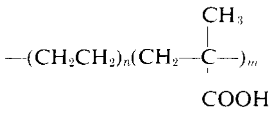
Communication to the Editor

Low Angle X-Ray Scattering from Ethylene–Methacrylic Acid Copolymers and Their Salts

A considerable body of literature exists concerning the structure and properties of ethylene–methacrylic (or acrylic) acid copolymers and their salts. Of the many experimental techniques which have been employed may be cited infrared spectroscopy,[1] X ray diffraction,[2] electron microscopy,[2] dynamic mechanical,[2-4] and dielectric[2,5] and nuclear magnetic resonance relaxation.[5] From these results, two distinct structural models have been proposed to account for the profound effects on the physical and mechanical properties of the copolymers caused by the presence of ionic groups. These are as follows. (1) The three-phase model[2,3,5] for ionized copolymers containing less than about 8 mol % ionizable groups consists of a polyethylene crystalline phase, a polyethylene amorphous phase which may also contain any remaining un-ionized acid groups, and an ionic phase consisting of clusters containing the ionized carboxylate groups. These clusters have been stated to be of the order of 100 Å in size[2] and are dispersed throughout the amorphous polyethylene phase. (2) The two-phase model[4] consists of a crystalline phase composed entirely of polyethylene and an amorphous phase consisting of polyethylene with the ionic groups uniformly dispersed at the molecular level through the amorphous phase.

We have carried out a low angle X-ray investigation in order to distinguish between the two proposed structural models. All the experiments were carried out using the same parent copolymer, which was a copolymer of ethylene and methacrylic acid containing 4.1 mol % methacrylic acid groups and having a weight average molecular weight of 300,000. Schematically, the structure of the copolymer may be represented by



$$-(CH_2CH_2)_n(CH_2-\underset{COOH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-)_m$$

with $n = 25$ for $m = 1$. Low angle X-ray scattering patterns were obtained on the un-ionized copolymer and on partially ionized sodium, cesium, and lithium salts.

Previous wide angle X-ray diffraction studies[2] have established that ionization, although effective in reducing the over-all crystallinity of the sample, does not affect the polyethylene crystal lattice spacings. However, upon ionization, a new peak is observed corresponding to a spacing of about 20 Å. This peak is little affected by the nature of the cation, persists to temperatures of at least 300°, and is virtually eliminated by saturating the polymer with water. It has been attributed[2] to a separate ionic phase within which clusters of carboxyl groups are arranged in some periodic fashion to give a repeat distance of 20 Å. We have also observed a peak corresponding to a 20 Å spacing in all the ionized samples investigated.

Results

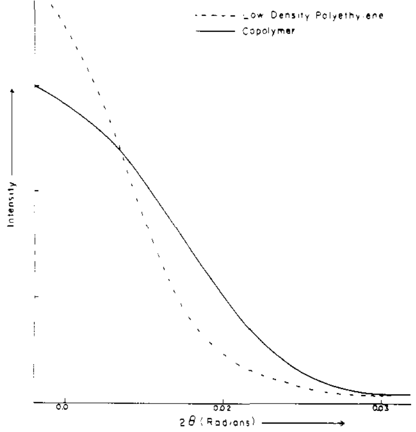


Figure 1. Angular dependence of low angle X-ray scattering pattern from low-density polyethylene and the un-ionized acid copolymer.

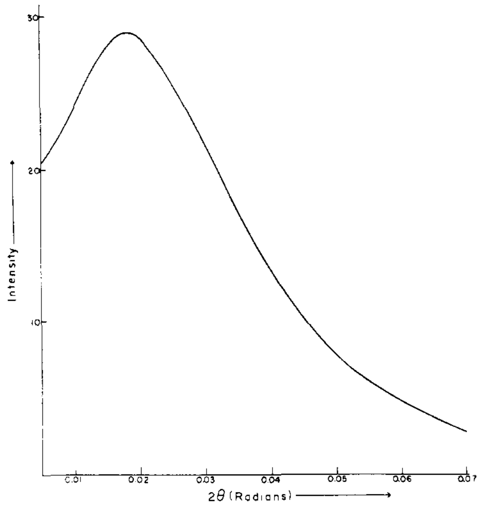


Figure 2. Angular dependence of low angle X-ray scattering pattern from 59% ionized cesium salt.

