

## Viscoelastic Study of Ionomers

THOMAS CARL WARD and ARTHUR V. TOBOLSKY,  
*Frick Chemical Laboratory, Princeton University,  
Princeton, New Jersey*

### Synopsis

Stress-relaxation curves were obtained for ionomers containing different cations, per cents of ionization, and thermal treatments. Differences in the rheological behavior were found to depend more on the ionization level than on the ion. A recently proposed model for ionomers is discussed and found to be consistent with these results. In terms of this model the degree of ionization in the polymer acts as a regulator for the growth of small oriented lamellar (crystalline) regions. In the most general terms, the mechanical behavior and strength of ionomers appears dominated by the existence of "hard" regions interspersed among "soft" regions. In the polymers studied here there was some slight crystallinity; however, similar effects and explanations are probably suitable for amorphous "ionomers." Toughness was also found in some completely amorphous carboxyl-containing copolymers without added ionic salts. The same explanation of "hard" regions interspersed among soft regions is also valid here. The "blocky" nature of the copolymerization may play a role in setting up this type of structure.

### Introduction

Recently copolymers based on  $\alpha$ -olefins and carboxylic acids have been combined with groups I and II cations to produce very interesting new materials.<sup>1-3</sup> These have been named ionomers. Interest has largely been in the 1 to 10 mole-% monobasic acid copolymers, and the present discussion will be similarly limited.

As is well known,  $\alpha$ -olefin polymers ordinarily derive their superior strength properties from crystallinity. Copolymerization usually disrupts the chain ordering in these materials which leads to large reductions in this crystallinity. However, in the case of ionomers, excellent strength properties comparable to those of the poly( $\alpha$ -olefins) are maintained even though in many ways the product seems to be an amorphous material. The most obvious example of this is provided by the clear optical properties of the ionomers which indicate that much of the crystallinity of the type that is found in polyethylene has vanished.

The ionomers are clear tough thermoplastics. At 140°C. they readily flow, illustrating the absence of covalent crosslinks. When compared to the acid copolymers from which they are made, the ionomers have remarkably high rigidity, yield points, and ultimate tensile strengths.<sup>1-3</sup> In this respect they resemble the metallocarboxylate rubbery copolymers which

have been known for many years.<sup>4</sup> The literature reveals that there has been considerable debate as to the role of the ions in the physical properties and viscoelastic behavior of these salt vulcanized rubbers.<sup>5-10</sup>

Since various concentrations of acid, degrees of ionization, and types of ions can be incorporated into the new ionomers, they are suggested as valuable materials for elucidating the role of ions in polymers.

### Materials

The ionomers used in this study were kindly donated by the Plastics Division of Union Carbide Corporation. Basic characterizations of the polymers were supplied to this study by Union Carbide and these are listed in Table I. Two relatively high levels of carboxyl content were chosen to

TABLE I  
Basic Properties of the Samples Studied

Sam- ple	Mole- % COOH (total)	Ion, and % ionized	Melt index	Tensile strength, psi	Elonga- tion, % elongation	Secant modulus, psi, 1%	H <sub>2</sub> O absorbed
A	8	0	5.2	2,100	490	6,000	0.063
B	8	Na <sup>+</sup> , 47%	0.66	4,900	320	57,700	4.445
C	6.5	Na <sup>+</sup> , 31%	2.6	4,550	420	42,300	0.168
D	8	Ca <sup>++</sup> 47%	0.15	5,070	233	46,500	0.084
E	6.5	Ca <sup>++</sup> 30.7%	1.3	3,840	380	31,830	0.046

keep crystallinity to a minimum. For completeness each of these was combined with a monovalent and a divalent cation. The per cents of acid and ionization were accurately determined by the supplier from the infrared spectra of pressed films. An internal standard was utilized in the measurements.

From the basic properties these samples are seen to be typical examples of ionomers. For example, comparison of samples A and B shows the great increase in modulus, the increase in tensile strength, and the decrease in elongation and melt viscosity that accompany the introduction of the ion.

