Effect of Water on Viscosity and Shear-Thickening Behavior of Telechelic Ionomers in Nonpolar Solvents

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ABSTRACT: Quantitative effects of water on the viscosity and rheology of magnesium- and sodium-neutralized dicarboxy-terminated polybutadiene in toluene are reported. A change in the water concentration from 50 to 500 ppm led to a viscosity decrease of 2 orders of magnitude for solutions near the gel concentration. Because of the hygroscopic nature of ionomer solutions, rheological experiments were conducted in a humidity-free environment. The dynamic measurements show that the viscosity reduction is related to a reduction in both the plateau modulus and the terminal relaxation time. The magnitude of shear-thickening decreases and the onset of shear-thickening shifts to higher shear rates with increasing water content.

Introduction

Ionomers are polymers containing covalently attached salt groups on less than 10% of the monomers. In the bulk, the ionic groups microphase separate into ion-rich domains in a matrix of the nonpolar polymer backbone. In a nonpolar solvent, similar ionic interactions lead to the formation of aggregates containing many chains at very low concentrations. This leads to a physically cross-linked network and gel formation in semidilute solutions. The aggregation results in an increase in viscosity by orders of magnitude over that of unneutralized materials which makes ionomers useful as viscosity enhancers in low-polarity solvents. This thickening ability in the semidilute region depends on the ion content,[1−5] neutralizing cation,[6−9] and solvent quality.[1,6,10] Further, nonpolar ionomer solutions often exhibit shear-thickening and shear-thinning behavior,[11−15] making them useful as rheology modifiers.

In the solid state, water is known to plasticize ionic aggregates and affect physical properties of ionomers. However, very few studies have systematically studied the effects of water in ionomers. In recent literature, Yang *et al.*[16] demonstrated that the T_g for sulfonated polystyrene neutralized with various metal counterions can vary by 8−10 °C depending on the water content of the sample. The amount of bound and absorbed water was determined from the change in mass upon heating the sample from 50 to 250 °C. If all the mass change corresponds to water as suggested by Yang *et al.*, this large change in glass transition is due to a small number of water molecules (0.2−0.7 molecules of water/acid group). The small amount of water plasticizes the cross-linking ionic aggregates which decreases T_g. Kim and Eisenberg[17] have looked at moisture effects on dynamic mechanical properties of poly(styrene-*co*-sodium methacrylate) ionomers, also using weight change in each sample as a measure of water content. Their results show that small amounts of water (0.06−0.26 water molecules/acid group) affected the dynamic behavior, resulting in a significant decrease in modulus in the rubbery region that occurs at temperatures exceeding 125 °C. It is important to note that the decrease in modulus with increasing moisture content was seen at temperatures from 125 to 225 °C which are above the boiling point of water, suggesting that tightly-bound water is affecting the modulus. These two studies put fourth two ideas. First, small amounts of water can have a large effect on the physical properties of ionomers. Second, the amount of water is difficult to quantify since it can be tightly bound to the ions and removed only with great difficulty. The extreme hygroscopic nature of ionomers has been demonstrated by Brozoski *et al.*[18] and Goddard *et al.*,[19] who observed significant water absorption by samples even during sample storage above calcium sulfate desiccant. We have made similar observations for ionomer solutions stored under the same conditions.

A number of studies[10,15,20−23] have pointed out that the addition of polar cosolvents to ionomers in nonpolar solvents results in a reduction in viscosity. Addition of small amounts of alcohol, as little as 0.25 wt %, reduces the sample viscosity by 1 order of magnitude. The reduction in viscosity is attributed to the solvation of ionic domains which results in a breakup of aggregates. It should be no surprise that water would affect the viscosity in a fashion similar to that of the polar cosolvents. However, unlike polar cosolvents which need to be added, water is already present at the time of neutralization and can be easily absorbed from the atmosphere. Lundberg and Phillips[1] have added 2, 5, and 10 wt % water to 1.7 mol % sulfonated polystyrene neutralized with sodium in tetrahydrofuran. They observed a decrease in viscosity by a factor of 3 at 2 g/dL; however, they did not measure the actual water content in the initial tetrahydrofuran solution. In this study, we show that very small amounts of water (50−500 ppm) have much more of a dramatic effect on viscosity.

