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New Polyisobutylene Based Model Ionomers

3. Further Mechanical and Structural Studies*

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Abstract

Three-arm star polyisobutylene ionomers ($\bar{M}_n$ = 8800) with terminal $\sim SO_3^{\ominus}M^{\oplus}$ ($M^{\oplus}$ = $K^{\oplus}$ or $Ca^{2\oplus}$) groups were synthesized and their mechanical properties investigated. Compression molded films displayed high elongations, i.e., ≈ 1000% for $Ca^{2\oplus}$ ionomers with lower values for the $K^{\oplus}$ counterions. Strain induced crystallinity was observed at higher elongations. Mechanical properties in general compared favorably with conventional covalently linked rubbery networks and were comparable and in some cases superior to EPDM-based ionomers carrying randomly distributed $\sim SO_3^{\ominus}M^{\oplus}$ groups.

Introduction

Over the last decade considerable interest has developed on the subject of ionomers. Initial investigations were focused on the structure/property correlations principally of nonelastomeric ionomer systems, e.g., ethylene methacrylic acid copolymers and sulfonated polystyrene (1-6). These investigations suggested that ionic groups randomly placed along a chain such as polyethylene or polystyrene would lead to the coulombic association of these groups in the presence of metal ions; for example, potassium, sodium, calcium, zinc. While considerable controversy still exists as to the nature of the "ionic cluster" or "ionic domain," there is general agreement that these aggregates act as physical crosslinks. In semi-crystalline polymers, e.g., polyethylene, a few ionic groups along the backbone strongly affect the crystalline morphology (7).

Recently, various authors began to investigate ionomers based on elastomers (8). For example, Lundberg et al. prepared elastomeric ionomers by sulfonating EPDM and neutralizing with various bases (8). These systems display characteristics of crosslinked networks but can be processed at elevated temperatures. Ionic plasticizers such as zinc stearate facilitate processing by solvating the ionic clusters; however, this plasticizer phase separates and recrystallizes upon cooling and behaves as a hard filler (9).

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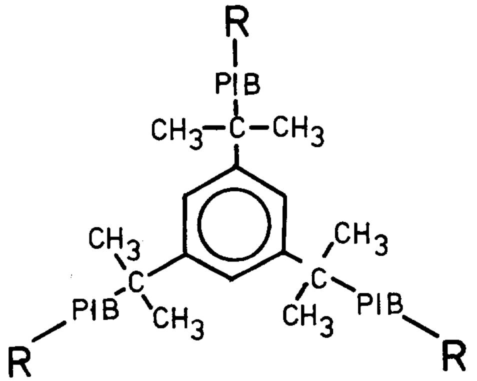
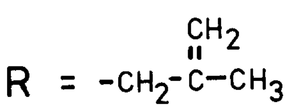
In the above elastomeric ionomers the ionic groups are randomly placed along the chain and give rise to an ill-defined network. An area of recent interest is model elastomeric systems where the network morphology is well defined by the use of precisely tailored chain elements; for example, polyurethanes obtained from a bi- or trifunctional alcohol and a tri- or bifunctional isocyanate (11). By the use of these systems the molecular weight between crosslinks, $\overline{M}_c$, can be defined and various theories of rubber elasticity can be tested. Teyssié et al. (12) have used this approach in preparing model ionomeric networks from linear polybutadienes endcapped with metal carboxylates. While anionic techniques are eminently useful for the accurate control of polybutadiene molecular weights, carboxyl termini have led to relatively weak ionomers (13).

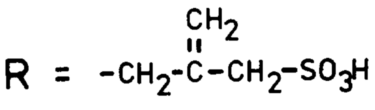
This paper concerns properties of new ionomers based on three-arm star polyisobutylene, PIB, carrying exactly one metal sulfonate group per chain terminus (14, 15). These networks contain both covalent (branch point of the PIB molecule) and terminal ionic junction points and therefore likely contain few dangling chain ends. By keeping the initial molecular weight of the PIB chains below that of the critical molecular weight for entanglement (i.e., $\sim$12,000 for linear PIB) (16), processing at elevated temperatures should be facile, in contrast to the EPDM-based ionomers.

