Table IV
Observed and Calculated values of d
(a = 6.68 Å, b = 7.42, c = 21.50 Å, β = 124°)

d(obsd), Å	d(calcd), Å	Index
17.7	17.8	001
4.47	4.44, 4.46	110, 004
4.20	4.23	$\bar{1}14$
3.71	3.71	020
3.08	3.08	120
3.01	3.01	$\bar{1}24$, 113
2.77	2.77	200
2.61	2.59, 2.61	210, 114
2.27	2.26, 2.23	130, 124
2.08	2.08	132

erentially to syndiotactic sequences.[13] Assuming that this preference still holds for PABA one can understand the "tolerance" of the crystalline lattice of this polymer to a small amount of methylation provided only the meso sequences are affected. As soon as a substantial number of racemic sequences become methylated, the crystalline lattice collapses.

In conclusion our results indicate that stereoregularity is not a necessary condition for the development of mesomorphic order and crystalline order in polymers with side group structure related to mesomorphic behavior. Two examples of such atactic polymers in which mesomorphic and crystalline order is present were given above. It appears that the development of mesomorphic order depends mainly on the nature of interactions between side groups. Crystallization depends, in addition, on the ease of packing of such side groups. Hydrogen bonding is useful inasmuch as it furthers arrangements between side groups in PMBA and PABA characteristic of mesomorphic order.[14] Furthermore, hydrogen bonding stabilizes the intermolecular lamellar arrangement of backbones and increases the glass transition temperature.

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The Morphology of Directionally Solidified Poly(ethylene oxide) Spherulites

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ABSTRACT: Poly(ethylene oxide) was crystallized from the melt by zone solidification under an imposed temperature gradient of 3 °C/mm. As the zone velocity was reduced to 15 μm/min, the nucleation rate was suppressed, and infinitely extended lamellae, oriented in the direction of motion, were grown in the melt from nucleation points at one end of the polymer rod. The texture of the spherulitic morphologies thus obtained at different zone rates was characterized by polarizing microscopy. While longitudinal sections exhibited fibrillar orientation in the axial direction of the polymer rods, no regular structure was apparent in the transverse cross sections. A theory explaining the observed phenomena and the parameters upon which they depend is developed.

The principal problem that exists in any effort to grow oriented crystals directly from the melt lies in the fact that polymers tend to form spherulites. As these are composed of spherical arrays of lamellae that radiate from a single nucleation point, the polymer chains within any group of spherulites are randomly oriented.[1]

Few attempts have been reported of the uniaxial crystallization of polymer solids from the melt in a manner that would result in a nonrandom spherulitic morphology. These include application of a shear stress[2,3] on the crystallizing melt, and transcrystallization[4–6] resulting from the massive nucleation on a foreign surface. By a restriction of the nucleation rate of new spherulites in the melt, the growth from existing nuclei can be made to proceed without interruption. Price and Kilb[7] have crystallized poly(ethylene oxide) from a single nucleation point within a very thin capillary. Sasaguri, Yamada, and Stein[8] unidirectionally crystallized a thin film of poly(butene-1) in a temperature gradient. Fujiwara,[9] using the technique of zone solidification, directionally crystallized poly(propylene) in a thin glass tube, as did Crissman for both poly(ethylene)[10] and poly(propylene).[11]

Of the methods outlined in the literature for the directional uniaxial crystallization of a polymer from the melt,

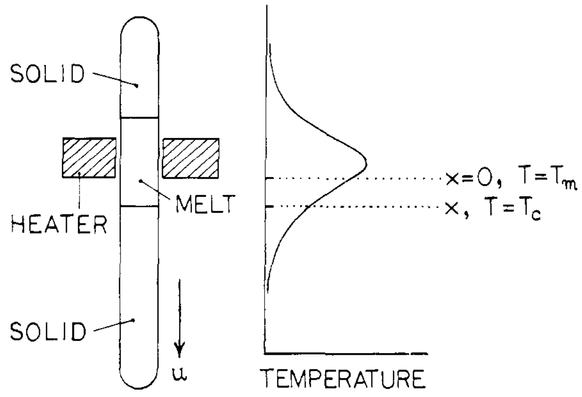

Figure 1. The general zone solidification apparatus.

zone solidification[12] is the most feasible one for preparing large samples of the material. As is seen in Figure 1, a rod of the material is passed through a heated region where the local temperature is high enough to cause melting; outside the zone, the material crystallizes. Zone refining and zone solidification are commonly applied to metals and inorganic materials and have been extended into the purification of organic substances.[13] However, zone purification is not easily evidenced in all organic compounds, mainly because the high viscosities in the melt make their diffusion very slow so that segregation of the impurities at the melt–solid interface is hindered. This implies that zone refining of purely polymeric substances should be difficult, although zone fractionation has been observed in solvent-extended systems.[14–16]

