Transient decay studies of photophysical processes in aromatic polymers:
2. Investigation of intramolecular excimer formation in copolymers of 1-vinyl naphthalene and methyl acrylate

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Transient decay studies of the copolymer system 1-vinyl naphthalene/methyl acrylate using pulsed laser excitation have shown that monomer and excimer decay rates are not described by dual exponential functions. Triple exponential decays are attributed to the existence of emission from two kinetically distinct monomer sites in addition to that of the excimer. Variation of intramolecular chromophore concentration in the copolymers allows adoption of a versatile series of extrapolation procedures to derive individual rate constants in the photophysical reaction scheme governing intramolecular excimer formation. Use of this procedure yields a rate parameter governing excimer formation in which the dependence upon local chromophore concentration within the polymer coil is removed to a degree not possible in studies of homopolymers alone.

INTRODUCTION

In a recent paper[1] we have demonstrated that the study of copolymer systems comprising a spectroscopically 'active' monomer with a monomer which does not absorb in the excitation wavelength region of interest allows the determination of individual rate parameters in the photophysical scheme descriptive of intramolecular excimer formation. In particular it has been show that it is possible to obtain information upon the rate coefficient, k_{DM}, governing excimer formation in which the dependence upon the local concentration of chromophore is removed to a degree not attainable in the application of transient decay studies to single polymers.

To date the majority of non-stationary state photophysical studies upon macromolecular species have been confined in the main to investigation of homopolymers[2-8]. In contrast, a number of reports have appeared in recent years upon the study of copolymer systems under steady state excitation conditions which have demonstrated the considerable potential of such systems in the elucidation of the parameters governing intramolecular excimer formation in polymers[9-18]. In particular, the ability to alter the steric constraints and overall chain flexibility by variation of the spectroscopically inactive comonomer whilst maintaining a common excimer-forming chromophore may be used to advantage.

Here, we extend our kinetic studies of copolymers of 1-vinyl naphthalene to the system 1-vinyl nephthalene/methyl acrylate to validate our previous extrapolation procedures used in derivation of photophysical rate coefficients[1] and to study the influence of macromolecular chain flexibility upon the processes of excimer formation and dissociation.

EXPERIMENTAL

Materials

Monomer purification and preparation and characterization of 1-vinyl naphthalene/methyl acrylate copolymers have been described[14].

A copolymer containing less than 0.5 mol % naphthalene chromophore was prepared by free radical polymerization under high vacuum conditions.

1-Methyl naphthalene was purified by high vacuum fractional distillation.

Tetrahydrofuran (THF) was purified, immediately prior to use, by refluxing over, and fractional distillation from $LiAlH_4$.

Techniques

Fluorescence decay curves and time-resolved emission spectra were recorded on a high resolution fluorimeter the operation of which has been described[19]. Sample excitation was achieved using an externally frequency-doubled, cavity-dumped dye laser (Coherent Radiation Ltd, Model 590) pumped using a 4 W argon–ion laser (Spectra-Physics Model 166). Conventional single photon counting equipment comprised the detection system.

Non-linear least square deconvolution analyses were performed on an ICL 2970 computer on data collected to

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a minimum of 30000 counts in the maximum.

Thoroughly degassed sample solutions (THF solvent) of optical density 0.1 were employed in all fluorescence measurements.

RESULTS AND DISCUSSION

The copolymer microcomposition data, the mole fraction of naphthyl chromophore, f_n, the fraction of linkages between naphthalene species in the macromolecule, f_{nn}, and the mean sequence length of chromophoric species, $\bar{l}_n$, necessary for the description of the photophysical behaviour of the polymers[14] are listed in *Table 1*.

Fluorescence decays in the monomer and excimer emission bands were recorded for all copolymers at 330 and 470 nm, respectively. Reduced χ^2 values[20] plots of weighted residuals[21] and plots of autocorrelation of residuals[22] were used to assess the 'goodness of fit' of trial functions to the observed decays. The kinetic scheme of Birks[23] applicable to intermolecular excimer formation in low molar mass species predicts a description of decay in the region of monomer, $i_M(t)$, and excimer, $i_D(t)$, emission as the sum and difference of two exponentials, respectively. In the present work, neither curve could be adequately matched by use of a single exponential function for any copolymer except that containing less than 0.5 mol % naphthyl chromophore. Of greater interest is the inability of dual exponential functions to provide an adequate fit of decay data. (χ^2 values were typically of the order of 3 and weighted residuals exhibited marked deviations from random distribution.) Similar deviations from 'expected' behaviour have been reported for the 1-vinyl naphthalene/methyl methacrylate[1] and for polymers containing acenaphthylene[24].

