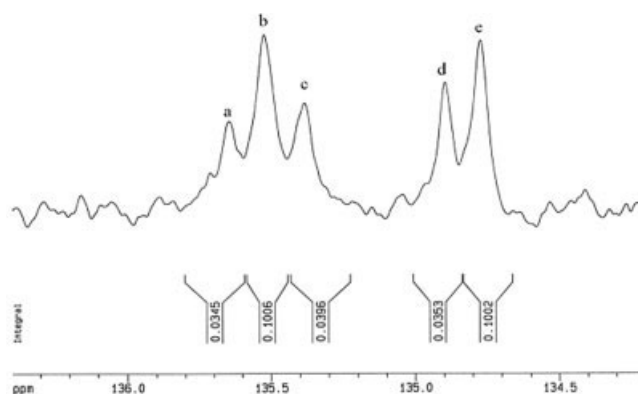


Figure 10 Enlargement of the range M4–M6 in Figure 7.

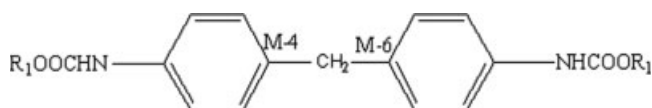


Figure 11 Chemical linkage of DMD.

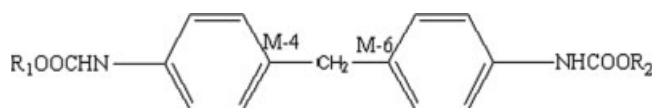


Figure 13 Chemical linkage of DMP.

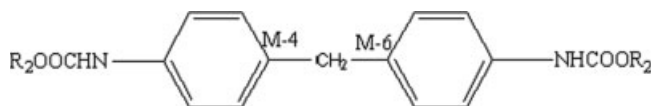


Figure 12 Chemical linkage of PMP.

In Figures 11–13, R_1 is in relation to DMPA, and R_2 to p756.

Except the peak “a,” there are four other peaks in Figure 10. By referring to Figure 9 (p756/MDI/p756) and Table IV, it is known that the peak “c” at δ 135.38 in Figure 10 should belong to M-4 and M-6 of the PMP linkage. For the DMP linkage, the chemical shift of M-4 is not the same as M-6. M-4 was influenced by DMPA, to which COOH group with stronger electron negativity was attached. M-6 was influenced by p756 of weaker electron negativity. The area of the M-4 peak and M-6 peak, however, should be nearly the same. It is easy to discover in Figure 10 that the area of the peak “e” is quite similar to the area of the peak “b.” Therefore, the peak “b” at higher δ value should be attributed to M-6 of the DMP linkage, while peak “e” at lower δ value to M-4 of the DMP linkage. Consequently, the peak “d” must be related to M-4 and M-6 of DMD linkage.

In Figure 10, the area of peak b, c, d, e is 0.1006, 0.0396, 0.0353, and 0.1002, respectively. Based on these data, the average length of hard segments \ln (DM) composed of DMPA and the average length of the soft segments \ln (PM) composed of p756 as well as the mol fraction of DMD, DMP, PMP could be calculated according the literature:¹¹

$$\ln(\text{DM}) = 1.35$$

$$\ln(\text{PM}) = 1.40$$

$$\text{Blockness} = 1/\ln(\text{DM}) + 1/\ln(\text{PM}) = 1.45$$

Polyurethane anionomer synthesized by using one-step process

Figure 14 is the partial enlargement of Figure 8. The area of peaks b, c, d, and e is 0.1027, 0.0498, 0.0831, and 0.0994, respectively. Accordingly,

$$\ln(\text{DM}) = 1.83$$

$$\ln(\text{PM}) = 1.50$$

$$\text{Blockness} = 1.21$$

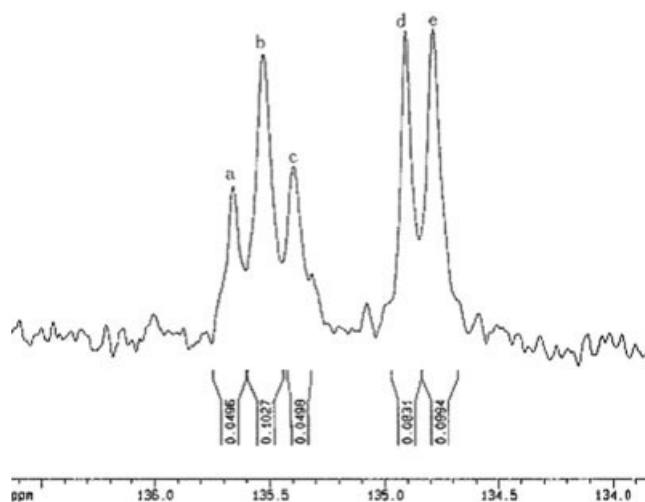


Figure 14 Enlargement of the range M4–M6 in Figure 8.

TABLE V
Sequence Distribution of Polyurethane Anionomers

	\ln (DM)	\ln (PM)	Blockness
Two-step process	1.35	1.40	1.45
One-step process	1.83	1.50	1.21

Relationship between sequence distribution of polyurethane anionomer and properties of the water dispersion of polyurethaneurea anionomer

The data in Table V make clear that the sequence length \ln (DM) or \ln (PM) of polyurethane anionomer synthesized by using two-step process is shorter than that by using one-step process. The blockness value of polyurethane anionomer synthesized by using two-step process is larger than that by using one-step process. These results mean that the distribution of hard segments composed of hydrophilic monomer DMPA is more uniform along the macromolecular chain of the polyurethane anionomer synthesized by using two-step process than that synthesized by using one-step process. It should be not difficult to understand that the distribution of hard segments composed of DMPA along the macromolecular chain of the polyurethaneurea based on the polyurethane prepolymer synthesized by using two-step process (WPUUa2) should also more uniform than that of the polyurethaneurea based on the polyurethane prepolymer synthesized by using one-step process (WPUUa1).

Combining Table VI with Table V, it could be discovered that more uniform distribution of the hydro-

TABLE VI
Properties of Polyurethaneurea Water Dispersions

	One-step process	Two-step process
Particle size (μm)	0.23	0.17
Polydispersity	0.802	0.599
ζ electric potential (mV)	-34.6	-44.1

philic monomer along the macromolecular chain could lead to smaller average size and polydispersity of the polymer particles dispersed in water, as well as higher stability (higher absolute value of ζ electric potential) of the water dispersion. The reason might be related to the fact that the anionomer WPUUa2 with hydrophilic DMPA units distributed more uniformly along macromolecular chain contained less DMD linkages (the calculated mol fraction = 0.128) and more DMP linkages (the calculated mol fraction = 0.728) in comparison with those of WPUUa1 (0.25 and 0.60, respectively). The DMD linkage (hard segment-hard segment) was unfavorable for transfer of the hydrophilic COOH groups, which were embedded originally in the macromolecular coils, onto the surface of the polymer particle, while the COOH group attached on the PMD (soft segment-hard segment) linkage was easier to move onto the particle surface, and stabilize more particles.

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