Formation of Molecular Composites through Hydrogen-Bonding Interactions

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ABSTRACT: The phase behavior of blends of poly(glutamates) (PMLG, PELG, and PBLG) with poly(vinylphenol) (PVPh) has been investigated by using FTIR and optical microscopy. The former polymers are α-helical rigid rods with flexible side chains and the latter is a random-coil polymer. The equilibrium number of hydrogen bond interactions was found between the side-chain esters of PMLG, PELG, and the OH group of PVPh in blends of these polymers but not found between PBLG and PVPh, indicating that this latter system is phase separated. The results of polarizing microscope observations demonstrated that at high rigid-rod concentrations the miscible blends displayed anisotropy. An association model has been applied to obtain a theoretical phase diagram for these systems.

Introduction

Helminiak et al.[1] patented the concept of a molecular composite in 1980, and in subsequent publications[2-6] this group, in collaboration with other laboratories, described the potential advantages of these systems and examined the problems of processing such materials from solution. The fundamental goal of this work, as also described by Takayanagi et al.,[7] was to extend the concept of fiber reinforcement to the molecular level, where the high aspect (length/diameter) ratio of individual rigid rods (or bundles of just a few rods) should lead to superior mechanical properties.

Unfortunately, there are fundamental difficulties associated with the formation of compatible rod/coil mixtures. On the basis of a lattice model, Flory[8] and, more recently, Ballauff[9] have demonstrated that, in a ternary *athermal* (i.e., $\chi = 0$) system of rods, coils, and solvent, the random-coil component is strongly excluded from the anisotropic phase and this separation persists in solvent-free mixtures. This predicted incompatibility of rods and coils has its origin in the entropic part of the mixing partition function but can be modified in various ways. Ballauff[9] demonstrated that by appending flexible side chains to the rigid-rod molecules miscibility in a wider region of composition can be obtained, even in binary rod/coil systems. In recent work Heitz et al.[10] have taken this a step further and grafted polystyrene side chains onto liquid-crystalline polyesters, obtaining an improved miscibility with polystyrene homopolymer. Another approach, which depends upon modifying the chemistry of the system, is to produce block copolymers of the rod/coil components, as described by Tsai et al.[11]

In this laboratory we have been characterizing blends of amorphous, random-coil molecules that are miscible as a consequence of hydrogen bonding.[12-21] Here we will report on the possibility that the favorable free energy of such interactions can balance the unfavorable entropic factors associated with mixing rods and coils and any other unfavorable contributions to the free energy of mixing, for example, from dispersion forces. We will demonstrate that in blends of various rigid-rod (α-helical poly(L-glutamates) with poly(4-vinylphenol) there is direct evidence for a degree of molecular level mixing and that it is indeed possible to obtain a thermodynamically stable dispersion of a rigid rod in a random-coil matrix.

Experimental Section

The rigid-rod polymers used in this study are the synthetic polypeptides poly(γ-methyl L-glutamate) (PMLG), poly(γ-ethyl L-glutamate) (PEGL), and poly(γ-benzyl L-glutamate) (PBLG), which were acquired from the Sigma Chemical Co. and used as received. The molecular weights of PMLG, PELG, and PBLG were 46 000, 160 000, and 248 000, respectively. The random-coil polymer is poly(4-vinylphenol) (PVPh) and was purchased from Polysciences, Inc. In most studies we used two different molecular weights of PVPh, 1500–7000 and 9000–11 000, respectively. Infrared spectra were recorded on an FTS-60 Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm^{-1}. A minimum of 128 scans were signal averaged. Polarizing optical observations were performed on an Olympus BH-2 microscope.

Thin films of the blends prepared for FTIR and polarizing microscope studies were cast from mixtures of a 0.4% (w/v) poly(L-glutamates)/chloroform solution and a 0.4% (w/v) PVPh/tetrahydrofuran solution onto potassium bromide windows or glass slides. The solvents were evaporated in dry air for 24 h to obtain the as-cast samples. These films were subsequently placed under vacuum at 130–140 °C for 10 h to give the annealed samples.

Simple Model

Before considering our experimental results, we will demonstrate using a simple model that it is, in principle, possible to obtain a thermodynamically stable molecular composite as a consequence of hydrogen-bonding interactions. In this paper we will confine our analysis to rigid-rod polymers with side chains that can form hydrogen bonds with the random-coil component of the mixture, as shown in Figure 1, which illustrates the self-association of phenolic OH groups and the formation of phenolic OH/ester hydrogen bonds. In a miscible mixture there will be a certain equilibrium distribution of free and bonded ester groups and it is these that we will later use as a probe of phase behavior.

Following Flory,[8] Ballauff[9] subdivided the mixing partition function Z_M into a combinatorial part, Z_{comb}, an orientational part, Z_{orient}, and an intramolecular or conformational part, Z_{conf}:

$$Z_M = Z_{comb} Z_{orient} Z_{conf} \quad (1)$$

In systems where the interactions are weak, Z_{conf} is assumed to be independent of the order of the respective phase and is therefore not considered. Here we will use Z_{conf} to obtain the contribution of hydrogen bonds to the

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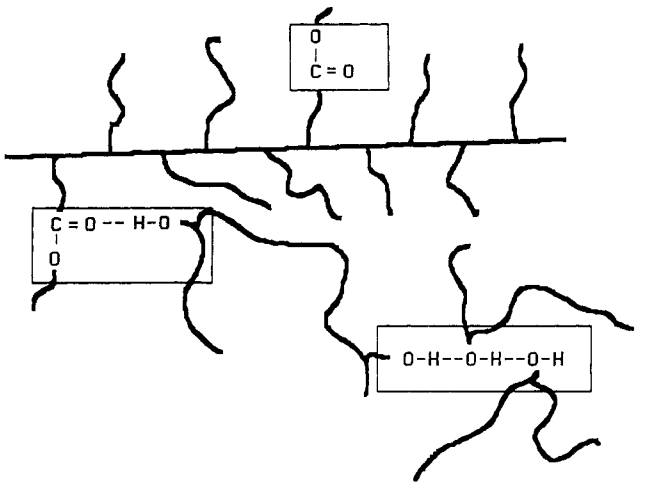

Figure 1. Illustration of the types of hydrogen bonds present in poly(L-glutamate)/poly(vinylphenol) blends.

