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Isodimorphism in Synthetic Poly(β-hydroxybutyrate-*co*-β-hydroxyvalerate): Stereoregular Copolyesters from Racemic β-Lactones

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ABSTRACT: Analogues of bacterial poly(β-hydroxybutyrate-*co*-β-hydroxyvalerate) have been synthesized by ring-opening polymerization of mixtures of racemic β-butyrolactone and β-valerolactone with a stereoselective alumoxane catalyst. Atactic fractions were removed by extraction with ethanol or acetone, leaving behind high molecular weight fractions with enhanced stereoregularity and sharp melting points. Whereas bacterial β-hydroxybutyrate/β-hydroxyvalerate polyesters are commercially available for only a limited range of comonomer compositions, the full composition range was obtained synthetically. Approximately the same random comonomer sequence distribution was found for the synthetic materials as for the natural copolyesters. Copolymer compositions were determined by 250-MHz ^{1}H NMR spectroscopy, which is also sensitive to tacticity effects. Tacticity and comonomer sequence effects were investigated in further detail by 63-MHz ^{13}C NMR spectroscopy. As was previously observed for the bacterial copolyesters, the fractionated synthetic analogues were highly crystalline and displayed isodimorphism, a phenomenon in which the crystal lattice of either homopolymer can accommodate the repeating unit of the other monomer.

Introduction

Poly(β-(*R*)-hydroxybutyrate) (PHB) and poly(β-(*R*)-hydroxybutyrate-*co*-β-(*R*)-hydroxyvalerate) (P(HB-*co*-HV)) are the first commercial thermoplastics from a bacterial source. Whereas PHB is a relatively abundant bacterial polyester,[1-6] poly(β-(*R*)-hydroxyvalerate) (PHV) has only been observed in a mixture with other polyalkanoates isolated from sewage sludge.[6-9] The Agricultural Division of ICI has developed a fermentation process for the production of these polyesters from petrochemical as well as nonpetrochemical feedstocks.[10,11] Acetate derived from these feedstocks is the building block for PHB homopolymer. The addition of propionate to the growing culture results in P(HB-*co*-HV).[12] These optically active copolyesters are manufactured in a large-scale fermenter by ICI from *Alcaligenes eutrophus* and are now available in kilogram quantities under the trade name Biopol.[11,12] Although copolymers containing up to 47 mol % β-hydroxyvalerate (HV) have been isolated,[13,14] the upper limit of HV content obtainable in the high-yield fermentation process is 20–30 mol %.[15] The apparent upper limit of HV incorporation is related not to enzyme selectivity but rather to the propionate level in the feed, since this is toxic to the bacteria in the culture. As a consequence, low copolyester yields are obtained for high propionate feeds. Nevertheless, copolyesters grown from *A. eutrophus* have a random comonomer distribution at all available compositions.[16,17]

The bacterial P(HB-*co*-HV) system has several unusual physical properties which have encouraged us to explore the entire composition range of synthetic analogues from 0–100% HV. Despite being a random copolymer, bacterial P(HB-*co*-HV) is crystalline at all accessible compositions. For bacterial samples containing 0–47 mol % HV we have measured degrees of crystallinity by wide-angle X-ray diffraction of 61–74% ± 5%.[16] Depending upon composition, individual copolyesters crystallize in either the PHB unit cell[18-21] or the PHV unit cell.[8,9,22] A crystal lattice transition occurs at ∼30 mol % HV.[16] The lattice transition manifests itself at a minimum or pseudoeutectic point in plots of melting point or enthalpy of fusion against copolymer composition[16] and is probably related to packing energy considerations. This phenomenon of mutually

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Table I
Stereoselective Copolymerization of Racemic β-Butyrolactone (β-BL) and β-Valerolactone (β-VL)[a]

		copolymer composition,[c] mol % HV		copolymer yield, wt %	
β-VL in feed, mol %	$CHCl_3$, vol %[b]	whole polymer	EtOH-insoluble fraction	whole polymer	EtOH-insoluble fraction
0	0	0	0[d]	53	28[d]
12	62	6	6	29	10
17	0	14	10	66	16
36	62	21	17	25	3
43	0	43	40	73	10
49	0	47	32	58	2
55	62	41	41	22	2
64	0	65	62	60	2
77	62	59	58	23	2
82	0	82	78	46	3
88	0	89	86	45	2
95	0	95	95	74	4
100	0	100	100	34	5

[a] For polymerization conditions see text and previous paper.[23] [b] Volume percent $CHCl_3$ in polymerization mixture (see text). [c] Determined by 250-MHz ^1H NMR spectroscopy. [d] Acetone-insoluble fraction.

cocrystallizable repeating units, called isodimorphism, is rare in polymers and requires similar main-chain conformations of the two homopolymers in the two crystal lattices.

