

The Role of Hard Segments of Aqueous Polyurethane-urea Dispersion in Determining the Colloidal Characteristics and Physical Properties

Tsutomu TAWA[†] and Shinzaburo ITO

Department of Polymer Chemistry, Kyoto University, Nishigyo, Kyoto 615-8510, Japan

(Received December 15, 2005; Accepted March 4, 2006; Published June 9, 2006)

ABSTRACT: A series of aqueous polyurethane-urea dispersions (PUDs) were synthesized to investigate the role of hard segments in determining the colloidal properties in water and the physical properties in PUD films. The chemical structures were modified in terms of, the fraction of the hard segment, the intra-chain distance between hard segments, the amount of ionic COOH group and the type of counterion. The particle size in water decreased with the increase in stabilization of micelles, which was determined by the homogeneity of the distribution of ionic units, flexibility of main chains and hydrophilicity of the neutralized counterions. The physical properties of PUDs were characterized by microphase separation of hard and soft domains. However, the microphase separation structure was not strict at the molecular chain level, that is, the hard domains containing some soft segments and the soft domains containing hard segments existed. The presence of the soft segment in the hard domain lowered the glass transition temperature of the hard domain, consequently affecting the mechanical strength etc., depending on the chain length of soft segment, the content of ionic units, and also on the bulkiness of the counterions. These results will be useful for designing molecular structures of PUDs to obtain the best performance for various applications. [doi:10.1295/polymj.PJ2005193]

KEY WORDS Aqueous Polyurethane-urea Dispersion (PUD) / Microphase Separation / Hard Segment / Colloidal Characteristic / Physical Property /

Polyurethane is a unique polymeric material with a wide range of physical and chemical properties. It has been used in various fields, such as foams, coatings, adhesives, and thermoplastic elastomers. These properties originate from the microphase separation structure in polyurethane films because the polyurethane chain consists of soft and hard segments as shown in Figure 1. A hard domain formed by hydrogen bonding of hard segments provides properties of both physical crosslinkage and filler-like reinforcement.^{1–7}

Recently, aqueous polyurethane-urea dispersion (PUD) is gathering considerable attention due to the growing concern to preserve the environment.^{8–15} PUD can be prepared by introducing ionic moieties into a polyurethane, neutralizing and then dispersing them into water if a sufficient amount of the ionic moiety is incorporated. The presence of an ionic group in the hard segment has a considerable effect on its physical properties and it is reasonable to suppose that the interaction between acid groups and their counterions is responsible for these effects. The degree of neutralization,^{16–19} the type of counterion,^{20–24} and the amount of ionic compound^{25,26} significantly influence the physical properties.

In this paper, we report the role of the hard segment of PUD investigated by using a few series of PUDs, which were prepared to have different distances and fractions of hard segments, the amount of ionic groups

and the type of counterions. After examining the colloidal characteristics and the physical properties of these PUDs in relation to the chemical structures, we discuss the role of hard segments from the molecular side.

EXPERIMENTAL

Materials

Polycarbonate diol (PC) was dried under N₂ bubbling at 75 °C for 4 h. 2,2-Dimethyl-1,3-propanediol (NPG, Wako Pure Chemical Industries, Ltd.) was dried under an N₂ atmosphere for more than 3 days. 1,3-Bis(isocyanatomethyl)cyclohexane (H6XDI, Mitsui-Takeda Chemical Industries, Ltd.), dimethylol propionic acid (DMPA), hydrazine monohydrate (HD, Wako Pure Chemical Industries, Ltd.), triethylamine (TEA, Wako Pure Chemical Industries, Ltd.), triisopropanolamine (TIPA, Wako Pure Chemical Industries, Ltd.), 2-dimethylaminoethanol (DMEA, Wako Pure Chemical Industries, Ltd.) and sodium hydrate (NaOH, Wako Pure Chemical Industries, Ltd.) were used without further purification.

Preparation of Aqueous Polyurethane-urea Dispersion

PUD was prepared as follows. A 500 mL four-neck round-bottom flask equipped with a stirrer, a ther-

[†]To whom correspondence should be addressed (Tel: +81-75-383-2614, Fax: +81-75-383-2617, E-mail: tawa@photo.polym.kyoto-u.ac.jp).

