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Deformation modes of poly(styrene-*co*-sodium methacrylate) ionomers

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The influence of ion content and ionomer morphology on deformation modes of poly(styrene-*co*-sodium methacrylate) ionomers has been examined. Dynamic mechanical thermal analysis indicates a morphology characteristic to amorphous ionomers: two separate loss peaks are observed, one associated with the glass transition of the multiplet-containing matrix phase and the higher temperature loss peak with the glass transition of an ion-rich cluster 'phase'. As ion content rises, the intensity of the matrix loss peak diminishes, while the intensity of the cluster loss peak rises. At a critical ion content of about 6 mol%, the cluster phase begins to dominate. Such 'two-phase' morphology of the ionomers has an appreciable effect on deformation modes. At low ion contents, where the matrix phase is the major one, only crazing is observed and the craze morphology is generally similar to that of polystyrene. At higher ion contents where the cluster phase becomes dominant, some shear deformation is present and the crazes tend to be shorter and less well defined. The effect of thermal treatment on crazing behaviour of the ionomers is also studied; two competing factors, i.e. simple physical aging and enhancement of the ion-rich cluster phase, determine the overall deformation modes. In general, thermal treatment enhances cluster formation, which in turn suppresses crazing and shifts the deformation mode towards shear deformation. Results of this study are compared with those reported on other types of ionomers, such as partially sulfonated polystyrene ionomers and ionomers based on poly(methyl methacrylate). Copyright © 1996 Elsevier Science Ltd.

(Keywords: deformation mode; poly(styrene-*co*-sodium methacrylate) ionomers; ion content effect)

INTRODUCTION

It is well established that many amorphous ionomers possess a 'two-phase' morphology as a result of aggregation of ionic groups into small aggregates, termed multiplets, and into larger units, comprised of many multiplets and interweaving polymer chains, termed clusters[1–7]. Perhaps the strongest evidence for this 'two-phase' morphology is the presence of two glass transitions, as evidenced in dynamic mechanical thermal analysis (d.m.t.a.) data by two separate moduli dispersions and two associated mechanical loss ($\tan\delta$) peaks. The first primary transition reflects the onset of appreciable chain mobility in the multiplet-containing matrix phase and the second higher temperature transition is associated with the onset of chain mobility in the cluster 'phase'. With increase of ion content, both glass transitions (T_gs) move to higher temperatures and the modulus or stiffness of the ionomer, especially in the plateau region between the two respective T_gs, rises appreciably. Ionomers in which similar effects have been noted include: sulfonated polystyrene (SPS) ionomers[8–10], carboxylated polystyrene ionomers[10], poly(styrene-*co*-sodium methacrylate) ionomers[11,12] and poly(methyl methacrylate) (PMMA) ionomers[13].

It is well known that in many ionomers there exists an 'ionomer' peak in intensity vs scattering angle curves from small-angle X-ray scattering (SAXS) or small-angle neutron scattering (SANS) measurements[14–17]. The peak is considered to arise from either intramolecular scattering of ionic clusters[14] or intermolecular scattering of multiplets[15–17]. For interpretation of scattering data and d.m.t.a. data, many possible models of ionomer structure have been proposed and these are discussed in some detail in recent papers[5,7]. Among them, a modified multiplet-cluster model proposed by Eisenberg *et al.*,[7] (designated as the EHM model), appears to be in accord with a wide variety of experimental results. In this model, the fundamental structural entity remains the contact ion pair; and multiplets, as in the classical multiplet-cluster model[6], consist of a small number of associated ion pairs bonded together by Coulombic interactions. It is suggested that polymer chains in the immediate vicinity of the multiplets have restricted mobility. As ion content rises, some overlap of these restricted mobility chains will occur. When the overlap region becomes great enough to have its own T_g, it constitutes what may be termed an ion-rich *cluster 'phase'*. In this model, the SAXS peak is considered to represent the average distance between multiplets within the cluster 'phase'. Here, d.m.t.a. and scattering data are both explained in the framework of a single model.

