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# Effect of Hydrogen Bonding and Ionic Aggregation on the Melt Rheology of an Ethylene–Methacrylic Acid Copolymer and its Sodium Salt

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## Synopsis

A study has been made of the dynamic and steady shear melt rheology of an ethylene–methacrylic acid copolymer, its methyl ester, and 70% neutralized sodium salt. Measurements were made with a Rheometrics mechanical spectrometer using the eccentric rotating disks and cone-and-plate geometries over a temperature range of 120–180°C and a frequency range of  $10^{-3}$  to  $10^2$  rad/sec. Correspondence was found between steady shear viscosity and the complex dynamic viscosity for the ester and acid materials. Over the temperature and frequency range studied the time–temperature superposition principle was applicable to  $G'$  data for each of the derivatives and a supermaster curve could be constructed from the three individual master curves. Time–temperature superposition was found not applicable to  $G''$  data for the sodium salt. Differences in rheological response between the ester and acid copolymers are explained by differences in  $T_g$ . It is suggested that differences in temperature shifts  $\Delta T$  required to produce  $G'$  superposition between the three derivatives reflect differences in  $\Delta H$  for interchain interactions. A mechanism for flow of clustered ionomers is suggested consisting of an initiation and a propagation step.

## INTRODUCTION

The most important molecular parameters determining polymer melt rheology are molecular weight, its distribution, and the amount of long chain branching. These factors have been studied extensively in the past by many workers and a wealth of data are available for such polymers as polystyrene and high and low density polyethylene. In recent years there has been interest exhibited in polymers containing polar, ionic, or other entities capable of intermolecular association. Longworth and Morawitz<sup>1</sup> investigated the melt rheology of styrene–methacrylic acid copolymers, finding large increases in viscosity with increasing methacrylic acid content and a corresponding increase in flow activation energy. Fitzgerald and Neilsen<sup>2</sup> explain the difference in viscosities of the acid copolymer and polystyrene as an effect of the higher  $T_g$  of the copolymer. Blyler and Hass<sup>3</sup> and Lim and Hass<sup>4</sup> investigated acrylic acid–ethylene copolymers to determine the significance of hydrogen bonding on the viscosity and flow activation energy. They conclude that the hydrogen bonds contribute to the increase in viscosity and are effective as temporary crosslinks, thereby increasing the activation energy. In their study of functionally terminated polybutadienes and butadiene–acrylonitrile copolymers, Collins et al.<sup>5</sup> conclude that the polarity of the polymer chain is most influential in increasing viscosity and activation energy over the parent polybutadiene polymers.

The influence of ionic groups attached along a polymer chain has also been investigated. A study conducted in this laboratory by Sakamoto et al.<sup>6</sup> on an

ethylene-methacrylic acid copolymer and its salts reveals time-temperature superposition for the acid copolymer but not for the Na or Ca salts. The viscosities of the salts were found to be approximately two orders of magnitude higher than the viscosity of the acid copolymer at comparable temperatures. Correspondence between steady shear and dynamic viscosities was found for the unionized acid copolymer, but for the salts, dynamic viscosities were lower than in the steady shear experiments and tended to converge at higher frequencies. Recently Shohamy and Eisenberg<sup>7</sup> investigated the melt properties of styrene-methacrylic acid copolymers and their corresponding sodium salts and methyl esters. They found time-temperature superposition of  $G'$  data applicable to the salts as well as the acid and ester copolymers, and that the shapes of the  $G'$  vs.  $\omega$  plots for each derivative were identical. They suggest that temperature shifts to gain superposition between derivatives are indicative of the strength of intermolecular interactions.

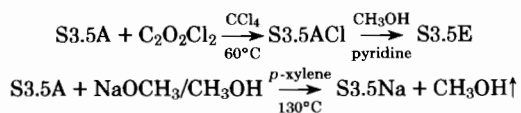
The present work was undertaken in an attempt to clarify the importance of hydrogen bonding and ionic interactions to rheological behavior in the melt. By using the same polymer backbone for ester, acid, and salt derivatives the complications of molecular weight and degree of branching could be avoided. By selecting the ester derivative as the reference material with no interchain effects, hydrogen bonding could be investigated through the acid copolymer and ionic interactions through the salt.

## EXPERIMENTAL

### Materials

The starting polymer (designated S3.5Zn) was a partially neutralized zinc salt of an ethylene-methacrylic acid copolymer kindly supplied by the DuPont Company. It was stated to contain 3.5 mole % methacrylic acid residues. This material was first converted to the free acid (S3.5A).

The zinc salt pellets (S3.5Zn) were dispersed in tetrahydrofuran (THF)-*p*-xylene solvent (95/5, v/v) at 80°C and H<sub>2</sub>SO<sub>4</sub> was added dropwise from a solution of the acid in THF. Since zinc sulfate is insoluble in THF, the reaction goes to completion. From S3.5A the methyl ester (S3.5E) and sodium salt (S3.5Na) were prepared according to the following schemes:



The acid chloride intermediate (S3.5ACl) was used to ensure complete conversion of the acid to methyl ester. The acid copolymer was first dissolved in CCl<sub>4</sub> (ca. 1% solids) at reflux. The hazy solution was then cooled to 60°C and the oxalyl chloride added dropwise over a period of 10 min. Gas was evolved and the resulting acid chloride solution was clear. After 1 hr reaction time, spectrograde methanol was added to the solution with a small amount of pyridine. Again gas was evolved and the solution turned hazy. After 3 hr reaction time, 100% of the methyl ester had formed. This was confirmed by the complete disappearance of the infrared (IR) absorbance at 1700 cm<sup>-1</sup> owing to the acid and the appearance of an absorption at 1735 cm<sup>-1</sup> assigned to the ester.

The neutralization of the acid copolymer followed the procedure described

earlier.<sup>8</sup> The percent neutralization, determined using the integrated IR absorbance at  $1700\text{ cm}^{-1}$ , was 70%.

Films were compression-molded at 10,000 lb pressure at  $150\text{--}160^\circ\text{C}$  for the acid and ester derivatives and  $210^\circ\text{C}$  for the Na salt. Films were removed hot then quenched to room temperature.

