# Ionomers Made from Terpolymers with Uniform Poly(methyl Methacrylate) Grafts

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## SYNOPSIS

Terpolymers with uniform poly(methyl methacrylate) (PMMA) grafts were prepared by terpolymerization of PMMA macromonomer, butyl acrylate, and acrylic acid in benzene using AIBN as initiator. During terpolymerization the macromonomer polymerizes faster than the monomers at the beginning but slower at the latter stage. The terpolymers were purified by solvent extraction and fractional precipitation. The average grafting number per chain of the terpolymers was determined to be 3–8. Ionomers were obtained by neutralization of the terpolymers with alkali hydroxide or metallic acetate. Dynamic mechanical spectrum of the ionomer shows the existence of two $T_g$'s, which implies the occurence of microphase separation. The ionomer exhibits high damping over a temperature range from $-25$ to $100°C$. Both PMMA grafts and metallic carboxylate content raise the tensile strength of the ionomer and lower the ultimate elongation. The tensile strength of ionomers neutralized with different metallic ions decreases in the following order: $Pb^{2+} > Zn^{2+} > Na^+ > Ca^{2+} > Mg^{2+} > K^+$. The ionomers with uniform PMMA grafts show much better mechanical properties than the terpolymer without neutralization or the ionomer without PMMA grafts.

## INTRODUCTION

Since Milkovich and his co-workers[1] reported the synthesis of copolymers with uniform grafts using the macromonomer technique, many research works about macromonomers have been published.[2-5] At the same time Bazuin and Eisenberg[6] and MacKnight and Lundberg[7] paid much attention to the ionomers. Recently, we have published the works concerning synthesis[8] and properties[9] of the ionomers made from terpolymers with uniform grafts of polystyrene. It was shown that there exist three phases in the ionomers containing polystyrene grafts, namely, polystyrene domains, ionic clusters, and continuous phase of poly(butyl acrylate) and that both glassy domains and ionic clusters influence the mechanical properties of the ionomers.

This paper deals with the synthesis, character-ization, and mechanical properties of the ionomers made from terpolymers containing uniform grafts of poly(methyl methacrylate), which were obtained through radical polymerization of PMMA macromonomer, butyl acrylate, and acrylic acid. The aim is to obtain a new thermoplastic elastomer with good properties using only radical polymerization in synthesis of macromonomer and terpolymer.

## EXPERIMENTAL

### Materials

$n$-Butyl acrylate and MMA were purified and dried by standard procedures. AIBN was purified by recrystallization from ethanol and vacuum dried. Thioglycollic acid was purified by distillation under reduced pressure. C. P. $N,N$-dimethyl benzylamine and benzyl triethyl ammonium chloride were used without purification. C. P. benzene was dried by standing over a 4A molecular sieve overnight. Glycidyl methacrylate was synthesized by neutralization of methacrylic acid with 20% NaOH, followed by

reaction with epichlorohydrin at 85°C using benzyl triethyl ammonium chloride as catalyst. After azeotropic distillation of water, the product was purified by vacuum distillation and kept in a refrigerator before use. Acrylic acid was dried with a 4A molecular sieve overnight and distilled under reduced pressure. The distillate was collected at 46°C/7 mm Hg and kept in a refrigerator before use.

## Synthesis of PMMA Macromonomers

Radical polymerization of MMA was carried out in benzene under nitrogen atmosphere using azobisisobutyronitrile (AIBN) as initiator and a different amount of thioglycollic acid as chain transfer agent at 65°C for 12 h, so as to obtain prepolymers with different molecular weight, which were then purified by precipitation in benzene with methyl alcohol. The yield was about 60%. Carboxylic acid end groups of the prepolymer were determined by titration in acetone with absolute ethyl alcohol solution of KOH using methanolic solution of phenolphthalein as indicator. The purified prepolymer was then reacted in xylene with glycidyl methacrylate (GMA) at a molar ratio of GMA/COOH = 2 using N,N-dimethyl benzylamine as catalyst at 139°C under nitrogen atmosphere for 8 h. The macromonomer thus obtained was purified by precipitation in benzene with methyl alcohol. Efficiency of the reaction between the prepolymer and GMA was determined to be nearly 100% by titration of the remaining carboxylic acid end groups in the macromonomer.

