Aqueous Dispersions of Polyurethane Anionomers: Effects of Countercation

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SYNOPSIS

The influence of counterions on the properties of aqueous dispersions of polyurethane (PU) anionomer have been investigated. The PU anionomers were prepared by polyaddition reaction of 4,4'-methylenebis(phenylisocyanate) with poly(propylene glycol) (PPG), dimethylolpropionic acid (DMPA), and 1,4-butanediol, followed by neutralization of pendant COOH groups by various bases. Stable dispersions are obtained for PU anionomers containing 0.8–1.1 wt % COOH groups (17.8–24.4 mmol/100 g polymer) that have been neutralized by ammonia, trimethylamine, triethylamine, LiOH, NaOH, and KOH, respectively. It is found that average particle size is determined mainly by the zeta potential of the dispersions. The number-average diameter of the dispersions containing metal cations (Li-, Na-, and K-0.9) is between 60–73 nm (zetal potential −65 to −70 mV), while that of the dispersions containing ammonium cations (AMM-, TMA-, and TEA-0.9) is between 104–251 nm (zeta potential −47 to −64 mV). The surface tension of the dispersions decreases with concentration rapidly and levels off at concentrations higher than 20 mmol/L. The decreased decomposition temperature of the PU anionomers, compared to unionized PUs, can be attributed to the disordering of hard domains after ionization or decomposition reaction catalyzed by alkali metal carboxylates. The thermal decomposition proceeds mainly via cyclic elimination.

INTRODUCTION

An ionomer can be defined as a copolymer consisting of a polymer main chain with a minority of the repeat unit carrying acid or tertiary nitrogen groups that are completely or partially neutralized or quaternized, respectively, to form salts.[1] The presence of ionic moieties in ionomers has a strong effect on many of their physical properties.[2] Polyurethane ionomers (PUIs) have received considerable attention in the past few decades due to their usefulness in coatings and adhesives.[3,4] Three types of PUI have been reported according to the ionic charges on the polymer main chain, i.e., cationomers,[5,6] anionomers,[7–10] and zwitterionomers.[11] One of the most important characteristics of many PUIs is their ability to disperse or dissolve in water if a sufficient

amount of ionic moiety is incorporated.[12,13] The component containing the ionogenic group is called the internal emulsifier to discriminate it from the conventional external emulsifier that is usually an added surfactant. Various processes have also been developed for the preparation of PU dispersions.[14,15] For example, the acetone process, in which the dispersions are obtained by adding water into solution of PUIs in acetone, is one of the most popular ones nowadays.

PU anionomers can be prepared by reaction of a chain extender containing COOH groups with NCO-terminated PU prepolymer, followed by subsequent neutralization of the COOH with base.[7–9] Countercations strongly affect the physical properties of PU anionomers containing carboxylate anions.[9] Lorenz et al. found that the acetone/water ratio affects the average particle size of the final dispersion and that the ion species distribute on the particle surface of the final dispersion.[16] Milligan et al. used 2,2-dihydroxymethyl carboxylic acid as ionogenic component

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to prepare PU anionomer dispersions.[17] However, research involving the influence of countercations on the property of PU anionomer dispersion is limited.[9]

The objective of this work is to report the preparation and the counterion effects of polyurethane anionomer dispersions derived from MDI, PPG, dimethylolpropionic acid, and 1,4-butanediol.

EXPERIMENTAL

Raw Materials

The raw materials are described in Table I. The polypropylene glycol (PPG) was dried and degassed *in vacuo* at 60°C for 2 days. The 4,4'-methylenebis(phenylisocyanate) (MDI) was purified by refluxing with hexane, followed by hot filtration to remove unsoluble solids. Other chemicals except dimethylformamide (DMF) and methyl ethyl ketone (MEK) were used without further purification. The DMF was dried by treatment with powdered barium oxide and vacuum-distilled from fresh alumina. The MEK was dried by distillation with P_2O_5 and then stored over 4A molecular sieves before use.

