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### Synthesis and Characterization of Ion-Containing Poly(Urethane-urea-imide) Block Copolymers

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## **SYNTHESIS AND CHARACTERIZATION OF ION-CONTAINING POLY(URETHANE-UREA-IMIDE) BLOCK COPOLYMERS**

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**Key Words:** Ionomers, Quaternizers, Soft and Hard Segment, Ionic Interaction, Young's Modulus, Tensile Strength

### **ABSTRACT**

Poly(etherurethane-urea-imide) (PEUUI) block copolymers containing a tertiary amine have been synthesized by reaction of amine-terminated poly(etherurethane-urea) (PEUU) prepolymer with 3,3,4,4-benzophenonetetracarboxylic dianhydride (BTDA) followed by solution imidization. The amine-terminated PEU prepolymer was prepared using poly(tetramethylene oxide) of molecular weight 2000 as soft segment, toluene diisocyanate (TDI), N-methyldiethanolamine (MDEA), and 4,4-oxydianiline (ODA). The PEUUI block copolymer was converted to ionomer by quaternizing the tertiary amine of MDEA with different diacids and alkyl halides. Properties of PEUUI ionomer films cast from solution were studied by infrared spectroscopy, differential scanning calorimetry, dynamic mechanical analysis and stress-strain testing. The quaternization of PEUUI shifted the soft segment glass transition temperature ( $T_g$ ) of PTMO to a lower temperature with subsequent development of hard segment ordering in comparison to nonquaternized PEUUI. The morphological changes of PEUUI upon quaternization were accompanied by dramatic improvements in mechanical properties and dynamic modulus that was extended

to much higher temperatures. The mechanical properties and thermal transitions were found to depend on the nature of quaternizer, provided that the system exhibited a two-phase interconnecting morphology. The improved mechanical properties and lowered soft segment  $T_g$  of PEUI ionomer samples were due to increased hard domain cohesiveness caused by ionic interchain interactions and aggregation of ionic groups.

## INTRODUCTION

Polyurethane block copolymer is an important class of thermoplastic elastomer and is composed of soft and hard segments. The soft segment usually consists of a polyether-, polyester-, or polyalkyl- diol with a molecular weight between 500 and 3000, while the hard segment is formed by extending an aromatic diisocyanate with low molecular weight diol or diamine. A wide spectrum of physical properties and morphology has been observed, depending on the chemical structure of the soft and hard segments [1-10]. Because of the immiscibility between the hard and soft segments, polyurethanes undergo microphase separation. The hard-segment domains act as physical crosslinks as well as filler particles for the soft segment matrix. The primary driving force for phase separation is the strong intermolecular interaction of hydrogen bonding between the hard-hard segments of urethane and/or urea linkages. It has also been shown that some of the urethane NH- groups will associate with the oxygen of the soft-segment matrix phase. The degree of phase separation is influenced by the introduction of ionic groups into the hard segment units; the resulting materials may be termed "polyurethane ionomers". The introduction of ionic groups improves the hard segment cohesion [11-18] and increases the driving force for phase separation because of the extreme polarity difference between the soft and hard segments. The increased phase separation and domain cohesion are responsible for the improvement of mechanical properties that typically accompanies ion introduction [15-23]. Polyurethane ionomers can be prepared by incorporation of a chain extender containing tertiary amine with NCO-terminated polyurethane prepolymer and subsequent modification with an ionizable component. There are three types of polyurethane ionomers: cationomers, anionomers, and zwitterionomers [15-18].

Polyimide-based elastomers have received wide spread attention due to their unique properties, including an extremely high thermal stability, high mechanical strength, and good dielectric properties [24-32]. The incorporation of imide group as hard segments in polyurethane-urea block copolymers has been successfully

accomplished and their interesting bulk properties have been reported in the literature [26, 28]. In previous work [26], we prepared PEOUI block copolymers from different types of amine-terminated polyurethane oligomers with BTDA. It was found that these block copolymers have considerable better thermal stability and tensile properties than typical linear polyurethane. Polyurethane ionomer chains extended with imide groups containing potential ionic moieties have not been synthesized and studied. The present study focuses on the synthesis of new type of ionomer based on poly(etherurethane-urea-imide) (PEUUI) block copolymers. This study also explores the effects of quaternizers on the properties of PEUUI ionomers. The materials investigated are cationomers based on toluene diisocyanate-N-methyl-diethanolamine-4,4'-oxydianiline-BTDA hard segments, and poly(tetramethylene oxide) (PTMO) of 2000 molecular weight soft segments. The tertiary amine of MDEA was quaternized with different quaternizers to produce cationomers. The structure-property relationships of the resulting cationomers were investigated using FTIR, differential scanning calorimetry (DSC), Dynamic mechanical spectroscopy (DMA), and stress-strain testing.

## EXPERIMENTAL

### Materials

Toluene diisocyanate (TDI, 80% 2,4 and 20% 2,6-isomers, Aldrich Chemical Co.), dibutyltin dilaurate (catalyst T-12, Air Products), adipic acid, malonic acid, oxalic acid, succinic acid, 1,2-dibromoethane, and iodomethane from Aldrich were used as received. Poly(tetramethylene oxide) (PTMO, E. I. DuPont De Nemours Co.,  $M_n = 2000$ ) was dehydrated under vacuum at 70°C for 24 hours. 4,4'-Oxydianiline (ODA, Aldrich) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, Aldrich) were vacuum sublimed to yield off white solids. 1-Methyl-2-pyrrolidone (NMP, Fluka), 1-cyclohexyl-2-pyrrolidone (CHP, Aldrich) and N-methyl-diethanol amine (MDEA, Aldrich) were distilled under vacuum prior to use.

