Effect of Composition on Aqueous Polyurethane Dispersions Derived from Polycarbonatediols

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ABSTRACT: Aqueous polyurethane dispersions derived from isophorone diisocyanate, various polycarbonatediols of different molecular weights, and dimethylol butyric acid were prepared by a dispersing procedure modified to enhance molecular weight. Particle size, average molecular weight, and tensile properties were determined. The molar ratio of reactants affected the properties of the polyurethane dispersions significantly, with the trends described as the effects of their ionic group and polycarbonatediol soft-segment contents. The molecular weight of the polycarbonatediols also significantly affected the particle size of the aqueous polyurethane dispersions and the film properties. As the molecular weight of the polycarbonatediols decreased, the particle size of the aqueous polyurethane dispersions decreased, and the moduli of the cast films increased, as expected. However, the tensile strength of the cast films decreased as the molecular weight of the polycarbonatediols decreased because of the decrease in elongation at break. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4419–4424, 2006

Key words: polyurethanes; dispersions; ionomers; polycarbonates

INTRODUCTION

Aqueous polyurethane dispersions have been considered an ideal low volatile organic concentration polyurethane coating system. They have used in various fields in applications including as coatings, modifiers for coatings, and polishes, in leathers and adhesives, and in paper and textile sizing because the trend has been for environmental regulations to require decreased levels of solvent emissions.[1–4] Incorporation of ionic groups into polyurethanes is a practical method for obtaining 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 polyurethane dispersions are related to their chemical structure.[17–22] Polycarbonatediols are recently commercialized polyols and are claimed to provide good resistance to hydrolysis, heat aging, oil, weathering, and fungi.[23] We have recently studied aqueous polyurethane dispersions derived from polycarbonatediols.[24,25]

Because mechanical strength is significantly affected by the molecular weight of the polyurethane resin, we found a practical method, a modified dispersing procedure that enhanced molecular weight, to prepare aqueous polyurethane dispersions derived from various polycarbonatediols.[24] Only one composition was studied; previously only polycarbonatediols with a molecular weight of 2000 were used. Stability of polyurethane dispersions is strongly influenced by composition and ionic content,[11,26–28] an important target in an investigation of the role of the composition. In the present study, aqueous polyurethane dispersions derived from isophorone diisocyanate (IPDI), various polycarbonatediols of different molecular weights and dimethylol butyric acid (DMBA) were prepared by the modified method. The effect of composition on the properties of the aqueous polyurethane dispersions was investigated.

EXPERIMENTAL

Materials

Three series of polycarbonatediols, L467m, L600m, and L565m, of different molecular weights were supplied by Asahi Kasei Corporation (Tokyo, Japan). The molecular weights of the polycarbonatediols are 2000, 1000 and 500 for m = 2, 1, and 0f, respectively. The polycarbonatediols are claimed to be produced from 1,6-hexanediol and another diol, either 1,4-butanediol or 1,5-pentanediol, by transesterification with ethylenecarbonate. The molar ratio of 1,4-buta-

nediol to 1,6-hexanedil in L467m is 70 : 30; the molar ratio of 1,5-pentanediol to 1,6-hexanedil is 5 : 95 in L60m and 50 : 50 in L565m. The polycarbonatediols were dried at 80°C and 5 mm Hg for 3 h.

Isophorone diisocyanate, Desmodur® I, was obtained from Bayer (Lever Kusen, Germany) and used as received. DMBA was obtained from Nippon Kasei, Fukushima, Japan. Tiethyl amine (TEA) and ethylene diamine (EDA) were Merck reagent grade (E. Merck, Darmstadt, Germany) and treated with molecular sieves (Merck reagent grade) before use. N-Methylpyrrolidone (NMP), dimethylformamide (DMF), and dibutyltin dilaurate were Merck reagent grade and used as received.

Preparation of polyurethane dispersions

The polyurethane dispersions were prepared by a method in which the dispersing procedure was modified as described previously.[24] The reaction procedure is shown in Scheme 1.