Some of the samples are seen to be hygroscopic so they were stored in desiccators until their use. Specimens were prepared for study by pressing rectangular strips at 15°C. and 30,000 psi for 5 min. These samples were then rapidly cooled to room temperature while still under pressure. If experiments were than immediately conducted on a specimen, it was classified as quick-quenched. For some investigations the ionomers were annealed. This was accomplished by placing quick-quenched samples in a vacuum oven for two days at 65°C.

### Experimental

Modulus-temperature studies were conducted using a Gehman apparatus<sup>11</sup> to obtain 10-sec. shear moduli below 10<sup>9</sup> dyne/cm.<sup>2</sup>. Above this

value the Clash-Berg procedure<sup>12</sup> was employed. A silicon oil bath of appropriate viscosity maintained the temperature. Heating rates were no faster than 1°C./min.

For stress-relaxation measurements on samples with moduli less than  $10^9$  dyne/cm.<sup>2</sup>, a thermostated ( $\pm 0.1^\circ\text{C}.$ ) relaxation balance was used.<sup>13</sup> Since low extension ratios,  $\alpha$ , were investigated in this study, the balance was carefully calibrated to account for small deflections in the sample supporting apparatus during an experiment. The initial sample length and the test length at some time were measured accurately with a cathetometer; corrections to the test length at all other times were applied using the calibration.

Where the modulus of a sample ranged above  $10^9$  dyne/cm.<sup>2</sup>, measurements were made with a Clash-Berg torsion tester fitted to a Tenney environmental chamber. The shear creep compliance,  $J_c(t)$ , obtained from this data was converted to the stress-relaxation modulus  $E_r(t)$  by the equation<sup>14</sup>

$$E_r(t) = (\sin m\pi/m\pi)[3/J_c(t)] \quad (1)$$

where  $m$  is the slope of a double logarithmic plot of compliance versus time. Considering that the value of  $m$  was generally less than 0.3, this equation should hold quite well.

### Preliminary Experiments

Stress-strain experiments were conducted and showed that the stress was proportional to  $(\alpha - 1/\alpha^2)$  up to about 4% elongation. Also, over small ranges of extensions at as much as 10% elongation this relationship was correct. Therefore, moduli were calculated from

$$E_r(t) = 3f(t)/A_0(\alpha - 1/\alpha^2) \quad (2)$$

where  $f(t)/A_0$  is the stress at time  $t$  based on the original cross-sectional area of the polymer. Except where noted, all tensile stress-relaxation experiments were conducted at approximately 1% elongation.

The effects of annealing and the absorption of water on the stress relaxation of ionomers are clearly illustrated in Figure 1. At  $50^\circ\text{C}.$  differences in thermal treatment are seen to affect the modulus considerably but not the rate of stress relaxation. At other temperatures the curves having different thermal histories are not exactly parallel, but the same trends are seen. On the other hand, absorption of water by the ionomers results in a low initial modulus; however, the stress decay rate is slower.

Much less difference in viscoelastic behavior was noticed between quick-quenched and annealed samples of polymer A, the acid copolymer. Both the shape of the stress-decay curves and the modulus were essentially unaffected by thermal history.

The extension ratio  $\alpha$  was investigated as a variable. Identical curves from stress-relaxation experiments were obtained at 1% extension and 10% extension. At 10% elongation the calculated modulus was slightly lower

