Low-Shear Melt Rheology of Partially-Neutralized Ethylene−Methacrylic Acid Ionomers

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ABSTRACT: We examine the melt rheology of a series of ethylene−methacrylic acid (E/MAA) ionomers, all based on the same E/MAA copolymer, with an emphasis on the low-shear-rate Newtonian region. All ionomers show Newtonian behavior at sufficiently low shear rates. The zero-shear viscosity η_0 is a strong function of neutralization level and is significantly higher for Zn ionomers than for Na ionomers at the temperatures and neutralization levels examined. The recoverable compliance J_e^0 is independent of cation type and neutralization level, indicating that the ionic associations bear no stress during steady flow in the terminal region. Therefore, the individual ionic associations have lifetimes much shorter than the terminal relaxation time of the polymer chain. We probe the effect of unneutralized acid groups on η_0 by removing these groups through esterification. Unneutralized acid groups substantially lower the viscosity of Na ionomers but have no discernable effect in Zn ionomers. An "acid-cation exchange" mechanism is proposed to explain these findings.

Introduction

Introducing even a few mole percent of ionic groups into polymer chains deeply influences the chemical, physical, and mechanical properties of the resulting materials, which are generally termed ionomers. Solubility, adhesive strength, glass transition temperature, and tensile strength can all be manipulated through the addition of ionic groups and lead to a range of applications for ionomers which are not adequately filled by nonionic polymers.[1−4] Numerous experimental and theoretical studies[1−6] have shown that ionomers are actually microphase-separated materials, where the ionic groups aggregate into nanometer-size domains dispersed in the nonpolar polymer matrix. These ionic aggregates act as cross-links and can impart elastomeric behavior to the material above the matrix glass transition temperature.

Nowhere is the impact of ionic aggregation more evident than in the flow behavior of ionomers.[7] The retardation of chain motion produced by the introduction of these ionic groups can raise the melt viscosity of an ionomer by several orders of magnitude over its "parent" unfunctionalized polymer. Sulfonated ionomers, such as sulfonated polystyrene and sulfonated ethylene−propylene copolymer, can be very difficult or impossible to melt process without the addition of plasticizers which mitigate ionic associations.[8,9] Carboxylated ionomers generally possess weaker associations, allowing these materials to be effectively melt processed. Early examples of such materials include carboxylated rubbers,[10] as well as the ethylene−methacrylic acid ionomers introduced by DuPont in the 1960s under the Surlyn tradename.[11] Though these ionomers are more viscous than their nonionic counterparts, they can nonetheless be processed in conventional apparatus.

The melt flow mechanism of ionomers remains poorly understood, however. Small-angle X-ray scattering experiments[12−14] consistently show that the ionic aggregates persist in the molten state up to temperatures as high as 300 °C, so flow clearly does not require the elimination of ionic associations. It is generally presumed that flow in ionomers proceeds via a mechanism of "ion hopping" (see Figure 1).[7,15] Ionic associations are assumed to be characterized by a finite lifetime τ which reflects the average length of time which an ionic group spends in a particular aggregate. At intervals of approximately τ, the ionic group can diffuse ("hop") to another aggregate, which allows the relaxation of stress in the polymer chain segment to which the ionic group is bound. For a polymer which contains many ionic groups, diffusion of the center of mass of the chain will require a very large number of these "hops", because these diffusive motions of short chain segments are uncorrelated. This "ion hopping" relaxation mechanism allows a macromolecule to diffuse without requiring all

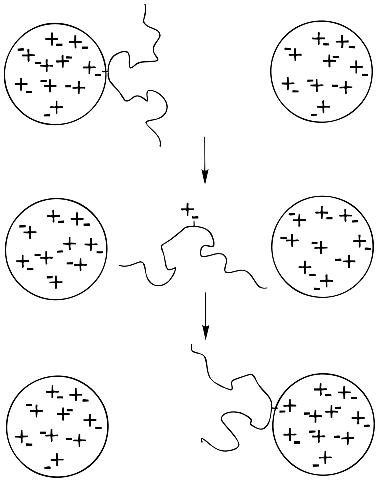

Figure 1. Schematic drawing of the "ion hopping" relaxation mechanism in ionomers. Circles represent ionic aggregates each containing several ionic groups, indicated by positive and negative charges. Area between the aggregates represents the nonpolar polymer matrix. The curved line represents a segment of a polymer chain bearing a single ionic group; the polymers studied here have many such segments per chain. Each ion pair within the aggregate is bound to such a polymer chain segment, but for clarity only one such segment is shown. Three snapshots in time are shown, from top to bottom: chain segment bound to left aggregate (top); segment dispersed in matrix (middle); segment bound to right aggregate (bottom).

