energy end of the domain of weaker surface–segment interactions adsorption must increase with increasing energy. This is obviously true, since for sufficiently weak interactions adsorption will not take place. Experimental evidence therefore indicates that, with all other factors the same, there is a surface–segment interaction energy which willl give a maximum adsorption. Since changing temperature changes the effective surface–segment interaction, the above argument may explain the conflicting reports of the temperature dependence of polymer adsorption. In general, however, it is very nearly impossible to change surface–segment interactions without changing the whole array of parameters that effect polymer adsorption, so it is not surprising that, except for the one case cited,[36] such an adsorption maximum has never been observed.

Acknowledgments. This work was supported in part by the Advanced Research Projects Agency of the Department of Defense. We are indebted to the Rohm and Haas Co. for PMMA samples and for doing the BET measurements on the adsorbents.

X-Ray Diffraction Studies of the Relaxation of Ethylene–Methacrylic Acid Copolymers and Their Salts[1a]

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ABSTRACT: The degrees of crystallinity and crystal orientation of quenched and annealed ethylene–methacrylic acid copolymers and their salts are studied by X-ray diffraction. The degrees of crystallinity of the annealed acid and salt are comparable with those of branched polyethylene but the crystallinity of the quenched acid is reduced by about half. Orientation functions for crystal axes have been determined as a function of the temperature of elongation and are used to calculate the crystalline component of birefringence. It is found that crystalline orientation makes an appreciable contribution to the birefringence. The change in orientation function with elongation varies with temperature in a very different manner for the acid and the salt, suggesting different orientation mechanisms for the two. At a temperature corresponding to the α mechanical dispersion, a marked increase is seen in the amorphous orientability of the salt, whereas no such increase is found for the acid. This suggests that a process occurs within the amorphous phase of the salt at this temperature, permitting greater orientation to occur. This is consistent with the assignment of this loss maximum to a softening temperature of a proposed ionic domain.

In a previous publication,[2] the results of birefringence studies of the relaxation processes of ethylene–methacrylic acid copolymers and their salts were presented. The variation of the strain optical coefficient, K, with temperature was determined for the un-ionized acid and the salt. A maximum in K was found at about 40° for the ionized salt but none was found for the un-ionized acid. This maximum occurs at a temperature corresponding to the α mechanical loss peak which has been associated with a glass temperature of a proposed ionic domain.[3] The birefringence maximum was associated with an increase in orientability of the amorphous part of the polymer as the ionic regions soften.

Since the copolymers are partly crystalline, it is likely that the crystallites may contribute significantly to the birefringence. It was a principal objective of the work described here to determine the temperature variation of this crystalline component of the birefringence in order to establish whether the α orientation maximum was of crystalline or amorphous origin.

Experimental Section

The samples studied were derived from the commercial Du Pont ethylene–methacrylic acid copolymer ("Surlyn") and are identical with those used in previous studies.[2,3b–7] The polymer has a weight-average molecular weight of about 300,000, a methacrylic acid content of 4.1 mol %, and around 25 methyl branches/1000 carbon atoms. The acid groups were ionized by a method described previously.[4] Quenched samples (Q) were prepared by molding in a laboratory press at 125° and rapidly cooling under pressure by transferring to a previously cooled laboratory press. The annealed samples (A) were prepared by holding the quenched samples in an oil bath at 94° for 24 hr and then cooling very slowly to room temperature.

Degrees of crystallinity were determined by the method of Mathews[8] using data obtained with a homemade spectrometer.[9] Data were corrected in the usual manner for polarization, absorption, and incoherent scattering. The diffracted intensity was resolved into a contribution from the amorphous scattering and diffraction from the 110 and 200 peaks by trial and error after making the following assumptions.

1. The form of the variation of the amorphous scattering with 2θ is the same over all temperatures of this study.
2. The diffracted intensity at $2\theta = 16.5°$ entirely results from amorphous scattering.
3. The 110 and 200 diffraction peaks are symmetrical in Bragg angle about their diffraction maxima.

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(1) (a) Supported by grants from the Petroleum Research Fund of the American Chemical Society and the National Science Foundation and a contract with the Office of Naval Research; (b) Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka, Kyushu, Japan.

