

# Synthesis and Properties of Polyurethane Ionomers Based on Carboxylated Polycaprolactone

HONG CHEN, DONGZHONG CHEN, QULI FAN, XUEHAI YU

Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210093, People's Republic of China

Received 7 July 1999; accepted 1 October 1999

**ABSTRACT:** Polycaprolactone containing carboxyl groups (CPCL,  $\bar{M}_n = 1200$ ) was prepared from caprolactone (CL) and dimethylol propionic acid (DMPA). Based on the CPCL, 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BD), a novel series of polyurethane ionomers could be synthesized with ions in the soft segment. The tensile modulus and ultimate elongation of the ionomer cast films increased, and the glass transition temperature of the CPCL-rich phase moved to a higher temperature after ionization. Moreover, this kind of ionomers showed small amounts of hard segment crystallinity by DSC. WAXD shows an ionic peak at  $2\theta = 8.6^\circ$  for the ionomer with carboxylate in the hard segment, which is not present in the ionomer with carboxylate in the soft segment. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 2049–2056, 2000

**Key words:** polyurethane ionomers; carboxylated polycaprolactone; ion in soft segment

## INTRODUCTION

Ionomers contain a certain number (usually 10 mol % or less) of inorganic salt groups attached to a polymer chain.<sup>1</sup> Ionization causes improved toughness, tear strength, and abrasion resistance.<sup>2</sup> Even small amounts of ionic groups can sufficiently modify specific properties of materials.<sup>3</sup> Their solid properties have been widely studied, and various models for their morphology have been proposed. The two chief models are the “homogeneous” model, in which the carboxylic salt groups are assumed to be randomly distributed in the amorphous phase of the polymer, and the “clusters” model, in which salt groups are thought to aggregate in clusters.<sup>4</sup> Currently, it is generally accepted that the ion pairs in organic polymer matrix tend to aggregate into microdomains with

two distinguished sizes—clusters and multiplets—which behave as physical crosslinks.

From a processing standpoint, it would be highly desirable if the aggregates could be made to dissociate at processing temperatures and reform at use temperatures, because the persistence of the ionic aggregates to high temperatures leads to melt viscosities that can be orders of magnitude greater than the analogous nonionic polymers.<sup>5</sup> To observe the aggregate dissociation, Register<sup>2</sup> chose to increase the matrix polarity by incorporating ethylene oxide (EO) units into the backbone of sulfonated polyurethane ionomers. However, no dissociation could be observed by small-angle X-ray scattering (SAXS) before the onset of degradation. We have synthesized a tailor-made polyurethane ionomer with a specific ionic structure, and observed a dissociation of ionic aggregates at elevated temperatures by means of hot-stage wide-angle X-ray diffraction (WAXD).<sup>6</sup> Although the dissociation of ionic aggregates is not complete, it means that the ionic

---

Correspondence to: X. Yu.

*Journal of Applied Polymer Science*, Vol. 76, 2049–2056 (2000)  
© 2000 John Wiley & Sons, Inc.

**Table I** The Synthesized CPCL and PCL

Sample	$M_n$ (Theory)	$M_n$ (HVT)	$M_n$ (AVT)	Yield (%)	$T_m$ (K)	$\Delta H$ (J/gdeg)
CPCL	1300	1200	1250	98	312.22	10.26
PCL	1260	1160	1200	97	321.46	20.62

aggregates could be dissociated when the polymer matrix and ionic structure were changed.

Therefore, further improving the compatibility between the ionic groups and the polymer matrix as well as changing the ionic type may destroy or weaken the ionic aggregation. Then the salt groups might be distributed in the polymer matrix in the form of ion pairs or multiplets, and no clusters would exist, because PCL is known for its good compatibility,<sup>7</sup> and carboxylate is more advantageous to ionic aggregate dissociation than the sulfonate group.<sup>2</sup> In this study, the carboxylate group was introduced into the PCL soft segment, and based on this, a new family of polyurethane ionomers was prepared. The microstructure and properties of these ionomers were studied by different techniques.

It could clearly be observed that the glass transition temperature of the CPCL-rich phase moved to a higher temperature, and the tensile modulus and ultimate elongation of the ionomer increased after ionization. Moreover, this kind of ionomer showed small amounts of hard segment crystallinity by DSC. What is expected and much more interesting is that the ionic peak at  $2\theta = 8.6^\circ$  for the ionomer with carboxylate in the hard segment is not present in X-ray scattering from the ionomer with carboxylate in the soft segment.

