

Preparation and Properties of Waterborne Polyurethane-Urea Anionomers. I. The Influence of the Degree of Neutralization and Counterion

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ABSTRACT: Two series of waterborne polyurethane-urea anionomers were prepared by a polyaddition reaction with isophorone diisocyanate, poly(tetramethylene oxide) glycol (weight-average molecular weight = 1000), dimethylol propionic acid (DMPA), and ethylene diamine as chain extenders. Triethylamine (TEA) or 28:1 mol/mol ammonium hydroxide (NH₄OH)/cupric hydroxide [Cu(OH)₂] was used as a neutralization agent [NH(C₂H₅)₃⁺ or NH₄⁺/Cu²⁺ counterion] for the pendant COOH group of DMPA. The effects of the degree of neutralization and counterion on the particle size of the dispersions, the conductivity, and the antibacterial and mechanical properties of polyurethane-urea anionomer films were investigated. The particle sizes of the two sample series dispersions decreased with an increasing degree of neutralization. Aqueous dispersions of polyurethane-urea anionomers with particle sizes of 30–120 nm

were stable for about 3 months. By infrared spectroscopy, it was found that TEA-based samples (T series) had higher fractions of hydrogen-bonded carbonyl groups in the ordered region than NH₄OH/Cu(OH)₂-based samples (S series). However, the fractions of hydrogen-bonded carbonyl groups in the disordered region of the S-series samples were higher than those of the T-series samples. The conductivities of the S-series film samples were higher than those of the T-series samples. However, the T-series film samples commonly had higher tensile strengths and initial moduli than the S-series samples. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2375–2383, 2002

Key words: waterborne; polyurethanes; neutralization agent; hydrogen bonding

INTRODUCTION

Waterborne polyurethane ionomers have been developed out of increasing concern over environmental pollution, health, and safety risks. Polyurethane ionomers contain a minor component carrying pendant acid or tertiary nitrogen groups (<10 mol %) that are completely or partially neutralized or quaternized, respectively, to form salts. One important feature of polyurethane ionomers is their ability to disperse or dissolve in water if a sufficient amount of the ionic moiety is incorporated,^{1,2} and this is a great advantage over conventional solvent-borne polyurethanes. The presence of ionic moieties in ionomers has a strong effect on their many properties.³

Polyurethane ionomers have received considerable attention in the past few decades because of their applications in coatings and adhesives for various substrates.^{4,5} The applications of polyurethane ionomers have rapidly increased in recent years. The structure-property relations of ionomers containing a small fraction of ionic repeat units have been the subject of numerous articles

and reviews. It is well recognized that a minimum ionic content is required for the formation of stable polyurethane dispersions, depending on the type of ionic species. In addition, the interactions between ions and their counterions are responsible for these effects.⁶

The degree of neutralization,⁷ the type of ionic component,⁸ and the counterion⁹ contributed significantly to the properties of polyurethane ionomers. Chen and Chen¹⁰ investigated the effects of neutralization agents [ammonia, trimethylamine, triethylamine (TEA), LiOH, NaOH, and KOH] on the properties of polyurethane anionomer dispersions. They found that dispersions containing metal cations always results in smaller particle sizes than dispersions containing ammonia cations. Hourston et al.¹¹ reported on the influence of the degree of neutralization, the ionic moiety, and the counterion on waterborne, dispersible polyurethanes. They also discovered that the degree of neutralization, the type of ionic component, and the counterion all contribute significantly to the properties of polyurethane ionomers. However, research on the influence of the counterion Cu²⁺ on the properties of waterborne polyurethane anionomers can hardly be found.

It is well known that unique properties of thermoplastic polyurethanes are obtained from the structures and compositions of components,^{12,13} the preparation methods, and the microphase separation of incompatible soft and hard segments that result in a hard-segment do-

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main, a soft-segment matrix, and a poorly characterized interphase. The nature of the hydrogen bonding of hard segments causes a strong mutual attraction leading to domain formation. Infrared spectroscopy has been employed extensively to study the hydrogen bonding and is a useful tool for characterizing the characteristics of hydrogen bonding in domains.^{14–16} The values of hydrogen bonding identified by a frequency shift are lower than those corresponding to the free groups (i.e., no hydrogen-bonded C=O and N—H groups). The magnitude of the frequency shift is usually used as an estimate of the hydrogen-bonding strength. Some researchers have reported that the band centered around 1725 cm^{-1} is attributable to the stretching of urethane carbonyl groups, whereas the urethane carbonyl stretching around 1710 cm^{-1} is due to hydrogen bonding in disordered regions.^{17,18} This urethane carbonyl stretching around 1710 cm^{-1} is attributable to the carbonyl participating in the urethane linkage of interfacial regions or being dissolved in the soft phase. The stretching of the stronger hydrogen bonds in ordered or crystalline regions occurs at a lower frequency around 1695 cm^{-1} . The band centered near 1665 cm^{-1} is assigned to the stretching of hydrogen-bonded carboxylic carbonyl groups, which come from the dimethylol propionic acid (DMPA) unit.