The Role of Hard Segment in PUD

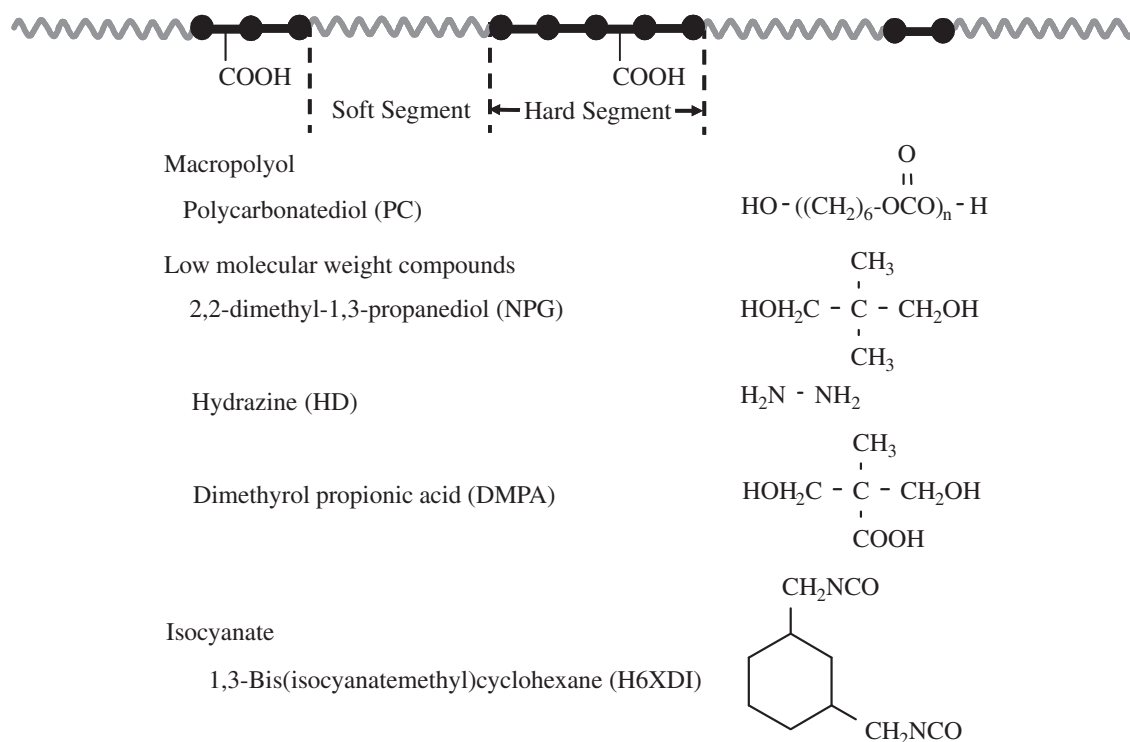


Figure 1. Schematic polyurethane-urea chain.

meter, a nitrogen inlet, and a condenser was charged with H6XDI (194.00 g, 1.0 mol) and acetonitrile (217.01 g) under nitrogen atmosphere. PC ($M_n = 2,000$, 246.91 g, 0.123 mol), NPG (25.73 g, 0.247 mol) and DMPA (39.70 g, 0.296 mol) were then added while stirring slowly, and the mixture was heated to 70 °C. They were allowed to react until the theoretical NCO content was detected by the dibutylamine back-titration method (ASTM D 1638). The NCO-terminated prepolymer thus obtained was poured into an aqueous solution of tertiary amines or NaOH as the neutralizing agent (counterions) under constant agitation (2,000 rpm). This dispersion was kept at 20 °C for 20 min to complete the neutralization reaction. DMEA, TEA, TIPA and NaOH were used as counterions. The stoichiometric ratio of counterions to COOH was 0.95. The neutralized NCO terminated polyurethane prepolymer was extended by adding a 10% hydrazine monohydrate solution. The stoichiometric ratio of the amine group of hydrazine to NCO of the prepolymer was 0.95. The PUD (30 wt % concentration) was obtained by the evaporation of acetonitrile and then by adding an adequate amount of water. Table I shows the sample designation and composition. Samples were named so that, for example in DM-20-2, the initial letter 'DM' refers to the counterion DMEA, 20 to the molecular weight 2000 of PC, and 2 to the COOH group weight content (%) in this polyurethane-urea dispersion.

