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Ion Hopping in Ethylene−Methacrylic Acid Ionomer Melts As Probed by Rheometry and Cation Diffusion Measurements

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ABSTRACT: The dynamics of chain and ionic group motion were investigated in a series of ethylene−methacrylic acid (E/MAA) ionomers of varying cation type and neutralization level, all formed from the same E/MAA copolymer. Low-shear-rate rheological measurements were utilized to determine the terminal relaxation time (t_d) of the polymer chains. The much faster ion-hopping time (τ) was measured through the use of cation diffusion studies, in which a finite slab of one ionomer diffuses into a matrix of a second ionomer. For the Mg/Ca, Mg/Li, Na/Ca, and Na/Li diffusion couples studied, the diffusion coefficient follows inversely with melt viscosity, though τ extracted from the diffusion coefficients depends more weakly on cation type than does t_d obtained from melt rheometry. For the highly neutralized E/MAA ionomers, τ is 4 orders of magnitude shorter than t_d, but the two relaxation mechanisms have a similar dependence upon temperature, in agreement with current theories of ionomer dynamics.

Introduction

Since their introduction more than 4 decades ago, ionomers—polymers that contain a small amount of covalently bound ionic functionality—have been recognized as important engineered materials utilized in applications ranging from adhesives to fuel cell membranes.[1−5] The ionic groups aggregate into nanometer-size domains within the relatively nonpolar polymer matrix[1−8] and act as temporary cross-links, strongly influencing ionomer melt flow behavior.[9] For example, ionomers typically have viscosities and terminal relaxation times orders of magnitude greater than those of comparable nonionic polymers.

The typical ionomer has many ionic groups distributed randomly along a high-molecular-weight polymer backbone. Since the ionic cross-links persist to temperatures in excess of the polymer degradation temperature,[10−12] melt processing must occur in the presence of these associations, which are frequently so strong as to make the materials intractable. For example, ionic plasticizers must typically be added to achieve significant melt flow in sulfonated ionomers.[13,14] However, some ionomers, such as the salts of ethylene−methacrylic acid (E/MAA) copolymers, can be readily melt-processed utilizing conventional equipment.[15] Flow in these associating polymers is thought to proceed by "ion hopping",[16,17] where bound ionic groups (cation−anion pairs, e.g., sodium methacrylate residues in Na-neutralized E/MAA) hop between aggregates in a thermally activated process with a characteristic time τ. Since these ionic groups are bound to the polymer chain, each hop allows a relaxation of any stress in the portion of the chain bearing that ionic group. The terminal relaxation time of the entire polymer chain, t_d, is thus increased relative to an analogous nonionic polymer, due to these temporary cross-links.

A comprehensive understanding of the dynamics of ionomer melts[18−20] necessitates accurate measurements of both τ and t_d on the same material at the same temperature. In a few favorable cases,[21−24] including select E/MAA ionomers,[24] rheological measurements have been able to access the terminal zone for ionomer melts, allowing t_d to be measured. While signatures of the faster ion-hopping time τ have been detected rheologically,[20,25] data are quite limited; most measurements of τ have employed dilute ionomer solutions[26,27] or specially synthesized short-chain telechelic ionomers[17] where complete chain relaxation accompanies each "hop".

An important consequence of this ion-hopping mechanism is that t_d should be proportional to τ; that is, the rate of chain relaxation is intimately tied to the rate of ion hopping. Here, we investigate the melt dynamics of Li^+, Na^+, Mg^{2+}, and Ca^{2+} ionomers prepared by neutralizing a single E/MAA copolymer to various levels. Mechanical rheometry is employed to measure t_d, while the ion-hopping process is quantified through X-ray microanalysis measurements of cation diffusion rate. While we refer to "cation diffusion" below, because it is the cation which is detected experimentally, we note at the outset that the ion-hopping mechanism presumes that the ions move as bound pairs through the nonpolar, polyethylene-rich matrix rather than as free ions.

Experimental Section

Materials. All ionomers were synthesized from the same statistical ethylene−methacrylic acid (E/MAA) copolymer previously studied by Vanhoorne and Register,[24] which contains 11.5 wt % methacrylic acid. Measurements on esterified derivatives of this polymer yield a weight-average molecular weight $M_w = 71$ kg/mol (high-temperature light scattering) and an apparent polydispersity $M_w/M_n = 4.0$ (high-temperature gel permeation chromatography calibrated with linear polyethylene standards). The high-pressure process used for E/MAA copolymerization is known to produce substantial long-chain branching.[28] Using the measured intrinsic viscosity $[\eta] = 56$ mL/g (1,2,4-trichlorobenzene, 135 °C), the known Mark−Houwink relationship for linear polyethylene,[29] and the assumption of random trifunctional branching,[30] we estimate

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that there is roughly one long-chain branch per 3000 g/mol of polymer.[31] The ionomers were prepared from the E/MAA copolymer by melt neutralization,[28] using the metal hydroxide; the actual neutralization level was determined by X-ray fluorescence. The ionomers are designated as "M*xx*" where "M" is the atomic symbol of the neutralizing metal cation and "*xx*" is the percent of acid groups that are neutralized.