Synthesis of Polyurethane Containing COOH Groups

The segmented PPG–PU used in this study was synthesized by a two-step condensation reaction. A 1000 mL four-necked glass reactor equipped with a stirrer, nitrogen inlet and outlet, and thermometer was charged with MDI (78.83 g, 0.315 mol) and MEK (40 g) under a nitrogen blanket. PPG (200 g, 0.1 mol) was then added slowly under gentle stirring, and the mixtures were allowed to react at 75°C until

the theoretical NCO content was reached as determined by the di-*n*-butylamine titration method. The NCO-terminated prepolymer was then chain-extended with 0.2 mol of DMPA and 1,4-butanediol at 75°C until complete disappearance of NCO absorption (2270 cm^{-1}) in its IR spectra. The COOH content was regulated by changing the relative amount of DMPA to 1,4-butanediol. The solid content of the final solution was adjusted to 40 wt % by adding a suitable amount of MEK.

Neutralization of COOH Groups

Into 60 g of the PU solution was added dropwise 10 g aqueous solution of the neutralizing agents (except triethylamine and tripropylamine, which were dissolved in a mixture of acetone and water). The mixtures were allowed to react at 60°C for 30 min to obtain PU anionomers in MEK. The amines used were ammonia, trimethylamine, triethylamine, and tripropylamine, while metal hydroxides used were LiOH, NaOH, and KOH. The stoichiometric ratio of amine to COOH is 1.2, while that of metal hydroxide is 1.0.

Dispersion of Polyurethane Anionomers

Deionized water was added slowly under constant agitation (300 rpm) to PU anionomer solutions at 25°C, from which samples were taken for viscosity measurement. During the addition of water, the viscosity increased slightly first and then dropped sharply. When the viscosity of the solution had dropped to about 10 cps, the addition was stopped. An aqueous dispersion of ca. 20 wt % solids was obtained after removal of MEK by a rotary vacuum evaporator. Samples were designated in such a way

Table I   Raw Materials

Designation	Chemical Identification	Suppliers
PPG	Polypropylene glycol (PPG), MW = 2000	Wako Chemical Co.
MDI	4,4'-Methylenebis(phenylisocyanate)	Tokyo Kasei Co.
DMPA	Dimethylolpropionic acid	Tokyo Kasei Co.
BDO	1,4-Butanediol	Wako Chemical Co.
Li	Lithium hydroxide	Wako Chemical Co.
Na	Sodium hydroxide	Wako Chemical Co.
K	Potassium hydroxide	Ishizu Seiyaku Co.
AMM	Ammonia water (25%) (AMM)	Wako Chemical Co.
TMA	Trimethylamine (30% in water) (TMA)	Wako Chemical Co.
TEA	Triethylamine (TEA)	Merck Chemical Co.
TPA	Tripropylamine (TPA)	Merck Chemical Co.

that, for example, Na-0.9 means anionomer (dispersion) obtained from a PU containing 0.9 wt % COOH that was neutralized by NaOH.

Film Preparations

Films for thermal testing were prepared by pouring the unionized solution or dispersions on polypropylene film, then vacuum-dried at 60°C for 48 h after standing at ambient air for 3 days. Sample designation is the same as mentioned above except for SOL-0.9, which stands for the film obtained from unionized PU containing 0.9 wt % COOH groups.

Measurements

Infrared spectra (IR) were recorded using an infrared spectrophotometer, Model IR-810, from Japan Spectroscopic Co., at a resolution of 4 cm^{-1}. The viscosity was determined using a Brookfield digital viscometer, Model DV-II, at 25°C. Particle size and distribution of the dispersions were measured by the laser scattering spectrophotometer of Otsuka Electronics Co. Ltd., Model DLS-700. A few drops of the dispersion were diluted in deionized water before the measurement.

Zeta potential of the dispersions was measured by the Lazer Zee Meter of Penkem, Inc., Model 501. The dispersion was first diluted to less than 1000 ppm, then put under an electric field of 100 V. The mobility of the particles to the anode was held up by applying an opposite electric field. Four applied electric potentials were averaged to obtain the zeta potentials cited. Surface tension of the dispersions

was measured using a face surface tensionmeter, Model LBVP-A3, from Kyowa Interface Science Co.

Differential scanning calorimetric (DSC) thermograms of the films over the temperature range of 50–350°C were recorded using a DuPont 910 thermal analyzer with a heating rate of 10°C/min and a sensitivity of 5 mcal/s under nitrogen purging. Thermogravimetric behavior of the films over the temperature range of 50–450°C was measured using a DuPont Model 951 thermogravimeter analyzer with a heating rate of 10°C/min under nitrogen purging.

