Light-Scattering Studies of Crystallite Organization in Ionomers[1]

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ABSTRACT: Photographic low-angle light-scattering patterns have been obtained for quenched and annealed samples of ionized and un-ionized copolymers of methacrylic acid and ethylene. It was found that patterns for the annealed un-ionized samples are similar to those for polyethylene itself, confirming their lamellar and spherulitic structures. As cooling rate and degree of ionization increase, the structure becomes more disordered and becomes more rodlike in nature. This variation is further confirmed by photometric measurements.

Mechanical,[2a] dielectric,[2b] optical,[3,4] and X-ray[5,6] studies have been published from this laboratory for methacrylic acid–ethylene copolymers. These have been interpreted in terms of a somewhat defective polyethylene structure for the un-ionized acid but in terms of a structure containing ionic domains for the ionized polymer. Mechanical properties of polyethylene in the α mechanical loss region have been interpreted in terms of processes involving lamellae and spherulites. Consequently, it is of interest to correlate changes in this superstructure with the observed dynamic mechanical property changes for the copolymer and its salts.

Spherulitic structure in these un-ionized copolymers as observed by light and electron microscopy has been reported,[7] but such structures are not seen for the ionized polymer. The characterization of less ordered structures by direct observation is difficult, so we have employed the light-scattering technique for this purpose.[8,9]

Experimental Section

The samples studied were of the same origin as for the previous investigations.[2-6] The 55% sodium ionized salt was the commercial Du Pont Surlyn-A copolymer containing 4 mol % methacrylic acid. This was converted to the un-ionized acid by Dr. Fred Emerson[10] using procedures previously described.

Samples of both polymers were prepared by molding in a laboratory press between sheets of metal for 15 min at 125°. Some samples were allowed to crystallize in the press at 91° for times of 30 min to 70 hr.

Others were removed from the press and allowed to cool at their natural rate, or else were quenched in a Dry Ice–methanol bath. The samples, preparation conditions, and the figure numbers where light-scattering results are given are summarized in Table I.

Photographic light-scattering patterns were obtained using the laser technique[11] utilizing a Spectra Physics Model 130 He–Ne laser. Patterns were recorded using Polaroid Type 57 film. Measurements are reported for H_v polarization (vertically polarized incident and horizontally polarized scattered radiation) and V_v polarization.

Photometric light-scattering measurements were made using a specially constructed low-angle light-scattering photometer[12] which permits intensity measurements down to 0.2° of scattering angle θ, from the incident beam in the horizontal plane. Provision is made for rotating the polarizer and analyzer through angles ψ_1 and ψ_2 from the vertical direction.

Results

Typical H_v photographic patterns obtained for air-cooled films are shown in Figures 1a and 1b for the un-ionized acid and the ionized sodium salt. The acid exhibits the four-leaf-clover pattern which is typical for scattering for spherulitic structures.[8,9] The scattering is a maximum at an azimuthal angle of 45° and at an angle θ_m between the incident and scattered beams related to the spherulite radius R by $4\pi(R/\lambda) \sin(\theta_m{}^0/2) = 4.1$, where $\theta_m{}^0$ is the angle measured within the sample (corrected for refraction by $\sin \theta_m{}^0 = \sin \theta_m/n$) and λ is the wavelength within the sample given by $\lambda = \lambda_0/n$ where λ_0 is the wavelength *in vacuo* and n is the refractive index of the film.

The pattern for the air-cooled acid in Figure 1a corresponds to $\theta_m{}^0 = 7° 30'$, which gives a spherulite radius of 2.1 μm. The air-cooled salt shows a scattered intensity which decreases monotonously with increasing scattering angle at ±45° azimuthal angles as is characteristic of scattering from anisotropic rods.[13] Spherulite scattering patterns approach these rodlike patterns as the spherulites become more imperfect as a result of incompleteness of shape[14] or of disorder of orientation of crystals within the spherulites.[15,16]

Photometric scans of the scattering as a function of θ are given in Figures 2a and 2b for the case of I_+ where $\psi_2 = \psi_1 + 90°$ at various values of ψ_1 (corresponding to the photographic variation at various values of the azimuthal angle μ). It is recognized that this definition of I_+ is an approximate one, but it is a good approximation at small values of θ. Contour plots of the scattered intensity are given in Figures 3a and 3b,

