Mechanical behaviour and water absorption properties of ionomers from copolymers with uniform polystyrene grafts

Hongquan Xie and Yanming Feng
Hua Zhong University of Science and Technology, Wuhan, Hubei, People's Republic of China

(Received 3 August 1987; revised 11 October 1987; accepted 14 December 1987)

Copolymers with uniform grafts were prepared by copolymerization of polystyrene macromer with butyl acrylate and acrylic acid. They were neutralized with alkali or metallic salts to form ionomers. The tensile strength of the ionomers can reach almost twice those of copolymers of butyl acrylate and acrylic acid without uniform polystyrene grafts or those of copolymers without neutralization. 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 water absorbency of the ionomers decreases with increasing amount or increasing molecular weight of the polystyrene grafts, but increases with metallic ions used in neutralization in the order: $Pb^{2+} < Zn^{2+} < Mg^{2+} < Ca^{2+} < K^{+} < Na^{+}$.

(Keywords: ionomer; graft copolymer; macromer; mechanical behaviour; water absorption; double physical crosslinks)

INTRODUCTION

Since the development of thermoplastic elastomers, it has been established that three types of physical crosslink exist in different thermoplastic elastomers, namely, glassy domains, crystallites and ionic clusters or multiplets. In recent years Milkovich *et al.*[1], using a macromer technique, successfully prepared poly(butyl acrylate-*co*-ethyl acrylate) with uniform polystyrene grafts—a new kind of thermoplastic elastomer, containing the polystyrene domains as physical crosslinks. MacKnight[2] reported the synthesis of ionomers used as thermoplastic elastomers with metallic-ion clusters or multiplets as crosslinks. More recently we[3] have synthesized poly(butyl acrylate-*co*-acrylic acid) with uniform polystyrene grafts and, after neutralization with salts, obtained ionomers that showed the existence of three phases under a transmission electron microscope, i.e. ionic clusters, glassy domains and continuous polyacrylate phase.

This paper deals with the mechanical behaviour of these ionomers as a function of structural parameters and neutralization conditions, such as neutralization method, degree of neutralization, type of metallic ion used, carboxylic acid content, molecular weight and content of polystyrene grafts, and also molecular weight of the copolymers. The effect of different factors on water absorption of the ionomers was also studied.

EXPERIMENTAL

Materials

Styrene and butyl acrylate (BA) were purified by first washing with 10% NaOH solution to remove inhibitors and then distilling under reduced pressure over CuCl. Acrylic acid (AA) was dried over 4 Å molecular sieves and distilled under reduced pressure. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Benzene, toluene, cyclohexane and n-butyl chloride were dried by standing over 4 Å molecular sieves for 24 h before use. Tetrahydrofuran (THF) was distilled over CaH_2. Solvents used for neutralization are chemically pure and used without purification. Ethylene oxide was purified by successive distillations over KOH and CaH_2. Methacryloyl chloride was synthesized by reaction of methacrylic acid with SO_2Cl at 65°C and purified by vacuum distillation over CuCl. n-Butyl lithium was synthesized by reaction of n-butyl chloride with lithium chips in cyclohexane at 50°C under nitrogen and its concentration was determined by double titrations.

Preparation of polystyrene macromers and copolymerization with BA and AA

Methacrylate-terminated polystyrene macromers[1] were prepared by capping living polystyrene anions with ethylene oxide, followed by terminating with methacryloyl chloride at 50°C for 2 h. The products were precipitated and washed with ethanol, then dried. Their molecular weight and molecular weight distribution were determined by g.p.c., carried out in an LC-4A type apparatus using a column filled with porous crosslinked polystyrene gels (HSG-40 and HSG-60) and using a u.v. detector and THF as eluent at 25°C.

Polystyrene macromer, BA and AA were copolymerized in benzene using AIBN as initiator at 61 ± 2°C for 24 h under nitrogen. After evaporating the solvent, the copolymer was vacuum dried. The dried copolymer was extracted with n-butanol three times to remove homopolymers and copolymers of BA and AA, then with mixed solvent of decalin and petroleum ether three times to remove homopolystyrene, followed by washing with petroleum ether and drying under vacuum. The carboxylic acid content of the copolymer was titrated in acetone with standardized NaOH solution in ethanol, using phenolphthalein as indicator. The number-average

0032-3861/88/071216-05$03.00

molecular weight of the copolymer was determined by a Bruss membrane osmometer using THF as solvent.