Shear-thickening behavior[11,13,24] has been observed in semidilute ionomer solutions. Typical viscosity *vs* shear rate behavior of ionomer solutions in nonpolar solvents is characterized by three regions of behavior. At low shear rates, a Newtonian plateau is observed. The interesting behavior is observed at intermediate shear rates where shear-thickening is exhibited, followed by

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shear-thinning at higher shear rates. Maus *et al.*[15] have found that the presence of small amounts of polar cosolvents affects the shear-thickening behavior. With the addition of 0.25 wt % octadecanol to a magnesium-neutralized carboxy-telechelic polystyrene in toluene, the viscosity enhancement (viscosity maximum/zero-shear viscosity) decreased dramatically and the critical shear rate for the onset of shear-thickening shifted to higher shear rates. Peiffer *et al.*[11] observed that shear-thickening behavior disappeared completely when low molecular weight alcohols were added to solutions of ionomers in xylene.

The purpose of this work was to show that extreme care needs to be taken to control the amount of water in ionomer solutions in nonpolar solvents in order to obtain reproducible data. Because of the extreme hygroscopic nature of these materials, a slight exposure of these materials to the atmosphere can result in water adsorption. Water content is an extremely important variable in ionomer rheology studies and its quantitative effects have not been previously measured. The challenge of this research was to accurately determine the water content in each sample and carry out rheological measurements in a controlled low-humidity environment.

Experimental Section

Sample Preparation. All solvents were obtained from Aldrich. Hycar CTB (B.F. Goodrich), dicarboxy-terminated polybutadiene with $M_n = 4600$ g/mol and a polydispersity of 1.8, was dissolved in tetrahydrofuran and neutralized with magnesium acetate tetrahydrate (Aldrich) dissolved in ethanol or sodium ethoxide in ethanol. Hycar possesses 15% 1,2-vinyl, 65% 1,4-trans, and 20% 1,2-cis microstructure. The neutralized materials were first dried in a rotovap and then in a vacuum oven for 2 days at 80 °C and 10^{-2} Torr. The degree of neutralization was confirmed by Galbraith Laboratories, Inc., Knoxville, TN, by inductively coupled plasma optical emission spectroscopy (ICPS). The reproducibility of neutralization level measurement by ICPS was within 5%. Each sample was successfully redissolved in anhydrous toluene to a concentration of 1.5 g/dL. After 1 week of stirring, water measurements were made. Each of the solutions was concentrated slowly (less than 15% volume change/h) in a rotovap at room temperature until the desired concentration was reached. The solutions were then transferred to several sample jars to allow variation of the water content.

Water Measurement. A coulimetric Karl-Fischer titrator, Mitsubishi MCI moisture meter Model CA-05, was used for water titration. Four to six measurements of water were made on each sample. The samples for water measurements were taken directly from the capillary or the rheometer immediately following the experiment. The overall reproducibility of the measurements was within 5% of the water content in the sample. Syringes used to transfer the solution to the titrator were rinsed with anhydrous toluene and the sample prior to each measurement. Chloroform was added to the anode solution to increase the solubility of the ionomer and keep the conductivity high.

Viscometry. Viscosity was measured with an automated Schott Gerate viscometer, Model AVS 300. Capillary sizes from 1 to 5 C were used to measure the complete viscosity range. A modification was made to the viscometer to use toluene-saturated vapor as the driving medium for filling the viscometer. Capillaries were washed with toluene and dried in a convection oven at 70 °C prior to each use. The solutions were poured into the capillaries in a toluene-saturated nitrogen environment. All viscosity measurements were performed at 25 °C in a temperature-controlled oil bath (accurate to ±0.05 °C).

Rheological Measurements. Steady-shear and dynamic data were obtained on a Bohlin VOR with a C-14 couette geometry at 25 °C. The rheometer was placed in an environmental chamber with less than 5% relative humidity (R.H.). Three torque bars (1.6, 11, and 90 g·cm) were used to capture up to 3 decades of steady and dynamic data. Complimentary data were also obtained on the Rheometrics RMS-800 with 0.04 rad cone and plate geometry. A standard procedure was used for all rheological measurements. Immediately after loading the sample, the sample was sheared for 3 min at 1 s^{-1}, followed by 7 min of rest. Then the dynamic-shear experiments and the steady-shear experiments were conducted.

