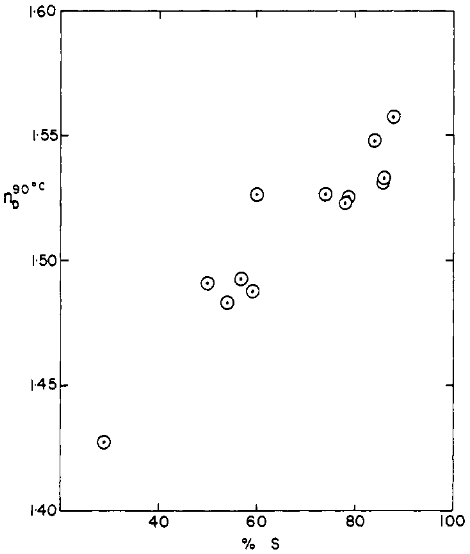

**Figure 3.** $n^{90}_{\mathrm{D}}$ vs. percent S in the S–DMS diblock copolymers. When $T_g$ of the S microphase was >90 °C, the $n^{90}_{\mathrm{D}}$ was extrapolated from data taken above $T_g$.

This increase in $|dn/dT|$ for $T > T_g$ of the block copolymer samples probably reflects the presence of the DMS in the block copolymers, especially since sample I29, the sample with the highest percent DMS, has the highest $|dn/dT|$, $T > T_g$.

It is tempting to try to use the refractive index values of these copolymers at a representative temperature as a method for determining their percent composition. But this will not work as can be seen in Figure 3, in which the points are the refractive indices of the block copolymers at 90 °C vs. percent S for all block copolymers with $T_g \leq$ 90 °C; for the five samples with $T_g >$ 90 °C, the high-temperature refractive index line was extrapolated back to 90 °C so that all refractive indices referred to fully rubbery polymers. As can be seen in Figure 3, there is only an imperfect correlation between $n^{90}_{\mathrm{D}}$ and percent S. There would be no improvement in this correlation if one picked $n^{30}_{\mathrm{D}}$, where all the S microphases are below their $T_g$. This imperfect correlation is exactly what should be expected since rubbery polymers have refractive indices that are quite molecular weight dependent. It was found previously that the refractive index of the PS standards above $T_g$ increased with molecular weight at each temperature,[3] reaching an asymptotic value at a molecular weight between $5 \times 10^4$ and $10^5$. In addition, although we found no molecular weight dependence for the refractive index of PS below $T_g$,[3] Fechner et al.[4] found a molecular weight dependence for the refractive index of PDMS up to a molecular weight $5.8 \times 10^4$ near room temperature, that is, well above the PDMS $T_g$. The molecular weight dependence of the refractive index of both PS and PDMS perturbs the correlation that may have been expected in Figure 3, while, at 30 °C, only the molecular weight dependence of the PDMS refractive index would perturb such a correlation. Therefore, at reasonable temperatures, refractive index cannot be used to determine percent composition in S–DMS diblock copolymers.

**Acknowledgment.** We thank the National Science Foundation, Polymers Program, for support of this study through Grant DMR 78-20774.

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# Optical Behavior and Polymorphism in Poly(ethylene sebacate). 1. Morphology and Optical Properties

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*Received July 13, 1981*

ABSTRACT: Depending upon crystallization temperature, poly(ethylene sebacate) crystallizes from the melt to form spherulites of three distinct types. Two of these, one unringed and one showing double extinction rings of the kind often found in spherulites of biaxial polymers, are comprised of crystals having the known monoclinic structure but with different preferred orientations. However, the third type, which shows uniformly spaced extinction rings, comprises crystals having a previously unknown structure. The new polymorph is metastable and, on heating, spherulites transform to the known stable form but with little visual evidence of the change other than a striking increase in magnitude of birefringence. The structure of this polymorph is closely related to that of the monoclinic form, and the transformation is accomplished without change in orientation of principal crystallographic axes. Optical properties of the two polymorphs have been studied in detail. It is shown that accurate alignment of the optic normal along the radius in double-ringed spherulites is the result of an averaging of electrical polarizabilities over two approximately equal populations of monoclinic crystals with opposite tilting of molecular chains with respect to the radius (a polymer analogue of mimetic twinning in simpler crystalline materials). Quantitative analyses of birefringences in ringed spherulites (including the change in birefringence accompanying transformation between the polymorphic forms) strongly reinforce the view, which has been challenged in some recent papers, that the crystallographic orientation averaged over neighboring lamellar crystals in these spherulites twists uniformly about the radius. Other properties of the new polymorph are described in a companion paper (part 2).

## Introduction

Linear aliphatic polyesters prepared by condensation of dibasic acids with ethylene glycol were among the first crystalline polymers to be subjected to systematic structural investigation by X-ray diffraction.[1-3] Members of the homologous series prepared from acids having an odd number of carbon atoms crystallize with orthorhombic unit cells, and those prepared from acids having an even number of carbon atoms crystallize with monoclinic unit cells. With the exception of poly(ethylene succinate), all share

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the features (a) that sequences of methylene groups deriving from the acid component exhibit planar zigzag conformations as found in polyethylene and (b) that as a consequence of distortion of glycol residues from planarity, axial repeat periods are about 0.5 Å shorter than values calculated for completely planar zigzag conformations of backbone chains. The most detailed structural investigation so far is that of Turner-Jones and Bunn for the adipate and suberate polyesters.[4]

Poly(ethylene adipate) was also chosen by Point[5] and by Takayanagi[6] as the subject of some of the earliest investigations of spherulitic morphology and crystallization kinetics in synthetic polymers by optical microscopic techniques. In an intermediate range of crystallization temperatures (approximately 25–40 °C, depending slightly upon molecular weight), Takayanagi observed the growth of double-ringed spherulites, that is, of spherulites exhibiting extinction rings which divide alternating wider and narrower annuli with birefringences of opposite signs. Above and below this temperature range, he found spherulites without rings showing uniformly positive birefringence in the first case and uniformly negative birefringence in the second. Point[5] recognized two of these forms and attributed the double-ringed extinction patterns to cooperative twisting of crystalline orientation about the radius and, specifically, to twisting of crystalline units of optically biaxial character about their optic normals which are aligned precisely parallel to the radius. Strong support for this interpretation was provided later by Keith and Padden,[7] who showed that modifications of the extinction patterns brought about by tilting spherulites on a Federow universal stage could be accounted for in detail on this basis.