### Measurements

Melting points determined on a Perkin-Elmer apparatus model DSC-2 are listed in Table I. The point of maximum excursion from the base line was taken as  $T_m$ . Dynamic mechanical measurements were carried out on a Vibron dynamic viscoelastometer, model DDV-II (Toyo Measuring Instruments Company). The temperature range was  $-160$  to  $100^\circ\text{C}$  and the frequencies employed were 3.5, 11, and 110 Hz. Samples were heated at  $1\text{--}2^\circ\text{C}/\text{min}$  under dry nitrogen. Relaxation temperatures are also listed in Table I.

TABLE I  
Characterization Data for S3.5 Derivatives

Material	$T_m^a$ ( $^\circ\text{C}$ )	$T_\gamma^b$ ( $^\circ\text{C}$ )	$T_\beta^b$ ( $^\circ\text{C}$ )	$T_\beta^c$ ( $^\circ\text{C}$ )	$T_\alpha^c$ ( $^\circ\text{C}$ )
S3.5E (quenched)	94	-126	-18	-2	$\sim 50$
S3.5A (quenched)	95	-110	25	45	—
S3.5Na (quenched)	—	-122	-10	3	$\sim 50^d$
S3.5Na (annealed)	83	—	—	—	—

<sup>a</sup> By DSC.

<sup>b</sup>  $E''_{\max}$  at  $110\text{ Hz}$ .

<sup>c</sup>  $\tan \delta_{\max}$  at  $110\text{ Hz}$ .

<sup>d</sup> No crystallinity present.

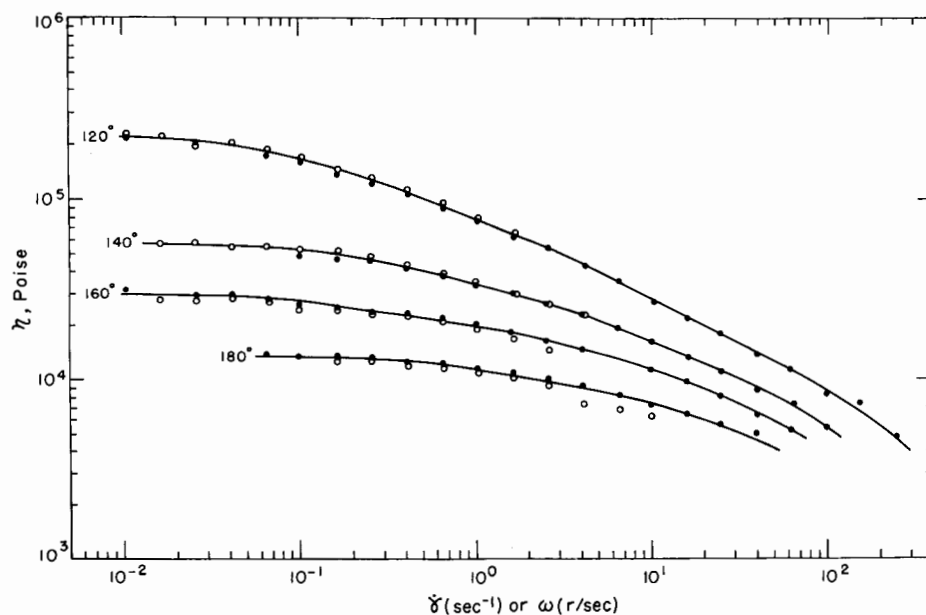


Fig. 1. Apparent viscosity  $\eta_a$  (O) vs. shear rate  $\dot{\gamma}$  and complex viscosity  $|\eta^*|$  (●) vs. angular frequency  $\omega$  for the S3.5 ester derivative.

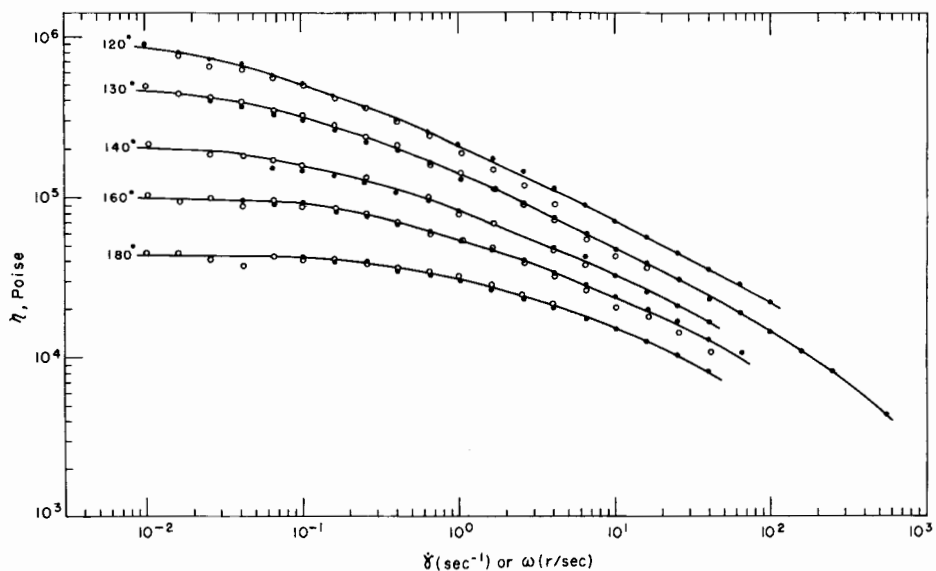


Fig. 2. Apparent viscosity  $\eta_a$  (●) vs. shear rate  $\dot{\gamma}$  and complex viscosity  $|\eta^*|$  (○) vs. angular frequency  $\omega$  for the S3.5 acid derivative.