Experimental

Materials: The synthesis of three-arm star olefin telechelic polyisobutylenes having exactly three $\sim CH_2\text{-}C(CH_3)\text{=}CH_2$ termini (I) has been described (17):



I

$$R = \text{-}CH_2\text{-}\overset{\overset{\displaystyle CH_2}{\|}}{C}\text{-}CH_3$$

II

$$R = \text{-}CH_2\text{-}\overset{\overset{\displaystyle CH_2}{\|}}{C}\text{-}CH_2\text{-}SO_3H$$

Hexane (Fisher Scientific Co.) was refluxed over fuming sulfuric acid, washed with water, dried over anhydrous $MgSo_4$, and finally distilled over CaH_2. Tetrahydrofuran (Fisher Scientific Co.) was freshly distilled from CaH_2. Acetic anhydride and sulfuric acid (both from Fisher Scientific Co.) were used without further purification. Calcium hydroxide and potassium hydroxide (Fisher Scientific Co.) were both A.C.S. certified reagents.

Sulfonation of I: Heterogeneous sulfonations were carried out in hexane solutions (10 g/100 ml) at room temperature (18, 19). Thus five grams of I ($\bar{M}_n$ = 8800 by VPO) were dissolved in 50 ml hexane and stirred at room temperature. Then 1.4 ml acetic anhydride was added, stirring was continued, and after ten minutes 0.65 ml sulfuric acid was added. After stirring for two hours the mixture was allowed to separate and the lower sulfuric acid layer was discarded. The sulfonic acid product II was either directly neutralized to the potassium salt (8) or was first isolated and then converted to the calcium salt. The latter procedure was employed to avoid $CaSO_4$ formation.

Direct Neutralization with KOH: A solution of KOH in ethanol (0.1N) was added to a portion of the sulfonated polymer solution. A two-fold excess of KOH was used to ensure complete reaction. After addition of the antioxidant Irganox 1010 to the slurry, the solvent was removed by pouring it into boiling water (8). The resultant polymer crumb was washed several times with water and then dried in a vacuum oven at 80° for two days.

Isolation of II: The free acid polymer was obtained by solvent flashing of the solution of sulfonated PIB in boiling distilled water. The polymer crumb was filtered, washed with distilled water and stirred in distilled water overnight to ensure the removal of traces of sulfuric and acetic acids. Since the dry acid tends to decompose (yellow) at room temperature, the wet crumb was stored in a freezer.

Titration of $\sim SO_3H$ endgroups: The wet crumb was dried in a vacuum oven at 70°C for 1 hour, then dissolved in THF and titrated against an alizarin-thymophthalein end point with enthanolic KOH (0.1N).

Neutralization with $Ca(OH)_2$: Pure II was dissolved (5 wt. %) in a mixture of ethanol-hexane (9/95 v/v) and the required amount of aqueous $Ca(OH)_2$ solution was added to achieve 2 equivalents of $Ca^{2\oplus}$ per one equivalent of $\sim SO_3H$. After addition of the antioxidant Irganox 1010 (0.2% by weight with respect to polymer) to the resulting polymer slurry, the solvent was removed by pouring in boiling water and the wet crumb was dried in a vacuum oven at 80°C for two days.

Film Preparation: Films were easily prepared by compression molding of dried ionomers at 150°C between Teflon sheets at ~1000 psi for 10 minutes followed by rapid quenching to room temperature on a steel plate.

Methods Used to Determine Mechanical Properties: Mechanical properties, i.e., stress-strain, stress relaxation and hysteresis, were determined on an Instron (Model 1122) at room temperature. Measurements were made at a constant elongation rate of 100% $\min^{-1}$ based on the initial length of the sample. The stress-strain data were used to determine the Mooney constants C_1 and C_2. Stress relaxation experiments were carried out by stretching at 5000% $\min^{-1}$ to a given elongation and then observing the decay in stress as a function of time.

Permanent set was determined by cyclic loading and unloading at an elongation rate of 100% $\min^{-1}$ to increasing strain levels in increments of 50% elongation. The end of the cycle occurred at zero stress during the unloading which prevented the material from further relaxing or recovering. The value of permanent set was taken as the elongation at this zero stress level.

Discussion

The number average functionality, F_n, of the ionomer has been determined by titration of the free acid and independently by sulfur analysis of the Na salt. Titration appears to be more accurate and produces more reliable data than sulfur determination. Results indicate essentially quantitative end group functionalization; i.e., exactly three sulfonic acid groups per molecule.

Stress/strain characteristics of compression molded films of the potassium and calcium ionomers have been determined. According to the results shown in Figure 1 high elongations were obtained. In these data, the calcium ionomer exhibits a higher degree of elongation than that of the potassium salt, however, we have found that the potassium salts can also display high elongation if prepared differently.

The stress/strain data were redrawn in the form of the classic rubber elasticity plot, i.e., by plotting engineering stress, σ_o, versus $(\lambda-(1/\lambda^2))$, where λ is the extension ratio. The data given in Figure 2 indicate linear or near linear behavior up to $\lambda \approx 3$.