free energy of mixing through the use of an association model. The energies of hydrogen-bonding interactions are significantly greater than kT at ambient temperatures, so that their lifetime is at least 1 order of magnitude longer than that of a molecular vibration. Accordingly, it is possible to treat the associated species, generally chains of hydrogen-bonded functional groups, as distinguishable entities for which a partition function can be constructed. In applying this approach to polymers, we have determined the free energy changes that are a result of these associations through a calculation of the modification in the number of configurations available to the chain in a hydrogen-bonded mixture, relative to a mixture where such interactions do not occur.[15] The formation of hydrogen bonds requires that specific segments be adjacent to one another and oriented in a specific manner. If the equilibrium or most probable distribution of hydrogen-bonded species at a particular temperature and composition is known from experimental measurement, however, then it is possible to define a parameter, usually an equilibrium constant, that accounts for all of the various enthalpic and entropic components of a particular interaction of this type. Infrared spectroscopy is a particularly powerful probe of hydrogen-bonding interactions and allows one to count the number of bonded and "free" groups, thus providing a basis for determining such equilibrium constants.

We have described this general approach elsewhere.[15] Here we will limit our analysis to the situation illustrated in Figure 1, where the random-coil component self-associates while the rigid-rod polymer does not but has an "acceptor" (ester) functional group located on a side chain that is capable of forming a hydrogen bond with the phenolic OH groups of the random-coil polymer. We will assume that the amide groups of the polypeptide backbone remain fully occupied in hydrogen bonding to one another and maintaining the α-helical backbone conformation. Therefore, the distribution of these hydrogen bonds does not change with composition and does not have to be considered (as we will see, infrared measurements show that this is a good assumption). We let the segments of the random-coil component (defined so that each contains just one functional group capable of forming a hydrogen bond) be represented by the letter B, so that in the pure self-associating polymer there is a distribution of B_h-mers, where there are h segments in a "chain" of groups linked by $h - 1$ hydrogen bonds. If A represents the non-self-associating component, then in the mixture there will be a distribution of B_h-mers, B_hA-mers, and A_1-mers (i.e., non-hydrogen-bonded groups), depending upon temperature and composition.

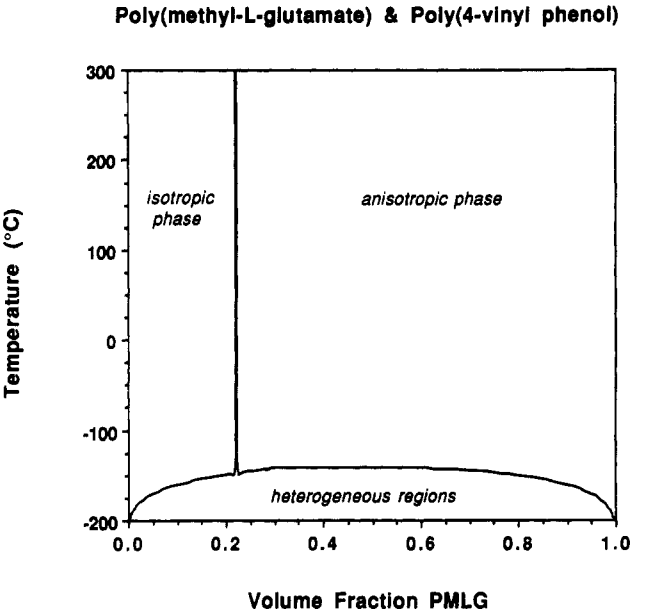

Figure 2. Calculated phase diagram for a PMLG/PVPh blend. Molecular weight of PMLG = 260 000.

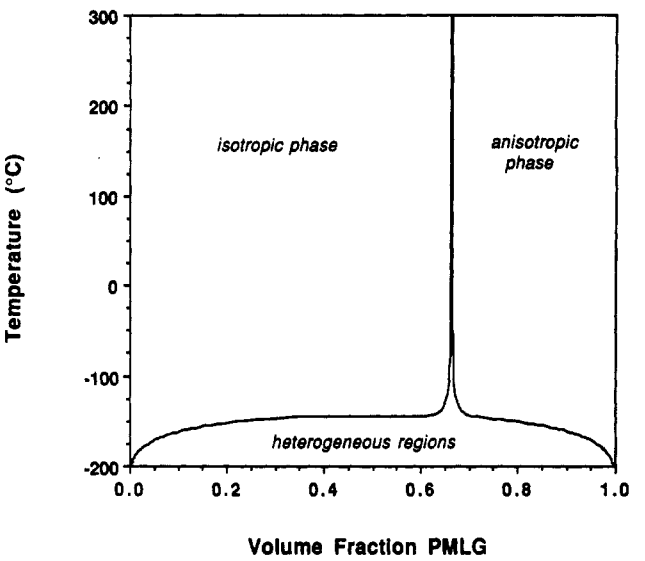

Figure 3. Calculated phase diagram for a PMLG/PVPh blend. Molecular weight of PMLG = 46 000.

Our procedure depends upon determining the probability that $h - 1$ B segments are adjacent to a chosen B segment in forming a B_h-mer, and so on, so that they could be linked to form hydrogen bonds. These probabilities are used to modify the usual expressions for the number of configurations available to the system, and for *flexible* polymers we write

$$Z_M^{\text{flexible}} = Z_F Z_H \tag{2}$$

where Z_F is the Flory expression of the mixing of non-hydrogen-bonded chains and Z_H accounts for the modifications to the configurations available to the chains as a result of forming the equilibrium distribution of hydrogen-bonded species. As a result, we obtain a Gibbs free energy that can be written

$$\Delta G_M = \Delta G_F + \Delta G_H \tag{3}$$

where ΔG_F is the usual Flory expression of the free energy

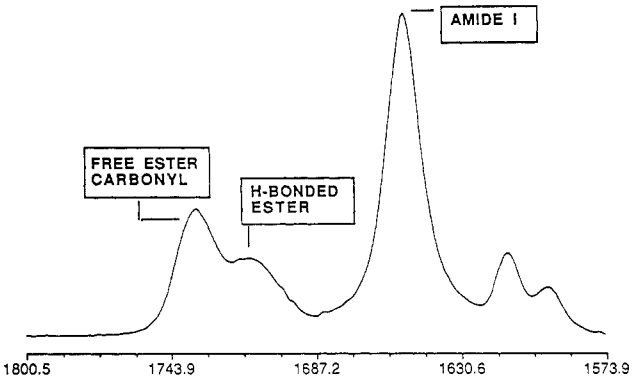

Figure 4. Infrared spectrum of a PELG/PVPh blend.