The question arises to what extent, if any, does the ion content, and the resulting microstructure, of ionomers affect their mechanical properties in the glassy state, i.e. at temperatures far below the matrix T_g? Although this is

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an area of study that has not received much attention to date, some effect on mechanical behaviour might be anticipated as the introduction of ionic interactions constitutes a type of physical cross-linking—as evidenced by an increase of T_g with ion content—and thereby increases the 'effective' entanglement density of the polymer[18,19]. Such an increase, as known from the studies of Kramer and coworkers[20–22], will affect the response of a glassy polymer to applied stresses. For example, when the entanglement density, ν_e, is low ($< 4 \times 10^{25}$ chains m^{-3}), as in polystyrene (PS), the polymer responds to tension only by localized crazing and strain to fracture is low; but when ν_e is high, as in polycarbonate (PC), the polymer responds through shear deformation and the material is ductile. It has also been noted by Henkee and Kramer[23] that if the effective entanglement (or strand) density of PS is raised by the introduction of covalent cross-links, the response to stress changes from crazing only, to crazing plus shear deformation, and then to shear deformation only as the degree of cross-linking rises. Ionic cross-linking may not be as stable as covalent cross-linking, as it can be overcome at elevated temperatures, but it does increase the 'effective' strand density and thereby will affect the mode of deformation and the resulting mechanical behaviour. In fact, in SPS ionomers, with sodium as the counterion, it has been noted, from transmission electron microscope (TEM) studies of strained thin films, that when the ion content approaches a critical value, which is near to 6 mol%, the mode of deformation changes from straight, long crazes, to shorter and branched crazes and then to crazing plus shear deformation[24]. Also, both the tensile strength and the energy to fracture show a significant increase at ion contents near to the critical value[25].

We have been studying mechanical, especially deformation and fracture, behaviour of glassy ionomers and have made extensive observations on deformation modes in strained thin film specimens of SPS ionomers. It is clearly of interest to examine other glassy ionomers to see whether the effects observed in the SPS ionomer are general in nature and whether comparable changes in deformation modes will occur in ionomers having a different backbone structure or a different ionic group. In the present paper, we report results obtained on poly(styrene-*co*-sodium methacrylate) ionomers, which have a comparable backbone chain to SPS ionomers but a different ionic group; and, in a separate communication, we present results on PMMA-based ionomers which have the same ionic units as poly(styrene-*co*-sodium methacrylate) ionomers, viz. sodium methacrylate, but a different backbone structure[26]. Our studies include TEM examination of the response to tensile stress of thin films of poly(styrene-*co*-sodium methacrylate) ionomers of two different ion contents, viz. 4.8 and 8.2 mol%; and also determination of dynamic mechanical properties of comparable ionomers over a broad temperature range from ambient to about 250°C.

The d.m.t.a. studies will provide information on the effects of ion content on morphology and microstructural features that will be useful in interpreting the data, obtained at ambient temperature, on the deformational response to applied stress. Since an extensive d.m.t.a. study has been recently reported for a similar ionomer of widely varying ion content by Kim *et al.*[12], our d.m.t.a. results will be briefly described and compared with their results. In their study, data are presented for temperatures above 100°C; hence, the possible influence of ion content on the modulus in the glassy state, reported in their study as negligible, may be better assessed from the d.m.t.a. data of this study which have been acquired down to temperatures well below T_g. In the study of the deformational response to applied stress, some consideration is also given to the effects of thermal treatment, as appropriate ageing at an elevated temperature can lead to the development of an equilibrium microstructure and enhance mechanical properties[19]. In fact, prior studies on SPS ionomers have shown that thermal treatment enhances cluster formation[27] and this is known to have a significant effect on mechanical properties[24,25].

EXPERIMENTAL

Preparation of the ionomers

Poly(styrene-*co*-methacrylic acid) samples were prepared by free-radical bulk copolymerization of styrene and methacrylic acid monomers. The ion contents were 4.8, 5.5 and 8.2 mol%, determined by titration of the acid copolymers in benzene/methanol (90/10, v/v) with methanolic NaOH solution. The copolymers were then converted to ionomers by neutralization in benzene/methanol (90/10, v/v). The ionomer solutions were freeze dried, followed by vacuum drying for 7 days. Details of sample preparation are described elsewhere[28].

Dynamic mechanical studies

All tests were made on samples ($12 \times 2.5 \times 0.5$ mm) cut from compression moulded plates. The samples were successively polished with emery papers of No. 400, No. 600 and No. 0000, before being installed in a Piezotron (Toyoseiki, Japan) for the d.m.t.a. tests. The tests were run at a frequency of 1 Hz and at a heating rate of 4°C min^{-1} with temperature control of ±0.5°C. Values of the storage modulus, E', the loss modulus, E'', and loss tangent, $\tan\delta (\equiv E''/E')$, were recorded at different temperatures, typically with 1°C interval. A more detailed description regarding the d.m.t.a. measurements is given elsewhere[13].

