epoxy-rich mixture goes into solution at elevated temperatures in DCE better than in TCE.

In the mixed solvents the trough in the bimodal CPC is significantly deeper. This, however, is not brought about by enhanced solubility of the 1:1 mixture only but also by an increase of the insolubility of both the epoxy-rich and copolyester-rich mixtures. The increases of the miscibility gaps are especially obvious in the 3:1 epoxy/copolyester mixture. A comparison of the 100, 105, and 110 °C isotherms in Figures 1 and 3 leads to the conclusion that the miscibility gap of the 3:1 epoxy/copolyester in the mixed solvent was brought about by the presence of TCE in the system. A similar comparison of the 80, 90, and 100 °C isotherms in Figures 2 and 3 for the 1:3 epoxy/copolyester shows that the broad miscibility gap of this mixture in the mixed solvent was brought about by the presence of DCE in the system.

Now, according to the Flory–Huggins solution theory[8,9] as expanded by Scott to cover the ternary case of polymer–polymer–solvent[10] for two polymers of the same molecular weight M and the same polymer–solvent interaction parameter $\chi_{12} = \chi_{13}$ the position of the phase boundary is solely dependent on the polymer–polymer interaction parameter χ_{23}. In our three phase diagrams the CPC are closed loops which do not touch the edges of the triangular phase diagrams, i.e., the binaries are completely miscible. The complete polymer–polymer miscibility indicates that $\chi_{23} = 0$ or negative.[11] From the nonsymmetry of our CPC and from the behavior of the two polymers in the mixed solvent one concludes that a large difference exists between χ_{12} and χ_{13}. In other words, the existence of a closed loop CPC in a ternary phase diagram consisting of two polymers and a solvent and the shape of this loop are dependent on the difference in magnitude between χ_{12} and χ_{13}.[5,11,12] We speculate that the large difference between the interaction parameters $|\chi_{12} - \chi_{13}| = |\Delta\chi| \gg 0$ may be responsible for the overall skewness of the CPC in our Figures 1 and 2. This point is, however, by no means verified.

In the cloud point isotherms belonging to ternary systems that showed bimodality, either in the literature[1,3–6] or in this work, the trough occurs always at a polymer/polymer ratio of about 1:1. Of the three literature systems showing bimodal CPC, two belong to compatible polymer pairs, polystyrene–poly(vinyl methyl ether)[5] and polyethylene–atactic polypropylene,[1,6] while the third (polystyrene–polybutadiene) belongs to an incompatible pair.[13] Therefore, the speculative explanation for the bimodality of the CPC we propose may fit only the systems containing compatible polymer pairs but may not explain the case where the polymers are incompatible, as in ref 3 and 4. Accordingly, in compatible polymers the molecular attraction between polymer 2 and polymer 3 molecules is higher than the attraction between each polymer and the solvent. At the ratio of 1:1 the large preponderance of polymer molecules are interacted with one another. In a system rich in one polymer, the amount of its molecules above the concentration of the second polymer is left uninteracted with the latter. The uninteracted part tends to separate out of the ternary solution, resulting in bimodal CPC whose maxima are at points not very close to exactly 1:1 polymer ratio, yet not corresponding to extreme dilution with respect to one polymer or the other.

Finally, it was recently calculated by Olabisi,[14] based on Flory's equation of state,[15] that for the binary system of polycaprolactone–poly(vinyl chloride) (PVC) when the polymer–polymer exchange energy parameter χ_{23} is negative and sufficiently large (a strong specific interaction) then a bimodal CPC is expected. The thermal instability of PVC precluded an experimental verification of the simulated curves. Nevertheless, we believe that Olabisi's treatment of binary systems is based on a line of reasoning that may also be applicable for ternary systems such as ours.

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High-Pressure Liquid Chromatography for Fractionating Oligomers from Degraded Poly(β-hydroxybutyrate)

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Poly(β-hydroxybutyrate) is an example of a thermoplastic polyester which is obtainable from nonpetrochemical sources. The study of this microbial polymer is important as part of a continuing effort to develop the technology for finding vegetative sources of polymers, oligomers, and monomers.