Biaxial optical character is to be expected of crystals possessing orthorhombic or lower symmetry and, to the extent that cooperative twisting of orientation about the appropriate crystallographic axis might occur in spherulites of other aliphatic polyesters, one would again expect to encounter double-ringed extinction patterns. A number of such polymers (synthesized some years ago for NMR investigations by W. P. Slichter, who kindly made them available to the author) were recently examined as part of a different study[8] and, indeed, double-ringed spherulites were found in poly(tetramethylene adipate), poly(ethylene suberate), and poly(ethylene sebacate). In the case of poly(ethylene sebacate), however, ringed spherulites of a second kind were also observed. These spherulites, which were optically negative and exhibited uniformly spaced extinction rings, were quite reminiscent of the familiar ringed spherulites found in polyethylene. Ringed extinction patterns of this kind are usually found (in association with cooperative twisting of orientation) only in optically uniaxial polymers or in polymers whose optical characters are effectively uniaxial (biaxial with optic angle $V \sim 0°$). The occurrence of such patterns in some spherulites of poly(ethylene sebacate) was seemingly inconsistent with a twisting of biaxial crystalline units whose optic angle is quite large (approximately 40°, as could be judged from the roughly equal widths of positively and negatively birefringent bands in double-ringed spherulites of the same polymer). Their presence at once signaled the likely existence of an unsuspected crystalline polymorph of uniaxial or pseudouniaxial optical character. This was the starting point of the present investigation, which, for convenience, will be reported in two parts. In part 1, which follows, are described morphological characteristics and optical properties of various types of spherulite found in poly(ethylene sebacate). In a companion paper, part 2,[9] we shall discuss the stability and structure of a new polymorph in this polymer, including the influence of moisture in suppressing its nucleation.

## Experimental Section

As noted earlier, preliminary observations were made on a sample of poly(ethylene sebacate) that had been stored for some years. This was of relatively low molecular weight, as judged by optical melting point. Experiments described later were carried out on fresh material prepared by D. J. Freed and A. M. Mujsce using the acid chloride synthesis as described by Billmeyer and Eckard.[10] This fresh polymer was purified by dissolution in methyl ethyl ketone and reprecipitation in methanol, followed by drying in a vacuum oven at 75 °C; its number-average molecular weight as determined by gel permeation chromatography was $M_n \sim 19000$.

Specimens for optical microscopic examination were melted briefly on or between glass cover slips on a hot plate at 150 °C and transferred to a Mettler FP52 microscope hot stage for crystallization at preset temperatures. Thin films for electron microscopic examination were deposited on freshly cleaved mica from a 0.1% solution of the polymer in methyl ethyl ketone and, when dry, melted and crystallized in the same manner; they were then shadowed at arctan (1/2) using Pt/C, coated with carbon, floated on water, and collected on a copper screen from which suitable areas were subsequently punched out as 3-mm disks. Thicker specimens (~0.5 mm) for X-ray diffraction studies were melted and crystallized on pieces of Kapton polyimide film from which they separated easily when cold. These were examined by using either a Guinier-de Wolff focusing powder camera of nominal radius 5.7 cm or a Rigaku vertical X-ray diffractometer, Cu K$\alpha$ radiation being employed in both cases.

## Observations

**Spherulitic Morphology.** Three distinct growth regimes are found in poly(ethylene sebacate) depending upon crystallization temperature ($T_c$). However, the corresponding temperature ranges are not sharply delineated. Below 50 °C, the polymer forms densely nucleated negatively birefringent spherulites exclusively. These are usually less than 40 $\mu$m in diameter and show no extinction features under the polarizing microscope other than Maltese crosses. X-ray powder patterns and selected-area electron diffraction patterns obtained from these spherulites are both consistent with the known monoclinic crystal structure,[11,12] the latter also indicating radial orientation of the *b* axis of the unit cell. Electron microscopy shows a finely textured lamellar morphology, which becomes more disordered with lower crystallization temperatures. Spherulites of this type, which we shall call type I, exhibit no unusual features and were not studied extensively.

As crystallization temperature is increased from 50 to 54 °C, type I spherulites become less common, and increasing numbers of small, negatively birefringent, ringed spherulites of the kind mentioned previously (type II) are formed. These type II spherulites grow up to 59 °C, but above about 57 °C they are found increasingly in admixture with double-ringed spherulites. Specimens crystallized at 56 °C consist exclusively of type II spherulites and were used for most of the further studies of these structures. The ring spacing is 2.1 ± 0.1 $\mu$m ($T_c$ = 56 °C) and the general appearance of the spherulites is as shown in Figure 6. Electron microscopy (Figure 1) shows these spherulites to consist of lamellar crystals not more than 100 Å thick and with a periodicity in orientation, corresponding to the optical ring spacing, indicative of a twisting of averaged crystallographic orientation about the radius. This morphology is very similar to that found in polyethylene, though less well ordered. X-ray powder patterns and selected-area electron diffraction patterns clearly indicate that these type II spherulites possess a crystallographic structure different from, though closely related to,

Table I
X-ray Powder Diffraction Data (Spacings in Å)

| | poly(ethylene sebacate) | | | | polyethylene | |
|---|---|---|---|---|---|---|
| | $T_c = 0$ °C[a] | $T_c = 56$ °C | $T_c = 63$ °C | calcd[b] | | |
| 001 | 14.90 | 14.75 m-d[c] | 14.95 m-d | 15.13 | | |
| 002 | | | 7.49 vw-d | 7.56 | | |
| $01\bar{1}$ | 6.60 | | 6.60 w | 6.58 | | |
| $11\bar{1}$ | 4.47 | | 4.41 m | 4.42 | | |
| $11\bar{2}$ | 4.32 | ~4.30 m | 4.32 mw | 4.34 | | |
| 110 | 4.16 | 4.17 vs-sd | 4.15 vs-sd | 4.15 | 110 | 4.13 vs |
| 020 | 3.66 | 3.80 mw-d | 3.66 s | 3.66 | 200 | 3.71 vs |
| ? | | 3.25 w | | | | |
| 005 | 3.01 | 3.03 w | 3.02 w | 3.03 | | |
| 120 | 2.95 | 2.96 mw-d | 2.96 mw | 2.96 | 210 | 2.97 m |
| 200 | 2.52 | $2.50_5$ mw | 2.52 w-d | 2.52 | 020 | 2.48 s |
| 130 | 2.19 | ~2.20 w-d | 2.19 m | 2.19 | 310 | 2.22 m |

[a] Intensities for these samples are essentially the same as for those crystallized at 63 °C. [b] Calculated from the unit cell of Kanamoto et al.[12] [c] vs = very strong, s = strong, m = medium, mw = medium weak, w = weak, vw = very weak, sd = slightly diffuse, d = diffuse.

