Macromolecules **1992,** *25,* 1405–1410

Study of the Crystal Phase and Crystallization Rate of Bacterial Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)

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Received July 31, 1991; Revised Manuscript Received October 18, 1991

ABSTRACT: The crystal phase of random 3-hydroxybutyrate/3-hydroxyvalerate (3HB/3HV) copolyesters (3HV content 0–95 mol %) has been investigated by wide-angle X-ray scattering. Isodimorphism of the copolymer system is confirmed, P(3HB-*co*-3HV) crystallizing in either a P(3HB) or P(3HV) lattice for 3HV contents lower or higher than 40 mol %, respectively. P(3HB-*co*-41% 3HV) shows the coexistence of both crystal phases and corresponds to the pseudoeutectic composition. With an increasing amount of counits, both P(3HB) and P(3HV) crystal lattices change: the P(3HB) cell expands (changes in both the *a* and *b* parameters), and the P(3HV) cell slightly contracts (changes in the *b* parameter). All P(3HB-*co*-3HV) are highly crystalline (>50%), but crystallinity develops at very different rates depending on composition: the slower crystallization rates are found close to the pseudoeutectic, where the spherulite radial growth rate is 4 orders of magnitude lower than that of P(3HB). Upon isothermal crystallization, 3HB/3HV copolyesters develop banded spherulites over rather wide ranges of crystallization temperature (T_c). The band spacing is found to increase with increasing T_c.

Introduction

Bacterial polyesters have attracted much attention in recent years, as biodegradable thermoplastic polymers with a number of potential applications in both medicine and agriculture or as a source of small-molecule specialty chemicals.[1] From the bacterium *Alcaligenes eutrophus*, ICI (U.K.) produces on an industrial scale both the optically active homopolymer poly(3-hydroxybutyrate) [P(3HB)] and random copolymers containing the 3-hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV) units, with a 3HV content up to 30–40 mol %. Using the same microorganism and a mixture of pentanoic and butyric acids as carbon sources, Doi et al.[2] have obtained P(3HB-*co*-3HV) containing up to 95 mol % 3HV units. The characterization studies of 3HB/3HV copolyesters have been recently reviewed by Doi.[3]

A property peculiar to P(3HB-*co*-3HV), which was first pointed out by Bluhm et al.[4] and further investigated on copolymers of both bacterial[5] and synthetic[6] origin, is isodimorphism,[7] i.e., cocrystallization of the two monomer units in either of the homopolymer crystal lattices, depending on copolymer composition. As a consequence of the cocrystallization of the 3HB and 3HV units, 3HB/3HV copolymers show a substantial crystalline phase over the whole composition range.[4–6,8] It has been reported that the rate at which crystallinity develops in P(3HB-*co*-3HV), both after quenching from the melt[5,9] and in films cast from solution,[10] markedly depends on copolymer composition. Analogous observations were made[8] regarding the ability of low-temperature (−100 °C) melt-quenched P(3HB-*co*-3HV) to crystallize on heating above T_g (cold crystallization): copolyesters rich in either 3HB or 3HV units crystallize more easily than those with an intermediate composition.

The above results point to a substantial effect of composition on the crystallization kinetics of P(3HB-*co*-3HV), worth studying in greater detail. An important issue to be addressed when investigating the overall crystallization rate of polymers is the actual elimination of any trace of crystallinity in the melt before quenching to the crystallization temperature (T_c). As a matter of fact, crystallization occurs at a faster rate if preexistent crystallization nuclei are present at T_c. To destroy all residual crystalline order, the polymer melt has to be heated to temperatures well above T_m. However, in the case of P(3HB) and of 3HB-rich copolymers, occurrence of thermal degradation[11,12] precludes access to high enough temperatures to meet the above requirement and allow correct interpretation of the overall crystallization rate results.

In the present work, the nucleation contribution to the crystallization process has been purposely skipped, confining the investigations to measurement of the radial growth rate of spherulites (G) during isothermal crystallization, with the aim of correlating the G parameter with copolyester composition.

