

# Sulfonated Polyisobutylene Telechelic Ionomers. XIV. Viscoelastic Behavior of Concentrated Solutions in Nonpolar Solvents

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## SYNOPSIS

The effect of molecular variables upon the dynamic viscoelastic behavior of solutions of sulfonated polyisobutylene telechelic ionomers in nonpolar solvents has been investigated. Intermolecular association of the ionic end groups in nonpolar media results in the formation of a transient ionic network which displays a viscous response at low frequencies and an elastic response at high frequencies. The frequency of the transition from viscous behavior to elastic behavior, as well as the plateau storage modulus, is dependent upon molecular variables such as architecture, molecular weight, neutralizing cation, and extent of neutralization. Variables which affect the strength of the ionic interactions, such as temperature and the type of solvent, also influence the viscoelastic response. Solutions of ionomers neutralized with cations of Groups IA and IIA, such as potassium and calcium, behave elastically over most of the experimentally accessible frequency range, while those neutralized with transition metals, such as zinc, display viscous flow over a rather wide range at low frequencies. As in previous studies of dilute solution viscosity behavior, the three-arm star trifunctional species was found to form a more extensive network in nonpolar solvents than the linear difunctional species at equivalent concentrations. The failure of time-temperature superposition indicates that these solutions are thermoheologically complex.

## INTRODUCTION

Although the bulk structure-property behavior of ionomers has been studied rather extensively for a number of years, only recently has the solution behavior of these materials attracted widespread attention. Ionomers generally contain less than about

15 mol% ionic groups along an otherwise nonpolar chain, and it is this difference in polarity between the main chain and the (usually) randomly placed ionic groups along the chain that imparts to these materials their unique properties in the bulk. Likewise, it is this same structural feature which leads to the unusual, and potentially very useful, behavior of ionomer solutions. Recent reviews of the behavior of ionomer solutions have been written by both Lundberg<sup>1</sup> and Tant and Wilkes.<sup>2</sup> In addition, Lundberg<sup>3</sup> has considered their potential utilization as fluid additives.

The behavior of ionomer solutions may vary greatly depending upon the solvent used. In nonpolar

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solvents the ionic groups tend to associate and thus viscosity is increased at all concentrations.<sup>4-10</sup> In polar solvents the ionic groups are ionized resulting in net positive charges (for cationomers) along the chain, and these solutions thus display the typical polyelectrolyte effect at very low concentrations.<sup>11-15</sup> Lundberg and Makowski<sup>7</sup> have found that solutions of polystyrene-based metal sulfonate ionomers in mixed solvents display a viscosity which may increase, remain relatively constant, or display maxima or minima over broad temperature ranges. Misra and Mandal<sup>9</sup> and Tant et al.<sup>16</sup> have observed similar effects for telechelic ionomers in mixed solvents.

Although viscosity effects in ionomer solutions are extremely important and give a good indication of molecular interactions, much more information concerning molecular dynamics may be obtained by studying the dynamic viscoelastic behavior, i.e., the response of the solution to a small amplitude oscillatory deformation. A recent series of papers by Agarwal and Lundberg<sup>17,18</sup> and Agarwal et al.<sup>19</sup> has focused on the viscoelastic behavior of concentrated solutions of sulfonated EPDM ionomers both in nonpolar solvents and nonpolar-polar solvent mixtures. Of particular interest is the fact that the storage modulus master curve of a 5 wt % solution of the zinc(II)-neutralized ionomer in a (nonpolar) paraffinic oil shows typical solution behavior in the low frequency terminal region, but displays a rubbery plateau extending several decades at high frequencies.<sup>17</sup> This master curve was obtained by shifting curves obtained isothermally at temperatures ranging from 0 to 135°C. Such a wide range of rheological responses for a single polymer solution is quite unusual. Similar results have been observed by Tant, Wilkes, and Kennedy<sup>20</sup> for decalin solutions of sulfonated polyisobutylene telechelic ionomers neutralized with zinc(II), although for these solutions this same diverse range of rheological responses may be observed at a single temperature. It is also significant that time-temperature superposition is successful for the zinc(II)-neutralized sulfonated EPDM solutions but not for the magnesium(II)- and barium(II)-neutralized sulfonated EPDM solutions.<sup>18</sup> The magnesium(II)-neutralized sulfonated EPDM solutions show much less flow in the low-frequency region than those neutralized with zinc(II), while the barium(II)-neutralized sulfonated EPDM solutions behave essentially as a rubbery network in the low-frequency region.

Agarwal et al.<sup>19</sup> have studied the dynamic viscoelastic behavior of sulfonated EPDM in nonpolar-polar mixed solvents. For a 2% solution of magnesium(II)-neutralized sulfonated EPDM (0.67 mol

% sulfonate groups) in a solvent mixture consisting of 98.5% paraffinic oil and 1.5% hexanol, an increase in  $G'$  is observed at all frequencies as the temperature is increased from 22.3 to 75.9°C. This would be expected, of course, from the viscosity behavior of such solutions since the viscosity is observed to increase with increasing temperature. The curves are also not superposable due to the fact that other mechanisms, such as the change in the association of the polar solvent with the ionic groups along the polymer chain, are occurring.

In a similar vein, Broze et al.<sup>21</sup> have studied the viscoelastic behavior of solutions of carboxy-telechelic polybutadiene having a number-average molecular weight of 4600 in decalin. The dynamic viscoelastic behavior of these solutions is highly dependent upon the cation used to neutralize the carboxylic acid groups. The curves for  $G'$  and  $G''$  are superposable, at least in the relatively narrow temperature range between 297 and 342°C, and the shift factors obey an Arrhenius type of dependence. For this series of materials neutralized with alkaline earth cations, the elasticity of the solution increases with decreasing cation size.

