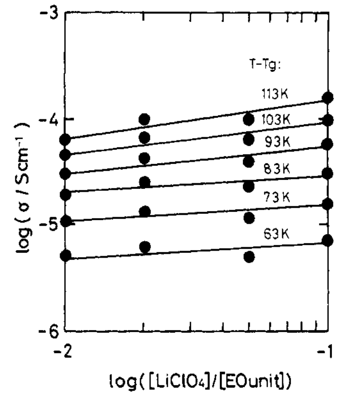

Figure 9. Ionic conductivity as a function of salt concentration for PEO–$LiClO_4$ complexes.

9 shows the ionic conductivity of the PEO–$LiClO_4$ complexes as a function of the salt concentration at constant reduced temperatures. The increase in the conductivity with the concentration was smaller than that expected by the complete dissociation. This also indicates that all of the incorporated salt does not function as carrier ions. The formation of ion pairs and other aggregates seems to occur at a higher concentration. We cannot deny at the present the possibility of long-range ion interaction which reduces the ionic mobility at constant reduced temperatures with increasing salt concentration.

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Sequence Distributions and a Phase Diagram for Copolymers Made from Poly(ethylene terephthalate) and *p*-Acetoxybenzoic Acid

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ABSTRACT: Copolymers made from poly(ethylene terephthalate) (PET) and *p*-acetoxybenzoic acid (PHB) have been examined in solution and as melts by NMR spectroscopy. Proton and carbon NMR spectra of solutions have shown that the sequence distributions for PET/PHB copolyesters can be described in terms of a probability model in which PHB has a slightly greater than random chance of being bonded to another PHB, which leads to significant deviations from randomness at higher PHB levels in the copolymer. Proton wide-line NMR spectra on melts show evidence of both liquid crystalline and isotropic phases for compositions at or above 35 mol % PHB. The compositions of the isotropic and anisotropic phases are found to contain approximately 35 and 80 mol % PHB, respectively, at 280 °C. The amount of each phase is estimated for several compositions up to 80 mol % PHB. A qualitative explanation of the formation of the liquid crystalline phase requires significant amounts of sequences of four or more PHB units to initiate liquid crystalline phase formation. At compositions with enough PHB to separate a liquid crystalline phase, shorter sequences of PHB partition between the phases to enrich further the PHB-rich phase.

Introduction

The series of copolyesters based upon poly(ethylene terephthalate) that has been copolymerized with *p*-acetoxybenzoic acid has been the subject of several investigations into their structure and properties. The copoly(ethylene terephthalate/*p*-oxybenzoyl) copolyesters, called PET/PHB, have been shown to exhibit liquid crystallinity at or above 35 mol % PHB.[1] The PET/60PHB and PET/80PHB copolyesters, having 60 and 80 mol % *p*-oxybenzoyl moieties, respectively, are reported to show domains,[2–5] and to have thermal properties[2,3,5,6] and diffraction patterns[2,4,7,8] domains[2–5] with phase separation into PHB- and PET-rich phases in their solids. Although the copolyesters have been reported to be random copolyesters based upon ^{13}C NMR spectra,[1,9] the phase separation[2,5] and morphology results[2,5] have been interpreted as evidence for blocked sequence distributions in these copolymers.

The NMR evidence for chain sequence statistics has been reexamined with a high-field spectrometer. It provides better sensitivity for carbon results and proton re-

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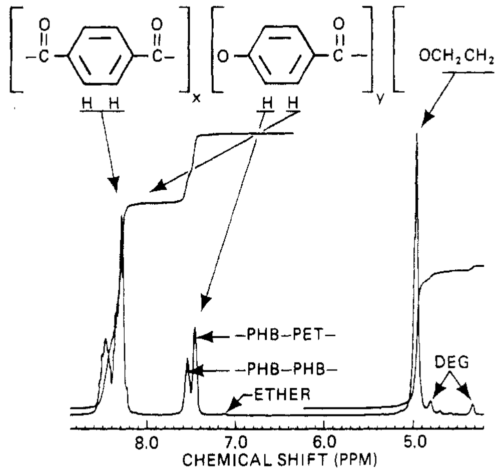


Figure 1. Proton NMR spectrum at 400 MHz with the assignments of the absorptions for PET/50PHB dissolved in trifluoroacetic acid.