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the ionic associations along the chain to be released simultaneously, the probability of which becomes vanishingly small as the number of ionic groups increases. Since the ionic cross-links are only temporary, their net effect is a reduction in the overall diffusion coefficient of the chains, resulting in a net increase in the viscosity and terminal relaxation time (t_d) of the material. A theory for a related case, where the interacting groups associate only pairwise, has been proposed recently by Leibler, Rubinstein, and Colby and found to be in good agreement with experiments on polymers with low levels of hydrogen-bonding groups.[16]

The often dramatic increase in t_d upon introduction of associating groups along the polymer chains can severely complicate rheological characterization of these materials.[7] Long relaxation times imply long equilibration times; for sulfonated materials, reports of vexing "slow drift" in the rheological properties over periods of days or even months are not uncommon.[17−19] A fundamental rheological quantity of practical interest is the zero-shear viscosity η_0. For a material to exhibit low-shear Newtonian behavior, the shear rate $\dot{\gamma}$ must be less than $1/t_d$. Conventional rheometers, which impose a fixed shear rate on the material, are thus unable to measure η_0 for materials with t_d much above 100 s, which includes typical ionomers.

These problems are reflected in the paucity of low shear rate rheometric data for ionomers. Systematic measurements of η_0 (and hence t_d) as a function of ion pair type or ion content would provide essential information regarding the influence of these key variables on the strength of the ionic associations and could provide the experimental basis for the development of a counterpart to the Leibler−Rubinstein−Colby theory[16] more closely applicable to ionomers. The present paper aims at investigating the effect of these variables, as well as the effect of unneutralized acid groups, on the melt rheology of ethylene−methacrylic acid ionomers at low shear rates. These materials contain many ionic groups (methacrylic acid salts) distributed randomly along the polymer backbone and thus are typical of conventional ionomers. Ethylene−methacrylic acid ionomers were chosen because they are known to be melt-processible, suggesting that t_d may be short enough to measure, in contrast to typical sulfonated systems. The ionomers studied here are all based on a single ethylene−methacrylic acid copolymer; ionic groups are introduced by neutralization of the methacrylic acid moieties. This provides control over cation type and neutralization level, while keeping the large-scale macromolecular architecture unchanged. Furthermore, to probe the effect of the unneutralized acid groups on the melt rheology, the partially neutralized ionomers have been compared with analogous materials wherein the acid groups have been esterified.

Experimental Section

Materials. The parent ethylene−methacrylic acid (E/MAA) copolymer (designated H100) was provided by DuPont; the methacrylic acid content (11.5 wt %) was determined by titration. Such E/MAA copolymers are highly polydisperse and can also contain long-chain branches, making a complete description of the molecular architecture difficult. The intrinsic viscosity [η] determined on H100 after esterification was 0.56 dL/g (trichlorobenzene, 135 °C); high-temperature gel permeation chromatography indicated an apparent polydispersity (uncorrected for long-chain branching) $M_w/M_n = 4.0$. Comparing the value of [η] with published correlations for typical low-density polyethylene[20] yields a viscosity-average molecular weight $M_v = 28$ kg/mol. Since [η] depends on the extent of long-chain branching, this number should be considered as a rough estimate only. Supercritical fluid fractionation of similar ethylene−methacrylic acid copolymers has shown only modest variation in methacrylic acid content between fractions, implying that the MAA units are distributed nearly randomly.[21] For the ionomers, the sample code employed here is M*xx*, where M represents the neutralizing cation (Na or Zn) and *xx* represents the percent of acid groups which are neutralized.

Neutralization. Na29, Na37, and Na39 were provided by DuPont. The other Na samples (Na26, Na35, Na47) were neutralized in toluene solution as follows. Typically, 20 g of H100 was dissolved in a mixture of 300 mL of toluene and 30 mL of *n*-butanol at 80 °C. After complete dissolution, the required amount of 0.5 M NaOH aqueous solution was added, and the two-phase mixture was stirred for 15 min. The reaction flask was then attached to a rotary evaporator and aspirator vacuum applied. After 200 mL of solvent had been distilled off, 200 mL of freshly mixed solvent (toluene/*n*-butanol 10/1 v/v) was added and the solution was allowed to homogenize at 80 °C for a minimum of 60 min. The distillation/redissolution process was repeated at least four times, until a homogeneous viscous solution was attained. The polymer was then evaporated to dryness and annealed for 16 h under vacuum at 170 °C.

Zn ionomers were neutralized by a similar procedure, replacing the NaOH solution by the required amount of zinc acetate dissolved in 25 mL of water. Distillation had to be conducted slowly to prevent the formation of visible heterogeneities within the sample. Usually 200 mL of distilled solvent was replaced with 250 mL of fresh mixed solvent, due to the lower solubility of the Zn ionomers compared with their Na counterparts. After at least four distillation/redissolution cycles, the polymer was evaporated to dryness and annealed under vacuum as for the Na samples.

Esterification. Typically, 20 g of H100 was dissolved in a refluxing mixture of 400 mL of toluene and 100 mL of ethanol. After complete dissolution, 15.2 g of *p*-toluenesulfonic acid (dissolved in a mixture of 160 mL of toluene and 40 mL of ethanol) was added. Conversion of methacrylic acid residues into ethyl methacrylate was followed by infrared spectroscopy. Typically, 50% of the acid groups were converted after 20 h, while 98% were converted after 1 week. When the required esterification level was reached, the polymer was precipitated in 4 L of methanol, filtered, redissolved in 500 mL of toluene, and reprecipitated in 4 L of methanol. It was then vacuum-dried following the same protocol described above. The material reacted for 1 week (designated E98) was found to have an esterification level of 98% by ^{1}H NMR. When it was desired to neutralize the acid groups remaining in a partially esterified polymer, the procedures used above to produce the corresponding ionomer (Na or Zn) were followed. These materials are denoted by the code M*xx*E, where M*xx* has the same significance as for the ionomers described above and the E suffix indicates that the remaining acid groups have been esterified.