Keith and Padden[17] have found that the spherulitic growth rate of isotactic polypropylene in atactic–isotactic blends is independent of the radius of the spherulite and dependent only upon the temperature and composition of the blend. This implies that in binary systems, even when one component does not crystallize, the second component is not rejected to the melt in front of the growing interface (zone refining) but rather to the side of the crystallizing lamellae (zone solidification). The growing front thus remains at a steady state. Recently, Mehta and Wunderlich[18] have presented experimental evidence that fractionation based on molecular weight may occur within a spherulite during the crystallization of a polydispersed material. However, even considering the impurities and the concentration gradient that will exist around the growing crystal, Keith and Padden[19] maintain that the process will occur at a steady state. This is substantiated by the results of Tanaka et al.[20] and Andrews and coworkers[21] who were unable to observe zone refining of impurities. Karasz and his associates[22] showed that a blend of different molecular weight poly(ethylene glycols) could not be separated by zone fractionation in the melt. Only upon addition of a solvent could any separation be made of the two materials.

Theory

The key to the uninterrupted growth of a crystal structure from a single nucleation point lies in the suppression of the nucleation within the subcooled melt ahead of the growing crystal front. In the ideal system where one need only consider homogeneous nucleation, the situation is relatively simple. As reviewed by Stookey[23] and experimentally verified by Koutsky, Walton, and Baer[24] for the case of crystalline polymers, the rate of homogeneous nucleation does not become significant until an undercooling of 50 to 70 °C is attained. The rate of homogeneous nucleation, N (nuclei/(cm^3 s)), is represented as a function of the undercooling by the Turnbull–Fisher expression in eq 1.

$$N = N_0 \exp(-\Delta F^*/RT_c) \tag{1}$$

The temperature coefficient of homogeneous nucleation according to the development of Hoffman and Lauritzen[25] for polymeric systems depends upon the crystallization temperature, T_c, and the free energy of formation of the nuclei in the melt, ΔF^*. Polymers crystallize from the melt in the form of spherulites. The rate of growth is characterized by G (cm/s), the radial growth velocity of the spherulite. Regardless of the nature of the nucleation process, the growth rate of a polymer spherulite can be described by eq 2,

$$G = G_0 \exp(-\Delta F^+/RT_c) \tag{2}$$

The radial growth velocity is, in addition to the crystallization temperature, T_c, also a function of the composition of the melt in the case of a multicomponent system. At low degrees of undercooling, G may have a very significant magnitude, whereas N, pertaining to homogeneous nucleation, may be very small. This region is a metastable zone of low subcooling in which growth of existing nuclei may proceed without further homogeneous nucleation. The zone solidification of pure low molecular weight materials occurs in this metastable zone.

However, in most crystallizing systems, the nucleation does not proceed by a homogeneous mechanism, but depends upon the presence of heterogeneous surfaces of low free energy, which induce nucleus formation at much lower degrees of undercooling. The rate of heterogeneous nucleation of poly(ethylene oxide) was found by Hay, Sabir, and Stevens[26] to be a function not only of the crystallization temperature but also of the temperature and time that the melt was held in the liquid state prior to the crystallization. Nevertheless, if conditions in the melt are held constant, the nucleation rate may follow a law similar in form to eq 1, but with a considerably lower energy of activation. The data of Flory and McIntyre[27] for the heterogeneous nucleation of poly(decamethylene sebacate) proceed in this manner.

To suppress heterogeneous nucleation, low degrees of undercooling must be used. However, the radial growth rate of polymer crystals formed from the melt at such degrees of undercooling is low. For example, at 5° under the melting point, tin crystallizes at 12.6 cm/s[28] and benzene at 15.4 cm/s.[29] Extrapolating the data of Hay et al.[26] to this same degree of undercooling for poly(ethylene oxide), the comparable rate is found to be 1.6×10^{-7} cm/s. Thus, there is a limit to the degree of undercooling that can be employed while at the same time having a reasonable rate of crystallization.

It is quite simple to determine the cases for which single crystal growth can be maintained under conditions where the nucleation rate is not completely suppressed. Consider an element of polymer melt at temperature T_m in Figure 1 having a cross-sectional area A (cm^2). If the sample is moving at a velocity u (cm/s) through a heated zone, then at steady state, a single crystal would be growing at a temperature T_c, such that the growth rate G (cm/s) is identical with the zone velocity u. If for a given crystallizing material the growth rate G and the nucleation rate N (nuclei/(cm^3 s)) are known as functions of the melt history and the temperature, then it is possible to predict the critical velocity of crystal growth such that the nucleation can be suppressed.

