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New Polyisobutylene-Based Model Ionomers

5. The Effect of Molecular Weight on the Mechanical Properties of Tri-Arm-Star Polyisobutylene-Based Model Ionomers

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Abstract

Mechanical properties of tri-arm polyisobutylene based ionomers have been investigated. Number average molecular weights ($\overline{M}_n$'s) of the polymers were varied from 8,300 to 34,000. The ionomer of lowest $\overline{M}_n$ (8,300) exhibits very low extension at break (∿ 150%) while the others with $\overline{M}_n$'s of 11,000, 14,000 and 34,000 show very high extensions, often exceeding 1,000%, and display relatively low permanent set and low hysteresis behavior. Since the ionic bonding is located exclusively at the chain ends, end-linked pseudo networks are formed due to coulombic attractions. At higher temperatures the coulombic interactions are weakened and the networks can be compression molded (∿150°C).

Introduction

Earlier work in the field of ionomers has been principally carried out on non-elastomeric polymer systems such as ethylene-methacrylic acid copolymers and sulfonated polystyrene (1-6). It has been observed that by introducing very small quantities of ions into polymers, the mechanical and structural properties change dramatically from those of the nonionized systems (1,2). Recently Lundberg et al. (7) have carried out research on elastomeric ionomers, specifically those based on sulfonated EPDM (7). However, in the latter systems the ionic groups were introduced at random along the polymer backbone resulting in an ill-defined ionomeric network.

The present study extends our earlier investigations (8,9) concerning the mechanical properties of new model ionomers based on tri-arm-star polyisobutylene (PIB) carrying a sulfonate group at the end of each arm. Upon neutralization, this system leads to a model network with ionic association only at the chain ends. The synthesis of these systems has been reported by Kennedy et al. (10,11) and developments concerning neutralization of the sulfonic acid PIB with various bases, i.e. KOH, $Ca(OH)_2$, was described by Mohajer et al. (8).

The critical molecular weight for entanglement formation of linear PIB is commonly reported as with some values as low as 9,000 and as high as 17,000 (12). Therefore, to study the effect of molecular weight on the mechanical properties and to determine the possible influence of entanglemnts, tri-arm-star ionomers with $\overline{M}_n$'s of 8,300, 11,000, 14,000 and 34,000 were studied. Stress-strain behavior, permanent set, stress relaxation, and hysteresis have been investigated for potassium ionomers produced by stoichiometric neutralization with KOH. Some comparisions have been made with calcium ionomers. Difunctional ionomers and mixed difunctional/tri-arm-star ionomer systems will also be considered in a later publication.

Experimental

The synthesis of tri-arm star sulfonic acid PIB has been described (10,11,13). End point neutralizations were carried out by the use of polymer solutions of hexane/ethanol (8) and stoichiometric quantities of ethanolic KOH or aqueous $Ca(OH)_2$. Since the number of variables involved in this study is large, a system of abbreviations will be used. This system is illustrated by an example. Specifically, a sample designated T-14-Ca-0 would be a tri-arm-star PIB ionomer of $\overline{M}_n = 14 \times 10^3$ which has been neutralized with calcium hydroxide to the exact stoichiometric end point, i.e., zero excess $Ca(OH)_2$ was added. Likewise, T-34-K-100 would indicate a tri-arm-star ionomer with $\overline{M}_n = 34 \times 10^3$ which has been neutralized with a 100% excess of KOH over that required for exact stoichiometric neutralization, i.e., twice the amount of KOH needed for end point neutralization. The ionomers under study are thus designated as T-34-K-0, T-14-K-0, T-11-K-0, T-8.3-K-0, T-34-Ca-0 and T-14-Ca-0.

$\overline{M}_n$'s were determined by titration using a standard KOH solution and by assuming exactly three sulfonic acid groups per PIB molecule (11). The sulfonated PIB sample utilized in previous studies (8,9) had an $\overline{M}_n$ = 9,000 as determined by titration and corroborated by VPO measurements of the sample prior to sulfonation (8). The $\overline{M}_n$ of this sample increased to 11,000 by loss of low molecular weight water-dispersible product during purification. Nevertheless, the mechanical properties of the material remained largely unchanged. The T-8.3-K-0 sample has a narrower molecular weight distribution than the other polymers because the PIB triolefin precursor was subjected to fractionation (13). The initial $\overline{M}_n$ of this sample was 6,600 but it increased to 8,300 during purification. Higher molecular weight samples generally do not undergo such changes in $\overline{M}_n$ during purification.

Ionomer films were compression molded at 150°C and were then stored in a vacuum dessicator until use; storage at ambient conditions had little influence on material behavior so long as the extent of neutralization was exactly stoichiometric.

