

Polyurethane anionomers.

I. Structure–property relationships

Show-An Chen* and Jen-Sung Hsu

Chemical Engineering Department, National Tsing-Hua University, Hsinchu, Taiwan 30043, China

(Received 29 January 1992; revised 15 October 1992)

Polyether polyurethane anionomers are prepared using poly(tetramethylene oxide) of molecular weight 2000 as soft segments, 4,4'-diphenylmethane diisocyanate (MDI) as diisocyanate, dimethylolpropionic acid (DMPA) as chain extender, and two ionization agents, triethylamine (TEA) and *N*-ethyl diethanolamine (EDEA). Properties of the films cast from solution are studied by infra-red spectroscopy, dynamic mechanical analysis, thermogravimetric analysis, differential scanning calorimetry, wide-angle X-ray diffraction, tensile-elongation testing, transmission electron microscopy and gel-permeation chromatography. In the unionized film, soft segment crystallites are not present. Ionization creates soft segment crystallites and produces increased cohesion in the hard domains, which leads to an increase in both tensile strength and elongation at break. The tensile strength of the two systems studied increases with increasing the ionic potential. The morphology of the films shows that the hard domains are dispersed in the soft domains and that the size of the hard domains increases greatly after ionization. The TEA system has larger hard domains than the EDEA system. After annealing, the unionized film has improved ordering in the soft domains and enhanced tensile strength, but annealing provides no appreciable effect on the ordering of soft and hard domains and mechanical properties for the ionized films.

(Keywords: poly(tetramethylene oxide); dimethylolpropionic acid; 4,4'-diphenylenemethylene diisocyanate; counterion; morphology)

INTRODUCTION

Polyurethane (PU) ionomers can be prepared by incorporation of a chain extender containing an amino group with NCO-terminated PU prepolymer and subsequent modification with an ionizable component¹. There are three types of PU ionomers: (1) zwitterionomers formed by use of a tertiary amine followed by reaction with a sultone to form a quaternary ammonium sultone^{2–6}; (2) anionomers formed by use of a secondary amine followed by reaction with a sultone or lactone¹; (3) cationomers formed by use of a tertiary amine followed by reaction with alkyl halide or acid⁷. Anionomers can also be formed by using either a diol or diamine chain extender that contains a pendent carboxylic or sulfonic acid group, which is subsequently neutralized with different cations or bases⁸.

Tensile strength and modulus of the zwitterionomers^{2–6} are higher than those of the corresponding conventional PU, resulting from strong interactions between cation and anion on hard segments of two neighbouring chains which lead to an increased hard domain cohesion. For the anionomers with metal counterions studied by Cooper and co-workers^{9,10}, crystallinity in soft domains was observed at low ionization levels for systems with higher molecular weight of soft segments; increasing

the ionization level decreased the crystallite melting temperature and endothermic area. For the anionomers studied by Al-Salah and co-workers⁸ the mechanical properties are greatly affected by the various types of metal counterions; anionomers containing transition metals exhibited good mechanical properties. The glass transition temperature of soft domains increased by increasing the ionic potential. For monovalent and non-transition metals, the mechanical properties of the anionomers improved by increasing the ionic potential. Al-Salah and co-workers¹¹ studied the viscometric properties and conductivity of PU anionomer solutions and the results show that the degree of dissociation of ion pairs depends on the polarity of the solvent and its solubility parameters; for a given polymer the specific conductance increases as the size of the metal counterion increases.

In a previous work⁷ three series of PU cationomers with various structures of hard segments were studied. It was found that in the unionized and ionized systems, the hard segments exhibit disordered and ordered arrangements, respectively. After ionization, disruption of the order and enhancement of cohesion through the coulombic interactions in the hard domains occur simultaneously.

One of the most important characteristics of many PU ionomers is their ability to disperse in water. This characteristic is important in adhesive and coating

* To whom correspondence should be addressed

applications. For anionomers, no study of the effect of non-metal counterions on the properties of the films and the phase-inversion mechanism, or on the effect of emulsification on the properties of the films is to be found in the literature.

In this work, films cast from solutions of polyether PU anionomers with two quaternary ammonium ions as counterions were prepared and characterized using various experimental techniques in order to elucidate the effects of ionization on physical properties.

EXPERIMENTAL

Materials

4,4'-Diphenylmethane diisocyanate (MDI) (Upjohn Co.) was purified by heating to 60°C and filtration by suction. Bromophenyl blue indicator (Wako Chemical Co.), dimethylolpropionic acid (DMPA) (Tokyo Kasei Co., extra pure), triethylamine (TEA), *N*-ethyl diethanol amine (EDEA) and methyl ethyl ketone (MEK) (Merck Chemical Co.) were used as received. *N,N*-dimethylacetamide (DMAc) (Merck Chemical Co.) was dried using a 4 Å molecular sieve before use. Poly(tetramethylene oxide) (PTMO) of molecular weight 2000 (DuPont Chemical Co.) was further dehydrated under vacuum at 50°C for 24 h.

Synthesis of PU anionomer solutions

PU prepolymer was prepared at 65–75°C under nitrogen in a stirred-glass reaction kettle with a reflux condenser. The MDI (4 mol) was charged into the kettle first and heated up to 65–75°C. Then PTMO (1 mol) in DMAc was added slowly such that one of the two hydroxyl groups in each polyol molecule could react with one molecule of MDI to yield prepolymers. The reaction was allowed to proceed until the theoretical isocyanate content was reached as determined by the di-*n*-butylamine method¹².