Spectral Analysis. Thin films (2−15 μm) of the ionomers and H100 were pressed between poly(ethylene terephthalate) sheets at 150 °C in a PHI hydraulic press. Mold release (tetrafluoroethylene oligomers) was applied to the PET sheets prior to molding; otherwise, the ionomer film adhered tenaciously to the sheets and could not be removed intact. For monitoring the progress of the esterification reaction, samples were cast into thin films by evaporating aliquots of the reaction mixture directly onto a NaCl plate; for the final products, spectra were also acquired on pressed films after polymer isolation and drying. Samples were analyzed on a Nicolet SX-300 FTIR spectrometer, at 4 cm^{-1} resolution. In all cases, the absorbance was kept below unity for the peaks in the 1800−1300 cm^{-1} region. Neutralization and esterification levels were calculated from the ratio of the area of the carboxylic acid dimer peak near 1700 cm^{-1} to the area of a neighboring polyethylene band (1464 cm^{-1}). We estimate the uncertainty of this method to be roughly ±3%. Esterified samples were analyzed by ^{1}H NMR at 80 °C in toluene-d_8, using a Bruker WM-250 spectrometer equipped with a variable temperature unit. The esterification level was calculated by comparing the integrated intensities of the ester methylene resonance (4.05

ppm) and the polymer methyl and methylene signals (0.8–1.8 ppm).

Rheological Measurements. Samples were molded under vacuum between poly(tetrafluoroethylene) sheets into 28 mm discs, using a closed mold and a PHI hydraulic press with heated platens. Polymers were melted at 130 °C for 15 min with no applied pressure, then pressed for 5 min at 70 bar, and then cooled to room temperature over 15 min. Steady shear measurements were performed on a Rheometrics stress rheometer (RSR) with 25 mm cone-and-plate fixtures (0.1 rad cone angle, 56 μm gap), applying constant stress to the material. Stresses used were 2–2000 Pa, allowing shear rates of 10^{-5} to 1 s^{-1} to be reached, depending on the sample viscosity. Samples were sheared for at least 40 min, by which time a steady shear regime was reached for all samples. Upon removing the stress, recovery curves were recorded for 20 min. Temperatures between 104 and 170 °C were investigated; whenever the sample temperature was changed, the thermal expansion of the tools was taken into account to keep the gap constant. Dynamic measurements were conducted on a Rheometrics mechanical spectrometer (RMS-800), using 25 mm parallel plate fixtures. Measurements covered frequencies from 10^{-3} to 10^2 rad/s, and temperatures ranged from 113 to 200 °C. Strain amplitudes were 5–15%; these strains were shown to be in the linear viscoelastic regime. The gap between the plates was 1–2 mm, and thermal expansion of the tools was taken into account. Capillary rheometry was performed at the DuPont Sabine River Laboratory, using an Instron capillary rheometer with a 0.76 mm diameter capillary having a length-to-diameter ratio of 33.

Results and Discussion

A. Melt Flow Behavior. Accessing the Newtonian regime (zero-shear viscosity η_0) requires that the shear rate be less than $1/t_d$. Because of the long relaxation times characteristic of ionomers, shear rates down to 10^{-5} s^{-1} were employed. Measurements could not be conducted at temperatures below 104 °C, due to crystallization of the polyethylene segments. At temperatures higher than 170 °C, sample viscosity progressively increased with measurement time; moreover, the recoverable compliance J_e^0, measured by recoil after shearing, systematically exceeded the value obtained from the approach to steady flow at the beginning of the experiment. We attribute these effects to the formation of interchain anhydride linkages, which act as branch points; some samples tested at 190 °C for several hours showed rheological behavior characteristic of cross-linked elastomers. However, peaks corresponding to anhydride groups could not be seen in the FTIR spectra of films pressed from samples tested at high temperatures, indicating that the level of such groups must be low. Fortunately, comparison of the values of J_e^0 obtained at the beginning and end of the test proved a sensitive indicator of whether any changes in the flow behavior had occurred. All data shown herein came from tests in which the starting and ending values of J_e^0 were identical within experimental error.

Figure 2 shows flow curves for sample Na37 at various temperatures. This sample clearly shows a Newtonian viscosity at shear rates below 10^{-2} s^{-1}; at the higher measurement temperatures, the Newtonian region extends to at least 1 s^{-1}. This should be contrasted with typical observations on other E/MAA ionomers in conventional (controlled strain rate) rheometers, where the materials remain shear thinning down to the lowest attainable shear rates,[22] or the lowest frequencies in dynamic viscoelastic testing.[22–25] Only a handful of prior rheological measurements on melts of “conventional” ionomers (high molecular weight polymers bearing many metal salt groups) have clearly demonstrated Newtonian or terminal behavior extending over a decade or more in shear rate or frequency; these studies employed materials with relatively polar (polymethacrylate[26] or polyester[27,28]) polymer matrices, which might be expected to reduce the barrier to ion-hopping. To our knowledge, the measurements reported here are the first to measure a similar Newtonian plateau in ionomers based on nonpolar polymers.