Film Preparation

Film samples for mechanical and viscoelastic measurements were prepared by casting the dispersions on a metal plate under ambient conditions. The films (about 0.1 mm thickness) were dried for longer than 1 d to avoid producing foam or bubbles in the film at annealing. When the aqueous dispersion forms the transparent film, the film formation process consists of three steps, water evaporation, particle deformation and particle coalescence.^{27–29} The mechanical properties are influenced by the condition of the film formation process. Furthermore, the microphase separation state also affects the mechanical properties, since the polyurethane, consisting of a soft and hard segment, takes the microphase separation structure. The film formation process and the microphase separation state are influenced by temperature being one of the annealing conditions. The temperature dependency of mechanical properties examined using DM-20-2 for 1 annealing hour showed the almost the same stress-strain (SS) curves above 110 °C. This result indicates that the disconnected PUD particles fully coalesce, are diffused mutually and formed the transparent film with the stable microphase separation structure above 110 °C for 1 annealing hour. On the basis of this experimental data, the annealing condition was determined at 130 °C for 1 h.

Measurements

The average particle size was measured by light

Table I. The designation and composition (mol ratio) of aqueous polyurethane-urea dispersions (PUD)

PUD	Polymer composition (mol ratio)				Counterion (0.95 eq.)	COOH weight content (%)	Hard segment weight fraction (%)
	H6XDI	PC	NPC	DMPA			
Series M							
DM-20-2	8.1	1	2	2.4	DMEA	2.6	52.6
DM-10-2	9.6	2	2	2.4	DMEA	2.4	55.8
DM-10-2H	8.1	1	2.6	1.8	DMEA	2.5	68.7
Series C							
DM-20-1	8.1	1	2.9	1.5	DMEA	1.6	52.3
DM-20-2	8.1	1	2	2.4	DMEA	2.6	52.6
DM-20-3	8.1	1	1	3.4	DMEA	3.6	52.9
Series N							
DM-20-2	8.1	1	2	2.4	DMEA	2.6	52.6
TE-20-2	8.1	1	2	2.4	TEA	2.6	52.6
TI-20-2	8.1	1	2	2.4	TIPA	2.6	52.6
Na-20-2	8.1	1	2	2.4	Na	2.6	52.6

The polyurethane prepolymer was prepared at NCO:OH = 1.5:1 ratio. The PUD was prepared by the chain-extending reaction between NCO group of polyurethane prepolymer and NH₂ group of hydrazine monohydrate. The ratio of NCO group of polyurethane prepolymer to NH₂ group of hydrazine monohydrate is 1 to 0.85.

scattering (Coulter N4 Plus), where a He–Ne laser with a wavelength of 632.8 nm was used. The sample was diluted in deionized water to adjust the concentration for measurement.

Viscoelastic properties of films were measured at 10 Hz using a DVA-200 instrument (IT Keisokuseigyō) at a heating rate of 5 °C/min in the temperature range from –100 to 200 °C.

Mechanical properties were measured at 25 °C using INTESCO Model 205 following the ASTM D-412 specifications. A crosshead speed of 300 mm/min was used throughout these investigations to determine the ultimate tensile strength and elongation at break for all the samples. The values quoted are the average of five measurements.

RESULTS AND DISCUSSION

Distance and Fraction of Hard Segment

In the polyurethane-urea molecule, the hard segment consists of urethane linkage generated by the reaction between H6XDI and low molecular weight diol or HD, and the soft segment is formed from macropolyol PC as shown in Figure 1. In a solid film, the hard segments aggregate by hydrogen bonding and form a hard domain. Therefore, the fraction of the hard segment in a polymer chain affects the number and the size of the hard domain. On the other hand, the length of soft segment, which is dependent on the PC molecular weight, determines the distance between the hard segments. In order to consider the influence of fraction and distance of the hard segments, three samples were prepared. Table I shows the specifications for these samples (Series M: DM-20-2, DM-10-2 and DM-10-

2H). The length of the soft segment in DM-20-2 was different from that in DM-10-2, but the weight fraction of the hard segment was kept constant by adjusting low molecular weight diols. Therefore, the mol ratio of PC in DM-10-2 was twice that in DM-20-2. In contrast, the mol ratio of PC to low molecular weight diol (NPG and DMPA) was kept constant for DM-20-2 and DM-10-2H, consequently increasing the weight fraction of the hard segment from 52.6 to 68.7. The last letter 'H' of DM-10-2H indicates that DM-10-2H has a larger hard segment fraction than the other samples. The differences of the three samples are schematically illustrated in Figure 2.

