Effect of Ion Valency on the Bulk Physical Properties of Salts of Ethylene–Acrylic Acid Copolymers

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ABSTRACT: A series of monovalent and divalent salts (Na, K, Li, Ca and Mg) of ethylene–acrylic acid copolymers have shown remarkable similarity in physical properties when the carboxyl groups were converted to equivalent degrees of ionization. Increasing salt conversion results in a modulus plateau with both monovalent and divalent salts, which suggests an optimum configuration of metallic ions and ionized carboxylic acid groups. The mobility of the ions in the polymer melt was demonstrated by blending a highly converted polymer with an unconverted polymer; moduli, tensile strengths and flow properties of the homogeneous blends were the same as those of directly converted materials. Valency in ionic interpolymers should not be considered analogous to functionality in covalent cross-linking. Other factors, such as spacing between ionized sites and the ratio of ionized groups to metal ions, play a dominant role. A structural model summarizing these results is presented. Our findings appear to resolve present conflicts in views regarding the role of mono- and divalent ions in polymers containing carboxylic acid groups.

As various types of polymers with pendant carboxyl groups became available, they were allowed to react with monovalent and divalent ions.[1,2] Some early investigators believed that reaction with divalent ions caused cross-linking analogous to covalent cross-linking because the resulting products were infusible and precipitated out of solutions.[2–6] Monovalent ions, on the other hand, produced thermoplastic, soluble products.[5,6] A few investigators reported that monovalent ions caused significant changes in tensile strength and other physical properties.[7–9] Still other investigators reported that use of divalent ions resulted in thermoplastic products that could be processed at elevated temperatures[8–12] and had considerable creep at room temperature.[13,14] Despite these publications, another group still held the view that divalent ions, such as calcium, caused true cross-linking similar to covalent cross-linking.[13,14]

Salts of ethylene–acrylic acid copolymers showed similar inconsistencies in our work. In this paper the physical properties of monovalent and divalent salts of ethylene–acrylic acid copolymers are described from the point of view of equivalent ionization of the pendant carboxyl groups. This approach appears to give a clearer picture of the role played by the valency of the ion.

Effect of Monovalent and Divalent Ions. A. General Properties and Viscosity. A number of metallic salts of ethylene–acrylic acid copolymers were prepared by milling the appropriate base with the copolymer on a two-roll mill. The degree of neutralization, or per cent conversion of the COOH group to COO^-, was determined by infrared techniques (See Appendix).

Table I shows results of experiments using a copolymer having 14.6% acrylic acid (AA) by weight (6.2 mol) and a melt index of 32 dg min^{-1} (see Appendix for test method). The compositions were designed to have an equivalent degree of neutralization of the carboxyl groups using ions of different valency. In order to ensure that the ion was actually acting toward the polymer in the indicated valence state and not as a "basic salt bond"[8] $[M^{2+}OH^-]^+$, the stoichiometric amounts of base were carefully added and, in addition, the per cent conversion of the carboxyl groups was checked by infrared measurements. Stoichiometric conversions with trivalent ions could not be achieved under the same experimental conditions.

The samples of Table I, as far as can be determined, do contain monovalent and divalent ions, each ion accounting for one or two ionized carboxyl groups on the polymer chain depending on its valence. The similarity of flow properties, modulus and per cent elongation between salts of monovalent and divalent ions is readily apparent.

Table II, showing results from a higher melt index copolymer, basically extends and confirms the data of Table I. Again we note a tendency toward greater interchain attraction as shown by lower flow properties and lower elongation at increasing degrees of neutralization. It is also apparent that using equivalent moles of divalent and monovalent ions result in very similar properties that could not be expected from conventional covalent cross-linking considerations.

