Thus the ir spectroscopy permits the observation of the state of aggregation of the ions in ionomers and the investigation of the influence of various factors on the aggregation of the ions. The possibility of observing two types of ion aggregates and the data presented which are in favor of a regular structure of ionic clusters are of great importance and probably may be of use in developing the theory of ionomer structure and properties.

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(25) It should be noted that polarized infrared studies of ethylene–methacrylic acid copolymer (4.1 mol % acid) and of its 78% neutralized sodium salts have been carried out by Stein et al.[4,5] They found that the 1700-, 1560-, and 720-cm^{-1} bands show perpendicular dichroism just as in our case.

Crystallinity and Order in Atactic Poly(acryloyloxybenzoic acid) and Poly(methacryloyloxybenzoic acid)

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ABSTRACT: It has been shown on two examples that α-substituted atactic polymers with sizable side groups can develop crystallinity. These polymers, poly(acryloyloxybenzoic acid) (PABA) and poly(methacryloyloxybenzoic acid) (PMBA), are endowed with hydrogen-bonded benzoic acid moieties. Under favorable circumstances the organization of side groups proceeds beyond the formation of a long range lamellar (smectic) order and crystallization takes place. Hydrogen bonding is shown to play an essential part in the formation of such crystalline structures for both polymers. X-ray data are consistent with a monoclinic unit cell for PABA.

The requirement of stereoregularity as prerequisite to the development of crystallinity in α-substituted polymers with sizable side groups is widely accepted. Atactic polymers of this kind are not considered as crystallizable. Crystallinity had at first been reported in the case of atactic polyacrylonitrile,[1] but it now seems that crystallization develops through long syndiotactic sequences.[2]

Until recently the only well-documented cases of crystallinity in atactic polymers were either those in which the substituant groups on the main chain can isomorphously replace each other, such as for example atactic poly(vinyl fluoride), atactic poly(trifluoroethylene), and possibly atactic poly(vinyl alcohol) or atactic polymers with long linear paraffinic side groups[3,4] in which the paraffinic chain length exceeds ten carbon atoms.[4]

We have shown recently[5] that some polymers with side groups characterized by chemical constitution related to mesomorphic behavior can organize spontaneously to give materials displaying long-range mesomorphic order in the solid state. A number of soluble polymers with flexible backbones and rigid, interacting side groups have been prepared. The long-range order (of the smectic or nematic type) results from the interaction and ordering of side groups.

By pursuing these studies we have discovered that the ordering process in some of these polymers goes beyond a smectic or nematic long-range order and leads to side group crystallization, the extent of which depends on the sample treatment and polymerization rate. The purpose of the present paper is to report on the development of crystallinity in two such polymers: atactic poly(acryloyloxybenzoic acid) (PABA) and atactic poly(methacryloyloxybenzoic acid) (PMBA).

Experimental Section

Monomers. *p*-Methacryloyloxybenzoic acid (MBA) and *p*-acryloyloxybenzoic acid (ABA) were synthesized by condensation of the corresponding acid chlorides with *p*-hydroxybenzoic acid. The procedure was previously described.[6] All monomers were extensively purified by repeated recrystallization from various solvents. MBA and ABA display sharp melting points at 182 °C and 201 °C, respectively.

Polymerization and Characterization of Monomers and Polymers. The bulk melt polymerizations were carried out without initiators due to the high melting points of the monomer. The samples of polymers PABA and PMBA were obtained by heating the corresponding monomers to 212 and 189 °C, respectively, and keeping the temperature constant for 3 h. Solution polymerization was carried out in dimethylforamide (DMF) at 115 °C. The monomer concentration was 30% by weight; the initiator was *tert*-butyl

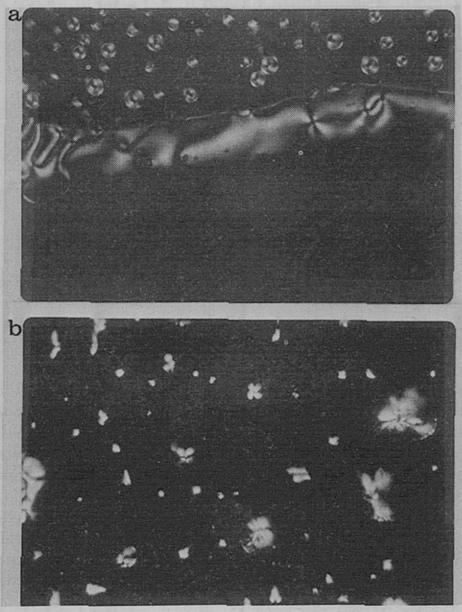

Figure 1. (a) Development of a nematic "schlierren" textures from a melt of *p*-acryloyloxybenzoic acid at 203 °C in the initial stages of polymerization (crossed polars). (b) Development of spherulitic structures from the melt of *p*-acryloyloxybenzoic acid at 203 °C at high conversions.

