α,α-Dinaphthylpropane: a model for polymer photophysics and a probe for the investigation of macromolecular dynamics?

Tom Annable and Ian Soutar*
The Polymer Centre, School of Physics and Materials, Lancaster University, Lancaster LA1 4YB, UK

and Garry Rumbles
Department of Chemistry, Imperial College of Science, Technology and Medicine, Exhibition Road, London SW7 2AY, UK

(Received 16 June 1992; revised 5 January 1993)

The time-resolved photophysical behaviour of α,α-dinaphthylpropane (αα-DNP) in iso-octane solution at temperatures greater than 30°C is in good agreement with the predictions of Birks kinetics. At temperatures below 30°C the fluorescence decay behaviour is more complex. This has serious implications for the attempted use of αα-DNP (or indeed any other bichromophoric compound) in attempts to probe macromolecular dynamics if '*forced* fits' to dual-exponential functions were to be employed. The complexity of the fluorescence decay behaviour of such a simple model molecule (in which the complication of 'tacticity' and/or energy migration effects are obviated) has implications regarding the interpretation of the photphyiscal behaviour of macromolecules derived from vinyl aromatic monomers.

(Keywords: α,α-dinaphthylpropane; photophysics; polymer dynamics; probe; fluorescence; kinetics)

INTRODUCTION

Amongst the ever-expanding battery of luminescence techniques used in the study of polymer systems (for overviews, see refs. 1 and 2), low-molar-mass bichromophoric species find applications both as models with which to assess the potential for stereoregular forms to exercise a 'ground-state control'[1a,3] over the photophysical characteristics of aromatic marcomolecules and as probes with which to interrogate the relaxational behaviour of bulk polymers[1b]. In this context we have synthesized 1,3-di(1-naphthyl)propane, (α,α-dinaphthylpropane, αα-DNP). We anticipated first using this molecule as a basic photophysical model for polymers and copolymers of 1-vinylnaphthalene and of the 'nearest-neighbour' interactions that dominate the photophysics of such species (cf. refs. 1c, 4 and references therein). Secondly, it was anticipated that αα-DNP might prove useful as a probe of 'free volume' or 'microviscosity' effects in polymer solids and concentrated solutions. However, as we report below, the photophysical behaviour of αα-DNP is more complex than might be expected at 'first sight' or indeed on the basis of behaviour previously reported[5].

EXPERIMENTAL

1,3-Di(1-naphthyl)propane (αα-DNP) and 1,2-di(1-naphthyl)ethane (αα-DNE) were synthesized by the method of Chandross and Dempster[6]. Purification was achieved through multiple recrystallization (from hexane) and vacuum sublimation.

Iso-octane (Aldrich spectrophotometric grade) was distilled immediately prior to use.

Solutions for spectroscopy (10^{-4} M; sufficiently dilute to preclude intermolecular excimer formation) were thoroughly degassed by a series of 'freeze–pump–thaw' cycles prior to sealing under high vacuum.

Steady-state fluorescence spectra were obtained using a Perkin–Elmer MPF3L spectrometer.

Time-resolved fluorescence measurements were made on an Edinburgh Instruments 199 spectrometer operating on the time-correlated single-photon-counting principle. Excitation pulses were generated using a 199F coaxial flashlamp using hydrogen as discharge medium leading to instrumental response functions of between 1.0 and 1.5 ns at f.w.h.m. (dependent upon gas pressure and spark gap) using a Philips XP2020Q photomultiplier tube as detector.

Temperature control was achieved using an Oxford Instruments 1704/DTC-2 cryostat.

RESULTS AND DISCUSSION

Steady-state fluorescence spectra

The fluorescence spectral characteristics of the αα-DNP in iso-octane under conditions of continuous excitation are as expected[6]. The spectra reveal evidence for the existence of two emissive states only, containing emission

---

* To whom correspondence should be addressed

0032-3861/93/173576-06

bands previously ascribed[6] to monomer and excimer, the relative intensities of which, consequent upon the dynamic interchange between these excited states, vary continuously as a function of temperature. The emission profile at any temperature is independent of excitation wavelength and the excitation spectra are typical of the unassociated monomeric naphthyl entity, indicative of the absence of significant ground-state interactions between the naphthyl chromophores.

