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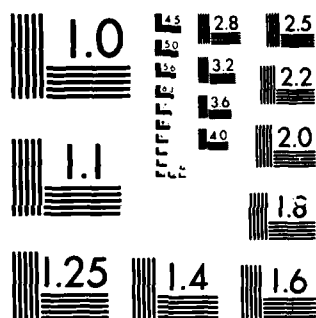
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be sensitive to the influence of solvent casting conditions on the morphology of the resulting polymer blends. Phase separation in methyl cyclohexane solutions of polystyrene is also examined and described satisfactorily using the same photophysical model developed for the solid polymer blends. Synthesis of probe polymers containing fluorescent groups at the chain ends is described as a means of determining the end-to-end distances from fluorescence depolarization measurements.

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THERMODYNAMIC AND KINETIC BEHAVIOR
OF THE POLYSTYRENE/POLY(VINYL METHYL ETHER) BLEND
AS STUDIED BY EXCIMER FLUORESCENCE

FINAL REPORT

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JANUARY 2, 1986

U. S. ARMY RESEARCH OFFICE

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A. STATEMENT OF THE PROBLEM STUDIED

It has been estimated that 15 to 20 percent of all engineering plastics produced in the United States today are polymer blends or alloys, which are physical mixtures of homopolymers and/or copolymers. Such physical blending is economically much more attractive as a materials development approach than the preparation of new homopolymers or copolymers through synthetic means. A serious problem exists, however, in that the bulk properties of the blend will depend on the degree of mixing achieved. Such mixing is difficult to accomplish on the molecular level and existing experimental techniques exhibit widely varying sensitivities to the distance scale over which inhomogeneities are detectible. A major objective of research sponsored by the Army Research Office has been to establish excimer fluorescence as a quantitative spectroscopic tool for the elucidation of morphology and dynamics in polymer blends.

The polymer blend of primary interest has been the polystyrene(PS)/poly(vinyl methyl ether)(PVME) system in which excimer fluorescence from phenyl-phenyl interactions in polystyrene is the main experimental observable. This blend was selected because it has been demonstrated by numerous other techniques that miscible one-phase blends may be prepared by solution casting from toluene solvent. Moreover, this blend exhibits a lower critical solution temperature (LCST) at a convenient point in the range of 370 to 400 K, depending on the molecular weights of the two components. Thus, the kinetics of phase separation may be followed easily. Several goals of the fluorescence studies were as follows: 1) to characterize the photophysical behavior of miscible PS/PVME blends over the whole concentration range as a function of the solvent casting conditions; 2) to develop a model for the photophysics of blends that have phase separated during the solvent casting process; 3) to follow the kinetics of thermally induced phase separation; 4) to verify existing theories of phase separation, particularly spinodal decomposition.

During early research on polymer blends it was generally felt that miscible systems would be encountered only infrequently because the unfavorable entropic factors associated with high molecular weight mixtures would overcome the (possibly) favorable enthalpic effects associated with the mixing process. In fact, a large number of miscible blends have been identified, but the process has been mainly based on empiricism. In an attempt to determine whether fluorescence spectroscopy could elucidate the molecular factors influencing miscibility, a series of blends related to the PS/PVME system through incorporation of either PS or PVME were examined. The fluorescent homopolymers selected for study were poly(1-vinyl naphthalene) (P1VN) and poly(2-vinyl naphthalene) (P2VN), both of which exhibit excimer fluorescence. The majority of homopolymer blend data was collected for P1VN/PVME and P1VN/PS, but several experiments were performed with P2VN/PVME and P2VN/PS. In addition, a copolymer of styrene with 2-vinyl naphthalene was prepared and blended with PVME and PS. The primary goal of these studies was to examine the effect of solvent casting and compare the concentration dependence of the excimer fluorescence for each blend with that observed for the PS/PVME system. Through this we hoped to learn more about the specific interactions that have been postulated as the

source of miscibility in PS/PVME blends.

Although the preceding discussion on blend research sponsored under this ARO contract has emphasized the binary nature of the solid state blends, the morphology of the final blend has been observed to depend upon the casting solvent. Thus, ternary thermodynamics must be applied and questions of whether equilibrium has been reached must be addressed. A truly binary system that is potentially simpler to analyze is a polymer solution undergoing phase separation. In order to determine whether the photophysical analysis originally developed for the PS/PVME blend would still work in such a situation, we examined the solution of polystyrene in methyl cyclohexane. As is usual for such polymer solutions, an upper critical solution temperature (UCST) is observed. The objective for this study was to induce phase separation by temperature decreases through the UCST and to analyze the photostationary state excimer fluorescence using the two phase model developed earlier.

With the exception of the miscible blends in which the fluorescent polymer is at very low concentration, the photophysical analysis based upon intermolecular excimer fluorescence is sensitive only to the local chromophore density; it is not possible to learn something about the chain statistics in the concentrated systems. In particular, the coil size of the fluorescent polymer is expected to decrease as the LCST is approached by an increase in temperature. Scattering techniques using light, X-rays or neutrons are the common methods used to determine such changes in configurational properties. However, as is to be expected, each method has its own limitations. In recent theoretical work performed in collaboration with Professor Hans C. Andersen of the Chemistry Department at Stanford we have developed a model that allows the mean squared end-to-end distance to be determined for a polymer chain labeled only at the chain ends with fluorescent chromophores. The approach relies on the concept that energy migration between the chain ends will lead to depolarization of an excitation produced by absorption of plane polarized light. The closer the chromophores, the more rapid will be the depolarization. Thus, transient fluorescence depolarization measurements will allow determination of changes in the coil size. To pursue this point, in the final year of the ARO contract we began synthesis of the fluorescently labeled polymers. The objective was to prepare polystyrene model compounds containing long-lived fluorescent chromophores different from the phenyl group at each chain end. These were then to be examined in PS/PVME blends near the LCST.