In this research, we investigated the preparation and properties of waterborne polyurethane ionomers from isophorone diisocyanate (IPDI), poly(tetramethylene oxide) glycol (PTMG), DMPA, and ethylene diamine (EDA) as chain extenders and TEA and 28:1 ammonium hydroxide (NH_4OH)/cupric hydroxide [$\text{Cu}(\text{OH})_2$] as neutralization agents. Infrared spectroscopy^{14–18} was used to assign the different kinds of hydrogen-bonded carbonyl groups in the polyurethane–urea anionomers prepared in this study. The effects of the types of neutralization agents and the degree of neutralization on the conductivity and antibacterial and mechanical properties were studied. In particular, we looked at the influence of TEA and $\text{NH}_4\text{OH}/\text{Cu}(\text{OH})_2$ on the properties.

EXPERIMENTAL

Materials

IPDI (Merck Co., Darmstadt, Germany), DMPA (Aldrich Chemical, Milwaukee, WI), TEA (Aldrich Chemical), NH_4OH (Aldrich Chemical), $\text{Cu}(\text{OH})_2$ (Aldrich Chemical), and *N*-methyl 2-pyrrolidinone (NMP; Aldrich Chemical) were used. EDA was dried over 4-Å molecular sieves, and PTMG [weight-average molecular weight = 1000; Aldrich Chemical] was degassed at 70°C under vacuum overnight.

Preparation of the waterborne polyurethane–urea anionomers

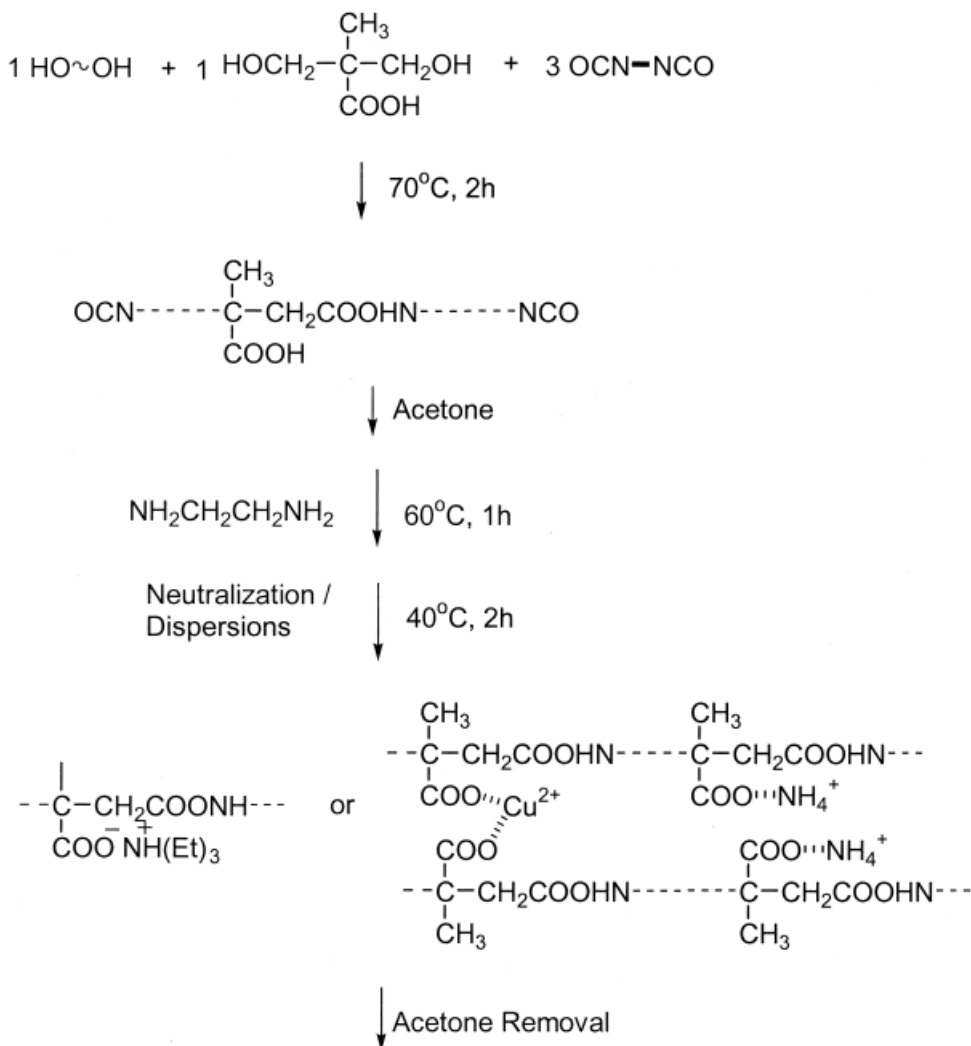
Two series of aqueous dispersions of polyurethane–urea anionomers were prepared as follows (Scheme 1). DMPA was dissolved in NMP (50/50 w/w) in a four-necked, round-bottom flask equipped with a thermometer, a stirrer, an inlet of dry nitrogen, a condenser, and a heat jacket. Then, PTMG was placed in the flask and degassed under vacuum at 60°C for 1 h. IPDI/acetone (12 g/5.6 g) was added slowly under moderate stirring, and the mixture was allowed to react at 70°C until the theoretical NCO content was reached, as described in the dibutylamine backtitration method. It took about 2 h to reach the theoretical value. The NCO-terminated prepolymer was chain-extended by EDA being dropped at 60°C for 1 h, and the reaction continued until the NCO absorption peak (2270 cm^{-1}) in infrared spectra had completely disappeared. The dispersion and neutralization were carried out simultaneously by the addition of distilled water/TEA or 28:1 mol/mol $\text{NH}_4\text{OH}/\text{Cu}(\text{OH})_2$ at a temperature below 40°C for 2 h under vigorous stirring. All the aqueous dispersions (30 wt % solids) were obtained by the evaporation of acetone. The sample designation and composition of the waterborne polyurethane–urea anionomers are listed in Table I. All samples contained the same hard-segment composition (molar ratio). Meanwhile, TEA and 28:1 mol/mol $\text{NH}_4\text{OH}/\text{Cu}(\text{OH})_2$ were used as neutralization agents for T-series and S-series samples, respectively. From the preliminary experiments, it was found that 40% neutralization was nearly the minimum value for the formation of a stable dispersion. Therefore, the degree of neutralization was varied from 40 to 100% in this study.