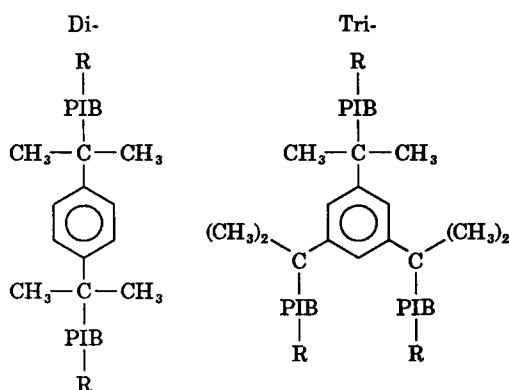
Finally, Gonzalez<sup>22,23</sup> has theoretically approached the problem of predicting the viscosity and viscoelastic behavior of ionomer gels. By regarding the system as a polymer solution with transient crosslinks, he was able to derive an expression for the viscosity of ionomer gels using reptation arguments. The deviatoric stress tensor was calculated, and, assuming small amplitude oscillatory shear flow, the values of the dynamic moduli  $G'$  and  $G''$  were calculated by using the classical equations from linear viscoelastic theory. The calculated plots of  $G'$  and  $G''$  as a function of frequency are remarkably similar, qualitatively, to the experimental results of Agarwal et al.<sup>17-19</sup> and Tant et al.<sup>20</sup> discussed above. That is, in the low frequency terminal region  $G'$  and  $G''$  display slopes of 2 and 1, respectively. Then at a critical frequency  $G'$  reaches a plateau and  $G''$  goes through a maximum as the solution/gel begins to respond in a more networklike manner.

As discussed above, we have previously reported the unique viscoelastic behavior displayed by sulfonated polyisobutylene telechelic ionomers in decalin.<sup>20</sup> Telechelic ionomers, which have the ionic groups located only at the chain ends, have served as model ionomers for experimental studies of structure-property behavior both in the bulk and in solution. This paper represents an extension of our previous work, and in particular addresses the variables of molecular architecture, neutralizing cation type, molecular weight, concentration, and temper-

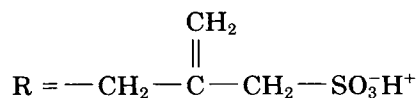
ature upon the viscoelastic behavior of sulfonated polyisobutylene telechelic ionomers in nonpolar solvents.

## EXPERIMENTAL

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



where PIB = polyisobutylene and



They were synthesized as previously described.<sup>24</sup>

The terminal sulfonic acid groups were neutralized to the end point with potassium hydroxide, calcium hydroxide, and zinc acetate using techniques described previously.<sup>25</sup> The procedure for neutralizing with cerium (III) acetate has been described by Tant.<sup>26</sup> Neutralizations were performed in solution, with the solvent being removed by evaporation and then drying under vacuum at 60°C for 3 days. The nomenclature used for sample designation in this paper is best described by example. D-12-ZnAc-100 refers to the linear difunctional ionomer of 12,000  $\bar{M}_n$ , which has been neutralized with zinc acetate to 100% excess, i.e., 100% excess neutralizing agent was added. The polydispersity index was about 1.7 for all ionomer samples. The pure polyisobutylene sample used was obtained from Scientific Polymer Products, Inc., Ontario, New York, and had an  $\bar{M}_v$  of  $1.3 \times 10^6$ .

Solutions were prepared by dissolving the bulk polymer in covered beakers using magnetic stirrers for agitation. The nonpolar solvents used were decalin and paraffinic oil. The paraffinic oil was 100N oil courteously provided by Dr. P. K. Agarwal of Exxon Research and Development Co. and is the

same solvent used by Agarwal et al.<sup>17-19</sup> in their studies of sulfo-EPDM solutions.

A Rheometrics mechanical spectrometer (Model 605) was used in the dynamic mode with cone (0.1 radian angle) and plate (2.5 cm diameter) geometry. Strain sweep measurements demonstrated a linear viscoelastic response at strain amplitudes up to 30%. A strain of 10% was used for the measurements. The frequency sweep covered frequencies from  $10^{-1}$  to about 631 rad/s. While the highest frequency measurements are at the upper limit of the Rheometrics device, the data obtained did not indicate any major instrumentation difficulties. The experiments were run isothermally at temperatures ranging from room temperature to 100°C.

## RESULTS AND DISCUSSION

### General Viscoelastic Behavior and the Effect of Molecular Architecture

Figure 1 shows the storage modulus  $G'$  and loss modulus  $G''$  for a 5 g/dL solution of the difunctional species, D-12-ZnAc-100, in decalin at 28°C. The striking features of the observed behavior are, as described previously,<sup>20</sup> that  $G'$  approaches a slope of 2 and  $G''$  approaches a slope of 1 in the terminal region, but at higher frequencies  $G'$  displays a rubbery plateau extending about two decades. According