Transmission electron microscope studies

For study of deformation modes by TEM, thin film samples were prepared by solution casting on to glass microscope slides with tetrahydrofuran (THF) as the solvent. The samples were examined in the TEM using a somewhat similar procedure to that described by Lauterwasser and Kramer[29]. The microscope used in these studies was a JEM-100CX11 (Jeol Ltd, Japan) and all micrographs were taken at an accelerating voltage of 100 kV. The samples, attached to copper grids, were deformed in tension and examined in the deformed state. Some samples were given an additional heat treatment of 8 h at 100°C under vacuum before being deformed and examined in the microscope. Further details of the procedures used in this study are given elsewhere[24,26].

Strand density of ionomers

Since we make use of the concept of molecular entanglements, or strand density, for understanding the deformation modes of ionomers, basic relations are explained. For linear polymers, such as homopolymers and copolymers, the strand density, v_e, is defined as

$$v_e = \rho N_A / M_e \tag{1}$$

where ρ is the density of the polymer ($g\,cm^{-3}$), N_A is Avogadro's number, and M_e is the entanglement molecular weight[22] (see *Figure 1a*). In a similar fashion, we can define an *ionic cross-link strand density*, ν_i, as

$$\nu_i = \rho N_A / M_i = f \rho N_A / M_o \tag{2}$$

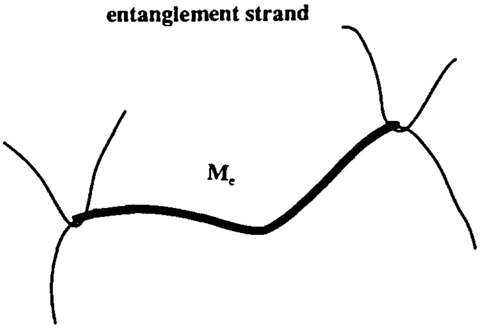
where M_i is the average molecular weight between ionic groups (see *Figure 1b*), f is the ion content (fraction), and M_o is the repeat unit molecular weight. We have proposed that, by combining these two quantities, an *effective strand density*, v_{eff}, may be defined as[26]

$$\nu_{eff} = v_e + k\nu_i \tag{3}$$

In equation (3), ν_{eff} is considered to be the strand density normalized in terms of the strength of the covalent bonds, since the strength of ionic bonds in ionomers is generally smaller than that of covalent bonds. Here, k is a coefficient reflecting the effectiveness of ionic cross-links as compared with covalent cross-links or physical entanglements (at temperatures far below T_g); therefore, the range of k is $0 < k < 1$. It may be expected that the k value of monovalent (e.g. Na) salt ionomers will be low, hence ν_{eff} will tend to be low; while the k value of divalent (e.g. Ca) salt ionomers of the same ion content is expected to be higher, leading to much higher ν_{eff} values. Therefore, it is anticipated that the replacement of counterions from monovalent to divalent may lead to a change in deformation mode[19]. In addition, since $\nu_i \propto f$ as seen from equation (2), the ν_{eff} value will increase with increasing ion content f, and this increase is expected to produce changes in the deformation modes of the ionomers[19]. It should be added that the k value may reflect the effectiveness of ionic cross-links according to their locations, i.e., whether they are in a matrix phase or in a cluster 'phase'. The k value of the latter should be higher as shown in the current result on poly(styrene-*co*-sodium methacrylate) ionomers and in the previous results on sulfonated polystyrene ionomers[19].

(a)

entanglement strand



(b)

ionic cross-link strand

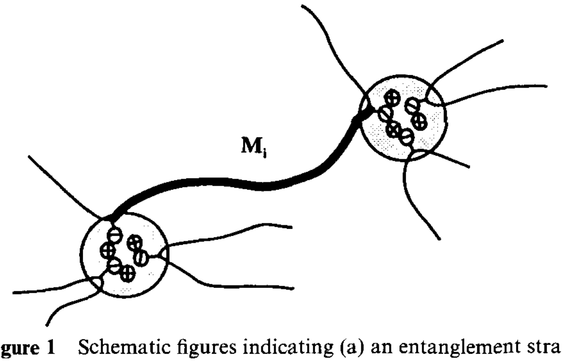


Figure 1 Schematic figures indicating (a) an entanglement strand and (b) an ionic cross-link strand

RESULTS AND DISCUSSION

D.m.t.a. studies and morphology

To examine morphology and to see whether our results were consistent with those reported by others, d.m.t.a. studies were conducted. The storage modulus and loss tangent vs temperature plots for polystyrene, and for two poly(styrene-*co*-sodium methacrylate) ionomers, having an ion content of 5.5 and 8.2 mol%, respectively, are shown in *Figures 2* and *3*. Our test results are in general accord with the results of more detailed studies taken over a wider range of ion content by Kim *et al.*[12].