Films for testing were prepared by the dispersions being cast onto a Teflon disk under ambient conditions. The films (typically ca. 0.5 mm thick) were allowed to dry at 50°C for about 1 day. The remaining moisture was removed at 60°C under 20 mmHg for 2 days.

Measurements

The particle size of the dispersions was determined with an autosizer (Malvern IIC, Malvern, Worcs, UK). Approximately 0.15 mL of an emulsion was diluted with deionized water to an appropriate concentration in the cell, and this was followed by the pinhole being set at 200 μm . The average particle diameters were measured at 25°C.

Fourier transform infrared spectra were acquired with a Fourier transform infrared spectrometer (Impact 400D, Nicolet, Madison, WI). For each sample, 32 scans at a 4- cm^{-1} resolution were collected in the absorption mode. The total fraction¹⁵ of the carbonyl absorption group participating in hydrogen bonding



Aqueous Dispersions of Polyurethane Anionomer

Scheme 1 Preparation process for polyurethane dispersion.

is expressed as $X_B = C_B/C_T$, where C_T is the total peak area of carbonyl groups and C_B is the peak area of hydrogen-bonded carbonyl groups.

Tensile properties were measured at room temperature with a United Data System (Instron SSTM-1, Canton, MA) tensometer according to the

TABLE I
Sample Designation and Composition (Molar Ratio) of Waterborne Polyurethane-Urea Anionomer and Their Particle Sizes

Sample designation	Degree of neutralization (%)	IPDI	PTMG (M_w -1000)	DMPA	EDA	Neutralization agent			Particle size (nm)
						TEA	NH ₄ OH	Cu(OH) ₂	
T-100	100	1	0.334	0.333	0.333	0.333	—	—	25.1
T-80	80	1	0.334	0.333	0.333	0.266	—	—	38.1
T-60	60	1	0.334	0.333	0.333	0.200	—	—	77.7
T-40	40	1	0.334	0.333	0.333	0.133	—	—	122.2
S-100	100	1	0.334	0.333	0.333	—	0.3111	0.0111	28.7
S-80	80	1	0.334	0.333	0.333	—	0.2488	0.0088	57.0
S-60	60	1	0.334	0.333	0.333	—	0.1866	0.0066	108.7
S-40	40	1	0.334	0.333	0.333	—	0.1244	0.0044	111.4