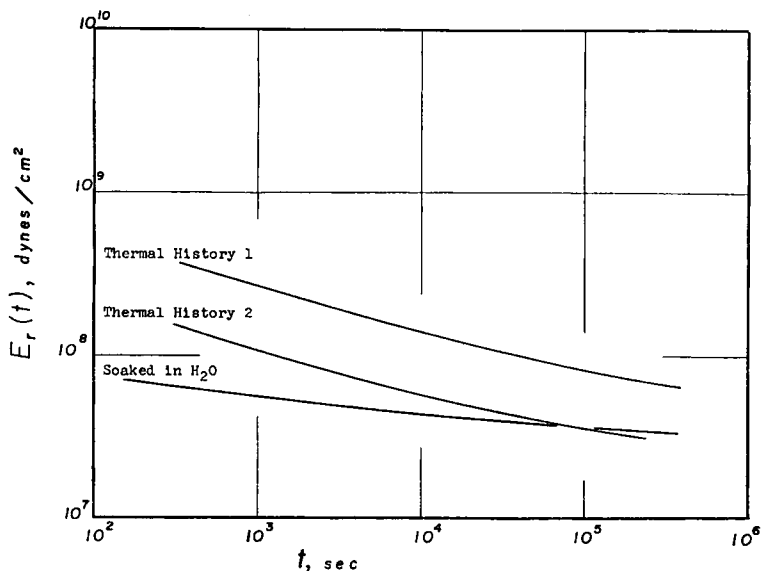


Fig. 1. Effects of thermal history and water on stress relaxation of ionomers. All curves are sample B at 50°C.

than that at 1%. This is to be expected in view of the nonlinearity of the stress-strain curve.

Choosing sample B as of greatest interest, x-ray photographs were taken of quick-quenched and annealed samples. A diffuse halo with only suggestions of sharpness was observed for the quick-quenched sample. Somewhat more molecular ordering was indicated in the annealed case, but it is small in comparison with a true semicrystalline polymer.

### Results and Discussion

Modulus-temperature curves for the ionomer samples were very similar to those previously reported.<sup>1,3</sup> In Figure 2 the data for polymer B are presented. The breadth of the curves is suggestive of a semicrystalline polymer, and the shape and position of the curves resemble those of low density polyethylene.<sup>1</sup>

Stress-relaxation data were obtained over a wide range of temperatures for quick-quenched samples of polymers A, B, and E. Figures 3-5 show the results. In Figure 6 are presented the stress-relaxation curves for annealed polymer B.

The shape of the curves is not indicative of a truly amorphous polymer.<sup>13</sup> The absence of a sharp transition region is very noticeable. Thus, the validity of applying the time-temperature superposition principle to this data was questioned. It is well known that semicrystalline polymers require shifts along the log-modulus axis as well as shifts along the log-time axis in order to produce satisfactory master curves.<sup>13</sup> It was discovered

that reasonably good superposition of the individual stress-relaxation curves could be obtained for all the samples studied; however, the shift factors,  $a_T$  of<sup>13</sup>

$$E_{r,T_{ref}}(t/a_T) = E_{r,T(t)} \quad (3)$$

did not fit a modified WLF equation<sup>15</sup>

$$\log a_T = -16.14(T - T_i)/56 + (T - T_i) \quad (4)$$

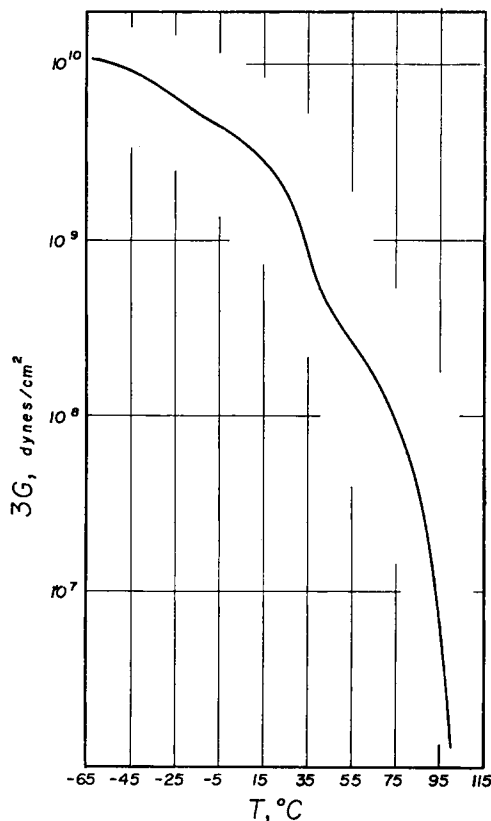


Fig. 2. Typical modulus-temperature behavior for sodium-linked ionomer.