The prepolymers were then diluted to 30 wt% with DMAc to lower the rate of heat generation and to avoid a substantial increase in viscosity during the subsequent chain extension reaction. DMPA (3 mol) in DMAc was added slowly to the diluted prepolymer solution at 65–75°C. The reaction was continued until the NCO groups were reacted, as confirmed by the disappearance of the i.r. absorption at 2270 cm⁻¹. The reaction mixture was then precipitated from water to give the crude product. The crude product was dried in a vacuum oven to give the carboxylic acid-containing polyurethane (unionized PU).

The unreacted carboxylic acid group content in the unionized PU was determined by acid–base titration with a KOH solution, about 88 mol% of the original carboxylic acid groups remain unreacted in the unionized PU, indicating that the reactivity of the COOH group with isocyanate is lower in comparison with the OH groups. Although about 12% of the COOH groups were reacted, the unionized PU could still dissolve in MEK completely to give a clear solution. Thus, it can be inferred that no crosslinking occurred in the unionized PU. A given quantity of the unionized PU was dissolved in MEK and then an appropriate amount of amine or potassium hydroxide was added to the PU solution. The ionization process was carried out at 60°C for 1 h. The degree of ionization was dependent on the amount of ionization agent added.

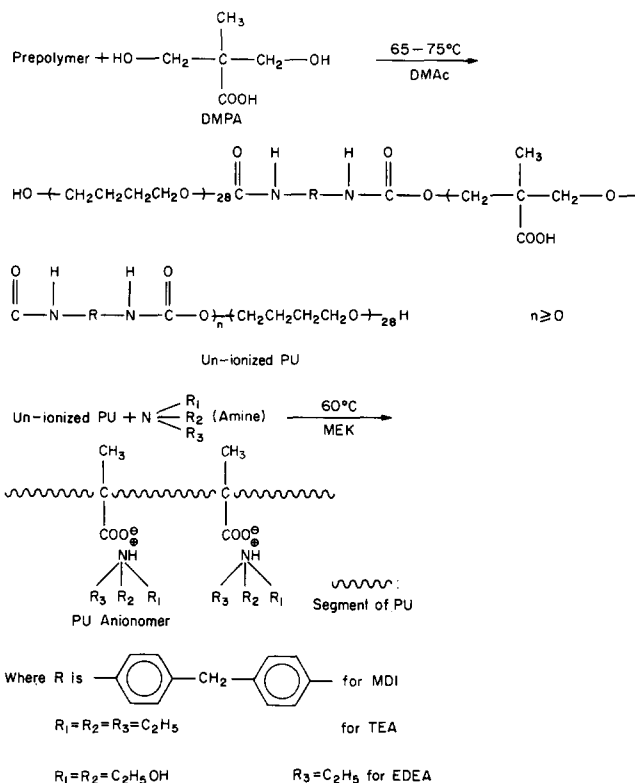


Figure 1 Reaction scheme of the PU anionomers with quaternary ammonium counterions

The above reaction procedure is summarized in Figure 1.

Film preparation

Films for physical testing were prepared by pouring the MEK solution into a Teflon mould, the inner dimensions of which were 8 cm × 8 cm × 1 cm. After standing at room temperature for 4 days to allow evaporation of the solvent, the film was vacuum-dried at 60°C for 48 h to remove residual solvent completely. The dry samples so obtained were about 0.3 cm thick and were stored in a desiccator at room temperature before testing.

Samples were designated so that, for example, MT-0.7 means 0.7 mole ratio of TEA to the carboxylic acid of the unionized PU, the initial letters 'M', 'T' and 'E' refer to MDI, TEA and EDEA respectively. The unionized PU was designated M-0.0.

Measurements

Since the carboxylic groups in the chain extender used can react with the isocyanate groups, the number of carboxylic groups in the unionized PU may be less than that initially added. The content of carboxylic group of the unionized PU was determined by acid–base titration as follows. A given weight (3–5 g) of the sample was dissolved in 200 ml of hot DMF and two drops of phenolphthalein solution as indicator were added with agitation. The resulting solution was titrated with 0.1 M KOH in isopropanol solution.

Chemical composition (C, H, N, O) of the films was measured by an elemental analyser, model CHN-O-RAPID (Heraeus Co.).

Tensile properties were measured at room temperature using a Shimadzu Universal Testing Machine, Model

502, with a crosshead speed of 20 mm min^{-1} . The dumbbell type specimen was 25 mm wide at the two ends, 0.1–0.4 mm thick, and 10 mm wide at the neck (JIS K6301 method).

Differential scanning calorimetric (d.s.c.) thermograms over the temperature range -30 to $+180^\circ\text{C}$ were recorded using a DuPont 910 apparatus with a heating rate of $20^\circ\text{C min}^{-1}$, under nitrogen purging.

Infra-red spectra (i.r.) were recorded using an i.r. spectrophotometer, Perkin-Elmer Model 983, at a resolution of 3 cm^{-1} .

Dynamic mechanical properties over the temperature range -150 to $+140^\circ\text{C}$ were measured using a Rheometric Dynamic Spectrometer Model RDS-II (Rheometrics Inc.).

Wide-angle X-ray diffractions (WAXD) were measured using a Shimadzu model XD-5 diffractometer. The X-ray beam was nickel-filtered $\text{CuK}\alpha$ ($\lambda = 0.1542 \text{ nm}$) radiation from a sealed tube operated at 30 kV and 20 mA. Data were obtained from 5° to 40° (2θ) at a scan rate of 4° min^{-1} with a smoothing time constant of 4 s.