Rheological Measurements. Samples were molded into disks at 130 °C under vacuum. Dynamic shear measurements covering 10^{-3}−10^{2} rad/s were conducted on a Rheometrics mechanical spectrometer (RMS-800) with 25 mm parallel plate fixtures, under a flowing dry N_2 atmosphere. The strain amplitude (15−25%) was determined to lie within the linear viscoelastic regime. Where possible, data were acquired from 105 to 180 °C. To access the lower end of this temperature range, samples were first heated to 135 °C to ensure complete melting and then cooled to the test temperature. In some cases, particularly at lower neutralization levels, measurements could not be conducted to temperatures above 155 °C, due to a progressive increase in viscosity with time which we attribute to the gradual formation of interchain anhydrides. Steady shear (creep) measurements were conducted using a Rheometrics dynamic stress rheometer (DSR) with a 40 mm cone-and-plate fixture (cone angle of 0.04 rad), also under a flowing dry N_2 atmosphere. Measurements were typically conducted at 135 °C, though for selected ionomers additional measurements were made at higher and lower temperatures. Applied stresses of 5−1000 Pa were used to obtain shear rates of 10^{-4}−10^{-2} s^{-1}. Creep durations of typically 10−20 times t_d were employed to ensure that steady state was achieved, where t_d was estimated from prior dynamic shear experiments; recoil measurements following steady creep were conducted for similar durations. Recoverable shear compliances measured on startup and recoil agreed to within error (<10%).

Cation Diffusion Measurements. Trilayer sheets were prepared, consisting of a thin Na- or Mg-neutralized ionomer film (≈40 μm thick, measured precisely) sandwiched between two thick layers (≈2 mm) of either Li- or Ca-neutralized ionomer. The sandwich was annealed in a temperature-calibrated oven under a dry nitrogen atmosphere for a predetermined time at the desired temperature and then rapidly cooled to room temperature. After annealing, the trilayer sandwich was cut in cross section at room temperature using a freshly prepared glass knife on a Leica Ultracut microtome. The smooth surface so obtained was then coated with approximately 24 nm of carbon to prevent charging during analysis.

A Philips XL30 field emission scanning electron microscope (SEM) fitted with a Princeton Gamma Tech Si(Li) energy-dispersive X-ray detector was used to measure the concentration of the Mg, Na, and Ca cations as functions of position across the cross-sectioned sandwich. A 6 keV electron beam was rastered for 515 μm across the specimen, perpendicular to the initial interfaces between the three layers in the sandwich. This low electron beam energy is required to avoid charging of the polymer during examination and to maintain good spatial resolution. The interaction volume for an E/MAA copolymer with 11.5 wt % MAA groups and 60% Mg^{2+} neutralization was determined by Monte Carlo simulations (Electron Flight Simulator; Vienna, VA) to be approximately 1 μm^3 and roughly spherical, meaning that the spatial resolution in the line scans is approximately 1 μm. The cation concentration profile was determined from the number of counts falling within energy windows characteristic for Na K (986.8−1095.2 eV), Mg K (1198.5−1309.5 eV), or Ca Kα (3633.4−3748.6 eV) X-rays, at each position along the line scan.

Results

Melt Rheology. Dynamic shear data for Na61, collapsed into master curves through time−temperature superposition, are shown in Figure 1. Good superposition was obtained over more than 5 decades of reduced frequency. We have examined numerous ethylene-based ionomers in addition to those described here,[31] with variations in comonomer type (acrylic acid vs methacrylic acid) and level and neutralizing cation type and level. For all ionomers examined, we find good superposition of dynamic shear data for temperatures ranging from 105 °C to the upper temperature limit (155−180 °C), indicating that the two relaxation mechanisms, t_d and τ, must be well separated in time and/or have very similar temperature dependences.

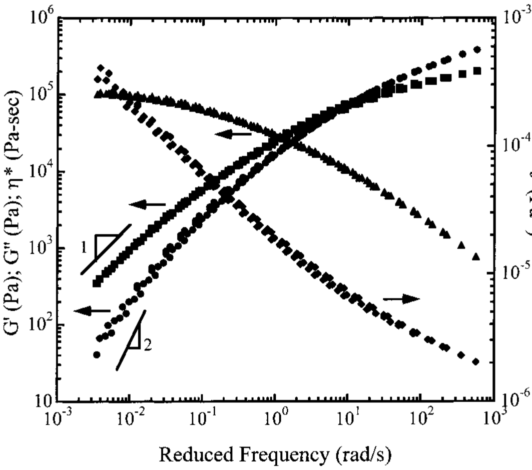

Figure 1. Master curves constructed by time−temperature superposition from dynamic shear data (105−180 °C) for Na61. Reference temperature T_r = 135 °C. Storage modulus, G' (●, left axis); loss modulus, G'' (■, left axis); complex viscosity, η^* (▲, left axis); storage compliance, J' (◆, right axis).

