Table II
Variations of Cloud Points of PVC Blends over the Composition Range

2nd component	cloud pt (°C) 2nd component compositions 15	25	40	50	60	75
PPrA	164	154	137	129	132	163
PBA	152	143	131	125	131	146
PPeA	130	121	109	106	111	129
50PBA/50PMA	149	144	139	137	142	152
50PBA/50PEA	148	141	134	132	134	148
50PBA/50PHA	117	112	107	105	105	112
25PBA/75PEA	142	137	131	130	134	148
49PPrA/51PPeA	147	137	128	124	126	143
27PMA/73PHA	145	130	118	115	120	149
55PBA/45PEA	155	145	136	132	138	157
40PEA/60PHA	148	137	128	125	128	141
40PEA/60PHA(L)	142	134	126	124	126	134

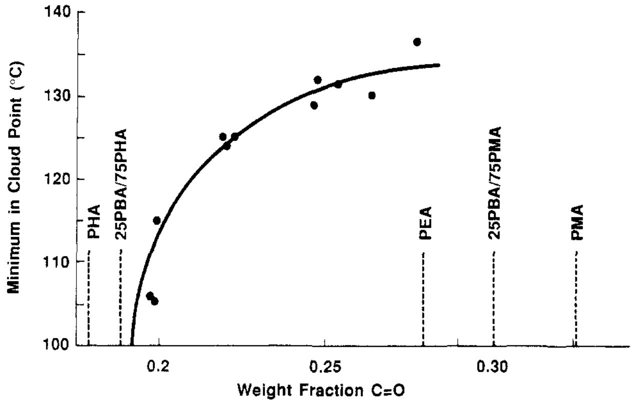

Figure 1. Plot of the minimum in the cloud-point curve for PVC/polyacrylate blends plotted against the weight fraction of C=O groups in the polyacrylate or copolyacrylate. Also shown are several immiscible compositions.

Results and Discussion

The cloud point data for the various blends are shown in Table II.

All of the miscible pairs show minima in the cloud-point data between 100 and 140 °C. It is also apparent that the sample prepared to low conversion gives essentially the same minimum in the cloud-point curve as the similar composition sample taken to high conversion, showing that the higher compositional variation does not affect the results.

Figure 1 shows a plot of the mimimum in the cloud-point curve against the weight fraction of C=O groups in the various polyacrylates, used as an arbitrary parameter depending on the fraction of polar groups in the polymer. Also shown are those compositions that give two-phase blends. It is apparent that the cloud point is simply a function of the weight fraction of C=O groups. For example, PBA, a PPrA/PPeA copolymer, and a PEA/PHA copolymer all contain a 0.22 weight fraction of C=O and have similar cloud points even though PEA and PHA individually form two-phase mixtures.

PEA is known to form two-phase mixtures when solvent cast with PVC but to form one-phase mixtures when prepared by the in situ polymerization of VCM with PEA.[4] PMA always produces two-phase mixtures. It is possible that the casting solvent is the cause of the two-phase mixtures in some cases, since phase separation in polymer/polymer/solvent systems is a common phenomena. It is unlikely that the cloud point is anything other than a smooth function of C=O content.

The cloud points do not appear to be much affected by molecular weights in the range studied. This would confirm that the cloud points are largely determined by the interactions, the temperature dependence of the interactions, and possibly free volume effects.

As the origin of the miscibility of these systems is concerned, this could be inferred to come from specific favorable interactions with PVC or from unfavorable cross terms between ester groups and hydrocarbon groups in the polyacrylates. One could equally have said that the miscibility of a PEA/PHA copolymer could be attributed to an unfavorable interaction between ethyl acrylate and hexyl acrylate units. This is not a particularly useful statement, however, since PBA shows identical miscibility. In theories that calculate cross terms, the division of a polymer into parts is essentially arbitrary. Whereas some divisions are mathematically equivalent, different divisions may lead you to believe that different effects cause miscibility. If one were to state that a favorable interaction of the type demonstrated in ref 10 was the origin of miscibility, then one would claim that miscibility occurred over a range of compositions where the normal unfavorable interactions nearly balanced out, that is, where the two polymers have similar solubility parameters. Whereas these appear to be very different descriptions of the system, it may be that in some cases such descriptions are not mutually exclusive when related to the individual group interactions.

