

Influence of Intermolecular Interactions on the Melt Rheology of a Propylene–Acrylic Acid Copolymer and its Salts

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Synopsis

Ionomers based on propylene–acrylic acid copolymer have been prepared and their rheological behavior studied. With different cations the melt viscosity at any shear rate increases as tributylamine salt < acid < zinc salt < sodium salt. Similarly, the activation energies for viscous flow follow the order polypropylene ~ tributylamine salt < acid ~ zinc salt < sodium salt. These results are a consequence of intermolecular interactions between salt groups for the metal acrylate derivatives and hydrogen bonding for the acid derivatives. Strong ionic interactions are absent in the tributylamine salt because of steric hindrance of the bulky amine substituents. The glass transition temperatures for these materials were equivalent. The elastic properties of these polymers follow a similar trend as does the viscosity.

INTRODUCTION

The melt rheology of nonpolar high-molecular-weight polymers is influenced primarily by the topological constraints on polymer molecules due because of, for example, chain lengths, long-chain branching, and entanglements. The flow behavior of polymers containing modest amounts of either polar or ionic substituents can, however, be dominated by the interactions of these groups. A number of investigators^{1–9} have observed that the introduction of either carboxylic acid or its salts into a predominantly hydrocarbon polymer results in a substantial increase in the melt viscosity and the flow activation energy relative to a nonpolar analogue.

For example, Longworth and Morawitz¹ found that the melt viscosity and the flow activation energy of styrene–methacrylic acid copolymers increased with increasing acid concentration. This they attributed to intermolecular hydrogen bonding between carboxylic acid groups. Similar results were reported by Blyler and Haas² and Lim and Haas³ for copolymers of ethylene and acrylic acid or methacrylic acid. These authors concluded that the increase in viscosity resulted from an increase in the apparent polymer molecular weight as a result of inter-chain hydrogen bonding and that the activation energy increase could be explained by an increase in the effective size of the flow unit. The latter effect is analogous to the effect of long-chain branching which is believed to be responsible for the differences in the flow activation energy of branched and linear polyethylenes.

Fitzgerald and Nielsen¹⁰ disagreed with these conclusions and argued instead that the increases in viscosity and the activation energy could be accounted for solely by changes of the glass transition temperature, T_g , owing to copolymer composition. More recently, Earnest and MacKnight⁹ found that the differences

in the rheological behavior of an ethylene-methacrylic acid copolymer and its methyl ester derivative could be accounted for by changes in T_g , but that changes in T_g alone could not account for differences between the sodium salt derivative and the acid.

While Blyler and Haas² report that the flow curves at different temperatures for ethylene-acrylic acid copolymers could not be superimposed to construct a master curve, Earnest and MacKnight⁹ and Sakamoto, MacKnight, and Porter⁶ found that time-temperature superposition could be obtained for both an ethylene-methacrylic acid copolymer and its methyl ester. Sakamoto et al.⁶ found, however, that time-temperature superposition was not possible for the sodium or calcium salts. Similarly, Earnest and MacKnight⁹ observed that while the reduced G' data for three derivatives of the ethylene-methacrylic acid copolymers (the acid, the methyl ester, and the sodium salt) could be superimposed to construct a super master curve, the G'' data for the salt did not superimpose with those for the acid and ester. This result was similar to that reported by Shohamy and Eisenberg⁷ for a styrene-methacrylic acid copolymer (1.5 mol % methacrylic acid). Earnest and MacKnight⁹ argued that the G' response of the ionomer is dictated primarily by the elastic response of the long-chain segments between the acid substituents and therefore should be essentially the same for all three derivatives. On the other hand, the failure of superposition of the G'' data suggests that more than one dissipative mechanism is involved in the flow of the salt. They postulated that, in the case of the salt, a loss mechanism may arise from an ion pair dissociation from an ionic domain or cluster.

All of the previously mentioned studies involved materials with either a predominantly ethylene or styrene backbone. The present investigation was undertaken to determine the effects of intermolecular hydrogen bonding and ionic association on the rheological properties of ionomers based on a propylene backbone.

EXPERIMENTAL

Materials

The acid modified polymer was a graft copolymer of acrylic acid onto polypropylene, prepared by a free-radical extrusion reaction described elsewhere.¹¹ The starting copolymer, designated Dexon 1001, was obtained from the Exxon Chemical Co. It contained 3.2 mol % acrylic acid as determined by infrared spectroscopy (IR), and had a melt flowrate (MFR) of 34.7 dg/min.¹² The molecular weight of the grafted species, that is, whether it is acrylic acid or poly(acrylic acid), was not determined and the effect of the graft chain length on the properties to be reported here is, at this time, unknown.

Because the grafting reaction results in considerable molecular weight degradation of the polypropylene backbone and a narrowing of the molecular weight distribution (MWD), the original polypropylene was not used for comparison purposes. Instead, a polypropylene which had undergone peroxide degradation, hereafter referred to as PP, was obtained from the Plastics Technology Division of the Exxon Chemical Co., and was used in this study as a reference polypropylene. This material had a MFR of 35 dg/min and the following molecular weights obtained from gel permeation chromatography: $M_n = 48,400$, $M_w = 131,000$, and $M_z = 167,000$.