## Terpolymerization of the PMMA Macromonomer with n-Butyl Acrylate (BA) and Acrylic Acid (AA)

The PMMA macromonomer, BA, AA, and AIBN (0.15% based on total weight of the monomers and macromonomer) were dissolved in benzene. The terpolymerization was carried out at 65°C during stirring under nitrogen atmosphere. After 24 h the product was precipitated with a mixed solvent of methanol and water (10/1 by volume) containing a small amount of antioxidant 264 and filtered, so as to remove the two residual monomers. The precipitate was redissolved in benzene and precipitated again with the methanol–water mixed solvent for three times. After evaporation of the solvent the precipitate was vacuum dried at 60°C to constant weight.

The crude product was purified by extraction with n-butanol at room temperature three times each for 24 h in order to remove homopolymers and copolymers of BA and AA into solution. The dried residue

was dissolved in n-butanol at 65°C and then cooled to 0°C in order to remove PMMA as precipitate, which was filtered and washed with cold n-butanol. Methanol was dropped into the mixture of filtrate and washings with stirring till the volume ratio of methanol/(butanol + methanol) was equal to 0.5–0.6. The precipitate obtained was the graft terpolymer. Subsequent addition of methanol will precipitate the homopolymer of BA at the volume ratio = 0.7–0.9.

Conversion of the macromonomer or the grafting efficiency (GE) can be calculated by the following equation according to the data obtained from the purification procedure:

GE (%) = (macromonomer charged

− macromonomer unreacted)

× 100/macromonomer charged.

Conversion of the monomers can be calculated as follows:

% conversion of BA = [wt crude product

(1 − AA %/100) − macromonomer charged]

× 100/butyl acrylate charged

% conversion of AA = MW of AA

× meq of KOH for titration/(AA charged × 10)

Content of PMMA and AA in the terpolymer can be calculated from the conversions.

## Preparation of Ionomers

The ionomers were prepared by neutralization in solution as follows: To an acetone solution of terpolymer of 5–7% concentration was added gradually 0.1N methanol solution of NaOH or KOH during stirring and the mixture reacted at room temperature for 2 h or 1% methanol solution of metallic acetate was added with reaction temperature at 50°C for 24 h. The product was precipitated and washed with water to remove the acetic acid formed. The ionomer was dried under vacuum at 60°C to constant weight.

## Characterization and Testing

Molecular weights of the PMMA macromonomers and the terpolymers were determined by Knauer VPO apparatus using chloroform as solvent and by Bruss membrane osmometer using tetrahydrofuran

as eluant, respectively. Molecular weight distribution was measured by LC-4A liquid chromatographic apparatus with refractive index detector. IR spectra of the terpolymer were obtained with PE-580B spectrophotometer using KBr disk coated with the terpolymer. Glass transition temperature ($T_g$) of the ionomer were measured with viscoelastometer DDV–III–EA with frequency of 110 Hz.

The ionomers or terpolymers were compression molded at 150–170°C. The tensile strength, ultimate elongation were determined on a DL-250 tensile tester at 25 ± 2°C with an initial gauge length of 25 mm and an extension rate of 250 mm/min. Permanent set was measured as % elongation after the specimen was broken and reunited after 3 min. The apparent crosslink density ($V_\alpha$) was calculated from the following equation:

$$V_\alpha = \sigma(RT)^{-1}(\lambda - 1/\lambda^2)^{-1}$$

where $\sigma$ is the tensile strength and $\lambda$ is the extension ratio.