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(1) H. P. Brown, *Rubber Chem. Technol.*, **30**, 1347 (1957).
(2) V. A. Miller (Firestone Tire and Rubber), U. S. Patent 2,604,668 (1952).
(3) M. Hagedorn, U. S. Patent 2,045,080 (1936); I. G. Farbenindustrie, British Patent 420,533 (1934).
(4) H. P. Brown (B. F. Goodrich), U. S. Patent 2,724,707 (1955).
(5) H. P. Brown, *Rubber Chem. Technol.*, **36**, No. 4, 931 (1963).
(6) L. E. Nielsen and W. E. Fitzgerald, *Proc. Roy. Soc.* (London), **A282**, 137 (1964).
(7) H. P. Brown and C. F. Gibbs, *Ind. Eng. Chem.*, **47**, 1006 (1955).
(8) B. A. Dolgplosk, *et al.*, *Rubber Chem. Technol.*, **32**, 328 (1959).
(9) B. A. Dolgplosk, V. N. Rakh, and S. B. Petrova, *ibid.*, **32**, 321 (1959).
(10) V. A. Miller (Firestone Tire & Rubber), U. S. Patent 2,849,426 (1958).
(11) R. Rees and D. J. Vaughan, presented at the 149th National Meeting of The American Chemical Society, Division of Polymer Chemistry, Detroit, Mich., April 1965; *Polym. Preprints*, **6**, No. 1, 287 (1965).
(12) W. Cooper, *J. Appl. Polym. Sci.*, **28**, 195 (1958).
(13) J. I. Cunneen, C. G. Moore, and B. R. Shephar, *J. Appl. Polym. Sci.*, **3**, 11 (1960).
(14) J. C. Halpin and F. Bueche, *J. Polym. Sci., Part A*, **3**, 3935 (1965).

TABLE I
METALLIC SALTS OF ETHYLENE–ACRYLIC ACID COPOLYMERS (6.2% MOL OF ACRYLIC ACID)

	Na^+	Ca^{2+}	Mg^{2+}	Na^+	Ca^{2+}	Mg^{2+}
Mol % COOH	6	6	6	6	6	6
Moles of COOH/100 g of resin	0.20	0.20	0.20	0.20	0.20	0.20
Moles of metal ions used/100 g of resin	0.0675	0.0337	0.0337	0.156	0.0675	0.0675
% ionization observed by ir	35	35	35	80	70	70
Melt index, dg min^{-1}	2.0	1.5	2.0	*a*	*a*	0.3[a]
Modulus, 1% extension, psi	50,600	45,200	42,500	37,400	35,600	41,500
Tensile strength (ultimate), psi	5,300	4,500	4,400	5,600	4,350	5,050
% elongation	420	400	400	300	250	370

[a] No flow at 43.25 psi, 190°.

TABLE II
SALTS OF ETHYLENE–ACRYLIC ACID COPOLYMER[a]

	Control starting material	Low conversion					High conversion				
		Monovalent ions			Divalent ions		Monovalent ions			Divalent ions	
		Na	K	Li	Ca	Mg	Na	K	Li	Ca	Mg
% ionized COOH[b]	0	30.0	25.0	28.5	30	37%	66%	63%	67%	63.5%	64%
Melt index (43.25 psi), dg min^{-1} (ASTM-D-1238)	67.0	3.8	4.5	5.2	3.1	2.5	0.3	0.6	0.2	0.1	0.2
Modulus, 1% extension, psi (ASTM-D-638)[c]	7,000	48,600	52,600	48,500	38,700	40,300	39,700	44,800	36,900	40,800	32,200
Tensile strength, psi	2,150	4,000	3,700	3,850	3,700	3,400	4,800	5,000	4,600	4,500	4,500
% elongation (ASTM-D-638)	470	330	410	350	390	330	282	388	250	200	220

[a] 14.8% by weight ethylene–acrylic acid copolymer (6.33 mol %), 67 dg min^{-1} melt index. [b] Determined from infrared spectra. [c] ASTM-D-638 procedure from which secant modulus is calculated 1% strain level.

Since viscosity was thought to be a sensitive index of cross-linking, samples containing different mole ratios of monovalent and divalent ions but with the same degree of ionization were examined by Dr. O. K. Spurr using a piston-driven capillary rheometer.

Figure 1 shows that there is little difference at 190° between the viscosity *vs.* shear rate behavior of monovalent and divalent salts at equivalent degree of neutralization. That is, when the polymer is neutralized in such a way that 1 mol of M^+ or 0.5 mol of M^{2+} are used to achieve the same degree of ionization of the pendant carboxyl groups, the viscosity behavior is the same except at low shear. When the degree of ionization is halved (the 0.5 NA^+ curve) a much larger difference is noted than when different ions were used. It then appears that viscosity at 190° is more sensitive to degree of ionization than to the valency of the ions investigated. These data confirm the melt index measurements.

