New Polyisobutylene-Based Model Elastomeric Ionomers. VIII. Thermal-Mechanical Analysis

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Synopsis

A series of well-characterized telechelic polyisobutylene-based sulfonated metal-neutralized ionomers have been studied using thermal-mechanical analysis (TMA). These ionomers serve as models in the sense that the ionic groups are located exclusively at the chain ends and hence the ionomeric character is well defined. The chemical parameters varied are (i) molecular weight, (ii) molecular architecture (linear or triarm products), (iii) addition of excess neutralizing agent, and (iv) type of cation. The effect of the above parameters on the glass transition temperature and the softening temperature (after the rubbery plateau region) is presented. It is observed that the glass transition temperature is only slightly affected by the above parameters due to the very low ionic content in these ionomers (<2 mol %). In the case of the triarm ionomer with excess neutralizing agent, the softening temperature following the rubbery plateau is much higher than that of the linear difunctional species. Linear monofunctional species do not show a rubbery plateau behavior and readily flow above their T_g in the absence or presence of excess neutralizing agent. The excess salt is most likely located at the ionic sites rather than being uniformly distributed throughout the matrix. Zinc-neutralized ionomers were found to have the lowest softening temperatures as compared to the corresponding calcium and potassium-neutralized ionomers. The covalent character of zinc is believed to be primarily responsible for this behavior. Thermal stability of these metal-neutralized ionomers is not significantly different from the sulfonated hydrocarbon precursor polymer. However, the unneutralized acid precursor polymers start to discolor at relatively lower temperatures, thereby suggesting poorer thermal stability.

INTRODUCTION

Hydrocarbon polymers containing ionic moieties (typically less than 15%) along their backbones are generally classified as ionomers. The unique properties of these materials are due to coulombic interactions between the ionic moieties present. The presence of small amounts of ionic groups in hydrocarbon polymers exerts a profound effect on their physical and thermal properties.[1,2] The polymers are ionically "crosslinked" through the association of ionic groups forming multiplets or, in some cases, through higher order associations termed as "clusters."[1] Either of these associations can be thermally relaxed to different extents depending upon the composition of ionic domains. If the degree of ionic association at the processing temperature is sufficiently reduced to permit adequate melt flow, ion-containing elastomers may be classified as thermoplastic elastomers.

Most of the earlier studies on ion-containing elastomers focused on carboxylate-containing elastomers.[1-4] In 1957 Brown reported the elastomeric

properties of carboxylated polybutadiene (PB) based ionomers.[3] More recently, Teyssié et al. have focused attention on the solution behavior of telechelic-carboxyl-terminated PB-based ionomers.[5-7] Lundberg and Makowski have investigated the effect of different acid functional groups on polystyrene (PS). They compared the behavior of carboxylated PS and sulfonated PS at the same level of functional groups with the same cation and backbone molecular weight and concluded that sulfonated ionomers are more strongly associated than the corresponding carboxylate ionomers.[8] Based on these studies, the sulfonates appear to show stronger association with higher temperatures. Therefore, one would have a higher temperature of application for thermoplastic esystems were then neutralized to obtain telechelic sulfonated PIB-based ionomers.[9-11] The molecular architecture (i.e., triarm trifunctional, linear difunctional, or linear monofunctional) and the molecular weight of these ionomers can be controlled, as described elsewhere.[11] Upon neutralization of the precursor sulfonic acid with specific cations, the resulting solid-state, thermal, and rheological properties change dramatically.[12-15]

The present study concerns the thermal mechanical behavior of several of these ionomers. Specifically, the variables studied are (i) molecular weight, (ii) extent of neutralization (including the excess addition of neutralizing agent above the exact stoichiometric requirement), (iii) molecular architecture, and (iv) cation (K, Ca, or Zn). The thermal behavior of neutralized ionomers, the precursor acid, and the unsulfonated telechelic olefin have been compared for a few select systems. This study enables one to estimate, at least qualitatively, the useful temperature range for application of these elastomeric ionomers. Moreover, this study reinforces an earlier hypothesis regarding the proposed morphological model for similar ionomers to which excess neutralizing agent has been added.[13] Based on the mechanical properties of these systems, it is postulated that the excess neutralizing agent (base or salt) is located at the site of the ionic association as opposed to being uniformly distributed throughout the low dielectric matrix.

Increasing the number of ionic species within the multiplets leads to increased coulombic attraction between these ions, similar to the concept of the Madelung constant in ionic crystals. Thus, the coulombic attraction due to the ionic moieties should increase and higher temperatures will be required to relax or dissociate the ionic crosslinks. It is with these ideas in mind that the thermal mechanical analysis (TMA) studies were undertaken.

EXPERIMENTAL

The synthesis, purification, and sulfonation of the parent triarm (T), monofunctional (M), and difunctional (D) linear olefin telechelic polyisobutylenes (PIB) has been described by Kennedy et al.[9-11] The acid forms of the ionomers were stored under refrigeration until use. Neutralization procedures of the telechelic sulfonic acids with various cations (K, Ca, or Zn) have been reported earlier.[13] The structures of the monofunctional, difunctional, and functional telechelic PIB based ionomers are shown in Figure 1.
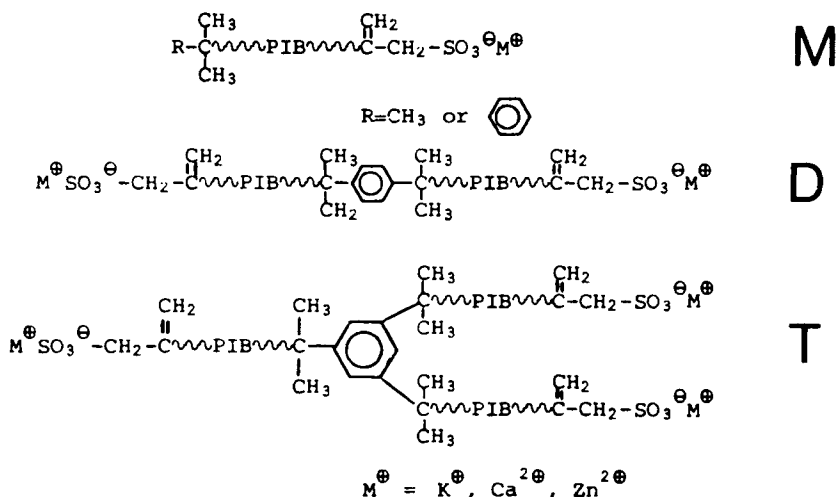
Fig. 1.   Structure of monofunctional (M), difunctional (D), and trifunctional (T) PIB ionomers.