Moreover, the crystal phase of P(3HB-*co*-3HV) has been analyzed through X-ray diffraction, to monitor the changes of the unit cell parameters with composition.

Experimental Section

Materials. Random 3HB/3HV copolyesters (3HV content 8–95 mol %) as well as poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (4HB content 16 mol %), isolated from *A. eutrophus*[2,13] were supplied by Prof. Y. Doi, Tokyo Institute of Technology. The composition and molecular weight were determined by ^{1}H NMR[14,15] and GPC,[8] respectively. The 3HB homopolymer was donated by ICI Biological Products, Billingham, U.K. (courtesy of Mr. A. Webb). One bacterial P(3HB-*co*-3HV) sample, whose 3HV molar content (19%, by ^{1}H NMR) was kindly determined by Dr. A. Ballestreri, University of Catania, Italy, was purchased from Aldrich Chimica (Italy). The compositions and molecular weights of the samples investigated are listed in Table I.

Crystallization Measurements. The isothermal rate of crystallization was measured through observation of the spherulite radial growth, using a Zeiss Axioscop optical polarizing microscope, equipped with a Linkham TH600 hot stage. A video camera, attached to the microscope through the Linkham VT0232 interface, allowed real-time measurement of the spherulite dimensions on a TV monitor, after calibration with a micrometric reticule. A video recording facility was used whenever crystallization was either too fast or too slow to be directly observed.

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0024-9297/92/2225-1405$03.00/0

Table I
Composition, Molecular Weight, and Melting of Bacterial Polyesters

composition, mol %		mol wt		T_m,[a]	ΔH_m,[a]
3HB	3HV	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	°C	J/g
100	0	35.0[b]	3.2[b]	176	95
92	8			170	70
81	19	c		117	62
66	34	30.2	2.5	96	48
59	41	25.5	2.4	83	48
45	55	25.5	2.5	83	57
29	71	20.7	1.6	86	71
18	82			104	83
5	95			106	87

[a] By DSC, 10 °C/min. [b] From ICI, by GPC. [c] From Aldrich, MW = 800 000.

Both P(3HB)[11,16] and P(3HB-*co*-3HV)[12] have been shown to undergo thermal degradation; the process involves random chain scission with a molecular weight decrease. Moreover, it is known[17] that the crystallization rate depends on polymer molecular weight, the effect being larger the lower the range of molecular weights considered. In order to minimize the risk of degradation of the copolyesters investigated and the consequent molecular weight decrease, a new sample was used for each crystallization measurement and great care was taken to expose it for the shortest possible time to high temperature during melting.

The experimental procedure was as follows: a small fragment of the "as-received" polymer sample was inserted between two microscope cover glasses and subjected to a five-step thermal program: (1) heating in the microscope hot stage at 20 °C/min to 15 °C above the melting temperature (T_m); (2) 1-min isotherm, during which the melt was squeezed into a film through a small pressure applied to the upper glass; (3) heating at 10 °C/min to either 200 °C (for 3HV contents 0–34 mol % and for the 4HB-containing copolymer) or 130 °C (for 3 HV contents 55–95 mol %); (4) quench to the crystallization temperature (T_c), by means of N_2 gas flow (cooling rate > 250 °C/min); (5) isotherm at the selected T_c. The whole procedure was carried out without removing the sample from the hot stage.

X-ray Diffraction. X-ray diffraction measurements were made with a Philips PW1050/81 powder diffractometer controlled by a PW1710 unit, using nickel-filtered Cu Kα radiation (λ = 0.1542 nm; 40 kV; 30 mA). The lattice constants were calculated from the well-determined positions of 8–10 of the most intense reflections, by least-squares refinements. The crystal sizes were determined by the Sherrer equation from the 020 reflection, using Warren's correction[18] for instrumental line broadening. The percentage of crystallinity was calculated from diffracted intensity data in the 2θ range 4–140° using Ruland's method.[19]

DSC Measurements. DSC measurements were carried out with a Du Pont 9900 thermal analyzer in the range −80 to 220 °C, at a heating rate of 10 °C/min. The temperature scale was calibrated with high-purity standards. From the melting endotherm appearing in the first scan of the as-received polyester sample, the peak temperature (T_m) and the melting enthalpy (ΔH_m), calculated from the area, were obtained. T_m and ΔH_m are reported in Table I.