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TABLE I
SUMMARY OF LIGHT-SCATTERING STUDIES

Figure	Sample	Preparation	Type	θ_m	R, μm	Comments
1a	Acid	Air cooled	Picture	7° 30′	2.1	H_v spherulitic
1b	Salt	Air cooled	Picture			H_v rodlike
2a	Acid	Air cooled	Photometric	7° 0′	2.3	H_v spherulitic scans
2b	Salt	Air cooled	Photometric			H_v rodlike scans
3a	Acid	Air cooled	Contour plot	7° 1′	2.3	H_v spherulitic
3b	Salt	Air cooled	Contour plot			H_v rodlike
4a	Salt	Crystallized 0.5 hr	Picture	3° 40′	4.1	H_v spherulitic
4b	Salt	Crystallized 18 hr	Picture	3° 50′	3.9	H_v spherulitic
5	Salt	Crystallized 18 hr	Photometric	3° 40′	4.1	H_v spherulitic
6	Salt	Crystallized 18 hr	Picture			V_v spherulitic
7a	Salt	Crystallized 18 hr	Picture	3° 40′	4.1	H_v spherulitic, 0° elongation
7b	Salt	Crystallized 18 hr	Picture			H_v spherulitic, 25% elongation
7c	Salt	Crystallized 18 hr	Picture			H_v spherulitic, 50% elongation
7d	Salt	Crystallized 18 hr	Picture			H_v spherulitic, 105% elongation

in which the differences in the character of the scattering patterns are clearly seen. The data are presented as a function of the scattering angle in air and are uncorrected for reflection, refraction, and secondary scattering,[17] since these corrections are not of consequence for the qualitative considerations in this paper. The spherulite radius calculated from the maximum of the photometric plot of Figure 2a is 2.3 μm and is in close agreement with the value of 2.1 μm obtained from the photograph.

The intensity of the scattering from the ionomer is comparable with that from the acid, suggesting the presence of crystalline aggregates of comparable size, but the absence of a maximum intensity with θ at $\psi_1 = 45°$ indicates the absence of spherical symmetry in the arrangement of these superstructures. Consequently, we conclude that lamellar morphology persists but that these lamellae are disordered with respect to each other. In view of this conclusion, it is not surprising that the α crystalline mechanical loss peak, associated at least in part with interlamellae motion, is not seen.

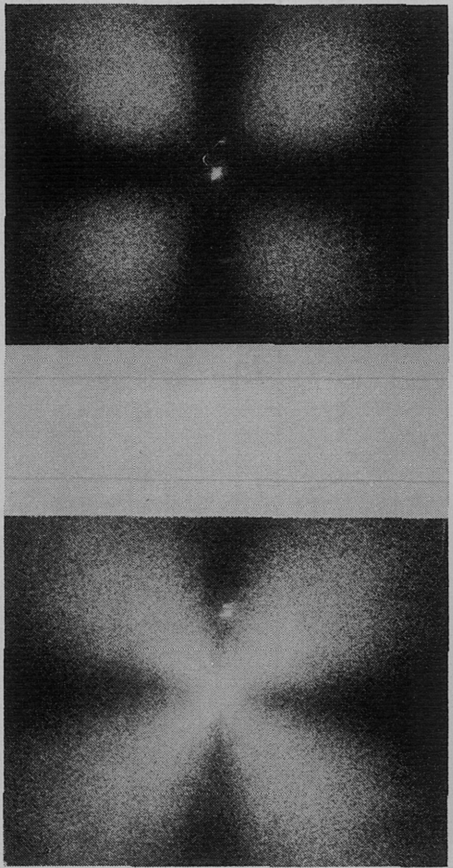

Figure 1. H_v scattering photographs for air-cooled samples of (a) un-ionized acid and (b) sodium salt.

