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Sulfonated Polyisobutylene Telechelic Ionomers

10. Effects of Architecture and Molecular Weight on Viscosity Behavior in a Nonpolar Solvent

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ABSTRACT

The gelation of polyisobutylene-based model ionomers with $-SO_3^-K^+$ terminal groups has been studied in hexane at 25°C. Both molecular architecture and molecular weight were found to significantly influence the concentration at which gelation occurs. Specifically, three-arm star trifunctional ionomers gel at lower concentrations than linear difunctional ionomers of similar molecular weight. In addition, the gelation concentration decreases with increasing molecular weight for the three-arm star trifunctional ionomer, but the results do not fit the relationship reported previously which relates gelation concentration and molecular weight for carboxylated linear telechelic polymers.

INTRODUCTION

The bulk structure-property behavior of ion-containing polymers has been studied quite extensively (1-3). The presence of low concentrations (usually <15 mole%) of ionic groups on an otherwise nonpolar polymer chain dramatically influences properties due to ion aggregation. These ionic associations essentialy result in an ionically crosslinked system. Although the bulk structure and properties of ionomers have been studied extensively, relatively little effort has been directed toward developing an understanding of their solution behavior. This is in spite of many potential applications such as viscosity control agents and gelling agents for tertiary oil recovery. A recent paper by Dieterich (4) reviews the application of polyurethane ionomers in aqueous dispersions and emulsions. Notable recent work on the solution properties of ionomers has been carried out primarily by Lundberg and coworkers (5-7) and by Teyssie and coworkers (8-12).

Lundberg and Makowski (5) have found that solutions of polystyrene-based metal sulfonate ionomers containing 0.3 to 6.3 mole percent sulfonate groups display unusual behavior in mixed solvents in that the viscosity may increase, remain relatively constant, or display maxima or minima over broad temperature ranges. Lundberg and Phillips (6) have shown that these ionomers in nonpolar solvents display a viscosity

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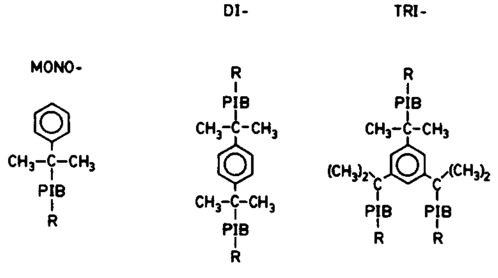
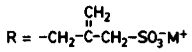
which increases with concentration at a rate much greater than that of the corresponding unneutralized polymer, while in polar solvents the typical polyelectrolyte behavior is observed at low concentrations. Broze, Jerome, and Teyssie (8-10) have studied the effect of cation, counteranion, backbone type, molecular weight, and solvent polarity on the gelation concentration of linear telechelic polymers with a single carboxylate group at each chain end. It was found that for the same polymer backbone the gelation concentration decreases with increasing molecular weight and decreasing solvent polarity. For the same molecular weight and solvent, the gelation concentration decreases with increasing root mean square end-to-end distance which, of course, depends on the type and flexibility of the polymer backbone. The effects of cation and counterion are somewhat more complex.

Previous publications from our laboratories have discussed the synthesis (13), sulfonation and neutralization procedures (14), and bulk structure-property behavior (14-19) of linear and three-arm star sulfonated polyisobutylene telechelic ionomers. Neutralization of the terminal sulfonic acid groups leads to well-defined elastomeric networks. In this paper we present our initial results concerning the effect of molecular architecture and molecular weight on the viscosity-concentration behavior of these PIB-based ionomers in a nonpolar solvent.

EXPERIMENTAL

The structures of the ionomers studied are:





$$R = -CH_2-\overset{\overset{\displaystyle CH_2}{\|}}{C}-CH_2-SO_3^-M^+$$

The terminal sulfonic acid groups were neutralized to the stoichiometric point with potassium hydroxide. The nomenclature used may be described by the example T-14-K-0. This refers to the three-arm star trifunctional ionomer with $\bar{M}_n$ = 14000 which has been neutralized with KOH to the endpoint (0% excess KOH). The precursor sulfonic acid would be designated by T-14-SO$_3$H, while the initial hydrocarbon polymer (prior to sulfonation) would be T-14-HC. The dispersity index is about 1.7 for all samples.