### Measurements

Fourier transform infrared spectra (FT-IR) of the polymers were recorded as neat films (prepared by casting a dilute solution of purified polymer in DMF over a KBr plates and evaporating the solvent at 60°C and further dried under vacuum) using a Nicole 400 spectrometer. A DuPont 910 differential scanning calorimeter (DSC) connected to a DuPont 2000 thermal analyzer was employed to study the

transition data of all polymers. The differential scanning calorimeter was run under a nitrogen stream at a flow rate of 50 cm<sup>3</sup>/min with a heating rate of 20°C/min. Dynamic mechanical analysis (DMA) measurements were conducted with a DMA 983, DuPont instrument with a frequency of 10 Hz in the extension mode and a heating rate of 2°C/min. The results have been measured in a temperature range from -100°C to 250°C. Tensile properties were determined from stress-strain curves with an Instron Tensile Tester Model 1026 at a strain rate of 5 cm/min. Measurements were performed at 25°C with a film thickness of about 300 μm and stamped out with a ASTM D412 die. The percent elongation recorded is the true strain determined from benchmarks placed on the sample. The stress was calculated as force/original cross-section area and an average of at least five individual determinations was used.

#### **Synthesis of Amine-Terminated Polyether Polyurethaneurea Oligomer (PEUU).**

The synthesis of PEUUI has been described previously [26] and has been slightly modified in this contribution. The synthesis scheme is diagrammed in Figure 1.

The polyol PTMO was homogeneously mixed with a calculated amount of MDEA to give an average value of  $M_n = 1014$  for the mixture. A resin kettle, equipped with a nitrogen inlet, stirrer, and thermometer was charged with one equivalent of polyol mixture. Two equivalents of TDI and 0.2% T-12 catalyst were slowly added with stirring under a dry nitrogen atmosphere at 40°C. The reaction temperature was maintained at 70-80°C until the isocyanate content (% NCO) reached the theoretical value of 6.17% NCO as determined by di-n-butylamine titration method.

The NCO-terminated polyurethane prepolymer was dissolved in NMP to form 20 wt% solution and cooled to 30°C. To the solution formed under stirring and nitrogen gas bubbling at ambient temperature, was added two equivalents of ODA dissolved in NMP. The reaction mixture was stirred for 1 hour at ambient temperature. The temperature was raised to 70°C and the reaction was allowed to proceed until the amine content reached the theoretical value as determined by non-aqueous titrimetry method [32].

#### **Synthesis of Poly(etherurethane-urea-imide) Copolymer (PEUUI)**

To 500-ml reaction kettle flask was added one equivalent of amine terminated PEUU solution. The solution was stirred, cooled in an ice bath and a stoichiometric amount of BTDA was added portionwise. The reaction mixture was stirred



under nitrogen for 3 hours at ice-bath temperature and then for 10 hours at room temperature to yield a viscous polyamic acid solution. The reduced viscosity of precipitated poly(amic acid) in NMP was 0.63 dL/g, measured at a concentration of 0.5- g/dL at 30°C in Ubbelohde viscometer.

The imidization of Polyamic was performed according to Waldbauer's technique [27]. A two-neck flask equipped with a Dean-Stark trap (half filled with CHP) and thermometer, was charged with (15% w/w) polyamic acid solution dissolved in a cosolvent system of NMP (80%) and CHP (20%). The reaction mixture was heated to 165°C in a hot silicone oil bath. Addition of CHP into polyamic acid solution as a azeotropic solvent in a 8:2 ratio was sufficient for the efficient removal of water which is formed upon the conversion of the amic acid to the imide and collected in the Dean-Stark trap. The reaction was allowed to heat for a total of 24 hours to ensure complete imidization as judged by FT-IR analyses [27, 29]. The imidization was confirmed by the observation of an appearance of characteristic imide related infrared absorption bands in the range 1770-1780  $\text{cm}^{-1}$  (asymmetrical amide I), 1721  $\text{cm}^{-1}$  (symmetrical amide I) and disappearance of amic acid band at 1535  $\text{cm}^{-1}$ . The homogeneous solution was then cooled to ambient temperature and precipitated in methanol in a high speed blender. The precipitated polymer was filtered off, washed with water, extracted with methanol and dried at 100°C under 5 mm Hg.