In eq. (4),  $T_i$  is a characteristic temperature, and was chosen as the temperature at which the 10-sec. modulus was  $10^9$  dyne/cm.<sup>2</sup>. Usually, for amorphous polymers,  $T_i$  is relatively close to  $T_g$ .

There is no reason to expect time-temperature superposition to be applicable in the ionomers. With the ionic bonds and some quantity of molecular orientation present, relaxation processes are probably not confined to one mechanism. Thus, it was decided not to place too much interpretation in the master curves for ionomers.

Several general tendencies become apparent from Figures 3-6. At a given temperature the increase in modulus due to incorporation of the ion is clear. Also obvious is that annealing is necessary for full development of the effect of the ion on the modulus. Above  $10^9$  dyne/cm.<sup>2</sup> the ionized samples have very similar relaxation behavior while the acid copolymer exhibits more of a transition region. The characteristic temperature is seen to vary as  $T_{iA} < T_{iE} < T_{iB} < (T_{iB})_{\text{annealed}}$ . In general, the inclusion of annealing and an increase in the percentage of ions result in a greater modulus

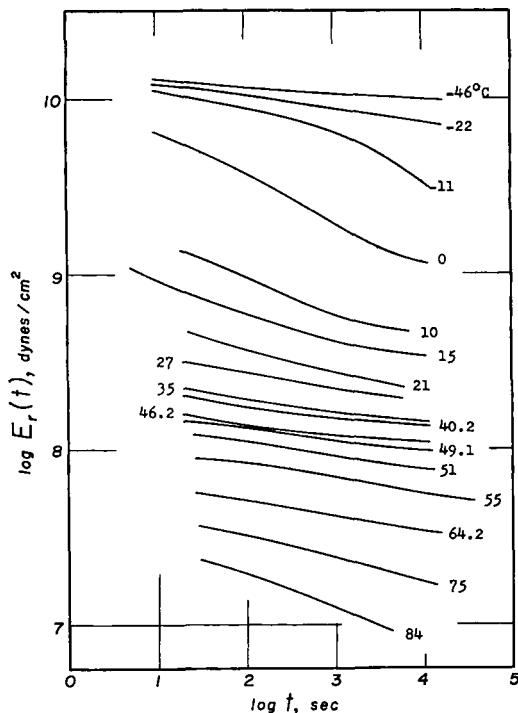


Fig. 3. Stress relaxation of the quick-quenched acid copolymer, sample A. Temperatures are in °C.

at a given temperature and time (over the range of  $10^4$  sec. of these experiments). More interesting than the moduli, however, are the shapes of the stress-relaxation curves.

Inspection of Figures 3-5 reveals that the major differences in viscoelastic behavior of the various samples are well illustrated (considering the time scale of the experiments) at 50°C. At temperatures around this, exactly the same relationships obtain between the slopes of the stress-relaxation curves. All of the quick-quenched samples are well above their  $T_i$ 's at this temperature. Consequently this appears to be a good temperature at which to illustrate the relaxation behavior of ionomers independently of time-temperature superposition.