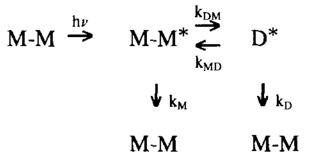
Time-resolved fluorescence data

At temperatures of 30°C and greater, the transient fluorescence decay profiles collected in the spectral regions dominated by monomer ($\lambda_a = 340$ nm) and excimer ($\lambda_a = 420$ nm) emissions could be described adequately ($\chi^2 < 1.3$; Durbin–Watson parameter[7] > 1.75; random distribution of residuals; etc.) by double-exponential functions of the form:

$$i(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) \qquad (1)$$

Furthermore, decays recorded at 420 nm, upon reconvolution with a model function of the form of equation (1) produced fits for which, within experimental error, $A_{1\mathrm{E}}$ and $A_{2\mathrm{E}}$ were virtually equal in magnitude but opposite in sign. In addition, $\lambda_{1\mathrm{E}}$ and $\lambda_{2\mathrm{E}}$ were identical to $\lambda_{1\mathrm{M}}$ and $\lambda_{2\mathrm{M}}$ respectively. (Subscripts E and M denote parameters derived according to equation (1) upon fitting to decays of excimer and monomer respectively.) The fitting parameters were confirmed using a global analysis[8] approach to the treatment of the monomer and excimer data set pairs. Typical data are shown in *Table 1*.

Such behaviour would be consistent with a photophysical reaction scheme (*Scheme 1*) whereby a single excimer moiety is formed from a single monomeric excited state (or at least an ensemble of excited states that behave as a single component, *vide infra*) and is consistent with the dual-exponential decay characteristics reported previously for αα-DNP[5]. The fact that in the excimer decay the magnitude of the negative 'growth' term $A_{1\mathrm{E}}$ is slightly (but consistently) less than $A_{2\mathrm{E}}$ could be ascribed to the fact that at 420 nm a small degree of spectral overlap exists between monomer and excimer emission bands. If, in such an instance, the fractions of monomer and excimer intensities apparent at 420 nm were f_M and f_E respectively, the growth term would be diminished (in magnitude) to $(f_\mathrm{M}A_{1\mathrm{M}} - f_\mathrm{E}A_{1\mathrm{E}})$ relative to an enhanced decaying component of pre-exponential factor $(f_\mathrm{M}A_{2\mathrm{M}} + f_\mathrm{E}A_{2\mathrm{E}})$ compared to the 'expected' values of $A_{1\mathrm{E}}$ and $A_{2\mathrm{E}}$ in the absence of spectral overlap. Alternatively, the deviation from 'ideal' behaviour might indicate that the simple scheme depicting intramolecular excimer formation between single excited-state populations of monomer and dimer species is not *strictly* applicable even in this high-temperature region.



Scheme 1

Table 1 Decay parameters obtained from double-exponential analyses of the high-temperature (⩾30°C) region data from αα-DNP in iso-octane. Units of λ are $10^7\ \mathrm{s}^{-1}$

T(°C)	$A_{1\mathrm{M}}$	$A_{2\mathrm{M}}$	$A_{2\mathrm{E}}/A_{1\mathrm{E}}$	$\lambda_{1\mathrm{M}}$	$\lambda_{2\mathrm{M}}$	$\lambda_{1\mathrm{E}}$	$\lambda_{2\mathrm{E}}$
60	0.46	0.051	−1.01	15.7	4.17	15.8	4.59
50	0.43	0.046	−1.06	14.5	3.90	14.5	4.06
40	0.39	0.030	−1.05	13.0	3.49	12.9	3.66
30	0.41	0.034	−1.03	10.1	2.91	10.1	2.98

Table 2 Kinetic parameters for αα-DNE in iso-octane

T (°C)	τ (ns)	k_M ($10^7\ \mathrm{s}^{-1}$)
60	60.5	1.65
40	62.5	1.60
20	67.9	1.47
0	71.9	1.39
−20	74.6	1.34
−40	75.1	1.33
−70	80.7	1.24
−90	85.1	1.17

It is apparent that the 'conventional' adaptation (*Scheme 1*) of the Birks[9] scheme as applied to intramolecular excimer formation is at least a *plausible* mechanism with which to model the kinetic behaviour observed at temperatures greater than 30°C. Within the limits imposed by adoption of this model, k_DM, the rate coefficient for excimer formation, may be evaluated at a series of temperatures and thence the associated activation energy, E_DM, estimated. The procedure is as follows:

Decay data derived by modelling decays in the region of monomer emission by functions of the form of equation (1) may be used to derive the parameter X defined as[9]:

$$X = \frac{B\lambda_1 + \lambda_2}{B + 1} \qquad (2)$$

where

$$B = A_{1\mathrm{M}}/A_{2\mathrm{M}}$$

Then k_DM may be derived from X as:

$$k_\mathrm{DM} = X - k_\mathrm{M} \qquad (3)$$

provided k_M, the rate constant for excited-state deactivation in the absence of excimer formation, may be independently evaluated. In this work, αα-DNE was considered a suitable 'model compound' from which k_M might be obtained. There is no evidence in either steady-state[6,10] or time-resolved[10] spectra for excimer formation in this compound, and the fluorescence decay has been shown to be well described by a single-exponential function over a range of solvents[10] and temperatures[10b].

