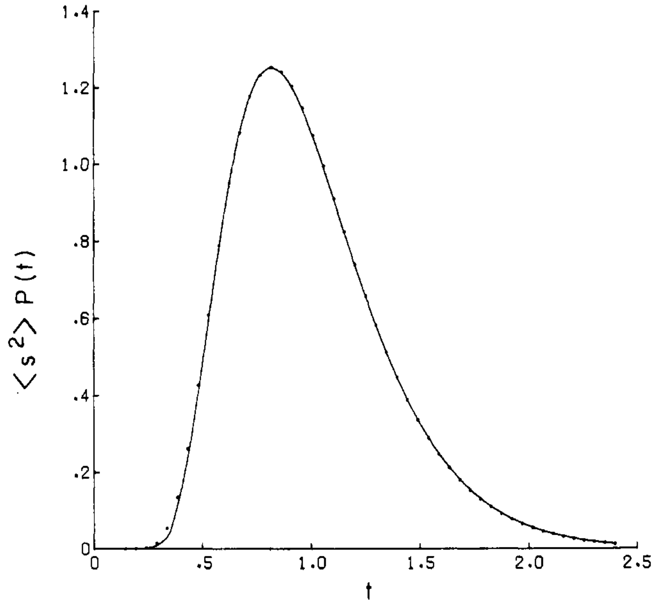

Figure 2. Distribution function of the reduced squared radius of gyration $t = s^2/\langle s^2\rangle$ for the circular chain as a function of t for large n. The solid curve is calculated from the exact distribution function given in ref 4. The points are values given by the empirical eq 3, with parameters listed in Table I.

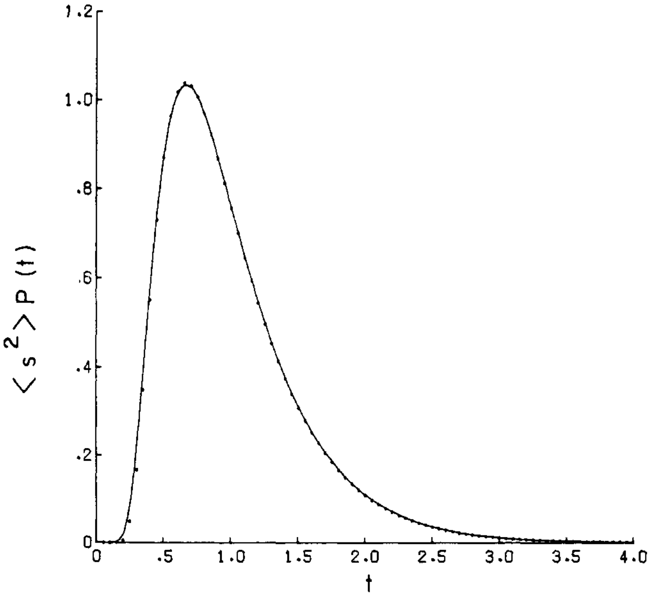

Figure 3. Distribution function for the linear chain. Exact curve calculated from ref 2. Otherwise the same as Figure 2.

greater than 1% is unwarranted in the spirit of approximation or in view of conceivable applications.)

The approximate function given by eq 3 suffers in that it can only be integrated numerically. However, a simple one-line FORTRAN statement suffices to evaluate the function. The numerical integrations required to construct Table II were accomplished with the International Mathematical and Statistical Libraries, Inc. (IMSL) program DCADRE, which uses cautious Romberg extrapolation.[10] Calculations were performed on the University of Washington CDC 6400 computer.

Although the approximate function is not easily integrable, it is readily differentiated. It is expected that functions of this class will find application to rubber elasticity,[6] should they be useful descriptions of the distribution functions of more complicated molecules.

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Bimodal Closed Cloud Point Curves of Ternary Systems

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There are several recent literature reports indicating bimodal cloud point curves (CPC) for polymer–polymer systems[1,2] and for ternary polymer–polymer–solvent (components 2, 3, and 1, respectively) systems.[1,3–6] Koningsveld et al.[1] explain the bimodal shape of the CPC as caused by a particular concentration dependence of the free enthalpy parameter, g. Welygan and Burns[4] present an explanation for the bimodal shape of the CPC in a ternary system, but the scarcity of data points and their scatter preclude a verification of the validity of the model. In this note we wish to report another ternary system that shows a bimodal shape of the CPC. This system is comprised of two compatible polymers and a solvent. The results obtained by changing solvents, and from the use of a mixed solvent, may aid in a better understanding of bimodal cloud point curves.