Molecular weight distributions of the polymers so prepared were measured by a model 201 Gel Permeation Chromatograph from Waters Associates at room temperature. The flow rate of the carrier solvent, DMF, was 0.5 ml min^{-1} . The average molecular weights were calculated on the basis of the molecular weight versus retention volume curve of monodisperse polystyrene standards.

A Jeol 200CX scanning transmission electron microscope (STEM) (Japan Electronic Optics Laboratory) operating at 120 kV and $20000\times$ magnification was used to examine the morphology of the samples. Microtomed specimens were mounted directly on the 400 mesh copper grids without a supporting film and then stained with OsO_4 by a well developed technique¹³ applicable to polyurethane¹⁴. During TEM observation, special precautions were taken to minimize electron beam damage of the specimens by focusing on an area and translating to an adjacent area for data recording.

RESULTS AND DISCUSSION

Elemental analysis (EA)

Results of elemental analysis of the films are shown in Table 1. The theoretical compositions were determined based on the raw materials added during the reaction. For the TEA system, as the degree of ionization increases, the number of atoms of carbon (C), hydrogen (H) and nitrogen (N) increase, while that of oxygen (O) remains unchanged. For the EDEA system, as the degree of ionization increases, the number of atoms of all four elements increase. The measured values are very close to the theoretical values, indicating that all the amine added was reacted completely and no appreciable amount of amine was retained in the sample.

Infra-red spectroscopy (i.r.)

I.r. spectra of the films of unionized PU (M-0.0) and two ionized systems with degree of ionization of 1.0 (MT-1.0 and ME-1.0) cast from MEK solutions are shown in Figure 2. For the unionized PU (M-0.0), the $\text{C}=\text{O}$ bands from the urethane group (NHCO) and the carboxylic acid group (COOH) overlap and have a peak at 1729 cm^{-1} (corresponding to unbonded $\text{C}=\text{O}$). In the

Table 1 Results of elemental analysis of the films

| Sample | Atomic ratio | | | | | | | |
|--------|--------------------------|-------|------|------|----------|-------|------|------|
| | Theoretical ^a | | | | Measured | | | |
| | C | H | N | O | C | H | N | O |
| M-0.0 | 187 | 296 | 8 | 49 | 187 | 290.7 | 8.4 | 48.3 |
| MT-0.7 | 197.8 | 323 | 9.8 | 49 | 197.8 | 318.2 | 10.1 | 49.4 |
| MT-1.0 | 202.8 | 335.6 | 10.6 | 49 | 202.8 | 332.4 | 10.5 | 49.6 |
| ME-0.7 | 197.8 | 326.6 | 9.8 | 52.6 | 197.8 | 324.3 | 9.7 | 53.1 |
| ME-1.0 | 202.8 | 340.9 | 10.6 | 54.3 | 202.8 | 337.2 | 10.5 | 54.9 |

^a The theoretical atomic ratios were calculated on the basis of the mole ratio of the unionized film $\text{PTMO/MDI/DMPA} = 1/4/3$

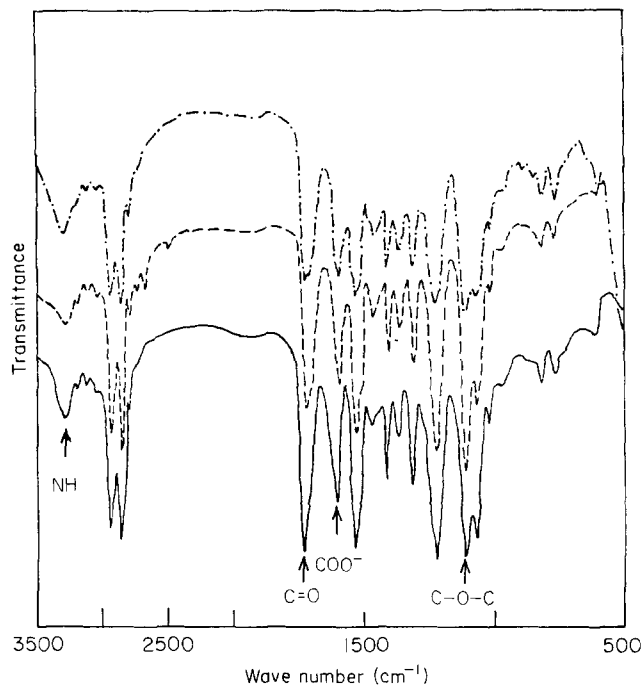


Figure 2 I.r. spectra of the films: (—) M-0.0, (---) MT-1.0, (- - -) ME-1.0

region of the NH band ($3000\text{--}3500 \text{ cm}^{-1}$), a peak at 3286 cm^{-1} is present due to the hydrogen-bonded NH group, but the peak at 3460 cm^{-1} due to free NH is not present, indicating that the NH groups appear to be completely hydrogen-bonded.

For the unionized PU, the C-O-C band from polyether soft segment has a peak at 1109.5 cm^{-1} . Upon ionization, this peak shifts to 1113.5 cm^{-1} for all the ionized films. Moreover, for all the ionized films, the absorption range of $-\text{COO}^-$ overlaps with that of aromatic $\text{C}=\text{C}$ bond and has a peak at 1600 cm^{-1} (Figure 2). Its relative intensity increases significantly after ionization, indicating that after ionization the carboxylate ion ($-\text{COO}^-$) actually exists in the films.

