

Synthesis and Characterization of Isocyanic Acid, *m*-Phenylenediiso-propylidene Based Poly(urethane-urea) Dispersions Containing Different Amount of 2,2-Bis(hydroxyl methyl)propionic Acid

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ABSTRACT: Isocyanic acid, *m*-phenylenediiso-propylidene (*m*-TMXDI)-based anionic poly(urethane-urea) dispersions were prepared by the prepolymer mixing process. The equivalent ratio of NCO/OH was kept constant at 1.8, while 2,2-bis(hydroxyl methyl) propionic acid (DMPA) used was varied from 3 to 10 wt %. The colloidal stability of poly(urethane-urea) dispersions arose entirely from the presence of ionized carboxylic acid groups. The chemical structure of poly(urethane-urea) dispersions with various amount of DMPA were identified by FTIR and ¹³C NMR analysis. The test results showed that the hydrophilicity of poly(urethane-urea) dispersions were increased with increase in DMPA content. The degree of chain extension was much lower than

the values predicted theoretically due to the side reaction of a small amount of hydrophilic isocyanate-terminated prepolymer with water. The average particle size of poly(urethane-urea) dispersions were decreased with an increase in DMPA content, and this lead to an increase in viscosity. Also, the thermal degradation behavior were measured and was shown that the initial degradation temperature shifted to lower temperature with an increase in DMPA content. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5737–5746, 2006

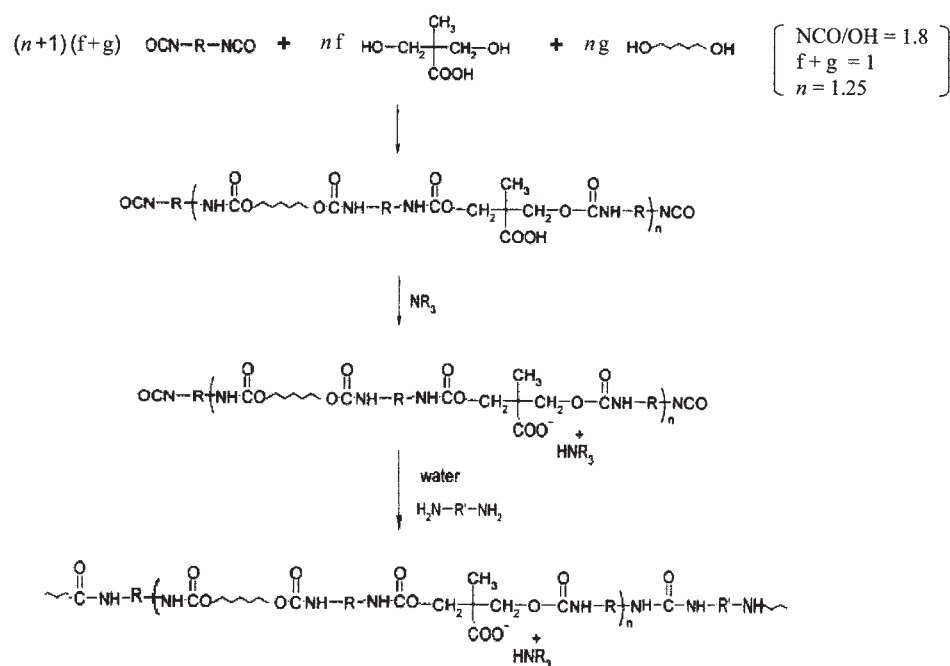
Key words: isocyanic acid; *m*-phenylenediiso-propylidene; poly(urethane-urea) dispersion; hard segment; soft segment; hydrophilicity; thermal degradation

INTRODUCTION

Waterborne polyurethane dispersions contained low volatile organic compound and nonflammable have been developed and widely used in coatings and adhesives.¹ An aqueous polyurethane dispersion is a binary colloidal system, where polyurethane particles are dispersed in a continuous aqueous medium. To be dispersible in water, polyurethane should contain ionic and/or non-ionic hydrophilic segments in its structure.² Lorenz et al.³ proved that the ionic centers in polyurethane dispersions are located predominantly on the surface of the dispersed particles, while the hydrophobic chain segments form the interior of the particles. There are a number of approaches for the preparation of polyurethane dispersions^{4,5} including the acetone process, the melt-dispersion process, the ketimine process, and the prepolymer mixing process. Recently, a lot of polyurethane dispersions have been prepared by different diisocyanates, e.g., isophorone diisocyanate (IPDI),^{6–9} hexamethylene diisocyanate (HDI),¹⁰ hydrogenated methylene bispheny-