The two polymeric components in our study are a copolyester and an epoxy system with a very broad molecular weight (M) distribution. The copolyester was prepared by melt polymerization to have the molar composition of 65:30:5 terephthalate/isophthalate/sebacate with 70:20:10 ethylene glycol/resorcinol di(β-hydroxyethyl) ether/poly(tetramethylene ether) glycol with M_n of 1000. The resultant copolyester had a glass transition temperature, T_g, of −3 °C, was found by x-ray techniques to be amorphous, and had an intrinsic viscosity in 60:40 tetrachloroethane/phenol in the order of 1.1–1.3 (depending on the batch). This polymer was found to be compatible with an epoxy system composed of 50 wt % 1:1 copolymer of bisphenol A and epichlorohydrin (Union Carbide's Phenoxy PKHH grade, $M_w \sim 80\,000$, $M_n = 23\,000$), 40% intermediate M epoxy (diglycidyl ether of bisphenol A, Ciba-Geigy Araldite 6099 grade with $M_w \sim 5000$–8000), and 10% low M epoxy (diglycidyl ether of bisphenol A, Ciba-Geigy Araldite 6010 grade, $M_w = 370$–390). This epoxy system is a transparent solid whose T_g is 85 °C and which is completely amorphous.

Intimate mixtures of the two components covering the range of 1:3 to 3:1 ratios were prepared by several means, as described by Aharoni and Prevorsek.[7] When a small amount of solvent (in the order of 5%) remained trapped in the solid mixture, dense polyester particles of ~5000 Å in diameter were

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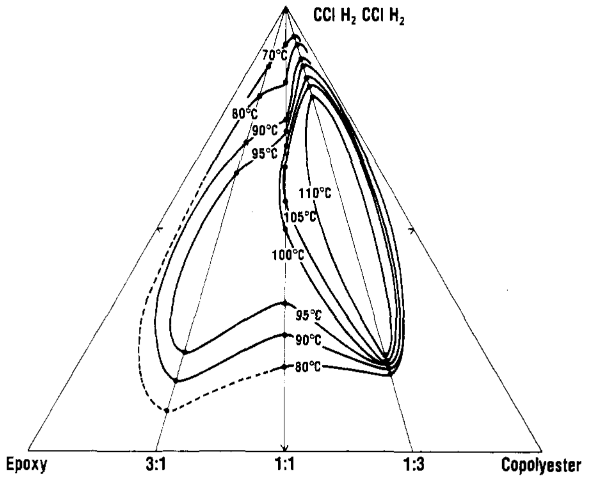

Figure 1. Phase diagram of epoxy and copolyester in dichloroethane at various temperatures. The system is turbid inside the closed regions and clear outside. Solution compositions are in volume fractions.

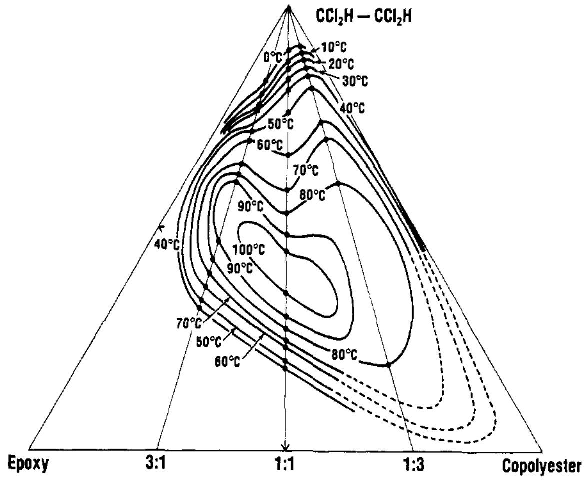

Figure 2. Phase diagram of epoxy and copolyester in tetrachloroethane. Details as in Figure 1.

