Infrared Dichroism Studies of the Relaxation of Ethylene–Methacrylic Acid Copolymers and Their Salts[1a]

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ABSTRACT: The change in infrared dichroism with elongation has been observed at a series of temperatures for several infrared bands of ethylene–methacrylic acid copolymers and their salts. The orientation functions of hydrocarbon and methacrylic acid parts of the molecule were calculated as a function of the temperature of stretching. It is found that the orientation function–strain coefficient for the un-ionized acid decreases uniformly with temperature, but that for the ionized salt passes through a maximum at about 40° where the strain-optical coefficient has been observed to pass through a maximum. Maxima are observed for the dichroism-strain coefficients for both the hydrocarbon and acid parts of the structure.

Previous mechanical and dielectric studies of the relaxation of ethylene–methacrylic acid copolymers and their salts have indicated the development of an α mechanical loss maximum upon ionization.[2-4] This maximum, occurring at about 40°, is relatively independent of the type of cation and is interpreted as a softening temperature, T_s, of ionic domains.

X-Ray diffraction measurements of crystalline orientation functions have indicated that in the vicinity of T_s there is a large drop in the orientation function–strain coefficient (orientational compliance) with increasing temperature for the ionized salt, whereas no such drop is observed for the un-ionized acid.[5] From these measurements, the crystalline contribution to the strain-optical coefficient was calculated and subtracted from the experimentally measured strain-optical coefficient.[6] The difference is mostly a result of the contribution of amorphous or disordered regions to the birefringence and is proportional to the amorphous orientation. This indicated that the amorphous orientational compliance for the ionized salt was less than that for the un-ionized acid at low temperature, but that there is an abrupt increase in amorphous orientation at T_s. These observations are consistent with the identification of T_s with a softening point of ionic domains.

In this paper, the technique of infrared dichroism is used to characterize the orientation of particular parts of the structure. The infrared dichroism is known to be related to the orientation of a molecular chain by[7,8]

$$f_i = C_i[(D - 1)/(D + 2)] \qquad (1)$$

where f_i is the orientation function of the ith molecular segment defined as

$$f_i = [3\langle\cos^2 \theta_i\rangle_{\text{av}} - 1]/2 \qquad (2)$$

where θ_i is the angle between the axis of the ith segment and the stretching direction. The dichroism, D, is defined as

$$D = A_{\parallel}/A_{\perp} \qquad (3)$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances for radiation polarized parallel and perpendicular to the stretching direction. The constant C_i is given by

$$C_i = (D_0 + 2)/(D_0 - 1) \qquad (4)$$

where

$$D_0 = 2 \cot^2 \phi_i \qquad (5)$$

The angle ϕ_i is that between the transition moment of the absorbing group and the segment axis.

The advantage of the dichroism technique is that wavelengths may be selected so that the absorption is characteristic of a group located in a particular part of a structure. Thus its dichroism characterizes the orientation of that particular part of the structure. Its quantitative interpretation is dependent upon the assignment of the normal mode of vibration associated with the particular absorption and the specification of its particular value of ϕ_i.

A specific application of this technique is the study by Cooper[9] and coworkers of the orientation of segmented polyurethanes in which the recovery of orientation of hydrocarbon and urethane linkages is distinguished by observing absorption bands associated with methylene groups and NH groups. Also, Onogi, *et al.*, have applied the method to analysis of orientation changes in stretching blends of polypropylene with ethylene–propylene copolymers.[10]

It was the intent of the investigation reported here to study orientation phenomena of the ethylene–methacrylic acid copolymer and its salts by observing the dichroism associated with absorption bands arising from the ethylene or the methacrylic acid parts of the structure.

The samples studied were derived from the same commercial Du Pont Surlyn A copolymer, containing 4.1 mol % methacrylic acid, which was used in our previous investigations.[2-6] Ionized samples were in the form of the 55% ionized sodium salt, while the un-ionized acid was prepared by refluxing the p-xylene solution with dilute hydrochloric acid as previously discussed.