In the preceding paper in this issue we described the coordination polymerization of racemic β-butyro- and β-valerolactone for the synthesis of high molecular weight PHB and PHV homopolymers.[23] Using high-field ^1H and ^{13}C NMR spectroscopy, we showed that the $AlEt_3/H_2O$ catalyst has significant stereoselectivity, yielding a stereoregular fraction which was highly crystalline. In the present paper we report a nonbiochemical synthesis of the full composition range of HB/HV copolyesters by polymerization of mixtures of racemic β-lactones utilizing the same alumoxane catalyst. We have explored both tacticity and comonomer sequence effects by ^1H and ^{13}C NMR.[24] The crystalline properties of the synthetic analogues are compared with those of the optically active bacterial copolyesters.

Experimental Section

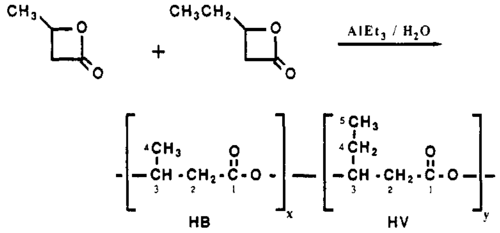
Materials. All chemicals except β-valerolactone (β-VL) were obtained commercially. The samples of bacterial PHB and P(HB-*co*-HV) were produced by ICI, Agricultural Division, Billingham, U.K., and are available through Marlborough Biopolymers Ltd., Hutton Rudby, U.K., under the trade name Biopol. The syntheses of racemic β-VL, PHB, and PHV are described in the preceding paper in this issue.[23] P(HB-*co*-HV) copolyesters were synthesized from mixtures of racemic β-BL and β-VL, following the general polymerization procedure and conditions also described in the preceding paper. All polymerizations were carried out in sealed ampules at 60 °C for 7 days with an alumoxane catalyst composition of $[AlEt_3]/[H_2O] = 1:1$.

Fractionation of Copolymers. After precipitation of the polymerization product into diethyl ether/petroleum ether, the samples were extracted with acetone (PHB) or ethanol (P(HB-*co*-HV) and PHV) for 5–10 h in a Soxhlet apparatus and subsequently stirred in acetylacetone (10 mL/g of polymer) for 2 days in order to remove the alumoxane catalyst.[25] The polymers were then precipitated with ethanol (5 mL/mL of acetylacetone), centrifuged at 10 000 rpm, washed twice with diethyl ether, recentrifuged, and air-dried. Destruction of the catalyst in this fashion removed a yellow impurity and greatly increased the polymer solubility.[23]

Copolymer Characterization. The procedures for the characterization of P(HB-*co*-HV) by ^1H and ^{13}C NMR spectroscopy, thermal analysis, X-ray diffraction, gel permeation chromatography, and viscometry were the same as those used previously for the corresponding homopolymers and are described in detail in previous publications.[14,16,23] Copolymer compositions were determined by integration of expanded 250-MHz ^1H NMR spectra of the methyl group resonances of the HB and HV comonomer units.[14]

Results and Discussion

Synthesis of Stereoregular P(HB-*co*-HV). Table I lists data for a series of β-hydroxybutyrate/β-hydroxyvalerate copolyesters prepared from (±)-β-butyrolactone/(±)-β-valerolactone mixtures by using the alumoxane catalyst from a 1:1 molar ratio of $AlEt_3$ and H_2O (eq 1).[23] This synthetic approach gives P(HB-*co*-HV) samples spanning the composition range 0–100% HV.



(1)

When the polymerization products were extracted with a solvent for the atactic polymer, samples having enhanced stereoregularity were obtained. In Table I the monomer feed composition, copolymer composition, and yield are compared for polymerizations in the presence and absence of $CHCl_3$ solvent. The copolymer composition is close to that of the comonomer feed for conversions ranging from 22% to 74%, a result which suggests that the reactivities of β-BL and β-VL are similar. The addition of $CHCl_3$ to the polymerization mixture, originally intended to facilitate workup, reduced the total yield of stereoregular polymer.[23] Tani et al. observed a lower total yield for PHV than for PHB (26% versus 78%) after precipitation into a mixture of diethyl and petroleum ethers and concluded that β-BL polymerized more rapidly than β-VL. A similar observation is made in the present study (34% versus 53% total yield); however, the alumoxane catalyst is slightly more stereoselective for β-BL than for β-VL,[23] leading to a larger fraction of ether-soluble (atactic) material for the latter. Moreover, for samples with ~85% isotacticity, PHB appears to be less soluble than PHV. Hence, any comparison of total yield in relation to percent conversion for samples of different comonomer composition is unreliable.