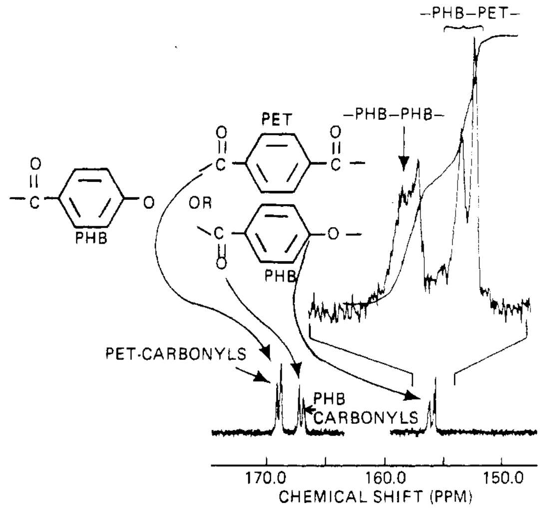


Figure 2. Portion of the ^{13}C NMR spectrum at 100 MHz with assignments for absorptions for PET/60PHB dissolved in trifluoroacetic acid.

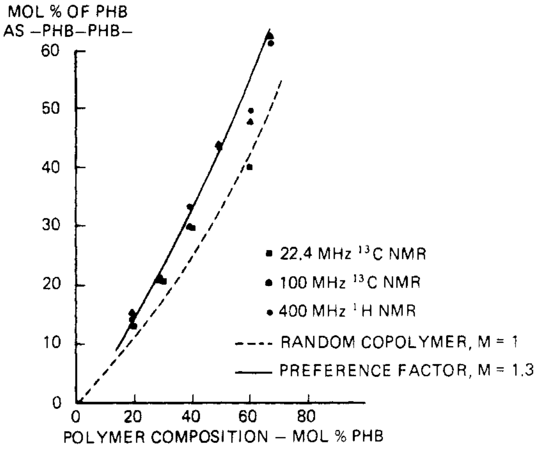


Figure 3. Mole percent of PHB connected directly to another PHB for several PET/PHB copolymers and from several measurements. Lines were calculated from a probability model described in the text.

sponses with sufficient resolution to measure chain statistics. Both measurements are consistent with previous results, but the improved sensitivity shows a small but measurable deviation from random chain statistics. The probable distributions are illustrated.

Previous proton wide-line NMR work[9,10] has been extended to measure the amount and composition of isotropic and liquid crystalline phases in melts at 280 °C. These results combined with the information on chain statistics and information on similar small-molecule liquid crystals provide insight into the formation of the liquid crystalline phase in PET/PHB copolyesters.

Methods

The polymer preparation has been described.[1] For the high-field NMR spectra, 1-5 wt % solutions of the polymer in deuteriated trifluoroacetic acid were made. With the exception of PET/70PHB, all solutions were clear and the polymer remained in solution. For PET/70PHB, the solutions were slightly turbid, and a small amount of polymer precipitated upon standing. Deviations from the nominal composition for the polymer in solution were not detectable. PET/80PHB would not dissolve and could not be measured by high-resolution NMR spectroscopy. The spectra were obtained on a JEOL Model GX-400 NMR spectrometer operating at 400 MHz for observing protons and 100 MHz for observing carbon.

For proton wide-line NMR spectra, the neat polymers were sealed in 5-mm tubes. Spectra were recorded on a Bruker Model SXP pulsed fast Fourier transform spectrometer operating at 90 MHz and equipped with a special 5-mm insert and heater. Temperatures up to 280 °C could be obtained at the sample in the insert. The free induction decays were collected with a Nicolet 1090A signal averager connected to a Nicolet Model 1080 data system. The signal averager provided 8-bit conversions at up to a 2-MHz rate to enable the rapidly decaying signals from the wide-line spectra to be obtained. The spectra were integrated by the data system using conventional techniques.