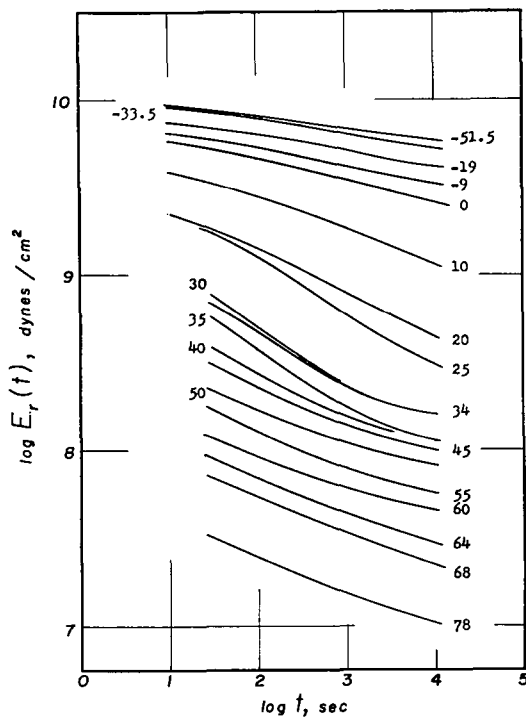


Fig. 4. Stress relaxation of the quick-quenched sodium ionomer, sample B. Temperatures are in  $^{\circ}\text{C}$ .

Figure 7 shows the stress-relaxation data for all the quick-quenched samples at  $50^{\circ}\text{C}$ . It is seen that the per cent of ionization, not the ion involved, is the important factor in the stress-relaxation rate. Thus, calcium and sodium ionomers of the same percentage ionization have stress-relaxation curves that are essentially parallel. The exact value of the modulus is not nearly as important in Figure 7 as the slopes of the curves. Sample D is probably shifted upward from sample B because it alone had a slight amount of excess salt incorporated into it in preparation in order to achieve the desired level of ionization. Also, differences in thermal histories of the quick-quenched samples caused small shifts in modulus values but not in the rates of stress relaxation.

Figure 7 predicts that even though incorporation of a salt into the acid copolymer produces an initially high modulus, the rate of stress relaxation of the resulting sample will be faster and eventually the modulus might drop below that of the parent polymer. The similarity between this observation and the results from previous studies on metalcarboxylate elastomers is notable. Earlier workers have incorporated salts into carboxylated rubbers to produce higher strength properties. Always accompanying these, however, were rapid increases in stress relaxation and creep.<sup>4-10</sup>

That the cation would have little effect on the ionomer rheology may seem surprising. However, in the original work on ionomers it was noticed that the ultimate properties and the modulus are much more dependent on the acid content and the per cent of ionization than on the cation that is present.<sup>1</sup> Other workers have come to similar conclusions.<sup>17</sup> Preceding researches have noticed differences in flow behavior of carboxylated rubbers containing different salts although these are small.<sup>5,8</sup> Especially puzzling has been the parallelism in response when either monovalent or divalent ions were utilized.<sup>1</sup>

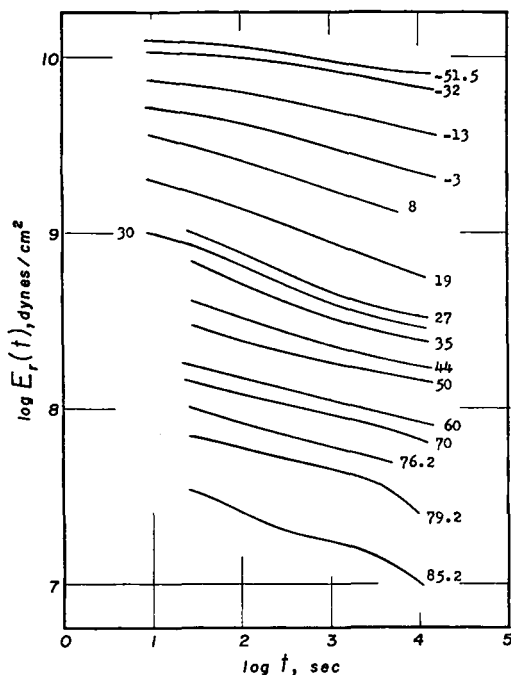


Fig. 5. Stress-relaxation curves for quick-quenched calcium ionomer, sample E. Temperatures are in °C.

In more recent work, Nielsen and Fitzgerald<sup>16</sup> find that stress-relaxation master curves for sodium and barium salts of a styrene-methacrylic acid copolymer (92.5-7.5 mole-%) are identical in shape but are shifted horizontally and vertically from one another. The divalent cation produced the higher modulus and delayed stress decay. Unfortunately, the degree of conversion of carboxyl to carboxylate is not quoted in this work.