## RESULTS AND DISCUSSION

### Terpolymerization

Figure 1 represents the individual conversion curves of the macromonomer, BA and AA vs. terpolymerization time. The conversion rate of the macromonomer seems higher than that of either BA or AA at the beginning of terpolymerization. This is
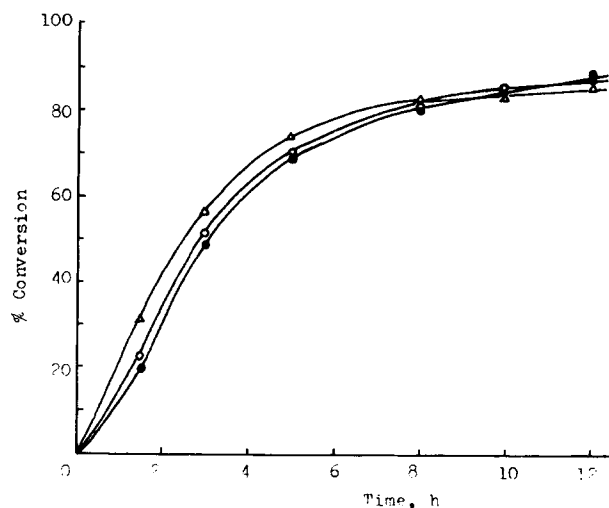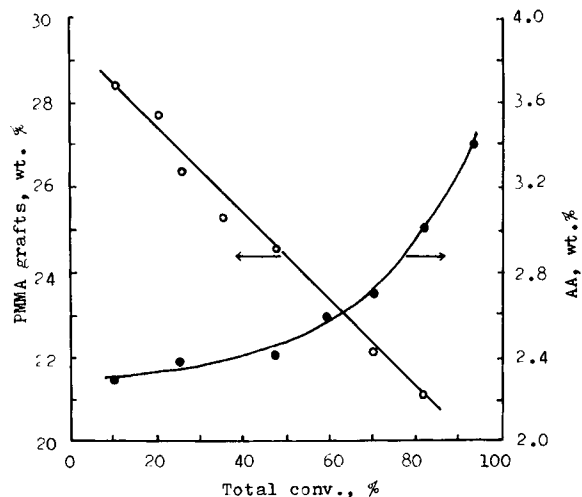


**Figure 2**   Change of PMMA graft content and AA content with total conversion of macromonomer and monomers.

due to the higher reactivity of the methacryloyl group of the macromonomer than that of acryloyl group of the monomers. At the latter stage rate of conversion of the macromonomer appears lower than that of BA or AA, since viscosity of the polymerization system increases with conversion, resulting in lowering diffusion rate and hence conversion rate of the macromonomer. The polymerization rate of BA was slightly higher than that of AA. As a result, content of AA in the terpolymer increases slowly with total conversion of the macromonomer and monomers at first and then quickly above 70% conversion, as shown in Figure 2. The same figure indicates the reduction of PMMA content in the terpolymer with increase of total conversion of the macromonomer and monomers.

### Structural Parameters of the Terpolymers

Since molecular weight of the macromonomer ($M_{ng}$), molecular weight of the purified terpolymer ($M_{nc}$), and weight fraction of AA ($W_A$) in the terpolymer can be determined by VPO, membrane osmometry, and titration with alkali, respectively, and the weight fraction of PMMA ($W_g$) can be calculated from conversion of the macromonomer and the monomers, the average grafting number per chain ($N_g$) and average number of acid groups per chain ($N_A$) can be calculated by the following equations:

$$N_g = M_{nc} \times W_g \times M_{ng}^{-1}$$

$$N_A = M_{nc} \times W_A \times M_{AA}^{-1}$$



**Figure 1**   Individual conversions of PMMA macromonomer ($\triangle$), BA ($\bigcirc$), and AA ($\bullet$) vs. terpolymerization time.

**Table I  Structural Parameters of the Terpolymers[a]**

| PMMA (%) | AA (%) | $M_{nc} \times 10^{-4}$ | $N_g$ | $N_A$ |
|----------|--------|------------------|-------|-------|
| 17.5 | 1.05 | 22.4 | 3.27 | 33 |
| 19.7 | 3.10 | 25.6 | 4.20 | 110 |
| 20.3 | 2.55 | 19.8 | 3.35 | 70 |
| 22.5 | 1.93 | 30.6 | 5.74 | 82 |
| 25.0 | 1.57 | 35.5 | 7.40 | 77 |

[a] $M_n$ of PMMA grafts = $1.2 \times 10^4$.

The data are summarized in Table I, which shows that the average grafting number per chain varies from 3 to 8 and the average number of acid groups per chain is 30–110.

## Characterization of the Terpolymers and Ionomers

The method of purification of the terpolymer was established by first testing the solubility of the ho-
mopolymers and copolymers of BA and AA, PMMA macromonomers in $n$-butanol and its mixture with methanol at 0 and 65°C separately, and then trying to separate a mixture of them according to the purification method, which showed that weight loss of the macromonomer PBA and copolymers of BA and AA during the purification was shown to be less than 1–2%. The purification method was also proved to be effective by the GPC curve of the purified product, which indicated only one peak without any shoulder and no peak for the macromonomer.