Results and Discussion

Sequence Distributions. Figure 1 illustrates the 400-MHz proton NMR spectrum of PET/50PHB in trifluoroacetic acid solution and shows assignments for the resonances. Figure 2 illustrates a portion of the 100-MHz ^{13}C NMR spectrum for PET/60PHB in trifluoroacetic acid with resonance assignments. The resonances of the quaternary carbons assigned to –PHB–PHB– and –PHB–PET– units show some further structure that has not been assigned and is likely owing to the moiety attached to the carbonyl of the PHB unit. Spectra of these types have been measured to determine the fraction of the PHB repeat units that are bonded to another PHB or to a PET unit. Figure 3 shows the fraction of the PHB bonded to another PHB for several compositions between 0 and 70 mol % PHB in the copolymer. Also included in Figure 3 are the data from a previous publication.[9] The present data are consistent among themselves and with the previous data.

The NMR measurements provide direct measures of the probability of a PHB being bonded to another PHB. For the case of a random copolymer,[11] the probability of a PHB being bonded to another PHB is given by

$$P(\mathrm{PHB}/\mathrm{PHB}) = P(\mathrm{PHB})/[P(\mathrm{PHB}) + 2P(\mathrm{PET})] = a \qquad (1)$$

While the previously available data were not sufficiently precise to be significantly different from the prediction of the random model, the data in Figure 3 are systematically above the prediction. If the PHB has a composition-independent preference for bonding to itself, then we might find

$$P(\mathrm{PHB}/\mathrm{PHB}) = ma \qquad (2)$$

where m is the preference factor. A preference factor of 1.3 for m provides predictions graphed as the solid line in Figure 3. Because of the size of the data set, no attempt was made to determine a "best" value for m. Rather, a

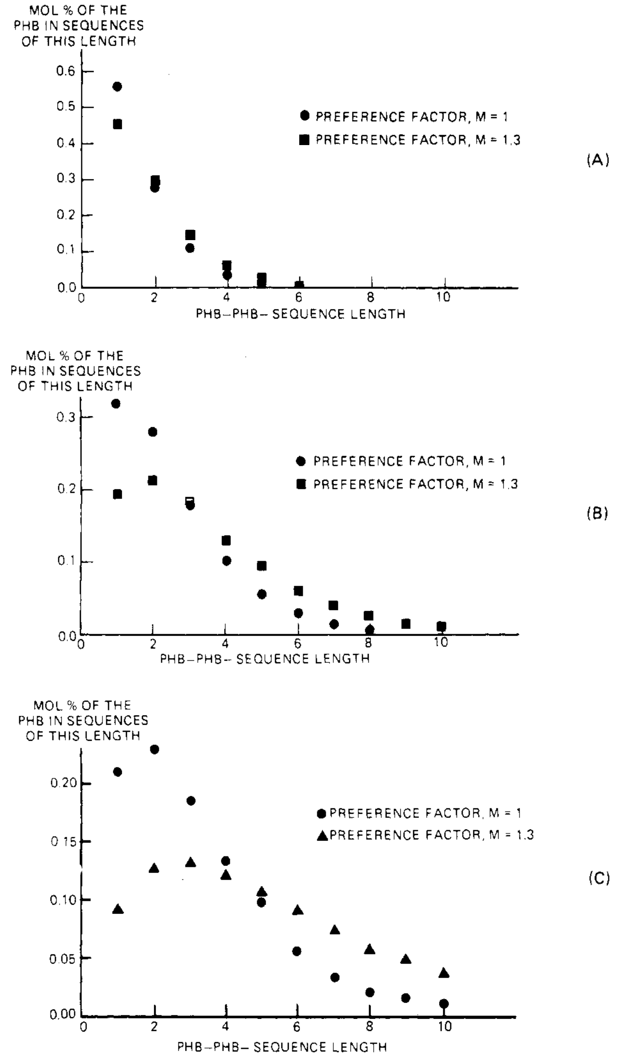


Figure 4. Mole percent of PHB units in (a) PET/40PHB, (b) PET/60PHB, and (c) PET/70PHB in sequences of various lengths as calculated from the probability model of sequencing used to describe the data in Figure 3.