First, we discuss the colloidal characteristics of PUDs. Table II shows the particle sizes of the PUDs. By comparing the particle sizes of DM-20-2 and DM-10-2H, we found that the particle size increases as the molecular weight of soft segment decreases. It is known that the ionic groups are located predominantly on the surface of particles and the ionomer dispersions are stabilized by the formation of electrical double layers. As the polyurethane chain becomes harder with decreasing length of soft segment, the formation of polymer micelles in water needs more chains to stabilize the micelle structure. In contrast with this result, the particle size decreased with the decrease of the soft segment length from DM-20-2 to DM-10-2 while the weight fraction of soft segment is fixed. This result was explained as an effect of homogeneous COOH group in a molecule. The smaller the molecular weight of PC is, the more uniformly the COOH group can be distributed. The uniform distribution of COOH group makes the formation of micelle easy, consequently the particle size becomes small.

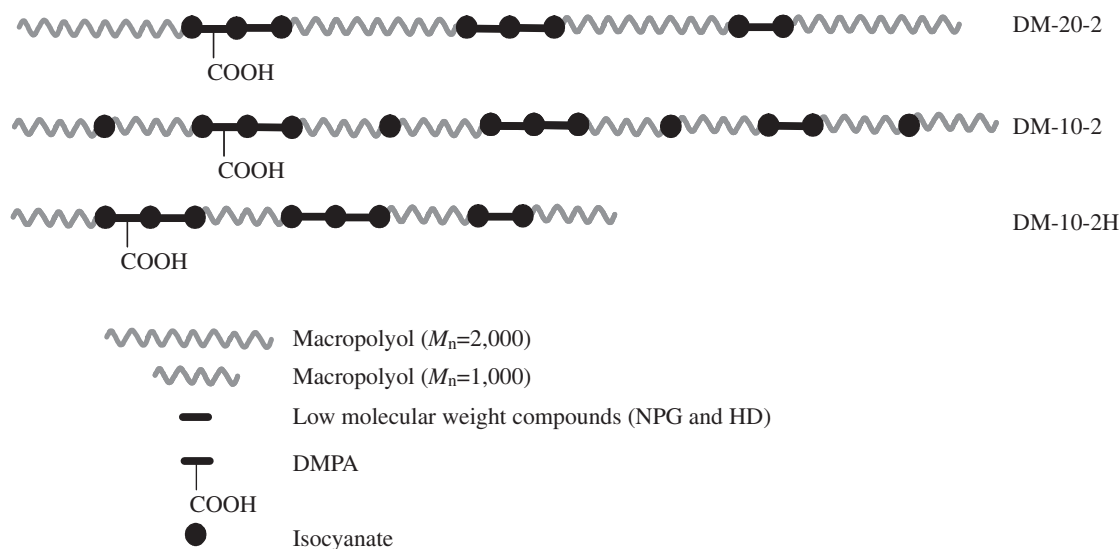


Figure 2. Illustration of the difference among three samples: DM-20-2 (top), DM-10-2 (middle) and DM-10-2H (bottom).

Table II. The colloidal and physical properties of aqueous polyurethane-urea dispersions (PUDs)

Sample	Particle size (nm)	T_{gs} ($^{\circ}\text{C}$)	T_{gh} ($^{\circ}\text{C}$)	Tensile strength (MPa)	Young's modulus (MPa)	Strain at break (%)
Series M						
DM-20-2	55.7	-29.0	118	47.2	236	388
DM-10-2	23.0	-14.5	105	50.6	313	391
DM-10-2H	115.0	-7.0	122	57.2	388	17
Series C						
DM-20-1	99.2	-28.7	116	47.8	200	365
DM-20-2	55.7	-29.0	118	47.2	236	388
DM-20-3	44.1	-28.3	122	46.6	271	335
Series N						
DM-20-2	55.7	-29.0	118	47.2	236	388
TE-20-2	112	-28.5	108	43.7	296	386
TI-20-2	57.6	-28.0	108	40.4	229	373
Na-20-2	49.0	-28.5	130	52.0	210	390

In viscoelastic properties, there are large differences among the three samples, as shown in Figure 3. Table II shows the T_g values determined from the maxima of $\tan \delta$. Two peaks are observed in the $\tan \delta$ curves. The lower temperature peak is considered as the glass transition temperature of the soft domains (T_{gs}) and the higher temperature peak is that of hard domains (T_{gh}). The comparison between DM-20-2 and DM-10-2 indicates that T_{gh} of DM-20-2 is higher than that of DM-10-2 and T_{gs} is opposite. These results can be explained as shown in Figure 4. Some hard segments existed in the soft domains and some soft segments existed in the hard domains, because the hard segments were more uniformly distributed in DM-10-2 due to the short length of the soft segment. Therefore, T_{gs} increases under the influence of hard segments and T_{gh} decreases under the influence

of soft segments.