The preparation of the propylene-acrylic acid copolymer also results in the homopolymerization of acrylic acid, and therefore, Dexon 1001 contains some free poly(acrylic acid). This was removed by preparing a 10% solution of Dexon 1001 in chlorobenzene at 90°C and adding to this approximately 1% hot distilled water. The propylene-acrylic acid copolymer was then reprecipitated in methanol and was, subsequently, washed two times with methanol in a Waring blender and dried under vacuum at 80°C. The acrylic acid concentration of the copolymer after extraction of the free poly(acrylic acid) was 1.3 mol % and its MFR was 33.3 dg/min.

The sodium, zinc, and tributylamine salts were prepared by titrating the copolymer in chlorobenzene at 90°C with a 50% excess of NaOH (aq), Zn(OAc)₂ (aq), and tributylamine, respectively. The neutralized copolymers were precipitated in methanol, washed two times with methanol in a Waring blender, and dried under vacuum at 80°C. The percent ionization was determined by comparing the intensities of the 1710-cm⁻¹ absorbance in the infrared spectra of the neutralized and unneutralized copolymers (Fig. 1) and are reported in Table I. Specific gravities at 23°C, determined by displacement of 2-propanol¹³ and MFR are also reported in Table I.

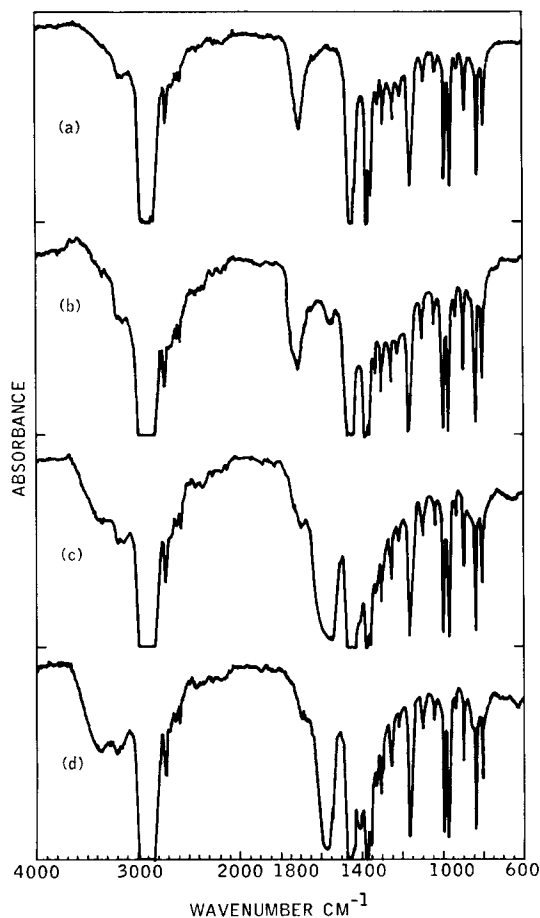


Fig. 1. Infrared spectra of propylene-acrylic acid copolymer and its neutralized derivatives.

TABLE I
Characteristics of Poly(Propylene-co-Acrylic Acid) Ionomers

Sample	% Neutralization	Specific gravity	MFR, dg/min
Acid derivative	0	0.9175	33.3
Sodium salt	85	0.9373	10.5
Zinc salt	85	0.9454	19.9
Tributylamine salt	30	—	57.1
Polypropylene	—	0.9049	35.0

Ionomer Characterizations

The crystalline structures of the propylene-acrylic acid ionomers were determined by x-ray diffraction using a Phillips verticle goniometer equipped with a diffracted beam monochromator (graphite crystal, CuK radiation). Powder samples were prepared by precipitating the polymer from solution in methanol and were used for intensity measurements.

Crystalline melting points and heats of fusion were measured with a Perkin-Elmer model 2 differential scanning calorimeter (DSC), using a heating rate of 10°/min. The melting temperatures reported represent the maxima or inflection points in the melting endotherm, and the heats of fusion were determined by integrating the area under the curve using a Tektronics model 31 programmable calculator which was interfaced with the DSC.¹⁴

Flexural modulus and strength were measured with an Instron testing machine using a crosshead speed of 1.3 mm/min.¹⁵ Rectangular samples measuring 3.2 × 12.7 × 127 mm were molded with a Boy, 20-ton, reciprocating screw, injection-molding machine. All samples were aged at room temperature and 50% RH for at least 48 hr prior to testing.

The complex shear modulus and its components, G' and G'' , were measured with a Rheometrics mechanical spectrometer at a frequency of 1 Hz, and covering the temperature range from -100 to 150°C. Samples approximately 50–60 mm in length were cut from injection-molded bars.

