

Sulfonated Polyisobutylene Telechelic Ionomers. XIII. Viscosity Behavior in Nonpolar Solvents and Nonpolar-Polar Solvent Mixtures

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Synopsis

The effect of molecular variables upon the dilute solution viscosity of sulfonated polyisobutylene telechelic ionomers has been studied in both nonpolar solvents and nonpolar-polar solvent mixtures. In nonpolar solvents, association of the terminal salt groups results in an increase in viscosity and gelation at very low concentrations. The concentration at which gelation occurs was found to be dependent upon molecular variables such as architecture, molecular weight, neutralizing cation, extent of neutralization, and the type of solvent. Addition of a small amount of a more polar cosolvent tends to break up ionic associations between polymer chains and thus reduces viscosity. Finally, such solutions with a small amount of polar cosolvent may display dramatic increases in viscosity with increasing temperature due to a dynamic equilibrium between the ionic groups on the polymer chain, the nonpolar solvent, and the polar cosolvent. The results of this work suggest that these ionomers may potentially be useful as viscosity modifiers or "thermal thickeners" in some applications.

INTRODUCTION

The bulk structure and properties of ionomers, i.e., polymers having less than about 15 mol% ionic groups on an otherwise low polarity chain, have been studied extensively in recent years.¹⁻⁵ In the bulk state the nonpolar matrix leads to association or aggregation of the ionic groups. Thus a two-phase morphology is developed in which the ionic aggregates serve as physical crosslinking sites. These ionic crosslinks have a dramatic effect upon the bulk viscoelastic and mechanical properties, potentially leading to increases in the glass transition temperature, higher tensile strength, development of an extended rubbery plateau, etc.

Until recently, relatively little effort had been directed at developing an understanding of the behavior of ionomer solutions. As might be expected, ionic groups may have a substantial effect upon solution behavior. These effects have led to many useful or potentially useful applications. Dietrich⁶

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has reviewed the application of polyurethane ionomers in aqueous dispersions and emulsions. More recently, Lundberg⁷ has considered the use of ionomers as fluid additives in a variety of applications. In addition to the need for research on ionomer solutions due to potential applications, such studies can also shed light on certain phenomena which affect the bulk structure and properties of ionomers. While segment-segment interactions are reduced when a polymer is diluted, the level of interaction between the ionic groups can be controlled by the choice of solvent. When an ionomer is dissolved in a nonpolar solvent, the nonpolar environment leads to association of the ionic groups just as in bulk ionomers. These associations act as physical crosslinks, which tend to increase the apparent molecular weight of the polymer in solution and thus result in an increase in viscosity. This viscosity increase may amount to several orders of magnitude above that of the nonionic polymer. As the polarity of the solvent is increased, the interaction of solvent molecules with the ionic groups increases. This decreases the intermolecular association of the ionic groups, thus decreasing the apparent molecular weight and the viscosity. Obviously, since at least 85% of the ionomer chain is nonpolar or relatively so, it may not be fully soluble in polar solvents. But ionomers may often be dissolved in nonpolar-polar solvent mixtures in which the concentration of the polar solvent, e.g., an alcohol, is very low. Such solutions may display quite unusual temperature effects. In this paper we describe the viscosity behavior of sulfonated polyisobutylene telechelic ionomers in nonpolar solvents and nonpolar-polar solvent mixtures. Before beginning a discussion of this work, however, some of the previous work concerning the viscosity behavior of ionomer solutions in a variety of solvents will be described.

BACKGROUND

As mentioned above, ionomers dissolved in nonpolar solvents associate very strongly due to the low polarity of the medium. Lundberg and Phillips⁸ have shown that sulfonated polystyrene dissolved in tetrahydrofuran (THF), a polar solvent, shows two different types of behavior, depending upon the concentration of the solution. At low concentrations the reduced viscosity of the sulfonated polystyrene solution is lower than that of the precursor polystyrene solution and decreases with increasing level of sulfonation. In this low concentration region, intramolecular associations predominate and the polymer coils are thus contracted. The viscosity is therefore reduced. As concentration increases, more intermolecular association occurs and the viscosity thus increases, becoming greater than that for the precursor polystyrene solution and increasing with increasing level of sulfonation.

Broze, Jérôme, and Teyssie⁹⁻¹¹ have extensively studied the dilute solution behavior of linear carboxylated telechelic ionomers based on polybutadiene and polyisoprene in nonpolar solvents. The unneutralized form of the carboxy-telechelic polyisoprene of 7000 \bar{M}_n (number-average molecular weight) displays a relative viscosity in toluene whose concentration dependence is typical of that for a low molecular weight polymer in solution, i.e., it increases slowly and linearly with concentration. However, upon neutralization with magnesium there is a very sharp increase in viscosity of several orders of magnitude at about 1.5 g/dL. Of course, this dramatic viscosity increase, or gelation, is a result of the intermolecular association of the Mg carboxylate

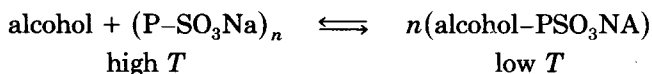
groups. This association increases the apparent molecular weight and/or network character, thus resulting in an increase in the viscosity. The gelation was observed to be strongest for the Mg cation and decreased in the order $Mg > Ca > Ba > Cu > Mn$. More polar solvents and higher temperatures were found to decrease the gelation effect as expected. The gelation concentration was found to decrease with increasing molecular weight according to the equation

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

where k is a proportionality factor. This equation, which was derived by Broze et al.,¹¹ was found to account for the behavior of several types of linear carboxylated telechelic ionomers in nonpolar solvents.¹⁰

Relatively little work has been done on solutions of ionomers in more polar solvents due to their limited solubility in such an environment. However, Lundberg and Phillips⁸ and Peiffer and Lundberg¹² have studied the viscometric behavior of sulfonated polymers in solvents such as dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). It was found that ionomers in these solvents display the typical polyelectrolyte effect at low concentrations, i.e., the viscosity increases with decreasing concentration. The ionic groups are solvated by the polar solvent, leaving high local charges along the chain which repel one another quite strongly. At low concentrations this mutual repulsion of like charges on the same chain expands the polymer coils and increases viscosity. The viscosity increases more dramatically for higher levels of sulfonation. Similar results have been found by Niezette, Vanderschueren, and Aras¹³ and Rochas, Domard, and Rinaudo.¹⁴ Hara and co-workers¹⁵ have recently observed very strong polyelectrolyte behavior for low molecular weight ($\bar{M}_w = 3500$) sulfonated polystyrene at low concentrations in DMF. Since only one to three ionic groups are present per chain, these workers suggest that the intermolecular ionic effects may also contribute to this effect.