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Differential scanning calorimeter (DSC) measurements were made using a Perkin-Elmer Model DSC-1B instrument which was calibrated with benzoic acid at a scanning speed of 10°/min.

Orientation functions were determined from an azimuthal scan of the diffracted intensity by graphical integration using a previously described procedure.[10] Samples were held at constant temperature using a homemade air thermostat. They were stretched in the thermostat and conditioned at each elongation for 30 min prior to measurement. Measurements of the time dependence of birefringence indicated that little orientation change occurred during the time of measurement.[11]

Birefringence was measured using a Babinet compensator as described in the preceding paper[2] for samples elongated at a constant rate of 0.02 in. (2%)/min.

Results and Discussion

Degree of Crystallinity. The variation of the degree of crystallinity (weight fraction) of the Q and A samples is plotted against temperature in Figure 1 for the acid and 78% sodium ionized salt. Data for the quenched salt are not given because the imperfect crystalline structure prohibits the resolution of the diffracted intensities into crystalline and amorphous contributions. Data are compared with those obtained by DSC calculated using an arbitrary heat of fusion of 33.6 cal/g for polyethylene crystals.

It is noted that approximate agreement is obtained between DSC and X-ray values of degree of crystallinity for the ΔH_f used. However, this value is low as compared with the value expected for a corresponding polyethylene homopolymer according to Knox's data.[12] From the melting point of 100°, he indicates a ΔH_f of 42 cal/g, while from the methyl content, a value of 50 cal/g is indicated. If these values were used for the DSC calculations, a degree of crystallinity somewhat less than the X-ray value would have been obtained for the annealed acid but fairly good agreement would be obtained for the quenched sample at low temperatures. It may be, however, that the X-ray values for the quenched sample at higher temperatures are too high since very low heating rates were necessary for the X-ray measurements so that considerable annealing of the quenched samples may have taken place.

The data indicate that ΔH_f for the annealed copolymer acid was less than that for a corresponding polyethylene homopolymer. This may be a consequence of crystal strain arising from the presence of crystal-excluded methacrylic acid groups at the crystal surface or else may be a consequence of ordering in the melt.

It may be that the X-ray crystallinity is in error because of disorder or small crystal size. It would be expected, however, that such errors would be in the direction of making our calculated X-ray crystallinities too low and would lead to an even smaller calculated heat of fusion for the ethylene crystals in the copolymer.

It is somewhat surprising that the degree of crystallinity of the A copolymer acid and salt are comparable with each other and with the degree of crystallinity of a corresponding polyethylene homopolymer even though the melting point is depressed from about 115 to 100°. The degree of crystallinity of the quenched acid is reduced to about one-half that of the annealed. Such a reduction is not observed for unsubstituted polyethylene. The ability to quench the copolymer must be a consequence of a reduction in its crystallization rate. This is in part a result of the decrease in supercooling of the copolymer because of its lower melting point and in part due to the decreasing diffusion rate of the amorphous chains arising from the association of acid groups or clustering of ions. Evidence for the latter is the higher glass temperature of the copolymer and higher melt viscosity as compared with those of the homopolymer.

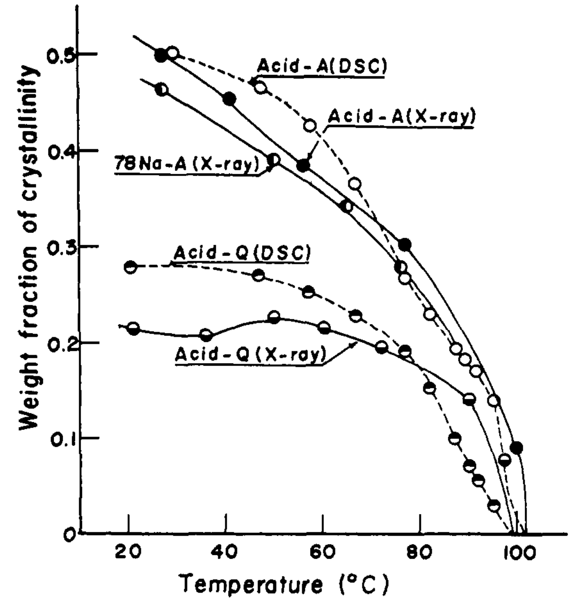

Figure 1. The variation of the weight fraction crystallinity as determined by X-ray diffraction and DSC with temperature for A and Q acid copolymer and A 78% sodium salt.

