position. The effect of molecular oxygen is also being studied. These reaction solutions absorb oxygen readily at 42°. A full report of these results and their implications for the mechanism of the cleavage of poly(vinyl alcohol) will be presented shortly.

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Domain Size in Ionomers

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Metal salts of carboxylic acid substituted hydrocarbon polymers (called ionomers) show considerably higher stiffness and tensile strength values than their free acid counterparts. This fact is attributed to aggregation of the ionizable groups into clusters, similar to the formation of micelles of metal salts of low molecular weight carboxylic and sulfonic acids in hydrocarbon solution.[1-3]

The size of the clusters in still in dispute, however. Some authors suggest the presence of a separate polar phase dispersed as domains of over 10 nm in size[4,5] with the clusters located in the domains; others state that the aggregation is nothing but dimerization of carboxylic groups.[6]

We take the view that the ionomers contain polar domains of a limited size, being identical with the clusters mentioned. This view is based on the following facts. (1) X-Ray diffractograms of metal salts of ethylene–methacrylic acids show a specific, rather broad peak[4,5] at about 4°, 2 ϑ, besides the ordinary ones due to crystalline polyethylene. Melting (of the crystalline polyethylene) does not cause this peak to disappear but soaking the material in water does. (2) Since alkali and alkaline-earth metal ions require a 6 coordination of oxygen (or other negatively charged atoms) electric neutrality requires most oxygens to be attached to more than one metal ion. This should lead to polar clusters of appreciable size. On the other hand, space requirements of the pendant polymer chains as well as the entropy of dilution associated with the breaking up of the clusters tend to reduce the size of the latter.

The 4° peak can be attributed to the clusters being areas of higher electron density than their surroundings. Uptake of water reduces the electron density of the clusters, causing disappearance of the peak.

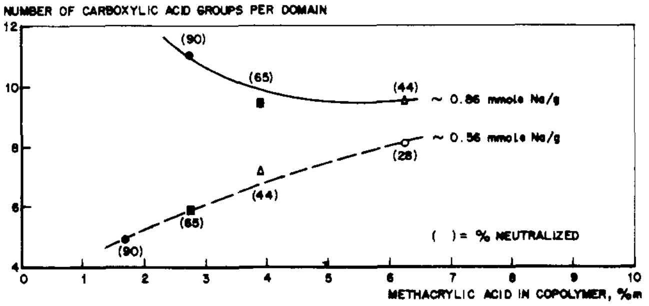

Figure 1. Size of polar domains in ethylene–methacrylic acid copolymers partially neutralized with sodium hydroxide.[4]

The idea of polar clusters being located in domains of at least 10 nm in size[4,5] is based on the general knowledge that in small crystals a repetition of at least five lattice planes is required for a well observable X-ray diffraction, the 4°, 2 ϑ, being related to a repeat distance of about 2.1 nm. However, the 4° peak might as well be due to a most frequently occurring distance between nearest-neighbor clusters, similar to the diffuse diffraction peaks observed with liquids. In accordance with this we may assume the domains to be located in the centers of spheres that are loosely and randomly packed, the packing density being roughly 55%. In this model, each cluster is, on an average, associated with a volume of d^3, d being the distance between nearest neighbors as determined from the peak at about 4°.

We can now calculate the number of carboxylic groups per cluster. If m is the equivalent weight per carboxylic group, the number of carboxylic groups per cluster is Nd^3/m, on the assumption that the density of the ionomer is 1 kg/l., while N is Avogadro's number.

Using the data of Wilson, Longworth, and Vaughan,[4] we have calculated the number of carboxylic groups per cluster for a series of ethylene–methacrylic acid copolymers and plotted these numbers *vs.* acid content in Figure 1.

In a theoretical treatment of the subject, Eisenberg[3] demonstrated that the number of carboxylic groups per cluster cannot be much higher than we have found here. Since the volumes associated with the clusters of the size calculated fill space completely, we can assume the clusters to be identical with the polar domains of the material. If, on the other hand, the clusters had been located in much larger domains, the former would have had to be of a much larger size, which is to be discarded according to Eisenberg.

The figure shows that at a high degree of neutralization the domain size strongly increases with acid content, but less so at a lower degree of neutralization. The change in domain size with acid content is small at constant content of ions.

This indicates that the functionality of the ionic crosslink depends both on carboxyl content and on degree of neutralization.

Since the position of the 4°, 2 ϑ peak is hardly dependent on temperature, the domain size is not either.

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(1) C. Singleterry, *J. Amer. Oil Chem. Soc.*, 32, 446 (1955).
(2) S. Bonotto and E. F. Bonner, *Macromolecules*, 1, 510 (1968).
(3) A. Eisenberg, *Macromolecules*, 3, 147 (1970).
(4) F. C. Wilson, R. Longworth, and D. J. Vaughan, *Polym. Prepr.*, 9, 505, 525 (1968).
(5) B. W. Delf and W. J. Macknight, *Macromolecules*, 2, 309 (1969).
(6) E. P. Otocka and T. K. Kwei, *Macromolecules*, 1, 401 (1968).