Solutions were prepared in stoppered volumetric flasks using magnetic stirrers for agitation. The nonpolar solvent was hexane. Drying the hexane over molecular sieves for several days did not affect the viscosities, so the hexane was used as received. The relative viscosities (defined as η/η_s, where η is the viscosity of the solution and η_s is the viscosity of the pure solvent) were measured with calibrated Ubbelohde dilution viscometers at 25±0.1°C in a thermostated bath. Due to the extremely wide range of viscosities encountered it was necessary to use several viscometers with different capillary sizes. In contrast to the typical procedure of calculating relative viscosity from a ratio of elution times when a single viscometer is used for both solvent and solution, absolute kinematic viscosities were first calculated and then used to calculate relative viscosities. Each data point shown in the figures represents the average of at least three experimental trials. When more than one data point is present for a particular ionomer at the same or nearly the same concentration, each data point represents results obtained from independently prepared solutions so as to check the solution preparation procedure.

RESULTS AND DISCUSSION

Figure 1a shows the effect of sulfonation and neutralization upon the relative viscosity vs. concentration behavior for the linear difunctional ionomer of 12000 $\bar{M}_n$. The linear increase in the logarithm of relative viscosity as a function of concentration for D-12-HC is typical of low molecular weight polymers in this concentration range. The nonlinear increase in the logarithm of relative viscosity for D-12-SO_3H indicates some association of the acid groups. Such association was not observed for the carboxylated linear telechelic polymers of Broze et al. (8-10), for which the logarithm of viscosity continued to increase linearly for the acid form at these concentrations. A high degree of association for the sulfonic acid form of these PIB-based ionomers was also previously observed in the bulk material (19). These associations are not maintained at room temperature due to decomposition of the sulfonic acid terminal groups, and viscosity is observed to decrease with time. The data shown were obtained as quickly as possible following dissolution of the polymer. Neutralization of the sulfonic acid groups with KOH greatly strengthens the ionic associations as shown in Figure 1a. The gelation observed for D-12-K-0 is similar to that observed by Broze et al. (8-10) for linear telechelic polymers (polybutadiene, polyisoprene, poly(α-methylstyrene) etc.) with neutralized carboxylic acid groups. Sulfonation and neutralization have a similar effect upon the viscosity behavior of the trifunctional structure, as shown in Figure 1b for the 14000 $\bar{M}_n$ polymer.

The gelation of telechelic polymers in a nonpolar solvent

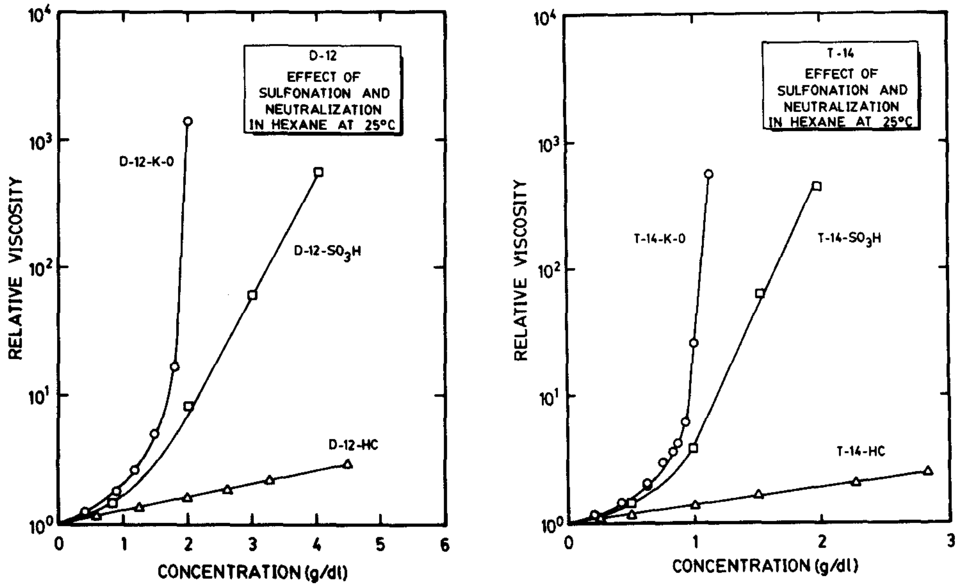


Figure 1. Effect of sulfonation and KOH neutralization upon relative viscosity for (a) D-12-K-0 and (b) T-14-K-0.