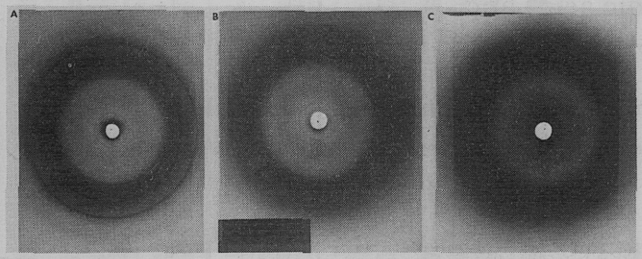

Figure 2. X-ray patterns of various PABA. (A) PABA prepared in bulk at 212 °C form I (film casting of form II on Mica). (B) PABA from (C) annealed several hours at 180 °C and slowly cooled (form II). (C) PABA prepared in solution in DMF at 115 °C, with *tert*-butyl perbenzoate as initiator.

perbenzoate (TBPB) (1% weight, with respect to monomer). The samples were degassed and polymerized for several hours. Conversions ranged from 50 to 80%; all polymers were dried in vacuo at 50 °C.

Hydrolysis of PABA to poly(acrylic acid) (PAA) was performed in concentrated sulfuric acid at room temperature, according to a procedure previously described.[6,8] The methylation procedure has also been previously described.[8]

The molecular weights of PABA samples were determined by measuring the intrinsic viscosity in dioxane at 30 °C[7] of PAA samples obtained by hydrolysis of the parent polymer.

X-ray diffraction patterns were recorded by means of a flat plate camera (Warhus) at a sample to film distance of 7.38 cm (Ni filtered Cu radiation was used). All samples were either powders or films and all diffraction patterns were recorded at room temperature. Films were prepared from polymer solution in DMF cast on mica or glass and dried in vacuo at 80–90 °C.

The extent of crystallinity in PABA was estimated using a Rigaku SG-7B diffractometer with Ni filtered Cu radiation. Intensity data were obtained on several highly crystalline samples, and an amorphous sample polymerized in solution. The crystallinity fraction for samples with the best developed crystallinity was estimated from the areas under the broad amorphous peaks (for crystalline and amorphous samples) from their inception at 12° to their maxima at 18° 2θ.

Electron diffraction patterns were obtained from single crystals of PABA, prepared by dissolving the crystalline, bulk polymerized sample in DMF at 90 °C; crystals formed upon slow cooling. These crystals were deposited on carbon substrates by transfer of a drop of suspension and subsequent solvent evaporation. They were examined in a JEM 100 electron microscope.

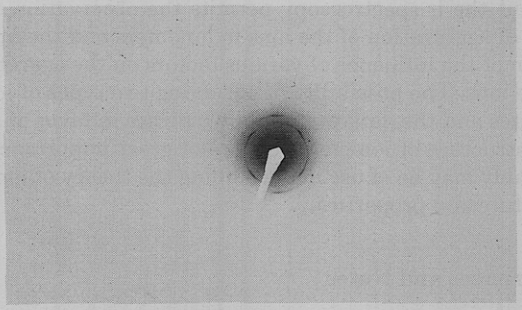

Figure 3. Electron diffraction pattern of a PABA monocrystal (form I). The three lines correspond with those in Figure 4.

Glass transition temperatures were estimated from deformation tests performed on pellets 0.1 cm thick and 1 cm in diameter with a Perkin-Elmer thermomechanical analyzer TMS-1.

Phase transition temperatures of monomers and polymers were determined by means of differential scanning calorimetry (Perkin-Elmer DSC-1B) and hot-stage polarizing microscopy (Leitz-Ortholux microscope with Mettler hot stage).

^{13}C NMR spectra were obtained in 15% weight solutions of PAA in D_2O with DSS as standard. Approximately 16 000 scans were accumulated at room temperature of a Jeol Co. PFT 100 instrument.