Evaluation of X and k_M (cf. *Table 2*) at a series of temperatures reveals the thermal dependence of k_DM and, in turn, allows expression in terms of an 'activation energy', E_DM. The resultant value of 13.0 kJ mol^{-1} is in good agreement with that of 13.8 kJ mol^{-1} reported by Chandross and Dempster[6] on the basis of steady-state fluorescence intensity data analysed on the assumption that *Scheme 1* is applicable. This concordance of results lends credibility to the proposal that *Scheme 1* offers a plausible mechanistic base for modelling of the

Table 3 Kinetic parameters for αα-DNP in iso-octane

T (°C)	k_{DM} ($10^7\,s^{-1}$)	k_{MD} ($10^7\,s^{-1}$)	k_D ($10^7\,s^{-1}$)
60	12.8	0.94	4.34
50	11.9	0.84	4.09
40	10.6	0.65	3.63
30	7.96	0.46	3.00

Table 4 Decay parameters obtained from double-exponential analysis of the low-temperature region data from αα-DNP in iso-octane. Units of λ are $10^7\,s^{-1}$; χ^2_M and χ^2_E refer to analyses of decays recorded at 340 and 420 nm, respectively

T(°C)	λ_{1M}	λ_{2M}	χ^2_M	λ_{1E}	λ_{2E}	χ^2_E
20	6.33	3.02	3.6	7.02	2.13	6.1
10	6.54	3.28	2.8	4.67	1.59	1.5
0	29.1	3.44	4.1	3.76	1.48	4.3
−10	24.4	3.05	3.7	3.31	1.33	4.0
−20	16.5	2.63	4.5	2.99	1.28	5.2
−30	14.3	2.26	4.2	2.94	1.15	3.6
−40	9.09	1.84	4.4	3.18	1.07	3.4
−50	5.75	1.55	2.9	2.47	1.04	2.5

photophysical behaviour of αα-DNP in this, the higher-temperature, regime.

The treatment may be extended to yield an estimate of the binding energy (equal to $E_{DM} - E_{MD}$) for the excimer. A value of 18.5 kJ mol^{-1} was derived for E_{MD} from the thermal dependence of k_{MD}, in turn derived from the dual-exponential fitting (equation (1)) to decays of *monomer* fluorescence as:

$$k_{MD} = \frac{(X - \lambda_2)(\lambda_1 - X)}{k_{DM}} \tag{4}$$

Within the limits of the applicability of *Scheme 1*, this estimate would represent the first published approximation to E_{MD}. (The earlier steady-state measurements[6] did not access the 'high-temperature region' of a Stevens–Ban[11] plot (defined such that $k_{MD} \gg k_D$) necessary in estimation of the binding energy from steady-state data.)

The k_{MD} data may be used, in addition, to estimate k_D via:

$$Y = \lambda_1 + \lambda_2 - X \tag{5}$$

and

$$k_D = Y - k_{MD} \tag{6}$$

The resultant data are listed in *Table 3*.

Deviations from Scheme 1

At temperatures below 30°C the ability (as judged by statistical fitting criteria) of dual-exponential fits to furnish adequate descriptions of the data becomes seriously impaired. More importantly, the resultant data show increasingly marked deviations from the behaviour expected on the basis of the kinetic scheme (*Scheme 1*). In particular $\lambda_{1M} \neq \lambda_{1E}$ and $\lambda_{2M} \neq \lambda_{2E}$. Typical data are shown in *Table 4*. Furthermore, the rate parameters resultant upon implementation of a dual-exponential fitting procedure become increasingly dependent upon the 'fitting range' (i.e. the region of the decay curve analysed), confirming the statistical evidence that dual-exponential model functions are inappropriate for simulation of decay characteristics. (For example, for the decay recorded at 340 nm amd 0°C, τ_{1M} changes from 3.4 to 22.7 ns when fitting over the whole decay, and from 5 ns after the peak of the decay, respectively.)

