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# Communications to the Editor

## Excimer Fluorescence as a Molecular Probe of Spinodal Decomposition in Polymer Fluids

Initial stages of spinodal decomposition and nucleation are not well understood even though we have a solid foundation based on experiments related to critical phenomena and the renormalization group approach.[1-3] Goldburg et al.[4] and Knobler et al.[5] have done some elegant experiments on spinodal decomposition of binary fluid mixtures using light scattering techniques as the main molecular probe to measure the droplet size.

The dynamics in the initial stages of spinodal decomposition or nucleation is difficult to measure partly because the time available for observation is fairly short and partly because the concentration difference in the very beginning of a droplet growth is small. If we are interested in the initial stages of droplet growth, the probe wavelength of visible light, which is of the order of a few thousand angstroms, is too large for detection of the formation of microdroplets at the molecular aggregation level. In this communication, we want to demonstrate that excimer fluorescence can be used as a molecular probe to study the dynamics of spinodal decomposition and nucleation in polymer fluids.

Excimer fluorescence has been used to study polymer blend miscibility and morphology of polymers containing aromatic ring structures.[6] Excimer-forming sites are produced by intramolecular interactions between aromatic rings on adjacent or nonadjacent repeating units of the same polymer chain and by intermolecular interactions between aromatic rings from different polymer chains. When the concentrations of the aromatic rings are low, such as in dilute solution of an aromatic vinyl polymer in a nonfluorescent solvent (or a nonfluorescent host polymer), intramolecular interactions dominate. At high ring concentrations, the aromatic vinyl polymer chains begin to overlap. Then, intermolecular entanglements tend to be the main reason for excimer fluorescence. Intramolecular interactions depend upon temperature, concentration, molecular weight, and solvent quality because excimer-forming sites can be related to polymer entanglement "points". In a dilute solution, only a small number of entanglement points, if any, within each polymer coil exists. If the polymer coil changes its dimension, the number of entanglement points will change, resulting in a slight change in the fluorescence emission spectrum. At higher concentrations in the semidulute region where different polymer chains overlap, the excimer-forming sites should have a different concentration dependence.

Vala et al.[7] concluded that the polystyrene fluorescence peak at 335 nm is due to excimer emission while the peak at 280–285 nm is due to monomer emission. The effects of molecular weight of polystyrene on fluorescence emission spectra in various solvents have been reported.[8]

We have been studying the phase behavior of polystyrene in methyl acetate.[9] The polymer–solvent system has an upper (~43 °C) and a lower (~114 °C) Θ temperature, both within the range of experimental accessibility. In the absence of a temperature or a pressure jump apparatus, we simply measured the fluorescence emission spectra of polystyrene ($M \sim 4 \times 10^5$) in methyl acetate at two different concentrations, 1 wt % ($<C^*$) and 15 wt % ($>C^*$), before, during, and after phase separation. We used a Perkin-Elmer MPF-44 fluorescence spectrophotometer, 1-cm square quartz cells, and right-angle excitation at 250-nm wavelength. As the solvent absorbs significantly at wavelengths below 265 nm, fluorescence measurements were performed with an excitation radiation of 240 nm in addition to those reported at 250 nm. The weaker spectra had similar forms, indicating an absence of unexpected effects on the emission spectra due to the penetration depth of the exciting radiation.

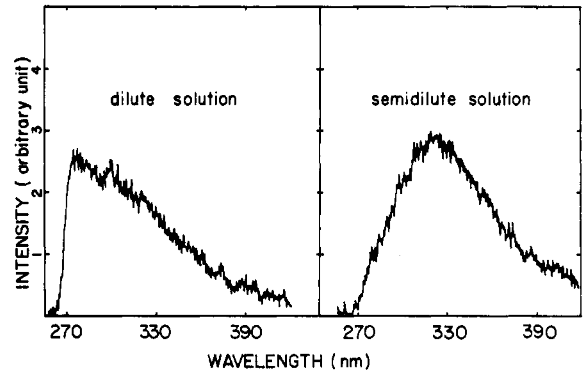


**Figure 1.** Fluorescence emission spectra of polystyrene ($M \sim 4 \times 10^5$) in methyl acetate at 1 and 15 wt % polymer concentrations in the homogeneous one-phase region at 25 °C.

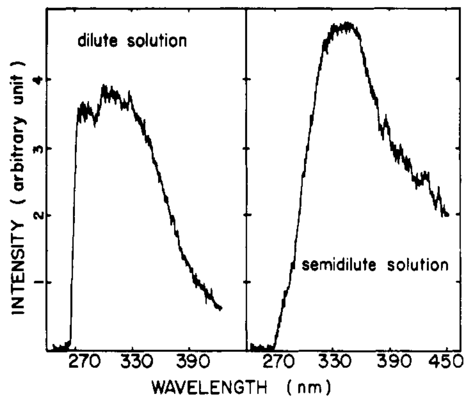


**Figure 2.** Fluorescence emission spectra of the same two polystyrene solutions as shown in Figure 1 measured at about 5 min after quenching the samples from 25 to 15 °C. Droplets were being formed.

