Morphological Changes in Polyesters and Polyamides Induced by Blending with Small Concentrations of Polymer Diluents

H. D. Keith* and F. J. Padden, Jr.

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

T. P. Russell

IBM Almaden Research Center, San Jose, California 95193.

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ABSTRACT: Unexpected morphological changes have been found in a number of aliphatic polyesters (poly(ϵ-caprolactone) and the suberate, azelate, and sebacate polyesters of ethylene glycol) upon blending with small concentrations (~1%) of compatible polar polymeric diluents, notably poly(vinyl butyral) and poly(vinyl chloride). Among these changes are striking reduction in frequency of nucleation of spherulites, marked enhancement in regularity of lamellar organization in banded spherulites (also manifested by improved regularity of banding), modification of interlamellar spacings, and, in some instances, modification of molecular packing in crystals. It is believed that adsorption of diluent on crystal boundaries (growth faces and fold surfaces of lamellae) underlies most of these effects. Preliminary experiments indicate that similar morphological changes may occur in nylon 66 and nylon 610 when blended with poly(vinylpyrrolidone).

Introduction

There have been numerous investigations of spherulitic crystallization from the melt in compatible blends in which an uncrystallizable polymeric diluent has been added to a crystallizable host polymer. Early work involved blends of isotactic and atactic isomers of the same polymer and in recent years has been extended to blends of chemically dissimilar polymers. In general, incidence of nucleation of spherulites and their subsequent rate of growth are both suppressed by incorporation of diluent. Seldom, however, are they suppressed by as much as an order of magnitude unless the diluent is present in substantial concentration (≥25%) and most blends previously studied have involved diluent concentrations of at least 10%. Associated changes in morphology usually appear unremarkable in that they reflect either segregation of relatively large amounts of diluent between lamellar crystals or changes in texture that, from their similarity to changes of texture brought about in undiluted host polymer by varying molecular weight, have been ascribed to modification of fluidity in the melt. Our purpose here is to report new observations of striking and more subtle morphological changes induced in aliphatic polyesters and in nylons by blending with certain diluents in small concentration (~1%). Incidence of nucleation is also acutely sensitive to the presence of these diluents whereas growth rates of spherulites are not.

The experiments outlined below derive originally from observations that addition of poly(vinyl butyral) (PVB), poly(vinyl formal) (PVF), or poly(vinyl chloride) (PVC) to poly(ϵ-caprolactone) (PCL) has the effect of inducing "banding" (occurrence of ringed extinction patterns) in spherulites of this host polymer in a range of crystallization temperatures in which it does not normally occur. Such a change upon addition of a diluent is not of itself without precedent in polymer morphology[1] and in blends involving PCL in particular[2–6] but, in this instance, it was attended by several unusual and unprecedented features. Among these were (a) substantial reduction in frequency of nucleation of spherulites so that those which did form grew to abnormally large sizes, (b) remarkable regularity in the ordering both of extinction bands and of twisted lamellar structures which give rise to them, and (c) the fact that these effects could be realized with addition of concentrations of additive as small as 0.5%. Marked changes in morphology encompassing similar features were also encountered when the experiments were extended to the suberate, azelate, and sebacate polyesters of ethylene glycol (PESUB, PEAZ, and PESEB, respectively). An exploratory survey of the phenomenology accompanying the striking changes first seen in these various host polymers by optical microscopy has now been carried out by using electron microscopy and electron diffraction, X-ray scattering (at small and wide angles), and differential scanning calorimetry. From observations noted so far it is already clear that the role of the diluents is not a passive one associated in conventional ways with segregation of an uncrystallizable species during crystallization. Rather, there appears to be an interaction between host and diluent polymers strong enough to cause significant modification of crystal growth processes on a molecular scale. This interaction is presumably polar in origin and may well require true thermodynamic compatibility between host and diluent. We have not seen evidence of corresponding behavior while surveying the influence upon PCL of other polar diluents [poly(ethyl acrylate), poly(methyl methacrylate), poly(vinyl acetate), and poly(vinylidene fluoride) among them] which, at 5% concentration, show visible signs of phase separation. It occurred to us that interaction with hydrogen-bonding diluents in small concentration might effect similar morphological changes in nylons. Preliminary indications suggest that this may be the case when poly(vinylpyrrolidone) (PVP) is blended with nylon 66 and nylon 610, but so far this is the only known diluent appearing to have this property.

Materials and Experimental Methods

Chemical structures and other characteristics of host polymers and diluents used in most of our experiments are listed in Table I. (In PVB, which is derived from polyvinyl alcohol, there are in addition to the ringed structures shown occasional hydroxyl groups pendant from backbone chains.) Samples of diluents and host polymers having different molecular weights from those quoted have also been used where available. In general, however, the new observations discussed later appear not to show major qualitative dependence upon these material parameters and, in order to simplify the presentation, we shall concentrate our discussion upon results obtained with the polymers listed. In the case of polyesters we shall devote attention principally to PVB as a diluent, this being more potent in its effects. (PVF has not been used extensively; in the few experiments conducted, however, its influence seemed essentially indistinguishable from that of PVB.) The contrasting behavior observed with PVC and the influence of variations in molecular weights or other material parameters will be noted as appropriate.

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Table I
Materials

polymer[f]	source	mp (optical), °C	molec wt	M_w/M_n
PCL	SPP[a]	62	33K	3.05
PESUB	*b*	65	*d*	
PEAZ	SPP[a]	42	51.4K	2.25
PESEB	*c*	80	19K	
PVB	Polysciences Inc.		116K	
PVC	SPP[a]		77.3K	1.95
nylon 66	Aldrich Chemical Co.	267	*e*	
nylon 610	Aldrich Chemical Co.	240	*e*	
PVP	Aldrich Chemical Co.		40K	

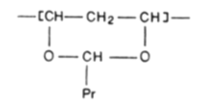
[a] Scientific Polymer Products, Inc. [b] Synthesized in these Laboratories by W. P. Slichter. [c] Synthesized in these Laboratories by D. J. Freed. [d] Uncharacterized: believed to be fairly low. [e] Uncharacterized. [f]

$—[(CH_2)_5—CO—O]—$

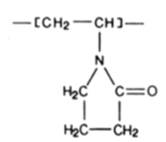
PCL

$—[O—CO—(CH_2)_n—CO—O—(CH_2)_2]—$

PESUB, $n = 6$
PEAZ, $n = 7$
PESEB, $n = 8$



PVB (in PVF, Pr is replaced by H)



PVP

In the range of compositions studied all of the blends examined appear to be compatible. In the case of PCL, compatibility with PVC and PVB over even wider ranges of composition has already been established by earlier work.[1,7,8] Corresponding information is not available for the other polyesters but, as might be expected from their chemical similarity to PCL, no indications of phase separation have been noted microscopically other than what is implied by the process of crystallization. Our blends of nylons with PVP have been judged compatible on similar grounds.

Specimens for experimental study, whether of undiluted host polymers or of blends, were cast from solution as thin films of melt on heated microscope cover slips and maintained above crystal melting points until solvent had evaporated and other cover slips were applied to form sandwiched layers. For optical microscopy, concentrations of 1–2% solids were used to prepare films which were subsequently crystallized isothermally in a Mettler FP82 hot stage fitted on a polarizing microscope. Spherulite growth rates were measured either by time-lapse photomicrography or by use of a filar eyepiece micrometer and stop watch. For electron microscopy and electron diffraction, films were cast from 0.1% solution on mica and, after crystallization, shadowed with Pt/C, coated with carbon, and transferred to specimen grids by conventional means; surface replicas were also prepared for electron microscopy by using standard techniques. X-ray powder diffraction patterns were recorded in a Guinier-de Wolff focusing camera of radius 5.7 cm, mostly with films cast upon Teflon-coated surfaces from which they could readily be detached after crystallization (in some instances the films were chopped into small particles to ensure random orientation of crystals[20]). In the case of PCL, PESEB, and their blends, compact stacks of similar films were employed for real-time small-angle X-ray scattering (SAXS) studies (carried out during heating at a constant rate) on beam line I-4 at the Stanford Synchrotron Radiation Laboratory. Details of the SAXS facility are given elsewhere.[9] Melting behavior was investigated both by hot-state optical microscopy and by using a Perkin-Elmer DSC-4 differential scanning calorimeter.