lene diisocyanate (H₁₂MDI),¹¹ and isocyanic acid, *m*-phenylenediiso-propylidene (*m*-TMXDI).^{12–15} In fact, high performance polyurethane dispersions prepared based on *m*-TMXDI provided significantly lower viscosity than corresponding polymers from IPDI or H₁₂MDI. Mequanint¹⁶ and Satguru et al.¹⁷ reported that a minimum amount of ionic group content is required for the formation of stable polyurethane dispersions. Chen and Chen¹⁸ found that a minimum value of 0.178 mmol COOH per gram of PU with full neutralization is required to form a stable dispersion for at least 1 month. The actual amount of ionic group content depends on the type of ionic species employed. 2,2-Bis(hydroxyl methyl)propionic acid (DMPA) is commonly used to provide anionic groups and neutralized to form internal salts in polyurethane dispersions,¹⁹ because the steric hindrance of carboxylic group prevents its reaction with isocyanate groups and so reduces the possibility of undesirable branching. In addition, both hydrophilic acid group contents and their degree of neutralization can affect particle size.^{20–22} The effect of anionic content on the surface tension of polyurethane dispersion has been studied.^{23,24} The surface tension of polyurethane dispersion decreased as the ionic content increased. Increasing the carboxyl content in polyurethane dispersions may lead to the generation of strong electro-

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Scheme 1 Prepolymer mixing process.

static repulsion. As a result, the polyurethane dispersion molecular chain may assume a more extended conformation, which causes the hydrophobic segment to loosely arrange at the air-water interface; therefore, the surface tension reduces. Polyether polyols and polyester polyols containing active hydroxyl groups are commonly used as the soft segment, and polyether polyols are generally preferred due to their better hydrolytic stability and greater flexibility. The mechanism of thermal degradation of polyurethanes is very complex due to the variety of products formed. It is well known that polyether moieties have a higher thermal stability than urethane and urea groups.²⁵ It is said that the early stage degradation occurred mainly in the hard segment for the polyether-type polyurethanes.

This article describes the preparation of isocyanic acid, *m*-phenylenediiso-propylidene (*m*-TMXDI)-based poly(urethane-urea) dispersions containing various amount of DMPA. FTIR and ¹³C NMR analysis are used to identify the molecular structure of poly(urethane-urea) dispersions. The effect of DMPA content on the hydrophilicity, particle size, and thermal stability is described.

EXPERIMENTAL

Materials

Isocyanic acid, *m*-phenylenediiso-propylidene (*m*-TMXDI, extra pure grade) was obtained from Tokyo Kasei Kogyo Co., Japan. 2,2-Bis(hydroxyl methyl) propionic acid (DMPA) was obtained from Lancaster Synthesis Co., USA. Poly(tetramethylene) ether glycol (PTMEG, $M_n = 2000$) was obtained from Scientific Polymer Products Inc., USA. Triethylamine (TEA), 1,2-ethylene diamine (EDA), and N-methyl 1-2-pyrrolidone (NMP) were obtained from Tedia Co., USA. Distilled water was used.

Preparation of anionic poly(urethane-urea) dispersions

Anionic poly(urethane-urea) dispersions were prepared by the prepolymer mixing process presented in Scheme 1.

TABLE I
Compositions of NCO-Terminated Prepolymer

Sample no.	NCO/OH	<i>m</i> -TMXDI (wt %)	PTMEG-2000 (wt %)	DMPA (wt %)	NMP (wt %)	NCO% of prepolymer predicted ^a
PUD-3	1.8	25.53	71.47	3	10	3.91
PUD-6	1.8	33.05	60.95	6	10	5.06
PUD-8	1.8	38.07	53.93	8	10	5.82
PUD-10	1.8	43.08	46.92	10	10	6.59

^a NCO% = $\frac{(\text{equiv. of TMXDI} - \text{equiv. of DMPA} - \text{equiv. of PTMEG2000})}{\text{weight of sample}} \times 42.02 \times 100$.

TABLE II
Compositions of Water Dispersion and Chain Extension

Sample no.	NCO% of prepolymer as determined by titration ^a	TEA (wt %)	Pure water (wt %)	EDA (wt %)	Hard/soft segment ratio
PUD-3	3.8	2.26	42.44	2.78	32/68
PUD-6	4.8	4.52	40.94	3.43	44/56
PUD-8	5.5	6.03	39.91	3.93	52/48
PUD-10	6.3	7.53	38.88	4.51	58/42

^a The NCO content of isocyanate terminated prepolymer was determined by the standard dibutyl amine back-titration method (ASTM D 2572).

$$\% \text{ NCO} = \left[\frac{42.02 \times (\text{equivalents of } (\text{C}_4\text{H}_9)_2 \text{ NH consumed})}{\text{weight of sample}} \right] \times 100.$$

Preparation of isocyanate-terminated urethane prepolymer

Isocyanate-terminated urethane prepolymer was synthesized in a 500-mL round-bottom, four-necked separable flask with a mechanical stirrer, thermometer, a reflux condenser, and temperature controller. The equivalent ratio of NCO/OH was kept at 1.8, while DMPA used was varied from 3 to 10 wt %. The compositions of the reaction mixtures are given in Table I.

Reactions were carried out under a nitrogen atmosphere at a temperature of 90°C in the presence of solvent, *N*-methyl-2-pyrrolidone (NMP). About 1 h of the reaction time is required to reach the expected NCO percentage. The NCO content of isocyanate-terminated prepolymer can be calculated and determined by the standard dibutyl amine back titration method (ASTM D 2572).

