Effect of soft segment length on the properties of polyurethane anionomer dispersion

Young Min Lee, Jong Cheol Lee and Byung Kyu Kim*
Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea
(Received 6 August 1993)

Aqueous polyurethane anionomer dispersions were prepared from isophorone diisocyanate, poly(tetramethylene adipate glycol) (PTAd) and dimethylol propionic acid as potential anionic centres. The effects of polyol molecular weight (M_n) on the state of dispersion, thermal, mechanical and viscoelastic properties and swelling of emulsion-cast film were determined. With increasing M_n of PTAd, the particle size of the emulsion and soft segment glass transition temperature, T_g, decreased, and solvent swelling, emulsion viscosity and hard segment T_g increased. Tensile strength showed a minimum with PTAd 1000, and elongation at break generally increased with the M_n of PTAd. These results could be interpreted in terms of soft segment–hard segment phase separation and crystallization of high molecular weight PTAd.

(Keywords: polyurethane; molecular weight; emulsion-cast film)

Introduction

Polyurethane (PU) ionomers are segmented copolymers that consist of alternating soft and hard segment units, with a minority of repeat units carrying pendent acid or tertiary nitrogen groups which are neutralized to form salts. The soft segment generally consists of polyether or polyester polyol, whereas hard segments are usually formed by the extension of a diisocyanate with a chain extender of a low molecular weight polyol or amine.

It is now generally accepted that the properties of PU ionomers are primarily due to the phase behaviour of soft and hard segments as well as ion character. The existence of the hard segment domain, in particular, may give PU ionomer its excellent mechanical strength[1,2]. An elevation in the soft segment glass transition temperature (T_g) is observed mainly as a result of the presence of dissolved hard segment[3,4]. In general, the polyester soft segment was found to contribute to phase mixing by hydrogen bonding between the oxygen of the soft segment and NH groups of the hard segment[5,6]. This behaviour also depends on the content, length and polarity of soft and hard segment. Many previous investigations[7–11] have reported on the characterization of this microdomain structure in segmented PU. However, with regard to PU aqueous dispersion, most work was done by industrial laboratories, and basic structure/property behaviour is sparse in the open literature[12–14].

In this paper we describe the preparation and properties of PU ionomer dispersions from poly(tetramethylene adipate glycol) (PTAd), isophorone diisocyanate (IPDI) and dimethylol propionic acid (DMPA). The effects of soft segment molecular weight ($M_n = 600$–2000) on the emulsion characteristics and properties of emulsion-cast films are studied.

Experimental

Materials. PTAd (Dongsung Chemicals) was dried and degassed at 80°C, 1–2 mmHg, for 5 h before use. DMPA (Aldrich) was dried at 100°C for 2 h in a drying oven. Extra-pure grades of IPDI (Huls Chemicals) and dibutyltin dilaurate (DBT) were used as received. Dimethylformamide (DMF), triethylene tetramine (TETA), triethylamine (TEA), and solvents used in titration were dried over 3 Å molecular sieves before use.

Prepolymer synthesis. The basic formulation is given in *Table 1*. A 500 ml round-bottom, four-necked separable flask with a mechanical stirrer, thermometer, condenser with drying tube and a pipette outlet was used as reactor. Reaction was carried out in a constant-temperature oil bath. PTAd, DBT (0.03 wt% based on the total solid weight), and DMPA dissolved in DMF (5 wt% based on the total weight) were charged into the dried flask. While stirring, the mixture was heated to 90°C for about 30 min, followed by adding IPDI to the homogenized mixtures. The mixture was heated to 90°C for about 3 h to obtain NCO-terminated prepolymers. The change of NCO value during the reaction was determined using a standard dibutylamine back-titration method[15]. Upon obtaining the theoretical NCO value, the prepolymers were cooled to 60°C, and the neutralizing solution, i.e. TEA dissolved in DMF (5 wt% based on the total weight), was added and stirred for 1 h while maintaining the temperature at 60°C. The 1:1 stoichiometry was obtained by adding TETA at the chain extension step. The amount of DMF used in each step, i.e. to dissolve the DMPA and to reduce the solution viscosity, was approximately the same (see the total amount in the tables).