value for m of 1.3 was chosen as probably above a best value to enable an examination of the possible deviations of the sequence distributions from randomness. The ability of the model to place a line near each of the data points while using a single value for m gives some support to the appropriateness of the model and the assumption that a single mechanism accounts for the sequencing of repeat units in this series of copolymers.

Figure 4 shows the probability model predictions for the sequence length distributions[11] in three copolyester compositions that are liquid crystalline as judged by their turbidity, wide-line NMR spectra, and other measures.[1] Figure 4A shows that PET/40PHB, which is liquid crystalline, has small deviations for m of 1.3 compared to the random model with m of 1. However, parts B and C of Figure 4 show that at higher PHB fractions the deviations of the distributions from the random model become more noticeable. This increasing deviation from the random distribution at higher fractions of a repeat unit with a preference for itself is a property of the model. At 70 mol % PHB, Figure 4C shows a significant tendency for longer runs of PHB than predicted by the random model. The fraction of PHB bonded to another PHB could not be observed for the PET/80PHB because no suitable solvent could be found. However, if similar statistics apply, PET/80PHB would have even more of a tendency to exhibit long runs of PHB units than PET/70PHB.

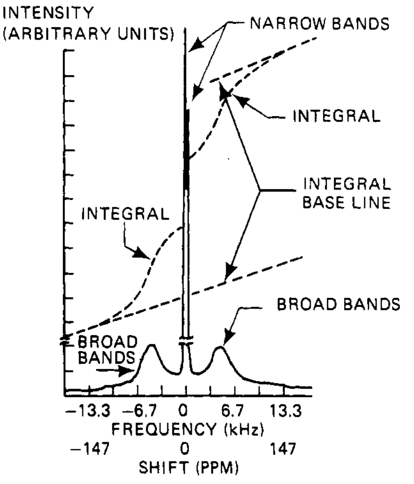


Figure 5. Pulsed fast Fourier transform proton NMR spectrum of neat PET/60PHB at 177 °C in a sealed, evacuated tube.

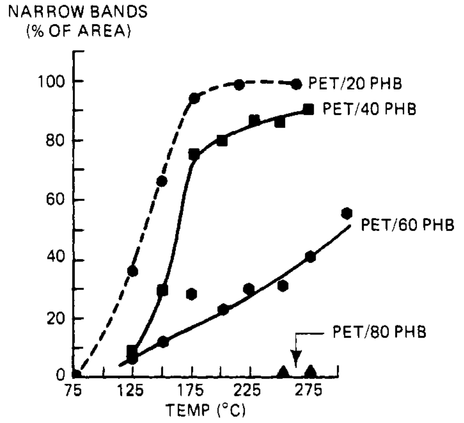


Figure 6. Percent of the proton absorption area in the narrow bands (illustrated in Figure 5) for several polymer compositions and at several temperatures.

Phase Diagram. Figure 5 shows a proton NMR spectrum for PET/60PHB at 177 °C. Similar spectra are observed up to 280 °C except that the ratio of the area of the narrow and broad bands changes with temperature. The description of the reasons for these band shapes has been given previously.[9] The illustration shown in Figure 5 has significantly better resolution than previously published spectra because a pulsed fast Fourier transform spectrometer was used to collect these data, whereas a field modulated continuous wave spectrometer was used in previous work. These higher resolution data allow for a more detailed interpretation of the material's behavior than previous data.[9,10]

Figure 6 shows the percent of the protons in the narrow bands for several polymers and at several temperatures. The PET/20PHB shows narrow bands prior to melting, which is common for semicrystalline polymers, but shows that all the protons are in the narrow bands after melting into a clear fluid at about 220 °C. At or above 35 mol % PHB, the polymers melt into turbid melts,[1] and Figure 6 shows that they give less than 100% of their area in the narrow lines. These data are an extension of previously published data.[9]