A typical procedure is as follows. In a 1-L glass reaction kettle, 33.3 g (0.15 mol) of IPDI, 100 g (0.05 mol) of L4672, 7.4 g (0.05 mol) of DMBA, 6.1 g (0.05 mol) of TEA, and 30 mL of NMP were reacted at 80°C for 2.5 h to obtain an NCO-terminated prepolymer solution. Then the prepolymer solution was mixed with a small amount (about 0.5 g) of deionized water for dispersion step by step. The torque of the stirrer increased on adding water, and the mixture was diluted with NMP if necessary. When the torque of the stirrer became steady and no significant increase in torque was observed, it meant enough water had been added. A solution of 1.5 g (0.0025 mol) of EDA in 2.0 g of deionized water was added to the prepolymer dispersion and stirred at 500 rpm at 30°C for 1 h. The mixture was heated to 80°C under vacuum to remove NMP in order to obtain a polyurethane dispersion with a solids content of 30%. This dispersion is denoted as I4672B(1.0), where I is IPDI, 4672 is the L4672 polycarbonatediol, B is DMBA, and 1.0 is the molar ratio of polycarbonatediol to DMBA. The formulations used in the preparation of the polyurethane dispersions are summarized in Table I.

Measurements

Particle size of the polyurethane dispersions was measured by a Photal Par-IIIs Photon Correlator (Otsuka Electrics) at 25°C.

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

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 a gauge length of 25 mm.
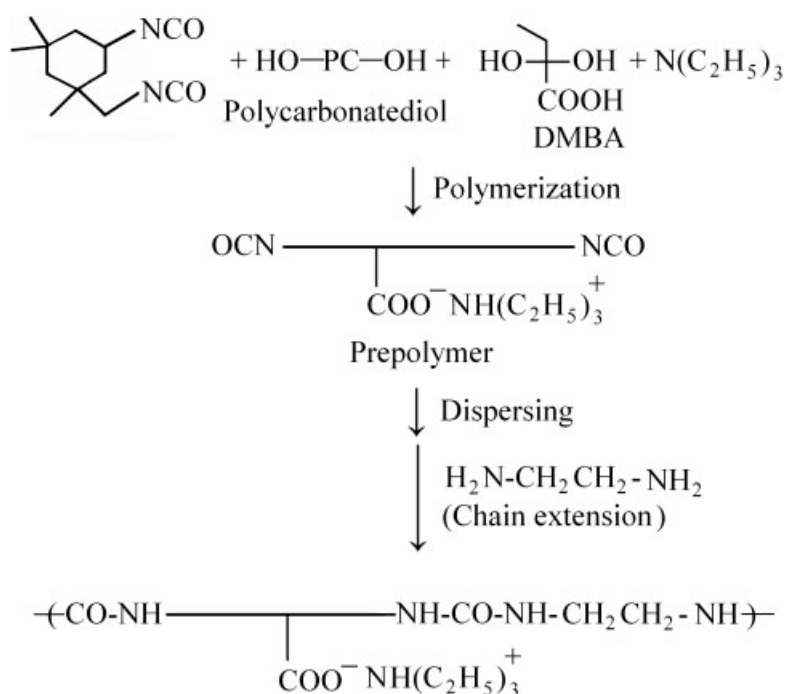
Scheme 1 Reaction procedure of the preparation of the polyurethane dispersions.

TABLE I
Formulations of the Polyurethane Dispersions

	IPDI (g)	Polycarbonatediol (g)	DMBA (g)	TEA (g)	T-12 (g)	EDA (g)	Water (g)
I4672B(0.5)	27.75	50	7.4	6.1	0.15	1.5	216.8
I4672B(1.0)	33.3	100	7.4	6.1	0.15	1.5	347.5
I4672B(1.5)	38.85	150	7.4	6.1	0.15	1.5	476.0
I4672B(2.0)	44.4	200	7.4	6.1	0.15	1.5	605.6
I4672B(2.5)	49.95	250	7.4	6.1	0.15	1.5	735.2
I4672B(3.0)	55.5	300	7.4	6.1	0.15	1.5	864.9
I4671B(1.0)	33.3	50	7.4	6.1	0.15	1.5	229.7
I4670fB(1.0)	33.3	25	7.4	6.1	0.15	1.5	171.4
I6002B(1.0)	33.3	100	7.4	6.1	0.15	1.5	347.5
I6001B(1.0)	33.3	50	7.4	6.1	0.15	1.5	229.7
I6000fB(1.0)	33.3	25	7.4	6.1	0.15	1.5	171.4
I5652B(1.0)	33.3	100	7.4	6.1	0.15	1.5	347.5
I5651B(1.0)	33.3	50	7.4	6.1	0.15	1.5	229.7
I5650fB(1.0)	33.3	25	7.4	6.1	0.15	1.5	171.4