Films were prepared by compression molding the dried triarm and linear difunctional ionomers at 150–170°C between Teflon sheets at approximately 1000 psi for about 5 min, followed by rapid quenching to room temperature on a steel plate. Higher molding temperatures were required for materials containing excess neutralizing agent. The monofunctional ionomers were very viscous tacky fluids at room temperature, even those containing excess neutralizing agent.

Thermal mechanical behavior (TMA) studies were carried out on a Perkin-Elmer Model TMS-2 instrument. The temperature range from $-110°C$ to where complete softening occurred ($< 300°C$) was investigated. A constant load of 10 g and a heating rate of 10°C/min was used.

The following nomenclature is used. The samples are designated by four symbols, for example, T-8.3-K-0. The first symbol T indicates a triarm ionomer; the second symbol, 8.3, expresses the number average molecular weight $(M_n) \times 10^{-3}$; the third symbol, K, indicates the cation the ionomer contains; and the fourth symbol, 0, indicates the percentage of excess neutralizing agent added past the equivalence point. Thus 0 indicates exact stoichiometric neutralization (no excess). The symbol T-8.3-K-100 represents the same material except containing 100% excess KOH. The ion content in these materials is very low, typically less than 2 mol %. Likewise, M-11-Ca-100 symbolizes a monofunctional PIB of number average molecular weight 11,000 neutralized with calcium hydroxide using a 100% excess of calcium hydroxide over the stoichiometric requirement. The symbol T-14-HC represents a triarm hydrocarbon (prior to sulfonation) and T-14-SO$_3$H represents the precursor sulfonic acid both of $\overline{M}_n = 14,000$.

RESULTS AND DISCUSSION

The softening behavior of a series of polymers, represented by T-14-HC, T-14-SO$_3$H, and T-14-K-0 is shown in Figure 2. The hydrocarbon precursor is a viscous fluid at room temperature, and it flows readily above the glass
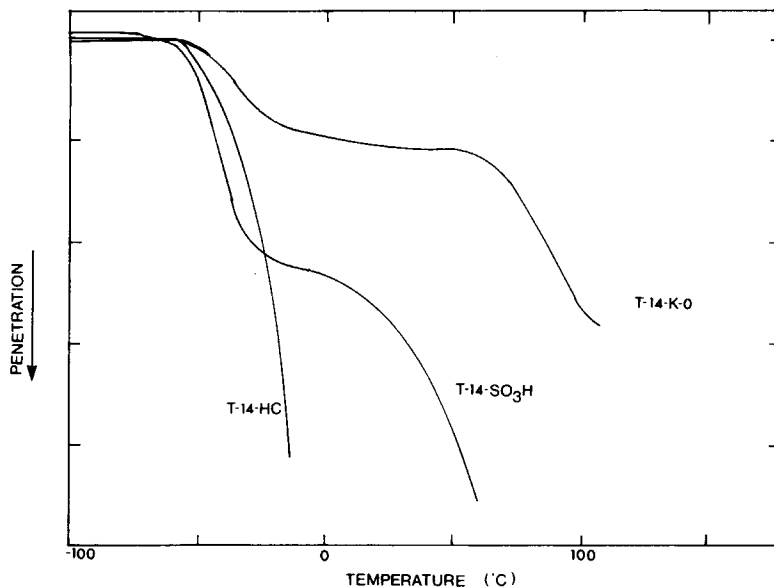
Fig. 2. The effect of sulfonation and neutralization on the TMA behavior of T-14-HC, T-14-SO₃H, and T-14-K-0.

transition temperature (ca. $-66°C$) as seen by TMA. In contrast, sample T-14-SO$_3$H displays a weak plateau behavior above T_g, which extends to approximately 20°C. This may be due to weak ionic association and hydrogen bonding present in the acid. However, when the sulfonic acid functions are neutralized by KOH to the exact equivalence point, the plateau region *extends dramatically* to about 100°C. The development of a rubbery plateau region upon neutralization is attributed to strong coulombic interactions between the terminal ionic moeities. In the case of univalent cations, e.g., K^+, two chain ends, each carrying a—SO$_3^-$K$^+$ ion pair, are held together by coulombic forces. This form of association may lead to the development of a network for the triarm species. Long-time stress–relaxation experiments have confirmed the existence of pseudoequilibrium networks in the triarm species but have not been observed for the linear difunctional systems.[14] At higher temperatures, these ionic associations become weaker (through thermal energy disruption), and the material may flow. By the introduction of three terminal ionic groups per molecule (i.e., in triarm polymers) the viscous fluid becomes a rubbery solid at ambient conditions.

