The Role of Excess Acid Groups in the Dynamics of Ethylene−Methacrylic Acid Ionomer Melts

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ABSTRACT: Ethylene−methacrylic acid (E/MAA) ionomers are commonly neutralized to substoichiometric levels, leaving unneutralized ("excess") carboxylic acid groups along the chain. Previous observations indicate that these excess acid groups interact preferentially with the ionic units and produce a reduction in viscosity. Here, we employ a combination of melt rheometry and cation diffusion experiments to elucidate the role of these excess acid groups in the chain and ion dynamics of E/MAA ionomers. We find that the excess acid groups act not by introducing a separate relaxation mechanism, but by accelerating the rate of ion hopping in these materials—a "plasticization" of the ionic interactions—which in turn speeds up chain relaxation proportionately. At low ion contents, the functional dependence of viscosity vs ion content is profoundly altered by excess acid groups, due to the competing effects of viscosity increase through interacid hydrogen bonding and viscosity reduction through plasticization of the ionic associations. A substantial dependence of the ion-hopping rate on the neutralization level is noted and quantified, with the ionic group diffusivity decreasing as neutralization level is increased. Finally, diffusion experiments pairing partially neutralized and unneutralized E/MAA ionomers show an additional contribution to the diffusion rate from a gradient in neutralization level, beyond that provided by the concentration gradient.

Introduction

The flow behavior of polymers bearing strongly associating groups ("stickers") is a fascinating subject of current interest.[1−7] Among these materials are ionomers, polymers bearing a small amount of ionic functionality (such as metal carboxylate groups) covalently bound to the polymer chain. These ionic groups aggregate into nanometer-scale domains, acting as transient physical cross-links; flow occurs through "ion hopping", where ionic groups (and the polymer chain segments to which they are connected) jump between aggregates with a characteristic time τ, which is much shorter than the terminal relaxation time t_d of the polymer chain (which bears many ionic groups).[2,3,7,8] We have recently presented a study of the ion and chain dynamics in ethylene−methacrylic acid (E/MAA) ionomers, using a combination of mechanical rheometry (to measure t_d) and cation diffusion measurements (to gauge τ).[7] These materials show an exponential increase in viscosity with increasing neutralization, with the viscosity of a typical E/MAA copolymer increasing more than 1000-fold as complete neutralization is approached.

To retain the manageable viscosities needed for melt processing, E/MAA ionomers are generally neutralized to levels well below 100%, meaning that a significant fraction of the MAA units—all of those in stoichiometric excess over the neutralizing agent—remain unneutralized. (These excess acid groups are sometimes termed "free" acid, though the MAA units are covalently bound to the polymer chain.) Though not ionic, these excess acid groups can also impact the flow behavior of the material. In unneutralized E/MAA copolymers, hydrogen bonding between MAA units raises the viscosity[8−10] relative to a nonassociating (esterified) derivative, but by a relatively modest factor (e.g., 5 times) compared with the orders-of-magnitude increase upon neutralization. However, when these E/MAA copolymers are partially neutralized with Na^+, Vanhoorne and Register[8] found that the excess acid groups produced a comparable *reduction* in viscosity (e.g., 3 times) relative to the esterified derivative.

For alkali metal and alkaline earth salts of E/MAA, FTIR spectroscopy demonstrates that the excess acid groups preferentially associate with the ionic aggregates.[8,11,12] Vanhoorne and Register[8] thus suggested two potential mechanisms for the observed viscosity reduction by excess acid groups: (1) a simple plasticization of the ionic associations, which can otherwise be achieved through the addition of polar small molecules ("ionic plasticizers") such as glycerol and water,[13,14] thus accelerating the basic "ion hopping" process (and consequently the rate of chain relaxation), or (2) an "acid-cation" exchange mechanism, where excess acid groups (and their associated chain segments) can rapidly jump between aggregates, exchange cations with another salt group in the aggregate (e.g., H^+ for Na^+), and allow a different chain segment to diffuse away in the acid form. This mechanism permits chain relaxation without requiring the transport of ionic groups between aggregates.

The objective of the present investigation is to elucidate the role of the excess acid groups upon the chain and ion dynamics in ionomers: to distinguish between the two possible mechanisms of viscosity reduction described above and to further quantify how excess acid affects the dynamics. As in our initial study,[7] the complementary techniques of rheometry and cation diffusion measurements are employed. Two routes were pursued to vary the content of acid groups while holding

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the metal methacrylate content constant: either varying the E/MAA ratio in the copolymer from which the ionomers were prepared or esterifying a fraction of the MAA units in a single E/MAA copolymer.