RESULTS AND DISCUSSION

Effect of molar ratio of the reactants

The molar ratio of the reactants was varied in the preparation of the polyurethane dispersions derived from L4672, as shown in Table I. The molar ratio of IPDI : L4672 : DMBA : TEA : EDA was varied as $(2 + x) : x : 1.0 : 1.0 : 0.5$, and each polyurethane dispersion obtained was denoted as I4672B(x).

The GPC data of this series of polyurethane dispersions are shown in Table II. The polyurethane dispersions were prepared by a novel method that had a modified dispersing procedure as described previously.[24] The modified dispersing procedure was essential to enhancing molecular weight. To decrease the overhydrolysis 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 allowed chain extension to be more effective. The M_n values of polyurethane dispersions prepared by a method without a modified dispersing procedure are always below 10,000.[24] The M_n values of the polyurethane dispersions prepared by the modified method were significantly greater than 10,000, indicating that the modified dispersing procedure was also effective for different molar ratios of the reactants.

Particle size values of the polyurethane dispersions are summarized in Table II. As the molar ratio of L4672 to DMBA (equal to x) increased, ionic group content decreased, and particle size followed an increasing trend, as shown in Table II. Particle sizes of I4672B(1.5) and I4672B(2.0) seemed to be lower than expected. This was possibly because of the difference in molecular weight. Although the dispersing procedure of our

modified method is rather complex, an interesting experience was encountered: as the molecular weight of the resin increased, the particle size of the polyurethane dispersions often followed a significantly increasing trend. For example, a polyurethane dispersion of the I4672B(1.0) composition prepared by a conventional dispersing procedure with an M_n of 9700 had a particle size of about 40 nm, that of I4672B(1.0) had an M_n of 32,800 and a particle size of 151 nm. The M_n of I4672B(1.0) was significantly greater than those of I4672B(1.5) and I4672B(2.0) because the effect of molecular weight competes with the effect of ionic group content. Thus, the increase in particle size was not so obvious for I4672B(1.5) and I4672B(2.0). The particle size of I4672B(2.5) increased to more than 300 nm. This dispersion showed little precipitation, indicating ionic

TABLE II
GPC Data and Particle Sizes of Polyurethane Dispersions

	M_n	M_w	M_w/M_n	Particle size (nm)
I4672B(0.5)	18,700	63,400	3.39	82
I4672B(1.0)	32,800	112,000	3.41	151
I4672B(1.5)	20,400	64,500	3.16	171
I4672B(2.0)	16,600	50,900	3.07	183
I4672B(2.5)	17,700	48,900	2.76	309[a]
I4672B(3.0)	13,600	29,400	2.16	—[b]
I4671B(1.0)	23,730	71,500	3.01	28
I4670fB(1.0)	14,600	34,900	2.39	15
I6002B(1.0)	30,500	97,100	3.18	109
I6001B(1.0)	19,700	56,200	2.85	42
I6000fB(1.0)	18,300	49,400	2.70	26
I5652B(1.0)	21,900	58,000	2.65	125
I5651B(1.0)	19,100	57,400	3.00	26
I5650fB(1.0)	18,800	60,100	3.20	21

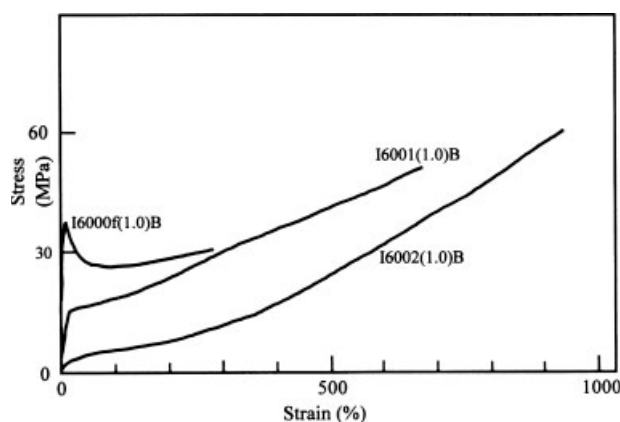[a] Mildly precipitated.
[b] Severely precipitated.