Observations

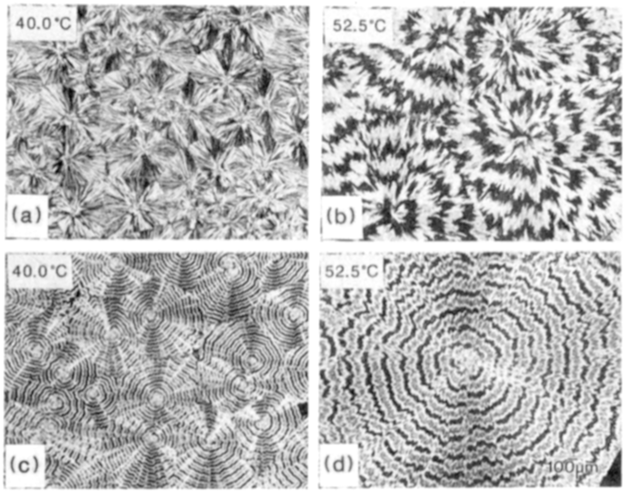


Figure 1. Transmitted light interference contrast micrographs, all at the same magnification, illustrating spherulites grown at the temperatures shown in PCL (a, b) and in PCL containing 1% PVC (c, d). Reproduction of this figure, and also of Figures 3 and 4, in black and white disguises the fact that weaker rings between prominent dark rings (of zero apparent birefringence) are bands of interference color; PCL has a relatively large inherent birefringence and the specimens are sufficiently thick that optical path differences between orthogonally polarized beams can exceed several wavelengths.

Poly(ε-caprolactone). When crystallized from the melt in undiluted form PCL grows spherulites which, for crystallization temperatures below about 50 °C, show simple extinction crosses under the polarizing microscope. Spherulites grown at higher crystallization temperatures additionally exhibit banding with large radial separations in the range 50–100 µm, increasing slightly with crystallization temperature.[10] This is illustrated in Figure 1 where, in order to show banding to best advantage, photomicrographs have been taken by using transmitted light interference contrast rather than conventional polarizing microscopy. As is well-known, such banding is common in polymer spherulites and is attributable to a twisting of crystallographic orientation about radii that apparently reflects cooperative twisting of radiating lamellar crystals about their axes of fastest growth. Its occurrence implies a high degree of coordination in packing of lamellae within fairly compact structures. A comparison of surface replicas of banded and unbanded spherulites of PCL is illustrated in Figure 2. The areas shown are small as compared with band spacing; both show clusters of many individual lamellae and the extent of ordering in directions both along radii and transverse to them is clearly much greater in the banded case. (In both instances electron diffraction shows that the crystallographic *b* axis is oriented radially.) We have previously observed very similar contrasts in lamellar organization between banded and unbanded spherulites in the cases of poly(ethylene oxide) and β-polypropylene.

Influence of PVC as Diluent. In an earlier study of blends of PCL and PVC, Khambatta et al.[2] have shown that banding occurs in spherulites grown at 30 °C with PVC concentrations in the range 10–50%. That the onset of banding in PCL is shifted to substantially lower temperatures by the presence of PVC has not only been confirmed in the present experiments but it has also been found that there is considerable sensitivity to diluent, 1% being sufficient to cause banding at temperatures as low as 35 °C (15 °C lower than in undiluted host polymer). At 40 °C banding is observed even with concentrations as small as 0.5%. A most notable feature of such banding induced by blending is that, relative to banding seen at higher temperatures in undiluted PCL, it is much more regular and exhibits smaller spacings (again see Figure 1). These spacings are commonly in the vicinity of 30 µm and decrease with decreasing temperature, with increasing PVC concentration, and with increasing molecular weight of host polymer. Unlike the behavior of PVB as a diluent (see later), PVC exerts only a moderate influence in reducing the density of primary nucleation centers for spherulitic

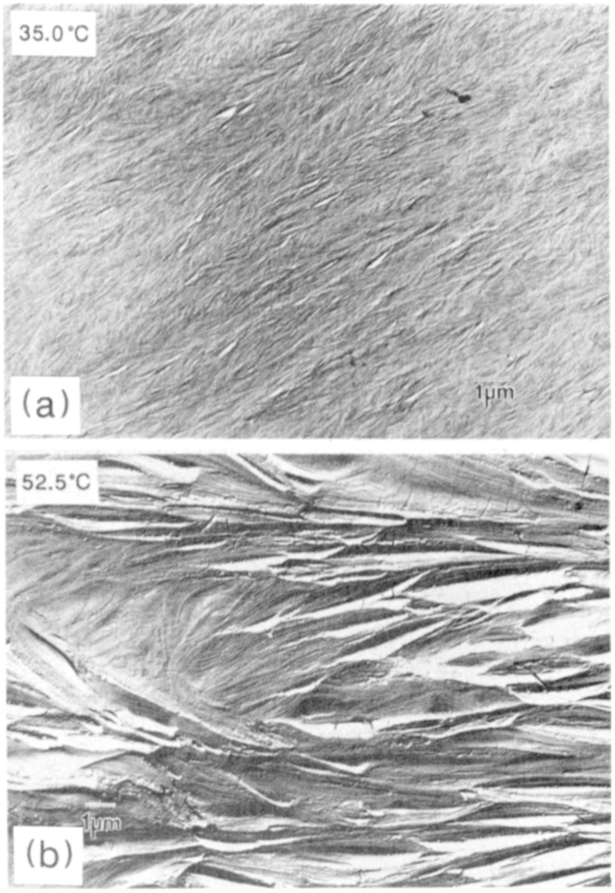


Figure 2. Comparison between lamellar structures in (a) an unbanded spherulite and (b) a banded spherulite in PCL (see text).

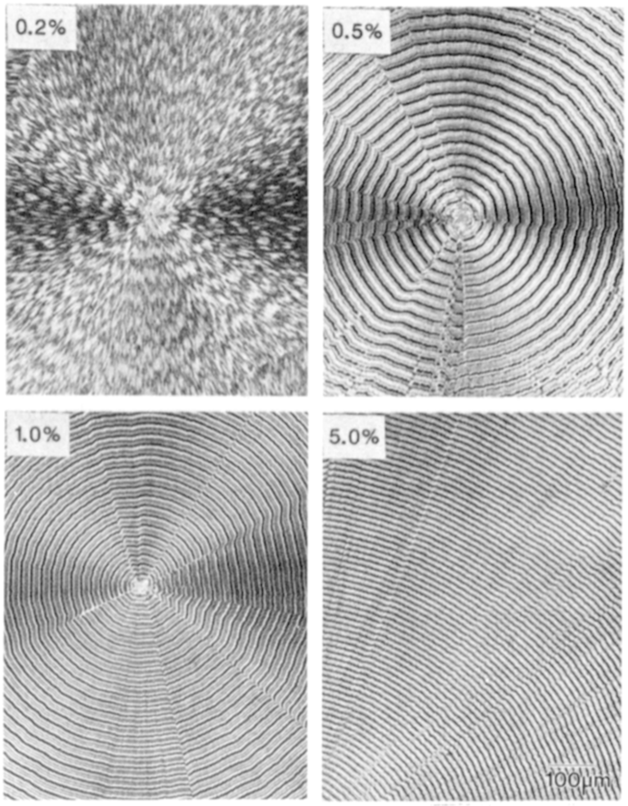


Figure 3. Transmitted light interference contrast micrographs of spherulites grown at 40 °C in PCL containing PVB at the concentrations shown.