## EXPERIMENTAL

### Materials

Monomer CL (Aldrich) was dried over calcium hydride at room temperature for 24 h, then distilled under reduced pressure (b.p.  $96^\circ\text{C}/15$  mmHg) before use. Dimethylol propionic acid (DMPA) was dried in a vacuum oven ( $100^\circ\text{C}$ ) for at least 5 h. 4,4'-Diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BD) were purified by vacuum distillation, *N,N*-dimethylformamide (DMF) was dried by calcium hydride and distilled before use. Toluene, cupric acetate, zinc acetate, sodium acetate, and stannous octoate catalyst were used as received.

### Sample Preparation

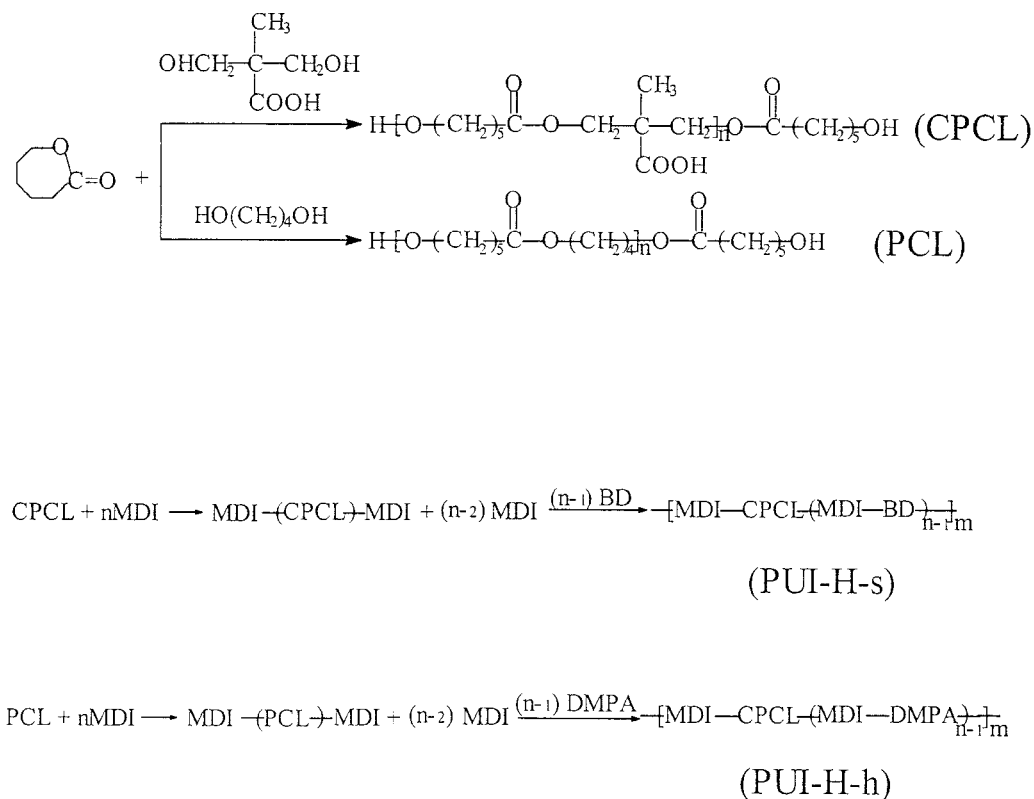
#### *Synthesis of Polycaprolactone (PCL) and Carboxyl Polycaprolactone (CPCL)*

The reaction proceeded under nitrogen protection in a three-necked flask equipped with a reflux condenser, a gas inlet, and a magnetic stirrer. Caprolactone was mixed with the stoichiometric amount of dimethylol propionic acid (or 1,4-butanediol and stannous octoate catalyst for the PCL synthesis). After reaction at  $80^\circ\text{C}$  for 24 h, the products were vacuum distilled to remove the unreacted CL, then washed with water to remove the DMPA (or BD and stannous octoate). The products were dried in a vacuum oven at  $80^\circ\text{C}$  for a week.

The oligomers were characterized by titration and DSC measurement. The results are shown in Table I.