Figure 1 Tensile stress–strain curves of I4672B(*x*)s.

group content was not more sufficient for good dispersibility. As the molar ratio of L4762 to DMBA was 3.0, the dispersion obtained showed severe precipitation. This means that at a molar ratio of L4762 to DMBA above 2.5, stable polyurethane dispersions would not be obtained with our method, which has a modified dispersing procedure.

The polyurethane dispersions were cast into films, and their tensile properties were determined. Tensile stress–strain curves of the cast films of the I4672B(*x*) dispersions are shown in Figure 1. Some tensile properties are summarized in Table III. As the molar ratio of L4672 to DMBA increased, the polycarbonate soft-segment content increased and the ionic group content decreased, the cast film became softer and the modulus decreased, as expected. It seems that I4672B(*x*) films have maximum tensile strength at a L4672 : DMBA molar ratio of 1.0, as shown in Table III. As shown in Figure 1, the elongation at break of I4672B(1.0) was higher than that of I4672B(0.5), and I4672B(1.0) was

able to sustain greater stress before break. Thus, the tensile strength of I4672B(1.0) was higher than that of I4672B(0.5). As the molar ratio of L4672 to DMBA increased further, the increase in flexibility caused a drop in tensile strength.

Effect of molecular weight of polycarbonatediols

Given the molecular weight and tensile strength values described above, a polycarbonatediol : DMBA molar ratio of about 1 seemed to be a better composition in preparing the polyurethane dispersions by our modified method. Thus, the molar composition of the reactants was held at a IPDI : polycarbonatediol : DMBA : TEA : EDA molar ratio of 3.0 : 1.0 : 1.0 : 1.0 : 0.5 for the preparation of the polyurethane dispersions derived from polycarbonatediols of different molecular weights.

The GPC data of the polyurethane dispersions are shown in Table II. Except for I4670fB(1.0), the M_n values of the polyurethane dispersions were around 20,000, indicating reasonably high molecular weights. The M_n of I4670fB(1.0) was 13,600, also significantly higher than 10,000, indicating that the modified dispersing procedure was also effective.

Polyurethane dispersion particle size is summarized in Table II. The effect of the chemical structure of the polycarbonatediols on the particle size of the polyurethane dispersions showed no obvious trend. However, the molecular weight of the polycarbonatediols affected the particle size of the aqueous polyurethane dispersions significantly. As the molecular weight of the polycarbonatediols decreased, the ionic group content of the polyurethane resin increased, and the particle size of the aqueous polyurethane dispersions decreased, as expected.

Typical tensile stress–strain curves of the cast films of the polyurethane dispersions derived from the L600m series of polycarbonatediols are shown in Figure 2, and some tensile properties are summarized in Table III. Two major factors may have affected the tensile modulus of the cast films: polycarbonate
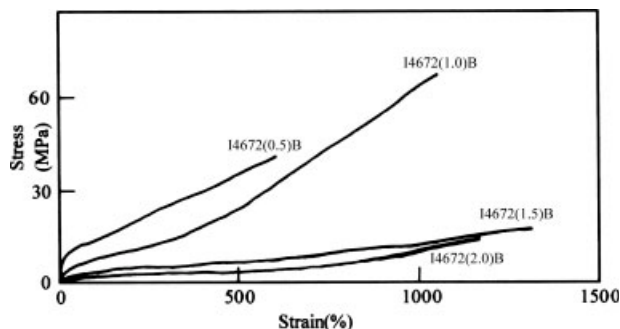
TABLE III
Tensile Properties of the Cast Films

	100% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
I4672B(0.5)	13.5	23.0	40.6	610
I4672B(1.0)	6.7	13.9	63.6	940
I4672B(1.5)	3.3	4.8	17.7	1310
I4672B(2.0)	1.9	2.5	14.2	1160
I4672B(2.5)	0.7	0.9	1.1	1120
I4671B(1.0)	20.0	30.5	53.5	700
I4670fB(1.0)	—[a]	—[a]	11.2	84
I6002B(1.0)	5.3	1.9	59.4	940
I6001B(1.0)	18.5	30.0	51.1	670
I6000fB(1.0)	26.0	—[a]	24.6	290
I5652B(1.0)	6.2	10.8	46.1	970
I5651B(1.0)	16.5	24.5	45.7	670
I5650fB(1.0)	34.5	—[a]	24.9	180

[a] Break occurred before measurement.