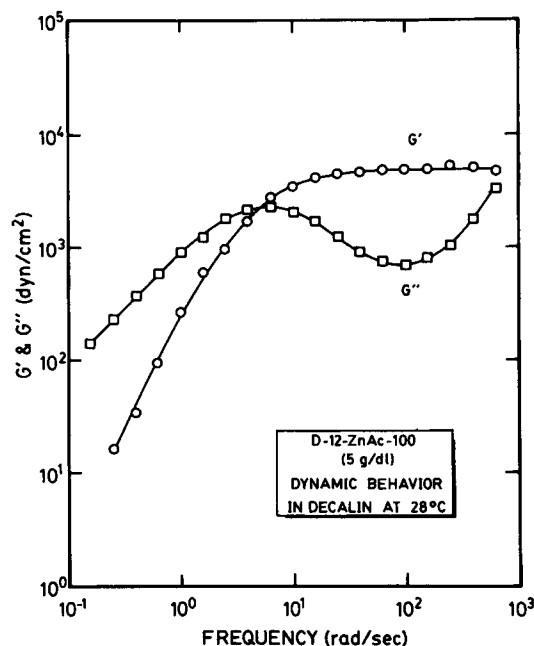


Figure 1 Dynamic moduli  $G'$  and  $G''$  vs. frequency for a 5 g/dL solution of D-12-ZnAc-100 in decalin at 28°C.

to the Rouse theory for linear flexible random coils,<sup>27</sup> the reduced intrinsic storage and loss moduli are given by

$$[G']_R = \sum_{p=1}^N \frac{\omega^2 \tau_p^2}{(1 + \omega^2 \tau_p^2)} \quad (1)$$

and

$$[G'']_R = \sum_{p=1}^N \frac{\omega \tau_p}{(1 + \omega^2 \tau_p^2)} \quad (2)$$

where  $p$  represents the  $p$ th normal mode of deformation of which there are  $N$  and  $\tau_p$  is the corresponding relaxation time. These equations are derived for a bead-spring model assuming no hydrodynamic interaction between neighboring beads, and apply strictly to infinitely dilute solutions. At finite concentrations sufficiently small that  $[G']_R$  can be approximated by  $G'M/cRT = G'/nkT$ , where  $n$  is the number of polymer molecules per volume, and, assuming that the relaxation times are not concentration dependent,<sup>28</sup> eqs. (1) and (2) can be written as

$$G' = nkT \sum_{p=1}^N \frac{\omega^2 \tau_p^2}{(1 + \omega^2 \tau_p^2)} \quad (3)$$

and

$$G'' = nkT \sum_{p=1}^N \frac{\omega \tau_p}{(1 + \omega^2 \tau_p^2)} \quad (4)$$

Thus it is clear that as frequency approaches zero,  $G'$  becomes proportional to  $\omega^2$  and  $G''$  becomes proportional to  $\omega$ . On a log-log plot the  $G'$  curve should therefore approach a slope of 2 and  $G''$  should approach a slope of 1. These results are independent of the effects of hydrodynamic interaction. Thus the slopes in the terminal region of the  $G'$  and  $G''$  curves shown in Figure 1 are those predicted for a linear viscoelastic fluid. Agarwal and Lundberg<sup>17</sup> observed very similar behavior in the master curves for a 5 wt% solution of a zinc(II)-neutralized sulfonated EPDM in a paraffinic oil. The  $\bar{M}_w$  of the sulfonated EPDM was about 84,000 and the sulfonation level corresponded to about seven sulfonate groups per molecule distributed randomly along the chain. The limiting slopes for  $G'$  and  $G''$  were obtained at low frequencies, and at high frequencies a broad rubbery plateau was observed. The primary difference between the viscoelastic response of the D-12-ZnAc-100 solution and the zinc(II)-neutralized sulfonated EPDM solution is that the same diverse responses

are observed over quite different frequency regions. For the D-12-ZnAc-100 solution these responses are observed to occur over the frequency range from  $10^{-1}$  to  $10^3$  rad/s, or *only* four decades. For the zinc(II)-neutralized sulfonated EPDM solution studied by Agarwal and Lundberg, the same responses extend from about  $10^{-5}$  to almost  $10^4$  rad/s, or *nine* decades. Also the  $G'$  and  $G''$  curves for the zinc(II)-neutralized sulfonated EPDM are master curves obtained by shifting isothermal data obtained over the range from 0 to 135°C. In contrast, the data in Figure 1 were obtained at a *single temperature*. For both solutions,  $G''$  shows a distinct peak in the frequency range where  $G'$  changes in behavior from a predominantly viscous response to a network response. Both solutions also display another increase in  $G''$  at the high frequency end of the rubbery plateau, suggesting the onset of a transition which would be observed at higher frequencies or lower temperatures. This anticipated transition is likely to be one to a more "glasslike" behavior. The minimum in  $G''$  occurs at about  $10^2$  rad/s for both solutions.

Figure 2 illustrates the viscoelastic behavior of a 5 g/dL solution of the trifunctional species, T-11.3-ZnAc-100, in decalin at 27°C. Several differences in behavior between this solution and that of the difunctional species of similar molecular weight, D-12-ZnAc-100, are evident. First,  $G'$  and  $G''$  do not approach the limiting slopes at low frequencies ex-