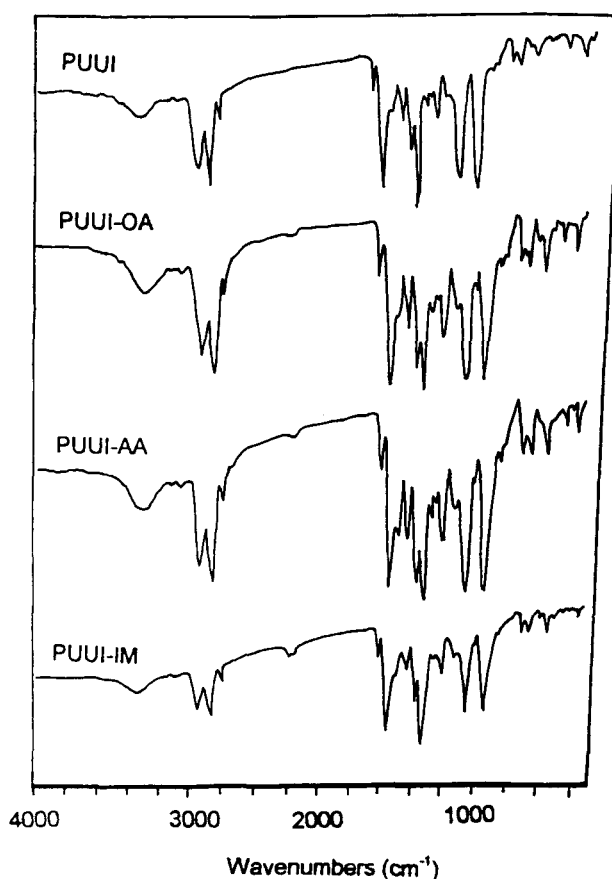
### Quaternization of Poly(etherurethane-urea-imide) Copolymer

The quaternization was performed according to a previously published procedure [18]. To obtain 100% degree of quaternization, a stoichiometric amount of quaternizing agent in NMP was added to the required amount of PEUUI (10% solution in NMP) containing tertiary amine and the whole system was stirred rapidly for at least 5 hours at 60°C. The quaternized PEUUI solution was cast onto soda-lime glass plates using a doctor blade with gaps set to ensure a final film thickness of 0.025mm and the solvent was removed at 80°C in an air oven for 24 hours. The semi-dried films were further dried at 80°C under vacuum for 48 hours. The resulting PEUUI films were tough, transparent and yellow to amber in color. All the quaternized PEUUI film samples were soluble in dimethylacetamide, N,N-dimethylformamide, dimethylsulfoxide, and NMP.

## RESULTS AND DISCUSSION

### Infrared Spectroscopy

Figure 2 shows the IR spectra of both PEUUI and PEUUI-ionomers cast



**Figure 2.** Typical FT-IR spectra of PUUI and PUUI ionomer series.

from NMP solutions. The characteristic of each major absorption band is listed in Table 1. Examination of the IR spectra of both nonquaternized and quaternized PEUUI reveals that all the spectra contain prominent characteristic bands of the imide, urea, and urethane groups. The NH band of the urethane linkage is observed at  $3286\text{ cm}^{-1}$  due to the hydrogen bonded NH group, but the peak at  $3460\text{ cm}^{-1}$  due to free NH is barely detectable. For the nonquaternized PEUUI, the C=O band (asymmetrical amide-I) has a peak at  $1774\text{ cm}^{-1}$ . Upon quaternization, this peak shifts to  $1780\text{ cm}^{-1}$ . For all the quaternized samples by dicarboxylic acids, where the -COOH group has been converted to a  $\text{-COO}^-$  groups, the frequency of the acid carbonyl overlaps with that of aromatic C=C bond and has a peak at  $1609\text{ cm}^{-1}$ . Its relative intensity increases significantly after quaternization, indicating that after quaternization the carboxylate ion  $[\text{-COO}^-]$  actually exists in the films. The C=O band at  $1656\text{ cm}^{-1}$  is assigned to the hydrogen-bonded urea carbonyl between the



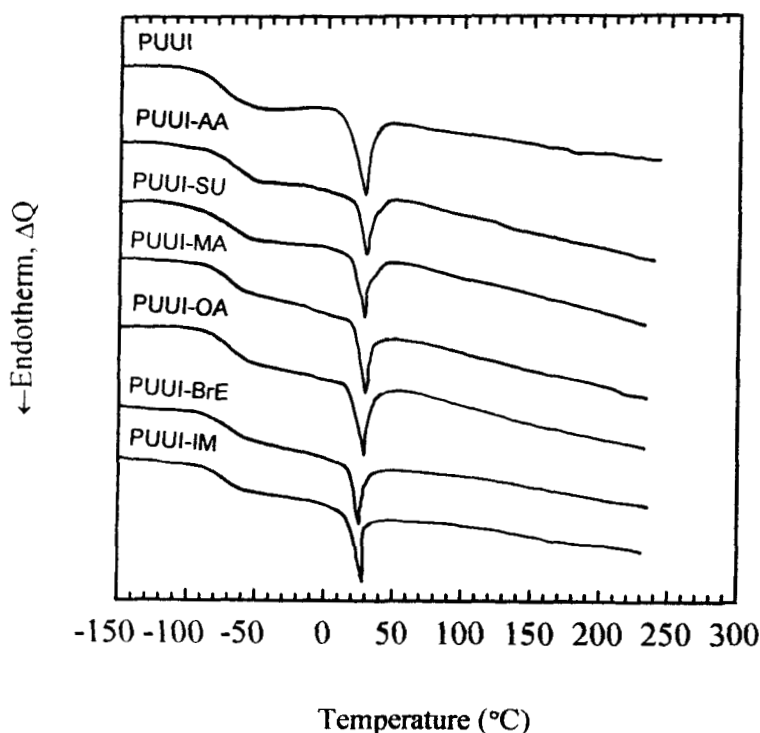
TABLE 1. FT-IR Absorption Bands with Assignments for Ion-Containing PUUI Block Copolymers