Preparation of ionomers

In the case of neutralization in solution, a 0.1 N ethanolic solution of univalent metal hydroxide was added to a 5% copolymer solution in acetone with stirring and the reaction was carried out at room temperature for 24 h. When a 1% solution of divalent metal acetate in methanol was used, the neutralization proceeded at 50°C for 24 h. The products were precipitated in water, washed with water several times and then dried under vacuum. If toluene or xylene was used as solvent, aqueous 10% zinc acetate solution was added dropwise and the reaction was carried out with agitation at 80°C for 5 h or 125°C for 40 min, respectively. The products were obtained by evaporating off the solvent.

Instead of neutralization in solution, the copolymers can also be neutralized in the melt. Copolymer (35 g) was mixed with the stoichiometric amount of metal acetate powder in a Brabender Plasticorder at 160–165°C and a shear rate of 30 rpm. Values of mixing torque were recorded in 5 min intervals till equilibrium. The ionomers obtained were vacuum dried.

Measurement

The ionomers or copolymers were compression moulded at 150–160°C between polyester films. The tensile strength, ultimate elongation and permanent set were determined on a DL-250 tensile tester at 25 ± 2°C, with an extension rate of $500\,\mathrm{mm\,min^{-1}}$.

The apparent crosslink density (V_α) was calculated from the following equation:

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

where σ is the tensile strength and λ is the extension ratio.

Water absorbency was measured according to the following procedure. The samples were first hot-pressed into 0.2–0.4 mm films, which were then cut to $1\,\mathrm{cm^2}$ and weighed. The samples were immersed in water at constant temperature and taken out at different time intervals. After removing water from the surface, the films were weighed. The water absorbency is given by:

$$\text{Water absorbency, } H_2O\ (\%) = [(W_a - W_b)/W_b] \times 100$$

where W_b is the weight of samples before water absorption and W_a is the weight of samples after water absorption.

RESULTS AND DISCUSSION

Effect of neutralization method on the mechanical properties of the ionomers

Table 1 compares the mechanical properties and apparent crosslink density between the ionomers neutralized in solution and those neutralized in the melt. It can be seen that ionomers neutralized in solution exhibit higher tensile strength, lower elongation and permanent set than those neutralized in the melt. This implies that neutralization in solution is more uniform, resulting in a higher degree of neutralization and higher crosslink density than neutralization in the melt.

Three solvent mixtures were tried in solution neutralization. The results in *Table 2* show that neutralization seemed perfect in either of these solvent mixtures, resulting in almost the same high tensile strength. However, the time needed for neutralization in methanol–acetone mixture was longer than that in the other two solvent mixtures, because of the lower neutralization temperature due to the lower boiling point of the methanol–acetone mixture, but the treatment after neutralization was easier.

Effect of metal carboxylate content on the mechanical properties of the ionomers

Copolymers of butyl acrylate with uniform polystyrene grafts containing no metal carboxylate also exhibit some tensile strength and elasticity, due to the presence of glassy domains formed by aggregation of polystyrene grafts. However, the ionomers from copolymers with uniform polystyrene grafts showed much better mechanical properties due to double crosslinks, formed by both ionic bonds and glassy domains (*Table 3*). With increase of carboxylic acid groups in the copolymer, which was neutralized by metal salts to the equivalence point, tensile strength, modulus and hardness increase, while ultimate elongation and permanent set decrease. When the carboxylic acid content of the original copolymer exceeded 5.6%, the ionomer behaved somewhat like a toughened plastic.