#### *Synthesis of PU Ionomers*

A 3 : 2 : 1 MDI : BD : CPCL ( $M_n = 1200$ ) segmented polycaprolactone–polyurethane used as the control polymer in this study was synthesized by a typical two-step condensation reaction.<sup>8</sup> The series of polyurethane ionomers with different composition were synthesized as follows. The reaction procedure is outline in Figure 1. The CPCL was dissolved in DMF with 15 wt % of toluene. The solution was stirred at  $110^\circ\text{C}$  for 1 h under dry nitrogen. The toluene was distilled off to dehydrate the system. After addition of 0.05 wt % stannous octoate catalyst, a 15 wt % solution of MDI in DMF was added. The solution was stirred for 1.5 h at  $60$ – $65^\circ\text{C}$  under dry nitrogen. Then the BD was added dropwise, and the reaction continued for an additional hour. To ensure a complete reaction, the mixture was stirred at  $80$ – $85^\circ\text{C}$  for 3–4 h. The synthesized ionomer was precipitated into toluene. The polymer was dried under vacuum for 1 week at  $50$ – $60^\circ\text{C}$ . The sample was dissolved in DMF and ionized by metal acetates, and then cast into a Teflon disk and kept in a vacuum oven for 1 week at  $65^\circ\text{C}$ . The composi-



**Figure 1** Synthetic route to polyurethane ionomers.

tions and designations of the samples are shown in Table II.

The nomenclature used in this article describes the chemical structure of the polymer chain. As an example, the designation “PUI3-Cu-s” is interpreted as follows: the number “3” indicates that the molar ratio of the polymer is MDI : BD : CPCL = 3 : 2 : 1. The letter “Cu” means that this sample has been converted to a  $\text{Cu}^{2+}$  base ionomer. The third part “s” means that the ionic group is in the soft segment.