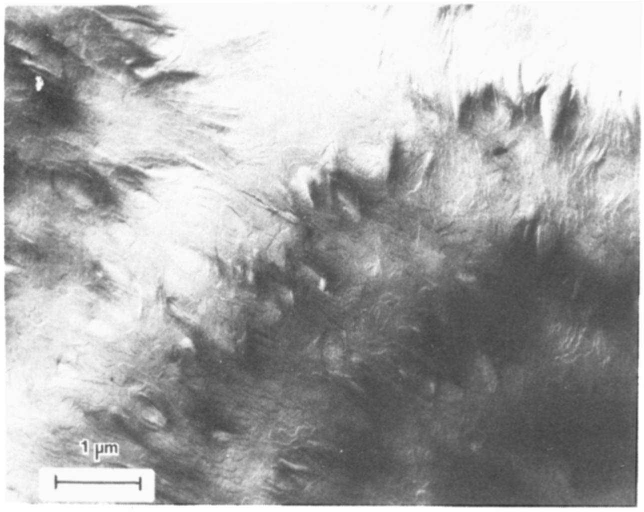


**Figure 1.** Electron micrograph of a boundary between two spherulites of type II (new polymorph).

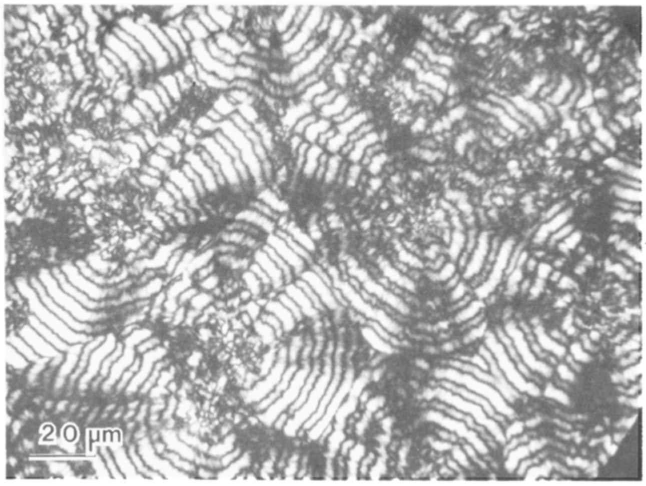


**Figure 2.** Optical micrograph of type III spherulites as viewed between crossed polarizers.

the known monoclinic structure. These aspects will be discussed in detail later.

Above 56 °C, and exclusively above 59 °C, the polymer forms spherulites in which the crystalline phase again has the known monoclinic structure. These are the double-ringed spherulites (type III) also referred to earlier and shown in Figure 2, for which electron microscopy again indicates twisting of orientation of lamellar crystals about the radius (see later, Figure 4). Primary nucleation being less dense at higher crystallization temperatures, these spherulites often achieve quite large radii (~50 μm). The ring structure rapidly becomes less clearly discernible in spherulites grown at temperatures above 66 °C. Above approximately 69 °C, spherulites are formed which have a patchy appearance with mixed sign of birefringence. These appear to differ from ringed type III spherulites only in that cooperativeness of the twisting of orientation breaks down progressively at higher crystallization temperatures and twisting may eventually cease; they do not represent introduction of a new regime involving a change either in crystal structure or in preferred crystallographic orientation.

**X-ray and Electron Diffraction.** Table I lists lattice spacings and relative intensities of reflections derived from X-ray powder patterns of samples crystallized at 0 (quenched in ice water), 56, and 63 °C and containing spherulites of types I, II, and III, respectively. Also shown for comparison are data obtained from crystals of linear polyethylene grown from dilute solution in xylene. First, it will be noted that patterns obtained from type I and type III spherulites are identical and can be indexed satisfactorily on the basis of the monoclinic unit cell ($a = 5.58$ Å, $b = 7.31$ Å, $c = 16.76$ Å, $\beta = 115.5°$) reported by Kanamoto et al.[12] Also evident is a close correlation between the *hk*0 spacings of this structure and corresponding *kh*0 spacings of polyethylene;[23] this reflects, in turn, a close similarity in chain-axis projections of the two structures, as will be discussed later in part 2. The crystal structure in type II spherulites is clearly different from that found in types I and III and represents a distinct polymorphic form. The most notable differences with respect to the known structure are (a) a striking reduction in intensity combined with appreciable broadening of the 020 reflection and its displacement from 3.66 to 3.80 Å, (b) a corresponding but less marked increased in intensity and sharpness of the 200 reflection, which is displaced slightly from 2.52 to 2.50 Å, and (c) disappearance of the moderately strong $11\bar{1}$ reflection at 4.4 Å, offset by appearance of a new reflection of appreciable intensity at 3.25 Å. Nevertheless, the two structures are closely akin, since *hk*0 reflections are essentially unchanged in position and, within experimental error, the long spacing, $d_{100}$, corresponding to $c \sin \beta$, is also unchanged.

It is already clear from these results that the polymorph might well be described by a monoclinic unit cell similar to that of Kanamoto et al. but in which the dimensions

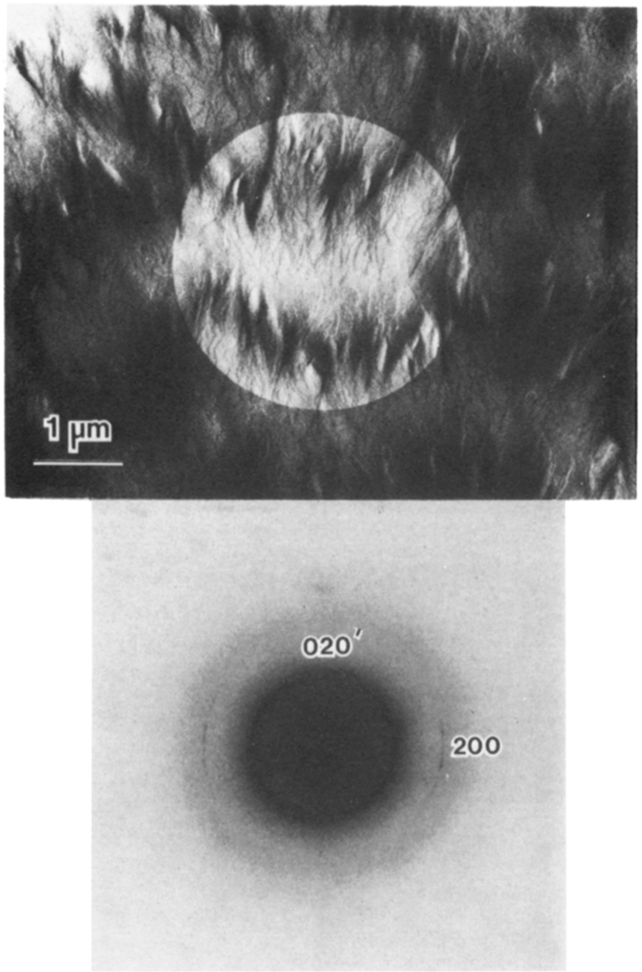


**Figure 3.** Selected-area electron diffraction pattern from a portion (circular area in micrograph) of a type II spherulite. The radius is vertical and the prime draws attention to the weak diffuse 020 reflection from the new polymorph as contrasted with strong sharp 020 reflections from the stable form (see Figures 4 and 5).

of the *c*-axis projection are increased by 3.8% in the *b* direction and decreased by 0.6% in the *a* sin *β* direction. Assuming no significant change in length of the *c* axis, as seems likely since *c* sin *β* is unchanged, this would imply a crystalline density approximately 3% less than that of the known polymorph. Such a density difference had already been suspected from optical microscopic examination of growing spherulites in which it could be seen that there is perceptibly less flow of melt around and between growing spherulites of type II than is the case with spherulites of type III. In the absence, as yet, of a complete structural analysis of the new polymorph, it is convenient for the moment to index reflections in terms of the monoclinic unit cell tentatively suggested above ($a = 5.55$ Å, $b = 7.60$ Å, $c = 16.76$ Å, $\beta = 115.5°$), even though this may later prove incorrect and may not accurately reflect the symmetry of the structure. For reasons to be substantiated later in part 2,[9] we shall refer to this in the following as the metastable polymorph, and to the previously known monoclinic form as the stable polymorph.