B. SUMMARY OF THE MOST IMPORTANT RESULTS

In the following we discuss the major results in each of the research areas sponsored by the ARO contract. Although much of the work has been published, there are several significant studies for which manuscripts are now being prepared. These areas are outlined in some detail in this Final Report. In addition, previously published studies are reviewed with the aim of placing the new work in the proper context. Taken as a whole this report should demonstrate the significance of fluorescence spectroscopy as a modern tool for polymer science.

1. Morphology and Kinetics of Phase Separation in PS/PVME Blends

a. Photophysics of Miscible and Immiscible PS/PVME Blends

Early work on the application of fluorescence spectroscopy to the study of polymer blends in this laboratory emphasized the correlation of variables expected to influence the free energy of mixing with changes in the ratio of excimer to monomer emission intensities, R . These studies included the effects of solubility parameter differences between the fluorescent guest polymer, generally poly(2-vinyl naphthalene), and the nonfluorescent host polymer matrix [1, 2], guest concentration [2 - 4], molecular weight of both host and guest [5 - 8], and the temperature at which the polymer blend is solvent cast [3]. In each case, an increase in R was interpreted as an increase in the local segment density, and could be rationalized on the basis of equilibrium Flory-Huggins thermodynamics. These studies demonstrated that excimer fluorescence was a useful addition to the battery of experimental tools available to study solid state polymer blends. However, the longer range goal of explaining the significance of the absolute value of R was not realized because there was insufficient companion information about the thermodynamics of the blends. The PS/PVME blend does not suffer from this limitation, and thus provides an excellent system for characterization of the photophysics under conditions for which miscibility or immiscibility are firmly established.

The first stage of the development of excimer fluorescence as a quantitative morphological tool was to understand the photophysics of miscible PS/PVME blends. We began with a consideration of the temperature and molecular weight dependence of R for blends containing low concentrations of PS. {ARO PUBLICATION NO. 1} In earlier work, energy migration in an isolated aryl vinyl polymer chain was treated as a one-dimensional random walk of the electronic excitation between adjacent pendent chromophores. [9] At each step in the walk, the excitation can be lost radiatively or nonradiatively from an isolated excited chromophore. Alternatively, the excitation can be trapped at an excimer forming site (EFS) composed of two adjacent chromophores suitably aligned in a coplanar sandwich configuration, leading to radiative or nonradiative emission from the excimer. The overall probability that an excitation absorbed anywhere in the chain will eventually be dissipated through radiative or nonradiative

decay is given by the quantity M . This is a probability function which may be predicted analytically, and which is related to the experimental observable R through the expression

$$R = \frac{Q_D}{Q_M} \left[\frac{1 - M}{M} \right] \quad (1)$$

where Q_D and Q_M are the intrinsic quantum yields for excimer and monomer emission.

From consideration of molecular models and the geometric requirements for excimer formation, we have concluded that the trans, trans meso rotational dyad is the predominant EFS in the aryl vinyl polymers. [9] The identification of the EFS trap with a particular rotational dyad state was a major breakthrough because it opened the way to utilize the powerful rotational isomeric state theory of Flory [10] to calculate the EFS population for the isolated PS chains. This trap population is relatively small. For example, assuming that an atactic PS chain has 45% meso dyads, the EFS concentration at 300 K was determined to be of the order of 0.026. [11] Since the EFS dyad configuration is at higher potential energy than the preferred ground state meso configurations, an increase in temperature will lead to an increase in the EFS population as long as conformational equilibrium may be maintained. At a fixed temperature only a slight molecular weight dependence of the EFS concentration was calculated. [11]

If the EFS population is calculated using RIS theory, the one-dimensional random walk model predicts that there should be a strong dependence of the observed R on the molecular weight of the aryl vinyl polymer. At very low molecular weights, there will be many chains that contain no EFS traps and there will be very little excimer fluorescence. As the PS chain length increases, the probability of finding an EFS trap within the ensemble of chromophores that is sampled by the random walking exciton will increase and the value of R will increase. At high molecular weights, however, the chain is sufficiently long such that not all chromophores may be sampled by the hopping excitation during the excited state lifetime. This will lead to a saturation effect with the value of R leveling off at some plateau characteristic of the trap concentration within some photophysically equivalent chain segment length.

The predictions of the one-dimensional random walk model were compared with fluorescence spectra of PS/PVME blends containing monodisperse PS with molecular weights ranging from 2200 to 390,000. Measurements of R were made at temperatures between 286 and 323 K. [11] A good fit was found to the experimental results for blends examined at temperatures of less than or equal to 300 K, but a consistent positive deviation of R above the plateau value was observed for the highest molecular weights. This was attributed to a decrease in the PS coil dimensions with increasing temperature as a result of adverse thermodynamic interactions with the PVME matrix upon approach of the phase separation binodal. As the chromophore density increases due to incipient coil collapse, the excitation almost certainly will cease to follow a strictly one-dimensional random walk and frequent

cross-loop hops will take place. This will lead to an increase in the dimensionality of the walk and an improved efficiency of sampling the existing EFS traps. The significant aspect for our work is that, with suitable further development in the theoretical analysis, possibly employing the pyrene end-tagged model compounds described in Section B.4 for the experimental studies, it may be possible to obtain the same type of information on polymer chain configurational statistics that is provided by SANS using much simpler and more accessible fluorescence instrumentation.