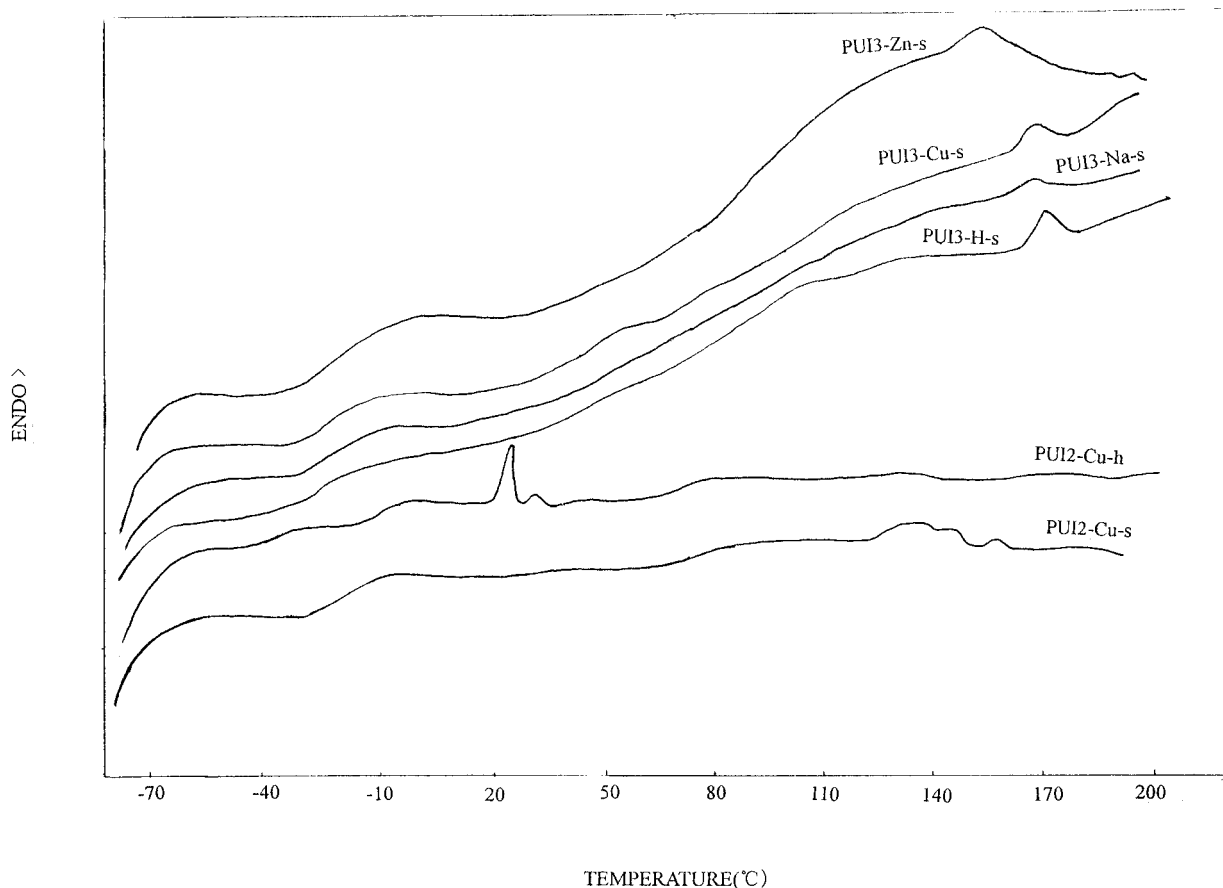
## CHARACTERIZATION

Differential scanning calorimetry thermograms were recorded over a temperature range beginning at 193 K and terminating at 453 K. Samples were run at a heating rate of 20 K/min.

The mechanical properties were determined on a table model Instron testing machine. The samples were stamped out of solution cast films ( $0.4 \pm 0.05$  mm) using an ASTM 1708 standard die and dried under vacuum for a minimum of 48 h

**Table II** The Synthesized Polyurethane Ionomers

Sample Designation	Molar Ratio					Cation	DSC		
	MDI	BD	CPCL	PCL	DMPA		$T_g$ (°C)	Endotherm (°C)	
PUI3-H-s	3	2	1			$\text{H}^+$	-26.8	171	
PUI3-Na-s	3	2	1			$\text{Na}^+$	-25.1	168	
PUI3-Cu-s	3	2	1			$\text{Cu}^{2+}$	-23.1	170	
PUI3-Zn-s	3	2	1			$\text{Zn}^{2+}$	-18.9	155	
PUI2-Cu-s	2	1	1			$\text{Cu}^{2+}$	-20.39	135	
PUI1-Cu-s	1		1			$\text{Cu}^{2+}$			
PUI2-Cu-h	2			1	1	$\text{Cu}^{2+}$	-36.5	24.5	30.5



**Figure 2** DSC parameters of polyurethane ionomers.

before testing. The samples with a gauge length of 1 cm were tested at room temperature using a crosshead speed of 5 cm/min.

Dynamic mechanical thermal analysis (DMTA) of the polymers was obtained at 110 HZ, using a microprocessor-controlled Rheovibron DDV-II. Solution cast films were cooled to 193 K and then heated at a rate of 2 K/min until the samples were too compliant to test.

The WAXD measurement was performed using a Rigaku D/MAX-RA rotating anode X-ray generator with a copper target, at a 30-KV cathode potential and a 60-mA emission current.

## RESULTS AND DISCUSSION

### Synthesis of Polycaprolactone and Carboxyl Polycaprolactone Diol

It has been reported<sup>9</sup> that the ring-opening polymerization of caprolactone in the presence of hydroxy carboxylic acid under lower temperature

has proven that the active propagation site is only on the hydroxy terminal; according to this rule, we used dimethylol propionic acid as an initiator to synthesize carboxyl polycaprolactone diol.

The number-average molecular weights of PCL and CPCL measured by hydroxyl value titration (HVT) and acid value titration (AVT) are listed in Table I. It can be seen that the results of hydroxyl value analysis, acid value analysis, and the yield were satisfactory, indicating that the polymerization was successful. It can also be noted that the  $T_m$  and  $\Delta H$  of CPCL were lower than those of PCL. It is because of this that the carboxylate disturbs the close packing of the CL and reduces the cohesions.

### Differential Scanning Calorimetry (DSC)

DSC traces are shown in Figure 2. Data obtained from the DSC traces are listed in Table II, where  $T_g$  is defined as the midpoint of the transition.