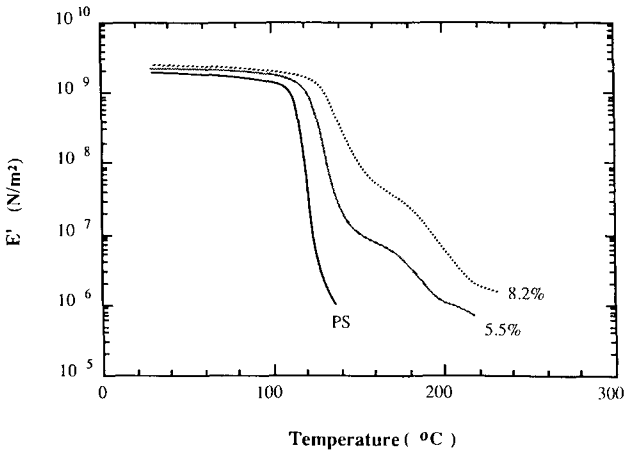


Figure 2 Storage modulus against temperature for polystyrene and poly(styrene-*co*-sodium methacrylate) ionomers of two different ion contents

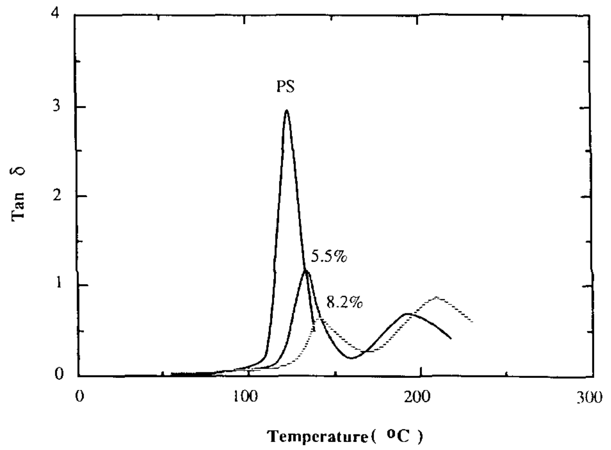


Figure 3 Loss tangent against temperature for polystyrene and poly(styrene-*co*-sodium methacrylate) ionomers of two different ion contents

First, two glass transitions are present, as evidenced by two large drops in moduli in two different temperature regions of *Figure 2* and by two corresponding tan δ peaks of *Figure 3*. In general accord with prior studies[11,12], we associated the lower temperature transition or loss peak with onset of chain mobility in the matrix phase containing isolated multiplets and the higher temperature modulus drop and loss peak with the glass transition of the cluster phase. Secondly, the modulus values in the plateau regions between the glass transition temperatures of the two phases increase markedly with ion content, even more rapidly than might be expected on the basis of the ionic aggregates acting as physical cross-links. Thirdly, both transition temperatures increase with ion content.

One difference between our results and those of Kim *et al.*[12] is that we find that the glassy modulus of the ionomer, here taken as the measured E' value at 30°C, does depend on ion content. Although only three points are plotted in *Figure 4*, it seems clear that the E' value increases with increasing ion content. The increase of the glassy modulus with ion content is not as great as that of the moduli above T_g but it is still significant, amounting to about 20% for an ion content of 8 mol%. It may be noted here that in a PMMA-based ionomer, having similar ionic groups to the ionomers studied here, the glassy modulus has also been observed to increase with ion content[13].

Figure 5 is a plot of the intensity of the two tan δ peaks vs ion content. The intensity of the multiplet-containing matrix peak decreases with ion content while that of the cluster phase increases. It appears that the critical ion content above which the cluster phase begins to dominate and above which it probably becomes continuous is about 6 mol%. This value is similar to that reported for SPS ionomers[9] and also similar to that cited, based on observations of both peak height and peak areas, for poly(styrene-*co*-alkali methacrylate) ionomers[11]. If we extrapolate the tan δ peak height of the matrix phase, shown in *Figure 5*, to higher ion contents, it appears that this phase would essentially disappear at an ion content of about 12 mol%; hence, at still higher contents, only a continuous ion-rich cluster 'phase' would be present, as suggested by Kim *et al.*[12].