In Figure 1, the time t required for the melt to reach any position x below the region at the melting point ($x = 0$, $t = 0$, $T = T_m$) is given by

$$t = x/u \tag{3}$$

If it is assumed that the temperature gradient C (°C/cm) is constant over the region in question, then the temperature at any position below the melting zone is given by

$$T = T_\mathrm{m} + Cx \tag{4}$$

The number of primary nuclei that are formed per unit volume in the time taken for the element to move from temperature T_m to the crystallization temperature T_c is

$$n = \int_0^{x/u} N\,\mathrm{d}t \tag{5}$$

Since the position and temperature are linearly related in a steady state operation, eq 5 may be integrated over the temperature interval from T_m to any temperature below the melting point. The crystallization temperature T_c is defined such that the growth rate G_c is identical with the zone velocity. The volume V of polymer crystallized in the time interval required for the melt to move in the zone heater from T_m to T_c is given in eq 6.

$$V = AG_\mathrm{c}\frac{T_\mathrm{c} - T_\mathrm{m}}{CG_\mathrm{c}} \tag{6}$$

Thus the total number of primary nuclei formed, n_T(nuclei), in a sample of cross-sectional area A as it moves from the melting point to the crystallizing point at a velocity u is

$$n_\mathrm{T} = A\frac{T_\mathrm{c} - T_\mathrm{m}}{G_\mathrm{c}C^2}\int_{T_\mathrm{m}}^{T_\mathrm{c}} N\,\mathrm{d}T \tag{7}$$

The critical condition for a single crystal to be formed that is continuous and devoid of primary nuclei (in the case of polymers, devoid of subsequent spherulites) is that n_T be less than or equal to unity.

Few data are available in the polymer literature for nucleation rates as a function of undercooling. One such case is the already mentioned results of Flory and McIntyre.[27] If the integration is carried out using these data for poly(decamethylene sebacate) for a sample of unit cross-sectional area, a critical velocity of 0.6 μm/min is calculated for a temperature gradient of 30 °C/cm. The significance of eq 7 lies not in the absolute value of the rate, but in the relation between the experimental conditions required to suppress nucleation. Small cross-sectional areas reduce the volume of material crystallized and thus it is expected that solidification in small capillaries will lead to uniaxial crystallization. Such results have been verified by Price[7] and Fujiwara[9] in small capillaries and by Stein and coworkers[8] in thin films.

More significant in eq 7 is the role of the temperature gradient. The number of nuclei at any given condition are reduced by the square of the temperature gradient. This permits the integration in eq 7 to be carried to lower crystallization temperatures and thus higher rates of crystallization. Temperature gradients in polymeric systems in the range of 30 to 300 °C/cm are readily attainable.[30,31]

It is the objective of this report to investigate the application of zone solidification to crystalline polymeric materials with the purpose of growing spherulites from the melt in a continuous fashion without interruption by subsequent nuclei.

Experimental Section

Materials. Zone solidification was performed on injection molded rods of poly(ethylene oxide), 1 cm in diameter and 10 cm in length. This polymer (Union Carbide WSR-205) has a high molecular weight (about 600 000).

Apparatus. The basic zone solidification apparatus (Figure 1) was modified to suit the conditions of polymer fusion. In particular, a cooler was placed beneath the heater to increase the temperature gradient. The heater was maintained at 100 to 110 °C and the cooler at −5 to −10 °C, while the resulting temperature gradient in the region of the crystallizing interface was linear at about 3.0 °C/mm. To establish and preserve this temperature profile, the space between the heater and cooler was insulated. A variable power supply was used to control the heater temperature. The cooling liquid passing through the zone cooler was provided from a constant temperature bath connected to a refrigerator.

A constant velocity was imparted to the polymer rods by use of a set of synchronous motors. Various speeds were obtained by a combination of pulleys and reducing gear mechanisms. To prevent interference from frost building between the polymer rod and the cooler with the motion of the ingot, a slow stream of dried air was used to keep humidity at low values.

Procedure. The polymer rods were initially placed under a vacuum of less than 1 mm for 24 h and enclosed within a glass tube containing dried nitrogen so as to exclude the effects of oxygen and humidity. Zone melting and solidification were then performed on the polymer ingots by passing them at a constant and controlled rate through the apparatus described above. After this procedure was completed, the rods were taken out of the glass tube for microscopic investigation. Thin sections, down to 20 μ, were obtained by use of a rotary microtome. These included both longitudinal (i.e., in the direction of growth, parallel to the cylinder axis) and transverse (i.e., circular cross sections normal to the cylinder axis). The sections thus obtained were then examined under the polarizing microscope.

Results and Discussion

It was observed that the spherical symmetry of the poly(ethylene oxide) spherulites is distorted in the direction of the zone motion as the velocity of the rod decreases below 400 μm/min. As the rate of travel through the heated zone was decreased, this elongation became more pronounced and the number of nucleation points was progressively reduced. At rates slower than 15 μm/min the entire rod was composed of extended sectors of the sperulites that had started at one end of the rod.

Figure 2a was obtained from a polarizing microscope with the polarizer and analyzer directions vertical and horizontal. It shows the usual shape of PEO spherulites formed from the melt between two glass slides, yielding a polygonal morphology upon intersection, as well as the typical Maltese cross. The fibrillar microstructure radiating from each nucleus is linear.