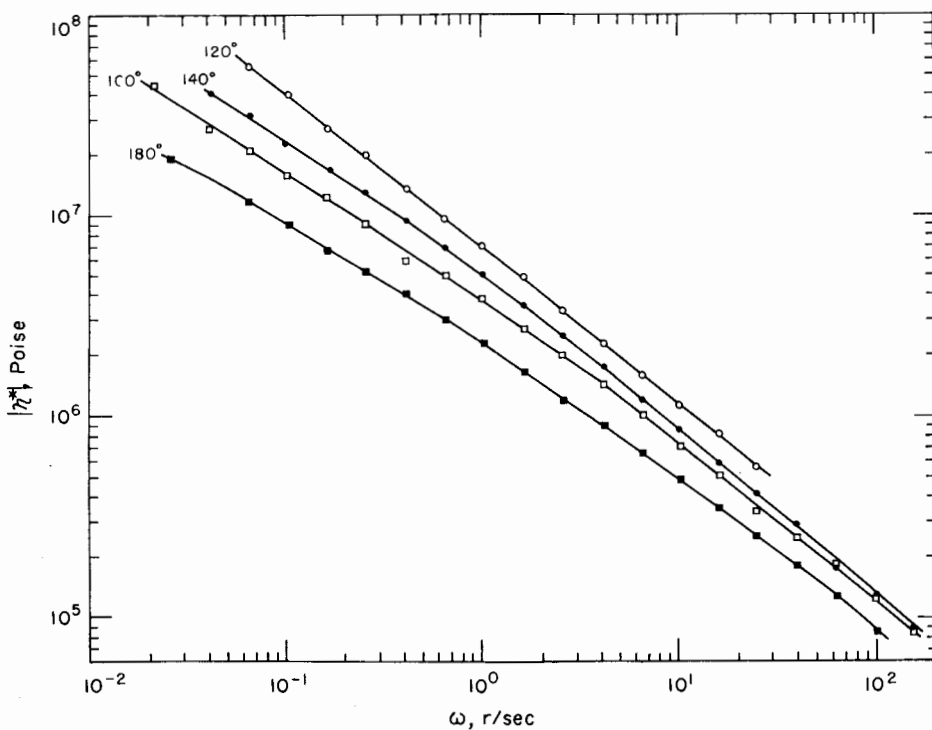


Fig. 3. Complex viscosity  $|\eta^*|$  vs. angular frequency  $\omega$  for the S3.5 sodium salt.

Association constants for hydrogen bonding in the acid derivative were determined by IR measurements using the  $935\text{ cm}^{-1}$  band assigned to the out-of-plane —OH bending in the dimer. Measurements were carried out on a Perkin-Elmer model 283 infrared spectrophotometer with a specially designed

heating cell. To attain temperatures below 40°C, precooled dry nitrogen was introduced through the purging inlet. Heating rates were 1–2°C/min, allowing readings to be made at  $\pm 2^\circ\text{C}$ .

Dynamic and steady shear data were taken in the melt using a Rheometrics model RMS 7220 mechanical spectrometer. The temperature range was 120–180°C and dry nitrogen gas was used to constantly purge the sample chamber. The cone-and-plate geometry was used for the steady shear experiments with a 25 mm diameter and a 0.1 rad cone. Accessible shear rates were  $10^{-2}$ – $10 \text{ sec}^{-1}$ . The eccentric rotating disk (ERD) geometry was used for the dynamic experiments. This technique has recently been reviewed by Macosko and Davis.<sup>9</sup> Twenty five millimeter platens were used and sample thicknesses were about 1 mm. Strains were corrected for displacement owing to instrument compliance. Replicate runs were found to have a precision of  $\pm 5\%$ .

## RESULTS

Figures 1 and 2 show the frequency dependence of the absolute value of the complex viscosity  $|\eta^*|$  and the shear rate dependence of the apparent viscosity  $\eta_a$  for the ester and acid derivatives, respectively. The frequency dependence of  $|\eta^*|$  for the Na salt is shown in Figure 3. Steady shear data were not attainable in the cone-and-plate geometry with this polymer. Extremely high apparent viscosities were noted for the lowest shear rates but the sample failed quickly by extruding out of the gap.

It is apparent from inspection of Figures 1 and 2 that there is excellent correspondence between the complex viscosity versus frequency and the apparent viscosity versus shear rate for the ester and acid derivatives. This result is predicted by molecular theories<sup>10</sup> and is shown to be the case for polyethylene and polystyrene melts.<sup>11,12</sup> Correspondence between  $\eta_a$  and  $|\eta^*|$  was also found to be the case for the methacrylic acid copolymer in a similar study by Sakamoto.

It can be seen that the zero shear viscosity  $\eta_0$  is asymptotically approached in the S3.5E and S3.5A polymers at the lowest shear rates or frequencies. In

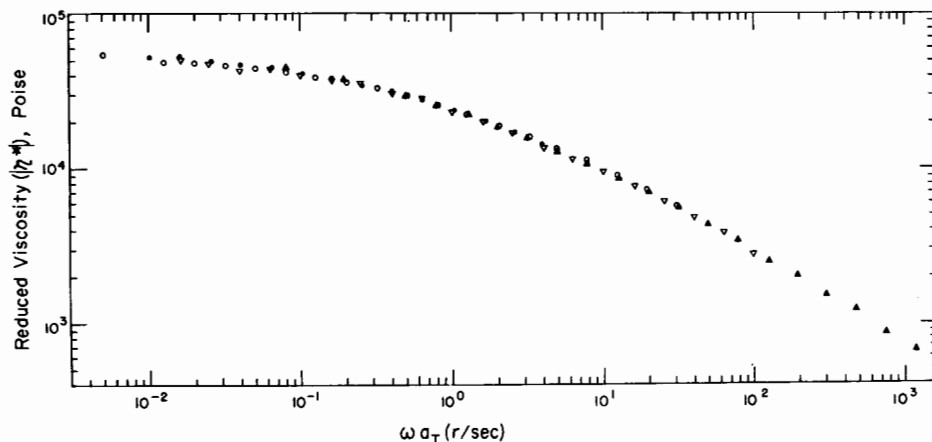


Fig. 4.  $|\eta^*|$  master curve of the S3.5 ester derivative. Reference temperature, 140°C: ( $\blacktriangle$ ) 120°C; ( $\nabla$ ) 140°C; ( $\circ$ ) 160°C; ( $\bullet$ ) 180°C.