Results and Discussion

X-ray Diffraction Analysis. Figure 1 shows X-ray diffraction spectra of the as-received powders of P(3HB) and P(3HB-*co*-3HV). The spectra are divided into two groups, according to the 3HV content: in Figure 1a, 0–41 mol %; in Figure 1b, 41–95 mol %. The spectrum of P(3HB-*co*-41% 3HV) has been included in both parts a and b for the sake of comparison. In agreement with previous evidence[4-6] of isodimorphism in the 3HB/3HV copolymer system, Figure 1 clearly indicates that up to a 3HV content of 34 mol % the P(3HB) crystalline phase develops (i.e., the 3HB lattice accommodates the 3HV counits), while above 55 mol % 3HV the opposite situation occurs, the X-ray diffraction spectra showing the pattern of the P(3HV) crystalline phase.

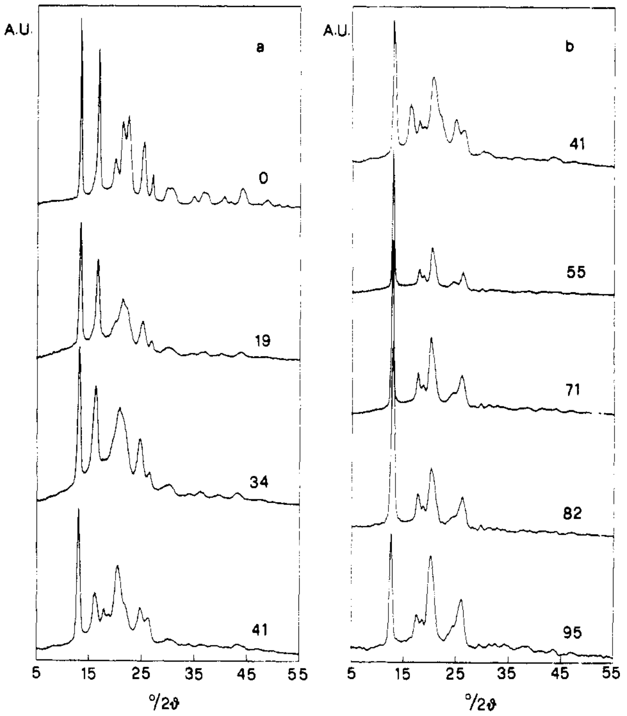


Figure 1. X-ray diffraction spectra of P(3HB-*co*-3HV) with different 3HV content (numbers on curves, in mole percent).

Quite interestingly, in the copolymer containing 41 mol % 3HV units P(3HB)- and P(3HV)-type crystals coexist. The composition of this copolyester corresponds to the so-called pseudoeutectic, where the crystalline phase of an isodimorphic system changes from that characteristic of one homopolymer to that typical of the other. It is expected[20,21] that the two crystals are found side by side close to the pseudoeutectic.

As a consequence of comonomer inclusion, the lattice parameters of both phases change, with the exception of the *c*-axis (fiber axis), as reported in Table II. It is seen that, in the P(3HB)-type phase, both *a* and *b* unit cell dimensions undergo a moderate but gradual increase with increasing 3HV content. On the basis of *d*(110), *d*(020), and *d*(002) spacings, previous papers[4,5] pointed out only *a*-axis variations for P(3HB-*co*-3HV) crystallizing in the P(3HB) lattice, but it is plausible that the side chain of the 3HV unit causes expansion in both directions of the plane perpendicular to the chain axis (i.e., the *ab* plane). When the present *d*-spacings are compared with the above-mentioned literature data,[4,5] the range is found to be the same, the only significant difference being a slight increase—rather than constancy—of the *d*(020) values with changing composition.