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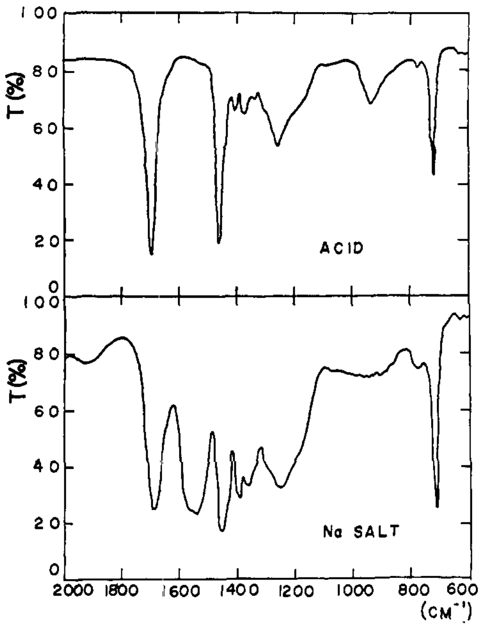

Figure 1. The infrared absorption spectra of the copolymer acid and the 55% ionized copolymer salt.

Films of thickness 0.025–0.050 mm were prepared by pressing at 138° for 6 min, after which they were rapidly cooled to room temperature. Thicker films of about 0.15 mm were used for birefringence measurements in order to obtain higher precision.

Infrared dichroism was measured using a Beckman IR-10 spectrometer and a Perkin-Elmer wire-grid polarizer, following the techniques described by Read and Stein.[11] The stretching direction of the film was inclined at 45° to the spectrometer slit in order to avoid machine polarization effects. The sample was enclosed in a heating chamber, and measurements were made in the range of 17–70°. The dichroism was calculated by taking ratios of absorbances at the band maxima relative to estimated base-line values at these wavelengths.

Birefringence was measured in the manner described by Kajiyama, Stein, and MacKnight,[6] using the system described by Keedy, Volungis, and Kawai,[12] in which an optical system is used in conjunction with an Instron tensile-testing machine. Samples of 1-in. length were stretched at a rate of 12 in./min.

Differential scanning calorimetry measurements were made using a Perkin-Elmer DSC-1B apparatus at a heating rate of 5°/min. Degrees of crystallinity were calculated using the arbitrary heat of fusion of 33.6 cal/g which was selected in the previous paper to give agreement between X-ray and dsc measurements.[5]

Measurements were made on quenched samples at temperatures at which annealing and structural reorganization may occur, as may be seen in the previous paper[5] by comparing results on quenched and annealed samples. This irreversibility with temperature change must be considered in interpreting the results.

Results

Infrared Dichroism. The infrared spectra of the copolymer acid and its sodium salt are presented in Figure 1. Important absorption bands are as follows.

1700 cm^{-1} (Acid and Salt). This is assigned to a stretching vibration of the hydrogen-bonded C=O bond in un-ionized carboxyl groups.[2b,11,13] Since the plane of the carboxyl group is believed to lie perpendicular to the axis of the chain, the angle ϕ_i between the C=O transition moment direction and the chain axis is believed to be close to 90°. Free rotation of the carboxyl group would also lead to $\phi_i = 90°$. However, if there were a tendency for the carboxyl group to lie in the plane of the chain, a much smaller ϕ_i would result. As indicated by Read and Stein,[11] these carboxyl groups are throught to be associated as dimers through hydrogen bonds.

1560 cm^{-1} (Salt). This band is assigned to an asymmetric vibration of the carboxylate ion. The band would have a transition moment angle, ϕ_i, close to 90° if the carboxylate group were oriented with its plane perpendicular to the chain axis as supposed. Parallel polarization ($\phi_i = 0°$) would result if the carboxylate group plane would lie in the chain direction.

1470 cm^{-1} (Acid and Salt). This is a CH_2 bending motion (B_{2u}) with its transition moment perpendicular to the chain.[14,15] There is a crystalline and an amorphous contribution to this band.

