

Aqueous Polyurethane Dispersions Derived from Polycarbonatediols

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ABSTRACT: Aqueous polyurethane dispersions derived from polycarbonatediols, isophorone diisocyanate, and carboxylic diols including dimethylol propionic acid and dimethylol butyric acid were prepared. The effect of dispersing procedure is investigated by FT IR, GPC, and the tensile film properties. The polyurethane dispersions prepared by a standard procedure exhibit lower molecular weights due to the overhydrolysis of the NCO groups. The polyurethane dispersions prepared by a modified procedure exhibit significantly higher molecular weights due to more effective chain extension, and their cast films exhibit higher tensile

strength. The particle size, tensile properties, thermal properties, and dynamic mechanical properties are investigated. The chemical structure of the polycarbonatediols seems to affect the tensile strength. The glass transition temperature of the soft segments, $T_g(S)$, of the polyurethane dispersions can be seen from the DSC and DMA data. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1723–1729, 2004

Key words: polyurethanes; dispersions; ionomers; molecular weight distribution; polycarbonatediols

INTRODUCTION

Polyurethanes have been found in wide applications such as coatings and adhesives¹ due to their unique properties, and great efforts have been made in chemistry and physics.^{2–10} In the polyurethane system, aqueous polyurethane dispersions are expanding their applications in coatings, adhesives, paper sizings, etc., due to the trend of environmental regulations to decrease the level of solvent emissions.^{11–13} The incorporation of ionic groups into polyurethanes is a practical method to obtain aqueous polyurethane dispersions, and various polyurethane dispersions have been described in the literature.^{11–21} The cost of raw materials and the dispersing technology are two important factors determining the feasibility of polyurethane dispersions for practical applications. Thus, one system with good commercial potential is the polyurethane dispersion derived from a diisocyanate, a commercial polyol and a carboxylic diol, which can provide ionic groups.^{11,17–21} The presence of ionic groups not only provides dispersibility in water, but also increases the intermolecular force and enhances the strength like other ionomers.^{22–25} The strength is also significantly affected by the molecular weight of the polyurethane ionomers.²⁰ High-molecular-weight polyurethane ionomers can be prepared first in a polar solvent such

as acetone and then dispersed in water.^{12,13,26} However, it is very difficult for the high-molecular-weight polyurethane ionomers to be dispersed uniformly in water. A large amount of solvent is often necessary.

In a more practical method, an NCO-terminated prepolymer ionomer, which is readily dispersible in water, is first prepared. After dispersion, a chain extender such as diamine is added to couple the NCO groups to enhance the molecular weight. Afterward, the solvent is removed to obtain the desired aqueous polyurethane dispersion. The effects of various factors such as the structure and content of diisocyanates, polyols, carboxylic diols, neutralizing agents, and chain extenders on the preparation of polyurethane dispersions and their properties have been studied extensively.^{14–21,27–30} Polycarbonatediols are recently commercialized polyols and are claimed to provide good hydrolysis resistance, heat aging resistance, oil resistance, weathering resistance, and fungi resistance.³¹ However, little effort has been made on characterizing polyurethane dispersions derived from polycarbonatediols.³²

In this article, various aqueous polyurethane dispersions based on polycarbonatediols are prepared, and the properties of the aqueous polyurethane dispersions and the effect of dispersing procedure are investigated.

EXPERIMENTAL

Materials

Three polycarbonatediols, L4672, L6002, and L5652, with a molecular weight of 2000 were supplied by

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TABLE I
Formulation of the Polyurethane Dispersions and Some Related Properties

	I4672P	I6002P	I5652P	I4672B	I6002B	I5652B
IPDI(g)	33.3	33.3	33.3	33.3	33.3	33.3
Polycarbonatediol (g)						
L4672	100	—	—	100	—	—
L6002	—	100	—	—	100	—
L5652	—	—	100	—	—	100
Carboxylic diol (g)						
DMPA	6.7	6.7	6.7	—	—	—
DMBA	—	—	—	7.4	7.4	7.4
TEA	6.1	6.1	6.1	6.1	6.1	6.1
T-12	0.15	0.15	0.15	0.15	0.15	0.15
MEK (mL)	30	30	30	30	30	30
Free NCO (%)	2.38	2.38	2.18	2.37	2.37	2.37
Water (g)	344.4	344.4	344.4	347.5	347.5	347.5
EDA (g)	1.5	1.5	1.5	1.5	1.5	1.5
Particle size ^a (nm)	152.6	178.8	140.2	151.2	108.6	124.8

^a Particle size of the polyurethane dispersions prepared by the modified procedure.