Effect of Tacticity on the ^1H NMR Spectra of Synthetic P(HB-*co*-HV). The ^1H NMR spectrum of synthetic P(HB-*co*-HV) is sensitive to the degree of stereoregularity of the polymer. Figure 1 shows the 250-MHz ^1H NMR spectrum of a whole sample containing 59 mol % HV. The two expanded regions are those of the methyl resonances of β-hydroxybutyrate and β-hydroxyvalerate repeating units. Whereas bacterial copolyesters, such as those shown in Figure 2, display a doublet and a triplet for the HB and HV methyl groups at 1.27 and 0.90

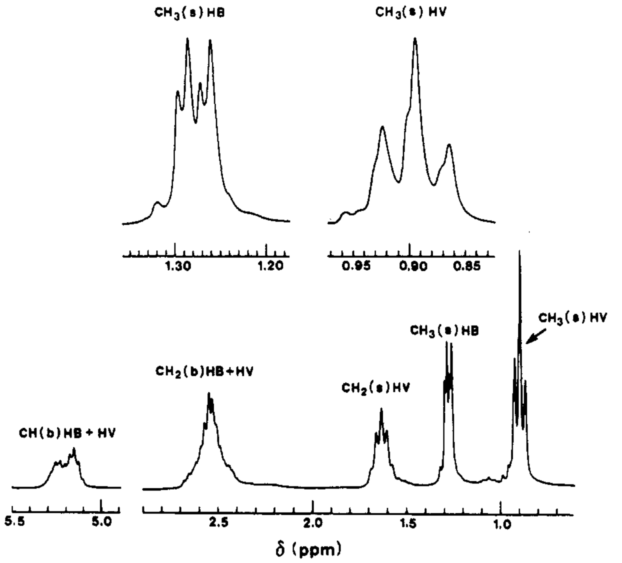


Figure 1. 250-MHz ^{1}H NMR spectra of synthetic P(HB-*co*-59%HV) in $CDCl_3$. Expanded spectra show the HB and HV methyl resonances; b and s refer to backbone and side group, respectively.

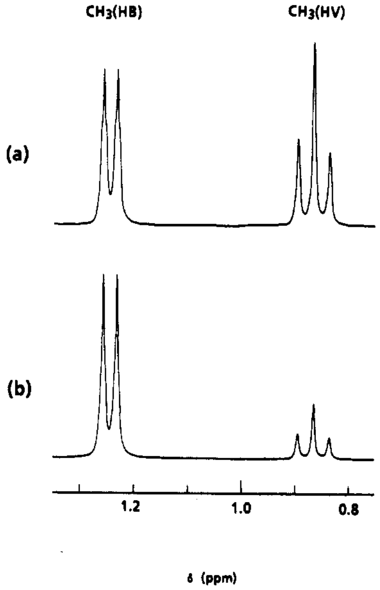


Figure 2. Methyl group region of the 250-MHz ^{1}H NMR spectra of (a) bacterial P(HB-*co*-47%HV) and (b) bacterial P(HB-*co*-20%HV) in $CDCl_3$.

ppm, respectively, synthetic samples (Figure 1) show two overlapping doublets and two overlapping triplets. Since the additional peaks are also observed for the methyl resonances of synthetic PHB and PHV homopolymers,[23] we attribute them to tacticity rather than comonomer sequence effects. After ethanol extraction the soluble, noncrystalline fraction of synthetic P(HB-*co*-HV) shows nearly equal intensities for the two doublets and the two triplets, as expected for an atactic copolymer. The ^{1}H NMR spectrum of the crystalline, insoluble fraction always shows a decreased intensity for the additional high-frequency doublet and triplet as compared with the whole sample, indicating a higher degree of stereoregularity.[24] Just as the ^{1}H NMR spectrum of PHB is more sensitive to tacticity effects than the spectrum of PHV,[23] the HB methyl resonance of synthetic P(HB-*co*-HV) shows a greater sensitivity to tacticity than the HV methyl resonance. Thus, it is difficult to use ^{1}H NMR as a measure of the degree of stereoregularity for copolyesters of high HV content.

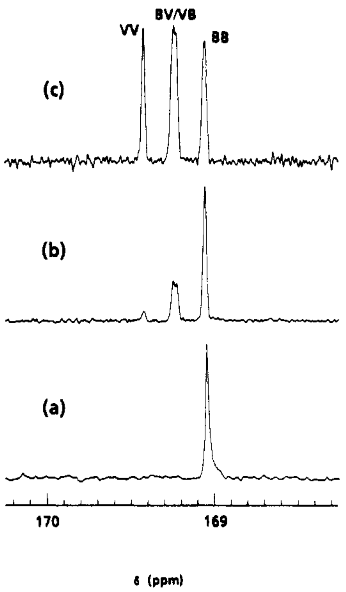
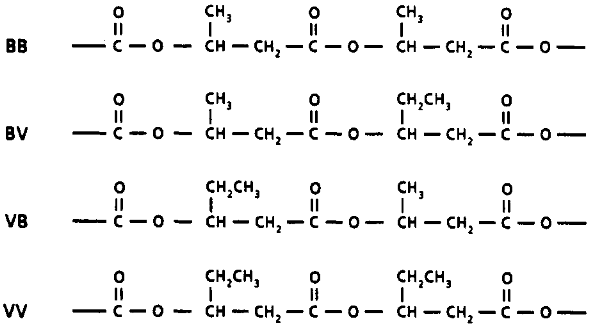


Figure 3. Carbonyl region of the 63-MHz ^{13}C NMR spectra of (a) bacterial PHB, (b) bacterial P(HB-*co*-20%HV), and (c) bacterial P(HB-*co*-47%HV) in $CDCl_3$.