In contrast, the emission analysed at 330 nm, $i_{330}(t)$, could be described (with χ^2 less than 1.5 for all copolymers) by triple exponential functions of the type:

$$i_{330}(t) = A_1\ \exp(-t/\tau_1) + A_2\ \exp(-t/\tau_2) + A_3\ \exp(-t/\tau_3) \tag{1}$$

Table 1 Copolymer composition data[14]

Copolymer	f_n	f_{nn}	$\bar{l}_n$
1	0.13	0.01	1.07
2	0.23	0.03	1.16
3	0.36	0.09	1.31
4	0.43	0.15	1.43
5	0.52	0.22	1.62
6	0.58	0.29	1.97
7	0.64	0.37	2.46
8	0.77	0.56	3.62

Credibility of the physical significance of triple exponential fitting is enhanced through the high signal-to-noise ratios obtained as a consequence of the stability of the excitation pulse and of collection to a minimum of 3 x 10^4 counts in the maximum (channel width 640 ps) combined with validation of the deconvolution procedure using synthetic test data[25].

Emission intensity decay in the spectral region of excimer fluorescence could not be modelled adequately by the use of dual exponential functions. Unfortunately, as we have discussed previously[1], the wavelength dependence of photomultiplier transit time precludes *meaningful* fits to triple exponential functions when excitation and emission wavelengths are widely separated.

Table 2 lists the empirical parameters obtained upon fitting $i_{330}(t)$ according to equation (1). The data imply the existence of three temporally distinct emitting species. However, time-resolved spectroscopic analyses of the copolymers revealed the presence of only two energetically distinct species. The situation is analogous to that obtained in the system 1-vinyl naphthalene/methyl methacrylate[1]. Following similar arguments to those employed to explain the photophysical behaviour of the latter system, it is assumed that conventional excimer and monomer decays are observed. If it is assumed that the long lived component (τ_1, A_1) is due to emission from the excimer and that the component described by A_2 and τ_2 is ascribable to that of monomeric chromophore from which excimer may be formed by a mechanism involving, in part, intramolecular energy migration. The reduction in fluorescence lifetime, τ_2, as the intramolecular concentration of chromophore is increased is consistent with such an assignment.

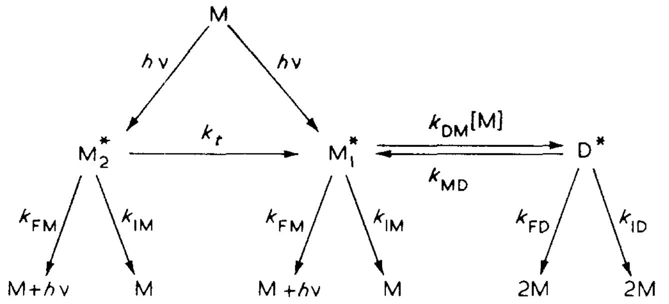
Since the third component is spectrally indistinguishable from the emission of one of the other species and since its relative contribution to the overall emission increases as the concentration of aromatic chromophore in the polymer decreases, it is proposed that the emission is due to a monomer chromophore which is isolated from the mechanismof excimer formation by 'down-chain' exciton hopping. Two plausible kinetic schemes applicable to such a situation are shown in *Figure 1*.

In scheme A it is proposed that M_1^* and D^* interact by the generally accepted energy migration mechanism. M_2^* is envisaged as an isolated monomeric entity which can transfer energy into sequences of naphthalene chromophores M_1^* with a transfer rate, $k_t[M_2^*]$. It is proposed that the reverse transfer out of the 'sequence length trap' is statistically improbable and negligible in the mechanism.

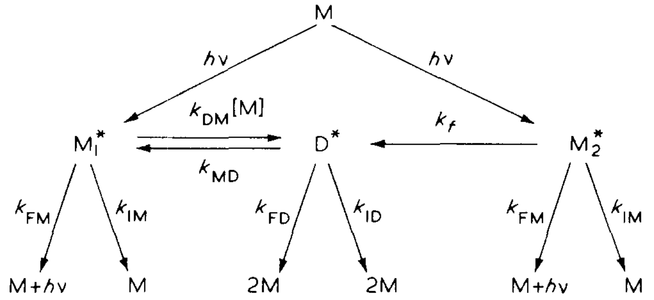
In scheme B, M_2^* is considered to be an isolated naphthalene chromophore which can attain the excimeric conformation through 'long range' interactions brought about by coiling of the macromolecule in solution with