Frequency, $\text{cm}^{-1}$	Relative intensity <sup>a</sup>	Main assignment <sup>b</sup>
3460	w, sh	$\nu$ (NH) - free NH
3280	s	$\nu$ (NH) - bonded NH
2940	s	$\nu_a$ (C-H) in ether
2848	s	$\nu_s$ (CH <sub>2</sub> ) in ether
2796	m	$\nu_s$ (CH <sub>2</sub> ) in ether
1780	s	$\nu_s$ (C=O) amide I
1721	vs	$\nu_a$ (C=O) amide I + ureth.
1656-1668	s	$\nu$ (C=O) - bonded urea
1600-1609	s	$\nu$ (C=C) in benzene ring
1539	s	$\delta$ (NH) + $\nu$ (C-N) amide II
1380	s	$\nu$ (C-N) amide III
1228	vs	$\delta$ (NH) + $\nu$ (C-N)[38]
1110-1116	vs	$\nu$ (CH <sub>2</sub> -O-CH <sub>2</sub> )
828	w	$\gamma$ (C-H) in benzene ring
730	w	$\gamma$ (C=O) amide IV

<sup>a</sup> Relative intensity based on sample at room temperature. W = weak; m = medium; s = strong; vs = very strong; sh = shoulder.

<sup>b</sup>  $\nu$  = stretching;  $\delta$  = bending;  $\gamma$  = out of plane bending;  $\nu_a$  = asymmetric stretching;  $\nu_s$  = symmetric stretching.

hard segment chains and could be attributed to the stretching vibration of disordered urea carbonyl [34]. Upon quaternization the C=O of urea carbonyl band shifts to a higher frequency, i.e., 1668  $\text{cm}^{-1}$ . A free urea carbonyl peak at 1695  $\text{cm}^{-1}$  is not detected [8]. The C=O bands from urethane group and the symmetrical amide I overlap and have a peak at 1721  $\text{cm}^{-1}$ . The C-O-C band from the PTMO soft segment is observed at 1110  $\text{cm}^{-1}$ , for the PEUI, indicating the presence of



**Figure 3.** DSC curves of PUUI and PUUI ionomer series: second heating at 20°C/min, after cooling from 200 to -120°C at 10°C/min.

hydrogen bonding between the soft and hard segments. Upon quaternization, the amount of hydrogen bonding is reduced, and the band shifts to a higher frequency, i.e., 1116  $\text{cm}^{-1}$ .

### Thermal Analysis

Figure 3 shows the DSC curves obtained for PEUUI and PEUUI ionomer films after cooling from 200 to -120°C at 10°C/min. The glass transition temperatures ( $T_g$ s) and the width of transition zones of all samples are listed in Table 2. Figure 4 shows the effect of heating end cooling on the transition temperatures of PEUUI-M ionomer and the other samples presented the same behavior. The most noticeable aspect of Figure 4 is the presence of high temperature endotherms at 196°C related to hard segment block copolymer, which is similar to those of the conventional polyurethane composed of PTMO/MDI/1,4-butanediol [35]. From these  $T_g$  data (Table 2), it is found that the  $T_g$  of the 2000 MW soft segment in the

TABLE 2. DSC Data of Ion-Containing PEUI Block Copolymer

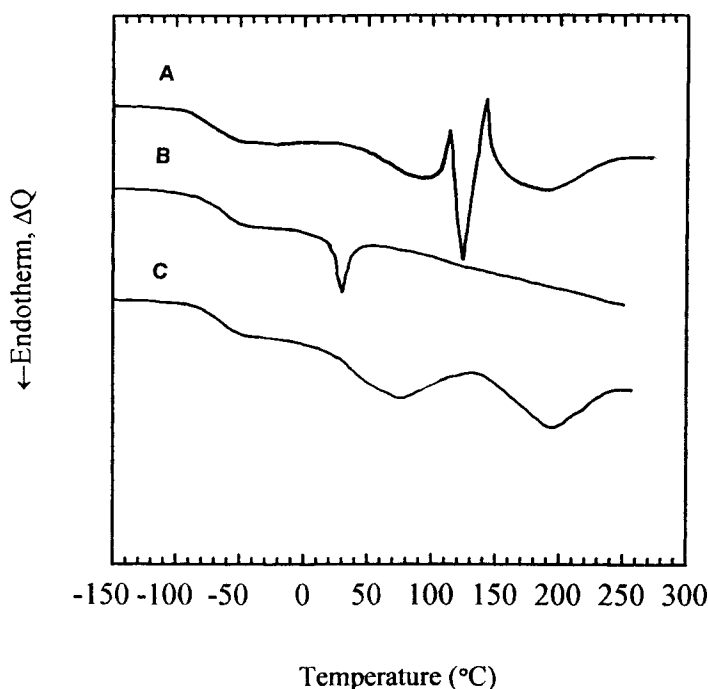
Sample**	T <sub>g</sub> .(°C) midpoint	T <sub>onset</sub> (°C)	T <sub>end</sub> (°C)	Zone width (°C)	E'' (β <sub>max</sub> ) (°C)
PUUI	-63	-80	-45	35	-50
PUUI-OA	-77	-88	-66	22	-68
PUUI-MA	-75	-86	-63	25	-65
PUUI-SU	-74	-88	-60	28	-62
PUUI-AA	-72	-87	-57	30	-60
PUUI-BrE	-76	-87	-64	23	-67
PUUI-IM	-78	-88	-69	19	-70