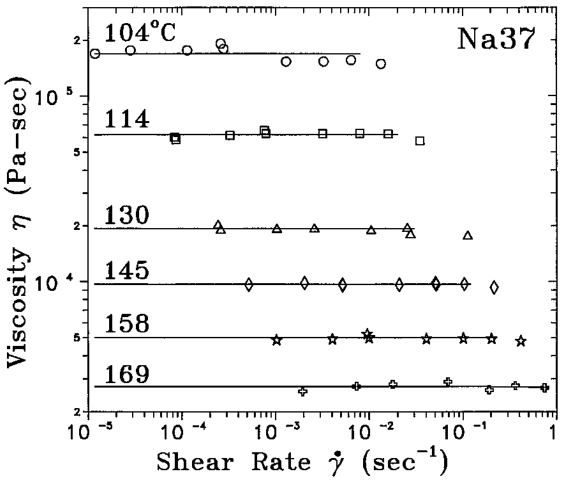

Figure 2. Steady-shear viscosity η obtained for sample Na37 at the temperatures indicated. Symbols are measured values; horizontal lines indicate best-fit Newtonian viscosity η_0.

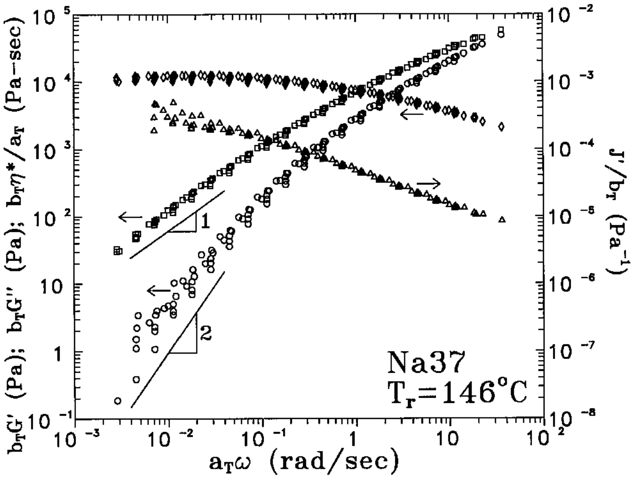

Figure 3. Pseudomaster curves constructed by time–temperature superposition from dynamic shear data on sample Na37. Reference temperature T_r = 146 °C. Storage modulus G' (○, left axis, Pa); loss modulus G'' (□, left axis, Pa); complex viscosity η^* (◊, left axis, Pa s); storage compliance J' (△, right axis, Pa^{-1}). Power-law slopes of 2 and 1 are indicated for G' and G'', respectively, as expected for terminal behavior.

Dynamic data on the same sample, collapsed into master curves by time–temperature superposition, are shown in Figure 3. Though ionomers are expected to be rheologically complex, as long as the two active relaxations (ion-hopping at time τ, terminal relaxation at t_d) are sufficiently well separated in time, it is possible to construct adequate master curves corresponding to one relaxation or the other. A more complete discussion of this point as applied to ionomers can be found elsewhere;[7] in Figure 3, we concentrate on the region in and near the terminal zone. The good superposition observed in Figure 3 suggests that the ion-hopping time τ lies outside the experimental window (τ < 100 ms). At low reduced frequencies, $G' \propto \omega^2$ and $G'' \propto \omega^1$, while the complex viscosity η^* becomes independent of frequency, all indicating terminal behavior. However, terminal behavior is barely reached for Na37, covering only about one decade of experimentally-accessible

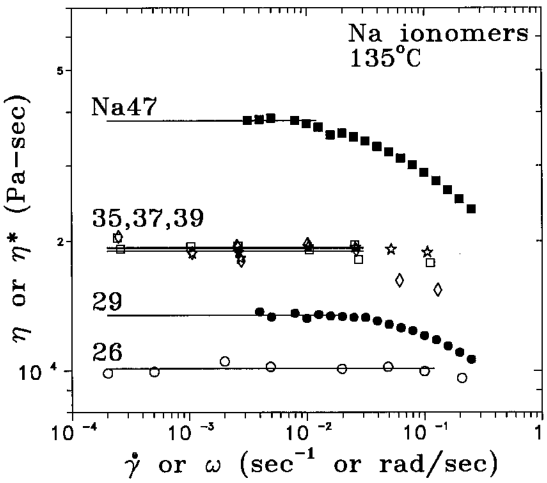

Figure 4. Flow curves at 135 °C for Na ionomers with various neutralization levels, as indicated. Open symbols show steady-shear viscosity η; solid symbols show complex viscosity η^*.