Figure 3 represents the dynamic mechanical spectrum of the zinc ionomer which shows two loss peaks at $-16$ and 95°C corresponding to $T_g$'s of PBA and PMMA, respectively. This demonstrates a microphase separation of PMMA grafts from PBA backbones in the ionomer made from the purified terpolymer. The plot of tan $\delta$ vs. temperature for the ionomer exhibits high tan $\delta$ values over a wide range of temperature from $-25$ to 100°C. This indicates that the ionomer exhibits good damping ability.

IR spectra of both the terpolymer and sodium ionomer are shown in Figure 4. Characteristic ab-
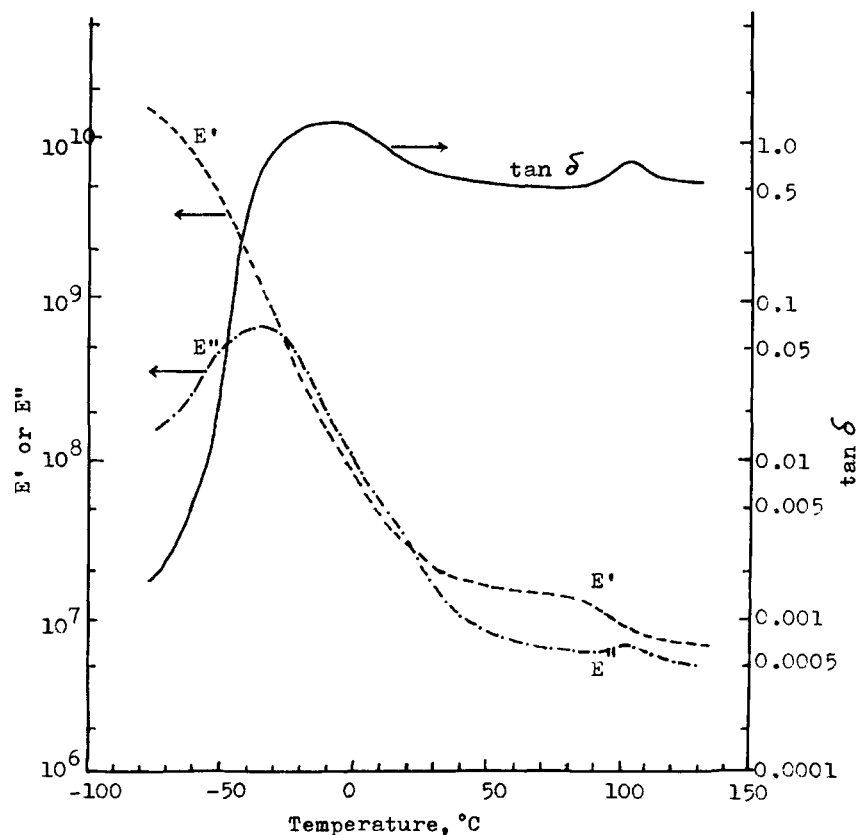