Lundberg and Makowski¹⁶ and Lundberg^{17,18} have made extensive studies of the unusual viscosity-temperature effects observed when ionomers are dissolved in a nonpolar solvent containing a small amount of more polar cosolvent. Typically, the viscosity of simple fluids, as well as polymer solutions, decreases with increasing temperature. These workers have found that solutions of ionomers in nonpolar-polar solvent mixtures may display dramatic increases in viscosity with increasing temperature. They interpret this behavior using the equilibrium



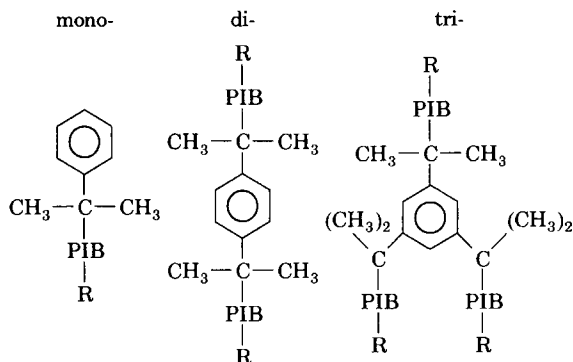
where the associating species (P-SO₃Na) is favored at high temperatures, while the solvated species (alcohol-PSO₃Na) is favored at low temperatures. These workers admit that this is an oversimplification since it ignores the hydrocarbon solvent and the polymer backbone. At higher temperatures, the strength of the ionic interactions is decreased, and thus the viscosity begins to decrease again. Such unusual viscosity-temperature effects in mixed solvents have also been observed by Misra and Mandal.¹⁹

Previous publications from our laboratories have concerned the synthesis,²⁰ sulfonation and neutralization,²¹ and bulk structure-property behavior²¹⁻²⁷ of

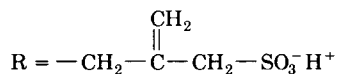
linear and three-arm star sulfonated polyisobutylene telechelic ionomers. The unique molecular structure of these ionomers, as well as the variety of controlled chain microstructures, suggested that study of their behavior in solution would be of interest. These ionomers are soluble in nonpolar solvents and nonpolar-polar solvent mixtures, but not in pure polar solvents due to the very low concentration of ionic groups. Previous reports have concerned initial studies of the viscometric behavior of dilute solutions²⁸ and the viscoelastic behavior of more concentrated solutions²⁹ of these ionomers. The work reported here is an extension of the initial studies of the viscometric behavior. The goal was to characterize the dilute solution behavior of the sulfonated polyisobutylene telechelic ionomers in nonpolar solvents and nonpolar-polar solvent mixtures. Also, we wished to determine the relationships between viscosity and molecular variables such as molecular architecture, molecular weight, neutralizing cation, excess neutralizing agent, etc.

EXPERIMENTAL

The sulfonated polyisobutylene telechelic ionomers used in this work were of three different molecular architectures—linear monofunctional, linear difunctional, and three-arm star trifunctional as illustrated below:



where PIB = polyisobutylene and



The terminal sulfonic acid groups were neutralized with various bases using procedures previously described.²¹ Neutralization was performed in solution, and the solvent was removed by evaporation followed by drying under vacuum at 60°C for 3 days. The nomenclature used to identify the various materials is best illustrated by an example. The designation T-14-K-0 refers to the trifunctional ionomer of 14000 \bar{M}_n neutralized with KOH to the end point (0% excess). The dispersity index was about 1.7 for all ionomer samples.

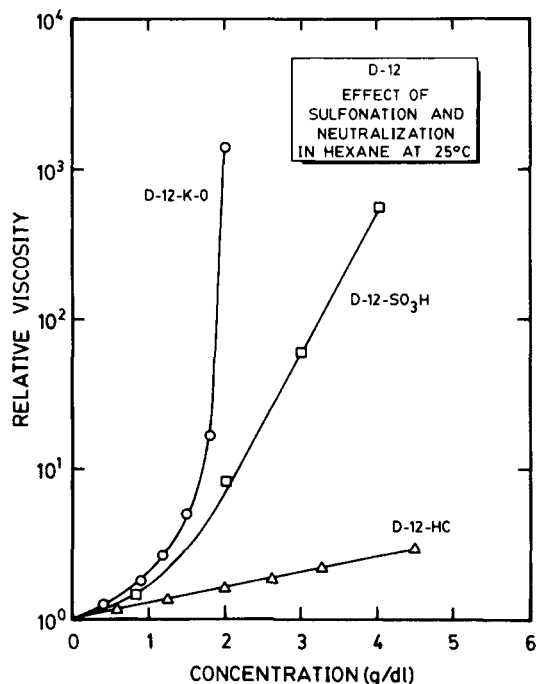
Solutions were prepared in stoppered volumetric flasks using magnetic stirrers for agitation. The solvent used was either hexane or decalin (decahydronaphthalene or DHN) or a mixture of hexanol and decalin. Drying the hexane and decalin over molecular sieves for several days did not affect the viscosities of the ionomer solutions, and so they were used as received. The hexanol was also used as received. The kinematic viscosities were measured using calibrated Ubbelohde dilution viscometers in a thermostated bath

maintained within $\pm 0.2^\circ\text{C}$. Relative viscosities (defined as η/η_s , where η is the kinematic viscosity of the solution and η_s is the kinematic viscosity of the pure solvent) were then calculated from these data. 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 determine 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 in order to check the solution preparation procedure.

RESULTS AND DISCUSSION

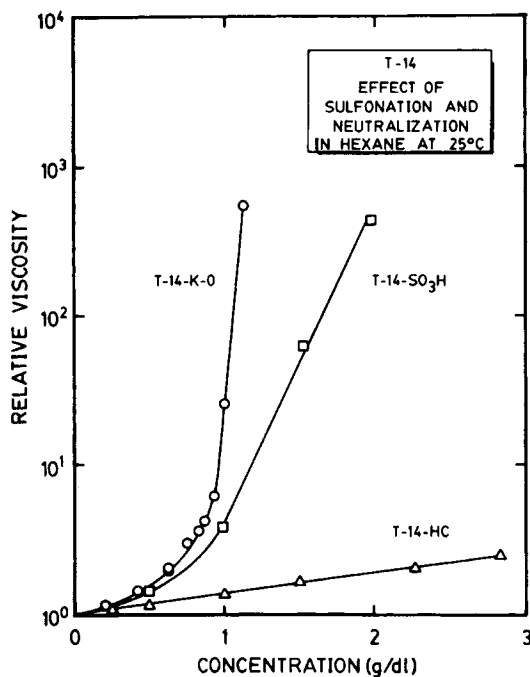
Effect of Sulfonation and Neutralization

Figure 1(a) shows the effect of sulfonation and neutralization upon the relative viscosity vs. concentration behavior in hexane for the linear difunctional ionomer of $12,000 \bar{M}_n$ which was neutralized to the end point with KOH (i.e., D-12-K-0). The linear increase in the logarithm of viscosity as a function of concentration for D-12-HC (the hydrocarbon form prior to sulfonation) is typical of low molecular weight polymers in this concentration



(a)

Fig. 1. Effect of sulfonation and KOH neutralization upon relative viscosity for (a) D-12 and (b) T-14 in hexane at 25°C .