Table 1. Zero-Shear Viscosities η_0, Terminal Relaxation Times t_d, and Activation Energies E_a at 135 °C

material	η_0 (kPa s)	t_d (s)	E_a (kJ/mol) (±1 std dev)
E98	0.22	0.08	48 ± 1
H100	1.3	0.5	69 ± 2
Na26	10.5	4	
Na29	13.6	5	79 ± 3
Na35	20.5	8	
Na37	19.6	8	80 ± 2
Na39	19.5	8	81 ± 3
Na47	39	16	
Na32E	52	20	70 ± 5
Zn48	160	60	99 ± 5
Zn53	300	120	92 ± 5
Zn58	450	180	109 ± 4
Zn54E	250	100	85 ± 5

reduced frequencies. Some of our ionomers have t_d values in excess of 100 s at 135 °C, meaning that terminal behavior could not be accessed in dynamic mode; therefore, steady data collected on the constant-stress rheometer will be emphasized in this paper.

Figure 4 shows similar flow curves, all at 135 °C, for a range of sodium ionomers with varying neutralization level. Both dynamic and steady data are included in Figure 4. In the terminal region, η^* must equal η_0, regardless of whether the Cox−Merz rule[29] holds at higher values of $\dot{\gamma}$ or ω; Sakamoto, MacKnight, and Porter,[22] in an investigation of other E/MAA ionomers, found stronger shear-thinning behavior in η^* than in η. In Figure 4, as the neutralization level is increased, η_0 increases, and the curves depart from Newtonian behavior at lower $\dot{\gamma}$ or ω, both reflecting an increase in t_d with neutralization level. The Na and Zn ionomers show qualitatively similar behavior, differing only in the values of η_0 and the frequency or shear rate at which the behavior ceases to be Newtonian; values of η_0 for all materials are given in Table 1.

The dependence of η_0 on neutralization level at 135 °C is shown in Figure 5 for both Na and Zn ionomers. Clearly, even partial neutralization (30−60%) can increase η_0 by 3 orders of magnitude or more. The limited range of neutralization levels examined, combined with the ±3% uncertainty in the neutralization level, precludes a detailed examination of the functional dependence of η_0 on neutralization level. However, there are clear differences in η_0 between Na and Zn ionomers of similar neutralization level; at 135 °C and 47−48% neutralization, Zn ionomers have η_0 four times larger than those of Na ionomers. This point will be discussed in greater detail below. Table 1 also shows that ionic interactions increase the flow activation energy of the molten polymers. From the temperature dependence of η_0, activation energies E_a = 80 ±2 kJ/mol for Na ionomers and E_a = 100 ±9 kJ/mol for Zn ionomers are calculated, which significantly exceed the value for the acid copolymer (69 ±2 kJ/mol). Values of E_a can also be extracted from the time−temperature shift factors obtained from constructing dynamic master curves such as Figure 3; agreement between the two methods was excellent. Our E_a value for the Na ionomers is also in good agreement with literature results[30,31] for carboxy-telechelic polybutadienes neutralized with Na.

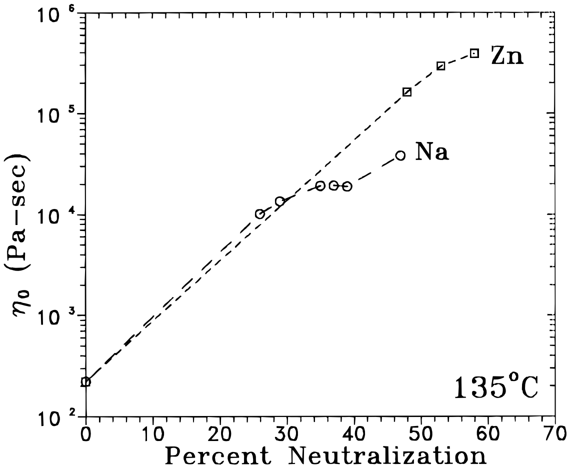

Figure 5. Dependence of zero-shear viscosity η_0 at 135 °C on neutralization level for Zn (□) and Na (○) ionomers. Dashed lines are guides to the eye. Zero percent neutralization corresponds to the E/MAA copolymer (H100).

B. Terminal Relaxation Time (t_d). Since we are able to access the Newtonian region for all the ionomers listed in Table 1, it is possible to directly compute t_d from[32]

$$t_d = \eta_0 J_e^{\,0} \tag{1}$$

where J_e^0 is the recoverable compliance, obtained from creep measurements (data from the RSR) by examining either the transient approach to steady shear or the recoil after the stress is removed. J_e^0 is a measure of the elastic energy stored in the material during steady flow, and as such, it should depend on the architecture of the polymer chain—in particular, the polydispersity and the extent of long-chain branching. Also, as noted above, J_e^0 is very sensitive to any changes in architecture occurring during the measurement, such as would be produced by interchain anhydride links. Since all materials examined in this study were derived from the same E/MAA copolymer, they should all have identical molecular architectures. During steady flow, the ionic groups should bear no stress, as the ion-hopping time $\tau \ll t_d$; the ionic groups merely serve to increase the time necessary to achieve steady flow (raise t_d). Therefore, all materials are expected to show the same value of J_e^0. In our case, measurements on all ionomers, as well as the acid copolymer and the esterified materials described in the next section, yielded a value of J_e^0 = (4 ± 2) × 10^{-4} Pa^{-1}. This value is also in good agreement with the low-frequency limit of the storage compliance J' measured during dynamic testing (see Figure 3); however, the difficulty in attaining terminal behavior in dynamic testing makes the creep−recovery method more reliable. Our value for J_e^0 is modestly larger than that reported[33] for narrow-distribution