DM-10-2H had the highest T_{gs} among the three samples due to the largest fraction of hard segments. It is interesting that T_{gs} s were quite different but T_{gh} s were almost the same at 120°C for DM-20-2 and DM-10-2H. These results obtained on DM-20-2 show that there are few soft segments in the hard domains, and the phase separation proceeds almost completely both in the hard and soft domains.

Figure 5 and Table II show the mechanical properties of these three samples DM-10-2H shows the most peculiar stress-strain curve of the three samples. The largest Young's modulus (388 MPa) and extremely small elongation are caused by the high fraction of hard segment in DM-10-2H. On the other hand, although the length of the soft segment is short in DM-10-2, it shows almost the same elongation as

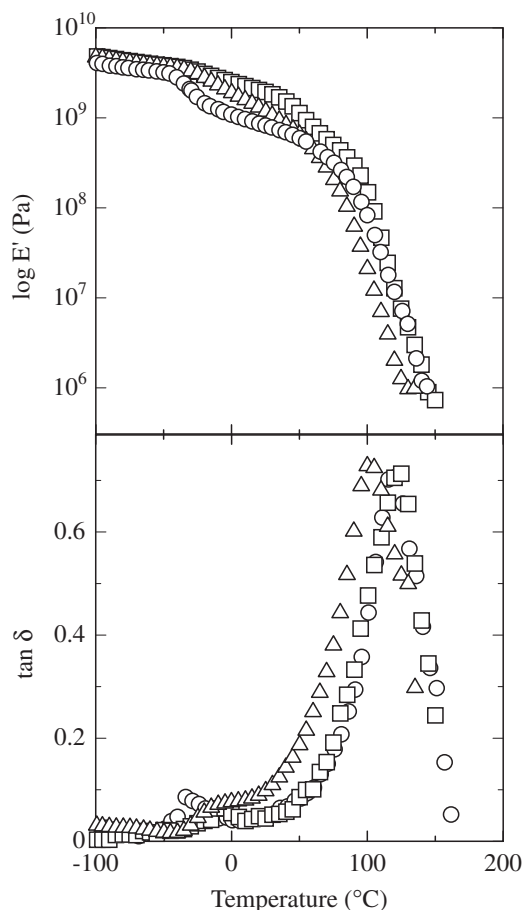


Figure 3. Storage modulus (E') and $\tan \delta$ for PUDs: (○) DM-20-2, (△) DM-10-2, (□) DM-10-2H.

DM-20-2. This result shows that two PCs connected by urethane linkage, as shown in Figure 2, behave as a long chain of the soft segment to large deformation. However, the Young's modulus has a big difference between DM-10-2 (313 MPa) and DM-20-2 (236 MPa). This is the contribution as the hard segment of the urethane linkage connecting two PCs. Therefore, the hard segment has larger influence in minute deformation.

Amount of Ionic Compounds

In the previous section, we focused on the distance

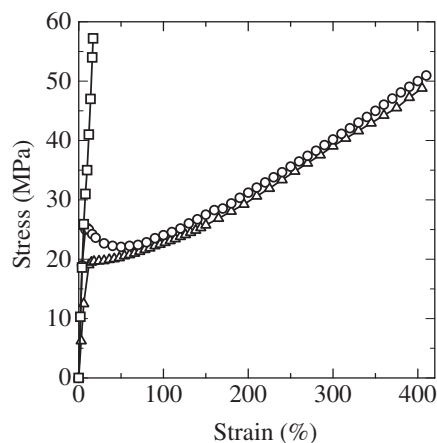


Figure 5. Stress-strain curves for PUDs: (○) DM-20-2, (△) DM-10-2 and (□) DM-10-2H.