Selected-area electron diffraction patterns from type I spherulites are essentially the same as that shown in Figure 5 and, as mentioned earlier, indicate radial orientation of the *b* axis of the stable polymorph. Markedly evident is the dominance, from the standpoint of intensity, of reflections from {020} and {110} planes, particularly relative to those from {200} planes. Figure 3 shows an electron diffraction pattern, and the field from which it was obtained, for a spherulite of type II. Preferred orientation in regions thick enough to show ringed structure in such spherulites is always poor, reflections from {110} planes being sufficiently arced to form a closed ring. Weak and diffuse 020 reflections are seen on the meridian and sharp 200 reflections on the equator (relative to the radius of the spherulite as axis), both agreeing in spacing with corresponding X-ray reflections from the metastable polymorph.

Figure 4 shows three electron diffraction patterns recorded successively from the same area of a ringed spherulite of type III in which crystalline lamellae lie es-

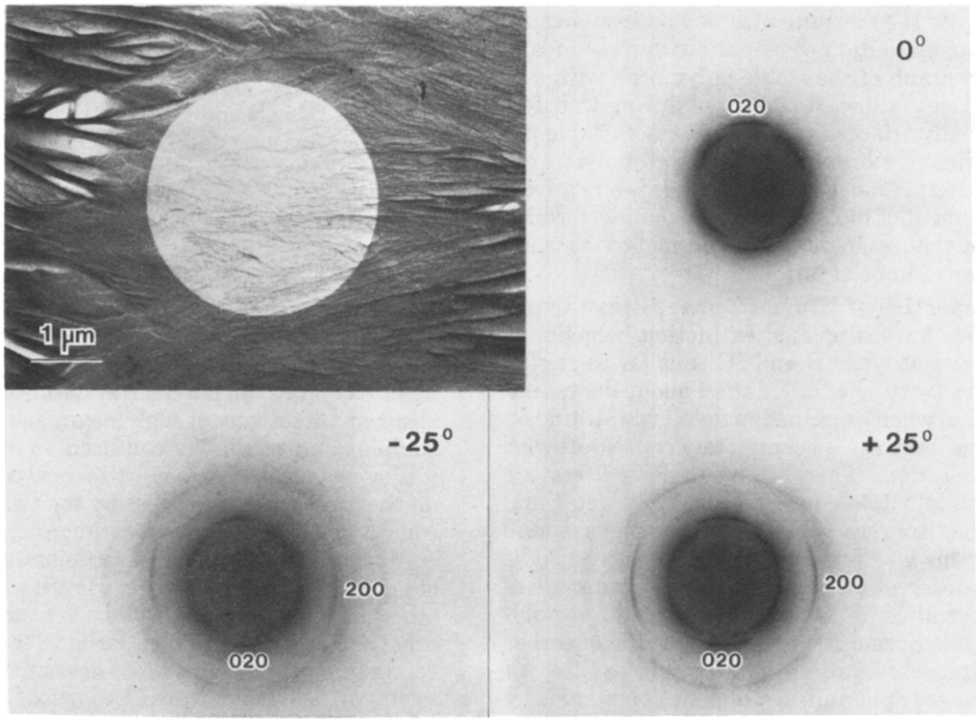


**Figure 4.** Selected-area electron diffraction patterns taken sequentially from the same area in a double-ringed type III spherulite. The radius is horizontal and the angles denote tilts of the specimen about a tangential [020] axis.

sentially flat in the plane of the specimen. The pattern denoted 0° was obtained with the specimen plane normal to the electron beam (zero tilt) and the strong sharp reflections designated 020 clearly show tangential orientation of the *b* axis of the stable polymorph. Four strong inner reflections corresponding in spacing to {110} planes are also seen; yet there is no clear indication of 200 reflections along the radial axis, the two weak reflections just discernible corresponding in spacing to $20\bar{2}$ and/or $20\bar{3}$ (whose calculated spacings are virtually identical, 2.774 and 2.782 Å, respectively). Since the *a* axis of the unit cell passes about midway between $20\bar{2}$ $20\bar{3}$ lattice points in the reciprocal lattice (these being close together owing to the long fiber repeat), it seems likely that the *a* axis is oriented radially, in which case the $a^*$ axis in the area under consideration would be raised from the plane of the specimen by 25.5° $(\beta - 90°)$. This is confirmed by the two patterns obtained by tilting the specimen about the *b* axis by ±25°. 200 reflections along the projection of the radial direction are seen in both cases, and with approximately equal intensity, indicating roughly equal populations of crystals oriented with $+a$ and $-a$ axes directed radially. This orientation is consistent with lamellae having the same growth habit, elongated along the *a* axis and with (001) as the broad (fold) surfaces, as found by Kanamoto et al.[12] in single crystals grown from dilute solution. In such crystals, the chains are tilted by approximately 25° from the normal to the plane of the lamellae. The presence of comparable populations of crystals with opposite directions of chain tilting will be discussed more fully later in relation to the optical properties of ringed type III spherulites. The appearance of 110 arcs in the zero-tilt pattern (Figure 4) probably reflects their inherently very strong intensity in combination with some spread in preferred orientation, and possibly some contribution from $(11\bar{2})$ and equivalent planes which have almost the same spacing as (110).

It is convenient to mention here, in anticipation of later discussion, that when heated to temperatures in the range 70–74.5 °C, the metastable polymorph undergoes a transformation to the stable polymorph. Figure 5 shows an electron diffraction pattern obtained from a relatively thin area of a type II spherulite after it had been heated to effect this transformation. The pattern corresponds to a rotation photograph of the stable polymorph with *b* as the rotation axis and shows further that during transformation the radially oriented *b* axis of the metastable polymorph becomes the *b* axis of the stable polymorph. During the transformation, apparently, there is a relatively minor rearrangement of molecules within a unit cell which undergoes slight changes in dimension normal to the chain axis but no change in orientation.