The second step in the quantitative analysis of the photophysics of PS/PVME blends was to examine the effect of concentration for blends that were solvent cast under conditions leading to both miscible and immiscible systems. {ARO PUBLICATION NO. 2} PS samples of molecular weights 4000 and 100,000 were blended with the same PVME sample used for the preceding study and cast from toluene and tetrahydrofuran (THF). As expected, the toluene cast films were optically clear over the entire concentration range, but the THF films were cloudy indicating that phase separation had occurred. It is important to note that the optical clarity is a poor measure of miscibility because optically clear films could simply mean that there is insufficient refractive index difference between the two components or that the domain size of a phase separated system is too small to give extensive scattering. When cloudy films result, however, it is certain that phase separation has occurred. Nevertheless, we are confident that the toluene-cast films are indeed miscible from all of the previous experimental and theoretical work that has been done on this blend.

The one-dimensional random walk analysis that was earlier applied to the 5% PS/PVME blends is not expected to be valid as the PS concentration increases. To understand this it is necessary to present some brief comments on the factors influencing each individual step in the random walk. It is generally accepted that excitation transport among chromophores that are randomly distributed, such as dye molecules in a glycerol solution, may be treated using Forster transfer. In this model the individual transfer steps depend upon the inverse sixth power of the distance of separation and the relative ring orientation. Generally, the orientation parameter is assumed to be statistically averaged to some finite constant value. However, the strong distance dependence makes the topology of the system very important. For isolated polymer chains the chromophore density is very high along the chain causing one-dimensional transport to predominate. As the concentration increases, however, the likelihood of off-chain transfer may become comparable to down-chain transfer, especially at bulk concentrations for which the average distance between chromophores on different chains is the same as along the chain. In the limit where there is no preference for intramolecular versus intermolecular excitation transport, a three-dimensional random walk model seems appropriate.

Assuming that a three-dimensional random walk process would apply at high concentrations, we developed a simple spatially periodic lattice model to calculate the probability function M . [12] This approach was analogous to the initial studies on the one-dimensional process and is of general interest because M may be related to R through Equation 1. The miscible toluene-cast blends exhibited a low initial value of R of the order of 1 for the 5% PS blend and with a strong convex upward curvature leading to a final

value of about 13 for pure PS. These data were fit with the two parameter lattice model to yield reasonable values for the ratio of the rate constant for the single step transfer to that of the overall monomer decay as well as for the probability that two chromophores located on adjacent lattice sites but from different polymer chains are in suitable EFS geometry.

The satisfactory fit of the R data for the PS/PVME blends cast from toluene is an encouraging result toward the goal of understanding the photophysics. However, a more significant feature may be that the general concept of the intimate relationship between M and R may be used to examine phase separated systems without any consideration of which energy migration model is more appropriate. This approach requires that data for R as a function of concentration first be obtained for a miscible blend allowing the probability function M to be determined experimentally through use of Equation 1. The M function may then be used in conjunction with a proposed model of the morphology to fit the observed R data for the multiphase system. The simplest possible model is to assume that the volume fractions of PS in the rich and lean phases are independent of the bulk concentration and that there is no energy migration between phases. [12] This allows one to calculate the individual contributions to the excimer and monomer fluorescence from PS chains in both the rich and lean phases. The resulting expression relates the concentration of PS in the rich phase, to the observed R.

The simple two phase morphological model was tested with data for phase separated PS/PVME blends cast from THF. The sensitivity of the PS/PVME blend to the casting solvent has been known for some time since Bank *et.al.* observed that optically clear films of PS/PVME were obtained by casting from toluene or benzene while optically cloudy films were obtained from trichloroethylene or chloroform. [13, 14] This behavior could result when the binary polymer-solvent interaction parameters are very different for the two polymers in the ternary system. To explore whether excimer fluorescence could provide information about the influence of the casting solvent, we prepared PS/PVME blends from tetrahydrofuran at room temperature that were then dried in air for 12 hours before taking the fluorescence spectra. The behavior of R was dramatically different than for the miscible toluene-cast films. Starting from an initial value of about 6, R increased rapidly and then leveled off to a plateau having the same R value of 13 exhibited for the pure PS. A good fit of the results for these blends was obtained when the rich phase PS volume fraction was set to 0.98 and the lean phase to 0.008.

In an extension of the studies of the influence of casting solvent, we have obtained experimental fluorescence results for PS/PVME blends prepared by solvent casting from additional solvents and have investigated the nonequilibrium aspects of the casting process. {ARO MANUSCRIPT IN PREPARATION - NO. 1} The additional solvents included chlorobenzene, dioxane, trichloroethylene, methylene chloride and chloroform. Films from chlorobenzene and dioxane were optically clear over the entire PS concentration range; films from trichloroethylene, methylene chloride and chloroform were all cloudy, in agreement with the literature [13, 14].

It was not possible to obtain reliable fluorescence data from the

chloroform and methylene chloride cast films due to the extremely low signal intensity. This was attributed to residual solvent in the films, which led to significant heavy atom quenching of the fluorescence. Good fluorescence data were obtained from the other casting solvents, however. The dioxane data were somewhat similar to those for the toluene-cast films measured earlier in that the R values started at about 2 and increased with concave curvature upward until a final R value of 9 was obtained. By contrast, the chlorobenzene data started at $R = 1$ and then increased linearly until a maximum value of 12 was reached for pure PS. Finally, the trichloroethylene data started at $R = 1$, increased very gradually until a PS volume fraction of about 0.6 and then increased dramatically to a final value of 20.