Figure 2b represents a longitudinal microtome section cut from a PEO rod that had been crystallized at 250 μm/min. The spherulites are distinctly oriented in the direction of growth. A much more pronounced orientation of the spherulitic structure is evident in Figure 2c which represents a similar section taken from a sample crystallized at 100 μm/min. As can be seen from these two pictures, there is an enormous variation in the apparent length of the spherulitic sectors in the growth direction with the result that no dimension is perfectly representative at each rate. This nonuniformity of length is caused by two factors: (1) the random appearance of nuclei which interfere with the growth patterns of the previously nucleated spherulites, and (2) the fact that any particular microtome section intersects each spherulite at a different distance from its axis of symmetry (i.e., the line passing through the nucleus in the direction of solidification). Thus, a section close to this axis would certainly be larger than one taken close to the periphery.

Figure 2d is a longitudinal section taken from a sample crystallized at 15 μm/min. At this rate, spherulites of un~~limited~~ length and oriented in the direction of solidification were grown from the initial nuclei. These spherulites appear as black horizontal lines resulting from the coincidence of the polarizer with the growth direction. The end of the sample was quenched to room temperature causing an interruption of the growing front by the massive nucleation at the lower degree of subcooling which results in the appearance of ordinary spherulites at the right end of Figure 2d.

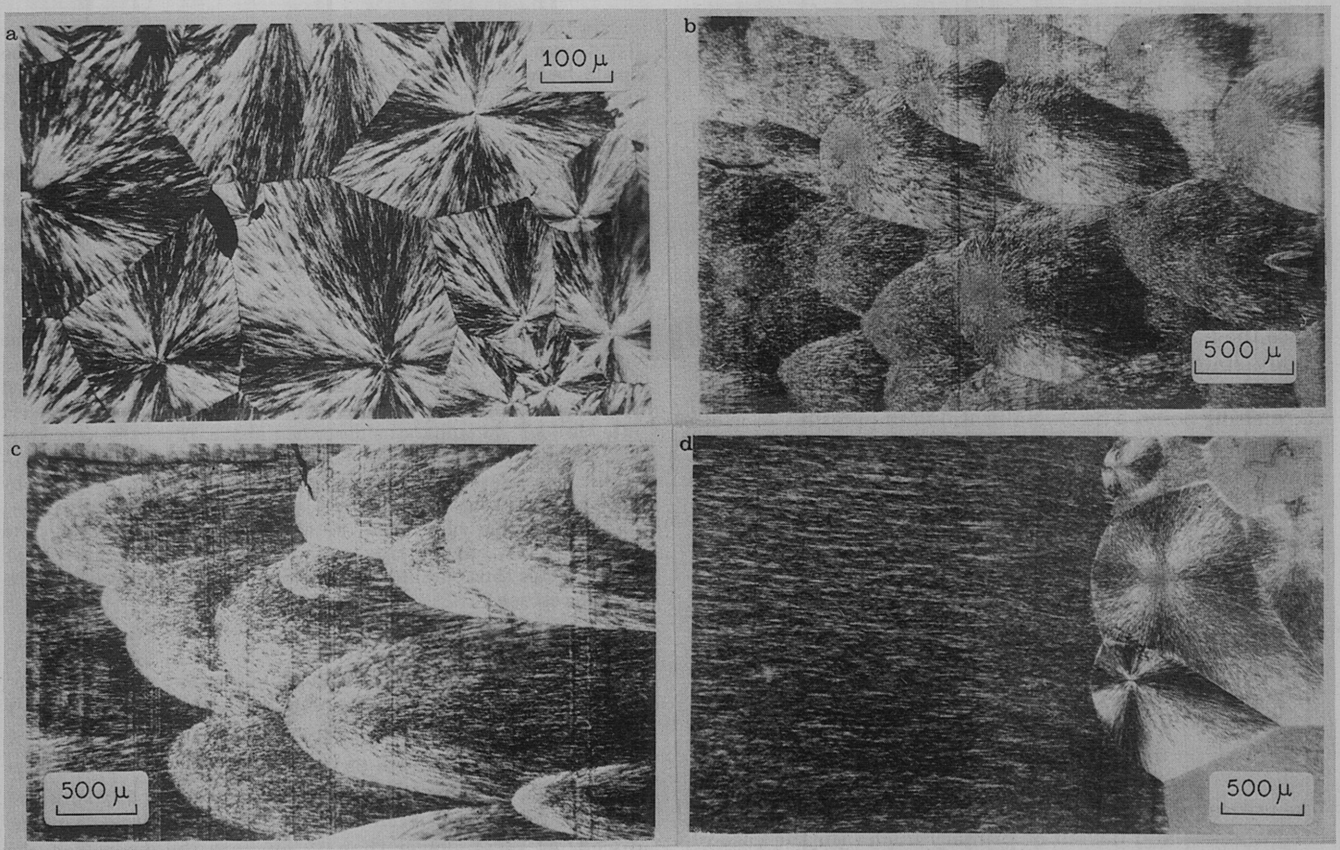

Figure 2. Spherulitic patterns in PEO: (a) bulk crystallized thin film; (b) longitudinal section, zone velocity = 250 μm/min; (c) longitudinal section, zone velocity = 100 μm/min; (d) longitudinal section, zone velocity = 15 μm/min. Right end quenched at room temperature.

