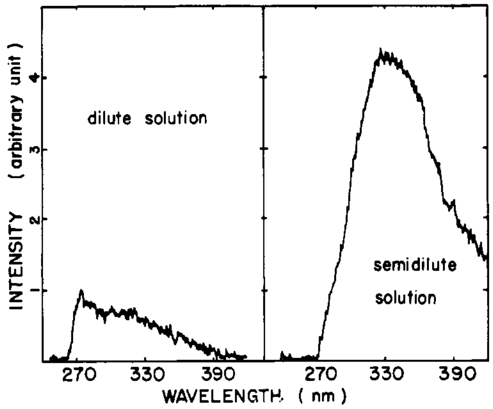

Figure 3. Fluorescence emission spectra of the same two polystyrene solutions as shown in Figure 1 measured at a very late stage of phase separation (~40 min after quenching the sample from 25 to 15 °C).

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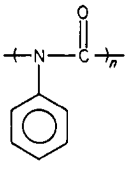
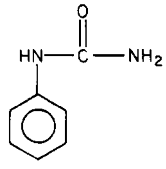
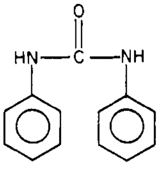
Fluorescence of Poly(phenyl isocyanate) and the Behavior of Some of Its Analogues

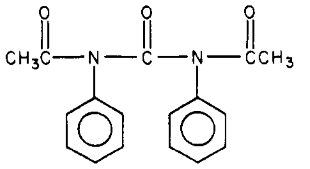
In comparing emission spectra of polymers to the spectral characteristics of their low molecular weight analogues, it is important to ensure that the analogue reflects the conformation of the polymer. For instance, 1,3-diphenylpropane is a less satisfactory analogue of polystyrene than 2,4-diphenylpentane, 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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Use of Azochromophoric Labels as a Molecular Probe of Physical Aging in Amorphous Polymers

When polymers are cooled from the rubbery state to the glassy state, they are in a nonequilibrium state with excess volume and enthalpy. They slowly reach an equilibrium state with concurrent loss of volume (densification) and enthalpy. This phenomenon, which is usually studied as a function of isothermal (sub-T_g) annealing time, is referred to as physical aging[1] as opposed to chemical aging. As well as densification, mechanical properties of polymers change as a consequence of physical aging; namely, the material becomes brittle. The current high level of research activity in this important area is directed at both experimental studies and theoretical studies.[2] Among the experimental studies, volume[3] or enthalpy relaxation,[4] mechanical[1c,5] or dielectrical,[6] and diffusion[7] measurements are often made. However, information obtained by these experimental measurements is macroscopic in nature rather than microscopic. It is well-known that physical aging is related to the loss of free volume, which has a certain distribution of sizes at a given temperature and time. It would be very desirable to have some information at the molecular level which can be related to the size distribution of free volume. Toward this goal, we have utilized one of the molecular labeling techniques by analyzing the kinetics of trans ⇄ cis photoisomerization of azochromophores covalently bonded to the main chain of amorphous polymers in small concentrations. As demonstrated by us,[8] such a molecular label, when properly designed in the polymer matrix, can be a sensitive molecular probe of the local environment surrounding the azo label. For example, in our most recent study,[9] we reported that as physical aging proceeds, photoisomerization of the azo label is progressively impeded, reflecting the disappearance of free volume above a certain size, since such isomerization would require free volume of a certain size in the immediate vicinity of the label.[10] We have now analyzed the kinetics of these photoisomerizations more fully. The results seem to provide information on the fraction of free volume above a critical size and its change as a function of temperature and aging time.

Three amorphous, single-phase polyurethanes were studied, whose chemical structures are shown in Chart I.

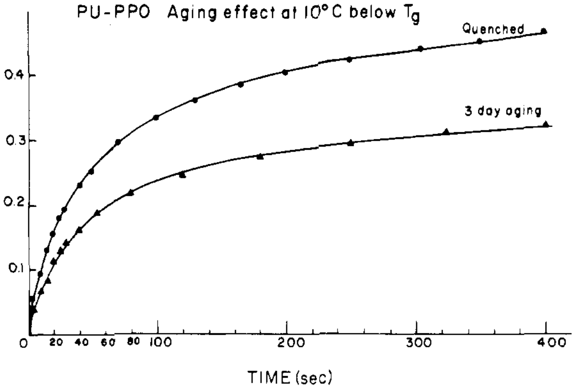
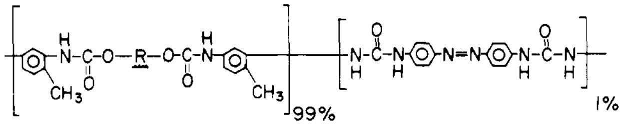


Figure 1. Course of the trans ⇄ cis photoisomerization of azobenzene residue in the main chain of PU–PPO at 10 °C below T_g (at −2 °C) as a function of physical aging.

Chart I
Chemical Structures and T_g's of Amorphous Polyurethanes with a Small Concentration of Azo Label in the Main Chain



R		T_g(°C)
$(CH_2)_4$	PU-BD	45
$(CH_2)_{10}$	PU-DD	15
$\{CH(CH_3)-CH_2-O\}_7$	PU-PPO	8

T_g was measured by DSC. A description of general polymer syntheses and kinetic studies can be found in ref 8. Quenching of the samples was done from 10 to 12 °C above T_g to their respective glassy temperatures, with the same cooling rate for all samples. This cooling rate in the DSC was 160 °C/min and in the kinetic studies was slower, about 4 °C/min. Therefore the quenched state in the kinetic studies actually corresponds to about 5–8 min of physical aging. Photoisomerization kinetics were always started with all-trans isomers, with similar radiation intensity.

The kinetics of reversible trans ⇄ cis photoisomerization were analyzed based on the following equations,[11] since thermal reaction is negligible at the temperatures we studied:

$$I(\delta) \equiv \left(1 + \frac{D_\infty}{2} + \frac{D_\infty^{\,2}}{12}\right)\ln|\delta| - \left(\frac{1}{2} + \frac{D_\infty}{6}\right)\delta + \frac{\delta^2}{24}$$

$$I(\delta) = At + \text{constant}$$

where $A = -I_0\phi_t\epsilon_t/y_\infty$, D_∞ and D are optical densities at the photostationary state and at time t, respectively, $\delta \equiv D_\infty - D$, I_0 is the radiation intensity, ϕ_t is the quantum efficiency, ϵ_t is the molar extinction coefficient, and y_∞ is the cis fraction at the photostationary state. In dilute solutions, the $I(\delta)$ vs. t plot gives a series of almost parallel straight lines up to 90% conversion in the ±20 °C range near T_g, meaning that the rate of photoisomerization is almost independent of temperature in this range. But in solid films there is a certain extent of relatively fast reaction followed by much slower reaction. Thus the plot of $I(\delta)$ vs. t results in a curvature if y_∞ is assumed to be 90%. In Figure 1, $I'(\delta)$ is plotted vs. time for convenience, where $I'(\delta)$ is $I(\delta)$ minus the intercept at $t = 0$. When

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