The work of Baptist[2] should be cited as the basic example of an attempt to exploit the original discovery by Lemoigne[3a] that an ether-insoluble polyalkanoate material was present in bacteria. This water-insoluble optically active polymer was shown[3b] to be based on the D(−), β-hydroxy acid isomer and has been synthesized in an optically active[4] and inactive[5] form by polymerization of the appropriate lactones.

Solution property studies of this polymer have been hampered by difficulties in obtaining suitably sharp fractions so that radius of gyration data could be unequivocally interpreted.[6,7] This communication describes a successful method for separating PHB into monodisperse oligomer fractions using reverse-phase high-pressure liquid chromatography.

Fractionation of PHB Oligomers

Low molecular weight samples of PHB can be prepared by alcoholysis[6] or alkaline[8] depolymerization methods. The acid conditions plus the presence of methanol leave the carboxyl end group in the ester form while from the alkaline conditions a salt or free acid end group can be obtained. The number average degree of polymerization of the various degraded samples studied were $\overline{\mathrm{DP}}_n = 10\text{–}20$. The melting point which has been shown to be closely related to solubility[9] and number average molecular weight[10] was between 106 and 125 °C for these samples.

A "Waters 6000" pump coupled with a "Waters 660" gradient programmer and a Perkin-Elmer LC 55 detector which was operated at 205 nm were the principal hardware components. The stainless steel column (25 cm × 4.2 mm) contained

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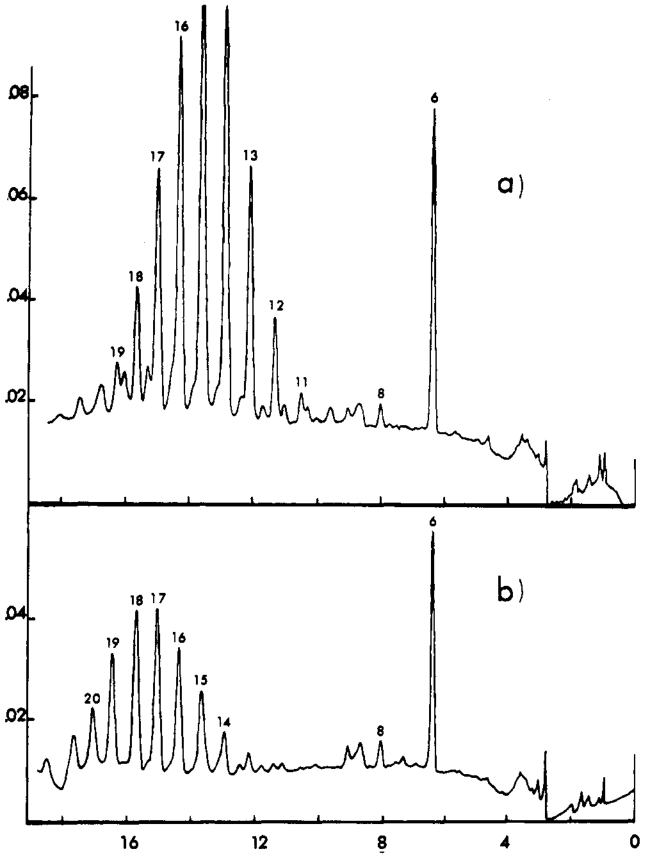

Figure 1. High-pressure liquid chromatographs of degraded PHB samples: (a) alkali degraded sample whose melting point is 106–109 °C; (b) alkali degraded sample whose melting point is 122–125 °C. The ordinate represents absorbance at 205 nm and the abcissa is retention time in minutes.

Lichrosorb RP 8 (10 μm). The latter is a silica gel which has been chemically modified with n-octane to provide a nonpolar stationary phase.

Solutions of polymer in acetonitrile (ACN, Burdich and Jackson) were made to be 0.1 g/100 mL; 20-μL samples were injected and gradient elution was started at a pump speed of 2 mL/min starting with purified (millipore) H_2O made up to pH 3 by addition of HCl. Using program no. 4, the gradient took 40 min to reach the final state of pure ACN.