Figure 7 shows an expanded view of the central part of the spectrum shown in Figure 5. The separation of the peaks is correct for the assignment of the peaks to aromatic and aliphatic protons as shown. The areas are measured for the separations shown by the line in Figure 7. The percent of the area for the aromatic protons for several compositions at 280 °C is shown in Figure 8. For less than

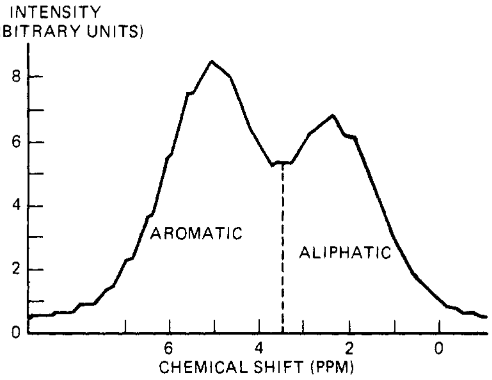


Figure 7. Expanded view of the narrow bands from the proton NMR spectrum shown in Figure 5 for neat PET/60PHB at 177 °C in a sealed, evacuated tube.

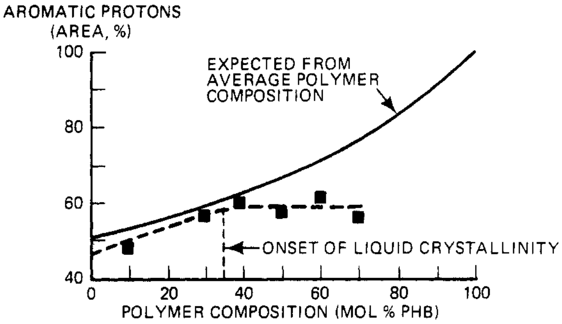


Figure 8. Percent of the narrow band area at 280 °C that is aromatic protons as illustrated in Figure 5 and which is expected on the basis of average composition of the copolymer for several PET/PHB copolymers.

about 35 mol % PHB, the polymers are isotropic, and they show a percentage of aromatic protons nearly the same as those expected from the average composition. The deviations from the expected results give an estimate of the accuracy of the spectral decomposition. In previous work, the narrow bands could not be assigned because of insufficient information.[9,10] Here, the narrow bands are interpreted as being from the polymer in isotropic phase domains. The appearance of the resolved peaks with the expected chemical shift difference and the smoothly changing composition indicated by the narrow bands upon formation of the liquid crystalline phase with changing composition support the interpretation. Above 35 mol % PHB, where the polymers exhibit liquid crystalline character, the composition measured by the narrow bands is nearly constant, and it is different from the average composition of the polymer. There data indicate that an isotropic phase exists for compositions above 35 mol % PHB at 280 °C and that the isotropic phase is richer in PET than the average polymer. The broad lines are interpreted as being from polymer in anisotropic or liquid crystalline domains.[9]

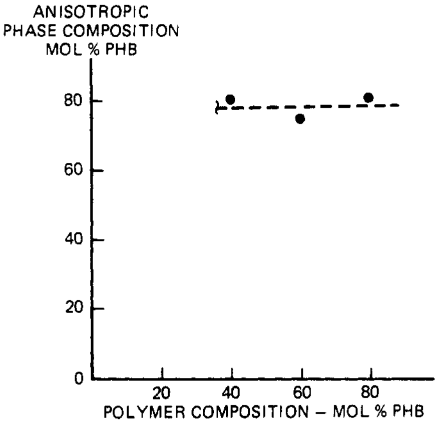


Figure 9. Estimated composition of the anisotropic phase at 280 °C for three copolymer compositions. The composition estimated in Figure 8 and amount of isotropic phase estimated in Figure 6 are used to estimate.