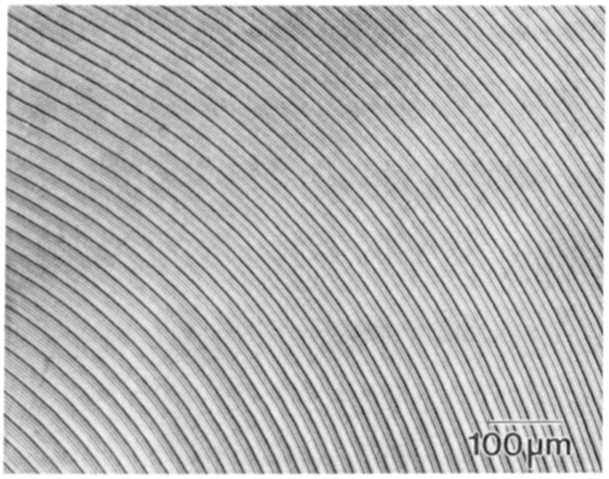


Figure 4. Extremely regular banding within a spherulite grown at 47.5 °C in PCL containing 1% PVB (transmitted light interference contrast micrograph).

growth. In crystallizations conducted at 40 °C nucleation density is least at a concentration of 2.5% PVC and the most regular banding then seems to occur at this same concentration.

X-ray powder patterns obtained from samples of PCL and from blends containing 5% PVC, all crystallized at 40 °C, are indistinguishable as was previously found by Ong and Price;[3] each shows a profusion of relatively sharp reflections consistent with the orthorhombic unit cell derived by Chatani et al.[11] and there is no evidence to suggest appreciable disordering of the lattice such as might be expected were diluent molecules to be incorporated within crystals.

Influence of PVB as Diluent. Morphology. Among the more notable effects of PVB as a diluent in PCL, and also in the other host polyesters considered later, is its remarkable potency in suppressing primary nucleation of spherulites at all crystallization temperatures. At a concentration of 1%, the nucleation density in PCL is reduced 30-fold or more, while at a concentration of 15%, specimens can be stored for weeks at 40 °C without nucleation occurring at all (in such cases, we have resorted to nucleating specimens at lower temperatures and then heating to desired crystallization temperatures). This behavior contrasts with that of miscible blends of PCL with PVC[2] and with chlorinated polypropylene[12] in which the nucleation density increases with diluent content at comparable concentration. Once nucleated, however, spherulites in PCL–PVB grow at radial rates comparable in order of magnitude to those observed in undiluted PCL at the same temperature. Growth rates are smaller in the blends and decrease with increasing diluent content but only to a degree (by a factor 5 in growth at 40 °C for a diluent concentration of 15%) that is not inordinate in comparison with what is commonly observed in polymers containing uncrystallizable diluents and in other blends involving PCL in particular.[13,14]

In other respects, the influence of PVB upon morphology is of a similar nature to that of PVC but more pronounced. The onset of banding is again observed to occur at considerably lower temperatures (30–35 °C) with as little as 0.5% diluent present. Banding in blends is even more regular (Figures 3 and 4), particularly at higher crystallization temperatures and in the middle of the range of PVB concentrations studied (0.2–15%). Spacings are again reduced relative to those found in undiluted PCL and decrease with increasing PVB content (from 40 µm at 0.2% concentration to 13 µm at 15% concentration in

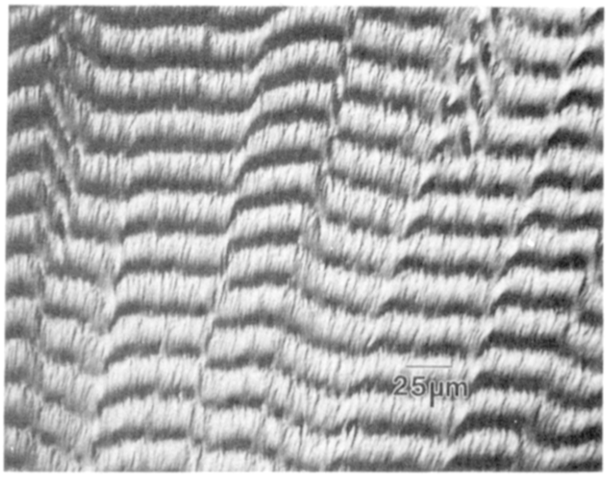


Figure 5. Reflected light interference contrast micrograph showing regularity of lamellar texture in a banded spherulite grown at 40 °C in PCL containing 1% PVB.

Table II
Optical Melting Point of PCL–PVB Blends[a]

% PVB	optical melting point, °C A	B	C
0	59.4	60.1	61.0
0.2	60.5	60.5	61.8
0.5	61.5	61.9	64.0
1.0	63.1	63.3	64.9
2.5	64.2	65.6	66.2
5.0	65.6	65.9	66.9
15.0	66.3	66.6	67.4

[a] Slow heating (0.2 °C/min.) near melting point. Samples crystallizes at 40.0 °C (A) 8 h; (B) 18 h; (C) 42 h.

crystallization at 40 °C); they also vary with crystallization temperature (from 18 µm at 35 °C to 36 µm at 50 °C in blends containing 0.5% diluent), though the temperature dependence becomes less pronounced with increasing concentration of diluent.[15] Blends of PCL with PVB, or with PVC, have so far resisted replication techniques.[16] A remarkably regular lamellar structure is nevertheless apparent under examination by optical microscopy (Figure 5); individual lamellae cannot be resolved but ordered clusters are readily discernible. As in the case of PCL–PVC blends, X-ray patterns of PCL–PVB blends are indistinguishable from those of PCL on its own; being a bulky molecule of irregular nonplanar structure, PVB might be expected a priori to be confined to amorphous regions.

Melting Behavior. When added in relatively small concentration to a crystalline polymer, an uncrystallizable diluent of reasonably high molecular weight is not expected to have much influence upon the equilibrium melting point T_m^0; if anything, there might be a slight depression. Melting temperatures as observed are sensitive, on the other hand, to lamellar thickness and to lamellar thickening upon heating prior to melting; these temperatures have been explored in the case of PCL–PVB blends for indications of changes in behavior occasioned at the level of individual crystals by the addition of diluent. Upon slow (~1–2 °C/min) heating under a polarizing microscope of spherulitic films which had been crystallized at 40 °C, followed by even slower (~0.2 °C/min) heating over the last 5 °C or so before ultimate melting, we have found a systematic increase with increasing diluent concentration in the temperature at which the last traces of birefringence disappears; an increase of ~7 °C was noted in blends containing 15% PVB (see Table II).

Table III
SAXS Long Periods (Å)

T_c, °C	PCL	1% PVB	5% PVB
30	129	124	127
40	148	146	147, 161
50	147	133, 148	137, 150
T_c, °C	PESEB	1% PVB	5% PVB
45	113	102	102

Melting endotherms of PCL and of similar blends (also crystallized at 40 °C) recorded by DSC provide corroborative evidence for these increases in melting temperature. For PVB concentrations up to 5% these endotherms all show single melting peaks, those recorded for given samples at heating rates of 1 and 10 °C/min being qualitatively similar in all cases. Quantitative differences between endotherms for pure PCL and for given blends also correspond closely at these two heating rates, almost to within experimental error, and may be illustrated by the following results obtained at the slower rate. Addition of 1% PVB has the effect of displacing the temperature of the melting peak by 0.6 °C upward in temperature and also of causing the tail of the peak to extend further by 2 °C on the high-temperature side. With 5% PVB the corresponding displacement of peak position is 1 °C and the high-temperature tail is extended by 3 °C. Endotherms were also recorded for PCL and for a blend containing 1% PVB with samples which had first been annealed at 55 °C for 2 h after crystallization at 40 °C. In the undiluted polymer this prior annealing raised the temperature of the melting peak by 2.5 °C and extended its high-temperature tail by 4 °C. In the blend, however, corresponding displacements relative to unannealed samples were 3 and 4.5 °C. In general, then, the influence of diluent, even at 1% concentration, is to produce a population of crystals which are more stable against melting, including some whose melting points are raised by several degrees. The effect is enhanced, but not markedly, by increasing concentration of diluent. As shown by the annealed samples, however, residence at higher temperature increases the stability of crystals considerably, this effect being more pronounced in the presence of diluent.

