

Clear Polyurethane Dispersions of Nanometer Size Derived from Carboxylic Polycaprolactonediol

Da-Kong Lee,¹ Hong-Bing Tsai,¹ Ruey-Shi Tsai²

¹Department of Chemical and Materials Engineering, National Ilan University, I-Lan 26041, Taiwan, Republic of China

²Department of Materials and Chemical Engineering, Ta Hwa Institute of Technology, Chung-Lin, Hsin-Chu, Taiwan, Republic of China

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ABSTRACT: Aqueous polyurethanes dispersions of nanometer size derived from various carboxylic polycaprolactonediol of different molecular weights, carboxylic diols, including 2,2-di(hydroxymethyl)propanoic acid (DMPA), 2,2-di(hydroxymethyl)butanoic acid (DMBA), and di(4-isocyanatocyclohexyl)methane (HMDI) were prepared by a method in which the dispersing procedure was modified to enhance the molecular weight. The molecular weight, particle size, and UV-vis spectra of the polyurethane dispersions were investigated. The tensile properties of the cast films were determined. The modified dispersing procedure gave polyurethane dispersions with higher molecu-

lar weight and better tensile strength. As the molecular weight of the carboxylic polycaprolactonediol decreases, the content of the ionic groups increases, the particle size decreases accordingly. As the molecular weight of the carboxylic polycaprolactonediol used is 1000 g/mol or below, the polyurethanes dispersions become completely clear. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1573–1577, 2008

Key words: polyurethanes; dispersions; ionomers; molecular weight distribution; carboxylic polycaprolactonediol; di(4-isocyanatocyclohexyl)methane; light transmittance

INTRODUCTION

Aqueous polyurethane dispersions have been considered to be one of the ideal low VOC (volatile organic concentration) polyurethane coating systems, and they can be found in various fields of application such as coatings, modifiers for coatings, polishes, synthetic leathers, adhesives, paper sizings, textile sizings, etc. because of the trend of the environmental regulations to decrease the level of solvent emissions.^{1–4} The incorporation of ionic groups into polyurethanes is a practical method to obtain aqueous polyurethane dispersions,^{1,2} and various polyurethane cationomers^{5–8} and polyurethane anionomers^{9–17} have been described in the literature. The properties of the polyurethane dispersions are related to their chemical structure.^{17–22}

The particle size is an important factor governing the properties of aqueous polyurethane dispersions, such as dispersion stability, film-forming properties, and optical properties.^{11,23–25} The average particle diameter of the aqueous polyurethane dispersions mentioned in the literature or the commercial ones is often greater than 100 nm. If the average particle di-

ameter of the aqueous polyurethane dispersions can be controlled to be smaller than 100 nm, namely nanometer-size dispersions, interesting properties such as higher transparency and better dispersion stability may be observed. This can be achieved by the increase of the ionic density. Polycaprolactonediol with a pendant carboxylic group are structurally interesting as a further source of ionic groups,²⁶ and are used here to replace the conventional polyols for the preparation of aqueous polyurethane dispersions with ultrafine particle size.

In this article, the preparation of ultra fine aqueous polyurethane dispersions derived from carboxylic polycaprolactonediol and the effect of composition on their properties are described.