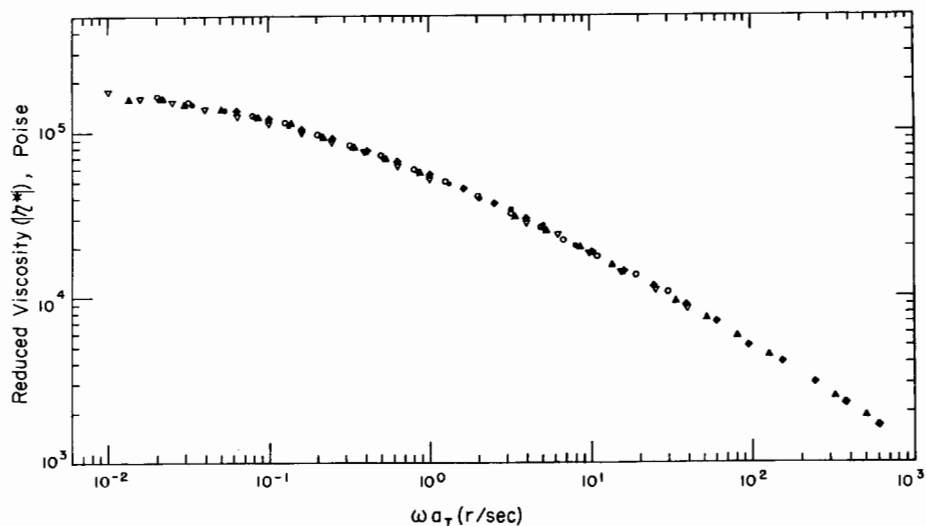


Fig. 5.  $|\eta^*|$  master curve of the S3.5 acid derivative. Reference temperature, 140°C: ( $\blacktriangle$ ) 120°C; ( $\blacklozenge$ ) 130°C; ( $\blacktriangledown$ ) 140°C; ( $\circ$ ) 160°C; ( $\bullet$ ) 180°C.

TABLE II  
Zero Shear Viscosities and Shift Factors for the Ester and Acid Derivatives

Derivative	Temperature (°C)	$\eta_0$ (P)	$a_T$ (calc)	$a_T$ (actual)
S3.5E	120	$2.39 \times 10^5$	4.49	7.64
	140	$5.6 \times 10^4$	1.0	1.0
	160	$2.9 \times 10^4$	0.491	0.491
	180	$1.35 \times 10^4$	0.22	0.155
S3.5A	120	$1.01 \times 10^6$	5.15	5.15
	130	$4.5 \times 10^5$	2.23	2.44
	140	$2.06 \times 10^5$	1.0	1.0
	160	$1.04 \times 10^5$	0.482	0.482
	180	$4.68 \times 10^4$	0.207	0.201

order to estimate  $\eta_0$  for each temperature the extrapolation method of Lim and Hass<sup>4</sup> was used for the dynamic data. A plot was made of reciprocal dynamic viscosity versus the loss modulus  $G''$ . As  $G''$  approaches zero,  $1/\eta'$  approaches  $1/\eta_0$ . A similar plot was constructed for  $1/\eta_a$  vs.  $\tau_s$ , the shear stress, and a double extrapolation was made to determine  $\eta_0$  for each temperature. These values of  $\eta_0$  were then used to apply time-temperature superposition to the viscosity data. Figures 4 and 5 show the excellent superposition obtained for each derivative at a reference temperature of 140°C. Vertical shifts were calculated as the ratio of  $\eta_0$  at 140°C to  $\eta_0$  at the temperature being shifted. Initial values of horizontal shift factors  $a_T$  were calculated by the method of reduced variables outlined by Ferry<sup>13</sup> using

$$a_T = \eta_0 T_{\text{ref}} / \eta_0^{\text{ref}} T \quad (1)$$

Values quite close to those calculated were actually used for the horizontal shift factors. Table II lists the values of  $\eta_0$  and  $a_T$  used for the superposition.

Determination of the zero shear viscosities also affords the advantage that the zero shear activation energy for flow  $\Delta E^\ddagger$  can be calculated. Since the  $\eta_0$  is

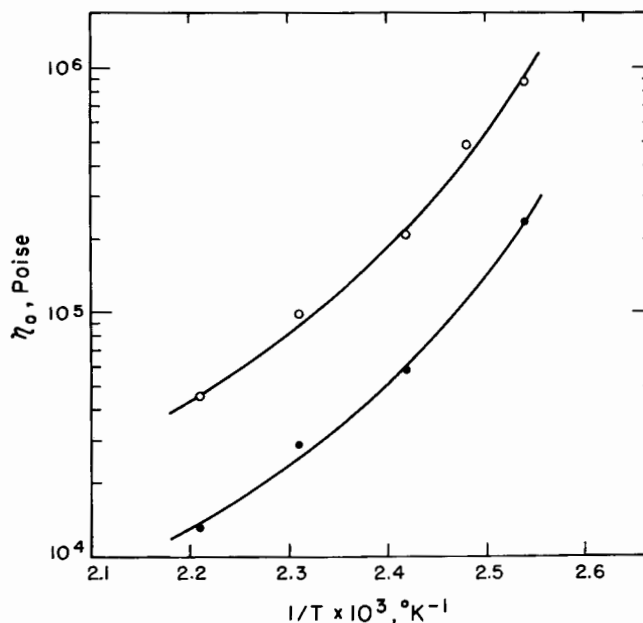


Fig. 6. Zero shear viscosity  $\eta_0$  vs. reciprocal temperature for the (●) ester and (○) acid derivatives.