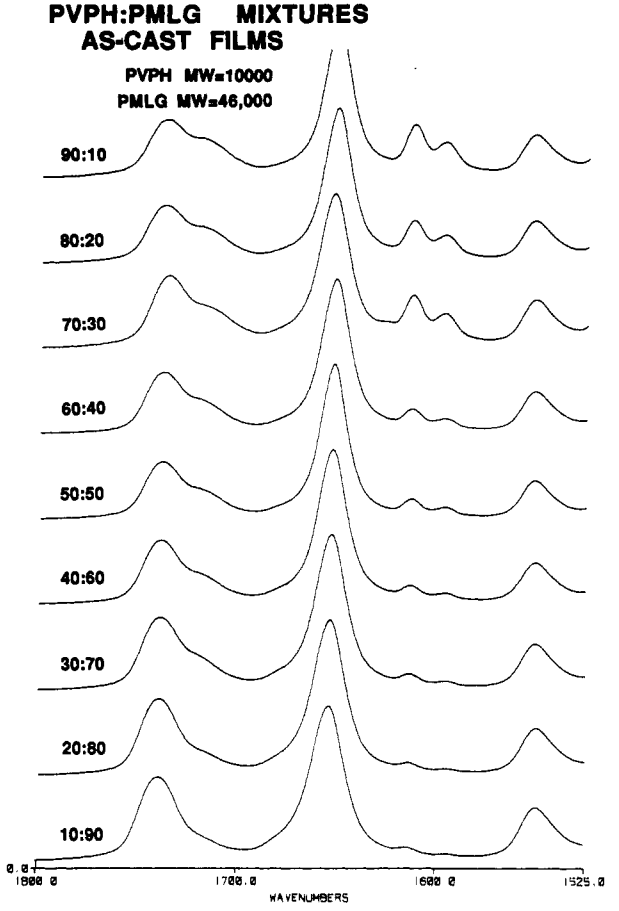

Figure 5. Infrared spectra of the "as-cast" films of PVPh/PMLG blends.

of mixing and ΔG_H represents the contribution of hydrogen-bonding interactions. If the "already formed" equilibrium distribution of associated species are allowed random contacts with one another and with non-hydrogen-bonded segments, then we can include the usual Flory χ term in ΔG_F to account for weak interactions (e.g., dispersion forces). The separation of strong polar interactions from weak nonpolar forces is thus a natural consequence of the model.

We can extend this approach to rigid-rod/random-coil mixtures but must now keep in mind that the a priori probabilities of finding certain segments adjacent to one another, such that they could be linked by hydrogen bonds, can depend upon the orientation of the rodlike component. If we were considering main-chain liquid-crystalline polyesters, for example, we could perhaps accomplish this through the use of the conditional probabilities given by DiMarzio[22,23] for the occupation of sites adjacent to rigid

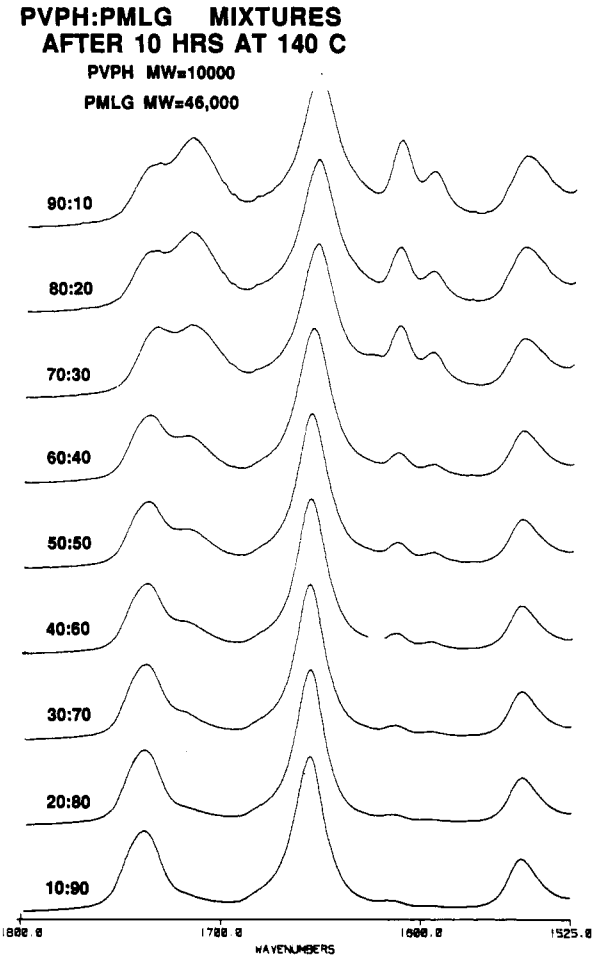

Figure 6. Infrared spectra of the annealed PVPh/PMLG blends.

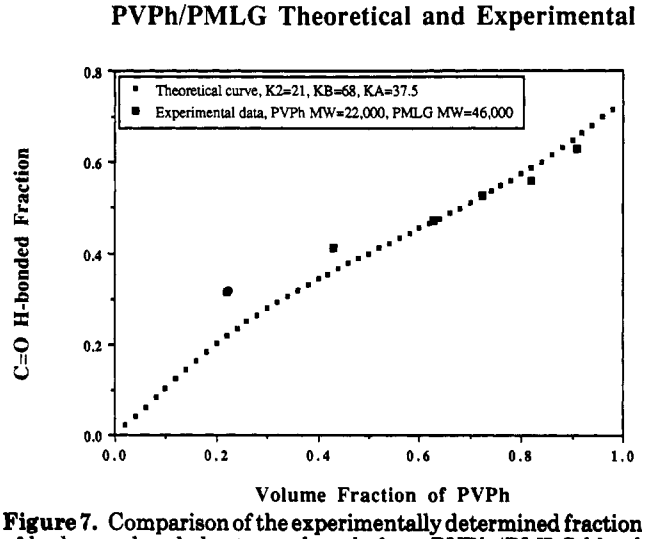

Figure 7. Comparison of the experimentally determined fraction of hydrogen-bonded ester carbonyls for a PVPh/PMLG blend to that predicted by using an association model.