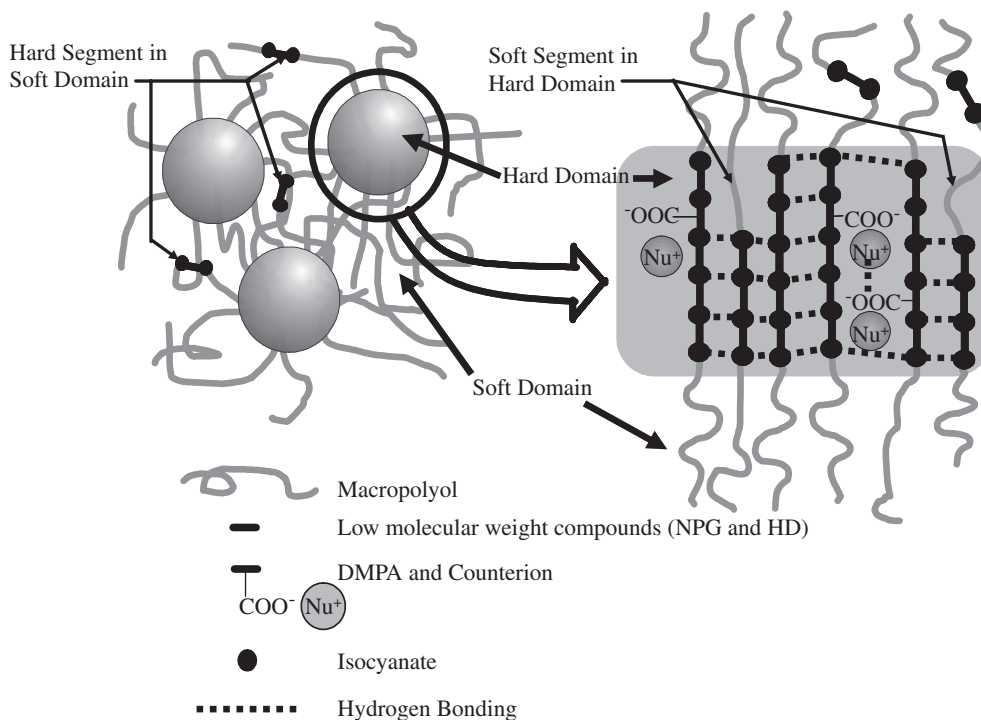


Figure 4. Schematic illustration for the microphase separation structure of a film produced from the PUD.

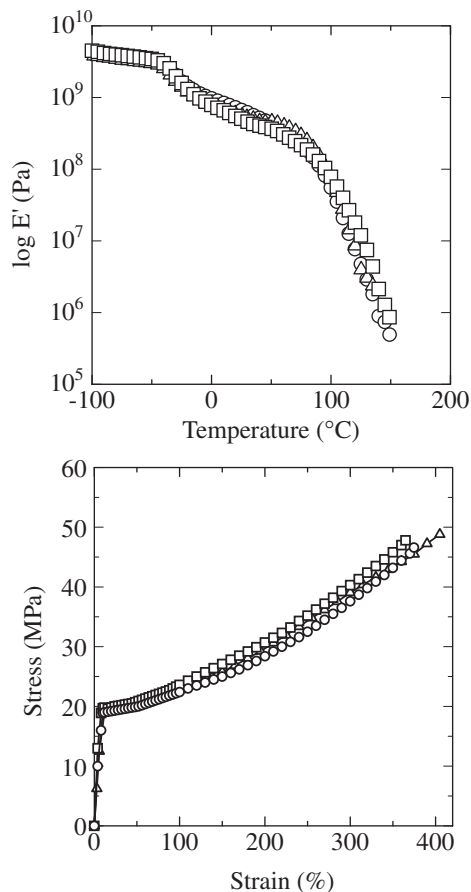


Figure 6. Storage modulus (E') and stress-strain curves for PUDs with different amounts of COOH group: (○) DM-20-1, (△) DM-20-2 and (□) DM-20-3.

and the fraction of hard segments in a polyurethane chain. In this section, we changed the amount of ionic COOH group in order to examine the cohesive force of the hard segment. The three samples of series C in Table I (DM-20-1, DM-20-2 and DM-20-3) were prepared to have COOH contents of 1.6, 2.6, or 3.6 wt % based on total solid. In colloidal characteristics, particle size decreased with increasing COOH content, as shown in Table II. Since the particle is stabilized by the hydrophilic groups in PUD,⁸ it is natural for the particle size to become smaller as the COOH content increases.

Figure 6 shows the dynamic modulus and the stress-strain curves of three samples, and Table II shows T_{ghs} . As shown in Table I, the hard segment fractions were almost the same among the three samples. Dynamic modulus, stress-strain curves and Young's modulus hardly changed among the three samples even when the content of hydrophilic DMPA increased. Only T_{gh} slightly rises with the increase of COOH content. These results show that microphase separation proceeds completely when the length of soft segment is long. Perhaps the COOH group contributes to promote microphase separation more strongly as com-

pared with other nonionic species. However, in this experiment the condensed state of hard segments was not influenced by the COOH content, since microphase separation proceeds depending completely on the presence of long chain hydrophobic PC.