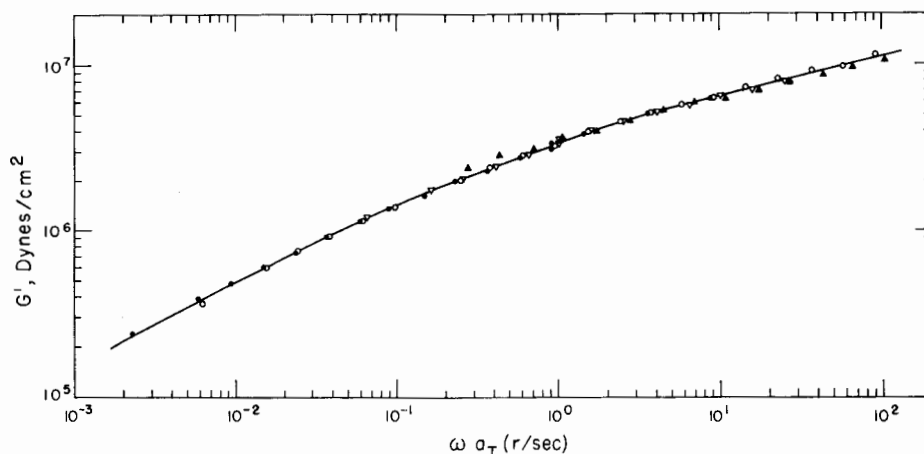


Fig. 7. Storage modulus  $G'$  master curve of the S3.5 sodium salt: Reference temperature, 140°C. Symbols same as in Fig. 4.

uniquely determined by temperature, an Arrhenius type equation (eq. (2)) can be used to calculate  $\Delta E^\ddagger$ :

$$\eta_0 = K \exp(\Delta E^\ddagger/RT) \quad (2)$$

However, plots of  $\log \eta_0$  vs.  $1/T$  are not straight lines, as is evidenced in Figure 6 by distinct curvature at the lower temperatures. For relative comparison, a least-squares fit of all the points indicates activation energies of 16.6 and 17.6 kcal/mole for S3.5E and S3.5A, respectively. If the points at the lowest temperature (120°C) are neglected, the  $\Delta E^\ddagger$  are calculated as 13.3 and 15.8 kcal/mole for the ester and acid derivatives. It is apparent that the activation energy of



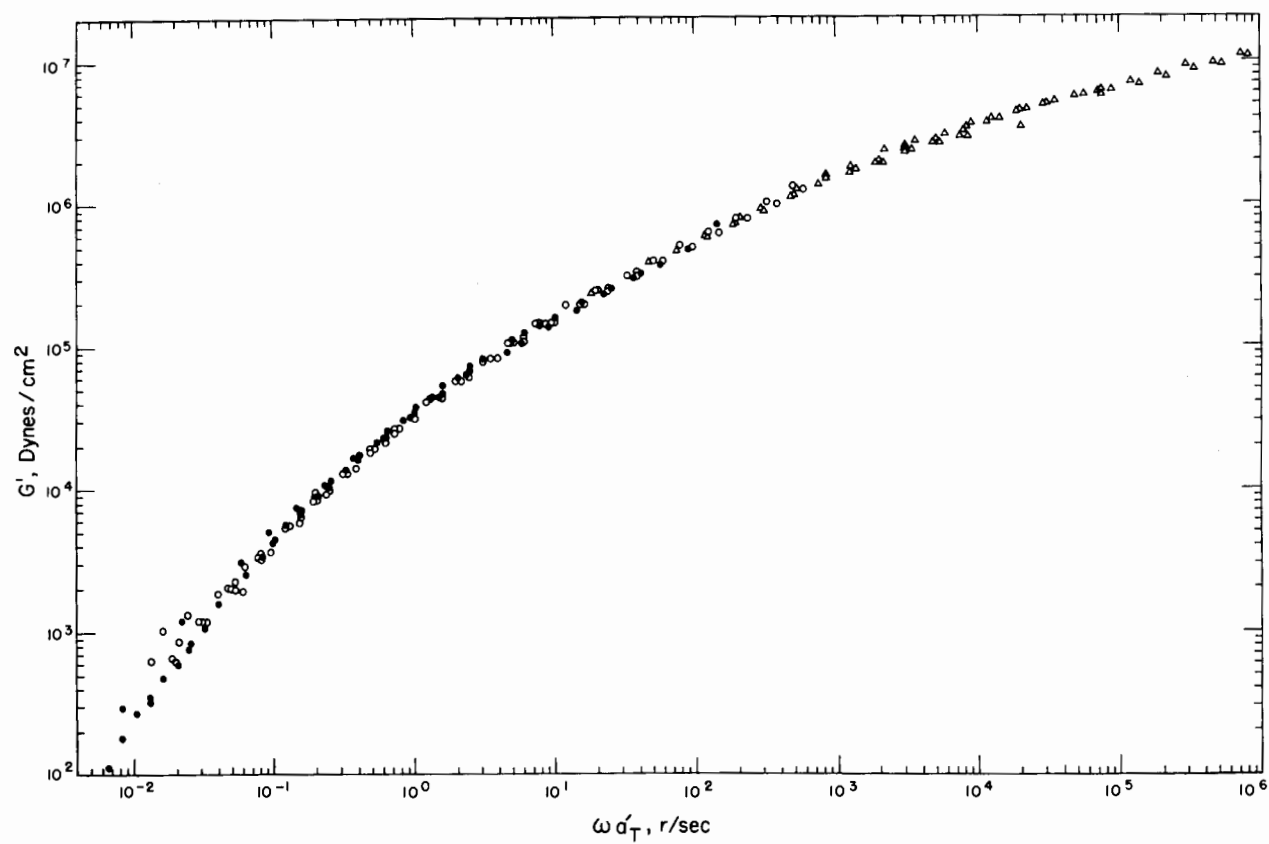


Fig. 8. Storage modulus  $G'$  super-master curve for the ester, acid, and sodium salt derivatives. Reference is the acid derivative at 140°C. (○) S3.5 acid (140°C), (Δ) S3.5 Na salt,  $a_T = 8200$ ; (●) S3.5 ester,  $a_T = 0.255$ .

viscous flow is larger for the acid form than for the ester form. However, the difference is not as large as that reported by Lim and Hass between a 5.3 mole % acrylic acid copolymer and its 85% ester. Their values are 8.5 and 15.7 kcal/mole for the ester and acid.<sup>4</sup>