**Figure 3**  Dynamic mechanical spectrum of the zinc ionomer made from terpolymer containing PMMA grafts with molecular weight of $1.35 \times 10^4$.
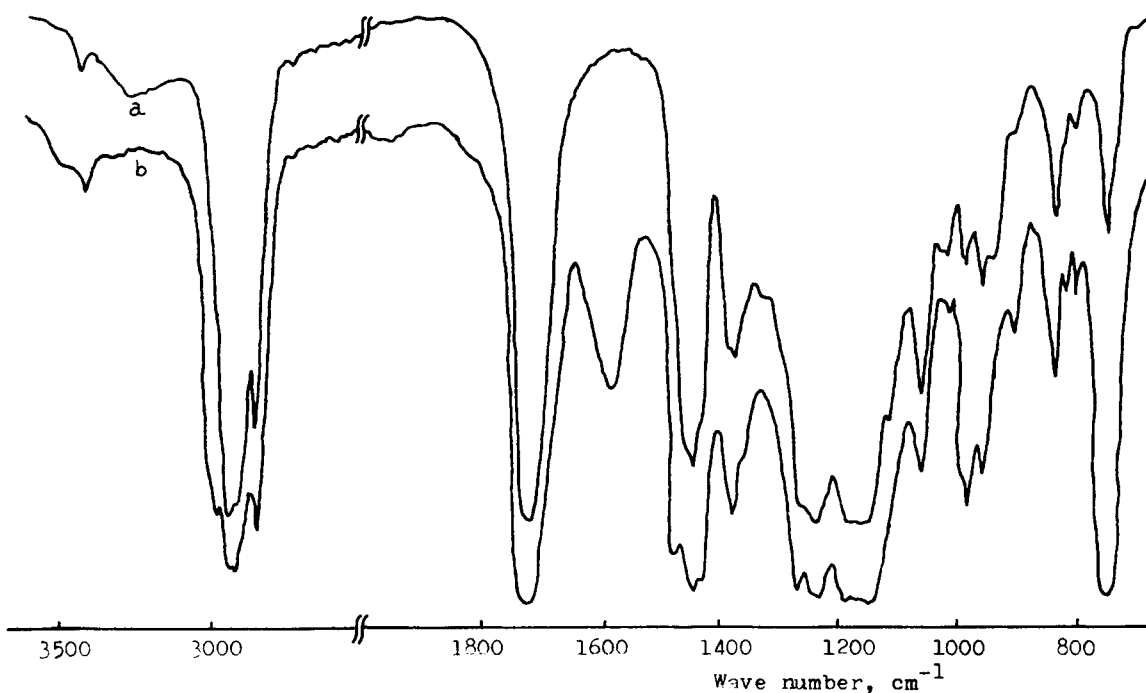
**Figure 4** IR spectra of the purified terpolymer (a) and sodium ionomer (b) made from it.

sorption peak of OH for COOH groups at 3250 cm$^{-1}$ appears in IR spectrum of the terpolymer (a) and disappears in that of the ionomer (b). The latter shows characteristic absorption peak of sodium carboxylate at 1565 cm$^{-1}$.

## Mechanical Properties of the Ionomers Formed from the Terpolymers

The mechanical properties of several zinc ionomers obtained from terpolymers synthesized with different amounts of PMMA macromonomer and neutralized to the equivalence point are listed in Table II and illustrated in Figure 5. Ionomer containing no PMMA grafts exhibits relatively low tensile strength and modulus with high ultimate elongation. For the ionomers containing PMMA grafts below 16%, the tensile strength increases only slightly as compared with the ionomers without PMMA grafts. This is probably because small amounts of the PMMA grafts are not able to form sufficient number and size of glassy domains and in this case the tensile strength of the ionomer is largely attributed to the ionic crosslinks. But, for the ionomers containing PMMA grafts above 16%, the tensile strength, modulus, and apparent crosslink density increase and the ultimate elongation decreases evidently, as PMMA content increases, while the permanent set exhibits a minimum at 23–29% PMMA content. All

the ionomers listed in the table behave like thermoplastic elastomer.

Table III shows the mechanical properties of zinc ionomers from terpolymers containing PMMA grafts of different molecular weight and neutralized with zinc acetate to the equivalence point. The tensile strength, modulus, and apparent crosslink density increase, while the ultimate elongation and permanent set decrease with increasing molecular weight of the grafts up to about $1.3 \times 10^4$. This may

**Table II  Effect of Amount of PMMA Macromonomer Used in Terpolymerization on Mechanical Properties[a] of Zinc Ionomers[b]**

| PMMA (%) | TS (MPa) | UE (%) | PS (%) | $M$ (MPa) | $V_a \times 10^4$ (mol/cm$^3$) |
|---|---|---|---|---|---|
| 0 | 7.4 | 595 | 22 | 1.1 | 4.4 |
| 15.5 | 7.7 | 520 | 17 | 1.5 | 5.2 |
| 23.5 | 9.8 | 410 | 13 | 3.0 | 8.0 |
| 28.7 | 10.4 | 350 | 13 | 3.8 | 9.7 |
| 30.0 | 10.8 | 290 | 17 | 5.3 | 11.6 |
| 35.5 | 11.2 | 205 | 21 | 7.1 | 15.7 |

[a] TS denotes tensile strength, UE ultimate elongation, $M$ modulus at 300% elongation, PS permanent set, and $V_a$ apparent crosslink density.

