

# Waterborne Polyurethanes: Spectroscopy and Stability of Emulsions

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**ABSTRACT:** We prepared waterborne polyurethanes based on isophorone diisocyanate, dimethylolpropionic acid, polyhexane neopentyl adipate glycol, or polyethylene-butylene adipate glycol through self-emulsion (a prepolymerization process). Their IR and NMR spectroscopic properties were investigated, and the peaks of these spectra were assigned. The stability of the emulsions was studied on the basis of the shelf life and particle size distribution of emulsions. The effects of solvents, hard-segment content, carboxylic group content, extenders, and feeding methods on the stability of the emulsions were determined to show that

*N*-methylpyrrolidone was a good solvent for retaining the stability of emulsions; particle sizes decreased with increasing COOH content and decreasing hard-segment content, whereas the extenders and feeding methods studied had little effect on the stability of the emulsions. The causes of the stability of the emulsions are discussed according to the analysis of the molecular and particulate structures. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 597–602, 2006

**Key words:** dispersions; ionomers; polyurethanes; stabilization

## INTRODUCTION

Since Schlack<sup>1</sup> first reported the formation of water-based polyurethanes (PUs) in 1942, the study of ionic PUs has been popular. Until 1970, potentially more industrially significant segmented PU ionomers were synthesized by Dieterich et al.<sup>2</sup> Waterborne PUs with equivalent properties to their solvent-borne counterparts are of great importance because of increasing environmental concerns.<sup>3</sup>

Waterborne PUs are PU ionomers consisting of PU backbones with a minority of pendant acid or tertiary nitrogen groups, which are completely or partially neutralized or quaternized, respectively, to form salts, and waterborne PU dispersions can be defined as binary colloidal systems in which PU particles are dispersed in continuous aqueous media.<sup>4</sup> Waterborne PUs represent a well-established area of polymer science, and their versatility and tailor-made properties have resulted in much research aimed at understanding their reactions and properties.<sup>5</sup> The polymer can be tailored for a specific application by variation of the chemical structure of the soft segments, the distribution and length of the hard segments or the molecular weight (MW), and the degree of branching of the chains. The hard segments govern the hardness, strength, and toughness of the polymers. The soft

segments determine the flexibility, low-temperature flexibility, and glass-transition temperature.<sup>6</sup>

Among PU ionomers, anionic PU dispersions have been most frequently used in many applications.<sup>7–11</sup> The preparation and properties of anionic PU dispersions have been fully researched.<sup>12–20</sup> Until now, however, no detailed research on the stability of dispersions has been reported, although this property is very crucial to the manufacture and application of waterborne PUs.

## EXPERIMENTAL

### Materials

Isophorone diisocyanate (IPDI; Degussa Corp., Germany) was used as received. Dimethylolpropionic acid (DMPA; Bayer, Germany) was dried at 105°C, and polyhexane neopentyl adipate glycol (HNA; MW = 2000) and polyethylene-butylene adipate glycol (PE-BA; MW = 2000) were dehydrated at 120°C *in vacuo* before use. *N*-methylpyrrolidone (NMP) was dried over 4-Å sieves before use. All percentages are listed by weight through this article unless otherwise indicated.

### Preparation of prepolymers

HNA was dehydrated in a reaction kettle equipped with a thermometer, stirrer, inlet and outlet of dry nitrogen, and heating jacket at 120°C *in vacuo* for 2 h. The reaction kettle was cooled to 80°C; then, IPDI, 0.1% dibutyl tin dilaurate, and DMPA dissolved in

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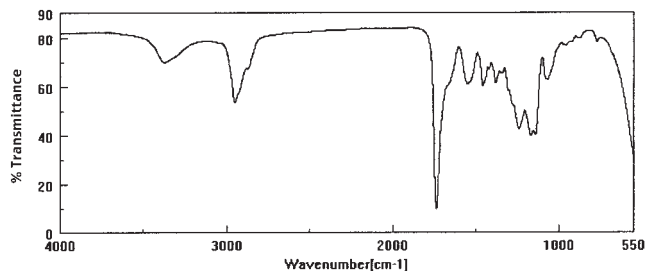


Figure 1 IR of waterborne PU.

NMP were placed simultaneously in the kettle with stirring. The reaction was carried out under the protection of a dry nitrogen atmosphere at a constant temperature of 80°C for about 5 h to obtain the NCO-terminated prepolymer. The NCO group content by weight was measured by titration with dibutylamine.