Birefringence. The variation of the static strain optical coefficient K_s with temperature is plotted in Figure 2 for the Q and A acid and its sodium salt. As previously pointed out,[2,11] the birefringence is not very time dependent for times longer than a few seconds so that the elongation rate is not

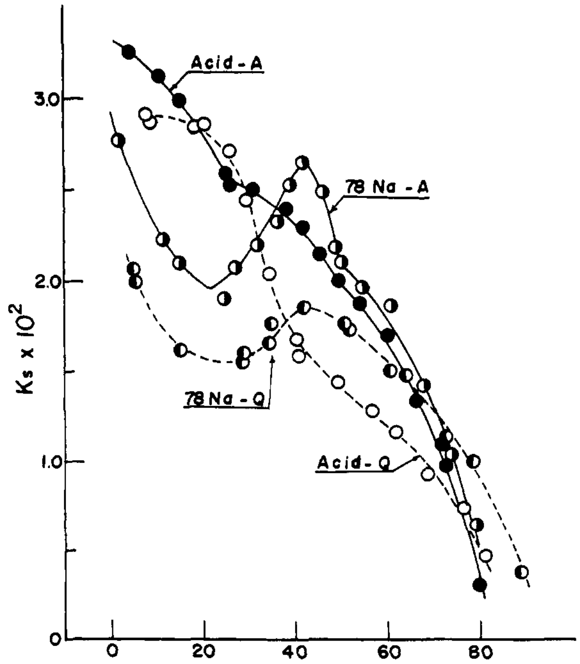

Figure 2. The variation of the static strain optical coefficient K_s with temperature for A and Q acid copolymer and 78% sodium salt.

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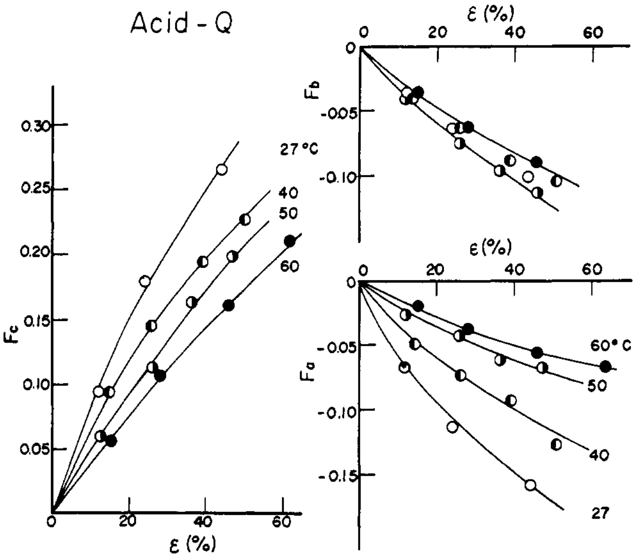

Figure 3. The variation of the orientation function for the *a*, *b*, and *c* crystal axes with per cent elongation at a number of temperatures for quenched acid copolymer.

critical for these measurements. It is noted that both the Q and A ionized samples exhibit a maximum in K_s at about 40° but that the unionized acid samples do not, in agreement with previous results.[2] It was proposed[2] that the maximum arises from a transition occurring in the ionic domains within the amorphous regions. Since the amorphous content of the annealed sample is lower than that of the quenched, the higher maximum for the A sample indicates that annealing favors the domain segregation within the amorphous regions.

The annealed acid copolymer exhibits a more pronounced shoulder in its K_s value in the range of 30–70° than the quenched acid copolymer. It will be shown that this greater K_s for the annealed sample is related to a greater degree of interaction between crystals arising from the more highly developed crystalline superstructure within these samples. In the following sections, these K_s values will be resolved into crystalline and amorphous contributions.