**Optical Properties of Ringed Spherulites (Types II and III).** We have discussed extinction behavior in ringed spherulites of types II and III thus far as arising from cooperative twisting of orientation about the radius, and this behavior, when examined in detail with tilting on a Federow universal stage, is completely consistent with such an interpretation. There is an extensive literature dating from the late 1950s (see, for example, ref 7 and 13–15 and other sources cited there) laying a sound foundation for this interpretation. Mention may also be made of direct observation by Fujiwara of twisting orientation in spherulites of polyethylene[16] and $\beta$-polypropylene[17] by microbeam X-ray diffraction and of earlier direct conoscopic observation of a similar twisting of orientation in ringed spherulites of organic compounds by Wallerant.[18] Nevertheless, occurrence of such twisting in ringed polymer spherulites (for which a satisfactory mechanistic explanation, admittedly, is still lacking) has been called in question quite recently. A model in which lamellar crystals undergo wavy distortions back and forth about a mean orientation has been suggested[19] to supplant the commonly held view that these crystals twist fairly uniformly over appreciable lengths, at least several ring spacings. Bassett and Hodge, on the other hand, while not doubting a twisting of orientation, have presented evidence suggesting that in polyethylene spherulites the orientation of lamellar crystals about the radius changes progressively in abrupt steps rather than continuously.[20] Other evidence exists, however, which appears to conflict with this (see, for example, Figure 6 of ref 21) or, at least, to imply that the behavior they describe is not the general case.

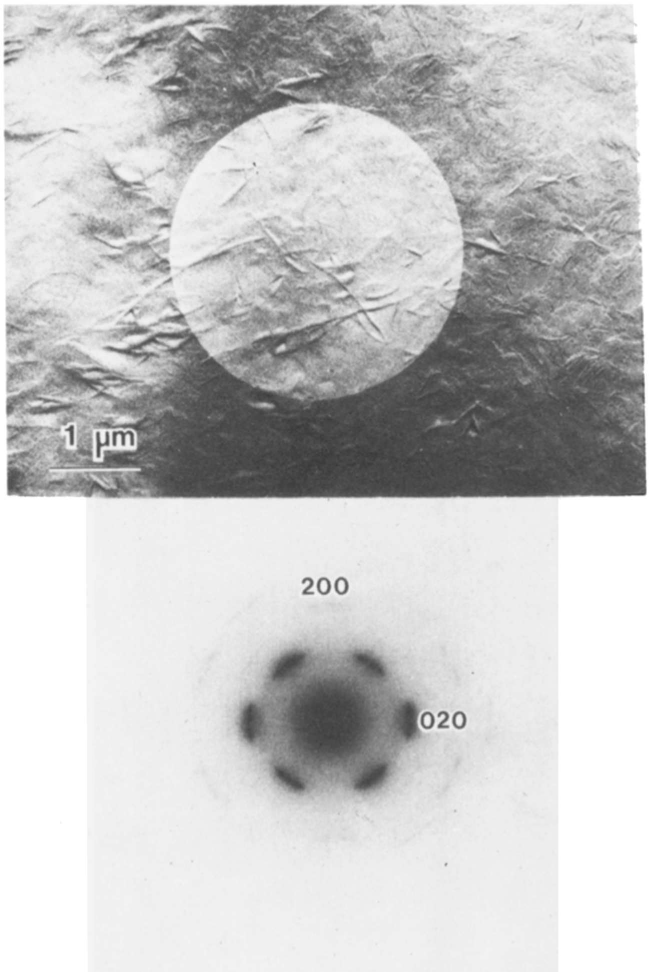
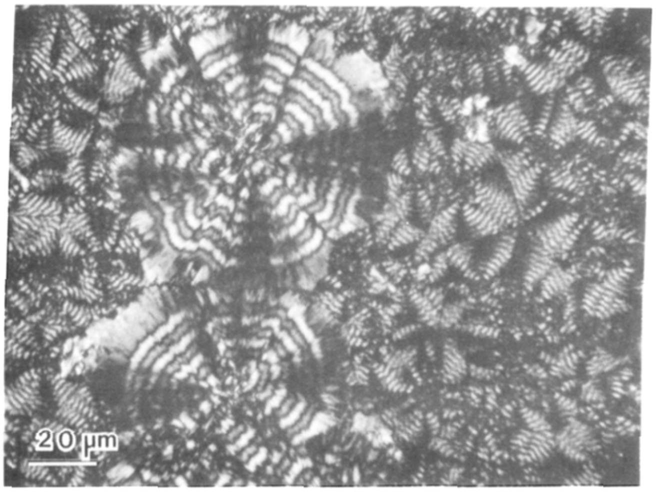


**Figure 5.** Selected-area electron diffraction pattern from a type II spherulite after transformation to the stable form at elevated temperature. The radius is horizontal.

In these contexts, the following comments may be made. It is now abundantly evident that the disposition of lamellar crystals in polymer spherulites, as revealed by electron microscopy at high magnification, is exceedingly complex and seemingly confused. Viewed on this scale, it is by no means easy to visualize how cooperative ordering on the grosser scale implied by the twisting model could come about. Nevertheless, extinction patterns calculated on the basis of this model, and assuming *uniform* twisting of orientation, conform in detail with what is observed (no other model permits this). This agreement, together with other evidence mentioned earlier, leaves no doubt that crystalline orientation, *when averaged over volume elements of the size sampled by optical microscopy or microbeam X-ray diffraction*, does, indeed, twist uniformly. How this should be interpreted in terms of distortions from a



b

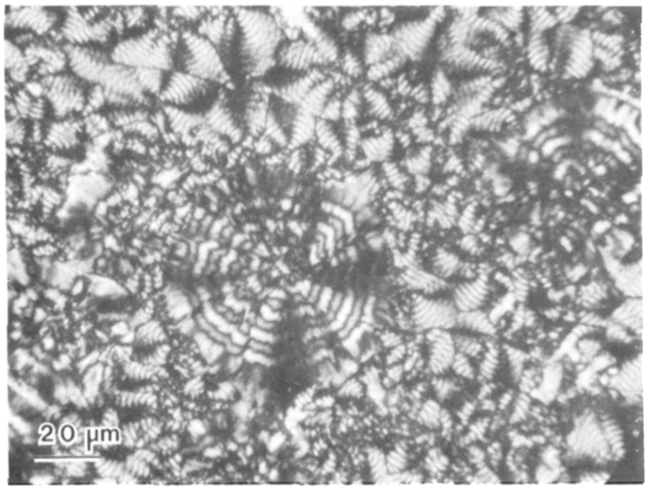


**Figure 6.** (a) Field comprising double-ringed spherulites (type III) grown at 63 °C surrounded by ringed negative spherulites (type II) subsequently grown at 56 °C by abrupt lowering of temperature. (b) Field as in (a) but photographed after transformation of type II spherulites to the stable form. Note the marked increase in birefringence which accompanies the transformation. Polarizing optical micrographs.

planarity in individual crystals and of relative dispositions of neighboring crystals, however, is a question that still remains to be more clearly resolved.

**Quantitative Measurement of Birefringences.** Conveniently for the ensuing discussion, Figure 6a shows in the same field spherulites of type III grown at 63 °C and spherulites of type II obtained by decreasing temperature abruptly to 56 °C during the course of crystallization. It will be noted that while the temperature was changing, type III spherulites underwent accelerated growth but seemingly with a cessation of cooperative twisting; this puzzling phenomenon is remarkable in that type III spherulites grown isothermally at temperatures down to 59 °C form rings in the usual way with, if anything, slightly smaller ring spacings. The broader, brighter bands in type III spherulites are negatively birefringent and the narrower, darker bands are positively birefringent; assuming uniform twisting of orientation, this implies that the indicatrix of the stable polymorph is biaxial positive with an optic angle $V = 40 \pm 2°$, as measured from the relative widths of these bands.