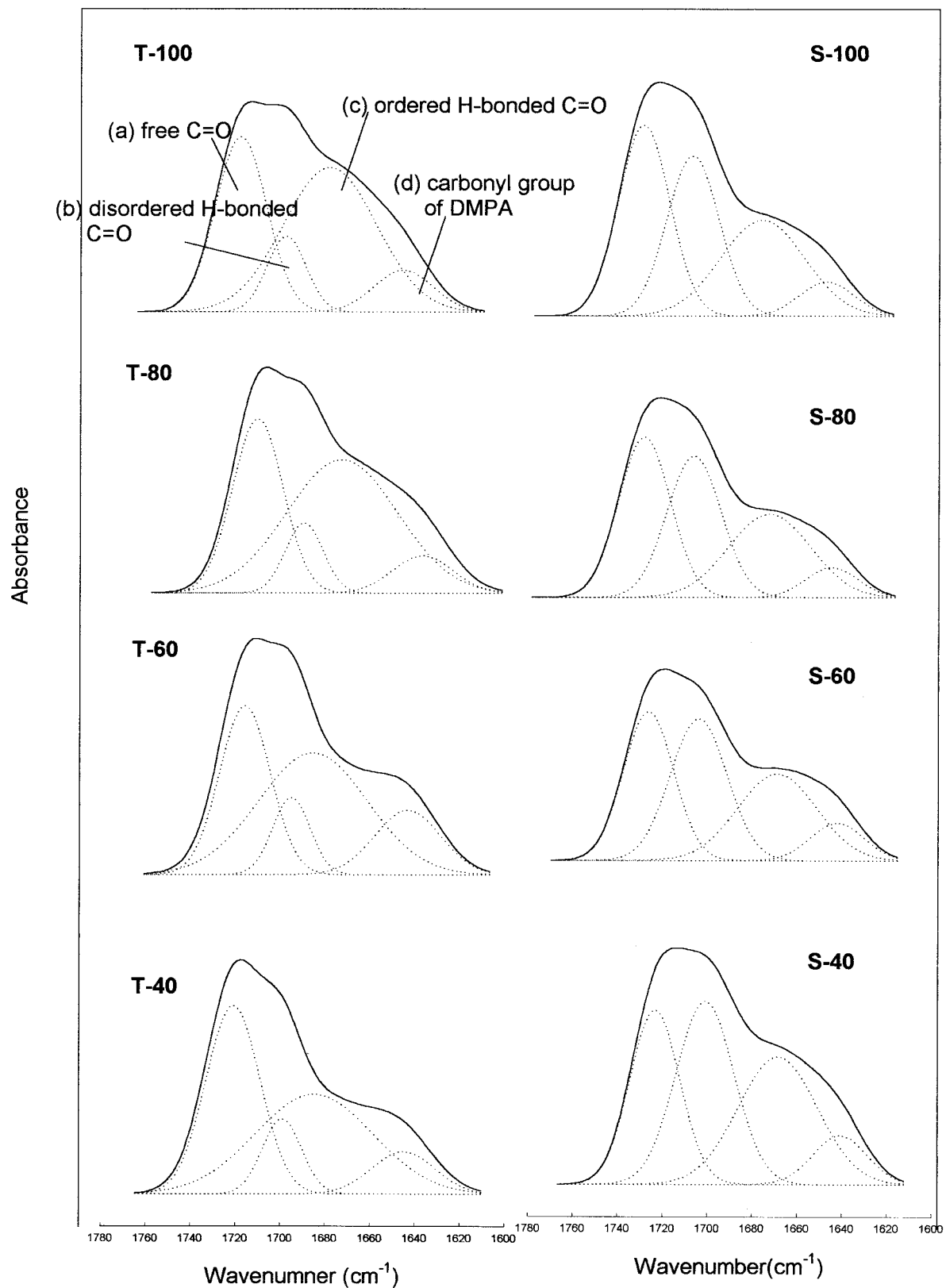


Figure 1 Decomposition of C=O stretching for T- and S-series samples.

ASTM Standard D 638 specifications. A crosshead speed of 20 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 averages of five measurements.

TABLE II
Decomposition Results of the C=O Stretching

Sample designation	Peak position (cm ⁻¹)			Fraction of peak area ^a				X _B (fraction)	
	Total	Free carbonyl group	Disordered H-bonded C=O	Ordered H-bonded C=O	Free carbonyl group	Disordered H-bonded C=O	Ordered H-bonded C=O		Carbonyl group of DMPA
T-100	1713	1720	1699	1679	0.30	0.09	0.53	0.08	0.62
T-80	1716	1720	1699	1681	0.31	0.09	0.52	0.08	0.61
T-60	1715	1720	1699	1688	0.34	0.10	0.46	0.10	0.56
T-40	1718	1721	1699	1684	0.37	0.11	0.42	0.10	0.53
S-100	1714	1722	1700	1668	0.35	0.30	0.29	0.06	0.59
S-80	1715	1722	1701	1666	0.34	0.31	0.29	0.06	0.60
S-60	1717	1723	1701	1665	0.33	0.32	0.29	0.06	0.61
S-40	1714	1723	1701	1668	0.30	0.32	0.32	0.06	0.64

^a The peak areas are based on the total C=O stretching band area.

The electrostatic properties of the films were determined with an Honestmeter (H-0110, Japan) at 60% relative humidity and room temperature. The half-life time was measured with the electrostatic meter (Honestmeter). The conductivity (1/s) of the polyurethane anionomer films was taken the 1/half life time of a given electrostatic charge.

A halo test was used to determine the antibacterial properties of samples with *Pseudomonas* as a bacterium. The films prepared in this study were put on a petri dish containing the cultured bacterium on an agar culture medium and then were cultured again for 2 days. The antibacterial property was determined by observation of the halo (clear zone) thereafter.

RESULTS AND DISCUSSION

Two series of waterborne polyurethane-urea anionomers were prepared from IPDI, PTMG, DMPA, EDA, and NH₄OH/Cu(OH)₂ (or TEA). The neutralization agents TEA or NH₄OH/Cu(OH)₂ (28:1) were used to produce the counterions, (C₂H₅)₃NH⁺ or NH₄⁺/Cu²⁺, of the waterborne polyurethane-urea anionomers. The influence of the degree of neutralization and counterion on the particle size of the dispersions, the conductivity, and the antibacterial and mechanical properties of the polyurethane-urea anionomer films was studied. The originality of this study is the use of Cu²⁺ as a counterion, as this is seldom found in literature studies.