Since the unionized PU has a COOH group on each hard segment, the COOH group can form a hydrogen bond both with another COOH group from neighbouring hard segments and with the C-O-C group of the soft segments. Upon ionization, the COOH group was converted to $-\text{COO}^-$ group and the number of hydrogen bonds between the soft/hard segments diminishes, hence the C-O-C band shifts from 1109.5 cm^{-1} to 1113.5 cm^{-1} .

For the TEA ionization films, the $\text{C}=\text{O}$ peak shifts downward. The extent of the shift increases with the

degree of ionization, and is 7.6 cm^{-1} at a degree of ionization of 1.0 (MT-1.0). The NH peaks remain unchanged upon ionization. For the unionized film, the NH group can form hydrogen bonds with another NH group and the C–O–C group of the soft segment. After ionization, some of the NH groups previously bonded to the C–O–C groups must shift to bond with the C=O group of the hard segment.

For the EDEA ionization films, the C=O band is split into two peaks; that centred at 1713 cm^{-1} is due to bonded C=O, and that at 1721 cm^{-1} to free C=O. The relative intensity of the bonded C=O increases as the ionization level increases. This is because each EDEA counterion has two OH groups and the OH group can form a hydrogen bond with both another OH group and the C=O group of the hard segment.

If the ionization does not affect the packing arrangement of both the soft and hard segments, the C=O band from the hard segments and C–O–C band from the soft segments will not change upon ionization. However, for the two ionization systems, these bands do change after ionization. Thus, the ionization process does change the packing arrangement of both the soft and hard segments.

Dynamic mechanical analysis (d.m.a.)

Dynamic mechanical measurements were carried out for the unionized PU and two amine ionization systems. Results for ionic content 0.7 and the unionized PU are shown in Figure 3. The transition temperatures determined from the maxima of $\tan \delta$ curves are listed in Table 2. Three peaks are observed in the $\tan \delta$ curves. The β peak is taken as the glass transition temperature of the soft domains (T_{gs}). The presence of the γ peak (below the β peak) between -131 and -148°C can be attributed to a relaxation process involving local motion of the methylene sequences of the polyether segments^{1,5}. The α peak is taken as the glass transition temperature of the disordered hard segments (T_{gh}).

For the TEA ionization system, after ionization to the content of 0.7 and 1.0, the T_{gs} drops by 58°C and 59°C , respectively, and the T_{gh} increases by 29°C and 26°C , respectively. These results would indicate that the incorporation of the ionic component increases the degree of phase separation and cohesion in the hard domains. MT-0.7 has a higher T_{gh} value than MT-1.0 due to more ordered hard domains in the former, since a larger

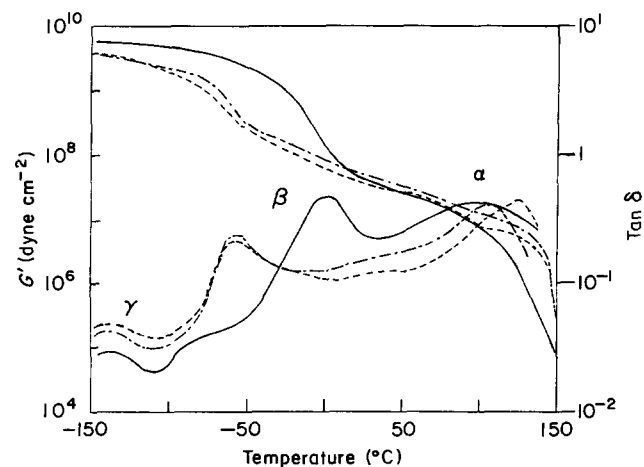


Figure 3 Dynamic mechanical analysis of the films: (—) M-0.0, (---) MT-0.7, (-.-) ME-0.7

Table 2 Characteristic peaks from dynamic mechanical curves of the films

| Sample | γ peak ($^\circ\text{C}$) | β peak ($^\circ\text{C}$) (T_{gs}) | α peak ($^\circ\text{C}$) (T_{gh}) |
|---------------------|------------------------------------|--|---|
| M-0.0 | -138 | +2 | +97 |
| MT-0.7 | -137 | -56 | +126 |
| MT-1.0 | -138 | -57 | +123 |
| ME-0.7 | -136 | -57 | +105 |
| ME-1.0 | -134 | -61 | +94 |
| AM-0.0 ^a | -139 | -12 | +96 |
| MC-0.0 ^b | -127.4 | -65.8 | +50.0 |
| MC-0.7 | -128.4 | -65.3 | +51.0 |
| MC-1.0 | -129.1 | -65.0 | +55.0 |
| MB ^c | | -60.0 | +135.0 |

^aThe prefix A denotes annealing at 60°C for 7 days

^bSystem of PTMO/MDI/MDEA/glycolic acid with mole ratio 1/6/5 of the first three compounds, where 'C' refers to cationomer

^cSystem of PTMO/MDI/1,4-butanediol with mole ratio of 1/4/3 (data taken from ref. 6)

amount of the bulky amine molecules are incorporated in the hard domains for MT-1.0, leading to more disordered hard domains.

For the EDEA ionization system, after ionization to the content of 0.7 and 1.0, the T_{gs} drops by 59 and 63°C , respectively, and the T_{gh} increases by 8°C and decreases by 3°C , respectively. These results would indicate that the degree of phase separation increases with the degree of ionization as in the TEA system. The increase and then decrease of T_{gh} might indicate an increased cohesion due to the increased degree of ionization and an overcompensation of the increased extent of disorder.