Figure 2 Tensile stress–strain curves of I460mB(1.0)s.

soft-segment content (based on weight and ionic group content. As the molecular weight of the polycarbonatediols decreased, the polycarbonate soft-segment content decreased, and the ionic group content increased; thus, there were modulus increases of 100% and 300%. Moreover, ductility decreased as the molecular weight of the polycarbonatediols decreased, and elongation at break decreased accordingly. Interestingly, the tensile strength of the cast films decreased as the molecular weight of the polycarbonatediols decreased. For some ionomers, strength increases as the ionic group content increases because of increasing intermolecular force.[29] Our cast films did not follow this trend. A major reason is that the elongation at break of the films was considerably different as the molecular weight of the polycarbonatediols varied. As shown in Figure 2, stress increased slowly with strain as the strain reached more than 100%. Thus, as the molecular weight of the polycarbonatediols decreased, the tensile strength of the cast films decreased because of the greater drop in the elongation at break.

Effect of ionic content on particle size

The stability and particle size of polyurethane dispersions are dependent on various factors such as chemical structure, composition, dispersing procedure and ionic content.[9–11,25–28] The effect of ionic group content on the particle size of 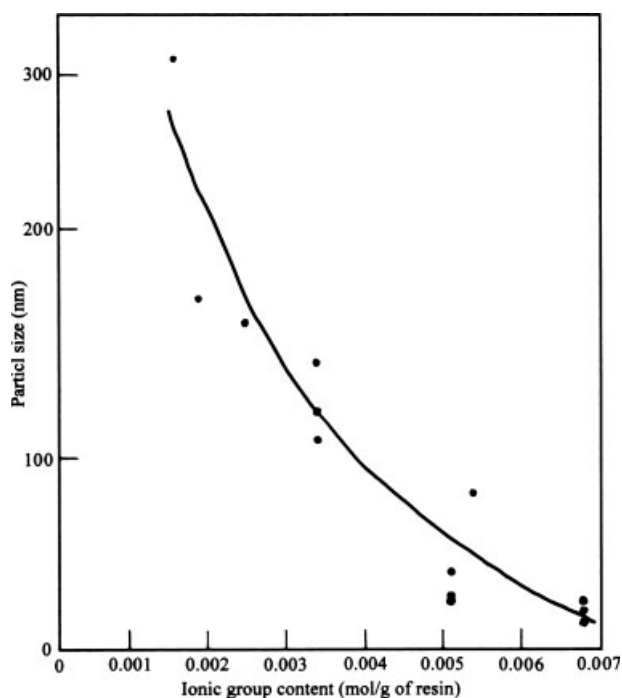our polyurethane dispersions is shown in Figure 3. It can be seen that ionic group content seems to have been a major governing factor in determining particle size. As ionic group content increased, the particle size of the polyurethane dispersions showed a decreasing trend.

CONCLUSIONS

Both the molar ratio of the reactants and the molecular weight of the polycarbonatediols affected the properties of the aqueous polyurethane dispersions significantly. As the molar ratio of L4672 to DMBA increased, ionic group content decreased and particle size followed an increasing trend. When the molar ratio of L4762 to DMBA was 2.5 or higher, the dispersions became unstable. As the molar ratio of L4672 to DMBA increased, the polycarbonate soft-segment content increased and the ionic group content decreased, and thus the modulus decreased, as expected. Because elongation at break is another factor that influences tensile strength, tensile strength was at its maximum at a molar ratio of L4672 to DMBA of 1.0. As the molecular weight of the polycarbonatediols decreased, the ionic group content increased, the particle size of the aqueous polyurethane dispersions decreased, and the modulus of the cast films increased, as expected. However, the tensile strength of the cast films decreased as the molecular weight of the polycarbonatediols decreased because of the decrease in the elongation at break.

Figure 3 Effect of ionic group content on the particle size of the polyurethane dispersions.

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