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New Polyisobutylene-Based Model Ionomers

IV. Strain Induced Crystallization of Low Molecular Weight Model Ionomers

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ABSTRACT

Strain induced crystallization has been observed at 25°C in low molecular weight three-arm star polyisobutylene ionomers at elongations exceeding about 550%. The sulfonated form of the polymer was neutralized with calcium hydroxide. The number average molecular weight of the polymer was only 9,000 with a dispersity ratio of about 1.7. This molecular weight is at the edge of the critical molecular weight for entanglements. Strain induced crystallization has been reported in the literature for very high molecular weight linear polyisobutylene. However, no such effects have been observed for linear, low molecular weight polyisobutylene and it has been stated it could not be induced. The cause for this strain induced crystallization in our materials is due to the presence of three ionic terminal groups per molecule which results in sufficient coulombic forces for maintenance of molecular orientation with strain without significant relaxation.

Introduction

Research in the field of ionomers has been continuing since the 1960's as evident by numerous excellent publications during this period (1-7). However, none of these has considered the strain-induced crystallization behavior of these various ionomeric polymer systems. This is likely due to the glassy or, in other cases, semicrystalline nature of these systems. Strain induced crystallization, first observed for natural rubber (8), leads to enhancement of mechanical properties. Linear, uncrosslinked, high molecular weight polyisobutylene (Mn = 5.9×10^5), which is a rubber at room temperature (Tg = -70°C) is known to crystallize upon stretching (9-11). However, in the case of uncrosslinked low molecular weight polyisobutylene, at this same temperature even well above the critical entanglement molecular weight, there is insufficient interaction between molecules to enable the chains to be held in the stretched condition without relaxation, thereby implying it cannot be crystallized upon stretching (10). In the present study it is shown that a low molecular weight ($\overline{M}n$ = 9,000) tri-star, polyisobutylene ionomer, neutralized with calcium hydroxide, exhibits very pronounced crystalline morphology upon stretching. The crystallinity induced upon stretching the polymer has a significant effect on the mechanical behavior of these systems, as expected and as will be published shortly by the authors. It may be noted here that the critical molecular weight for entanglement for linear polyisobutylene (PIB) is reported to be about 12,000 (12). Thus,

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in order to strain induce crystallinity in the tri-star PIB ionomers of about only 9,000 molecular weight, it is very important that the chains do not slip-by each other upon stretching as there is not much entanglement in these systems. However, the coulombic forces between the ion pairs are strong enough to hold the chains together, even at high elongations. Due to the alignment of the chains in the stretch directions, a high degree of orientation results in promoting crystallinity.

Experimental

The synthesis of the three arm star olefin telechelic polyisobutylenes with each arm having a SO_3H terminal group has been discussed by Kennedy et al. (13). The subsequent neutralization of the acid form with calcium hydroxide has been carried out by Mohajer et al. (14). The neutralized samples were compression molded between teflon sheets at 150°C, for a period of fifteen minutes. For the first five minutes they were heated at atmospheric pressure and 150°C. They were then very slowly compressed (5 minutes) to the final pressure of about 1000 psi, and it was held for another five minutes. Subsequently, they were quenched to room temperature on a steel plate.

Thin strips of polymer film were stretched to various elongations, up to 900%. A Phillips table-top X-ray generator model PW1170 was utilized with a standard vacuum sealed Statton photographic camera. The exposure time was about 16 hours in each case. The polymer under study is designated as T-9-Ca-100, indicating it is a 9,000 molecular weight tri-arm polyisobutylene polymer having sulfonated ions at the chain ends which have been reacted with calcium hydroxide in excess of 100% of the required quantity for exact stochiometric neutralization.

Results

Figure 1 (a-c) shows the wide angle X-ray scattering (WAXS) pattern for the system under study at elongations of (a) 400%, (b) 575%, and (c) 900%. It is readily observed that figure 1(a), provides a diffuse amorphous halo, indicating absence of any significant crystallinity. However, upon further stretching the sample to 575% elongation, (Figure 1b) a sharp diffraction pattern is observed, indicating the presence of pronounced oriented crystalline morphology. It may be pointed out here that certain mechanical properties also show significant changes around 400% - 500% elongation which can be explained in terms of the development of strain induced crystallinity in this material. Upon further stretching the sample to very large elongations the diffraction pattern becomes sharper, indicating increased crystallinity (see Figure 1c).

Discussions

Thermodynamically, for any phase change, the change in the Gibb's free energy, ΔG, is given by the following relation:

$$\Delta G = \Delta H - T\Delta S$$

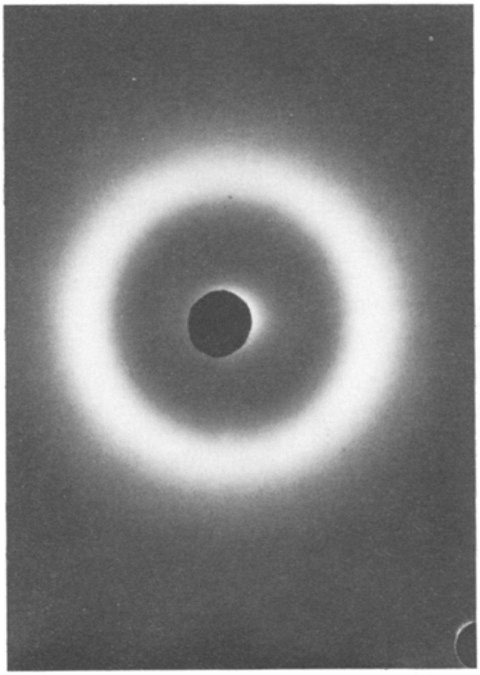

Figure 1a

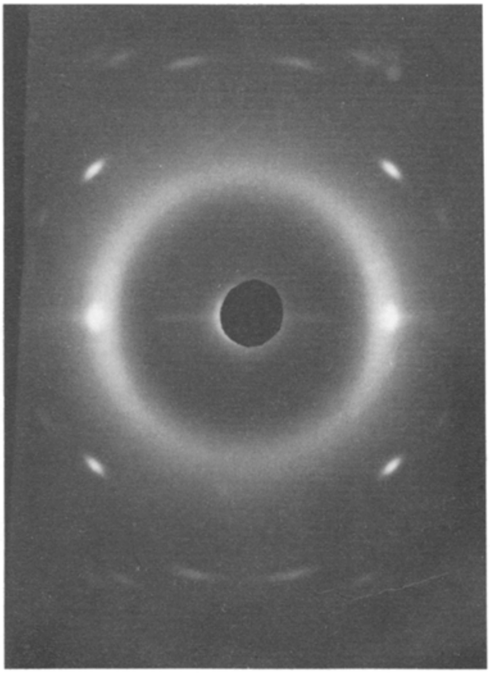

Figure 1b

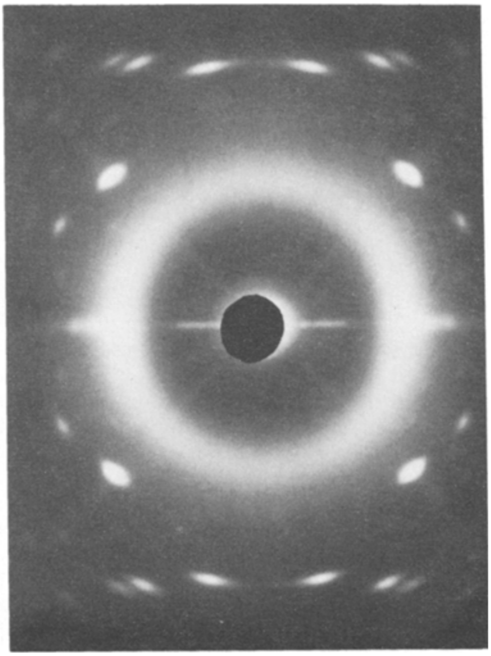

Figure 1c

Figure 1. WAXS patterns for the 9,000 molecular weight, three-arm star polyisobutylene, at (a) 400%, (b) 575% and (c) 900% elongation at room temperature.

At equilibrium, $\Delta G = 0$, and the melting temperature, $Tm = \Delta H/\Delta S$. It is also well known that crystal nucleation is promoted at a higher degree of supercooling, i.e.,(Tm-Tc) where Tc is the crystallization temperature. Unoriented polyisobutylene is non-crystalline under ambient conditions, however, upon stretching, the chains become oriented. If these chains can be held together, without relaxation, the chain orientation greatly reduces the conformational entropy, ΔS, from the amorphous to that of the semi-crystalline phase, while ΔH, the enthalpy change is much less influenced by this variable. This results in an appreciable elevation in the melting point, Tm which enhances the supercooling and the driving force for crystallization. Thus, the polymer crystallizes in an oriented fashion at room temperature. In the present system, there is one sulfonate group at each end of the tri-arm PIB molecule. Upon neutralization with calcium hyldroxide, these terminal ionic groups form ion pair bridging between molecules (and in some cases possibly between two arms of the same molecule). The coulombic forces of attraction between these ion-pairs are strong enough to maintain orientation and limit molecular relaxation upon stretching even for the low molecular weight systems so far above Tg. It may be noted here that the ionic content is only about 1.5 mole percent. Thus, we recognize the significant effect of ionic moieties upon the strain induced crystallization behavior. It is interesting to note that the molecular weight of the PIB ionomer under study is only 9,000, while the critical molecular weight for entanglement of linear PIB has been reported to be about 12,000 (12). It is therefore apparent that it is the ionic interaction at the chain ends which lowers the rate of relaxation and thus promotes the orientation and subsequent crystallization behavior. Absence of crystallinity at 400% elongation indicates that the chains are not oriented enough to promote nucleation and growth.

It may be mentioned here that strain induced crystallization was also observed for other samples of different molecular weights and neutralized to the exact or excess stochiometric requirements. In addition, following the several hour WAXS exposure for any of these samples as well as that discussed here, release of the loading, resulted in very high recovery indicating low permanent set. Further details in this regard will be detailed in later publications.

Conclusions

The present study dramatically shows that low molecular weight polyisobutylene–based ionomers (Mn = 9,000) can be strain induced crystallized following neutralization with calcium hydroxide. These molecules which each possess only three terminal ionic groups demonstrate that coulombic forces of attraction between the chain ends are sufficient to provide orientation with stretching, i.e. limit molecular relaxation. Since the molecular system involved is at the edge or below the critical molecular weight for entanglements for polyisobutylene as reported in the literature, it is clear that ion pair formation between molecules must be established within these ionomer systems which lead to a considerable increase in the relaxation time behavior of these materials thereby promoting orientation and enhancing the supercooling at a given stretching temperature. We belive this short report dramatically demonstrates the effect of ionic moieties on the bulk properties of this interesting elastomer.

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