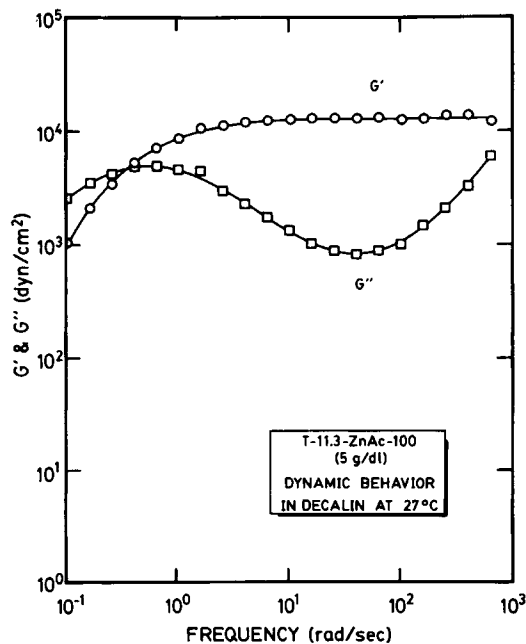
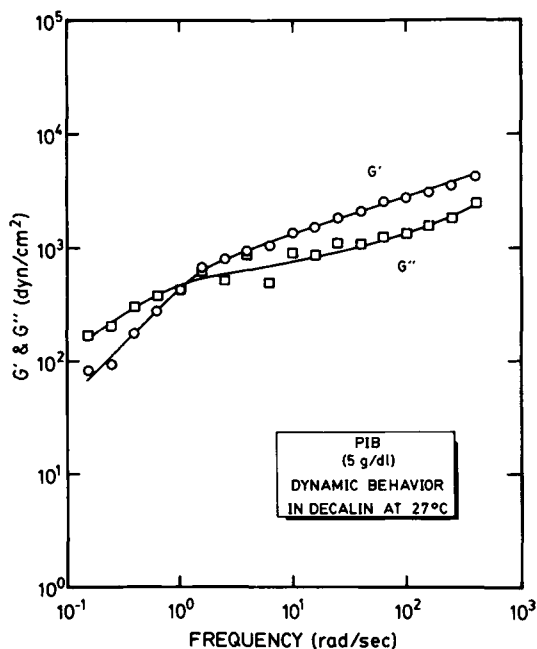


Figure 2 Dynamic moduli  $G'$  and  $G''$  vs. frequency for a 5 g/dL solution of T-11.3-ZnAc-100 in decalin at 27°C.

pected for a linear viscoelastic fluid. Second, the onset of the rubbery plateau occurs at least a decade lower for the trifunctional ionomer. Third, the plateau modulus  $G_N^0$  of the T-11.3-ZnAc-100 solution is  $1.4 \times 10^4$  dyn/cm<sup>2</sup> whereas that of the D-12-ZnAc-100 solution is only  $5.2 \times 10^3$  dyn/cm<sup>2</sup>. Finally, the peak in the loss modulus  $G''$  occurs at a lower frequency for the trifunctional ionomer. Each of these factors is strong evidence that the trifunctional ionomer solution possesses a more extensive network character. This would be expected since each trifunctional molecule already has a permanent covalent network junction. Thus only ion pair association is necessary for network formation. For the difunctional ionomer some triplet or higher order associations are required for network formation. These statements are supported by dilute solution viscosity data which show that the trifunctional ionomer forms a gel at a lower concentration than the difunctional ionomer of similar molecular weight.<sup>10,16</sup>

In Figure 3 the viscoelastic behavior of a solution of high molecular weight ( $\bar{M}_v = 1.3 \times 10^6$ ) linear polyisobutylene at the same concentration of 5 g/dL is shown. According to Ferry,<sup>29</sup> the crossover between  $G'$  and  $G''$  corresponds approximately to the onset of entanglement coupling. Obviously, below this frequency there are entanglements, but they do not couple as strongly at low frequency and thus do not contribute significantly to the elastic response



**Figure 3** Dynamic moduli  $G'$  and  $G''$  vs. frequency for a 5 g/dL solution of linear polyisobutylene ( $\bar{M}_v = 1.3 \times 10^6$ ) in decalin at 27°C.

(i.e., by storing energy) as they do at higher frequencies. But it is clear that above this frequency there is not a flat plateau region as is observed for the zinc-neutralized ionomer solutions. Rather, there is only a decrease in the slope of  $G'$ . At low frequencies the limiting slopes corresponding to a linear viscoelastic fluid are not even approached by the PIB solution due to the high molecular weight of the PIB and the resulting intermolecular entanglements which are effective even at these very low frequencies.

Apparently, at low frequencies and low molecular weights the average lifetime of the zinc sulfonate association is short compared with the deformation rate, thus allowing the polymer molecules to flow past one another. As the frequency increases, the time scale of the deformation approaches that of the lifetime of the ionic associations. As this occurs the molecular interactions fall more within the time scale of deformation. Polymer molecules are not as free to flow past one another and the slopes of  $G'$  and  $G''$  begin to deviate from the limiting slopes in the terminal region. Finally, the time scale of the deformation becomes shorter than the time scale of the average zinc sulfonate association, and the solution begins to behave as a network. A distinct plateau in the storage modulus is observed which indicates networklike behavior and the fact that the effective crosslink density has reached a maximum.

The Deborah number, introduced by Reiner,<sup>30</sup> offers a quite convenient way to describe the transition from a predominantly viscous response to a networklike response, and is defined by

$$N_{De} = \lambda_c / t_s \quad (5)$$

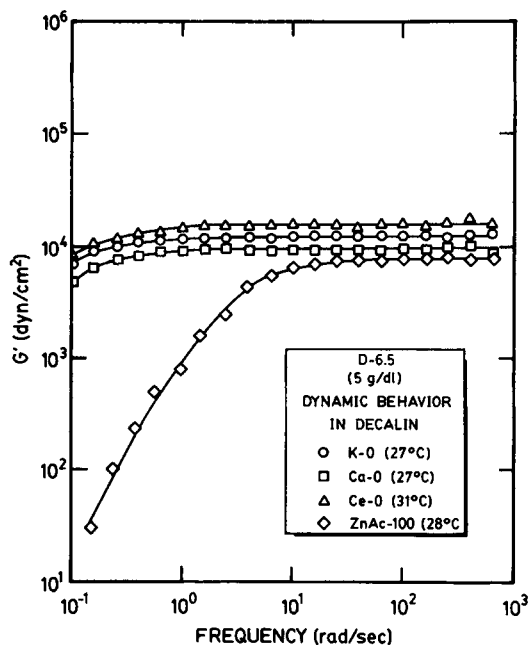
where  $\lambda_c$  is a characteristic relaxation time of the material and  $t_s$  is the time scale of the experiment. For this case we can consider  $\lambda_c$  to be the average lifetime of an ionic association and  $t_s$  as the inverse frequency, giving

$$N_{De} = \lambda_c \omega \quad (6)$$

From eq. (6), high frequencies will result in high Deborah numbers ( $>1$ ) and an elastic response, and low frequencies will result in low Deborah numbers ( $<1$ ) and a viscous response. This, of course, is the observed behavior.