Melt viscosities were measured in steady shear with an Instron capillary rheometer and in dynamic shear with a Rheometrics mechanical spectrometer using a cone and plate configuration. Temperature was varied between 180 and 240°C. The capillary die had an aspect ratio ($L:R$) of 80, and the apparent shear rate was varied from 0.2–3000 sec⁻¹. All capillary data reported here have been corrected for non-Newtonian behavior using the Rabinowitsch equation.¹⁶ For the dynamic viscosity measurements, an angle of 4×10^{-3} rad was used, and the oscillatory frequency covered the range of 0.02–20 Hz. The strain amplitude was chosen so as to confine the measurements to the linear range.

RESULTS AND DISCUSSION

Polymer Crystallinity

The x-ray diffraction patterns for polypropylene and the acid, sodium salt, and zinc salt copolymers corresponded to the monoclinic or α -crystal structure of polypropylene.¹⁷ The intensities of the crystalline diffraction patterns for the copolymers were greater than for the polypropylene, indicating higher degrees

of crystallinity in the copolymers. The width of the 6.37Å reflection at half-maximum was smaller for the copolymers than for polypropylene, indicating that the crystalline domains in the copolymers are larger.

Differences in the DSC thermograms of these polymers were observed as shown in Figure 2. The temperature at the maximum rate of melting is depressed in the copolymers several degrees below that for polypropylene, and a single endotherm near 160°C is observed rather than the double endotherm seen for the polypropylene. In addition, for the acid, zinc salt, and sodium salt derivatives of the copolymer a small but distinct endotherm occurs at ~146°C, a temperature characteristic for melting of the hexagonal or β form of polypropylene crystallites.¹⁸ This result is, however, inconsistent with the x-ray diffraction results which indicated no β -form present in any of these materials. This discrepancy between the x-ray and thermal analyses, however, may be due to differences in the sample preparations. The DSC samples were prepared by compression molding and it is possible that quenching the polymers from the melt to room temperature results in the formation of some β -form crystallites. This is somewhat speculative, since no x-ray data were obtained for the compression-molded films. Still, it is interesting that the lower temperature endotherm is absent in the thermogram for polypropylene and the tributylamine salt derivatives.

The heats of fusion measured by DSC for all the materials are similar, which indicates that the degrees of crystallinity were not greatly different; and, in general, it appears that the incorporation of 1.3 mol % acrylic acid or its salts into polypropylene does not significantly inhibit the ability of polypropylene to crystallize. Therefore, because many of the solid-state properties of semicrystalline polymers are dependent on the extent of crystallinity, one might suspect that this modification of polypropylene should not have a deleterious effect on its physical properties. This will be shown to be the case later in this article.

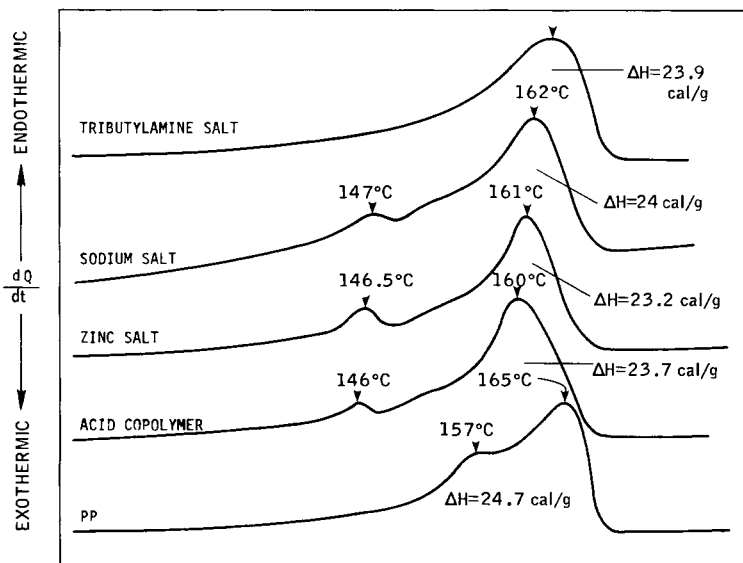


Fig. 2. DSC thermograms for polypropylene and its copolymer derivatives.

Rheology

The viscosity-shear rate curves for the various copolymer derivatives are compared in Figure 3. Whereas the melt viscosity increases upon conversion of the acid derivative to a metal salt, the viscosity actually decreases for the tributylamine salt. The first result is consistent with those of previous investigations^{6,7} of carboxylate ionomers, and can be adequately explained by an increase in the apparent polymer molecular weight due to intermolecular associations of the ionic groups. That the monovalent cation, sodium, leads to a greater increase in viscosity than does the divalent cation, zinc, was somewhat unexpected, but is consistent with similar results reported by Makowski et al.,¹⁹ for various sulfonated EPDMs. Comparing the viscosity curve of the tributylamine salt with that of the acid reveals that the low shear rate viscosity of the former is somewhat lower, suggesting that the intermolecular interactions in the tributylamine salt are weaker than in the acid, the latter resulting from hydrogen bonding. This is perhaps due to the bulky nature of the tributylamine cation which inhibits strong ionic association such as occur with the metal salts. Because of changes in the molecular weight and MWD of the original polypropylene polymer caused by the grafting reaction, comparisons between the flow curves of the copolymers and polypropylene are not straightforward. Therefore, it is not immediately apparent how the rheology of the tributylamine salt copolymer derivative compares to that of polypropylene. It will be shown later in this article, however, that the tributylamine salt of the propylene-acrylic acid copolymer exhibits much the same behavior as polypropylene, which suggests that ionic interactions are negligible with this cation.