Orientation Functions. The variation of the orientation function of the *a*, *b*, and *c* axes with elongation for the Q acid sample at a number of temperatures is presented in Figure 3, while values for the A acid are given in Figure 4 and for the A 78% sodium salt in Figure 5. The variation of the orientation functions with elongation has been extensively studied for the stretching of both low- and high-density polyethylene as a function of temperature. It is observed that the *a* and *b* crystal axes orient differently from each other, in contrast to what might be expected if we thought the polyethylene crystals to behave as individual crystals immersed in an amorphous matrix. The difference between the behavior of the *a* and *b* axes has been explained on the basis of the spherulitic structure of polyethylene.[13,14] The *b* axes of polyethylene crystals are uniquely oriented in the radial direction in the spherulites. The deformation of polyethylene has been explained in terms of the deformation of the spherulites from spheres to ellipsoids accompanied by the bending and twisting of lamellae within the spherulites and also tilting of chain axes with respect to lamellae axes. The orientability of these crystals is restricted because of their inclusion in the spherulitic superstructure, since the crystals must orient as a part of a larger lamella which in turn is part of a spherulite.

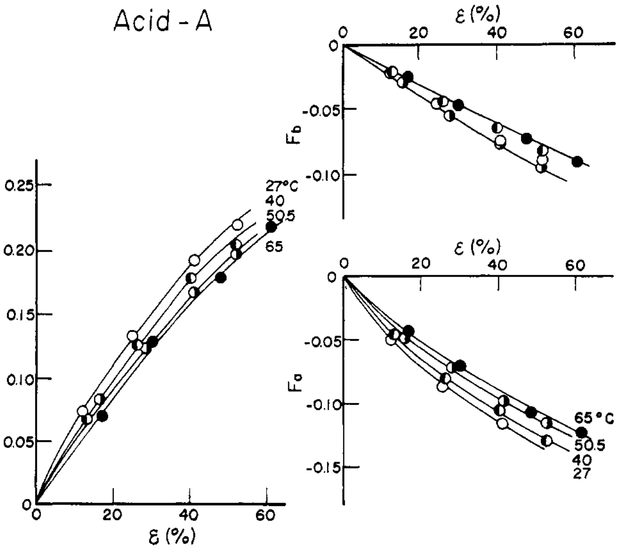

Figure 4. The variation of the orientation function for the *a*, *b*, and *c* crystal axes with per cent elongation at a number of temperatures for annealed acid copolymer.

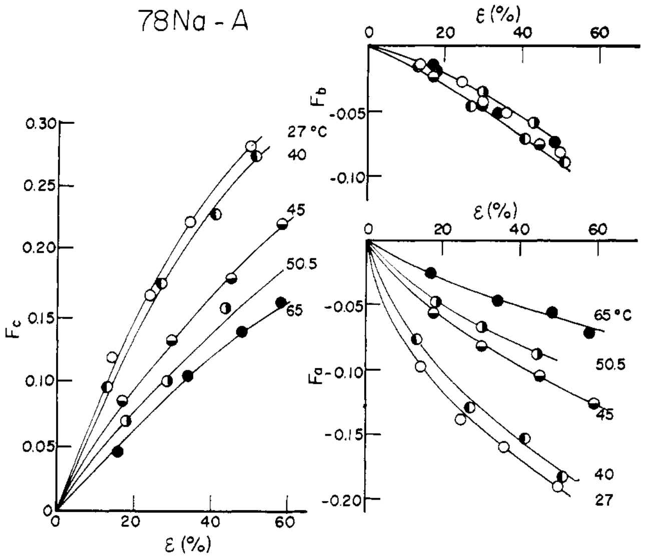

Figure 5. The variation of the orientation function for the *a*, *b*, and *c* crystal axes with per cent elongation at a number of temperatures for annealed 78% sodium copolymer salt.