B. Physical Properties *vs.* Per Cent Conversion. The secant modulus (1% elongation) or stiffness of a polymer is generally considered an indication of the degree of crystallinity in polyolefins. However, in the case of ethylene–acrylic acid copolymer salts, this is not the case. Figure 2 shows that increasing the per cent neutralization of the available carboxylic acid groups results in an increase in modulus. This was not accompanied by an increase in crystallinity. As also suggested by Rees and Vaughan[11] for ethylene–methacrylic acid copolymers, it probably represents an increase in interchain attraction. It is interesting to note that this increase in modulus is directly proportional to the per cent of ionized carboxyl up to about 33% conversion where an apparent maximum in modulus is observed. Figure 2 also shows that a copolymer having greater carboxyl content (18.7% AA) will attain a higher modulus level at equivalent per cent conversion.

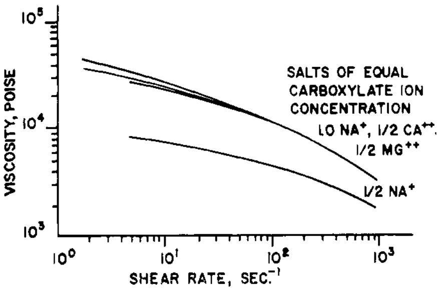

Figure 1. Viscosity *vs.* shear rate at 190° (data from O. K. Spurr). Salts with the same ionization of pendant carboxyl groups induced by monovalent and divalent ions.

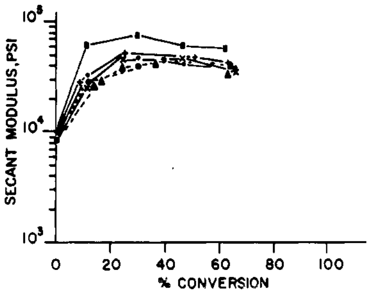

Figure 2. Modulus *vs.* per cent neutralization, ethylene–acrylic acid copolymer salts: (6.33 mol % acrylic acid copolymer) •, Na salts; + K salts; ×, Li salts; ●, Ca salts; ▲, Mg salts; (8.07 mol % acrylic acid copolymer) ■, Na salts.

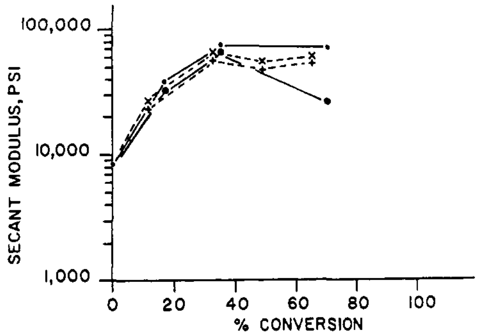

Figure 3. Effect of moisture on ethylene–acrylic acid copolymer salts, modulus *vs.* per cent conversion (6.35 mol % acrylic acid copolymer): •, Na salts dried in a vacuum oven; +, Ca salts dried in a vacuum oven; ●, Na salts after 24 hr water immersion; ×, Ca salts after 24 hr water immersion.

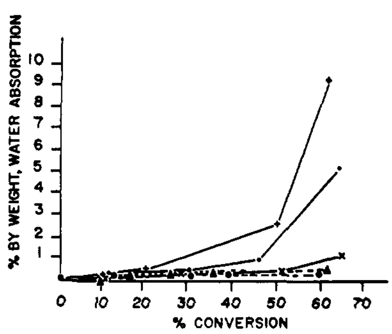

Figure 4. Water absorption *vs.* per cent conversion, per cent weight increase after 24 hr immersion at room temperature (6.33 mol % acrylic acid copolymer): •, Na salts; +, K salts; ×, Li salts; ●, Ca salts; ▲, Mg salts.

The peaking of modulus at about 33% neutralization is interesting. It suggests that the spacing of the carboxyl groups relative to metallic ions is important. This spacing probably determines the most effective configuration for optimum physical properties in a nonoriented state.

Another plausible explanation for the peaking of modulus is that increasing the salt conversion beyond 33% makes the polymer more water sensitive and susceptible to the plasticizing effect of moisture. However, this explanation is probably not valid. Although water immersion for 1 day does exaggerate the loss in modulus at high neutralization of the carboxyls (Figure 3), careful drying under vacuum at 50° for 72 hr did not significantly change the over-all pattern of a limiting modulus value at a given carboxyl content. Use of less water sensitive ions such as calcium and magnesium did not give a higher modulus level at high neutralization (See Figures 4 and 2). A more sensitive test using thermal gravimetric analysis equipment showed that although there was a substantial amount of water in an 80% sodium converted salt, there was very little in a calcium salt. Yet the calcium, the magnesium, and the dried sodium showed roughly the same moduli patterns.