In regards to the copolymers crystallizing in the P(3HV) lattice, it is found that replacement of 3HV with 3HB units induces a decrease of the *b* parameter, in agreement with the smaller steric hindrance of the methyl side chain. Lack of any corresponding appreciable change of *a* can be tentatively correlated with the fact that, in the P(3HV) unit cell, the methyl group in the valerate side chain is directed essentially along the *b*-axis[22] and replacement with 3HB units allows contraction mainly in this direction. From the data reported in Table II it is seen that the unit cell parameters of P(3HB-*co*-95% 3HV) better compare with those of P(3HV) obtained from a bacterial source[23] than with the values of the synthetic racemic polymer.[22]

As far as volume changes with composition are concerned, it is found that expansion of the P(3HB) lattice

Table II
Crystallographic Parameters, Degree of Crystallinity, and Heat of Fusion of Bacterial Polyesters

sample	lattice type	a, Å	b, Å	c, Å	V, Å^3	cs,[a] Å	X_c,[b] %	$\Delta H°$, J/g
P(3HB)		5.73 (1)	13.15 (3)	5.96 (1)	449 (2)	270	73	130
P(3HB-*co*-19% HV)	P(3HB)	5.80 (2)	13.30 (3)	5.99 (2)	462 (2)	163	54	115
P(3HB-*co*-34% HV)	P(3HB)	6.04 (5)	13.53 (7)	6.00 (3)	490 (5)	136	52	92
P(3HB-*co*-55% HV)	P(3HV)	9.53 (3)	9.95 (3)	5.59 (3)	530 (4)	200	60	95
P(3HB-*co*-71% HV)	P(3HV)	9.60 (7)	10.04 (6)	5.58 (6)	538 (8)	174	64	111
P(3HB-*co*-82% HV)	P(3HV)	9.59 (6)	10.08 (6)	5.60 (6)	541 (7)	118	65	128
P(3HB-*co*-95% HV)	P(3HV)	9.58 (5)	10.17 (5)	5.58 (4)	544 (6)	146	68	128
P(3HV)[c]		9.52	10.08	5.56	534			
P(3HV)[d]		9.32	10.02	5.56	519			
P(3HB-*co*-16% 4HB)	P(3HB)	5.69 (7)	13.16 (6)	6.00 (5)	449 (10)	127	43	

[a] Crystal size; $\sigma = \pm 5\%$. [b] $\sigma = \pm 5\%$. [c] From ref 23. [d] From ref 22.

on increasing 3HV content is larger than contraction of the P(3HV) unit cell on introduction of 3HB units. It appears therefore that a stronger perturbation to the crystalline lattice occurs on incorporation of a larger-size comonomer than a smaller size comonomer.

The crystallinity degree (X_c) is found to decrease as the relative fraction of foreign monomer units becomes larger. Again the P(3HB) lattice, where the crystalline fraction changes from 73% (P(3HB)) to 52% (P(3HB-*co*-34% 3HV)), is seen to be more sensitive to comonomer inclusion than the P(3HV)-type phase, where X_c = 68% and 60% for P(3HB-*co*-95% 3HV) and P(3HB-*co*-55% 3HV), respectively.

Knowledge of X_c, together with the experimental heat of fusion obtained by DSC (Table I), allows calculation of the enthalpies of fusion ($\Delta H°$, Table II) of hypothetical perfect crystals of P(3HB) and P(3HB-*co*-3HV). The value for P(3HB) is in the range of previously reported data: 136 J/g (crystallinity from X-ray),[4] 146 J/g (crystallinity from density),[24] 130 J/g (crystallinity from ^{13}C NMR).[25] In regards to the $\Delta H°$ values for P(3HB-*co*-3HV), they tend to be higher than those recently obtained by Kamiya et al.[25] through evaluation of the crystallinity degree from solid-state ^{13}C NMR but show an analogous behavior with changing composition, with a minimum around the pseudoeutectic.