Material PUI3 was used to study the effect of neutralizing cation type on properties. Three dif-

ferent cations were studied:  $\text{Na}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ . The carboxyl polyurethane (PUI3-H-s) exhibited a PCL-rich phase glass transition at a temperature lower than that of ionized PUI. In another words, the glass transition temperature of the PCL-rich phase moved to a higher temperature after ionization. The  $T_g$  increased in the order of PUI3-H-s < PUI3-Na-s < PUI3-Cu-s < PUI3-Zn-s. The increased  $T_g$  provided the best evidence for a better phase-mixing morphology. In contrast, a better phase separation resulted in a polyurethane ionomer with ionization in the hard segment.<sup>10</sup>

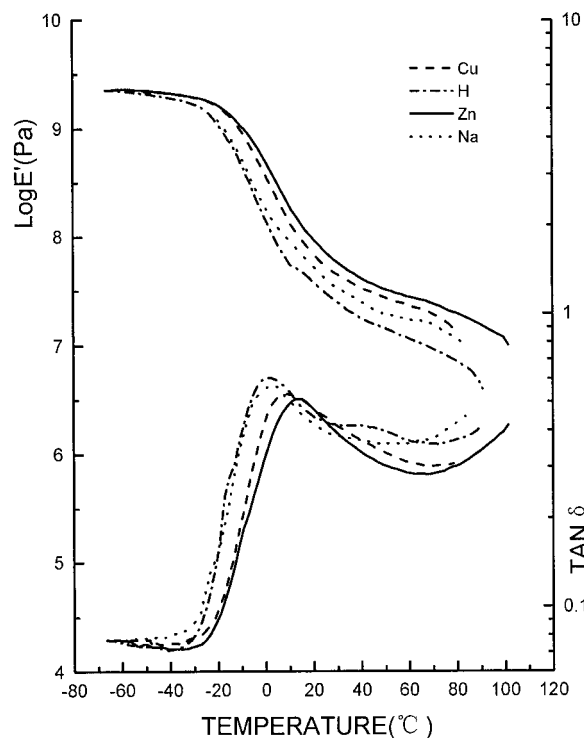
It is interesting that endotherms at about 170°C were observed on the trace of the ionomers showing that the hard segment in the ionomer system possesses a regular array. As we expected, that ionization of the soft segments did not disturb this regular structure, small crystallites or short range ordered structure could exist in the hard segment of these PU ionomers.

Comparing the DSC traces of “PUI2-Cu-s” and “PUI2-Cu-h,” it can be observed that a copper-based sample “PUI2-Cu-h” with ions in the hard segments exhibited a strong endotherm near room temperature, representing the melting of polycaprolacton crystallites, and the melting endotherm of PCL crystallites could no longer be found for the sample “PUI2-Cu-s” with ions in the soft segments. On the contrary, a broad endotherm above 100°C can be found on the curve of “PUI2-Cu-s,” represented the melting of the hard segment ordered structure while no endotherm above 100°C can be found on the curve of “PUI2-Cu-h.” These results suggest that crystallites of soft segments existed in PCL-based PU ionomers with ions in the hard segments and small crystallites or short-range ordered structures of hard segments existing in the CPCL-based PU ionomers with ions in the soft segments.

It can also be noted that the PCL-rich phase glass transition temperature of the “PUI2-Cu-s” was much higher than that of the “PUI2-Cu-h.” This suggest that ionization of the PCL soft segments causes better phase mixing, which is consistent with the reported literature.<sup>11</sup>

#### Dynamic Mechanical Thermal Analysis (DMTA)

DMTA results, expressed as the loss tangent ( $\tan \delta$ ) vs.  $T$  and the absolute modulus ( $|E|$ ) vs.  $T$  on logarithmic scales are shown in Figure 3. As Figure 3 shows, ionization of the soft segments obviously improved the phase compatibility of these polyurethanes, producing a higher  $T_g$  of the soft



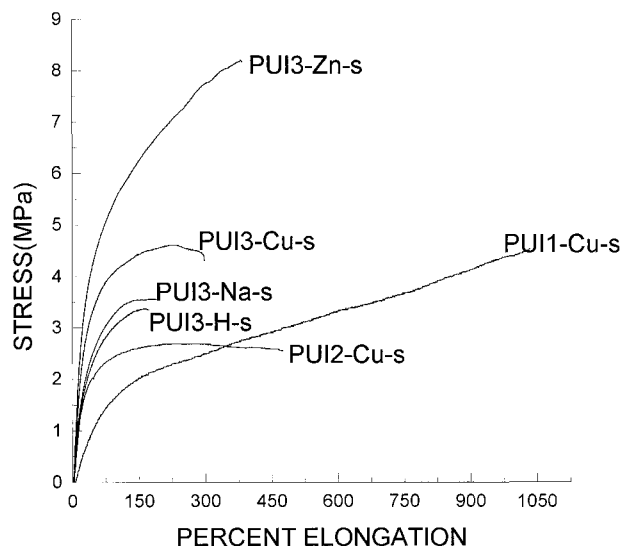
**Figure 3** Dynamic mechanical testing results for polyurethane ionomers.

segments. This result is consistent with the DSC result. For the ionomers, the choice of the cation also has profound effects on the character of the DMTA curves and microstructure of the samples. PUI3-Zn-s showed a higher  $T_g$  than PUI-Cu indicated that the ionic species based on  $\text{Zn}^{2+}$  had obvious influence on the relaxation of polymer matrix.