Asahi Kasei Corp. The polycarbonatediols are claimed to be produced from 1,6-hexanediol and another diol of either 1,4-butanediol or 1,5-pentanediol by transesterification with ethylene carbonate. The molar ratio of 1,4-butanediol to 1,6-hexanediol in L4672 is 70:30. The molar ratio of 1,5-pentanediol to 1,6-hexanediol in L6002 is 5:95 and that in L5652 is 50:50. L4672 and L5652 are liquid at room temperature, and they are easy to handle. L6002 is white solid at room temperature. The polycarbonatediols were dried at 80°C and 5 mm Hg for 3 h.

Isophorone diisocyanate (IPDI), Desmodur I, was obtained from Bayer and used as received. The equivalent weight of IPDI was determined by a di-*n*-butylamine back titration method¹² to be 113.5 g/mol. Dimethylol propionic acid (DMPA) was Aldrich reagent grade and dimethylol butyric acid (DMBA) was obtained from Nippon Kasei. Triethylamine (TEA) and ethylenediamine (EDA) were Merck reagent grade and treated with a molecular sieve before use. Butanone (MEK), dimethylformamide (DMF), and dibutyltin dilaurate (T-12) were Merck reagent grade and used as received.

Preparation of the polyurethane dispersions

The polyurethane dispersions were prepared by a method similar to that described in the literature³³ as a one-shot process or by a method in which the dispersing procedure was modified. The former is denoted as the standard procedure, and the latter is denoted as the modified procedure.

A typical standard procedure for I4672P(S), where I represents the IPDI diisocyanate, 4672 represents the L4672 polycarbonatediol, P represents the DMPA carboxylic diol, and S is the standard procedure, is as follows. Into a 1-L glass reaction kettle equipped with

a mechanical stirrer containing a torque meter, a thermometer, a condenser for reflux, and a nitrogen gas inlet, 33.3 g (0.15 mol) of IPDI, 100 g (0.05 mol) of L4672, 6.7 g (0.05 mol) of DMPA, 6.1 g (0.05 mol) of TEA, and 30 mL of MEK were added. Under nitrogen, the mixture was stirred at a speed of 100 rpm and heated to 80°C for about 2.5 h to obtain an NCO-terminated prepolymer solution. Its NCO content was determined to be 2.38%. Then, 342.4 g of deionized water was added and mixed with the prepolymer solution at a stirring speed of 500 rpm at 35°C to obtain a prepolymer dispersion. 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. Then, the mixture was heated to 80°C to remove MEK 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.

In the modified procedure, only the dispersing stage was varied. For example, in the preparation of I4672P(M), where M means the modified procedure, 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 upon the addition of water and the mixture was diluted with MEK if necessary. After 2.0 g of water was added, the torque of the stirrer became steady and no significant increase in torque was observed; then enough water was added. Other stages followed the same operations as in the standard procedure.

Measurements

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

TABLE II
Tensile Film Properties of Polyurethane Dispersions Prepared via the Standard Procedure

Sample	100% modulus (MPa)	200% modulus (MPa)	300% modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
I4672P(S)	4.9	5.8	6.7	21.3	1010
I6002P(S)	5.9	8.1	12.3	34.6	630
I5652P(S)	4.9	6.0	7.1	22.7	910
I4672B(S)	6.2	8.1	11.3	35.6	720
I6002B(S)	6.4	8.6	12.4	41.9	780
I5652B(S)	5.1	6.4	8.0	32.4	1060

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 a RI detector. The eluent was 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 IR spectra of the prepolymer dispersions were measured by a Perkin-Elmer 1600 series FTIR.

The polyurethane dispersions were casted into films and dried. The tensile stress-strain data of dumbbell-shape 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.

The DSC heating curves of the casted film samples from -100 to 200°C were determined by a Du Pont DSC 910 at a heating rate of 20°C/min under nitrogen.

The dynamic mechanical properties of strip specimens (20 × 5 × 0.5 mm) were measured by a Perkin-Elmer, dynamic mechanical analysis, DMA7, with a tensile mode at a forced vibration frequency of 1 Hz and a heating rate of 5°C/min.