Constant Humidity Tests. A beaker containing toluene and another containing a saturated sodium bromide solution in water were placed in a closed jar for 2 h. The saturated sodium bromide solution maintains a constant humidity in a closed environment of approximately 58% R.H. The magnesium- and sodium-neutralized solutions were placed in this toluene-saturated environment with this constant humidity. A precipitate was observed in both the samples within 2 days of exposure to this environment. The sodium- and magnesium-neutralized samples contained 390 ppm (2.5 water molecules/Na) and 1300 ppm of water (~4 water molecules/Mg). The precipitate is believed to be metal oxide particles, since no precipitate is observed for non-neutralized materials in toluene with a similar water level. Precipitate in the sodium-neutralized material redissolved within 2 days. This experiment showed that solutions adsorb moisture when atmospheric moisture is present, making it very difficult to carry out solution characterization experiments.

Results and Discussion

Sample Preparation, Observations, and Viscometry. A coulimetric Karl-Fischer titrator easily provides quantitative water measurements of hydrated ions and salts in the solid state and in solution. The only requirement is that water in the sample should be easily accessible by the reagents, which is not possible for ionomers in bulk because nonpolar polymeric material shields the ionic groups. In recent literature, Zhu *et al.*[25] have performed a detailed study of sodium- and magnesium-neutralized nedocromil hydrates, which are low molecular weight carboxylates. Their work shows that water measured by coulimetric Karl-Fischer titration agrees well with the water analysis performed by FTIR, TGA, and ^{13}C NMR. Coulimetric Karl-Fischer titration can also measure tightly-bound water which may be difficult to measure by TGA if sample degradation occurs close to the water desorption temperature.

The neutralized samples, after heating in a flask at 80 °C and 10^{-2} Torr, contained approximately 2 water molecules/magnesium counterion and 0.2 water molecules/sodium counterion, as calculated from water measurements on dilute solutions prepared with anhydrous toluene. The samples were only heated to 80 °C to avoid any chemical change such as decarboxylation, anhydride formation, or cross-linking of the unsaturated polymer backbone. Concentrating the solutions slowly under reduced pressure at room temperature allowed the preparation of homogeneous, relatively water-free (less than 40 ppm) solutions at room temperature. The low-boiling toluene−water azeotrope (bp 85 °C) consisting of 80% toluene and 20% water aided in removal of water. Previous work in ionomer solutions has shown that exceedingly long times are required to prepare a homogeneous solution.[12,26] This technique was especially useful in reducing the preparation time.

The effects of moisture became quickly evident when 10−30 μL of deionized water was added to a few of the sample jars containing 40 mL of solution. Large changes in viscosity were noticeable as the water droplets mixed with the solution. Addition of more than 700 ppm of water or a large droplet results in a precipitate which often resolubilized over several days. Realizing that polymer precipitation will reduce viscosity, all the viscosity measurements were conducted on visibly clear samples. The upper limit of water which could be added to the solutions depended on the concentration and neutralization level.

Several researchers[10,12,27] have studied the time required to reach a steady viscosity for ionomers in nonpolar solvents. Tant[10] has shown that reaching a steady viscosity in a solution can take as long as 10 h after a temperature jump. Peiffer *et al.*[12] reported that viscosity increases with time and that a steady-shear viscosity is achieved in 4−6 days. These observations led us to explore the time required for reaching steady viscosity when the water content is changed. The viscosity of a mixture formed from two solutions of the same concentration of magnesium-neutralized sample but with different amounts of water (one with less than 50 ppm water and one with water content greater than 500 ppm) reached a stable viscosity within 1 min with proper mixing. This viscosity varied less than 10% from the aged samples containing the same amount of water. Further, in a capillary closed to the atmosphere, no viscosity change occurred over 2 days for the magnesium-neutralized samples.

The sodium-neutralized samples, however, showed time-dependent behavior along with moisture-dependent behavior. These samples increased in viscosity by as much as 80% when the sample was allowed to sit in the closed capillary over 2 days. Repeated measurements on the sample or a change in stirring speed for the stirbar in the capillary resulted in a change in viscosity, suggesting the aged samples are shear-sensitive. As a result, these complications led us to discontinue experiments on the sodium-neutralized materials. This increase in viscosity is expected to result from changes in the ionic aggregate structure. A decrease in the functionality or an increase in association strength of the ionic aggregates could explain the observed behavior. Future experiments on monocarboxylate sodium-neutralized ionomers and our current theoretical work on aggregation in solution will address this effect.

After the short-time aging experiments, we tested samples aged over 1 month. The solutions were stored in a sample jar in a desiccator over anhydrous calcium sulfate. Over the month, the viscosity of the magnesium-neutralized samples decreased. The water tests on these samples revealed that the viscosity decrease resulted from the solutions gaining moisture from the desiccant rather than from aging.