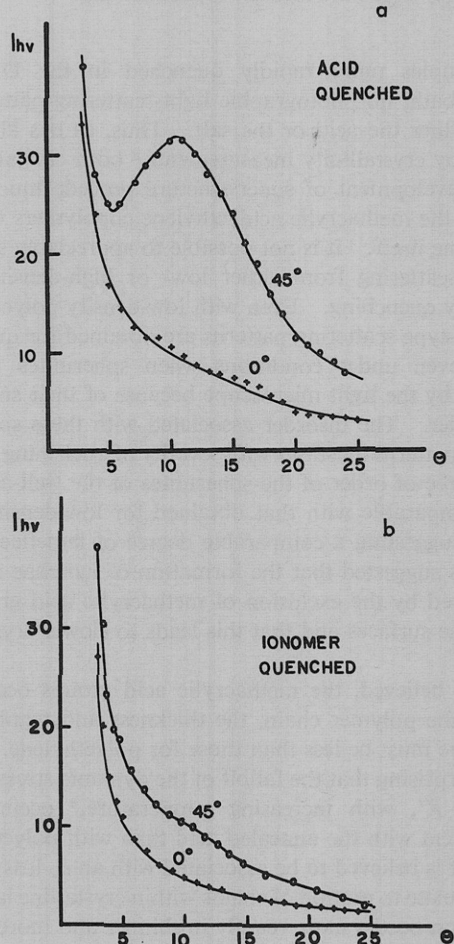

Figure 2. Photometric I_+ scans at $\psi_1 = 0$ and 45° for samples of (a) un-ionized acid and (b) sodium salt.

(17) R. S. Stein and J. J. Keane, *J. Polym. Sci.*, 17, 21 (1955).

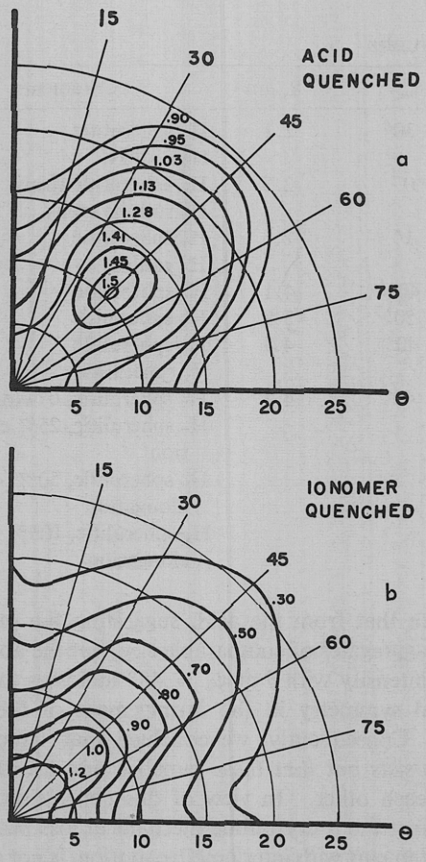

Figure 3. Contour plots of the I_+ light-scattered intensity for samples of (a) un-ionized acid and (b) sodium salt.

For samples more rapidly quenched in the Dry Ice–methanol bath, no photographic light-scattering patterns are seen for either the acid or the salt. Thus, as has also been indicated by crystallinity measurements,[6] both crystallization and the development of superstructure procede much more slowly for the methacrylic acid–ethylene copolymers than for polyethylene itself. It is not possible to appreciably suppress the light scattering from either low- or high-density polyethylene by quenching. Even with low-density polyethylene, spherulitic-type scattering patterns are obtained for quenched samples, even under conditions when spherulites are not resolvable by the light microscope because of their small size and disorder. The disorder associated with these spherulite scattering patterns increases with severity of quenching.

The degree of order of the spherulites of the well-annealed acid is comparable with that obtained for low-density polyethylene, suggesting a comparable degree of lamellae formation. It is suggested that the formation of lamellae must be accompanied by the exclusion of methacrylic acid groups to the lamellae surfaces and that this leads to slower crystallization.

If, as is believed, the methacrylic acid groups occur randomly in the polymer chain, the thickness and regularity of the lamellae must be less than those for polyethylene. Thus, it is not surprising that the falloff of the dynamic stress optical coefficient K', with increasing temperature,[3] occurs to a greater extent with the annealed acid than with polyethylene. This falloff is believed to be associated with an α_2 loss process which we relate to motion of chains within crystalline lamellae. Such motion occurs more readily in thinner and more imperfect lamellae.

