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 $\pm 1\%$ (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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Received June 18, 1968

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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[1] To whom all correspondence should be addressed at E. I. du Pont de Nemours and Co., Experimental Station, Pioneering Research Laboratory, Wilmington, Del. 19898.

[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).

Table I
Influence of Ions on the Bulk Properties of a Carboxylic Copolymer

Polymer and treatment	Tensile strength, psi	Elongation, %
Butadiene–methacrylic acid copolymer (0.12 ephr[a] COOH)	100	1600
Treated with NaOH (0.12 ephr NaOH)	1700	900
Treated with ZnO (0.12 ephr ZnO)	6000	400
Sulfur vulcanizate (gum)	<500	

[a] Equivalent parts per hundred.

of the high strength. They differ in the interpretation of the molecular process responsible for the relaxation.

Cooper postulated that the relaxation occurred *via* a chemical mechanism.[3] The salt cross-links were thought to take part in an interchange reaction thereby relieving localized stress concentrations. Halpin and Bueche assigned the relaxation to a viscoelastic process which they claimed was a natural reflection of the sparse cross-link density in the metal oxide vulcanizates.[4] No special importance was attached to the ionic cross-links in this theory. A concise summary of the evidence leading to these two interpretations is given in ref 4.

The "labile cross-link" hypothesis apparently first suggested by Cooper has also been adopted as the explanation for the higher tensile strengths of hydrocarbon rubbers cross-linked with polysulfide linkages as contrasted with those cross-linked by monosulfide, disulfide, or carbon–carbon links.[5] The nonreinforced polysulfide cross-linked rubbers are, however, much weaker than the metallocarboxylate rubbers.

An alternative explanation for the high (relatively) strengths of polysulfide cures has recently been presented by us.[6] We proposed that the high tensile strength results from an internally relaxed network formed by the thermal lability of the polysulfide cross-links *at the vulcanization temperature* rather than at the temperature of the tensile test.

The recent discovery of ionomers (plastics in which a copolymer of ethylene and an acid is combined with a metal) has promoted a renewed interest in the structural effect of combining ions with organic macromolecules.[7] In a viscoelastic study of ionomers by one of us, it appeared that the mechanical behavior and strength of these transparent plastics was dominated by the existence of ionic clusters interspersed throughout a predominantly amorphous matrix.[8] Some slight crystallinity was also present; this affected the properties somewhat and also made interpretation more complex.

The viscoelastic study of metallocarboxylate rubbers reported here indicates that a similar clustering phenomenon obtains in these completely amorphous systems. The high strength of these rubbers is consequently ascribed to the presence of hard ionic clusters which give rise to a two-phase, reinforced structure. Since the ionic clusters are integrally bonded to the elastomer phase, they function as excellent reinforcing fillers.

The tendency to segregate and form clusters (following neutralization of the acid groups by the metal oxides) is motivated by the highly unfavorable thermodynamic situation of ionic salts essentially dissolved in a hydrocarbon medium. The aggregation of the ionic groups from different chains relieves this energetically unfavorable condition. The long-range coulombic interactions between ions undoubtedly assists in setting up the clusters.

This mechanism of "vulcanization" effects the formation of an internally relaxed "network" structure with the ionic clusters acting as "filler" and "crosslink." The result is a high-strength rubber.

The viscoelastic effect of the presence of ions in polymers is more readily demonstrated in the two-phase carboxylic rubbers than in the three-phase ionomers. The viscoelastic response characteristics are similar to those observed with linear segmented elastomers—an enhanced and extended "rubbery plateau" region above a major glass transition temperature.[9] The characteristics are also similar to very slightly crystalline polymers in which the transition region is broadened on the temperature scale.[10] The classic example is highly plasticized poly(vinyl chloride). The microcrystalline regions present in this system act as quasi-cross-links.

Toughness was also found in some completely amorphous carboxyl-containing polymers *without* added ionic salts. The same explanation of hard clusters dispersed throughout a rubbery matrix is also valid here. However, in this instance the clusters are composed of un-ionized acid groups. The segregation in the ion-free systems reported here is undoubtedly fostered by the heterodisperse or "blocky" nature of the copolymerization. This occurs at high conversions if the reactivity ratios differ appreciably from unity.