The viscosity-shear rate curves taken at 180 and 200°C for various samples are shown in Figures 4-7. Both the steady-state viscosity and the dynamic viscosity data are shown. As expected, in the limit of low shear rates, a satisfactory correspondence between the two experiments was observed in all the samples except the sodium derivative. Owing to the rather strong ionic associations in this latter system, the limiting zero shear viscosities could not be

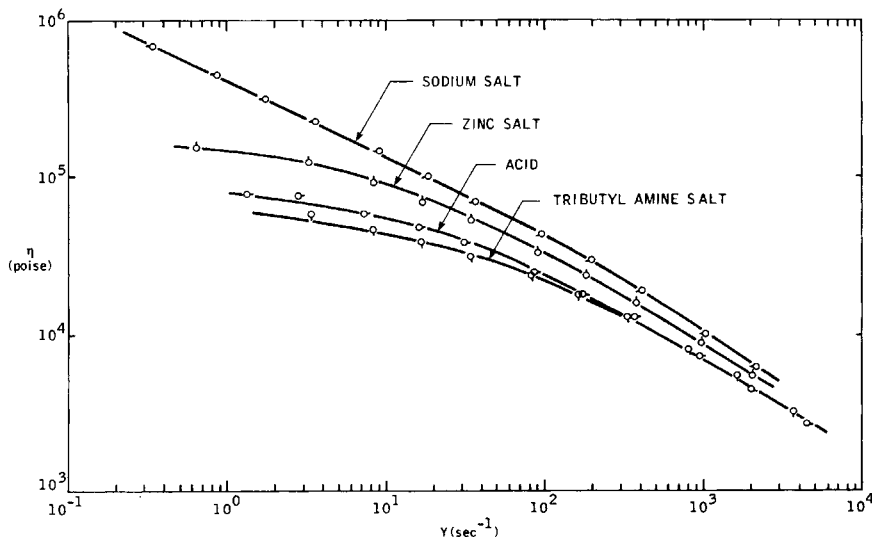


Fig. 3. Steady-state viscosity vs. shear rate for various copolymer derivatives at 180°C. $L:R = 80$.

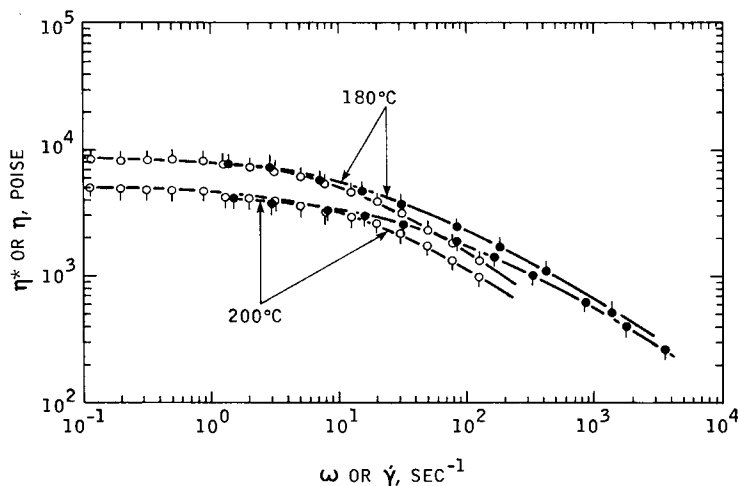


Fig. 4. Viscosity vs. shear rate for propylene-acrylic acid copolymer at 180 and 200°C. O, Dynamic data; ●, steady-state data.

achieved even at the highest temperature of measurement, 240°C. The sample response was highly nonlinear at the experimentally accessible strain rates and the lack of a good superposition of the dynamic data with that of steady state is not surprising.

Time-temperature superposition of the capillary data for all the polymers was attempted by vertically shifting the viscosity-shear stress data along the viscosity axis using 200°C as a reference temperature. The master curves obtained are shown in Figure 8. In general, superposition worked for each of these ionomers. Similar results were obtained by Earnest and MacKnight⁹ for the acid and ester derivatives of an ethylene-methacrylic acid copolymer, while Blyler and Haas² found that superposition was not applicable to ethylene-acrylic acid copolymers. This latter result is somewhat surprising in view of the similarity of the ethylene-methacrylic acid copolymers and the ethylene-acrylic acid copolymers.

