ENERGY RELAXATION IN SYNTHETIC POLYMER SOLUTIONS

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A detailed knowledge of the kinetics of energy relaxation in polymer
solutions is essential to obtain a complete understanding of the ultimate
fate of excitation energy residing in these molecules. The application of
time-resolved fluorescence techniques provides a valuable addition to
existing methods for studying the time-dependent photophysical processes
occurring in many polymer systems. We have developed in our laboratories
an apparatus based on a mode-locked, cavity-dumped laser excitation source
which allows the recording of fluorescence lifetimes and time-resolved
emission spectra with time and wavelength resolution and data acquisition
times superior than conventional techniques. Features of this system are
the very high laser repetition rate (5MHz), the exact reproducibility of
the laser pulse profile and the use of photon counting detection methods.
The system stability and deconvolution techniques allow the analysis of
multiple decay kinetics in the sub-nanosecond time domain with great
confidence and the recording of time-resolved spectra provides a complete
description of the fluorescence decay processes.

The apparatus has been used to study the kinetics of excimer
formation and decay in a number of synthetic polymers containing pendant
aromatic groups. The formation of an intrachain excimer from the
association of an electronically excited aromatic moiety with a similar
ground state chromophore has been shown to occur in a number of vinyl
aromatic polymers and a red-shifted structureless fluorescence is often

observed in addition to normal monomeric fluorescence. Such excimer sites have been implicated as traps involved in photodegradation pathways.

The kinetics of monomer and excimer fluorescence decay in these systems may be shown to be of the general form

$$i_M(t) = A_1 e^{-\lambda_1 t} + A_2 e^{-\lambda_2 t}$$

$$i_D(t) = A_3 (e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

where $i_M(t)$ and $i_D(t)$ are the time dependent intensities of monomer and excimer emission respectively and λ's are related to rate constants. Data obtained from analysis of the fluorescence decay curves for several polymers in dilute dichloromethane solutions is shown in Table 1.

Table 1

	τ(nsec)	
	Monomer	Excimer
Poly(styrene)	0.76	13.9
Poly(α-methyl styrene)	1.0	8.40
Poly(vinyl naphthalene)	7.43	43.1
*Poly(N-vinyl carbazole)	–	2.5, 21.3

*Only dual excimer emission present.

In the case of the poly(styrenes) no reverse dissociation of the excimer once formed is observed while in poly(vinyl naphthalene) dissociation of the excimer site to excited monomer is a major process at room temperature. The recording of time-resolved emission spectra (Figure 1) provides unambiguous confirmation of these excited state processes. Fluorescence emission from solutions of poly(N-vinyl carbazole) arises solely from two excimer sites within the polymer chain and analysis of the time-resolved spectra confirm the

interconversion of these sites during the excited state lifetime.

This technique thus allows a detailed insight into energy migration and transfer processes occurring in polymer systems and further studies in this area are in progress.
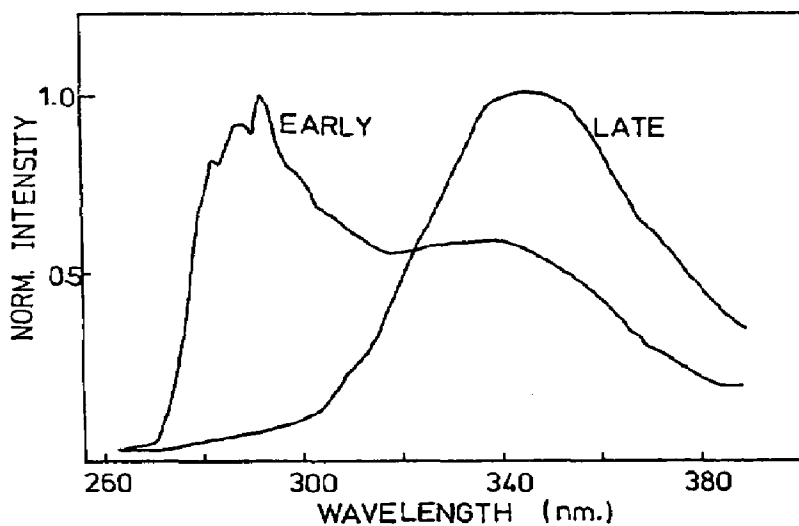

<u>Figure 1</u> Time-resolved emission spectra for 0.01% poly(α-methyl styrene). Early gate $\Delta t = 0$, $\delta t = 0.2$ns; Late gate $\Delta t = 41$ns, $\delta t = 0.2$ns.