Registry No. PVC, 9002-86-2; PPrA, 24979-82-6; PBA, 9003-49-0; PPeA, 37017-37-1; (PBA)(PMA) (copolymer), 25852-39-5; (PBA)(PEA) (copolymer), 26353-42-4; (PBA)(PHH) (copolymer), 26353-42-4; (PBA)(PPeA) (copolymer), 120411-53-2; (PMA)(PHA) (copolymer), 120411-55-4; (PEA)(PHA) (copolymer), 120411-56-5.

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Microstructures of Commerically Available Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)s

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The bacterially synthesized polyesters, poly(3-hydroxybutyrate) (PHB) and its copolyester with 3-hydroxyvalerate (PHB–HV), are optically active and biodegradable polymers. These polymers are very interesting materials because of their unique properties.[1-3]

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Table I
Sequence Distributions and Melting Points of PHB–HV Samples

sample	D	model[a]	F_V	F_B	F_{VV}	F_{BV}	F_{BB}	F_{VVV}	F_{BVV}	F_{BVB}	T_m	SD[b]
1	0.994	exptl	0.183	0.817	0.034	0.149	0.668	0.008	0.027	0.121	109.0	R
		1	0.184	0.816	0.034	0.150	0.666	0.006	0.028	0.122		
		2	0.180	0.820	0.032	0.148	0.672	0.006	0.026	0.122		
		3	0.182	0.828	0.033	0.149	0.669	0.008	0.027	0.120		
2	1.27	exptl	0.122	0.878	0.018	0.104	0.774	0.005	0.016	0.085	112.0, 140.8	B
		1	0.122	0.878	0.015	0.107	0.771	0.002	0.013	0.094		
		2	0.125	0.875	0.019	0.106	0.769	0.003	0.016	0.090		
		3	0.122	0.878	0.021	0.101	0.777	0.005	0.016	0.085		

[a] Exptl, 1, 2, and 3 indicate experimental data and that calculated by a Bernoullian model, by a Markovian model, and a mixture of two Bernoullian models, respectively. [b] Sequence distribution; R and B indicate random copolymer and blend of random copolymers, respectively.

We have reported previously[4] the microstructures of a series of PHB–HV samples which were isolated from *Alcaligenes eutrophus* in our laboratory. It was concluded that some of PHB–HV samples are random copolymers of HB and HV units, but others are mixtures of PHB–HV random copolymers with different compositions.

PHB and PHB–HV are biosynthesized industrially.[5,6] In this paper, the microstructures of commercially available PHB–HV samples of natural origin are analyzed by NMR spectra and DSC melting curves. Two PHB–HV samples are investigated. It is found that one of these is a random copolymer, but another is a mixture of two random copolymers. Even in the commercial PHB–HV's, there are some mixture samples. In general, properties of the polymer mixture are different from those of respective components. So, before the properties of PHB–HV's are investigated, we must characterize their microstructures, that is, whether these samples are true random copolymers or not.

PHB–HV samples of natural origin were purchased from Aldrich Chemical Co., Inc.[7] Sample 1 is lot no. 8231ML, MW 800 000. Its HV fraction is 30% from the indication on its label, but estimated composition by us is 20.2% by ^{1}H NMR spectra[8,9] and 18.3% by ^{13}C NMR. Sample 2 is lot no. 8331ML, MW 150 000. Its HV fraction is 14% from the label but 13.9% by ^{1}H NMR and 12.2% by ^{13}C NMR. The details of NMR and DSC experiments and the procedures for data analysis are similar to those described in a previous paper.[4]

The sequence distributions of samples were obtained from 67.9-MHz ^{13}C NMR spectra[8,10] and are shown in Table I. In order to characterize the microstructures of these samples, three statistical models are assumed; models 1, 2, and 3 are a Bernoullian, a Markovian, and a mixture of two Bernoullians, respectively. The sequence distributions calculated from these models are also shown in Table I. The parameter D, which indicates whether the sample is a random copolymer or not, is defined as follows:

$$D = F_{VV}F_{BB}/F_{VB}F_{BV}$$

A sample with a D value of 1 or near 1 is characterized as a random copolymer. D values are 0.994 for sample 1 and 1.27 for sample 2. Accordingly, sample 1 is a random copolymer. Its sequence distribution is well described by model 1, although it is also well reproduced by models 2 and 3. But if model 3 is adequate, sample 1 is a mixture with 98.7 mol % of PHB-HV with an HV mole fraction 17.9% (PHB–17.9%-HV) and 1.3 mol % of PHB–52.6%-HV. In practice, it is not regarded as a mixture. In the case of sample 2, the D value is larger than 1. According to the calculation on the basis of model 3, sample 2 is made up of 76.9 mol % PHB–8.0%-HV and 23.1 mol % PHB–26.1%-HV. Sample 2 may be a mixture of two random copolymers.