[b] Ionomers made from terpolymers containing 3% AA and PMMA macromonomer with a molecular weight of $1.35 \times 10^4$.
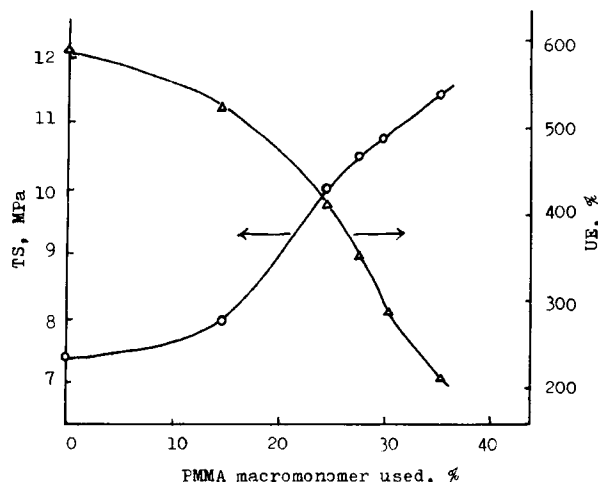
**Figure 5** Effect of wt % PMMA macromonomer used in terpolymerization on the tensile strength and ultimate elongation of the ionomers.

be interpreted as that increase of molecular weight of the PMMA grafts enhances the formation of PMMA domains due to the increasing tendency of microphase separation with increasing molecular weight, resulting in increment of physical crosslinks which need more stress to destroy them during stretching. Microphase separation was demonstrated by the above-mentioned dynamic mechanical spectrum of the ionomer containing PMMA grafts with molecular weight of $1.35 \times 10^4$. It was also indicated by DSC curve of the BA copolymer containing PMMA grafts with molecular weight of 1.35 $\times 10^4$ in another paper[10] of ours that two glass transition temperatures existed, which implies the phase separation between PMMA grafts and PBA backbones.

The molecular weight of the terpolymer before neutralization also affects the mechanical properties

**Table III    Effect of Molecular Weight of PMMA Macromonomers on Mechanical Properties of the Zinc Ionomers[a]**

| $M_{nPMMA}$ $\times 10^{-3}$ | TS (MPa) | UE (%) | PS (%) | $M$ (MPa) | $V_\alpha \times 10^4$ (mol/cm$^3$) |
|---|---|---|---|---|---|
| 5.0 | 8.4 | 630 | 20 | 1.2 | 4.8 |
| 8.6 | 8.8 | 525 | 18 | 1.9 | 5.9 |
| 11.5 | 9.1 | 455 | 16 | 2.5 | 6.8 |
| 13.5 | 9.7 | 375 | 12 | 3.2 | 8.5 |
| 17.5 | 9.8 | 320 | 12 | 4.8 | 9.8 |

[a] Ionomers made from terpolymers with weight ratio of PMMA macromonomer : BA : AA = 24.3 : 72.3 : 3.0.

**Table IV    Effect of Molecular Weight of the Terpolymers on Mechanical Properties of the Zinc Ionomers[a]**

| $M_{nc} \times 10^{-5}$ | TS (MPa) | UE (%) | PS (%) | $M$ (MPa) | $V_\alpha \times 10^4$ (mol/cm$^3$) |
|---|---|---|---|---|---|
| 1.75 | 9.1 | 610 | 19 | 1.4 | 5.3 |
| 1.95 | 9.3 | 560 | 18 | 2.1 | 5.9 |
| 2.67 | 9.7 | 490 | 13 | 2.8 | 6.8 |
| 3.55 | 10.0 | 450 | 12 | 3.8 | 7.4 |
| 4.20 | 10.4 | 390 | 12 | 5.1 | 8.8 |

[a] Ionomers made from the terpolymers obtained by terpolymerization at weight ratio of PMMA macromonomer ($M_n = 1.15 \times 10^4$) : BA : AA = 24.3 : 72.3 : 3.0.

of the ionomers made from them, as shown in Table IV. The higher the molecular weight of the terpolymer is, the larger are the tensile strength and modulus at 300% elongation and the less are the ultimate elongation and permanent set. This may be because the number of both PMMA grafts and ionic crosslinks per chain increase and also the entanglement of chains are enhanced with increasing molecular weight of the terpolymers.