Table 2 Effect of solvent used in neutralization on mechanical properties of the ionomers

Solvent (vol. ratio)	Temp. (°C)	Time (h)	*TS* (MPa)	*UE* (%)	*M* (MPa)	*PS* (%)
Acetone/methanol (4/1)	50	24	12.8	430	3.0	10
Toluene/water (20/1)	80	5	13.1	410	3.0	8
Xylene/water (10/1)	125	0.66	13.3	430	2.9	10

Table 1 Comparison of mechanical properties[a] of ionomers obtained by different neutralization methods

Reagent	Method	*TS* (MPa)	*UE* (%)	*M* (MPa)	*PS* (%)	$V_\alpha \times 10^4$ (mol cm^{-3})
$ZnAc_2$	Soln.[b]	12.8	430	3.0	10	10.1
$ZnAc_2$	Melt	8.7	520	1.7	14	5.9
$MgAc_2$	Soln.[b]	9.0	380	2.5	10	7.7
$MgAc_2$	Melt	8.0	470	1.8	14	5.8

[a] *TS* denotes tensile strength, *UE* ultimate elongation, *M* modulus at 300% elongation, *PS* permanent set and V_α apparent crosslink density
[b] Acetone–methanol mixture used as solvent

Table 3 Effect of carboxylic acid content[a] of the graft copolymers on mechanical properties of the ionomers

AA (wt%)	*TS* (MPa)	*UE* (%)	*M* (MPa)	*PS* (%)	*H*[b]	$V_\alpha \times 10^4$ (mol cm^{-3})
0	3.0	820	–	–	30	1.3
1.11	4.6	630	0.6	14	44	2.6
2.33	8.4	500	1.4	10	48	5.7
3.10	12.8	430	3.0	10	56	10.1
4.23	14.4	320	4.2	8	62	14.3
5.62	14.6	180	9.2[c]	8	66	22.4

[a] The carboxylic acid groups were neutralized with zinc acetate to the equivalence point

[b] *H* represents Shore hardness

[c] This modulus is at 100% elongation

Table 4 Effect of degree of neutralization on the mechanical properties of the ionomers

Equivalent $ZnAc_2$/COOH	*TS* (MPa)	*UE* (%)	*M* (MPa)	*PS* (%)	*H*	$V_\alpha \times 10^4$ (mol cm^{-3})
0	5.9	630	1.4	18	30	3.3
0.5	10.1	450	2.7	10	48	7.6
1.0	12.8	430	3.0	8	56	10.1
1.5	15.1	460	3.1	12	58	11.1
2.0	13.3	350	3.4	12	58	12.3

Effect of degree of neutralization on the mechanical properties of the ionomers

The amount of zinc acetate used in the neutralization has a significant influence on the mechanical properties of ionomers, as shown in *Table 4*. Increase of degree of neutralization enhances the modulus, hardness 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 tensile strength decreases.

These phenomena may be interpreted as follows. When a stoichiometrically equivalent amount of metallic salt was used in neutralization, only a certain portion of the zinc salt was used in effective chemical crosslinking, leaving some free carboxylic acid groups, some unlinked metal bonds and some intramolecular bonds. 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 salt was distributed into the ionic clusters, thus increasing the size of the clusters and also reinforcing the polymer. This results in an increase of the tensile strength. However, if the zinc acetate used for neutralization is in too great an excess, the excess zinc salt not used in neutralization is separated out as a filler, thus inducing a decrease of the tensile strength.

Effect of type of metallic ion on the mechanical properties of the ionomers

The mechanical properties of the ionomers neutralized with different types of cation are listed in *Table 5*. The tensile strength of the ionomers decreases in the following order: $Pb^{2+} > Zn^{2+} > Na^{+} > Ca^{2+} > Mg^{2+} > K^{+}$.

Eisenberg *et al.*[4] indicated that the ionic potential (Z/r, charge-to-ion-size ratio) of the metallic ions is an important factor influencing the properties of ionomers. 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. Thus the tendency for formation of ionic clusters is: $Pb^{2+} > Ca^{2+} > Zn^{2+} > Mg^{2+}$. The electronic configurations of metallic ions also exert an important influence on the formation of ionic bonds. The existence of external d-level electrons makes Pb and Zn more covalent[5]. These two cations exhibit lower electrostatic attraction than Ca^{2+} and Mg^{2+}, and it is easier to interchange their ionic bonds. When stress was applied to the ionomer, cation exchange between neighbouring groups through dissociation and re-formation of ionic bonds may occur so as to prevent the formation of local stresses and hence premature failure. Thus the tendency for cation exchange decreases in the order: $Pb^{2+} > Zn^{2+} > Ca^{2+} > Mg^{2+}$. Experimental results of tensile strength (*Table 5*) indicated that cation exchange seemed to be the main factor influencing the tensile strength of the ionomers. The ultimate elongation of Pb or Zn ionomer and permanent set of the Pb ionomer were larger than those of other divalent cations.