Figure 1 is a plot of the scattering intensity as a function of angle for the un-ionized acid copolymer together with a similar plot for a sample of low-density polyethylene. The two materials show qualitatively similar behavior, although the copolymer exhibits a somewhat broader pattern. On the other hand, the scattering pattern of a sample in which 59% of the acid groups are ionized with cesium is entirely different as shown in Figure 2. The maximum present in the curve corresponds to a characteristic length of 83 Å. Further experiments established that the sodium salts show

---

(1) W. J. MacKnight, L. W. McKenna, B. E. Read, and R. S. Stein, *J. Phys. Chem.*, 72, 1122 (1968).

(2) R. Longworth and D. J. Vaughan, *Nature*, 218, 85 (1968).

(3) W. J. MacKnight, T. Kajiyama, and L. W. McKenna, *Polym. Eng. Sci.*, 8 (4), 267 (1968).

(4) E. P. Otocka and T. K. Kwei, *Macromolecules*, 1, 401 (1968).

(5) B. E. Read, E. A. Carter, T. M. Connor, and W. J. MacKnight, *Brit. Polym. J.*, Jan 1969.

patterns similar to Figure 2 but the lithium salts are quite different, exhibiting no maximum and being very similar to the un-ionized acid copolymer. In addition, although annealing is known to increase the degree of crystallinity as measured by the wide angle X-ray technique,[2] it had very little or no effect on the low angle maximum in the cesium salt.

Conclusions

(1) The comparison between the scattering pattern obtained from the un-ionized acid copolymer and low-density polyethylene indicates that these two materials are structurally similar.

(2) The comparison between the scattering patterns obtained from the un-ionized acid copolymer and the cesium salt proves that there are fundamental structural differences between these two materials and hence that the cesium salt, in contrast to the un-ionized acid copolymer, possesses a structure different from that of low-density polyethylene.

(3) The maxima observed with cesium and sodium salts are unaffected by annealing which is known to alter the crystalline fraction. These maxima are, therefore, interpreted as being due to electron dense regions in the amorphous fraction which are almost certainly caused by aggregations of ions. The fact that no maximum is observed with the lithium salt supports this view inasmuch as lithium scatters X-rays very weakly. However, the similarity between the mechanical and viscous properties of the lithium salt and those of other salts indicates structural similarities between them.

(4) Therefore, the preliminary low angle X-ray results provide direct evidence for the three-phase structural model for the ionized copolymers. Further work is in progress and will be described in due course.

Experimental Section

The starting copolymer was kindly provided by the Du Pont Co. It was stated to have a weight average molecular weight of 300,000 and oxygen analysis established the presence of 4.1 mol % methacrylic acid units. The finely divided starting material was refluxed in tetrahydrofuran with hydroxides of lithium, sodium, and cesium in order to produce the ionized copolymers. Infrared analysis established that the following ionizations were obtained: Li salt, 65%; Na salt, 60%; Cs salt, 59%.

After ionization the samples were precipitated twice in a methanol–water mixture, washed thoroughly several times, and dried *in vacuo* at 100°. Samples were compression molded for X-ray analysis. Annealing was carried out by heating the samples at 10° below their melting points for 24 hr under vacuum, followed by slow cooling to room temperature.

Low angle X-ray scattering patterns were obtained using a Warhus low-angle camera with 0.020-in. pin holes and a 29-cm sample-to-film distance. The camera was evacuated during exposures and the scattering patterns, which were all obtained with nickel-filtered copper radiation, were microdensito-metered using a Joyce–Lobel instrument.

Acknowledgments. Thanks are due to Dr. Ruskin Longworth of the Du Pont Co. for providing the starting material and to Mr. F. A. Emerson for preparation of the ionized copolymers. We are grateful to the National Science Foundation for partial support of this research.

B. W. Delf,[6] W. J. MacKnight

Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01002

Received February 10, 1969

---

[6] On leave from the Physics Department, University College, Cardiff, Great Britain.

ERRATA

Volume 2, 1969

Michael H. Theil: Thermochemical Aspects of Polymerization. Equilibrium Copolymerization.

Page 137. In the last sentence of the subsection entitled Description of Model and Notation N_0 should be redefined as a molar quantity.

Page 138. Equation 2 is incorrect. It should read

$$\Delta S_D/N_0 = -R\{X_A[(1 - P_{AA}) \ln (1 - P_{AA}) + P_{AA} \ln P_{AA}] + X_B[(1 - P_{BB}) \ln (1 - P_{BB}) + P_{BB} \ln P_{BB}]\}$$

Page 141. The parentheses in the subscript in the upper right hand corner of Figure 4 should be eliminated.

MICHAEL H. THEIL