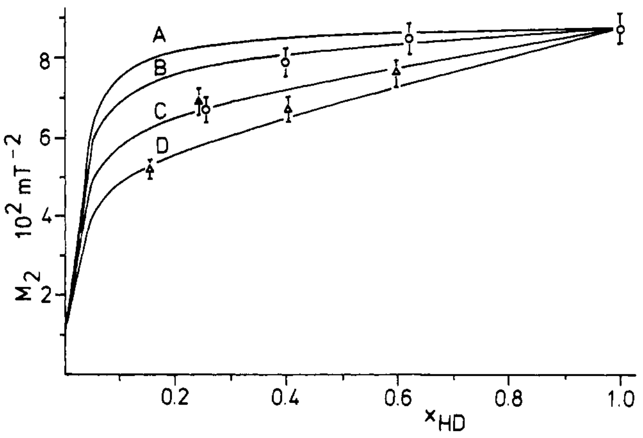

Figure 2. ^1H NMR second moments for cocrystallized PEHD/PED. Circles and triangles refer to L and H samples, respectively. Full lines are calculated for the models of complete segregation (A), molecular clustering (B), adjacent reentry (C), and random reentry (D).

xylene solution. The striking influence upon the solid echo may be related to the fact that the random coils start to overlap in this concentration region thus affecting the crystallization kinetics, but this effect needs further investigation.

In Figure 2, M_2 values calculated for four different models of chain folding are compared with experimental M_2's as obtained from the solid echos of Figure 1. Curve A corresponds to the case of "complete segregation" mentioned above. Curve B has been obtained for a cluster model where 80% of the PEHD protons are at the surface (or edge) of a molecular cluster, the other protons inside the cluster having the same second moment as in pure PEHD. Curve C corresponds to chain folding by adjacent reentry along the (110) plane and curve D to the random reentry (or random switchboard[1]) model. The M_2 values of the L samples are close to curve B for the cluster model (see below for $x_{HD} = 0.25$). A "molecular cluster" can be formed by regime II crystallization[13] where a row of PE stems folds back on itself forming a stack of two or more parallel rows. Neutron scattering results have also been interpreted in terms of this superfolding[14] or stacked sheets[15] model. The low value of M_2 at $x_{HD} = 0.25$ (Figure 2) may be due to an isotope effect[14] whereby PEHD grows preferentially at the beginning of the crystallization process causing a gradient of x_{HD} in each crystal. Although this effect should be small at our crystallization temperature of 60 °C and further reduced in PEHD/PED as compared with PEH/PED, it may be nonnegligible at $x_{HD} < 0.3$. Thus, a distribution of x_{HD} about the average $\bar{x}_{HD} = 0.25$ lowers the value of M_2 if we exclude the extreme case of complete segregation where this "distribution" would become singular, and M_2 is given by curve A.

The M_2 values of the H samples are closest to curve D for random reentry if we exclude the value (full triangle in Figure 2) due to the dotted line of Figure 1 (see above). However, further work is necessary in order to discriminate unambiguously between the random and adjacent reentry models. We can qualitatively understand the lower M_2 values of the H as compared to the L samples assuming that the crystallization is diffusion controlled. The entanglement of the high molecular weight chains should then impede the mobility and thus the ability to form adjacent reentry lamellae. It should be noted that there are ~100 stems per molecule in the H series as compared with ~15 stems in the L series.

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Excimer Fluorescence as a Molecular Probe of Polymer Blend Compatibility. 1. Blends of Poly(2-vinylnaphthalene) with Poly(alkyl methacrylates)

As a result of interest in polymer–polymer interactions in the solid state,[1] a number of experimental tools have been employed to study blend compatibility. These include small angle neutron scattering, pulsed nuclear magnetic resonance, optical transmission, density measurement, vapor sorption, calorimetry, dynamic mechanical, and dielectric spectroscopy.[2-8] However, no single technique can answer all questions about interactions at the molecular level. Thus it is desirable to extend the range of methods. One promising approach along these lines has been made recently by Morawetz[9] in a study where nonradiative energy transfer was used as a tool. We present evidence in this paper that another very powerful probe of interaction in physical blends is provided by excimer fluorescence.