Experimental Section

Materials. E/MAA statistical copolymers containing 11.5, 15, and 19 wt % MAA (equivalent weights of 750, 570, and 450 g/equiv, respectively) were provided by Dr. John W. Paul of DuPont Packaging and Industrial Polymers (Orange, TX). The 11.5 wt % MAA material is that examined previously;[7,8] MAA contents of the other two copolymers were determined at DuPont. Partially neutralized Li^+, Na^+, Mg^{2+}, and Ca^{2+} ionomers were prepared from these E/MAA copolymers at DuPont by melt neutralization;[15] neutralization levels were determined by X-ray fluorescence, and the melt index (MI) was measured according to ASTM D-1238 condition E (190 °C). In addition, several Na^+ ionomers were prepared from the 11.5 wt % MAA copolymer at Princeton by a solution neutralization process;[8] previous measurements[8] have shown that the two neutralization routes produce Na^+ ionomers with indistinguishable rheological characteristics. Partially esterified materials were prepared at Princeton from the 11.5 wt % MAA copolymer as described previously, with the esterification levels determined via FTIR.[8] The remaining acid groups were subsequently neutralized in solution with the stoichiometric amount of sodium hydroxide or calcium acetate. For the partially esterified ionomers, FTIR confirmed that the ester groups were retained through the neutralization process and that there were no detectable unneutralized acid groups in the final product.

Measurements. As described in detail elsewhere,[7] dynamic viscoelastic measurements were conducted over 10^{-3}−10^{2} rad/s and 105−180 °C on a Rheometrics RMS-800, with strain amplitudes (10−20%) confirmed to lie within the linear regime. Steady-shear measurements were conducted on a Rheometrics DSR-200 at 135 °C; applied stresses of 5−1000 Pa were used in creep and recovery experiments to obtain shear rates of 10^{-4}−10^{-2} s^{-1}, from which the zero-shear viscosity η_0 was extracted. Cation diffusion studies were conducted using the method described previously.[7] In brief, trilayer specimens were prepared consisting of a thin Na- or Mg-neutralized ionomer film (≈30−50 μm, measured precisely) sandwiched between two thick films of a Li- or Ca-neutralized ionomer or of the unneutralized E/MAA copolymer (≈0.7−2.0 mm). After annealing for prescribed times at specified temperatures, the specimens were cut in cross section, and X-ray microanalysis (Philips XL-30 scanning electron microscope with energy-dispersive X-ray detection) was used to measure the concentration profile of Na or Mg. The cation diffusion coefficient, $\mathscr{D}_{ion}$, was obtained by fitting the measured concentration profiles to the Fickian solution for diffusion from a finite-thickness slab into two semiinfinite media.[7] The cases in which Fickian behavior is, and is not, obeyed are discussed in detail below.

Results and Discussion

A. Rheological Behavior of E/MAA Ionomers of Varying MAA Content.

Table 1 contains the compositions and selected rheological characteristics of the three E/MAA copolymers and the Na ionomers prepared therefrom by melt neutralization. Activation energies E_a were obtained from the temperature dependence of the time−temperature superposition shift factors used in creating master curves from dynamic viscoelastic data;[7] the temperatures and frequencies used correspond to the approach to terminal flow,[7] so the E_a values reflect the temperature dependence of polymer chain diffusion (t_d). For the three unneutralized E/MAA copolymers, E_a increases modestly with MAA content, as expected for increased hydrogen bonding. As the neutralization level increases, the zero-shear viscosity η_0 increases rapidly.[7,8] Note that the recoverable compliance J_e^0 does not vary substantially among ionomers prepared from the same E/MAA copolymer, which confirms that no major changes in molecular architecture (e.g., additional branching created via the formation of interchain anhydrides) occur with the neutralization procedures employed.[2,7]

Table 1. Compositions and Rheological Characteristics of E/MAA Copolymers and Na Ionomer Derivatives

wt % MAA	wt % Na	% neutralization	melt index (190 °C)	η_0 (kPa·s) at 135 °C	$J_e^0 \times 10^4$ $(Pa^{-1})^a$	E_a $(kJ/mol)^b$
11.5	0.0	0	100	1.1	2.0	71 ± 1
	0.87	29	14	16	2.1	69 ± 1
	1.11	37	10	18	1.9	73 ± 1
	1.20	40	9.2	22	1.9	76 ± 2
	1.83	62	2.1	86	2.0	78 ± 1
	2.53	87	0.62	590	3.1	62 ± 5
15	0.0	0	60	2.2	1.8	74 ± 2
	0.95	24	5.9	35	2.2	83 ± 1
	1.31	34	2.9	57	2.6	82 ± 2
	1.96	51	1.8	110	2.7	84 ± 1
	2.17	57	1.0	150	2.9	90 ± 3
	2.55	67	0.40	500	2.4	91 ± 8
19	0.0	0	60	2.5	1.5	81 ± 3
	0.39	8	12	16	1.9	81 ± 2
	0.69	14	6.4	39	1.9	80 ± 1
	1.08	22	3.4	62	1.7	84 ± 2
	1.73	35	1.6	270	1.7	90 ± 1
	2.47	51	0.67	480	1.4	95 ± 2

[a] Typical standard deviation in J_e^0 (determined from creep and recovery measurements at several stresses in the terminal region) is 0.3×10^{-4} Pa^{-1}. [b] Uncertainty intervals correspond to ±1 standard deviation of the Arrhenius fit.