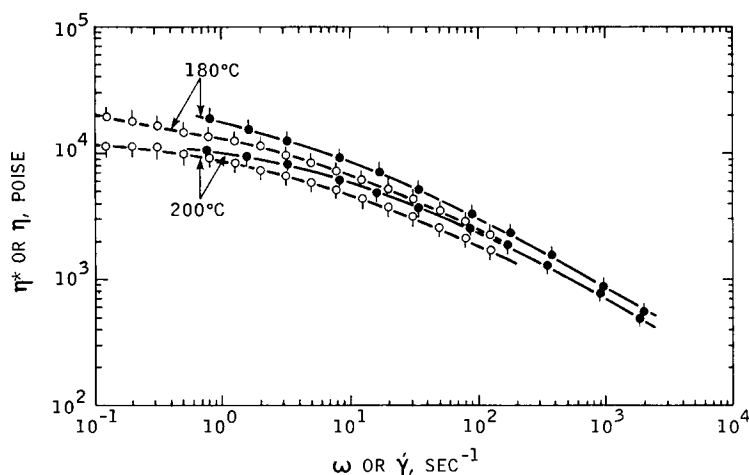


Fig. 5. Viscosity vs. shear rate for propylene-acrylic acid copolymer (zinc salt) at 180 and 200°C. O, Dynamic data; ●, steady-state data.

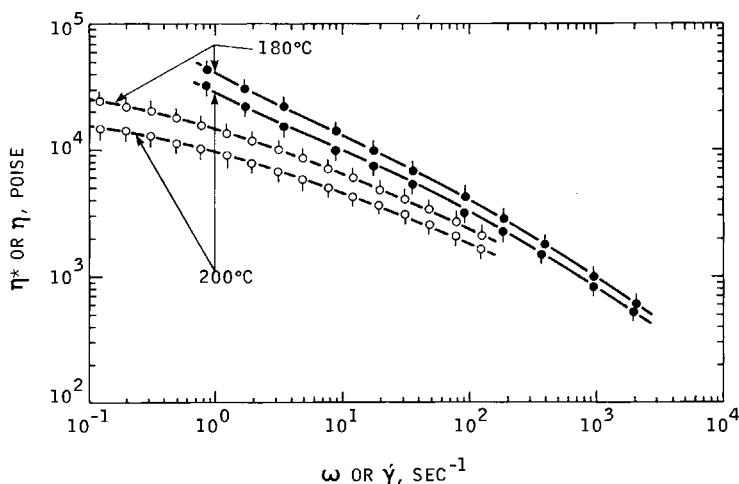


Fig. 6. Viscosity vs. shear rate for propylene-acrylic acid copolymer (sodium salt) at 180 and 200°C. O, Dynamic data; ●, steady-state data.

The viscosity shift factors, a_T , were used to calculate an Arrhenius-type activation energy for viscous flow and are given in Table II for PP and the different copolymer derivatives. The activation energy for the acid copolymer is greater than for polypropylene, and that for the sodium salt derivative is greater than for the acid copolymer. The activation energy for the zinc salt is roughly the same as for the acid derivative. These results are consistent with those of Lim and Haas³ and Earnest and MacKnight⁹ for similar systems, the increases in E_a being a consequence of the restriction of chain motions due to the intermolecular interactions.

A somewhat surprising result was found in the case of tributylamine salt. It was shown previously (see Fig. 3) that this material behaved as if ionic interactions were weaker than the hydrogen bonding occurring in the acid or were

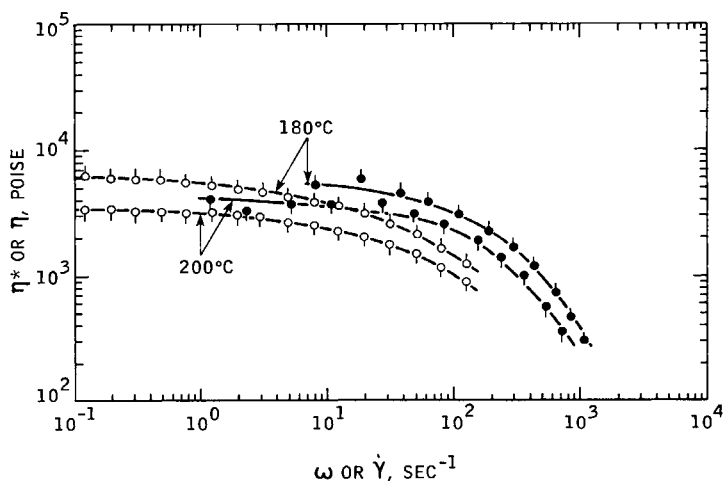


Fig. 7. Viscosity vs. shear rate for propylene-acrylic acid copolymer (tributylamine salt) at 180 and 200°C. O, Dynamic data; ●, steady-state data.