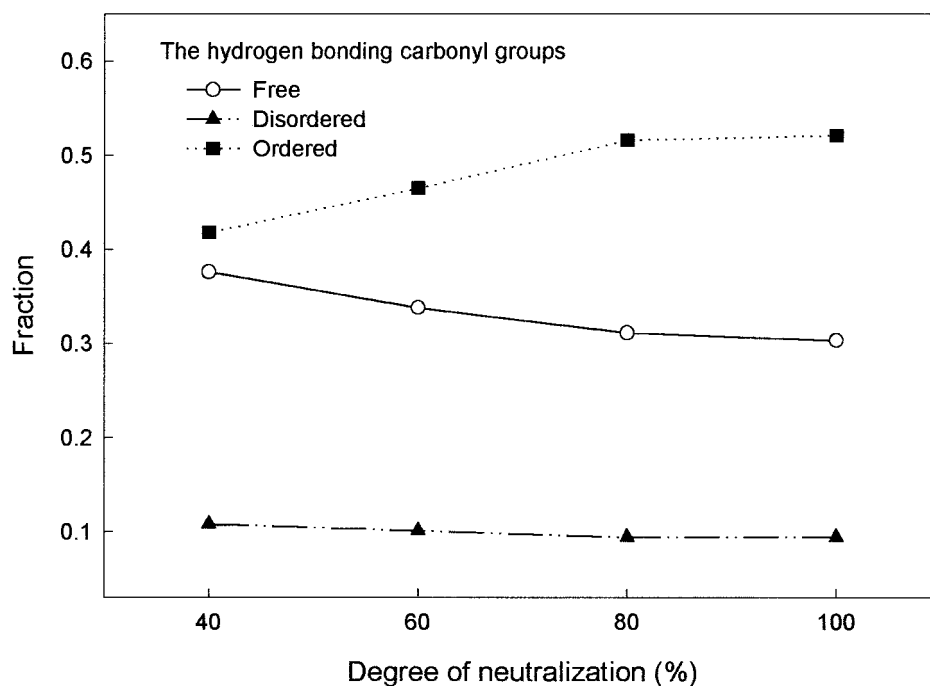


Figure 2 Relationship between fractions of three kinds of hydrogen-bonded carbonyl groups for T-series samples.

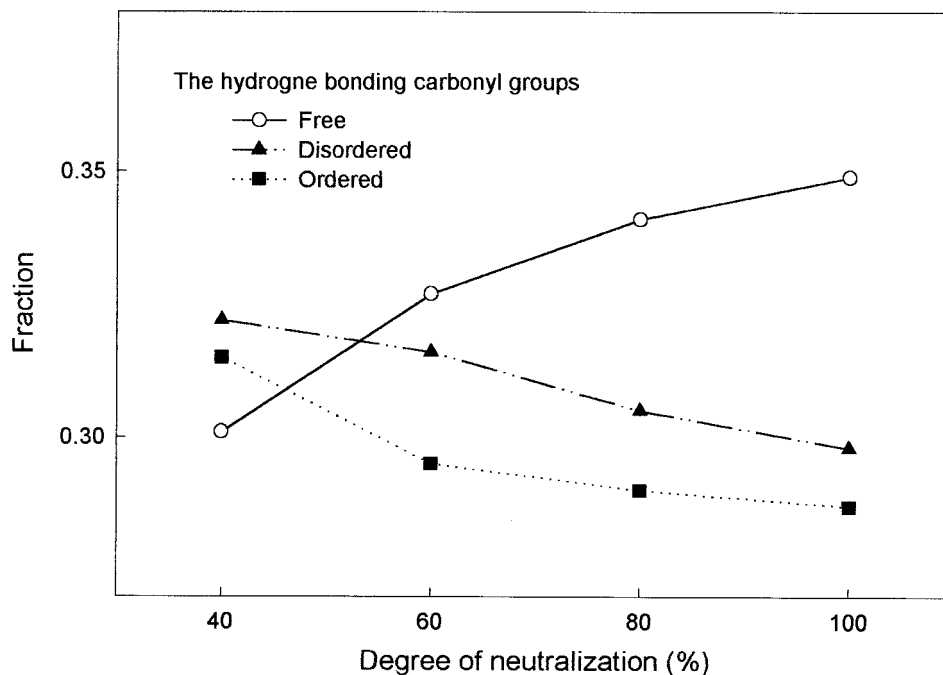


Figure 3 Relationship between fractions of three kinds of hydrogen-bonded carbonyl groups for S-series samples.

The effects of the degree of neutralization and counterion type on the particle sizes of dispersions for the two series of samples (T and S) are shown in Table I. Stable dispersions were obtained when neutralization agent concentrations greater than 40% were used. However, TEA-based dispersions were more stable than those based on $\text{NH}_4\text{OH}/\text{Cu}(\text{OH})_2$ at the same degree of neutralization. The obtained aqueous dispersions with

particle sizes of 25–122 nm were stable for about 3 months. The average particle size of the dispersions significantly decreased with an increasing degree of neutralization. However, there was no meaningful difference in particle sizes between the dispersions with different kinds of counterions at the same degree of neutralization. The particle size of the dispersions obtained in this study was mainly dependent on the degree of neutralization.