Mechanical properties were determined on an Instron Model 1122 at room temperature. Stress-strain behavior was obtained by stretching microdumbbells (10.0 mm long) at a constant crosshead speed of 100% $min.^{-1}$. Permanent set was determined by cyclic loading and unloading at a rate of 100% $min.^{-1}$ to increasing strain levels in increments of 50% elongation. The end of a cycle was taken at zero stress during the unloading which prevented the material from further relaxing or recovering. The value of the permanent set was defined as the instantaneous elongation at the end of the cycle. The percent hysteresis for a given cycle was calculated as the ratio of the area bounded by the loading-unloading curves to the total area under the corresponding loading curve. The areas were determined by using an electronic digital planimeter. Stress relaxation experiments were carried out at either 25% or 100% elongation.

Discussion

Stress-strain data for the four molecular weight systems are shown in Figure 1. With increasing molecular weight the stress is lower at any given elongation for the three higher molecular weight samples. Assuming that this system forms a "pseudo end-linked rubbery network" held together by coulombic forces at the chain ends where the ionic species are located, then according to the Gaussian theory of rubber elasticity the stress is given by (14):

$$\sigma = \frac{\rho RT}{\overline{M}_c}\left(\lambda - \frac{1}{\lambda^2}\right)$$

Thus, for the same extension ratio, λ, the stress will be lower for a higher M_c ($\overline{M}_c$ = the number average molecular weight between two "crosslink" points). Assuming only two ion pairs per ion-pair multiplet, the $\overline{M}_c$ would be equal to the average molecular weight of two arms, i.e., $\overline{M}_c$ = 2/3 $\overline{M}_n$. For example, $\overline{M}_c$ for a polymer of $\overline{M}_n$ = 8,300 would be $\sim$5,500. The observed behavior of higher stresses at a given extension ratio for lower molecular weight polymers in line with the predicted trend.

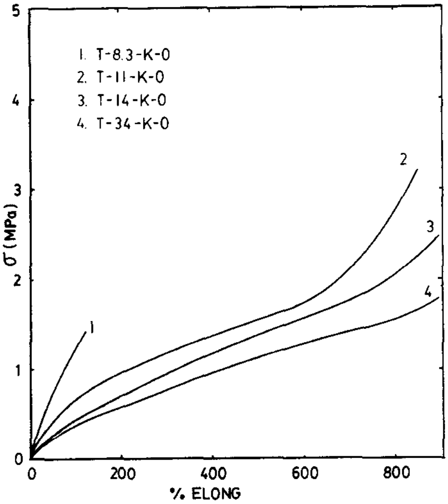

Figure 1: Stress vs. percent elongation for the T-8.3-K-0, T-11-K-0, T-14-K-0 and T-34-K-0 materials.

Sample T-8.3-K-0 displays only a moderate extension to break ($\sim$150%) which is less characteristic of elastomers. However, the rest of the ionomers exhibit elongations in excess of 800%, often exceeding 1000%.

The upturn in the stress at about 600% elongation suggests either development of crystallinity at higher elongations or deviation from Gaussian behavior due to limited chain extensibility. Previous work on strain induced crystallization for the low molecular weight ($\overline{M}_n$ = 9,000) PIB ionomer has shown the onset of crystallinity at about 500% elongation (9). Reversible crystallinity promotes chain-chain interaction and thereby improves tensile properties and subsequent recovery following load removal. The corresponding permanent set of this series of ionomers is shown in Figure 2.

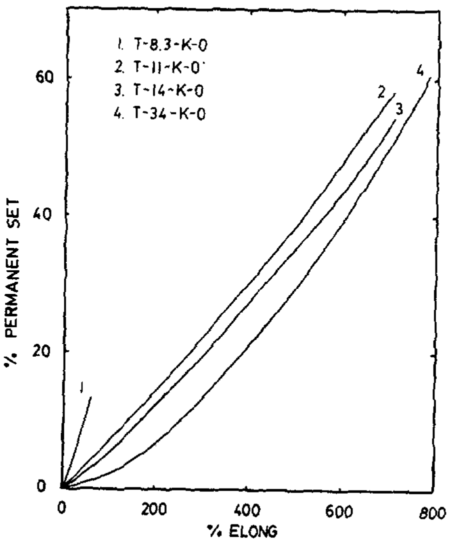

Figure 2: Percent permanent set vs. percent elongation for the T-8.3-K-0, T-11-K-0, T-14-K-0, and T-34-K-0 materials.

As previously observed (8), the instantaneous permanent set, of these systems is relatively small, e.g., only 50-60% even at 700% elongation. Additional recovery occurs quickly with time further implying network integrity. The mechanical hysteresis of samples T-34-K-0 and T-34-Ca-0, and T-14-K-0 and T-14-Ca-0 is shown in Figures 3 and Figure 4, respectively. Even at very high elongations, the hysteresis is only about 20%, which is quite small considering that these samples are uncrosslinked polymers of relatively low molecular weight and that these tests are performed far above the Tg (-65°C). Crystallinity at high elongations restricts chain relaxation and flow because the crystallites serve as anchor points. Thus, except for T-8.3-K-0, the elastic properties of these systems are surprisingly good for a low molecular weight system with no permanent crosslinks.

