Studies of Cocrystallization of Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) by Solid-State High-Resolution ^{13}C NMR Spectroscopy and Differential Scanning Calorimetry

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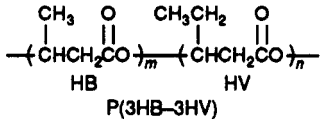
Received May 7, 1990; Revised Manuscript Received July 20, 1990

ABSTRACT: The solid-state structures of bacterially synthesized copolymers of 3-hydroxybutyrate (HB) and 3-hydroxyvalerate (HV) (P(3HB–3HV)) have been studied in detail by means of solid-state high-resolution ^{13}C NMR spectroscopy and differential scanning calorimetry. The observed ^{13}C chemical shifts of P(3HB–3HV) containing more than 40 mol % HV are different from those of P(3HB–3HV) containing less than 40 mol % HV; this indicates that the structural transition in the P(3HB–3HV) crystals occurs at the comonomer composition of ca. 40 mol % HV. It is shown that the higher (>40%) and lower (<40%) HV-containing copolymers crystallize in the crystalline lattices similar to those of P(3HV) and P(3HB), respectively. From the partitioning of comonomer units between the crystalline and noncrystalline regions, it is concluded that the two kinds of comonomer units cocrystallize in the P(3HB–3HV) crystals. The heat of fusion of the P(3HB–3HV) crystals depends on comonomer composition, while their crystallinity is almost unchanged. These results also support the occurrence of cocrystallization in the P(3HB–3HV) crystals. In the P(3HB) lattice, the HB units are easier to crystallize than the HV units and vice versa in the P(3HV) lattice. The crystallizing ability of the HV units in the P(3HB) crystalline lattice was determined to be about twice that of the HB units in the P(3HV) lattice.

Introduction

Poly(3-hydroxybutyrate) (P(3HB)) and its copolymer with 3-hydroxyvalerate (P(3HB–3HV)) have attracted much attention because they are thermoplastic biopolyesters. They are naturally occurring[1,2] and harmlessly



P(3HB–3HV)

biodegraded to water and carbon dioxide[1] by a wide variety of bacteria. They are statistically random[3–6] and highly crystalline[7,8] copolymers. The mechanical and physical properties of P(3HB–3HV) copolymers vary widely with their comonomer composition.[3,7–11] Such composition dependence of the properties should be ascribed to structural changes of the copolymer in the solid state. Thus, it is important to investigate the composition dependence of the solid-state structures of P(3HB–3HV) copolymers in detail.

The crystalline structures of P(3HB), P(3HV), and their copolymers were analyzed by X-ray diffraction. P(3HB)[12,13] and P(3HV)[14] have similar crystalline structures: both exist in 2_1 helices with fiber periods of 0.596 and 0.556 nm, respectively. P(3HB–3HV) copolymers containing less than 40 mol % HV crystallize in the P(3HB) crystalline lattice, while those containing more than 40 mol % HV crystallize in the P(3HV) lattice.[3,8] The transition from the P(3HB) to P(3HV) crystalline lattices occurs at a comonomer composition of ca. 40 mol % HV. Only the *a* parameter of the crystalline unit cell of P(3HB) increases slightly as the HV content increases. The other parameters, *b* and *c*, of the P(3HB) lattice and all of the P(3HV) lattice parameters are kept constant, irrespective of comonomer composition.

The melting point vs composition curve has a minimum at the comonomer composition where the lattice transition occurs.[3,8] The melting point is depressed steeply as the HV content increases from 0 to 40 mol %. This cannot be predicted by the Flory[15] equation for melting point depression.[3] The Flory equation was based on the assumption that copolymer crystals are composed of only one kind of comonomer unit and that all of the other comonomer units exist in the noncrystalline region. Thus, another model for crystallization of copolymers is required to explain the observed melting point depression of P(3HB–3HV). One possible model is based on the assumption of isomorphism of HB and HV units; that is, both types of comonomer units are simultaneously included in the same copolymer crystals.[3] In fact, such isomorphism is expected because the chemical structure of the HB unit is not so different from that of the HV unit and the crystalline structures of P(3HB) and P(3HV) are geometrically quite similar.[3]

However, the data of other crystalline structure analyses for P(3HB–3HV) containing up to 30 mol % HV indicate that only a small fraction of HV units are included in the P(3HB) crystalline lattice as defects.[16,17] These two results differs in the comonomer composition of the crystalline region. It remains unclear how much of the minor component enters a crystal of the main component.