Halpin and Bueche<sup>10</sup> reviewed some of the conflicting ideas concerning metalcarboxylate elastomers in addition to presenting their own viscoelastic data on the problem. These authors conclude that the properties of these materials are due to the unique response of sparsely crosslinked networks and are independent of the nature of the crosslink bonding.



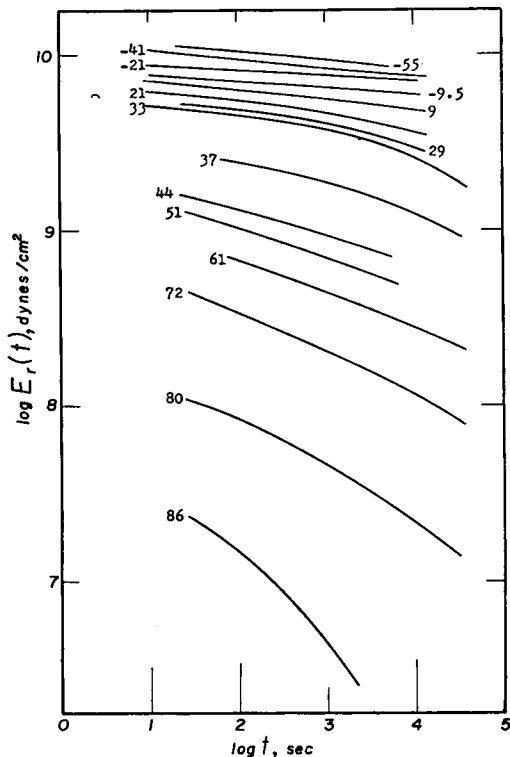


Fig. 6. Stress-relaxation curves for an annealed sodium ionomer, sample B. Temperatures are in  $^{\circ}\text{C}$ .

It appears that for ionomers none of the relaxation mechanisms such as bond exchange,<sup>5,6</sup> simple molecular flow, or sparse network response<sup>10</sup> can fully account for the observed phenomena in the time-temperature regions investigated. The thermal history and per cent of ionization dependence and the cation independence of stress-decay rates as well as the relative modulus values must be explained by a successful model.

Thoughts of crystallinity linger in the discussion of these ionomers. Rees has published the results of x-ray, infrared, electron microscope, and DTA studies on ionomers of the type used in this work.<sup>1</sup> Crystallinity was found to be submicroscopic and low enough in degree so that accurate x-ray measurements could not be made. However, on annealing, infrared and x-ray examination showed that there are definite increases in the parameters associated with crystallinity in, for example, polyethylene. Rees feels that a high nucleation rate produces microcrystalline order in the ionomer, but he maintains that these regions contribute negligibly to the mechanical properties in comparison to the ionic interactions.

A model for ionomers has been proposed by Bonotto and Bonner of Union Carbide Corporation which seems consistent with the present work and the