The thermal behavior for three difunctional polymers D-12-HC, D-12-SO$_3$H, and D-12-K-0 is shown in Figure 3. The behavior is very similar to that displayed by the triarm species in that the TMA data shows a rubbery plateau region which in turn implies a 3-dimensional network structure. However, as indicated above, long-time stress–relaxation experiments at ambient indicate that, for the difunctional species, the stress decreases to zero after about 24 h.[14,15] This implies that a pseudo equilibrium network does not exist with the difunctional ionomers. Thus, one must take into account the time scale of the experiment in analyzing these data. If one considers only the TMA behavior of the difunctional species, one may er-
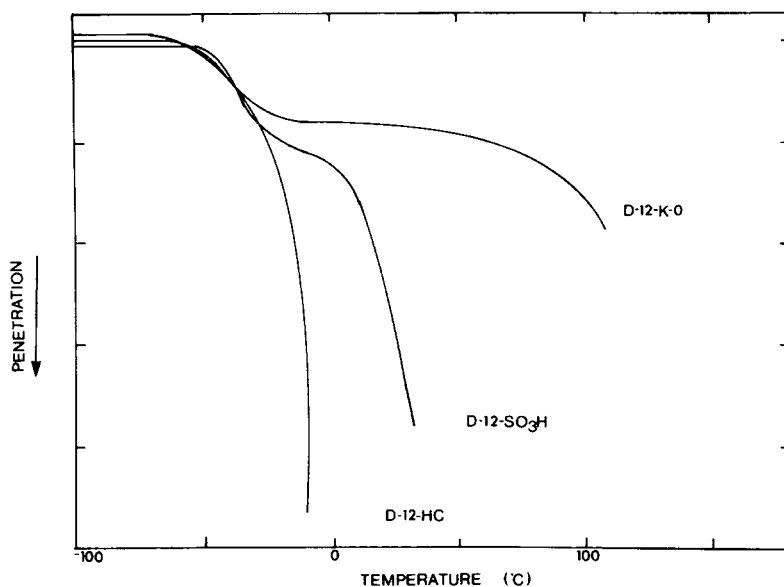
Fig. 3.   The effect of sulfonation and neutralization on the TMA behavior of D-12-HC, D-12-SO₃H, and D-12-K-0.

roneously conclude that they may also have a 3-dimensional near equilibrium network structure. Recall that the TMA experiments were performed at a heating rate of 10°C/min. Previous mechanical property experiments indicated[14] that ionic associations in the difunctional species predominantly lead to chain extension with very little network character. Thus the observed TMA behavior for the difunctional species may be attributed to chain entanglements acting as pseudocrosslinks at short times. This behavior is analogous to the viscoelastic response to amorphous long chain homopolymers. For example, Tobolsky[16] observed that the relaxation modulus of polystyrene at short times displays a plateaulike behavior characteristic of the rubbery region; however, at longer times, the relaxation modulus does not show a pronounced rubbery region, due to relatively slow disentanglement.

The softening behavior of the monofunctional species, which carry only one ionic group per molecule, is shown in Figure 4. These materials begin to flow just above the glass transition temperature and behave more like the unsulfonated species rather than the sulfonic acids which exhibit weak association. In other words, a plateau region does not exist for the monofunctional ionomers. Indeed all the monofunctional sulfonated species are very tacky at room temperature. Since these materials carry only one ionic moiety per chain, multiple chain extension cannot occur so that networklike behavior cannot arise. The ionic chain ends may, however, associate to form "ionic centers" with the polyisobutylene chains at the periphery. A "micellar" type of structure is thus possible. The number of ionic groups within a micelle would be limited by packing considerations. Based on our studies of bulk properties of the triarm and difunctional systems, at ambient temperature, we believe that the monofunctional systems may principally as-
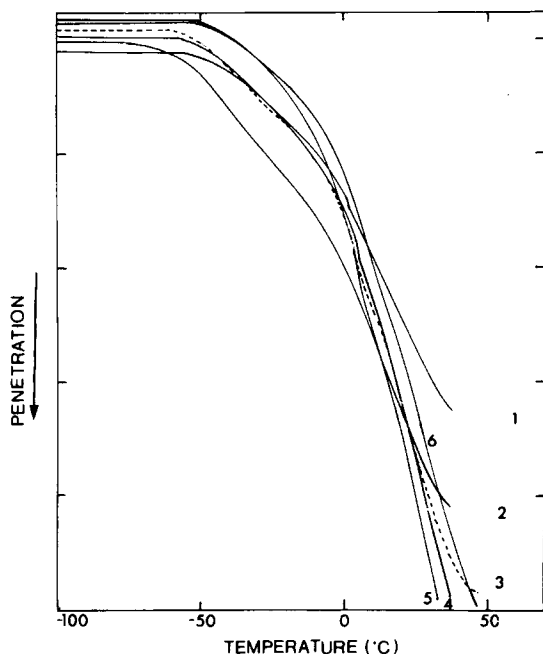
Fig. 4.   TMA scan for (1) M-11-K-0, (2) M-11-Ca-0, (3) M-11-Zn-100, (4) M-11-K-100, (5) M-11-Ca-100, and (6) M-11-CaAc-100 [Ca = neutralized by Ca(OH)$_2$, CaAc = neutralized by Ca(AcO)$_2$].

sociate by two chains and not into higher-order micelles. This micelle character is being further investigated by solution and melt rheological property measurements.[17]

The monofunctional species may serve as models for investigating the effect of loose or "dangling" chain ends in blends with the triarm ionomers. Since these PIB-based ionomers carry metal sulfonate groups only at the chain ends, these systems form a model end-linked network with few or no dangling ends. Mechanical studies (bulk property data) imply that, in the triarm species, on the average two chain ends are linked by the coulombic interactions between the ion pairs.[14] Thus, the blending of the monofunctional ionomers to the three-arm ionomers is tantamount to deliberately introducing "dangling end effects" in the model networks. Since conventional elastomers have random crosslinking sites, the nature of defects is not precisely known.