All of the materials in Table 1 contain a fraction of unneutralized acid groups. Variation of the weight percent MAA at constant weight percent Na thus corresponds to variation in the number of excess acid groups at a constant ionic group content. For example, 87% neutralization of the 11.5 wt % MAA copolymer and 51% neutralization of the 19 wt % MAA copolymer produce very similar levels of sodium methacrylate units (2.5 wt % Na), but the concentration of excess acid in the latter is more than 6 times that in the former. This comparison provides a simple means for exploring the impact which excess acid groups have on rheology, but it is critical to note that the three E/MAA copolymers are not identical. These materials are prepared in a high-pressure free-radical polymerization process which is known[15] to produce substantial long-chain branching and chain length polydispersity; it would be exceedingly difficult to precisely match these quantities between copolymers with varying MAA content.

Obviously, variations in molecular architecture will also impact the rheology, so as a first step toward correcting for these differences, we divide each ionomer's zero-shear viscosity η_0 (or melt index, MI) by that of the E/MAA copolymer ("base resin") from which it was prepared. Figure 1 shows that this approach effectively collapses both the η_0 and MI data onto master curves (for reference, 1 wt % Na = 0.435 mequiv Na per gram of ionomer). No systematic trend with excess acid level is evident when comparing data for ionomers based on the three copolymers at the same weight percent Na; the η_0 and MI ratios appear to each lie within factor-of-4 bands. As a gauge of the magnitude of experimental error in the η_0 and MI measurements, Figure 1 also shows the product of the η_0 and MI ratios. For Newtonian materials of equal activation energy, this ratio should be unity; the large stresses used in the MI

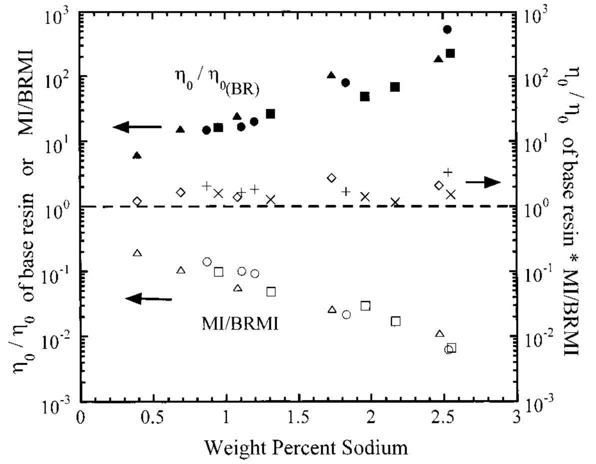

Figure 1. Ratio of Na-neutralized ionomer to E/MAA copolymer zero-shear viscosity at 135 °C (filled symbols, top half of figure, left axis) and melt index at 190 °C (open symbols, bottom half of figure, left axis). Both are plotted vs weight percent Na in the material. Symbols near the center of the figure (just above the horizontal dashed line) denote the cross-product of the η_0 and MI ratios (right axis). MAA contents in base resin are 11.5 (●, ○, +), 15 (■, □, ×), and 19 wt % (▲, △, ◇).

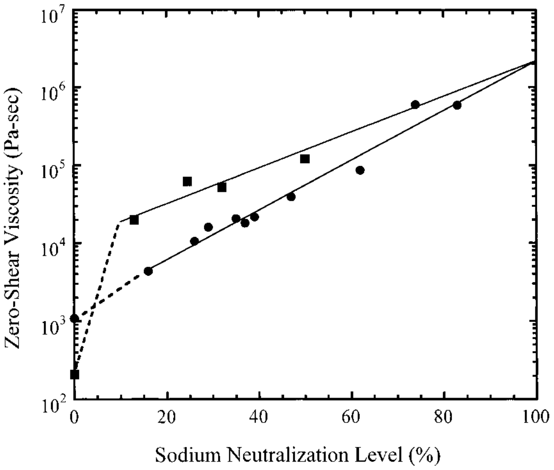

Figure 2. Zero-shear viscosity at 135 °C for both "conventional" ionomers (●) and partially esterified ionomers (■). Both data sets are plotted against the percentage of MAA residues present as sodium methacrylate; for the conventional ionomers, the balance of the units exist in the acid form (excess acid), while for the partially esterified ionomers, the balance of the units are ethyl methacrylate residues. Solid lines are least-squares fits to the data (for neutralization levels > 0), subject to the constraint that the lines must coincide at 100% neutralization. Dashed lines at low neutralization levels, where the two curves cross, are guides to the eye.

measurement cause this cross-product to slowly increase with ion content (t_d), but the curves for the ionomers made from all three E/MAA copolymers still lie within a factor-of-2.5 band. Given the simplicity of the approach taken to correct for differences in molecular architecture (dividing ionomer η_0 and MI by that for the base resin), it is perhaps not surprising that modest effects such as that from excess acid cannot be discerned. A more discriminating (though more experimentally challenging) approach is described in the following section.