(b)

Fig. 1. (Continued from the previous page.)

range. The nonlinear increase in the logarithm of relative viscosity for D-12-SO₃H clearly indicates some association of the acid groups. Such association was not observed by Broze et al.⁹⁻¹¹ for the carboxylated linear telechelic polymers, i.e., the logarithm of viscosity continued to increase linearly for the acid form at these concentrations. This difference is another indication that sulfonic acid groups associate more strongly than carboxylic acid groups. A high degree of association for the sulfonic acid form of these ionomers was also previously observed in the bulk material.³⁰ The viscosity is observed to decrease with time at room temperature due to decomposition of the sulfonic acid terminal groups. The data shown were obtained as quickly as possible following dissolution of the polymer. Neutralization of the sulfonic acid groups with KOH greatly enhances the ionic associations as shown in Figure 1(a). The potassium sulfonate groups are also thermally stable, and thus the viscosity is observed to remain constant with time. The gelation observed for D-12-K-0 is similar to that observed by Broze et al.⁹⁻¹¹ 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 ionomer, as shown in Figure 1(b) for the 14,000 \bar{M}_n polymer. It should be noted that, following dissolution of the neutralized ionomers, viscosity measurements were made at various times up to 2 weeks after solution preparation. Viscosities were found to be stable over this period of time.

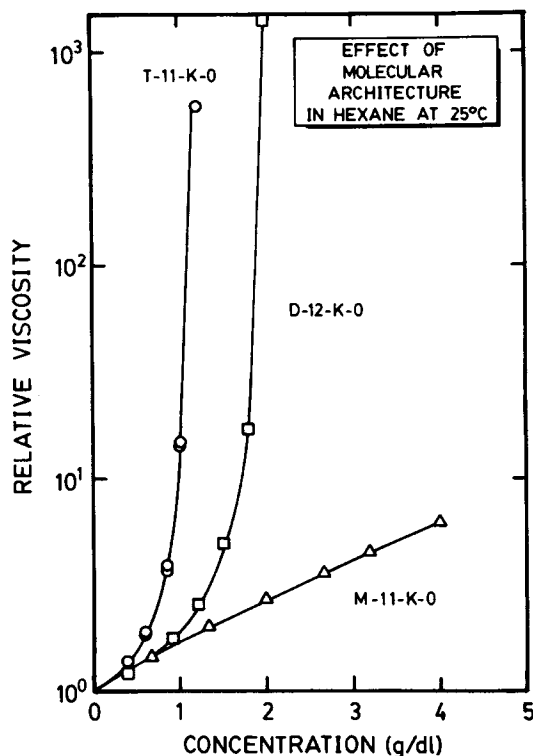


Fig. 2. Effect of molecular architecture upon relative viscosity in hexane (25°C) at an approximately constant number-average molecular weight of 11,000–12,000.

Effect of Molecular Architecture

The effect of molecular architecture upon the relative viscosity of the potassium-neutralized species is shown in Figure 2 where the architecture is varied while holding the number-average molecular weight approximately constant at 11,000–12,000. The solution of the monofunctional species 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 starlike molecules or micellar structures with a central ionic region. The slight downward curvature of the relative viscosity vs. concentration curve 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 of the aggregate.^{31,32} 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 1(a) and 2, the solution of D-12-K-0 does display gelation. The solution of T-11-K-0 also gels but at a much 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 and higher order associations are necessary for network formation. As discussed above, the probability of triplets and higher order associations increases with increasing polymer concentration. Therefore, at the gel concentration for T-11-K-0 the ionic associations are predominantly ion pairs—sufficient for gelation of the three-arm star trifunctional 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.

It is of interest to observe the gelation curves of D-12-K-0 and T-11-K-0 on the basis of ion concentration rather than concentration of polymer. This can be done by using the molecular weight to calculate the *moles of molecules per volume* from the weight per volume and then multiplying by either 2 or 3, depending upon functionality, to obtain the *moles of ions per volume* or the *ionic concentration*. These data are presented in Figure 3. Clearly, for these two ionomers of similar molecular weight but different chain microstructures,

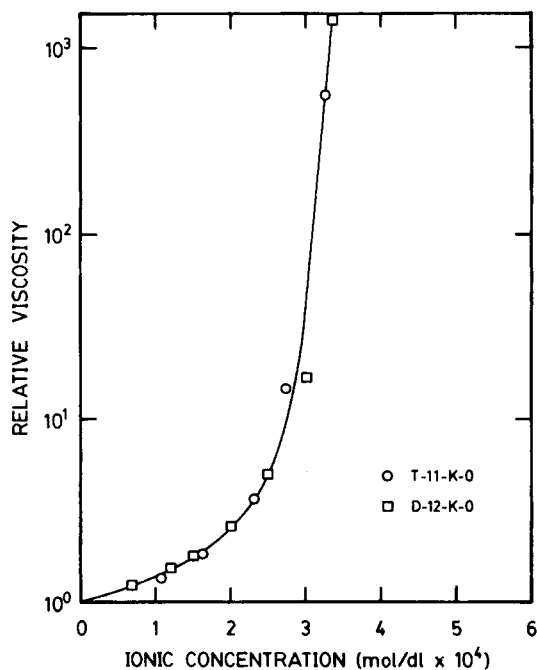


Fig. 3. Gelation curves for D-12-K-0 (□) and T-11-K-0 (○) in hexane at 25°C based on ionic concentration.

the data fall on essentially the same curve. It thus appears from the data, at least in this molecular weight range, that ionic concentration is more important than molecular architecture in determining the gelation concentration. It would certainly be of interest to perform similar studies at other molecular weights to determine if such behavior is observed over a wide range of molecular weights.

Effect of Molecular Weight

The effect of molecular weight of the three-arm star trifunctional ionomer, $\bar{M}_n = 11,000, 14,000, \text{ and } 34,000$, on relative viscosity is shown in Figure 4. The T-8.3-K-0 material 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 eq. (1) for linear difunctional ionomers, i.e., gelation concentration decreases with increasing molecular weight. However, the exponent for the trifunctional molecules 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.^{10,11} The differences in both the nature of the ionic groups and the molecular architecture may contribute to this. The value of k is 3.16. The plot of $\log C_{\text{gel}}$ vs. $\log \bar{M}_n$ from which the values of k and the exponent were determined is shown in Figure 5.

Figure 6 shows the effect of molecular weight upon the gelation behavior of the linear difunctional ionomer neutralized with KOH. The trend here is different from that observed by Broze et al.^{10,11} for the linear carboxylated ionomers and different also from that reported here for the three-arm star sulfonated polyisobutylene telechelic ionomers. That is, the low molecular

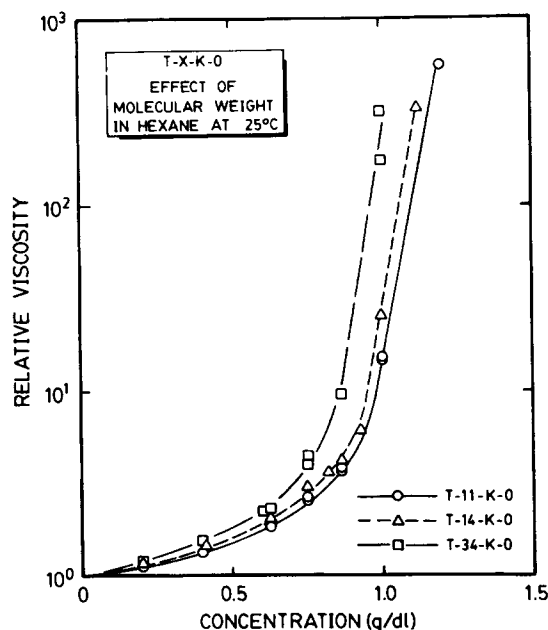


Fig. 4. Effect of molecular weight upon the relative viscosity-concentration behavior of the three-arm star trifunctional ionomer in hexane at 25°C: (—○—) T-11-K-0; (---△---) T-14-K-0; (□) T-34-K-0.