### Chain extension of prepolymers

When we achieved the theoretical NCO value, the prepolymer was neutralized with triethylamine at the same temperature for 10 min and then cooled to 50°C; an emulsion was obtained on the addition of deionized water to the reaction mixture under stirring rapidly for 5 min. Ethane diamine dissolved in water was added dropwise over 5 min. This reaction kettle was kept at 50°C for another 2 h to finish the chain extension. The milk white product was a PU anionomer dispersion with a solid content of about 35%.

### Photon correlation spectroscopy

Particle sizes were determined for the dispersions by light scattering with a ZetaSizer 1000 model (Malvern, Instruments, UK).

### IR and NMR spectroscopy

IR and NMR analysis were carried out with a FT/IR-430 (Jasco, Tokyo, Japan) spectrophotometer and a

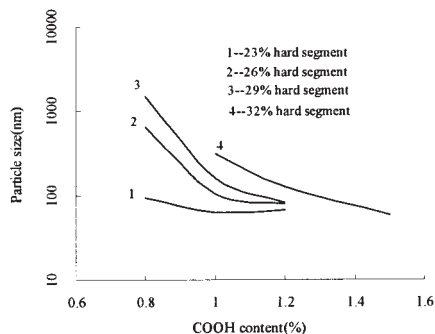


Figure 2 Effect of COOH% on particle size with PE-BA as the soft segment.

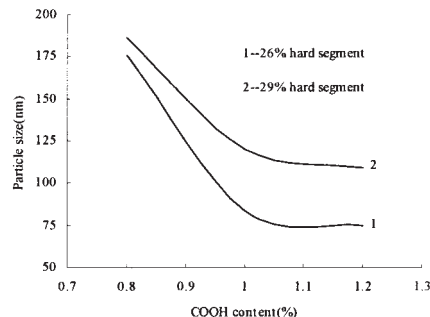


Figure 3 Effect of COOH% on particle size with HNA as the soft segment.

Varian 400 spectrometer, respectively. Samples submitted to NMR measurement were dissolved in deuterated dimethyl sulfoxide solutions.

## RESULTS AND DISCUSSION

### Spectral analysis of waterborne PU

A typical IR spectrum of waterborne PU prepared from HNA and IPDI is shown in Figure 1. The characteristic peaks at about 2270  $\text{cm}^{-1}$  (NC=O stretching vibration) and 3530  $\text{cm}^{-1}$  (O—H stretching vibration) from IPDI and HNA, respectively, disappeared, and the characteristic peaks of PU centered at 3370  $\text{cm}^{-1}$  (N—H stretching vibration) and 1530  $\text{cm}^{-1}$  (N—H deformation vibration) emerged in this spectrum. The peak centered at 3370  $\text{cm}^{-1}$  was assigned to a combination of the partially hydrogen-bonded and free NH groups, as we believed that the hard segments of PUs were partially crystalline at ambient conditions. Generally, vibrational absorption curves are expected to be symmetric, however, both hydrogen-bonded NH and carbonyl absorption peaks showed some skewness, with the right half of the area broader than the left half. It has been suggested that the NH stretching peak is composed of four overlapping symmetric peaks at 3440, 3320, 3270, and 3180  $\text{cm}^{-1}$  attributed to the free NH, hydrogen-bonded NH, and trans and cis

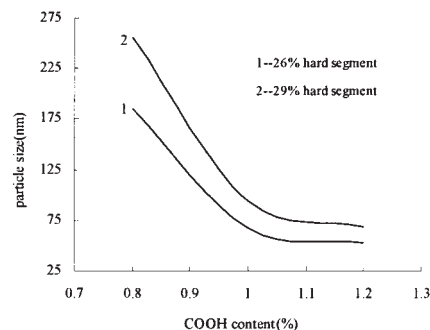
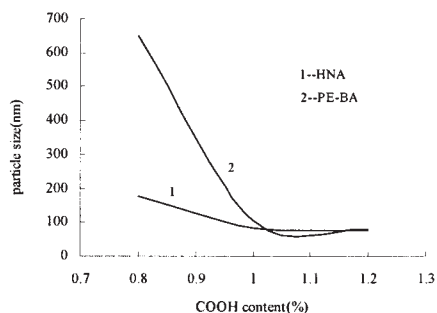


Figure 4 Effect of COOH% on particle size with a mixture of PE-BA and HNA as the soft segment.