We relate the greater suppression of superstructure formation in the ionized salt to postulated segregation of ionized carboxylic acid groups into "domains." Since the light-scattering results do indicate a lamellae morphology for the salt, it seems likely that these ionized regions must occur on the lamellar surfaces so that the ionized domains must be interlamellar. We feel that this morphology is more reasonable than are spherical domains. These present a spacial problem of organizing the ionized groups into a sphere which possesses enough surface area to accommodate the hydrocarbon parts of the molecule. A lamellar domain has a greater surface-to-volume ratio.

The results of photographic experiments for ionized samples slowly crystallized at 91° for 0.5, 2, 18, 63, and 70 hr indicate spherulite formation. It is noted that while the air-cooled samples exhibited rodlike morphology, these samples are definitely spherulitic, as illustrated by the H_v pictures for the 0.5- and 18-hr crystallized samples in Figure 4. The pattern for the 0.5-hr crystallized sample of Figure 4a has the "tennis-racquet" appearance described by Kawai, *et al.*,[18] characteristic of disordered spherulites with θ_m 3° 40′ and radius 4.1 μm, while the pattern for the 18-hr crystallized sample of Figure 4b has the four-leaf-clover appearance of a fairly perfect spherulite with θ_m 3° 50′ and radius 3.9 μm. A photometric scan for the 18-hr crystallized sample of I_+ at $\psi_1 = 0°$ and 45° is shown in Figure 5, which clearly shows the scattering maximum in the 45° plot.

Thus it is evident that with slow crystallization, even the ionized samples can develop well-organized spherulitic structure, confirming that these polymers can form lamellae. In Figure 6, the V_v photographic light-scattering pattern is presented which is also typically spherulitic.

The variation of the H_v scattering patterns with elongation

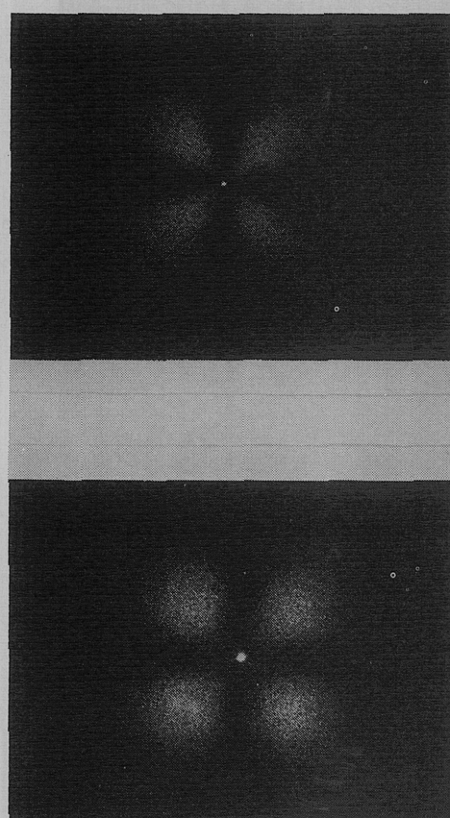
(a)
(b)

Figure 4. H_v scattering photographs for samples of the sodium salt crystallized at 91° for (a) 0.5 and (b) 18 hr.

(18) M. Motegi, T. Oda, M. Moritani, and H. Kawai, *Polym. J.*, 1, 209 (1970).