Results and Discussion

The family of *p*-*n*-alkoxybenzoic acids displays nematic and/or smectic liquid crystalline organization, beginning with the *n*-propoxy homologue. On the other hand, neither of the monomers studied in the present investigation displays mesomorphic behavior. Both MBA and ABA give a sharp transition from crystal to isotropic melt. Rapid polymerization of the melt can be observed. If the polymerization is performed on the hot stage of a polarizing microscope, it is possible to see between crossed polars the formation of mobile, nematic schlierren textures. Out of these textures a growth of sperulites can be observed as the polymerization progresses. Figures 1a and 1b illustrate this phenomenon. It must be pointed out that the development of spherulitic structures is more pronounced for poly(acryloyloxybenzoic acid) (PABA) than for the poly(methacryloyloxybenzoic acid) (PMBA).

It is apparent from our observations that the development of crystallinity in both polymers depends strongly on the preparation conditions. Thus in the case of PABA one can distinguish two crystalline forms: form I with a higher degree of crystallinity and a higher crystallite perfection than the form II. Form II is obtained on rapid polymerization of the monomer at or above its melting point (201 °C). It can also be obtained through annealing at 215 °C and slow cooling of an amorphous PABA obtained by polymerization of ABA at 115 °C in DMF.

Form I with a degree of crystallinity which may reach 40% can be obtained either on casting of a film of form II from DMF (mica) or on slower polymerization in a thin layer of the molten monomer. The latter method, however, is not well reproducible and leads to mixtures of form II and form I. Finally, monocrystals of form I can be grown from dilute solution and give sharp electron diffraction patterns.

Figures 2A, 2B, and 2C illustrate typical x-ray patterns for form I, form II, and amorphous PABA. Figure 3 gives the sharp electron diffraction pattern of monocrystals of the form I of PABA. The diffraction peaks correspond to the 4.47, 3.71, and 3.08 Å peaks obtained by x-ray diffraction.

Table I
Configuration and Order in PABA

Method of polymerization	T^0 of polymerization, °C	T_g, °C	Values of x-ray spacings, Å Monomer	 Polymer	Tacticity P(I)	 P(S)	 mr
Bulk, form II (fast polymerization)	210	125	13.7 ± 0.1 (w)	17.7 (m); 5.57 (m); 5.09 (m); 4.73 (m)	^{13}C spectra show random steric configuration with mr triads and P(I) diads at approximately 0.5		
Bulk, form I (film casting of form II; also obtained from slower polymerization)	210	125	6.2 (s); 5.45 (s); 4.7 (m); 4.3 (m); 3.87 ± 0.05 (m); 3.47 (w); 3.34 (m); 2.94 (m)	17.7 (w); 4.47 (s); 4.20 (m); 3.71 (s); 3.08 (m); 3.01 (m); 2.77 (w); 2.61 (w); 2.27 (w); 2.08 (w)			
$\bar{M}_v \sim 100\,000$							
Isotropic solution (dimethylformamide) TBPB used as initiator	115	90		Amorphous halo			
$\bar{M}_v \sim 30\,000$							

Table II
Configuration and Order in PMBA

Method of polymerization	T^0 of polymerization, °C	T_g, °C	Values of x-ray spacings, Å Monomer	 Polymer	Tacticity P(I)	 P(S)	 mr
Bulk	185	110	17.5 (m) ± 0.1; 7.16 (s)	19.0 (s); 9.8 (s); 6.25 (w); 4.44 (m); 3.13 (w)	0.29	0.71	0.42
Isotropic solution (heptyloxybenzoic acid) TBPB used as initiator	150		6.72 (s); 6.22 (m) 4.95 (s); 4.88 (m) 4.15 (m); 3.75 (s) 3.57 (s); 3.44 (s) 3.24 (s); 3.17 (m)	Amorphous halo	0.31	0.69	0.41

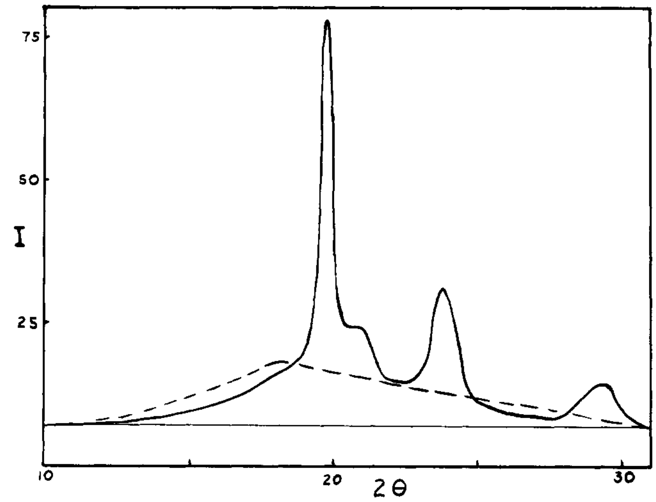

Figure 4. X-ray diffractometer intensity from PABA (form I). The most intense peaks correspond to 4.47, 3.37 and 3.09 Å. The dashed line is from an amorphous sample.