The crystal size decreases parallel to crystallinity along the P(3HB)-type copolymer sequence, while the trend of the P(3HV)-type samples is not easily understandable, unless substantial disorder and lattice strain effects—not accounted for by the present data elaboration—are postulated.

Table II also reports the unit cell parameters of P(3HB-*co*-16% 4HB), a copolyester whose monomer units do not show isomorphism;[5] accordingly, the experimental parameters reflect the occurrence of an undeformed P(3HB)-type crystalline phase, whose amount (X_c) and "quality" (crystal size) are however lower than those found in P(3HB-*co*-3HV) with analogous comonomer content (compare with P(3HB-*co*-19% 3HV)), where cocrystallization occurs.

Isothermal Crystallization. The 3HB/3HV copolymers crystallize from the melt showing a well-developed spherulitic morphology. Through measurement of the spherulite radius as a function of time at selected crystallization temperatures, linear plots are obtained whose slope, the radial growth rate G, changes with changing T_c. As an example, Figure 2 illustrates the crystallization behavior of P(3HB-*co*-82% 3HV). The same procedure was applied to all copolyesters, and the resulting dependence of spherulite growth rate on crystallization temperature is shown in Figure 3. No curve is reported for (3HB-*co*-41% 3HV), which did not develop a well-defined spherulitic texture. This observation has to be related to the X-ray evidence that crystals of both P(3HB)- and P(3HV)-type concomitantly grow at this particular composition.

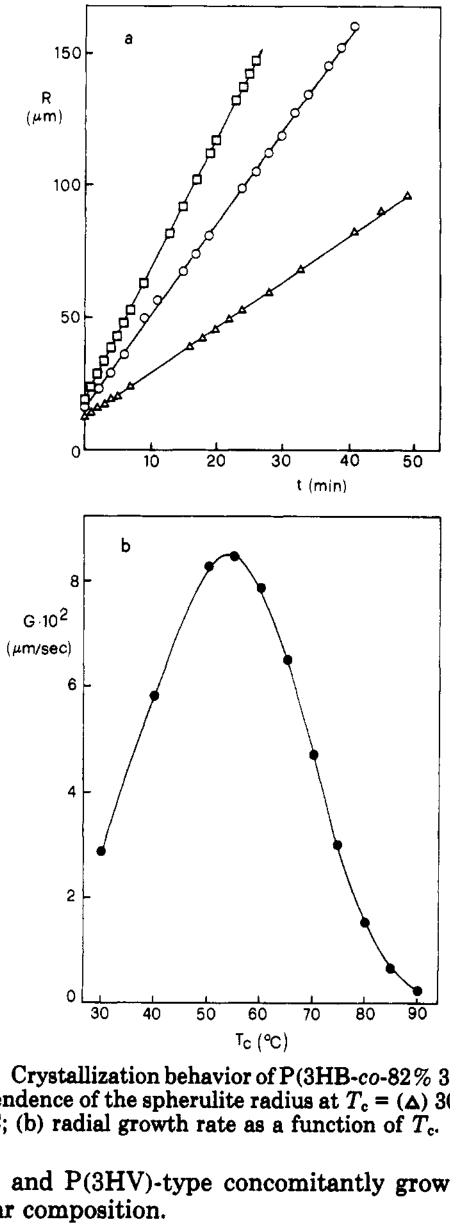


Figure 2. Crystallization behavior of P(3HB-*co*-82% 3HV): (a) time dependence of the spherulite radius at T_c = (△) 30, (○) 40, (□) 50 °C; (b) radial growth rate as a function of T_c.