It is probable that in any polymeric system containing acid groups in a predominantly hydrocarbon environment, there is a thermodynamic tendency for the acid groups to segregate themselves. The hydrocarbon matrix is simply not the best "solvent" for acid groups. This segregation can occur more easily when the copolymerization results in the formation of blocky sequences of the acid and hydrocarbon components. But even without blockiness the presence of ions in a neutralized system creates such an unfavorable thermodynamic situation that a massive reorganization to form hard ionic clusters is effected.

Experimental Section

The apparatus for the modulus–temperature studies and the stress relaxation measurements has been described elsewhere.[8,9]

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(5) L. Mullins, *et al.*, "The Chemistry and Physics of Rubber-Like Substances," L. Bateman, Ed., MacLaren, London, 1963, Chapter 19, p 730.

(6) A. V. Tobolsky and P. F. Lyons, *J. Polym. Sci., Part A-2*, **6**, 1561 (1968).

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

(9) S. L. Cooper and A. V. Tobolsky, *Text. Res. J.*, **36**, 800 (1966); *Polym. Preprints*, **8**, 52 (1967).

(10) A. V. Tobolsky, "Properties and Structure of Polymers," John Wiley & Son, Inc., New York, N. Y., 1960, p 198.

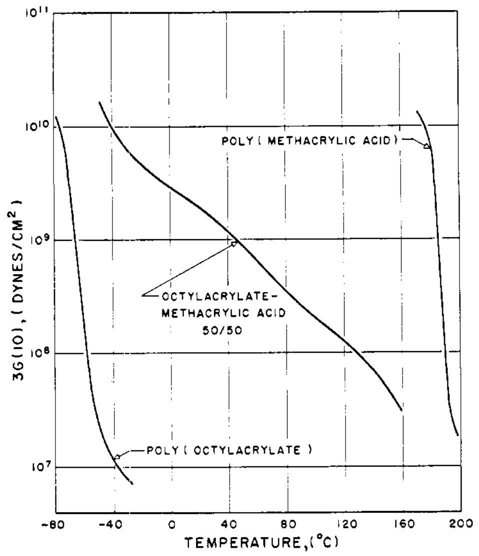

Figure 1. Modulus-temperature curves of an octyl acrylate-methacrylic acid copolymer (50:50) and the respective homopolymers.

TABLE II
CURE RECIPES OF CARBOXYLIC TERPOLYMER

Cure type	Zinc oxide, wt %	Combination (salt/ sulfur)	Sulfur, wt %
Polymer (Hycar 1072)[a]	100	100	100
Stearic acid		1	
Sulfur		1.5	4
Tetramethylthiuram monosulfide		0.4	
Diphenylguanidine			1.75
ZnO	5		
ZnO coated with ZnS		5	
Cure temp, °C	152	152	152
Cure time, min	30	30	40 20[b]

[a] Butadiene–acrylonitrile–methacrylic acid terpolymer, wt % 69/25/6.3. [b] A lower cross-link density sample prepared by us.

The vulcanizates of the butadiene–acrylonitrile–methacrylic acid terpolymer (Hycar 1072) were kindly supplied by Dr. K. Scott of the Goodyear Tire and Rubber Co. Their preparation is described in Table II.

The unvulcanized polymers studied included the Hycar 1072 and a butadiene–acrylonitrile copolymer (Chemigum N 600) as well as a butadiene–methacrylic acid copolymer and an octylacrylate–methacrylic acid copolymer. The polymerization conditions in the latter two acid copolymers were probably instrumental in the formation of the "blocky" sequences.

Results and Discussion

The viscoelastic effect of cluster formation is most easily observed in measurements of modulus *vs.* temperature. Evidence for the presence of ion-free acid clusters set up by a "blocky" copolymerization is given in Figures 1 and 2. The octylacrylate–methacrylic acid copolymer (50:50) gave an extremely diffuse modulus–temperature curve, was hazy if not opaque, and showed very high strength, all characteristic of some highly heterodisperse copolymers, almost a block copolymer. The butadiene–methacrylic acid copolymer (95:5) also gave a very shallow modulus–temperature curve. The enhancement and extension of the "rubbery modulus" region by the acid clusters is readily apparent.