According to the rubber elasticity theory, an ideal Gaussian network should give a linear plot when the data are plotted as in Figure 2 and the initial slope should provide the shear modulus and be directly related to $\bar{M}_c$. This calculation gave $\bar{M}_n \approx 6{,}700$. Assuming that only two PIB chain ends are joined at each ionic bridge, then $\bar{M}_c$ between permanent

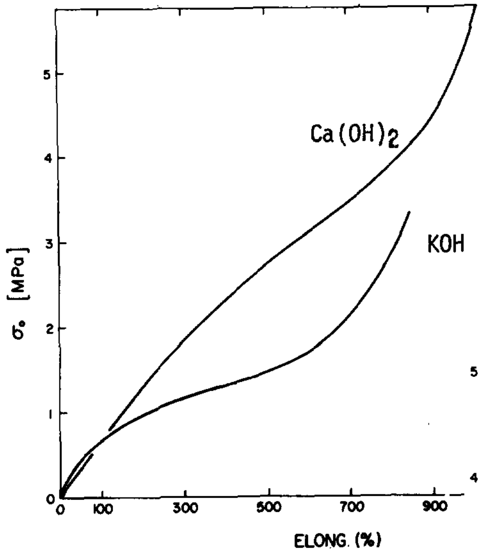


Figure 1. (left) Engineering stress versus elongation behavior for three-arm star PIB ($\overline{M}_n$ = 8800) neutralized with KOH and Ca(OH)$_2$

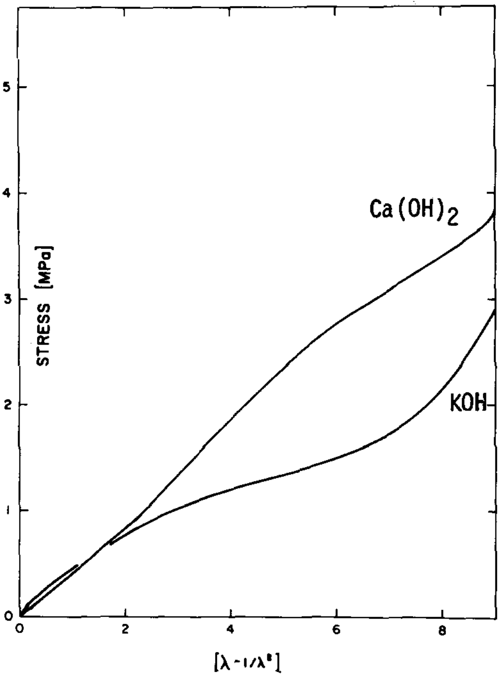


Figure 2. (right) Rubber elasticity plot for three-arm star PIB ($\overline{M}_n$ = 8800) neutralized with KOH and Ca(OH)$_2$

crosslinks, i.e., the crosslinks emanating from a phenyl ring (inspect II), is the sum of two arms of II; i.e., (8800/3) x 2 ≈ 6000. This value is close to the one obtained from the stress/strain data.

On the other hand, stress relaxation data have yielded a near equilibrium modulus which led to $\overline{M}_c \approx 12,000$, i.e., twice the value suggested from the above simplified model. Undoubtedly a portion of the difference in the two values is due to the nonequilibrium character of the stress/strain measurement relative to the stress relaxation experiment. However, at this time we will offer no additional explanation.

In Figure 3 we have replotted the data in terms of the Mooney-Rivlin equation, i.e., by plotting $\sigma_o/(\lambda-(1/\lambda^2))$ versus $1/\lambda$, and have obtained linear relationships with very small slopes indicating that C_2 is small - particularly for the calcium salt. This behavior is similar to many conventional covalently crosslinked elastomers. Experimentation in this area is continuing.

Figure 4 shows percent permanent set obtained following cyclic deformations to increasing elongations with a single sample. The percent set is rather small. For example, at 200% elongation the permanent set is ≈ 10% i.e., lower than that of sulfonated EPDM ionomers containing zinc stearate (19). Further, the permanent set of a lightly crosslinked polybutadiene with $\bar{M}_c \approx 12{,}000$ gave nearly the same values under comparable elongations and drawing conditions. Evidently our material behaves much like a true network and exhibits properties comparable to conventional covalently crosslinked elastomers.