Water dispersion and chain extension

Once the NCO content of isocyanate-terminated prepolymer had reached the expected value, triethylamine (TEA) was added into prepolymer at 60°C for 30 min. The stoichiometric amount of TEA added was calculated to ensure the complete neutralization of the carboxylic group of prepolymer.

An aqueous prepolymer dispersion was obtained by adding the neutralized prepolymer into a flask containing distilled water at temperature lower than 20°C and mixed for 20 min. To accomplish rapid dispersion in water, the process requires powerful dispersion equipment with high shear impeller. To extend the molecular weight of aqueous prepolymer dispersion, chain extension was carried out by adding stoichiometric amount of 1,2-ethylene diamine (EDA) slowly for 30 min. The compositions of dispersion and chain extension are given in Table II.

Film formation

Films were prepared by casting the aqueous dispersions on silicone-coated surface and they were then allowed to dry at room temperature for 2 days. After drying for 2 days, the residual water and NMP solvent were removed by placing the films into a vacuum oven at 120°C for 30 min.

Characterization

To ascertain the molecular structure of urethane (NHCOO), urea (NHCONH) and hydrophilic carboxylate group (COO⁻) bonded in the hard segments and ether group (C—O—C) in the soft segments. Fourier-transform infrared (FTIR) and ¹³C nuclear magnetic

TABLE III
Average Molecular Weight of NCO-Terminated Prepolymer

Sample no.	DMPA (wt %)	Repeat unit ($n = 1.25$) ^a	$\bar{M}_n(\text{prepolymer})$ (g mol ⁻¹)
PUD-3	3	$[(\text{X}-\text{Y}_1)_{0.38}-(\text{X}-\text{Y}_2)_{0.62}]_{1.25}$	2163
PUD-6	6	$[(\text{X}-\text{Y}_1)_{0.60}-(\text{X}-\text{Y}_2)_{0.40}]_{1.25}$	1650
PUD-8	8	$[(\text{X}-\text{Y}_1)_{0.69}-(\text{X}-\text{Y}_2)_{0.31}]_{1.25}$	1440
PUD-10	10	$[(\text{X}-\text{Y}_1)_{0.76}-(\text{X}-\text{Y}_2)_{0.24}]_{1.25}$	1276

^a $[(\text{X}-\text{Y}_1)_f-(\text{X}-\text{Y}_2)_g]_n-\text{X}$, where X = TMXDI, Y₁ = DMPA, Y₂ = PTMEG2000, equiv. of DMPA, equiv. of PTMEG2000
 $f = \frac{\text{equiv. of DMPA}}{\text{equiv. of DMPA} + \text{equiv. of PTMEG2000}}$ $g = \frac{\text{equiv. of PTMEG2000}}{\text{equiv. of DMPA} + \text{equiv. of PTMEG2000}}$
 and n = degree of polymerization of prepolymer.

TABLE IV
Molecular Weight of Chain-Extended Poly(urethane-urea) Dispersions

Sample no.	\overline{M}_n^a (10^3) (g mol ⁻¹)	\overline{M}_w^b (10^3) (g mol ⁻¹)	PDI ^c	m^d
PUD-3	6.4	9.7	1.52	2.9
PUD-6	8.4	14.8	1.68	4.9
PUD-8	7.6	13.1	1.73	5.1
PUD-10	8.1	12.7	1.57	6.1

^a \overline{M}_n : number-average molecular weight.

^b \overline{M}_w : weight-average molecular weight.

^c PDI: polydispersity index, $\overline{M}_w/\overline{M}_n$.

^d Degree of chain extension (m) $\cong \frac{\overline{M}_n \text{ of chain extended poly(urethane-urea)}}{\overline{M}_n \text{ of prepolymer} + M_w \text{ of EDA}}$.

resonance (NMR) spectrum were recorded by Nicolet-NEXUS 870 FTIR and Bruker-AVANCE DRX 400 MHz NMR, respectively.

The average particle size of poly(urethane-urea) dispersions were measured by Horiba LB-500 Dynamic Light Scattering Particle Size Analyzer.

The average molecular weights of poly(urethane-urea) dispersions and its distribution were measured by Waters-717 gel permeation chromatography (GPC).

The NCO content of isocyanate-terminated prepolymer was determined by the standard dibutyl amine back-titration method (ASTM D 2572).

% NCO

$$= \left[\frac{42.02 \times (\text{equivalents of } (C_4H_9)_2 \text{ NH consumed})}{\text{weight of sample}} \right] \times 100$$

The viscosity of poly(urethane-urea) dispersions were measured by a Brookfield-DV-I+ viscometer at 25°C.

The nonvolatile content of poly(urethane-urea) dispersions were measured by A&D-MX50 moisture analyzer.

pH values of polyurethane dispersions were measured by Janco-6171 pH meter at 25°C.

The surface tension of poly(urethane-urea) dispersions were measured by Kyowa CBVP-A3 surface tensionometer (Wilhelmy plate method).

The thermal degradation of polyurethane dispersions were carried out using TA Instruments Q-500 TGA (thermal gravimetric analyzer) from room temperature to 600°C at heating rates 10°C/min under nitrogen at a flow rate of 50 mL/min.