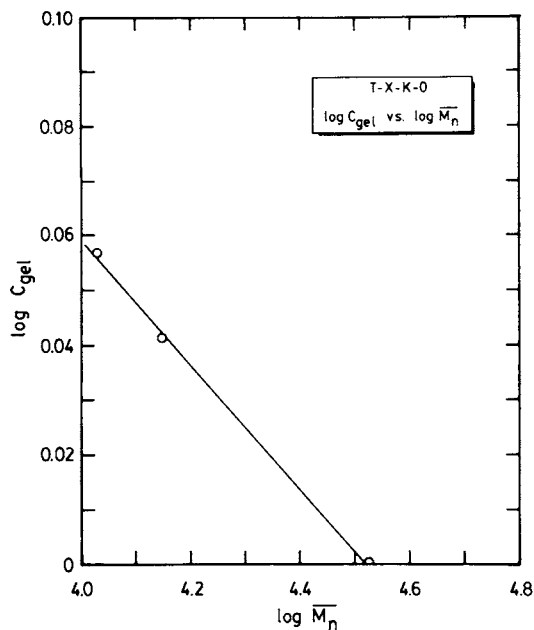


Fig. 5. Plot of log of gelation concentration vs. log of molecular weight for the three-arm star trifunctional ionomers, T-X-K-0.

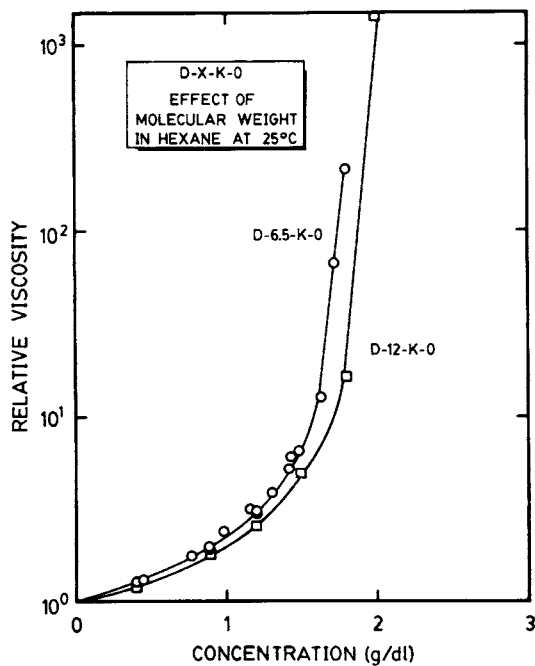


Fig. 6. Effect of molecular weight upon the relative viscosity-concentration behavior for the linear difunctional ionomers, D-X-K-0, in hexane at 25°C.

weight ionomer, D-6.5-K-0, gels at a lower concentration than the higher molecular weight ionomer, D-12-K-0. Even though the trend observed for these ionomers is different, it does agree with the idea that higher ionic concentrations result in a higher degree of association, thus leading to gelation at lower concentrations. It seems possible that in this low molecular weight region the ionic concentration may be more important than the molecular weight. As molecular weight increases, there should be a point where molecular weight becomes the important variable due to the occurrence of entanglements, resulting in a decrease of the gelation concentration as molecular weight increases. Such a transition has been observed for the bulk storage modulus for linear carboxylated telechelic ionomers by Jérôme and Broze³³ as well as the bulk storage modulus for the three-arm star sulfonated polyisobutylene telechelic ionomers by Tant et al.³⁴ Such a transition has not, however, been observed for solutions. In order to test this hypothesis, it would be necessary to investigate the gelation behavior of a broader series of molecular weight materials in solution.

The gelation of telechelic ionomers in a nonpolar solvent results from association of the ionic endgroups. If triplet or higher order associations are possible, as suggested by Broze et al.,¹¹ then linear telechelic polymers may indeed form networks 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 to simple chain extension. If it is assumed that only chain extension occurs, it is possible to calculate the apparent degree of polymerization, DP, as a function of concentration from the relative viscosity. In other words, the apparent DP is that DP which would be necessary to cause the observed relative viscosity. (It is important to note here that DP does not refer to the number of monomer groups but to the number of telechelic chains which are joined end-to-end to produce a single chain.) The specific viscosity η_{sp} is given as a function of the intrinsic viscosity $[\eta]$ by the well-known Huggins equation,³⁵ i.e.,

$$\eta_{sp} = [\eta] + k_1[\eta]^2 c \quad (2)$$

The specific viscosity is given by

$$\eta_{sp} = \eta_{rel} - 1 \quad (3)$$

and the intrinsic viscosity by

$$[\eta] = \eta_{sp}/c|_{c \rightarrow 0} \quad (4)$$

The intrinsic viscosity is also related to the viscosity-average molecular weight \bar{M}_v by the empirical Mark-Houwink equation, i.e.,

$$[\eta] = k\bar{M}_v^a \quad (5)$$

where k and a are constants dependent upon the polymer-solvent system.

Substituting eq. (5) into eq. (2) gives

$$\eta_{sp}/c = k\bar{M}_v^a + k_1k^2\bar{M}_v^{2a}c \quad (6)$$

Assuming that only chain extension occurs, the apparent \bar{M}_v may be calculated at various concentrations since η_{sp}/c is measured directly and $a = 0.7$, $k = 2.6 \times 10^{-4}$, and $k_1 = 0.3$ for the polyisobutylene-cyclohexane system.³⁶ The apparent degree of polymerization, \bar{DP} , is then calculated by dividing the apparent \bar{M}_v by \bar{M}_n , where the apparent \bar{M}_v is determined from experimental viscosity measurements and eq. (6). Of course, this calculation is accurate only for a narrow molecular weight distribution and becomes exact for a polydispersity of 1.0. For these ionomers, $\bar{M}_w/\bar{M}_n = 1.7$ and therefore the calculation is an approximation. The results for D-6.5-K-0 and D-12-K-0 are shown in Figure 7. It is certainly not clear why there should be an abrupt increase in the apparent degree of polymerization below 2 g/dL, which would occur if chain extension was solely responsible for the viscosity increase. It is likely that the ionic associations which occur are of both types, i.e., triplets and higher order associations, which result in multifunctional network junction points and ion pair associations, which result in simple chain extension. Dynamic experiments on gels formed by these linear difunctional species, and which are the subject of a separate publication,³⁷ suggest that an elastomeric network is indeed formed since the storage modulus G' is in some cases constant over the entire range of experimentally accessible frequencies. Intramolecular ion pair associations may also occur, resulting in cyclic structures. These cyclic species may be mutually independent or they may be