In the case of univalent cations, the tensile strength of the ionomers decreases with decreasing ionic potential, i.e. $Na^{+}(1.03) > K^{+}(0.75)$. This is contrary to the divalent ions. The reason is probably due to the different behaviour 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[6]. For univalent cations, the higher the ionic potential, the more dispersed the ionic clusters and therefore the greater the strength of the ionomer.

Effect of polystyrene graft content on the mechanical properties of the ionomers

The mechanical properties of different zinc ionomers obtained from copolymers with constant AA/BA ratio but different proportions of polystyrene grafts and neutralized to the equivalence point are listed in *Table 6*. This shows that ionomers containing no uniform polystyrene grafts possess only low tensile strength and modulus with higher elongation and permanent set. With increase of polystyrene graft content, the tensile strength increases and the elongation decreases, while permanent set exhibits a minimum at 20–30% polystyrene content. The apparent crosslink density increased with polystyrene graft content and the products changed gradually from elastomer to toughened plastic.

Table 5 Mechanical properties of the ionomers neutralized with different types of cation

Cation	*TS* (MPa)	*UE* (%)	*M* (MPa)	*PS* (%)	$V_\alpha \times 10^4$ (mol cm^{-3})
K^{+}	7.3	480	1.5	12	5.3
Na^{+}	11.6	350	2.6	10	10.6
Ca^{2+}	9.7	400	2.6	8	8.0
Mg^{2+}	9.0	380	2.5	8	7.7
Zn^{2+}	12.8	430	3.0	8	10.1
Pb^{2+}	13.7	470	2.8	14	9.9

Table 6 Effect of polystyrene graft content on the mechanical properties of the ionomers

Graft content (wt%)	*TS* (MPa)	*UE* (%)	*M* (MPa)	*PS* (%)	*H*	$V_\alpha \times 10^4$ (mol cm^{-3})
0	5.3	520	1.0	14	36	3.5
10	7.6	440	1.9	10	45	5.8
16	11.7	420	2.8	10	50	9.3
22	12.8	430	3.0	8	56	10.1
27	14.7	300	4.9	8	64	15.3
32	15.5	240	8.2[a]	12	72	19.2
38	16.9	160	12.3[a]	30	88	28.1
50	17.2	60	–	50	94	58.5

[a] This modulus was at 100% elongation, while others were at 300% elongation

Table 7 Effect of molecular weight of polystyrene grafts on mechanical properties of the ionomers

$M_n \times 10^3$	*TS* (MPa)	*UE* (%)	*M* (MPa)	*PS* (%)	*H*	$V_\alpha \times 10^4$ (mol cm^{-3})
6.7	6.2	570	1.2	14	40	3.8
10.0	12.1	420	2.1	10	54	9.6
11.0	12.5	410	2.9	10	54	10.1
12.0	13.1	370	3.1	10	56	11.6
14.0	14.4	300	4.8	8	60	15.0
19.0	13.7	260	–	10	60	15.8

Table 8 Effect of molecular weight of the copolymers on mechanical properties of the ionomers

$M_n \times 10^4$	*TS* (MPa)	*UE* (%)	*M* (MPa)	*PS* (%)
11.0	9.5	550	1.3	20
18.5	11.5	440	2.5	14
21.0	13.2	420	3.0	10
41.0	15.5	340	4.1	10
43.0	17.2	300	5.6	8

Effect of molecular weight of polystyrene grafts on mechanical properties of the ionomers

Table 7 shows the mechanical properties of zinc ionomers prepared by copolymerization of BA, AA and polystyrene macromers of different molecular weights and consequent neutralization to the equivalence point with zinc acetate. The tensile strength increased and the ultimate elongation and permanent set decreased with increasing molecular weight of polystyrene grafts up to 1.4×10^4, exceeding which both tensile strength and ultimate elongation decreased. The latter phenomenon may be attributed to the relative decrease in the number of polystyrene grafts per macromolecule as a constant proportion of polystyrene was used, resulting in a reduction of the physical crosslinks formed by polystyrene grafts.