RESULTS AND DISCUSSION

Synthesis of anionic poly(urethane-urea) dispersions

A series of *m*-TMXDI-based anionic poly(urethane-urea) dispersions were prepared by the prepolymer mixing process. The equivalent ratio of NCO/OH was kept constant at 1.8, while DMPA used was varied from 3 to 10 wt %.

Isocyanic acid, *m*-phenylenediisopropylidene (*m*-TMXDI) contains two tertiary aliphatic diisocyanate groups. This functionality provides unique properties as compared to primary and secondary aliphatic isocyanates. The steric hindrance created by the dimethyl groups inhibits the self-condensation reactions leading to allophanate, biuret, and isocyanurate formation, this reduced side reactions in prepolymers based on *m*-TMXDI. Moreover, the reactivity of the tertiary isocyanate is lower than other primary or secondary aliphatic isocyanate, which allows prepolymers to be prepared at higher temperature while maintaining excellent stability.¹²

TABLE V
Ionic Content of Anionic Poly(urethane-urea) Dispersions

Sample no.	f	n	m	Ionic content ^a (10^{-2}) (mequiv. g ⁻¹)
PUD-3	0.38	1.25	2.9	21.5
PUD-6	0.60	1.25	4.9	43.8
PUD-8	0.69	1.25	5.1	57.9
PUD-10	0.76	1.25	6.1	71.5

^a Ionic content (milli-equiv. g⁻¹) = $\frac{f \times n \times m \times 1000}{\overline{M}_n \text{ of chain extended poly(urethane-urea)}}$.

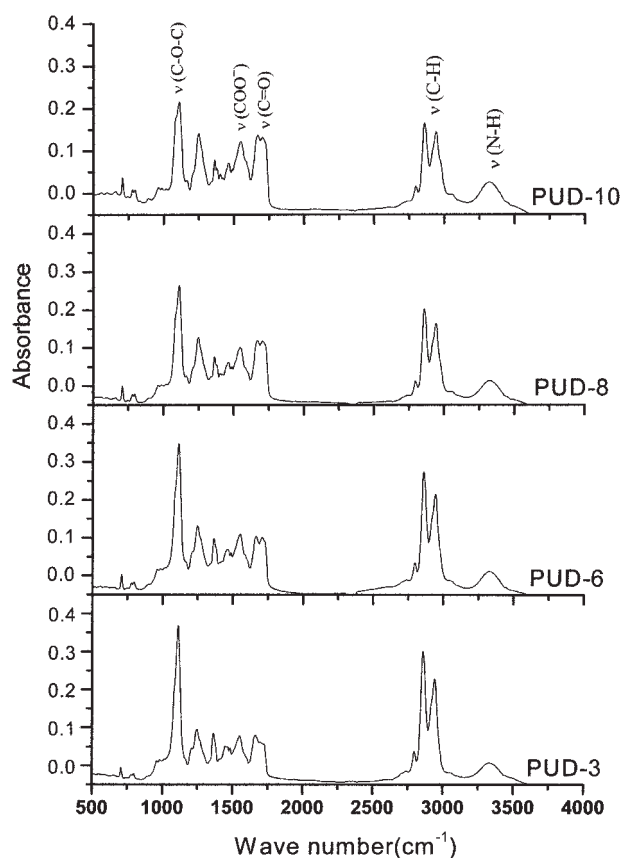
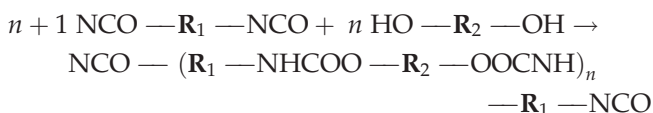


Figure 1 FTIR spectra of the polyurethane dispersions containing different DMPA content.

Excess of diisocyanate is needed to produce an isocyanate-terminated urethane prepolymer presented as follows.



The optimum equivalent ratio of NCO/OH is $(n + 1)/n$ ($n > 1$), where n is the degree of polymerization of prepolymer.

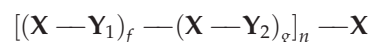
The stoichiometry is chosen to yield an isocyanate-terminated prepolymer of low molecular weight, along with the presence of a small volume of water soluble solvent such as *N*-methyl-2-pyrrolidone (NMP), which ensures that the viscosity is low enough for the successful dispersion of the prepolymer in water. The degree of polymerization of this isocyanate terminated prepolymer is varied with the equivalent ratio of NCO/OH.