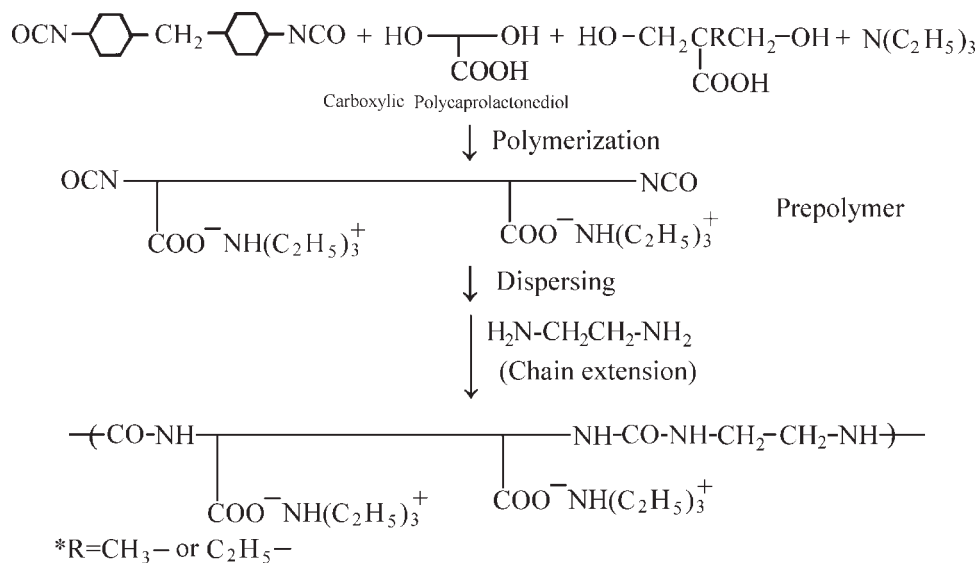
EXPERIMENTAL

Materials

Di(4-isocyanatocyclohexyl)methane (HMDI), Desmodur[®] W, and isophorone diisocyanate (IPDI), Desmodur[®] I, were obtained from Bayer (Leverkusen, Germany) and used as received. 2,2-Di(hydroxymethyl)propanoic acid (dimethylolpropionic acid; DMPA) was Aldrich (Munich, Germany) reagent grade. 2,2-Di(hydroxymethyl)butanoic acid (dimethylol butyric acid; DMBA) was obtained from Nippon Kasei (Fukushima, Japan). Three polycaprolactonediol with a pendent carboxylic group, Placel205BA, Placel210BA and Plac-

Correspondence to: H.-B. Tsai (hbtsai@niu.edu.tw).

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Scheme 1 Reaction procedure of the preparation of the polyurethane dispersions.

cel220BA with molecular weights of 500, 1000, and 2000, respectively, were supplied by Daicel Co. Ltd. (Tokyo, Japan). These carboxylic polycaprolactonediol were dried at 80°C and 5 mmHg for 3 h before use. A polycarbonatediol, L5652, with a molecular weight of 2000 were supplied by Asahi Kasei Corp. (Tokyo, Japan). Triethyl amine (TEA) and ethylene diamine (EDA) were Merck (Darmstadt, Germany) reagent grade and treated with molecular sieve before use. Dibutyltin dilaurate (T-12) and *N*-methylpyrrolidone (NMP) were Merck reagent grade and were used as received.

Preparation of the polyurethane dispersions

The polyurethane dispersions were prepared by a method similar to that described previously in which the dispersing procedure was modified.²⁷ The reaction procedure is shown in Scheme 1.

A typical standard procedure for H220B is as follows. In a 1-L glass reaction kettle, 39.3 g (0.15 mol) of di(4-isocyanatocyclohexyl)methane (HMDI), 100 g

(0.05 mol) of Placel 220BA, 7.4 g (0.05 mol) of 2,2-di(hydroxymethyl)propanoic acid (DMBA), and 12.2 g (0.10 mol) of triethylamine (TEA) were reacted in 30 mL of *N*-methylpyrrolidone (NMP) at 80°C for 2.5 h to obtain an NCO-terminated prepolymer solution. The prepolymer solution was mixed with a small amount (0.5 g) of deionized water for dispersion step by step. The torque of the stirrer increased on the adding of water and the mixture was diluted with NMP if necessary. After the torque of the stirrer became steady and no significant increase in torque was observed, enough water was added (totally 372.6 g) to obtain a prepolymer dispersion. A solution of 1.5 g (0.025 mol) of ethylene diamine (EDA) in 2.0 g of deionized water was added to the prepolymer dispersion for chain extension. Then, the mixture was heated to 80°C under vacuum to remove NMP and to obtain a polyurethane dispersion with a solid content of 30%. The formulations in the preparation of other polyurethane dispersions are summarized in Table I.

TABLE I
Formulation of the Polyurethane Dispersions

	H205P	H210P	H220P	H205B	H210B	H220B
HMDI (g)	39.3	39.3	39.3	39.3	39.3	39.3
Carboxylic polycaprolactonediol						
Placel205BA (g)	25	—	—	25	—	—
Placel210BA (g)	—	50	—	—	50	—
Placel220BA (g)	—	—	100	—	—	100
Carboxylic diol						
DMPA (g)	6.7	6.7	6.7	—	—	—
DMBA (g)	—	—	—	7.4	7.4	7.4
TEA (g)	12.2	12.2	12.2	12.2	12.2	12.2
T-12 (g)	0.15	0.15	0.15	0.15	0.15	0.15
Water (g)	198.0	256.3	373.0	199.6	257.8	374.6
EDA (g)	1.5	1.5	1.5	1.5	1.5	1.5

TABLE II
GPC Data and Particle Size of Polyurethane Dispersions

Sample	M_n (g/mol)	M_w (g/mol)	M_w/M_n
H205P	17,600	45,100	2.56
H210P	18,400	51,000	2.77
H220P	19,300	62,700	3.25
H205B	16,600	43,700	2.63
H210B	21,500	65,300	3.04
H220B	34,800	115,600	3.32

Measurements

The molecular weight and molecular weight distribution of the polyurethane dispersions were determined by the gel permeation chromatography (GPC) performed on a Tosoh HLC-8220 GPC equipped with a TSK gel Super HM-H*4 column and a RI detector. The eluent was dimethyl formamide (DMF), the flow rate was 0.5 mL/min, the operation temperature was set to be 40°C, and the molecular weight was calibrated with polystyrene standards.