\*\* OA = Oxalic acid; MA = Malonic acid; SU = Succinic acid; AA = Adipic acid

BrE = 1,2-Dibromoethane; IM = Iodomethane

PEUI ionomer samples is 15°C lower than that of PEUI sample. In addition, a narrowing in the width of the transition zone of PEUI ionomers is observed. This suggests that the degree of phase purity of the soft domain increases dramatically upon quaternization of the hard segment. All the samples exhibited short range order-disorder transition temperature of hard domains at about 80°C. This temperature disappeared when the samples were quenched from 200°C to -120°C and the scan repeated. This implies that short-range ordering of hard domains is a kinetic effect which can be changed by a material's thermal history [35].

Figure 4 shows that when the PEUI-AA sample quenched from 200°C to -120°C at 10 or 5°C/min, a crystalline melting endotherm of PTMO appears at about 29°C, while the short-range hard domain ordering endotherm disappears. The appearance of the PTMO melting endotherm at about 29°C suggests that soft segment crystallization proceeds more completely under a slower cooling rate. Van Bogart *et al.* [36] and Miller *et al.* [37] observed the same phenomena in 2000-MW soft segment polyester- and polyether- polyurethanes. The semicrystalline soft do-

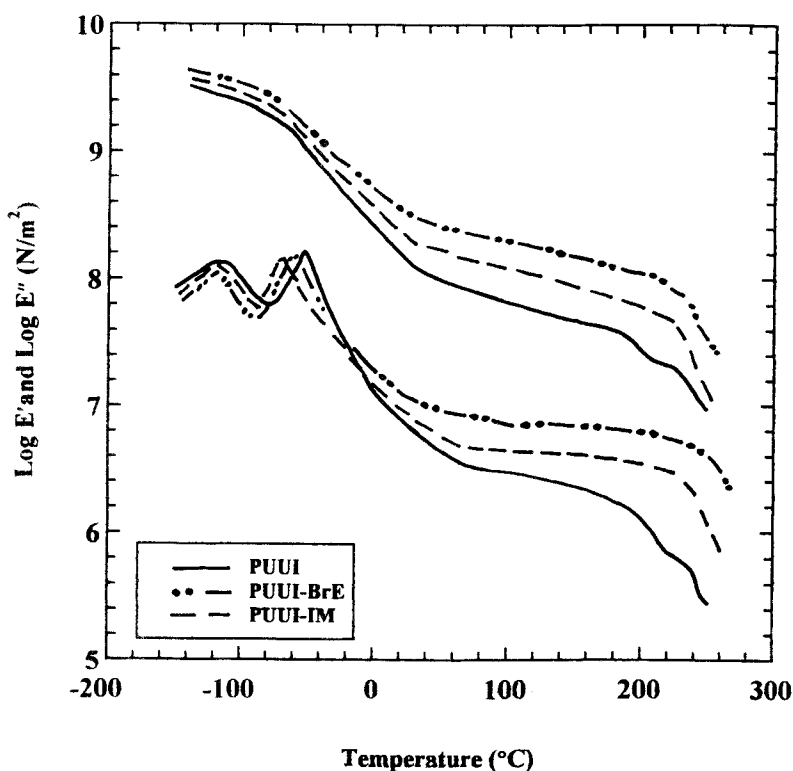


**Figure 4.** DSC curves of PUUI-AA ionomer sample: (A) first heating at 20°C/mini (B) second heating at 20°C/min, after cooling from 200 to -120°C at 10°C/mini (C) third heating at 20°C/min, after quenching from 250 to -100°C

mains inhibit the short-range ordering of the hard domains, and hence, no endotherm is seen.

#### Dynamic Mechanical Analysis

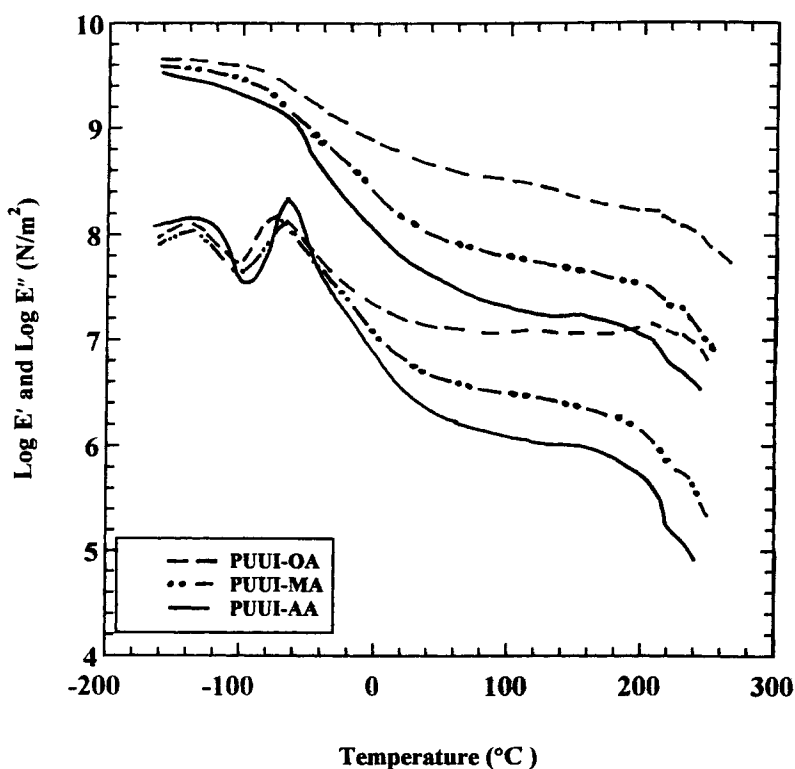
The loss modulus,  $E''$ , and the storage modulus,  $E'$ , for PEUUI and PEUUI ionomer films quaternized by alkyl halides and dicarboxylic acids are plotted as a function of temperature in Figures 5 and 6, respectively. The soft segment glass transition is listed in Table 2. The  $E''$  curves in Figures 5 and 6 show two relaxation processes in the materials. The relaxation at approximately -125°C results from the local-mode motions of the methylene sequences in the PTMO soft segment. The high-temperature relaxation corresponds to the soft-segment glass transition,  $\beta_s$ . It is seen very distinctly that the position of the  $\beta_s$  peak in the  $E''$  curves depends on the type of quaternization agent and follows the same trend as the glass transition temperature measured by DSC. Figures 5 and 6 show that the