The data in Figure 1 begin to approach the terminal region, where η^* is independent of frequency and $G' \sim \omega^2$ and $G'' \sim \omega^1$, which permits an estimation of t_d. However, more precise measurements of t_d may be obtained from steady-shear creep and recovery experiments at low deformation rates, which provide values for the zero-shear viscosity η_0 and recoverable shear compliance J_e^0. The terminal relaxation time can be calculated from these two quantities as

$$t_d = aJ_e^0\eta_0 \qquad (1)$$

where the order-unity prefactor a depends on the chain architecture: $a = 10/\pi^2$ (≈1.013) for monodisperse entangled linear polymers,[32] while early[33] and recent[34] models for the dynamics of monodisperse star polymers predict $a = 2$ and $a \approx 3.2$, respectively. For our ionomers, all based on a polydisperse and highly branched E/MAA copolymer, a is unknown. However, this is not a serious impediment, as a is a constant across all our ionomers (and hence in all comparisons in this work), since all are prepared from the same E/MAA copolymer. For order-of-magnitude calculations, we will take $a = 1$ below. J_e^0 is only weakly dependent upon temperature[35] and so, like a, should depend only upon the molecular architecture of the polymer and not on the cation type or level of neutralization. From measurements conducted on both the E/MAA copolymer and its ionomer derivatives, we found $J_e^0 = (2.2 \pm 0.5) \times 10^{-4}$ Pa^{-1} (one standard deviation, across all materials at various applied shear stresses in the Newtonian region).[36]

Since both J_e^0 and a are constant in this study, t_d is simply proportional to η_0, so variations in t_d achieved through neutralization or temperature are directly

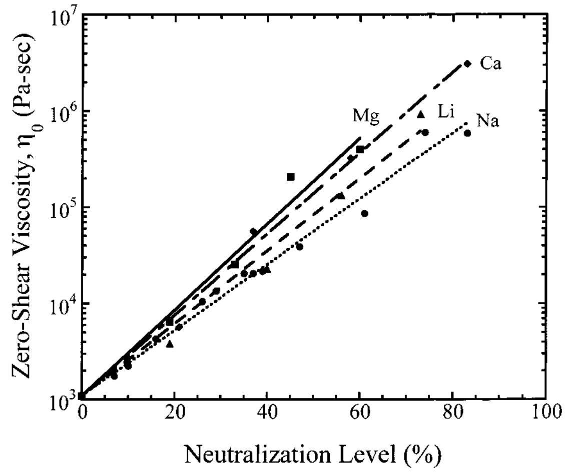

Figure 2. Measured zero-shear viscosities (η_0) for Mg (■), Ca (◆), Li (▲), and Na (●) ionomers determined via steady-shear creep experiments at 135 °C, plotted against neutralization level. Lines correspond to exponential fits to each data set. Zero neutralization corresponds to the E/MAA copolymer.

manifested in η_0. Figure 2 shows the dependence of η_0 (at 135 °C) on neutralization level for ionomers neutralized with all four cations. In each case, a strong (exponential) dependence of η_0 on neutralization level is observed, with η_0 increasing by more than 3 orders of magnitude upon neutralization of 80% of the methacrylic acid groups. The choice of cation type has a modest effect here, with η_0 going in the order Mg > Ca > Li > Na. Similar results can be inferred from the melt index measurements of Bonotto and Bonner on ethylene–acrylic acid copolymers partially neutralized with these same cations.[37]

Activation energies E_a were determined from Arrhenius fits to the time–temperature shift factors used in constructing master curves such as Figure 1 from dynamic data. Values of E_a were also obtained for selected ionomers from the temperature dependence of the zero-shear viscosity measured in steady shear; the two methods produced identical E_a values within error. Figure 3 shows the E_a values plotted against neutralization. For Li, Mg, and Ca, a general increase in E_a with neutralization level is found, while for Na, the activation energy is practically independent of neutralization level and equal to that determined for the E/MAA copolymer, $E_a = 71 \pm 1$ kJ/mol. These activation energies correspond to the terminal relaxation behavior of the polymer chains, as this is the principal relaxation evident in Figure 1; we will compare these values to those obtained for the faster ion-hopping process in the next section.