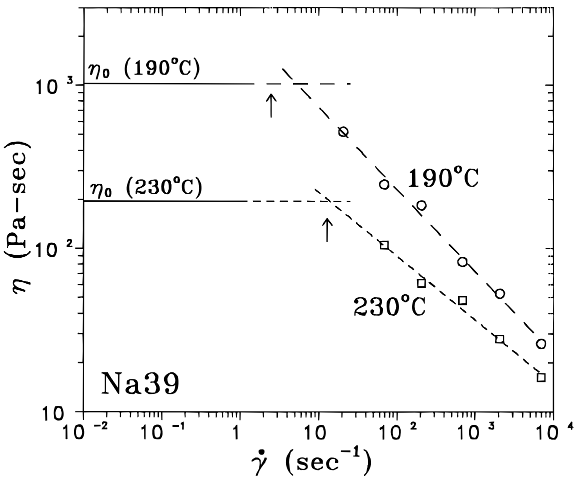

Figure 6. Composite of low-shear (cone-and-plate) and high-shear (capillary) flow curves for sample Na39. Solid horizontal lines represent the values of η_0 at the indicated temperature, calculated from the values of η_0 at 170 °C and the activation energy E_a given in Table 1. Symbols represent capillary rheometer data at 190 °C (○) and 230 °C (□); dashed lines are power-law fits. Arrows mark the values of $1/t_d$ calculated from the low-shear rheometry, via $t_d = \eta_0 J_e^0$.

linear polyethylene (2.2×10^{-4} Pa^{-1}), most likely due to the polydispersity and long-chain branching present in our E/MAA copolymer. Longworth[11] previously reported that J_e^0 was essentially invariant with neutralization level in a series of Na ionomers; the E/MAA copolymer from which his ionomers were derived had J_e^0 roughly an order of magnitude higher than our E/MAA copolymer exhibits, presumably due to higher molecular weight and correspondingly more long branches per chain in Longworth's polymer. To our knowledge, there are only two other reports relevant to the effects of ion type and content on J_e^0. From data on carboxy-telechelic polybutadiene ionomers,[31,34] it can be shown that[7] J_e^0 for the acid form and four alkali metal salts is constant to within 50%. Additionally, data on Zn-neutralized sulfonated ethylene−propylene polymers in solution[35] show that J_e^0 is similarly unaffected by sulfonation level.

Since J_e^0 is constant across all our materials, variations in η_0 (see Figure 5) translate directly into variations in t_d. Actual values of t_d for each material at 135 °C are reported in Table 1. For our Na ionomers, t_d is on the order of 10 s at 135 °C, whereas it is closer to 10^2 s for the Zn ionomers. The value of t_d can also be estimated from measurements at higher shear rates: the Newtonian plateau should extend to $\dot{\gamma} \approx 1/t_d$, beyond which the polymer becomes shear thinning. Measurements to high shear rates are not possible for these ionomers in a cone-and-plate geometry because the flow becomes unstable with respect to ejecting the polymer from the gap.[7,23] Therefore, a combination of cone-and-plate (for low $\dot{\gamma}$) and capillary rheometry (for high $\dot{\gamma}$) is necessary to access the wide range of shear rates required. Figure 6 is a composite of results from both cone-and-plate and capillary measurements made on Na39. The solid horizontal lines represent the values of η_0 obtained by extrapolating the values of η_0 determined on the RSR to higher temperatures, using the measured E_a. The symbols represent data acquired with a capillary rheometer, with the dashed lines indicating least-squares power-law fits. The horizontal and power-law lines for each temperature should intersect at roughly $1/t_d$; the values of $1/t_d$ calculated as $(\eta_0 J_e^0)^{-1}$ are shown by the arrows. Agreement between the two methods is quite satisfactory.

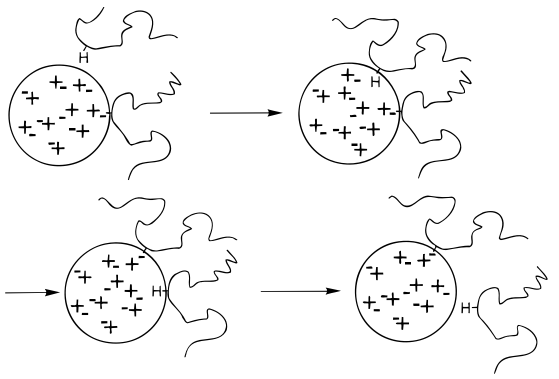

Figure 7. Schematic drawing of the proposed "acid−cation exchange" relaxation mechanism in ionomers, analogous to Figure 1. H represents the acid proton on a polymer chain segment. Only one aggregate is shown, in four snapshots going from upper left to lower right. This mechanism allows chain segments to diffuse without transporting any ions between aggregates.