rods. Here our problem is simplied if we make Ballauff's[9] assumption that there is no correlation of the conformation of the side chain, where the hydrogen-bonding group that is of interest to us is located, with the orientational order of the main-chain rigid rod. The probabilities used to describe the distribution of hydrogen-bonded species would then be identical with those given in our previous work,[15] and we can write

$$\Delta G_M = \Delta G_{FB} + \Delta G_H \quad (4)$$

where ΔG_{FB} is the Flory–Ballauf result and ΔG_H is equal

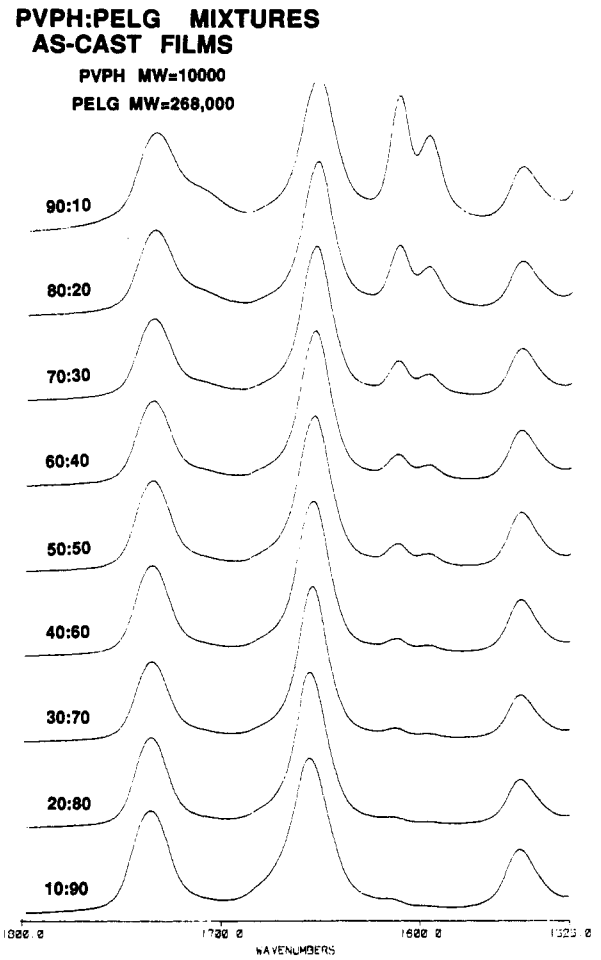

Figure 8. Infrared spectra of the as-cast films of PVPh/PELG blends.

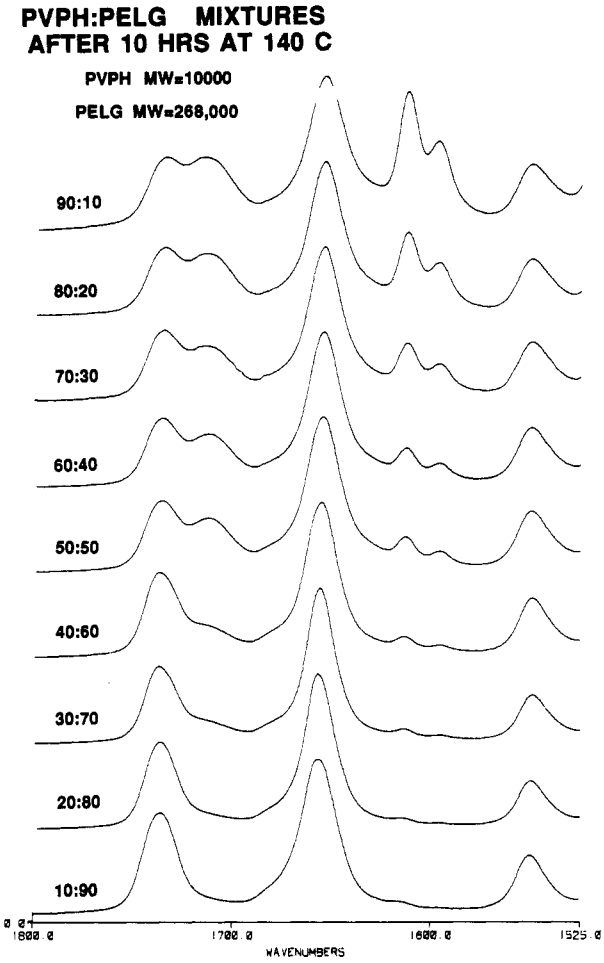

Figure 9. Infrared spectra of the annealed PVPh/PELG blends.

to that given previously[15] in terms of the composition of the components and equilibrium constants describing hydrogen bond formation.

If we now mark all quantities that refer to the anisotropic phase by a prime, we can equate the chemical potentials of the two phases in the usual manner and write

$$\frac{\Delta\mu'_{rod} = \Delta\mu_{rod}}{RT} = 0$$

$$= \ln\left[\frac{\phi'_A}{\phi_A}\right] - rM_A\left[\frac{\phi'_A - \phi_A}{rM_A} + \frac{\phi'_B - \phi_B}{M_B}\right] +$$

$$rN_A\frac{2}{\bar{y}}\frac{V_s}{V_A} + 2\ln\left[\frac{8}{\Pi\bar{y}}rM_A\frac{V_r}{V_A}\right] - rM_A\phi'_A\left[\frac{V_r}{V_A} - \frac{\bar{y}}{rM_A}\right] +$$

$$rM_A(\phi'_B{}^2 - \phi_B{}^2)\chi + rM_A[(\Delta\bar{G}'_H)_A - (\Delta\bar{G}_H)_A] \quad (5)$$

and

$$\frac{\Delta\mu'_{coil} - \Delta\mu_{coil}}{RT} = 0$$

$$= \ln\frac{\phi'_B}{\phi_B} - M_B\left[\frac{\phi'_A - \phi_A}{rM_A} + \frac{\phi'_B - \phi_B}{M_B}\right] +$$

$$M_B\frac{2}{\bar{y}} - M_B\phi'_A\left[\frac{V_r}{V_A} - \frac{\bar{y}}{rM_A}\right] + M_B(\phi_A{}'^2 - \phi_A{}^2)\chi +$$