B. Rheological Behavior of Partially Esterified Ionomers. A more direct method to evaluate the effect of excess acid groups is to compare ionomers prepared from the same base resin (here, the 11.5 wt % E/MAA copolymer) but with and without excess acid groups, a comparison which can be achieved by converting the excess acid groups to the ethyl ester derivatives. "Conventional" ionomers (containing excess acid groups, such as the materials in Table 1) are denoted here by "C*x*", where C corresponds to the cation type and *x* represents the percent neutralization. To prepare the esterified derivatives, the E/MAA copolymer was first partially esterified; the remaining acid groups were subsequently neutralized with either Na^+ or Ca^{2+}. These ionomers are designated as "C*x*E", where E denotes the ester derivative. Two unneutralized materials are also discussed below: H100 (the E/MAA copolymer, underivatized) and E98 (E/MAA copolymer with 98% esterification of the acid groups).

Figure 2 shows η_0 for both sets of Na ionomers. At 0% neutralization, η_0 for E98 is approximately 5 times smaller[8] than for H100, due to the elimination of hydrogen-bonding interactions through esterification. However, partial neutralization with Na quickly inverts this order; at 13% neutralization, η_0 for the esterified derivative is 6 times *larger* than for the "conventional" ionomer containing excess acid groups. This demonstrates that, in the absence of excess acid, the incorporation of ionic groups causes a very steep initial increase in viscosity, which diminishes at higher levels, leading to an overall downward curvature of the data for the esterified materials in Figure 2. With 11.5 wt % MAA in the base resin (equivalent weight 750 g/equiv), 13% neutralization corresponds to one ionic group per 5800 g/mol of polymer, which is still well below one group per entanglement strand for polyethylene.[16]

In Figure 2, η_0 for the two types of ionomer must coincide at 100% neutralization, where all MAA residues exist as the Na salt (neither ester nor excess acid present). The solid lines in Figure 2 are best exponential fits to the η_0 values for both sets of ionomers (*excluding* H100 and E98), subject to this constraint. However, considering the entire range of data for the partially esterified ionomers (*including* E98), η_0 is certainly *not* well-described by an exponential dependence on neutralization level; rather, the downward curvature in the data suggests a power-law form, as explored further in the following section. Figure 2 clearly shows that the presence of excess acid in conventional ionomers strongly modifies the functional dependence of η_0 on ion content, especially at low levels of neutralization (where many excess acid groups exist per salt group).

At 50% neutralization, Figure 2 demonstrates that the presence or absence of excess acid groups alters η_0 by only a factor of 3 for Na ionomers, consistent with the satisfactory master curves in Figure 1. However, the magnitude of the viscosity reduction by excess acid groups need not be same for all neutralizing cations. For the cation diffusion studies described in the following section, we prepared a partially esterified, Ca-neutralized ionomer, Ca50E, which showed $\eta_0 = 1600$ kPa·s at 135 °C; the "conventional" analogue of this material, Ca50, has[7] $\eta_0 \approx 150$ kPa·s, a full order of magnitude lower. Thus, even at higher ion contents, the quantitative impact of excess acid on the viscosity can be substantial.

C. Cation Diffusion Measurements. 1. Partially Esterified Ionomers. To discriminate between the two proposed mechanisms—plasticization (weakening) of ionic associations vs "acid-cation exchange"—we conducted cation diffusion measurements (of $\mathscr{D}_{\mathrm{ion}}$) on comparable esterified and "conventional" ionomers, to

Table 2. Rheological Characteristics of Select E/MAA Ionomers with and without Excess Acid

ionomer	η_0 (kPa·s) at 135 °C	$J_e^0 \times 10^4$ (Pa^{-1})
Na61	86	2.0
Na50E	120	2.8
Ca58	320	2.6
Ca50E	1600	2.2
average, with acid[a]	170	
average, without acid[a]	440	

[a] Average viscosity for materials with acid (Na61/Ca58) and without acid (esterified, Na50E/Ca50E) calculated as the logarithmic average: $\log \eta_{\text{average}} = 0.5 \log(\eta_{\text{Na}}) + 0.5 \log(\eta_{\text{Ca}})$.

complement the rheological measurements (of η_0). Acid-cation exchange would permit chain relaxation without the motion of cations; while only acid groups move between ionic aggregates, exchange of cations between MAA residues within an aggregate would eventually permit every chain segment bearing an MAA unit to relax. Therefore, if acid-cation exchange were simply active in parallel with the usual ion hopping, excess acid groups should reduce η_0 but leave $\mathscr{D}_{\text{ion}}$ unchanged. By contrast, if plasticization is the mechanism, then $\mathscr{D}_{\text{ion}}$ will be accelerated by the same factor by which η_0 is reduced.