The curves of Figure 3 show that the rate of spherulite growth strongly depends on copolymer composition: at first, with increasing 3HV content the crystallization process markedly slows down and the whole crystallization curves move to lower temperature. The decrease of crystallization rate is impressive: copolyesters containing 34 and 55 mol % 3HV show G values 3–4 orders of magnitude lower than P(3HB). At compositions higher than 55 mol % 3HV, an opposite trend is observed: with increasing 3HV content, the crystallization rate increases and the curves slightly shift to higher temperature. It

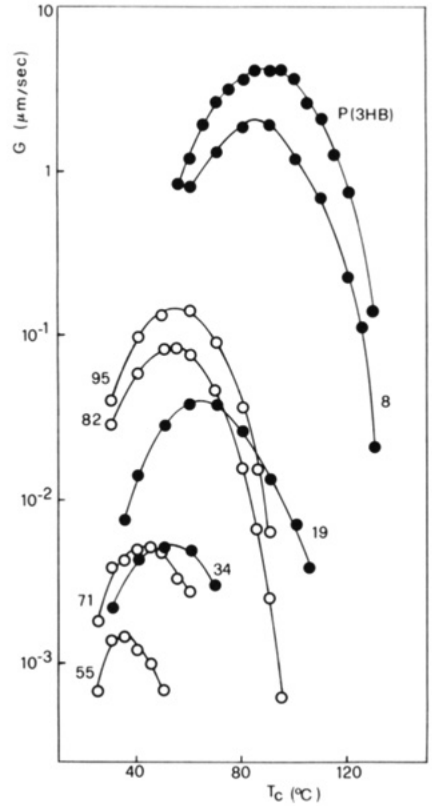


Figure 3. Radial growth rate as a function of T_c for P(3HB) and P(3HB-*co*-3HV) with different 3HV contents (numbers on curves, in mole percent).

turns out that the pseudoeutectic, i.e., the composition where the crystalline phase changes from the P(3HB) to the P(3HV) lattice, discriminates between two different behaviors of the crystallization rate of P(3HB-*co*-3HV) with increasing 3HV content.

Figure 4 reports the composition dependence of both the calorimetric melting temperature (T_m, from Table I) and of the crystallization temperature (T_c^{max}, from the curves of Figure 3) at which the copolyesters exhibit the maximum spherulite radial growth rate. T_c^{max} is used to indicate the temperature about which the crystallization curve of the different copolymers is centered. Both T_m and T_c^{max} exhibit a minimum in the range 40–50 mol % 3HV. Since T_m represents the upper temperature limit to crystallization, it is very clear from Figure 4 that it is the composition dependence of T_m that dictates the trend of T_c^{max}, i.e., the location on the temperature scale of the crystallization curves of Figure 3. As for T_g, which conversely represents a lower limit to crystallization, no appreciable effect has to be expected, due to the much less dramatic T_g than T_m change with composition: T_g decreases linearly as a function of 3HV mole fraction from +4 °C to −17 °C over the composition range P(3HB) ÷ P(3HB-*co*-95% 3HV).[8]

The dependence of the maximum spherulite growth rate (G^{max}, from the curves of Figure 3) on composition is also shown in Figure 4. Again a minimum is observed: the crystallization process undergoes a severe rate decrement as the copolymer composition approaches the pseudoeutectic. This experimental observation clearly reflects the increasing difficulty for either crystal lattice to accommodate increasing amounts of guest monomer units during cocrystallization.