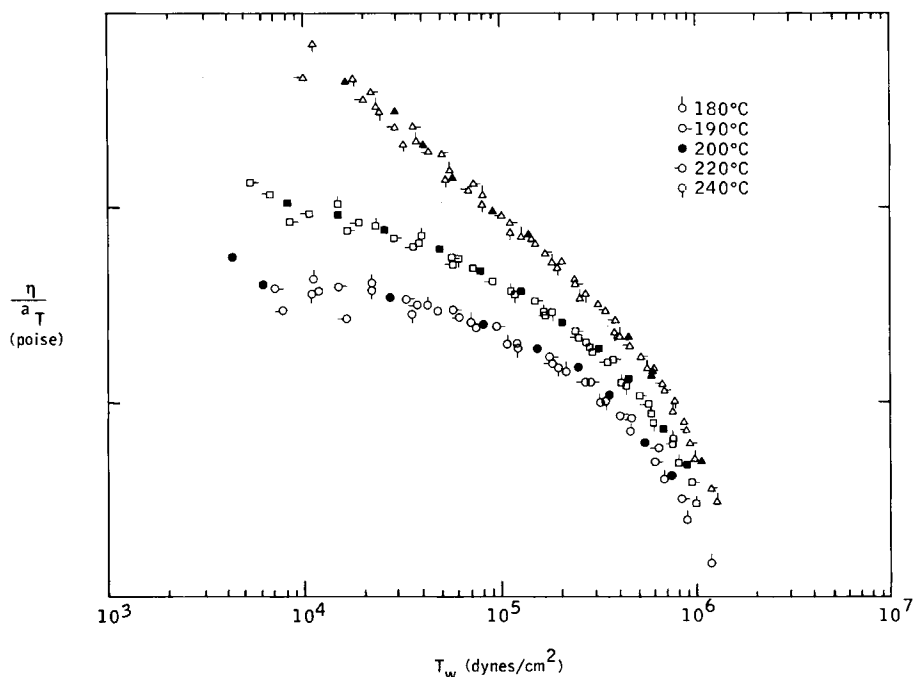


Fig. 8. Viscosity-shear stress master curves for propylene-acrylic acid copolymer, O; its zinc salt, \square ; its sodium salt, Δ . Ref. temp. = 200°C; $L:R = 80$.

perhaps nonexistent. The activation energy for this sample is similar to that for polypropylene, which suggests that the introduction of a tributylamine acrylate into polypropylene results in no restriction of chain motions such as occur when the grafted species is acrylic acid or a metal acrylate. This result indicates that the ionic interactions which normally occur in an ionomer can be controlled by the choice of the size of the cation, in this case tributylamine.

As noted earlier, the master curve of the propylene acrylic acid copolymers clearly shows a Newtonian flow region, while the flow curves for the metal salts, especially that of sodium salt, do not. The low shear viscosity for the sodium salt appears to be unbounded, behavior which is analogous to what would be expected for an extremely high-molecular-weight polymer. The linearity of the viscosity-shear stress data for the sodium salt derivative at low shear rates suggests that the flow of this material is characterized by a yield stress, similar to that which accompanies plastic flow of a solid. These characteristics of the metal salt ionomers are consistent with the concepts of strong ionic crosslinking, but whereas a covalent crosslink is permanent, the ionic crosslink is time de-

TABLE II
Flow Activation Energies for Propylene-Acrylic Acid Copolymers

Derivative	E_a (kcal/mol)
Polypropylene	10.3
Acid	11.4
Tributylamine salt	10.0
Zn salt	11.6
Na salt	12.3

pendent with an extremely long relaxation time. Therefore, unlike chemically crosslinked polymers, these polymers exhibit melt flow under suitable conditions of shear rate or shear stress and temperature.

One important fact distinguishes the results reported here from those previously reported for ethylene-based ionomers. Whereas in those systems interpretation of the rheological data is complicated by differences in the T_g for the various derivatives, no such complication exists in the present study. The T_g of all the materials discussed here are identical as evidenced by the β transition in the dynamic mechanical data shown in Figure 9. The major difference between the behavior of the two systems, the ethylene-based and propylene-based ionomers, is that in the ethylene systems the functional group is attached to the main chain and in the propylene system it is attached to a grafted branch. The constancy in T_g observed in these systems suggests that the acrylic acid groups are present in a distinct dispersed phase, as has been previously shown to be the case by Pegoraro.²⁰ Therefore, the viscosity differences for the various polymers described here are clearly due to a reduction of chain mobilities resulting from the ionic interactions and not differences in T_g .