#### Effect of Neutralizing Cation Type

Figure 4 illustrates the effect of neutralizing cation type upon the storage modulus of the D-6.5 ionomer



**Figure 4** Dynamic storage modulus  $G'$  vs. frequency for 5 g/dL solutions of D-6.5, neutralized with various cations, in decalin at  $29 \pm 2^\circ\text{C}$ .

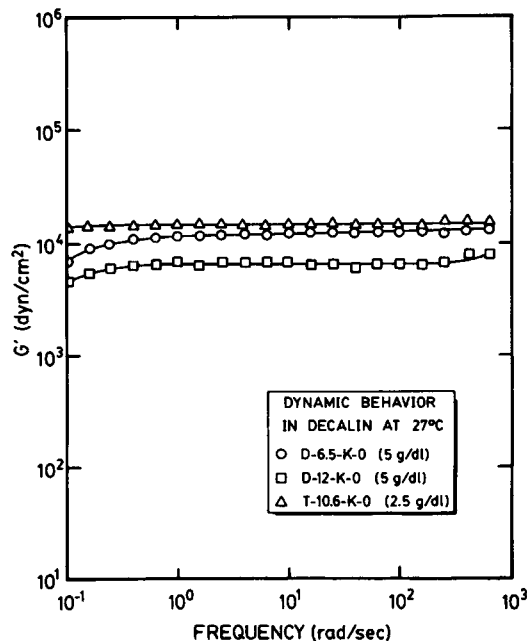
at a concentration of 5 g/dL in decalin and in the temperature range of  $29 \pm 2^\circ\text{C}$ . Clearly, the behavior of the D-6.5 solutions stoichiometrically neutralized with  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Ce}^{3+}$  is very similar, but there is no trend with the valence of the cation. The rubbery plateau is seen to persist over essentially all four experimentally accessible decades of frequency, with a slight decrease in  $G'$  at the lowest frequencies. Thus these solutions display a networklike behavior over the entire experimentally accessible frequency range. The solution with 100% excess zinc acetate displays a predominantly viscous response, as described earlier, and is thus very different from the other solutions. This results from the less ionic, more coordinative character of the zinc bonds.<sup>31</sup> Similar results have been found for the dilute solution behavior of these ionomers in nonpolar solvents.<sup>10,16</sup> The fact that the plateau modulus  $G_N^0$  of D-6.5-K-0, D-6.5-Ca-0, and D-6.5-Ce-0 are all very similar suggests that the network and crosslink densities are all similar despite the variation in cation valence.

#### Effect of Molecular Weight

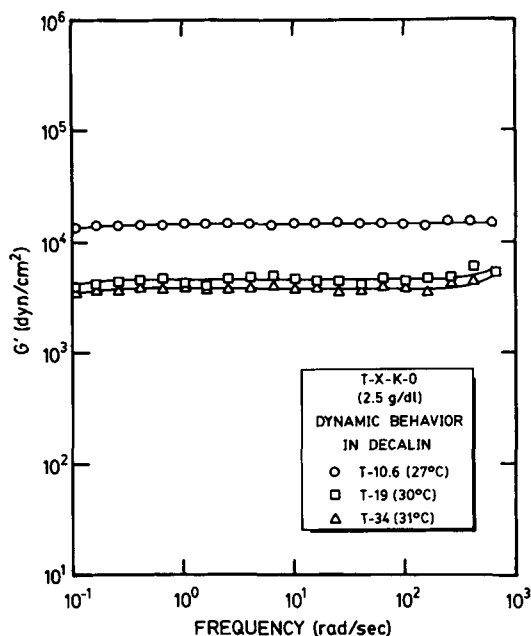
Two of the curves in Figure 5 show the effect of molecular weight for the linear difunctional species stoichiometrically neutralized with KOH and at a concentration of 5 g/dL in decalin. The plateau modulus of the D-6.5-K-0 solution is substantially

higher than that of the D-12-K-0 solution over the entire range of frequencies. This result supports the dilute solution studies which showed that the D-6.5 gels at a lower concentration than D-12. Again, both findings indicate that the D-6.5 material forms a network with a higher ionic crosslink density than the D-12 material as would be expected. It is interesting to compare the  $G'$  of these two solutions with that of the solution of T-10.6-K-0 at exactly half the concentration of the latter, i.e., 2.5 g/dL. The T-10.6-K-0 solution displays a slightly higher plateau modulus than the D-6.5-K-0 solution, even though it is only half the concentration. This is another indication that the trifunctional molecules find it much easier to form a network than the difunctional molecules.