An excimer is an excited molecular complex which is formed between two identical aromatic rings, one of which is in a singlet excited state.[10] Three types of nominal excimer forming sites exist in the aromatic vinyl polymers. First, intermolecular interaction between rings on different chains leads to sites which are important in neat homopolymer films and in regions of aggregation in blended systems. The second type results from intramolecular interaction between rings on nonadjacent chain segments; we shall consider it as a subclass of the intermolecular case. A third type which is important in very dilute blends is the intramolecular site formed between aromatic rings on adjacent chain segments. This is of interest because it provides a measure of the population of racemic g^-t and tg^- dyads in syndiotactic sequences and meso tt dyads in isotactic sequences.[11] Experimentally, the population of suitable excimer forming sites is proportional to the ratio of the excimer emission intensity I_D to the emission from the isolated aromatic ring I_M.[11-13] These values are taken at 400 and 340 nm, respectively.

In this study, the excimer probe technique is used to examine the compatibility of blends formed from dispersion of 0.2 wt % poly(2-vinylnaphthalene) (P2VN) in a series of poly(alkyl methacrylates). This system was selected for several reasons. First, maximum interpenetration of two dissimilar polymers is expected when the two polymers have the same solubility parameter. The poly(alkyl methacrylate) host matrices provide for such molecular dispersion since the range of their solubility parameters brackets the solubility parameter of P2VN. Second, these host matrices are transparent to both the incident excitation and the P2VN fluorescence. Finally, the glass transition temperatures of the host matrices are all above room temperature, making it possible to "freeze in" the chain conformational distribution of the guest polymer when films are cast at room temperature.[11] We note, however, that this condition may not be met as easily for two of the hosts, poly(*n*-butyl methacrylate) and poly(vinyl acetate), which have T_g's of 27 and 30 °C, respectively.

The 2-vinylnaphthalene monomer was bulk thermally polymerized at 80 °C for 72 h using 0.1% benzoyl peroxide as initiator. The polymer was freed of residual monomer by multiple precipitation from toluene into methanol. Twelve of the host matrices were poly(alkyl methacrylate) derivatives: methyl (PMMA, 9.25), ethyl (PEMA, 8.99), *n*-propyl (PnPMA, 8.80), isopropyl (PiPMA, 8.70), *n*-butyl (PnBMA, 8.60), isobutyl (PiBMA, 8.53), *sec*-butyl (PsBMA, 8.72), *tert*-butyl (PtBMA, 8.65), phenyl (PPhMA, 9.92), isobornyl (PiBoMA, 8.1), benzyl (PBzMA, 9.29), and cyclohexyl (PCMA, 8.90). Here the acronym and solubility parameter δ for the polymer are listed in parentheses. Two other hosts were polystyrene (PS, 9.04) and poly(vinyl acetate) (PVAc, 10.01). All host matrices were purified by multiple precipitation using toluene–methanol, acetone–water, or methanol–water solvent–nonsolvent systems. In most cases solid films of the blends were prepared by solvent casting from spectrophotometric grade toluene on glass plates which were covered and left to dry at 295 K. Final film thickness was 15–20 μm. Films with PsBMA, PPhMA, and PiBoMA hosts were cast on a water surface due to difficulties in removal from the plates. All films were dried to constant weight.

The spectrofluorometer was of modular construction consisting of a Schoeffel 1000 W Xenon arc lamp, a Schoeffel quarter meter exciting monchrometer, a sample compartment, and a Schoeffel quarter meter analyzing monochrometer. Detection was with a cooled EMI 9558 QB photomultiplier. The film sample was placed between two sapphire plates and mounted at 45° to the exciting beam with fluorescence being measured at right angles to the exciting beam. Back face illumination was used.

Typical fluorescence behavior is shown in Figure 1 which includes uncorrected emission spectra for five different hosts. The slightly structured emission at high energy corresponds to the isolated naphthalene "monomer" and the broad structureless band at low energy corresponds to the excimer complex. The disappearance of the two highest energy P2VN bands in the PiPMA host is also observed in PsBMA; these bands do appear in PtBMA and PnPMA but are of lower intensity than for all other hosts. We have no good explanation of this observation at this time although it appears to be associated with the extent of interpenetration of the guest and host, cf. below.