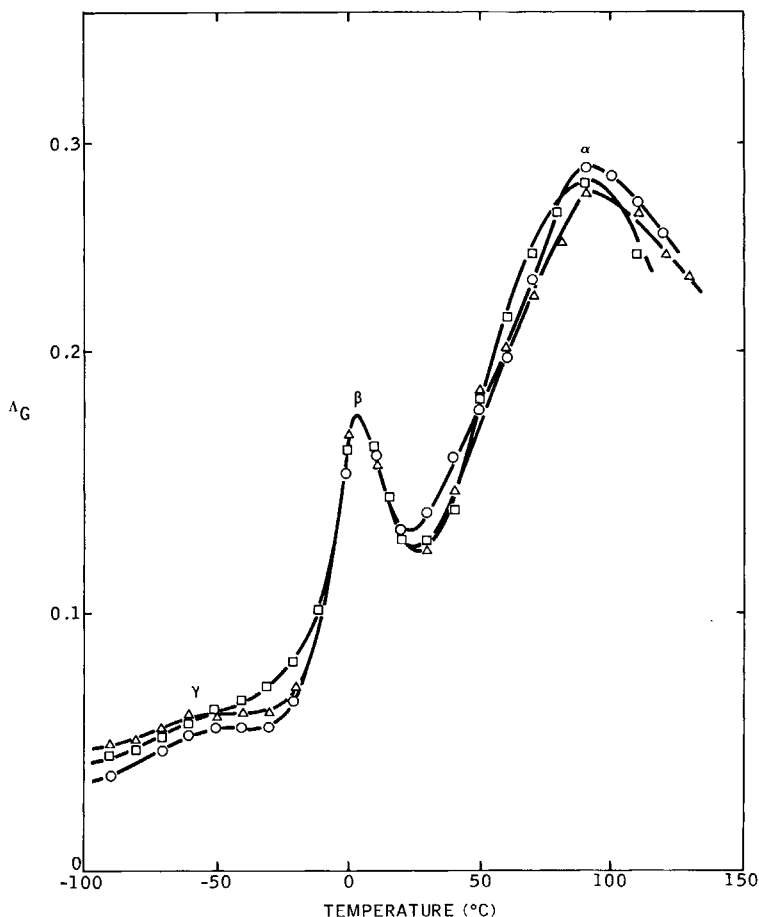


Fig. 9. Logarithmic decrement vs. temperature for propylene-acrylic acid copolymer and its metal salts. O, Acid; □, sodium salt; Δ, zinc salt.

Another rheological property which should be sensitive to differences in the intermolecular associations exhibited by these materials is elasticity. With the exception of the polypropylene sample used, all the polymers discussed in this article have the identical backbone molecular weight and distribution. Based on the method of its preparation and MFR information, it is believed that the polypropylene sample, PP, also has a similar molecular weight and MWD.

Extrudate (die) swells were measured at 180°C in a melt indexer using a short capillary die, $L/D = 3.8$. The data for polypropylene and the copolymers are given in Figure 10 as a function of the shear rate at the capillary wall. Han²¹ has reported that die swell ratios for a given polymer increase with increasing weight-average molecular weight. Intermolecular hydrogen bonding or ionic associations which increase the effective polymer molecular weight should then, as a consequence, increase the die swell ratio. The data in Figure 9 are consistent with this hypothesis. Thus, the acid copolymer behaves as if it were of higher molecular weight than the polypropylene and the sodium-neutralized copolymer acts as if it were of even higher molecular weight. The data for the zinc salt are somewhat confusing. This material exhibited the highest die swell ratio of any of the polymers evaluated and the die swell ratio decreased with increasing shear rate. Although reproducible, the explanation for this behavior is not apparent.

Mechanical Properties

The dynamic mechanical properties of the acid copolymer and its metal salts are given in Figure 11. At any given temperature, the dynamic shear moduli, G' , follow the order sodium salt > zinc salt > acid. In the bottom half of this

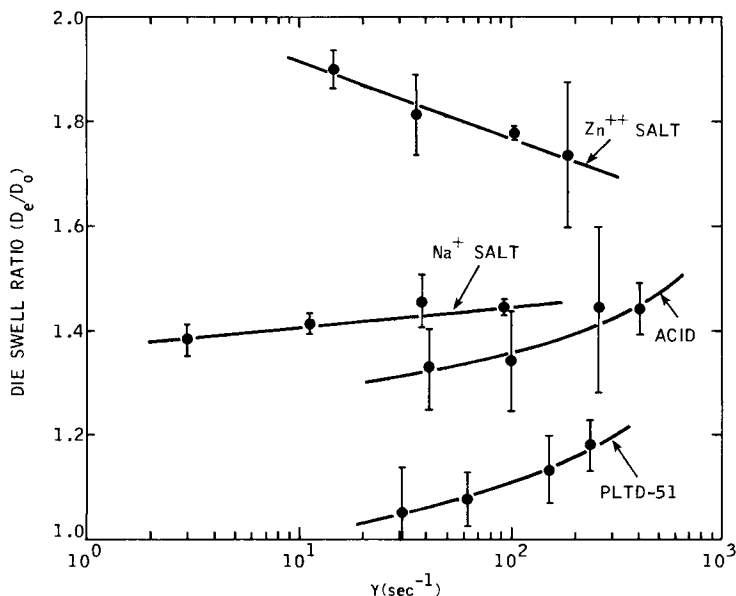


Fig. 10. Die swell vs. shear rate for polypropylene and its copolymer derivatives. $T = 180^\circ\text{C}$; $L/D = 3.8$.