As presented in Table V and Figure 6, when terpolymers containing different amounts of acrylic acid were neutralized with their equivalent amount of zinc ions, tensile strength, modulus at 300% elongation, and apparent crosslink density, all increase while ultimate elongation decreases, as the carboxylic acid group content of the terpolymer increases. The ionomers made from the terpolymers with uniform PMMA grafts show much better mechanical properties than copolymers of BA with only uniform PMMA grafts and containing no carboxylic acid group. This phenomenon is due to the double cross-

**Table V    Effect of Carboxylic Acid Content of the Terpolymers on Mechanical Properties of the Ionomers[a]**

| AA (%) | TS (MPa) | UE (%) | PS (%) | $M$ (MPa) | $V_\alpha \times 10^4$ (mol/cm$^3$) |
|---|---|---|---|---|---|
| 0 | 4.6 | 690 | 21 | 0.6 | 2.4 |
| 1.05 | 5.7 | 605 | 18 | 0.9 | 3.3 |
| 1.97 | 7.8 | 535 | 15 | 1.5 | 5.1 |
| 2.71 | 9.1 | 465 | 13 | 2.4 | 6.7 |
| 3.11 | 10.7 | 400 | 13 | 3.0 | 8.9 |
| 4.08 | 11.5 | 320 | 13 | 4.1 | 11.4 |

[a] Ionomers made from the terpolymer containing 28.3% PMMA ($M_n = 1.35 \times 10^4$).
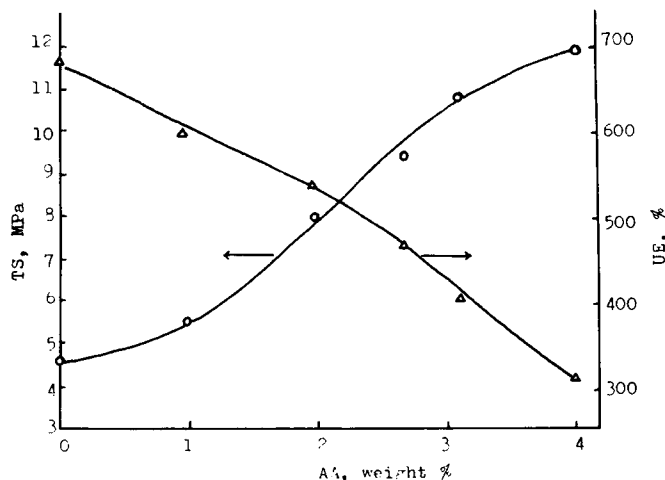
**Figure 6**  Effect of AA content on the tensile strength and ultimate elongation of the ionomers.

links, formed by both ionic bonds and glassy domains in these ionomers.

If Figure 6 is compared with Figure 5, the same tendency can be observed. This implies that either ionic crosslinks or crosslinks by glassy domains have a somewhat similar effect on the mechanical properties.

Tensile strength of the ionomers made from terpolymers with uniform PMMA grafts seems lower than that of the ionomers with uniform polystyrene grafts, as reported by us previously.[9] It may be due to the possibility that compatibility of PMMA grafts with PBA backbone is better than that of polystyrene grafts with PBA backbone, resulting in somewhat imperfect domains of PMMA in the PBA continuous phase.

The amount of zinc acetate used in the neutralization of terpolymers exerts a significant influence on the mechanical properties of the ionomers, as shown in Table VI. Increase of degree of neutral-

ization enhances the tensile strength, modulus, and crosslink density of the ionomer, but reduces the ultimate elongation. Tensile strength increases with neutralization degree until the equivalent salt to COOH ratio reached 1.5, above which the tensile strength decreases. This phenomenon may be explained as follows: When an equivalent amount of metallic acetate was used in neutralization, only a certain portion of zinc acetate was used in effective crosslinking, leaving some free carboxylic acid groups, some unlinked zinc ion bonds, and some intramolecular bonds, due to the reaction between the weak acid and zinc acetate, a salt of weak acid and weak base. Since not all the zinc ions play a role in crosslinking, the tensile strength of the ionomer neutralized at the equivalence point was not the highest. When a moderate excess of zinc acetate was used, the number of zinc ions that functioned as crosslinks increased and a small amount of zinc acetate was distributed into the ionic clusters, thus increasing the size of the clusters and also reinforcing the polymer. But if the zinc acetate used for neutralization is in too great an excess, the excess salt not used in neutralization is separated out as a filler, thus inducing a decrease of the tensile strength.