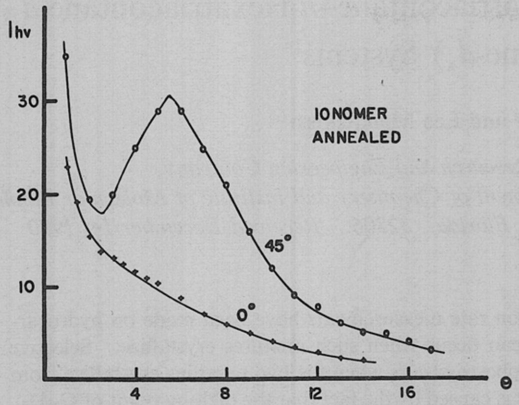

Figure 5. Photometric I_+ scans at $\psi_1 = 0$ and 45° for the sodium salt crystallized at 91° for 18 hr.

for the 18-hr crystallized ionized salt is shown in Figure 7 for samples uniaxially stretched at room temperature by 0, 25, 50, and 105%. The changes in patterns with elongation are typical of those previously observed for polyethylene[8] and polypropylene[19] and theoretically explained on the basis of the deformation of anisotropic spheres to ellipsoids.[19–21] A photometric measurement indicates, for example, that the intensity maximum for a 35% stretched sample is shifted toward the equator from an azimuthal angle of 45 to 55°.

Thus it is evident that the deformation mechanism of the annealed ionomer is affected by the spherulitic texture. The variation of the crystallite orientation functions described in a previous paper[6] is a consequence of the participation of the crystallite in this spherulite deformation process. It should be realized, however, that the mobility of crystals with respect to each other within the deforming spherulite depends upon the intercrystalline interaction which should depend upon the deformability of the interlamellar ionized regions.

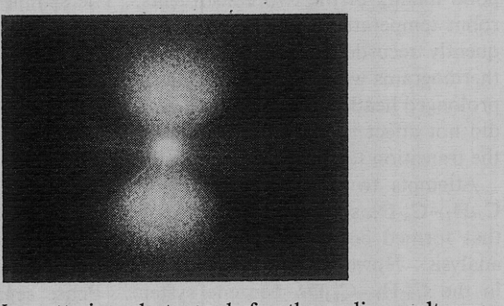

Figure 6. A V_v scattering photograph for the sodium salt crystallized at 91° for 18 hr.

(19) R. Samuels, *J. Polym. Sci., Part C*, **No. 13**, 37 (1966).
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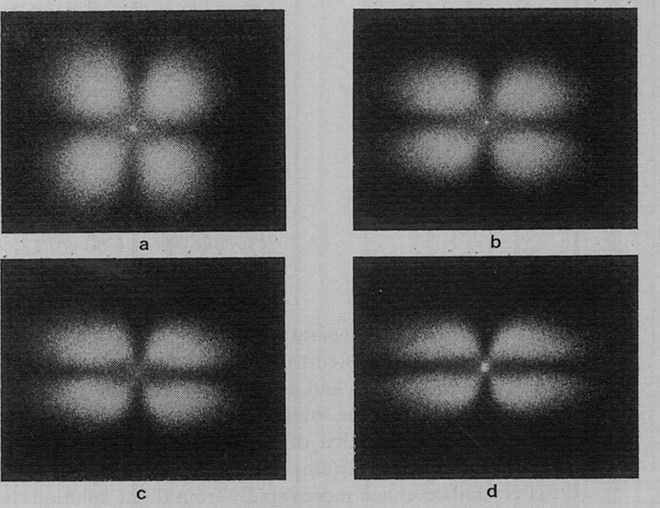

Figure 7. H_v scattering photographs for the 18-hr crystallized sample stretched (a) 0, (b) 25, (c) 50, and (d) 105%.

Such a dependency was evident in the previously reported studies of the temperature dependence of the change in X-ray orientation functions.[6]

It was hoped that this influence might be seen in the temperature dependence of the light-scattering pattern variation with deformation. Such a study was carried out by the photographic and photometric techniques, but no appreciable difference was seen on comparing changes in H_v scans upon deformation at 25 and 45°. It is planned to study this phenomena further by the dynamic light-scattering technique, which is more sensitive to changes on internal spherulite orientation accompanying spherulite deformation.[12,22]

Conclusions

The light-scattering studies have indicated that both the ionized and un-ionized forms of methacrylic acid–ethylene copolymers are lamellar in their morphology and, given enough crystallization time, the lamellae organize into spherulitic structures. With faster crystallization, these spherulites are disordered and, in the case of the ionized acid, degenerate into rodlike lamellar aggregates. The spherulites deform upon stretching samples in much the same manner as do spherulites of polyethylene.

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