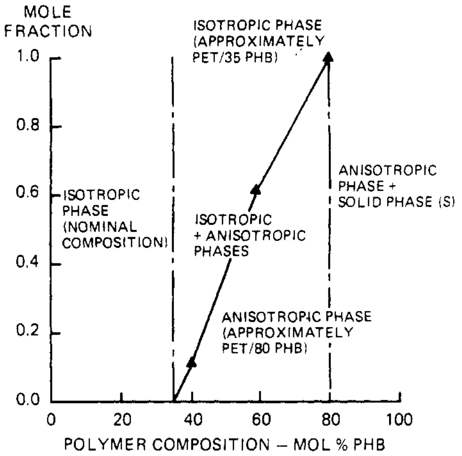
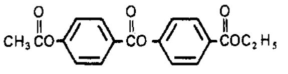
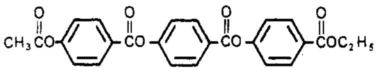
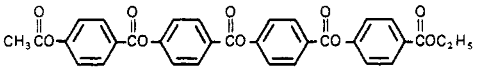


Figure 10. Phase diagram for PET/PHB copolymers at 280 °C.

Table I

Nematic Liquid Crystals Derived From p-Hydroxybenzoic Acid

compound	nematic range, °C.
	115
	142-282
	187-Dec. At Red Heat

The data in Figure 6 provide an estimate of the amount of isotropic phase for each polymer at several temperatures. At 280 °C the average composition of the isotropic phase in the polymer having the liquid crystallinity is estimated to be PET/35PHB, as shown in Figure 8. Then the amount of isotropic phase (Figure 6) along with its composition (Figure 8) leads to the composition of the anisotropic phase by difference with results shown in Figure 9. These data indicate the approximate composition of the anisotropic phase is PET/80PHB. Although these data are not sufficient to assure the composition of the two phases, they are reasonably interpreted as indicating compositions at or above 35 mol % at 280 °C have PHB- and PET-rich phases of approximately constant composition.

The interpretation of the data may be summarized in a phase diagram as shown in Figure 10. At the composition where turbidity and other unusual properties are noticed,[1] an anisotropic phase separates and increasing amounts of the anisotropic phase are present at higher PHB levels. A solid phase probably separates at some composition depending upon temperature, also. This work provided no way to measure any such solid phase, however.

Amount of Anisotropic Phase. The sequence distribution data and the phase composition data can now be brought together to give an improved interpretation of the amount of anisotropic phase present in a PET/PHB

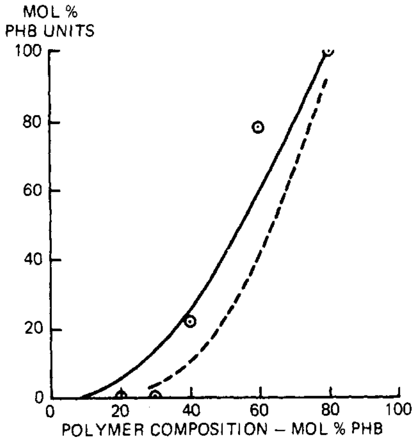


Figure 11. Mole percent of the total PHB units observed in the anisotropic phase (⊙) at 280 °C for several polymer compositions. Mole percent of the total PHB units calculated by the probability model with $m = 1.3$ to be in sequences of three PHBs or longer (–) or four PHBs or longer (- - -).

copolymer. Table I shows data on the liquid crystallinity of the isolated sequences of PHB.[12] The data on small molecules show that at 280 °C three repeat units are near their isotropic transition and four repeat units are a stable liquid crystal. Thus, liquid crystallinity might occur when there are significant concentrations of four or more PHB units in a sequence. The fraction of PHB in sequences of four or more units as calculated by the probability model is displayed in Figure 11 along with the experimental data for mole percent of the PHB in the anisotropic phase. The data on these polymers show that the anisotropic phase occurs near the same composition for which there are significant amounts of PHB in sequences of four or more PHBs.