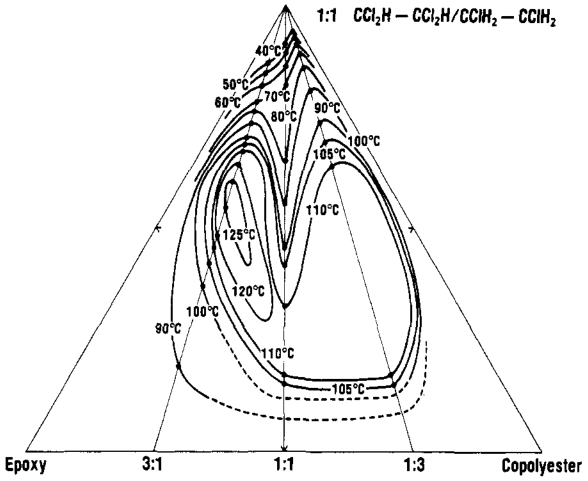

Figure 3. Phase diagram of epoxy and copolyester in a 1:1 mixture of dichloroethane and tetrachloroethane. Details as in Figure 1.

observed in the electron microscope. Flash heating, for 90 s at 140 °C, was sufficient to drive the solvent remnants away and to make the solid uniform on a microscopic scale. At this point the system had a single T_g at 27 °C (for the 1:1 mixture) and its density, as determined by pycnometry and from the position and shape of the amorphous halo obtained from x-ray diffraction, was higher than the algebraic average of the two ingredients. These observations fulfill the criteria for a single phase solid solution, leading to the conclusion that an intimate mixture of the two components, copolyester and epoxy system, in 1:1 ratio, is a single-phase solid solution[7] and that the two components are compatible with one another. The observed transparency of the polymer–polymer solid solution throughout the whole composition range, its single T_g, and higher than calculated density all indicate a polymer–polymer compatibility over a very broad composition range.

The polymers were put into solution by heating them, or their mixtures in 1:3, 1:1, and 3:1 ratios, with the desired solvent in the desired concentration (all concentrations were in volume/volume). The solutions were placed in glass tubes which were subsequently sealed under nitrogen, facilitating heating at temperatures somewhat higher than the normal boiling points of the solvents by a moderate increase in pressure. The cloud temperature was taken as the first definite haze upon slowly cooling the solution or the disappearance of such haze upon slowly heating the solution. Each cloud temperature determination was repeated not less than four times, twice going up in temperature and twice going down, and the reported cloud point temperature is the average of all determinations. The temperature difference between going up and down changed from less than 1 °C in the dilute solutions up to about 10 °C in the highly concentrated solutions. Nonetheless, the cloud points were reproducible even at the high concentrations. In the regime of very high polymer concentration only a few points were obtained, owing to the high viscosity of the systems.

The results of the observations in three solvents, namely 1,2-dichloroethane (DCE), 1,1′,2,2′-tetrachloroethane (TCE), and a mixture of 1:1 of these solvents, are presented in Figures 1, 2, and 3, respectively. In them, the areas enclosed by the curves represent the regions showing two phases, while the areas out of the closed loop curves represent single-phase systems. The pure copolyester showed no cloud point in DCE over the whole range of freezing, at -35 °C, to above boiling, at 90 °C; in TCE above the glass termperature of -58 °C; and in their mixture above a cloud point of -30 °C at concentrations of $<10\%$ and a glass point of ~ -15 °C at concentrations of 10% and above. The pure epoxy system had a CPC in DCE with a peak at 50 °C for a concentration of 2.5%; in TCE its CPC peaked at -11 °C at 4% concentration; and in the mixed solvent the epoxy CPC peaked at 2 °C for 2% concentration while turning into a clear glass at -35 °C in concentrations higher than 20%. As was indicated above, the binary polymer mixtures were found to be compatible. Hence, there are no miscibility gaps reaching any side of the triangular phase diagrams at the temperature ranges indicated therein.

The three systems are characterized by their CPC being closed and bimodal, showing a trough at the 1:1 epoxy/copolyester mixture. The troughs are, as in ref 2, 4, and 6, on the high solvent concentration side of the CPC, but in DCE a trough appears also on the high polymer concentration side of the curves, similar to the case in ref 5. Close observation reveals that the troughs become prominent only in intermediate temperature ranges, 80–95 °C in DCE, 60–90 °C in TCE, and 80–110 °C in the mixed solvent.

Comparison of Figures 1 and 2 shows that DCE is a poorer solvent than TCE, especially toward copolyester-rich mixtures. This is indicated, for instance, by the fact that in DCE at 80 °C the 3:1 copolyester/epoxy system shows a miscibility gap covering the solvent 17–88% concentration range, while in TCE at the same temperature the miscibility gap narrowed to 19–60% solvent. On the other hand, it appears that the 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 $\overline{\mathrm{DP}}_{\mathrm{n}} = 10\text{–}20$. 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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