**Figure 5** Comparison of particle size with either PE-BA or HNA as the soft segment.

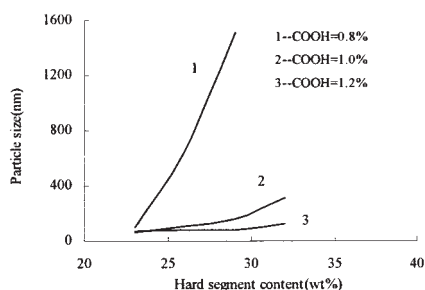
NH conformations, respectively.<sup>21</sup> Likewise, the free and bonded properties of NH and the existence of the C=O urea groups (from extension of diamine) could explain the skewness of the PU carbonyl absorption peak, which was present at the same frequency as the HNA centered at  $1730\text{ cm}^{-1}$ .

Although the NMR of waterborne PUs is rarely studied, a considerable amount of information can be obtained from the  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of waterborne PUs. If NMR spectra are measured under high-resolution conditions, small chemical-shift differences can be observed that differentiate between similar PU structures. We thoroughly investigated the NMR spectra in a previous study.<sup>22</sup>

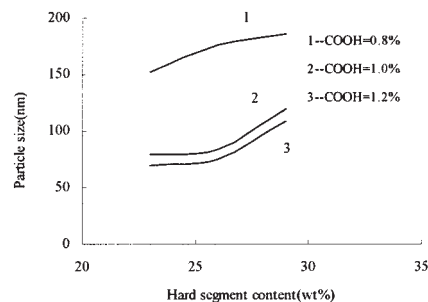
### Effect of COOH content

A stable emulsion is the premise of practical application; many factors, for example, solvents and the content of COOH and hard segments, may have effects on the stability of emulsions. In addition to the shelf life of emulsions, the size distribution of particles is also a key parameter for evaluating the stability of an emulsion. In general, the smaller the particles in an emulsion are, the more stable the emulsion is.

Hydrophilic groups are very crucial to the stability of PU emulsions, and carboxylic groups are often present in PU ionomers. The COOH content is defined as follows:<sup>8</sup>



**Figure 6** Effect of hard-segment content on particle size with PE-BA as the soft segment.

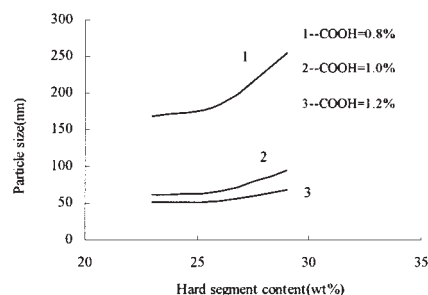


**Figure 7** Effect of hard-segment content on particle size with HNA as the soft segment.

$$\text{COOH content (wt\%)} = \frac{\text{Weight of COOH in PU}}{\text{Total Weight of PU}} \times 100$$

It has been proven that the average weight percentage of hydrophilic ionic sites, rather than the average number of DMPAs per prepolymer, is the critical factor in good dispersion.<sup>13</sup> The effect of COOH content on the stability of the PU emulsions was investigated on the basis of waterborne PUs with PE-BA, HNA, and a mixture of PE-BA and HNA as the soft segment, as shown in Figures 2–4, respectively.

According to Figures 2–4, the particle size of the emulsions decreased with increasing carboxylic group content. When the content of hard segments was lower than 29%, the particle size reached a minimum value when the content of carboxylic groups was over 1.2%. With increasing COOH content, the number of carboxylic groups in each PU molecule increased, which resulted in the improvement of the hydrophilicity of the PU structures. COOH groups arrange outside particles due to their hydrophilic nature, which causes interaction between the COOH groups and water. Compared with bigger particles, smaller particles have larger relative surface areas, so if smaller particles in the PU emulsions were formed, more COOH groups were needed. As the content of COOH groups decreased, bigger particles were



**Figure 8** Effect of hard-segment content on particle size with a mixture of PE-BA and HNA as the soft segment.

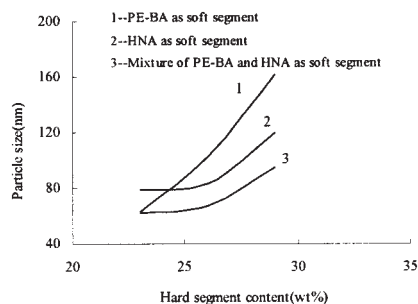


Figure 9 Effect of soft segments on particle size.

formed to lower the surface energy of the emulsion system. This increase was the consequence of the decreasing number of carboxylate anions present, which resulted in the decrease to stabilize the total particle surface area.<sup>5</sup> If the content of carboxylic group reached a critical value, a PU emulsion was not given. On the contrary, a water-soluble PU ionomer, not an emulsion, was obtained if the carboxylic groups were as high as 1.5%.