Table 2 Decay parameters descriptive of $i_{330}(t)$

Copolymer	A_1	τ_1/ns	A_2	τ_2/ns	A_3	τ_3/ns
1	0.038	65.1	0.027	9.5	0.077	39.7
2	0.030	64.3	0.052	7.1	0.067	29.1
3	0.031	59.3	0.097	4.4	0.079	19.3
4	0.030	56.3	0.125	3.9	0.072	16.3
5	0.028	53.1	0.197	3.0	0.068	13.6
6	0.026	53.8	0.228	2.3	0.064	13.6
7	0.023	45.7	0.225	1.9	0.043	12.2
8	0.029	40.1	0.504	1.1	0.055	12.4



Scheme A



Scheme B

Figure 1 Photophysical reaction schemes

rate characterized by the coefficient k_f. Whilst such interactions do not appear to be of significance in describing the photophysical behaviour of the copolymer system under stationary state conditions[14] they would become evident only at low mole fractions of chromophore and would therefore not be distinguishable in an analysis of total spectral profile. (During the writing of this manuscript Guillet *et al.*[26] have proposed a general mechanism, based upon observations of dual exponential decays in homopolymers containing naphthalenes, in which the long-lived monomer emission results from singlet naphthalene unable to form excimer within the excited state lifetime. The kinetic schemes A and B correspond to specific mechanisms within the generalized scheme of Guillet *et al.*[26]. Indeed, as we have remarked[1] the dual exponential decays observed in homopolymers are consistent with either scheme A or B since the decay of monomer capable of excimer population by migration will become so fast as to be below the temporal resolution of sampling systems which do not employ sub-nanosecond excitation sources.)

If it is assumed that:

$$k_{M_2} = k_{M_1} = k_M = k_{FM} + k_{IM} \tag{2}$$

$i_M(t)$ and $i_D(t)$ are given by[1]

$$i_M(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) + A_3 \exp(-\lambda_3 t) \tag{3}$$

$$i_D(t) = A_4 \exp(\lambda_4 t) + A_5 \exp(-\lambda_5 t) + A_6 \exp(-\lambda_6 t) \tag{4}$$

where $$\lambda_{1,2} = \frac{1}{2}[(X+Y) \pm \{(Y-X)^2 + 4k_{MD}k_{DM}[M]\}^{1/2}] \tag{5}$$

and $$X = k_M + k_{DM}[M] \tag{6}$$

$$Y = k_D + k_{MD} \tag{7}$$

where $$k_D = k_{FD} + k_{ID}; \tag{8}$$

and $$\lambda_1 + \lambda_2 = k_M + k_{DM}[M] + k_D + k_{MD}; \tag{9}$$

and $$\lambda_3 = k_t + k_M \text{ (Scheme A)} \tag{10a}$$

or $$\lambda_3 = k_f + k_M \text{ (Scheme B)} \tag{10b}$$

The rate parameters A_i and τ_i listed in *Table 1* according to equation (1) may be equated with those descriptive of $i_M(t)$ from equation (3) such that $\tau_i = \lambda_i^{-1}$.

Derivation of individual rate coefficients

The rate coefficients descriptive of intermolecular excimer formation in low molar mass systems may be derived by two procedures.

(1) Kinetic data derived for a single chromophore concentration may be combined with the independent measurement of the lifetime of chromophore in the absence of quenching through excimer formation at low concentrations[23]. Such a procedure has been involved, with a single exception[1], in previous determinations of rate coefficients governing intramolecular excimer formation in macromolecules[6,7,8,27]. Difficulties inherent in such a procedure include those associated with the choice of an adequate model compound to produce an unquenched rate parameter, k_M; and the fact that the resultant rate constant, k_{DM}, for excimer formation is a pseudo-first order function of the form $k_{DM}[M]$ where [M] is, for a given polymer, a constant but undefined local concentration of chromophore within the polymer coil. The adoption of external, dynamic quenchers of chromophore emission[8,26] does not circumvent either limitation.

(2) A more rigorous approach requires the variation of chromophore concentration and the adoption of extrapolation procedures as outlined below[23,28]:

(a) k_M is estimated from the unquenched monomer lifetime. In the case of intramolecular excimer formation in macromolecular species the 'alternative' procedure (b) is more satisfactory[1].

(b) Since $\lambda_1 \to k_M$ as $[M] \to 0$, k_M is estimated by extrapolation to zero chromophore concentration.