It is at once tempting to interpret these results in terms of the diluent causing changes in the thicknesses of crystals and different recrystallization and/or thickening behavior upon heating. However, relatively small changes in thermodynamic parameters, such as surface energy σ_e, enthalpy, or entropy of melting, might also be invoked, and independent evidence from small-angle X-ray scattering is desirable.

Small-Angle X-ray Scattering. X-ray long periods indicative of interlamellar spacings were determined from peaks in small-angle scattering profiles (after correction for the Lorentz factor) recorded for samples of PCL and of blends containing 1% and 5% PVB which had been crystallized at various temperatures. Such periods as measured at room temperature are given in Table III. In specimens crystallized at 50 °C, or in those containing 5% PVB and crystallized at 40 °C, the influence of diluent is to cause a doubling of scattering peaks, indicating the presence of two roughly equal populations of crystals giving rise to two different long periods. One of these long periods is more or less unchanged from the single long period observed in pure PCL crystallized at the same temperatures, the other is either larger (crystallization at 40 °C)[17] or smaller (crystallization at 50 °C). On the other hand, in specimens crystallized at 30 °C or those containing 1% PVB and crystallized at 40 °C, the influence of diluent is

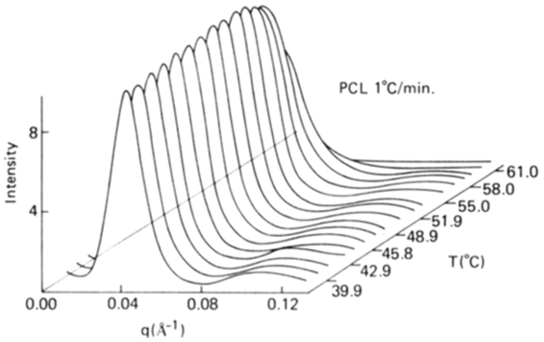


Figure 6. SAXS profiles (with correction for Lorentz factor) of PCL (crystallized at 40 °C) measured at various temperatures during heating at 1 °C/min.

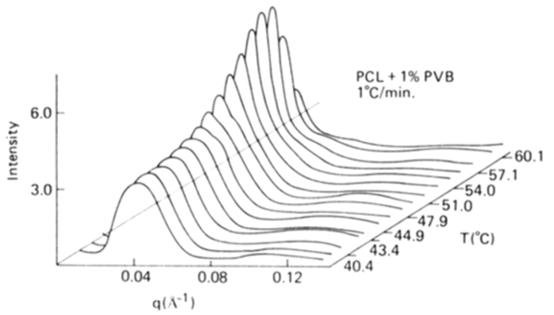


Figure 7. SAXS profiles as in Figure 6 for a blend of PCL containing 1% PVB.

slight. Scattering profiles are perceptibly broadened and accompanying reductions in the long period are very small, although, from consistency in the results, seemingly real. Figures 6 and 7 show representative results of experiments conducted during heating at 1 °C/min, in this case of specimens crystallized at 40 °C. Intensity profiles (after Lorentz correction, i.e., Iq^2) are plotted versus scattering vector $q = (4\pi/\lambda) \sin \theta$, where 2θ is the scattering angle. In pure PCL (Figure 6) there is little change in scattering at temperatures below 50 °C. The long period then begins to increase smoothly, reaching a value of about 240 Å at melting, while the shape and intensity of the scattering peak remain relatively unchanged until the onset of final melting. Behavior in the blend (Figure 7), however, is significantly different. Changes in peak shape occur between 45 and 50 °C, which indicate rapid disappearance of crystals that give rise to smaller interlamellar spacings and, at the same time, an increase of intensity at smaller angles which then continues until the onset of final melting; this increase appears to imply development of an appreciably enhanced population of crystals that give rise to increased interlamellar spacings. However, the long period before final melting, as indicated by the peak position, is commensurate with that in undiluted polymer.

Insofar as variations in the X-ray long period, which is strictly a measure of interlamellar spacing, are also indicative of changes in crystal thickness,[18] it would appear that PVB is capable of modifying thicknesses of PCL crystals in specimens to which it has been added as a diluent in small concentration. If it were to accumulate within amorphous layers between otherwise unchanged crystals one might expect small increases in the long period, whereas, if anything, we have observed decreased long periods; in specimens crystallized at 50 °C the decrease is appreciable. The appearance in some instances of roughly equal populations of crystals giving rise to two different long periods is a further indication of significant change. Differences in behavior between host polymer and blends upon heating support the view, already suggested by our experiments on melting, that PVB accentuates the formation of thicker crystals in the course of whatever recrystallization processes occur at higher temperatures. The nature of these processes, however, remains uncertain.

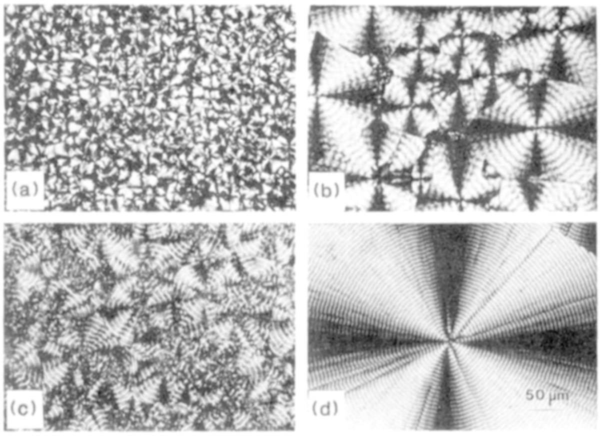


Figure 8. Comparison between spherulites formed (a) in PESEB at 45 °C, (b) in PESEB containing 1% PVB at 45 °C, (c) in PESEB at 63 °C, and (d) in PESEB containing 1% PVB at 63 °C. All photographed between crossed polarizers at the same magnification.

Poly(ethylene sebacate). The morphology of PESEB in undiluted form has already been studied extensively using the same polymer as employed in the present work.[19] At crystallization temperatures below 50 °C and above 59 °C, spherulites comprising crystals having a stable monoclinic structure (α-form) are produced; they differ in that the b axis is oriented radially in those formed in the lower range while a is so oriented in those grown in the higher. The former are negatively birefringent and unbanded while the latter are banded (spacing $\sim$7.3 μm) and show double-ringed extinction patterns attributable to twisting of optically biaxial crystals about their optic normals (see Figure 8). At crystallization temperatures above 66 °C the banding becomes poorly coordinated and is no longer discernible above 69 °C. In the intermediate range of crystallization temperature (50–59 °C), small negatively birefringent and finely banded (spacing $\sim$2 μm) spherulites are also formed (they alone are produced in a narrow temperature interval close to 56 °C) which comprise crystals having a metastable polymorphic structure (β-form). Upon heating to 70 °C this polymorphic form (also monoclinic) undergoes solid-state transformation to the stable α-form, spherulitic morphology appearing unchanged except for a substantial increase in magnitude of birefringence.