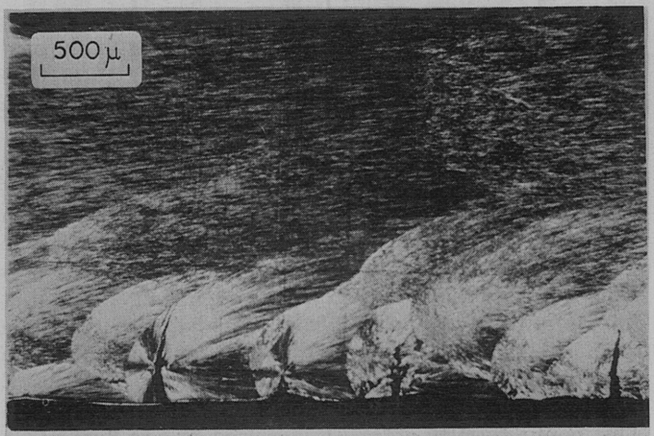

Figure 3. Wall effect on the spherulitic pattern of directionally solidified PEO; zone velocity = 15 μm/min.

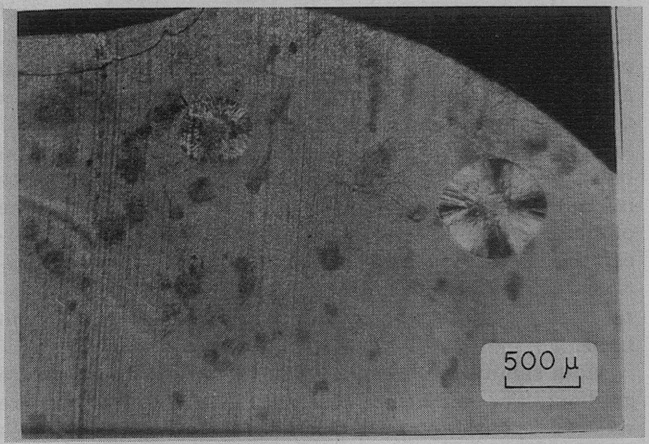

Figure 4. General appearance of the transverse cross section in directionally solidified PEO; zone velocity = 15 μm/min.

There seems to be no restriction regarding the ultimate length of these directionally oriented spherulites. Lengths covering the entire sample (10 cm) have been obtained. Although thermal analysis is not a definite criterion regarding fractionation, the melting points of the polymer at each end of the rod were found to be identical. During zone solidification, the interface between the melt and the solid was observed to remain flat and stationary. This indicates that the crystallization temperature was constant and uniform over the cross-sectional area.

A surface effect was observed with regard to the glass tubes causing surface nucleation. The spherulites thus produced extended into the main oriented matrix by no more than 1 mm (Figure 3). Occasionally, there also exists sporadic nucleation of spherulites within the bulk of the oriented material, which is most probably caused by persistent heterogeneous nuclei. The calcium salts that are used in the manufacture of PEO are present to an extent of up to 0.8% in the polymer rods. However, only a very minute fraction of these serve as heterogeneous nuclei during the crystallization process. This is evidenced by the fact that not more than about 20 nuclei are seen in any longitudinal section of the entire polymer rod, whereas thousands would have been expected if most of the calcium salts had offered preferential nucleation sites.

In contrast to the continuous macrocrystalline morphology in the longitudinal section, the transverse cross sections are considerably different. Their general appearance,

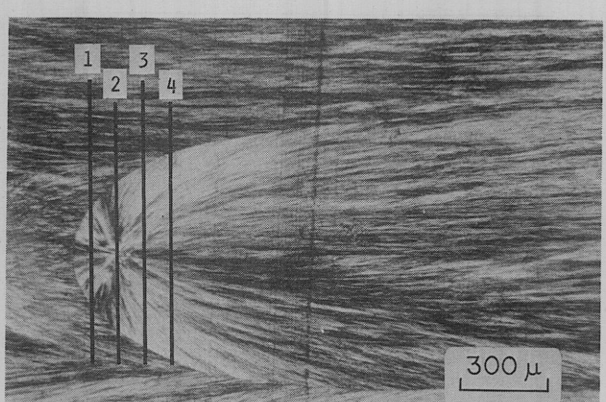

Figure 5. Longitudinal section of PEO spherulite, showing position of transverse cross sections in Figure 6.

viewed under cross polarizers, is shown in Figure 4. Although the polymer is birefringent, there is no observable spherulitic structure and certainly no Maltese cross at the magnifications used in this work. There happens in this figure to be an isolated spherulite in the right-hand corner that results from the fact that this section contains the nucleus of one of the infrequent sporadic spherulites discussed earlier. To understand this phenomenon, a series of transverse cross sections was made in sequence through an elongated spherulite similar to that shown in Figure 5. As the figure depicts, the first section was made normal to the axis through a line 1, i.e., cutting the section through the backward growing part of the spherulite just before the nucleus. Section 2 was made in a similar manner but through the nucleus while the third and fourth sections were made consecutively in the forward growing portions of the PEO spherulite. These four transverse cross sections are seen in Figure 6.