In addition to viscosity master curves of the ester and acid derivatives, master curves of  $G'$  data were constructed using the same horizontal shift factors. Horizontal shift factors were empirically estimated for the sodium salt and a  $G'$  vs.  $\omega$  master curve for this derivative was also successfully constructed (Fig. 7). Furthermore, a super-master curve could be constructed for the three chemically different samples by using horizontal shifts of the individual master curves, each with 140°C as the reference temperature. This curve (Fig. 8) shows excellent juxtaposition of the data onto a single smooth curve. The empirical shift factors necessary for superposition of the three master curves were found to be  $a'_T = 0.255$  for S3.5E and  $a'_T = 8200$  for S3.5Na, with the master curve of the acid as the reference. To relate these frequency shifts to temperature shifts at constant frequency, an analysis used by Shohamy and Eisenberg<sup>7</sup> was utilized where a plot of  $|\eta^*|$  versus temperature was constructed for  $\omega = 1$  rad/sec. As is shown in Figure 9, data for the ester and acid are essentially parallel, giving a temperature shift  $\Delta T$  of 33°C. Constructing another parallel line through the S3.5Na data and extrapolating to the viscosity range of the ester gives a  $\Delta T$  of 165°C. Results are comparable if other frequencies or viscoelastic functions are used.<sup>7</sup>

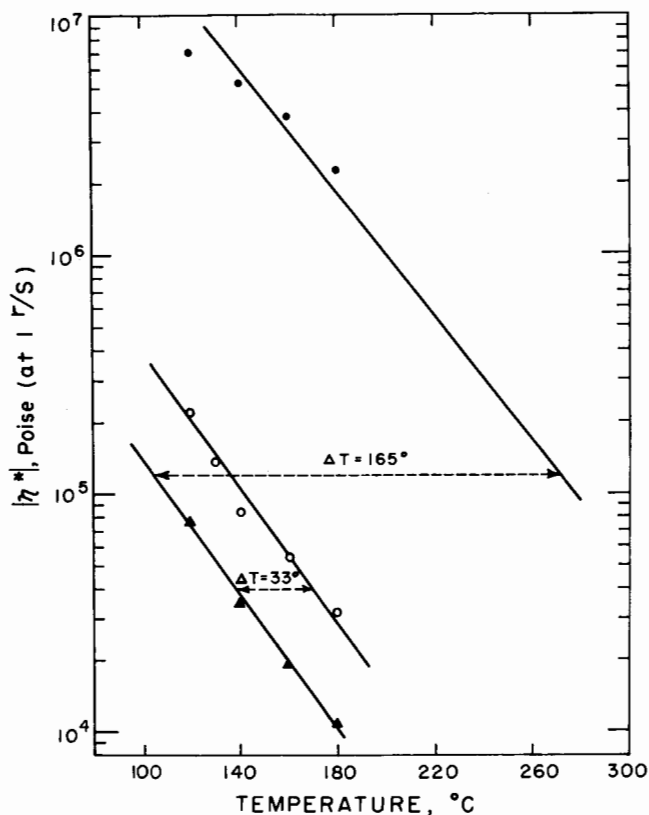


Fig. 9. Complex viscosity  $|\eta^*|$  at 1 rad/sec, as a function of temperature.

According to Ferry,<sup>13</sup> if the shift factors  $a_T$  are not the same for long and short retardation times, any attempt to fit the data will give one set of apparent  $a_T$  values for  $G'$  and another for  $G''$ ; and no master curves can be drawn without subjecting the data to additional analysis. To test the data for any anomaly, a super-master curve of  $G''$  vs.  $\omega a'_T$  was constructed using the same shift factors as for the  $G'$  plot. As is shown in Figure 10, the data superimpose fairly well except at high reduced frequencies. These points are for the Na salt and indicate a clear breakdown of time-temperature superposition. The salt data at their lowest reduced frequencies do overlap with data from the acid derivative, but at  $\omega a'_T = 10^3$ , curves at different temperatures begin to diverge.

## DISCUSSION

The obvious effect of replacing methacrylate groups with carboxylic acid groups is to increase the viscosity of the polymer melt. For styrene-acrylic acid copolymers Fitzgerald and Nielsen<sup>2</sup> have explained this increase in viscosity as a result of an increase in  $T_g$  of the copolymer over the homopolymer. Indeed the  $\beta$  relaxation temperature of S3.5A is 45°C higher than for S3.5E. This temperature difference roughly corresponds to the results of Figure 9 where  $\Delta T = 33^\circ\text{C}$  between the ester and acid forms. In a study of ethylene-acrylic acid copolymers, Otocka and Kwei<sup>14</sup> support the conclusion that the  $T_g$  increase of the copolymer is due to two effects. The first is copolymer composition where the much higher  $T_g$  of the comonomer raises the overall glass transition temperature. The second effect is that due to crosslinking. Near room temperature, essentially all the acid groups participate in stable cross-linking dimers;<sup>14,15</sup> however, at the elevated temperatures employed in this work (120–180°C) only 10–40% of the carboxylic acid groups are dimerized, thus the "crosslink density" is greatly reduced and this second effect is less prominent. In light of this,  $\Delta T$  from Figure 9 should be less than the difference in  $T_\beta$  as measured in the Vibron experiments.

Interchange between pairs of hydrogen bonding dimers is, of course, taking place in the polymer melt. Whether this interchange perturbs the flow behavior must be determined by the rate of dissociation and association. Low molecular weight acid dimerization reactions are diffusion controlled processes having rate constants of the order of  $10^6$ – $10^{10}$  mole  $\text{sec}^{-1}$  in dilute solution.<sup>16</sup> Since diffusion is the controlling factor, the rate constants will be inversely proportional to the viscosity of the medium.<sup>17,18</sup> Dilute solutions of low molecular weight acids have viscosities about  $10^{-2}$  P, while the bulk viscosities of the polymer melts investigated are  $10^4$ – $10^6$  P. If the most favorable conditions were selected, the rate constants could be within the time scale of the rheological experiments (up to  $10^2$   $\text{sec}^{-1}$ ). However, the local viscosity experienced by the carboxylic acid groups would certainly be lower than the bulk viscosity and the molar concentration of the acid group is small. Therefore, we conclude that the association and dissociation of hydrogen bonds occurs more quickly than the rheological measurements, revealing only the effect of the equilibrium concentration of dimers. Reinforcing this conclusion is the excellent correspondence of steady shear and dynamic viscosities for the acid derivative, as seen in Figure 2, and the excellent time-temperature superposition of viscosity data for S3.5A. If the content of dimers in the melt has a significant effect on the flow behavior, then

we might expect that viscosity curves at different temperatures would have different shapes, but this was not found.