C. Influence of Unneutralized Acid Groups. While sulfonated ionomers are invariably neutralized to the stoichiometric point or beyond, because of thermal instability when unneutralized sulfonic acid groups are present, carboxylated ionomers are often neutralized to less than the stoichiometric point, providing an additional means for controlling rheological behavior. The question arises as to whether the remaining "free" (unneutralized) acid groups have an effect beyond reducing the overall neutralization level, *i.e.*, do they participate in the ion-hopping process? A possible mechanism for this participation is shown schematically in Figure 7. If the acid groups preferentially associate with the ionic aggregates, as is known to occur for sulfonated ionomers,[36] and counterions (either H^+ or M^+) can rapidly exchange "partner" carboxylate anions within an ionic aggregate, then it is possible for chain segments to diffuse through the material *without* requiring any transport of ionic groups from one aggregate to another. The idea that cations are rapidly redistributed between partner anions in the melt is supported by the experiments of Bonotto and Bonner,[37] who showed that melt-mixing an ethylene−acrylic acid ionomer with its acid copolymer produced a material with properties indistinguishable from those of the corresponding partially-neutralized ionomer.

Ideally, we would like to compare two E/MAA ionomers: for example, one containing 10 wt % MAA neutralized to 50% and another containing 5 wt % MAA neutralized to 100%. However, such a comparison would require the synthesis of two E/MAA copolymers closely matched in molecular weight, molecular weight distribution, and long-chain branching; this is an exceedingly difficult task. However, we can approximate this comparison by preparing two ionomers with identical neutralization levels, but in one of the materials we remove all the unneutralized acid groups by converting them to the ethyl esters. The ester groups have no discernable tendency to associate.[23,38,39] With this approach, a perfect match in the molecular architectures is assured. We present three such comparisons below: (1) the acid copolymer vs its fully-esterified analog, (2) an ionomer neutralized 32% with Na and 68% esterified (Na32E) vs analogous Na materials containing unneutralized acid, and (3) an ionomer neutralized 54% with Zn and 46% esterified (Zn54E) vs analogous Zn ionomers.

The E/MAA copolymer H100 and the 98% esterified derivative (E98) show Newtonian behavior over the

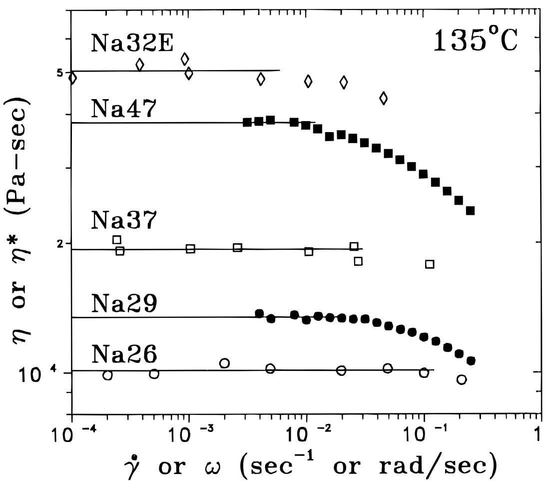

Figure 8. Flow curves at 135 °C for Na ionomers with various neutralization levels, as indicated, as well as the partially-esterified sample Na32E. Open symbols show steady-shear viscosity η; solid symbols show complex viscosity η^*. Note the higher viscosity for Na32E than for Na47, despite the much higher ion content of the latter.

entire range of shear rates employed. As shown in Table 1, η_0 drops by a factor of 6 at 135 °C when the acid copolymer is esterified. Blyler and Haas[38] and Earnest and MacKnight[23] have previously reported similar results; the decrease in η_0 is due to the fact that the carboxylic acid groups in E/MAA and E/AA copolymers are strongly dimerized through hydrogen bonding, as is evident in their infrared spectra. These hydrogen bonds raise the viscosity in the same way that ionic groups do, though much less substantially; the LRC treatment provides a good description of the hydrogen-bonded case.[16] Eliminating the unneutralized acid groups (and thus the possibility of hydrogen bonding) thus *lowers* the viscosity when no ions are present. Note also that the activation energy measured for E98 (48 ± 1 kJ/mol) is in excellent agreement with literature values[40,41] for low-density polyethylene (53 ± 9 kJ/mol) containing similar long-chain branching.

Figure 8 shows the data for sample Na32E, as well as several Na ionomers containing unneutralized acid groups. By interpolating between the η_0 values found for Na29 and Na37, it is clear that Na32E has a viscosity about three times higher than an analogous ionomer containing unneutralized acid; that is, η_0 *increases* on esterification, exactly the opposite of what happens for the acid copolymer. Figure 9 shows analogous data for Zn54E and Zn ionomers containing unneutralized acid; in the Zn case, esterification has no detectable effect on η_0, as Zn54E and Zn53 behave essentially identically. For both the Na and Zn cases, the activation energy E_a appears to decrease slightly on esterification, though given the limited temperature range of the data, this decrease is only marginally significant.