In the diffusion experiments discussed in this section, concentration profiles for the Na cations were determined after annealing a trilayer "sandwich" containing a thin Na-neutralized ionomer film laminated between two thick Ca-neutralized ionomer sheets. (Though we refer to "cation diffusion" here, it is important to note that the ion-hopping mechanism presumes that the metals diffuse as metal carboxylate salts, rather than as dissociated cations; the level of ionization in these systems is expected to be trivially small, as the matrix is polyethylene.) Two sets of diffusion sandwiches were constructed, in which all ionomers had neutralization levels of approximately 50−60% but in which excess acid groups were either present (Na61/Ca58) or absent (Na50E/Ca50E). As we have reported previously[7] for "matched" diffusion pairs (Na61/Ca58, Mg60/Ca58, and Mg60/Li56), $\mathscr{D}_{\text{ion}}$ values determined for the Na61/Ca58 and Na50E/Ca50E sandwiches after various annealing times were identical to within error, confirming that diffusion is Fickian. Fickian diffusion is expected in such "matched" experiments, where the neutralization levels and viscosities are similar for the two ionomer types comprising the sandwich, and the value of $\mathscr{D}_{\text{ion}}$ so extracted should be a good approximation to the self-diffusion coefficient of the ionic groups in both the inner and outer layers. In a following subsection headed "ionomer pairs with unmatched neutralization levels", we demonstrate that when a close matching of viscosity and neutralization level is *not* achieved between the components of the diffusion sandwich, Fickian diffusion is no longer obtained.

Table 2 lists the η_0 values for these four ionomers; because Na^+ and Ca^{2+} ionomers have somewhat different viscosities at the same neutralization level,[7] there is some spread in the η_0 values, so we take a log-mean η_0 to represent the average viscosity of each pair. By this measure, the esterified materials have viscosities 2.6 times larger than the "conventional" ionomers (despite a 10% lower neutralization level). At 150 °C, $\mathscr{D}_{\text{ion}} = 1.3 \times 10^{-10}$ cm^2/s for the Na61/Ca58 pair, while $\mathscr{D}_{\text{ion}} = 4.0 \times 10^{-11}$ cm^2/s for the Na50E/Ca50E pair—a ratio of 3.3 in the $\mathscr{D}_{\text{ion}}$ values, in the direction expected from the η_0 values (lower $\eta_0 \leftrightarrow$ higher $\mathscr{D}_{\text{ion}}$). The close similarity between these results (factors of 2.6 and 3.3) strongly supports the plasticization hypothesis; relaxation still proceeds exclusively by ion hopping, with no need to postulate an additional mechanism. However, the excess acid groups (which interact with the ionic aggregates) weaken the ionic associations and shorten τ.

2. Ionomers of Varying Neutralization Level. The observations in the previous sections indicate that the strong increase in η_0 with neutralization level in E/MAA ionomers[7,8] may result not from introducing ionic associations per se, but rather from *removing* (via neutralization) the excess acid groups which act to plasticize these associations. This raises a more general question: does the ion-hopping time τ vary with the neutralization or functionalization level? Theories for the dynamics of reversible networks[1,3] composed of linear, monodisperse polymer chains with interacting sites predict $t_d \sim n^2\tau$, where n is the average number of ionic groups per chain. Previous applications of this scaling relationship to experimental data for ionomers have generally assumed[3,7] that τ depends solely on temperature and is independent of n. Here, because all ionomers are prepared from the same E/MAA copolymer, $n \sim N$, where N is the neutralization level; alternatively, we may ask whether τ is independent of N.

Qualitatively, a decrease in $\mathscr{D}_{\text{ion}}$ with increasing N was noted by Van Alsten,[12] who measured $\mathscr{D}_{\text{ion}}$ by attenuated total reflectance FTIR in diffusion couples of partially neutralized and unneutralized E/MAA copolymers. The dependence of $\mathscr{D}_{\text{ion}}$ upon neutralization level was manifested as a departure from Fickian diffusion, with diffusion accelerating as the neutralization level dropped, but the magnitude by which $\mathscr{D}_{\text{ion}}$ varied was not quantified. For an ion-hopping process, $\mathscr{D}_{\text{ion}}$ and τ should be related[7] as $\mathscr{D}_{\text{ion}} = d^2/\tau$, where d is the average hop distance—the average separation between ionic aggregates. While d can in principle also change with neutralization level, the peak spacing measured by small-angle X-ray scattering for Na ionomers prepared from the 11.5 wt % MAA copolymer decreases by less than 25% when neutralization is increased from 47 to 83%.[17] Therefore, we consider d to be essentially constant as neutralization level is varied, so that changes in $\mathscr{D}_{\text{ion}}$ directly reflect changes in τ.

To assess the effect of neutralization level on τ, we measured $\mathscr{D}_{\text{ion}}$ at 150 °C for E/MAA ionomers of varying neutralization level, using thin layers of Mg-neutralized ionomers diffusing into Li- or Ca-neutralized ionomers (Mg19/Li19; Mg33/Ca37; Mg45/Li40; and Mg60/Li56 and Mg60/Ca58 data taken from our previous work[7]). The results are shown in Figure 3, where each point is plotted against the neutralization level of the Mg film used as the center layer in the sandwich. For all the systems shown in Figure 3, the measured value of $\mathscr{D}_{\text{ion}}$ was independent of annealing time to within experimental error, again confirming the expected Fickian behavior ("expected" since N and η_0 are matched between the two components comprising any of these diffusion sandwiches, though N and η_0 vary substantially across the series of sandwiches for which data shown in Figure 3). $\mathscr{D}_{\text{ion}}$ decreases substantially with increasing neutralization level, by a factor of 7 on increasing from 20 to 60% neutralization. A portion of this reduction can be attributed to the elimination of excess acid groups (reduction from 80% to 40% of the MAA units), though τ could also be lengthened simply

