polymer communications

# Transient decay studies of photophysical processes in aromatic polymers:
## 4. Intramolecular excimer formation in homopolymers of 1-vinylnaphthalene, 2-vinylnaphthalene and 1-naphthyl methacrylate

**D. Phillips and A. J. Roberts**
*The Royal Institution of Great Britain, 21, Albermarle Street, London W1X 4BS, UK*

**and I. Soutar**
*Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh EH14 4AS, UK*
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*Introduction*

The considerable potential of transient decay measurements in the analysis of photophysical phenomena in polymers has long been recognised. In particular the phenomenon of intramolecular excimer formation in macromolecules has attracted interest[1–6]. However, it has generally been assumed in the study of such aromatic homopolymer systems that the kinetic scheme of Birks[7], derived for the description of intermolecular excimer formation in low molecular weight species, can be applied directly to the intramolecular phenomenon in polymers. Such an assumption has resulted in the adoption of kinetic parameters derived from dual exponential analyses of decay data in the regions of monomer and excimer emission.

Recently high resolution time-resolved spectroscopic measurements on copolymers containing varying concentrations of aromatic chromophores have indicated that the conventional kinetic scheme of Birks[7] is not applicable in such systems[8–10]. Furthermore, it has been suggested that the photophysical behaviour of poly(acenaphthylene)[11] and poly(*N*-vinylcarbazole)[12,13] cannot be adequately modelled in terms of dual exponential decay functions. In view of such studies, it might appear that deviations from Birks[7] scheme are to be expected in polymer species in general. This would imply that previous reports of two decay times for emission from macromolecules are the result of forcing the data into dual exponential analytical functions which do not truly represent the photophysical characteristics of the system. Furthermore, doubts concerning the applicability of Birks[7] scheme in polymer systems have been expressed by Holden *et al.*[14,15] and De Schryver *et al.*[16].

In the light of our observations upon copolymer systems[8–10] and of confidence generated in the meaningful analysis of decay data in terms of triple exponential fits through use of synthetic test data[17] it seemed appropriate to re-examine the photophysical behaviour of aromatic homopolymers. Here we report on studies of poly(1-vinylnaphthalene), poly(2-vinylnaphthalene) and poly(1-naphthyl methacrylate).

*Experimental*

*Materials.* 1-Vinylnaphthalene (Koch–Light) was purified by multiple fractional distillation under high vacuum. 2-Vinylnaphthalene (Koch–Light) was recrystallized from benzene and thrice from ethanol (m.p. = 64–66°C).

1-Naphthyl methacrylate was synthesized by reaction of equimolar amounts sodium 1-naphtholate and methacroyl chloride in aqueous medium. The product was extracted with ether and purified by recrystallization from ethanol/water (twice) followed by recrystallization from 40/60 petroleum ether (m.p. = 65–66°C).

Polymers were synthesised by free radical polymerization to less than 10% conversion, AIBN initiator in benzene under high vacuum at 60°C. Polymers were purified by multiple reprecipitation.

Tetrahydrofuran was purified by reflux over and fractional distillation from $LiAlH_4$.

*Techniques.* Fluorescence decay measurements were made on thoroughly degassed solutions in THF of optical density 0.1. The high resolution spectrometer employed has been previously described[8–10].

*Results and discussion*

*Poly(1-vinylnaphthalene)[P1VN].* Fluorescence decay curves were recorded at 330 nm and 475 nm in the regions of monomer and excimer fluorescence respectively. In contrast to previous reports for this polymer[1,2] neither curve could be adequately represented by dual exponential decay functions. For the decay at 330 nm attempted fitting to a function of the form

$$i(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) \qquad (1)$$

produced $\chi^2$ values in excess of 3.3. Similarly for the decay at 475 nm employment of a function of the type depicted in equation (1) resulted in high $\chi^2$ values (in excess of 5.7). Non random plots of weighted residuals[18] and autocorrelation of residuals[19] in addition to use of the serial

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correlation coefficient[20] and $\chi^2$ criterion[21] indicated that the description of the intensity of decay in terms of equation (1) was inappropriate. More seriously, it should be noted that inspection of the resultant kinetic parameters detailed in *Table 1* reveals that

(i) the decay times $\tau_1$ and $\tau_2$ do not coincide when evaluated from the decay data in the spectral regions of monomer and excimer emission.