RESULTS AND DISCUSSION

Dispersity of PU Anionomers

It is well known that a minimum ionic content is required for the formation of stable PU dispersion, depending on the type of ionic species.[12] In this work, PUs with different contents of DMPA were prepared in order to study the influence of ionic contents. However, the total fraction of the chain extender (DMPA + BDO) in PU was kept constant to alleviate the influence of microstructure on the dispersity. The COOH content is defined as follows:

COOH content (%)

$$= \frac{\text{weight of COOH in PU}}{\text{total weight of PU}} \times 100$$

As shown in Table II, dispersity of the PU anionomers depends both on COOH content and countercations (neutralizing agents used). Depend-

Table II Effects of COOH Content and Neutralizing Agents on Dispersity of the PU Anionomers in the Aqueous Phase

COOH Content[a] (wt %)	Neutralizing Agents						
	LiOH	NaOH	KOH	AMM	TMA	TEA	TPA
0.6 (13.3)[b]	↓[c]	↓	↓	↓	↓	↓	↓
0.7 (15.6)	↓	↓	↓	↓	↓	↓	↓
0.8 (17.8)	Disp[d]	Disp	Disp	Disp	Disp	Disp	↓
0.9 (20)	Disp	Disp	Disp	Disp	Disp	Disp	↓
1.0 (22.2)	Disp	Disp	Disp	Disp	Disp	Disp	↓
1.1 (24.4)	Disp	Disp	Disp	Disp	Disp	Disp	↓
1.2 (26.7)	—[e]	—	—	—	—	Paste[f]	↓

[a] Weight percentage of COOH groups before neutralization.
[b] The values in parentheses represent millimoles of COOH groups per 100 grams of PU.
[c] Precipitation.
[d] Dispersible: stable for at least 1 month.
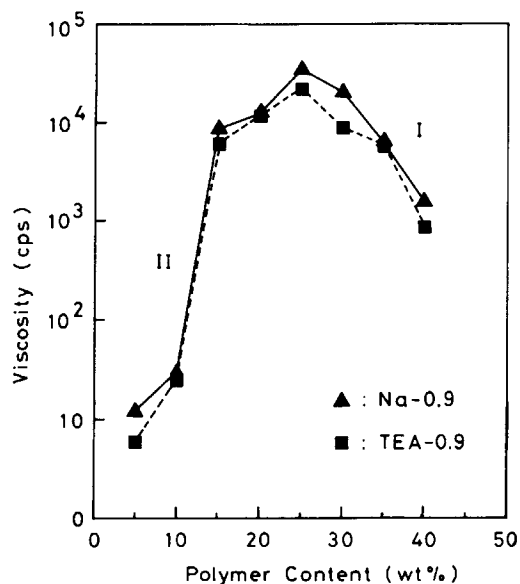[e] Not measured.
[f] Pastelike mixture.

Figure 1 The viscosity variations of (▲) Na-0.9 and (■) TEA-0.9 solutions during water addition at the dispersion temperature of 25°C.

ing on their macroscopic appearance, the dispersions can be classified as stable dispersion, precipitation, and paste. Except for the TPA series, stable dispersions are obtained for PU anionomers having COOH content between 0.8 and 1.1 wt % (17.8–24.4 mmol per 100 g of PU). However, when COOH contents are lower than 0.8 wt %, the dispersions sediment quickly. The dispersion of TEA-0.9 results as a pastelike mixture.

From these results, clearly there exists an optimum range of COOH contents to obtain stable dispersion. When COOH content is less than 0.8 wt %, the ionic groups are not enough to stabilize the dispersed particles. In case of the TPA series, the tripropylammonium cations are too hydrophobic to form a stable dispersion. For TEA-1.2, the pastelike

mixture would result from the excessive swelling of the particle surface by water. It is expected that water–soluble PUs could be obtained if an excess of ionic groups was incorporated. These results can also be explained by the zeta potential, which is the main factor in determining the stability of dispersed particles (see later section).

Viscosity Variations during Dispersion

The viscosity variations of Na-0.9 and TEA-0.9 solutions during water addition are shown in Figure 1. With the addition of water, the viscosity first increases from ca. 2000 cps to a maximum value of ca. 30,000 cps and then falls sharply to about 10 cps. The viscosity changes of other PU anionomers during dispersion are similar, except for a slight difference in viscosity. The reason for the viscosity increase in region I is that, as a result of a decrease in MEK content, the polyether segments lose their solvation sheath and come together to form hydrophobic associates that act as physical cross-linking.[4] Further addition of water increases turbidity and decreases the viscosity sharply (region II), suggesting that the associates have been rearranged to form microspheres during the phase inversion. The viscosity changes during phase inversion is very similar to that reported by Lorenz et al.[18] Thus, obtained dispersion consists of a continuous aqueous phase with dispersed particles of PU swelled by MEK.