The narrowed modulus plateau supports the above analysis and the DSC results. Although ionization gives the materials better phase compatibility, the synthesized polyurethane ionomers still exhibit a typical elastomeric property of normal polyurethanes, for each sample still has a typical rubbery plateau. Unlike the polyurethane ionomers with ions located in the urethane group, our ionization process is not involved in the removal of hydrogen bond in the hard segments as a physical linkage.

#### Mechanical Properties

The stress–strain curves are shown in Figure 4. The tensile strength, elongation at break, and tensile modulus are list in Table III. For the PUI3 series, the value of Young’s modulus and tensile



**Figure 4** Stress-strain curves of polyurethane ionomers.

strength were found to depend upon ionization and different metals in the order of  $Zn > Cu > Na > H$  in the same way as the rubbery plateau modulus in the DMTA testing. This results are similar to the ionization upon the hard segment PU.<sup>12</sup> However, the elongation at break of such samples also increases in the same order, which can possibly be attributed to the increasing of phase mixing within the ionized soft segment.

It is reasonable to explain that the modulus increases due to the hard segments of the series samples increasing in the order of  $PUI3-Cu-s > PUI2-Cu-s > PUI1-Cu-s$ .

#### Wide-Angle X-ray Diffraction (WAXD)

WAXD has long been recognized as a powerful tool to characterize the morphology of the ionic domains.<sup>13</sup> Figure 5 represents data of wide-angle X-ray diffraction intensity as a function of the angle for the PUI2-Cu-s and PUI2-Cu-h ionomers. No evidence of crystallization showed in Figure 5(a) and 5(b), although the sample "PUI2-Cu-h" showed small amounts of soft segment crystallinity by DSC. It appears that the amount of crystallinity in the ionomer is too small to produce peaks in WAXD under the experimental condition.