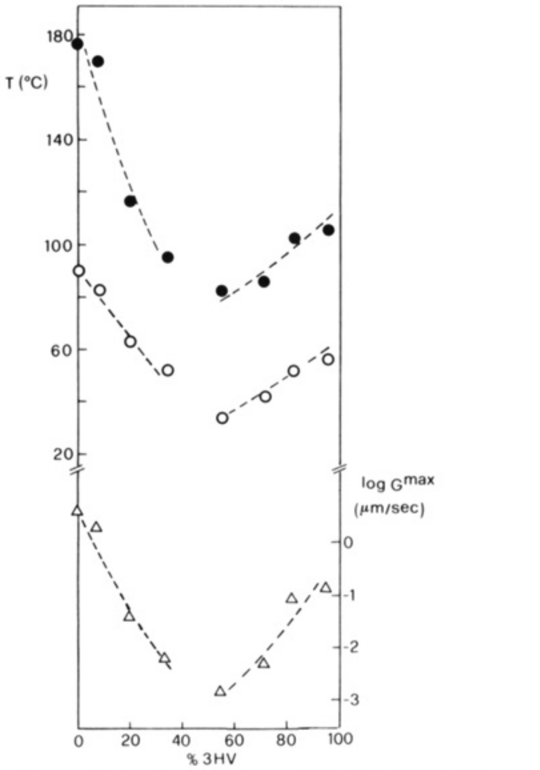
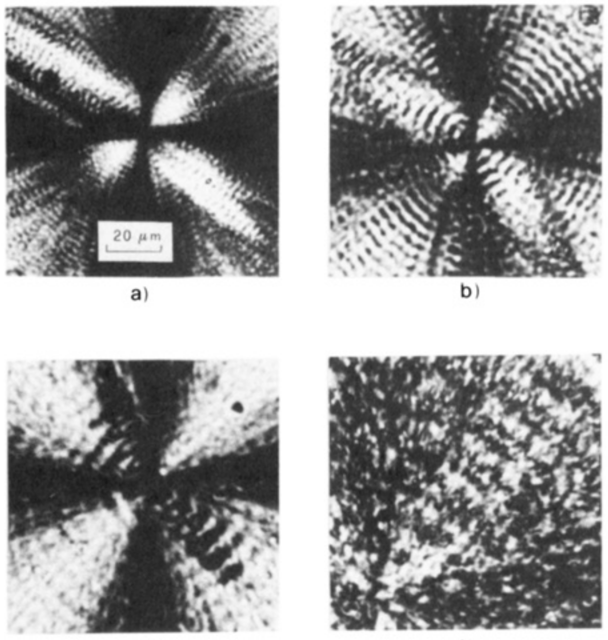


Figure 4. Composition dependence of T_m (●), T_c^{max} (○), and G^{max} (△) in P(3HB-*co*-3HV). See text.



a) b)

c) d)

Figure 5. Optical micrographs of spherulites of P(3HB-*co*-82% 3HV) isothermally crystallized at 65 °C (a), 75 °C (b), 85 °C (c) and 95 °C (d).

Morphology. As already reported for P(3HB),[24] P(3HB-*co*-3HV) also form spherulites with concentric extinction rings (bands). According to Keller,[26] helical torsion of the crystalline lamellae is the cause of the appearance of bands in spherulites, though nontwisting S-shaped lamellae[27] as well as asymmetric development around screw dislocations[28] have also been proposed as the reason for the observed periodic extinction. Despite the broad acceptance of the twisted lamellae model, no general agreement is found on the origin of the lamellar torsion.[26,29–31]

Figure 5 shows a series of optical micrographs of spherulites of P(3HB-*co*-82% 3HV) isothermally crystallized at various temperatures. It is clearly seen that the band spacing (S) changes with changing T_c, a dependence that

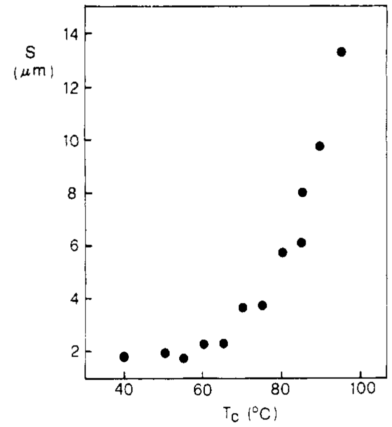


Figure 6. T_c dependence of the band spacing S for P(3HB-*co*-82% 3HV) spherulites.