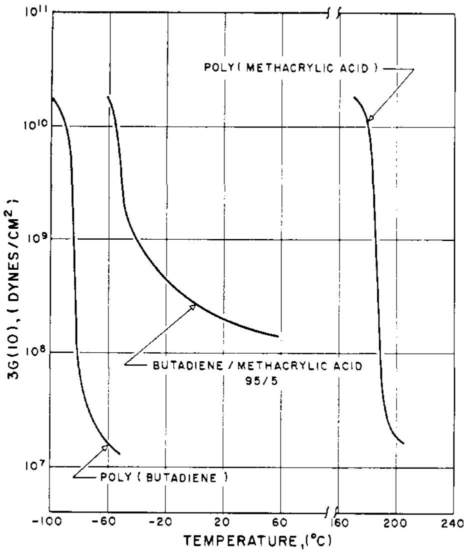

Figure 2. Modulus–temperature curves of a butadiene–methacrylic acid copolymer (95:5) and the respective homopolymers.

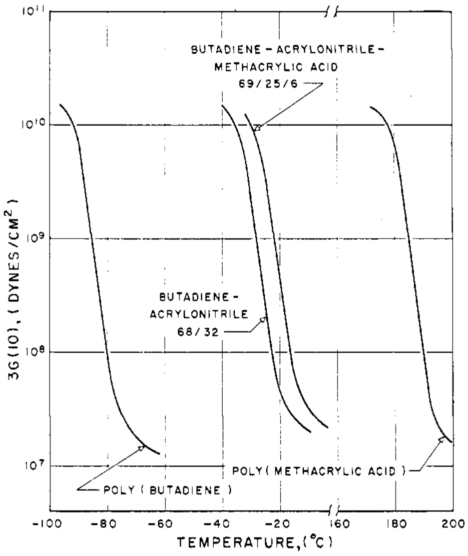

Figure 3. Modulus–temperature curves of a butadiene–acrylonitrile copolymer (68:32), a butadiene-acrylonitrile–methacrylic acid terpolymer (69:25:6), and the butadiene and methacrylic acid homopolymers.

Figure 3 contains the modulus–temperature curves of the raw carboxylic rubber and the analogous butadiene–acrylonitrile copolymer (68:32). The carboxylic rubber is a terpolymer of butadiene, acrylonitrile, and methacrylic acid (69:25:6). The strict parallel character of the two curves over the whole region indicates the absence of a viscoelastic effect due to any interactions of acid groups as, for example, by hydrogen bonding. The slight displacement of the entire carboxyl curve

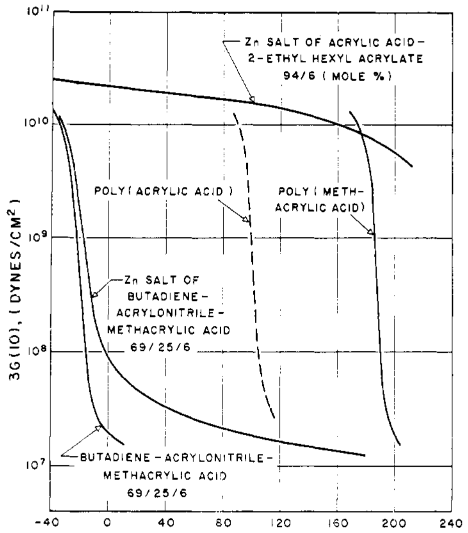

Figure 4. Modulus–temperature curves of poly(acrylic acid), a butadiene–acrylonitrile–methacrylic terpolymer (69:25:6), and their zinc salts.

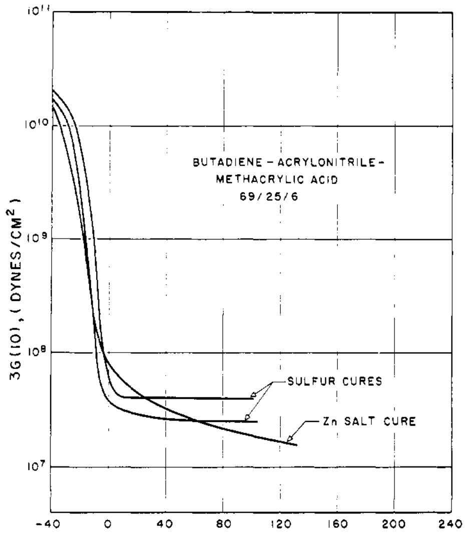

Figure 5. Modulus–temperature curves of the butadiene–acrylonitrile–methacrylic acid terpolymer with sulfur cures and a zinc salt cure.

to a higher temperature is expected from the additive contribution of the acid groups distributed in a random fashion along the chain.