Effect of molecular weight of the terpolymer on the mechanical properties of the ionomers

The molecular weight of the copolymer also affects the mechanical properties of the ionomers, as shown in *Table 8*. With increase of molecular weight of terpolymers, tensile strength and modulus of the ionomers increased, while ultimate elongation and permanent set decreased. This may be because the number of both polystyrene grafts and ionic crosslinks per macromolecule increased as the molecular weight of the copolymer increased, resulting in an increase of the crosslink density.

Comparison of the mechanical properties of copolymers with a single crosslink and double crosslink

Table 9 summarizes the mechanical properties of the copolymers with only polystyrene grafts or only ionic clusters or with both polystyrene grafts and ionic clusters as crosslinkages. It can be seen that tensile strength and apparent crosslink density of the copolymers with a double crosslinkage are higher and the permanent set is lower than those with only a single crosslinkage, while the ultimate elongation was still satisfactory.

Water absorption of the ionomers

Ionomers neutralized with different cations showed the following order of decreasing water absorbency: $Na^+ > K^+ > Ca^{2+} > Mg^{2+} > Zn^{2+} > Pb^{2+}$, as illustrated in *Figure 1*. The water absorbency of the alkali-metal ionomers is the highest and that of Pb and Zn ionomers the lowest in the temperature range 20–80°C. This is probably due to univalent cations forming weak crosslinks through the association of oppositely charged ions, which may allow water molecules to penetrate, while divalent cations form chemically bonded crosslinks between macromolecules, which prevent penetration of water molecules. Also, sodium and potassium ions are easier to solvate by water than zinc and lead ions, which are of more covalent character.

Table 9 Comparison of mechanical properties between copolymers with single and double crosslinkage

Samples[a]	*TS* (MPa)	*UE* (%)	*PS* (%)	$V_\alpha \times 10^4$ (mol cm^{-3})
PBA-*g*-PSt (BA/PSt = 74.9/22)	3.0	820	–	1.3
PBA-*g*-PSt (BA/PSt = 60/40)	7.3	360	20	6.6
P(BA–AA)–Zn (BA/AA = 74.9/3.1)	5.3	520	14	3.5
P(BA–AA)–Zn (BA/AA = 74.9/6.2)	8.8	290	14	9.5
P(BA–AA)–Zn–PSt (BA/AA/PSt = 74.9/3.1/22)	12.8	430	10	10.1

[a] All the ratios in the parentheses are weight ratios

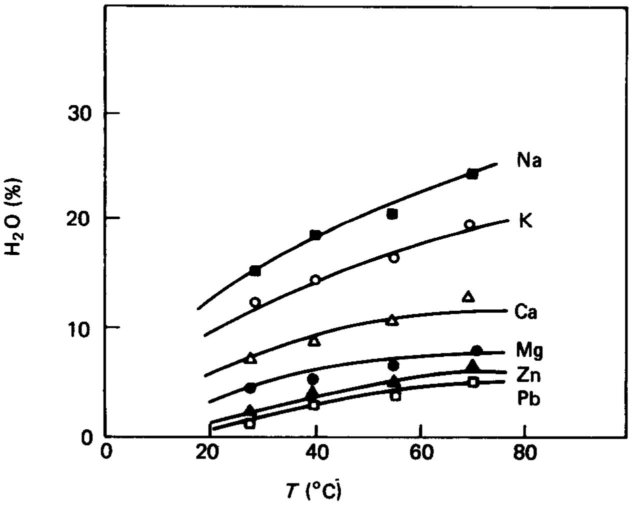

Figure 1 Water absorption *versus* immersion temperature for ionomers with different types of cation