In this study, the equivalent ratio of NCO/OH was kept constant at 1.8.

$$\frac{\text{equiv. of NCO}}{\text{equiv. of OH}} = \frac{\text{equiv. of TMXDI}}{\text{equiv. of DMPA} + \text{equiv. of PTMEG2000}} = 1.8$$

$$\frac{n + 1}{n} = 1.8 \quad \text{or} \quad n = 1.25$$

The repeat unit of NCO-terminated urethane prepolymer can be presented as below.



in which X = TMXDI, Y₁ = DMPA, and Y₂ = PTMEG2000

$$f = \frac{\text{equiv. of DMPA}}{\text{equiv. of DMPA} + \text{equiv. of PTMEG2000}} \quad (1)$$

$$g = \frac{\text{equiv. of PTMEG2000}}{\text{equiv. of DMPA} + \text{equiv. of PTMEG2000}} \quad (2)$$

$$f + g = 1$$

$$\text{equiv. of NCO} = (f + g) (n + 1) \quad (3)$$

$$\text{equiv. of OH} = (f + g) (n) \quad (4)$$

The value of f , g , n and \overline{M}_n of NCO-terminated prepolymers with various amount of DMPA are given in Table III. The value of $\overline{M}_n(\text{prepolymer})$ decreased with increasing value of f at a constant equivalent ratio of NCO/OH.

Water dispersibility can be obtained on neutralization of the acid groups to form internal salts. The stoichiometric amount of triethylamine (TEA) was calculated to ensure the complete neutralization of the carboxylic group of DMPA. In the water dispersion step, a turbid solution was obtained, which indicated the beginning of the transformation of an organic solution into an aqueous dispersion, where spontaneous particle formation occurred and the appearance would be varied from milky white to opaque translucent with increasing in DMPA content due to an increase in hydrophilicity. It is also important to consider the side

TABLE VI
Assignment of IR Spectrum of Anionic Poly(urethane-urea) Dispersions

Wave length (cm ⁻¹)	Assignment
3400	ν(N-H) of urethane group
3300	ν(N-H) of urea group
2800-3000	ν(C-H) in CH ₂ (symmetric and asymmetric)
2270	ν(N=C=O) of isocyanate group
1720	ν(C=O) of urethane group
1680	ν(C=O) of urea group
1590	ν(C=O) of carboxylic group
1120	ν(C-O-C) of aliphatic ether

ν: stretching mode.

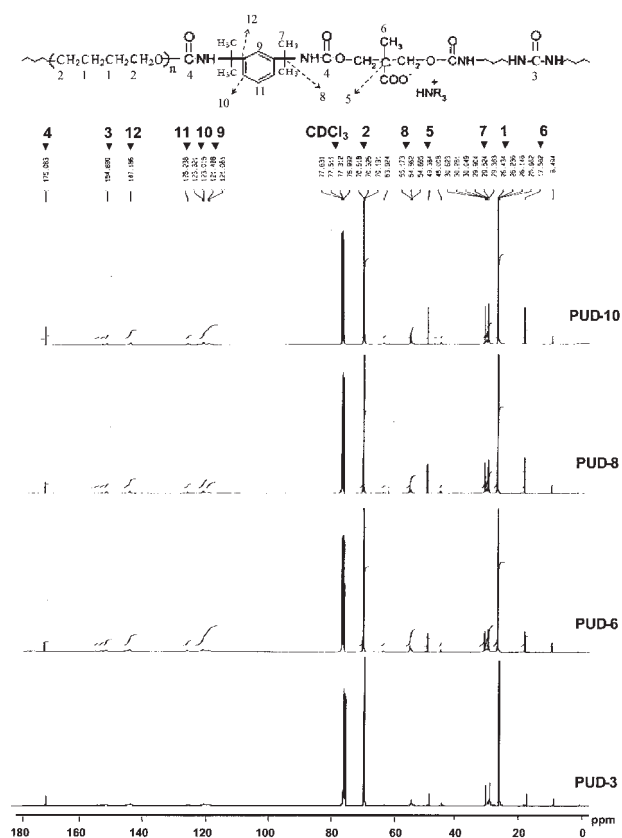
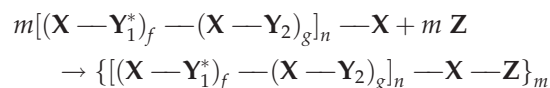


Figure 2 ^{13}C NMR spectrum of polyurethane dispersions containing different DMPA content.

reaction of the NCO end groups with water. This can be minimized at temperatures below 20°C , because the reactivity of terminated NCO group of *m*-TMXDI-

based prepolymer toward water is very slow at low temperature.

In the chain extension step, poly(urethane-urea) dispersion was obtained by adding stoichiometric amount of 1,2-ethylene diamine (EDA) chain extender into NCO-terminated prepolymer dispersion gradually. The reaction of chain extension is as follows.



in which $X = \text{TMXDI}$, $Y_1^* = (\text{DMPA}-\text{R}_3\text{N})$, $Y_2 = \text{PTMEG2000}$ and $Z = \text{EDA}$.

Degree of chain extension (m)

$$\cong \frac{\bar{M}_n \text{ of chain extended poly(urethane-urea)}}{\bar{M}_n \text{ of prepolymer} + \bar{M}_w \text{ of EDA}} \quad (5)$$

The average number molecular weight (\bar{M}_n , \bar{M}_w), polydispersity (PDI), and degree of chain extension (m) of poly(urethane-urea) dispersions are given in Table IV.

Referring to the general Carothers equation, the degree of chain extension (m) can be stated as follows.