**Table III** Mechanical Properties of Polyurethane Ionomers

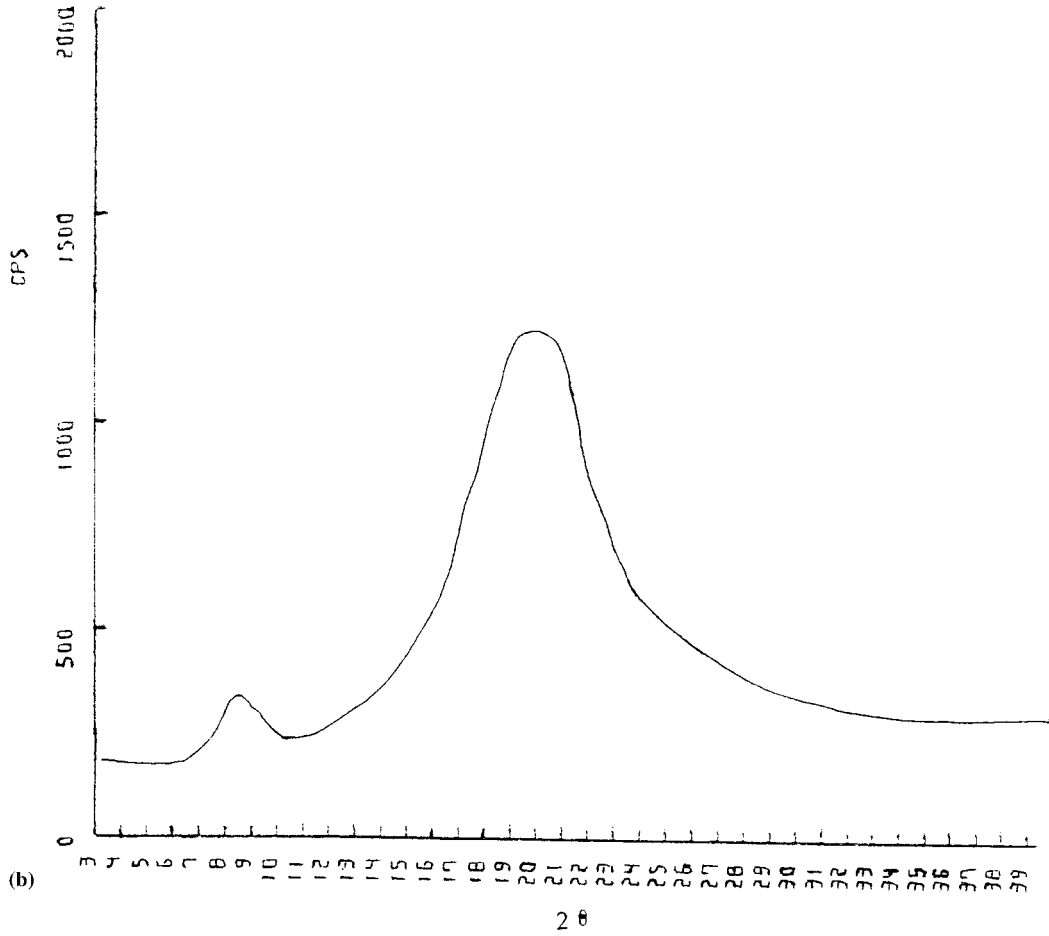
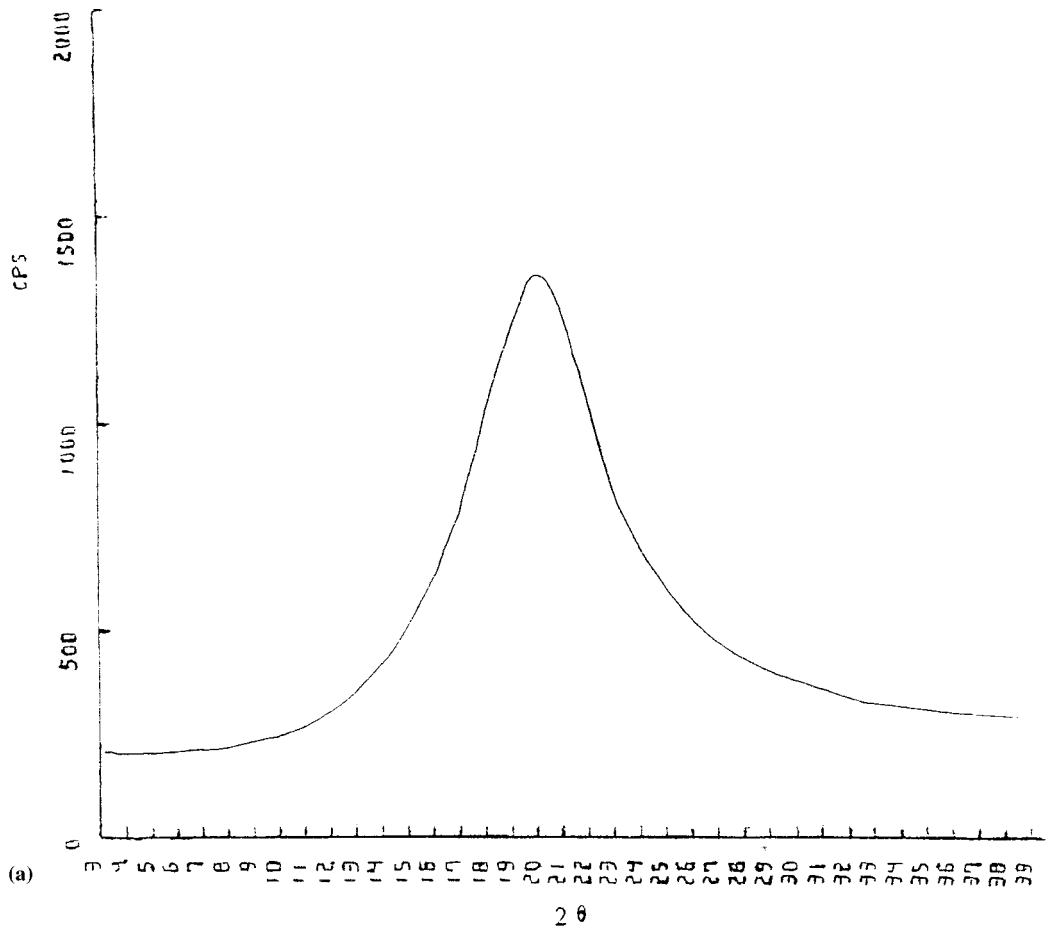
Sample	Stress (MPa)	Strain (%)	Modulus (MPa)
PUI3-H-s	3.183	165.549	7.321
PUI3-Na-s	3.637	196.092	10.288
PUI3-Cu-s	4.493	209.681	13.272
PUI3-Zn-s	7.662	385.186	15.391
PUI2-Cu-s	2.831	343.185	9.054
PUI1-Cu-s	4.239	919.474	2.882