The value of ion content at which the cluster phase begins to dominate appears to have about the same value for PS-based ionomers, even when the nature of the ionic group changes from sulfonate to carboxylate. However, if the ionic group is kept the same but the base polymer is altered, the situation changes. For example, in our study of PMMA-based ionomers, having the same sodium methacrylate ionic groups as in the PS-based ionomers of this study, we find that the critical ion content is about 12 mol%[13]. One reason for the higher value for the PMMA-based ionomers is that PMMA has a higher dielectric constant than PS and hence, the tendency for multiplets to cluster is reduced. Or in terms of the more

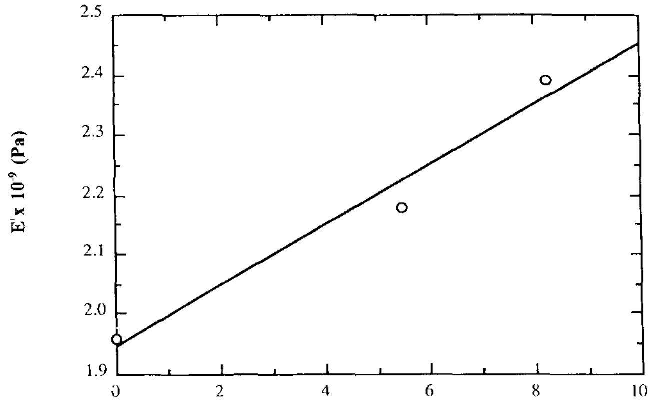


Figure 4 Glassy modulus at 30°C against ion content for poly(styrene-*co*-sodium methacrylate) ionomers

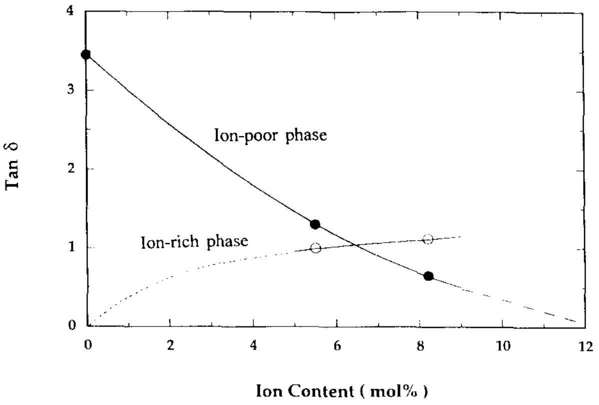


Figure 5 Loss tangent peak heights against ion content for poly(styrene-*co*-sodium methacrylate) ionomers

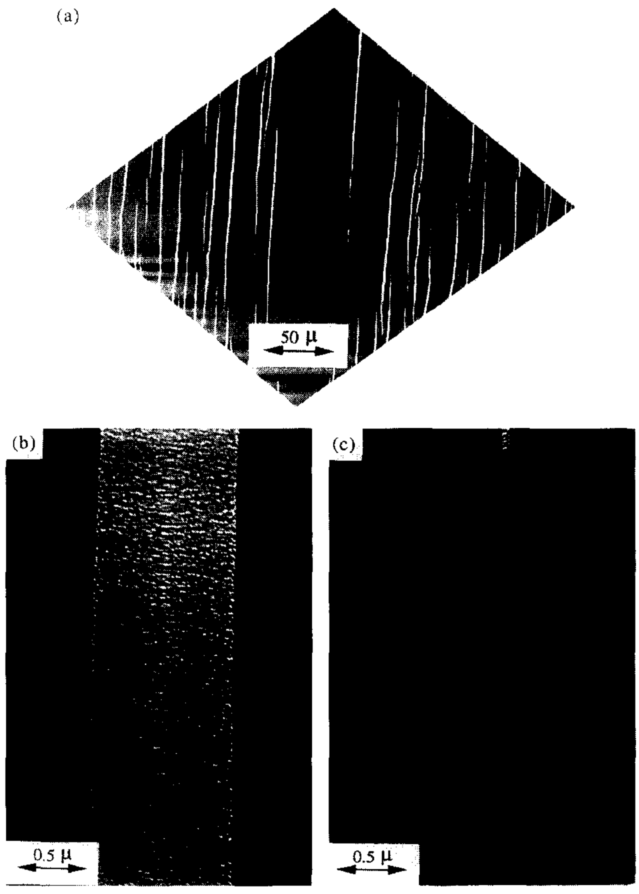


Figure 6 TEM micrographs of deformed thin films of the S-4.8% MAA-Na ionomers cast from THF: (a) low magnification scan; (b) typical craze morphology; (c) craze tip region

recent EHM model[7], PMMA has a smaller persistent length (or higher flexibility) and this leads to a higher value of the critical ion content.

Mechanical deformation studies

To determine the influence of ionomer morphology on deformation mechanisms in poly(styrene-*co*-sodium methacrylate) ionomers, we have examined ionomers having an ion content, 4.8 mol%, that is below the critical value at which the cluster 'phase' becomes dominant and also ionomers with an ion content, 8.2 mol%, that lies above the critical value.