Cation Diffusion. As described in the Experimental Section, a trilayer sandwich was prepared such that a thin midlayer of one ionomer (neutralized with Na or Mg) is allowed to diffuse into two thick outer layers of another ionomer (neutralized with either Li or Ca). The diffusion of the cations is monitored by the use of X-ray microanalysis. The energy spectra for ionomers neutralized with Na, Mg, and Ca are shown in Figure 4. Unfortunately, Li K X-rays cannot be detected due to their low energy (54 eV). Moreover, at the 6 keV electron energy employed, the Ca Kα X-ray peak is barely distinguishable above background. Therefore, Na and Mg are the cations which can be best profiled using this technique.

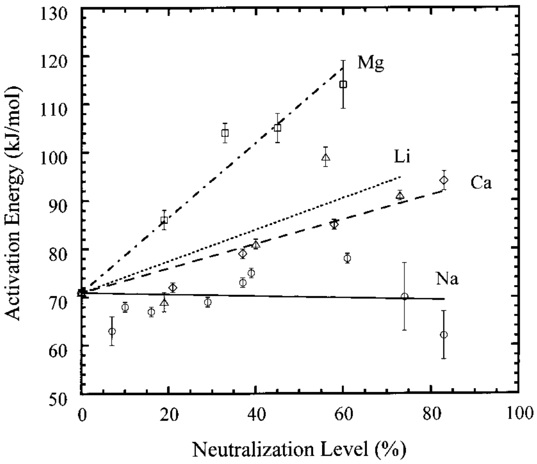

Figure 3. Activation energies for Mg (□, dot–dashed curve), Li (△, dotted curve), Ca (◇, dashed curve), and Na (○, solid curve) ionomers determined via time–temperature superposition of dynamic shear data, plotted against neutralization level. Best-fit lines are intended as guides to the eye, rather than rigorous representations of the variation in E_a with neutralization level. Error bars correspond to one standard deviation of the Arrhenius fit.

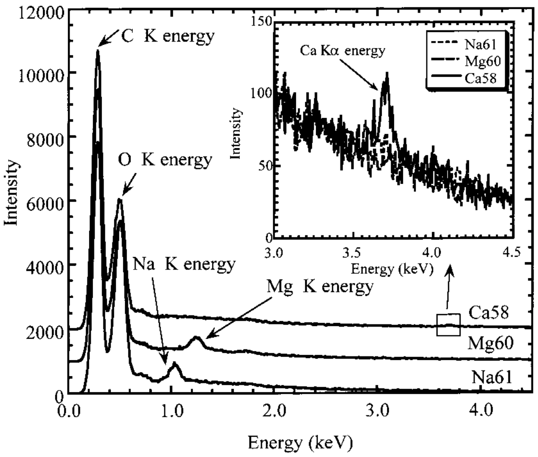

Figure 4. X-ray energy spectra for Na, Mg, and Ca ionomers measured at an electron beam energy of 6 keV. Successive spectra have been shifted vertically by +100 arbitrary intensity units for clarity. Inset shows the Ca Kα region (no intensity shift).

A series of representative diffusion profiles are shown in Figure 5 for Mg60 (midlayer) diffusing into Ca58 (outer layers). The sandwich is initially prepared by bringing the three layers together at 150 °C under minimal pressure to generate bubble-free interfaces. The sharp edges of the concentration profile for the “time zero” sample in Figure 5 shows that, during this initial treatment, the extent of cation diffusion is not more than 3 μm, only moderately higher than the calculated 1 μm resolution of the microanalysis method. Frequently, several days elapsed between the end of the annealing process for any trilayer sandwich and its examination by X-ray microanalysis, during which time the specimens were stored at room temperature. To test for diffusion during this period, the “time zero” sample was reexamined 4 months later. The profiles in Figure 5 show that there is no substantial difference between the two—as expected,[38] given the high activation energies and the fact that the polyethylene matrix is partially crystalline at room temperature.[10,39] The initial thickness of the midlayer was precisely determined from

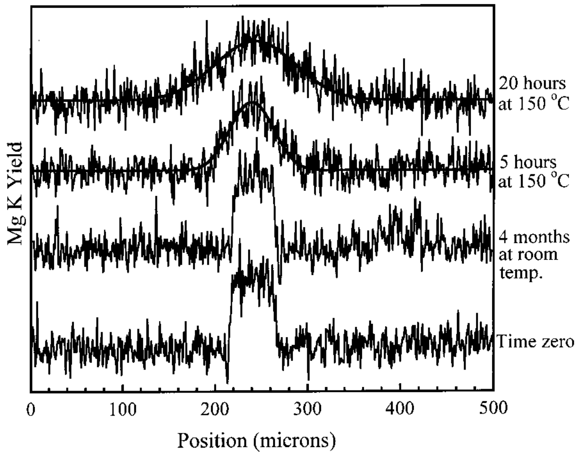

Figure 5. Mg concentration profiles for Mg60 diffusing into Ca58. From bottom to top, profiles are shown at "time zero", after 4 months of room temperature annealing, and after 5 and 20 h of annealing at 150 °C. Profiles have been shifted vertically for clarity.