However, at 40 mol % PHB in the polymer, the amount of PHB in the anisotropic phase is much above the fraction in sequences of four of more PHB units. Actually, it is much nearer the fraction in sequences of three or more PHB units, as shown in Figure 11. It is likely that, once the liquid crystalline phase separates, the remaining PHB sequences partition between the two phases. At 40 mol % PHB, the mole fraction of PHB in the liquid crystalline phase is right for all of the sequences with three or more PHB units in a run to be included. Furthermore, at 60 mol % PHB, the fraction of PHB in the liquid crystalline phase is right for all sequences with two or more PHB units in a run to be included in the liquid crystalline phase. Although the detailed interpretation is likely not as simple as presented here, the concept of longer sequences being required to initiate phase separation followed by partition of the remaining PHB units between the phases is a reasonable expectation. Furthermore, as more PHB-rich phase is present, it is more likely that other shorter runs of PHB can find a PHB-rich domain in which to dissolve even in the face of the constraints of being bonded into a chain.

Relation to Other Work. There is general agreement based upon a variety of measurements[2,8] that the PET/xPHB polymers are two-phase systems for x above 30. The results reported here support that conclusion and add details about the composition and amount of the phases. However, there is disagreement about how the chain sequence statistics relate to the phase separation. Zachariades, Economy, and Logan[2] concluded from etching and diffraction measurements that PET/80PHB is a blocky copolymer with long sequences of PHB. Joseph, Wilks, and Baird[5] concluded from etching and DSC data that the polymers are nonrandom copolyesters. Meesiri, Menczel, Gaur, and Wunderluch concluded[6] that the polymers cannot contain longer blocks of pure poly(oxybenzoate) unless they are made that way by special techniques described by Lenz, Jin, and Feichtinger[13] and that they have made random copolymers. Blackwell, Lieser, and Gutierrez[7] and Blackwell, Gutierrez, and Chivers[8] have argued that extensive blockiness is not necessary to explain the diffraction data. In the work presented in this paper, the probability model of the sequences which predicts the NMR data shows that for PHB contents below 60 mol % the deviation of the sequences from those for a random sequence is so small as to be negligible. Even in PET/60PHB, Figure 4 shows that the differences between the models is small and extended blocks of PHB are unlikely to be the reason for any unusual properties such as domains found by etching.

However, the PET/80PHB is likely to represent a different case. Consider the differences between the two distributions illustrated in Figure 4C for PET/70PHB. The probability model may also apply to PET/80PHB, which cannot be measured. If so, the predictions of the probability model show even more extreme differences between the two distributions. Thus, a slight preference of PHB to bond to itself has a much bigger effect at higher PHB levels, leading to a larger portion of longer sequences of PHB than a random model would predict. This reasoning tends to best support the model described by Blackwell et al.[7,8] in which the PHB-rich phase is pictured as a PHB-like lattice with PET inclusions as defects. At the higher PHB levels the expected sequence distributions are a sensitive function of the value of m in the model. This work is not sufficient to provide a highly reliable value for m. To quantitatively model the PET/80PHB case will require that the model be shown to apply by some direct measurement of the PET/80PHB polymer and a measurement of a better value of m obtained.

Conclusion

Proton and carbon NMR spectra of solutions have shown that the sequence distributions for PET/PHB copolyesters can be described in terms of a probability model in which PHB has a slightly greater than random chance of being bonded to another PHB. While the deviations from randomness of the sequence distributions are slight at lower PHB fractions, they become more significant at higher PHB levels in the copolymer. There is no evidence for significant blocking in any of the copolyesters up to PET/70PHB, although the deviations from randomness lead to perturbations in the distributions of sequence lengths at the higher PHB levels.

Proton wide-line NMR spectra on melts show evidence of both liquid crystalline and isotropic phases at compositions at or above PET/35PHB. The compositions of the isotropic and anisotropic phases are found to be approximately PET/35PHB and PET/80PHB, respectively, at 280 °C. The amount of each phase is estimated for several compositions up to PET/80PHB.