(ii) the pre-exponential factors $A_1$ and $A_2$ for the decay observed for the excimer are not equal in magnitude.

These observations are inconsistent with the predictions of Birks[7] kinetic scheme which requires that monomer and excimer decays be described as

$$i_M(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) \qquad (2)$$

$$i_D(t) = A_3[\exp(-t/\tau_1) - \exp(-t/\tau_2)] \qquad (3)$$

In contrast, the use of a triple exponential function of the form

$$i(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) + A_3\exp(-t/\tau_3) \quad (4)$$

produced a significant improvement in fit as assessed by the previously mentioned criteria. The derived parameters are detailed in *Table 2*. The data are consistent with the predictions made following transient kinetic studies of copolymers incorporating 1-vinylnaphthalene chromophores[8,9]. In the latter studies it was proposed that there are two kinetically distinct monomer species in addition to an excimer. A similar proposal has been made by Holden *et al.*[14,15] from studies of the kinetics of excimer formation in poly(naphthylalkyl methacrylates).

According to our previous analysis $\tau_1$ and $\tau_2$ are associated with the decay of excimer and monomer species which interact via a mechanism involving energy migration and rotational sampling. $\tau_3$ is ascribed to emission from monomer which is unable to participate in the formation of excimers by this mechanism but may be involved in alternative routes to excimeric sites[8-10,22]. This model implies that extrapolation of $\tau_3$ data for the copolymers should yield a value of 11.4 ns for the homopolymer which is in reasonable agreement with that of 12.6 ns reported here. Furthermore, the high local chromophore concentration of the homopolymer results in the approximation that $\tau_1^{-1} = k_D$, the rate parameter governing deactivation of the excimer by processes other than dissociation to excited monomer. The value of $2.56 \times 10^7$ s$^{-1}$ obtained from $\tau_1$ for the homopolymer agrees well with those of $2.2 \times 10^7$ s$^{-1}$ [8] and $2.4 \times 10^7$ s$^{-1}$ [9] obtained by extrapolation over a range of intramolecular concentrations in the copolymer series[8,9].

The association of $\tau_1$ and $\tau_2$ with an excimer/monomer interaction involving intramolecular energy migration suggests that the monomer lifetime should be subject to considerable quenching relative to that of ~50 ns for an unassociated chromophore[8,9]. This prediction is borne out by the trends in $\tau_2$ observed with increasing aromatic content in series of copolymers of vinylnaphthalene[8,9] and by the present work in which $\tau_2$ for the homopolymer is 1.6 ns.

As discussed in earlier publications in this series[8-10] it is not justifiable within the limits imposed by the current experimental techniques to attempt description of the decay at 475 nm in terms of a triple exponential function.

*Poly(2-vinylnaphthalene)[P2VN]*. Dual exponential functions of the type described in equation (1) were found to be inappropriate for the description of the decays of emission intensity both at 330 nm and 475 nm. As with P1VN the decay data for P2VN at 330 nm could be adequately matched by use of triple exponential functions. The resultant kinetic parameters are detailed in *Table 2*.

It is apparent from consideration of the relative magnitude of the pre-exponential factors that the contribution of the overall fluorescence profile from 'conventional' monomer (characterised by $A_2$, $\tau_2$) is greater in P2VN than in P1VN. This may be due either to the influence of the goemetry of the chromophore with respect to the polymer backbone or to influences of tacticity within the polymer samples. The importance of tacticity in determination of the photophysical properties of P2VN and other polymers has been discussed[16,23]. However, $\tau_1$ is observed in the decay at 330 nm as a consequence of reverse dissociation of excimer to excited monomer. The small value of $A_1$ is indicative of a relatively small value for $k_{MD}$, the rate coefficient for this process, rather than indicating a low excimer yield.

It is worthy of note that $\tau_3$ the lifetime of the monomer species which according to our previous proposals[8,9] is excluded from excimer formation via the conventional mechanism is comparable to the corresponding lifetime for P1VN. Such an observation might lend greater credibility to a kinetic scheme in which such monomers could be involved in excimer formation through excitation transfer rather than the alternative mechanism whereby excimer formation is consequent upon long range interactions between chromophores as a result of chain coiling since the latter mechanism would be expected to be critically dependent upon polymer structure and thence coil dimension.