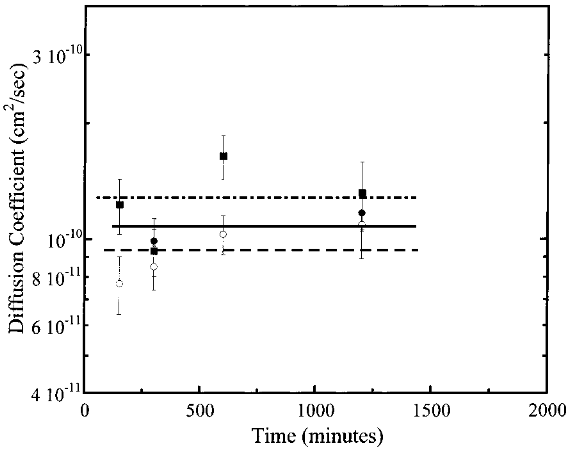

Figure 6. Fitted values of $\mathscr{D}_{\mathrm{ion}}$ plotted against annealing time at 150 °C for Ca58/Na61/Ca58 (■, dot–dashed line), Ca58/Mg60/Ca58 (●, solid line), and Li56/Mg60/Li56 (○, dashed line) trilayer sandwiches, where the cation initially in the midlayer was monitored. Error bars correspond to one standard deviation in the fit used to determine $\mathscr{D}_{\mathrm{ion}}$. Horizontal lines are drawn at the average value of $\mathscr{D}_{\mathrm{ion}}$ for each system.

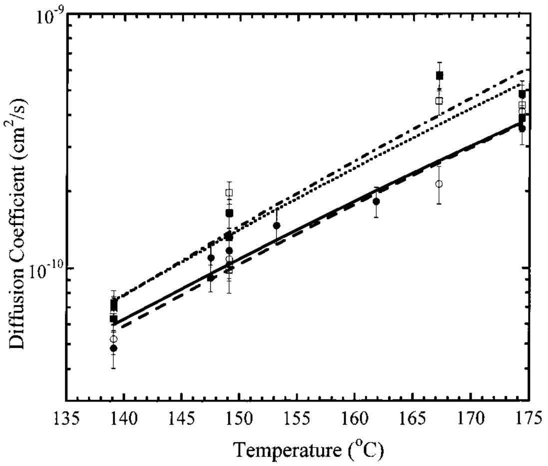

Figure 7. $\mathscr{D}_{\mathrm{ion}}$ as a function of temperature for Ca58/Mg60/Ca58 (●, solid curve), Li56/Mg60/Li56 (○, dashed curve), Ca58/Na61/Ca58 (■, dot–dashed curve), and Li56/Na61/Li56 (□, dotted curve) trilayer sandwiches. Error bars correspond to one standard deviation in the fit used to determine $\mathscr{D}_{\mathrm{ion}}$. Continuous curves are Arrhenius fits.

the time zero profile; the variation (one standard deviation) in initial midlayer thickness was approximately 1.5 μm for specimens cut from any particular sandwich.

After 5 and 20 h of annealing at 150 °C, Figure 5 shows that significant diffusion of the Mg cations has occurred, resulting in near-Gaussian profiles. We model the cation motion as Fickian diffusion of a finite pulse (the thin Mg60 film) into an infinite medium (the thicker Ca58 films). The solution to this diffusion profile is[40]

$$\bar{c}(x,t_{\mathrm{a}}) = \frac{1}{2}\left[\mathrm{erf}\left(\frac{h-x}{\sqrt{4\mathscr{D}_{\mathrm{ion}}t_{\mathrm{a}}}}\right)+\mathrm{erf}\left(\frac{h+x}{\sqrt{4\mathscr{D}_{\mathrm{ion}}t_{\mathrm{a}}}}\right)\right] \qquad (2)$$

where $\bar{c}(x,t_{\mathrm{a}})$ is the normalized cation concentration (initially unity in the center of the trilayer sandwich), x is the distance normal to the center plane of the sandwich, t_{a} is the annealing time, h is the initial half-thickness of the midlayer, and $\mathscr{D}_{\mathrm{ion}}$ is the cation diffusion coefficient. Figure 5 shows the best fits of this expression to the $t_{\mathrm{a}} = 5$ and 20 h data; good fits are obtained, though the noise in the profiles is so large as to obscure any modest deviations from eq 2. A better test of the key assumption underlying eq 2—Fickian diffusion, with a concentration-independent $\mathscr{D}_{\mathrm{ion}}$—is to examine whether the best-fit value of $\mathscr{D}_{\mathrm{ion}}$ is independent of t_{a} (and hence cation concentration). Indeed, Figure 6 shows that $\mathscr{D}_{\mathrm{ion}}$ does *not* vary substantially with time for any of the diffusion pairs examined here, confirming that Fickian diffusion is a satisfactory approximation.