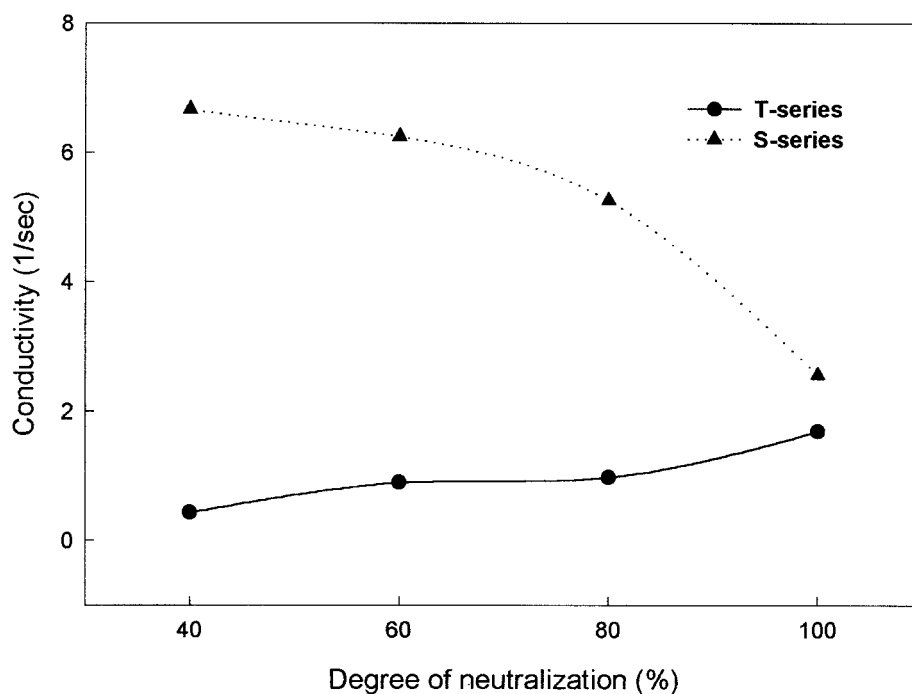


Figure 4 Effect of the degree of neutralization on the conductivity for T- and S-series samples.

TABLE III
Physical Properties of Waterborne Polyurethane-Urea Anionomer Films

Sample designation	Conductivity ^a (1/s)	Tensile strength (kgf/cm ²)	Tensile modulus (kgf/cm ²)	Antibacterial performance ^b
T-100	1.69	1031.88	2881	X
T-80	0.98	978.47	2832	X
T-60	0.90	774.86	2588	X
T-40	0.44	509.64	1478	X
S-100	2.56	386.81	1551	O
S-80	5.26	493.13	1780	O
S-60	6.25	593.18	2312	O
S-40	6.67	657.65	2676	O

^a The conductivity (1/s) of film is reciprocal of the electrostatic half-life time (s) determined with a Honestmeter.

^b O = the existence of antibacterial function; X = nonexistence.

Infrared spectroscopy¹⁴⁻¹⁸ was used to evaluate the different kinds of hydrogen-bonded carbonyl groups. In this study, the effects of the counterion and degree of neutralization on hydrogen bonding were also investigated with infrared spectroscopy. The spectra were analyzed with a curve-resolving technique based on linear least-squares analysis to fit the combination of Lorentzian and Gaussian curve shapes. Curve fitting of the C=O stretching region was performed for all samples. Figure 1 shows the results of the curve-fitting procedure for T- and S-series samples with various degrees of neutralization. The fractions and frequency of the free, disordered, and ordered hydrogen-bonded carbonyl groups for T- and S-series samples are presented in Table II. The bands centered around 1720 and 1722 cm⁻¹ were attributed to the stretching of free carbonyl groups for the T and S series, respectively, whereas the bands around 1699 and 1701 cm⁻¹ were assigned to the hydrogen-bonded carbonyl groups in the disordered regions for the T and S series. T-series samples had bands centered around 1683 cm⁻¹ that were assigned to the stretching of ordered hydrogen-bonded carbonyl groups; however, those stretching bands of S-series samples appeared near 1667 cm⁻¹. The stretching of hydrogen-bonded carboxylic carbonyl groups from the DMPA unit for T- and S-series samples was around 1645 and 1639 cm⁻¹, respectively. The frequency of hydrogen-bonded carbonyl groups in disordered and ordered regions shifted to lower values than those corresponding to the free carbonyl group around 1720 and 1722 cm⁻¹ for both T- and S-series samples. It is remarkable that S-series samples presented higher shifts to lower frequency values than T-series samples. This may be due to the higher linking power between chains due to the presence of bivalent Cu²⁺ in S-series samples.

Figure 2 shows the fraction changes of three kinds of carbonyl groups for T-series samples as the degree of neutralization varied. As the degree of neutralization in T-series samples increased, the fractions of total hydrogen-bonded carbonyl groups (X_B) and the fractions of hydrogen-bonded carbonyl groups in the or-

dered region significantly increased, whereas the free carbonyl groups decreased and the fractions of hydrogen-bonded groups in the disordered regions showed almost no change. The T-series samples had much higher values of hydrogen-bonded carbonyl groups in the ordered region (ordered or crystalline domain) than the others. The existence of this domain may be the reason for their excellent mechanical properties.

Figure 3 shows the fraction changes of three kinds of carbonyl groups for S-series samples with various degrees of neutralization. For S-series samples, the fractions of hydrogen-bonded groups in ordered and disordered regions decreased slightly with an increasing degree of neutralization, but the fractions of free carbonyl groups increased. The higher fractions of hydrogen-bonded carbonyl groups in the disordered region (disordered interface or amorphous domain) in comparison with those of hydrogen-bonded carbonyl groups in the ordered region are remarkable in S-series samples. From this result, we could deduce that the counterions NH₄⁺/Cu²⁺ in S-series samples might disrupt the order of the hard domain, indicating that the counterions might alter the ordered region into a disordered region. Therefore, the salt groups might be distributed in the interface region between hard and soft domain or be dissolved in the soft phase. This suggests that the higher S-series property values were related to the disordered region.