TEM scans of strained thin films are given in *Figure 6* for the 4.8 mol% sample, in which the cluster 'phase' is the minor component. Samples of this ion content deform by localized crazing and, as *Figure 6a* shows, most of the crazes, which grow in a direction perpendicular to the applied stress axis, tend to be long and straight. At higher magnification, *Figure 6b*, the craze morphology is similar to that observed in the PS homopolymer[21,30]. The craze-bulk interfaces are well-defined, oriented fibrillar elements, interspersed with voids, span the craze, and a thin central section, the so-called midrib, contains chains of a higher draw ratio. Also, as noted in *Figure 6c*, the craze tapers at the end to a relatively fine point. In general, the deformation behaviour of this ionomer is analogous to that of PS, except that a few of the crazes observed had somewhat less defined edges and some of the tapered craze tips were not quite as sharp.

The situation changes when tests are made on films having an ion content that is high enough so that the cluster phase becomes dominant. This is evident from the TEM scans of *Figure 7*, taken on a sample having an ion content of 8.2 mol%. In this sample, as *Figure 7a* shows, crazes are much shorter and less straight and some waviness, probably due to the coexistence of some shear deformation at the craze tips, is present. Many of the crazes are branched and bifurcated and they coexist with shear bands, as seen in the high magnification micrograph (*Figure 7b*). Note the presence of several very thin crazes that have formed within the angled shear band. The deformation patterns seen in the present ionomer at high ion content are reminiscent of those reported to occur in SPS ionomers having an ion content about the critical value of about 6 mol%. For example, both crazes and shear deformation zones have been found to coexist in SPS ionomers of 6.1 mol%[31] and bifurcated crazes and shear bands were noted in a sample of 8.5 mol%[24]. Rather similar deformation patterns showing interactions between crazes and shear zones have been noted in non-ionomeric glassy polymers where a higher network strand density has been achieved by blending PS with poly(2,6-dimethyl-1,4-phenylene oxide), PPO[32,33].

Based on results obtained on poly(styrene-*co*-sodium methacrylate) ionomers, it may be concluded that when the ionic cross-linking is primarily associated with the multiplet-containing matrix phase, there will be little, if any, changes in deformation mode; but when the ion content is above the critical value at which the cluster 'phase' becomes the dominant one, the network structure formed will have a higher effective entanglement density and shear deformation as well as crazing will be induced. This should lead in these ionomers to an enhancement of mechanical properties, as has already been noted for SPS ionomers having a dominant cluster 'phase'[25].

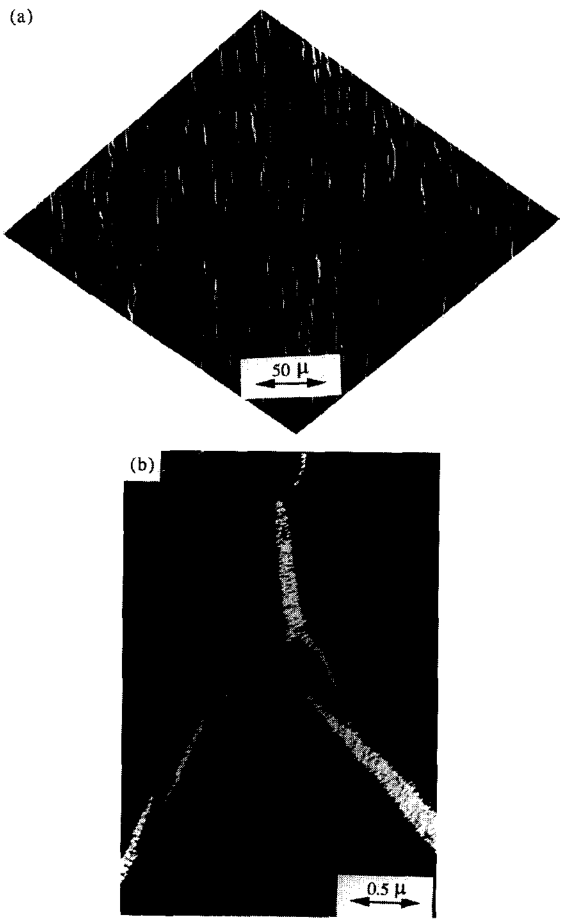


Figure 7 TEM micrographs of deformed thin films of the S-8.2% MAA-Na ionomers cast from THF: (a) low magnification scan; (b) crazes and shear deformation