*Poly(1-naphthylmethacrylate)[PNMA]*. The data presented in *Table 2* substantiate our proposal that in general the simple kinetic scheme applicable[7] to low molar mass intermolecular excimer formation, is not appropriate in general to description of the intramolecular phenomenon in macromolecules. Recently, Holden *et al.*[14] have proposed a kinetic scheme involving three kinetically distinct emitting species in poly(naphthylalkyl methacrylates). In contrast to the mechanisms proposed in our work[8-10], Holden *et al.*[14] have proposed that one monomer species is 'isolated' from the excimer formation scheme and will

*Table 1* Kinetic parameters derived from dual exponential fits for PIVN

| λ nm | $A_1$ | $\tau_1$ ns | $A_2$ | $\tau_2$ ns |
|---|---|---|---|---|
| 330 | 0.06 | 30.09 | 0.17 | 5.60 |
| 475 | 0.16 | 44.05 | −0.04 | 15.47 |

*Table 2* Decay data for triple exponential analysis

| Sample | $A_1$ | $\tau_1$ ns | $A_2$ | $\tau_2$ ns | $A_3$ | $\tau_3$ ns | $\chi^2$ |
|---|---|---|---|---|---|---|---|
| PIVN | 0.029 | 39.1 | 0.290 | 1.6 | 0.079 | 12.6 | 1.19 |
| P2VN | 0.005 | 54.6 | 0.479 | 2.1 | 0.011 | 13.6 | 1.12 |
| PNMA | 0.011 | 20.5 | 0.547 | 0.9 | 0.160 | 4.1 | 1.19 |

produce an emission lifetime characteristic of an unquenched chromphore. The relatively short value of $\tau_3$ observed in the current work might suggest that such a mechanism does not hold for PNMA although further work e.g. with copolymer series in which individual rate constants could be examined would be necessary to clarify the situation.

As for P1VN and P2VN the value of $\tau_2$ associated with the monomeric entity involved in energy migrative population of excimer sites is short as is to be expected in such a kinetic scheme.

## *Conclusions*

The kinetic schemes proposed on the basis of studies of the intramolecular concentration dependence of excimer formation in a variety of copolymer systems appear to be valid for the aromatic homopolymers studied. Consequently, analysis of fluorescence data in terms of the direct application of the Birks kinetic scheme must be viewed with caution.

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# Experimental studies of poly(vinyl acetate) networks swollen in isopropyl alcohol below the $\theta$-temperature

**M. Zrinyi, T. Molnár* and E. Horváth**
*Department of Colloid Science, L. Eötvös University, H-*1088 *Budapest, Puskin u.* 11–13., *Hungary*

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## *Introduction*

At the $\theta$-temperature the repulsive and attractive forces balance each other, and the mean size of a polymer molecule is that of a random coil. Below the $\theta$-temperature the attractive forces predominate, and a phase transition of polymer networks marked by a sudden change in the degree of swelling has been theoretically predicted[1-3]. Although this phenomenon attracted attention in the past and is still the subject of many theoretical discussions, only a small number of experimental studies have been reported[4-7].

## *Experimental*

Various poly(vinyl acetate) networks were prepared according to a previously described method[8]. The crosslinking density which is the average number of crosslinks on a primary chain was varied from 5 to 72. Several series of networks have been prepared differing from each other not only in their crosslinking densities ($l$) but also in the initial polymer concentration ($c_0$) at which the crosslinks were introduced (3, 6, 9 wt%).

Cylindrical gel pieces and films were prepared for the optical and swelling degree measurements. The swelling degree, that is the ratio of the total mass of the swollen gel to that of the dry polymer within the network, was determined by weighing the samples after 2 weeks at each temperature in order to obtain the equilibrium swelling degree of the network.

Turbidity measurements were carried out by a BRICE PHOENIX universal light scattering photometer. The turbidity of the films was determined at a wavelength of 546 nm as a function of the temperature which was measured nearby the gel samples by a platinium resistance sensor connected to a KNAUER universal

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* Magyar Viscosagyar, H-2537 Nyergesujfalu, Hungary

‡ Clinic of Psychiatry, Semmelweis Medical University, H-1083 Budapest, Balassa u. 6., Hungary

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