The glass transition temperature has been treated as an isoviscous state where the viscosity of a polymer would be about  $10^{13}$  P. Viscous behavior is, therefore, a function of the temperature elevation above  $T_g$ . As discussed above, there is little direct effect of any intermolecular hydrogen bonding occurring in the melt; however, the crosslinking effect near room temperature probably does contribute significantly to an increase in  $T_g$  for the acid over the ester derivative. We may conclude then that for the system studied, the melt behavior of the acid derivative is determined primarily by the glass transition temperature regardless of the molecular interactions that determine it.

Neutralization of the acid groups in the copolymer has a great effect on rheological and other physical properties.<sup>6,19</sup> It has been established that in the concentration range and degree of neutralization studied, ionic clusters exist giving rise to domains of an ionic phase which remain intact well above the melting point.<sup>20-22</sup> Preliminary small-angle x-ray studies on S3.5Na show an x-ray scattering peak at  $2\theta = 2.5^\circ$  which persists in the melt to at least  $135^\circ\text{C}$ .<sup>23</sup> As was mentioned above and in previous studies, the steady shear viscosity is observed to be greater than the dynamic viscosity of ionomers. It is therefore interesting to find that the ester, acid, and salt derivatives of the same polymer backbone give time-temperature superposition on a plot of  $G'$  vs.  $\omega a'_T$  (Fig. 8). At first glance this result seems unlikely; however, the mechanism for storing energy via  $G'$  depends on the elastic nature of the polymer chain; i.e.,  $G'$  results from the elastic response of the long chain segments between any crosslinks that may exist. In the theory of rubber elasticity the modulus is considered proportional to the number of crosslinks, but the shape of the modulus-time curve does not depend on crosslink density. Therefore the action of ionic domains to crosslink the polymer results only in an increased storage modulus without the incorporation of additional mechanisms for energy storage. According to theoretical treatments of thermorheologically simple materials, if superposition is applicable for  $G'$ , then it must also be applicable to the loss function  $G''$ .<sup>13,24</sup> However, ionomers are not thermorheologically simple materials, as evidenced by the failure of  $G''$  data to superimpose using the same shift factors as for  $G'$ . The lack of superposition is not an effect of experimental scatter. Because of the large values of modulus for the salt, the instrumental signal-to-noise ratio is extremely high, allowing precise measurements of the force components to be made.

The same type of  $G'$  superposition was recently reported by Shohamy and Eisenberg<sup>7</sup> for a styrene-methacrylic acid copolymer system (98.5:1.5 mole %) below the so-called critical cluster concentration for the polymers. They found superposition applicable for ester, acid, and sodium salt derivatives over a similar temperature and frequency region. They also mention that time-temperature superposition was not as successful for viscoelastic loss functions,  $G''$  or  $\eta'$ , although no details were given. From Figure 10 it can be seen that superposition does not apply to  $G''$  data of the salt derivative at the higher reduced frequencies. Stress-relaxation studies of various ionomers have also shown this failure of time-temperature superposition over extended time (or frequency) when ionic clusters are evident.<sup>25,26</sup> This anomaly is presumably due to secondary dissipative mechanisms involving the ionic domains, but our data are not sufficiently