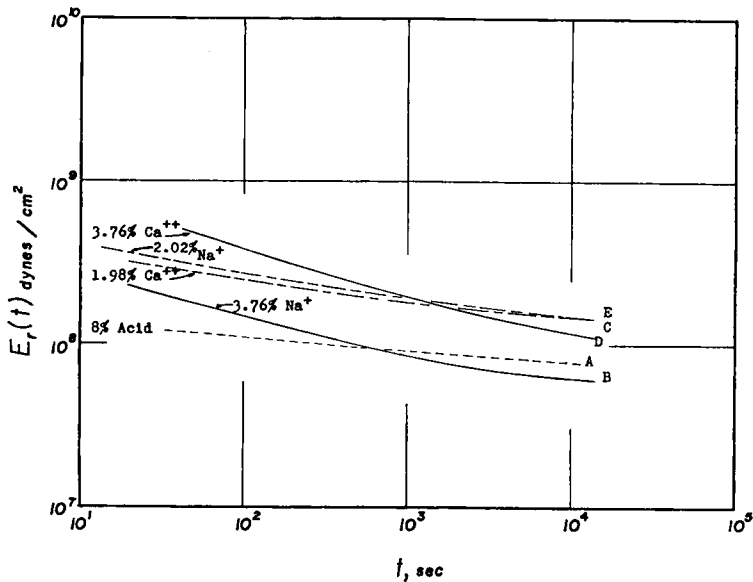


Fig. 7. Summary of viscoelastic response of quick-quenched samples, all at 50°C.

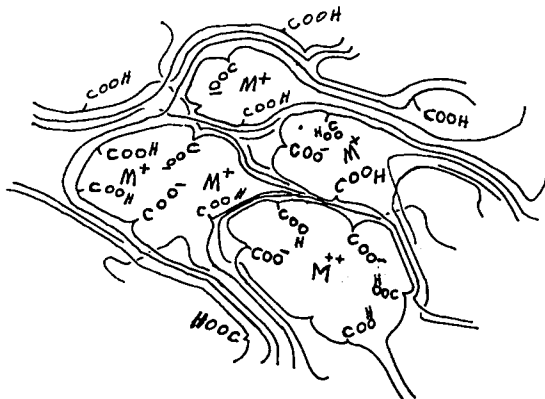


Fig. 8. A model for ionomer structure.

previous x-ray, infrared, etc., data.<sup>17</sup> A rough drawing of what a section of this model looks like is shown in Figure 8. According to this view there are submicroscopic regions of the polymer in which lamellar domains are interspersed with "ionic pockets." In these ionic regions there may be several intermolecular associations involving carboxyl, carbonyl, and carboxylate groups and the cations. The number of regions of ionic association is determined primarily by the per cent of ionization and the original acid content of the copolymer. Growth of the surrounding lamellae is governed by the size and number of "ionic pockets." As the concentration and size of these regions increases, the ability of chains immediately around

them to associate is decreased. The pockets are probably "soft" compared with the crystallites.

It is helpful to consider the "pockets" as multifunctional ionic "filler" units reinforcing the dispersed lamellae. In these terms it is easy to see why the strength properties of the polymer are improved by the ionization. Also, the type of cation employed in the "vulcanization" is seen to be much less important than in models where ionic crosslinks depending strictly on the valence of the ion are postulated. The latter proposals have never adequately explained the effectiveness of monovalent cations in carboxylic rubbers.

The observed rheological behavior of the ionomers is easily explained by this model. It appears that the microcrystalline regions are dominating the stress-relaxation response as presented in Figures 3-7. The results are similar to those for plasticized poly(vinyl chloride) in which microcrystalline regions were found to be important.<sup>18</sup> Difference in the present polymer and plasticized poly(vinyl chloride) is in the strength-contributing nature of the "pocket" regions of ionomers. The increases in stress-relaxation rate accompanying increases in degree of ionization reflect the effect of the number of ionic nucleating sites on the microcrystallinity. Comparison should be made with the previously studied ethylene-vinyl acetate copolymers.<sup>19</sup>

To summarize the above ideas, the relatively cation independent ionic domains that form on cooling melted ionomers control the degree of crystallite growth in the other regions of the polymer largely by the number of carboxyls that are ionized. Above  $T_i$ , these strength contributing "ionic pockets" initially produce relatively high modulus values in the ionomers; but at longer times and higher temperatures the reduction in microcrystallinity overtakes their reinforcing effect and stress rapidly relaxes. Annealing the samples probably produces better "alignment" in the ionic as well as lamellar regions and results in a higher modulus. Annealing in the lamellar regions probably levels out at amounts dictated by the per cent of ionization. Thus, the properties of ionomers are controlled by the ionic bonds but only in an indirect manner.