RESULTS AND DISCUSSION

Preparation of polyurethane dispersions via two different procedures

The formulation in the preparation of the polyurethane dispersions is summarized in Table I. In the preparation of the polyurethane dispersions, the molar composition of the reactants was held constant (molar ratio of IPDI:polycarbonatediol:carboxylic diol:TEA:EDA = 3.0:1.0:1.0:1.0:0.5). As in a standard procedure, IPDI, polycarbonatediol, carboxylic diol, and TEA were mixed and reacted in MEK to form a prepolymer solution. The prepolymer solution was then dispersed in enough water, and water-soluble EDA was added to couple the NCO end group for chain extension. The molar amount of the isocyanate group used was stoichiometrically greater than that of the hydroxy group and amine groups due to the hydro-

lysis of the NCO groups by water during dispersion. Fortunately, the hydrolytic reaction formed amine groups that reacted with the isocyanate group to enhance the molecular weight. If the NCO/(OH+NH₂) ratio is 1:1, there will be excess amine groups remaining in the polyurethane dispersions that may cause yellowing and a storage stability problem.¹ After chain extension, MEK was removed to form polyurethane dispersions with a solid content of 30%.

The polyurethane dispersions were cast into films and their tensile properties were determined. The results are shown in Table II. Typically, a tensile strength of as high as 40 MPa is required for some aqueous polyurethane dispersions in furniture and automobile applications.³⁴ The tensile strength of the polyurethane dispersions prepared via the standard procedure may be not high enough to meet this requirement. This is probably due to the fact that the molecular weight of these polyurethane dispersions is not high enough. The GPC data of these polyurethane dispersions are listed in Table III. The M_n (number average molecular weight) values are around 10,000. This means that these polyurethane dispersions may not possess enough molecular weight. Another interesting phenomenon is that the polydisperse index (M_w/M_n) is close to 2, which seems to be a molecular weight distribution result of the step polymerization conducted in a homogeneous system.³⁵ Probably the chain extending step was not as effective as expected. This might be due to the overhydrolysis of the NCO groups of the prepolymer by water at the dispersing step.

TABLE III
GPC Data of Polyurethane Dispersions Prepared via the Standard Procedure

Sample	M_n	M_w	M_w/M_n
I4672P(S)	10,912	22,322	2.046
I6002P(S)	9188	16,369	1.782
I5652P(S)	11,574	23,157	2.009
I4672B(S)	9668	17,835	1.845
I6002B(S)	8489	15,658	1.844
I5652B(S)	8408	14,575	1.734

The overconsumption of the NCO groups of the prepolymer can be verified by IR analysis. During the dispersing of the prepolymer solution in a large amount of water, the mixing medium was taken out at a time interval of 10 min. After drying, the IR spectrum was measured. The results are indicated in Figure 1. The peak at 2267 cm^{-1} corresponds to the absorption of the NCO groups, and the C-H stretching at 2939 cm^{-1} can be used as a reference to quantify the content of NCO groups. Before dispersing in water, there was a high content of NCO groups in the prepolymer solution. After being mixed with a large amount of water, the content of NCO groups decreased drastically. And there was only small amount (estimated to about 15% of original amount) of NCO groups left at the end of the dispersing step as shown in Figure 1. In other words, the chain extending step would not be as effective as required.

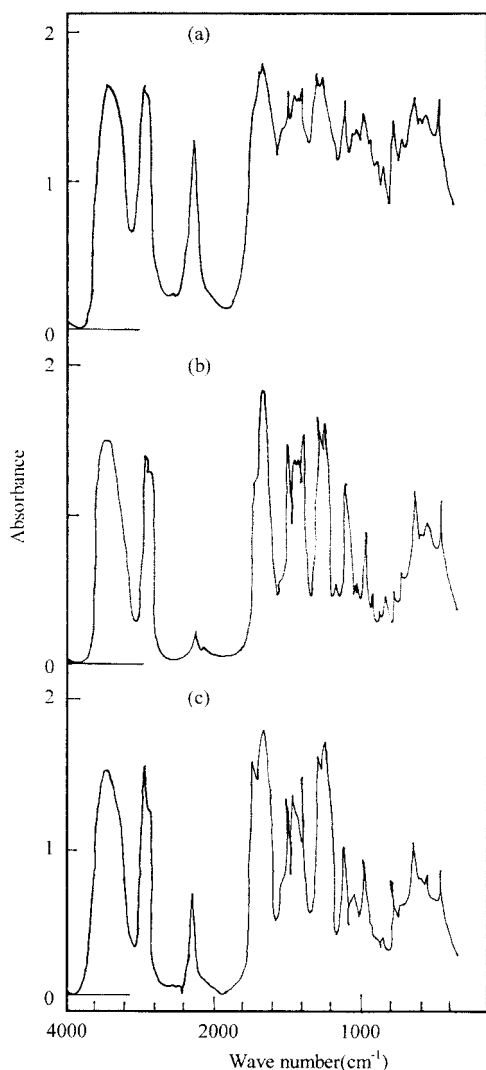


Figure 1 IR spectra of (a) NCO-terminated prepolymer before dispersion, (b) prepolymer dispersion via the standard procedure, and (c) prepolymer dispersion via the modified procedure for I6002P.