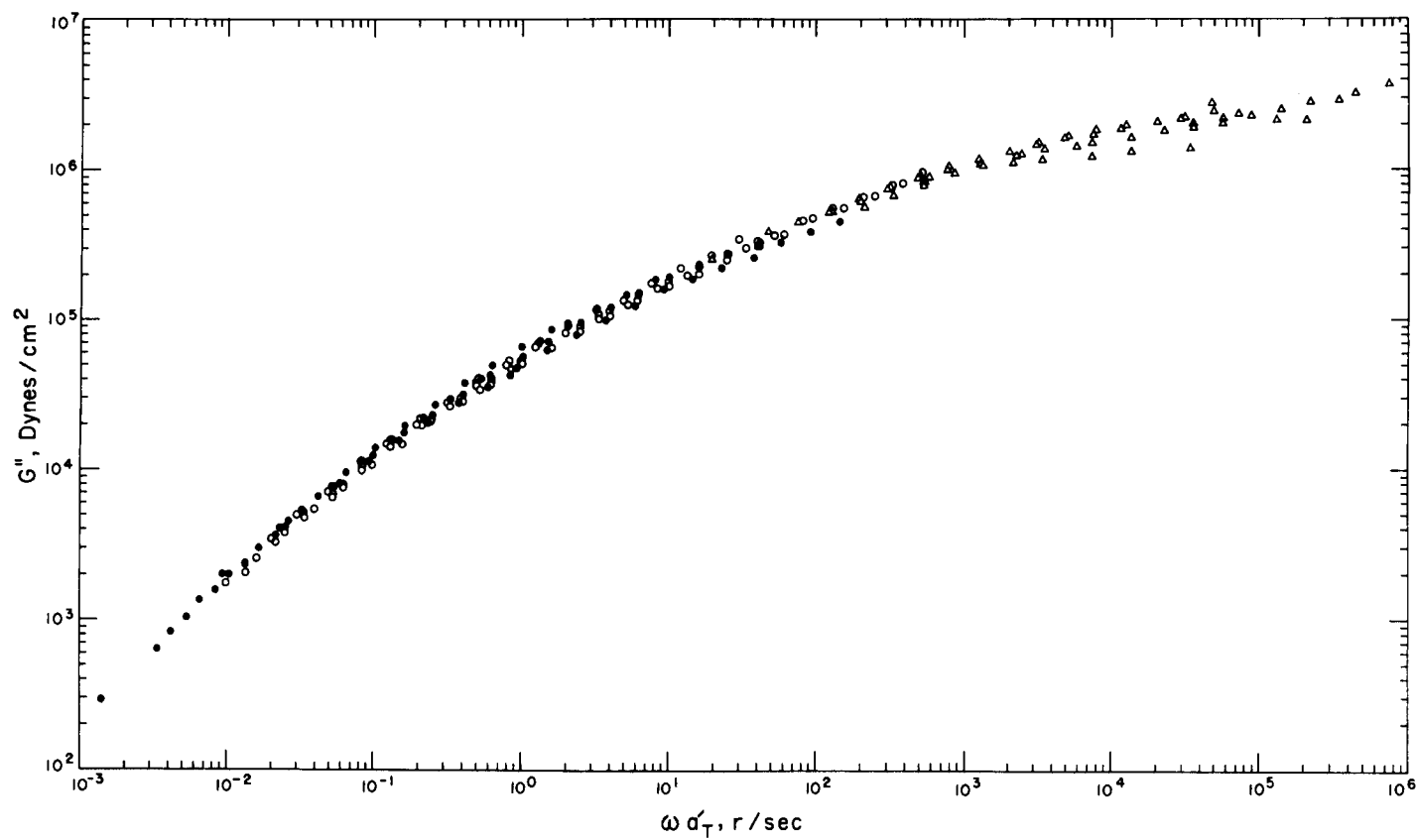


Fig. 10. Loss modulus  $G''$  super-master curve for the ester, acid, and sodium salt derivatives. Reference is the acid derivative at 140°C. Symbols same as in Fig. 8.

precise for further quantitative analysis, as were data from previous stress relaxation experiments.<sup>26</sup>

Since it is assumed that the nature of the polymer chain determines the storage modulus properties, we may speculate on the importance of interchain interaction. The temperature differences  $\Delta T$  needed to obtain superimposed plots of  $G'$  should give insight here. Infrared measurements of similar systems indicate  $\Delta H$  values for dissociation of hydrogen bonded dimers to be about 6–12 kcal/mole,<sup>14,15</sup> and the value calculated for our S3.5A is 10.6 kcal/mole. Otocka calculates  $\Delta H$  for the process of two ion pairs yielding a quartet to be 25 kcal/mole,<sup>27</sup> and Potts et al. calculate  $\Delta H$  for a sodium carboxylate quadruple ion to be 30 kcal/mole.<sup>28</sup> Shohamy and Eisenberg<sup>7</sup> suggest that  $\Delta T$  values between ester and acid and ester and salt simply reflect differences in  $\Delta H$  values for the two types of interactions and, indeed, the ratio for their nonclustered styrene ionomers give values quite close to the calculated ones in Table III. The ratio of  $\Delta T$ 's in this work gives approximately the same result even though the polymers are based on a polyethylene backbone and, more importantly, contain ionic clusters.

It may be fortuitous that the  $\Delta T$  ratio for this system agrees so closely with the results of Shohamy and Eisenberg. For the polyethylene based ionomers it has been seen that the viscosity increases with increasing neutralization,<sup>20</sup> suggesting that  $\Delta T$  between ester and salt would also increase with increasing ionization. In models thus far proposed, unionized carboxyl groups act to plasticize the ionic domains, thereby lowering the degree of interaction among ion pairs. Making a correction for partial ionization Longworth and Vaughn<sup>29</sup> report a linear relation between log viscosity of sodium salts and mole percent methacrylic acid relative to polyethylene of the same molecular weight. A similar curve with lower slope is shown for unionized acid copolymers. Correlation of this linear increase in log viscosity with a temperature shift  $\Delta T$  and an interaction energy  $\Delta H$  implies a constant ratio between salt and acid derivatives, which is exactly what was found by Shohamy and Eisenberg and by us.

Two additional factors influencing the rheological response of an ionomer are the equilibrium number of salt residues in a cluster and their rate of association and dissociation. Available data indicate that the clusters are intact in the melt and the concentration and size do not change significantly with temperature. A high temperature mechanical and dielectric relaxation is seen to occur in similar polyethylene ionomers at 50–100°C.<sup>8,30,31</sup> It is thought that this relaxation reflects the softening of the ionic domains, somewhat like a glass transition. The viscosities of the two phases (cluster and matrix) in the melt would then be very different because the cluster would be closer to its  $T_g$ . Therefore the translation of a polymer segment through the melt would have to be coupled with the removal of an ion pair from a more viscous cluster which would be the rate controlling process.

TABLE III  
Theoretical and Calculated Interaction Ratios

	$\Delta T$ (°C) Ester–Acid	$\Delta T$ (°C) Ester–Salt	Ratio
Shohamy and Eisenberg	8	38	4.8
This work	33	165	5.0
Theory	—	—	2.5–4.2

## CONCLUSIONS

At the concentration investigated, incorporation of hydrogen bonding carboxylic acid groups in a polyethylene-based polymer leads to an increase in melt viscosity and a slight increase in activation energy for viscous flow. These effects can be explained satisfactorily by an increase in glass transition temperature. Time-temperature superposition of viscosity data for the acid copolymer indicates that the presence of any hydrogen bonded network is not influenced by the equilibrium concentration of acid dimers. Neutralization of acid comonomer units produces a different polymer morphology owing to ionic clustering. The superposition of  $G'$  data for the three derivatives suggests that the chain dynamics, not the method or form of any crosslinking, determines this behavior. Failure of the sodium-salt  $G''$  data to superimpose suggests additional mechanisms of flow in this derivative. It is postulated that  $\Delta T$  differences required for superposition among the three derivatives reflect differences in  $\Delta H$  for interchain interactions.

Our proposed mechanism of flow in ionomers can be divided into two steps. The  $\Delta T$ 's would reflect an energy increase needed to initiate polymer segmental flow (initiation step). The propagation step, involving the motion of a segment through a hydrocarbon matrix, is essentially the same for all three derivatives, as shown by the superposition of the  $G'$  data. Failure of  $G''$  data to superimpose reflects the dependence of this viscoelastic function on the initiation step. As clusters become more ordered the initiation step becomes more significant and is reflected in an increased  $\Delta T$  between ester and salt.

These conclusions are consistent with the hypothesis that flow in clustered ionomers results from an ion pair dissociating from a cluster, then "jumping" to another cluster, leaving the clusters intact on a time-averaged basis.

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