With increasing temperature and decreasing degree of annealing lamellae become thinner and more disordered, and the ordering of these lamellae within the spherulite becomes less. This may be seen from the departure of the H_v low-angle light-scattering patterns of the ideal spherulite.[15–17]

The annealed acid copolymer is spherulitic as seen from microscopic observations and by low-angle light scattering.[18] The less crystalline quenched acid and the salt exhibit less spherulitic order. Spherulites cannot be resolved with the polarizing microscope even though a somewhat diffuse,

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spherulite-type structure may be characterized from the four-leafed-clover form of low-angle light-scattering patterns which are obtained.[18]

For annealed low-density polyethylene, $-f_a$ exhibits a (negative) maximum at about 60° at a given elongation.[13] The increase in $-f_a$ with temperature up to 60° is attributed to the α_1 relaxation process which is believed to be related to the twisting of lamellae about the crystal b axes so as to align the c axis parallel to the stretching direction. This process becomes easier for quenched samples of polyethylene where the lamellae are less perfect and the disordered interlamellar layer is thicker. In such cases, the $-f_a$ maximum is shifted to lower temperatures.[19] We believe that this α_1 process becomes correspondingly easier for the lower spherulitic order found in the quenched acid and the salt. In these cases, we believe that lamellae can easily rotate about their b axes, leading to a high degree of a axis orientation perpendicular to the stretching direction.

The decrease in $-f_a$ found for polyethylene at temperatures higher than 60° is ascribed to an α_2 process related to intracrystalline motion of chains above this "crystal disordering temperature." This process becomes easier with increasing crystal imperfection. We believe that this α_2 process occurs in the lower temperature range of 27–60° for the imperfect crystal structure probably occurring in the quenched acid and the salt and is largely responsible for the large temperature dependence of f_a seen in Figures 3 and 5.

A particularly large drop in $-f_a$ is seen in Figure 5 in the temperature interval from 40 to 45°. This is the temperature range which has been ascribed to a glass temperature of a proposed ionic domain.[3] This observation suggests a second reason for the change of f_a with temperature. We believe that the forces tending to twist crystalline lamellae are transmitted between crystals through the interlamellar amorphous phase. The ionic domains serve to reinforce and cross-link this phase, increasing its modulus and its ability to transmit force between lamellae. This may, in part, be responsible for the high value of $-f_a$ found for the ionized salt. Upon heating past 40°, these domains are believed to soften so that the transmission of force between crystals decreases, leading to the observed decrease in $-f_a$.

Orientational compliances, C_i, were calculated by dividing the orientation function by the static strain and extrapolating to zero strain. These are plotted in Figure 6 for the a and c axes for the three types of samples. These values reflect the changes in the orientation functions themselves and are used to calculate crystalline contributions to the birefringence in the next section.

Resolution of Birefringence into Crystalline and Amorphous Contributions. As with polyethylene,[20,21] it is assumed that the total birefringence may be expressed as a sum of crystalline and amorphous parts

$$\Delta = \phi_{cr}\Delta_{cr} + (1 - \phi_{cr})\Delta_{am} + \Delta_F \tag{1}$$

where ϕ_{cr} is the volume fraction of crystals. Δ_{cr} is the specific birefringence of the polyethylene crystals given by[21]

$$\Delta_{cr} = (n_a - n_c)f_a + (n_b - n_c)f_b \tag{2}$$

where n_a, n_b, and n_c are the refractive indices of polyethylene crystals given by[22] $n_a = 1.514$, n_b 1.519, and $n_c = 1.575$ as derived from measurements on $C_{3,4}$ crystals.

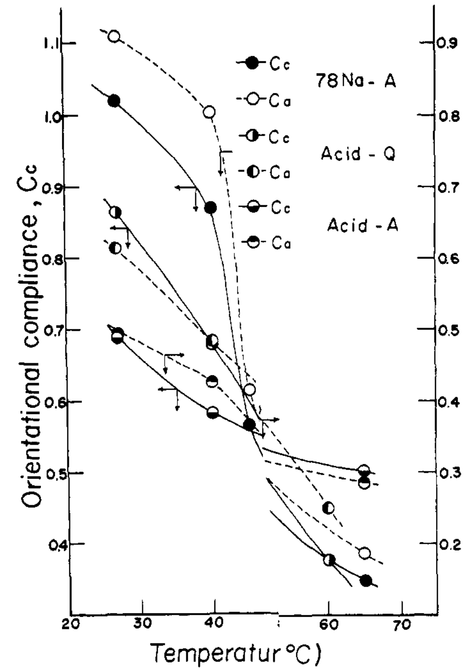

Figure 6. The variation of the entational compliance with temperature for the a and c axes of nd A acid copolymer and A 78% sodium salt samples.