For the particular case of Mg60 diffusing into Ca58, $\mathscr{D}_{\mathrm{ion}} = (1.2 \pm 0.1) \times 10^{-10}$ cm²/s at 150 °C for the Mg ions. As noted above, the Ca diffusion profile can also be measured on the same annealed sandwiches (though with poorer statistics), yielding $\mathscr{D}_{\mathrm{ion}} = (1.1 \pm 0.3) \times 10^{-10}$ cm²/s for the Ca ions. We note that strict counterdiffusion of Mg and Ca is not required in this system, as all the layers of the sandwich are only partially neutralized; that is, there are three cations present: Mg^{2+}, Ca^{2+}, and H^{+}. However, unequal values of $\mathscr{D}_{\mathrm{ion}}$ for Mg and Ca would produce a neutralization gradient in the film, which evidently does not occur.

Diffusion experiments were conducted using four cation combinations, all at roughly 60% neutralization: Mg60 or Na61 (midlayers) into Li56 or Ca58 (outer layers), at annealing temperatures ranging from 139 to 174 °C. Figure 7 shows the diffusion coefficients for these four cases plotted against temperature. There is a significant difference—approximately 30%— between the values of $\mathscr{D}_{\mathrm{ion}}$ for Na (faster) and Mg, though there is no clear effect of the identity of the outer layer in the sandwich. Arrhenius fits to the data yielded E_{a} values of 80–90 kJ/mol (see Table 1).

Discussion

Interpretation of $\mathscr{D}_{\mathrm{ion}}$. Though there are in fact three cations present in these diffusion experiments (two metal cations and H^{+}), we believe that the design of the experiments produces values of $\mathscr{D}_{\mathrm{ion}}$ which are close to the self-diffusion coefficient of the cation of interest, for the following reasons. First, the ionomer pairs used in the diffusion trilayers were chosen to have similar neutralization levels and, by Figure 2, similar viscosities. This is particularly true for the matched-valency pairs Mg/Ca and Na/Li, where the η_0 values

Table 1. Activation Energies E_a for E/MAA Ionomers Neutralized with Various Cations

method	ionomer or diffusion pair	E_a (kJ/mol)[a]
rheometry	Li56	99 ± 2
	Na61	78 ± 1
	Mg60	114 ± 5
	Ca58	85 ± 2
diffusion	Na61 into Li56	85 ± 18
	Na61 into Ca58	90 ± 10
	Mg60 into Li56	82 ± 7
	Mg60 into Ca58	80 ± 8

[a] Quoted uncertainties correspond to one standard deviation in the Arrhenius fit.

differ by 50% or less. Since all ionomers are prepared from the same E/MAA copolymer, then the similar viscosities should reflect similar rates of ion hopping in the two materials, as discussed further below. In other words, if the self-diffusion coefficients of the cations in the two ionomers forming the trilayer are similar, then the measured $\mathscr{D}_{\text{ion}}$ should correspond closely to both. Second, Figure 7 shows a surprising insensitivity of the value of $\mathscr{D}_{\text{ion}}$ to the identity of the outer layers, even when the diffusion experiments pair divalent and monovalent cations (Na61 into Ca58, Mg60 into Li56). If counterdiffusion occurs such that no gradient in neutralization level results, then the flux of monovalent cations must be exactly double the counterflux of divalent cations. However, close inspection of Figure 2 shows that the two ionomers neutralized with monovalent cations (Na61, Li56) have η_0 values approximately 3 times lower than the ionomers neutralized with divalent cations (Mg60 and Ca58), so faster diffusion of the monovalent cations is expected in the particular diffusion experiments conducted here. If the inner and outer layers were not chosen to have similar neutralization levels (and hence η_0 values), then a substantial effect of the identity of the outer layer on $\mathscr{D}_{\text{ion}}$ would be expected; we have indeed observed this effect,[31] which will be reported on subsequently.