TABLE IV
GPC Data of Polyurethane Dispersions Prepared via the Modified Procedure

Sample	M_n	M_w	M_w/M_n
I4672P(M)	33,293	147,122	4.419
I6002P(M)	31,808	109,326	3.437
I5652P(M)	25,079	75,180	2.998
I4672B(M)	32,783	112,019	3.417
I6002B(M)	30,461	97,137	3.189
I5652B(M)	21,921	58,048	2.648

To decrease the extent of the hydrolysis of the NCO groups, the prepolymer solution was mixed with a small amount (0.5 g) of water for dispersion step by step in a modified procedure. By this procedure, the amine groups formed by the hydrolysis of the NCO groups had enough time to couple the remaining NCO end groups as indicated by the increasing viscosity of the dispersing medium (increasing torque value of the stirrer). After the torque of the stirrer became steady, enough water was added. The obtained prepolymer dispersion exhibits a rather high content of NCO groups (estimated to about half of the original amount) as indicated by the IR data shown in Figure 1. The prepolymer dispersion was chain extended with EDA. Afterward, MEK was removed to obtain the desired polyurethane dispersions.

The GPC data of the polyurethane dispersions prepared via the modified procedure are shown in Table IV. The M_n values of these polyurethane dispersions are over 20,000, indicating that their molecular weights are significantly greater than those of the polyurethane dispersions prepared via the standard procedure. More interesting, their polydisperse indices are significantly higher than 2, indicating the more heterogeneous nature of the chain extension. Thus, the chain extension would be more effective in these polyurethane dispersions prepared via the modified procedure.

The tensile properties of the polyurethane dispersions prepared via the modified procedure are summarized in Table V. Their tensile strength is significantly higher than that of the corresponding polyurethane dispersions prepared via the standard procedure due to the increase in molecular weight, as expected (Fig. 2). The tensile strength of these polycarbonatediol-based polyurethane dispersions can meet the requirement of commercial polyurethane dispersions.

Properties of polyurethane dispersions prepared via the modified procedure

The particle size of the polyurethane dispersions prepared via the modified procedure is summarized in the last row of Table I. Since the dispersing procedure

TABLE V
Tensile Film Properties of Polyurethane Dispersions Prepared via the Modified Procedure

Sample	100% modulus (MPa)	200% modulus (MPa)	300% modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
I4672P(M)	6.2	8.5	12.3	54.8	880
I6002P(M)	5.5	8.2	12.5	57.3	940
I5652P(M)	5.9	7.5	9.9	36.1	940
I4672B(M)	6.7	9.6	13.9	63.6	940
I6002B(M)	5.3	7.6	11.9	59.4	940
I5652B(M)	6.2	8.2	10.8	46.1	970

is rather complex, the effect of the chemical structure of polycarbonatediols on the particle size of the polyurethane dispersions shows no obvious trend. However, the chemical structure of the carboxylic diols seems to affect the particle size of the polyurethane dispersion to some extent. The particle size of the polyurethane dispersions derived from DMBA seems smaller than that of the corresponding polyurethane dispersion derived from DMPA.

Typical second run DSC heating curves of the polycarbonatediols and the cast films of the polyurethane dispersions prepared via the modified procedure are shown in Figure 3. The DSC heating curve of L6002 exhibits a step inflection and a melting endotherm. The mid-point of the step inflection is taken as the glass transition temperature (T_g) and the peak temperature of the melting endotherm is taken as the melting point (T_m). The heat of fusion (ΔH_m) of L6002 is rather high as shown in Table VI. This indicates that L6002 can crystallize significantly after cooling from the molten state at a slow cooling rate. The DSC heating

curves of L4672 and L5652 show only a T_g , but no T_m . These two polycarbonatediols cannot crystallize significantly and are liquid at room temperature.