Emulsification and chain extension. Aqueous dispersion of PU was obtained by adding water (35°C) to the mixture (60°C). Since the water addition rate, in addition to the viscosity ratio between prepolymer solution and water, is a critical parameter in obtaining stable dispersion, a tubing pump was used, and water was added for 6 min at a constant flow rate. The phenomena of phase inversion, viscosity and conductivity change during the emulsification process are well documented[16–18]. TETA

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* To whom correspondence should be addressed

0032-3861/94/05/1095-05

dissolved in water was then fed to the emulsion for a period of 40 min, and chain extension was carried out for the next 2 h. The resulting product was a stable (over 6 months at room temperature) urea–urethane dispersion with a solids content of about 35%.

Tests. Particle size and distribution were measured with an Autosizer (Malvern IIC), and the state of dispersion was investigated by transmission electron microscopy (TEM, Hitachi H300). To obtain the micrographs, samples were stained with OsO_4 for 1 week. Tensile properties of the emulsion-cast films were measured using an Instron Tensile Tester at a crosshead speed of 100 mm min^{-1} and an average of at least five measurements was taken. Films were prepared by casting the emulsion onto a Teflon plate, followed by drying at 80°C for 5 h. The resulting films were then heated overnight in an oven at 60°C under 2–3 mmHg. Microtensile test specimens were prepared according to ASTM D-1822. Dynamic mechanical tests were performed with a dynamic mechanical thermal analyser (d.m.t.a., Polymer Lab.) from −100°C to 100°C at a frequency of 1 Hz. To measure the swelling in water and dimethylformamide (DMF), films were immersed in solvent for 24 h at room temperature and the percentage swelling was determined by measuring the weight increase:

$$\%\ \text{swelling} = \frac{w - w_0}{w_0} \times 100$$

where w_0 is the weight of dried film and w is the weight of film at equilibrium swelling.

Results and discussion

Particle size and emulsion viscosity. Throughout the experiments, the average molecular weight of NCO-terminated prepolymer was fixed at 4500. As the M_n of PTAd increases from 600 to 2000, the hard segment content decreases from 48 to 38%. *Table 2* shows that the particle size decreases linearly with increasing M_n of PTAd. The Autosizer result was visually confirmed from TEM (*Figure 1*). In PU dispersion, the average particle size is governed mainly by the hydrophilicity of the PU[16–18]. However, the hydrophilicity increases marginally with increasing M_n of PTAd in the present system (to be shown later). The decrease of particle size with increasing M_n of PTAd has to be related to the increased chain flexibility of PU.

Table 1 Basic formulation of the feed[a]

M_n of PTAd	PTAd (g)	DMPA (g)	IPDI (g)	TEA (ml)	TETA (g)
600	18.6	1.93	12.45	2.0	1.18
1000	20.8	1.93	10.09	2.0	1.18
1500	22.2	1.93	8.68	2.0	1.18
2000	22.9	1.93	7.91	2.0	1.18

[a] NMP, 300 ppm; H_2O, 55 g; DMF, 10 ml

The effects of chain flexibility on the particle size reduction should be at least two-fold. First, flexible particles are more deformable in shear field[19,20]. During phase inversion, the dispersed phases are broken many times into smaller ones. Second, chain flexibility reduces the solution viscosity, which directly contributes to the fine break-up of the dispersed phase. Assuming stress continuity at the interface, smaller dispersed-phase viscosity leads to greater dispersed-phase deformation according to[21]:

$$\eta_c\gamma_c = \eta_d\gamma_d$$

where η and γ are viscosity and rate of shear, and the subscripts c and d designate continuous and dispersed phase, respectively. These two contribute to the fine break-up of PU ionomer phase in water, leading to a smaller particle size. Conversely, when the particle-size decrease is mainly caused by the increased hydrophilicity, an equilibrium particle size is generally obtained due to the increased swelling of water at high hydrophilicity.