Influence of PVB as Diluent. As in the case of PCL, blending with PVB (in the following we confine our remarks to a PVB concentration of 1%) causes both a dramatic reduction in nucleation density and an accompanying improvement in regularity of morphological texture. These effects are most clearly evident in the case of spherulites of α-form as illustrated in Figure 8. It is noteworthy, first, that the negatively birefringent spherulites now exhibit coarse banding with spacings which increase from 14.5 to 65 μm as crystallization temperature is increased from 30 to 50 °C and, second, that regular banding (with spacings reduced slightly to $\sim$6 μm) now persists in the double-ringed spherulites to the highest crystallization temperatures (above 70 °C) at which nucleation and growth are observable on a time scale of many hours. Figure 9 shows electron micrographs obtained by replication of spherulites crystallized at 63 °C in PESEB and in a blend containing 1% PVB. It will be noted in this comparison that although band spacings are compa-

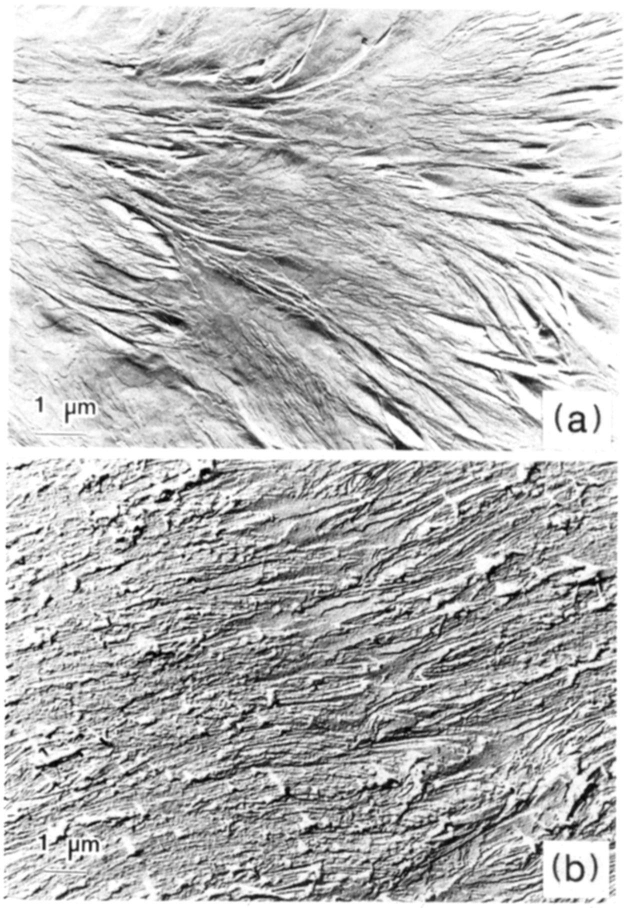


Figure 9. Electron micrographs of replicas of spherulites crystallized at 63 °C in (a) PESEB and (b) PESEB blended with 1% PVB. Detachment of a poly(acrylic acid) replica in (b) has resulted in deformation of the polymer in small localized regions.

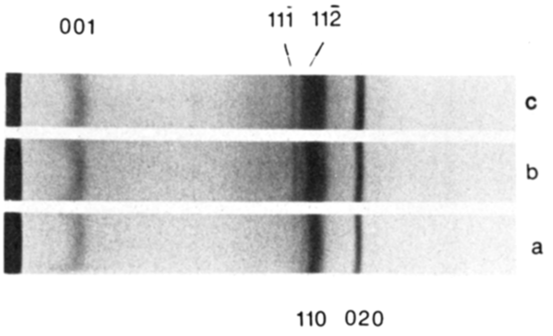


Figure 10. Enlargement of X-ray powder patterns of PESEB crystallized at 63 °C (a) and PESEB containing 1% PVB crystallized at 63 °C (b) and at 40 °C (c).

rable, packing in terms of more homogeneous and intimate stacking of lamellae seems appreciably more ordered in the blend.

Comparison between X-ray powder patterns obtained from these various spherulites of α-form in the blend with corresponding patterns obtained from undiluted host polymer reveals easily recognized changes in the relative intensity of certain reflections that suggest subtle variation of structure within the unit cell. These patterns are all dominated by two strong reflections, 110 at $d \sim 4.15$–4.2 Å and 020 at $d \sim 3.65$ Å. Two additional reflections in this region appear as weaker satellites to 110 which have been identified from lattice spacings, $d \sim 4.4$ Å and $d \sim 4.3$ Å, as $11\bar{1}$ and $11\bar{2}$, respectively. As is evident from Figure 10, and has also been confirmed by densitometry, the relative intensities of these latter reflections are enhanced in patterns obtained from the blend.[20] The degree of enhancement increases steadily in blends crystallized at progressively lower temperatures. It would appear that registry of chains along the chain axis c has been modified to a varying extent since this would influence intensities of hkl reflections but leave $hk0$ reflections unchanged.

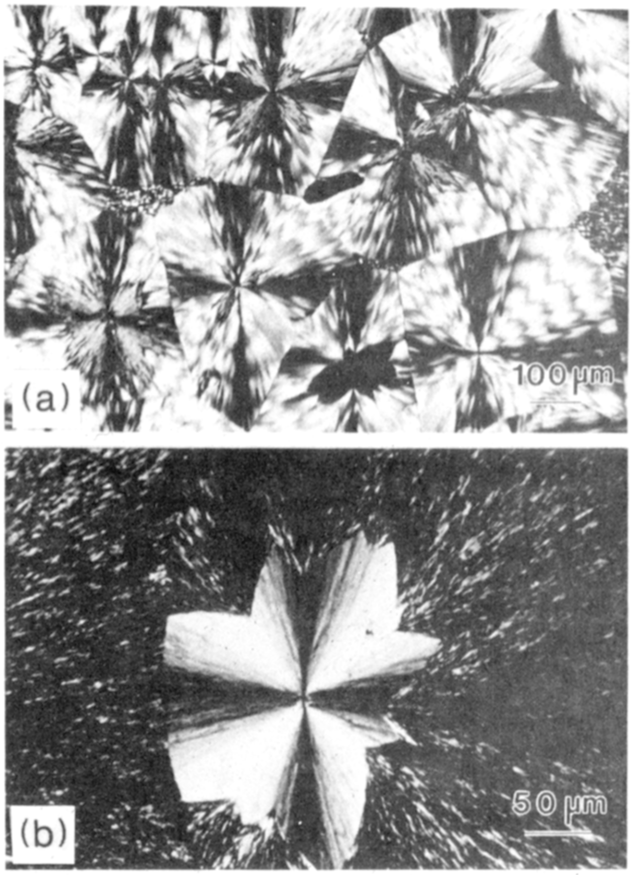


Figure 11. Spherulites in PESEB containing 1% PVB crystallized at (a) 52 °C and (b) 57 °C. Note in this temperature range that many spherulites nucleate in a finely banded form (the bands are barely resolved in (b), not at all in (a)) but undergo transition during isothermal growth to other morphological forms (see text); most of the area shown in (b) is a single spherulite nucleated near the center but extending in a low birefringence form to and beyond the right-hand margin.