The specific birefrigence of the arphous part may in turn be resolved into contributions frome ionic domains and the un-ionized acid[2]

$$\Delta_{am} = \phi_{ion}\Delta_{ion} + (1\ \phi_{ion})\Delta_{acid} \tag{3}$$

where ϕ_{ion} is the volume fraction the amorphous phase which is ionized and Δ_{ion} and Δ_{acid}e the specific birefringence values for the ionized and uonized regions of the amorphous phase. These are given

$$\Delta_{ion} = \Delta_{ion}{}^0 f_{i} \tag{4}$$

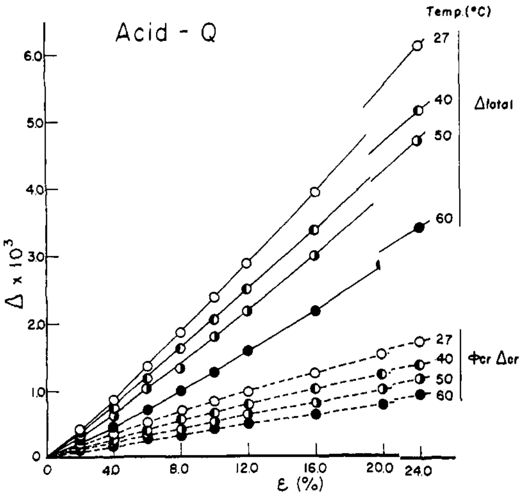

Figure 7. The variation of the total birefringe and the crystalline contribution with elongation for a number temperatures for the Q acid copolymer sample.

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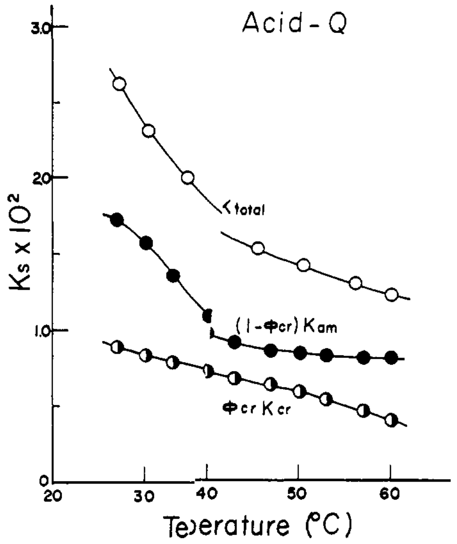

Figure 8. The variation of͏e total strain optical coefficient, the crystalline contribution, a) the amorphous contribution with temperature for the Q acid c͏olymer sample.

and

$$\Delta = \Delta_{\text{acid}}{}^{0} f_{\text{acid}} \quad (5)$$

where f_{ion}, for examp(s the orientation function of the ionized region and Δ_{ion}s the intrinsic birefringence of the perfectly oriented ionizregion.

The form birefringe, Δ_F, in eq 1 is believed to be small and is neglected in the considerations.

From the measured eight fraction crystallinity and density, ϕ_{cr} may be calculd. The values of f_a and f_b are used in eq 2 to obtain $\phi_{cr}\Delta_{cr}$ hich is plotted along with the total birefringence Δ_{total} in igure 7 for the Q acid sample at a number of temperatu. It is seen that the crystalline contribution represents out one-third of the total birefringence. Similar plots have be obtained for the other samples. From the orientational co liance of the crystals, the crystalline and amorphous co ibutions to the strain optical coefficients have been de mined and are plotted against temperature in Figures 8, 9, d 10.

A significant obs ation is that $\phi_{cr}K_{cr}$ decreases with temperature and does t show a maximum as is seen for polyethylene homopolymer.[19] The maximum in K_{cr} for polyethylene is interpreted[13] as being a result of the competition between two processes as discussed earlier, the α_1 which results in an increase in K_{cr} with temperature and which is associated with interlamellar slip and the α_2 which is related to intracrystalline chain motion which causes K_{cr} to decrease with increasing temperature. The absence of a maximum for the copolymer suggests that these processes are shifted to lower temperatures. Such a shift has been observed for quenched polyethylene.[19] Thus, it is apparent that the α maximum in K_s observed for the ionized copolymer salt is not a consequence of the same sort of crystalline processes that leads to the K_s maximum for polyethylene.