Influence of Countercations on Particle Size

As shown in Table III, the number (D_N) and weight (D_W) average diameter of particles can be arranged in the order of TEA-0.9 > TMA-0.9 > AMM-0.9 > K-0.9 > Li-0.9 > Na-0.9, while the absolute values of the zeta potential are in the opposite order.

Studies performed by Lorenz prove that in PU

Table III Average Particle Size and Zeta Potential of PU Anionomer Dispersions

PU Anionomer	Number-Average Diameter : D_N (nm)	Weight-Average Diameter : D_W (nm)	D_W/D_N	Zeta Potential (mV)
Li-0.9	60.5 (22)[a]	98.1 (49)	1.62	−68.6
Na-0.9	59.9 (22)	97.7 (47)	1.63	−70.3
K-0.9	72.8 (26)	116.6 (57)	1.60	−64.7
AMM-0.9	103.6 (33)	142.1 (51)	1.37	−64.1
TMA-0.9	158.9 (45)	204.4 (65)	1.32	−61.2
TEA-0.9	250.9 (86)	365.1 (145)	1.46	−46.7

[a] The values in parentheses are the standard deviations.

ionomer dispersions the ionic centers are located on the surface of the dispersed particles, while the hydrophobic chain segments form the interior of the particle.[8] From this structure, particle stabilization can be decided by the well-known model of a diffuse double layer.[19] The double layer is formed, at the interface, by the dissociation of carboxylate salt groups. The carboxylate anions, which are chemically bound to the PU backbone, remain fixed to the particle surface, whereas the countercations migrate into the aqueous phase as far as they are allowed by the attractive forces of the carboxylate anions. This forms a layer of decreasing electrical charge and possesses an electrokinetic or zeta potential in the surface of shear. The repulsive force of the zeta potential between particles is responsible for the overall stabilization of the dispersion.

The variations of average particle diameter and polydispersity (D_W/D_N) of the dispersions with the zeta potential are shown in Figure 2. Smaller particle sizes are obtained at higher zeta potential (negative value), indicating that particle size is determined by the stability of the dispersed PU anionomers. Stable dispersions prevent coagulation during the dispersion process and result in finer particles. However, polydispersities of the dispersions containing alkali metal cations are almost constant ($D_W/D_N = 1.60-1.63$) regardless of the difference
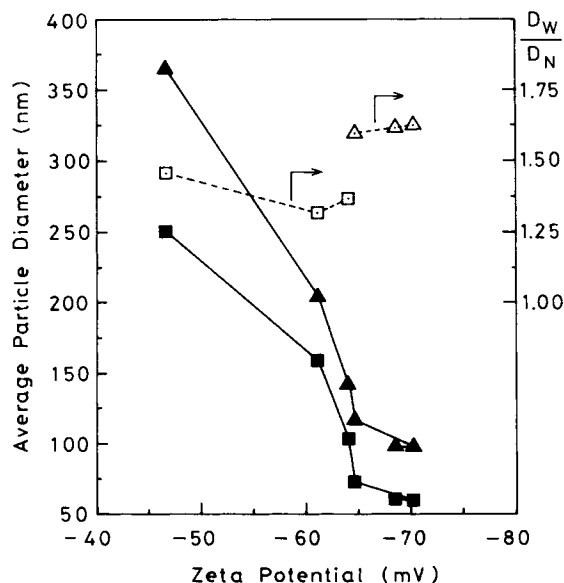