In Figure 6a, the beginnings of a Maltese cross are just discernible. However, the branches of this cross should not intersect at a central point as this can happen only at the nucleus. Instead, a small central circle is seen formed by the fibrils that are growing in directions almost normal to the plane of the photograph. Since the cross section of Figure 6b is made through the nucleus, there is evident a sharp Maltese cross emanating from the spherulitic center. It is only this cross section which contains the nucleus that can have the sharp radial symmetry shown. For this reason, cross sections taken farther away from the origin of the spherulite (see Figures 6c and 6d) show only a faint radial pattern. The crystal lamellae in this case are growing almost normal to the plane of the photograph and the transverse order has disappeared.

It should be noted that the appearance of a Maltese cross is obviously not restricted to transverse sections but takes place in all planes containing the nucleus. The longitudinal section of Figure 5 shows this effect with the right horizontal branch of the cross greatly distorted as it branches off widely in the direction of orientation. The faint vertical lines that appear in all cross-sectional photographs are the result of minute imperfections in the microtome blade.

In Figure 7, a schematic representation is given for the birefringent structure that is observed in the transverse cross section of the zone solidified PEO. It is assumed that the extended unidirectional propagation of the PEO from the original spherulitic nucleus does not change the basic microstructure of the growing front. The crystallographic *c* axis of the PEO should be tangential to the original spherulite, i.e., in a plane perpendicular to the growth direction. This condition in a normal spherulite results in a Maltese