For the unionized PU annealed at 60°C for 7 days, the d.m.a. result, given in Table 2, shows a drop in the T_{gs} of 14°C . This result would indicate that annealing increases the degree of phase separation of the film.

A comparison between TEA and EDEA ionization systems shows that the TEA system has more ordered hard domains than the EDEA system, since the TEA molecule is more symmetrical than the EDEA molecule. The results of tensile-elongation, morphology and thermal measurements also support this interpretation as will be discussed below.

Differential scanning calorimetry (d.s.c.)

D.s.c. curves for all the films without and with annealing are shown in Figures 4 and 5, respectively. The temperatures and heats for the characteristic peaks of all samples are listed in Table 3.

For all films except the unionized PU, an endothermic peak was found in the temperature range of 10 – 23°C (Figure 4). The temperature of this peak corresponds to the melting peak of the flexible soft domains^{9,10,16}, while the hard domain has no detectable order, in contrast to those of the conventional PU (composed of PTMO/MDI/1,4-butanediol¹⁷) and PU cationomers studied by Chen and Chan^{7,18} for which the short range order-disorder transition temperatures of hard domains are 70°C and 82 – 90°C . For both amine ionization systems, the film with a degree of ionization of 0.7 has lower melting temperature (T_{ms}) and smaller heat of melting (ΔH_{ms}) than that with a degree of ionization of 1.0, possibly due to smaller crystallite size and degree of crystallinity of the former caused by the lower degree of phase separation as indicated by d.m.a.

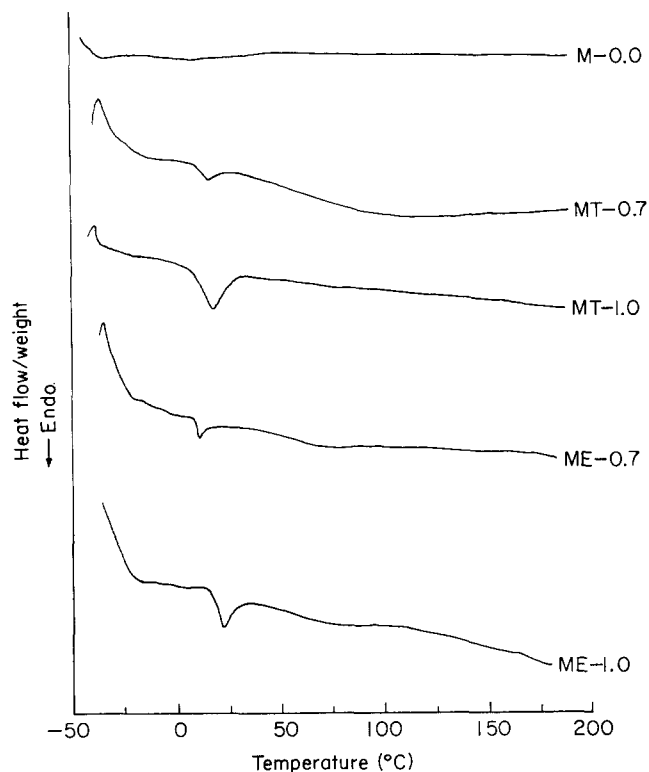


Figure 4 D.s.c. curves of the films

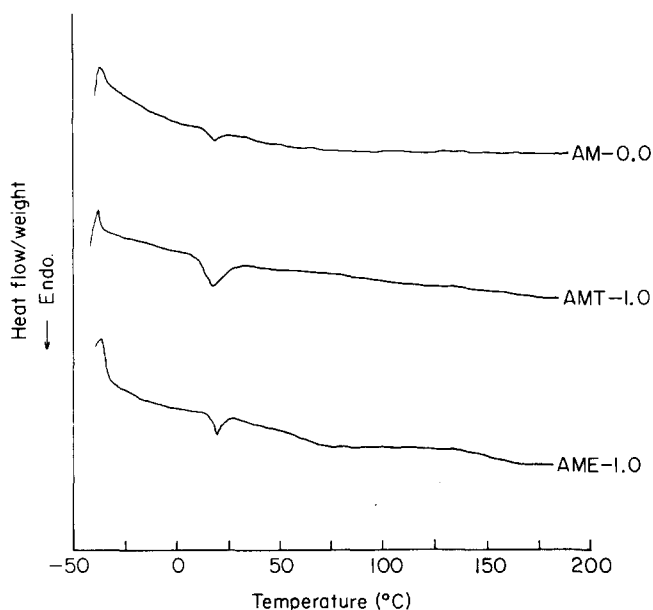


Figure 5 D.s.c. curves of the films annealed at 60°C for 7 days

Table 3 Characteristic peaks from d.s.c. curves of the films

| Sample ^a | T_{ms} (°C) | ΔH_{ms} (J g ⁻¹) |
|---------------------|---------------|--------------------------------------|
| M-0.0 | — | — |
| MT-0.7 | 15.5 | 1.2 |
| MT-1.0 | 18.4 | 3.7 |
| ME-0.7 | 10.3 | 0.9 |
| ME-1.0 | 21.0 | 2.8 |
| AM-0.0 | 15.4 | 0.9 |
| AMT-1.0 | 17.0 | 3.6 |
| AME-1.0 | 19.2 | 2.7 |

^aThe prefix A denotes annealing at 60°C for 7 days

For the amine ionization films annealed at 60°C for 7 days, the d.s.c. results are shown in Figure 5. The unionized film generates an endothermic peak at 15°C, indicating that annealing can improve the order of the soft domains and enhance phase separation as confirmed by d.m.a. For the ionized films, the d.s.c. curves are similar to those of the unannealed case, indicating that the annealing has no appreciable effect on the order of soft and hard domains.