From a comparison of these results, we found that the fractions of hydrogen-bonded carbonyl groups in the ordered region of T-series samples had much higher values than those of S-series samples, whereas the fractions of hydrogen-bonded carbonyl groups in the disordered region of S-series samples had much higher values than those of T-series samples (see Table II). It is reasonable to suppose that the origin of notably different properties between T- and S-series samples was related to the different structures of domains having complex multiphases. Therefore, the relationship between the fractions of different hydrogen-bonded groups and the properties (e.g., the conduc-

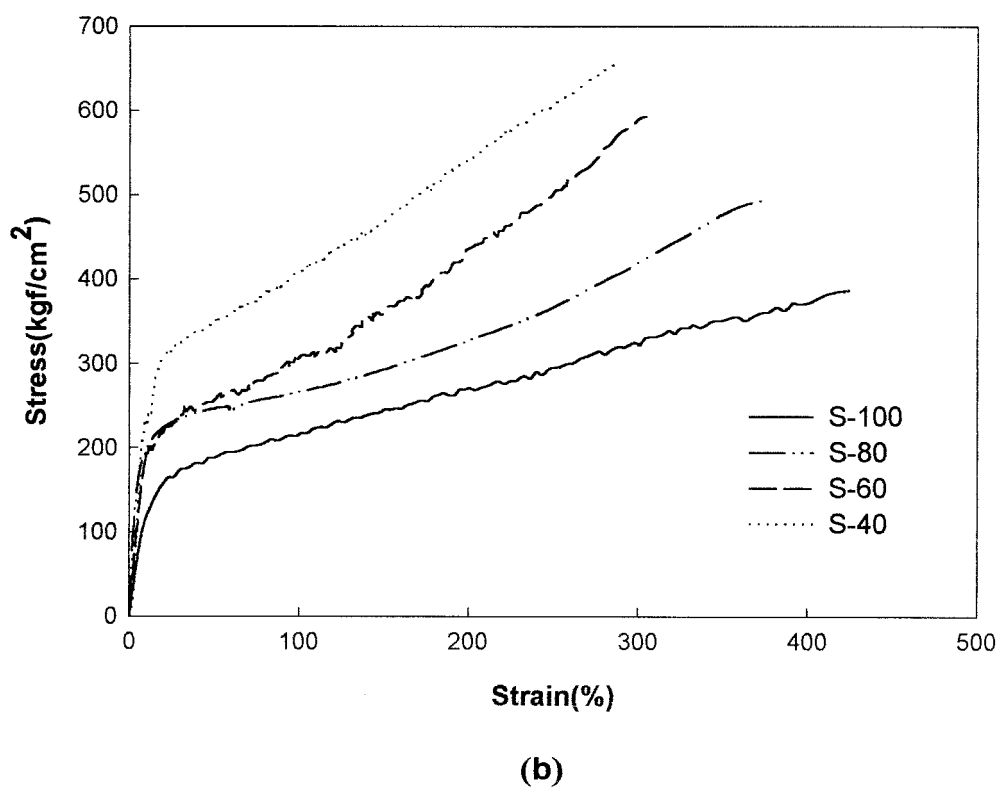
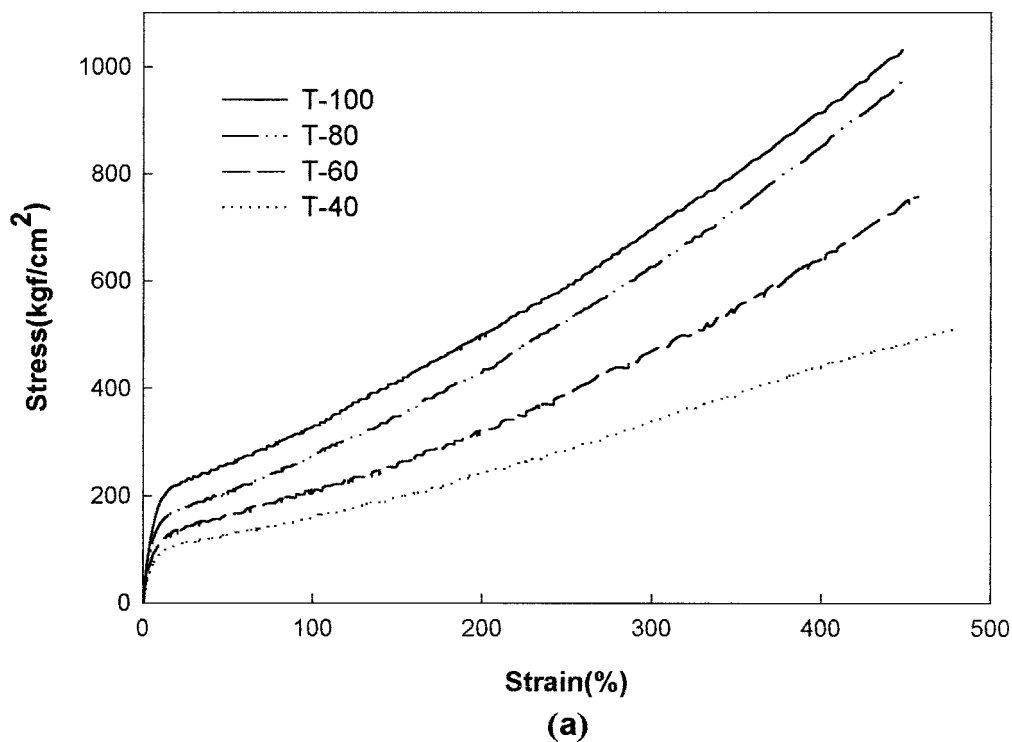


Figure 5 Effect of the degree of neutralization on the tensile properties of (a) T-series and (b) S-series samples.

tivity and tensile strength and modulus) was investigated in this study.