We have attempted to understand the effect of dangling ends by the use of these model PIB-based ionomers. Mechanical studies reveal that both Young's modulus and tensile properties decrease with an increase in the amount of monofunctional species in the system.[15] Blends of T-10.5-K-0 and M-11-K-0 materials were prepared (by codissolution) to study this behavior. The TMA behavior of (i) 100% T-10.5-K-0, (ii) a blend of 10% M-11-K-0 and 90% T-10.5-K-0, and (iii) a blend of 22% M-11-K-0 and 78% K-1.5-K-0 is shown in Figure 5. The softening behavior of the blends is almost identical to that of T-10.5-K-0. However, since these experiments were performed at a heating rate of 10°C/min, the data also must be considered within the time frame of the experiment. Long-term room temperature permanent set
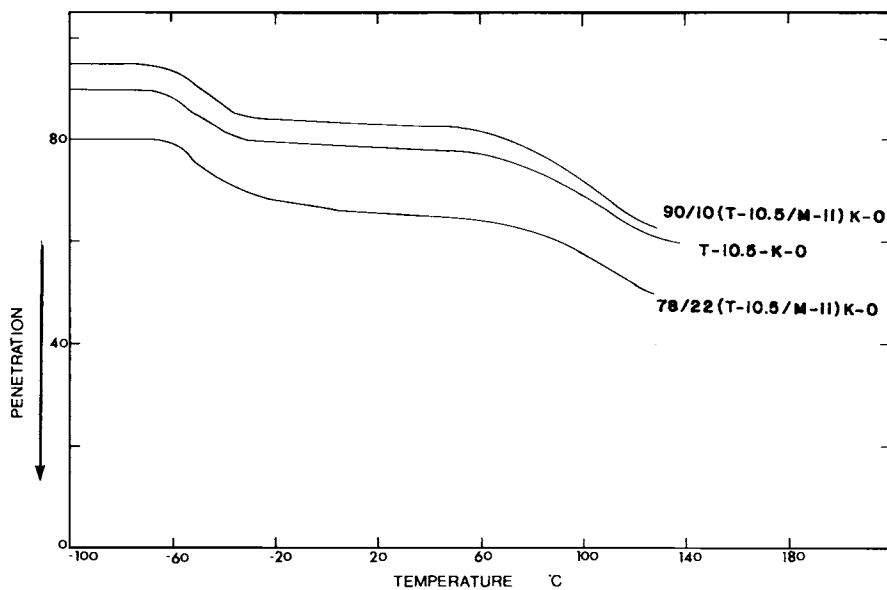
Fig. 5.   TMA scan for T-10.5-K-0, and two mixtures of this polymer with M-11-K-0.

studies have shown that percent recovery decreases with increasing the concentration of the monofunctional species.[14] Also, the stress–strain behavior of these blends indicate that both the Young's modulus and the tensile properties decrease with an increase in the concentration of monofunctional species in the system.[15]

The softening behavior of the difunctional species of $\overline{M}_n = 6500$ is shown in Figure 6. All the difunctional materials show a rubbery plateau within
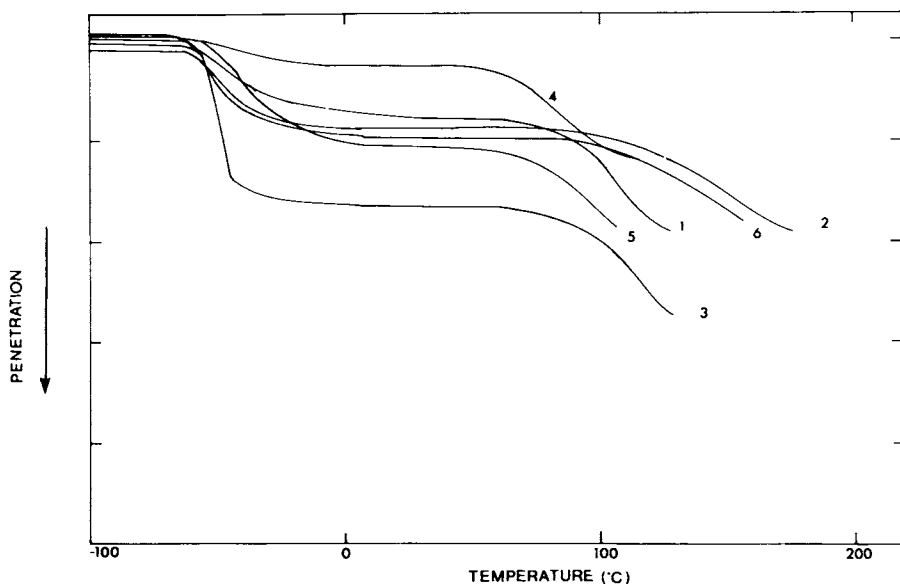

Fig. 6.   TMA scan for (1) D-6.5-Ca-0, (2) D-6.5-Ca-100, (3) D-6.5-CaAc-100, (4) D-6.5-Zn-100, (5) D-6.5-Kn-100, and (6) D-6.5-K-100.

the time frame of the experiment, as did a higher molecular weight difunctional system (D-12-K-0, data not shown). The chain extension through Coulombic association in the linear difunctional species extensively increases the relaxation time, and, therefore, within the time scale of the experiment, significant penetration (relaxation) does not occur. The softening temperature after the rubbery plateau shifts to higher temperatures with the addition of excess neutralizing agent. The zinc neutralized ionomer exhibits the lowest softening temperature, signifying that the ionic associations are weakest in this material at elevated temperatures. However, a word of caution regarding the thermal behavior of the difunctional species is warranted here. We have observed that the stress for D-12-K-0 at 25% elongation vanishes over a day at ambient temperature. Evidently, a pseudoequilibrium network is virtually absent, and only chain extension takes place. Network points with three functionalities may exist in these linear difunctional systems; however, their concentration is too low for a near or pseudo equilibrium network to develop.