All second run DSC heating curves of the casted films of the polyurethane dispersions exhibit only a step inflection corresponding to the glass transition temperature of the soft segments (T_{gS}). The results are summarized in Table VI. It can be seen that the T_{gS} values of the polyurethane dispersions are about 20°C higher than those of the corresponding polycarbonatediols as shown in Table VI. This may be due to the presence of the ionic groups, which hinder the motion

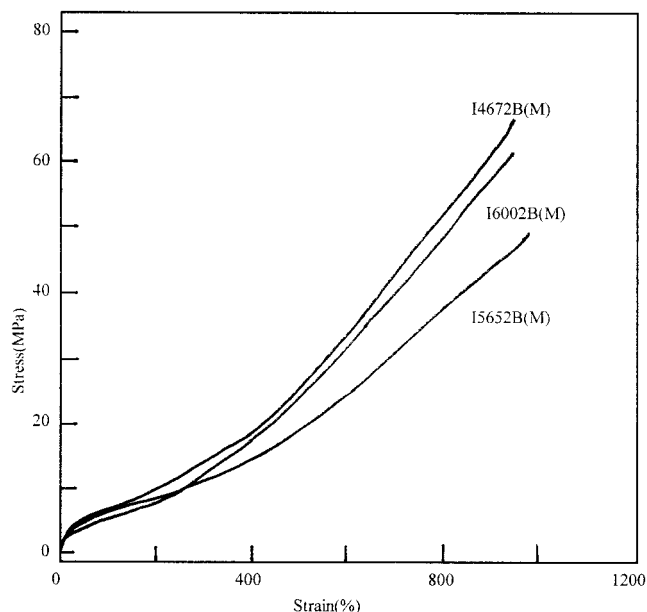


Figure 2 Tensile stress-strain curves of I4672P(M), I6002P(M), and I5652P(M).

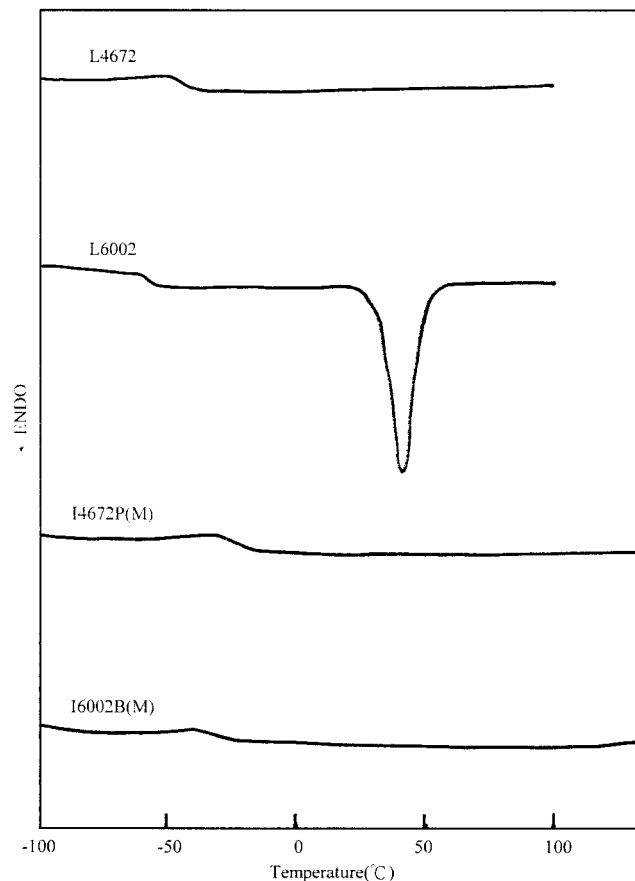


Figure 3 DSC heating curves of L4672, L6002, I4672P(M), and I6002P(M).

of polycarbonate soft segments. The presence of the ionic groups might also hinder the crystallization of the polycarbonate soft segments in I6002-P(M) and I6002-B(M), and thus no T_mS was found.

Typical DMA (dynamic mechanical analysis) curves of the casted films of the polyurethane dispersions prepared via the modified procedure are shown in Figure 4. All the casted films show similar real modulus (E') versus temperature curves. There is a great drop in E' around -30°C corresponding to the T_gS . Moreover, there is another drop in E' around 80°C . As the E' dropped to a value below about 10^6 Pa, the DMA measurements could not be done successfully, indicating that the films no longer sustained enough stress. The corresponding temperature may be a limit service temperature for the polyurethane dispersions. This means that the temperature resistance of these polyurethane dispersions may be about 80°C . If better heat resistance is required, a stiffer diisocyanate such as bis(4'-isocyanatocyclohexyl)methane (H_{12} MDI) may be involved. All the casted films show similar $\tan\delta$ versus temperature curves. As shown in Figure 4, the film samples exhibit a major damping peak at -25°C corresponding to the glass transition temperature of the soft segments (T_gS). The results are tabulated in Table VI. It can be seen that the observed T_gS data are consistent with the DSC data.