$$M_B[(\Delta\bar{G}'_H)_B - (\Delta\bar{G}_H)_B] \quad (6)$$

Because we use the molar volume of the chemical repeat unit of the self-associating polymer, V_B as a reference volume. In order to describe the hydrogen-bonding interactions, we have rewritten Ballauf's equations in terms of the same reference volume. The volume fraction of the poly(L-glutamate) under consideration is given by ϕ_A, and each repeat unit has a molar volume V_A. Accordingly, the volume fractions of the rod and side-chain components are given by

$$\phi_A\frac{V_r}{V_A} \text{ and } \phi_A\frac{V_s}{V_A}$$

respectively, where V_s is the molar volume of the side chain and $V_r = V_A - V_s$. The degree of polymerization of the rod is equal to M_AV_A/V_B or M_Ar ($r = V_A/V_B$), while that of the coil is given by M_B. The disorder index $\bar{y}$ is as defined by Flory and Ronca[24] and Ballauff,[9] and we have used the "asymptotic approximation"[9,24] in our calculations. The χ term is defined following Ballauf[9] and in terms of solubility parameters can be written as

$$\frac{V_rV_sV_B}{RTV_A}\left[\frac{(\delta_{coil} - \delta_{rod})^2}{V_s} + \frac{(\delta_{coil} - \delta_{side\ chain})^2}{V_r} - \frac{(\delta_{rod} - \delta_{side\ chain})^2}{V_A}\right] \quad (7)$$

The quantities $(\Delta\bar{G}_H)$ are the contributions of the hydrogen-bonding interactions to the chemical potentials. These are defined in terms of the equilibrium constants that are required to reproduce the experimentally observed distribution of hydrogen-bonded species, and expressions for these quantities have been reported previously.[15] It is a consequence of the model we employ that equilibrium constants should be transferable between molecules that

have the same functional groups by simply adjusting for the differences in the molar volumes of the molecules or segments under consideration,[13] so for reasons that will become apparent later we took the equilibrium constants for phenolic OH groups from a detailed study of phenol by Whetsel and Lady,[25] while the equilibrium constant describing phenolic OH/ester hydrogen bonds was taken from our recent studies of PVPh/polyacrylate blends.[19]

Using these quantities and solubility parameters calculated from group contributions,[21] we obtained the phase diagrams shown in Figures 2 and 3 for PMLG/PVPh blends. The calculated phase diagrams for PELG and PVPh blends are similar, and all predict that we should obtain a thermodynamically stable anistropic single-phase mixture or molecular composite for blends of poly(L-glutamate) rods with PVPh coils of appropriate composition. The position of the biphasic gap separating isotropic and anisotropic phases depends upon the rigid-rod chain length, and, to illustrate this, phase diagrams for two different PMLG samples are compared in Figures 2 and 3.

Results and Discussion

From our previous work on blends of PVPh with various acrylates and methacrylates, we know that hydrogen bonds between esters groups and phenolic hydroxyl's can result in the formation of miscible blends.[16,18,19] In mixtures of this type there is a competition for formation of hydrogen bonds between self-associated OH groups (i.e., OH···OH hydrogen bonds) and between OH and ester carbonyls. The proportion of "free" (i.e., non-hydrogen-bonded) and bonded carbonyl groups thus varies systematically with composition and temperature. Infrared spectroscopy is an extraordinarily useful probe of these systems, not only because the carbonyl band shifts upon hydrogen bonding, which can only occur in detectable amounts if there is a degree of molecular level mixing, but also because it allows us to probe the backbone conformation of the polypeptides to ensure that a helix/coil transition has not occurred. This is accomplished through observation of the conformationally sensitive amide I mode. A spectrum obtained from a PELG/PVPh blend is shown in Figure 4. The characteristic sharp amide I mode corresponding to the α-helical structure is clearly observed near 1650 cm^{-1}, as is the presence of both free and hydrogen-bonded ester carbonyls near 1735 and 1715 cm^{-1}, respectively.

As might be expected from the predictions of Flory[8] and Ballauff[9] and the experimental studies of Hwang et al.,[3-5] anisotropic single-phase systems are not readily obtained from solution, because of the propensity of the anisotropic phase to exclude random-coil polymers. This is presumably modified by hydrogen-bonding interactions, but to an extent that we have yet to examine in rod/coil/solvent systems. By trial and error we found that the optimum approach was to dissolve the poly(L-glutamate) under consideration in chloroform and the PVPh in THF, mix these two solutions, and cast films. Even so, phase separation at the scale of the hydrogen-bonding functional group clearly occurs. This is illustrated in Figure 5, which shows the infrared spectra of the "as-cast" films of various mixtures of PVPh with PMLG. There is clearly some degree of hydrogen bonding, but far less than we would expect, based on our experience with miscible PVPh/polyacrylate and polymethacrylate blends.[16,18,19] Upon annealing these samples in a vacuum oven at 140 °C for 10 h, above the T_g of the PVPh polymers used in this study, the proportion of hydrogen-bonded carbonyl groups increased markedly, as can be seen from the spectra shown

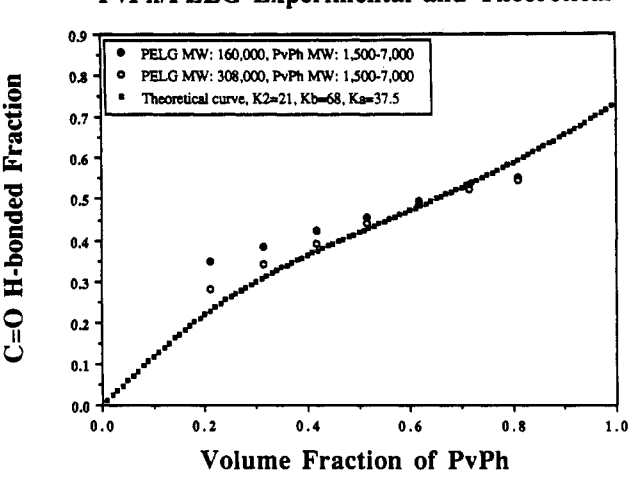

Figure 10. Comparison of the experimentally determined fraction of hydrogen-bonded ester carboyls for a PVPh/PELG blend to that predicted by using an association model.