Wide-angle X-ray diffraction (WAXD)

Wide-angle X-ray diffraction (WAXD) measurements on the unionized PU and all ionized films each render a single, diffused scattering peak with an intensity maximum at $2\theta = 20^\circ$, indicating that no crystallinity of either hard or soft segments was detected by WAXD¹⁶. Since the d.s.c. data (Table 3) show that the PTMO melts below room temperature, the degree of crystallinity of the soft domains cannot be detected by WAXD at room temperature.

Morphological changes after ionization

TEM micrographs of the unionized film and two ionized films cast from solutions are shown in Figure 6. The M-0.0 sample (Figure 6a) shows a morphology with soft domains as the continuous phase and hard domains as the dispersed phase. Upon ionization, for the TEA system (MT-1.0), the hard domains aggregate to form agglomerates and still present as the dispersed phase (Figure 6b).

For the EDEA system, upon ionization (ME-1.0), its hard domains have less order than those of the TEA system resulting from higher asymmetry of EDEA. Thus the size of hard domains increases to a much lesser extent than that of the TEA system and still present as the dispersed phase (Figure 6c). This result is in agreement with those from d.m.a. and t.g.a. measurements.

Tensile properties

Tensile properties of all the films are shown in Figure 7. The tensile strength and elongation at break are listed in Table 4. For all the films, the tensile-elongation curves are all concave upwards and the specimens under test show whitening during elongation. Thus crystallization evidently occurs in the soft domains during the deformation. This result reflects the fact that the hard domains must aggregate so tightly as to act as 'physical cross-links'.

Upon ionization, both the tensile strength and elongation at break increase, owing to the significant increase in phase separation and hard-segment cohesion. Since the TEA ionization system has more ordered hard domains than the EDEA ionization system as confirmed by the d.m.a. and morphological studies, the former has higher tensile strength than the latter. For both ionization systems of amine type, the degree of ionization of 0.7 has more ordered hard segments than the degree of ionization of 1.0 as confirmed by the result of d.m.a., so the former has higher tensile strength than the latter.

According to the studies by Al-Salah and co-workers⁸, the tensile strength of PU anionomers increases with increasing ionic potential of metal counterion (the ionic potential is defined as the ratio of the cation charge to the cation radius). For monovalent metal counterions, the cation charge is equal and all the cations are spherical,

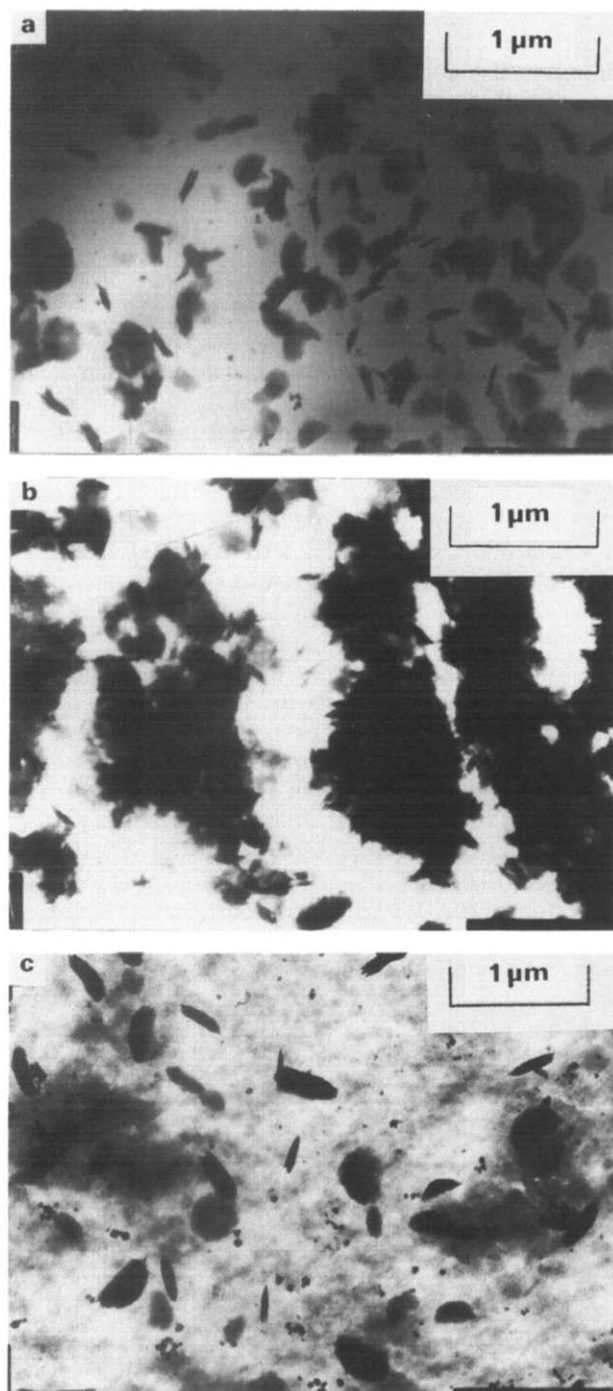


Figure 6 TEM micrographs of the films: (a) M-0.0; (b) MT-1.0; (c) ME-1.0

so the extent to which anions of the polymer backbone are polarized increases with decreasing cation radius. For the PU anionomers in this study, the sequence of the radii of the counterions are EDEA > TEA. Thus, the TEA system has more ordered hard domains and stronger coulombic interactions than the EDEA system, thus the former has higher tensile strength than the latter, which is consistent with the results of Al-Salah *et al.*⁸.