Figures 1−3 show the viscosity of magnesium-neutralized (160%) carboxy-terminated polybutadienes at 1.44, 3.10, and 4.11 g/dL as a function of water in solution. The samples contain 1.6 times the stoichiometric amount of neutralizing magnesium cation. The degree of neutralization affects the influence of water. For example, 4.91 g/dL solution of the sample neutralized to 110% of the stoichiometric amount shows a more gradual decrease in viscosity with water content. Each data point is a composite of three to six water measurements and three viscosity measurements. The deviations at the same water level are from different capillary sizes or from different sample aging. But the differences are much smaller than those of the viscosity reduction with water. Viscosity was measured for the four aged samples with different water levels. Intermediate water levels were achieved by mixing two aged solutions.

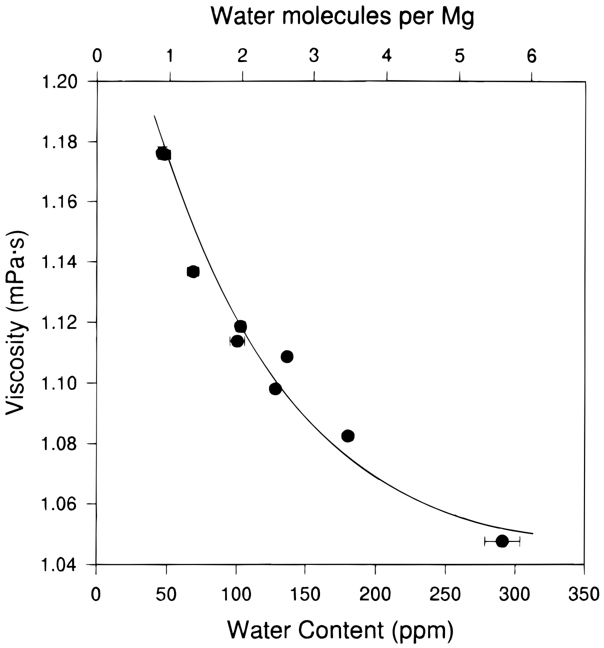

Figure 1. Viscosity of 1.44 g/dL Mg (160%) dicarboxypolybutadiene in toluene plotted as a function of water content. Error bars on each data point in both directions indicate the uncertainty in measurement of the viscosity and water content as obtained on a sample in a given capillary. The deviations between data points at similar water levels are from a different shear history or changes in the capillary diameter. The solid line indicates the trend in the data.

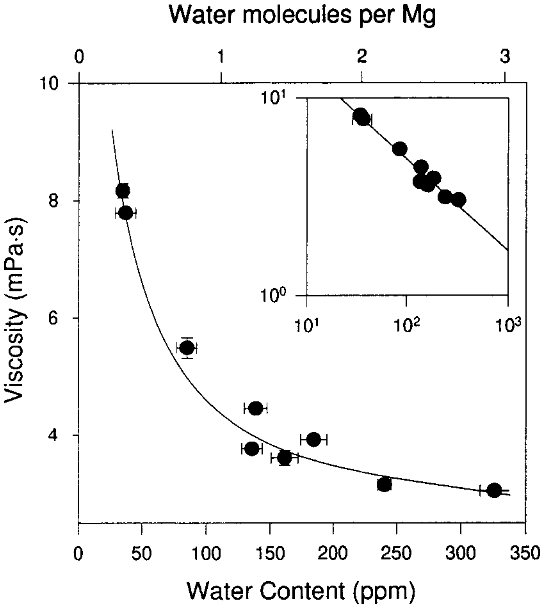

Figure 2. Viscosity of 3.09 g/dL Mg (160%) dicarboxypolybutadiene in toluene plotted as a function of water content. Note: 220 ppm of water corresponds to 2 water molecules/magnesium cation. The inset displays the same data in a log−log plot, with a solid line displaying the best fit line with a slope of −0.46.