The effect of water on the ionomer's flow properties fits into this picture nicely. The water presumably migrates to the ionic areas and lowers the effectiveness of interchain bonding. Therefore the initial modulus is lower than with dry samples, but the stress relaxation is correspondingly slower due to less limitations on lamellar growth demanded by the water-containing "ionic pockets."

### A More General Explanation

In more general terms, the mechanical behavior and strength of ionomers appears dominated by the existence of hard "regions" interspersed among "soft" regions. In the polymers studied here there was some slight crystallinity; however, similar effects and explanations are probably suitable for amorphous "ionomers."

The "blocky" nature of the copolymerization undoubtedly plays a role in setting up this kind of structure.

Toughness was also found in some completely amorphous carboxyl-containing copolymers without added ionic salts, as discussed below. The same explanation of "hard" regions interspersed among "soft" regions is also valid here.

In previous experiments in this laboratory, we measured the modulus-temperature curves of some carboxyl-containing copolymers. An octyl acrylate-methacrylic acid copolymer (50:50) gave an extremely shallow modulus-temperature curve, was hazy if not opaque, and showed very high strength, all characteristic of some highly heterogeneous copolymers; almost a block copolymer. The copolymers of butadiene-acrylic acid (90:10) also gave a very shallow modulus-temperature curve. The metalcarboxylate rubbers derived from this latter copolymer may owe some of their strength to the "hard" region "soft" region type of structure.

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### Résumé

Des courbes de relaxation-tension ont été obtenues pour des ionomères contenant différents cations, des pourcentages d'ionisation différents et ayant subi des traitements thermiques divers. Des différences dans le comportement rhéologique ont été trouvées et elles dépendent plus du niveau d'ionisation que de l'ion lui-même. Un modèle récemment proposé pour les ionomères est discuté et est en accord avec ces résultats. Sur la base de ce modèle le degré d'ionisation du polymère agit comme régulateur pour la croissance de petites régions lamellaires (cristallines) orientées. De façon générale, le comportement mécanique et la force des ionomères semblent dominés par l'existence de

régions "dures" réparties au sein de régions "souples." Dans les polymères étudiés, nous avons noté une certaine cristallinité, bien que faible. Toutefois des effets semblables et une explication peuvent être utilisées dans le cas d'ionomères amorphes. On a également trouvé une dureté dans certains copolymères complètement amorphes carboxylés sans addition de sels ioniques. La même explication de régions "dures" réparties au sein de régions "souples" est également valable ici. La nature séquencée de la copolymérisation peut jouer un rôle dans les propriétés de telles matières.

### Zusammenfassung

An Ionomeren mit verschiedenen Kationen, verschiedenem Ionisierungsausmass und verschiedener thermischer Behandlung wurden Spannungs-Relaxations-Kurven gemessen. Die Unterschiede im rheologischen Verhalten hingen, den Ergebnissen zufolge, mehr vom Ionisierungsausmass als von der Art des Ions ab. Ein kürzlich vorgeschlagenes Modell für Ionomere wird diskutiert und ist, wie gefunden wurde, mit diesen Ergebnissen vereinbar. Gemäss diesem Modell wirkt der Ionisierungsgrad im Polymeren regulierend auf das Wachstum der kleinen, orientierten, lamellaren (kristallinen) Bereiche. Ganz allgemein gesehen scheint das mechanische Verhalten und die Festigkeit der Ionomeren von der Existenz "harter," in "weiche" Bereichen gebetteter Regionen beherrscht zu sein. In den hier untersuchten Polymeren trat eine gewisse geringe Kristallinität auf, jedoch treffen ähnliche Einflüsse und Erklärungen wahrscheinlich auch für amorphe "Ionomere" zu. Einige völlig amorphe carboxylhaltige Copolymere ohne ionische Salzzusätze erwiesen sich ebenfalls als zähe. Auch hier gilt die gleiche Erklärung, dass "harte" Bereiche in "weiche" Regionen eingebettet sind. Der blockartige Charakter der Copolymerisation kann für den Aufbau dieses Strukturtyps verantwortlich sein.

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