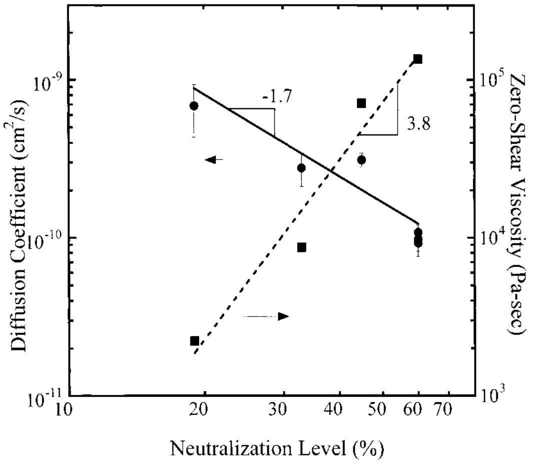

Figure 3. Cation diffusion coefficients (●; left axis) and zero-shear viscosities (■; right axis), both at 150 °C, for Mg-neutralized ionomers as a function of neutralization level. Steady-shear viscosities were measured at 135 °C and shifted to 150 °C using the activation energies measured from dynamic viscoelastic measurements. Error bars on diffusion coefficients correspond to ±1 standard deviation of the values obtained at different annealing times. Solid and dashed lines are least-squares power-law fits to the two sets of data, with the slopes indicated.

by the increase in ion content—ionic groups in a larger aggregate may be bound more tightly.

Figure 3 also shows the η_0 values for the same Mg ionomers and power-law fits to both $\mathcal{D}_{\text{ion}}$ (exponent -1.7) and η_0 (exponent 3.8). The results for $\mathcal{D}_{\text{ion}}$ imply that $\tau \sim N^{1.7}$, where N is the fractional neutralization level; this suggests that the observed $\eta_0(N)$ dependence reflects not only the variation in ionic group content (since the average number of ionic groups per chain, n, is proportional to N) but also the $\tau(N)$ dependence. For ionomers prepared from a given E/MAA copolymer, η_0 should be proportional to t_d (indeed, to within a factor of order unity,[18] $t_d \approx \eta_0 J_e^0$). Incorporating the observed $\tau(N) \sim N^{1.7}$ dependence into the theoretical result for monodisperse linear chains[1,3] ($\eta_0 \sim t_d \sim n^2\tau$) thus yields $\eta_0 \sim N^{3.7}$, within error of the observed exponent of 3.8. Such a direct comparison with theory should be viewed with caution, given the long-chain branching and polydispersity present in our E/MAA copolymers. However, our results clearly show that the dependence of τ on n must be accounted for even in future studies of model ionomers (linear chains of narrow length distribution).

3. Ionomer Pairs with Unmatched Neutralization Levels. Elucidating the functional form of $\mathcal{D}_{\text{ion}}(N)$, as in Figure 3, is quite tedious; it requires the preparation and analysis of separate diffusion "sandwiches" for each value of N, and each of these sandwiches in turn requires the preparation of a pair of ionomers neutralized with different cations (e.g., Mg and Ca) at closely matched neutralization levels. An alternative would be to prepare a single diffusion "sandwich", but from ionomers of *different* neutralization level (and cation type) so that the neutralization level varies continuously throughout the annealing process. To investigate this approach, we prepared trilayer sandwiches of Mg60 diffusing into either H100 or Ca21, such that the average neutralization level seen by the Mg cations would decrease continuously upon annealing, as magnesium methacrylate groups hop into the less-neutralized outer layers of the sandwich. These experiments are thus reminiscent of those of Van Alsten,[12] but since X-ray microanalysis provides the entire concentration profile (rather than an integrated measure of the ion content), a quantitative analysis of $\mathcal{D}_{\text{ion}}(N)$ is possible.

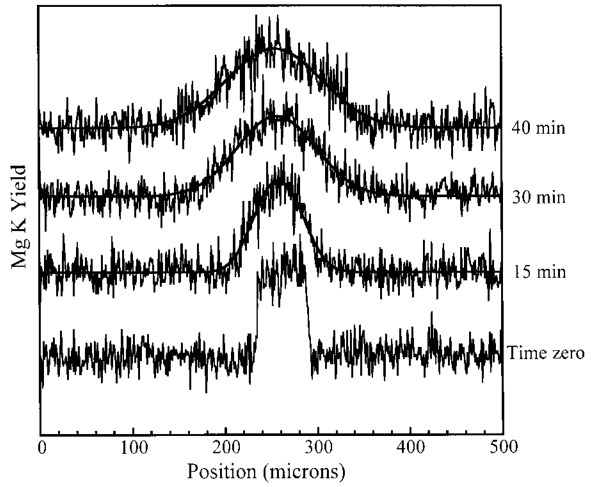

Figure 4. Mg concentration profiles for Mg60 diffusing into H100. From bottom to top, profiles are shown at "time zero" and after 15, 30, and 40 min of annealing at 150 °C. Profiles have been shifted vertically for clarity. Smooth solid curves are best-fit solutions to the Fickian model, with $\mathcal{D}_{\text{ion}}$ as the sole adjustable parameter.

