labeled butyl rubber fractions of different $\bar{M}_n$. Their spectra recorded at 220 K indicate that the line shape starts to change markedly only at low molecular weights, which is in accordance with Bullock's finding that the independence of τ_R of the chain length at higher molecular weights is characteristic of a segmental or local mode relaxation.[38]

In summary, the method of nitroso spin labeling offers a simple and versatile route for obtaining nitroxyl functionalized macromolecular chains. The only requirement is the presence of appropriate C=C double bonds along the polymer chain. It is to be noted that the so-called forced ideal quasi-living (FIQL) copolymerization method[39,40] provides a particularly good procedure for preparing tailor-made copolymers with controlled composition and molecular weight. By use of this technique, even a very small relative amount of diene as comonomer can be incorporated into the polymer chain in a way that the microstructure of the copolymer, i.e., the sequence distribution along the chain, remains uniform. Another and so far not yet fully exploited feature of the FIQL copolymerization technique is that it works best in producing low molecular weight polymeric species, an inexhaustible pool of starting materials to obtain labeled polymers and macromolecular spin probes.

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Communications to the Editor

Synthesis of Crystalline β-Hydroxybutyrate/β-Hydroxyvalerate Copolyesters by Coordination Polymerization of β-Lactones

Optically active poly(β-hydroxybutyrate-*co*-β-hydroxyvalerate), P(HB-*co*-HV), is manufactured in a fermentation process by ICI and marketed as Biopol through Marlborough Biopolymers, Billingham, U.K.[1] The copolyesters are offered in a range of compositions and are thermoplastics varying in such physical properties as melting point, toughness, and flexibility. Although copolymers containing up to 47 mol % β-hydroxyvalerate (HV) have been isolated,[2,3] the upper limit of HV content obtainable in a high-yield fermentation process is 20–30 mol %.[4]

The P(HB-*co*-HV) system has several remarkable physical properties which make it desirable to explore the entire composition range from 0 to 100% HV. In spite of being random copolymers,[1,5-7] bacterial P(HB-*co*-HV) from *Alcaligenes eutrophus* is crystalline at all accessible compositions.[5,6] Depending upon composition,[5,6] individual copolyesters crystallize in either the poly(β-hydroxybutyrate) (PHB)[8-10] unit cell or the poly(β-hydroxyvalerate) (PHV)[11] unit cell. The lattice transition, at about 30 mol % HV, appears as a pseudoeutectic in plots of melting point and enthalpy of fusion against copolymer composition.[6] This phenomenon of mutually cocrystallizable repeating units, relatively uncommon in polymer science, is called isodimorphism and is a consequence of the similar crystalline conformations of the two homopolymers.

In the present paper we report the synthesis of high molecular weight P(HB-*co*-HV), by a nonbiochemical route, having statistical sequence distributions similar to

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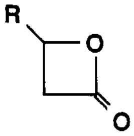
those of the bacterial copolymers. By coordination polymerization of racemic β-lactones using a stereoregulating organoaluminum catalyst we have prepared crystalline copolyesters containing 0–100 mol % HV.

Copolymer Synthesis. Copolyesters were prepared from mixtures of racemic β-butyrolactone and β-valerolactone by an adaptation of the procedure used by Tani and co-workers, who prepared PHB and PHV homopolymers.[12] The catalyst for the polymerization of these lactones was the reaction product of triethylaluminum with water, as used by Agostini, Lando, and Shelton in the original synthesis of PHB.[13] The product of the polymerization was partially stereoregular and by adjusting the ratio of [$AlEt_3$]/[H_2O] to 1:1 the stereoregularity of the product could be maximized.[14] By extraction with ethanol, a fraction could be isolated which was highly stereoregular.[12] Both of these fractions were characterized by solution NMR, wide-angle X-ray diffraction, and differential scanning calorimetry.