For the unionized film after annealing at 60°C for 7 days, the tensile properties increase significantly as shown in Table 4. This result indicates that annealing can improve the order of the soft domain and enhance phase separation as confirmed by d.s.c. and d.m.a. For the ionized films, annealing does not produce a significant

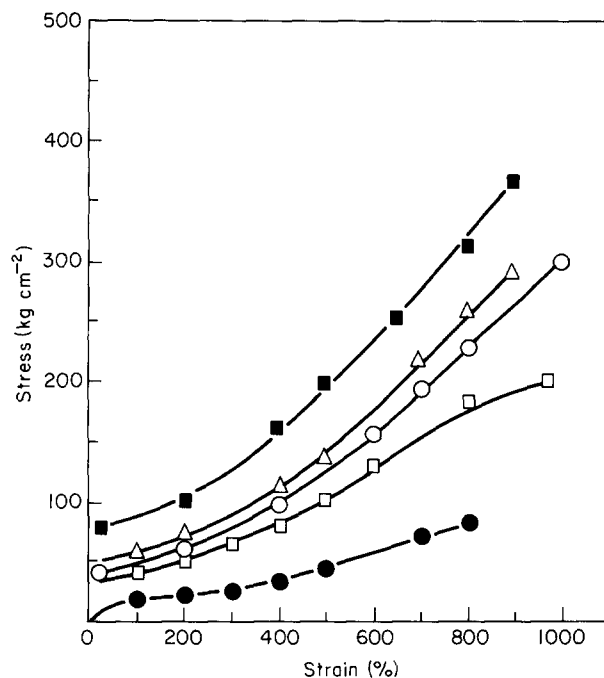


Figure 7 Stress-strain curves of the films: (●) M-0.0; (■) MT-0.7; (○) ME-0.7; (△) MT-1.0; (□) ME-1.0

Table 4 Characteristic values of tensile-elongation curves and molecular weight of the films

| Sample | Tensile strength (kg cm ⁻²) | Elongation (%) | Molecular weight (× 10 ⁴) | |
|---------------------|---|----------------|---------------------------------------|-------------|
| | | | \bar{M}_n | \bar{M}_w |
| M-0.0 | 82 | 796 | 28.1 | 106 |
| MT-0.7 | 363 | 900 | 28.0 | 108 |
| MT-1.0 | 290 | 892 | 27.6 | 103 |
| ME-0.7 | 298 | 999 | 29.1 | 109 |
| ME-1.0 | 200 | 976 | 28.3 | 105 |
| MB ^a | 234.6 | 860 | 7.5 | |
| MC-0.0 ^b | 51 | 1328 | 9.2 | 13.9 |
| MC-0.7 | 59 | 1257 | 9.2 | 13.9 |
| MC-1.0 | 71 | 959 | 9.2 | 13.9 |
| MZ-0.0 ^c | 4.7 | 1940 | | |
| MZ-0.47 | 382.5 | 720 | | |
| MZ-0.99 | 369.6 | 480 | | |
| AM-0.0 | 216 | 820 | | |
| AMT-1.0 | 296 | 874 | | |
| AME-1.0 | 207 | 955 | | |

^a System of PTMO/MDI/1,4-butanediol with mole ratio of 1/4/3 (data taken from ref. 6)

^b System of PTMO/MDI/MDEA/glycolic acid with the same number designation as in the present system, where 'C' refers to cationomer (data taken from ref. 18)

^c System of PTMO/MDI/MDEA/propane sultone with the same number designation as in the present system, where 'Z' refers to zwitterionomer (data taken from ref. 4)

effect on the tensile properties, since these films are already highly phase-separated before annealing.

Comparison with other PU ionomers

Comparing the unionized film of the present anionomer (M-0.0) with conventional PU of PTMO/MDI/butanediol (MB)⁶, the chain extender DMPA of the former has a COOH group, which can form a hydrogen bond with the ether group of the soft segments and thus causes an increased phase mixing between soft and hard segments as reflected by the higher T_{gs} of the former (+2°C) than of the latter (-60°C) (Table 2). In addition, the

asymmetrical structure of DMPA would lead to an increased hindrance to the alignment of the hard segment, while for the latter, the chain extender butanediol is symmetrical, allowing the hard segments to be crystallizable and aligned in an ordered fashion⁶. Thus, in spite of the higher molecular weight of the former, the T_{gh} and tensile strength of the former are lower than those of the latter (Tables 2 and 4). This would mean that the ordering of hard segment is the dominant factor in determining the tensile strength of the films.

For the PU cationomers of PTMO/MDI/MDEA/glycolic acid studied by Chen and Chan^{7,18}, ordering in the hard domains appears for both the unionized and ionized films. In the PU anionomers of PTMO/MDI/DMPA/amine, since the chain extender DMPA is more asymmetrical than MDEA in the cationomers and the anionomers are branching (resulting from the reaction of COOH with NCO) instead of linearity as in the cationomers, only the soft domain is crystallizable, and no order-disorder transition in the hard domains was observed. Thus for the unionized films, one would expect a T_{gh} and tensile strength of the cationomer (MC-0.0) higher than those of the anionomer (M-0.0). However, the T_{gh} (Table 2) and tensile strength (Table 4) of the anionomers are higher than those of the cationomers. This must be due to the higher molecular weight of the anionomers (Table 4). Further comparing the counterions of these two ionomers, the size of the quaternary ammonium ions for the anionomers is larger than the glycolate ion for the cationomers, leading to a weaker coulombic interaction in the former. Thus, the anionomers with more disordered hard domain and weaker coulombic interaction would be expected to give T_{gh} and tensile strength lower than those of the cationomers with the same molecular weight. However, from Tables 2 and 4, the anionomers have T_{gh} and tensile strength values higher than the cationomers. This must be also due to the higher molecular weight of the anionomers, over seven times that of the cationomers. The number of physical crosslink sites between chains of the former are much larger than those of the latter (as also reflected in the presence of a rubbery plateau of the anionomers in Figure 3), which leads to higher T_{gh} and tensile strength, so the molecular weight is the dominant factor in determining the tensile strength of the films.