Although the data have not yet been fit to either the one-phase or two-phase models, some qualitative observations may be significant. In the region over which the three-dimensional spatially periodic lattice model should apply, i.e. PS volume fractions greater than 0.6, the concave upward dioxane results should fit well with slightly altered fitting parameters compared to the toluene case. The linear chlorobenzene data are particularly interesting because this functional form has been observed to result when the lattice model is modified to eliminate the possibility of an increase in the number of intermolecular EFS with increasing PS concentration. [15] This may mean that some form of specific interaction between the solvent and the phenyl rings that arises in the ternary casting solution may lead to a nonequilibrium structure in the cast film that prevents intermolecular EFS formation. Finally, it may be possible to fit the trichloroethylene results at high concentration using the two-phase model, but the origin of the initial plateau at low R remains unclear.

In the second part of the study on solvent casting, we have examined nonequilibrium phenomena in PS/PVME blends cast from THF and have compared the results to blends prepared from toluene and chlorobenzene. The first indication of possible kinetic limitations to the attainment of thermodynamic equilibrium was the observed dependence of the optical appearance on the rate of solvent evaporation from the THF casting solution. Rapid drying yields very cloudy films while slow drying produces films with extremely finely dispersed domains such that the films appear almost clear. We note that the former case might lead to a polymer "skin" being formed on the surface of the casting solution, which could actually impede the solvent evaporation and lead to more entrapped solvent than in the latter case. The rapid and slow cast films were kept under vacuum at room temperature for five days before measurement of the fluorescence spectra. Both sets of films gave R values that were considerably higher than for the toluene cast blends, as described above. In addition, the excimer band position was at much higher energy than for the toluene cast films; the shift was 700 cm for the 30% PS blend and 900 cm for the 70% PS blend.

In order to determine whether the effects of the THF could be removed by annealing, the films prepared as described above were placed under vacuum for 10 hours at 383 K and then sealed between two sapphire plates before annealing an additional 1 1/2 days at 383 K. This led to a very slight reduction in R for the toluene and chlorobenzene cast films and the initially clear THF cast films dropped sharply to almost equal the toluene results. By contrast, whereas the initially cloudy THF cast films did

become clear upon annealing and the R value did decrease to about 1/3 of its initial value, it was still 30 to 100% higher than the toluene or chlorobenzene results. At the same time the excimer band position shifted red leveling out at about 500 cm⁻¹ higher energy than the toluene and chlorobenzene films. Further annealing did not change either R or the excimer band position. However, when the top sapphire plate was removed exposing the film again to the ambient atmosphere and the films annealed for two more days at 383 K, the R value and the excimer peak position for all films, regardless of casting solvent and processing history, came to within 15% of common values. Similar results were obtained for a fresh set of samples cast from THF and annealed for three days under vacuum without any cover seal at 383 K.

The interpretation of the solvent casting results should introduce some caution into the processing protocol used for film preparation. We first note that there clearly is residual THF in the ten micron thick films even after ten hours annealing under vacuum at 383K. Thus, even highly volatile solvents can be retained in the film particularly if there is some source of specific interaction between the solvent and one of the polymers. The second point is that the molecular packing around the phenyl rings and the potential EFS traps is strongly influenced by the solvent. This may allow excimer fluorescence to be used as a sensitive probe not only of these nonequilibrium solvent casting effects but also of such processes as physical aging in which there is a volume relaxation over long time periods.

b. Thermally Induced Phase Separation in PS/PVME Blends

Polymer-polymer blends typically show a decrease in miscibility with increasing temperature. McMaster has used a modified Flory equation of state thermodynamic model to show that the existence of a lower critical solution temperature (LCST) is caused mainly by differences in the pure component thermal expansion coefficients. [16] The mechanism of the phase separation depends upon the region of the phase diagram that is occupied immediately after a temperature jump above the LCST. The binodal, defined as the locus of points for which the chemical potentials of each component are equal in both phases, separates the stable one-phase region from the region in which two phases coexist at equilibrium. The spinodal, which is the locus of points for which the second derivative of the Gibbs free energy of mixing equals zero, divides the two-phase region into metastable and unstable portions. In the metastable region between the binodal and spinodal curves small fluctuations in volume fraction decay with time. Only if there is a large fluctuation leading to formation of a nucleus of critical concentration will phase separation take place; this is referred to as the nucleation and growth mechanism. In the unstable region within the spinodal there is no thermodynamic barrier against phase separation and small fluctuations in concentration may grow with time; this is the spinodal decomposition mechanism.

All experiments with the PS/PVME blends were performed under conditions that should lead to spinodal decomposition. This allows us to compare the

experimental results with existing theories. The first series of experiments {ARO PUBLICATION NO. 3} was designed to demonstrate the feasibility of using excimer fluorescence to test Cahn's kinetic treatment of the early stages of spinodal decomposition. [17] This is a linearized theory that predicts that the volume fractions of the two phases remain constant with time while the compositions change gradually. This is in contrast to the nucleation and growth mechanism in which the composition of the growing phase remains constant but the phase itself increases in size.

The development of the morphological model for interpreting the photophysical behavior of blends phase separated by virtue of the solvent casting process was the first essential component for understanding the kinetics of phase separation in PS/PVME blends. The second component was the measurement of the phase diagram using light scattering turbidity measurements. In the first study [18] we determined the phase diagram simply by reporting the minimum temperature at which a given blend showed visual signs of phase separation after fifteen minutes of annealing in an oil bath. This phase diagram was then used to determine the volume fraction of the rich phase for a bulk PS concentration of 10%. Assuming that spinodal decomposition was occurring and that the volume fraction of the rich phase would remain constant allowed determination of R as a unique function of the rich phase PS concentration. From use of the two-phase morphological model we concluded that R only increases to about 90% of the equilibrium value when the 10% blend is subjected to a temperature jump to 423 K. Analysis of the very early stages of the phase separation allowed estimation of the macroscopic diffusion coefficient, found to be of the order of -10^{-10} cm²/sec.