R = - CH_3
- CH_2CH_3

Stereochemical Notation. The polymerization of racemic lactones introduces stereochemical features into the synthetic copolyesters which are not present in the bacterial copolyesters. These natural copolyesters are optically pure poly(β-(*R*)-alkanoates), where *R* refers to the stereochemistry of the chiral centers. The synthetic analogues are prepared from racemic monomers and are optically inactive. Because of stereoregulation by the catalyst, however, blocks of *R* or *S* monomers are incorporated in the polymer chains. The monomer sequence can be analyzed in terms of *RR*, *RS*, *SR*, and *SS* diads or *RRR*, *RRS*, *SSR*, *RSR*, *SRS*, and *SSS* triads by NMR as discussed in the following section. Since *RR* and *SS* diads are NMR equivalent because of their enantiomeric relationship, they are referred to as isotactic (i) diads. *RS* and *SR* diads are collectively referred to as syndiotactic (s) diads.[15] Similarly, *RRR* and *SSS* triads are referred to as isotactic (I) triads, *RRS* and *SSR* are collectively referred to as heterotactic (H) triads, and *RSR* and *SRS* are collectively referred to as syndiotactic (S) triads.

Studies of Stereochemistry and Sequence Distribution by NMR. Both bacterial and synthetic copolyesters reveal similar comonomer sequence effects in ^{13}C NMR. The comonomer sequence distribution of bacterial copolyesters has been determined previously from analysis of the carbonyl region in ^{13}C NMR spectra.[6,7] This carbonyl region comprises four resonances, two of which are poorly resolved; these were assigned to BB, (BV,VB), and VV diad sequences, where B and V refer to β-hydroxybutyrate and β-hydroxyvalerate units, respectively.[6] For synthetic copolyesters the NMR analysis is more complex, since in addition to comonomer sequence effects, tacticity effects are observed. For synthetic P(HB-*co*-HV) both ^{13}C and ^{1}H NMR provide information on tacticity, whereas ^{13}C NMR provides additional information on comonomer sequence effects.

Figure 1 shows the ^{13}C NMR spectrum of a synthetic copolyester containing 32 mol % HV. In the expanded carbonyl region, six resonances are observed. Because bacterial copolyesters are optically pure, they display only isotactic diad resonances in the carbonyl region of their ^{13}C NMR spectra, corresponding to the BB-i diad at 169.1 ppm, the BV/VB-i diad at 169.3 ppm, and the VV-i diad at 169.5 ppm.[6] The synthetic copolyesters have one additional resonance approximately 0.10 ppm downfield from each of the three i diad resonances. On the basis of peak position and intensities, and knowledge of the overall copolymer compositions, we assign these peaks to s diads.[18]

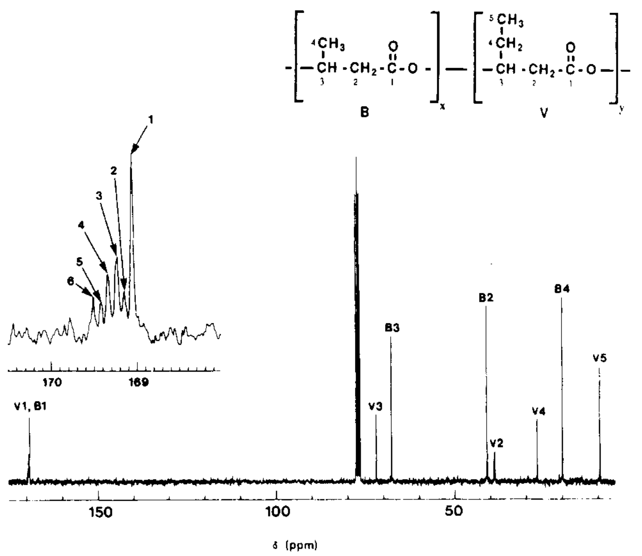


Figure 1. ^{13}C NMR spectrum, 63 MHz, of synthetic P(HB-*co*-32% HV), $M_v = 1.81 \times 10^5$ (M_v was calculated from the intrinsic viscosity measured in $CHCl_3$ at 30 °C, using *K* and *a* constants from ref 16 and 17). Diad peaks are identified as follows: (1) BB-i; (2) BB-s; (3) BV/VB-i; (4) BV/VB-s; (5) VV-i; (6) VV-s.