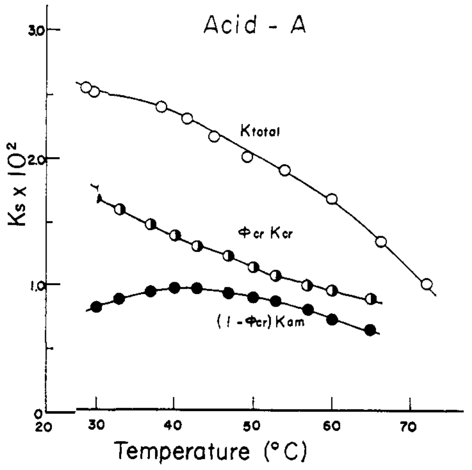

Figure 9. Thariation of the total strain optical coefficient, the crystalline co bution, and the amorphous contribution with temperature f he A acid copolymer sample.

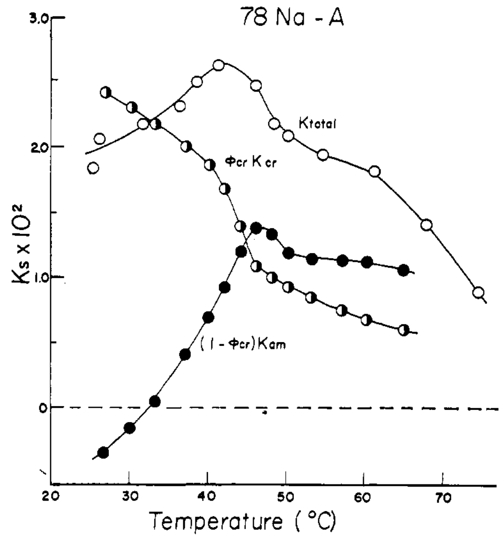

Figure 10. The variation of the total strain optical coefficient, the crystalline contribution, and the amorphous contribution with temperature for the A 78% sodium salt sample.

A comparison of Figure 10 with Figures 8 and 9 indicates that the contribution of the crystals to the birefringence at low temperatures is greatest for the ionized acid and the contribution of amorphous regions is least. The temperature region of the α transition is characterized by a large increase in amorphous orientation occurring simultaneously with a decrease in crystalline orientation. We have seen that both of these changes are consistent with an explanation in terms of the softening of ionic domains. Below this transition temperature we believe that the amorphous regions are interlaced with glasslike ionic domains which lead to a low compliance, so that the major change produced by external strain is to orient crystals. At the α transition, the domains may soften, permitting greater amorphous orientation. As discussed previously, when this happens, less force is transmitted to crystal lamellae so that the crystal orientation becomes less. In the same temperature region, mobility increases within the crystal, leading to a slipping of chains through the crystal, also resulting in lower crystal orientation.

The increase in birefringence with increasing temperature resulting from the increase in amorphous orientation is greater than the decrease resulting from the decrease in crystal orientation. Consequently, the value of K_{total} is observed to increase in the temperature region of 27–45°.

After the ionized regions have softened, further heating leads to viscous flow in the amorphous regions so that a decrease in the amorphous birefringence contribution occurs at temperatures above 45°. The amount of this decrease is related to the molecular weight of the polymer, the amount of residual hydrogen bonding between chains, and the time scale of the experiment. This decrease in $(1 - \phi_{cr})K_{am}$ at higher temperatures results in a maximum in the vicinity of the α transition temperature.

The contribution of $\phi_{cr}K_{cr}$ continues to decrease at temperatures above 45° because of the increasing contribution of the α_2 process as well as the decreasing transmission of force between lamellae. Thus K_{total} will decrease as a consequence of the decrease in both the crystalline and amorphous contributions to birefringence. A maximum in K_{total} will be found in the vicinity of the temperature of the α dispersion as a result of the competition of the low- and high-temperature processes. This maximum will be near but not precisely at the same temperature as the maximum in $(1 - \phi_{cr})K_{am}$.