Because of the reverse-phase conditions the more polar oligomers (monomer, dimer, etc.) are eluted first in their acid form. To identify the fractions, previously prepared[11] acid form oligomers were used to calibrate the system:

sample	t_R, min
hexamer	6.4
octamer	8.0

When these two controls were added to an ACN solution of two different PHB samples whose melting points were 106–109 and 122–125 °C, respectively, the resulting chromatograms were as shown in Figure 1. The various peaks are identified in accordance with the above calibration information.

The two chromatograms show clear separation into the peaks which are characteristic of what was a near Gaussian distribution in each sample. The sample with the lower melting point has clearly a lower average DP as has been confirmed by separate molecular weight measurements. The potential of the method for preparative studies is clear. On the other hand, the presence of small satellite peaks is clearly evident in the chromatograms. These are thought to be due to the nature of the saponification reaction used to prepare the samples since it has been shown that some ethylenic end groups are formed during saponification.

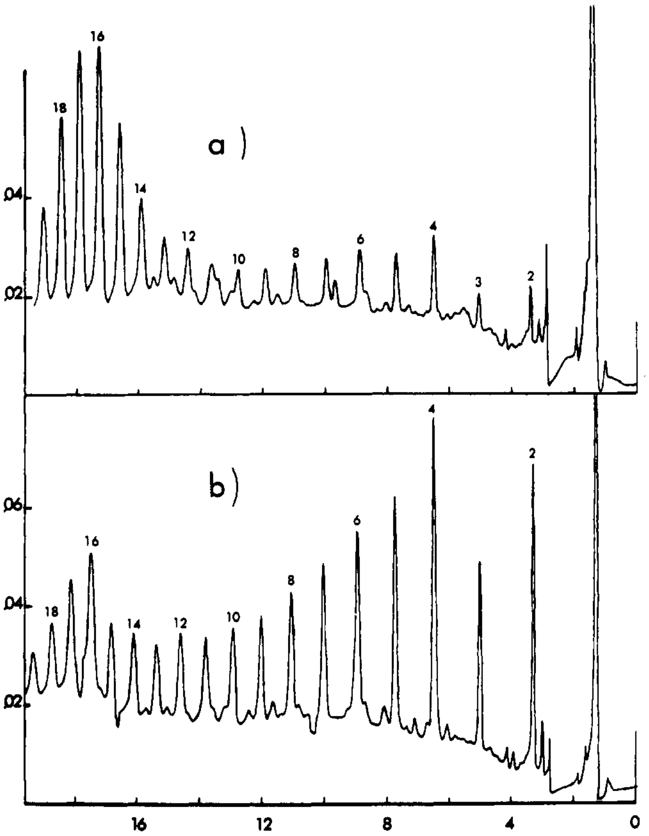

Figure 2. Depolymerization of a degraded PHB by a solution of BF_3 in methanol (sample in Figure 1B above): (a) after 4.5 h; (b) after 23 h. The ordinate represents absorbance at 205 nm and the abcissa is retention time in minutes.

Continuous Hydrolysis Study

A PHB sample whose melting point was 122–125 °C was dissolved in ACN and 25% by volume of methanol with 2.5% BF_3 was added. The reaction mixture was kept at 35 °C and 20 μL volumes were removed and injected regularly.

Figure 2 shows the chromatograms corresponding to different times of hydrolysis and it is clear that the displacement of the starting distribution toward smaller sized oligomers is in accordance with the expected homogeneous depolymerization scheme. However, the peaks identified in the chromatograms of Figure 2 have a slightly longer retention time in the column even when exposed to the depolymerization conditions. This difference is due to the transformation of the end carboxyl group into an ester function which is less polar hence retained longer in the column. This was confirmed by separate experiments with a trimer ester. The solution of BF_3 in methanol is known to esterify rapidly[13] while the ester interchange reaction which is responsible for the depolymerization is expected to proceed more slowly.

In previous[12] studies the heterogeneity of the molecular weight distribution of the saponification product was noted. In the case of BF_3 in methanol it seems that some components in the distribution may be deficient. No explanation is available at this time.

Conclusion

In view of the current interest in solution properties[6] of PHB this study should be the basis of a preparative method for preparing pure fractions of this important biopolymer.