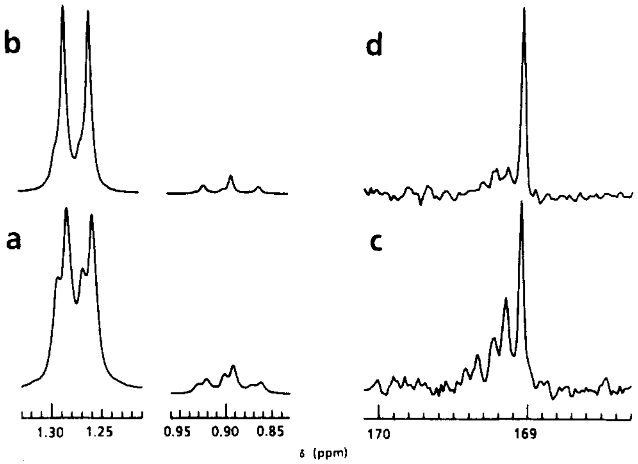


Figure 2. Effect of extraction of synthetic P(HB-*co*-10% HV) on NMR spectra: (a,b) expanded 250-mHz ^{1}H NMR spectra of the methyl resonances of (a) the whole polymer sample and (b) the EtOH-insoluble fraction; (c,d) expanded 63-MHz ^{13}C NMR spectra of the carbonyl resonances of (c) the whole polymer sample and (d) the EtOH-insoluble residue; whole sample refers to as-synthesized material after precipitation from a nonsolvent such as diethyl ether/petroleum ether.

As an example of tacticity effects in ^{1}H NMR, Figure 2a shows sections of the 250-MHz spectrum of synthetic P(HB-*co*-10% HV). Whereas bacterial copolyesters display an HB-CH_3 doublet at 1.27 ppm and an HV-CH_3 triplet at 0.90 ppm, the HB and HV methyl resonances of synthetic P(HB-*co*-10% HV) show two overlapping doublets and two overlapping triplets. Since this effect is also observed in the HB-CH_3 resonance of synthetic PHB homopolymer, in which comonomer sequence effects are absent, we attribute the doubling of these two methyl resonances to tacticity effects, corresponding to partial resolution of triads. When the whole sample of Figure 2a was extracted with ethanol, which is a solvent for nonstereoregular material,[12] the soluble noncrystalline fraction

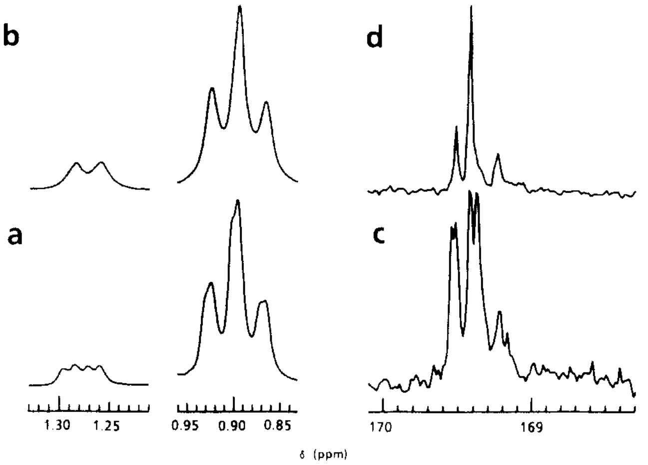


Figure 3. Effect of extraction of synthetic P(HB-*co*-86% HV) on NMR spectra: (a,b) expanded 250-MHz ^{1}H NMR spectra of the methyl resonances of (a) the whole polymer sample and (b) the EtOH-insoluble fraction; (c,d) expanded 63-MHz ^{13}C NMR spectra of the carbonyl resonances of (c) the whole polymer sample and (d) the EtOH-insoluble residue.

was found to have equal intensities of the two doublets and of the two triplets. This is to be interpreted as an atactic configuration, as will be clarified below. The ^{1}H NMR of the crystalline, insoluble fraction given in Figure 2b displays a decreased intensity of the second doublet and triplet. Clearly, this sample is more stereoregular than the whole sample of Figure 2a. At least one of the contributions to the high-field doublet and triplet is due to I triads, since the doublet and triplet have the same chemical shift as observed for bacterial P(HB-*co*-HV). The additional downfield doublet and triplet are assigned to H triads; no separate set of signals is observed corresponding to S triads. Equal intensity of the two sets of signals appears to correspond to the absence of stereoregularity (atacticity) since in the ^{13}C NMR spectrum of the same samples there are as many *RS*/*SR* as *RR*/*SS* diads giving rise to equal intensity signals. A low relative intensity of the downfield doublet and triplet appears to correspond to a high degree of stereoregularity (isotacticity) since in the ^{13}C NMR spectrum of the same samples a low relative intensity of s versus i diads is observed.