Scheme I



$$\text{BB}\quad -\overset{O}{\overset{\|}{C}}-O-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-O-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-O-$$

$$\text{BV}\quad -\overset{O}{\overset{\|}{C}}-O-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-O-\overset{CH_2CH_3}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-O-$$

$$\text{VB}\quad -\overset{O}{\overset{\|}{C}}-O-\overset{CH_2CH_3}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-O-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-O-$$

$$\text{VV}\quad -\overset{O}{\overset{\|}{C}}-O-\overset{CH_2CH_3}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-O-\overset{CH_2CH_3}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-O-$$

^{13}C NMR Analysis of Comonomer Sequence and Tacticity Effects. Both bacterial and synthetic P(HB-*co*-HV) samples reveal similar comonomer sequence effects in their ^{13}C NMR spectra. Comonomer sequence distributions in bacterial copolyesters have previously been determined from an analysis of the carbonyl ^{13}C NMR spectra.[16,17] Figure 3 shows that for bacterial P(HB-*co*-HV) the carbonyl region comprises four resonances, corresponding to BB, BV, VB, and VV diads (Scheme I, where B and V refer to β-hydroxybutyrate and β-hydroxyvalerate repeating units, respectively); the peaks for BB and VV sequences are well resolved, while those of BV and VB diads partially overlap.[16]

For synthetic P(HB-*co*-HV), the NMR analysis is more complex, since signals arise from tacticity as well as from comonomer sequence effects. Figure 4 shows the ^{13}C NMR spectrum of a synthetic copolyester containing 59 mol % HV. In the expanded carbonyl region, multiple resonances are observed. Whereas bacterial P(HB-*co*-HV) displays only isotactic (*i*) diad resonances, spectra of the synthetic copolyesters show an additional syndiotactic (*s*) diad resonance ca. 0.10 ppm to high frequency of each of the three resolved *i* diad (i.e., VV, VB + BV, and BB) resonances.[24] This assignment, based on peak positions and intensities, was made by comparing ^{13}C NMR spectra of synthetic copolyesters of different HV content (Figure 5). Figure 6 shows a hypothetical structure for P(HB-*co*-HV) in which the diad structures responsible for each of the resonance peaks in Figure 5 are identified. If synthetic P(HB-*co*-HV) formed long blocks with respect to comonomer distribution, significant resonances due to BV/VB

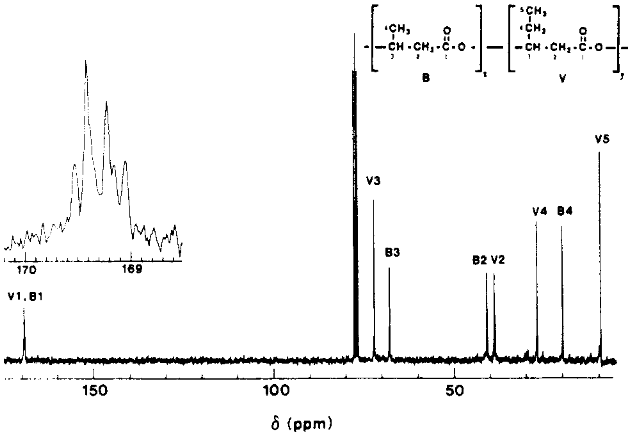


Figure 4. 63-MHz ^{13}C NMR spectrum of synthetic P(HB-*co*-59%HV) in $CDCl_3$. The expanded spectrum shows the carbonyl region.

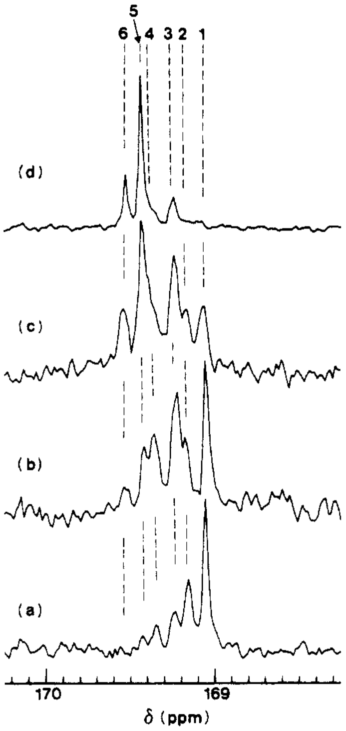


Figure 5. Carbonyl region of the 63-MHz ^{13}C NMR spectra of synthetic P(HB-*co*-HV) in $CDCl_3$ containing (a) 14, (b) 41, (c) 59, and (d) 86 mol % HV. Diads are identified as follows: 1, BB-*i*; 2, BB-*s*; 3, BV/VB-*i*; 4, BV/VB-*s*; 5, VV-*i*; 6, VV-*s*.