1263 cm^{-1} (Acid and Salt). The assignment of this band is not certain, but it is probably associated with the carboxyl group.

935 cm^{-1} (Acid). This is assigned as a deformation of the hydrogen-bonded O–H bond of the un-ionized carboxyl group believed to be out of the plane of this group.[13] To the extent that the carboxyl group plane is perpendicular to the chain axis, the transition moment angle of this band, ϕ_i, is 0° and is parallel to the chain axis.

720 cm^{-1} (Acid and Salt). This is a CH_2 rocking motion consisting of two components.[14,15] One is at 720 cm^{-1} and arises from amorphous trans sequences, whereas the other is a crystalline doublet with a *b*-axis-polarized component at about 720 cm^{-1} (B_{2u}) and an *a*-axis-polarized component at about 730 cm^{-1} (B_{1u}). Because of low crystallinity, the two components are not clearly resolved in our spectra. Both components are polarized perpendicularly to the chain direction.

The methacrylic acid group is too large to be accommodated in the polyethylene unit cell, so all bands associated with the carboxyl group or the carboxylate ion must arise from amorphous parts of the polymer. It is possible, of course, that these groups may be localized at chain folds in the polyethylene folded-chain morphology of this polymer so that their orientation may be constrained by the orientation of the crystals.

The variation of dichroism with elongation for the various absorption bands of the copolymer acid at 40° is shown in Figure 2, while that for the ionized salt is shown in Figure 3. Each measurement represents the average of several determinations, and its estimated precision is indicated by the length of the vertical lines on the graph. Similar results were obtained at other temperatures. Birefringence measurements have indicated that there is little variation of orientation with time, so relaxation is probably not important in the dichroism measurements.

At each temperature, all bands except that at 935 cm^{-1} show monotonously decreasing dichroic ratios with increas-

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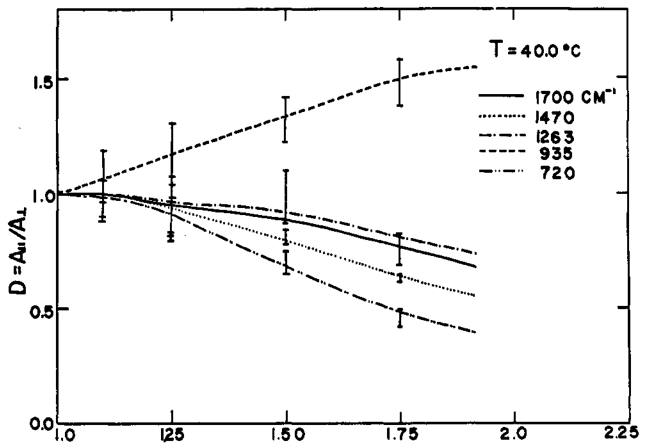

Figure 2. The variation of dichroism with elongation for the various absorption bands of the copolymer acid at 40°.

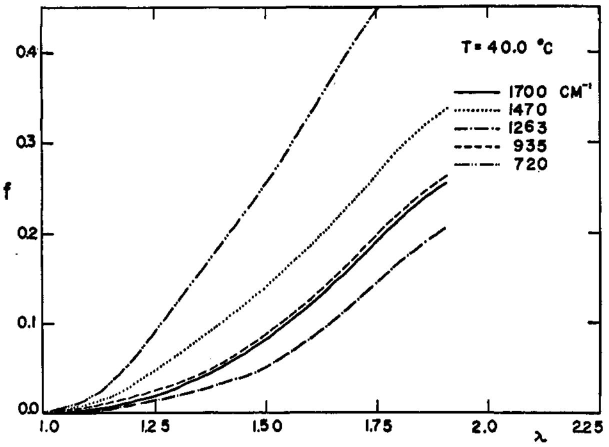

Figure 4. The variation of the orientation function with elongation for the various absorption bands of the copolymer acid at 40°.

ing elongation. This is expected on the basis of the preceding band assignments.