A decrease in viscosity with increasing water content was observed at all concentrations. At the lowest concentration studied, 1.44 g/dL (Figure 1), the viscosity decreased less than 10% when the water content was increased from 35 to 290 ppm. In contrast, the solution at 4.11 g/dL (Figure 3) exhibited a decrease in viscosity

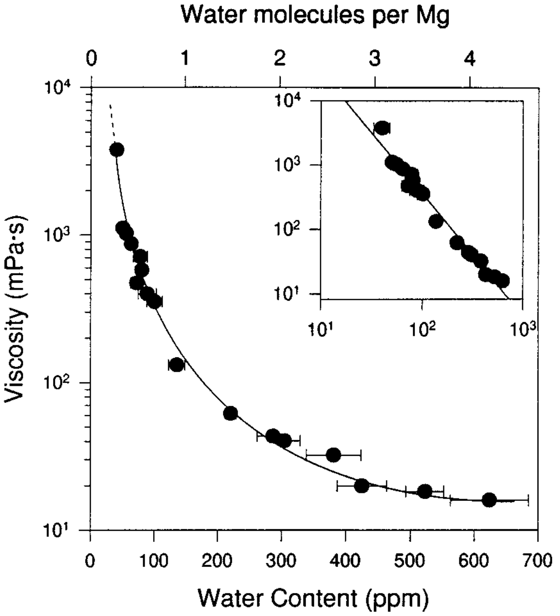

Figure 3. Viscosity of 4.11 g/dL Mg (160%) dicarboxypolybutadiene in toluene plotted as a function of water content. Note: 295 ppm of water corresponds to 2 water molecules/magnesium cation. The inset displays the same data in a log–log plot, with a solid line displaying the best fit line with a slope of −1.89. A “gel” is obtained at water levels below 35 ppm and is indicated with a dashed line.

by 2 orders of magnitude when the water level was increased from 35 to 285 ppm. Less than a 35% decrease in viscosity was observed upon the addition of another 250 ppm of water to this solution. Below a water concentration of 35 ppm, the 4.11 g/dL solution was a gel, which is indicated with a dashed line. The upper axis on each graph corresponds to the number of water molecules per magnesium ion. Note that the ppm range of water measured by Karl-Fischer titration corresponds to 0.3−4 water molecules/magnesium ion.

To illustrate the effect of water per cation on the viscosity, the viscosity of unneutralized polybutadiene in toluene and magnesium-neutralized (160%) samples with 0.5, 1.0, and 2.0 water molecules/magnesium are plotted in Figure 4. As the concentration increases, the intermolecular associations increase, resulting in a viscosity enhancement. At the higher concentrations the water has much more of an effect than at lower concentration, suggesting that intermolecular associations are affected by absorbing moisture. At 4.11 g/dL, the ionomer solution containing 2 water molecules/magnesium exhibits a viscosity which is 1 order of magnitude greater than the unneutralized polymer, suggesting that significant association still exists.

A lesser effect on viscosity with increasing water content is observed for the sodium-neutralized (85%) materials at 3.50 g/dL (Figure 5). No gelation was observed in this solution even at water concentrations less than 10 ppm. The viscosity of the solution decreased by a factor of 10 when 500 ppm of water was added to the solutions. Solutions with greater than 550 ppm water were possible; however, they were not tested because of the aging and shear sensitivity of the solutions. The viscosity at two concentrations of water was measured after 2 days of rest. These data (■) show that the viscosity increased by as much as 80% during rest.

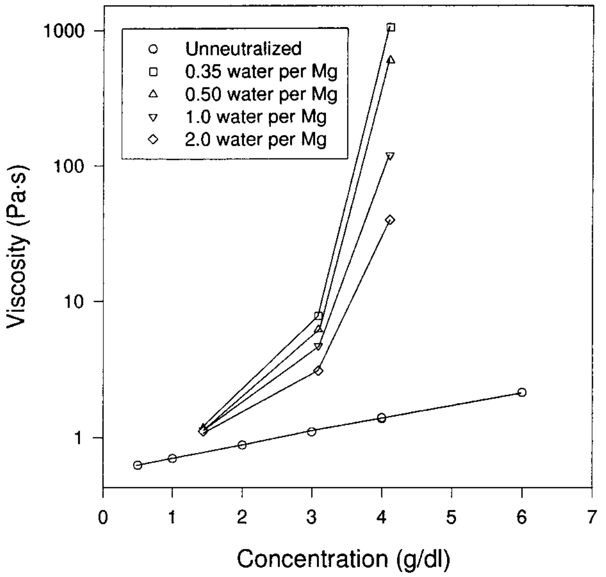

Figure 4. Viscosity of unneutralized dicarboxypolybutadiene and the Mg (160%) dicarboxypolybutadiene in toluene as a function of concentration. The lines are drawn to show the trends in the data.