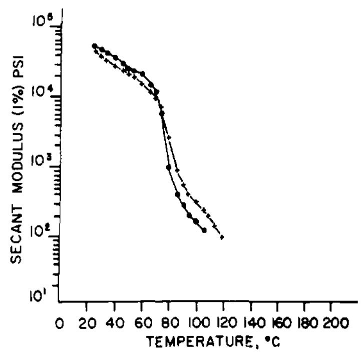

Figure 5. Secant modulus (1% extension, Instron) *vs.* temperature curves, Ca and Na salts at similar % neutralization (6.36 mol % acrylic acid copolymer): ●, Na salt 70% neutralized; +, Ca salt 70% neutralized.

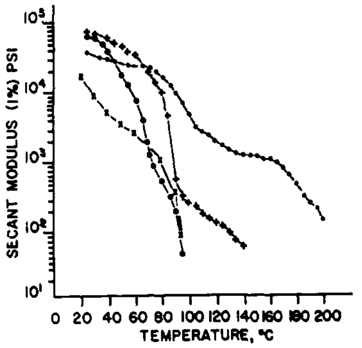

Figure 6. Secant modulus (1% extension Instron) *vs.* temperature curves, ethylene–acrylic acid copolymers sodium salts, effect of increasing per cent neutralization (6.35 mol % acrylic acid copolymer): ×, 0% neutralized; ●, 34.5% neutralized; +, 70% neutralized; •, 100% neutralized.

Modulus–temperature curves should be sensitive to the distances between cross-links or, in this case, to the distances between areas of high interchain attraction. At 30–43% conversions the modulus temperature curves are very similar. At 70% conversion the similarity persists but the polymer containing calcium ions tends to have a slightly higher modulus at elevated temperatures (Figure 5).

Figure 6 shows modulus *vs.* temperature curves for sodium salts having different per cent conversion. These curves may be viewed as the result of two opposing forces. On the one hand, increasing conversion lowers the residual polyolefin crystallinity so that there is a drop in stiffness in the 70–90° range. On the other hand, increasing ionic bonding increases the modulus at room temperature. Increasing conversion also gives rise to a rubbery plateau at elevated temperatures. The attainment of a maximum modulus value at 33% conversion only holds true at lower temperatures; at higher temperatures the greater the per cent conversion, the greater the modulus.

These modulus–temperature curves indicate that these salts behave in different ways at different temperatures. Below 90°, crystallinity and the possibility of hydrogen bonding may cause a maximum in modulus at 33–35% neutralization which is equivalent to a ratio of COOH to $-COO^-$ of 2:1; also there is little difference between divalent and monovalent salts. Between 90° and 150° ionic forces predominate and a few differences have been noted between monovalent and divalent ions (Figure 7). At 150° and above, the melt index data again show little difference between

TABLE III
PROPERTIES OF ETHYLENE–ACRYLIC ACID COPOLYMER SALTS. MONOVALENT IONS

	% ionized[a]	Melt index (43.25 psi), dg min^{-1}	Melt index (43.25 psi), dg min^{-1}	Secant modulus, 1% extension, psi	Tensile strength (ultimate), psi	% elongation at break	Density,[b] g/cc
Control–starting material 14.8% acrylic acid	0	67	2,570	7,000	2,150	470	0.949
Sodium salt	12.0	12.2	256	33,400	3.150	420	0.9568
	30.0	3.9	92	48,600	4,000	330	0.9586
	47.5	1.0	30	42,500	4,600	310	0.9603
	66.0	0.3	7.6	39,700	4,800	280	0.9633
Potassium salt	8.0	16.3	360	29,300	3,050	470	0.9588
	25.0	4.5	110	52,600	3,700	410	0.9626
	51.0	2.7	49	49,500	4,450	370	0.9684
	63.0	0.57	15	44,800	5,000	390	0.9750
Lithium salt	12.0	18.7	442	26,300	3,150	410	0.9516
	28.5	5.2	116	48,900	3,850	350	0.9510
	52.5	1.4	38	48,500	4,100	260	0.9493
	67.5	0.2	5.4	36,900	4,600	250	0.9446

[a] Infrared measurements. [b] Density 23°/4° (ASTM-D-1505-57T).