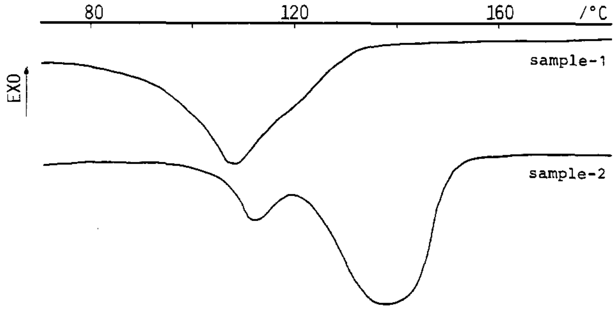

Figure 1. DSC melting curves of PHB–HV samples.

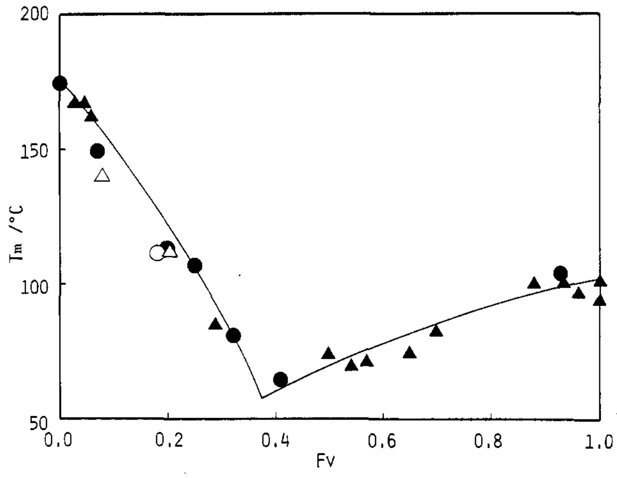

Figure 2. Melting points of bacterial PHB–HV's: (○, ●) melting point versus HV mole fraction of the sample for a random copolymer; (△, ▲) two melting points versus two HV mole fractions of binary mixture calculated with model 3; (○) sample 1; (△) sample 2; (●, ▲) data cited from a previous paper.[4]

Melting temperatures are determined by DSC melting curves, as shown in Figure 1. The melting curve of sample 1 has one peak, but that of sample 2 has two peaks. The melting curve peak did not change its position significantly even when heating rates were changed. So, the two peaks did not result from the recrystallization and sample 2 was suggested to be a mixture. Considering that the melting points of a mixture are the same as that of random PHB–HV's before mixing,[4] sample 2 shows the true melting points of component PHB–HV's. The melting points were plotted from the previously reported data[4] in Figure 2. One melting point of sample 1 is plotted against the HV mole fraction while two points of sample 2 against two components' HV mole fractions calculated with model 3. The plots correspond well with the data of the previous paper[4] and of Bluhm et al.,[10] suggesting that sample 1 is a simple random copolymer but that sample 2 is a mixture of random copolymers. Thus, it is concluded that some of commercial PHB–HV's are mixtures of PHB–HV random copolymers.

In DSC measurements, a mixture of PHB–8%-HV and PHB–26%-HV may have two melting points, as shown in sample 2. But for the mixture of PHB–30%-HV and PHB–70%-HV, only one melting point is observed because the melting points of the two copolymers are almost the same (see Figure 2). In this case, it is impossible to judge from melting points only whether the PHB–HV sample is a random copolymer or a mixture. On the other hand by NMR analysis of sequence distributions, a mixture of PHB–8%-HV and PHB–26%-HV cannot be distinguished from a PHB–14%-HV random copolymer. But a mixture of PHB–30%-HV and PHB–70%-HV can be easily identified as a mixture from sequence analysis. Both the data for sequence distributions from NMR and the melting points from DSC melting curves are needed to judge whether a PHB–HV sample is a random copolymer or a mixture. Before investigation of physical and mechanical properties of PHB–HV copolymers, the microstructures of the samples must be checked.