In the blend, as in undiluted PESEB, finely ringed negative spherulites are produced at temperatures in the range 50–59 °C. Identification of their structure is now uncertain, however, since they invariably appear in admixture with a preponderance of other spherulites of α-form, some of kinds not seen in undiluted host polymer. Nevertheless, we believe them to be of the polymorphic β-form since similar spherulites produced almost exclusively under certain conditions in the presence of PVC (see later) can be so identified unambiguously by X-ray diffraction. An interesting feature concerning their formation is that only within the range 54–56 °C do they grow uninterrupted until they abut with other spherulites. They otherwise exhibit unusual behavior in that they consistently undergo change during growth to whatever morphology obtains for spherulites of α-form grown at the same temperature (see Figure 11). Such behavior is not only different from anything seen in undiluted PESEB but also stands in sharp contrast to common experience with other polymers. Regardless of differences in growth rate, when spherulites of two different polymorphic forms grow simultaneously in the same polymer, each usually continues without change of form until it impinges upon its neighbors (see, however, Lovinger[21]); generally, there is continuity of a given crystal structure (possible disorder notwithstanding) throughout radial growth. In the present case, differences in growth rate clearly seem irrelevant since, although finely ringed spherulites represent the slower growing form in Figure 11b, the reverse is the case in Figure 11a.[22] It appears, rather, that diluent occasionally promotes nucleation of α-form crystals at growth fronts of β-form crystals, possibly by adsorbing on these fronts and interfering with molecular attachment. Other effects involving interrupted growth and seemingly indicative of adsorbed PVB modifying molecular attachment at growth faces have also been noted and will be described below in the corresponding case of PESUB where they are particularly striking (see, later, Figure 13).

In terms of small-angle X-ray scattering the most notable influence of PVB added as diluent to PESEB is a significant reduction in the long period, as measured at room temperature, from 113 to 102 Å (again see Table III). (Shapes and breadths of scattering profiles are not changed.) This apparently indicates a commensurate reduction in crystal thickness and in lengths of molecular stems between folds; as seen from Figure 10, unit cell dimensions are not altered appreciably and interpretation of the reduced long period in terms of a further increase in chain tilt within crystals would imply fold surfaces that do not correspond even remotely to a crystallographic plane with a small Miller index l. Melting points, as indicated by high-temperature tails of DSC melting peaks or disappearance of birefringence under the polarizing microscope, are not altered appreciably.

Influence of PVC as Diluent. In terms of its influence upon density of nucleation, PVC is less potent than PVB, although, relative to undiluted PESEB, there is again a substantial decrease at all crystallization temperatures. Spherulites found in blends with PVC at 2–5% concentration and at crystallization temperatures below about 55 °C are of the same form as those produced under similar conditions in the presence of PVB and shown earlier in Figure 8a,b. Behavior is significantly different, however, at higher crystallization temperatures. The most notable change is that double-ringed spherulites are not formed at all; in their stead we find growth almost exclusively of the finely ringed negatively birefringent form. From X-ray powder diffraction patterns it has been determined that these spherulites represent the metastable β-form, now nucleating and growing at temperatures considerably higher than they do in the undiluted host polymer. A further aspect of this behavior is that whereas such spherulites in undiluted PESEB undergo solid-state transformation to the α-form upon heating (as noted earlier), in blends with PVC they persist without change until they melt at about 78 °C.

Poly(ethylene suberate). This polymer has a monoclinic crystal structure very similar to that of PESEB,[23,24] differing principally in that the c axis of the unit cell in smaller by about 2.5 Å as a consequence of its chemical repeat being shorter by two methylene groups. Not suprisingly, its morphology is also similar to that of PESEB, negatively birefringent spherulites forming at lower and double-ringed spherulites at higher crystallization temperatures; as in PESEB, banding in the latter loses coordination and becomes no longer discernible at higher temperatures (above 42 °C). No evidence has been found for existence of a metastable β-form similar to that known in PESEB.

The influence of PVB added at 1% concentration also follows a pattern closely similar to that noted in PESEB. Nucleation density is greatly decreased and regular banding in double-ringed spherulites again persists to the highest crystallization temperatures studied (see Figures 12 and 13). In this case, X-ray powder diffraction patterns show an even more marked enhancement of $11\bar{1}$ intensity

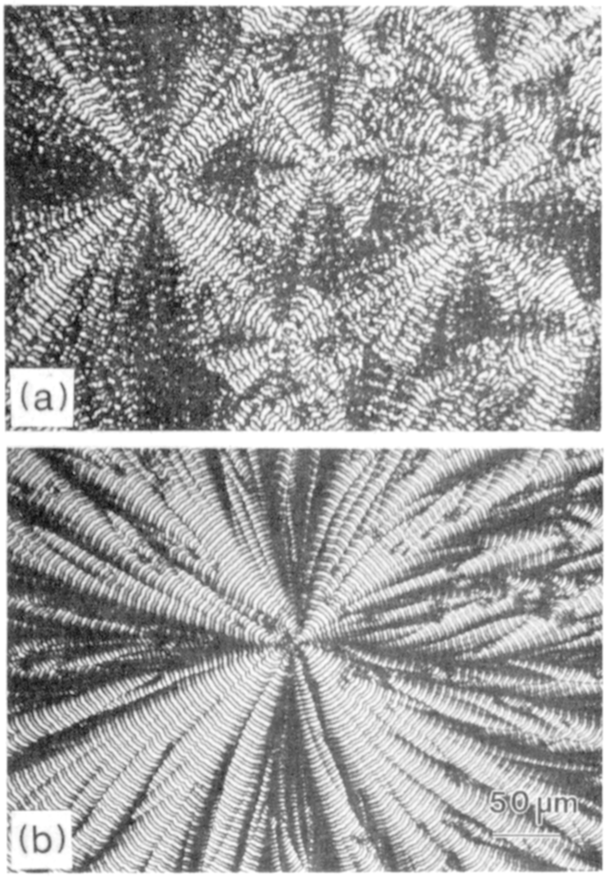


Figure 12. Comparison at the same magnification between banding in (a) spherulites of PESUB grown at 42 °C and in (b) a spherulite grown in PESUB containing 1% PVB at 48 °C.

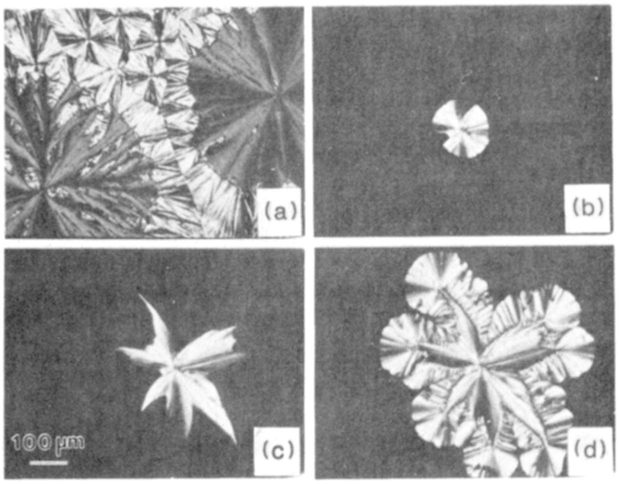


Figure 13. (a) Two banded spherulites grown in PESUB containing 1% PVB at 52 °C for 40 min before quenching to room temperature. The spherulite on the right had a scalloped profile when quenched; that on the left consisted mostly of discrete arms each nevertheless with finely textured and banded morphology. (b) Stunted growth in two sectors of a spherulite in the same blend which was nucleated at 48 °C and taken to 52 °C for continuing crystallization. (c) Same spherulite after further crystallization at 52 °C; note the highly irregular radial growth. (d) Same spherulite after further crystallization had been allowed to proceed at 48 °C; growth has now resumed even at positions where it had previously ceased. All photographed between crossed polarizers at the same magnification.