In the present study, the solid-state structures of P(3HB–3HV) were analyzed by solid-state high-resolution ^{13}C NMR spectroscopy and differential scanning calorimetry (DSC). The solid-state NMR is expected to provide an independent means for discriminating chemically equivalent carbons distributed among different

0024-9297/91/2224-2178$02.50/0

Table I
^{13}C T_1 Values[a] of P(3HB) and P(3HB-55.4% 3HV) Obtained on the Assumption of Biexponential Decay

		C=O	CH	CH_2	s-CH_2(V)	CH_3(B)	CH_3(V)
P(3HB)	slow	180	98	130		2.8	
	rapid	18	5.7	4.3		0.3	
P(3HB-55.4% 3HV)	slow	120	70	58	42	4.0	4.5
	rapid	17	7.5	4.5	2.2	0.4	0.8

[a] Given in seconds.

environments, including more than two types of crystalline lattices and a noncrystalline phase. It is shown that the ^{13}C chemical shifts of P(3HB-3HV) sensitively reflect structural changes of the crystalline phase, such as the lattice transition. The partitioning of HB and HV units is determined between the crystalline and noncrystalline regions. These data provide direct evidence of the occurrence of cocrystallization in the P(3HB-3HV) crystals and make possible a quantitative analysis of cocrystallization.

Experimental Section

Samples. P(3HB) and five kinds of P(3HB-3HV) copolymers containing 18.3, 31.6, 40.7, 55.4, and 93.1 mol % HV were used in this study. P(3HB) and P(3HB-3HV) containing 18.3 mol % HV, hereafter abbreviated as P(3HB-18.3% 3HV), were purchased from Aldrich Chemical Co. The other samples were isolated from *Alcaligenes eutrophus* (ATCC 17699, NCIB 11599). The details of bacterial preparation of P(3HB-3HV) were described elsewhere.[5] Every P(3HB-3HV) sample has a random sequence distribution and not a mixture of random copolymers, which was confirmed by the ^{13}C NMR analysis of its chloroform solution and by DSC measurements.[5,6] The HV content of each sample was determined from its ^1H NMR spectrum in chloroform solution.[3,4]

NMR Measurements. To avoid recrystallization, as-received samples were heated above their melting points in vacuo, then quenched to room temperature, and left for more than 5 days.

Solid-state high-resolution ^{13}C NMR spectra were recorded at 67.9 MHz on a JEOL GSX-270 spectrometer equipped with cross-polarization magic-angle sample spinning (CPMAS) accessories. A sample was packed in a ceramic cylindrical rotor with polyimide end caps. All NMR spectra were acquired with high-power dipolar decoupling (DD) of ca. 60 kHz and MAS at 5.0–5.5 kHz. CPMAS NMR spectra were measured with a 2-ms contact time, a 5-s pulse repetition time, a 27-kHz spectral width, 8K data points, and 1000 accumulations. DDMAS NMR spectra were measured with a 27-kHz spectral width, 8K data points, and 1200–3600 accumulations. ^{13}C chemical shifts were calibrated indirectly by the methyl resonance of solid hexamethylbenzene (17.4 ppm relative to TMS).

The pulse repetition time for quantitative DDMAS NMR measurements was adjusted to be longer than 5 times the spin-lattice relaxation time of a carbon nucleus (T_1^C) of interest. The T_1^C data were obtained by using the pulse sequence developed by Torchia.[18] The T_1^C decay curves were practically reproduced on the assumption of a biexponential decay. The T_1^C data are listed in Table I. The longer and shorter T_1^C values seem to arise from the crystalline and noncrystalline regions, respectively. The T_1^C values for the main-chain carbons are longer than 40 s, indicating the necessity of very long repetition times for quantitative DDMAS NMR measurements. On the other hand, all of the T_1^C values for the side-chain methyl carbons are shorter than 5 s. Thus, quantitative analysis was carried out only for the peaks of the side-chain methyl carbons. Their DDMAS NMR spectra were measured with a pulse repetition time of 25 s.