Figure 7 shows the temperature dependence of penetration for various triarm ionomers of $\overline{M}_n = 34,000$. As observed earlier, upon stoichiometric neutralization, or with the addition of excess neutralizing agents, the rubbery plateau region is extended significantly. The existence of a plateau region strongly suggests network formation by strong coulombic interactions between the ionic groups. The plateau region extends to about 100°C for both T-34-K-0 and T-34-Ca-0. The softening temperature is only marginally higher for the T-34-Ca-0. It is of particular interest that upon the addition of excess neutralizing agent the softening temperature for T-34-K-100 increases to 140°C while for T-34-Ca-100 it reaches nearly 200°C! The corresponding softening temperature for T-34-K-0 and T-34-Ca-0 is only about 100°C. Evidently, the excess neutralizing agent significantly strengthens ionic interactions and thus extends the rubbery plateau region. The
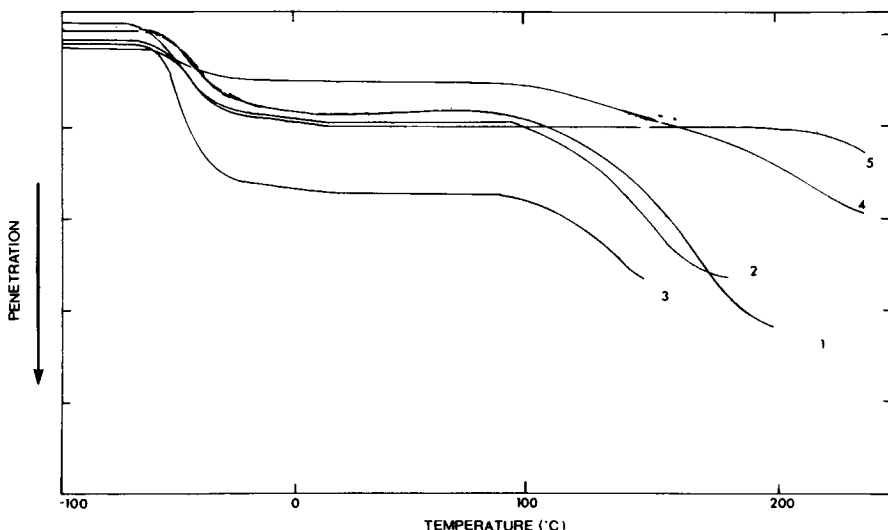

Fig. 7.　TMA scan for (1) T-34-K-0, (2) T-34-Ca-0, (3) T-34-Zn-100, (4) T-34-K-100, and (5) T-34-Ca-100.

excess neutralizing agent most likely resides at the ionic sites rather than being uniformly distributed throughout the matrix. This behavior further reinforces the model presented in Figure 8, which was based on prior high temperature viscosity studies.[13]

It may also be noted from Figure 7 that the T-34-Zn-100 material begins to flow around 90°C, i.e., at a somewhat lower temperature than the same material containing potassium or calcium ions. Although this result may appear surprising at first sight, a similar trend has been observed for all the Zn-neutralized systems studied by us. Interestingly, neutralization with zinc acetate results in comparable mechanical properties at ambient conditions to those neutralized with calcium hydroxide or acetate. However, according to the results of thermal and rheological experiments, zinc-neutralized materials flow more readily and can be processed more easily than those neutralized with potassium or calcium salts. Similar trends for the D-12 and T-8.3 series materials are shown in Figures 9 and 10, respectively.

The effect of excess neutralization on the TMA behavior of the T-14-K-X series (where X is percent excess neutralizing agent) is shown in Figure 11. The softening temperature for T-14-K-(-10) is only 60°C, while for T-14-K-0 it is 100°C. With a further increase in the amount of neutralizing agent, the softening temperature reaches an upper limit of about 160°C. According to the stress–strain behavior of this T-14 series ionomers,[13] the initial modulus does not change significantly with the addition of excess neutralizing agent. This implies that the number of network points remain essentially constant upon addition of excess salt. The proposed morphological model (see above) is consistent with the mechanical and thermal data.

Lundberg and Makowski[8] have shown that the properties of sulfonated EPDM ionomers are strongly dependent upon the nature of the cation used for neutralization and that the melt viscosity at elevated temperatures is much less for the zinc-acetate-neutralized material than with Na, Mg, Ca, neutralized ionomers. However, at ambient temperature the tensile properties of the zinc sulfonate EPDM were comparable if not better than those of the other systems. This behavior was explained in terms of a combination of the following two phenomena: plasticization of the ionic associations by excess zinc acetate at elevated temperatures, and conversion of disulfonates
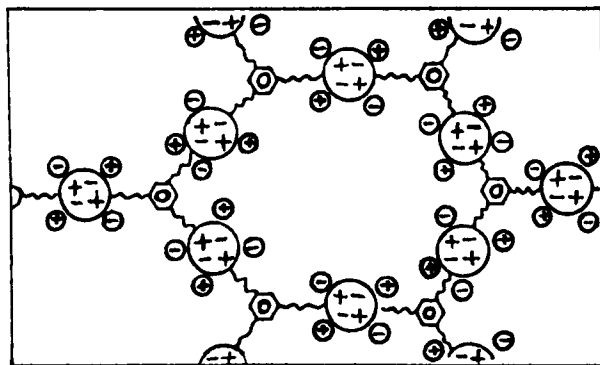