(c) k_{DM} is estimated as $\partial(\lambda_1 + \lambda_2)/\partial[M]$.

(d) k_{DM} may be obtained, as an alternative to procedure (c) as the intercept of a plot of λ_2 as a function of $[M]^{-1}$ since $\partial\lambda_2/\partial[M] \to k_{DM}$ as $[M] \to \infty$.

(e) The intercept of $(\lambda_1 + \lambda_2)$ plotted as a function of [M] in combination with (b) [or (a)] may be used to yield $(k_{MD} + k_D)$, since $(\lambda_1 + \lambda_2) \to (k_M + k_{MD} + k_D)$ as $[M] \to 0$.

(f) As an alternative to (e), $(k_{MD} + k_D)$ may be derived from a plot of $(\lambda_1\lambda_2)$ against [M] by substitution of k_M from (b), since $(\lambda_1\lambda_2) \to k_M(k_{MD} + k_D)$ as $[M] \to 0$.

(g) $\partial(\lambda_1\lambda_2)/\partial[M] = k_{MD}k_D$. Thus k_D may be estimated in combination with the result from (c) or (d) for k_{DM}.

(h) As $[M] \to \infty$, $\lambda_1 \to k_D$.

(i) k_{MD} may be estimated by combinations of (e) and (f) with (g) and/or (h).

The application of the extrapolative procedures outlined in (2) above require that:

(i) the kinetic scheme of Birks[23] is applicable to the intramolecular phenomenon in polymers or that suitable modification (as in the case of triple exponential decays) is possible; and

(ii) a term descriptive of the concentration of chromo-

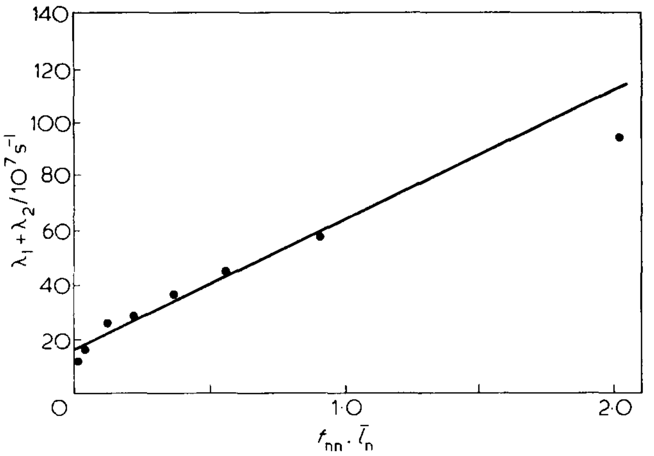


Figure 2 $(\lambda_1+\lambda_2)$ as a function of $\bar{l}_n f_{nn}$

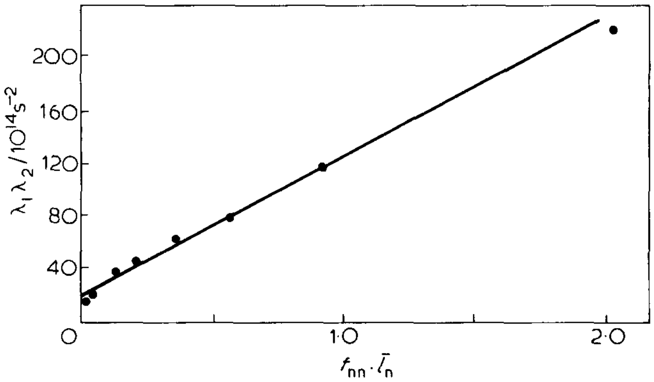


Figure 3 $(\lambda_1\lambda_2)$ as a function of $\bar{l}_n f_{nn}$

phore capable of formation of intramolecular excimers may be substituted for [M].

The assumptions made regarding the first of these restrictions in terms of the identity of species primarily responsible for decay parameters λ_1 and λ_2 have been detailed above and in a prior publication[1]. With respect to the second limitation, it is proposed that the concentration of potential excimer sites may be characterized by the function $\bar{l}_n f_{nn}$ which has been demonstrated to be the appropriate concentration term for descriptions of intramolecular excimer formation in several vinyl aromatic systems under steady state excitation[11,12,14].