Figure 4 shows concentration profiles for the Mg60/H100 sandwich annealed for various times at 150 °C. On the basis of the results of Figure 3, we expect $\mathcal{D}_{\text{ion}}$ to increase as N decreases, so in contrast to all the results presented thus far (here and in our previous work[7]), we expect the diffusion in these "unmatched" sandwiches to be *non*-Fickian. In particular, the "wings" of the concentration profile, where diffusion is more rapid (lower N), should be broader than in the Fickian case. However, the noise in the profiles (especially in the wings, where the number of accumulated counts above background is small) obscures any departures from Fickian behavior; the solid curves shown in Figure 4 are Fickian fits to each profile and match the data to within experimental error. However, deviations from Fickian behavior are manifested in our experiments in another way: the values of $\mathcal{D}_{\text{ion}}$ which provide the best fits to the profiles in Figure 4 are not constant, but rather increase with annealing time, as shown in Figure 5. Since the average neutralization level in the immediate vicinity of the Mg cations decreases as diffusion proceeds, the average $\mathcal{D}_{\text{ion}}$ increases with annealing time. Mg60 diffusing into Li56, a "matched" sandwich where Fickian diffusion (time-independent $\mathcal{D}_{\text{ion}}$) is both expected and observed, is also shown in Figure 5 as a reference case; at 150 °C, $\mathcal{D}_{\text{ion}}$ determined for the Mg60/H100 pair is between 20 and 60 times larger than for Mg60/Li56 and increases steadily with annealing time.

As a measure of the "average" Mg neutralization level (N_{avg}) in the diffusing layer at any time, we use the second moment of the concentration profile:

$$N_{\text{avg}} = N_0 \frac{\int \bar{c}^2(x)\,\mathrm{d}x}{2h \int \bar{c}^2(x)\,\mathrm{d}x} \qquad (1)$$

where N_0 is the initial neutralization level of the diffusing layer (e.g., 60% for Mg60), $\bar{c}$ is the Mg concentration normalized by the initial Mg concentration in the diffusing layer, x is the distance normal to

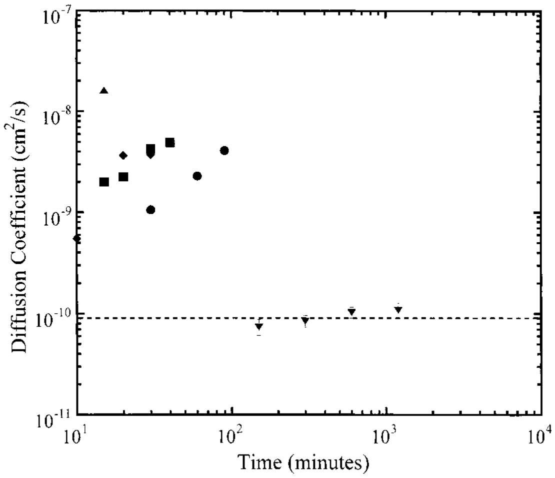

Figure 5. Cation diffusion coefficients for Mg60/Li56 at 150 °C (▼) and Mg60/H100 at several temperatures: 140 (●), 150 (■), 165 (◆), and 175 °C (▲). For Mg60/Li56, the average value of $\mathscr{D}_{\text{ion}}$ is shown by the dashed horizontal line. For the other data sets, a pronounced increase in the apparent $\mathscr{D}_{\text{ion}}$ with annealing time is seen, reflecting the fact that the actual diffusion process is non-Fickian. Error bars shown on the Mg60/Li56 data correspond to ±1 standard deviation of the $\mathscr{D}_{\text{ion}}$ value obtained by nonlinear regression of the Fickian model to the concentration profiles; the error bars on the data derived from the "unmatched" experiments are of similar relative magnitude.

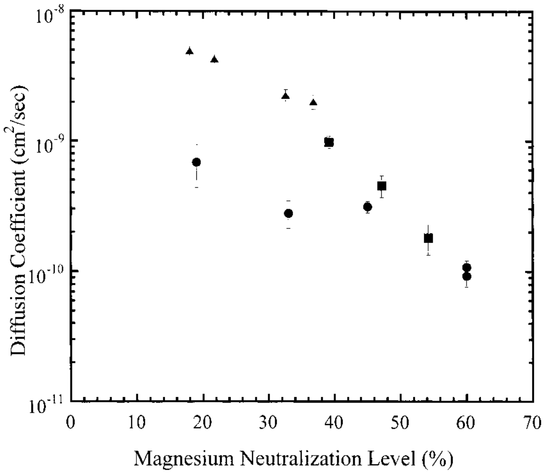

Figure 6. Cation diffusion coefficients as a function of Mg neutralization level (N) for both "matched" (●, data of Figure 3) and "unmatched" (▲, Mg60/H100; ■, Mg60/Ca21) diffusion pairs. In the "matched" experiments, N corresponds to the initial neutralization level within the Mg-neutralized ionomer film, while for the "unmatched" experiments, N corresponds to N_{avg} as defined by eq 1. Error bars correspond to ±1 standard deviation of the $\mathscr{D}_{\text{ion}}$ value obtained by nonlinear regression of the Fickian model to the concentration profiles.