The conductivity [$1/s$, or the reciprocal of the electrostatic half-life time (s)] of the polyurethane-urea

anionomer films prepared in this study is shown in Figure 4 and Table III. The conductivity of T-series samples increased with an increasing degree of neutralization, but the conductivity of S-series samples

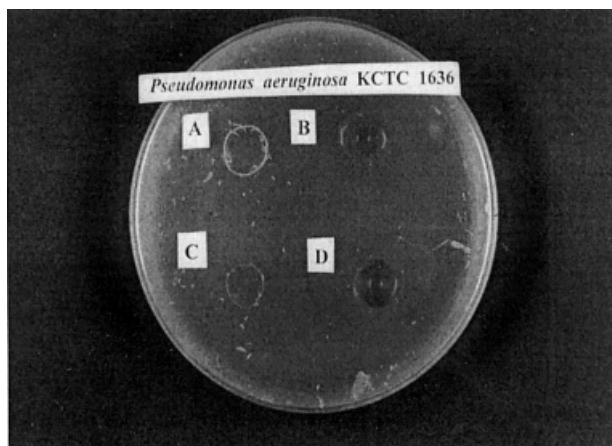


Figure 6 Photomicrograph of an antibacterial halo for typical T- and S-series samples: (A) T-40, (B) S-100, (C) T-100, and (D) S-40.

decreased with an increasing degree of neutralization. The decrease in the conductivity of S-series samples might be attributed to the decrease in the fraction of disordered hydrogen-bonded carbonyl groups with the degree of neutralization. However, we estimated that the increase in the conductivity of T-series samples might be due to the increase in the salt content with the degree of neutralization, but S-series film samples had much higher conductivity than T-series samples. This might be related to the higher content of the disordered region in S-series samples, indicating the greater possibility of the existence of the metal cation Cu^{2+} in disordered regions such as interface regions or amorphous soft-phase regions. In addition, the high concentration of the Cu^{2+} cation itself might have contributed to the higher conductivity for S-series samples.

The tensile properties of the polyurethane-urea anionomer film samples are shown in Figure 5 and Table III. As the degree of neutralization increased, the tensile strength and initial modulus of T-series samples also increased, but those of S-series samples decreased. These changes are coincident with the trend of changes in the fractions of the hydrogen-bonded carbonyl groups in the ordered region with an increasing degree of neutralization for the two series of samples, whereas the tensile strength and modulus of T-series samples commonly were higher than those of S-series samples. This might be due to the value of the hydrogen-bonded carbonyl groups in the ordered region of T-series samples being higher than that of S-series samples.

Figure 6 shows a photomicrograph of the antibacterial halo (clear zone) for the typical samples T-100, T-40, S-100, and S-40. S-100 and S-40, containing $\text{NH}_4^+/\text{Cu}^{2+}$ cations, had a strong antibacterial halo, but T-1 and T-2, having $\text{NH}(\text{C}_2\text{H}_5)_3^+$, did not. This may be attributed to the bactericidal power of the Cu^{2+} cation itself. However, we could not find a difference in the antibacterial performances of S-100 and S-40. Therefore, we con-

cluded that the content of the Cu^{2+} cation in S-40 was enough to make a halo (clear zone) of the bacteria.

CONCLUSIONS

Polyurethane ionomers from IPDI, PTMG, DMPA, and EDA as chain extenders and from TEA and $\text{NH}_4\text{OH}/\text{Cu}(\text{OH})_2$ as neutralization agents were prepared. The effects of the types of neutralization agents and degrees of neutralization on the particle size of the dispersion, the conductivity, and the antibacterial and mechanical properties of the films were studied. The properties of polyurethane anionomers (T-series samples) containing the countercation $(\text{C}_2\text{H}_5)_3\text{NH}^+$ were compared with those (S-series samples) containing $\text{NH}_4^+/\text{Cu}^{2+}$. The aqueous dispersions of polyurethane-urea anionomers with particle sizes of 30–120 nm were stable for about 3 months. The particle size decreased with an increasing degree of neutralization. Infrared spectroscopy was used to assign the types of hydrogen-bonded carbonyl groups in the polyurethane-urea anionomers prepared in this study. T-series samples had higher fractions of hydrogen-bonded carbonyl groups in the ordered region than S-series samples. However, S-series samples had higher fractions of hydrogen-bonded carbonyl groups in the disordered region than T-series samples. The conductivity and antibacterial properties of S-series sample films were superior to those of T-series samples. However, T-series films presented higher tensile strength and initial modulus than S-series films.

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