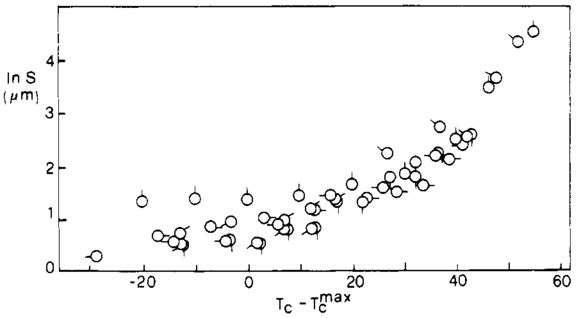


Figure 7. Dependence of band spacing on ($T_c - T_c^{max}$) for (○) P(3HB), (○) P(3HB-*co*-8% 3HV), (○) P(3HV-*co*-19% 3HV), (○) P(3HB-*co*-34% 3HV), (○) P(3HB-*co*-71% 3HV), (○) P(3HB-*co*-82% 3HV), and (○) P(3HB-*co*-95% 3HV).

is better visualized in the plot of Figure 6. The increase of band spacing with crystallization temperature, which often corresponds to a coarsening of the sperulite, is a well-documented phenomenon[24,26,32-34] whose interpretation will be possible only when the debate on the origin of lamellar torsion is satisfactorily concluded. Early work by Hoffman and Lauritzen[29] correlated the increase of S with T_c with the increase of lamellar thickness with temperature; along the same lines, a dependence of S on ΔT^{-n}, where ΔT is the undercooling and $2 < n < 4$, has been more recently proposed.[30] On the other hand, on the assumption that lamellar torsion is due to a sequence of transverse screw dislocations of the same sign, a linear dependence of $\ln S$ on $1/T(\Delta T)^3$ has also been suggested.[35] While none of the proposed dependencies satisfactorily describe the experimental data of Figure 6, recent evidence[36] that anisotropy of the melt enhances ring formation in polyethylene spherulites points to the role possibly played by stresses set up during crystallization in inducing banding. The final morphology of isothermally crystallized polymers appears therefore to be dictated by a number of different parameters whose relative importance is still difficult to evaluate.

In an attempt to compare the T_c dependence of band spacing for all P(3HB-*co*-3HV)s examined, the plot of Figure 7 has been devised where the abscissa ($T_c - T_c^{max}$) represents the crystallization temperature normalized toward T_c^{max} for each copolymer. The S data of Figure 7 indicate a common trend, the band spacing increasing rather markedly with crystallization temperature above T_c^{max}, in a way that is apparently independent of copolymer composition and consequently of the crystallization rate, which is markedly composition dependent.

Conclusions

3HB/3HV copolyesters have been shown to crystallize in either of the P(3HB) or P(3HV) lattices, depending on composition, in line with previous evidence of isodimorphism of the P(3HB-*co*-3HV) system. All experimental evidence agrees in locating the pseudoeutectic composition in the vicinity of 40% 3HV content.

Both P(3HB) and P(3HV) crystalline cells undergo changes with changing copolymer composition, the former in the sense of an expansion (monitored by differences in both *a* and *b*) and the latter of a more modest contraction mainly along the *b*-axis. Very recent solid-state ^{13}C NMR results[25] indicate that the 3HB/3HV ratio in the crystalline phase of P(3HB-*co*-3HV) does not correspond to the overall copolymer composition; in other words, the minor component enters the main component crystal in a lower amount than expected on the basis of pure composition considerations. Though it seems reasonable that each crystal phase will preferentially accept the parent monomer, the present results demonstrate the actual inclusion of comonomer units in either crystal lattice, i.e., real occurrence of cocrystallization. The crystalline phase of P(3HB-*co*-3HV) has been shown to be conspicuous (>50%) over the whole composition range, with X_c slightly changing with 3HV content. Conversely, the rate at which crystallinity develops during isothermal crystallization strongly depends on composition, being slower the closer to the pseudoeutectic, where the crystallization rate is 4 orders of magnitude lower than that of P(3HB).

In summary, the present results clearly support the occurrence of cocrystallization in P(3HB-*co*-3HV) and point out concomitant impressive kinetic effects on the crystallization process.

Acknowledgment. We thank Andrea Magni for performing the crystallization measurements.

This work was partially supported by CNR (Progetto Finalizzato Chimica Fine II).

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