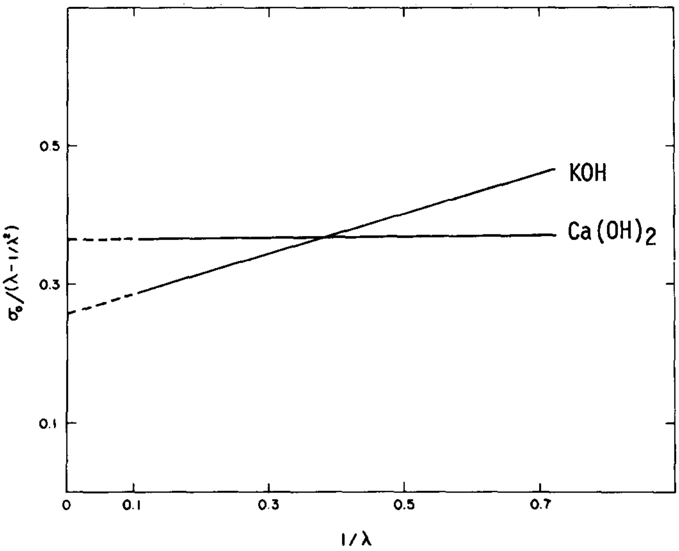


Figure 3. (above) Mooney-Rivlin plot for three-arm star PIB ($\bar{M}_n$ = 8800) neutralized with KOH and $Ca(OH)_2$

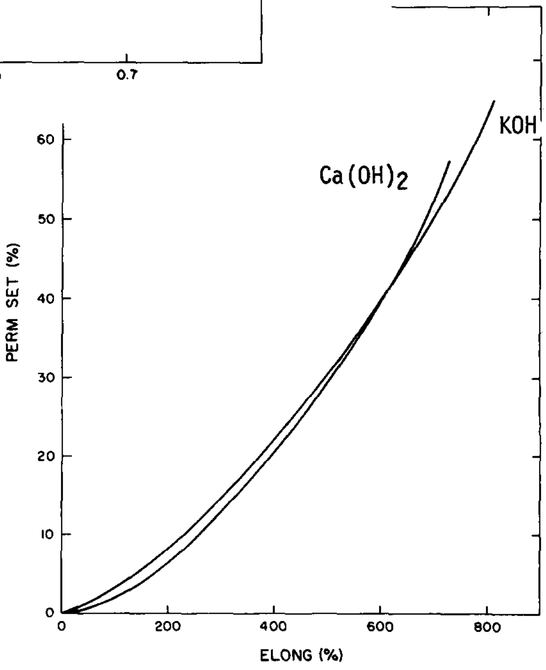


Figure 4. (right) Permanent set versus elongation behavior for three-arm star PIB ($\bar{M}_n$ = 8800) neutralized with KOH and $Ca(OH)_2$

Recalling Figure 1 it is noted that high elongations were obtained with these systems. This is suprising in view of the relatively low molecular weight chain segments bridging the ionic clusters. The upturn above $\lambda \simeq 6$ suggests crystallization of PIB chain segments. Strain induced crystallization is indicated by the wide angle X-ray diffraction pattern shown in Figure 5, obtained on a calcium hydroxide ionomer. Evidently a high degree of orientation occurs as a result of strain. The presence of crystallinity assists in maintaining low permanent set even at high elongations. At elongations below the onset of strain induced crystallization the permanent set compares favorably to conventional noncrystallizable covalently crosslinked elastomers. We view crystallinity to be an asset in this system that provides additional tensile strength and elongation that would not be achieved if only an amorphous character were retained upon elongation.

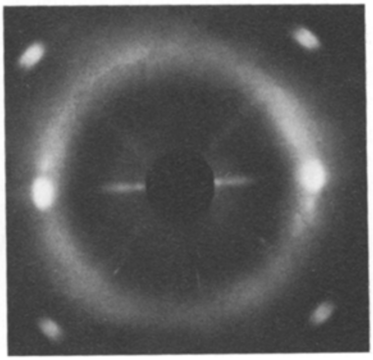


Figure 5. WAXS pattern for a Ca salt three-arm star PIB ionomer strained to 700% elongation

Conclusions

Model ionomer networks can be generated from a three-arm star PIB prepolymer that is of lower molecular weight ($\bar{M}_n$ = 8800) than that critical for the onset of entanglements (at least for a linear PIB). These networks contain a combination of covalent and ionic junction points and dangling chain ends are speculated to be few in number. These materials exhibit strain induced crystallization which is desirable for applications under high elongation. The properties of these systems are in many respects superior to conventional crosslinked elastomers. Due to the low molecular weight of the prepolymers, these ionomers undergo facile processing at reasonably low temperatures and hence are superior to EPDM-based ionomers which require higher temperatures and possibly the presence of an ionic plasticizer for processability.

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