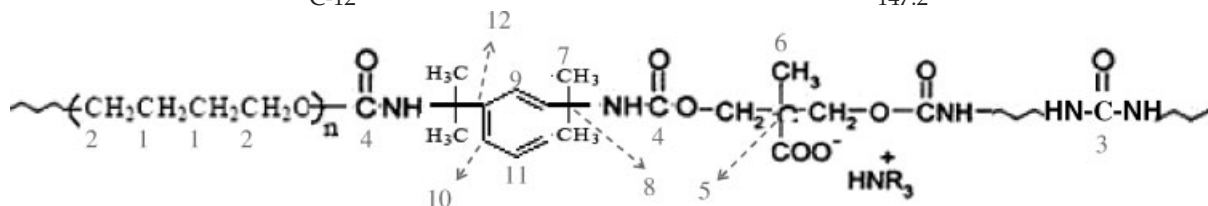
$$m = \frac{1 + r}{1 + r - 2rp} \quad (6)$$

where $r = N_{\text{NCO}}/N_{\text{NH}_2} \leq 1$; $p =$ extent of reaction; N_{NCO} , N_{NH_2} : number of functional groups present initially.

In this study, the equivalent ratio of NCO/NH₂ was kept at 1 (stoichiometric) initially. If the extent of reac-

TABLE VII
Assignment of ^{13}C Chemical Shifts of Anionic Poly(urethane-urea) Dispersions.

Assignment (Carbon no.)	Chemical shift (ppm)
C-1	26.2
C-2	70.5
C-3	154.9
C-4	175.1
C-5	49.4
C-6	17.8
C-7	29.5
C-8	55.2
C-9	121.5
C-10	123.1
C-11	128.3
C-12	147.2



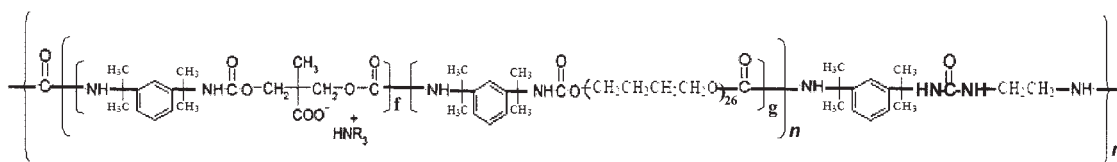
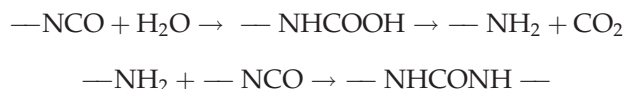


Figure 3 Chemical structure of anionic poly(urethane-urea) dispersions.

tion (*p*) reached 0.90, the degree of chain extension (*m*) would be 19, calculated according to the eq. (6). But we found that the degree of chain extension (*m*) in Table IV were still very much lower than the values predicted theoretically. This meant that a near stoichiometric amount of NCO/NH₂ was not actually present in the reaction system, but instead there was an excess concentration of amine groups. This result was attributed to the side reaction of a small amount of hydrophilic NCO-terminated prepolymer with water.



The side reaction is probably due to the presence of high concentration of water in the aqueous dispersion system.

A minimum amount of ionic content required for the formation of stable polyurethane dispersions have been reported.^{16–18} The ionic content of chain-extended poly(urethane-urea) dispersion can be stated as below.

$$\begin{aligned} & \text{Ionic content (milliequiv./gram of PUD)} \\ & = \frac{f \times n \times m \times 1000}{\bar{M}_n \text{ of chain extended poly(urethane-urea)}} \quad (7) \end{aligned}$$

As shown in Table V, the ionic content of poly(urethane-urea) increased with increase in DMPA content. With increase in the ionic content, the hydrophilicity of poly(urethane-urea) dispersions increased.

Chemical structure of poly(urethane-urea) dispersions

The chemical structure of the anionic poly(urethane-urea) dispersions synthesized was characterized by FTIR and ¹³C NMR.

In the FTIR spectrum, the absorption spectrum is shown in Figure 1. The assignment of the most characteristic IR bands are given in Table VI. Four major spectrum regions are presented.

- 3250–3400 cm⁻¹, N—H stretching, a broad absorption band.
- 1620–1750 cm⁻¹, C=O stretching, the band centered at around 1720 cm⁻¹ is attributed to the stretching of urethane carbonyl groups, whereas the band at around 1650 cm⁻¹ is assigned to the stretching of urea carbonyl groups.
- 1550–1600 cm⁻¹, COO⁻ stretching, characteristic of the pendant group from DMPA unit.
- 1050–1150 cm⁻¹, C—O—C stretching, the ether groups in PTMEG2000.

As expected, the increase in the DMPA content causes an increase in the relative intensity of N—H stretching and C=O stretching corresponding to the urethane and urea linkage. Therefore, the hard segment content of poly(urethane-urea) dispersions is increased with increase in DMPA content.