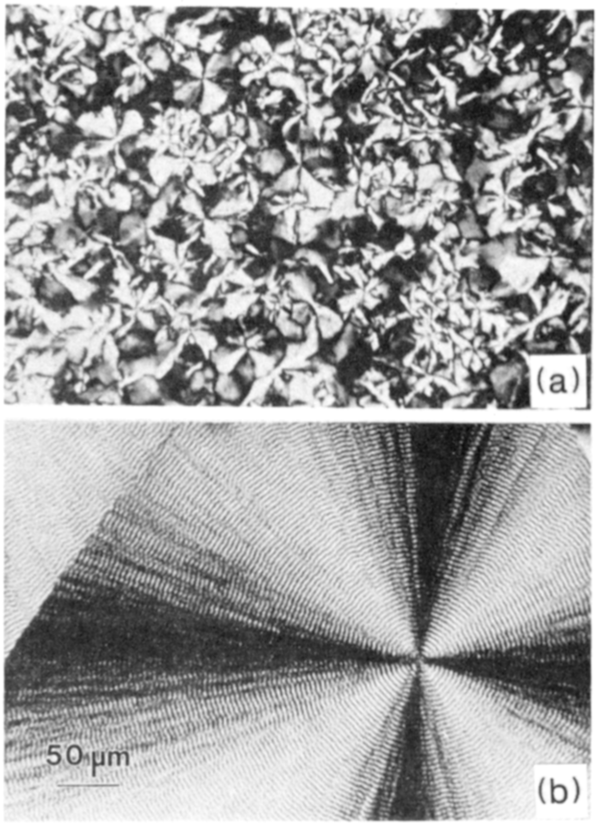


Figure 14. Comparison between spherulites grown at 25 °C in (a) PEAZ and (b) PEAZ containing 2% PVB. The latter represents the host polymer in a new polymorphic form (see text).

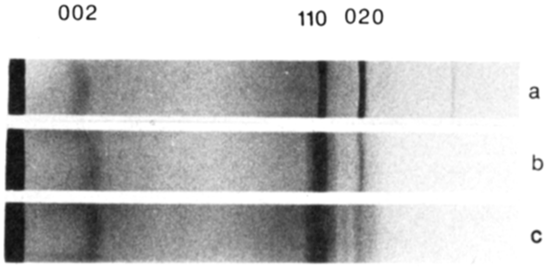


Figure 15. X-ray powder patterns of PEAZ (a) and of PEAZ containing 2% PVB (b) and 5% PVB (c). Note that, relative to pattern a, patterns b and c show displacement of 002 reflections and the presence of new reflections (weak) in the neighborhood of the 110 and 020 reflections.

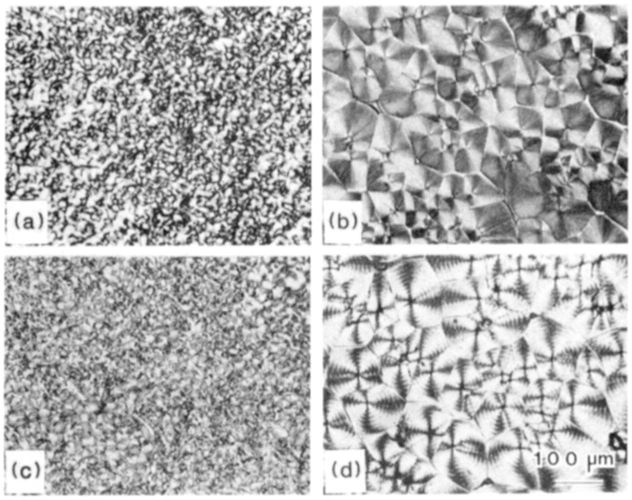


Figure 16. Polarized light micrographs, all at the same magnification, showing the influence of 5% PVP added as diluent (a, b) to nylon 610 crystallized at 200 °C and (c, d) to nylon 66 crystallized at 240 °C.

than in the corresponding blend with PESEB; 11$\bar{2}$ reflections, however, are too weak to be recorded in patterns either from undiluted PESUB or from the blend.

At crystallization temperatures above about 48 °C double-ringed spherulites in the blend develop scalloped or deeply indented profiles, indicating variability of growth rate along their perimeters (Figure 13a). Such variability becomes more marked at 50 °C, and at 52 °C growth actually stops more or less indefinitely in some sectors while radial projections (still showing a compact and well-coordinated ringed morphology) continue growing elsewhere (Figure 13b,c). When the crystallization temperature is reduced radial growth commences again at points where it had ceased, but it is notable that in spherulites initially grown at 52 °C such further growth begins only upon reducing the temperature by as much as 4 °C (Figure 13d). Commonly, this further growth does not begin uniformly across existing growth fronts but tends to be initiated at isolated local sites.

Poly(ethylene azelate). PEAZ is the lowest melting of all the polyesters studied and its morphology has been examined only in a restricted range of crystallization temperature between 20 and 35 °C. Spherulites in the undiluted polymer commonly show mixed birefringence with no hint of banding, and blending with PVC at concentrations up to 5% appears to have no effect other than to cause moderate reduction in nucleation density. Blending with 1% PVB, however, again causes marked reduction in nucleation density and pronounced morphological changes. Spherulites of two kinds are now produced, one highly negatively birefringent without banding and one showing weaker negative birefringence together with banding at a spacing of about 4 μm. At 2% concentrations the banded form alone is produced (Figure 14). This banding is more regular and also more widely spaced in host polymer of higher molecular weight.

X-ray powder diffraction patterns show that these ringed spherulites are of a crystalline form different from the orthorhombic structure found in undiluted polymer[25] or in blends with PVC. This is clearly indicated (see Figure 15) both by significant reduction in the 002 lattice spacing from 15.6 to about 13.9 Å and by the appearance of a cluster of new reflections in the vicinity of strong 110 and 020 reflections (to avoid confusion we have reversed the traditional identification of *a* and *b* axes in this polymer in order to preserve similarity of indexing of *hk*0 reflections with other polyesters discussed previously). The structure of this polymorph has yet to be determined but is probably monoclinic and similar to the structures of PESUB and α-PESEB. Reflections are found in close correspondence with *hk*0 reflections from the orthorhombic form, and from their spacings it is clear that, within experimental error, axes of the unit cell as viewed in chain-axis projection remain orthogonal to one another. A smaller 002 spacing, however, indicates that the *c* axis is inclined to the *ab* plane by an angle β (given by $\sin \beta \approx 13.9/15.6$) of roughly 117°, comparable to corresponding monoclinic angles in PESUB (114.3°) and PESEB (115.5°). Whether or not ester groups are regularly aligned in the new structure, their disposition in adjacent chains is certainly different from that in orthorhombic crystals formed in the absence of diluent.

Nylon 66 and Nylon 610. Figure 16 illustrates the influence of PVP upon the morphology of nylon 66 and nylon 610 crystallized at 240 and 200 °C, respectively. In both cases the nucleation density has been reduced significantly and spherulites in the blends exhibit well-defined and more regular banding than is commonly found in pure nylons. The concentration of PVP in these examples is 5%; however, nucleation density is suppressed to essentially the same degree by 1% diluent although regular banding develops consistently only with slightly larger concentrations (~2%). As yet, these systems have not been studied extensively.

Discussion

In previous sections we have summarized rather than attempted a detailed description of new phenomena encountered in a study which, although extensive in the case of polyesters, was nevertheless far from exhaustive. We have identified certain polymeric diluents that in very small concentrations clearly modify crystallization behavior in these host polymers quite significantly at a molecular level. Such modification is manifested in several ways including changes in axial registry of chains within unit cells, changes in crystal thickness and the manner in which this varies upon heating, promotion of new and stabilization of known polymorphs, and pronounced influence upon lamellar organization. There are also indications from our observations of nylons that such behavior may find expression in some other systems as well. It may ultimately prove to have useful application with respect to modification of structure and control of properties in crystalline polymeric blends.