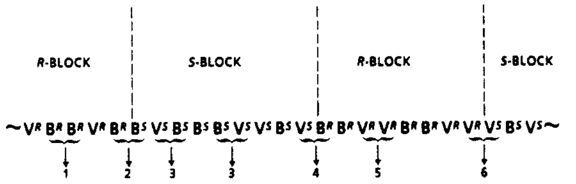


Figure 6. Schematic representation of a P(HB-*co*-HV) copolymer containing 50 mol % HV. Diads are labeled as follows: 1, BB-*i*; 2, BB-*s*; 3, BV/VB-*i*; 4, BV/VB-*s*; 5, VV-*i*; 6, VV-*s*.

diads would not be observed. However, such resonances are clearly seen in Figure 5, and their variation in intensity with comonomer composition further suggests that the synthetic copolyesters are close to random in comonomer distribution. On extraction with ethanol the *s* diad content of P(HB-*co*-HV) is significantly reduced; Figure 7 shows ^{13}C NMR spectra of the highly stereoregular insoluble fractions. Whether these polymers are stereoblock (as in Figure 6 with longer sequences of ~*RRRRR*~ and ~*SSSSS*~) or consist of independent isotactic *R* and *S* chains[21,22] containing occasional defects (i.e., ~*RRSRR*~ and ~*SSRSS*~) cannot be determined from the carbonyl ^{13}C NMR spectra since only diads are resolved. However, as pointed out in the previous paper,[23] it is difficult to envision how a racemic mixture of isotactic *R* and *S* polymers can be produced from racemic comonomers by an achiral homogeneous catalyst.

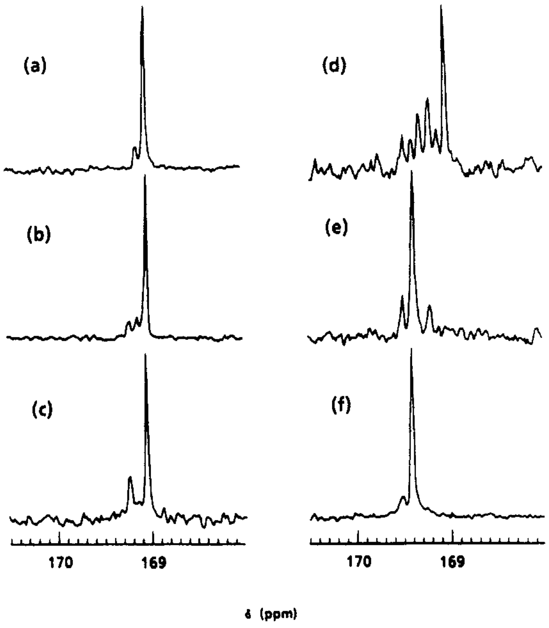


Figure 7. Carbonyl region of the 63-MHz ^{13}C NMR spectra of fractionated synthetic P(HB-*co*-HV) in $CDCl_3$: (a) 0, (b) 6, (c) 17, (d) 32, (e) 95, and (f) 100 mol % HV.

Table II
Molecular Weight Analysis of Bacterial and Synthetic P(HB-*co*-HV)

P(HB-*co*-HV), mol % HV	$[\eta]$, dL/g	$M_v \times 10^{-3}$, g/mol	$M_n \times 10^{-3}$,[a] g/mol	M_w/M_n[a]
		Bacterial		
0	2.17	293	161	2.1
4	1.03	113		
8	1.16	131		
17	3.42	526		
20	1.59	197	51.7	3.6
		Synthetic[b]		
0	1.46	177	21.4	5.6
6	1.69	213		
32	1.49	181	35.5	3.5
95	1.64	205	33.8	4.1
100	1.78	228	52.1	3.5

[a] Gel permeation chromatography. [b] Fractionated synthetic samples.

Molecular Weight of Synthetic P(HB-*co*-HV). The molecular weights of bacterial and synthetic P(HB-*co*-HV) are similar; however, the synthetic copolyesters have a slightly broader molecular weight distribution. Table II lists the intrinsic viscosities of representative bacterial and fractionated synthetic P(HB-*co*-HV) samples. The viscosity-average molecular weights, M_v, are also listed in Table II. These values were calculated from the intrinsic viscosities by using Mark–Houwink–Sakurada constants *K* and *a* for PHB from the literature.[26,27] Values of *K* and *a* for PHV and P(HB-*co*-HV) have not previously been reported. If the estimation procedure of Van Krevelen[28] is used to derive *K* for the copolyesters, the calculated value varies little with composition.[23] The results in Table II show that the alumoxane catalyst yields high molecular