Cahn's linearized theory of spinodal decomposition was extended recently by de Gennes [19] and Pincus [20] through scaling techniques applied to polymer blends in the melt. A critical feature of the modified analysis is the proposal by Pincus [20] that the growth rate of the concentration fluctuation that controls the kinetics during the early stages of decomposition is proportional to the melt reptation diffusion coefficient. As a result the kinetics of the early region of spinodal decomposition is predicted to depend strongly upon molecular weight.

Our second study on phase separation kinetics of PS/PVME blends was designed to test this prediction. {ARO PUBLICATION NO. 4} To ensure that all blend components were above the critical entanglement length of about 200 monomer units, high molecular weights were used. The monodisperse polystyrene samples were of 100,000 and 1,800,000 molecular weight and the polydisperse PVME ($M_w/M_n = 1.8$) was 44,600 molecular weight. The cloud point measurements of the preceding study [18] were improved by using the same sapphire substrate as for the fluorescence measurements and by taking the cloud point temperature as the point at which the first signs of visual opalescence occurred upon linear heating of the films at 5 K/min. In addition, bright field optical transmission optical microscopy was used to examine the morphology of the phase separated films. Finally, a spectral correction procedure was developed to analyze films with high nominal bulk PS concentrations.

Thermally induced phase separation was followed in the same manner as previously [18] for 10% and 50% PS blends of both molecular weights. [21]

It is significant to note that excimer fluorescence is a more sensitive measure of phase separation at short times because films annealed for about one minute showed no visual signs of opalescence while R increased between 10 and 50% for the different blends. Analysis of the fluorescence data using the two phase model allowed determination of the enhancement of the rich phase composition over the nominal bulk value as a function of annealing time at 423 K. In order to compare the fluorescence results at short times (less than two minutes annealing) with the de Gennes - Pincus theory, we had to first modify their theoretical approach to account for the fact that the PS and PVME were of different molecular weights. With this done and an empirical expression for the binary interaction parameter selected, an expression for the growth rate of the fastest growing concentration fluctuation was determined.

For both the 10% and 50% blends the de Gennes - Pincus theory predicted that the growth rate of the dominant concentration should decrease and; thus, the initial slope of the enhancement of the rich phase concentration over the bulk as a function of time should decrease with increasing molecular weight. Although this was observed experimentally, the effect was smaller than predicted, with the theory and experiment differing by a factor of four. The difference was attributed to the polydispersity of the PVME in which the presence of short unentangled PVME chains that can diffuse rapidly during the early stages of phase separation is expected to weaken the molecular weight effect.

Another possible explanation for the discrepancy between experiment and theory lies in the phase diagram. It is essential that accurate values of the equilibrium binodal compositions for a particular temperature be available in order to calculate the volume fraction of the rich phase in the two component system because this volume fraction is assumed to be constant during the early stages of spinodal decomposition. Unfortunately, it is quite difficult to ensure that equilibrium is achieved for PS/PVME blends at high PS concentrations due to the high T_g of the PS. For this reason we determined, for the third time and with $\bar{M}_w$ we believe the highest accuracy of the studies to date, the cloud point curves for PS(100,000)/PVME and PS(1,800,000)/PVME blends. (ARO MANUSCRIPT IN PREPARATION - NO. 2) The cloud point curves were determined using a film turbidity device based upon a helium-neon laser and phototube detection. The system was designed to utilize the same sample chamber that is used for the fluorescence measurements. This chamber has excellent thermal control and can be evacuated and back-filled with nitrogen or argon in order to eliminate oxidative degradation of the sample.

The cloud point curves were determined by heating at a slow rate until commencement of phase separation, as evidenced by a rapid increase in the scattered light from the sample. The temperature was then decreased by several degrees and the decrease in scattering intensity monitored. This was followed by a temperature jump, smaller than the preceding temperature drop, and the process was repeated a sufficient number of times such that equilibrium was ensured. This could take of the order of many hours for the high PS concentration blends. Using this technique, a cloud point curve was obtained for each of the PS molecular weights. As proof of the closer approach to equilibrium for these measurements as compared to the previous

determinations, both curves were approximately parallel to each other and did not cross at high PS concentration.

An important extension of the experimental analysis for this phase diagram determination was the evaluation of an expression for the PS/PVME binary interaction parameter from the cloud point curves. This was done by assuming a functional form for the interaction parameter and then calculating the binodals using a free energy of mixing calculated from the Flory-Huggins configurational entropy of mixing combined with an enthalpy of mixing term based on the assumed interaction parameter. The criterion for the fit was that the same expression for the interaction parameter should yield binodal curves that passed through both sets of cloud point curves. Although we initially attempted to use an expression that was only temperature dependent, as was done in the previous work [18, 21], we found that a concentration dependent term was essential to obtain good fits. Once an expression for the interaction parameter was determined, we then calculated the spinodal curves for each PS series.

With the phase diagram firmly established, the fluorescence kinetic data determined in the earlier phase separation study [21] were re-evaluated. This analysis showed much better agreement with the de Gennes - Pincus theory; the predicted growth rate of the fastest growing concentration fluctuation was within 50% of the experimental results. Of course, the caveat with regard to the polydispersity still applies since the kinetic measurements have not yet been repeated. Nevertheless, we have been successful in our application of excimer fluorescence as a quantitative tool of polymer blend morphology.

2. Morphology of Blends Containing Either PVME or PS

The most distinctive photophysical feature of the PS/PVME blends is the dependence of R on concentration. As discussed above; the shape of the curve depends strongly upon the casting solvent with the miscible toluene-cast blends exhibiting strong concave upward curvature, the immiscible unannealed blends cast from THF exhibiting strong convex upward curvature and the chlorobenzene films showing linear behavior. Since this functional form seems to be quite sensitive to the phase morphology, we chose it as the relevant photophysical feature for study of several additional blend systems that contain either PS or PVME as one of the components. The objective was to correlate the molecular structure of the constituents and the photophysical behavior of these blends with the PS/PVME results so that new insight on the miscibility of PS/PVME might be obtained.