The relative peak intensities were determined after the curve resolution of overlapping peaks, using the NMR 1 program for spectral analysis obtained from New Methods Research, Inc.

DSC Measurements. The DSC thermal data were recorded on a Seiko DSC-20 equipped with an SSC-580 thermal controller. A heating rate of 20 °C min^{-1} was used. To avoid recrystallization, all samples for DSC measurement were heated to 200 °C, then quenched to room temperature at a rate of ca. 200 °C min^{-1}, and left for 5 days.[5,6] The molecular weights of P(3HB) and P(3HB-3HV) are known to decrease rapidly above 200 °C.[19-21] To avoid the influence of thermal degradation on DSC measurements, samples were freshly prepared for each run.

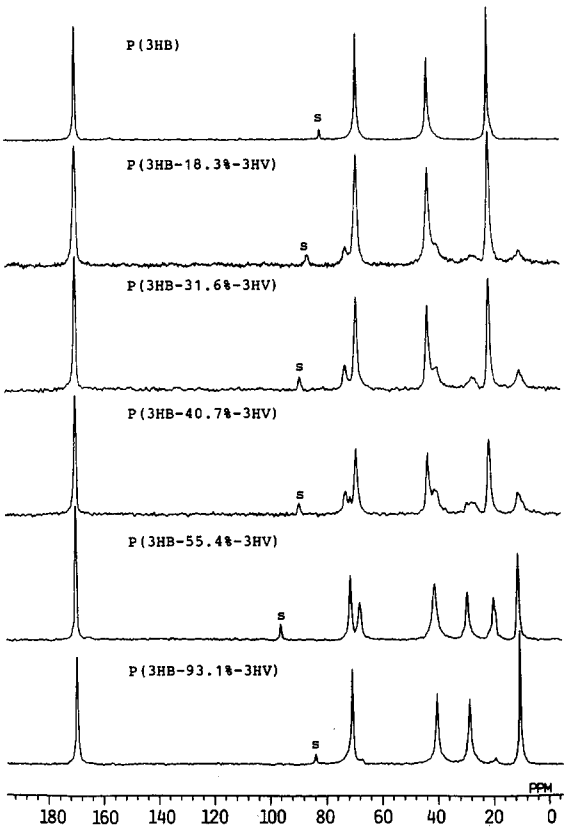


Figure 1. 67.9-MHz ^{13}C CPMAS NMR spectra of a series of P(3HB-3HV) samples.

Results

Crystal Lattices of P(3HB-3HV) Copolymers. Figure 1 shows the 67.9-MHz ^{13}C CPMAS NMR spectra of a series of P(3HB-3HV) samples. Table II lists the chemical shifts for the ^{13}C resonances of the HB and HV units. The main-chain methine carbon resonance of the HV units shows a large discontinuous chemical shift change of ca. 2 ppm between the comonomer compoisitions of 31.6 and 55.4 mol % HV. The other carbon resonances also shift in the same comonomer composition range. Since the CP efficiency of the crystalline region is larger than that of the noncrystalline region in CPMAS NMR of polymer samples, the chemical shift differences seen in Table II should reflect predominantly the differences in crystalline environments such as comonomer sequence distribution, crystallinity, and/or crystalline lattice structures. In solution,[5] the ^{13}C chemical shifts of P(3HB-3HV) are affected by first-order short range structures such as diad and triad comonomer sequences but do not exhibit an apparent dependence on their distribution over a polymer chain. Thus, the variation of the comonomer sequence distribution is not responsible for the chemical shift changes observed here. As described later, the

Table II
Chemical Shifts of ^{13}C Resonances of P(3HB-3HV) Samples in the Solid State

	chem shift/ppm[a]													
		CH(V)[b]		CH(B)[b]		CH_2(B)[b]		CH_2(V)		s-CH_2(V)[b]		CH_3(B)[b]		CH_3(V)[b]	
X/%[c]	CO	LB	LV	LB	LV	LB	LV	LB	LV	LB	LV	LB	LV	LB	LV
0.0	170.0			68.6		42.9						21.4			
18.3	169.8	72.5		68.5		42.9		40.2[d]		26.7[d]		21.1		9.7	
31.6	169.8	72.6		68.6		42.9		39.4[d]		26.9		20.9		9.9	
40.7	169.8	72.6	70.8	68.7		42.9			40.5	27.2		21.0			10.5
55.4	169.9		70.9		67.5		40.6		40.6		29.0		19.5		10.7
93.1	169.8		70.7		67.2		40.3		40.3		28.7		19.4		10.5