Neutralization of the acid groups with zinc oxide has a profound effect on the modulus–temperature curve of the carboxylic rubber. As shown in Figure 4, the curve is much shallower with the transition region extending over a wider temperature span. The enhanced "rubbery plateau" modulus extends to high temperatures but decreases slowly with increasing temperature without ever reaching a plateau.

Also shown in Figure 4 are the curves for poly(acrylic acid) before and after the formation of the zinc salt. The "after" curve is taken from Nielson's paper and actually represents the zinc salt of an acrylic acid copolymer which is 96% acid.[11]

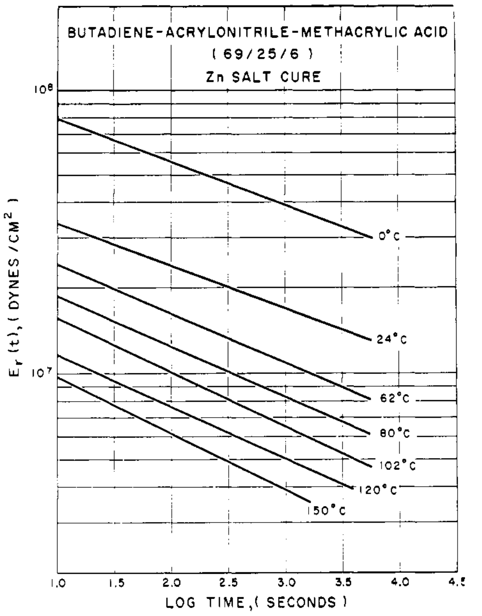

Figure 6. Stress relaxation curves of the butadiene–acrylonitrile–methacrylic acid terpolymer with the zinc salt cure.

The ionic clusters which are dispersed in the "vulcanized" carboxylic rubber and which form a continuous phase in the acrylic acid system appear to maintain their structural integrity up to at least 180°.

The viscoelastic effect of the ionic clusters is strikingly illustrated by comparing the modulus–temperature curve of the zinc salt cure of carboxylic rubber with curves of covalent sulfur-cross-linked networks (Figure 5). The distinct character of the zinc salt vulcanizate, that is ultimately reflected in the unique strength properties, is indeed apparent.

The effect of cross-link density in covalent networks is also shown. Reducing the cross-link density results in a decrease of the modulus at all temperatures; the characteristic shape of the modulus–temperature curve is unchanged, however. It is unreasonable to expect that low cross-link density could give rise to the high rubbery modulus exhibited by the metallocarboxylate rubber.[4]

A combination zinc salt–sulfur cure which contains both ionic clusters and covalent cross-links exhibits the broader transition region and the enhanced rubbery modulus of the zinc salt cure but eventually does reach a plateau around 80°. The plateau modulus is approximately the same as that of the lower cross-link density sulfur cure. The curve has not been drawn in Figure 5 for reasons of clarity.

Stress relaxation curves of the metallocarboxylate rubber are shown in Figure 6. The stress continually decays over the entire temperature region between 0 and 150°. The curves are merely shifted downward with increasing temperature on log–log plots of modulus *vs.* time. A similar effect in stress relaxation has been observed for the high-strength, two-phase thermoplastic elastomers (S/B/S block copolymers).[12]

It is of interest to contrast the actual stress relaxation

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(11) L. E. Nielson and W. E. Fitzgerald, *Proc. Roy. Soc.* (London), **A282**, 137 (1964).

(12) C. W. Childers and G. Kraus, *Rubber Chem. Technol.*, **40**, 1183 (1967).

data of the metallocarboxylate rubber with the data that would result from systems corresponding to the two current theories.[3,4] Corresponding plots of covalently cross-linked rubbers (even with low network densities) would show decreasing rate and amplitude of stress relaxation with increasing temperature.[13] Such curves are convex to the time axis with a plateau effect. The curves would approach a horizontal line with increasing temperature because of the decrease in the entanglement relaxation time. On the other hand, the chemical exchange mechanism would result in increasing concavity of the curves toward the time axis with increasing temperature due to chemical flow. It is significant that the high permanent set expected from this mechanism has not been observed.[4]