It is widely accepted that the ionic groups are located predominantly on the surfaces of particles and the ionomer dispersions are stabilized by the formation of electrical double layers[1,2]. As the flexibility of PU chain increases with increasing soft segment content, the formation of micelle structure in water, having ionic sites on the surface, will be more plausible. This augments the thickness of electrical double layers due to the effective structuring of the micelles, leading to an increase in effective volume of the dispersed phase of the emulsion. The rate of water swelling also increases as the particle size decreases, due to the increased total surface area of the particles. In addition, at fixed total volume the effective hydrodynamic volume increases with decreasing particle size[22]. These all contribute to the increased effective hydrodynamic volume of the dispersed phase, and the effect should be more pronounced with increasing chain flexibility, leading to a dramatic rise in viscosity with high M_n of PTAd.

Thermal analysis. *Figure 2* shows the d.s.c. thermograms of PUs containing PTAds with different M_n values. Generally, the shorter the segments, the more compatible the hard and soft segments[23]. Therefore soft segments prepared from PTAd of higher M_n are more likely to be phase separated with hard segments. With phase-separated morphology, PTAd can be crystallized. Our d.s.c. thermogram shows the melting peaks for PTAd

Table 2 Effect of M_n of PTAd on emulsion characteristics and film properties

M_n of PTAd	Particle diameter (μm)	Emulsion viscosity (cPs, 20°C)	Hardness (Shore A)	Modulus[a] (kg cm^{-2})		Tensile strength (kg cm^{-2})	Elongation at break (%)	% Swelling (20°C)	
				200%	300%			Water	DMF
600	0.192	10.3	78.1	13.2	10.2	232	311	48	351
1000	0.126	10.8	79.0	20.1	11.3	203	321	57	612
1500	0.107	12.9	90.4	27.8	54.2	291	473	74	836
2000	0.048	42.0	92.2	9.3	7.8	325	582	92	1276