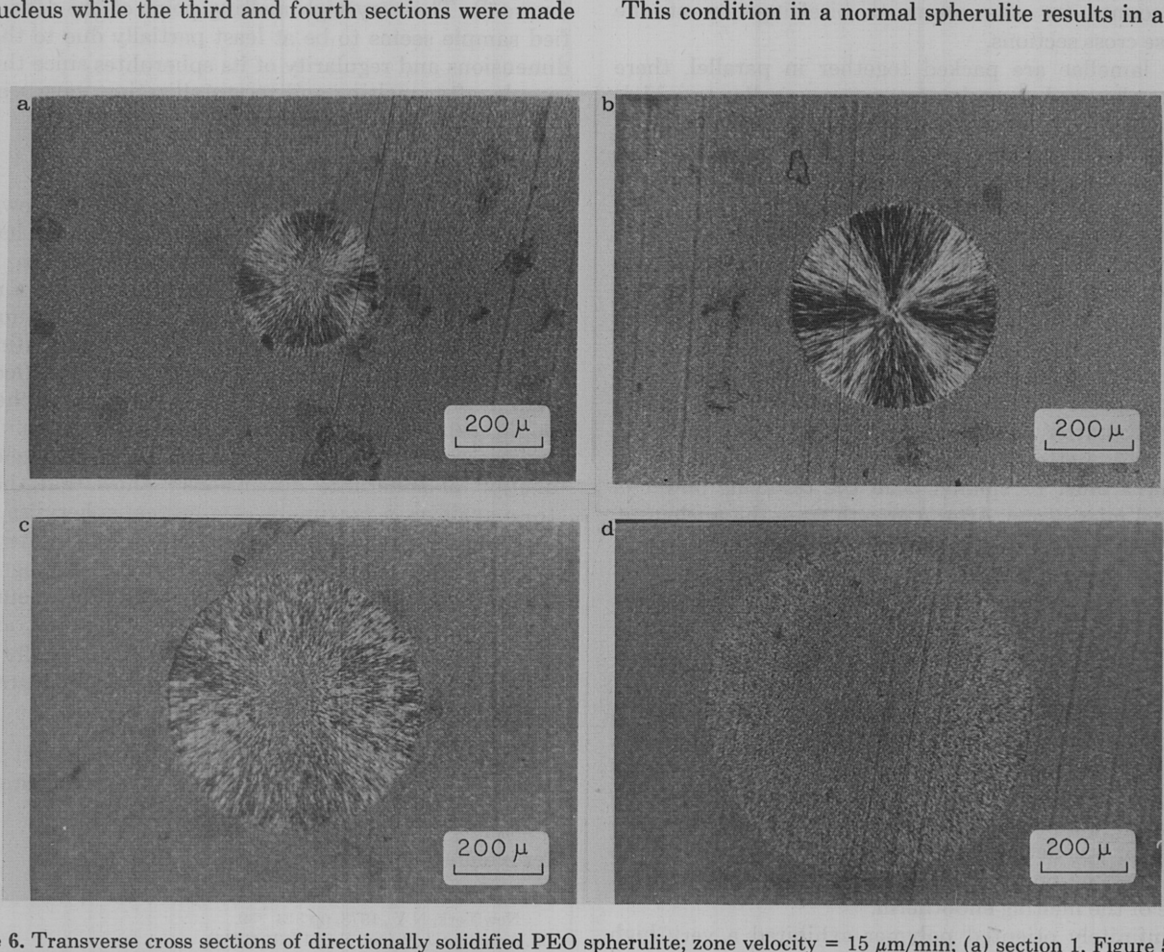

Figure 6. Transverse cross sections of directionally solidified PEO spherulite; zone velocity = 15 μm/min; (a) section 1, Figure 5; (b) section 2, Figure 5; (c) section 3, Figure 5; (d) section 4, Figure 5.

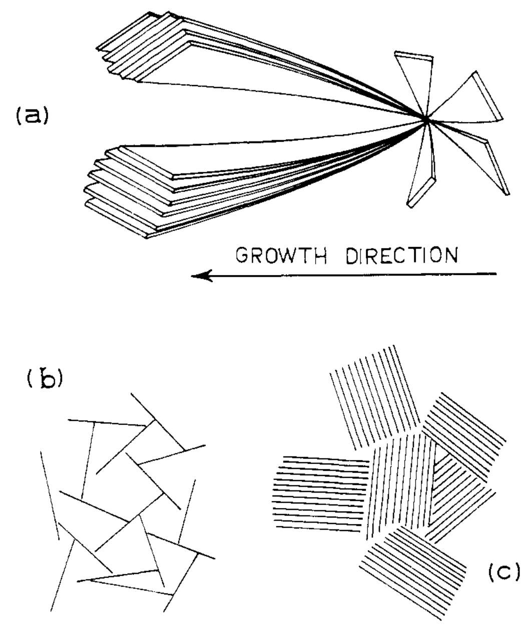

Figure 7. Macrofibrillar structure of PEO spherulites: (a) general appearance of lamellae; (b) random packing; (c) efficient packing.

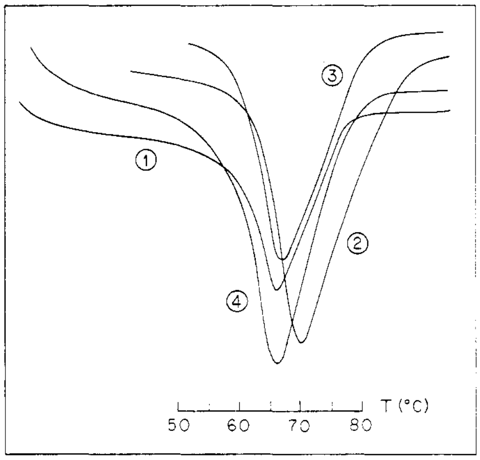

Figure 8. Melting curves of PEO samples (DuPont 900 Differential Thermal Analyzer); heating rate = 10 °C/min; ΔT = 2 °C/in: (curve 1) melt crystallized; (curve 2) directionally solidified at 15 μm/min; (curve 3) melt crystallized and annealed at 55 °C for 2 days; (curve 4) directionally solidified at 15 μm/min, after melting and recrystallization.

cross extinction pattern when viewed under crossed polarizers. If the *c* axis is perpendicular to the growth direction, then the transverse cross sections should contain the *c* axes of the PEO unit cell regardless of the distance from the origin of the nucleus. The individual lamellae viewed in the transverse cross section are optically nonisotropic and thus, depending on their orientation, will rotate polarized light. This accounts for the observed birefringence of the transverse cross sections.

If the lamellae are packed together in parallel, there should be observed an extinction pattern similar to a Maltese cross in the transverse cross section. This is not observed. A random packing of the lamellae, Figure 7b, would account for the observed birefringence, but this would be unlikely since the growing crystal front would not form with such packing of the lamellae. It is more reasonable to assume that bundles of lamellae pack together to form fibrils and these propagate out from the nucleus in the growth direction (Figure 7c). The transverse section should then contain a mosaic of these fibrils in cross section. Keith and Padden[17] have shown that such growth is possible when spherulite crystallization occurs in highly dilute blends of isotactic and atactic poly(propylene). Since no Maltese cross patterns are observed, the cross sections of these fibrils must be smaller than the resolving power of the optical microscope. After a growth from the nucleus of about 100 μm, the fibrils become indistinguishable from those emanating from other nuclei and at that point the spherulitic boundaries cease to have any meaning. After this point the macrofibrillar structure of the lamellae is the only meaningful supermolecular structure that is apparent in the material.

In almost all cases, the polymer samples stayed in the melt for very long periods of time. At the slower rates (e.g., 15 μm/min) each zone remained in the molten state for more than 2 days. In order to check that no degradation had occurred during the directional solidification, the melting behavior was determined by differential thermal analysis. The melting point was defined as the minimum temperature of the melting endotherm.