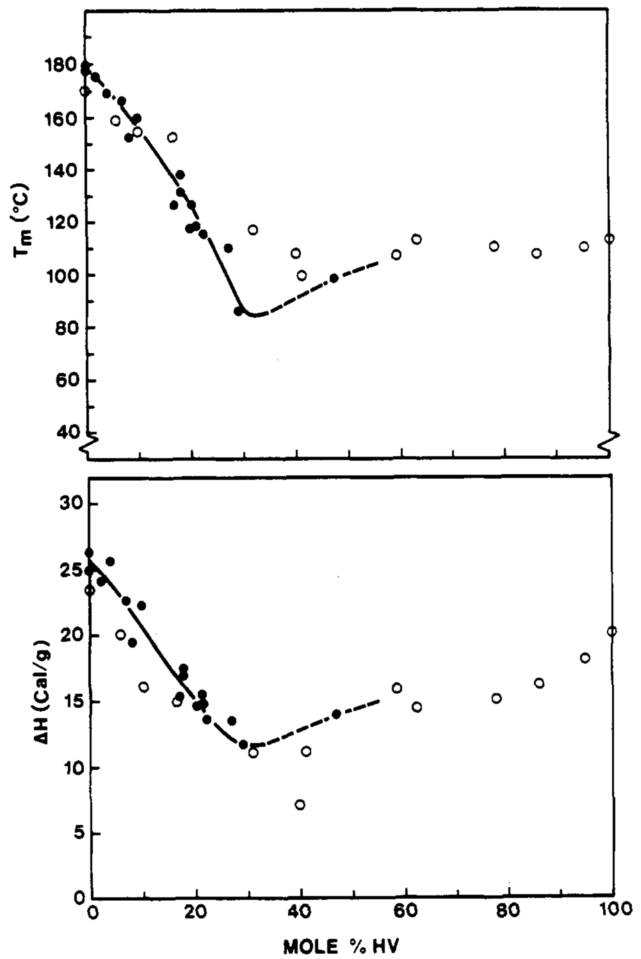


Figure 8. Variation of melting point (T_m) and enthalpy of fusion (ΔH_m) with composition for bacterial (solid circles) and fractionated synthetic P(HB-*co*-HV) (open circles).

weight analogues of the bacterial copolyesters. This is confirmed by gel permeation chromatography. It is noteworthy that molecular weights measured for both bacterial and synthetic P(HB-*co*-HV) are higher than those of conventional polyesters prepared by condensation polymerization.

Crystallinity of Fractionated Synthetic P(HB-*co*-HV). The insoluble fractions of ethanol-extracted synthetic P(HB-*co*-HV) are highly crystalline and display relatively sharp melting endotherms. The effect of extraction on the DSC thermograms of synthetic P(HB-*co*-HV) has been reported in detail elsewhere.[24] Figure 8 shows plots of melting point (T_m) and enthalpy of fusion (ΔH_m) against copolymer composition for the bacterial and fractionated synthetic copolyesters.[30] In general, good agreement was observed for T_m and ΔH_m between bacterial and synthetic materials over the composition range where samples from both sources were available. Copolymers containing more than 47 mol % HV, synthesized via the nonbiochemical route, appear to follow the previously predicted pattern[16] based on bacterial P(HB-*co*-HV). Minima in T_m and ΔH_m are observed (Figure 8) at ~30 mol % HV, a pseudoeutectic point which corresponds to the transition from the PHB to the PHV crystal lattice.[16] DSC thermograms of bacterial and fractionated synthetic copolyesters are compared in Figure 9. As with the bacterial polymers, the synthetic samples display broad melting endotherms in the composition midrange. With increasing HV content, the endotherms sharpen. Bacterial PHB and synthetic PHV both display very sharp melting endotherms, but synthetic PHB shows a significant low-temperature shoulder. This suggests that the PHB crystal lattice is less accommodating of stereoirregularities than the PHV lattice. The smaller change in ΔH_m (i.e., the difference in ΔH_m between the pure homopolymer and the pseudoeutectic composition) for PHV as opposed to PHB (9 versus 15 cal/g, respectively) and the location of the pseudoeutectic point (~30 mol % HV) also suggest that the PHV lattice more easily accommodates the smaller methyl side group of HB than the PHB lattice accommodates the ethyl group of HV. The existence of multiple peaks and a broad melting range is a complex phenomenon which could be explained by a distribution of crystallite sizes.[31,32] Wide-angle X-ray diffraction has shown, however, that the average crystallite size for both bacterial[14] and synthetic copolyesters is independent of composition. Alternatively, the relatively broad melting endotherms could be a result of differing degrees of crystal imperfection or could arise from the melting range and composition range corresponding to solidus and liquidus lines in a true two-component liquid/solid phase diagram.[33]

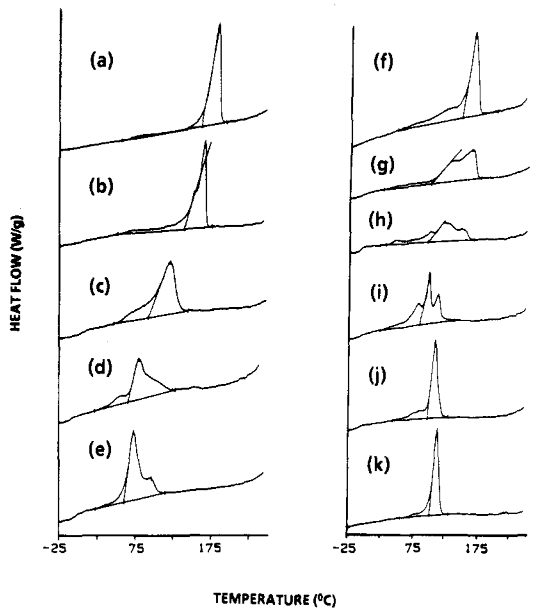


Figure 9. DSC thermograms. Bacterial P(HB-*co*-HV): (a) 0, (b) 7, (c) 21, (d) 29, and (e) 47 mol % HV. Fractionated synthetic P(HB-*co*-HV): (f) 0, (g) 10, (h) 32, (i) 78, (j) 86, and (k) 100 mol % HV.