TABLE IV
PROPERTIES OF ETHYLENE–ACRYLIC COPOLYMER SALTS. DIVALENT IONS

	% ionized[a]	Melt index (43.25 psi), dg min^{-1}	Melt index (43.25 psi), dg min^{-1}	Secant modulus, 1% extension, psi	Tensile strength (ultimate), psi	% elongation at break	Density,[b] g/cc
Control–starting material 14.8% acrylic acid	0	67	2,570	7,000	2,150	470	0.949
Calcium salt	11	16.8	410	25,600	2,850	465	0.9563
	30	3.1	72	38,700	3,650	390	0.9604
	39	0.7	24	45,400	3,750	265	0.9618
	63.5	0.08	2.3	40,800	4,500	200	0.9621
Magnesium salt	12	26	600	24,000	2,400	400	0.9529
	15	19	335	26,900	2,550	390	0.9577
	25[c]	8.5	139	36,400	3.200	385	0.9613
	37.5[c]	2.5	67	40,300	3,400	330	0.9662
	64[c]	0.16	4.3	32,200	4,500	220	

[a] Infrared measurements. [b] Density 23°/4° (ASTM D1505-57T). [c] Contains some unreacted $Mg(OH)_2$.

types of salts as long as the same degree of ionization is maintained (Figure 1).

Tensile strength and per cent elongation data (Tables III and IV) show that increasing per cent conversion increases ultimate tensile strength and decreases per cent elongation; also there is no inflection point at 33% conversion. This indicates that the maximum in the modulus is only noticed in a relaxed state since modulus is measured at 1% elongation. Ultimate tensile strength, on the other hand, reflects properties of an oriented structure at 200–400% elongation. Melt index both at 43.25 and 432.5 psi for these same resins substantiate the over-all similarity of flow properties of different salts as well as a fairly linear relationship between the neutralization of the copolymer and the log of the melt index (Tables III and IV and Figure 7).

C. Mobility of Ions. To determine if the ions could be redistributed in a polymer matrix, a series of experiments were run comparing directly neutralized samples with blends of a 15.3% acrylic acid copolymer (54 dg min^{-1} melt index) with its 70% neutralized form (0.5 dg min^{-1} melt index). It should be noted that the products before blending are very dissimilar in terms of clarity, flow properties and solubility characteristics.

These blends, on the other hand, appeared homogeneous, had very similar tensile strengths, per cent elongation, melt indices and infrared spectra as directly neutralized samples of equivalent conversion.

Although the evidence is circumstantial, it appears that in the process of milling, the sodium ions were redistributed in the same random order obtained in directly neutralized samples. Similar results were obtained with calcium salts, although longer milling time was required to homogenize the blends.

In other words, a sequence of acrylate salt groups in a highly neutralized product does not behave as a normal, permanently located segment of a block co-

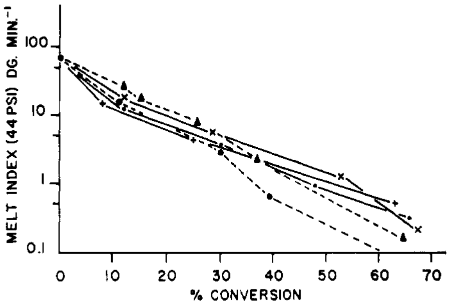

Figure 7. Melt index *vs.* per cent neutralization, ethylene–acrylic acid copolymer salts (6.33 mol % acrylic acid copolymer): •, Na salts; +, K salts; ×, Li salts; ●, Ca salts; ▲, Mg salts.

polymer. Given sufficient heat and shear, ion rich portions act as ion donors for the system.

D. Proposed Model. It has been useful to view ethylene–acrylic acid copolymer salts as polymers containing crystalline areas of very short sequences and amorphous areas of great cohesive strength due to ionic forces.[15] Figure 8 graphically summarizes some of the thoughts expressed in this paper.