The infinitely oriented polymer exhibited a very high melting point at 70.1 °C (curve 2 in Figure 8) while the ordinary injection molded material melted along curve 1 at 66.1 °C. The thermodynamic melting point of poly(ethylene oxide) had initially been estimated to be 68.5 °C.[32] However, Mandelkern et al.[33,34] have pointed out by analogy with other polymers that it must lie between 74 and 80 °C, and the more current references[35–37] agree on a value of 76 °C obtained by extrapolation.

For comparison, the melting point of an injection molded sample, annealed at 55 °C for 48 h, was found to be 67.2 °C (curve 3). The very high melting point of the zone-solidified sample seems to be at least partially due to the large dimensions and regularity of its spherulites since the same sample, after melting and recrystallization, gave a melting point of only 66.3 °C (curve 4).

Conclusions

Zone solidification to form infinite lamellae grown from the melt originating at a single nucleation point has been demonstrated to be possible for poly(ethylene oxide). Whether such a technique can also be applied at a reasonable rate to other crystalline polymers depends upon the relative temperature coefficients of the nucleation and growth processes. It is expected that zone-solidified polymers composed of infinitely long oriented spherulites should exhibit improved mechanical properties. Recent studies on the tensile properties of poly(propylene) as a function of spherulite dimensions[38] show that the yield stress achieves a maximum at a critical spherulite radius. The reduced strength obtained at larger spherulite sizes is attributed to the voids left during the cooling of the spherulite and to the yield at the spherulite boundaries where impurities tend to concentrate. Therefore, expectation of better tensile properties in the directionally solidified sample with infinitely long spherulitic microstructure is consistent with these results.

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Morphological Studies of Semicrystalline Poly(2,6-dimethylphenylene oxide)

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ABSTRACT: A sample of poly(2,6-dimethylphenylene oxide) (PPO) has been crystallized by exposure to 2-butanone (MEK) vapor. This sample has been investigated by wide and small angle x-ray scattering (WAXS and SAXS), differential scanning calorimetry (DSC), and light-scattering techniques. The WAXS and DSC experiments reveal a maximum crystallinity of about 30%. The SAXS, analyzed according to the linear paracrystal model of Hosemann, indicates a high degree of order in the superlattice with an average crystal lamellar thickness of 38 Å. Extensive peak broadening occurs in the WAXS curve arising from crystal lattice distortions or defects. These distortions or defects most probably are a consequence of the removal of solvent molecules from the lattice during the drying process. The light-scattering studies show a rodlike morphology apparently made up of fibrous bundles. The exact nature of the structures responsible for the observed light-scattering patterns cannot be conclusively demonstrated.

Wide angle x-ray-scattering (WAXS) studies of single crystals of poly(2,6-dimethyl-1,4-phenylene oxide) have been reported by a number of authors.[1–3] The results of the studies indicate that the structure of PPO single crystals depends on the solvent used for the crystallization and the subsequent drying procedures. Barrales-Rienda and Fatou[2] have shown that the relatively sharp diffraction maxima obtained in the WAXS pattern of PPO single crystals in the presence of α-pinene solvent become very broad and ill defined when the crystals are thoroughly dried. It is generally accepted that solvent molecules incorporate into the PPO crystal lattice.[2]

It is well known that bulk PPO cannot be thermally crystallized but crystallizes fairly readily in the presence of solvent or solvent vapor. Horikiri and Kodera[3] have reported the growth of spherulitic superstructures in PPO when thin films were exposed to α-pinene or tetralin. It was noted that spherulites are not formed when the crystallization is carried out in tetralin vapor at temperatures greater than 50 °C. This work demonstrates the dependence of the morphology as well as the crystal structure of PPO on the nature of the solvent and the conditions of crystallization. Solvents having solubility parameters close to that of PPO produce a morphology which is stable over a wide range of temperatures.[5,6] For the present study, 2-butanone (MEK) has been selected as the solvent. (MEK has a solubility parameter of 9.3 while PPO has a solubility parameter of 8.8.) In all cases the polymer films were thoroughly dried subsequent to crystallization. In the case of some solvents, such as acetone, the drying process leads to extensive crazing,[6] but no crazing was observable with MEK. The morphology and structure of the semicrystalline PPO thus obtained were studied by small angle x-ray scattering (SAXS), differential scanning calorimetry, (DSC), and light scattering, in addition to WAXS.

Experimental Section

(1) Sample Preparation. PPO was obtained from the General Electric Co. (courtesy of A. Katchman) in powder form. The powder was dissolved in toluene at 25 °C and precipitated with an excess of methanol. The PPO purified in this way was used for the crystallization experiments. $[\eta]$ was measured in toluene at 25 °C and interpreted with the aid of the viscometric equation of Barrales-Rienda[2]

$$[\eta] = 5.74 \times 10^{-2} \bar{M}_n^{0.69} \qquad (1)$$

This resulted in an $\bar{M}_n$ of 2.3×10^4.