Fig. 8.   Morphological model for triarm ionomers containing excess neutralizing agent.[13] Smaller circles represent the excess ions.
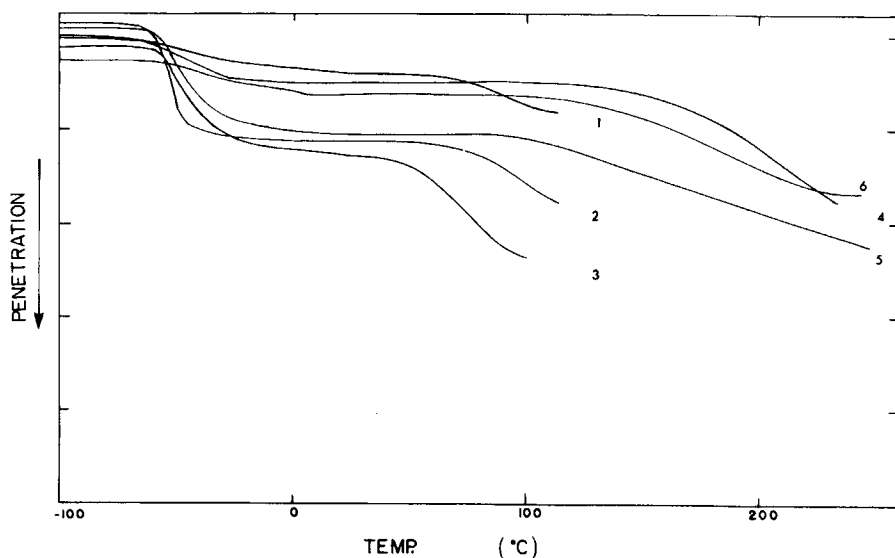
Fig. 9.　TMA scan for (1) D-12-K-0, (2) D-12-Ca-0, (3) D-12-Zn-100, (4) D-12-K-100, and (5) D-12-Ca-100.

—SO_3—Zn—SO_3— to less strongly associating monosulfates, —SO_3—Zn—OOC—CH_3—, at an excess zinc acetate concentration. These observations may be due to the covalent nature of the transition metal zinc.

Several factors may affect ionomer properties neutralized with different cations: (i) ionic radii, (ii) effective charge of the cation, (iii) charge and size of ligands, (iv) ionic/covalent character of the cation, and its electronic configuration, (v) dielectric constant of the polymer (surrounding medium),
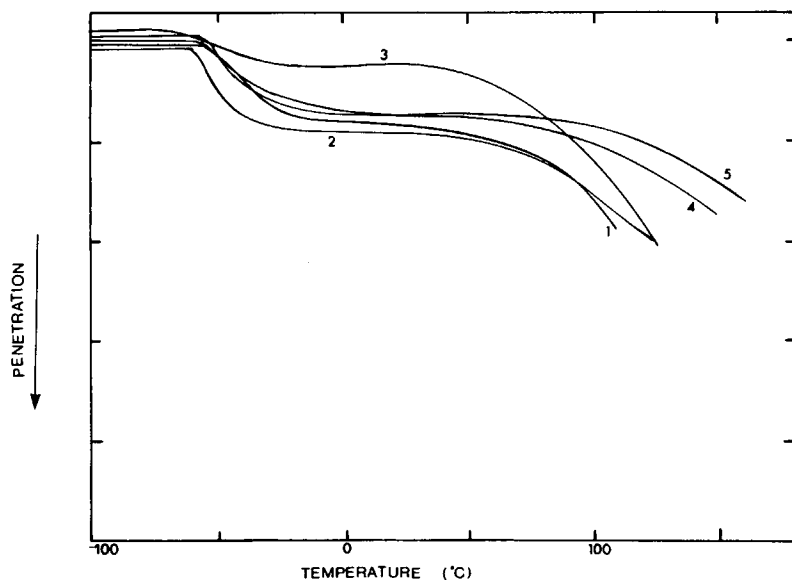

Fig. 10.　TMA scan for (1) T-8.3-K-0, (2) T-8.3-Zn-0, (3) T-8.3-Ca-100, (4) T-8.3-Ka-100, (5) T-8.3-Ca-100, and (6) T-8.3-CaAc-100.
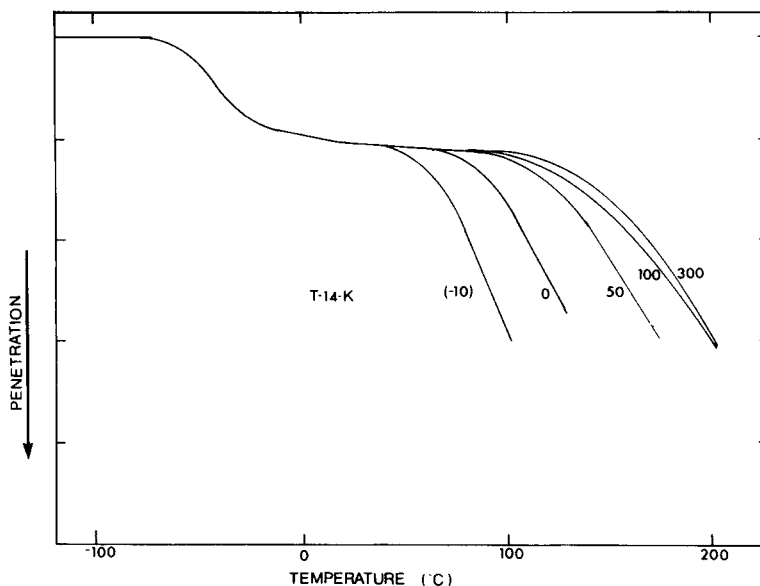
Fig. 11.   Effect of excess neutralizing agent: TMA scans for T-14-K-(-10), T-14-K-0, T-14-K-50, T-14-K-100, and T-14-K-300.