[a] Ppm from TMS. [b] B, V, LB, and LV indicate the HB unit, the HV unit, the P(3HB) lattice, and the P(3HV) lattice, respectively. s-CH_2 indicates side-chain methylene of HV units. [c] X indicates HV mol % content of P(3HB-3HV) copolymers. [d] Broad peak.

Table III
Chemical Shifts and Peak Intensities of Methine Carbon Resonances in CPMAS NMR Spectra

	chem shift/ppm[a]						rel peak intensity/%					
	HV unit[b]			HB unit[b]			HV unit[b]		HB unit[b]			
X/%[c]	NV	LB	LV	LB	NC	LV	LB	LV	LB	LV	lattice	X_c/%[c]
0.0				68.70	69.66				100.0		LB	0.0
18.3	72.48			68.49	68.93				100.0		LB	0.0
31.6	72.52	73.04		68.90	68.51		11.5		88.5		LB	11.5
40.7	72.78	72.19		68.99	68.57		11.4		65.6		LB	14.8
			70.94			67.53		15.1		7.9	LV	65.8
55.4	72.52		71.05		67.99	67.48		75.4		24.6	LV	75.4
93.1	72.15		70.80		68.06	67.17		96.7		3.3	LV	96.7

[a] Ppm from TMS. [b] NC, LB, and LV indicate noncrystalline component and crystalline components in the P(3HB) and P(3HV) lattices, respectively. [c] X and X_c indicate HB mol % content of whole P(3HB-3HV) copolymers and that in the crystalline region, respectively.

crystallinity of the P(3HB-3HV) samples is almost independent of the variation of the comonomer composition. Thus, the change of the crystalline lattice seems to be the main source of the characteristic chemical shift changes of P(3HB-3HV) in the solid state.

Since the chemical shifts of P(3HB-18.3% 3HV) and P(3HB-31.6% 3HV) are almost the same as those of P(3HB), these copolymers are considered to crystallize in the P(3HB) crystalline lattice. It is also reasonable to assign the crystalline lattice of P(3HB-55.4% 3HV) and P(3HB-93.1% 3 HV) to that of P(3HV). These assignments are summarized in Table II. In the CPMAS spectrum of P(3HB-40.7% 3HV) shown in Figure 1, two peaks were clearly observed for the main-chain methine carbon resonances of HV units. They can be assigned to the contributions from the P(3HB) and P(3HV) lattices, respectively. This indicates that the transition from the P(3HB) to P(3HV) lattices takes place at a comonomer composition of ca. 40 mol % HV, which is consistent with the results of X-ray studies.[3,8] In conclusion, the ^{13}C chemical shifts sensitively reflect the change in the crystalline lattice of P(3HB-3HV).

Comonomer Composition in the Crystalline and Noncrystalline Regions of P(3HB-3HV) Copolymers. Among all the carbons, the main-chain methine carbons exhibit the largest chemical shift changes on going from the P(3HB) to P(3HV) lattices. The CPMAS NMR peaks of the main-chain methine carbons of both HB and HV units are unambiguously resolved into the contribution from the crystalline and noncrystalline regions by computer simulation. The resulting chemical shifts and the relative peak intensities are shown in Table III.

In the CP experiments, the relative peak intensities do not reflect the exact compositions because the strength of the ^{13}C–^{1}H dipole interaction depends on the environments surrounding the carbon atoms of interest. In general, the CP efficiency is very different between the crystalline and noncrystalline components so that the crystallinity cannot be determined by the CPMAS NMR method alone.