In the ¹³C NMR spectrum, the spectrum recorded are shown in Figure 2. The observed chemical shifts are given in Table VII, and those assignments correspond with the published values.²⁶ The aliphatic region is dominated by the two soft segment carbon peaks at 26.2 ppm (C-1) and 70.5 ppm (C-2) arising from the PTMEG2000 soft segment. The peaks at 154.9 ppm (C-3) and 175.1 ppm (C-4) are assigned to the carbonyl carbon position relevant to the urea and urethane moieties, respectively. In particular, the peak at 49.4 ppm (C-5) is assigned to the tertiary carbon position of DMPA, and the peak at 17.8 ppm (C-6) is assigned for the methyl carbon position of DMPA molecule. There are six different peaks (C-7 to C-12) that can be assigned to the carbon position of isocyanic acid, *m*-phenylenediisopropylidene (*m*-

TABLE VIII
Colloid Properties of Anionic Poly(urethane-urea) Dispersions

Sample no.	Viscosity at 25°C (cP)	Nonvolatile (wt %)	pH	Particle size (nm)	Surface tension (mN/m)
PUD-3	45	36.8	8.1	1350 ± 300	41.3
PUD-6	68	37.7	8.2	800 ± 200	39.5
PUD-8	112	35.7	8.5	450 ± 100	38.0
PUD-10	175	35.4	8.3	150 ± 50	36.7

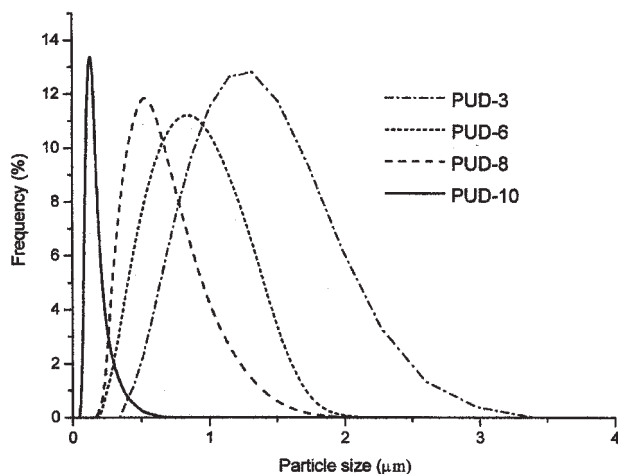


Figure 4 Effect of DMPA content on the particle size and distribution of the dispersions.

TMXDI). As a result, it is shown that the intensity of peaks (C-4, C-5, and C-6) are increased with increasing DMPA content.

Under such results, it was reasonable to expect that the poly(urethane-urea) molecule designed by synthesized successfully.

The chemical structure of anionic poly(urethane-urea) dispersions is presented in Figure 3.

These poly(urethane-urea) dispersions are segmented block copolymers whose structure and properties depend on a number of parameters including the materials used in their synthesis, the relative proportion of the starting materials, and the method used in their synthesis. Basically, it consists of a relatively flexible component, the so-called soft segment, and a relatively polar and stiff component known as the hard segment. In this study, the soft segment is

PTMEG, and the hard segment consists of *m*-TMXDI, DMPA, and EDA chain extender. The properties of poly(urethane-urea) dispersions are significantly influenced by the ratio of hard and soft block components, and the average block lengths employed. Of particular interest to us is the chemical structure, which provides for urethane linkages between hard segments and soft segments and urea linkages between hard segment units.

Effect of DMPA content on colloid properties

There are three possible interchain physical interactions within poly(urethane-urea) dispersions: (a) electrostatic forces between ionic centers, (b) hydrogen bonding between urethane and urea groups, and (c) association of hydrophobic segments. These interchain interactions control the aqueous dispersion properties.

In this work, the viscosity, particle size, and surface tension of poly(urethane-urea) dispersions with various amount of DMPA were measured and shown in Table VIII. It was found that smaller particle sizes and narrower particle size distributions were obtained with higher DMPA content in poly(urethane-urea) dispersions as shown in Figure 4. The asymptotic decrease of particle size with DMPA content is due to the stabilizing mechanism of the ionomer dispersions. With an increase in the ionic content, the number of $-\text{COO}^-\text{HN}^+(\text{C}_2\text{H}_5)_3$ ionic groups in poly(urethane-urea) dispersions increased, each particle in the dispersion is absorbed by a thin layer of water due to the presence of ionic groups on the surface of particle, while the chain segments form the interiors of the particles. At the interface between particle and water, a double layer is formed by the dissociation of ionic