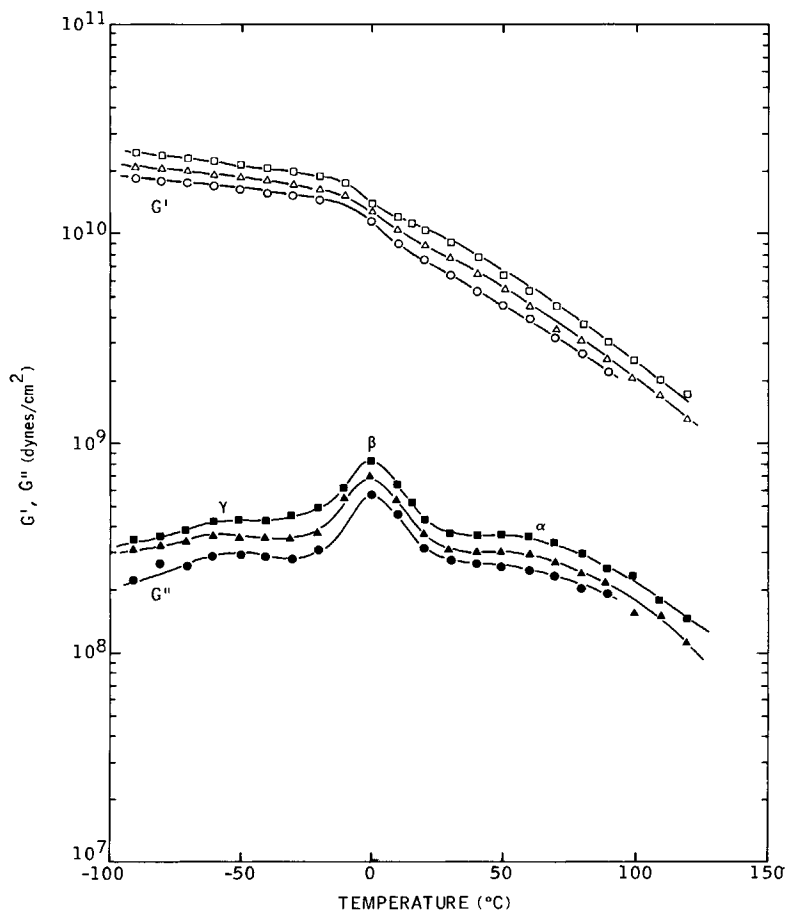


Fig. 11. Temperature dependence of G' and G'' for propylene-acrylic acid copolymers ($f = 1$ Hz). \circ , \bullet , acid; \square , \blacksquare , sodium salt; \triangle , \blacktriangle , zinc salt.

figure, G'' data for these polymers are also given, and from the position of the β peak, it is clear that all the samples have identical glass temperatures as was shown earlier in Figure 9.

The mechanical properties were also determined by a three-point flexural test at three different temperatures and these are given in Table III. Whereas the static mechanical data do not distinguish between the properties of the acid copolymer and its salts, the enhancement of the flexural properties over those of polypropylene are clear. These results are consistent with the hypothesis of physical crosslinking in these systems, owing to hydrogen bonding for the acid derivative and ionic interactions for the salts. The improvement of the strength for the copolymers versus polypropylene can be attributed to a restriction of the chain mobility caused by the network formed by the physical crosslinks, and consequently more force is required for a given deformation. This is supported by the fact that whereas the ultimate strengths of the copolymers were greater than for polypropylene, the strains at which the ultimate strength was achieved were in every case less.

TABLE III
Flexural Properties of Propylene-Acrylic Acid Copolymers

Sample	25°C	100°C	140°C
Modulus dyne/cm ²			
PLTD-51 (PP)	1.09×10^{10}	2.21×10^8	9.58×10^7
P-0.013AA	1.65×10^{10}	3.89×10^8	1.78×10^8
P-0.013AA-.85 Zn	1.71×10^{10}	3.91×10^8	1.85×10^9
P-0.013AA-.85 Na	1.80×10^{10}	3.85×10^8	1.67×10^9
Strength, dyne/cm ²			
PLTD-51 (PP)	3.77×10^7	1.02×10^7	4.34×10^6
P-0.013AA	5.20×10^7	1.55×10^7	6.79×10^6
P-0.013AA-.85 Zn	5.42×10^7	1.55×10^7	7.76×10^6
P-0.013AA-.85 Na	5.60×10^7	1.57×10^7	6.93×10^6

CONCLUSIONS

Ionomers based on a polypropylene backbone with acrylic acid pendant groups have been prepared and studied. These materials exhibit many of the rheological characteristics found in other ionomer systems, namely, ethylene-acrylic acid, ethylene-methacrylic acid, and styrene-methacrylic acid copolymers. The melt viscosity at any shear rate increases as tributylamine salt < acid < zinc salt < sodium salt. Similarly, the activation energies for viscous flow follow the order polypropylene ~ tributylamine salt < acid ~ zinc salt < sodium salt. These results are a consequence of intermolecular interactions between salt groups for the metal acrylate derivatives and hydrogen bonding for the acid derivative. Strong intermolecular interactions are apparently absent in the tributylamine salt which is most likely due to steric hindrance of the bulky amine substituents. Whereas some authors have attributed similar behavior in ethylene and styrene ionomers to changes in the glass transition temperature, for the propylene ionomers T_g was invariant.

The elastic properties of these polymers follow a similar trend as does the viscosity. That is, the sodium salt exhibits a higher die swell than does the acid which is greater than polypropylene. The die swell data for the zinc salt are anomalous, being higher than for the sodium salt and decreasing with increasing shear rate.

The introduction of the acid and ionic species into polypropylene at a level of 1.3 mol % did not appreciably affect the extent of the polymer crystallinity. In addition, the presence of intermolecular associations resulted in improved tensile properties—that is, increased modulus and strength, though the ultimate elongations declined.

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