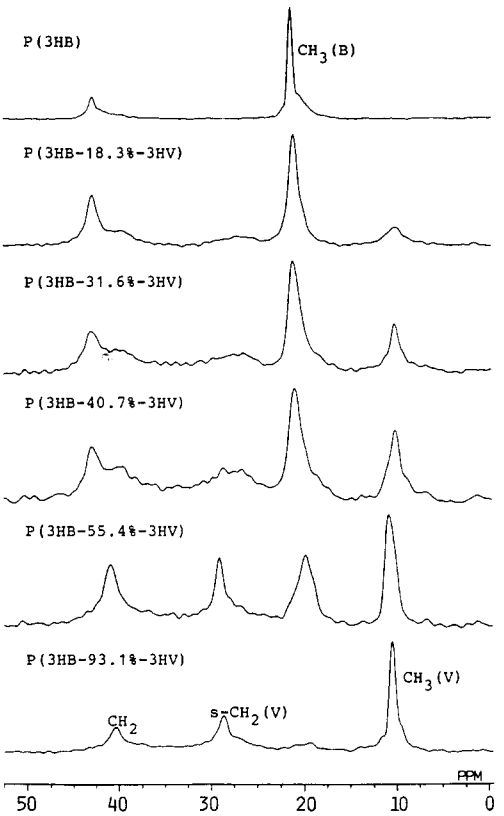


Figure 2. Methyl resonances in the 67.9-MHz ^{13}C DDMAS NMR spectra.

However, the CP efficiencies of comonomer units included simultaneously in a crystal should be similar to each other, because ^{1}H spin diffusion should be effective.[22] Thus, it can be assumed that the CP efficiency of the HB and HV units is the same in the same crystalline lattice. Then the comonomer composition in the crystalline regions is estimated from the relative peak intensities of CPMAS NMR spectra.

Table IV
Chemical Shifts and Peak Intensities of Methyl Carbon Resonances in DDMAS NMR Spectra

	chem shift/ppm[a]						rel peak intentisy/%					
	HV unit[b]			HB unit[b]			HV unit[b]			HB unit[b]		
X/%[c]	LB	LV	NC	LB	LV	NC	LB	LV	NC	LB	LV	NC
0.0				21.34		20.06				72.3		27.7
18.3			10.11	21.24		20.45			19.4	59.4		21.1
31.6	11.32		10.29	21.34		20.74	6.2		25.7	54.0		14.2
40.7	11.56	10.74	9.73	21.42	21.89	20.62	24.5	14.2	18.0	4.1	20.1	19.1
55.4		11.01	10.31		20.77	19.98		42.5	13.2		16.5	27.9
93.1		10.78	10.22			19.73		68.1	25.8			6.1

[a] Ppm from TMS. [b] NC, LB, and LV indicate noncrystalline component and crystalline components in the P(3HB) and P(3HV) lattices, respectively. [c] X indicates HV mol % content of P(3HB-3HV) copolymers.

Table V
Comonomer Composition, Crystallinity, and Heat of Fusion for P(3HB-3HV) Samples

X[a]/%	X_c[a]/%	X_a[a]/%	E[b]	λ[c]/%	ΔH_f[d]/kJ mol^{-1}
0.0				72.3	11.2
18.3	0.0	47.8	0	59.4	6.2
31.6	10.2	64.4	0.246	60.2	3.6
40.7	14.2	48.6	0.242	62.9	4.8
	58.6		0.484		
55.4	72.1	32.1	0.481	58.9	7.6
93.1	100.0	80.8	1	68.1	10.0

[a] X, X_c, and X_a indicate HV mol % content of whole P(3HB-3HV) copolymers, that in the crystalline region, and that in the noncrystalline region, respectively. [b] E indicates the crystallizing ability of the secondary component. [c] λ indicates the degree of crystallinity. [d] ΔH_f indicates the heat of fusion of the pure crystal.

The HV mol % content, X_c, in the crystalline region of each P(3HB-3HV) sample is also listed in Table III. For P(3HB-40.7% 3HV), X_c values were estimated individually for the P(3HB) and P(3HV) lattices. In every sample except for the comonomer composition near 0 or 100% HV, X_c values are not 0 or 100%; i.e., the cocrystallization of the comonomer units was indeed found to occur in P(3HB-3HV). For the copolymer crystals with the P(3HB) lattice, the HV mol % content (X) is larger than X_c, while $X < X_c$ for those with the P(3HV) lattice. Thus, the HB units are easier to crystallize than the HV units in the P(3HB) lattice, and similarly the HV units are easier to crystallize than the HB units in the P(3HV) lattice.