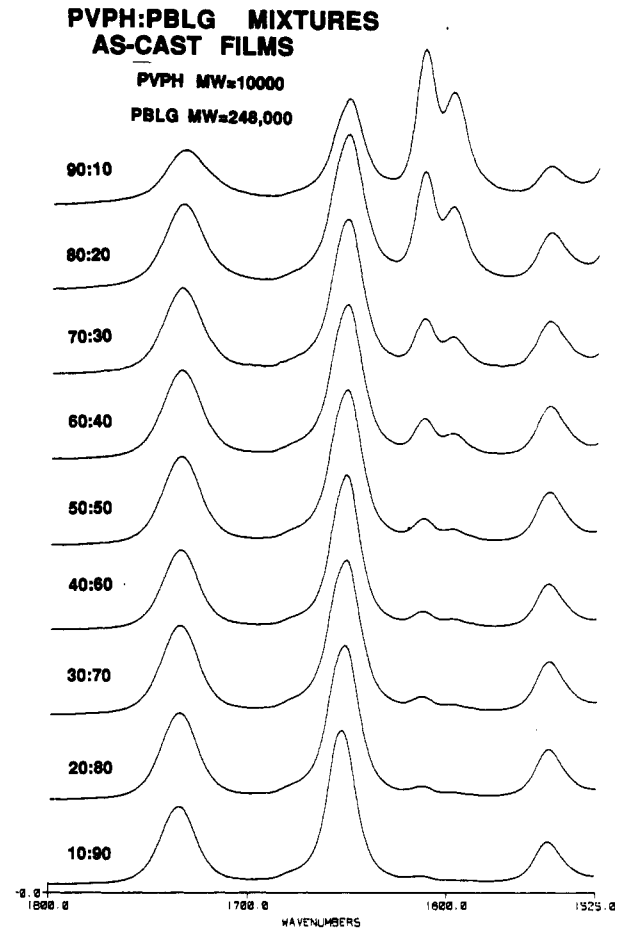

Figure 11. Infrared spectra of the as-cast films of PVPh/PBLG blends.

in Figure 6. The detection of these hydrogen-bonded groups does not necessarily mean that we have made a true molecular composite, as this requires that the fraction of hydrogen-bonded groups must be equal to the equilibrium distribution characteristic of a single-phase system for a particular composition and temperature. If the system is phase separated, the proportion of hydrogen-bonded groups will always be less than this fraction, but there could still be a significant concentration of such species.

Clearly, we cannot use equilibrium constants calculated from the fraction of bonded groups measured in this study

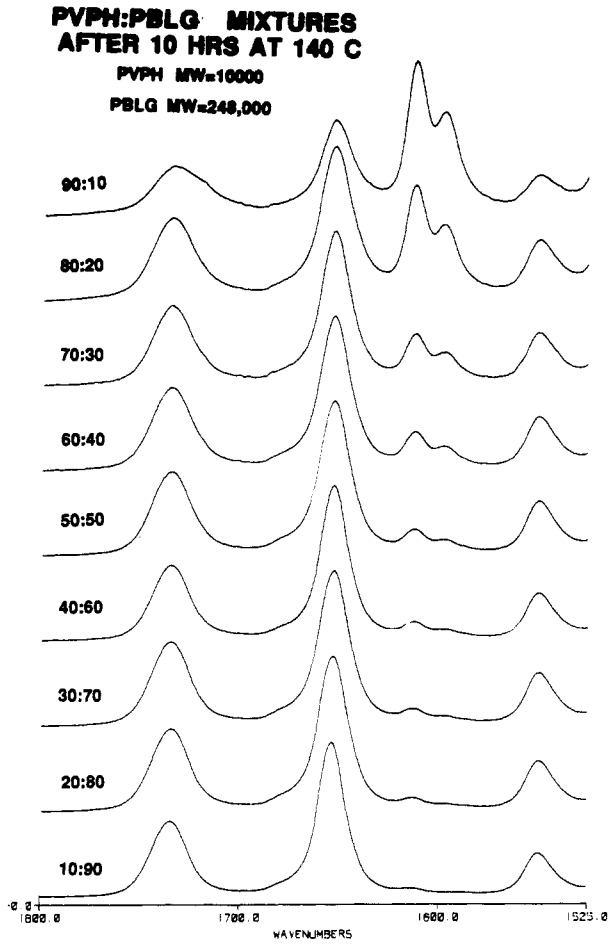

Figure 12. Infrared spectra of the annealed PVPh/PBLG blends.

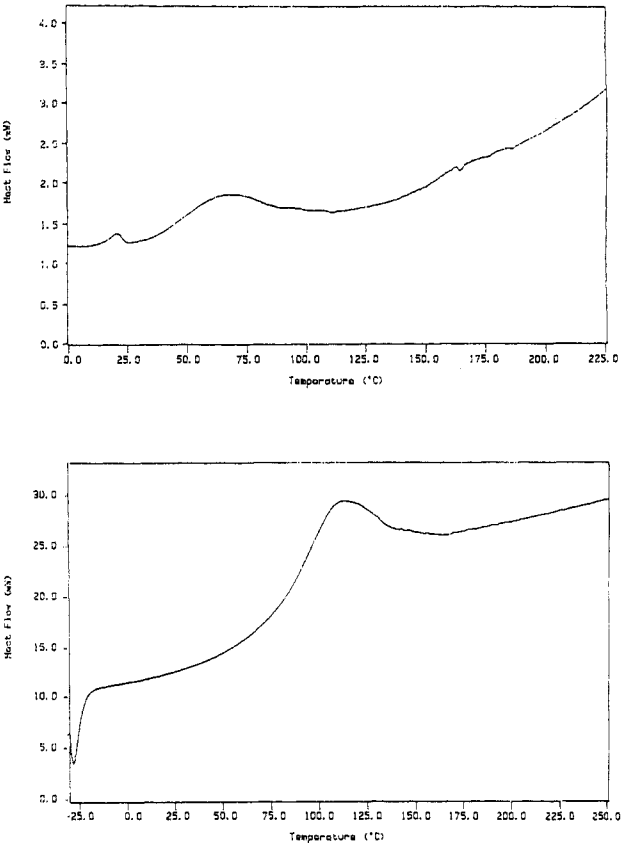

Figure 13. Bottom: DSC thermogram of PVPh. Top: DSC thermogram of an annealed PVPh/PELG (50/50) blend.