Type of Counterion

The type of counterion also affects the physical properties of PUDs. In this section, we discuss series N in Table I. As to colloidal characteristics, TE-20-2 with the TEA counterion had a large particle size (112 nm) in comparison with the other dispersions with Na, DMEA and TIPA counterions. TEA had the weakest hydration ability among them because it has the hydrophobic ethylene group, but DMEA and TIPA have the hydrophilic hydroxyl units. Na-20-2 has the smallest particle size because it has the strongest hydrated ability of metal cations among the four samples.

Figure 7 shows the $\tan \delta$ values and the stress-strain curves of N-series samples. T_{gs} of four samples are almost the same, because the same PC was employed as the soft segment. On the other hand, T_{ghs} and mechanical properties were in the decreasing order

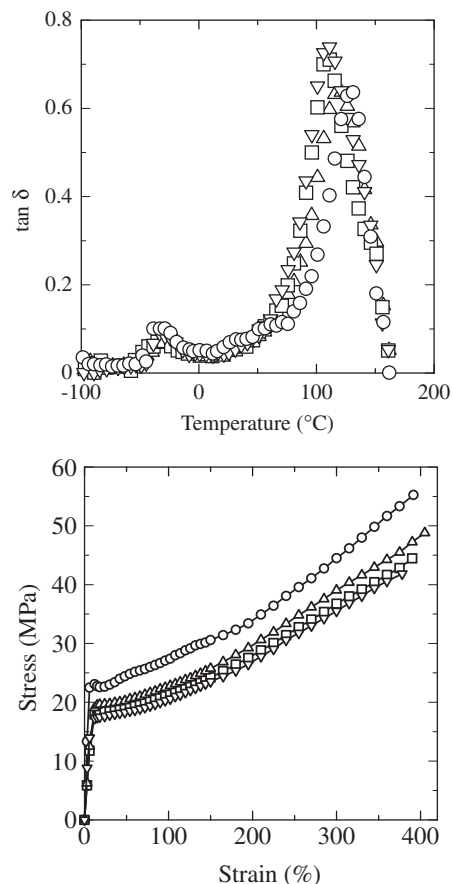


Figure 7. $\tan \delta$ and stress-strain curves for PUDs with different counterions: (○) Na-20-2, (△) DM-20-2, (□) TE-20-2 and (▽) TI-20-2.

of Na, DMEA, TEA and TIPA. These results indicate that counterions affect the condensed state of the hard segment. Assuming that the size of counterion is proportional to the molecular weight, their size increases in the order of Na (23), DMEA (89), TEA (101), and TIPA (192). This is consistent with the order of T_{gh} s, suggesting that the mechanical properties and Young's modulus are subjected to the plasticizing capacity of the counterion. It exists near the COOH group in the hard domains as shown in Figure 4, and the effect as a plasticizer in the hard domain becomes larger as its size becomes large, resulting in a weak cohesive force between the hard segments.

CONCLUSION

Differences in the fraction and distance of hard segments, the amount of COOH groups and the type of counterions appeared as the colloidal characteristics and physical properties of three series of PUDs.

The hard segment affected the colloidal characteristics of PUD. The increase in the fraction of hard segment enlarged the particle size of PUD micelles, because the polyurethane chain becomes harder with increasing fraction of hard segment and the formation of polymer micelles in water needs more chains to stabilize the micelle structure. Under a certain fraction of the hard segment, the homogeneous distribution of COOH group in the polyurethane chain results in a small particle size. The amount of COOH groups as hydrophilic unit also influenced the particle size of PUD, indicating that the larger amount of COOH groups led to the smaller particle size of PUD. Moreover, the hydrophilicity and hydration ability of the counterions affected the particle size of PUD.

In physical properties, the role of the hard segment is more important. The results of viscoelastic measurement showed that PUD had a microphase separation structure and two T_g s: T_{gh} derived from the hard domain and T_{gs} from the soft domain. The distance of the hard segments affected the microphase separation structure, resulting in an increase in T_{gs} and decrease in T_{gh} by the mutual penetration of the hard and soft segments into the soft and hard domains with the reduction of the distance between the hard segments. In mechanical properties, the influence of the hard segment appears most clearly in the Young's modulus. And the increase of the fraction of hard segment led to the high modulus and short elongation.