results from association of the ionic endgroups. If triplet or higher order associations are possible, as suggested by Broze et al. (8-10), then linear telechelic polymers may indeed form a network in solution. Intermolecular ion pair association would result in simple chain extension and an increase in viscosity due to the increase in apparent molecular weight. However, it seems difficult to attribute increases in viscosity of several orders of magnitude within such a small concentration range to simple chain extension. It is likely that the ionic associations which occur are of both types, i.e. triplets and higher order associations which result in network junction points and ion pair associations which result in simple chain extension. Recent dynamic experiments on gels formed by the linear difunctional materials suggest that an elastomeric pseudo-network may indeed exist since the storage modulus, G', is constant at room temperature over the entire frequency range (20). Intramolecular ion pair associations may also occur, resulting in cyclic structures. These cyclic species may be mutually independent or they may be interlocked to form catenates as suggested by Broze et al. (11). Recently, Misra and Mandal (21) have suggested, based upon osmotic pressure measurements, that the degree of association remains essentially constant in the concentration region where gelation occurs. These workers assert that a high degree of association exists even at very low concentrations and that this should be reflected in an abnormally large Huggins coefficient.

The effect of molecular architecture upon the relative viscosity is shown in Figure 2 where architecture is varied

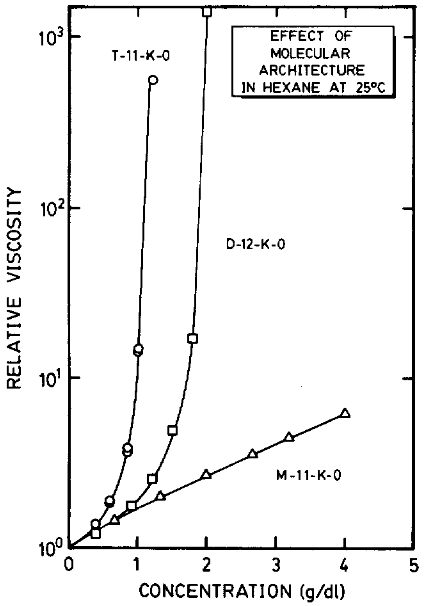
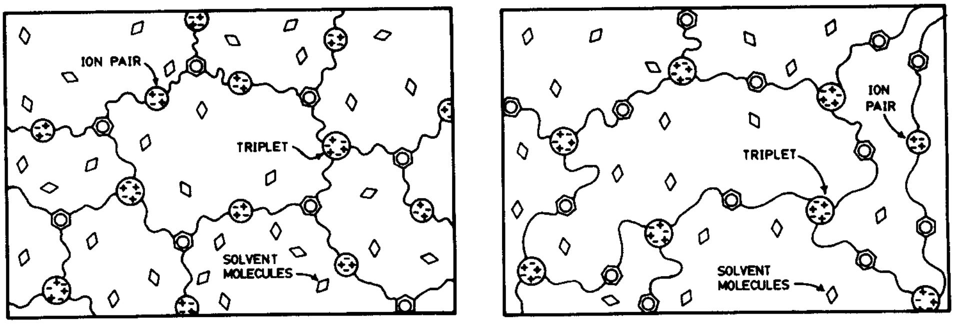


Figure 2. Effect of molecular architecture upon viscosity at an approximately constant molecular weight of 11000-12000.

while holding molecular weight approximately constant. The solution of M-11-K-0 does not gel even at higher concentrations since ion pair association would lead only to dimerization. In fact, ionic associations which involve three or more ion pairs would result in the formation of star-like molecules or micellar structures with a central ionic region. The slight downward curvature of the relative viscosity vs. concentration plot for M-11-K-0 may indicate that as concentration is increased the average number of arms per star increases. The probability of triplets and higher order associations should increase with increasing concentration. Once a few arms are present, however, the addition of more arms of common length has very little effect on the radius of gyration (22,23). Therefore, as the concentration of the linear monofunctional ionomer is increased, the viscosity increases due to the presence of more polymer; however, it does not increase linearly since some of the added molecules are incorporated into stars which already exist and to which they contribute very little additional hydrodynamic volume. (The ultimate number of arms per star would be limited by steric considerations.) The viscosity vs. concentration curve would then be expected to exhibit a decreased rate of viscosity increase as observed. As shown in both Figures 1a and 2, the solution of D-12-K-0 does display gelation. The solution of T-11-K-0 also gels but at a lower concentration than the D-12-K-0. This behavior most likely occurs for two reasons. First, the number of ionic groups per molecule is greater for the trifunctional ionomer, so that for molecules of the same molecular weight the ionic content is 1.5 times higher. Second, since each three-arm star ionomer already possesses a permanent network junction point, only ion pair association of the terminal ionic groups is necessary for network formation. However, the linear difunctional ionomers do not possess a permanent network junction point, and thus triplets or higher order associations are necessary for network formation. As discussed above, the probability of triplets and higher order associations increases with increasing concentration. Therefore, at the gel concentration for T-11-K-0 the ionic associations are probably predominantly ion pairs -- sufficient for gelation of the three-arm star trifunctional