Orientation functions were calculated from these dichroism values using eq 1–5 and arbitrarily assuming that $\phi_i = 90°$ for the 1700-, 1560-, 1470-, 1263-, and 720-cm^{-1} bands and $\phi_i = 0°$ for the 935-cm^{-1} band. Typical values are plotted as a function of elongation in Figure 4 for the copolymer acid and in Figure 5 for the 55% ionized salt at 40°. It is noted that all bands indicate appreciable orientation of the amorphous chain parallel to the stretching direction, but different values of the orientation function are deduced from data obtained using different bands. This result is somewhat similar to that observed for the amorphous regions of polyethylene by Read and Stein[11] and for poly(vinyl chloride) by Shindo, Read, and Stein,[8] where it is found that different values of the amorphous orientation function of the amorphous chain are deduced from observations at different wavelengths. This effect has been ascribed to two causes. (1) The actual values of ϕ_i may not be exactly 90 or 0° for the various bands. A rigorous normal-mode analysis with consideration of the extent of orientation of the plane of the carboxyl group may lead to deviations from these ϕ_i values and hence lead to a variation of C_i of eq 1 from band to band. (2) The bands may not be associated with the conformation of a single monomer unit on the chain but may depend upon the conformational sequence of several monomer units. The theory of this effect has been described by Flory and Abe.[16]

In addition to the above factors, differences among the bands may result from differences in location of the absorbing group within the structure. Thus, it is seen in Figure 5 that the orientation functions calculated from the 1263-, 1560-, and 1700-cm^{-1} bands associated with the methacrylic acid part of the molecule are less than those calculated from the 720- and 1470-cm^{-1} bands associated with the hydrocarbon part of the chain. This may be understood upon realizing that the hydrocarbon part of the molecule resides partially within polyethylene-type crystals which orient upon stretching to a greater extent than do the amorphous chains, as indicated by the X-ray measurements of Kajiyama, *et al.*[5] Furthermore, the methacrylic acid part of the molecule may lie partly within ionized domains which do not deform as readily as do the hydrocarbon regions, or else they may be restricted in motion because of intermolecular association.

It is noteworthy that at 20° an appreciable orientation function is found (0.03 at 50% elongation) for the 1560-cm^{-1} band arising from the carboxyl ion (Figure 7). While this is only about one-eighth of the orientation function of the hydrocarbon part of the chain, it does indicate that orientation of the ionized regions takes place at temperatures lower than the postulated softening temperature of the ionized domains.

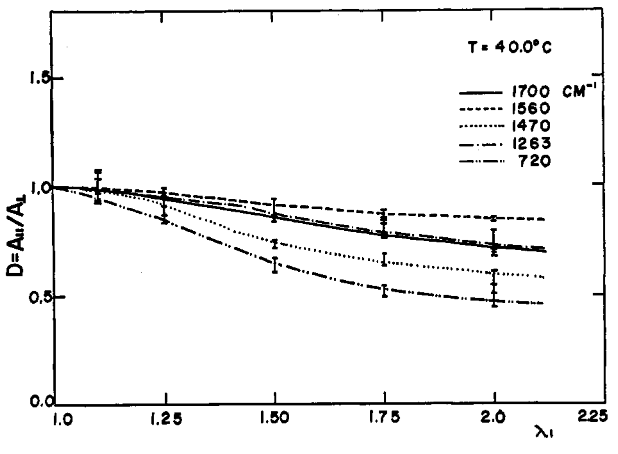

Figure 3. The variation of dichroism with elongation for the various absorption bands of the 55% ionized sodium salt at 40°.