Figure 10 displays the X-ray powder diffraction patterns of some fractionated synthetic copolyesters. All samples except P(HB-*co*-40%HV) show a significant level of crystallinity. However, this sample was incompletely extracted with ethanol, as indicated by ^{13}C NMR spectroscopy. As a result, a larger weight fraction was isolated than for similar copolyesters (Table I), and a lower enthalpy of fusion was observed (Figure 8). A clear transition in the X-ray powder pattern is observed (Figure 10) as the HV content increases. As reported previously for bacterial P(HB-*co*-HV),[16] the PHB crystal lattice persists up to ~30 mol % HV, while the PHV lattice is observed for copolyesters containing 40–100 mol % HV. It should be noted that the synthetic sample containing 32 mol % HV, which is close to the pseudoeutectic composition, displays both PHB and PHV crystal lattices (Figure 10). Whether this reflects the nature of the true pseudoeutectic, or is the result of slight comonomer composition drift, is not known.

Conclusions

The evidence presented previously for isodimorphism in bacterial P(HB-*co*-HV) was incomplete in the sense that only half the composition range was accessible, and only

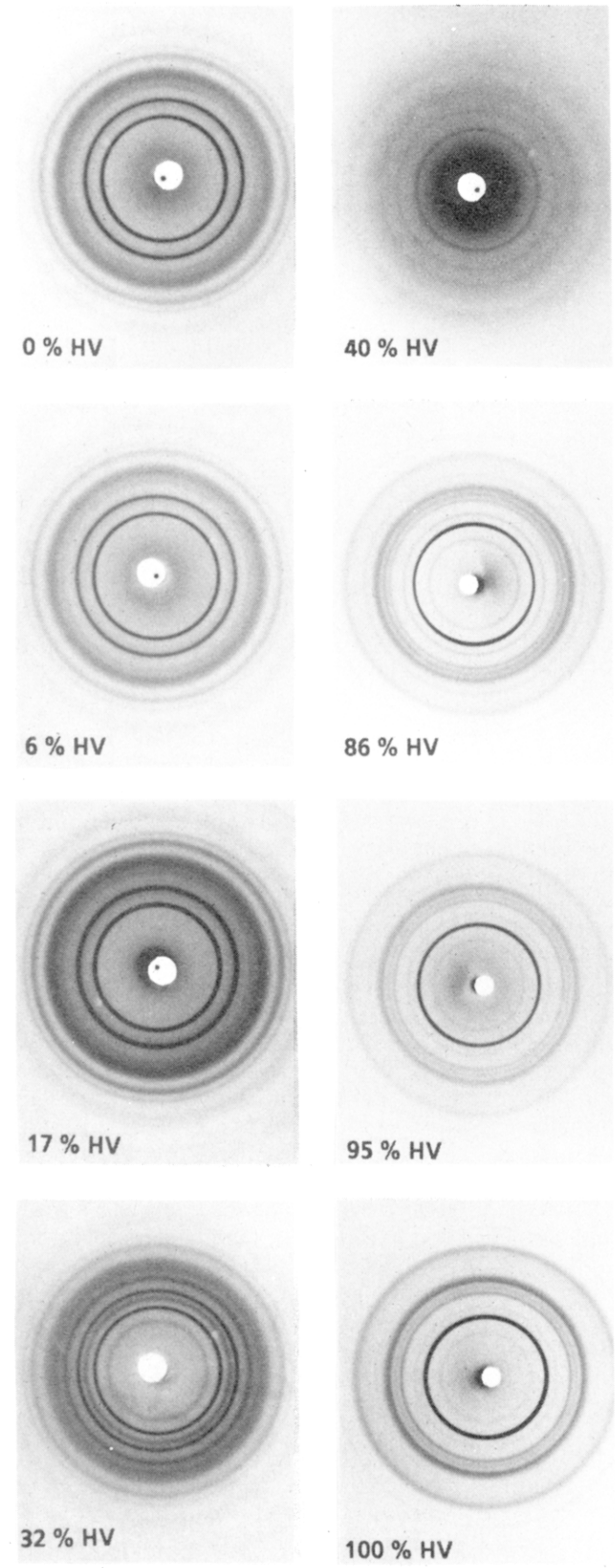


Figure 10. Wide-angle X-ray powder diffraction patterns of fractionated synthetic P(HB-*co*-HV). Copolymer compositions are indicated in mol % HV.