in order to establish the equilibrium distribution, as we would be engaging in a circular argument and would produce self-fulfulling predictions. Accordingly, as noted above, the equilibrium constants we used for the self-association of PVPh were taken from a detailed study of phenol by Whetsel and Lady,[24] while those describing phenolic OH to ester hydrogen bonds were obtained from our studies of blends of PVPh with polyacrylates.[19] Using these parameters, we calculated the theoretically predicted fraction of hydrogen-bonded groups shown in Figure 7, using the equations for the stoichiometry of hydrogen bonding given in our previous work.[12-15,19] It can be seen that there is a very good agreement. There are some deviations at low PVPh concentrations, but this is probably due to experimental errors in curve-resolving the infrared bands observed in the spectra of these blends, where the fraction of bonded groups is relatively small. (Note also that the measured fraction of hydrogen-bonded species is somewhat *greater* than that predicted. It would be *less* in a phase-separated system.) Similar results were obtained for the blends of PVPh with PELG. Spectra of the as-cast and annealed films are shown in Figures 8 and 9, and a comparison of the measured fraction of hydrogen-bonded species is compared to that theoretically predicted in Figure 10. Again there is a good agreement, and this is strong evidence that we have produced a single-phase system, as we have apparently obtained the equilibrium distribution of hydrogen-bonded species. This could only occur if the molecules are mixed at the molecular level.

In contrast to PVPh/PMLG or PELG blends, we could not obtain blends with PBLG that displayed the equilibrium distribution of species, as can be seen from Figures 11 and 12, which show the spectra of the as-cast films and annealed samples. The proportion of hydrogen-bonded groups is negligibly small over most of the composition range.

The use of infrared spectroscopy as a probe of molecular level mixing is not, as yet, common. We believe it can be employed in systems where the number of interacting species can be directly measured and compared to theoretical predictions, as long as the latter are based on parameters obtained independently (i.e., from other mixtures). We have explored this approach in some recent papers,[25,26] but this work is, at the time of writing, still in the review process. As further confirmation of the single-phase nature of these mixtures, we therefore performed some DSC studies on a PVPh/PELG blend. The PVPh used in this study has a T_g near 120 °C, as shown in Figure 13. PELG also shows a transition of some kind near 120 °C. A similar endotherm has been observed near 132 °C in PBLG,[27] but we are not concerned with these here. We did not observe any low-temperature transitions in our DSC studies of PELG, but there is a prominent relaxation process attributed to side-chain motions, near −11 °C and +27 °C for PMLG and PBLG, respectively, that can be observed in dynamic-mechanical studies.[28,29] The mixing and interaction of PVPh with the polypeptide side chains might then be expected to produce a T_g at some intermediate temperature (i.e., between 120 and about 0 °C). This is indeed what is observed, as can be seen in Figure 13, for a 50/50 PELG/PVPh blend, where a T_g near 65 °C is now apparent.

Together with the infrared results this is strong evidence that the PVPh blends with PMLG and PELG are miscible, but have we maintained the α-helical structure of the polypeptide backbones or induced a helix–coil transition? The amide I band has the same width at half-height throughout the composition range (although at low polypeptide concentrations it *appears* to be broader at first glance,

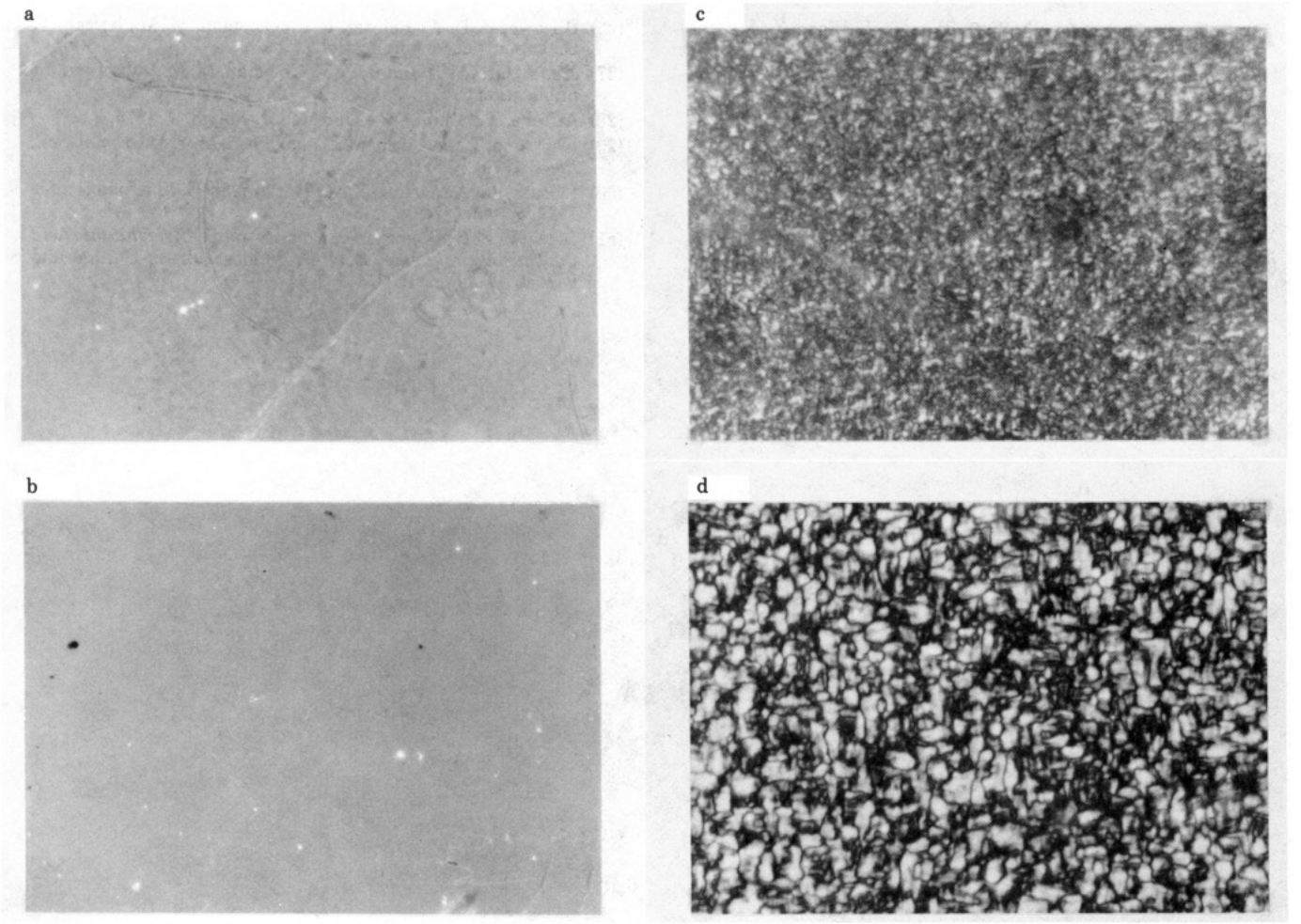

Figure 14. Polarizing microscope observations of annealed mixtures of PELG and PVPh: (a) 20/80, (b) 40/60, (c) 60/40, (d) 80/20.