These qualitative differences in the effect of unneutralized acid between Na and Zn ionomers implies that the acid groups interact to a greater extent with Na carboxylates than with Zn carboxylates. Qualitative differences are also observed in the infrared spectra of the Na and Zn ionomers. For Zn, the peak corresponding to the C=O stretch of dimerized COOH groups (at 1700 cm^{-1}) maintains its position and width as the neutralization level is increased. By contrast, in the Na ionomers the peak broadens and moves to lower wavenumber as the Na level is increased, reaching 1685 cm^{-1} in an 83% neutralized sample. Similar observations

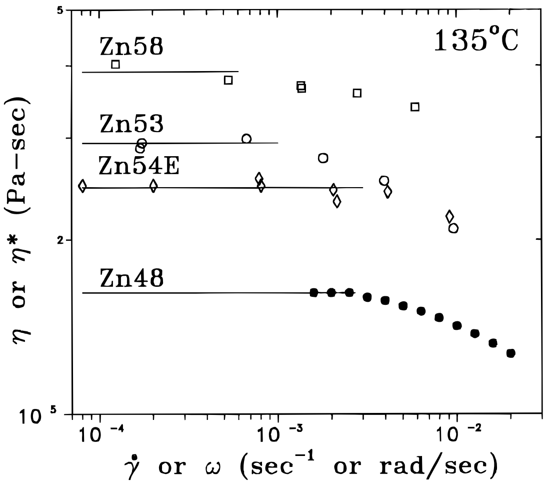

Figure 9. Flow curves at 135 °C for Zn ionomers with various neutralization levels, as indicated, as well as the partially-esterified sample Zn54E. Open symbols show steady-shear viscosity η; solid symbols show complex viscosity η^*.

were made by Han and Williams[42] on potassium- and zinc-neutralized E/MAA ionomers; from a detailed analysis of the spectra, they concluded that zinc forms specific coordination complexes, which do not permit further association with free acid groups. These spectral changes indicate that the local environment of the acid groups in Na ionomers changes continuously as the neutralization level is increased (as would be expected if the acid groups are associated with the ionic aggregates); conversely, the lack of change in the Zn ionomer spectra as neutralization level is increased implies that the unneutralized acid groups are dispersed in the polymer matrix. These inferences are consistent with the rheological results, where acid groups effectively plasticize the associations in Na ionomers but have no discernable effect in Zn ionomers. It is also possible that partitioning of the unneutralized acid groups into the ionic aggregates serves to "plasticize" the aggregate and accelerate the ion-hopping process as sketched in Figure 1. The effects of certain polar plasticizers, notably glycerol,[8,43,44] on ionomers have been well-documented; by coordinating to the metal cation, glycerol reduces the strength of the associations between ionic groups and hence the melt viscosity. The excess carboxylic acid groups may play a similar role here. However, it is important to note that while glycerol molecules can easily "hop" along with the ions to which they are coordinated, in our case the carboxylic acid groups are also tied to the polymer chains, making the two cases somewhat different.

These observations regarding the association behavior of the unneutralized acid groups may also relate to the unexpected result that the Zn ionomers show higher viscosities at 135 °C than the Na ionomers. In sulfonated ionomers, it has been repeatedly shown[45−47] that Zn produces lower melt viscosities than do other cations, including Na. For carboxylated materials, such comparisons are rarer; early work[48,49] on carboxylated rubbers neutralized beyond the stoichiometric point indicates that Zn produces lower viscosities and tensile strengths than most cations, but the excess neutralizing agent may affect such comparisons. One complicating factor is that the activation energies for Na and Zn ionomers differ; however, using the activation energies we have determined, the ratio of Zn to Na viscosities drops only a factor of 2.2 on increasing the temperature from 135 to 200 °C, so the difference in activation energy should not dominate the comparison. Interestingly, qualitative agreement with our results (higher η_0 for Zn ionomer than Na) was found by Iwakura and Fujimura,[50] who studied styrene−methacrylic acid copolymers neutralized to very low levels (11−13% of stoichiometric). We consider that, at low levels of neutralization, the presence of the acid−cation exchange mechanism may depress the viscosity of Na carboxylate ionomers to levels below those of their Zn counterparts, in which acid−cation exchange appears to be negligible. Such an effect would be evident in plots of η_0 vs neutralization level for the different cations, such as Figure 5, once a wider and more extensively overlapping range of neutralization levels is examined.

Conclusions

The melt flow behavior of a series of Na and Zn ethylene−methacrylic acid ionomers has been investigated over a wide range of shear rates and temperatures. All polymers exhibited Newtonian behavior at sufficiently low shear rates, demonstrating the existence of a true zero-shear viscosity η_0 in "conventional" ionomers with nonpolar matrices. While η_0 is a strong function of the neutralization level and choice of cation, the recoverable compliance J_e^0 is independent of cation type and level. Thus, ionic associations bear no stress during steady flow, demonstrating that the individual ionic associations have much shorter lifetimes than the terminal relaxation time of the polymer chain (t_d). For our ionomers, t_d ranges from 4 to 200 s at 135 °C, whereas t_d for the esterified derivative of the same copolymer is only 80 ms. Unneutralized acid groups substantially reduce the viscosity of Na ionomers, presumably through an acid−cation exchange mechanism or through "plasticization" of the ionic aggregates; however, free acid groups do not substantially affect the viscosity of our Zn ionomers. These differences are consistent with differences in the local environment of the free acid groups as seen in infrared spectra.

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