Since we are interested here in comparing the time scales for ion hopping (τ) and chain diffusion (t_d), we need to relate the measured $\mathscr{D}_{\text{ion}}$ to τ. We begin by assuming that within an aggregate rapid exchange of cations between anions should be possible, such that a polymer segment bearing a carboxylate anion has an equal chance of leaving the aggregate with any metal cation inside that aggregate. In this case, each hop is statistically independent, and a sequence of such hops yields a diffusive motion of the cations which can proceed much more rapidly than the diffusion of polymer chains.[20,38] A diffusion coefficient can be related to a characteristic time t through a characteristic length l:

$$t = \frac{l^2}{\mathscr{D}} \tag{3}$$

For cation diffusion, $\mathscr{D} = \mathscr{D}_{\text{ion}}$, $t = \tau$, and $l \approx d$, the average distance between ionic aggregates. For chain diffusion, $\mathscr{D} = \mathscr{D}_{\text{chain}}$, $t = t_d$, and $l \approx R_g$, the radius of gyration the polymer chain.[32] Thus, the chain and ion dynamics can be compared either in terms of $\mathscr{D}$ or in terms of t, provided the appropriate value for l is determined independently.

Some comparisons may be made even in the absence of values for l. Since small-angle X-ray scattering (SAXS) indicates little change in melt structure with temperature in E/MAA ionomers,[11,39] d may be taken as temperature-independent, meaning that the activation energy determined for $\mathscr{D}_{\text{ion}}$ also corresponds to the activation energy for τ. Table 1 compares the E_a values determined in the cation diffusion experiments and by mechanical rheometry; though the E_a values in the diffusion experiments carry a much greater uncertainty, the general agreement between the two supports the idea that t_d is proportional to τ, which is a fundamental principle of the ion-hopping mechanism: speed up the individual hops, and one speeds up the terminal relaxation proportionally. Second, Figure 7 shows that $\mathscr{D}_{\text{ion}}$ for Mg is lower than for Na, by approximately a factor of 1.3. By comparison, Figure 2 shows that the ratio of viscosities is approximately 3 (log-mean of Mg/Ca and Na/Li), with Mg having the higher viscosity. Thus, the effects of changing cation type from Na to Mg are consistent: an increase in η_0, a decrease in $\mathscr{D}_{\text{ion}}$. The quantitative disagreement (factors of 1.3 vs 3) remains a puzzlement, however. This difference may result from differences in the details of the ion-hopping process for monovalent cations (which are accompanied by only one anion) vs divalent cations (which are coordinated to two anions, each connected to an independent polymer chain segment).

We can obtain order-of-magnitude estimates for the rates of cation and chain motion through eq 3. In terms of diffusivities, we estimate $R_g \approx 7$ nm, which is the value for linear polyethylene[41] with the same intrinsic viscosity[29] as our branched E/MAA; this value of R_g produces $\mathscr{D}_{\text{chain}} \approx 2 \times 10^{-14}$ cm^2/s for Mg60 at 150 °C, taking $a = 1$ in eq 1. This may be compared with $\mathscr{D}_{\text{ion}} = 1.2 \times 10^{-10}$ cm^2/s measured directly for the Mg cations in Mg60 at 150 °C—a ratio of nearly 10^4. To make the comparison in terms of times, we take $d \approx 4$ nm, determined from the position of the “ionomer peak” in molten Na61 (treating the peak simply as a Bragg reflection).[39] This yields $\tau \approx 1.3$ ms for Mg60 at 150 °C, which may be compared directly with $t_d = 73$ s (taking $a = 1$ in eq 1), a ratio of nearly 10^5. By either measure, it is clear that cation motion occurs far more rapidly than chain motion, as previously deduced both by Van Alsten[38] and by Colby et al.[20] This confirms, post facto, our assumption of facile cation exchange within an aggregate: if cations remained bound to particular anions throughout the diffusion process, then $\mathscr{D}_{\text{ion}}$ and $\mathscr{D}_{\text{chain}}$ would be equal.

It is reasonable to ask whether the ion-hopping relaxation at τ could be seen mechanically as well, as has been reported in sulfonated polystyrene ionomers.[20,25] In our rheological experiments, we are able to obtain data to reduced frequencies as high as 10^3 rad/s at 135 °C (see Figure 1). For Na61, τ is estimated as 2.7 ms at 135 °C, following the procedure described above; thus, the relaxation would be expected at $\omega = 1/\tau = 400$ rad/s, but no such peak in G'' is evident in Figure 1. Moreover, in Figure 1 the highest value of G' is approximately 4×10^5 Pa, which is still much lower than the plateau modulus for linear polyethylene (2.3×10^6 Pa at 170 °C).[35] Indeed, G' is still increasing strongly with frequency at 10^3 rad/s, rather than leveling out into a plateau. These observations lead us to believe that some relaxation due to chain disentanglement must occur at shorter times (higher frequencies) than can be measured in our dynamic shear experiments. However, since all the chains contain some ionic groups, this also suggests that τ may be broadly distributed, allowing significant relaxation to occur even at frequencies several times the value of $1/\tau$ calculated from the diffusion measurements. This relaxation is likely favored by the broad molecular weight distribution and moderately entangled long branches which are present in these E/MAA copolymers, allowing some parts of the system[42] to relax much faster than t_d. If τ is broadly distributed and overlaps with relaxation due to chain disentanglement (the leading edge of the t_d relaxation), then we would not expect to see a clear peak corresponding to τ, emphasizing the need for the cation diffusion measurements for its determination.