the interfaces between layers of the sandwich (i.e., the abscissa in Figure 4), and h is the initial half-thickness of the diffusing layer. In practice, the Fickian fits (as shown in Figure 4) were used to evaluate the integrals in eq 1 rather than the noisy raw data. Figure 6 shows $\mathscr{D}_{\text{ion}}$ as a function of N_{avg} for Mg60 diffusing into H100 and into Ca21, along with the $\mathscr{D}_{\text{ion}}$ values measured in the matched neutralization level experiments described in the previous section (where diffusion is Fickian). As in Figure 3, $\mathscr{D}_{\text{ion}}$ decreases with neutralization level in these "unmatched" diffusion experiments also, but the numerical values of $\mathscr{D}_{\text{ion}}$ do not coincide with those from the "matched" diffusion experiments. Indeed, comparison of the three data sets suggests that $\mathscr{D}_{\text{ion}}$ systematically increases with the mismatch in neutralization level between the layers initially comprising the sandwich; the mismatch is near zero for the "matched" diffusion experiments and largest for the Mg60/H100 pair. While some of this discrepancy could be attributed to our chosen definition for N_{avg} (eq 1)—there is in fact no clear-cut definition, since the actual diffusion process is non-Fickian—the horizontal shift required to bring the three data sets in Figure 6 into coincidence would be unjustifiably large. (Note that even the shortest-time value for $\mathscr{D}_{\text{ion}}$ in the Mg60/H100 experiment substantially exceeds that for the "matched" pair Mg19/Li19.)

Rather, these results indicate that cation diffusion truly *is* more rapid into an acid copolymer than into an ionomer of similar neutralization level—even when the comparison is made at the same *average* neutralization level as defined by eq 1, meaning that the neutralization level in the vicinity of the Mg cations is similar. Recall that diffusion is driven by gradients not in concentration per se, but in activity,[19] and it is entirely plausible that the activity coefficient of the metal carboxylate groups decreases in the presence of excess acid. Thus, in these "unmatched" diffusion experiments, we infer that there exists a gradient in Mg carboxylate activity coefficient through the sandwich, providing an additional driving force for diffusion from regions of high neutralization level to low, beyond the usual driving force arising from the concentration gradient.

Previously, we had observed[7] strict counterdiffusion of metal cations in "matched" diffusion experiments on the Mg60/Ca58 pair (where concentration profiles for both Mg and Ca could be acquired on the same sandwich). Strict counterdiffusion is not fundamentally required in this system, as both the Mg and Ca ionomer layers are only partially neutralized; that is, H^+ "cations" on the excess acid groups are present in addition to Mg^{2+} and Ca^{2+}. Therefore, Mg^{2+} and Ca^{2+} could diffuse at different rates, though this would produce a gradient in excess acid content through the sandwich specimen. The observation of strict counterdiffusion in the Mg60/Ca58 pair is thus consistent with a metal salt activity coefficient which decreases as ion content is reduced.

Conclusions

Parallel rheometry and cation diffusion measurements demonstrate that excess acid groups in E/MAA ionomers accelerate the rates of ion hopping and chain diffusion proportionately. Consequently, the observed viscosity reduction results from a plasticization of the ionic interactions, rather than from a separate "acid-cation exchange" mechanism, wherein acid groups (rather than ionic groups) would be transported between aggregates. At intermediate neutralization levels, these free acid groups reduce the viscosity by approximately a factor of 3, and this modest effect does not prohibit the construction of satisfactory master curves of η_0(ionomer)/η_0(E/MAA copolymer) vs ion content for ionomers derived from copolymers of different MAA content. However, at low neutralization levels, the impact of the excess acid groups is much more pronounced, since the excess acid groups can also increase η_0 through interchain hydrogen bonding. Consequently, at low ion contents, viscosity is far more weakly dependent on ion content when free acid groups are present. In addition, cation diffusion measurements indicate a strong inverse dependence of $\mathscr{D}_{\text{ion}}$ on neutralization level N, implying an increase in the ion-hopping time with N ($\tau \sim N^{1.7}$). This $\tau(N)$ dependence, not previously considered, contributes approximately half of the observed dependence of viscosity upon neutralization level ($\eta_0 \sim N^{3.8}$). Finally, the ion-hopping process can be tracked directly by measuring the time evolution of the concentration profiles of the neutralizing cations. When the diffusion pair comprises ionomers of differing neutralization level, we find an additional positive contribution to $\mathscr{D}_{\text{ion}}$ created by the gradient in neutralization level.

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