The effect of molecular weight upon the storage modulus  $G'$  of the trifunctional species stoichiometrically neutralized with KOH is illustrated in Figure 6 for 2.5 g/dL solutions in decalin between 27 and  $31^\circ\text{C}$ . The plateau modulus is highest for the T-10.6-K-0 solution due to its lower molecular weight and thus higher crosslink density. Upon increasing  $\bar{M}_n$  from 10,600 to 19,000  $G_N^0$  is observed to drop from  $1.5 \times 10^4$  to  $4.7 \times 10^3$  dyn/cm<sup>2</sup>. This large decrease in  $G_N^0$  is due to the large decrease in ionic crosslink density as molecular weight is increased. Increasing  $\bar{M}_n$  from 19,000 to 34,000 results in only a slight reduction in the plateau modulus



**Figure 5** Dynamic storage modulus  $G'$  vs. frequency for D-6.5-K-0 and D-12-K-0, both at 5 g/dL, and T-10.6-K-0 at 2.5 g/dL in decalin at  $27^\circ\text{C}$ .

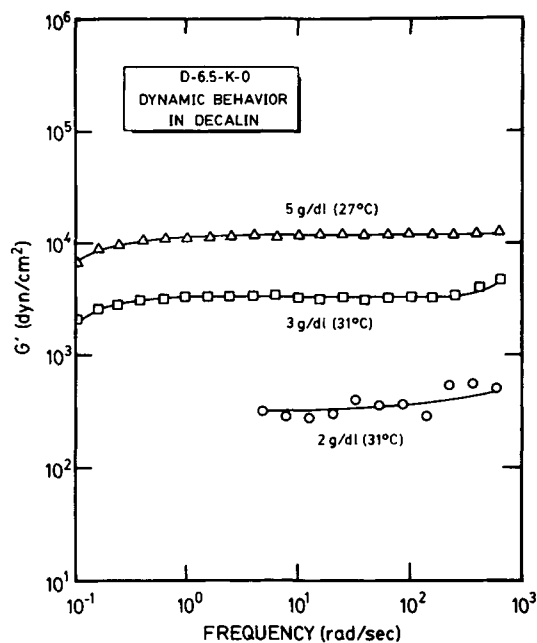


**Figure 6** Dynamic storage modulus  $G'$  vs. frequency for 2.5 g/dL solutions of T-X-K-0 in decalin at  $29 \pm 2^\circ\text{C}$  showing the effect of molecular weight.

$G_N^0$ —from  $4.7 \times 10^3$  to  $3.8 \times 10^3$  dyn/cm<sup>2</sup>. This small decrease in  $G_N^0$  can be attributed to the onset of entanglement coupling as  $\bar{M}_n$  is increased from 19,000 to 34,000. Thus, while the crosslinks which determine  $G_N^0$  for the T-10.6 and T-19 solutions are primarily the result of ionic associations, the crosslinks which determine  $G_N^0$  for the T-34 solution are the result of both the ionic associations and entanglements.

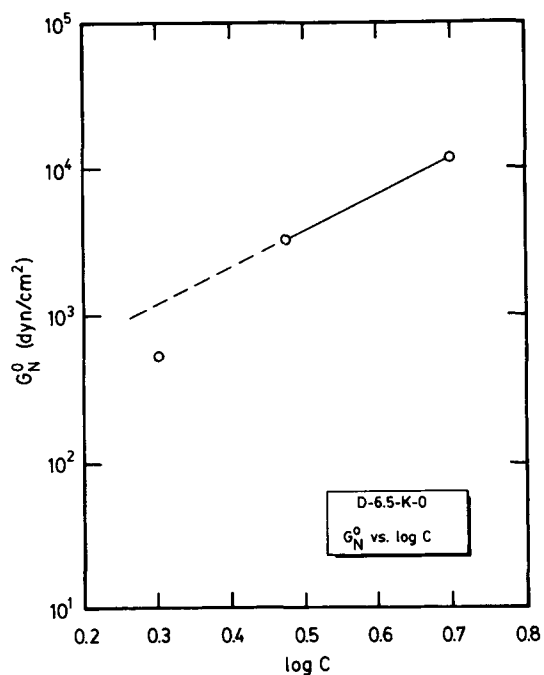
#### Effect of Concentration

Figure 7 shows the effect of concentration on the behavior of D-6.5-K-0 in decalin at  $29 \pm 2^\circ\text{C}$ . The plateau modulus  $G_N^0$  is observed to increase with increasing concentration as expected. Agarwal and Lundberg<sup>17</sup> have found that unsulfonated EPDM solutions display a  $G_N^0$  which is proportional to  $c^2$  whereas solutions of sulfonated EPDM show a stronger dependence on concentration, i.e.,  $G_N^0 \propto c^{2.5}$ . The values of  $G_N^0$  from Figure 7 are plotted in Figure 8 in terms of  $\log G_N^0$  vs.  $\log c$ . Since the 2 g/dL solution is near the gelation point and not well into the gel region, a line was drawn only between the points for the 3 and 5 g/dL solutions. Although the data are obviously very limited, the slope of the line is 2.5—the same as that found by Agarwal and Lundberg for their sulfonated EPDM solutions. Similar data on D-12-K-0 solutions at



**Figure 7** Dynamic storage modulus  $G'$  vs. frequency for 2, 3, and 5 g/dL solutions of D-6.5-K-0 in decalin at  $29 \pm 2^\circ\text{C}$ .

concentrations of 5 and 10 g/dL revealed a  $c^{2.15}$  dependency. Clearly, additional data must be obtained to accurately establish the dependence of  $G_N^0$  upon



**Figure 8** Effect of polymer concentration  $C$  on the plateau storage modulus  $G_N^0$  of D-6.5-K-0 in decalin at  $29 \pm 2^\circ\text{C}$ .