Comparing the anionomers with the zwitterionomers of PTMO/MDI/MDEA/propane sultone⁴, the hard domain of the former is more disordered than that of the latter, resulting from the branching structure of the former. For the anionomer, two neighbouring hard segments with negative charges are bridged by a counterion, but for the zwitterionomers, two neighbouring hard segments can interact directly via coulombic force, and therefore the cohesion is strongly enhanced. From these considerations, the mechanical properties of the anionomer should be inferior to those of the zwitterionomer at the same molecular weight. However, the anionomers have tensile strength approximately equal to the zwitterionomers (Table 4). This indicates that the present PU anionomers must have higher molecular weight than the zwitterionomers.

CONCLUSIONS

For the NCO-terminated polyurethane (PU) prepolymer, chain extension by use of the chain extender, dimethylol-

propionic acid, can lead to a PU with some branching and phase mixing between soft and hard segments as compared with PU with other chain extenders. The ionization can induce crystallization in the soft domains resulting from the increased phase separation and enhanced cohesion through the coulombic interactions in the hard domains. The TEA ionization system has higher hard segment cohesion and slightly lower extent of phase separation than the EDEA ionization system. For both amine ionization systems, the degree of ionization of 0.7 has more ordered hard domains than the degree of ionization of 1.0. The tensile strength of the two systems of anionomers increases with increasing ionic potential and falls in the sequence: TEA > EDEA.

The morphologies of the unionized and ionized films both show that the hard domains are dispersed in the soft domains. The size of hard domain increases significantly after ionization. The TEA system has a larger size of hard domain than the EDEA system.

Comparing the anionomers with other PU ionomers, the physical properties of PU ionomers are strongly dependent on the molecular weight of polymers, ordering in the hard domains, and coulombic interactions between hard segments.

ACKNOWLEDGEMENTS

The authors wish to thank the National Science Council of the Republic of China for financial aid through the project Studies on Emulsion Polymer Systems, NSC 79-0405-E007-05.

REFERENCES

- Dieterich, D., Keberle, W. and Witt, H. *Angew. Chem. Int. Edn* 1970, **9**, 40
- Hwang, K. K. S., Yang, C. Z. and Cooper, S. L. *Polym. Eng. Sci.* 1981, **21**, 1027
- Yang, C. Z., Hwang, K. K. S. and Cooper, S. L. *Macromol. Chem.* 1983, **184**, 651
- Speckhard, T. A., Hwang, K. K. S., Yang, C. Z., Laupan, W. R. and Cooper, S. L. *J. Macromol. Sci.-Phys.* 1984, **B23**, 175
- Yu, X.-H., Nagarajan, M. R., Grasel, T. G., Gibson, P. E. and Cooper, S. L. *J. Polym. Sci., Polym. Phys. Edn* 1985, **23**, 2319
- Yu, X., Nagarajan, M. R., Li, C., Gibson, P. E. and Cooper, S. L. *J. Polym. Sci., Polym. Chem. Edn* 1986, **24**, 2681
- Chen, S. A. and Chan, W. C. *J. Polym. Sci., Polym. Phys. Edn* 1990, **28**, 1499
- Al-Salah, H. A., Frisch, K. C., Xiao, H. X. and Mclean, J. A. Jr *J. Polym. Sci., Polym. Chem. Edn* 1987, **25**, 2127
- Lee, D. C., Register, R. A., Yang, C. Z. and Cooper, S. L. *Macromolecules* 1988, **21**, 1005
- Miller, J. A., Hwang, K. K. S. and Cooper, S. L. *J. Macromol. Sci.-Phys.* 1983, **B22**, 321
- Al-Salah, H. A., Mclean, J. A. Jr, Frisch, K. C. and Xiao, H. X. *J. Macromol. Sci.-Phys.* 1987, **B26**, 447
- Malec, E. J. and David, D. J. in 'Analytical Chemistry of Polyurethane' (Eds D. J. David and H. B. Staley), Wiley, New York, 1969, pp. 86-90
- Wegner, G., Zhu, L. L. and Leiser, G. *Makromol. Chem.* 1981, **182**, 231
- Chan, K. W. and Geil, P. H. *Polymer* 1985, **26**, 490
- Kajiyama, T. and Macknight, W. J. *Trans. Soc. Rheol.* 1969, **13**, 527
- Kazmierczak, M. E., Fornes, R. E., Buchanan, D. R. and Gilbert, R. D. *J. Polym. Sci., Polym. Phys. Edn* 1989, **27**, 2173
- Seymour, R. W. and Cooper, S. L. *Macromolecules* 1973, **6**, 48
- Chan, W. C. *Doctoral Dissertation*, National Tsing-Hua University, Hsinchu, Taiwan, 1988