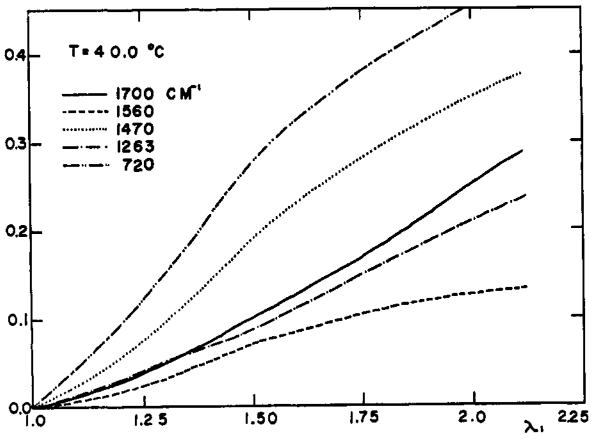

Figure 5. The variation of the orientation function with elongation for the various absorption bands of the 55% ionized sodium salt at 40°

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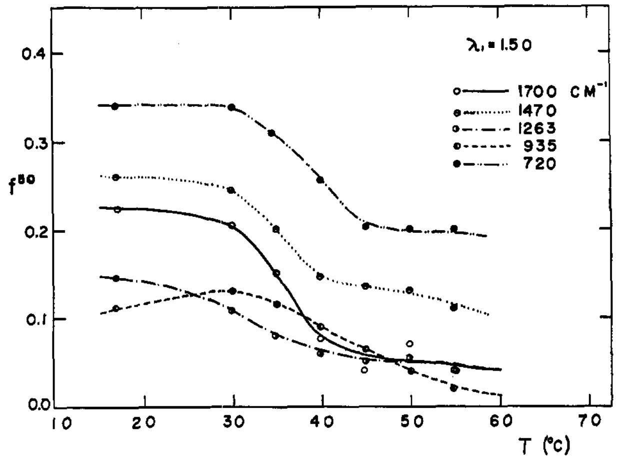

Figure 6. The variation of the orientation function at 50% elongation, f^{50}, with temperature for the copolymer acid.

As a measure of the temperature dependence of the orientability of various parts of the structure, values of the orientation function f^{50} at 50% elongation are plotted as a function of temperature for the acid in Figure 6 and the salt in Figure 7. For the acid, the orientation function f^{50} decreases monotonously with increasing temperature (with slightly different behavior of the 935-cm^{-1} hydroxyl band). The decrease is more abrupt in the range of 30–40°, in a manner somewhat like the change in birefringence which is shown in Figure 8. This decrease may be associated with the broad β-transition region of this copolymer. On the other hand, a maximum in f^{50} is seen for the ionized salt at about 40°, as is seen in the orientation function of the ionized salt, which is similar to the maximum in the birefringence as is shown in Figure 9.

It is of interest to note that the maximum is seen in values of f^{50} obtained from all of the absorption bands, including those obtained from both the hydrocarbon and the methacrylic acid part of the structure. It is apparent that the largest percentage increase in f^{50} is observed for the 1560-cm^{-1} band from the ionized methacrylic acid groups. It is noted that an f^{50} maximum is seen for the 720-cm^{-1} band. This band arises from both crystalline and amorphous regions. Since X-ray diffraction results indicate that no orientation maximum is seen for the crystals,[5] the maximum observed at 720 cm^{-1} must come from the amorphous contribution.

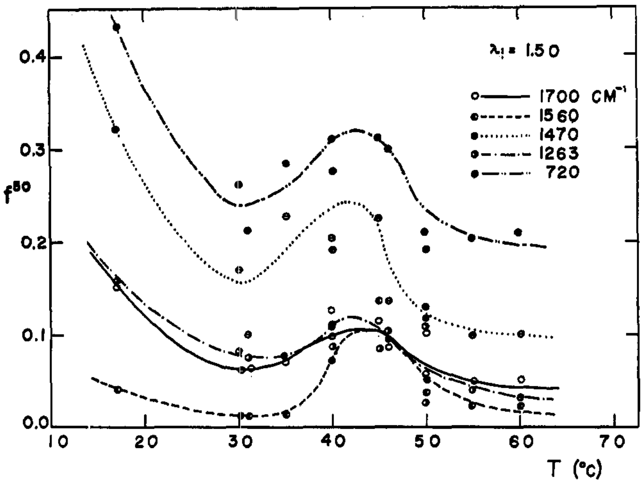

Figure 7. The variation of the orientation function at 50% elongation, f^{50}, with temperature for the 55% ionized sodium salt.