(a) (b)

Figure 3. Schematic of ion association resulting in formation of gel structure with similar crosslink density for (a) the three-arm trifunctional ionomer and (b) the linear difunctional ionomer.

ionomer but not for the linear difunctional ionomer. As concentration increases, the probability of triplet ionic associations (rather than ion pairs) increases until the number of triplets is sufficient for gelation of the difunctional ionomer to occur. These ideas are depicted schematically in Figure 3, where network structures of approximately the same crosslink density are compared. Figure 3a shows that only ion pair association is necessary for network formation for the three-arm trifunctional ionomer, while Figure 3b shows that triplets (or higher order associations) are required for the linear difunctional ionomer to form a network.

The effect of molecular weight upon the gelation concentration, C_{gel}, of linear telechelic polymers was observed experimentally and predicted theoretically by Broze et al. (8-10) to be given by:

$$C_{gel} = k\ \bar{M}_n^{-1/2} \qquad (1)$$

where k is a constant depending on the nature of the polymer backbone. This equation was found to fit experimental data for several types of linear telechelic polymers for which the dispersity index ranged from less than 1.2 to 1.8. The effect of molecular weight upon viscosity behavior of the three-arm star trifunctional ionomer, where $\bar{M}_n$ = 11000, 14000, and 34000, is shown in Figure 4. (T-8.3-K-0 swells but is not soluble at these low concentrations due to the high concentration of ionic groups.) The gelation curves for the three trifunctional ionomers occur in the order predicted by Equation (1) for linear difunctional ionomers, i.e. gelation concentration decreases with increasing molecular weight. However, the exponent for the trifuctional polymers is -0.11 rather than -0.5, so that molecular weight has less of an effect for these ionomers compared to those studied by Broze et al. This may be due to the difference in both the

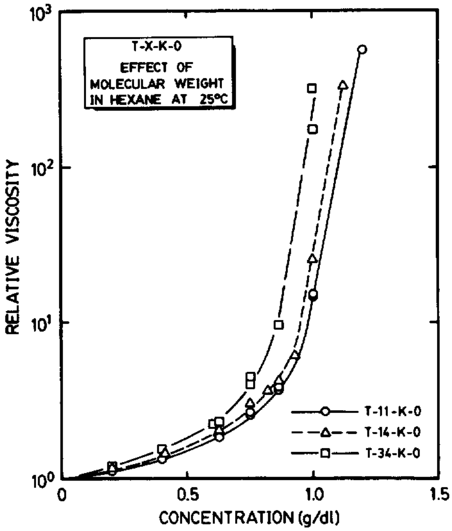


Figure 4. Effect of molecular weight upon the viscosity-concentration behavior of the three-arm star trifunctional ionomer.

nature of the ionic groups and the molecular architecture. The value of k is 3.16. Equation (1) was not obeyed for the two available linear difunctional ionomers. Work is underway on a broader range of molecular weights to confirm this finding and to further investigate molecular weight effects for the linear difunctional ionomers.

CONCLUSIONS

Linear and three-arm star PIB's with $-SO_3^-K^+$ terminal groups display unique solution behavior in a nonpolar solvent, in particular gelation with increasing concentration arising from association of ionic groups. The concentration at which gelation occurs is dependent upon both molecular architecture and molecular weight. Three-arm star trifunctional ionomers gel at lower concentrations than linear difunctional ionomers of the same molecular weight, since their ionic content is greater by a factor of 1.5 and three-arm star ionomers already contain a permanent network junction point. For the three-arm star trifunctional ionomers the gelation concentration decreases with increasing molecular weight.

Further studies are underway to determine the effects of excess neutralizing agent, cation type, solvent polarity, polar cosolvent, and temperature upon the solution behavior of the polyisobutylene-based model ionomers. Additional studies on architecture and molecular weight effects are also in progress.

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