Using an Ehringhaus compensator to measure optical path differences, the ratio of the absolute magnitudes of maximum birefringences at the centers of the negatively and positively birefringent bands is 1.75 ± 0.01. (Careful focusing of the microscope is needed to judge compensation of these maximum birefringences accurately.) The corresponding ratio between maximum birefringences in negatively birefringent bands of type III spherulites and in negatively birefringent type II spherulites is 0.88 ± 0.01 (the qualification "maximum" has additional meaning here in that birefringence tends to be variable in type II spherulites, though whether this reflects variations in crystallinity or in degree of preferred orientation is uncertain). Radial repeat periods of the ringed patterns (corresponding to twisting by 180° about the radius) are 2.1 ± 0.1 μm for type II and 7.5 ± 0.2 μm for type III spherulites grown at 56 and 63 °C, respectively. These twist periods increase with crystallization temperature as is commonly (though not invariably) the case in polymer spherulites; in this instance, however, the variation is scarcely noticeable, corresponding to the limited range of temperatures over which the ringed spherulites are formed. There is a more marked *inverse* variation with molecular weight, since twist periods for spherulites of types II and III grown in the lower molecular weight sample used in preliminary studies were approximately 3 and 15 μm, respectively. Such an inverse dependence of twist period upon molecular weight in spherulites of a given type appears to be a general rule in ringed polymer spherulites.[8]

The axis about which twisting occurs in type III spherulites is clearly parallel to the optic normal, that is, to the intermediate principal axis of the indicatrix, which necessarily lies orthogonal to the optic axes. Denoting the principal refractive indices of the stable polymorph by $N_3 > N_2 > N_1$, the maximum birefringences mentioned above for negatively and positively birefringent bands would then be proportional to $N_2 - N_3$ and $N_2 - N_1$, expressed algebraically. These birefringences cannot easily be measured as accurately as the ratio between them (owing to experimental error in measuring thickness of a thin film); we have determined the following values: $N_2 - N_3 = -0.034 \pm 0.003$, $N_2 - N_1 = 0.019 \pm 0.001$, no allowance being made for incomplete crystallinity. In a similar fashion, we find for type II spherulites a maximum birefringence −0.038 ± 0.003.

Figure 6b shows a specimen prepared exactly as that in Figure 6a but subsequently heated at 1 °C/min from 56 to 74 °C and maintained at that temperature for 10 min to ensure complete transformation of the metastable polymorph in type II spherulites to the stable form. (Fuller details of this transformation will be described in part 2.) Apart from a scarcely perceptible decrease in definition and darkness of extinction in the rings, the transformation is accomplished without apparent change in morphology. There is, however, a striking increase in magnitude of the negative birefringence. This is quite evident in comparing the brightness of type II spherulites in Figures 6a and 6b and using the birefringence of type III spherulites as reference. Careful measurement of ratios of birefringence in such specimens, as well as direct measurements on particular type II spherulites chosen for observation in the same specimen before and after transformation, agree in showing that the negative birefringence increases in the ratio 1.35 ± 0.01.

**Consistency of Optical Properties with the Model of Uniformly Twisting Averaged Orientation.** For a biaxial positive indicatrix, optic angle and principal refractive indices are related by $n_2 = n_1 \cos^2 V + n_3 \sin^2 V$, where $n_i = 1/N_i^2$.[7] This can be rearranged to yield

$$\cos^2 V = \frac{N_3 - N_2}{N_2 - N_1}\,\frac{N_2 + N_3}{N_1 + N_2}\left(\frac{N_1}{N_2}\right)^2$$

The first factor on the right has been measured as 1.75 and the two remaining factors, each close to unity, can be estimated with very little error from the measured birefringences noted earlier and from an assumed reasonable value for $N_3$. We have chosen $N_3 = 1.55$, and the value of $N_\parallel$ for oriented polyethylene fibers, and, on this basis, we calculate $V = 37.7°$, quite close to the value 40 ± 2° measured from ring widths. Again, we have seen earlier that the maximum birefringence of type II spherulites has the value $(N_3 - N_2)/0.88$, $N_3 - N_2$ being the maximum negative birefringence in type III spherulites. After transformation to the stable polymorph, the maximum birefringence of type II spherulites should be $N_3 - N_1$, since the $b$ axis is now radial. Assuming no change in crystallinity, the increase in the magnitude of birefringence during transformation should be in the ratio $R = 0.88(N_3 - N_1)/(N_3 - N_2) = 0.88\{1 + (N_2 - N_1)/(N_3 - N_2)\}$. The measured ratio $(N_3 - N_2)/(N_2 - N_1)$, as we have seen, is 1.75, giving $R = 1.38$. This agrees remarkably well with the measured ratio 1.35.

**Relation between Orientations of Indicatrix and Unit Cell. A. Type III Spherulites.** The only symmetry rule applicable to optical properties of monoclinic crystals is that the unique axis ($b$) of the unit cell must be parallel to one principal axis of the indicatrix. In type III spherulites, this places one such axis in the tangential plane, in which the acute and obtuse bisectrices of the indicatrix, that is, the directions of the greatest and least electrical polarizability at optical frequencies, must also lie. Inspection of the likely chain-axis projection of the stable polymorph (see later, Figure 4 of part 2[9]) shows that polarizability along the $b$ axis is almost certainly less than along the $a^*$ direction. We must suppose, therefore, that $b$ corresponds to the obtuse bisectrix (axis of least polarizability and smallest refractive index, $N_1$). On this basis, then, the acute bisectrix (axis of greatest polarizability and largest refractive index, $N_3$) would lie along $c^*$, and the optical normal along $a$.

However, this cannot be a satisfactory identification of axes for an individual single crystal. This may be seen by reference to the diagram in the upper left of Figure 7 showing a side elevation of a chain-folded single crystal of poly(ethylene sebacate); axes of both the real and reciprocal unit cells are indicated, $b$ and $b^*$ being perpendicular to the page. If we suppose, for the moment, that the tilted molecular stems are of polyethylene (without ester linkages), then the $N_3$ and $N_2$ axes would obviously lie parallel to $c$ and $a^*$, respectively. Introduction of ester linkages in (001) planes increases polarizability along the $a$ axis but causes $N_3$ and $N_2$ to rotate about $b$ only *part way* toward $c^*$ and $a$; rotation into the $c^*$ and $a$ directions would require the polarizability of ester linkages along $a$ so to dominate that along $c$, the chain axis, that the $a$ axis would then correspond to the largest refractive index, $N_3$, which is clearly not the case. We therefore show the principal refractive indices of the single crystal, $N_3^{(c)}$ and $N_2^{(c)}$, at angles $\phi$ with respect to $c$ and $a^*$, $\phi$ being undetermined but probably ~5°.