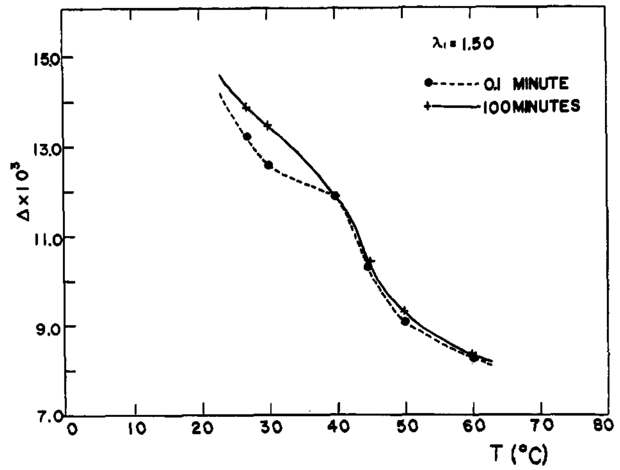

Figure 8. The variation in birefringence at 50% elongation with temperature for the copolymer acid. Values at various time intervals after stretching are plotted.

Discussion

On the basis of the mechanical, dielectric birefringence, and X-ray studies reported in the earlier papers, it was postulated that the α mechanical loss process was a softening temperature of the ionized domains. One might expect that this process would lead to a much greater increase in orientation of groups associated with the ionized domains than for those residing in the hydrocarbon regions. The observation that the orientation of groups in both regions increases at this temperature indicates that orientational changes in the two regions must be coupled. This conclusion has structural implications.

If the ionized domains were dispersed in a hydrocarbon continuum, the softening of such regions would increase their orientation but not affect or even decrease the orientability of the continuous hydrocarbon phase. Also, if one stretched the polymer at a temperature below the softening temperature of the ionized domain, most of the orientation should occur in the softer hydrocarbon phase, with little orientation occurring in the ionized domain. Such a model would imply that the hydrocarbon and ionic regions would effectively behave as though they were mechanically connected in series with each other.

The observation that orientation of both regions occurs

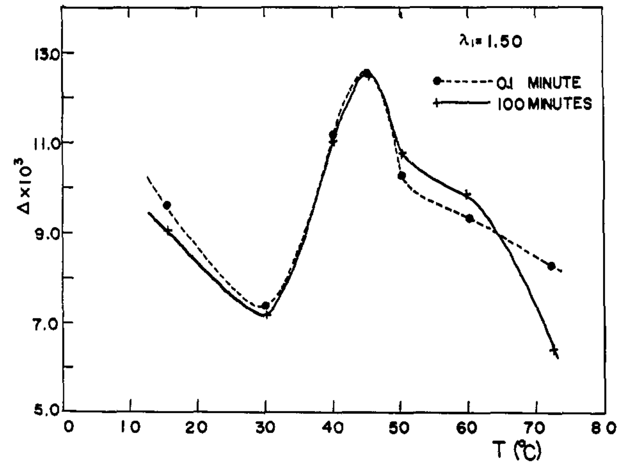

Figure 9. The variation in birefringence at 50% elongation with temperature for the 55% ionized sodium salt. Values at various time intervals after stretching are plotted.