Figures 2 and *3* illustrate the applicability of the function of $\bar{l}_n f_{nn}$ to non-stationary state kinetic data through plots of $(\lambda_1+\lambda_2)$ and $(\lambda_1\lambda_2)$, respectively, as functions of the concentration term. Moreover the function $\bar{l}_n f_{nn}$ produced more satisfactory fits than any other terms descriptive of copolymer microcomposition. Indeed the approximation to linearity evident in *Figures 2* and *3* is as good as that generally displayed by similar plots for intermolecular excimer formation in low molar mass species[29].

The kinetic parameters resultant upon extrapolation techniques detailed as (a) to (i) above are collated in *Table 3*.

The linearity of the dependence of $(\lambda_1+\lambda_2)$ or $(\lambda_1\lambda_2)$ upon $\bar{l}_n f_{nn}$ inspires confidence in the analytical procedure. (Deviations at low $\bar{l}_n f_{nn}$ are to be expected at low concentrations due to uncertainty in kinetic data and at high concentrations due to breakdown of the copolymer model as the homopolymer condition is approached, as evident in stationary state data[14].) The credibility of the treatment is further enhanced by the agreement shown between kinetic parameters derived by alternative extrapolation procedures and by the applicability of the method to the 1-vinyl naphthalene/methyl methacrylate system[1]. In particular the agreement between values of k_D determined by methods 2(g) and 2(h) validates assumptions regarding assignment of λ_1 and λ_2 outlined previously since method 2(g) is independent of identity of the individual λ functions whereas 2(h) requires the correct limiting condition to be valid for λ_1. Furthermore since k_D characterizes the total 'spectroscopic' decay of excimer (i.e. through emission of radiation and internal non-radiative processes), its value should be independent of comonomer. The value of $2.35 \times 10^7 s^{-1}$ obtained in the current work is in excellent agreement with that of $2.2 \times 10^7 s^{-1}$ obtained for the 1-vinyl naphthalene/methyl methacrylate system[1].

The designation of the rate coefficient for excimer formation as αk_{DM} in *Table 3* takes cognizance of the fact that whilst the dependence of the rate parameter of excimer formation upon intramolecular concentration in the macromolecule has been removed to an extent, the concentration term $\bar{l}_n f_{nn}$ is at best proportional to the local excimer-forming chromophore concentration. However, it should be stressed that the term αk_{DM} is independent of chromophore concentration in a manner which is not satisfied in single point determinations of the type described in method (1) above.

Comparison of the values of k_M in *Table 3* illustrates the influence of copolymer composition and characteristics upon k_M. The difficulty in choice of appropriate model compounds evident in our analysis of 1-vinyl naphthalene/methyl methacrylate[1] is reinforced in the current work and further illustrates the undesirable features of the single point method[1].

Comparison of the value of the rate constant, k_{MD}, governing excimer dissociation with that obtained for the 1-vinyl naphthalene/methyl methacrylate copolymer series[1] reveals the influence of 'spectroscopically inactive' monomer upon excimer dynamics. It is apparent that the increased flexibility of the methyl acrylate copolymers leads to an enhanced dissociation rate for the excimer.

Reference to *Table 1* reveals that λ_3 is dependent upon the local chromophore concentration in the polymer as would be required by either mechanism for excimer

Table 3 Kinetic data

Rate coefficient	Value x $10^{-7}/s^{-1}$	Procedure
k_M	1.91 1.72 1.5	(a)* (a)† (b)
αk_{DM}	46.5 43.0	(c) (d)
$k_{MD}+k_D$	14.5 14.0	(e) (f)
k_D	2.36 2.35	(g) (h)
k_{MD}	11.95	(i)

* Determined using 2×10^{-5} M 1-methyl naphthalene
† Determined using copolymer containing less than 0.5 mol % chromophore

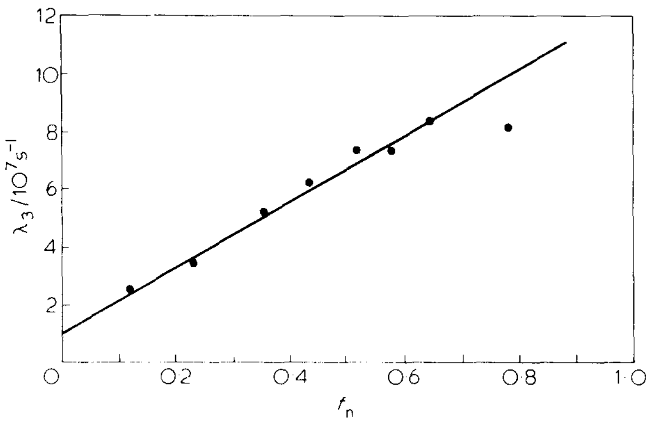


Figure 4 λ_3 as a function of f_n

formation as shown schemes A or B of *Figure 1*. *Figure 4* demonstrates the linear dependence of λ_3 upon the mole fraction of naphthyl chromophore, f_n, in the polymer. Such an observation would be consistent with either of the proposed mechanisms. For either scheme λ_3 is of the form:

$$\lambda_3 = k_M + k_i \qquad (11)$$

where $k_i = k_t$ or k_f according to the relevant reaction scheme. The linear dependence of λ_3 upon f_n, considering the concentration independence of k_M implies that k_i may be designated as[1]:

$$k_i = k'_i f_n \qquad (12)$$

The slope and intercept of *Figure 4* yield values of 11.4 $\times 10^7 s^{-1}$ for k'_i and $1.0 \times 10^7 s^{-1}$ for k_M, respectively. The latter value is, within experimental error, in agreement with that obtained by extrapolative procedure 2(b) (*Table 3*). The rate parameter k'_i is a 'pseudo-first order coefficient', since f_n has been adopted as a function representative of the true 'intracoil local concentration' of aromatic. Therefore, k'_i is proportional to the true second order rate constant.

Comparison of the value of k'_i of $11.4(\pm 0.5) \times 10^7 s^{-1}$ for the 1-vinyl naphthalene/methyl acrylate copolymer series with that of $7.8(\pm 0.3) \times 10^7 s^{-1}$ obtained for the 1-vinyl naphthalene/methyl methacrylate system shows a slight dependence of the rate coefficient upon chain flexibility. Since dielectric relaxation measurements upon poly(methyl methacrylate) and poly(methyl acrylate) in solution indicate that the segmental motion of the latter system is an order of magnitude faster at 298K[30], it is tempting to assume that the mechanism outlined in scheme A of *Figure 1* is more appropriate than that of scheme B which requires long range interactions via polymer chain coiling. However, the situation is complicated by the considerable modification of polymer flexibility induced by vinyl naphthalene chromophores, particularly at high concentrations. Furthermore, fluorescence depolarization measurements of the relaxation of PMMA and PMA bearing fluorescent probes of differing molar volume indicate[31,32] that the difference in relaxation rate may not be as marked as indicated by dielectric relaxation techniqyues.

The values of αk_{DM} of $\sim 4.5 \times 10^8 s^{-1}$ and $1.2 \times 10^8 s^{-1}$ for vinyl naphthalene/methyl acrylate and 1-vinyl naphthalene/methyl methacrylate show a remarkable, but fortuitous, similarity in ratio to relaxation data for segmental motion in PMMA and PMA obtained by fluorescence depolarization[31,32]. We might be tempted into the conclusion that lesser steric constraints upon excimer formation in the copolymers of methyl acrylate relative to methyl methacrylate, which are undoubtedly operative[14], are reflected in the kinetic data. Unfortunately, the values of αk_{DM} are not capable of direct comparison since the dependence upon the local concentration parameter, $\bar{l}_n . f_{nn}$, may not be characterized by the same proportionality constant from one copolymer series to another. It is likely that studies of the temperature dependence of excimer formation under pulsed excitation will produce a more meaningful comparison through examination of activation energy data for the process. Such studies constitute a current research programme.

CONCLUSIONS

(1) The results of the current work provide evidence of the validity of the extrapolation procedure previously employed to derive rate coefficients of individual processes in the photophysical scheme applicable to excimer formation in macromolecules.

(2) The photophysical scheme of Birks[23] descriptive of intermolecular excimer formation in low molar mass media is not generally applicable to polymer systems.

(3) The contribution of monomer, M_1^*, involved in the 'conventional' monomer–excimer interaction scheme increases as a function of chromophore concentration in the polymer relative to that of M_2^*. However, M_1^* decays with an ever increasing rate as the intramolecular fluor concentration increases (as would be expected for excimer state population by migration). The result is that the decay of M_1^* in homopolymer is liable to be too rapid for detection in excitation with pulses of nanosecond duration. This observation would account for the apparent validity of dual exponential fits to the decay of monomer and/or excimer in homopolymers evident in the literature (see for example ref 1–8). However, since the decays observed in homopolymer systems would correspond to interaction of D* and M_2^* care is necessary in interpretation of data derived from observations upon such systems. Support for our assertions is to be found in the observation of subnanosecond decays from a 'third species' in poly (*N*-vinyl carbazole)[33,34].

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