In the first portion of this research {ARO MANUSCRIPT IN PREPARATION - NO. 3} blends of poly(1-vinyl naphthalene) (P1VN) with PVME and with PS were examined. The P1VN sample selected was of low molecular weight, about 3800, such that entropic factors that might prevent miscibility were reduced, thus placing more emphasis on enthalpic interactions. The PVME was the same sample examined previously and the PS samples were monodisperse materials of molecular weights 35,000, 233,000 and 1,800,000. In order to have a comparison with a classical method for evaluating miscibility, we determined

the glass transition temperatures for the P1VN/PVME blends cast from 1,3,5-mesitylene and P1VN/PS(35,000) blends cast from toluene over the entire concentration range using differential scanning calorimetry. Although a single T_g was observed for all cases, there were slight but noticeable breaks in the plots of T_g versus P1VN concentration between 50 and 60 weight percent P1VN. At concentrations higher and lower than this region there were continuous changes in the T_g values toward the pure component values. We conclude from these results that extensive mixing is taking place at the concentration extremes, but that neither blend system is truly miscible on the molecular level in spite of the fact that all blends were optically clear.

The P1VN/PVME system was selected to examine the influence of the casting solvent, by analogy with the previous study on the PS/PVME blend. From observations of optical clarity it was obvious that immiscible blends were obtained by casting from toluene, chlorobenzene and THF for P1VN concentrations between 40 and 70 percent. However, the fluorescence behavior of the phase separated blends was qualitatively identical to that for the optically clear blends prepared from 1,3,5-mesitylene. In each case there was a slight convex upward curvature with the deviation from linearity reaching a maximum at about 50 percent P1VN. This deviation was larger for the 1,3,5-mesitylene and THF cast films than for the chlorobenzene and toluene-cast films. Values of R for 10% P1VN blends were 2.3, 2.5, 2.8 and 3.0 for the 1,3,5-mesitylene, THF, chlorobenzene and toluene casting solvents, respectively. Similar data for the 90% P1VN blends were 12.8, 13.1, 13.5 and 14.5.

The effect of molecular weight of the PS was examined in a series of P1VN/PS blends cast from toluene, all of the films appearing to be optically clear. Although the shapes of the R versus P1VN concentration curves were qualitatively similar to the P1VN/PVME blends, the slight convex upward curvature exhibited in the PS(35,000) host matrix changed to a more linear functional form as the PS molecular weight increased. The R values at 10% P1VN concentration were similar to the PVME results at about 2.2 for each PS host but the R values at 90% P1VN were larger at 16.5, 17.1 and 18.4 in order of increasing PS molecular weight.

In a final series of P1VN concentration studies blends were prepared by toluene casting of P1VN with poly(cyclohexyl methacrylate) (PCMA) and with poly(methyl methacrylate) (PMMA). Although all of the P1VN/PCMA blends appeared optically clear, the P1VN/PMMA blends were cloudy and definitely phase separated for P1VN concentrations between 40 and 70%. The R values at 10% P1VN were 2.1 and 2.8 and at 90% P1VN they were 18.6 and 20.2 for the PCMA and PMMA hosts, respectively. Again the functional form of the R plot was similar to the P1VN/PVME data with slight convex upward curvature.

A smaller amount of data was collected for blends involving homopolymers or copolymers containing the 2-vinyl naphthalene unit. In the first study poly(2-vinyl naphthalene) (P2VN) of molecular weight 72,000 was blended with the same PVME sample used previously or with PS(1,800,000) and cast from toluene. Both sets of blends were phase separated for all P2VN compositions. The PVME series gave a linear plot of R versus P2VN concentration with R values of 4.3 and 18.3 at 10 and 90% P2VN. The

PS(1,800,000) series yielded a slightly convex upward shaped R plot with R values of 5.0 and 19.5 at 10 and 90% P2VN.

The final series of blends was made with a copolymer of styrene and 2-vinyl naphthalene prepared by radical polymerization and having composition determined by ultraviolet absorption to be 57% styrene and 43% 2-vinyl naphthalene by weight. The number average molecular weight measured by gel permeation chromatography was 56,000. This P(S-co-2VN) copolymer was blended with PVME and cast from 1,3,5-mesitylene and toluene. In addition, toluene cast blends were prepared for PS samples of molecular weights 2200, 35,000 and 1,800,000. All blends cast from 1,3,5-mesitylene were optically clear but the P(S-co-2VN)/PVME blends prepared from toluene were phase separated for concentrations between 50 and 90% copolymer.

The fluorescence behavior for P(S-co-2VN) in the PVME host was dramatically different from the P2VN/PVME results. First, the R values were lower by a factor of 20 for P(S-co-2VN) compared to the P2VN homopolymer system. At 10% P(S-co-2VN) the 1,3,5-mesitylene cast films yielded an R of 0.11 while the toluene gave 0.16. At 90% copolymer the corresponding R values were 0.43 and 0.45. Second, the results showed concave upward curvature, the only blend to show behavior qualitatively similar to the PS/PVME case.