and (vi) solution equilibrium characteristics of the neutralization reaction (stability/solubility constant). The electronic configuration of the cation, which in turn governs its covalent character, may be particularly important in determining the properties of ionomers. According to the TMA data, the more covalent character of the zinc cation as compared to highly ionic potassium and calcium cations plays a major role in the observed behavior, as we have discussed in detail elsewhere utilizing the acid base concept of Pearson.[18]

It is interesting to compare the behavior of these ionomers with respect to molecular architecture. Thus Figure 12 compares the TMA scans for T-8.3-SO$_3$H, M-11-K-0, D-6.5-K-0, and T-8.3-K-0. The difunctional linear and triarm species show a significant rubbery plateau region upon exact neutralization; however, the acid form, i.e., T-8.3-SO$_3$H, shows a much weaker association. The monofunctional species behaves like the hydrocarbon precursor and shows no rubbery plateau region. The thermal behavior of these telechelic sulfonated PIB-based ionomers with respect to the molecular architecture is as expected; i.e., the softening temperature after the rubbery plateau is highest for the triarm species while the monofunctional species readily flows above the T_g.

Figure 13 shows the DSC scans for T-14-Zn-100, T-14-Ca-0, T-34-K-0, T-14-K-0, and T-8.3-K-0. The glass transition temperature of the ionomers does not change with the variables studied, as has already been indirectly suggested by TMA results.[15] The glass transition temperature (T_g) of PIB is $-73°C$.[19] In all the systems studied by TMA, the T_g was found to be somewhat higher (approximately $-66°C$), as might be expected due to the presence of a low concentration of ionic moieties. Similar observations were
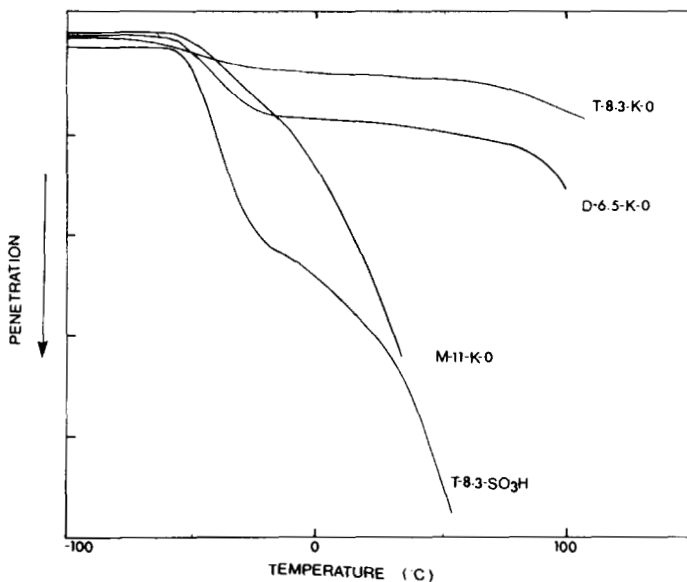
Fig. 12.   Effect of molecular architecture: TMA scans for T-8.3-SO$_3$H, T-8.3-K-0, M-11-K-0, and D-6.5-K-0.

made by Teyssé et al. while studying the effect of neutralization on the glass transition temperature of carboxy-terminated telechelic polybutadiene based model ionomers.[20] However, this behavior seems to contrast somewhat with the carboxylated polystyrene system studied by Eisenberg and King, where the ionic groups were randomly located along the polymer backbone.[1] They observed that the glass transition temperature increased with an increase in ionic content. The somewhat lower T_g sensitivity in the PIB-based systems may be due to the very low ion concentration.
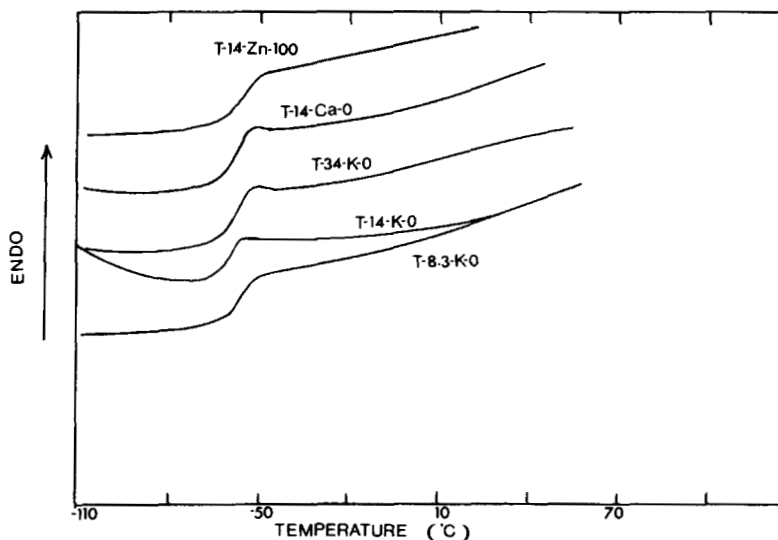

Fig. 13.   DSC scans for T-14-Zn-100, T-14-Ca-0, T-34-K-0, T-14-K-0, and T-8.3-K-0.