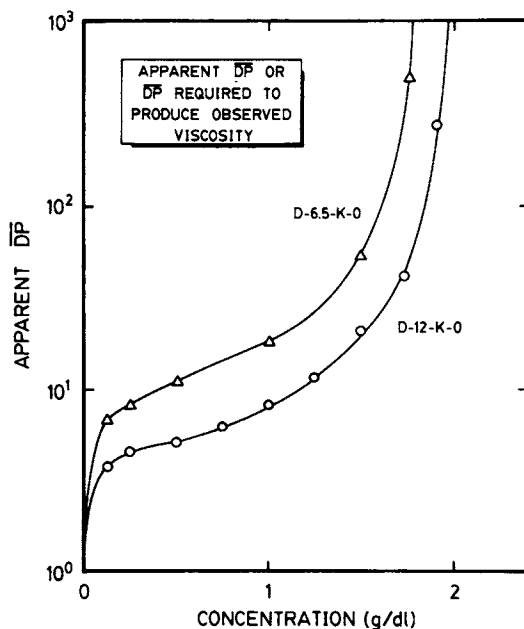


Fig. 7. Apparent degree of polymerization required to produce observed viscosity for D-6.5-K-0 and D-12-K-0 in hexane at 25°C.

interlocked to form catenates as suggested by Broze et al.¹¹ Recently, Misra and Mandal¹⁹ have suggested, based upon osmotic pressure measurements, that the degree of association remains essentially constant in the concentration range 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.

Effect of Excess Neutralizing Agent

The fact that excess neutralizing agent strongly affects the solid state mechanical properties of the sulfonated polyisobutylene telechelic ionomers²⁵ suggests that this variable may also have a strong effect upon the viscosity behavior in nonpolar solvents. Figure 8 shows the effect of both the type of neutralizing agent and excess neutralizing agent upon the viscosity behavior in hexane of the D-6.5 and D-12 materials. As shown in Figure 8(a), the gelation curves for D-6.5-K-0, D-6.5-Ca-0, and D-6.5-Ca-100 are essentially the same, while D-6.5-K-100 apparently gels at a slightly lower concentration. It is not clear why the D-6.5-K-100 should associate more strongly in solution than the D-6.5-Ca-100. The difference cannot be attributed to experimental

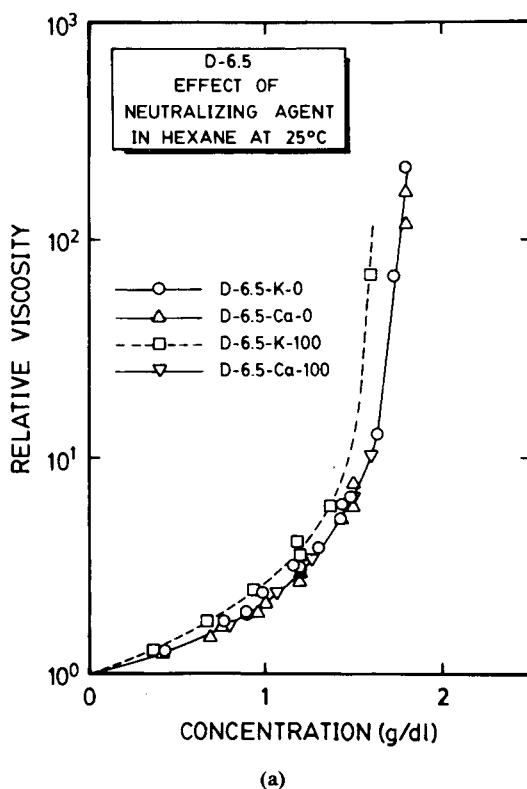


Fig. 8. Effect of neutralizing agent and excess neutralizing agent on viscosity behavior of (a) D-6.5 and (b) D-12 in hexane at 25°C. (a) (—○—) D-6.5-K-0; (—△—) D-6.5-Ca-0; (—□—) D-6.5-K-100; (—▽—) D-6.5-Ca-100. (b) (—○—) D-12-K-0; (—△—) D-12-Ca-0; (□) D-12-K-100; (▽) D-12-Ca-100; (—◇—) D-12-ZnAc-100.

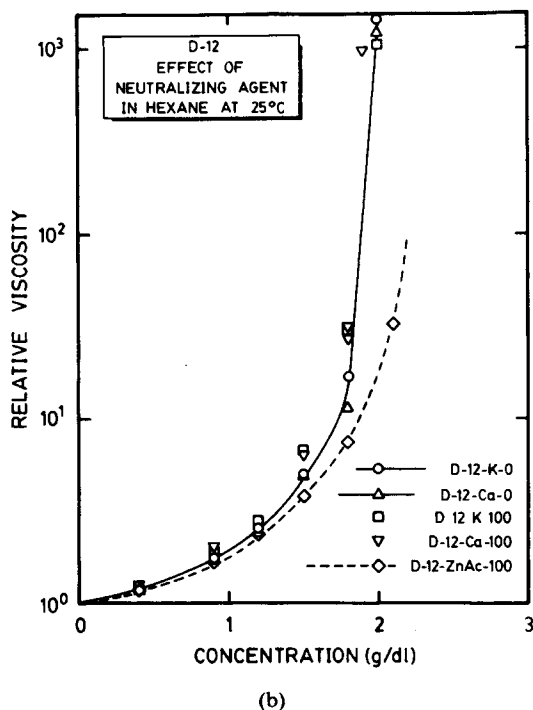


Fig. 8. (Continued from the previous page.)

error in either the solution preparation procedure or the measurements, since the results were found to be quite reproducible. It also cannot be attributed to the difference in number of cations present (twice as many K^+ as Ca^{2+}) since the D-12 materials show somewhat different behavior. In Figure 8(b) it is clear that at each concentration (except the highest) the viscosities of the D-12 solutions containing excess neutralizing agent (for both potassium and calcium) are higher than that of the solutions of stoichiometrically neutralized material. Thus, excess neutralizing agent results in somewhat stronger association but not to the extent found for bulk properties. The likely reason for the smaller effect in solution is that much of the excess neutralizing agent is dispersed in the solvent, leaving less associated with the ionic regions. Thus less reinforcement of the ionic associations occurs due to the dilution of the excess neutralizing agent. Figure 8(b) also shows the behavior of the D-12-ZnAc-100 solution. The weaker association of zinc is due to its less ionic, more coordinative character,³⁸ which has also been clearly observed in the bulk.²⁷

Effect of Solvent

Figure 9 shows the viscosity behavior of T-11-K-0 in hexane and tetrahydrofuran (THF). The gelation in hexane, as has been discussed, is due to the association of the terminal ionic groups in the low dielectric environment provided by the solvent and the PIB chains. In THF, a more polar solvent, the solvent molecules interact more strongly with the ionic groups on the polymer chains. Thus the ionic groups interact less strongly with each other,