Paralleling Childers' observation concerning the stress relaxation of the S/B/S system,[12] it is perhaps surprising that the stress relaxation data exhibit no plateau region corresponding to a pseudoequilibrium relaxation modulus of the butadiene–acrylonitrile network joined by ionic clusters. The observed behavior suggests that relaxations *involving* the ionic clusters are occurring. The possibilities suggested in the S/B/S system might also obtain in the metallocarboxylate rubber. These include motions of the ionic clusters as a whole, detachment of individual groups from such clusters, and restricted mobility of butadiene–acrylonitrile.[12,14] While the exact mechanism of relaxation remains an open question, restricted mobility of the entanglement network appears to be the most reasonable interpretation at the present time.

It is of interest to illustrate the magnitude of the stress relaxation in the two-phase salt cure by comparing it with the sulfur cures and the combination cure. As shown in Figure 7, the sulfur cures give the expected curves—convex to the time axis in log–log plots of modulus *vs.* time.[13] The lower cross-link density sulfur cure does exhibit a slightly higher rate and amplitude of stress relaxation but nowhere near that of the zinc salt cure. The combination (salt–sulfur) cure again reflects the characteristics of the clusters and the covalent network. The stress relaxation initially follows the high rate of the salt cure but then begins to exhibit the convex curvature of a covalent network.

The viscoelastic effect of the hard clusters can be significantly diminished by a selective solvation of the ionic domains. This was accomplished by swelling samples in a *p*-xylene solution containing about 5% glacial acetic acid. The *p*-xylene acted as a carrier for the acid. After deswelling the sample at ambient conditions for 1 day, a 6% concentration of plasticizer remained.

The acid plasticizes the "rubbery plateau" modulus of the zinc salt cure by a factor of 3 while only slightly affecting the major transition temperature. In contrast, an equivalent amount of *p*-xylene swollen into another sample of this cure shifted the transition temperature but had a negligible effect upon the enhanced rubbery modulus.

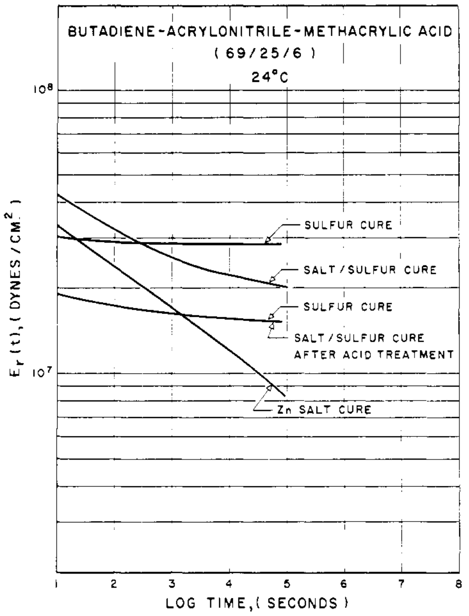

Figure 7. Stress relaxation curves of the butadiene–acrylonitrile–methacrylic acid terpolymer with sulfur cures, a zinc salt cure, and a combination zinc salt–sulfur cure.

Selective solvation of the ionic clusters in the combination (salt–sulfur) cure resulted in a stress relaxation curve exactly the same as the low cross-link density sulfur cure.

Summary and Conclusions

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 motivation to form clusters presumably arises from the highly unfavorable thermodynamic situation of ionic salts essentially dissolved in a hydrocarbon medium. The aggregation of the ionic groups into clusters relieves this energetically unfavorable condition. The long-range coulombic interaction between ions undoubtedly assists in setting up the clusters.

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 vulcanization results in the formation of an internally relaxed network structure with the ionic clusters acting as a reinforcing "filler" and quasi-cross-link.

Toughness due to clustering can also occur in carboxyl-containing polymers in the absence of ionic salts. The clusters in this instance are composed of un-ionized acid groups. The segregation is fostered by the "blocky" nature of the copolymerization in these systems.

(13) R. Chasset and P. Thirion, "Physics of Non-Crystalline Solids," J. A. Prins, Ed., North Holland, Publishing Co., Amsterdam, 1965, p 345.

(14) R. Zelinski and C. W. Childers, *Rubber Chem. Technol.*, **41**, 161 (1968).