The diagram at the lower left of Figure 7 shows the same situation in mirror image for a crystal with oppositely directed $a$ axis and chain tilt. The significance of our earlier observation (Figure 4) of roughly equal populations of crystals with $\pm a$ axes directed radially in type III spherulites is now evident. If these lamellar crystals are interleaved in either a regular or a random manner, the optical properties of the spherulites will be determined by an averaged indicatrix, as shown at the right of Figure 7, in which $N_3$ lies along $c^*$, the common lamellar normal, and $N_2$ lies along the radius. The third principal refractive index, $N_1$, is tangential as before and accurately reflects the corresponding refractive index of each individual crystal, i.e., $N_1^{(c)} = N_1$. Using established methods,[7] one can relate the optic angle of the single crystal, $V^{(c)}$, to the measured optic angle $V$ of the averaged indicatrix by $\cos^2 V^{(c)} = \cos^2 V/\{\sin^2(\beta - \phi) - \cos^2(\beta - \phi)\sin^2 V\}$. $V^{(c)}$ varies from 26.9° for $\phi = 0$ to 36.1° for $\phi = 10°$; for $\phi = 5°$, $V^{(c)} = 32.6°$, probably fairly close to the real value.

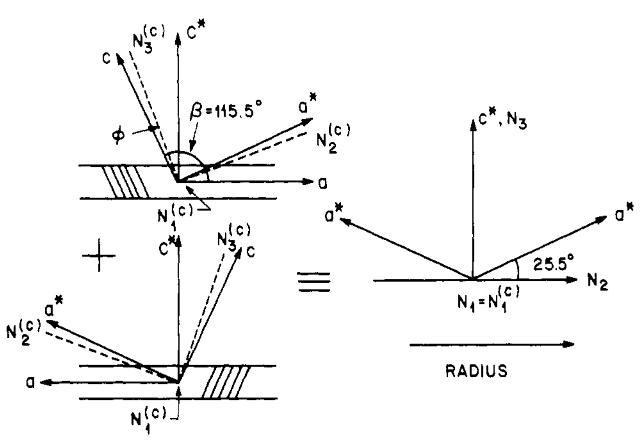


**Figure 7.** Diagram illustrating assignment of crystallographic axes and directions of principal refractive indices in crystals with oppositely directed $a$ axes, and the directions of principal refractive indices in the effective (averaged) indicatrix which determines optical properties of an ensemble comprising crystals of both kinds in approximately equal numbers.

Representation of the optical properties of these spherulites by an averaged indicatrix calls for some comment. In a formal sense, the sum of two symmetric second rank tensors (the indicatrix is the ellipsoid representation of such a tensor) is still a tensor of the same kind. However, for this to have physical meaning in the present context, the electrical polarizabilities which are being averaged over the crystal population must vary on a scale small with respect to the wavelength of light, a condition seemingly met adequately. What is surprising, perhaps, is how close, in contributing to the average, is the compensation between crystals with each of the two orientations. Even in the thinnest films in which birefringence can be seen in type III spherulites, extinction patterns show very close alignment of the averaged optic normal along the radius. This is apparent from the fact that when radial crystalline fibers are oriented accurately normal to the axis of the polarizing microscope, extinction rings intersect the arms of the extinction cross orthogonally in a simple fashion. Such orthogonality is not usually seen in thicker films as shown in Figures 2 and 6, however, because of appreciable inclinations (whose cause is well understood[7]) of radial fibers with respect to the specimen plane; nevertheless, the resulting zigzag intersections reduce to the simpler orthogonal condition when the films are tilted to bring the axes of radial fibers at the region being examined into the plane of focus. If there were a slight perponderance of crystals with one direction of chain tilt sufficient to cause the optic normal to be inclined to the radius by a small angle, 2° say, extinction behavior would be as in Figure 8. This could easily be distinguished from what, in fact, is observed. The populations of crystals of

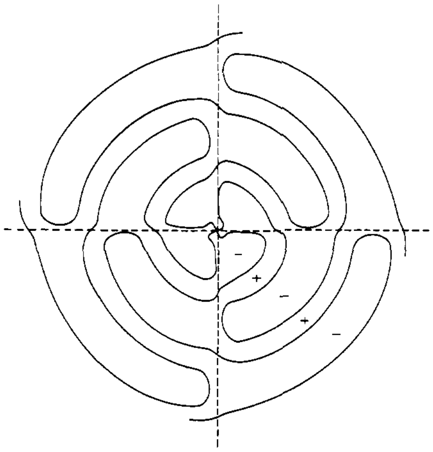


**Figure 8.** Computed extinction pattern for a spherulite with uniformly twisting orientation in which the optic normal makes an angle of 2° with respect to the radial axis of twist. The indicatrix is taken to be biaxial positive with $V = 30°$. Note the loops which come within 2° of the pass directions of polarizer and analyzer.

the two kinds must be very close indeed to being equal; there may be statistical fluctuations in population assuming equal a priori probabilities but no perceptible bias in a given region in favor of one kind of crystal or the other.

This point has some significance because, if lamellar crystals proliferate during growth through the agency of screw dislocations, as in commonly believed, the sense of chain tilt in a parent crystal ought to be preserved unchanged in new crystals branching from it. Progressive branching might then be expected to give rise to sector-shaped domains comprising a preponderance of crystals with one or other direction of chain tilt. Since this is clearly not the behavior observed, we infer either that intimately interleaved crystals of both kinds are produced at the outset as might, for example, occur with heterogeneous primary nucleation or that proliferation (branching) of radial crystals is a more complex process than currently realized.

Whatever the underlying causes, presence in roughly equal numbers of crystals with opposed directions of chain tilt results in an apparent symmetry not necessitated by crystallographic rules for monoclinic crystals. This is reminiscent of mimetic twinning such as occurs in potassium chlorate in which repeated reflection twinning on a submicroscopic scale causes an apparent increase in symmetry from monoclinic to orthorhombic.[22] An identical situation exists in poly(ethylene adipate) (probably in double-ringed spherulites of other "even" linear aliphatic polyesters as well) in which precise radial orientation of the optic normal is not a direct consequence of symmetry rules, an observation noted many years ago but not before understood.[7] Presence in this polymer of crystals with opposed radial orientation of *a* axes has been confirmed by means of an experiment exactly parallel to that illustrated in Figure 4. It is obvious that similar averaging of optical properties could also arise in other polymers of monoclinic or triclinic symmetry and should be borne in mind when interpreting their optical behavior.