The very low value of R may be rationalized on the basis of both intramolecular and intermolecular effects. Incorporation of styrene units in the 2-vinyl naphthalene chain will effectively break up any down chain energy migration forcing the majority of the excitation transport to be three-dimensional between chains. At the same time, it is likely that the concentration of intramolecular EFS traps would be reduced due to the sharply restricted sequence length of 2-vinyl naphthalene units. The most intriguing explanation for the small value of R comes from consideration of the intermolecular interactions, however. As discussed above, we have determined that the interaction parameter for the PS/PVME blend is both concentration and temperature dependent, and that it is negative, indicating some form of specific interaction between the dissimilar repeating units. We expect then that the styrene units of the copolymer will be extensively solvated with the vinyl methyl ether units of the PVME. This will effectively act as an insulating barrier decreasing the likelihood of intermolecular excitation transport and of intermolecular EFS formation. Both features will cause a reduction in R. It appears from these results that, although P2VN and PVME are definitely immiscible, a sufficient concentration of styrene units has been incorporated among the naphthalene chromophores such as to force the apparent miscibility of the styrene-2-vinyl naphthalene copolymer when blends are prepared from 1,3,5-mesitylene solution.

The fluorescence results for the P(S-co-2VN)/PS blends showed a significant variation in the shape of the R versus P(S-co-2VN) concentration plot. For the PS(2200) host the curve was sigmoidal with an initial low plateau starting at $R = 0.11$ for 10% copolymer and increasing slightly to $R = 0.23$ at 50% copolymer before a much sharper increase with an inflection point at about 75% copolymer and a final value of 0.68 at pure copolymer. As the PS molecular weight increased, the initial plateau disappeared such

that the PS(1,800,000) results showed linear behavior between 10% and 90% copolymer.

To interpret these results it is instructive to refer to earlier work on P2VN/PS blends in which it was demonstrated by both differential scanning calorimetry and by fluorescence methods that blends of P2VN(70,000) with PS(2200) were miscible at least up to 35% P2VN. [6, 8] Furthermore, blends of P2VN(70,000) with PS having molecular weights greater than about 10,000 are expected to be immiscible at virtually all concentrations, even though the films were optically clear. [8] Thus, we conclude that the P(S-co-2VN)/PS(2200) blends are miscible at least below 40% P(S-co-2VN) and that the initial plateau with concave upward curvature is a characteristic "signature" of such miscible systems. The tendency toward linear behavior on the R plot as the PS molecular weight increases is characteristic of systems that are most likely phase separated on the microscopic scale. This is to distinguish them from blends in which macroscopic phase separation has taken place. In this latter case, the two-phase model seems to be an adequate representation of the photophysics.

3. Phase Separation in PS/Methyl Cyclohexane Solutions

Although the current interest in the thermodynamics of polymer blends may be technologically driven, there has been a fundamental interest in polymer solution thermodynamics that extends back at least five decades. As an extension of the PS/PVME blend work we wished to explore the applicability of the photophysical analysis to a binary polymer solution. [ARO PUBLICATION NO. 5] This was done for the PS(17,500)/methyl cyclohexane system, which was selected because very accurate coexistence curve data were available in the literature. The importance of high accuracy in the phase diagram has already been discussed. The experiments were analogous to the thermally induced phase separation studies for the PS/PVME blends except that, as is usual, the polymer solution exhibited UCST behavior such that phase separation occurred as a result of a temperature quench, rather than an increase. A significant difference between these experiments and the earlier blend work was that phase separation in solution was followed as a function of time at the temperature at which the solution was demixing, rather than by quenching to a lower temperature before measurement of the fluorescence spectra.

The magnitude of the changes in R with time compared favorably with those predicted by the two-phase model. [22] For samples at their critical composition, R changed about 10 to 15% during phase separation for temperature quenches of less than 0.7 K below the critical temperature, increasing steadily at long times in rich-phase regions while decreasing steadily at long times in lean-phase regions. Considerable spatial inhomogeneity was observed throughout the sample cell, indicating that macroscopic layering was occurring and that the fluorescence probe was sensitive to such aggregation. A particularly interesting result was the observation of a sharp increase in R with increasing PS content for PS volume fractions less than 0.04 for miscible solutions near the critical temperature. This could be due to coil contraction caused by the trend

toward segregation and, if so, would be highly significant in providing an experimental test for current theories of coil collapse.

4. Synthesis of Polymer Chains Having Fluorescent Terminal Groups

The excimer fluorescence technique, while quite powerful as a method of determining segment density in the aryl vinyl polymers, is not particularly well suited for studying global chain statistics. Although we were able to suggest that there was a reduction in coil size as the critical temperature was approached for both the PS/PVME solid blends and for the PS/methyl cyclohexane solutions, it was not possible to obtain a quantitative measure of the reduction. An alternative fluorescence method that does show promise of yielding such configurational information is fluorescence depolarization.

In a fluorescence depolarization experiment, plane polarized light is used to illuminate a sample. Those chromophores having transition dipoles aligned with the incident light will then become excited and will retain the polarization upon decay unless the transition dipole orientation relative to the laboratory frame is changed due to molecular motion or unless the excitation is transferred to another chromophore with different dipole alignment. The first case has been widely utilized in the biophysical community to determine rotational diffusion constants. The second case is one which people generally try to avoid by doing experiments at extremely low chromophore concentrations. However, in collaboration with Professor Hans C. Andersen of the Department of Chemistry at Stanford we have developed a theoretical treatment that allows fluorescence depolarization of a small number of chromophores attached to a polymer chain to be used to obtain quantitative information about the chain statistics.

The theoretical model of most interest for the ARO research is for the case when there are two identical chromophores attached to a polymer chain only at the chain ends. [23] Measurement of the transient anisotropy from such a probe molecule dispersed at low concentration in an otherwise identical polymer matrix will then allow calculation of the mean squared end-to-end distance. Having this theoretical work as our foundation, our goal was to prepare polystyrene chains containing fluorescent groups on each end and to disperse them in the PS/PVME matrix. We would then measure the transient anisotropy as a function of separation from the binodal in order to determine whether there was a reduction in the PS chain size as the condition of phase separation approached. At the termination of the present ARO contract, we had been able to synthesize a variety of end-tagged polymer samples, but had not yet obtained any fluorescence anisotropy measurements.