A qualitative explanation of the formation of the liquid crystalline phase requires significant amounts of sequences of four or more PHBs to initiate liquid crystalline phase formation. At compositions with enough PHB to separate a liquid crystalline phase, shorter sequences of PHB partition between the phases to enrich further the PHB-rich phase.

Acknowledgment. We gratefully acknowledge help with the probability model by Dr. L. D. Moore and Dr. J. R. Overton and the samples and encouragement provided

by Dr. W. J. Jackson and H. F. Kuhfuss.

Registry No. (*p*-Acetoxybenzoic acid)(ethylene glycol)(terephthalic acid) (copolymer), 52237-98-6.

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Relationships between Molecular Structure and Immiscibility of Liquid Crystalline Side-Chain Polymers in Low Molecular Weight Nematic Solvents

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Received June 6, 1986

ABSTRACT: The so-called "contact method" is used to investigate the problems of incomplete miscibility newly encountered in binary solutions of liquid crystal side-chain polymers and low molecular weight (LMW) nematogenic compounds. We first demonstrate the possibilities and the limits of this technique applied to the observation of the phenomenon of phase separation in these systems. Then we analyze how the critical demixing temperature is influenced by various modifications of the molecular structure of the polymer solute and of the LMW solvent. The experimental results are interpreted in order to specify the relevant solute–solute, solvent–solvent, and solute–solvent interactions. We infer from this discussion that the solute–solvent interactions are favored by more flexible mesogenic parts in the liquid crystalline polymer and, in contrast, by stiffer LMW molecules.

Introduction

Prior to the discovery of polymers with mesomorphic properties, no example was known of a gap of miscibility in binary mixtures of liquid crystals. Furthermore the properties of easy miscibility have been long and widely applied to characterize the nature of the mesophases by using a reference method.[1,2]

Thus a novel difficulty was introduced in the study of phase diagrams of liquid crystals by the first discovery of a nematic–nematic immiscibility in binary systems of side-chain polymers with low molecular weight (LMW) mesogens by Casagrande et al.[3]

Such an incompatibility does not seem to be really outstanding, and numerous cases of liquid–liquid immiscibility are obvious. One must consider, however, that among the hundreds or even thousands of binary phase diagrams of liquid crystals studied previously this behavior was never before observed. One can contrast the chemical vicinity of the components of most mixtures, but even when two very different nematogens are associated, such as a rodlike mesogen with a disklike one, this usually generates the disappearance of the nematic properties.[4]

The mechanism of this phase separation has been explored experimentally in order to discover whether it is a spinodal decomposition or not.[5] In addition, theoretical calculations varying interactions between the two components have been used to describe the behavior of such binary solutions.[6] We propose an experimental study in which we outline what kinds of interactions would be relevant in this phenomenon.

For this purpose we have first chosen an experimental means of investigation for this peculiar immiscibility property: the phase diagrams are observed by using the contact method in order to determine the critical temperature T_c below which the domain of the homogeneous nematic phase is divided by a gap of miscibility. These choices concerning the method are discussed and substantiated in the Experimental Section. The various classes of binary diagrams are also described in this section.

Starting from a large family of side-chain polysiloxanes with liquid crystalline (LC) properties, we have varied the nature of the low molecular weight (LMW) nematogen used as solvent. In each case the critical demixing temperature is measured. These results are presented in the second part of the paper. Finally, use is made of these results to estimate what chemical parameters are more likely to induce a phase separation.

Experimental Section

To describe the contours of the gap of miscibility, the simplest method would be elaboration of homogeneous binary mixtures with fixed fractions X in polymer units, studying their evolution with decreasing temperature (e.g., by means of light scattering) in order to determine the temperature of the phase separation as performed by Casagrande et al.[3] and Benthack-Thoms and Finkelmann.[7] Such an approach appeared absolutely unthinkable to us: the study under consideration in this paper implies dozens of variations of the constituents of the binary mixture. This would require hundreds of mixtures in order to draw precisely enough the demixtion curve for all the systems. Consequently, one needs a large quantity of each compound (at least 1 g) and a great deal of time because of the difficulties in getting well-homogenized

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