The films made from the polyurethane dispersions prepared via the modified procedure show interesting tensile properties as shown in Table IV. The elongation at break of the films is high, indicating that the films are ductile. Compared with the properties of the segmented polyurethane elastomers with a hard segment content of 40 wt % derived from IPDI or other diisocyanates and a poly(tetramethylene ether) glycol³⁶ and other thermoplastic polyurethane elastomers³⁷ based on IPDI, the films made from the polyurethane dispersions exhibit significantly higher tensile strength. It seems that the ionic groups play an important role in the development of high tensile strength, like other polyurethane ionomers.^{14,16,19,20,25}

TABLE VI
Thermal Transitions of the Polycarbonatediols and the Casted Films of the Polyurethane Dispersions Prepared via the Modified Procedure

Method	DSC $T_gS(^{\circ}\text{C})$	DSC $T_mS(^{\circ}\text{C})$	DSC $\Delta H_mS(\text{J/g})$	DMA $T_gS(^{\circ}\text{C})$
L4672	-46	—	—	—
L6002	-54	42	43.5	—
L5652	-51	—	—	—
I4672P(M)	-28	—	—	-18
I6002P(M)	-35	—	—	-32
I5652P(M)	-34	—	—	-25
I4672B(M)	-30	—	—	-22
I6002B(M)	-35	—	—	-27
I5652B(M)	-31	—	—	-21

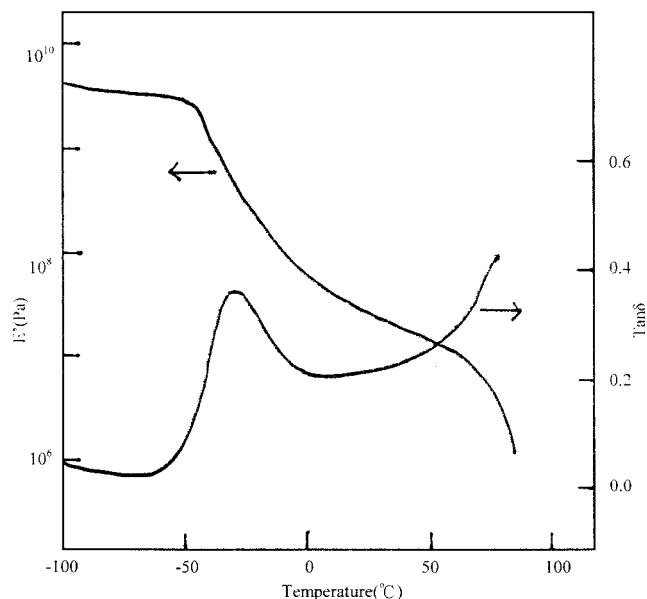


Figure 4 DMA curves of I6002P(M).

The structure of polycarbonatediols also influences the tensile strength of the films to some extent as shown in Table V and Figure 2. The tensile film properties of the polyurethane dispersions derived from L4672 are similar to those of the polyurethane dispersions derived from L6002, but the tensile strength of the polyurethane dispersions derived from L5652 are significantly lower than those of the polyurethane dispersions derived from L4672 and L6002. For example, the tensile strength of I5652P(M) is significantly lower than that of I4672P(M) and I6002P(M). The lower tensile strength of the polyurethane dispersions derived from L5652 might be due to the difficulty of the soft segments to crystallize owing to the composition and random structure of L5652.

CONCLUSION

In the preparation of the aqueous polyurethane dispersions derived from polycarbonatediols, the dispersing procedure significantly influences the molecular weight and thus the tensile strength of the polyurethane dispersions. The polyurethane dispersions prepared by the standard procedure exhibit lower molecular weights due to the overhydrolysis of the NCO groups. The molecular weight of the polyurethane dispersions prepared by the modified procedure is significantly higher and their casted films exhibit higher tensile strength. The DSC and DMA data consistently show that the polyurethane dispersions exhibit a main glass transition temperature corresponding to the polycarbonate soft segments. The tensile properties of the polyurethane dispersions are dependent on the compositions. The polyurethane disper-

sions derived from L5652 exhibit a lower tensile strength.

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