Salts of ethylene–acrylic acid copolymers contain residual polyethylene crystallinity, the greater the per cent ionization the shorter the crystalline sequences become. This change can be followed by infrared spectroscopy, differential thermal analysis and X-ray diffraction.[16]

The amorphous regions in the polymer are due to a variety of causes. Some are caused by typical short chain olefin branches, some by pendant carboxyl groups that may be hydrogen bonded,[17] and some by ionized carboxyl groups. The model also shows various possible types of ionic domains, for instance, one or two monovalent ions surrounded by carboxyl groups preferentially drawn from the crystalline areas. Note that a divalent ion in such an ionic pocket might behave like two monovalent ions provided it was surrounded by the same number of ionized carboxyl groups. Up to now, proposed models showed divalent ions as ionically cross-linking polymer molecules while the "cross-linking effects" of monovalent salts were not explained.[1]

The clustering of polar groups, or if one prefers it, the rejection of the polar portions during the growth of the polyolefin crystals, would lead to a kind of blockiness. In order to differentiate it from block copolymers, we call it domain blockiness or morphological blockiness.

This clustering may be why creep studies by Ward and Tobolsky on these materials suggested the presence of a block copolymer.[18] Actually, we believe that the carboxyl groups are fairly randomly distributed along the polymer chain.

Within the ionic domains, the ionic forces, unlike the covalent bonds found in chemical cross-linking, are diffuse, nondirectional and act at greater distances because they decay as the square of the distance. In such a case, the valency of the ions is a convenient way to measure the intensity of the forces involved, but should not be confused with functionality concept of chemical cross-linking.

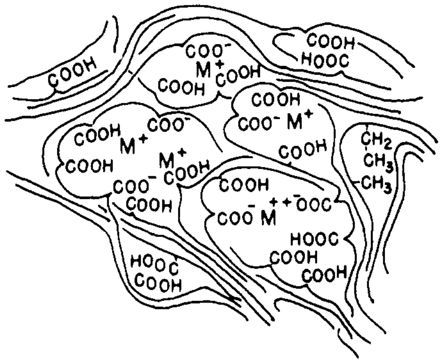

Figure 8. Proposed model for ethylene–acrylic acid copolymer salts.

The degree of ionization on the polymer chain has a fundamental effect on physical properties for two reasons. It represents the intensity of the coulombic forces in the ionic domains, and, at the same time, it gives an indication of the spacing between sites of high interchain attraction. This is analogous to cross-linking density concepts in elastomers and would be the reason for an increasingly higher rubbery plateau at elevated temperatures with increasing salt conversion.

It is reasonable to assume that each ion species will behave differently because of the ratio of charge intensity to ionic radius effect. This q/a effect, where q is in units of one electron and a is the sum of the cation radius and the oxygen anion radius in Ångströms, was noted by Eisenberg in his work with ionic phosphates.[19] Calcium, for instance (q/a = 84), should have a higher cross-linking bonding power than sodium (q/a = 42). Our data show some of this effect (Figure 7) but it is not as pronounced as we expected from Eisenberg's experiments where calcium polyphosphate had a glass transition of 525° compared to 280° for the sodium salt.

Robeson,[20] using a dynamic torsional pendulum, also found that the sodium and the calcium salts of ethylene–acrylic acid copolymers (30% neutralized) had very similar mechanical loss (Q^{-1}), shear modulus (G') and loss modulus curves (G''). It appears that, with products of relatively low salt content, the effect of ion size and charge is subordinate to the effect of ionization of the pendant carboxyl group.

The same figure also shows the possibility of two ions in the same amorphous pocket. This may happen as the per cent conversion is increased and the volume of available crystalline matrix is decreased. "Quadruple ions" showing a somewhat similar structure have been proposed by Erdi and Morawetz[21] in the case of sty-

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(15) S. Bonotto and C. L. Purcell, *Mod. Plastics*, **42**, No. 7, 135 (1965).

(16) G. Foster and W. Niegish, personal communication.

(17) W. J. McKnight, L. W. McKenna, B. E. Read, and R. S. Stein, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967; *Polym. Preprints*, **8**, No. 2, 1, 130 (1967).

(18) T. C. Ward, and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **11**, 2403 (1967).

(19) A. Eisenberg, H. Farb, and L. G. Cool, *J. Polym. Sci., Part A-2*, **4**, 855 (1966).

(20) L. Robeson, personal communication.

(21) N. Z. Erdi and H. Morawetz, *J. Colloid Sci.*, **19**, 708 (1964).

rene–acrylic acid copolymer salts in media of low dielectric constant.