because the band is now less intense than other modes), so that the polymers have maintained their α-helical structure to within the limits that can be detected by infrared spectroscopy. Accordingly, for PMLG and PELG blends, we should obtain the isotropic and anisotropic phases predicted by the simple model described above. Optical micrographs for PELG/PVPh blends are shown in Figure 14, and it is clear that at low PELG concentrations the films are indeed isotropic, while above a certain critical concentration, mesomorphic regions can be seen. To reiterate, these samples have the equilibrium distribution of hydrogen-bonded species characteristic of a single-phase system. Accordingly, we believe that these films are thermodynamically stable "molecular composites".

For PELG and PMLG the observations of phase behavior are in general agreement with the predictions of a simple model. No agreement was found for PBLG. This could simply be because the model is too crude. Certainly, the estimation of χ for rod/coil interactions from solubility parameters is not likely to be accurate. It should also be kept in mind that the morphology of PBLG films is influenced by solvent and composition, so that an ordered crystalline phase could have been produced. It has been proposed that stacking of the side-chain benzene rings of PBLG plays a role in stabilizing various structures (ref 31 and citations therein). More work is required in order to elucidate the origin of these differences in the behavior of PBLG relative to PMLG and PELG.

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References and Notes

(1) Helminiak, T. E.; et al. U.S. Patent 4,207,407, 1980.
(2) Wellman, M.; Husman, G.; Kulshreshtha, A. D.; Helminiak, T.; Wiff, D.; Benner, C.; Hwang, W. F. *Coat. Plast. Prepr. Pap. Meet.* (*Am. Chem. Soc., Div. Org. Coat. Plast. Chem.*) **1980**, *43*, 783.
(3) Hwang, W. F.; Wiff, D. R.; Helminiak, T. *Coat. Plast. Prepr. Pap. Meet.* (*Am. Chem. Soc., Div. Org. Coat. Plast. Chem.*) **1981**, *44*, 32.
(4) Hwang, W. F.; Wiff, D. R.; Benner, C. L.; Helminiak, T. E. *J. Macromol. Sci.* **1983**, *B22*, 231.
(5) Hwang, V. F.; Wiff, D. R.; Verschoore, C.; Price, G. E.; Helminiak, T. E.; Adams, W. W. *Polym. Eng. Sci.* **1983**, *23*, 784.
(6) Krause, S. J.; Haddock, T.; Price, G. E.; Lenhert, P. G.; O'Brien, J. F.; Helminiak, T. E.; Adams, W. W. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 1991.
(7) Takayanagi, M.; Agata, T.; Morikawa, M.; Kai, T. *J. Macromol. Sci., Phys.* **1980**, *B17*, 591.
(8) Flory, P. J. *Macromolecules* **1978**, *11*, 1138.
(9) Ballauff, M. *J. Polym. Sci., Part B, Polym.* **1987**, *25*, 739; *Mol. Cryst. Liq. Cryst.* **1986**, *136*, 175.
(10) Heitz, T.; Rohrback, P.; Hocker, H. *Macromol. Chem.* **1989**, *190*, 3295.
(11) Tsai, T. T.; Arnold, F. E.; Hwang, W. F. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1985**, 64.
(12) Painter, P. C.; Park, Y.; Coleman, M. M. *Macromolecules* **1988**, *21*, 66.
(13) Painter, P. C.; Park, Y.; Coleman, M. M. *Macromolecules* **1989**, *22*, 580.
(14) Painter, P. C.; Park, Y.; Coleman, M. M. *Macromolecules* **1989**, *22*, 580.
(15) Painter, P. C.; Graf, J.; Coleman, M. M. *J. Chem. Phys.* **1990**, *92*, 6166.
(16) Coleman, M. M.; Lichkus, A. M.; Painter, P. C. *Macromolecules* **1989**, *22*, 586.
(17) Coleman, M. M.; Hu, J.; Park, Y.; Painter, P. C. *Polymer* **1988**, *29*, 1659.

(18) Coleman, M. M.; Lee, J. Y.; Serman, C. J.; Wang, Z.; Painter, P. C. *Polymer* **1989**, *30*, 1298.
(19) Serman, C. J.; Zu, Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1989**, *22*, 2015.
(20) Hu, J.; Painter, P. C.; Coleman, M. M.; Krizan, T. D. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, *28*, 149.
(21) Coleman, M. M.; Sherman, C. J.; Bhagwagar, D. E.; Painter, P. C. *Polymer* **1990**, *31*, 1187.
(22) DiMarzio, E. A. *J. Chem. Phys.* **1962**, *36*, 1563.
(23) DiMarzio, E. A. *J. Chem. Phys.* **1977**, *66*, 1160.
(24) Flory, P. J.; Ronca, G. *Mol. Cryst. Liq. Cryst.* **1979**, *54*, 289.
(25) Whetsel, K. B.; Lady, J. H. In *Spectrometry of Fuels*; Friedel, H., Ed.; Plenum: London, 1970; p 259.
(26) Bhagwager, D. E.; Painter, P. C.; Coleman, M. M.; Krizan, T. D., submitted for publication.
(27) Xu, Y.; Graf, J.; Painter, P. C.; Coleman, M. M., submitted for publication.
(28) Aritake, T.; Tsujita, Y.; Uematsu, I. *Polym. J.* **1975**, *7*, 21.
(29) Kajiyama, T.; Kuroishi, M.; Takayanagi, M. *J. Macromol. Sci., Phys.* **1975**, *B11*, 121.
(30) Hiltner, A.; Anderson, J. M.; Borkowski, E. *Macromolecules* **1972**, *5*, 446.
(31) Block, H. *Poly(γ-benzyl L-glutamate) and Other Glutanic Acid Containing Polymers*; Polymer Monographs 9; Gordon and Breach: London, 1983.