The particle size of the polyurethane dispersions was measured by a Photal Par-III's Photon Correlator (Otsuka Electric) at 25°C.

The UV-vis spectra of the polyurethane dispersions were determined by a Hitachi 2001 UV spectrophotometer at a scanning rate of 200 nm/min. Deionized water was used as the reference.

The polyurethane dispersions were cast into films and dried. The tensile stress-strain data of dumbbell shaped film specimens were determined by an Instron 4469 Universal Testing Machine at an extension rate of 100 mm/min at 23°C, and the gauge length used was 25 mm.

RESULTS AND DISCUSSION

The formulations in the preparation of the polyurethane dispersions are summarized in Table I. The molar composition of the reactants was held constant: molar ratio of HMDI : carboxylic polycarbonatediol : carboxylic diol : TEA : EDA = 3.0 : 1.0 : 1.0 : 2.0 : 0.5. The GPC data of the polyurethane dispersions pre-

pared by a novel method in which the dispersing procedure was modified as described previously²⁷ are summarized in Table I. The modified dispersing procedure is essential to enhance the molecular weight. To limit too extensive hydrolysis of the NCO groups, the prepolymer solution was mixed with a small amount of water for dispersion step by step in our modified procedure. By this procedure, the amine groups formed by the hydrolysis of the NCO groups had enough time to couple the remained NCO end groups as indicated by the increasing viscosity of the dispersing medium. This procedure let chain extension be more effective. The M_n values of the polyurethane dispersions prepared by a conventional method without modified dispersing procedure are always below 10,000 g/mol. The M_n values of the polyurethane dispersions prepared by the modified method are significantly greater than 10,000 g/mol as shown in Table II, indicating that the modified dispersing procedure is effective.

The appearance and the average particle diameter of the polyurethane dispersions prepared by the modified procedure are summarized in Table III. It can be seen that the molecular weight of the carboxylic polycaprolactonediol affects the particle size significantly. As the molecular weight of the carboxylic polycaprolactonediol decreases, the content of ionic groups in the polyurethane resin increases, and the particle size of the aqueous polyurethane dispersions decreases, as expected.

Typical UV-vis spectra of the polyurethane dispersions are shown in Figure 1. H205P, H210P, H205B, and H210B show similar UV-vis spectra, and exhibit little absorption in the visible region. These four polyurethane dispersions are clear and look transparent, the light transmittance is more than 90% as the wavelength is longer than 500 nm. The transmittance is almost 100% around 800 nm. Thus the transmittance at 800 nm is used as the reference to compare the effect of light scattering. The data are listed in Table III. H220P and H220B look slightly turbid and exhibit close spectra. As shown in Figure 1 and Table III, the transmittance in the visible region drop

TABLE III
Particle Size, Appearance, and Light Transmittance at 800 nm of the Polyurethane Dispersions

Sample	Particle size (nm)	Appearance	Transmittance at 800 nm (%)
H205P	9	Clear	100.0
H210P	12	Clear	99.9
H220P	27	Clear to translucent	74.5
H205B	8	Clear	99.9
H210B	13	Clear	99.9
H220B	35	Clear to translucent	69.2
I5652P(S) ^a	68	Translucent	21.8
I5652P(M) ^a	140	Opaque	0.0

^a Ref. 27.

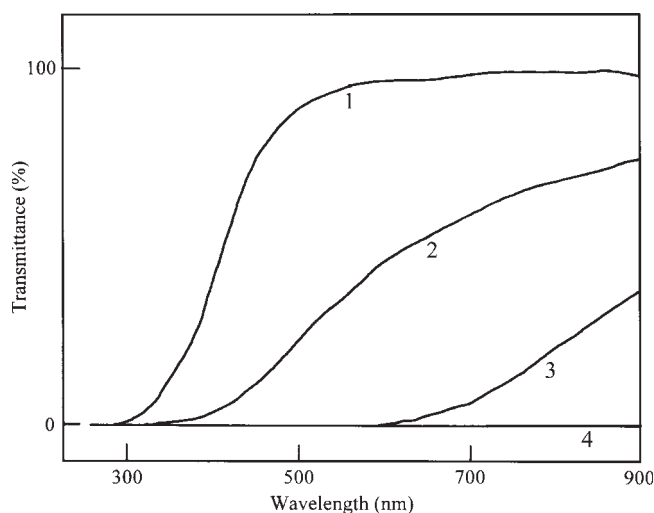


Figure 1 UV-vis spectra of (1) H205P, (2) H220P, (3) I5652P(S) PUD of 68 nm, and (4) I5652P(M) PUD of 140 nm.

significantly for these two polyurethane dispersions. Since the UV-vis spectra were recorded as the transmittance referred to water, $T = I/I_{ref}$, the loss in transmittance should be due to light scattering. This means that the dispersed particles scatter the visible light significantly for H220P and H220B. Two polyurethane dispersions derived from IPDI, L5652 polycarbonatediol, and DMBA prepared previously²¹ are used for comparison. The polyurethane dispersion with an average particle diameter of 68 nm, I5652(S), looks translucent. Its transmittance at 800 nm drops to 21.8%, indicating strong light scattering by the dispersed particles. The polyurethane dispersion with an average particle diameter of 140 nm, I5652(M), looks opaque. Its transmittance in the visible region reaches zero. The visible light is completely scattered.