**Figure 5.** Temperature dependence of dynamic storage modulus  $E'$  and loss modulus  $E''$  of the PUUI and PUUI ionomer series quaternized by alkyl halides.

quaternized PEUI samples exhibit a higher rubbery plateau modulus than the corresponding non-quaternized sample. This suggests increased hard-domain cohesion due to the aggregation of ionic groups, as the ionic groups provide interchain crosslinking within the hard domains. Quaternization also slightly increases the hard domain volume fraction, which causes an increase in the modulus due to a filler effect. The effect of methylene group length of the diacid quaternizers  $\text{HOOC}(\text{CH}_2)_n\text{COOH}$  ( $n = 0, 1, 2, 4$ ) on the rubbery plateau modulus is seen in Figure 6. As the methylene group length increases from  $n = 0$  to  $n = 4$ , the level of plateau modulus decreases due to the free volume between the hard-segment chains increasing and the inter-molecular associations diminishing.

The PEUI ionomers quaternized by mono- and dialkyl halides exhibit the same qualitative features as diacid quaternizers. The dynamic mechanical curves of these materials (Figure 5) do indicate a high degree of ionic association as evidenced

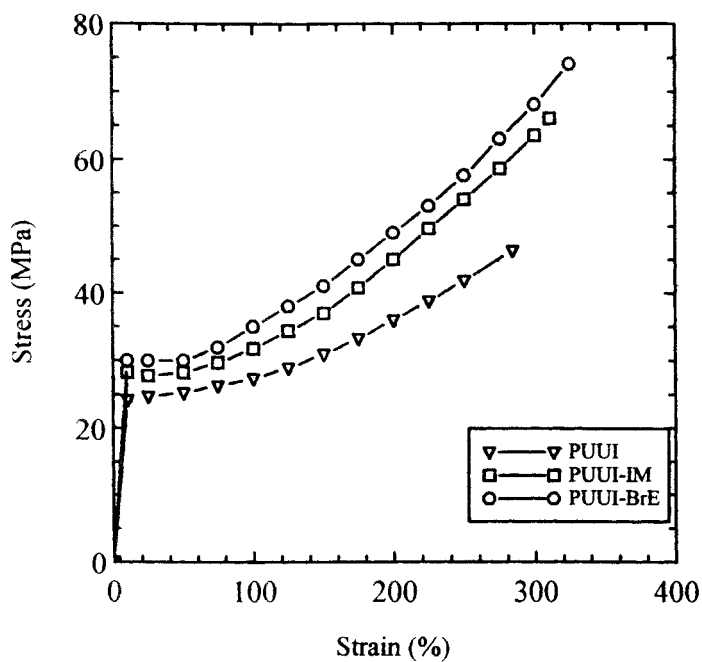


**Figure 6.** Temperature dependence of dynamic storage modulus  $E'$  and loss modulus  $E''$  of the PUUI and PUUI ionomer series quaternized by dicarboxylic acids.

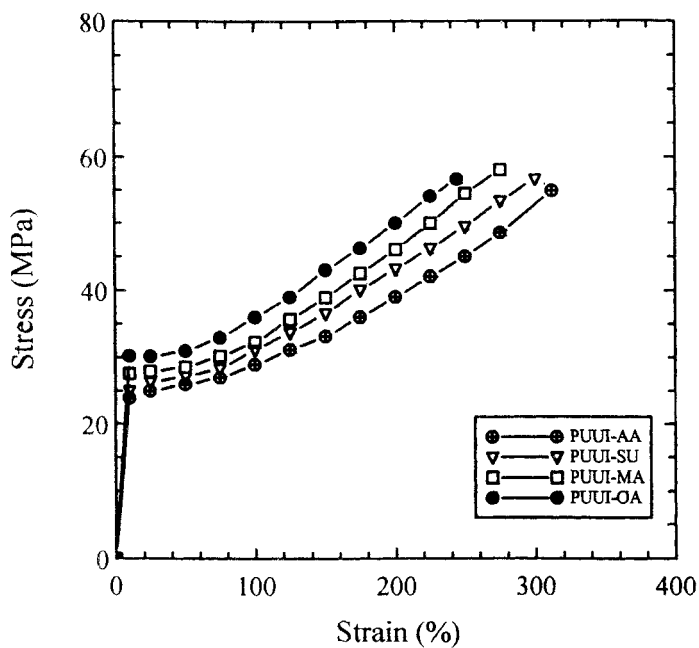
by the somewhat elevated rubbery plateau modulus. In all cases, the differences can be attributed to differences in the interchain interactions. The relative degree of ionic interaction in these materials can be summarized as follows:  $OA \cong BrE > MA > IM > SU > AA$ . This result is consistent with those obtained from DSC analysis and supports the conclusion drawn from the DSC data.