Recently, it has been reported[11] that a blend of PHB and PHB–8%-HV has one melting point, which depends on blend composition.

Registry No. (HB)(HV) (copolymer), 119878-76-1.

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Crystalline Structure of Poly(β-benzyl L-aspartate)

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Poly(β-benzyl L-aspartate) (abbreviated PBA) is an unusual homopolypeptide since it may exist in three different helical conformations: left-handed α-helix, right-handed α-helix, and ω-helix, as well as a β-pleated sheet.[1] For this reason we decided to study by electron microscopy the crystals of this polymer as grown from solution. Blais and Geil[2] reported that this polymer formed fibrillar aggregates by isothermal precipitation from a saturated solution in either 2-nitropropane or cyclopentanone. In our case we have used hexafluoroisopropyl alcohol as a solvent in order to promote the formation of single crystals of helical PBA, as it is known to happen with the related polymer poly(γ-benzyl L-glutamate).[3]

For our experiments we used a commercial sample (Sigma) of PBA with a nominal molecular weight of 60000. A 0.1% solution of polymer in hexafluoroisopropyl alcohol was prepared at 40 °C. Upon slow cooling to room temperature, crystals appeared in the preparation. A droplet of solvent-containing crystals was deposited onto a carbon-coated copper grid. Excess solvent was removed with filter paper. The grids were then shadowed with Pt–C at an angle of 14°. The grids were observed in a Philips 301 electron microscope.

In order to ascertain that the crystals contained α helices, the X-ray diffraction pattern of a mat of crystals was obtained. Only a sharp ring at 12.7 Å plus a diffuse ring at 4.6-Å spacings were observed. These features coincide with those previously observed by Bradbury et al.[1] and Malcolm[4] for α-helices of PBA.

The crystals that we obtained are shown in Figure 1. They all are about 50 Å thick and display three types of morphologies: (a) triangles, with two sharp and one irregular side (The tip of the triangle opposite to the irregular side is not sharply defined but appears rounded or irregular); (b) hour-glass-like crystals, with sharp sides and irregular bases; (c) complex structures, which appear to be formed by accumulation of the two previous types of crystals.

These morphologies are quite different from other structures observed with the same polymer such as the fibers reported by Blais and Geil[2] or the irregular plates obtained by Masuda et al.[5] using a low molecular weight material.

In spite of the well-developed habit of the crystals apparent from Figure 1, no electron diffraction pattern could be detected. Even at extremely low beam intensities, only an amorphous halo was observed. The absence of diffraction may either indicate that the chains are considerably tilted or that the molecular order has been lost when it was subjected to the vacuum of the electron microscope or even of the evaporator, due to the presence of solvent in the original crystals.

The crystals of PBA in the α-helical conformation, which we have described, show two puzzling features. They are 3 or 4 times thinner than the crystals found in other α-helical polypeptides.[6] Although in a 50-Å thickness it is possible to accommodate a sufficient length of α-helix (about 33 residues in 9 turns), there is no obvious reason to explain why these crystals are so thin. It cannot be excluded that the helical stems are inclined with respect to the crystal, so that a longer helical section might be accommodated in a 50-Å thickness.

Another puzzling feature of these crystals is the hour glass (Figure 1b) or irregular triangular shape (Figure 1a) that we have found. One possible explanation for these shapes would be that the crystals contain a mixture of right-handed and left-handed helices. It was shown by Crick[7] that right-handed α-helices cannot be packed with regularity, whereas alternating layers of left-handed and right-handed helices would have a better interlocking of the helical grooves. In fact Elliot et al.[8] have prepared crystals of 1:1 poly(γ-benzyl L-glutamate) and poly(γ-benzyl D-glutamate) as an equimolecular mixture of right-handed and left-handed helices. In our case regular alternating layers of right-handed and left-handed PBA could be deposited on the two straight crystal faces. It is then not possible to have a regular alternation on a third side, so that in the tip of the triangles and in the irregular edge of the crystals irregular shapes may appear as observed.

We have also studied the influence of temperature on the structure of such crystals. When they are heated above 150 °C, a transition to the ω-form takes place, as described

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