The relative insensitivity of the T_g by the presence and/or concentration of ions (within the range studied) and the dramatic effects on the thermomechanical spectrum of the PIB ionomers (in terms of a rubbery plateau) is strongly reminiscent of the behavior of thermoplastic elastomers, e.g., styrene–butadiene–styrene (SBS) block copolymers and segmented polyurethanes.[21] For example, in SBS block copolymers containing 20% polystyrene (PS), the styrene domains act as physical crosslinks in the rubbery polybutadiene matrix. However, upon heating above the T_g of PS, the initially glassy domains soften and begin to flow. The SBS block copolymer starts to flow and becomes processable. It is interesting to compare the viscous flow behavior of the two common thermoplastic elastomers, namely, the SBS triblock copolymers and the segmented polyurethane (PU) systems, with the PIB-based ionomers. In the SBS triblock copolymers a two-phase system exists in the melt while in the segmented PU systems mixing occurs often between the hard and soft segments at the processing temperature, thereby facilitating flow. In the ionomer systems, while the ionic associations exist in the melt, these "physical ionic crosslinks" become somewhat thermally more relaxed and viscous flow occurs at elevated temperatures.

In order to assess the thermal processing of these ionomers at elevated temperatures, the thermal stability of these materials has been studied to a limited extent. Figure 14 shows the thermal degradation behavior (TGA) of T-8.3-Zn-100, D-12-Zn-100, and M-11-Zn-100 in a nitrogen atmosphere. In the time scale of the experiment (min) these ionomers are stable up to 300°C. The precursor acid is much less stable and begins to discolor above 80°C. The same ionomers were also studied by TGA in air at a heating rate of 10°C/min, and the results are shown in Figure 15. The thermal degra-
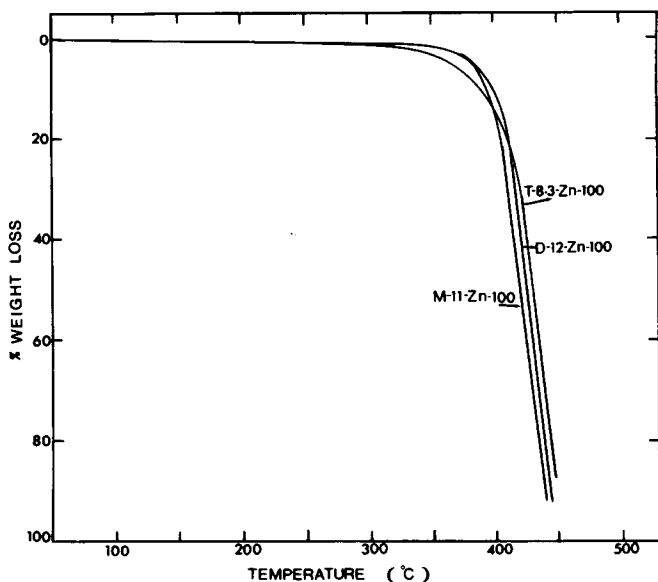

Fig. 14. Percent weight loss as a function of temperature for T-8.3-Zn-100, D-12-Zn-100, and M-11-Zn-100 in nitrogen.
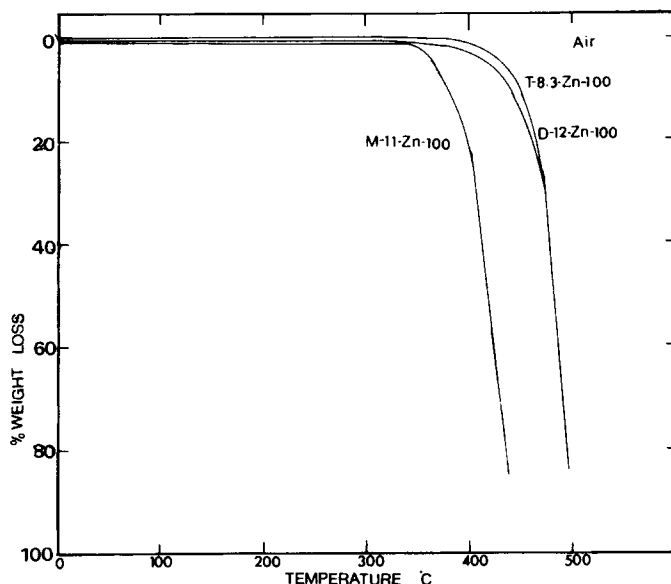
Fig. 15. Percent weight left as a function of temperature for T-8.3-Zn-100, D-12-Zn-100, and M-11-Zn-100 in nitrogen.

dation behavior of triarm and linear difunctional materials in air is similar to that in a nitrogen atmosphere. However, the monofunctional ionomer, M-11-Zn-100, begins to degrade at a slightly lower temperature (260°C) in air. Thus, from a processing point of view, all these ionomers can be safely processed in air up to approximately 300°C.

CONCLUSIONS

(i) Triarm and linear difunctional ionomers display a significant rubbery plateau behavior, while the monofunctional species flow readily above the glass transition temperature. Monofunctional species can serve as models for "dangling ends" and, with an increase in their concentration in a triarm matrix, the softening (flow) temperature is slightly lowered. Based on earlier studies[13,14] in conjunction with those reported here, in the linear difunctional species primarily chain extension occurs, whereas in the triarm species a pseudo equilibrium network structure prevails. Only weak ionic associations exist in the sulfonic acid polymers.

(ii) The softening temperature increases with an increase in the extent of neutralization, particularly in the presence of excess neutralizing agent above the exact stoichiometric endpoint. The TMA results support the simple morphological model proposed earlier[13] based on melt viscosity studies. According to this model the excess ions are preferentially located at the multiplets rather than being uniformly distributed throughout the matrix.

(iii) Ionomers neutralized with zinc acetate have much lower softening temperatures than those neutralized with either potassium or calcium salts. This is most likely due to the more covalent nature of zinc.

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