A comparison of particle size with PE-BA as the soft segment and with HNA as the soft segment is shown in Figure 5. At a lower concentration range of COOH, the particles from HNA were much smaller than the ones from PE-BA. When the content of carboxylic groups was over 1%, they had nearly the same particle size. This indicated that the structures of polyester diols had an effect on the stability of the PU emulsions, whereas when the content of carboxylic groups was higher than 1%, the effect was negligible.

#### Effect of hard-segment content

Hard-segment content could greatly influence the stability of PU emulsions.<sup>23,24</sup> As the content of hard segments increased, the particle size of the PU emulsions increased, as shown in Figures 6–9.

Polymer molecules of PU ionomers gather to form particles of emulsions through hydrophobic interaction. The more hydrophobic the polymer molecules are, the stronger the interaction between the polymer molecules is. An increase of hard segments causes an increase in carbamic groups and an increase in the

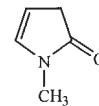


Figure 10 NMP structure.

hydrophilicity. With increasing hard segments, the number of water molecules entering into the interior of particles of the emulsions rise, so the particles are bigger compared those with a with lower content of hard segments. The function of hard segments is different from that of carboxylic groups in contributing to the particle size because carboxylic groups, which increase to cause a decrease in particle size, distribute on the surface of particles, whereas carbamic group distribute on the inside.

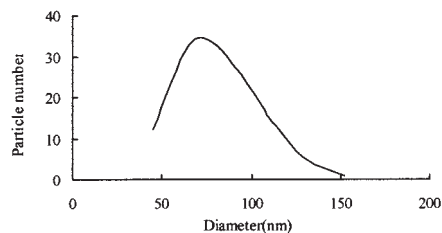
#### Effect of solvents

In some cases, a small amount solvent (ca. 10–30% accounts for the weight of the prepolymer) is necessary to lower the viscosity of prepolymer; also, the existing solvent can make the dispersion process easier and the emulsion more stable.<sup>25,26</sup> Several solvents, *N,N*-dimethyl formamide, acetone, methyl ethyl ketone, and NMP, were used to investigate the stability of the emulsions prepared. The emulsion prepared from NMP was more stable than those prepared from the other three solvents, as it is generally believed. When the content of COOH was kept at a constant value of 1.5%, the stability of different contents (26 and 29%) of hard segments were evaluated according to the solvents used. The emulsion from NMP could be kept for over 6 months without apparent appearance change; all emulsions from other solvents coagulated during the period, some even on the 2nd day after the preparation of the emulsions.

It is thought that the stabilization ability of NMP for emulsions comes from its structure, as shown in Figure 10. The other three solvents are very easily soluble in water (acetone: miscible; dimethylformamide: miscible; methyl ethyl ketone: 25.6 g/100 mL at 20°C), so they tended to remain in water when the emulsions were formed. However, NMP is not so soluble in

TABLE I  
Dependence of Emulsion Stability on Chain Extenders

Segment content (%)	COOH (%)	Extender	Appearance of emulsions	Shelf life
26	0.8	Ethylenediamine	Milk white	Over 6 months
		Diethylene triamine	Milk white	Over 6 months
26	1.0	Ethylenediamine	Milk white with blue	Over 6 months
		Diethylene triamine	Milk white with blue	Over 6 months
29	1.0	Ethylenediamine	Milk white with blue	Over 6 months
		Diethylene triamine	Milk white with blue	Over 6 months



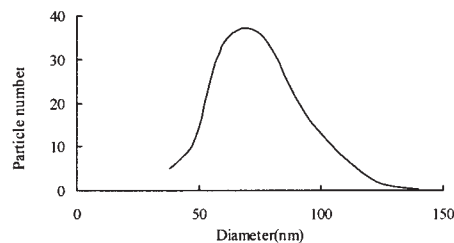
**Figure 11** Particle distribution with ethylenediamine as the chain extender.

water (10 g/100 mL at 20°C), the molecules are more likely to stay at the interface of the particles as surfactants do. This arrangement improves the stability of the emulsions, as shown in this study. On the other hand, NMP has a high boiling point; this is beneficial to the formation of films from emulsions on drying. This is the reason NMP can stabilize PU emulsions and is widely studied and used.

#### Effect of extenders

Extenders are needed to ensure that polymers grow large enough with appropriate properties. In the process of waterborne PU manufacturing, more active extenders than water and alcohols, including amines, are often used because prepolymers are already dispersed in water before extension in the prepolymer process.<sup>27,28</sup> Ethylenediamine and diethylene triamine were used as extenders to investigate the effects of extenders on the stability of emulsions. The appearance and shelf life properties are shown in Table I, and typical particle size distributions are illustrated in Figures 11 and 12, respectively.