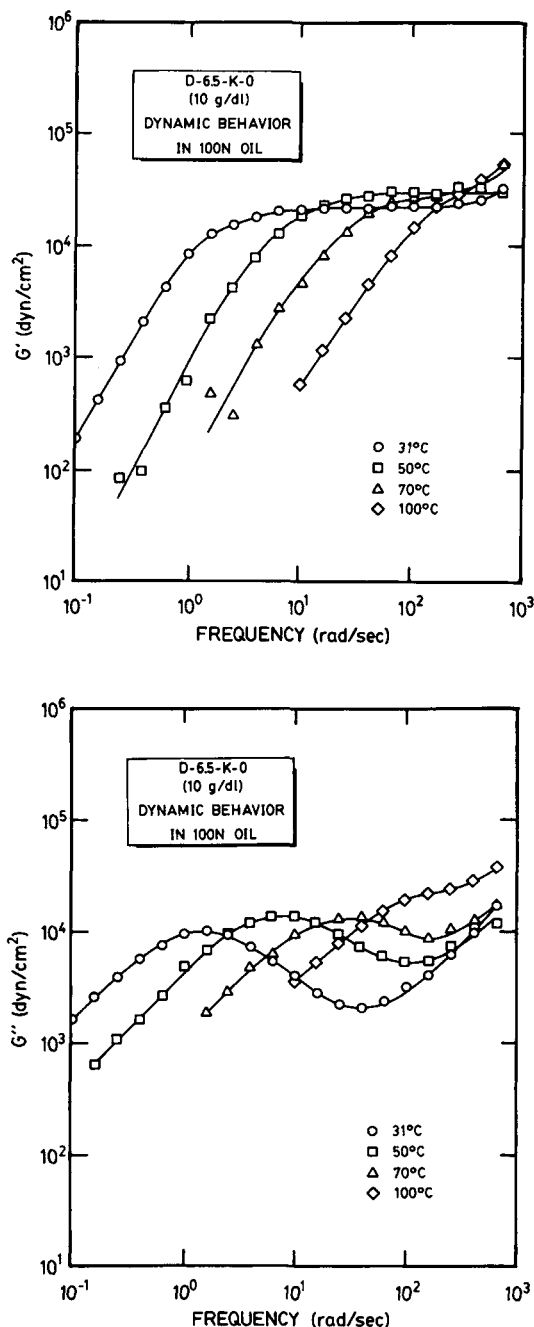
concentration. Limitations on the present study were imposed by a lack of sufficient amounts of material.

### Effect of Temperature

In order to investigate the effect of temperature upon the viscoelastic behavior of these ionomers, experiments were conducted on solutions of D-6.5-K-0 and T-34-K-0 in 100N oil—the same paraffinic oil utilized by Agarwal and Lundberg<sup>17-19</sup> in their studies of sulfonated EPDM solutions. This paraffinic oil was selected due to its very high boiling point as well as to facilitate comparison with the sulfonated EPDM solution data. The D-6.5-K-0 ionomer was selected for study because it possesses the highest concentration of ionic groups and does not have a permanent covalent network junction point. Its behavior is therefore dominated by ionic interactions. On the other hand, T-34-K-0 was selected because it has the lowest ionic content and it does have a permanent network junction point.

One difference between 100N oil and decalin that became obvious at an early stage is that the kinetics of the dissolution process are much slower in 100N oil than in decalin. This may be due to the long chain nature of the 100N oil which would be expected to reduce the mobility of the ionomer and thus retard dissolution. Preparation of solutions in decalin normally required 2-3 days, whereas preparation of solutions in 100N oil often required 2-3 weeks.

Composite plots of  $G'$  and  $G''$  are shown in Figure 9 for D-6.5-K-0 in 100N oil at a concentration of 10 g/dL and at temperatures of 31, 50, 70, and 100°C. The terminal slopes for 2 for  $G'$  and 1 for  $G''$  are clearly reached. It may be recalled that for the D-6.5-K-0 in decalin, and at 5 g/dL instead of 10 g/dL, the storage modulus was essentially constant over all four decades of frequency. Apparently, the mobility of the chain ends in 100N oil is so much lower than in decalin that the ionic groups have a much more difficult time locating other ionic groups with which to associate. This both shortens the plateau region and reduces the plateau modulus. Increasing the temperature further reduces the breadth of the plateau by shortening the lifetime of the ionic interactions. When the temperature reaches 100°C, a clear rubbery plateau is no longer observed—just an inflection in the  $G'$  curve. Nor is a peak in the  $G''$  curve, which indicates a transition in behavior, now observed. The composite plots of  $G'$  and  $G''$  in Figure 9 clearly show the shifting of the terminal



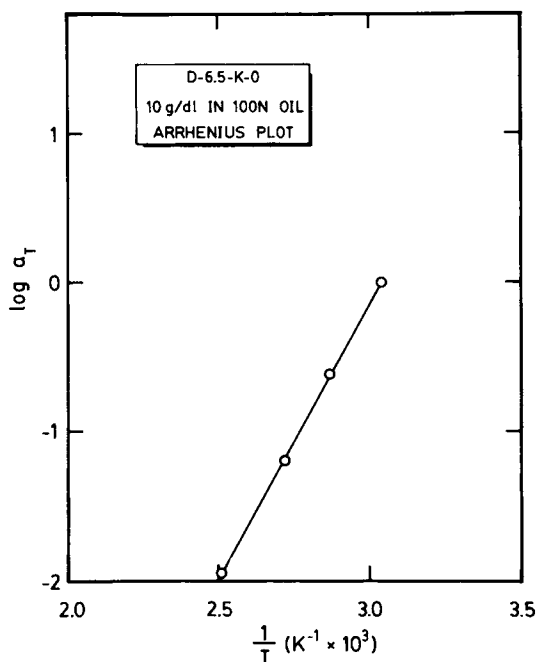
**Figure 9** Composite plots of (a) dynamic storage modulus  $G'$  and (b) dynamic loss modulus  $G''$  vs. frequency for 10 g/dL solution of D-6.5-K-0 in 100N oil at various temperatures.