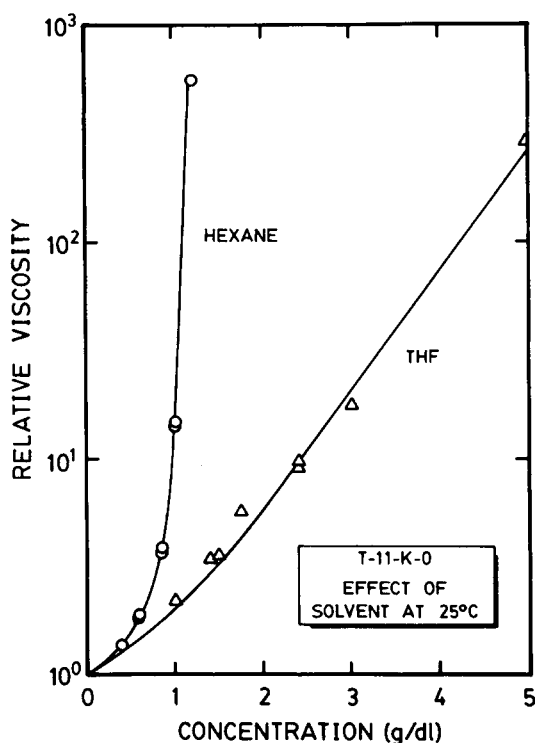
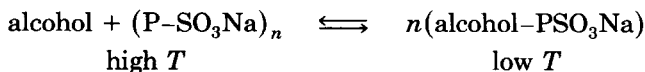


Fig. 9. Relative viscosity behavior of T-11-K-0 in hexane and THF at 25°C.

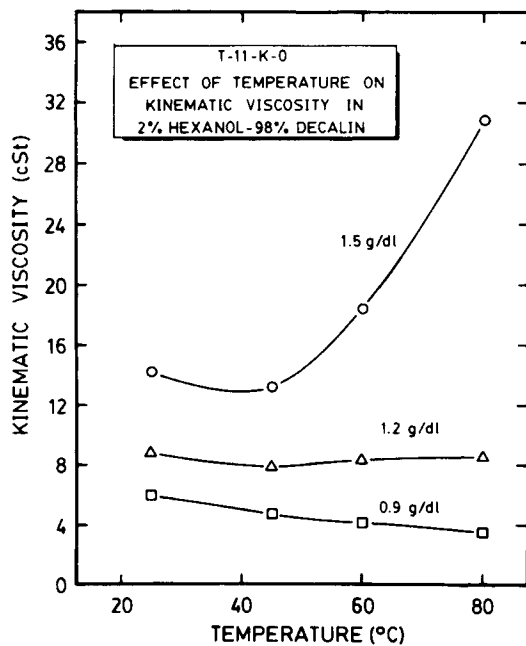
and the viscosity is greatly reduced. As expected, the type of solvent has a large effect upon the strength of the association between the ionic groups.

Effect of Temperature in Nonpolar-Polar Solvent Mixtures

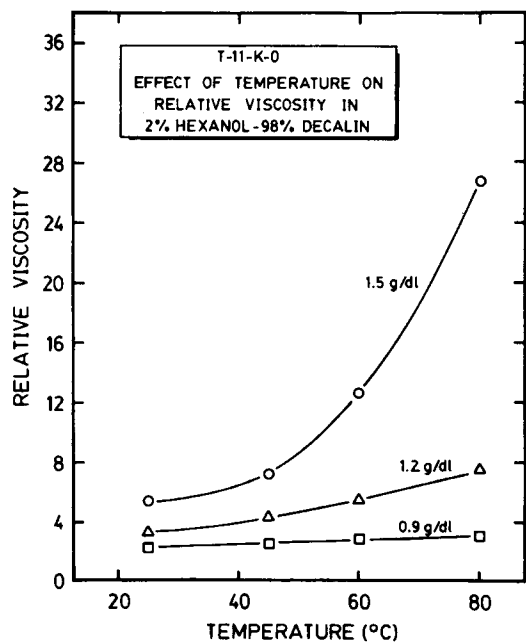
In typical fluids, both low molecular weight substances and high polymers, viscosity is normally observed to decrease with increasing temperature. This decrease in viscosity is due to the higher thermal energy which causes more rapid molecular motions (shorter relaxation times) and more free volume in which these motions may occur. As mentioned previously, Lundberg and Makowski,¹⁶ Lundberg,¹⁷ and Misra and Mandal¹⁹ have observed that the viscosity of an ionomer solution may increase with temperature when the solvent is a mixture of a nonpolar solvent and a small amount of a polar solvent. This increase in viscosity is due to the alteration of the strength of ionic interaction with temperature according to the relationship



so that the associating species (P-SO₃Na) is favored at high temperatures. This same type of behavior may be observed for the sulfonated polyisobutylene telechelic ionomers in mixed solvents. Figure 10(a) shows the effect of temperature on the kinematic viscosity of T-11-K-0 in a 2% hexanol-98%



(a)



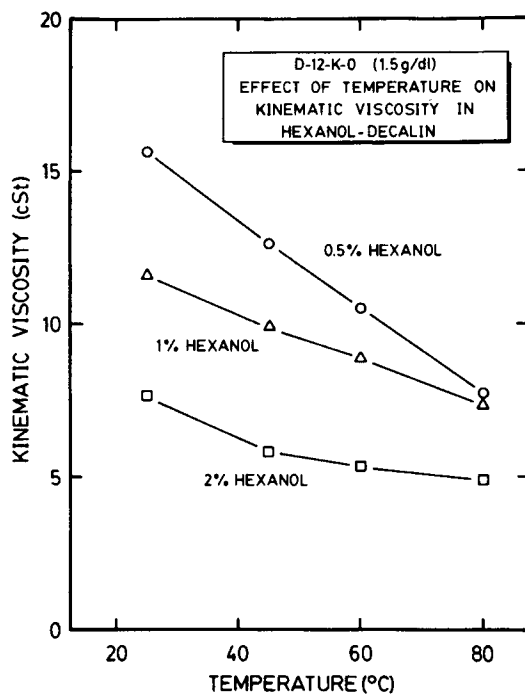
(b)

Fig. 10. Effect of temperature on (a) kinematic viscosity and (b) relative viscosity of T-11-K-0 in 2% hexanol-98% decalin.

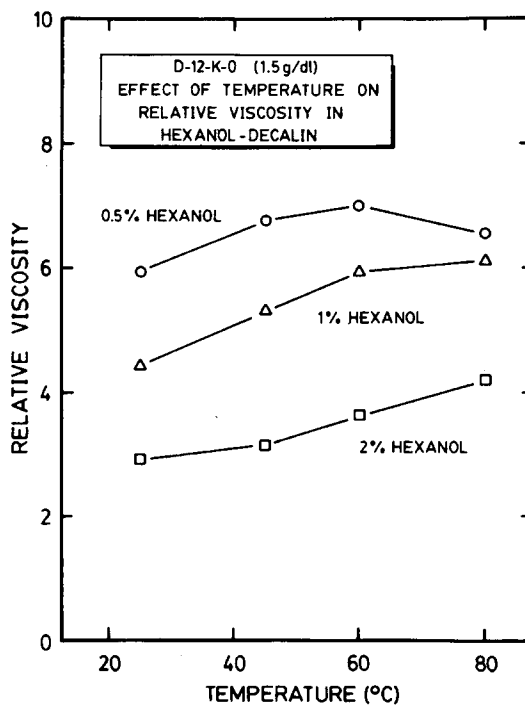
decalin mixture at three different polymer concentrations. At a concentration of 0.9 g/dL the kinematic viscosity decreases over the entire temperature range studied, i.e., 25–80°C. At 1.2 g/dL the kinematic viscosity is relatively constant over this temperature range. Upon increasing the concentration from 1.2 to 1.5 g/dL, the kinematic viscosity is observed to decrease slightly from 25 to 45°C. It then increases dramatically in the temperature range from 45 to 80°C, increasing by a factor of 2.5. Figure 10(b) shows this same data plotted in terms of *relative viscosity* instead of *kinematic viscosity*. Since the relative viscosity is simply the kinematic viscosity of the solution divided by the kinematic viscosity of the solvent, the effect of the decreasing solvent viscosity is removed in these data. Thus the effect of temperature upon the solute itself is being observed. For this particular case the relative viscosity increases throughout the temperature range of 25–80°C at all three concentrations and the effect becomes stronger with increasing concentration and increasing temperature. The fact that the effect increases with increasing concentration is certainly because of the more extensive interaction of the ionic groups at higher concentrations.