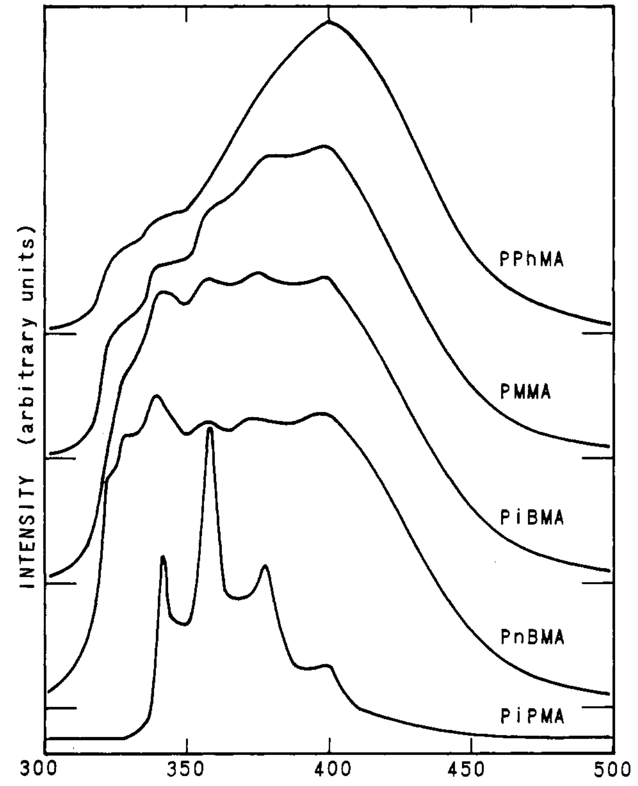

Figure 1. Uncorrected fluorescence spectra for solid films of blends of 0.2% poly(2-vinylnaphthalene) with five poly(alkyl methacrylate host matrices. See the text for the host identification key.

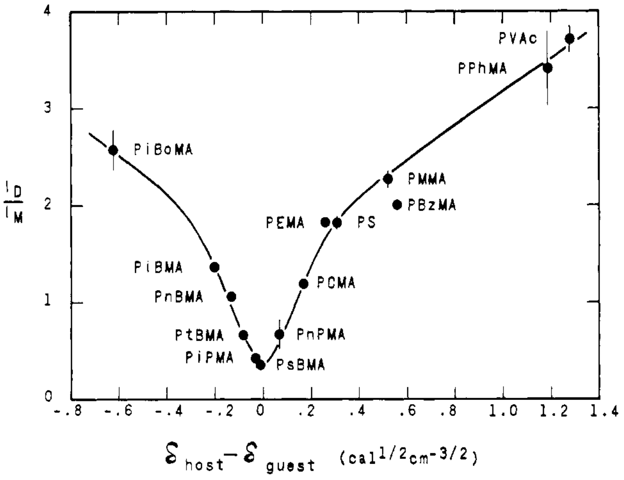

Figure 2. Excimer to monomer intensity ratio vs. the difference in solubility parameters between the guest and host polymers. See the text for the host identification key. Standard deviations are indicated by vertical bars where they are larger than the size of the solid circle.

To obtain an estimate of the tendency toward molecular compatibility in the blends, solubility parameters were evaluated for all pure polymers using empirical estimation techniques.[14,15] Densities of previously melted polymer samples were determined by water displacement or flotation. This procedure gave results which agreed with experimental literature values and were internally consistent.

Figure 2 shows the average values of the excimer to monomer ratio (I_D/I_M) plotted against the difference in host and guest solubility parameters. A symmetric curve has been drawn through the data. Note that it passes through a well-defined minimum at $\Delta\delta = 0$. This general type of curve is analogous to the behavior observed for swelling of cross-linked elastomers or to the change in intrinsic viscosity as a function of the solubility parameter of the solvent. However, a most significant difference in this case is that information is being obtained on the molecular in contrast to the bulk level.

It is quite clear that the excimer probe is sensitive to the host matrix. However, before we may proceed with an analysis of the molecular morphology in these blends, we must determine which type of excimer site is displaying the host sensitivity.