**B. Type II Spherulites.** At the outset, we pointed out the resemblance between extinction behavior in type II spherulites and in spherulites of polyethylene, leading to the preliminary conjecture that the metastable polymorph of poly(ethylene sebacate) is effectively uniaxial. This assessment needs further consideration. First, it is clear that after transformation to the stable polymorph, type II spherulites cannot be comprised of uniaxial crystals, yet they also exhibit similar extinction patterns. The optical properties of these spherulites are presumably governed by an averaged biaxial indicatrix with principal axes $N_1$, $N_2$, and $N_3$ as before but with $N_1$ as the rotation axis parallel to the radius. In this case, the indicatrix twists about the obtuse bisectrix and the birefringence should always be negative and oscillate in magnitude. Careful measurement using the Ehringhaus compensator confirms this to be the case, the magnitude of the birefringence in the "extinction" rings being approximately 0.15 of the maximum birefringence midway between them. We have noted earlier that these rings are less dark than extinction crosses in the same spherulites (again see Figure 6b); they obviously stand out by contrast in brightness against their background. On the basis of our discussion, the decimal fraction just mentioned would be expected to have the value $(N_2 - N_1)/(N_3 - N_1) = 0.36$. This is rather poor agreement. However, birefringence at the rings is quite sensitive to tilting of crystalline fibers with respect to the plane of the specimen (a common phenomenon in thin films[7]) or to some spread of crystallographic orientation about the radius; either circumstance would tend to bring an optic axis toward the direction of viewing, hence reducing both the birefringence observed at the rings and the measured fraction.

Similar observation of birefringence in type II spherulites as grown (in the metastable crystal form) again shows negative birefringence at all points, but the ratio of minimum to maximum values in this case is 0.10. If, then, we set $(N_2^{m} - N_1^{m})/(N_3^{m} - N_1^{m}) = 0.10$ and recall earlier results that $(N_3^{s} - N_1^{s}) = 0.053$ and $(N_3^{s} - N_1^{s})/(N_3^{m} - N_1^{m}) = 1.35$, the superscripts m and s denoting the metastable and stable polymorphs, respectively, we see that $N_3^{m} - N_1^{m} = 0.039$ and $N_2^{m} - N_1^{m} = 0.004$, from which we may deduce $V^{m} = 19°$. On the other hand, if orientation effects cause the measured ratio $(N_2^{m} - N_1^{m})/(N_3^{m} - N_1^{m})$ to be reduced by a factor 2.4, in the manner that seemingly occurs in the corresponding case of type II spherulites after transformation, we would have to revise these values of $N_2^{m} - N_1^{m}$ and $V^{m}$ to 0.010 and 30°, respectively. In either event, the metastable polymorph is certainly not uniaxial but biaxial positive, with an optic angle appreciably smaller than that of the stable polymorph. As in the stable polymorph, we again identify $N_3^{m} > N_2^{m} > N_1^{m}$ of an averaged indicatrix with $c^*$, $a$, and $b$ axes of the metastable polymorph, respectively, assuming that the analogue of mimetic twinning is again a factor (but in this case with chain tilts in the tangential plane). Then the optic angle of the single crystal must be appreciably less than 30°, probably $\sim 15°$.

Having reached the present understanding of how uniformly spaced "extinction" rings can arise in the biaxial polymer, it is now evident that the observation that initiated this investigation should not necessarily have occasioned surprise. This observation did not indicate the presence of a new polymorph unambiguously although, in fact, such a polymorph does exist; ignorance can be a more useful stimulus to curiosity than incomplete knowledge.

## Conclusions

Principal conclusions of this part of the study are as follows: (a) the optical properties of ringed spherulites in poly(ethylene sebacate) are quantitatively consistent with uniform twisting of crystallographic orientation about the radius; (b) the indicatrix governing these properties is not related directly to crystal structure but is, rather, an average of indicatrices of crystals having two specific but different orientations; (c) because of this averaging, there is an apparent increase in symmetry which, in turn, explains why in double-ringed spherulites the optic normal is aligned precisely in the radial direction although no such requirement is set by symmetry rules applicable to monoclinic crystals; and (d) over a limited range of crystallization temperature, poly(ethylene sebacate) solidifies in a hitherto unknown polymorphic form. Properties of this polymorph are to be described in part 2.

**Acknowledgment.** It is a pleasure to acknowledge assistance from several colleagues. Thanks are due to W. P. Slichter for a sample of polymer, to D. J. Freed and A. M. Mujsce for synthesis of a sample of relatively high molecular weight, to M. Y. Hellman for characterization of molecular weight, and to F. J. Padden, Jr., and A. J. Lovinger for helpful criticism of the manuscript.

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# Optical Behavior and Polymorphism in Poly(ethylene sebacate). 2. Properties of the New Polymorph

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ABSTRACT: The newly recognized polymorph of poly(ethylene sebacate) is shown to be metastable and to undergo transformation to the stable monoclinic form at temperatures in the range 70–74.5 °C. The transformation is extremely slow at the lower limit of this range and virtually instantaneous at the upper limit; it appears to occur in the solid state. It is shown that nucleation of the polymorph is suppressed by the presence of moisture absorbed in the polymer, by contact of "dry" polymer with water at crystallization temperature, or by the presence of sebacic acid often remaining as a contaminant after synthesis. These phenomena appear to be related to a more congested packing of polar groups than is found in the known monoclinic form. Carbonyl groups of one molecule are deeply interdigitated with ester linkages of the next, providing an energetically propitious head-to-tail arrangement of aligned dipoles but leaving no room for favorable interaction with other dipoles of foreign origin. A likely crystal structure is proposed in which the dipole alignment just referred to seems certain but many important details still remain to be resolved definitively.

In a companion paper[1] (part 1), evidence has been presented for the existence of a new polymorphic form of poly(ethylene sebacate). We shall now describe the properties of this polymorph and, in particular, its metastability and transformation to the known monoclinic form, the sensitivity of its nucleation to the presence of polar contaminants (notably moisture), and its likely crystal structure.

## Metastability and Transformation to the Stable Form

Distinctive differences between X-ray diffraction patterns of the two polymorphic forms of poly(ethylene sebacate) have already been noted in part 1. These are seen again in the diffractometer traces shown in Figure 1, which illustrates very clearly the relative displacement and marked difference in intensity of 020 reflections from the two crystal forms. Traces such as these provide a convenient and rapid means of assessing the relative amounts of the two forms present in a given sample. By this means, we find that the new polymorph is stable indefinitely at room temperature and remains unchanged if maintained at its crystallization temperature (56 °C in most of our experiments—see part 1 for fuller details) for at least 20 h after solidification. If the polymorph is heated at 1 °C/min to various higher temperatures and then examined by X-ray diffraction at room temperature, we find that the first sign of transformation occurs at 70 °C in the form of a slight shoulder on the 020 peak similar to, but much less pronounced than, that shown in Figure 1c. This new reflection continues to grow very slowly in intensity with further heating at 70 °C over a period of several hours. In specimens heated to 73 °C, transformation to the stable form is essentially complete after 5-min residence at this temperature. In specimens heated to 74 °C and examined immediately, however, there is still a discernible 020 peak due to the new polymorph but, when specimens are maintained at this temperature, it disappears very rapidly and leaves a trace corresponding to the pure stable form. If specimens are heated at 1 °C/min under the polarizing microscopy, there is an abrupt increase in birefringence of type II spherulites (of the new polymorphic form) in passing through 74.5 °C, indicating that at this temperature the transformation is essentially instantaneous. The transformed spherulites then melt at the same temperature as type I or type II spherulites (of the stable form).

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