It is commonly believed that a network of polymer structure that causes the instability of emulsions is formed on the basis of the extension of diethylene triamine with three functional amino groups. According to Table I and Figures 11 and 12, the emulsions from ethylenediamine and diethylene triamine, respectively, had almost the same stability and particle size. It is known<sup>4,29</sup> that the particles in emulsions are



**Figure 12** Particle distribution with diethylene triamine as the chain extender.

formed before the extension; the extension reaction occurs inside these particles formed beforehand with many carboxylic groups arranged outside. This ensures the polymer molecules do not grow too large, as each particle acts as a separated reactor in which the extension process is accomplished. The network structure from the extension of triamine can be accommodated in these particles like the linear ones from the diamine.

#### Effect of feeding method

According to ref. 30, stability is related to feeding methods of polydiols and DMPA. The stability of the emulsions was investigated on the basis of feeding methods: HNA and DMPA simultaneously (method A, as described according to the Experimental section), HNA first (reaction time = 3 h) and then DMPA (reaction time = 2 h; method B), and DMPA first (reaction time = 2 h) and then HNA (reaction time = 3 h; method C), respectively. The stability of the emulsions in which ethylenediamine was used as extender from the three methods is compared in Table II.

It is generally believed that emulsions from a one-shot method (A) are not as stable as those from a two-shot method (B and C) because carboxylic groups are not evenly distributed in the backbone of the polymers attributed to the reaction active difference between HNA and DMPA, in which it is believed that DMPA is more active than HNA.<sup>13</sup> Our previous study<sup>31</sup> showed that HNA was more active than

**TABLE II**  
Effect of Feeding Method on Emulsion Stability

Hard segment content (%)	COOH (%)	Feed method	Appearance of emulsions	Shelf life
29	1.0	A	Milk white with blue	Over 6 months
29	1.0	B	Milk white with blue	Over 6 months
29	1.0	C	Milk white with blue	Over 6 months
26	0.8	A	Milk white	Over 6 months
26	0.8	B	Milk white	Over 6 months
26	0.8	C	Milk white	Over 6 months
26	1.0	A	Milk white with blue	Over 6 months
26	1.0	B	Milk white with blue	Over 6 months
26	1.0	C	Milk white with blue	Over 6 months

**TABLE III**  
Average Particle Sizes With Different Feeding Methods

	Feeding method		
	A	B	C
Average particle size of emulsions (nm)	76.2	57.1	69.9

DMPA, whereas no direct evidence proved that the even distribution of carboxylic groups was more favorable than uneven distribution for the stability of emulsions. According to the results, the emulsions from the three methods had almost the same appearance, shelf life, and average particle size, which indicates that feeding methods had little effect on the stability of the emulsions (Table III). This also supports the observation that regular distribution of ionic sites in PUs is not a critical factor for good dispersion.

### CONCLUSIONS

Waterborne PUs are a developmental trend in the PU industry because of the more and more stringent regulations concerning the protection of environment. Many emulsions were prepared through prepolymerization processes in this article. IR spectra showed the appearance of characteristic absorption peaks centered at  $3370\text{ cm}^{-1}$  (N—H stretching vibration) and  $1530\text{ cm}^{-1}$  (N—H deformation vibration) from waterborne PUs. The free NH, hydrogen-bonded NH, and trans and cis NH conformations explained the skewness of the peaks. According to the shelf life and particle size distribution, the stability of the emulsions was explained. The particle size of the emulsions decreased with increasing carboxylic group content, and a water-soluble PU ionomer, not an emulsion, was obtained if the carboxylic group content was as high as 1.5%. The structures of polyester diols had effects on the stability of the PU emulsions, whereas when the content of carboxylic groups was higher than 1%, the effect was negligible. Particle sizes decreased with decreasing hard-segment content; the function of hard segments was different from that of the carboxylic group in contributing to the particle size decrease, as carboxylic groups were distributed on the surface of particles, whereas carbamic groups were distributed inside. NMP was a good solvent for retaining the stability of the emulsions, as the molecules of NMP were more likely to stay at the interface of particles as surfactants do. The extenders studied made no difference on the stability of emulsions because the extension reaction occurred inside these particles before-

hand. Feeding sequences had little effect on the stability of the emulsions, as the regular distribution of ionic sites in the PUs was not a critical factor for good dispersion. This investigation was helpful for the manufacture of stable emulsions and for the further discussion of the stability of PU emulsions.

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