Parts c and d of Figure 2 show part of the ^{13}C NMR spectrum of the whole sample and fractionated, insoluble fraction of synthetic P(HB-*co*-10% HV), respectively. The BB-i and -s, BV/VB-i and -s, and the VV-i diad resonances are clearly visible in Figure 2c, but because of the low HV content of this particlar synthetic sample, the VV-s diads are not intense enough to be observed. Figure 2d shows the effect of removal of atactic material by extraction with ethanol, as demonstrated by the decreased intensity of the resonances corresponding to BB-s and BV/VB-s diads.

Figure 3 is the same plot as Figure 2 but for a sample of P(HB-*co*-86% HV). As was the case with the 10 mol % HV sample, this synthetic copolyester could be extracted with ethanol to leave behind an insoluble stereoregular fraction. Whole samples containing 70–100% HV show additional resonances (Figure 3c), as compared with whole samples of low HV content (cf. Figure 2c). Extraction of these high HV samples, however, greatly simplifies the spectrum (Figure 3d) so that again only the s diad peaks are observed downfield of i diad resonances. We attribute the additional resonances in high-HV samples to long-range effects.

Figures 2 and 3 show that there is good agreement between the tacticity information in the ^{1}H and ^{13}C NMR spectra. If these synthetic copolymers formed blocks with respect to comonomer distribution, resonances arising from BV/VB diads would not be observed. However, such resonances are clearly seen in both Figures 2 and 3 (parts c and d), and the variation of their intensity with comonomer composition suggests that these synthetic copolyesters are close to random in comonomer distribution.

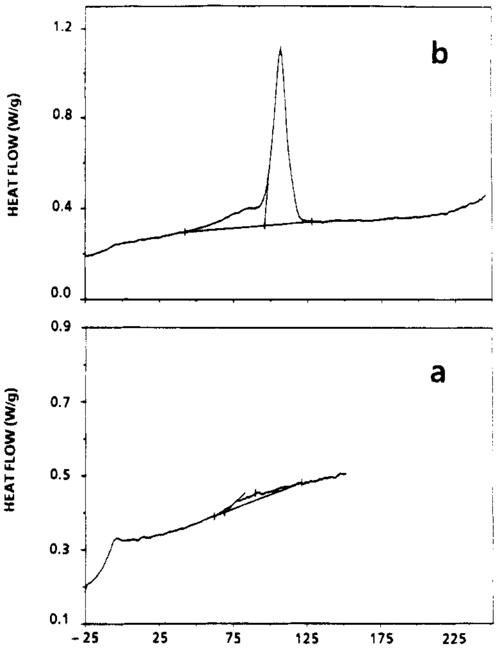


Figure 4. Effect of extraction of synthetic P(HB-*co*-86% HV) on DSC thermograms: (a) whole polymer sample and (b) EtOH-insoluble residue (T_m = 107 °C; ΔH_m = 16 cal/g).

Crystallinity of Synthetic Copolymers. The practical consequence of the increased stereoregularity achieved by the extraction procedure is demonstrated by differential scanning calorimetry (DSC). Figure 4 compares DSC traces for the whole 86% HV sample and for the isotactic fraction. The increase in melting temperature T_m and increased sharpness of melting, combined with an increase in enthalpy of fusion ΔH_m, are all characteristic of a stereoregular polymer. In addition, the whole sample in Figure 4a shows an inflection near −20 °C attributable to the glass transition, which is almost absent in the isotactic fraction in Figure 4b. Both T_m and ΔH_m of the crystalline 10 and 32% HV samples are in good agreement with those of bacterial copolyesters of similar composition.[6] For example, from Figure 5 in ref 6, in which T_m is plotted against copolymer composition for bacterial P(HB-*co*-HV), 10 and 32% HV copolymers would have values close to 160 and 85 °C, respectively; values for T_m of 155 and 115 °C were measured for synthetic isotactic samples of these compositions. From the same figure in ref 6, one can predict T_m of bacterial P(HB-*co*-86% HV) to be about 105 °C; a value of 107 °C was measured for the synthetic isotactic sample of that composition. Wide-angle X-ray diffraction showed that the 10% sample crystallized in the crystal lattice of PHB homopolymer, whereas the 86% sample was found to exhibit the PHV homopolymer lattice. Extraction and characterization of a range of compositions has fully confirmed the isodimorphic behavior of these synthetic copolyesters, as first reported for the equivalent bacterial specimens.[6]