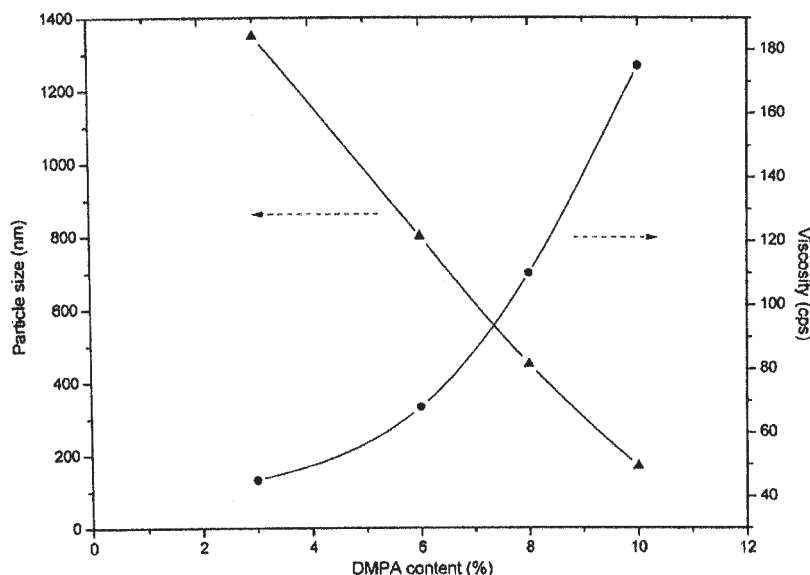


Figure 5 Effect of DMPA content on the average particle size and viscosity of the dispersions.

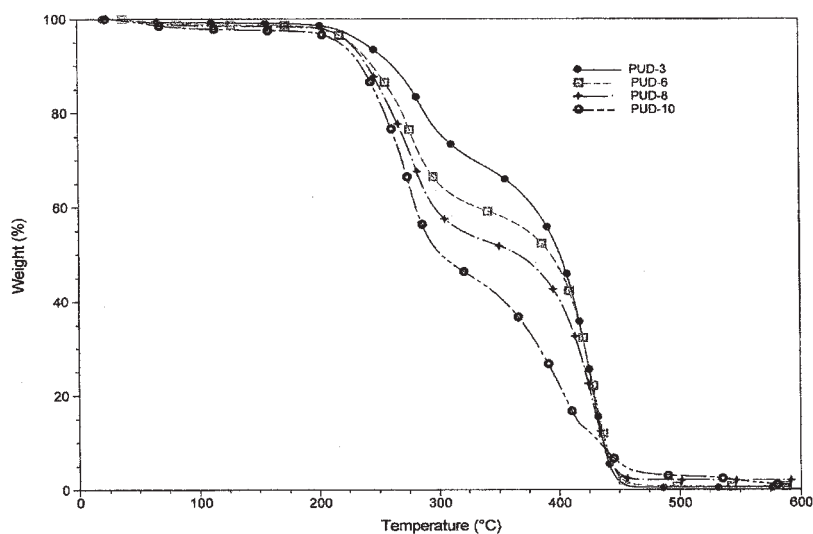


Figure 6 Thermal gravimetric curves of anionic polyurethane dispersions.

groups. The electrical double layer is based on a physical model,²⁷ in which the liquid layer surrounding the particle exists as two parts; an inner region (stern layer) where the ions are strongly bound and an outer region (diffuse layer) where they are less firmly associated. Therefore, the electrical double layer stabilizes these dispersions in the water. With a decrease of particle size, the relative size of water layer increased. Concurrent with the particle size decrease, there is an increase in the number of particles. Hence, the effective volume of the dispersed phase increases, resulting in an increase in viscosity as shown in Figure 5.

The surface tension of poly(urethane-urea) dispersions were measured by surface tensiometer (Wilhelmy plate method). It is shown that the surface tension is slightly decreased as the ionic content increased. Increasing the ionic content in dispersions may lead to the generation of strong electrostatic repulsion. As a result, the polyurethane dispersion molecular chain may assume a more extended conformation, which causes the hydrophobic segment to loosely arrange at the air-water interface; therefore, the surface tension reduces.

The thermal degradation behavior of poly(urethane-urea) dispersions were measured by thermal gravimetric method and shown in Figure 6. It is obvious that two stages of the thermal decomposition were observed, and the initial degradation temperature shifted to lower temperature with an increase in DMPA content. Chang et al.²⁵ reported that the pyrolysis product for PTMEG-based polyurethane in the first stage of thermal decompositions is mainly carbon dioxide, whereas the main gas product in the second stage is butyl ether. It is said that the early stage degradation occurred mainly in the hard segment of polyurethanes. In the present study, the first stage occurred at about 220°C, which resulted from hard

segment through degradation of the urethane and urea groups, and weight loss percentage were increased with increasing DMPA content, because DMPA molecules formed hard segment in polyurethane main chain. The second degradation was related to the soft segments and occurred at about 350°C, it was also shown that the onset temperature of second stage degradation were decreased with an increase in DMPA content.

CONCLUSIONS

Isocyanic acid, *m*-phenylenediiso-propylidene-based anionic poly(urethane-urea) dispersions were successfully synthesized by the prepolymer mixing process. The colloidal stability of poly(urethane-urea) dispersions arose entirely from the presence of ionized carboxylic acid groups. An increase in the hydrophilicity of poly(urethane-urea) dispersions were obtained by increasing the DMPA content. The degree of chain extension was found much lower than the values predicted theoretically due to the side reaction of a small amount of hydrophilic NCO-terminated prepolymer with water. The average particle size of poly(urethane-urea) dispersions were decreased with increase in DMPA content due to an increase in the hydrophilicity, and this lead to an increase in viscosity of poly(urethane-urea) dispersions.

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