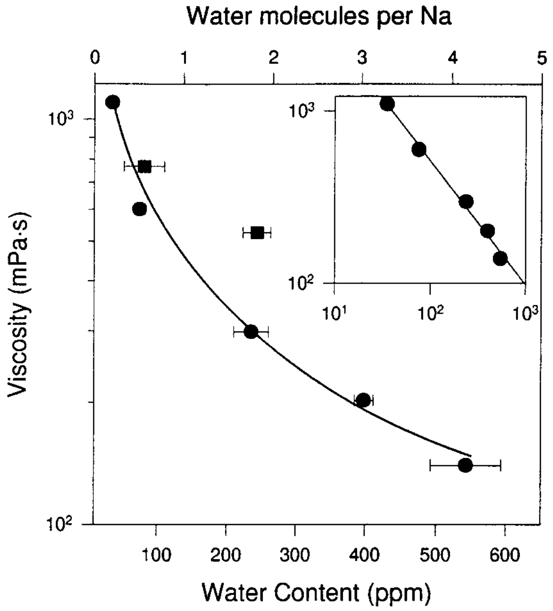

Figure 5. Viscosity (●) of 3.50 g/dL Na (85%) dicarboxypolybutadiene in toluene plotted as a function of water content. Note: 250 ppm of water corresponds to 2 water molecules/magnesium cation. The inset displays the same data in a log–log plot, with a solid line displaying the best fit line with a slope of −0.71. The viscosity data after 2 days of rest in a closed capillary are shown as ■.

Rheological Measurements. The dynamic-shear measurements probe the structure and relaxation spectrum. At low frequencies, long-time or large-scale motions are probed, while at high frequencies, short-time or subsegment motions are probed. In Figure 6, the storage modulus G' and loss modulus G'' for 4.91 g/dL of magnesium-neutralized (110%) solution at 55 ppm/water is plotted. The higher concentration solution with a lower neutralization level sample permitted shear experiments over a broader range of water levels. At low frequencies, terminal relaxation slopes of 2 and 1 are observed for G' and G'', respectively. Based on the simplest rheological model, the Maxwell model, we can obtaine quantitative information about the material. The relationships between G' and G'' and the terminal relaxation time, τ, and plateau modulus, G_∞, are shown

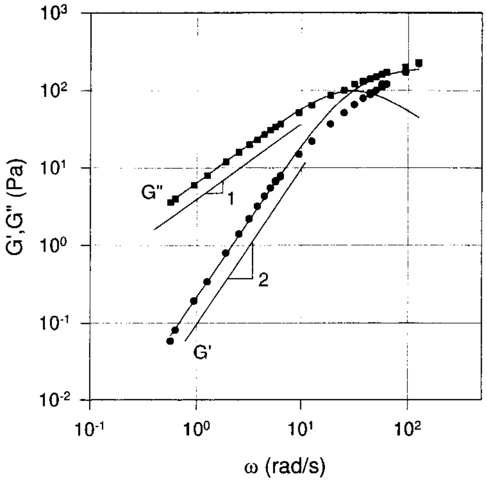

Figure 6. Storage modulus (G') and loss modulus (G'') plotted as a function of frequency at a water content at 55 ppm for a 4.91 g/dL solution of Mg (110%) dicarboxypolybutadiene in toluene. The plot includes a composite of data obtained at several strain amplitudes. The Maxwell model fits are shown as solid lines.

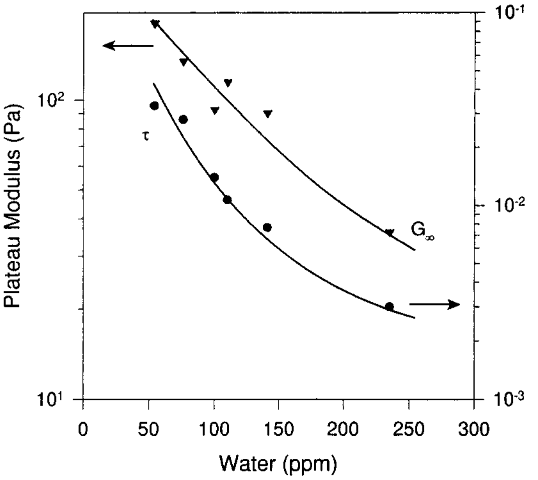

Figure 7. Terminal relaxation time (τ) and plateau modulus (G_∞) plotted as a function of the water content for a 4.91 g/dL solution of Mg (110%) dicarboxypolybutadiene in toluene.