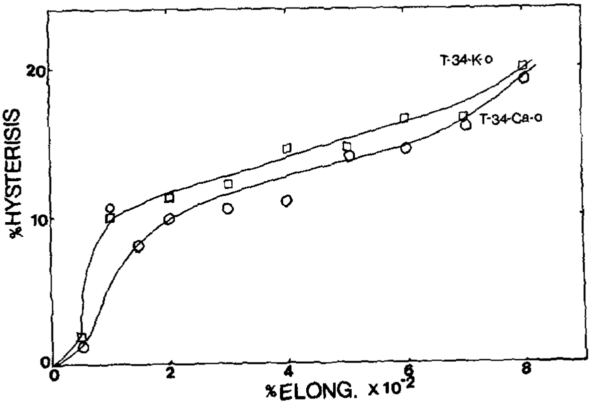

Figure 3: Percent hysteresis vs. percent elongation for the T-34-K-0 and T-34-Ca-0 materials.

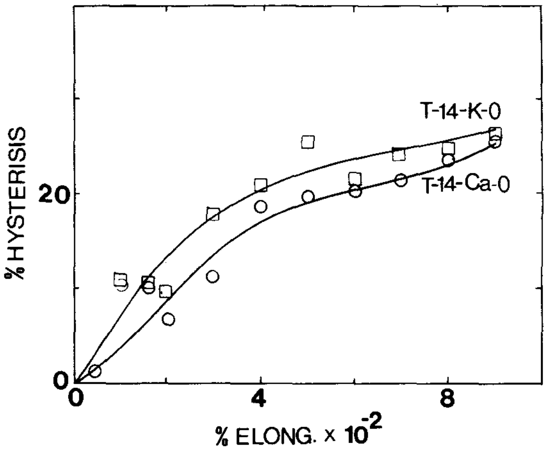

Figure 4: Percent hysteresis vs. percent elongation for the T-14-K-0 and T-14-Ca-0 materials.

Results of stress-relaxation experiments on the three higher molecular weight ionomers at 25% and 100% elongation are shown in Figure 5. The near equilibrium stress level for the 11,000 molecular weight polymer is higher than that for the 14,000 molecular weight sample which in turn is higher than that of the 34,000 molecular weight sample. The near equilibrium stress is 50% to 80% of the initial stress in all cases. At 100% strain the relaxation is faster, likely due to the higher driving force to increase the conformational entropy. The increase in the near equilibrium stress with decrease in molecular weight is again in accord with the Gaussian theory of rubber elasticity. Comparison of stress values at a given time for the two different strain levels for a particular sample indicates that at 100% strain, these systems do not quite behave as perfect linear viscoelastic materials. Evidently the ratio of stress at 100% and at 25% elongation is not constant at all times for a given polymer, however, this is not uncommon for elastomers at these extensions.

The above mechanical properties render these low molecular weight ionomers potentially good thermoplastic elastomers. Since the "crosslinks" between the chain ends are ionic in nature, the materials can be processed at elevated temperatures. With the increasing temperature the coulombic forces of attraction between the ion pairs decrease, while the elastic forces of retraction increase, thereby causing the system to flow at elevated temperatures. Detailed studies concerning the melt rheology of these systems will be reported (15).

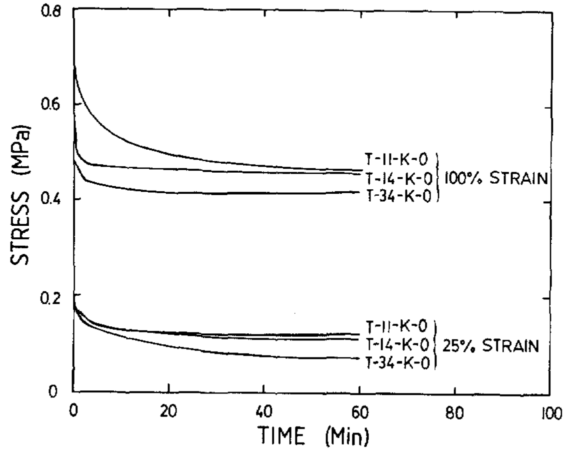

Figure 5: Stress relaxation behavior for T-11-K-0, T-14-K-0 and T-34-K-0 materials at 25% and 100% elongation at ambient temperatures.

Conclusions

The present study indicates that tri-arm-star PIB ionomers of relatively low molecular weight (11,000 $\leq \bar{M}_n$ 34,000) are interesting new thermoplastic elastomers. They have high tensile properties and low permanent set and hysteresis at ambient conditions, and they can be thermally formed above ∿150°C. The presence of crystallinity at higher elongations helps to enhance mechanical properties. The lowest molecular weight ionomer studied ($\bar{M}_n$ = 8,300) exhibits less attractive properties due to low extensions at break. It is remarkable that the introduction of three terminal ionic groups per molecule is sufficient to transform room temperature liquid PIB prepolymers into elastomers with good mechanical properties.

Acknowledgement

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