Figure 2   The variations of particle size and polydispersity (D_W/D_N) with zeta potential: (■) number-average diameter; (▲) weight-average diameter; (□) D_W/D_N of dispersions containing ammonium cations; (△) D_W/D_N of dispersions containing alkali metal cations.
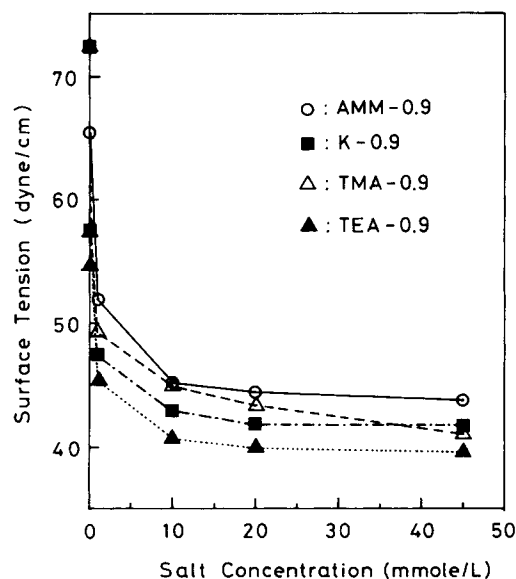

Figure 3   Effect of salt concentration on the surface tension of PU anionomer dispersions.

in the zeta potential. Dispersions containing ammonium cations (AMM-, TMA-, TEA-0.9) result in a narrower particle-size distribution ($D_W/D_N = 1.32-1.46$), which can be attributed to the sharpening effect of the particle coagulation caused by the low zeta potential.

From the above-mentioned results, clearly the dispersions containing metal cations always result in smaller particle size than do those containing ammonium cations. These results suggest that the alkali metal cation is more easily hydrated in the aqueous phase than is ammonia and results in a higher zeta potential on the particle surface. The hydrophobic alkyl substituent of the ammonium cation reduces its hydration ability in the aqueous phase. In the extreme case of the TPA series, no stable dispersion could be obtained irrespective of the COOH content.

The variations of surface tension with salt concentration are shown in Figure 3. The surface tension decreases rapidly with salt concentration and levels off at concentrations higher than 20 mmol/L. Dispersions containing alkali metal cations exhibit similar surface tension and show a value of ca. 42 dyne/cm at a concentration of 45 mmol salt groups/L. However, the surface tension of dispersions containing ammonium cations decreases with the alkyl length of the ammonium cation. This means that the surface energy depression of the dispersions depends not only on the concentration of the PU anionomer but also on the surface activity of the countercations.
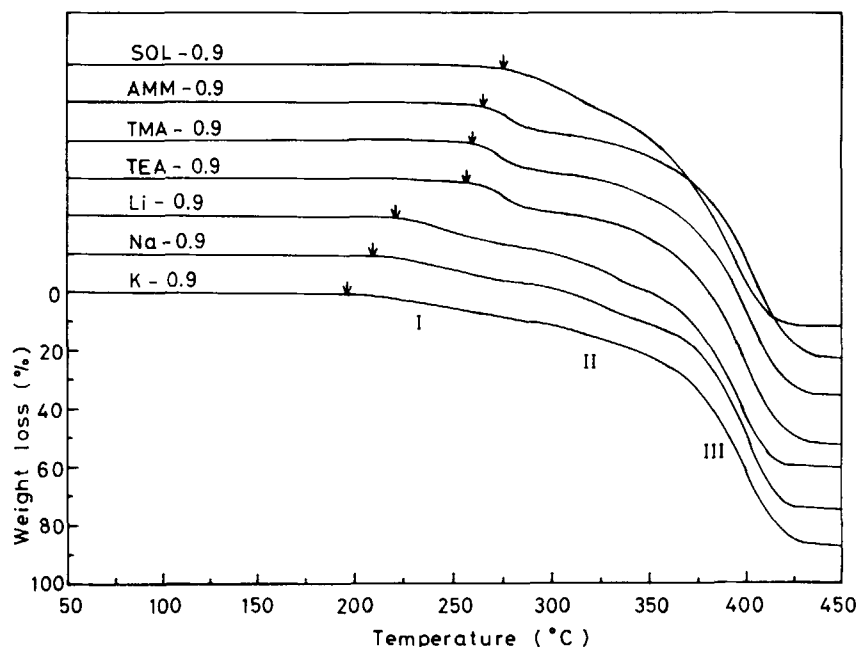
Figure 4   TGA curves of the films cast from unionized solution and aqueous PU anionomer dispersions.

Thermal Behaviors

TGA curves of the films are shown in Figure 4. The films from SOL-0.9 and dispersions containing ammonium cations (AMM-, TMA-, and TEA-0.9) lose weight in two stages, but films containing alkali metal cations (Li-, Na-, and K-0.9) lose weight in three stages. The onset temperature and weight loss of each stage are summarized in Table IV.