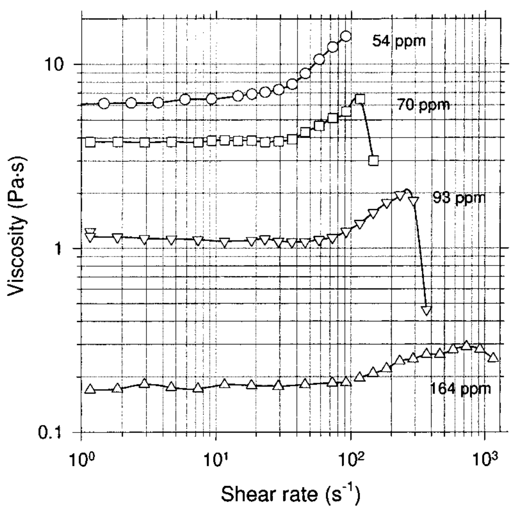

Figure 8. Viscosity plotted as a function of shear rate at different water levels for a 4.91 g/dL solution of Mg (110%) dicarboxypolybutadiene in toluene.

in eqs 1 and 2. A fit of the single-mode Maxwell model

$$G' = G_\infty\left(\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\right) \tag{1}$$

$$G'' = G_\infty\left(\frac{\omega\tau}{1+\omega^2\tau^2}\right) \tag{2}$$

is shown as the solid lines connecting the data points in Figure 6. A single-model Maxwell model does not fit the entire spectrum as it deviates at higher frequencies. For telechelic associating polymers, a single-mode Maxwell model often describes the dynamic shear data.[28,29] Even though we do not obtain perfect agreement over the entire frequency range, the terminal region shows the expected limiting behavior, allowing us to get good fits to the Maxwell model over 1.5 decades of frequency. In Figure 7, the plateau modulus, G_∞ and the terminal relaxation time, τ, are plotted as a function of water content. Both the plateau modulus and the terminal relaxation time decrease with the addition of water. In terms of the Green–Tobolsky model[30] for a physically cross-linked network, the plateau modulus relates to the elastically effective chains, ν, as shown in eq 3. A decrease in the elastically effective chains

$$G_\infty = \nu kT \tag{3}$$

suggests either that water hydrates the ionic groups, thus breaking up the ionic aggregates and reducing the number of elastically effective chains, or that there is a rearrangement in the network, creating fewer effective chains. Since an equilibrium viscosity is reached with 1 min and no precipitate is observed in these solutions, it is believed that water is hydrating both the carboxylic chain end and the magnesium ion to reduce the number of effective chains.

The Tanaka–Edwards transient network model[31] with a chain breakage potential independent of molecular weight predicts a single relaxation time directly relating to the association strength. A decrease in relaxation time thus suggests a decrease in association strength which is equivalent to plasticization of the ionic domain. In fact, several researchers have reported plasticization of ionic domains in bulk ionomers by polar species.[32],[33]

The zero-shear viscosity is a product of the plateau modulus and terminal relaxation time as shown in eq 4. Thus, a decrease in viscosity in telechelic nonpolar

$$\eta_0 = G_\infty\tau \tag{4}$$

ionomer solutions is due to plasticization of ionic aggregates and hydration of chain ends.

The steady-shear viscosity of 4.91 g/dL solutions with different water levels is shown in Figure 8. Three features of the effect of moisture are seen. First, the onset of shear-thickening and shear-thinning occurs at higher shear rates with the addition of water. Second, the magnitude of shear-thickening declines with an increasing amount of water. Third, the region between the onset of shear-thickening and the onset of shear-thinning increases with water content. The data points in the shear-thinning region were not obtained in the steady-state regime. The viscosity in this regime takes an exceedingly long time to reach steady state. Also, flow instabilities are often observed in this regime.

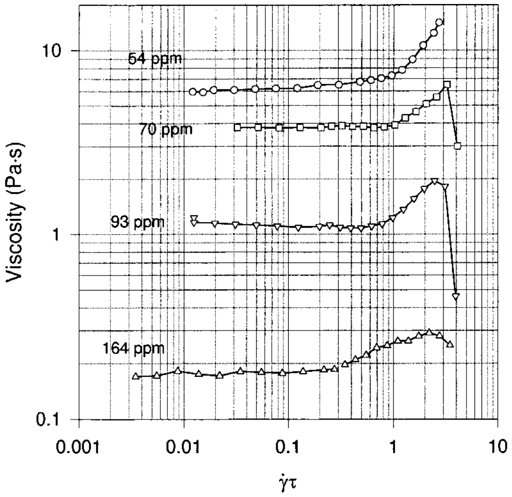

Figure 9. Same data from Figure 7 replotted as a function of dimensionless shear rate ($\dot{\gamma}\tau$).