In order to determine the degree of crystallinity and the comonomer composition in the noncrystalline region, quantitative DDMAS NMR spectra of the methyl carbons were carbons were measured with a pulse repetition time of 25 s. Figure 2 shows the methyl resonances in 67.9-MHz ^{13}C DDMAS NMR spectra. These spectra were resolved into component peaks by using the NMR 1 program. The resulting chemical shifts and the relative peak intensities are listed in Table IV. The lattice transition is again indicated from the trends of the chemical shift changes. The HV mol % content in the crystalline (X_c) and noncrystalline (X_a) regions and the degree of crystallinity (λ) were estimated from the relative peak intensities. These data are listed in Table V. For P(3HB-40.7% 3HV), coexistence of the two types of crystalline lattices was again confirmed from the DDMAS NMR spectrum. Thus, we obtained two values for X_c, corresponding to the different crystalline lattices, respectively. The values of λ represent the sum of the contributions from the two crystalline lattices. Both comonomers of P(3HB-3HV) are distributed among the crystalline and noncrystalline regions irrespective of lattice type. The degrees of crystallinity of the P(3HB-3HV) samples studied are ca. 60-70% and are independent of comonomer composition. Such high degrees of crystallinity observed over a wide range of comonomer composition also indicate the occurrence of cocrystallization.[3]

Heat of Fusion of P(3HB-3HV) Copolymers. The values of the heat of fusion of the pure crystal, ΔH_f, were estimated from the degrees of crystallinity and the peak intensities of DSC thermograms (Table V). The ΔH_f value of P(3HB) is determined to be 11.2 kJ mol^{-1}, which is consistent with previous reported values (12.6 kJ mol^{-1} [23] and 10.1 kJ mol^{-1} [3]). The ΔH_f values reach a minimum at a comonomer composition around 40 mol % HV. This tendency is similar to that of the melting point.[3,8] Such comonomer composition dependence of ΔH_f again supports cocrystallization in the P(3HB-3HV) crystals.

Discussion

The X_c values in Table III are in general agreement with those in Table V, although serious deviations are found in several cases. The assumption that the CP efficiency is the same for the HB and HV units in the same crystalline lattice may not be correct. Thus, on the basis of the X_c values estimated from DDMAS NMR spectra (Table V), the crystallizing ability of a secondary component is discussed below. The secondary component is the HV unit for P(3HB-3HV) copolymers with comonomer compositions up to 40 mol % HV, and the HB unit for higher HV-containing copolymers ($X > 40\%$). The secondary component is more difficult to crystallize than the main component.

The crystallizing ability, termed E, was defined as follows: When a crystal has the P(3HB) lattice, i.e., $X < 40\%$, the E value is given by

$$E = \frac{(1 - X)X_c}{X(1 - X_c)} \tag{1}$$

When a crystal has the P(3HV) lattice, i.e., $X > 40\%$, the E value is given by

$$E = \frac{X(1 - X_c)}{(1 - X)X_c} \tag{2}$$

Equations 1 and 2 are rewritten as follows:

$$X_c = \frac{EX}{(1 - X) + EX} \quad (X < 40\%)$$

$$1 - X_c = \frac{E(1 - X)}{X + E(1 - X)} \quad (X > 40\%) \tag{3}$$

The E value represents the fraction of the secondary component that is capable of crystallizing. The crystallizing ability of the main component is defined to be unity. When the E value is equal to unity, the comonomer

composition in the crystalline region is the same as that of the overall copolymer. The secondary component is excluded from the crystal when the E value is equal to zero. The E values obtained are also listed in Table V. The E values for the HV units in the P(3HB) lattice are approximately 0.24, and those for the HB units in the P(3HV) lattice are 0.48. Thus, the crystallizing ability of the secondary component is 1/4 and 1/2 that of the main component in the P(3HB) and P(3HV) crystalline lattices, respectively, or the crystallizing ability of the HB units in the P(3HV) lattice is twice as large as that of the HV units in the P(3HB) lattice. This indicates that the P(3HV) lattice is less destabilized by incorporation of the secondary component than the P(3HB) lattice. In other words, the P(3HV) lattice is less disturbed by incorporation of HB units. This is reasonable considering that a HV unit is more bulky than a HB unit by one methylene unit. However, it is surprising that such a slight structural difference causes such a large (twice) difference in crystallizing ability.