The decomposition of urethane generally follows a combination of reaction paths **a** and **b** as shown in Figure 5.[20] The cyclic elimination (reaction **b**) is particularly favored in urethane derived from aromatic isocyanates and alcohols carrying a hydrogen or methyl group in the beta position to the hydroxyl group.[21]

Table IV shows that, for both films from SOL-

0.9 and dispersions containing ammonium cations, the weight loss in stage I is about equal to that calculated from reaction **b** of Figure 5, suggesting that these films mainly decompose via cyclic elimination. The lower weight loss of the films containing metal cations in stage I seems to be due to the involatility of the resulting metal carboxylates. The SOL-0.9 film shows a higher onset temperature than do those containing ammonium cations, indicating that ionization can disrupt the ordering in the hard domains and, accordingly, lowers decomposition temperature.[22] From the order of AMM-0.9 > TMA-0.9 > TEA-0.9 in onset temperature, clearly, the bulkier is the ammonium cation, the lower is the decomposition temperature. The much lower onset temperature of films containing metal cations seems to
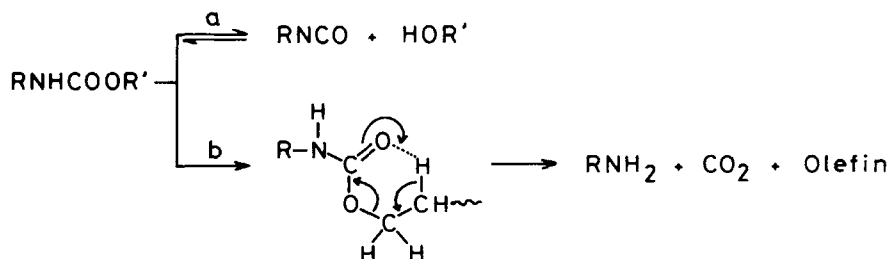

Figure 5   Thermal decomposition modes of urethane.

Table IV   The Characteristic Values of the TGA Curves of Films Cast from Solution and Dispersion

| Sample | Calcd Weight Loss (%)[a] | | Onset Temperature of Each Stage (°C) | | | Found Weight Loss (%) | |
	Reaction a	Reaction b	I	II	III	Stage I	Stage II
SOL-0.9	6.90	12.4	275	316	—	11.8	—
AMM-0.9	7.21	12.6	263	298	—	12.3	—
TMA-0.9	7.99	13.4	258	298	—	12.0	—
TEA-0.9	8.74	14.1	255	296	—	12.4	—
Li-0.9	7.02	12.4	220	301	349	9.7	12.3
Na-0.9	7.32	12.8	209	299	348	9.0	12.8
K-0.9	7.62	13.1	196	295	346	9.6	12.9

[a] Weight percentage loss calculated from reactions a and b as shown in Figure 5.

be due to the decomposition catalyzed by the metal carboxylates, which are well-known catalysts for the addition reaction of isocyanate with hydroxyl groups.[23]

DSC curves of the films from SOL-0.9 and dispersions are shown in Figure 6. The temperatures of the characteristic peaks of all samples are listed in Table V. For SOL-0.9, only one broad peak I is found at 62–160°C. For the films cast from the dispersion containing ammonium cations, another peak II (172–239°C) appears in addition to the broad peak I. The broad peak I can be assigned to dissociation of the dispersed phases of the hard segment, while peak II would be attributed to the dissociation of the ion clusters formed in the film state. Both TMA-0.9 and TEA-0.9 show two peaks II with a temperature difference of about 10°C, indicating that at least two types of ionic cluster are formed.

For the films from dispersions containing alkali

Table V   The Characteristic Peaks Determined from DSC Curves of Films Cast from Solution and Dispersion[a]

Sample	Peak I Range (°C)	Peak II (°C)
SOL-0.9	62–130 (broad)	—
AMM-0.9	68–160 (broad)	239
TMA-0.9	63–135 (broad)	229, 239
TEA-0.9	63–132 (broad)	172, 180
Li-0.9	—	161
Na-0.9	—	150
K-0.9	—	162, 181

[a] Only the peaks before decomposition are presented.

metal cations, only peak II at 150–181°C can be observed. The disappearance of peak I can be attributed to the distinct phase separation caused by the strong ionic strength of metal cations. Peak II can be assigned to the phase transition from a regular ionic cluster to an irregular one.[24]

CONCLUSIONS

Aqueous dispersions of PU anionomers have been prepared and the effects of counterion on the properties of the dispersions and films have been investigated. During dispersion, the viscosity increases from ca. 2000 cps to a maximum value of ca. 30,000 cps and then drops sharply. Stable dispersions are obtained for PU anionomers containing 0.8–1.1 wt % COOH groups that are neutralized by ammonia, trimethylamine, triethylamine, LiOH, NaOH, and KOH, respectively.