The component in hard segments, such as the amount of the COOH unit and the type of counterions, influenced the T_{gh} . The T_{gh} slightly rose with the increase of COOH content due to promotion of micro-

phase separation by hydrogen bonding of the ionic COOH species. Furthermore, T_{gh} and Young's modulus were influenced by the plasticizing capacity proportional to the size of counterion.

These experimental results indicate that the detailed internal structure in the hard domain, as illustrated in Figure 4, is important knowledge for designing the chemical structure of PUDs.

REFERENCES

1. S. Sakurai, Y. Okamoto, H. Sakaue, T. Nakamura, L. Banda, and S. Nomura, *J. Polym. Sci., Part B: Polym. Phys.*, **38**, 1716 (2000).
2. W. Tang, R. J. Farries, W. J. Macknight, and C. D. Eisenbach, *Macromolecules*, **27**, 2814 (1994).
3. G. Consolati, M. Levi M, and S. Turri, *Polymer*, **42**, 9723 (2001).
4. M. F. Sonnenschein, N. Rondan, B. L. Wendt, and J. M. Cox, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 2715 (2004).
5. D. J. Martin, G. F. Meijs, G. M. Renwick, S. J. Mccarthy, and P. A. Gunatillake, *J. Appl. Polym. Sci.*, **62**, 1377 (1996).
6. H. Tan, M. Guo, R. Du, X. Xie, J. Li, Y. Zhong, and Q. Fu, *Polymer*, **45**, 1647 (2004).
7. L. F. Wang and Y. H. Wei, *Colloids Surf., B*, **41**, 249 (2005).
8. D. Dieterich, *Prog. Org. Coat.*, **9**, 281 (1981).
9. S. Asaoka, T. Sakurai, M. Kitajima, and H. Hanazawa, *J. Appl. Polym. Sci.*, **73**, 741 (1999).
10. B. K. Kim and J. C. Lee, *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 1095 (1996).
11. S. Turri, M. Levi, and T. Trombetta, *J. Appl. Polym. Sci.*, **93**, 136 (2004).
12. Y. S. Kwak, S. W. Park, Y. H. Lee, and H. D. Kim, *J. Appl. Polym. Sci.*, **89**, 123 (2003).
13. T. Tawa and S. Ito, *Colloid Polym. Sci.*, **283**, 731 (2005).
14. Y. M. Lee, J. C. Lee, and B. K. Kim, *Polymer*, **35**, 1095 (1994).
15. D. J. Hourston, G. Williams, R. Satguru, J. D. Padget, and D. Pears, *J. Appl. Polym. Sci.*, **66**, 2035 (1997).
16. D. J. Hourston, G. D. Williams, R. Satguru, J. C. Padget, and D. Pears, *J. Appl. Polym. Sci.*, **74**, 556 (1999).
17. S. L. Hsu, H. X. Xiao, H. H. Szmant, and K. C. Frisch, *J. Appl. Polym. Sci.*, **29**, 2467 (1984).
18. J. E. Yang, J. S. Kong, S. W. Park, D. J. Lee, and H. D. Kim, *J. Appl. Polym. Sci.*, **86**, 2375 (2002).
19. D. C. Lee, R. A. Register, C. Z. Yang, and S. L. Cooper, *Macromolecules*, **21**, 1005 (1988).
20. Y. Chen and Y. L. Chen, *J. Appl. Polym. Sci.*, **46**, 435 (1992).
21. S. A. Chen and J. S. Hsu, *Polymer*, **34**, 2769 (1993).
22. Y. S. Kwak, S. W. Park, and H. D. Kim, *Colloid Polym. Sci.*, **281**, 957 (2003).
23. H. A. Al-salah, K. C. Frisch, H. X. Xiao, and J. A. Mclean Jr., *J. Polym. Sci., Part A: Polym. Chem.*, **25**, 2127 (1987).
24. S. A. Chen and J. S. Hsu, *Polymer*, **34**, 2776 (1993).
25. B. K. Kim and J. C. Lee, *Polymer*, **37**, 469 (1996).
26. H. Xiao, H. X. Xiao, K. C. Frisch, and N. Malwitz, *J. Appl. Polym. Sci.*, **54**, 1643 (1994).

27. Y. Wang, C. L. Zhao, and M. A. Winnik, *J. Chem. Phys.*, **95**, 2143 (1991).
28. E. M. Boczar, B. C. Dionne, Z. Fu, A. B. Kirk, P. M. Lesko, and A. D. Koller, *Macromolecules*, **26**, 5772 (1993).
29. Y. Wang and M. A. Winnik, *J. Phys. Chem.*, **97**, 2507 (1993).