The observed changes in deformation mechanisms with increasing ion content are qualitatively consistent with results obtained on covalently cross-linked polystyrene[23]. There, too, it was noted that, as the total strand density increased, the deformation mode changed from crazing only to combined crazing and shear. However, in the covalently cross-linked PS, the transition from crazing only to crazing plus shear occurred at a strand density that was only (1.3–2.5) times the entanglement density of PS, while we find, in the ionically cross-linked ionomer of the current study, that the same transition occurs at a strand density of about 12 times the ν_e value, assuming that all ionic groups form effective cross-links. One possible reason for this difference, is that the craze surface energy Γ, a key parameter that increases with strand density and causes the craze stress to rise[22] is probably considerably smaller for ionomeric cross-linking involving monovalent counterions, such as Na, than for covalent cross-linking because association and disassociation of monovalent ion pairs in ionic aggregates is easier than chain scission. Hence, a higher degree of ionic cross-linking as compared to covalent cross-linking, may be required in these materials to induce similar deformation mode changes. Ionomers, however, have the advantage of processability as they can be melt-processed or readily dissolved in solvents. It should be added that ionic cross-linking involving divalent counterions, such as Ca, are much more effective than those involving monovalent ions in increasing the 'effective' strand density, thereby enhancing mechanical properties[26].

Effects of thermal treatment on deformation modes

To determine whether an equilibrium morphology had been realized in the ionomer films cast from solution, it was decided to give the samples an extra heat treatment and then repeat the mechanical deformation tests. The principle reason for adopting this procedure is that several reports given in the literature[27,34] indicate that appropriate thermal treatments in ionomers of low ion content favour ionic aggregation and increase the extent of the cluster phase that is present at any given ion content.

In one study, it was reported that a Na-salt, SPS ionomer of 2.5 mol% ion content, compression moulded at 135°C, developed no high temperature loss peak in d.m.t.a. tests and exhibited no rubbery plateau region above the matrix T_g; however, after the sample was given an additional thermal treatment (24 h at 200°C), a high temperature cluster peak was observed in tan δ vs T data and an extended rubbery modulus plateau region was realized[27]. In a second report concerning Mn salts of SPS ionomers, samples cast from THF/H_2O solution showed no SAXS peak indicative of the presence of a cluster phase; but, after ageing (4 h at 120°C) an ionomer aggregate peak was found[24].

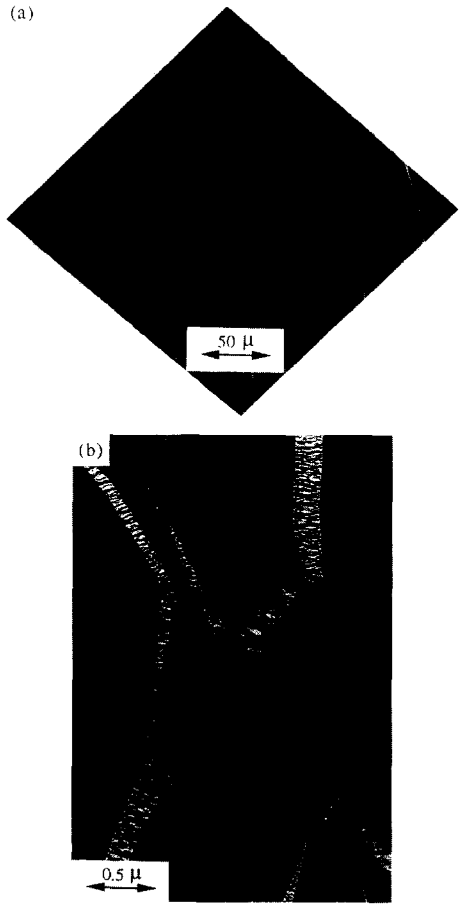


Figure 8 TEM micrographs of deformed thin films of the S-4.8% MAA-Na ionomer cast from THF followed by ageing for 8 h at 100°C: (a) low magnification scan; (b) branched crazes mixed with shear deformation

In the present study we decided to give cast specimens of polystyrene and several poly(styrene-*co*-sodium methacrylate) ionomers a thermal treatment of 8 h at 100°C under vacuum and then redo the thin film tests. The ageing treatment was found to have no effect on the deformation mode (crazing) of the PS homopolymer[35]. For the ionomer sample of 4.8 mol% ion content, in which the multiplet-containing matrix phase is the dominant one, deformation patterns as shown in *Figure 8* were obtained. At low magnifications, the craze pattern that developed in this heat treated film, *Figure 8a*, is seen to consist of many short crazes; and, at high magnification, *Figure 8b*, we obtain a complex deformation pattern that includes curved and branched crazes and shear bands. The deformation pattern seen here is clearly different from that of the specimen prior to heat treatment of the same ion content (*Figure 6*). Instead, the pattern is more representative of that observed in the non-heat-treated ionomer sample of 8.2 mol% ion content (*Figure 7*). We infer from these results that the additional time at elevated temperature has given the polymer chains of the 4.8 mol% ionomer sufficient mobility to enhance the formation of ionic aggregates and to increase the extent of the cluster 'phase' at the expense of the matrix phase. This conclusion, based on mechanical deformation mode observations, is consistent with the reported results of the effects of heat treatment on d.m.t.a. and SAXS observations of other PS ionomers[27,34].