Figure 11 shows the effect of temperature upon the kinematic and relative viscosities of D-12-K-0 at a concentration of 1.5 g/dL in hexanol/decalin mixtures containing 0.5, 1.0, and 2.0% hexanol. Clearly, the kinematic viscosity of all three solutions steadily decreases as temperature is increased from 25 to 80°C. The relative viscosity, however, is observed to increase, except for the lowest hexanol content solution, between 60 and 80°C. Lundberg and Makowski¹⁶ observed similar decreases in viscosity of ionomer/mixed solvent systems at high temperatures, which they attributed to the decreasing strength of ionic association which would be expected to occur at these temperatures. But it is difficult to explain on that basis alone why the 0.5% hexanol solution in Figure 11(b) displays a decrease in relative viscosity between 60 and 80°C, while the 1 and 2% hexanol solutions display an increase. This behavior might be interpreted in the following way. At room temperature the hexanol is principally dispersed within the ionic regions, which it tends to solvate, and the remainder of the solution. As temperature increases, the polar hexanol molecules become more soluble in the nonpolar decalin, and thus the equilibrium distribution of the hexanol molecules between the ionic and nonionic regions changes. As the polar molecules are removed from the ionic aggregates, the aggregates associate more strongly and the viscosity increases. There is likely a critical number of hexanol molecules associated with the ionic aggregates which will remain associated no matter how high the solubility of hexanol in decalin becomes. This critical point would be expected to be reached at a lower temperature for the solution with the lowest concentration of hexanol, which is indeed the observed behavior.

Figure 12 shows the same type of data for the same material, D-12-K-0, except at a polymer concentration of 2.0 instead of 1.5 g/dL. The behavior is clearly quite similar except that the increase in viscosity with temperature is much stronger, since the molecules interact with one another much more at this higher concentration. Figure 13 shows this same data plotted in terms of relative viscosity vs. percent hexanol at each of four different temperatures. There is a sharp decrease in relative viscosity at each temperature up to 1% hexanol. Above this hexanol content the further decreases in viscosity become

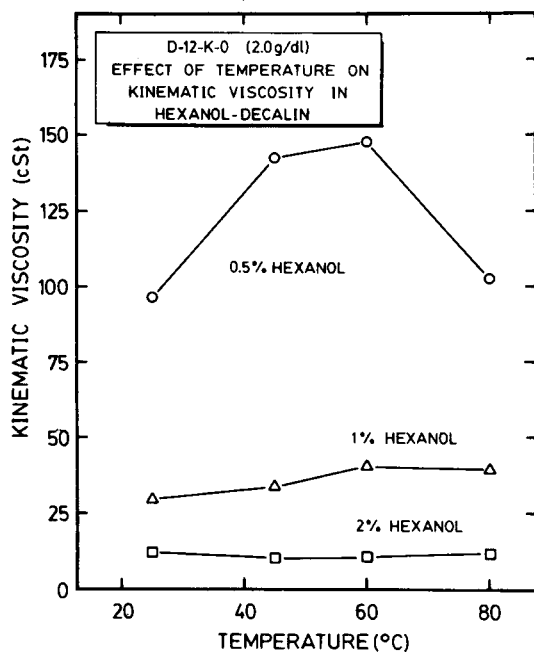


(a)

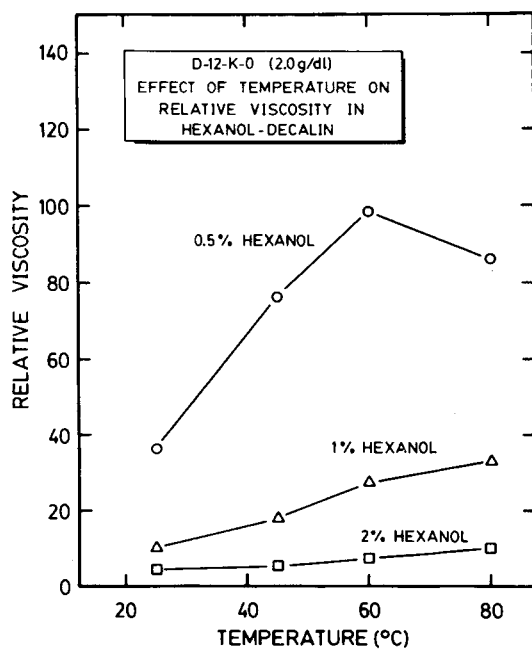


(b)

Fig. 11. Effect of temperature on (a) kinematic viscosity and (b) relative viscosity of D-12-K-0 at a concentration of 1.5 g/dL in hexanol-decalin.



(a)



(b)

Fig. 12. Effect of temperature on (a) kinematic viscosity and (b) relative viscosity of D-12-K-0 at a concentration of 2.0 g/dL in hexanol-decalin.

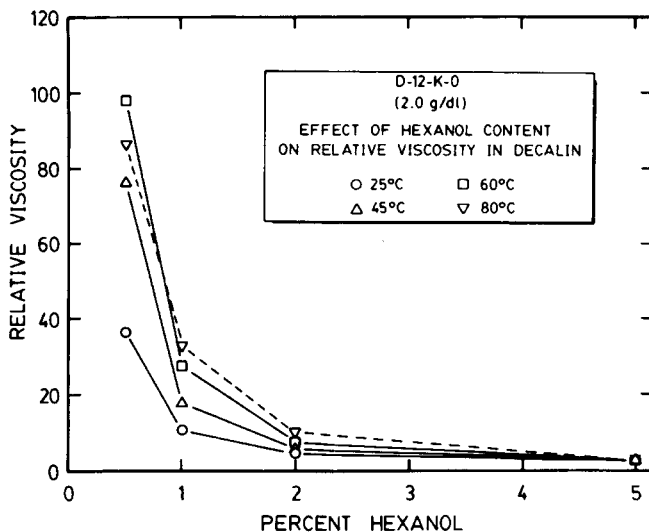
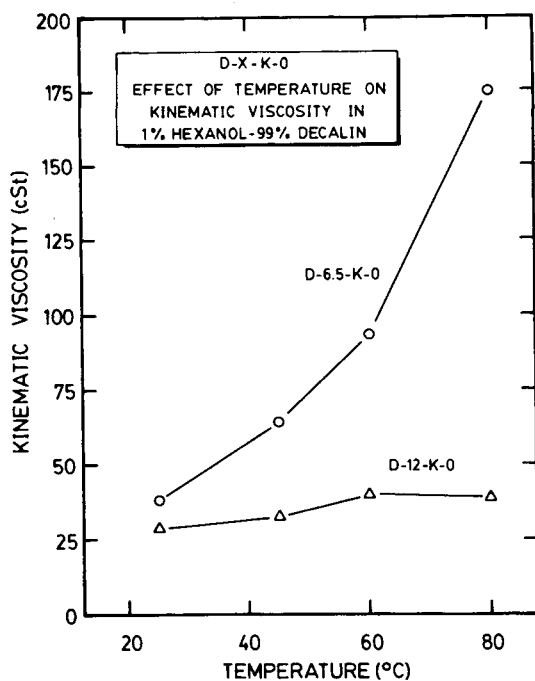


Fig. 13. Effect of hexanol content on relative viscosity in decalin of D-12-K-0 at a concentration of 2.0 g/dL: (○) 25°C; (△) 45°C; (□) 60°C; (▽) 80°C.