region to higher frequencies. It is quite apparent, particularly from the  $G''$  curves, that these curves cannot be shifted to superpose and therefore the solution is thermorheologically complex. In fact, while the terminal region shifts toward the right with in-

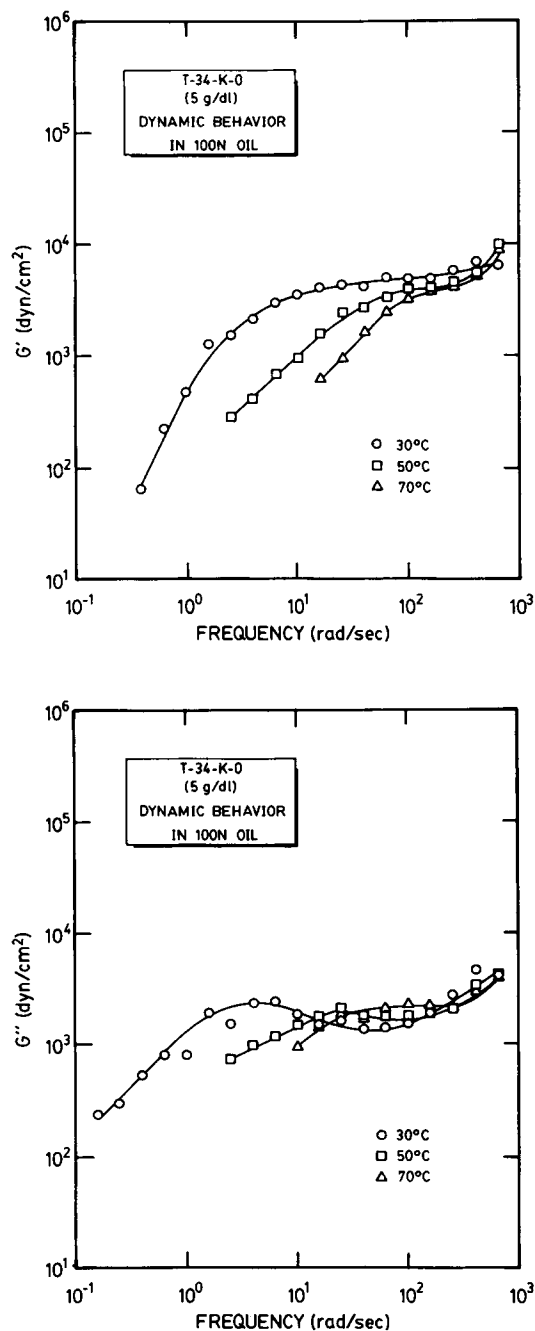


creasing temperature, the high frequency transition to more rigid behavior, which is indicated by the increase in both  $G'$  and  $G''$ , seems to remain at essentially the same frequency. Even though the curves are not superposable, it was considered of interest to determine shift factors for the temperature dependence of the terminal flow region. The onset of the terminal flow region was arbitrarily defined to occur at the frequency where  $G'$  is  $10^4$  dyn/cm<sup>2</sup>. A reference temperature of 31°C was selected and a shift factor  $a_T$  was determined for each of the other three curves so that shifting would cause these curves to intersect the 31°C curve at a  $G'$  of 10 dyn/cm<sup>2</sup>. These shift factors are plotted in Figure 10 in terms of  $\log a_T$  vs.  $1/T$ . Clearly, the relationship is linear, indicating an Arrhenius temperature dependence for the onset of the terminal flow region. Of course, these data were obtained over a limited temperature range and should not be extrapolated far beyond this region.

Composite plots of  $G'$  and  $G''$  are shown in Figure 11 for T-34-K-0 in 100N oil at a concentration of 5 g/dL and at temperatures of 30, 50, and 70°C. The curves are obviously not superposable. Again, the terminal region is observed to shift to higher frequencies with increasing temperature, while the transition to glasslike behavior seems to remain at essentially the same frequency. It is clear that the



**Figure 10** Arrhenius plot,  $\log a_T$  vs.  $1/T$ , for the onset of flow for 10 g/dL solution of D-6.5-K-0 in 100N oil.



**Figure 11** Composite plots of (a) dynamic storage modulus  $G'$  and (b) dynamic loss modulus  $G''$  vs. frequency for 5 g/dL solution of T-34-K-0 in 100N oil at various temperatures.

terminal slopes of 2 for  $G'$  and 1 for  $G''$  are reached only by the 30°C curve and not by the two higher temperature curves. The reason for this change in behavior is not clear, but it does further illustrate the complexity of these solutions.

## CONCLUSIONS

The dynamic behavior of sulfonated polyisobutylene telechelic ionomers in decalin is highly dependent upon the neutralizing cation. Neutralization with ionic cations such as  $K^+$  and  $Ca^{2+}$  can result in solutions which behave as networks over the range of experimentally accessible frequencies, while less ionic cations such as  $Zn^{2+}$  result in solutions which behave as networks at high frequencies but as viscous fluids at low frequencies. The concentration dependence for solutions of the difunctional species is the same as that for the sulfonated EPDM solutions while it is somewhat less for the trifunctional species. The molecular weight dependence is affected by both ionic content and chain microstructure.

A higher molecular weight solvent such as a paraffinic oil apparently interferes with ionic interactions enough to cause these solutions to flow at lower frequencies and exhibit much lower viscosities. The solutions are found to be thermorheologically complex since curves obtained at various temperatures are not superposable.

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