In summary, we have synthesized close analogues of bacterial P(HB-*co*-HV) over the full range of composition, including the range 47–100 mol % HV not available from commercial sources.[2-4] Although the synthetic copolyesters are highly crystalline, they are not optically active and the low yield of stereoregular material (<25 wt % of the total polymer) is a drawback. Given the improvements in degree of tacticity of poly(α-olefins) that were forthcoming from advances in Ziegler–Natta catalysis, it is reasonable to expect that the same improvements in stereoregulation may be forthcoming for P(HB-*co*-HV) synthesis.

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Registry No. $AlEt_3$, 97-93-8; H_2O, 7732-18-5; ((±)-β-butyrolactone)((±)-β-valerolactone) (copolymer), 110774-30-6.

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Anomalous Association Behavior of an Ethylene Oxide/Propylene Oxide ABA Block Copolymer in Water

In analogy to conventional, low molecular weight surfactants, one of the characteristic properties of ABA (or AB)-type block copolymers in solution is that they form micelles[1] in selective solvents which are thermodynamically good solvents for one block and precipitants for the other block. It is now well accepted that the micelles formed are composed of a relatively compact core of "insoluble" blocks and a highly swollen shell of "soluble" blocks. In most cases, block copolymer micelles are spherical in shape in dilute solution and have a narrow distriubtion of both mass and size. Micellization of block copolymers obeys the closed association model,[1] resembling thus the behavior of conventional detergents. However, a peculiar phenomenon has been reported by a number of research groups[2-10] on the micellization process of some block polymers in selective solvents. The so-called anomalous behavior manifests itself essentially in strong angular asymmetry of scattered light. In general, such an anomaly in micellization is absent in common detergents.

The aim of this paper is to try to elucidate the cause of the anomalous association behavior observed in ABA block copolymers in the transition region between molecular and micellar solutions. By designing and carrying out a filtration experiment in the anomalous region for aqueous solutions of poly(oxyethylene–oxypropylene–oxyethylene) (PEO–PPO–PEO) block copolymer, poloxamer 184, we have succeeded in eliminating the anomalous behavior, as evidenced by light-scattering intensity and line-width measurements. Based on these results we have reached a tentative conclusion that composition heterogeneity could be one possible cause to explain the anomaly in micellization behavior of (PEO–PPO–PEO) block copolymers in selective solvents. A more detailed study is under way.

Two commercial poloxamer 184 (also called Pluronic L64) samples, obtained from Fluka Co. and Polysciences Co. were used in this study without further purification. Poloxamer 184 is a PEO–PPO–PEO block copolymer containing approximately 40% oxyethylene with a nominal molecular weight of 2900 and a hydrophilic–lyophilic balance (HLB) value of 15. For light-scattering measurements, aqueous solutions were first centrifuged at 12 000 rpm ($\sim$17000*g*) and then filtered through Millipore filter GS (nominal pore size 0.22 μm) into 17-mm-o.d. cells, which were then sealed under vacuum. We used a standard, laboratory-built light-scattering spectrometer[11] capable of both absolute integrated scattered intensity and photon correlation measurements at different scattering angles. A Spectra-Physics argon ion laser (Model 165) was operated at 488 nm with an output power in the range of 200–400 mW, depending on the scattered light intensity level of the sample solution. The photoelectron count time correlation function was measured with a Brookhaven BI-2030 64-channel correlator. The temperature was controlled within 0.02 °C and data were analyzed by using either the cumulants method[12] or a double-exponential fitting method.[13]

The association process of poloxamer 184 in water has been studied via the temperature dependence of either the scattered light intensity (I) or the effective hydrodynamic radius (R_h) of the particles. Figure 1 shows the scattered intensity results obtained on an aqueous solution of poloxamer 184 (Fluka product, c = 10.0 mg/mL) before and after filtration. Similar results could be observed by using the Polysciences product. There are three distinct regions

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