[a] At 200% and 300% elongation

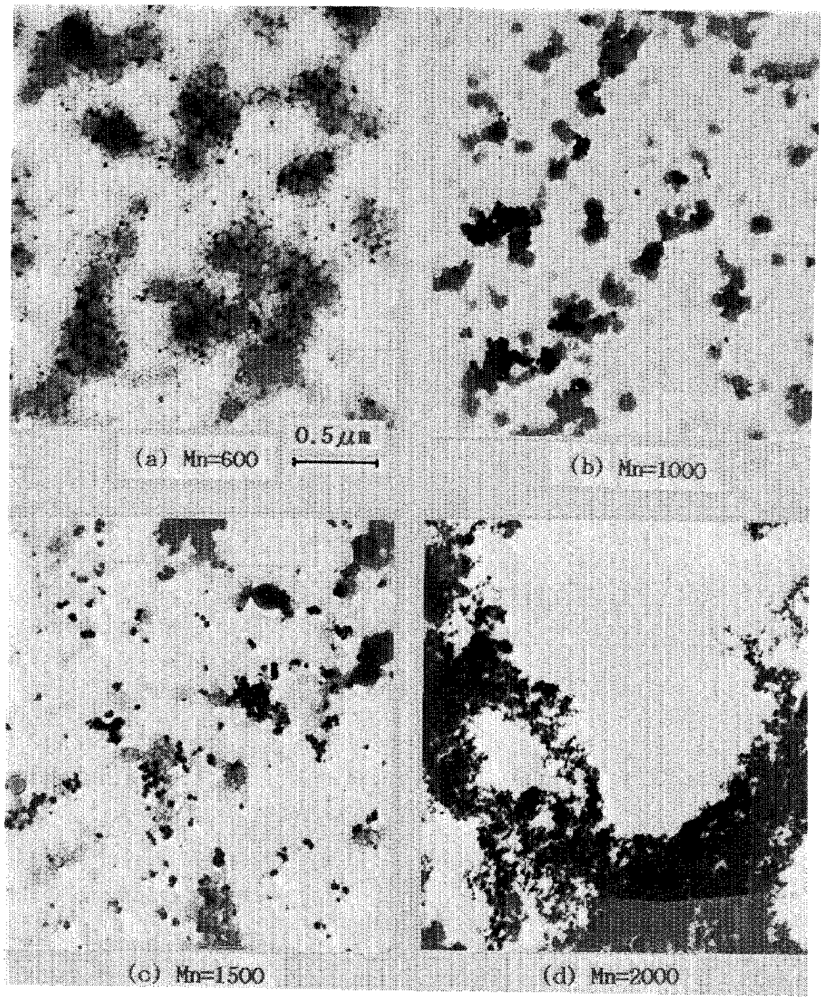

Figure 1 TEM micrographs for PU ionomer dispersions

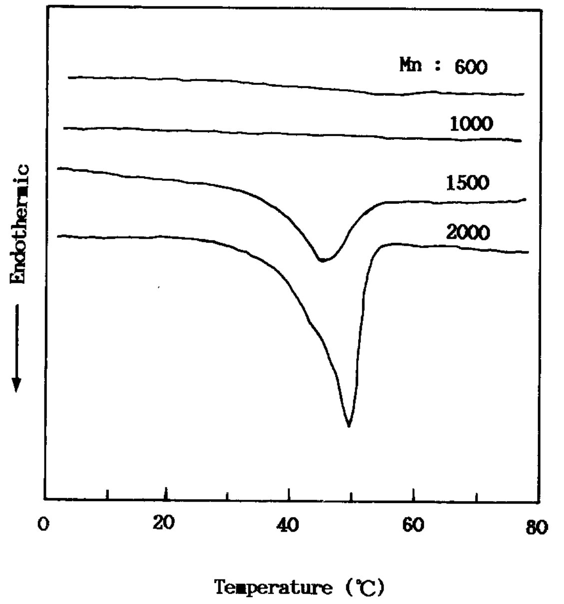

Figure 2 D.s.c. thermograms of the emulsion-cast films

1500 and 2000. Among these two, soft segment crystallization is more perfect and the crystalline melting temperature is higher for PTAd 2000 than for PTAd 1500. The increase of the melting point is attributed to an increase in the size of the crystallites or an increase of complete crystalline phase due to the greater phase separation between the hard and soft segments.

Viscoelastic properties. The dynamic mechanical properties of the emulsion-cast films as a function of temperature are shown in *Figure 3*. The storage moduli (E') (*Figure 3a*) of PU from PTAd 600 and 1000 show similar behaviour to the thermoplastic, whereas those from PTAd 1500 and 2000 show an upturn at about 0°C. The upturn, leading to a higher value of E' at ambient temperature, should be related to the prevention of soft–hard phase mixing and soft segment crystallization[24]. When the phase mixing is relatively complete, the backbone mobility of soft segments is greatly restricted by the hard segments within the soft segments, and the hard segments are solubilized by the soft segments within the hard segments, and lose their effectiveness as a filler or a physical crosslink[23]. The loss modulus (E'') peak (*Figure 3b*) at -25 to -35°C, corresponding to the T_g of the soft segment, is broader at lower M_n of PTAd, especially at PTAd 600, and it moves towards the lower temperature as the M_n of PTAd increases. The decrease of soft segment T_g with increasing M_n of PTAd is due to the increased degree of soft–hard phase separation. A broad shoulder in PTAd 600 is an indication of intimate phase mixing, and the overall effect would be to hinder the motion of soft segments and broaden the distribution of their relaxation times[23]. The peak at about -85°C can be attributed to the relaxation process involving the