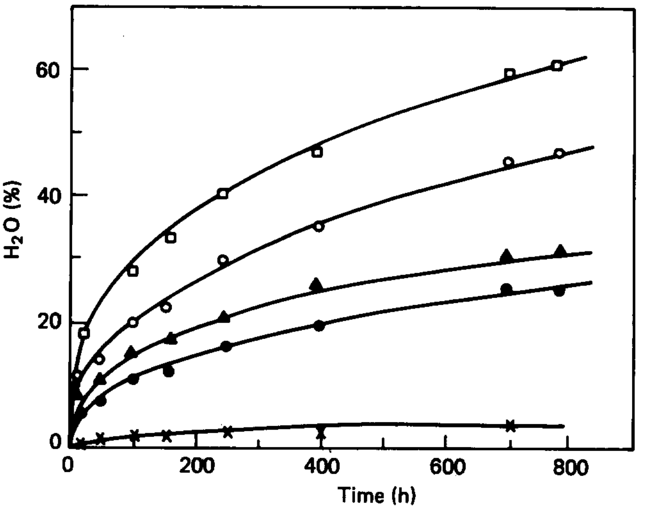

Figure 2 Water absorption *versus* immersion time for ionomers with different original carboxylic acid content. Weight per cent of AA in copolymer: (□) 4.23, (○) 3.10, (▲) 2.33 and (●) 1.11 for Na ionomer; (×) 3.10 for Zn ionomer

Raising the temperature accelerates movement of chains, thus facilitating diffusion and penetration of water molecules.

Figure 2 indicates that water absorbency of sodium ionomer increased markedly at the beginning of immersion in water, then gradually with time, and also increased significantly with ion content. However, zinc ionomer behaved in a quite different manner. Not only immersion time but also ion content affect the water absorbency of zinc ionomer slightly.

In the case of zinc ionomers, water absorbency decreased with increase of molecular weight and content of polystyrene grafts (*Figure 3*). This can be explained by the increase of physical crosslinks and hydrophobic component, resulting in limitation of chain movement and also hindrance of water molecule diffusion. Hence the water absorbency is lowered.

The ionomers are transparent before absorption of water. With increase of water absorption, the surface of the samples became emulsified and they gradually turned milky white, but after drying turned transparent again. This demonstrates that the water absorption process is a physical process.

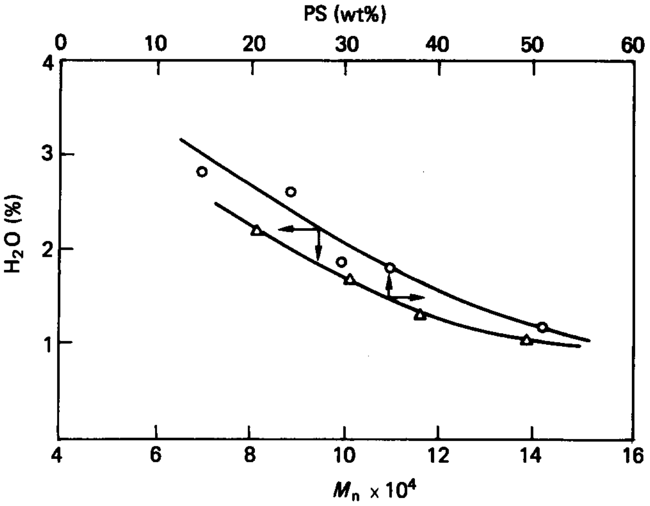

Figure 3 Effect of molecular weight or content of the polystyrene (PS) grafts on water absorbency of the ionomers

The copolymers before neutralization are easily soluble in toluene, benzene, ethyl acetate, acetone or diethyl ether, but after neutralization with metallic salts the ionomers obtained do not dissolve but swell to different degrees in the above solvents. However, if a solvent such as toluene was used to swell the ionomer first and then a small amount of alcohol was added, the ionomers can be dissolved.

ACKNOWLEDGEMENT

Support by the National Science Foundation Committee of China is gratefully acknowledged.

REFERENCES

1 Schulz, G. O. and Milkovich, R. *J. Appl. Polym. Sci.* 1982, **27**, 4773
2 MacKnight, W. J. and Lundberg, R. D. *Rubber Chem. Technol.* 1984, **57**, 652
3 Xie, H. Q. and Feng, Y. M. *Polym. Bull.* in press
4 Martsura, H. and Eisenberg, A. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 1201
5 Bagrodia, S. and Wilkes, G. L. *Polym. Bull.* 1984, **12**, 389
6 Jenkins, D. K. and Duck, E. W. 'Ionic Polymers' (Ed. L. Holliday), Applied Science, London, 1975, p. 184