A negative value of $(1 - \phi_{cr})K_{am}$ is observed for the copolymer salt at temperatures less than 33° where the crystalline contribution to the birefringence is greater than the total. The variation of $(1 - \phi_{cr})\Delta_{am}$ with elongation at low temperature, as shown in Figure 11, shows an initial decrease toward a minimum at 5% elongation at 27° followed by an increase to positive values at elongations past 10%. This behavior is similar to that found for branched polyethylene homopolymer[20] and for polypropylene[23] and has been attributed to an initial perpendicular orientation of the amorphous chains with respect to the crystalline orientation within the crystalline superstructure. It may result in part from a contribution from distortional birefringence at low temperatures associated with processes such as bond bending as is found, for example, for poly(vinyl chloride).[24]

These changes observed for the ionized salt may be compared with the observations for the quenched and annealed acid in Figures 8 and 9. In these cases, no abrupt increase in $(1 - \phi_{cr})K_{am}$ is found in the vicinity of 40°, indicating the absence of a process believed to occur in the amorphous regions of the ionized salt.

It is seen from Figure 8 that $(1 - \phi_{cr})K_{am}$ for the Q acid copolymer sample decreases appreciably with temperature in the vicinity of 30°. This is consistent with the proposed explanation that the amorphous phase undergoes a glass transition at about 23°.

The amorphous birefringence contribution does not decrease with temperature in the range of 27–40° for the annealed acid (Figure 9) as it does for the quenched acid. In fact a slight increase in $(1 - \phi_{cr})K_{am}$ with temperature is observed. We believe that the difference is a consequence of the acid approaching the morphology of low-density polyethylene with increasing annealing. For polyethylene, it is thought that at low elongations, forces are transmitted directly between crystals.[13,19,25] A decrease in $(1 - \phi_{cr})K_{am}$ with increase in temperature is not observed for low-density polyethylene at temperatures below the α dispersion.[19]

Further interpretation requires the resolution of the amorphous birefringence into contributions from the hydrocarbon, acid, and ionic regions. Such resolution is, in principal, possible through use of infrared dichroism as has recently been demonstrated, for example, for polyurethanes, by Cooper, *et al.*[26] Preliminary measurements on such copolymers have been reported by Read and Stein,[27] where different degrees of orientation are found for hydrocarbon and carboxyl group parts of the chain. Measurements on the copolymer acid and salts as a function of temperature have been carried out by Uemura and will be reported in a following publication.[11]

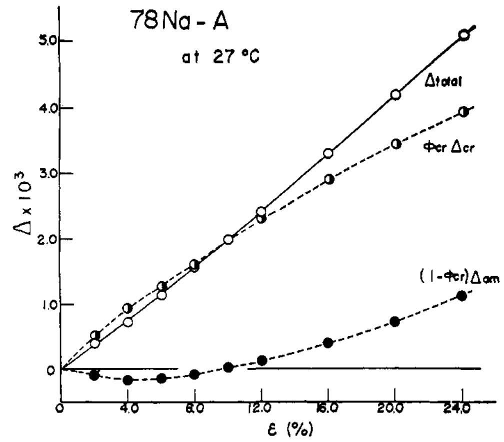

Figure 11. The variation of the total birefringence and the crystalline and amorphous contributions for the A copolymer sodium salt at 27°.

Conclusions

It has been possible, through a combination of birefringence and X-ray diffraction measurements to resolve orientational changes occurring upon stretching ethylene–methacrylic acid copolymers and their salts into contributions arising from crystalline and amorphous regions. The results of this resolution clearly demonstrate that there is a basically different relaxation process occurring in the ionized salt in the vicinity of 40° than in the acid. The relaxation in this α dispersion region of the salt is dominated by an abrupt increase in amorphous orientation with increase in temperature of stretching, whereas little change or a small decrease is found for the acid. This observation indicates that some structural restriction which has prevented amorphous orientation at the lower temperatures is "melted out" at about 40°, and is consistent with the proposed glass transition of ionic regions at this temperature.

The detailed examination of the variation of the orientation functions for the *a*, *b*, and *c* crystal axes leads to conclusions which are consistent with the above interpretation of the α dispersion. Differences are observed between the orientational changes for quenched and annealed samples of the copolymer acid which may be interpreted in terms of the observation that the acid approaches a more perfectly spherulitic polyethylene-type morphology with increased annealing.

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