The intramolecular site depends upon the population of suitable local conformational states of the chain, i.e., rotational dyads. The intermolecular site, on the other hand, is independent of local conformational structure and is sensitive solely to aggregation of guest aromatic vinyl polymers. At this stage of the study it is not clear whether any differences in spectral parameters between intermolecular and intramolecular excimer sites should be expected. Thus, direct experimental measurement is not yet possible. Nevertheless, a distinction may be made if what is known about the effect of solvent on chain conformational structure in fluid solutions is applied to these solid state blends. It is generally accepted that increasing the solvent quality will lead to expansion of the coiled polymer chain. However, only the long-range conformational structure of the chain is affected; the local conformational distribution is insensitive to the solvent medium. Thus we would not expect the intramolecular excimer site distribution in the solid blends to depend upon the host matrix.

The situation is quite different for the intermolecular sites. These arise entirely from clustering of the guest polymer chains or the chain bending back upon itself. In a good host medium there will be extensive interpenetration of the guest and host chains causing the local concentration of aromatic rings to drop. In addition, expansion of the chain will reduce the likelihood of chain "back-bending". Both effects will lead to reduction in I_D/I_M as is observed in Figure 2 for $|\Delta\delta| = 0$. As the host matrix becomes a thermodynamically poorer solvent for the P2VN guest, chain expansion will decrease and the extent of mutual interpenetration of the guest and host will also decrease causing the local concentration of aromatic rings to rise. These effects will lead to an increase in the number of intermolecular excimer sites and I_D/I_M will increase. As an alternative explanation,[18] it is also possible that the higher molecular weight components of our unfractionated P2VN sample which initially are compatible with the host matrix become incompatible as the host polymer becomes a poorer solvent.

A more complete study is in progress.

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Effect of D_2O on the Thermal Stability of the β Conformation of Poly[*S*-((3-hydroxypropyl)-carbamoylmethyl)-L-cysteine]

Poly(*S*-(carboxymethyl)-L-cysteine) is known to undergo a pH-induced β-coil transition in aqueous solution,[1,2] and we have recently published a paper concerning its circular dichroism and β-coil transition in detail.[3] In order to avoid the complication arising from the electrostatic effect of ionized groups, we have prepared a water-soluble, nonionizable polypeptide, poly[*S*-((3-hydroxypropyl)carbamoylmethyl)-L-cysteine] (poly[Cys(CamPrOH)], and investigated its conformation in aqueous solutions by measurement of circular dichroism. In this communication we report the characteristic temperature dependence of its conformation in D_2O.

Poly[Cys(CamPrOH)] was synthesized by a method similar to that for preparing poly[N^5-(3-hydroxypropyl)-L-glutamine].[4] Poly(*S*-(carbobenzoxymethyl)-L-cysteine)[5] was amidated by a large excess of 3-aminopropanol at 60 °C for a few days, and the reaction mixture was poured into a 3% acetic acid solution. After the solution was dialyzed against distilled water, poly[Cys(CamPrOH)] was isolated by lyophilization. Poly[Cys(CamPrOH)] is soluble in dichloroacetic acid (DCA) but is sparingly soluble in water. Sample code, TX-4071: $\bar{M}_n$ 12 000 in 0.1% CH_3COOH solution, $[\eta]$ 0.31 dL g^{-1} in DCA at 25 °C.

The infrared spectra of solid film cast from an aqueous solution shows an amide I band at 1625 cm^{-1} and an amide II band at 1528 cm^{-1}. Then poly[Cys(CamPrOH)] is in the β structure in the solid state.

Figure 1 shows the circular dichroism of poly[Cys(CamPrOH)] in H_2O at 25 °C and in D_2O at different temperatures, the concentrations of which are about 0.02 g dL^{-1} or 10^{-3} N. Circular dichroism of an H_2O solution does not change appreciably with temperature; it has two negative bands around 198 and 225 nm. This spectrum is similar to that of poly(*S*-(carboxymethyl)-L-cysteine) in the fully ionized state,[3] and the conformation of poly[Cys(CamPrOH)] in H_2O is, therefore, assigned to the random coil. On the other hand, circular dichroism of a D_2O solution is strongly dependent on temperature. At 1.5 °C the spectrum has a strong positive band at 198 nm and a negative band at 227 nm and is similar to that of poly(*S*-(carboxymethyl)-L-cysteine) at low degrees of ionization.[3] Then poly[Cys(CamPrOH)] is in the β conformation in D_2O solution at low temperature. With increasing temperature, the circular dichroism changes markedly, both positive and negative bands becoming

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