Two classes of polymer chains have been prepared, each having pyrene groups at the chain ends. Pyrene was selected as the chromophore because of its long lifetime, its inherent stability and the ease of synthetic preparation. The first experiments were based on reaction of hydroxy-terminated poly(ethylene glycol)(PEG) with pyrene-butyric acid. This system was selected for the initial work in order to become acquainted with the

general approach to fluorescent labeling. We successfully prepared samples having molecular weights of 1400, 4800 and 9200. The second set of samples, having PS backbones that are of more relevance to the phase separation work, was prepared in collaboration with Dr. Georges Hadziioannou of IBM Laboratories in San Jose. The synthesis was performed using anionic polymerization techniques in which bifunctional living polystyrene is terminated by reacting with 1-bromobutylpyrene. Five samples having relatively narrow dispersity and number average molecular weights of 2000, 400, 8000, 32,000 and 64,000 have been prepared.

Although no physical measurements have yet been performed on the phase separation problem, we have utilized the pyrene labeled PEG samples in two separate studies sponsored by the Polymers Program of NSF. These involve the study of hydrogen bond formation between a polymeric donor and polymeric acceptor in aqueous solution. The systems selected for study were poly(acrylic acid)/poly(ethylene glycol) and poly(methacrylic acid)/poly(ethylene glycol). In both cases, pyrene labeled PEG was used as a probe molecule and the experimental observable was intramolecular and intermolecular excimer formation between the terminal pyrene groups. The contributions of ARO in the preparation of the labeled compounds will be acknowledged as partial support: {ARO MANUSCRIPTS IN PREPARATION - NO. 4 AND 5}

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C. LIST OF PUBLICATIONS AND TECHNICAL REPORTS

1. Publications

- (1) R. Gelles and C. W. Frank; "Energy Migration in the Aromatic Vinyl Polymers. 2. Miscible Blends of Polystyrene with Poly(vinyl methyl ether);" *Macromolecules* 1982, 15, 741-747.
- (2) R. Gelles and C. W. Frank; "Energy Migration in the Aromatic Vinyl Polymers. 3. Three-Dimensional Migration in Polystyrene/Poly(vinyl methyl ether);" *Macromolecules* 1982, 15, 747-752.
- (3) R. Gelles and C. W. Frank; "Phase Separation in Polystyrene/Poly(vinyl methyl ether) Blends As Studied by Excimer Fluorescence;" *Macromolecules* 1982, 15, 1486-1491.
- (4) R. Gelles and C. W. Frank; "Effect of Molecular Weight on Polymer Blend Phase Separation Kinetics;" *Macromolecules* 1983, 16, 1448-1456.
- (5) J. M. Torkelson, M. Tirrell and C. W. Frank; "Polystyrene-Methylcyclohexane Solutions Undergoing Phase Separation: A Study by Fluorescence Spectroscopy;" *Macromolecules* 1984, 17, 1505-1512.
- (6) C. W. Frank and R. Gelles; "Rotational Dyad Statistics and Energy Migration in Miscible and Immiscible Polystyrene/Poly(vinyl methyl ether) Blends;" NATO Advanced Study Institute on Photochemical and Photophysical Tools in Polymer Science, San Miniato, Italy, October, 1985.

2. Manuscripts in Preparation

- (1) C. Leigh, W.-C. Zin and C. W. Frank; "Effect of Casting Solvent on Morphology in PS/PVME Blends"
- (2) W.-C. Zin and C. W. Frank; "Phase Separation in PS/PVME Blends"
- (3) W.-J. Cho and C. W. Frank; "Concentration Studies on the Photophysics of Polymer Blends"
- (4) H. T. Oyama, W. T. Tang and C. W. Frank; "Effects of Complexation on the Chain Configuration in the Poly(acrylic acid)/Pyrene Labeled Poly(ethylene glycol) Complex"
- (5) H. T. Oyama, W. T. Tang and C. W. Frank; "Effects of

Complexation on the Chain Configuration in the
Poly(methacrylic acid)/Pyrene Labeled Poly(ethylene glycol)
Complex"

3. Technical Reports

- (1) Technical Report No. 1; Reprint; Energy Migration in the Aromatic Vinyl Polymers. 2. Miscible Blends of Polystyrene with Poly(vinyl methyl ether)
- (2) Technical Report No. 2; Reprint; Energy Migration in the Aromatic Vinyl Polymers. 3. Three-Dimensional Migration in Polystyrene/Poly(vinyl methyl ether)
- (3) Technical Report No. 3; Manuscript; Phase Separation in Polystyrene/Poly(vinyl methyl ether) Blends as Studied by Excimer Fluorescence
- (4) Technical Report No. 4; Manuscript; Effect of Molecular Weight on Polymer Blend Phase Separation Kinetics
- (5) Technical Report No. 5; Reprint; Phase Separation in Polystyrene/Poly(vinyl methyl ether) Blends as Studied by Excimer Fluorescence
- (6) Technical Report No. 6; Reprint; Effect of Molecular Weight on Polymer Blend Phase Separation Kinetics
- (7) Technical Report No. 7; Reprint; Polystyrene-Methylcyclohexane Solutions Undergoing Phase Separation: A Study by Fluorescence Spectroscopy
- (8) Technical Report No. 8; Manuscript; Rotational Dyad Statistics and Energy Migration in Miscible and Immiscible Polystyrene/Poly(vinyl methyl ether) Blends

D. LIST OF ALL PARTICIPATING SCIENTIFIC PERSONNEL

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