A common feature of all the host polyesters and corresponding diluents we have used is their polar character; the opportunity this affords for intra- and intermolecular dipolar interaction may well underlie many of the new observations described. Structural specificity appears not to play a simple role, however, since chemical repeats vary from one host polymer to another and the chemical structures of PVB and PVC are quite different. A contributory factor may be that crystal structures of the aliphatic polyesters are inherently labile. From the fact that some have orthorhombic unit cells in which ester groups are confined within sheets normal to a chain axis and some have monoclinic unit cells with corresponding sheets inclined to a chain axis,[16] while at least one (PEAZ) appears capable of assuming either form, it is clear that interdigitation of protuberant carbonyl oxygen atoms with ester groups on adjacent chains is not tightly regulated. In these terms, our observations upon blending with PVB of formation of a new polymorph in PEAZ, and of the likelihood of modified or disordered registry of chains along chain axes in corresponding blends of PESEB and PESUB with PVB, should perhaps occasion little surprise. In the case of PCL there is evidence to suggest that even in undiluted polymer the disposition of ester groups may already be staggered within the unit cell.[11] Of the four polyesters we have studied this in the only one in which blending with diluents has no apparent influence on X-ray powder patterns. We note that polymorphism in the nylons is indicative of similar lability with respect to the registry of hydrogen-bonded sheets of molecules.

Being segregated from the solid phase, the diluents we have used are concentrated at growth fronts during crystallization and ultimately become dispersed between lamellar crystals within spherulites in a concentration appreciably larger than that in the virgin melt. We believe that, in general terms, their adsorption both on growth faces and on fold surfaces of crystals underlies most of the unusual phenomena we have encountered.[26] Much would depend upon specific circumstances created by segments of diluent molecules adsorbed on growth faces and upon whether or not such adsorption is transitory on a time scale commensurate with addition of new molecular layers, a consideration likely to involve competition between attachment of host and diluent molecules in dynamic situations. Stunted crystal growth at small supercooling when the driving force for crystallization is small as in Figure 13 might well result. Under less extreme conditions, diluent molecules adsorbed transitorily upon growth faces may present polar groups to crystallizing molecules in positions other than those to be expected in their absence and, in this way, encourage their deposition with disordered axial registry or with modified packing in a polymorphic form. Transition between polymorphic forms during the growth of a spherulite might also occur readily in a temperature range in which both of the forms are relatively stable. On the other hand, changes in crystal thickness, whatever their implication in terms of modified molecular folding, more likely reflect an influence of diluent upon the thermodynamic variables that govern growth of chain-folded lamellae. That development of more stable and seemingly thicker crystals upon heating may be more pronounced in PCL–PVB blends than in pure PCL is particularly puzzling. To the extent that thickening may occur within individual crystals of PCL at higher temperatures on the time scale of our experiments[10,27] it seems unlikely that it would be enhanced by a diluent adsorbed at fold surfaces. On the other hand, if thinner crystals melt and thicker ones are formed within the semicrystalline matrix the diluent in these circumstances would appear to accelerate the recrystallization.

We turn now to the two influences of diluents that first aroused our interest, those concerning reduction of nucleation density and enhancement of regularity of morphological texture. Primary nucleation of polymer spherulites generally takes place at heterogeneities whose character and mode of functioning are both too uncertain for useful speculation about possible roles of diluents, other than to make the obvious point that adsorption on foreign particles is likely involved. Causes of markedly enhanced regularity of morphogical texture upon incorporation of diluent, despite indications of greater molecular disorder on the scale of individual crystals, are also elusive. Similar effects have not previously been observed in blends of crystallizable polymers with their uncrystallizable atactic isomers; consequently, segregation and/or concentration gradients at crystal growth fronts appear to have little direct influence. However, most prior experience has been with blends in which molecular interactions are exclusively of van der Waals character and in which, as far as is known, molecular folding during crystallization is not affected by diluents. In the present context, diluents appear to be more assertive in their influence. Two possible manifestations of this influence that might bear directly upon regularity of texture are increased frequency of lamellar branching at screw dislocations now formed at more irregular growth fronts and stronger intercrystalline connectivity promoted by bridging diluent molecules adsorbed on neighboring fold surfaces; both would encourage a compactness that in lamellar structures would also improve regularity of organization.

A general observation throughout our work, not previously mentioned, was that even small concentrations of PVB in solutions from which films were cast caused significant improvement in ease and uniformity of spreading upon both glass and Teflon-coated substrates. This is presumably related to tendency of this diluent to adsorb upon solid surfaces and is not surprising perhaps in terms of its known adhesive properties. Blending of PVB in modest concentration with compatible structural polymers may afford an alternative to existing methods for promoting adhesion with fillers or with reinforcements in composites. Finally, we note a parallel between our observations and the well-known properties of Sclair polyethylene which from the melt readily grows large spherulites with unusually regular banding; one wonders if the adventitious presence of a potent diluent is responsible for this behavior even in such an unreactive polymer.

Acknowledgment. We are grateful to Dr. J. P. Bell, University of Connecticut, for communicating results of his researches with Y. K. Choun prior to publication.

Registry No. PCL, 24980-41-4; PCL (SRU), 25248-42-4; PESUB, 25776-26-5; PESUB (SRU), 26762-06-1; PEAZ, 26760-99-6; PEAZ (SRU), 26762-07-2; PESEB, 25037-32-5; PESEB (SRU), 25034-96-2; PVC, 9002-86-2; PVP, 9003-39-8; nylon 66, 32131-17-2; nylon 610, 9011-52-3; nylon 610 (SRU), 9008-66-6.

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(15) Spherulites in films of the blends can easily be grown to diameters approaching 1 cm and, because of their regularly spaced banding, behave like circular diffraction gratings when viewed in transmitted or reflected white light.
(16) In later experiments small areas of replica torn from the polymer surface have shown, among areas of still-attached and deformed polymer, evidence of finely scaled lamellar packing similar to that illustrated in Figure 9.
(17) Occurrence of the component peak corresponding to the larger long period in this blend is unlikely to represent a consequence of isothermal thickening, since the residence time at crystallization temperature of faster growing spherulites in the undiluted PCL was greater and did not produce evidence of such thickening.
(18) We have learned in private communication from J. P. Bell and Y. K. Choun that, from studies they have conducted of selective degradation of PCL by aqueous methylamine, the thickness of interlamellar amorphous layers remains essentially constant as X-ray long periods vary with crystallization temperature.
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Small-Angle Scattering from Anisotropic Systems in the Guinier Region

Ravi F. Saraf

T. J. Watson Research Center, Yorktown Heights, New York 10598.
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ABSTRACT: A general formula for scattering in the Guinier region is derived for uniaxially symmetric system in terms of the inertia of ellipsoid. It is shown that the azimuthal angle dependence of the scattering pattern is independent of the shape of the particle and depends only on the axial and lateral dimensions. A method involving double-tilt is proposed and discussed to quantitatively estimate the size when the Guinier region is difficult to access for the long axis parallel to the detector plane (e.g., voids scattering from highly drawn fibers) or in cases when the axis of symmetry cannot coincide with the detector plane (e.g., single chain scattering from planar oriented films). A family of "particle" shapes ranging from convex to concave surface is considered to quantitatively estimate the error between the actual and measured aspect ratio.

Introduction

There have been various theoretical calculations and small-angle neutron scattering (SANS) studies to estimate the aspect ratio of a single chain on deformation in the condensed state[1–8] in the past 15 years. In some cases, the data are interpreted by assuming an ellipsoidal shape[2–8] for amorphous polymer and a cylindrical shape for semicrystalline polymers[7] to estimate the molecular draw ratio, defined as the aspect ratio of a single chain. In a different type of study, estimation of shape and size of voids in high strength fibers and metallic alloys is important to determine the ultimate mechanical strength. Small-angle X-ray scatterins (SAXS) is a commonly used method for estimating void size.[10–15] The shape of the void is interpreted ellipsoidal to account for the elliptical scattering pattern (for example, ref 14 and 15). The conjecture on the shape of the scatterer from Guinier region analysis may not be valid as discussed in this paper. Other motivation for this

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