Crystallinity in PMBA is much less pronounced. On fast polymerization PMBA displays no crystallinity and gives an x-ray pattern characteristic of smectic layered arrangements of macromolecules.[5] Annealing or slower polymerization brings out some crystallinity which is however less extensive than that shown by form I of PABA.

Both polymers display a remarkable heat stability of their crystallites. The crystallinity in PABA and PMBA persists until the onset of decomposition which under air starts at 220 °C for PMBA and 250 °C for PABA. PABA displays at 252 °C a sharp endothermic peak which could well be due to the melting of crystallites just before the decomposition sets in.

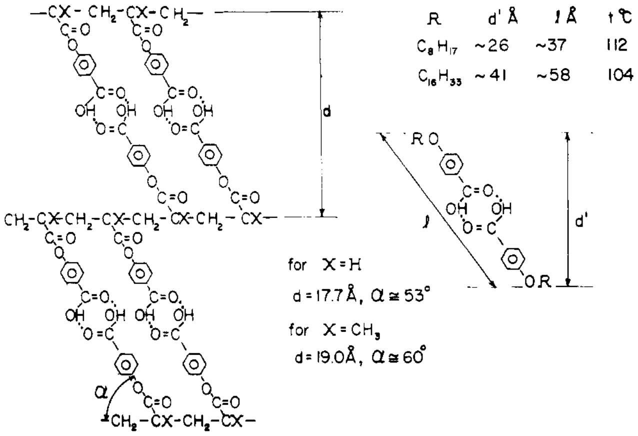

Figure 5. Disposition of benzoic acid moieties in smectic phases of alkoxy benzoic acids and in PABA and PMBA.

Data relative to both polymers are given in Tables I and II. In both polymers the x-ray data are consistant with a lamellar structure in which the side groups are tilted with respect to the lamellar planes. Crystallization seems to be the result of orderly packing of side groups into a tridimensional lattice. The macromolecule of PABA with its more flexible backbone can form a three-dimensional lattice more easily than the PMBA macromolecule which is crowded by the presence of α-methyl groups along its backbone. The crystallinity of PABA can reach 40% (Figure 4), while the crystallinity of PMBA is much less extensive.

Abrupt precipitation of the dissolved PABA or PMBA leads to the destruction of order. Annealing experiments performed on the amorphous PABA show that this sample can acquire some crystallinity (Figures 2B and 2C).

Figure 5 sketches some interconversions between differ-

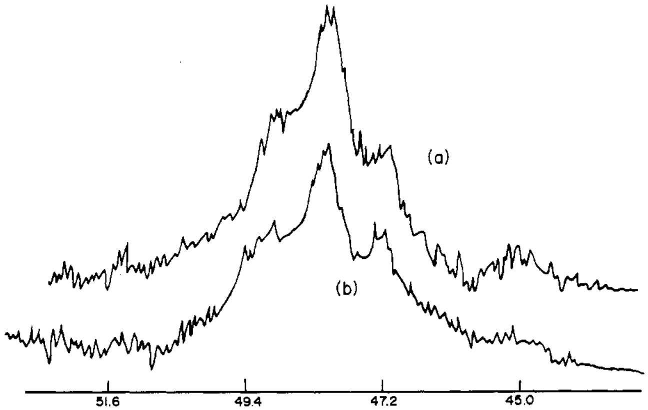

Figure 6. ^{13}C NMR spectra (methine region) of poly(acrylic acids) derived from: (a) bulk polymerized, crystalline PABA (form I); (b) solution (DMF) polymerized, amorphous PABA.

Table III
Crystallinity and Methylation of PABA

% methylation	Crystallinity (x ray)
0	Crystallinity (40%)
10	Weak crystallinity
20	Very weak crystallinity
30	Traces of crystallinity
50	Amorphous
100	Amorphous

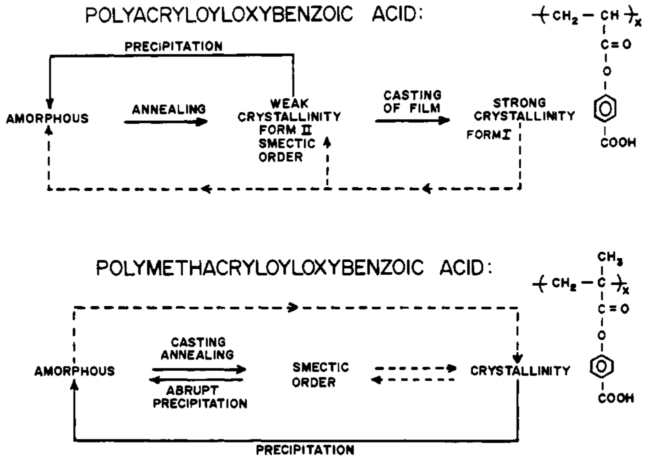

Figure 7. Schematic diagram of attempted interconversions between various morphologies of PMBA and PABA. Full lines represent the observed transformations, dotted lines the unsuccessful attempts at interconversions.

ent morphologies of both polymers. Full lines represent observed transformations, while the dotted lines represent unsuccessful attempts at interconversion.