Furthermore it should be possible to study reaction mechanism using this method not only to follow molecular weight changes but also the proportions of modified end units (free acid vs. methyl ester or ethylenic vs. hydroxylated) in the reaction product. When suitable calibrated oligomers are available the retention time is a useful measure of degree of polymerization.

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Communications to the Editor

A New Method for the Study of Polymer Compatibility[1]

It is well known that most polymer pairs form incompatible mixtures.[2] The cause of this phenomenon has been clarified by Gee[3] who pointed out that for the mixing of two polymeric species the entropy of mixing per unit volume is negligible, so that only pairs of polymers which mix with an evolution of heat will form thermodynamically stable mixtures.

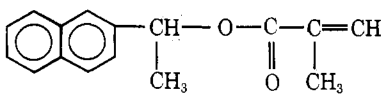
A number of methods have been employed for the characterization of polymer compatibility. Optical clarity of mixtures[4] is frequently used as a test but it suffers from the obvious limitation that light scattering will only be observed if the two polymers have significantly different refractive indices. A comparison of the heat of solution of the components of a mixture and the mixed polymers yields the heat of mixing and this experimentally exacting method has been shown to give results which correlate with other criteria of compatibility.[5–7] DSC measurements of glass transition,[8,9] measurements of dynamic mechanical properties,[9,10] and electron microscopic studies[11] are the methods used most frequently for compatibility studies. Various aspects of studies of multicomponent polymer systems have been reviewed in a recent monograph.[12] It should be noted that different methods have different powers of resolution. For instance, blends of poly(2,6-dimethyl-1,4-phenylene ether) and isotactic polystyrene exhibit two-phase behavior by dynamic mechanical testing, while DSC studies give results typical of a single phase.[9] On the other hand, dynamic mechanical testing was found to be less sensitive than electron microscopy which will reveal separate phases even if their domains have dimensions as small as 10 nm.[11]

We have found that the phenomenon of nonradiative energy transfer[13] is a powerful tool for the study of polymer compatibility. If the emission spectrum of a donor (D) overlaps the absorption spectrum of an acceptor chromophore, light absorbed by D may be emitted by A. The dependence of the efficiency of this process on the distance r between the two chromophores is of the form

$$\mathrm{Eff} = [1 + (r/R)^6]^{-1} \quad (1)$$

when R is a characteristic distance depending on the refractive index of the medium and the mutual orientation of the chromophores, with R^6 proportional to the overlap integral of the emission spectrum of D and the absorption spectrum of A. In favorable cases R may be as large as 4 nm. Thus, if two polymers are labeled with D and A, respectively, the efficiency of energy transfer in a system containing both polymers characterizes the extent of their interpenetration.

We have employed in our studies copolymers of I and II.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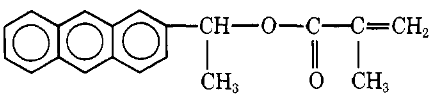
II

The naphthyl group has an absorption maximum at 287 nm and its emission spectrum has maxima between 325 and 336 nm, which overlap the absorption spectrum of the anthryl group. The anthryl group emission has maxima at 388, 408, and 432 nm, with the central peak most intense. Nonradiative transfer efficiencies were determined by recording the reflectance fluorescence spectrum of films cast from a mixed polymer solution irradiated at 278 nm. The results were characterized by I_D/I_A, the ratio of the fluorescence intensity of the donor at 336 nm and the acceptor at 408 nm.

Figure 1 shows results obtained with blends, containing equal weights of poly(methyl methacrylate) labeled with 1.4 wt % of II and methyl methacrylate–butyl methacrylate copolymers labeled with 1.2 wt % of I. As expected, I_D/I_A increased with an increasing butyl methacrylate content of the copolymer, reflecting the decrease in energy transfer accompanying decreasing compatibility. The most striking result is the demonstration that the technique is able to characterize the decreasing interpenetration of the polymeric components, rather than make the merely qualitative distinction between a "compatible" and "incompatible" system. The high sensitivity of our technique may be illustrated by comparison with the use of dynamic mechanical measurements for the characterization of compatibility. In a study of the compatibility of methyl methacrylate–butyl acrylate copolymers,[10] the components of the system had to differ by 20 mol % in their composition before two damping maxima could be resolved. By contrast, in the similar system used by us, a change in I_D/I_A

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