Figure 1 shows the emission spectra in the homogeneous one-phase region at 25 °C. At low concentrations ($C < C^*$, with $C^*$ being the overlap concentration), the monomer emission at ~280 nm dominates. At high concentrations ($C > C^*$), the polystyrene fluorescence peak at ~335 nm due to excimer emission dominates. As the critical solution concentration of a binary polymer–solvent fluid is in the neighborhood of the overlap concentration, the concentrations of the two phases are likely to have one phase greater than $C^*$ and the other less than $C^*$. Figure 2 shows the fluorescence emission spectra of the same two polystyrene solutions as shown in Figure 1 measured at about 5 min after quenching the samples from 25 to 15 °C. In the dilute solution (1 wt % overall polystyrene concentration) small droplets of more concentrated solutions are formed, creating the excimer peak at ~335 nm. As the excimer peak was very weak in Figure 1 for the dilute solution, the fluorescence excimer technique becomes a

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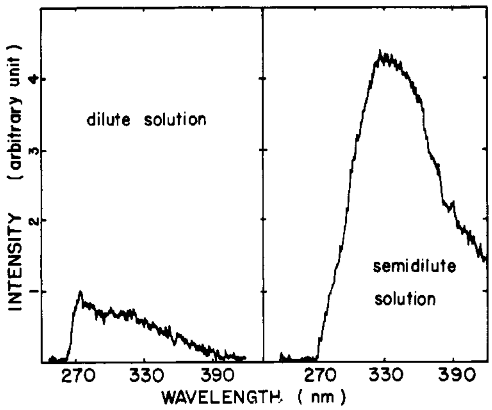


**Figure 3.** Fluorescence emission spectra of the same two polystyrene solutions as shown in Figure 1 measured at a very late stage of phase separation (~40 min after quenching the sample from 25 to 15 °C).

very sensitive probe to study the microphase separation of polymer solutions (or blends) when the initial concentration of the aromatic ring containing polymer is low. At high concentrations, such as the 15 wt % polystyrene solution, the intensity of the excimer peak is increased because of an increase in the concentration of the more concentrated phase while droplets of more diluted solutions contribute toward the monomer excitation peak at ~280 nm. Figure 3 shows the fluorescence emission spectra of the the two-phase solution. The incident radiation sees essentially the more dilute upper phase. Therefore the spectrum is similar to that of the dilute solution in Figure 1. The intensity peak for the monomer excitation is lower because of lower polymer concentration. At high concentrations, the droplets which have lower polymer concentrations still intermingle with the more concentrated phase even after 40 min. Therefore, the net excimer peak at ~335 nm is lower than that in Figure 2.

In Figures 1–3, we have demonstrated that excimer fluorescence can be used to study the structure and morphology of microphase formation during spinodal decomposition and nucleation. More quantitative and detailed studies are under way. While theoretical treatment of the rate constants associated with monomer and excimer peaks is very difficult, we can, nevertheless, determine the concentrations of those droplets empirically.

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## References and Notes

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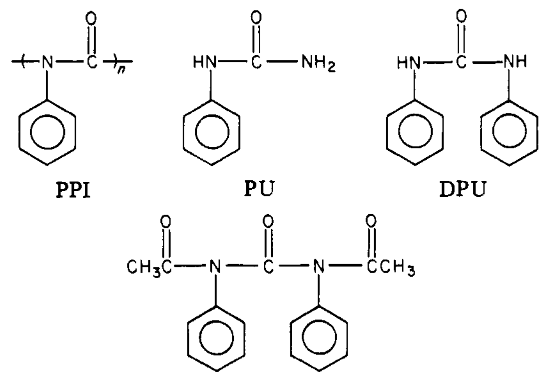
## Fluorescence of Poly(phenyl isocyanate) and the Behavior of Some of Its Analogues

In comparing emission spectra of polymers to the spectral characteristics of their low molecular weight analogues, it is important to ensure that the analogue reflects the conformation of the polymer. For instance, 1,3-diphenylpropane is a less satisfactory analogue of polystyrene than 2,4-diphenylpentane, whose meso form exhibits much more excimer emission than the racemic isomer,[1] in analogy with the higher excimer yield from isotactic as compared to atactic polystyrene.[2]

We have compared the behavior of poly(phenyl isocyanate) (PPI) with that of phenylurea (PU), diphenylurea (DPU), and diacetyldiphenylurea (DADPU).



PPI PU DPU

DADPU

In dilute tetrahydrofuan solution, PU fluoresces with an emission maximum at 308 nm. Solutions of the polymer PPI exhibit an emission spectrum similar to that of PU but with a quantum yield about one-tenth as large.

The compound PU is not a good analogue of PPI and we have, therefore, investigated DPU and particularly DADPU, which has an electronic system quite close to that of the polymer. Yet, neither of these compounds fluoresced and the question then arises why DADPU should behave so differently from the polymer. We should like to suggest the following interpretation: In DPU and DADPU internal quenching by the second phenyl group eliminates the fluorescence observed in PU. This is analogous to the difference between the fluorescent benzylamine and the nonfluorescent dibenzylamine.[3] In the polymer, conformational restraints apparently reduce the internal quenching. It is well-known that aliphatic polyisocyanates are almost rodlike[4] and they may assume in solution a helical conformation similar to that characterizing their crystals.[5] On the other hand, poly(tolyl isocyanate) has been found to be quite flexible[4a] and a higher flexibility of PPI is also implied by its failure to form liquid crystals.[6] Thus, although the conformational restraints in PPI should be much less severe than in the alkyl-substituted polyisocyanates, they are apparently still sufficient to inhibit to a large extent internal quenching of the excited phenyl groups.

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