The qualitative behavior of reduction in the magnitude of shear-thickening and the increase in the critical shear rate for the onset of shear-thickening when polar cosolvents are present agree well with our results on the steady-shear behavior with increasing water content (Figure 8). Peiffer *et al.*[11] showed that, on a lightly sulfonated poly(styrene-*co*-vinylpyridine) zinc-neutralized ionomer in xylene, an addition of oleyl alcohol caused a reduction in zero-shear viscosity and moved the onset of shear-thickening to higher shear rates. Since Peiffer *et al.*[11] do not show the start of shear thinnning, no comparison can be made on the magnitude of shear-thickening. Maus *et al.*[15] made similar observations for Mg-neutralized carboxy-telechelic polystyrene ionomer in toluene with an addition of 0.25 wt % octadecanol. They also found the magnitude of shear-thickening decreased with the presence of alcohol.

Shear-thickening behavior in associating polymers can be explained by several possible mechanisms: shear-induced transfer of intramolecular associations to intermolecular associations (Witten and Cohen[34] and Ballard *et al.*[35]); association of aggregates containing many chains under shear, which is similar to the mechanism proposed for shear-thickening in colloidal suspensions[36] (Peiffer *et al.*,[11] Dupuis *et al.*[37]); shear-induced coagulation of free chain ends to enhance the network in solution (Wang[38]); changes in the rates of chain creation and destruction (Ahn and Osaki[39]); and chain stretching in the non-Gaussian regime (Vrahopoulou and McHugh,[40] Jenkins,[41] and Marrucci *et al.*[42]). The theories which predict shear-thickening based on non-Gaussian chain stretching differ in the starting network model and in the assumptions for chain breakage and attachment rates under shear.

In Figure 9, the steady-shear viscosity data are plotted as a function of reduced shear rate, shear rate multiplied by the terminal relaxation time $\dot{\gamma}\tau$. The plot shows the onset of shear-thickening, and shear-thinning moves to the common reduced shear rates of approximately 1 and 3, respectively. This suggests that the location and the interval of shear-thickening are both related to the terminal relaxation time of the system. Further, a decrease in the magnitude of shear-thickening is observed with decreasing terminal relaxation time or decreasing association strength.

The location for the onset of shear-thickening ($\dot{\gamma}_c\tau > 1$) is predicted by the Witten–Cohen[34] model and by Ahn and Osaki.[39] The data also support the prediction of the Free path model of Marrucci *et al.*[42] where a reduced critical shear rate for the onset of shear-thickening between 1.0 and the square root of the number of Kuhn segments is predicted. However, the Wang model[38] predicts the reduced critical shear rate for the onset of shear-thickening as being smaller than unity.

The presence of water decreases the association strength and the magnitude of shear-thickening. This has consequences in differentiating between the various models describing such phenomena. Both the non-Gaussian stretching mechanism[40–42] and the interaggregate aggregation mechanism[11] predict a decrease in the magnitude of shear-thickening with a decrease in the association strength.

Conclusions

This study details the effects of water on the viscosity and rheology of magnesium- and sodium-neutralized dicarboxy-terminated telechelic polybutadiene. The viscosity of magnesium-neutralized samples was reduced by 2 orders of magnitude when the water concentration was increased from 0.27 to 2 water molecules/magnesium ion. The viscosity reduction was greatest at concentrations near the "gel" concentration and decreased with decreasing concentration. The moisture affected the viscosity of the sodium-neutralized samples less; however, the samples exhibited time-dependent behavior.

A reduction in the plateau modulus and the terminal relaxation time was observed with increasing water content. This implies that water plasticizes the ionic aggregates, making it easier to remove chain ends from an aggregate. Water also hydrates ionic groups which reduces the number of intermolecular associations. The shear-thickening magnitude decreased and the interval for shear-thickening increased with increasing amounts of water in the system. A common location and interval for shear-thickening is obtained when shear rate is scaled with the terminal relaxation time. These observations support the theoretical models of shear-thickening of Peiffer et al.[11] and Marrucci et al.[42] The location of shear-thickening is qualitatively correctly predicted by Ahn and Osaki[39] and Witten and Cohen;[34] however, these two models do not make predictions for the effect of the association strength on the magnitude of shear-thickening. A further comparison of experimental data to the predictions of the various theories will be presented in subsequent publications.

The hygroscopic nature of ionomers makes them difficult to work with in a normal laboratory environment. Care must be taken to avoid or account for moisture adsorption to obtain reproducible results.

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