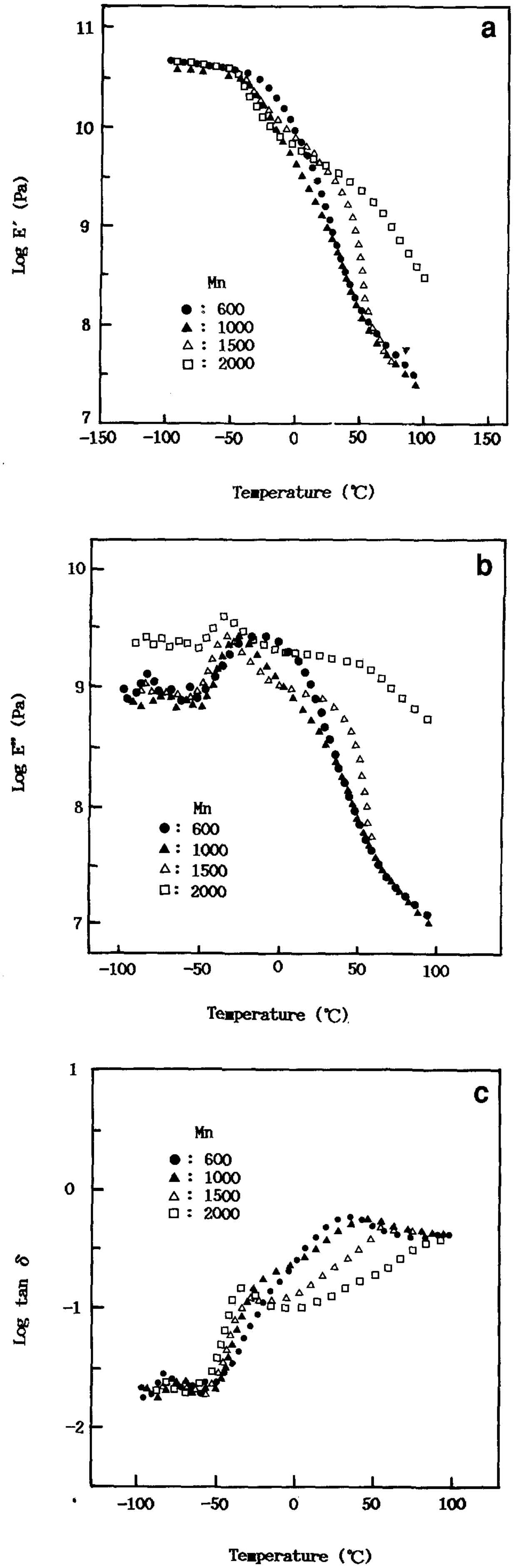

Figure 3 Dynamic mechanical properties of the emulsion-cast films: (a) storage modulus (E'); (b) loss modulus (E''); (c) tan δ

local motion of methylene sequence of the polyester segment[12,13].

The increased phase separation with increasing M_n of PTAd is again demonstrated in the tan δ curve (*Figure 3c*). With the increase of M_n, the lower peak (soft segment or soft-segment-rich phase T_g) moves towards the lower temperature, and the higher peak (hard segment or hard-segment-rich phase T_g) moves towards the higher temperature. The higher peak is defined for PTAd 600 and 1000 only, due to their relatively high hard segment content.

Mechanical properties. The tensile strength and elongation at break (*Table 2*) show that a minimum strength is obtained with PTAd 1000. The basic structure–property relationship in PU states that hard segments affect hardness and strength, and are controlled by the total NCO content[25]. As the M_n of PTAd increases, fewer hard segment and urethane linkages are formed, resulting in decreased strength for PTAd 1000. As the M_n of PTAd increases further, soft–hard phase separation becomes evident and soft segments crystallize. These two factors, i.e. phase separation and soft segment crystallization, contribute to the strength[26]. The increase of elongation with M_n of PTAd comes primarily from the augmented phase separations, which provide PU with more perfect physical networks than in the phase-mixed morphology[23].

Swelling in water and DMF. With the increase of M_n of PTAd from 600 to 2000, swelling in DMF (*Table 2*) increases over five-fold, whereas in water it increases only slightly. The overall hydrophilicity of PU slightly increases with the soft segment content. It seems that DMF is preferentially dissolved in the soft domain. At low M_n ($\leqslant 1000$), swelling is favoured by the amorphous nature of the soft segment, and is retarded by the hard domains dissolved in soft segments. At high M_n, swelling is augmented by phase separation and retarded by the crystallinity of the soft domain; it seems that the former dominates.

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