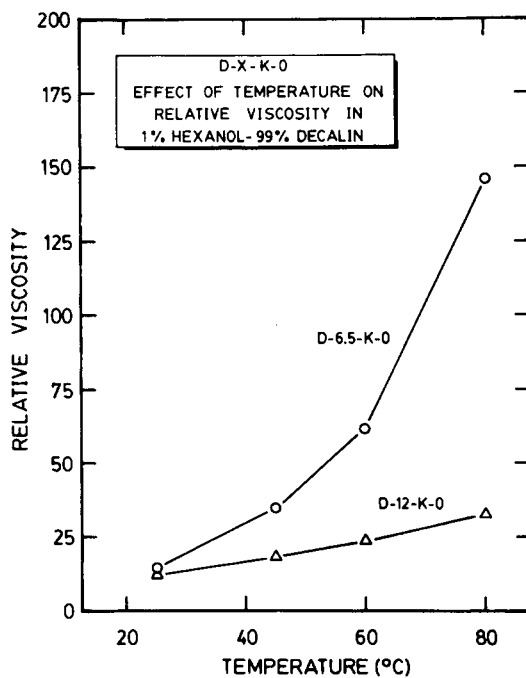
progressively smaller until at a 5% hexanol concentration the viscosities at all four temperatures are the same. Lundberg and Makowski¹⁶ have observed similar behavior for sulfonated polystyrene in mixed solvents, and have suggested that as additional polar cosolvent is added the ionic groups are, in a way, being "titrated." It is clear that the "end point" in this case must be near 1–2% hexanol since further addition of hexanol has little effect upon viscosity.

Figure 14 compares the kinematic and relative viscosities for D-6.5-K-0 and D-12-K-0 at a concentration of 2 g/dL in 1% hexanol–99% decalin. Clearly, the increase in viscosity is much greater for the D-6.5 solution than for the D-12 solution because there are almost twice as many ionic groups present. Between 25 and 80°C the D-6.5-K-0 solution experiences a kinematic viscosity increase of 360% and a relative viscosity increase of 870%! Thus very low concentrations of ionomer in mixed solvents may result in phenomenal viscosity increases with increasing temperature, thereby providing a unique "thermal thickening" behavior.

The kinetics of these viscosity changes are also of importance. Figure 15 shows the time dependent relative viscosity of D-6.5-K-0 at a concentration of 2.0 g/dL in 1% hexanol–99% decalin following a temperature jump from 25 to 45°C. It is clear from these data that it takes about 10 h for the viscosity to reach equilibrium following the temperature jump. Equilibrium viscosities were typically reached more quickly at higher temperatures, with a time of about 2 h being required to establish equilibrium at 80°C. The viscosities reported in this paper for these ionomers in mixed solvents are all equilibrium viscosities, and were found to be quite reproducible provided that sufficient time was allowed for equilibrium to be reached.



(a)



(b)

Fig. 14. Effect of temperature on (a) kinematic viscosity and (b) relative viscosity of D-6.5-K-0 and D-12-K-0 at 2.0 g/dL in 1% hexanol-99% decalin.

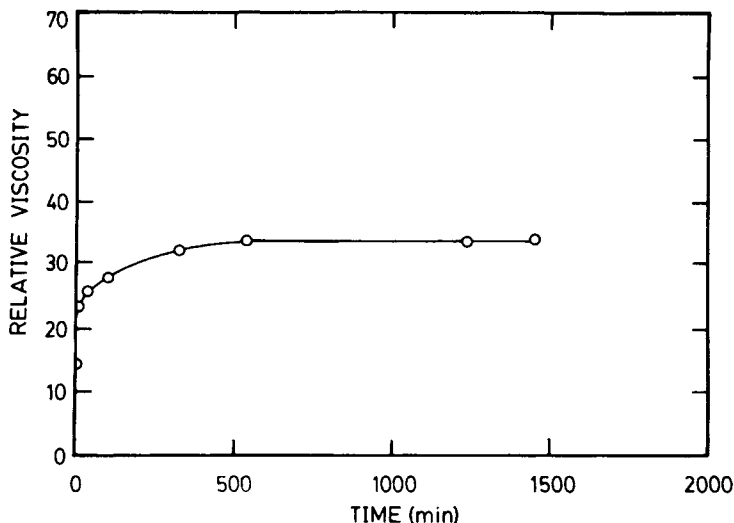


Fig. 15. Time-dependent relative viscosity of D-6.5-K-0 in 1% hexanol-99% decalin following a temperature jump from 25 to 45°C.

CONCLUSIONS

The sulfonated polyisobutylene telechelic ionomers were observed to gel in nonpolar solvents such as hexane at concentrations as low as 1–2 g/dL. The gelation concentration was found to be lower for the trifunctional ionomer than for the difunctional ionomer of similar molecular weight due to its higher concentration of ionic groups as well as the presence of a permanent covalent network junction. However, when plotted vs. ionic concentration rather than polymer concentration, the gelation curves were found to coincide, at least for the particular molecular weight range studied. For the trifunctional ionomers, the gelation concentration decreases with increasing molecular weight, while the reverse trend was found for the difunctional ionomers. This unexpected result for the difunctional ionomers may be due to the low molecular weights of the difunctional species studied, i.e., \bar{M}_n of 6500 and 12,000. It is possible that in this low molecular weight range the ion content becomes more important than entanglements. Ionomers neutralized with potassium and calcium gel at about the same concentration, while those neutralized with zinc gel at a somewhat higher concentration due to the less ionic, more coordinative character of zinc. Excess neutralizing agent was found to slightly decrease the gelation concentration.

In nonpolar-polar solvent mixtures, an increase in relative viscosity is observed with increasing temperature. The viscosity increase is a function of both the concentration of the ionomer and the concentration of polar cosolvent. The molecular weight, and therefore the ion content, was also found to be a factor. Fluids which display increasing viscosity with increasing temperature are obviously quite unusual. The fact that these ionomers in nonpolar-polar solvent mixtures display this type of viscosity-temperature behavior suggests that they may be useful as viscosity control agents or "thermal thickeners" in applications requiring viscosity to be maintained or increased at high temperatures.

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