Comparison with Theories of Ionomer Dynamics. The long-chain branching and broad molecular weight distribution in our E/MAA copolymer hamper a quantitative comparison with theories of ionomer dynamics, as these have been developed for linear, monodisperse chains. However, selected comparisons are still possible. The first theory for ionomer dynamics was that due to González,[18] who assumed that chains move by reptation but only when all ionic association are broken, such that

$$t_d = \exp(n) t_d^0 \tag{4}$$

where n is the average number of ionic groups per (linear) chain and t_d^0 is the terminal relaxation time of the chain in the absence of ionic associations. The González model thus predicts an exponential increase of viscosity with ion content, in agreement with the results of Figure 2. However, important disagreements between this model and our results exist as well. First, since n is not significantly temperature dependent (ionic aggregates persist up to the decomposition temperature with no discernible change),[10,11,39] the temperature dependence of t_d matches that of t_d^0. For an esterified (nonassociating) derivative of this E/MAA copolymer, we[24] previously measured $E_a = 48 \pm 1$ kJ/mol, in significant disagreement with the values found here for the ionomers. More importantly, in the González model, ionic groups move only during the fraction of the time during which the chain reptates. Thus, unless additional mechanisms are postulated, cation and chain diffusion proceed only in tandem, yielding $\mathscr{D}_{\text{ion}} = \mathscr{D}_{\text{chain}}$, in complete disagreement with our results and the previous conclusions of Van Alsten[38] and Colby et al.[20]

More recent theories of the dynamics of reversible networks consider the chain to move through a series of "hops", occurring at intervals τ, of chain segments containing an associating unit. The theories of Leibler et al.[19] and Colby et al.[20] lead to expressions for t_d scaling as

$$t_d \sim n^2 \tau \tag{5}$$

This expression captures the essential feature that t_d scales with τ, consistent with both the temperature dependences (similar E_a for $\mathscr{D}_{\text{ion}}$ and t_d) and cation effects (Mg produces higher η_0 and lower $\mathscr{D}_{\text{ion}}$ than Na) which we have presented here. The exponential dependence of t_d on n reflected in Figure 2 is not consistent with the n^2 dependence predicted by eq 5; this could result from the substantial departure of our E/MAA from the ideal monodisperse linear case (given the dramatic differences between the dynamics of linear and branched polymers[42]) or from a dependence of τ on the neutralization level. At least two mechanisms can be envisioned for the latter. One is simply that the association number of the aggregates, and by inference the binding strength, increases with the density of ionic groups; in polystyrene-based ionomers, evidence exists for an increase in aggregate size with functionalization level.[43] Second, recall that as one neutralizes these materials to greater levels, one is also removing the unneutralized ("free") acid groups from the system. These free acid groups associate with the aggregates and produce a viscosity reduction.[24] Thus, progressive removal of these groups through increased neutralization should produce a steeper-than-predicted dependence of t_d on n. The role of these unneutralized groups on the dynamics of partially neutralized E/MAA ionomers will be described in a future communication.

Conclusions

The rates of both polymer chain and ionic group motion in E/MAA ionomers can be quantified through parallel melt rheometry and cation diffusion measurements. While these methods give either a relaxation time or a diffusion coefficient, one may convert between the two using the relevant characteristic distance (radius of gyration for chain diffusion, interaggregate distance for ionic group diffusion) estimated independently. The zero-shear viscosities η_0 for E/MAA ionomers neutralized with Li^+, Na^+, Mg^{2+}, and Ca^{2+} were found to depend exponentially on neutralization level, with the choice of neutralizing cation having only a modest effect upon η_0. Since the recoverable compliance is independent of neutralization level and cation type, these changes in η_0 directly reflect changes in the terminal relaxation time t_d upon neutralization. For Mg/Li, Mg/Ca, Na/Li, and Na/Ca diffusion couples prepared from highly neutralized ionomers, the diffusion coefficients of the ionic groups are approximately 5 orders of magnitude higher than the diffusion coefficients of the polymer chains, reflecting the underlying "ion-hopping" process: ionic groups are transported between aggregates through the micro-Brownian motion of polymer subchains, thus permitting a diffusive motion of cations at a rate greatly exceeding that of the motion of the polymer chain's center of mass. However, the terminal time (polymer chain relaxation) and ion-hopping time (ionic group motion) have similar activation energies, as predicted by current theories for the dynamics of associating polymers.

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References and Notes

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