### Mechanical Properties

Mechanical properties of PEUUI ionomers as determined by stress-strain analysis generally depends on the type of quaternization agent, concentration of the hard domains, intermolecular bonding within the hard domains, and the ability of the soft segment to crystallize under strain. Figures 7 and 8 show the stress-strain curves of the PEUUI and PEUUI ionomer samples quaternized by alkyl halides and dicarboxylic acids, and the results are summarized in Table 3. The stress-strain



**Figure 7.** Stress-strain curves of PUUI and PUUI ionomer series quaternized by alkyl halides.



**Figure 8.** Stress-strain curves of PUUI ionomer series quaternized by dicarboxylic acids.

TABLE 3. Tensile Properties of Ion-Containing PUUI Block Copolymers

Sample **	Tensile Strength, MPa	Elongation at Failure, %	Secant Modulus, MPa		Young's Modulus, MPa
			100%	200%	
PUUI	46.3	284	27	36	42
PUUI-OA	56.6	244	36	50	132
PUUI-MA	58.0	275	32	46	120
PUUI-SU	56.6	300	30	43	116
PUUI-AA	54.8	312	29	39	112
PUUI-BrE	74	325	35	49	138
PUUI-IM	66	311	32	45	118

\*\* OA = Oxalic acid; MA = Malonic acid; SU = Succinic acid; AA = Adipic acid

BrE = 1,2-Dibromoethane; IM = Iodomethane

curves of PEUUI quaternized by SU, BrE, AA, and IM materials are all concave upwards and the samples under test show whitening during elongation. Thus, crystallization evidently occurs in the soft domains during deformation. It is seen that the quaternization of PEUUI leads to higher Young's modulus and tensile strength and their values depend on the type of quaternization agent. This may be attributed to hard domain cohesion which has more of an interconnected morphology. It is also possible that the improved phase separation increases the volume fraction of the hard phase, thereby increasing the modulus by enhancing the filler effect. Figure 8 illustrates the effect of methylene group length of the diacid quaternizers  $\text{HOOC}(\text{CH}_2)_n\text{COOH}$  on the mechanical properties of PEUUI ionomers. The results show that the Young's modulus and tensile strength decreases, whereas elongation at break increases with increasing methylene group length. This is due to the phase cohesion of the hard domains by ionic interchain interactions and their reduced ability to deform which decrease with increasing methylene group length.



Whereas the increase of ultimate elongation at break with increasing methylene group length is due to stress-induced crystallization of the soft segment, which prevents premature failure. The stress-strain curve of PEUII-BrE ionomer (Figure 8) shows a higher tensile strength, Young's modulus and elongation at break than PEUII-OA ionomer. This result is consistent with those obtained from DMA analysis and clearly shows that the strength of ionic interactions that occur in PEUII-BrE is greater than in PEUII-OA ionomer. The greater ionic interactions drives the system to more phase separation and possibly enhances the system's ability to crystallize further under strain.

## CONCLUSION

Poly(etherurethane-urea-imide) block copolymer containing tertiary amine was successfully prepared by reaction of amine-terminated poly(etherurethaneurea) prepolymer and BTDA and followed by solution imidization. Ion-containing PEUII was accomplished by quaternizing the tertiary amine of MDEA with different diacids and alkyl halides and the effects of quaternizers on the morphology and mechanical properties have been investigated. The resulting PEUII ionomer films were tough, transparent, and yellow to amber in color. The nonquaternized PEUII material was not highly phase separated, and quaternization improved both the degree of phase separation and hard segment domain cohesion. The changes in morphology of PEUII upon quaternization led to a greater tensile strength, Young's modulus and dynamic modulus that was extended to much higher temperatures. The quaternization of PEUII shifted the glass transition temperature of soft segment to a lower temperature and well developed hard segment ordering. In general, mechanical properties and thermal transitions were found to depend on the type of quaternizing agents. The effects of quaternization level and tertiary amine content on the morphology and physical properties of PEUII ionomers, PEUII zwitterionomers, and metal-containing PEUIIs are being investigated.