In order to evaluate the influence of tacticity on the development of crystalline order in PABA, we have recorded the NMR spectra of poly(acrylic acid) (PAA) obtained by hydrolysis of the parent PABA.

Figure 6 gives the ^{13}C NMR spectra of the methine region of poly(acrylic acids) obtained through acid hydrolysis of a crystalline sample of PABA with a degree of crystallinity in excess of 40% (spectrum a) and of a reference amorphous PABA prepared in solution in DMF (spectrum b). Both spectra show clearly the regions of mm, rm, and rr triads, and both are essentially identical with those published by Schaffer for an atactic PAA.[11] Similarly, in a previous work[5] we have shown that PMBA polymerized in bulk is an atactic polymer. Tables I and II give some NMR data for PABA and PMBA. These indicate that a high content of heterotactic triads is tolerated in the formation of crystalline structures in both polymers.

In order to investigate the influence of hydrogen bonding on the development of order in PABA we have partially methylated some of the PABA samples with 1-methyl-3-*para*-tolytriazene.[8] Methylation data are given in Table III.

It can be seen from the table that hydrogen bonding plays an important part in the development of order in PABA and PMBA. The completely methylated polymers are amorphous glasses. They display neither birefringence nor crystallinity on annealing and their x-ray diffraction patterns are typical of amorphous compounds. However, partly methylated samples of PABA can still crystallize up to a composition of 0.2–0.3 of methyl groups.

The low-angle x-ray line at 17.7 Å suggests a strong tilt of the side groups with respect to the lamellar planes. We have assumed that hydrogen bonding between the benzoic acid moieties is the factor responsible for the mesophase order formation. Linear dimerization through hydrogen bonding is recognized as responsible for the mesomorphic behavior of *para-n*-alkoxybenzoic acids,[9] although there appears to be a degree of dynamic equilibrium between linear dimers and open chain aggregates.[10] Figure 7 illustrates schematically the organization of alkoxybenzoic acids in their smectic state together with the organization of macromolecules of PABA and PMBA. One can see that in both cases a strong tilt of the molecular groups with a dimerized benzoic acid moiety is present.[5,9] The value of the angle of tilt cannot be easily determined for the smectic phases of the alkoxy benzoic acids. This is due to the structure of the molecule in which the rigid hydrogen-bonded benzoic acid moiety can assume an orientation which differs from that of the flexible hydrocarbon chain which is in the "liquid paraffin" conformation. The interlamellar spacings d' for both the octyloxy- and hexadecyloxybenzoic acids recorded in the smectic state are much shorter than the corresponding hydrogen-bonded "dimer", indicating a tilt of both parts of the molecule.[12]

The x-ray data on form I PABA may be indexed to a monoclinic unit cell with the following dimensions: $\beta = 124°$, $a = 6.68$ Å, $b = 7.42$ Å, and $c = 21.50$ Å.

Table IV compares calculated and observed values of d. The azimuthal positions of the three-electron diffraction peaks are consistent with this indexing.

The side groups are believed to be closely aligned with the c axis, with the main polymer chain in the ab plane. Thus the angle of tilt of the side groups from the planes containing the main chains is near 60°.

The value of the angle of tilt α of the benzoic acid moieties in PMBA is also near 60°. The values in Figure 7 were obtained from estimation of the length of the side groups and the low-angle x-ray spacing.

We believe that it is the predominantly racemic disposition of mesomorphic side groups which allows the development of the lamellar order of the backbones. Such ordering is furthered by hydrogen bonding between benzoic acid moieties contained in the side groups. The structure of such networks is not without analogy to the β form or "pleated sheet" structure of polypeptides. The fact that complete methylation destroys the ability of both polymers to crystallize or even to display limited long-range smectic order does suggest that hydrogen bonding plays an important part in the development of such order. The results of partial methylation bear out this point of view. It is known, for example, from methylation studies performed on polymethacrylic acid, that isotactic sequences methylate pref-

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,