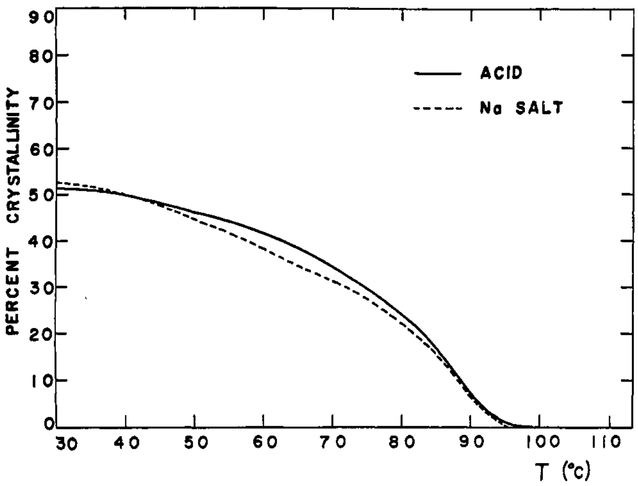

Figure 10. The weight-fraction crystallinity as measured by the differential scanning calorimeter as a function of temperature for the un-ionized copolymer acid and the 55% ionized sodium salt. A crystalline heat of fusion of 33.6 cal/g for branched polyethylene is assumed.

below the softening temperature and that the softening of the ionized regions also leads to an increase in the orientation of the hydrocarbon regions implies a parallel connection between the two.

Microscopic observations and low-angle light-scattering (LALS) studies of the annealed un-ionized acid demonstrate that the structure is spherulitic, probably being composed of chain-folded lamellae.[17] The spherulitic order is almost as good as that in a branched low-density polyethylene. Also, degrees of crystallinity of the annealed acid by X-ray diffraction are of the order of 0.50, again comparable with branched polyethylene. Degrees of crystallinity and spherulitic order of the acid are appreciably decreased for samples quenched from the melt—much more so than for polyethylene itself.

It is apparent that a bulky methacrylic acid group cannot be accommodated within a polyethylene crystal lattice. Thus, if high degrees of crystallinity and spherulitic order can persist for samples containing 4 mol % methacrylic acid, it is likely that the acid groups occur on the irregular fold surface of the ethylene lamellae. For rapidly crystallized samples, there is insufficient time for the chains to arrange themselves so as to allow these groups to occur on lamellae surfaces, so the degree of crystallinity and spherulitic order is suppressed.

While spherulites are not observed for the salt, degrees of crystallinity of the annealed samples as shown in Figure 10 approach those of the un-ionized acid. Also, light-scattering patterns indicate the presence of rod-like aggregates of crystals which may be identified with lamellae.[17] Thus, it seems likely that the ionized regions may occur on lamellae surfaces. This suggests a sandwich type of structure in which the ionized domains may occur between crystalline lamellae. This model would seem consistent with the postulated parallel connectivity between the regions. While the domains may contain some hydrocarbon groups associated with the carboxylate groups, the high crystallizability and spherulitic order suggest that most of the hydrocarbon residues exist outside of the domain in the crystallizable regions. Indeed, there seems to be a competition for the hydrocarbon between the domains and the crystals.

We believe that these infrared studies confirm that the α loss maximum observed for the ionized copolymer is associated with a process which permits greater orientation of amorphous regions of the polymer to take place. The identification of this process with a softening temperature of ionic domains is consistent with this postulate.

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Electrical Properties of 7,7′,8,8′-Tetracyanoquinodimethane Salts of Ionene Polymers and Their Model Compounds[1a]

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ABSTRACT: Electrically conducting polymeric salts were prepared by the reaction of ionene polymers with LiTCNQ in the presence or absence of neutral TCNQ. The specific resistivity, the activation energy for conductivity, and the Seebeck coefficient were determined as a function of the number of CH_2 groups between positively charged nitrogens. The wide variations of electrical properties could not be correlated with the length of the polymethylene chain in the polymer. X-Ray analysis of single crystals of model compounds revealed that the electrical properties depend mainly on crystal geometry.

The discovery of highly conducting 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) paramagnetic salts constitutes an important advance in the study of electronic conductivity of purely organic materials. This high conductivity is exhibited by mono- or polysalts, provided the TCNQ radical anion ($TCNQ\cdot^-$) is associated with a neutral TCNQ molecule[2,3] ($TCNQ^0$). Although the electronic conductivity of this type of material has already been well established,[4] no data

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(1) (a) This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract No. NAS 7-100; (b) NRC–NASA Resident Research Associate.

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