Table VII lists the effect of type of cation used in neutralization of the terpolymers on the mechanical properties of the ionomers. The results demonstrate that tensile strength of the ionomers decreases in the order: for univalent cations, $Na^+ > K^+$ and for divalent cations, $Pb^{2+} > Zn^{2+} > Ca^{2+} > Mg^{2+}$. Matsura and Eisenberg[11] indicated that the higher the ionic potential of a metallic ion, the larger the repulsive force between the cations and the more difficult it becomes to form ionic clusters. Ionic potentials for the divalent cations such as $Pb^{2+}$, $Zn^{2+}$, $Ca^{2+}$, and $Mg^{2+}$ are 1.67, 2.70, 2.02, and 3.03, respectively, and hence the tendency for formation of ionic clusters is $Pb^{2+} > Ca^{2+} > Zn^{2+} > Mg^{2+}$. How-

**Table VI    Effect of Neutralization Degree on Mechanical Properties of the Ionomers[a]**

| Equivalent Zn(OAc)$_2$ : COOH | TS (MPa) | UE (%) | PS (%) | M (MPa) | $V_\alpha \times 10^4$ (mol/cm$^3$) |
|---|---|---|---|---|---|
| 0 | 5.7 | 610 | 19 | 1.0 | 3.3 |
| 0.50 | 9.2 | 500 | 14 | 2.1 | 6.4 |
| 1.00 | 10.6 | 430 | 13 | 2.6 | 8.4 |
| 1.50 | 11.6 | 390 | 13 | 3.2 | 9.9 |
| 2.00 | 10.5 | 335 | 13 | 3.4 | 10.2 |

[a] Ionomers were made from the terpolymers obtained by terpolymerization at weight ratio of PMMA macromonomer ($M_n$ = 1.35 × 10$^4$) : BA : AA = 28.3 : 68.7 : 3.0.

**Table VII Mechanical Properties of the Ionomers[a] Neutralized with Different Types of Cations**

| Cation | TS (MPa) | UE (%) | PS (%) | $M$ (MPa) | $V_\alpha \times 10^4$ (mol/cm$^3$) |
|--------|----------|--------|--------|-----------|-------------------------------------|
| Na$^+$ | 9.5 | 400 | 15 | 2.4 | 7.9 |
| K$^+$ | 7.8 | 485 | 18 | 1.6 | 5.6 |
| Mg$^{2+}$ | 8.6 | 400 | 13 | 2.2 | 7.2 |
| Ca$^{2+}$ | 9.1 | 385 | 13 | 2.4 | 7.8 |
| Zn$^{2+}$ | 10.6 | 430 | 12 | 2.6 | 8.4 |
| Pb$^{2+}$ | 11.3 | 450 | 13 | 2.6 | 8.5 |

[a] Ionomers were made from the terpolymers obtained by terpolymerization at weight ratio of PMMA macromonomer ($M_n$ = 1.35 × 10$^4$) : BA : AA = 28.3 : 68.7 : 3.0.

ever, the existence of external d-level electrons makes Pb and Zn more covalent[12] and it is easier to interchange their ionic bonds. When stress was applied to the ionomer, cation exchange between neighboring groups through dissociation and reformation of ionic bonds may occur so as to prevent the formation of local stresses and hence premature failure. Table VII indicates that cation exchange seemed to be main factor influencing the tensile strength of the ionomers. The ultimate elongation of Pb or Zn ionomer was larger than that of Ca or Mg ionomer.

In the case of univalent cations, the tensile strength of the ionomers decreases with decreasing ionic potential: Na$^+$ (1.03) > K$^+$ (0.75). This is contrary to the divalent cations. It is probably due to the different behavior of univalent and divalent cations in the formation of crosslinks. The former forms weak crosslinks through association of oppositely charged ions, while the latter forms chemically bonded crosslinks through ionic bonds. For

univalent cations, the higher the ionic potential is, the more dispersed are the ionic clusters and therefore the greater is the strength of the ionomer.

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