Conclusion

P(3HB–3HV) copolymers crystallize in the same crystalline lattice as homopolymers of the main component. The main component is the HB unit for the copolymers containing up to 40 mol % HV, while the HV unit is the main component for those containing more HV. The main component is easier to crystallize than the secondary component. The crystallization ability of the secondary component is 1/4 and 1/2 that of the main component in the P(3HB) and P(3HV) crystalline lattices, respectively. This is due to the excess free energy of the secondary component incorporating in the crystal. The HB units in the P(3HV) crystalline lattice are easier to crystallize than the HV units in the P(3HB) lattice and vice versa. This may be ascribed to the smaller size of the HB units. This study shows evidence for the P(3HB–3HV) isomorphism hypothesis.

References and Notes

(1) Holmes, P. A. *Phys. Technol.* **1985**, *16*, 32.
(2) Doi, Y.; Tamaki, A.; Kunioka, M.; Soga, K. *Appl. Microbiol. Biotechnol.* **1988**, *28*, 330.
(3) Bluhm, T. L.; Hamer, G. K.; Marchessault, R. H.; Fyfe, C. A.; Veregin, R. P. *Macromolecules* **1986**, *19*, 2871.
(4) Doi, Y.; Kunioka, M.; Nakamura, Y.; Soga, K. *Macromolecules* **1986**, *19*, 2860.
(5) Kamiya, N.; Yamamoto, Y.; Inoue, Y.; Chûjô, R.; Doi, Y. *Macromolecules* **1989**, *22*, 1676.
(6) Inoue, Y.; Kamiya, N.; Yamamoto, Y.; Chûjô, R.; Doi, Y. *Macromolecules* **1989**, *22*, 3800.
(7) Bloembergen, S.; Holden, D. A.; Hamer, G. K.; Bluhm, T. L.; Marchessault, R. H. *Macromolecules* **1986**, *19*, 2865.
(8) Kunioka, M.; Tamaki, A.; Doi, Y. *Macromolecules* **1989**, *22*, 694.
(9) Owen, A. J. *Colloid Polym. Sci.* **1985**, *263*, 799.
(10) Bauer, H.; Owen, A. J. *Colloid Polym. Sci.* **1988**, *266*, 241.
(11) Mitomo, H.; Barham, P. J.; Keller, A. *Polym. Commun.* **1988**, *29*, 112.
(12) Cornibert, J.; Marchessault, R. H. *J. Mol. Biol.* **1972**, *71*, 735.
(13) Yokouchi, M.; Chatani, Y.; Tadokoro, H.; Teranishi, K.; Tani, H. *Polymer* **1973**, *14*, 267.
(14) Yokouchi, M.; Chatani, Y.; Tadokoro, H.; Tani, H. *Polym. J.* **1974**, *6*, 248.
(15) Flory, P. J. *Trans. Faraday Soc.* **1955**, *51*, 848.
(16) Mitomo, H.; Barham, P. J.; Keller, A. *Sen-i Gakkaishi* **1986**, *42*, 589.
(17) Mitomo, H.; Barham, P. J.; Keller, A. *Polym. J.* **1987**, *19*, 1241.
(18) Torchia, D. A. *J. Magn. Reson.* **1978**, *30*, 613.
(19) Grassie, N.; Murray, E. J.; Holmes, P. A. *Polym. Degrad. Stab.* **1984**, *6*, 47.
(20) Grassie, N.; Murray, E. J.; Holmes, P. A. *Polym. Degrad. Stab.* **1984**, *6*, 95.
(21) Grassie, N.; Murray, E. J.; Holmes, P. A. *Polym. Degrad. Stab.* **1984**, *6*, 27.
(22) VanderHart, D. L.; Perez, E. *Macromolecules* **1986**, *19*, 1902.
(23) Barham, P. J.; Keller, A.; Otun, E. L.; Holmes, P. A. *J. Mater. Sci.* **1984**, *19*, 2781.

Registry No. P(3HB–3HV) (copolymer), 80181-31-3.