It can be seen from Table III that the particle size of the polyurethane dispersions affects the transparency significantly. As the average particle diameter is in the range of 8–13 nm, the polyurethane dispersions (H205P, H210P, H205B, and H210B) are clear and transparent. As the average particle diameter is 27 nm or greater, the transparency seems to decrease with particle size for the polyurethane dispersions because of light scattering. The data show that as the average particle diameter is less than about 20 nm, the polyurethane dispersions become clear and transparent.

Typical tensile stress versus strain curves of the cast films of the polyurethane dispersions are shown in Figure 2. The results of some tensile properties are summarized in Table IV. Two major factors may affect the tensile modulus of the cast films, one is the content (based on weight) of the polycaprolactone soft segments, and the other is the content of the ionic groups. As the molecular weight of the carboxylic polycaprolactonediol decreases, the content of the polycaprolactone soft segments decreases, and

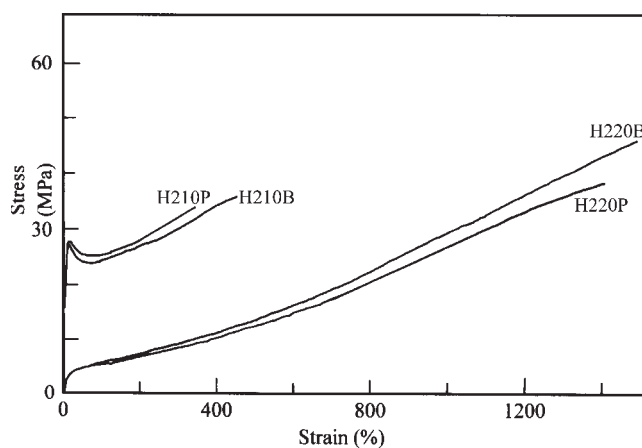


Figure 2 Tensile stress-strain curves of H210P, H220P, H210B, and H220B.

the content of ionic groups increases, thus 100% modulus and 300% modulus increases, as expected. It can be seen that the increase in modulus values for H210P and H210B (M_n of carboxylic polycaprolactonediol = 1000 g/mol) from H220P and H220B (M_n of carboxylic polycaprolactonediol = 2000 g/mol) is large. H205P and H205B are derived from the carboxylic polycaprolactonediol with a molecular weight of 500 g/mol, it is not surprising that they become very hard and the obtained films are very brittle. Thus, no tensile test result could be obtained.

The ductility of the cast film decreases as the molecular weight of the carboxylic polycaprolactonediol decreases, and the elongation at break decreases accordingly. Interesting is that the tensile strength values of the cast films of H220P and H220B are greater than those of H210P and H210B. For some ionomers, the strength increases as the content of ionic groups increases because of the increasing of the intermolecular force.²⁸ But, our cast films do not follow this trend. A major reason is that the values of the elongation at break of the films are considerably different as shown in Figure 2. The very high ductility let H220P and H220B exhibit higher tensile strength.

TABLE IV
Tensile Properties of Cast Films of Polyurethane Dispersions

Sample	100% modulus (MPa)	300% modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
H205P ^a	—	—	—	—
H210P	25.5	32.5	34.2	350
H220P	5.3	8.3	34.8	1400
H205B ^a	—	—	—	—
H210B	24.5	30.0	36.6	450
H220B	5.6	9.0	46.6	1490

^a Brittle films.

CONCLUSIONS

Aqueous polyurethanes dispersions of nanometer size were prepared by a method in which the dispersing procedure was modified through mixing the prepolymer solution with a small amount of water step by step to enhance the molecular weight. As the molecular weight of the carboxylic polycaprolactone-diol decreases, the ionic group content increases, the particle size of the polyurethanes dispersions decreases accordingly. As the molecular weight of the carboxylic polycaprolactone-diol used is 1000 g/mol or below, the polyurethanes dispersions become completely clear. The data show that as the average particle diameter is less than about 20 nm, the polyurethane dispersions become clear and transparent. The tensile properties are influenced considerably by the molecular weight of the carboxylic polycaprolactone-diol used.

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