For the ionomer of 8.2 mol% ion content, the effects of the ageing treatment are much less significant than for the 4.8 mol% sample. TEM observations for this sample are given in *Figure 9*. As for the non-heat-treated sample, both crazes and shear deformation are present. However, as seen in *Figure 9a*, the crazes tend to be somewhat longer on the average and less restricted in their growth than for the unannealed sample (*Figure 7a*). Some branched and bifurcated crazes are also present, as may be seen by the high magnification scan of *Figure 9b*. Thus, for high ion content samples, where the cluster phase is already the dominant one even in non-heat-treated samples, the primary effect of the additional thermal treatment is simply to act as a physical ageing process rather than to further enhance the extent of the cluster 'phase'. Physical ageing, viz annealing of a glassy polymer at a temperature close to but below T_g, has been shown by Donald and Kramer to favour craze development and growth and to suppress or reduce the extent of shear deformation[33].

The overall effect of heat treatment on crazing behaviour in ionomers depends on which of two competing factors, viz. simple physical ageing or enhancement of the ion-rich cluster 'phase', is the dominant one. From our results it appears that when the ion content is low and the annealing temperature is close to the matrix T_g, the second effect dominates; but when the ion content is already above the critical value at which the cluster phase dominates, the two effects essentially balance one another, although there is some tendency, as a result of the first effect, to shift the induced deformation mechanisms more toward crazing.

It is interesting to compare the results of this study with results of similar tests carried out on both non-heat-treated and heat-treated samples of PMMA-based ionomers having the same type of ionic groups present[26].

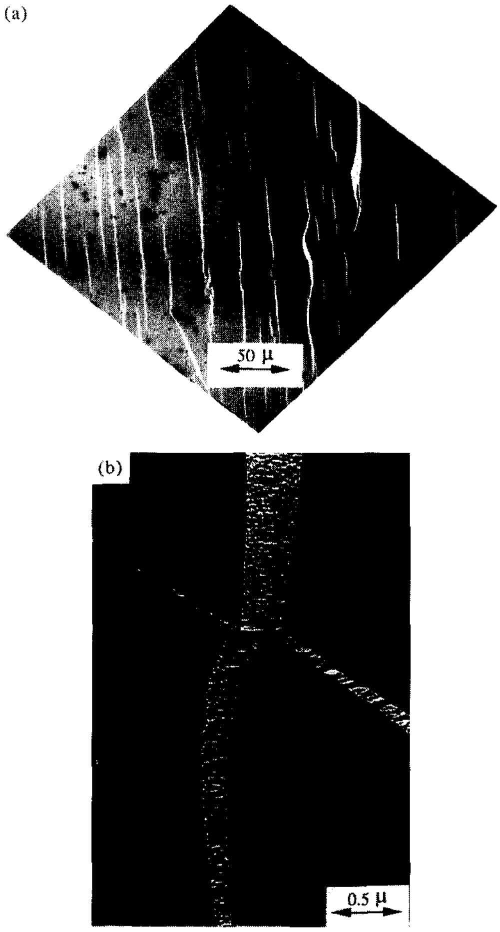


Figure 9 TEM micrographs of deformed thin films of the S-8.2% MAA-Na ionomer cast from THF followed by ageing for 8 h at 100°C: (a) low magnification scan; (b) a bifurcated and curved craze

As noted earlier, in these PMMA-based ionomers, the critical ion content at which the cluster 'phase' becomes dominant is about 12 mol%. Deformation tests have been made on cast thin films of this ionomer having an ion content of 6 mol%, a value at which the morphology is dominated by the multiplet-containing, matrix phase. These tests show that the only mode of deformation at this ion content is localized crazing[26], a result similar to that noted in the present study when tests were made on a sample (4.8 mol%) having the cluster phase as a minor component. However, when the PMMA-based ionomer samples were given an additional heat treatment, it was found that both craze and shear deformation modes were present. Hence the effects observed in the present study—viz. a transition from crazing only to combined crazing and shear as the ionic microstructure is modified by thermal treatment so as to intensify the extent of the cluster 'phase'—are not confined to poly(styrene-*co*-sodium methacrylate) ionomers but are probably representative of other amorphous, glassy ionomers as well.

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