The average particle size of the dispersions depends heavily on cation type. The number-average particle diameters of the dispersions containing alkali metal cations are in the range of 60–73 nm (Na-0.9 < Li-0.9 < K-0.9), while those of the dispersions containing ammonium cations are in the range of 104–251 nm (AMM-0.9 < TMA-0.9 < TEA-0.9). These results have been explained by the measured zeta potentials, which are determined mainly by the hydration ability of the cations in the aqueous phase. The surface tension of the dispersions decreases rapidly with the concentration and levels off at concentrations higher than 20 mmol salt groups/L.

Thermal properties of the films also depend on the cation types. Ionization of the COOH groups decreases the onset temperature of decomposition, which has been attributed to the disordering of the
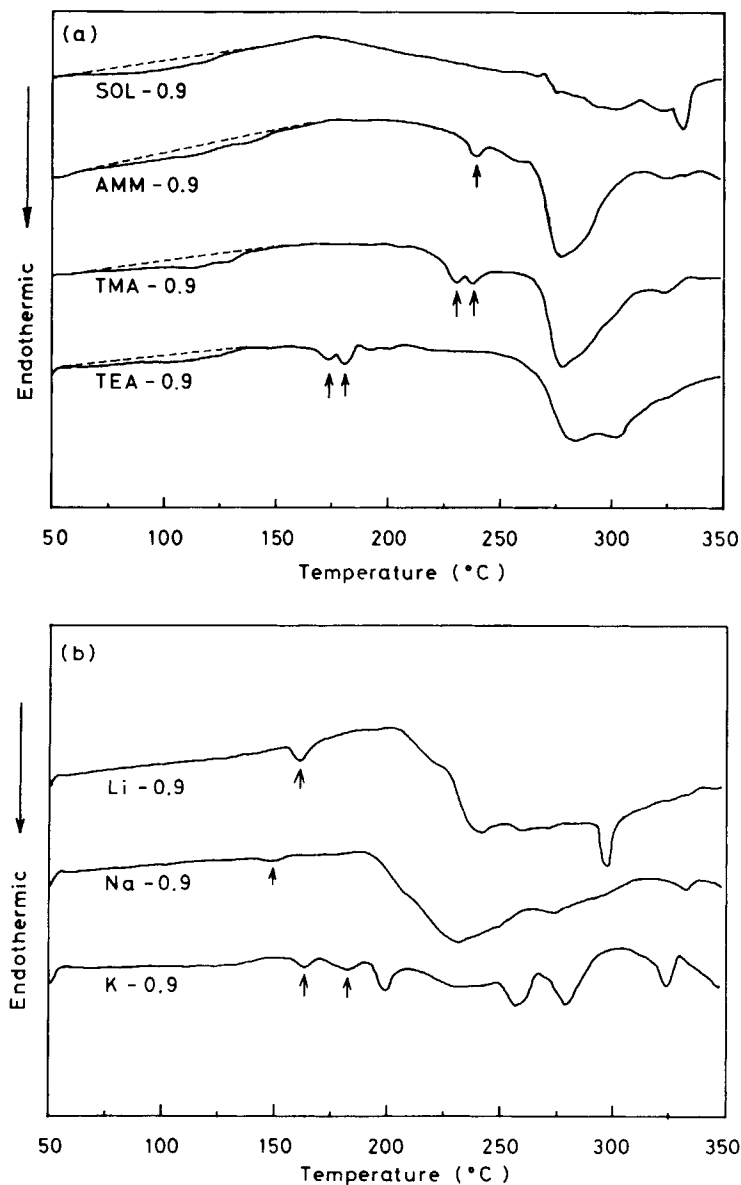
Figure 6   (a) DSC curves of SOL-0.9 and PU anionomers containing ammonium cations;
(b) DSC curves of PU anionomers containing alkali metal cations.

hard domains or decomposition catalyzed by metal carboxylates. The thermal decomposition proceeds mainly via cyclic elimination.

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