one of the eight samples studied, namely, P(HB-*co*-47%-HV), crystallized in the PHV lattice.[16] We have now synthesized close analogues of bacterial P(HB-*co*-HV) over the full range of compositions, including the range 47–100 mol % HV not available from commercial sources.[34] Sharp melting copolyesters with a high degree of stereoregularity were obtained by solvent fractionation. The synthetic copolyesters are optically inactive and are apparently random in comonomer distribution. Like bacterial P(HB-*co*-HV), the fractionated synthetic analogues are highly crystalline and display isodimorphic behavior. Despite containing a small fraction of stereoirregularities, the fractionated copolyesters prepared in this study are remarkably similar to optically active bacterial P(HB-*co*-HV) in melting point, enthalpy of fusion, and X-ray crystal structure. The bacterial copolyesters provide thermoplastic materials with a range of properties of potential interest for a variety of commercial applications.[35-37] The range of mechanical properties (e.g., toughness, flexibility) is expected to be extended by the synthetic analogues.

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Registry No. (H3)(HV) (copolymer), 110774-30-6.

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Ring Flips as a Probe of the Structure of Polyanilines

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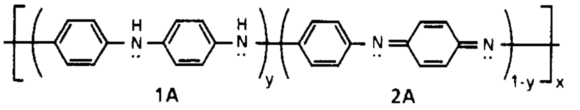
ABSTRACT: Deuterium solid–echo and carbon magic angle spinning NMR measurements have been performed in order to investigate the structure and dynamics of insulating and conducting forms of polyaniline. For all of the polymers studied, the primary motion of the chains from room temperature to over 400 K is phenyl ring 180° flipping, which is commonly observed in the amorphous regions of polymers. Deuteron spin alignment and carbon spin–lattice relaxation data show that there is a very broad distribution of correlation times for ring flips, extending from less than 10^{-7} s to at least 1 s. However, the deuterium spectra can be deconvoluted into two line-shape components, attributable to fast and slow flippers, and the ratio of these components is shown to be a convenient indicator of the polymer dynamics and a sensitive probe of free volume. For the conducting salt form, emeraldine hydrochloride, approximately one-third as many rings can be classified as fast flippers as for the emeraldine base. The decrease in the number of fast flippers is caused by partial π-character of the ring–nitrogen bonds and/or steric interactions with adjacent chloride counterions. This result is shown to be consistent with a structure for the salt containing poly(semiquinone radical cation) segments and residual reduced units.

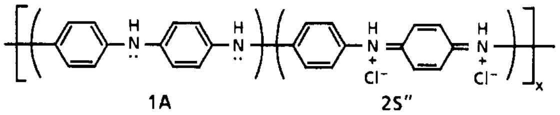
Introduction

Polyaniline has been the subject of considerable scientific inquiry because of its unique electrical behavior and its potential as an environmentally stable conducting polymer. It is synthesized by the electrochemical or chemical oxidative polymerization of aniline and can exist as a number of unique structures, characterized by the oxidation state, i.e., the ratio of amine to imine nitrogens, and the extent of protonation.[1-3] These different structures can be interconverted by acid/base or oxidation/reduction treatment. Six basic repeat unit building blocks have been proposed from which the different forms of polyaniline are composed.[2] They are designated by 1 = reduced or 2 = oxidized, followed by A = amine or imine base, S′ = monoprotonated salt, or S″ = diprotonated salt. The unprotonated forms of polyaniline consist of reduced base units, 1A, and oxidized base units, 2A, as follows:



(I)

where the oxidation state of the polymer increases with decreasing values of y ($0 \leq y \leq 1$). Claims have been made that polyaniline polymers having the following compositions (and others) have been isolated: the fully reduced leucoemeraldine base ($y = 1$), the half-oxidized emeraldine base ($y = 0.5$), and the fully oxidized pernigraniline base ($y = 0$).[2] Protonation of the base forms leads to polymers whose conductivity depends upon the ratio of reduced and oxidized units as well as the extent of protonation. Of particular interest is the highest conductivity form, the emeraldine salt, which has an idealized composition corresponding to an equal number of 1A and 2S″ units:



(II)

Structural characterization of the various forms of polyaniline has been limited because, like most conducting polymers, they are largely insoluble in common organic solvents. A number of spectroscopic studies have been carried out, however, in the solid state. X-ray diffraction measurements of emeraldine base and emeraldine hydrobromide salt indicate these forms of polyaniline to be completely amorphous.[4] Raman studies of emeraldine base have identified the presence of para-disubstituted benzene and quinone diimine moieties and, taken together with infrared spectra, have provided evidence for a head-to-tail polymerization of aniline, with no ortho incorporation of phenylenediamine groups.[5] The same conclusion was reached by comparison of the infrared spectrum of emeraldine base with that of a regiospecifically synthesized polymer.[6] Difficulties have been encountered in establishing the polyaniline secondary structure, such as sequence distribution and chain conformations, because of broad line widths measured in ^{13}C NMR[7,8] and photoemission[9] spectra. Possible reasons for the low spectroscopic resolution are compositional defects, a distribution of torsion angles between adjacent rings, variations in syn and anti conformational arrangements about the benzenoid

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