## ACKNOWLEDGEMENTS

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## REFERENCES

- [1] N. S. Schneider, C. R. Desper, J. L. Illinger, and A. O. King, *J. Macromol. Sci. Phys., B11*, 527 (1975).
- [2] J. L. Illinger, N. S. Schneider, and F. E. Karasz, *Polym. Eng. Sci.*, *12*, 25 (1972).
- [3] P. E. Gibson, M. A. Vallance, and S. L. Cooper, *Properties of Polyurethane Block Polymers, in Developments in Block Copolymers*, I. Goodman, Ed., Elsevier, London, 1982.
- [4] L. R. Schroeder and S. L. Cooper, *J. Appl. Phys.*, *47*, 4310 (1976).
- [5] J. T. Koberstein and I. Gancarz, *J. Polym. Sci., Polym. Phys. Edn.*, *24*, 2487 (1986).
- [6] C. M. Bruntte, S. L. Hsu, and W. J. Macknight, *Macromolecules*, *15*, 71 (1982).
- [7] J. W. C. Van Bogart, P. E. Gibson, and S. E. Cooper, *J. Polym. Sci., Polym. Phys. Edn.*, *21*, 65 (1983).
- [8] L. Ning, W. De-Ning, and Y. Sheng-Kang, *Polymer*, *37*, 3045 (1996).
- [9] L. S. Teo, C. Y. Chen, and J. F. Kuo, *Macromolecules*, *30*, 1793 (1997).
- [10] C. D. Eisenbach and L. Stadler, *Macromol. Chem. Phys.*, *196*, 1981 (1995).
- [11] D. Dietrich, W. Keberle, and H. Witt, *Angew. Chem., Int. Ed. Engl.*, *9*, 40 (1970).
- [12] D. C. Lee, R. A. Register, C. Z. Yang, and S. L. Cooper, *Macromolecules*, *21*, 998 (1988).
- [13] S. A. Visser and S. L. Cooper, *Macromolecules*, *24*, 2576 (1991).
- [14] H. A. Al-Salah, J. A. Maclean, Jr., K. C. Frisch, and H. X. Xiao, *J. Macromol. Sci.-Phys. B26*, 447 (1987).
- [15] A. Eisenberg and M. King, *Ion Containing Polymers: Physical Properties and Structure*, Academic Press, New York, 1977.
- [16] S. Ramesh and G. Radhakrishnan, *J. Appl. Polym. Sci.*, *48*, 2095 (1993).
- [17] S. Yang, H. X. Xiao, D. P. Higley, J. Kresta, K. C. Frisch, W. B. Farnham, and M. H. Hung, *J. Macromol. Sci.-Pure Appl. Chem.*, *A30*, 241 (1993).
- [18] H. A. Al-Salah, H. X. Xiao, J. A. McLean, Jr., and K. C. Frisch, *J. Polym. Sci., Polym. Chem. Edn.*, *26*, 1609 (1988).
- [19] J. A. Miller, K. K. S. Hwang, C. Z. Yang, and S. L. Cooper, *J. Elast. Plast.*, *15*, 174 (1983).

- [20] B. Grassl and J. C. Galin, *Macromolecules*, **28**, 7035 (1995).
- [21] P. Charlier, R. Jerome, Ph. Teyssie, and L. A. Ultracki, *Macromolecules*, **21**, 2894 (1990).
- [22] H. A. Al-Salah, K. C. Frisch, H. X. Xiao, and J. A. MacLean, Jr., *J. Polym. Sci., Polym. Chem. Edn.*, **25**, 2127 (1987).
- [23] T. A. Speckhard, K. K. S. Hwang, C. Z. Yang, W. R. Laupan, and S. L. Cooper, *J. Macromol. Sci.-Phys.*, **B23**, 175 (1984).
- [24] C. A. Arnold, J. D. Summers, Y. P. Chen, R. H. Bott, D. Chen and J. E. McGrath, *Polymer*, **30**, 986 (1989).
- [25] S. A. Nye and S. A. Swint, *J. Appl. Polym. Sci.*, **43**, 1539 (1991).
- [26] H. A. Al-Salah, *Polym. J. (Japan)*, **23**, 815 (1991).
- [27] R. O. Waldbauer, M. E. Rogers, C. A. Arnold, G. A. York, Y. Kim, and J. E. McGrath, *Polym. Preprints (ACS)*, **31(2)**, 432 (1990).
- [28] H. A. Al-Salah, *Mu'tah, J.*, **6(2)**, 65 (1991).
- [29] I. K. Varma and B. S. Rho, *J. Appl. Polym. Sci.*, **28**, 2805 (1983).
- [30] B. Masiulanic and R. Zielinski, *J. Appl. Polym. Sci.*, **30**, 2731 (1985).
- [31] B. Masiulanic and K. Gostanski, *Polimery*, **38(8-9)**, 414 (1993).
- [32] A. C. De Visser, A. A. Driessen, and Johannes G. C. Wolke, *Makromol. Chem. Rapid Comm.*, **1**, 177 (1980).
- [33] N. Yui, K. Nojimar K. Sanui, and N. Ogata, *Polym. J.*, **17**, 969 (1985).
- [34] A. Dine-Hart and W. M. Wright, *Makromol. Chem.*, **143**, 189 (1971).
- [35] L. Born and H. Hesse, *Coll. Polym. Sci.*, **263**, 335 (1985).
- [36] J. W. C. Van Bogart, D. A. Bluemke, and S. L. Cooper, *Polymer*, **22**, 1428 (1981).
- [37] J. A. Miller, K. K. S. Hwang, and S. L. Cooper, *J. Macromol. Sci.-Phys.*, **B22**, 321 (1983).
- [38] H. Ishihara, I. Kimura, K. Saito, and H. Ono, *J. Macromol. Sci.-Phys.*, **B10**, 591 (1974).

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