Recent calculations by Potts and Ashcraft indicated that such a sodium carboxylate quadruple ion could have a fairly high bond energy of the order of −30 kcal/mol.[22]

Conclusions

Monovalent and divalent salts of ethylene–acrylic acid copolymers have similar properties at similar degrees of ionization of the pendant carboxyl group.

There is a maximum modulus at room temperature at about 33% conversion for a variety of ions. This effect is not due to the plasticizing action of water. It probably represents an optimum configuration in the relaxed state. This effect is not present at elevated temperatures.

Metallic ions are not permanently associated to any particular carboxyl group; under heat and shear a redistribution can be obtained.

A model of ionomer structure is presented which incorporates both polyolefin and ionic regions. The possibility of domain blockiness may make these products appear less random than they really are.

In such a model the degree of ionization of the pendant carboxyl groups plays a more dominant role than ion valency. This would help to explain the similarity in physical properties between monovalent and divalent salts.

Acknowledgments. The authors are grateful to Dr. O. K. Spurr for rheological measurements, and to Mr. J. V. Atkinson, Mr. R. C. Hazelton and Mrs. J. C. Clinnard for developing the analytical methods.

Appendix

1. **Thermal gravimetric analysis** was performed on a Du Pont 950 thermogravimetric analyzer (5° heating rate, in air, 2-sec time constant).

2. **Sample Preparation.** Samples were prepared from plaques compression molded at 140–160° and conditioned in a desiccator for at least 24 hr. Specially dried samples were conditioned in a vacuum oven for 72 hr at 50° before testing.

3. **Infrared measurements** were obtained with Perkin-Elmer Model 221 instrument. The carboxylate ion content was determined by measuring the absorbance ratio of the 6.4 μ/13.9 μ absorption bands. The absorbance ratio was correlated with a calibration curve established by direct titration procedures. The titration curve was fitted to a quadratic curve by a least-squares procedure (IBM 1620 polynomial regression program) with a standard deviation of ±1% (absolute) within the calibration range. The determination of the un-ionized acid was obtained by measuring the absorbance ratio of 10.65 μ/13.9 μ absorption bonds correlated to a calibration curve obtained by direct titration.

4. **Melt Index Measurement. ASTM 1238 65 T.** The melt index in decigrams per minute is the amount of molten polymer extruded through an orifice of specified length and diameter under prescribed conditions of temperature and pressure. Unless otherwise specified, melt index, refers to the flow (decigrams per minute) of a polyolefin under ASTM procedure A, conditions E. These are 190°, 3.04 kg/cm^2 or 43.25 psi.

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(22) J. E. Potts, E. G. Hendricks, C. Wu, and A. C. Ashcraft, paper presented at the American Chemical Society Middle Atlantic Regional Meeting, Feb 2, 1968.

Ionic Clusters in High-Strength Carboxylic Rubbers

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ABSTRACT: The viscoelastic effect of ionic linkages in carboxylic rubber is indicative of the presence of hard ionic clusters dispersed throughout an amorphous rubbery matrix. The viscoelastic response characteristics of the metallocarboxylate rubbers are similar to those observed with linear segmented elastomers—an enhanced and extended "rubbery plateau" region above a major glass transition temperature. The high strength of the carboxylic rubbers cured with metal oxides is ascribed to the presence of ionic clusters which give rise to a two-phase, reinforced structure.

The unusual physical properties that result from the combination of ions with organic polymers were first noted in 1954.[2a] Copolymers of butadiene containing small amounts of acid groups were cross-linked by metal oxides to give rubbers characterized by a high tensile strength *without* the addition of reinforcing fillers. High strength was observed with both monovalent and divalent ions. The corresponding sulfur vulcanizates were very weak products by comparison. These early results are summarized in Table I.[2]

Subsequent study of metallocarboxylate rubbers over the past decade has generated some debate concerning the source of the unusual properties.[3,4] The two current theories invoke the concept of a relaxation process occurring during the tensile stress test as the source

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(2) (a) B. F. Goodrich, British Patent 707,425 (1954); (b) H. P. Brown, *Rubber Chem. Technol.*, **30**, 1347 (1957).

(3) W. Cooper, *J. Polym. Sci.*, **28**, 195 (1958).

(4) J. C. Halpin and F. Bueche, *ibid., Part A*, **3**, 3935 (1965).