The cluster model was proposed by Longworth and Vaughan to account for results obtained by wide-angle X-ray scattering measurements on polyethylene ionomers.<sup>13</sup> A peak appeared at  $2\theta = 4^\circ$  in the X-ray scattering of ionomers, which was not present in the scattering from the unionized copolymers. Because the peak was observed for all cations studied, it was concluded that the peak did not result from the electron-density difference between the cation and the polymer, but from an electron-density difference resulting from a change of morphology upon ionization. In our experiments, we could also clearly observe an ionic peak for the ionomer with carboxylate in the hard segment at  $2\theta = 8.6^\circ$ , which corresponds to a Bragg spacing of  $10.3 \text{ \AA}$  [Fig. 5(b)], but it is not present in the X-ray scattering from the ionomer with carboxylate in the soft segment [Fig. 5(a)]. We also could not find the ionic peak in all X-ray scatterings from the PUI3 series. However, the only difference between the "PUI2-Cu-s" and "PUI2-Cu-h" samples is the ionic position. It was concluded that the ionic peak disappeared at  $2\theta = 8.6^\circ$  in Figure 5(a) results from the ionic position moving from the hard segment into the soft segment. This observation might be explained by the fact that the ion pairs are randomly distributed in the soft segment matrix and not isolated in large ionic clusters due to the improvement of compatibility between the polycaprolactone matrix and ionic groups by moving ionic groups from the hard segment into the soft segment.

#### CONCLUSION

1. A novel series of polyurethane ionomers with carboxylate in the polycaprolactone

**Figure 5** WAXD patterns of PUI2-Cu-s and PUI2-Cu-h. (a) WAXD patterns of PUI2-Cu-s; (b) WAXD patterns of PUI2-Cu-h.



soft segments were successfully synthesized, and their properties were characterized with various methods.

2. The mechanical properties of the new polyurethane ionomers increased, and the glass transition temperature of CPCL-rich phase moved to a higher temperature in the order of PUI3-H-s < PUI3-Na-s < PUI3-Cu-s < PUI3-Zn-s.
3. The new polyurethane ionomers did not disturb the hard segment ordered structure.
4. The ion pairs are randomly distributed in the soft segment matrix and do not aggregate to larger ionic clusters in such are ionomer system.

## REFERENCES

1. Lundberg, R. D. *Encyclopedia of Chemical Technology* 1984, p. 546, 3rd ed., Supplement Volume.
2. Register, R. A.; Yu, X.; Cooper, S. L. *Polym Bull* 1989, 22, 565.
3. Yu, X.; Grady, B. P.; Reiner, R. S.; Cooper, S. L. *J Appl Polym Sci* 1993, 47, 1673.
4. Marx, C. L.; Caulfield, D. F.; Cooper, S. L. *Macromolecules* 1973, 6, 344.
5. Fenton, D. E.; Parker, J. M.; Wright, P. V. *Polymer* 1973, 14, 589.
6. Wei, X.; Jin, B.; Yu, X. *Polym Bull* 1997, 39, 729.
7. Yoshida, E.; Osagawa, Y. *Macromolecules* 1998, 31, 1446.
8. Petrovic, Z. S.; Ferguson, J. *Prog Polym Sci* 1991, 16, 695.
9. Xei, D. Nanjing University PH.D. Thesis (1998).
10. Yang, C.-Z., et al. *J Polym Sci Part B Phys* 1991, 29, 581.
11. Wei, X.; Yu, X. *J Polym Sci Part B Polym Phys* 1997, 35, 225.
12. Miller, J. A.; Hwang, K. K. S.; Cooper, S. L. *J Macromol Sci-Phys* 1983, B22, 321.
13. Longworth, R.; Vaughan, D. J. *Nature* 1968, 218, 85.