Clearly, *Scheme 1* is not appropriate for characterization of the photophysical behaviour of the αα-DNP at temperatures lower than 30°C. The deviations from 'predicted' behaviour are shown dramatically when the data are plotted in 'lifetime' format (where $\tau_i = 1/\lambda_i$), and over a more extensive temperature range, as revealed in *Figure 1*. The potential danger in application of dual-exponential fitting to the region of monomer emission *alone* is clearly demonstrated. *Were* the αα-DNP to be used as a probe of medium mobility *and* the dual-exponential fitting deemed adequate (as *might* be the case e.g. in highly scattering media such as micelles or bulk polymers, where whole curve fitting might not be adopted in analysis), conclusions based upon dual-exponential analyses of monomer emission in the lower-temperature region would be misleading in the extreme. The trends in 'monomer lifetimes' for the αα-DNP dispersed in the fluid solvent iso-octane would

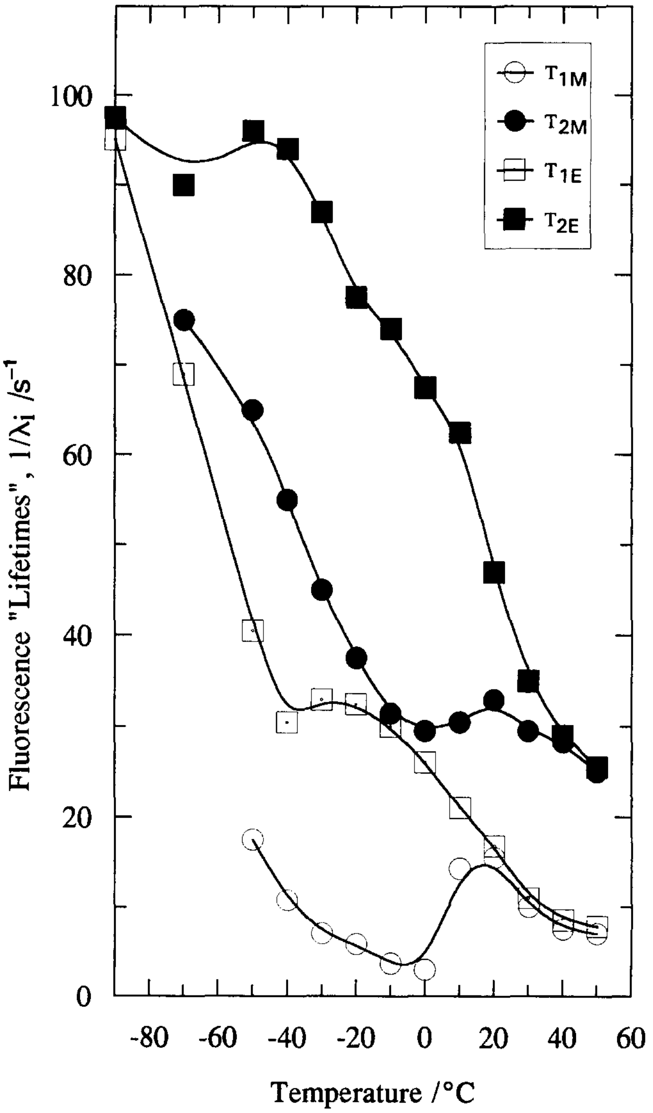


Figure 1 Fluorescence 'lifetimes' of αα-DNP in iso-octane resultant upon dual-exponential fitting of decay data recorded in the regions of monomer (open symbols) and excimer (filled symbols) emissions

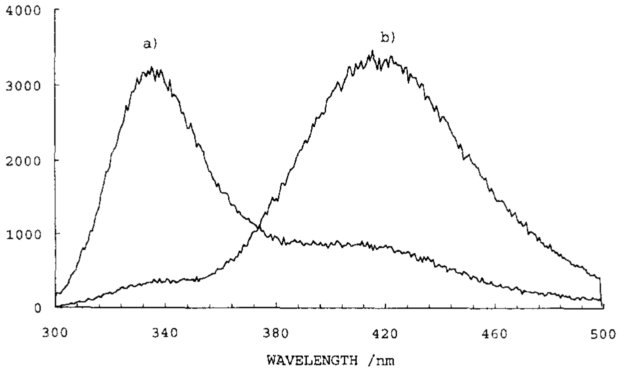


Figure 2 Time-resolved emission spectra of αα-DNP in iso-octane at 25°C recorded using a gate width of 3.3 ns and delays of (a) 0 ns and (b) 30 ns following excitation

imply (assuming the 'validity' of *Scheme 1*) the existence of a physical transition within their local environment. This is untenable since:

(i) No such transition occurs. In the 'transition region' (between ca. 0 and 30°C) the fluid solvent displays no abnormalities in its thermal dependence of viscosity.

(ii) The transition would be anomalous in the extreme. The increase in apparent 'monomer lifetimes' would imply that the medium was exerting, as temperature increases, a stabilizing influence upon the monomeric excited state against the deactivation incurred by the process of intramolecular excimer formation. This would require that the medium, at the microscopic level, becomes more rigid with increasing temperature. Such a conclusion is clearly fallacious in this instance.

It does not matter whether the primary interest in the study of the excimer-forming characteristics of bichromophoric (or indeed polychromophoric) molecules lies in elucidation of the photophysics or in 'harnessing' the photophysics with a view to interrogating the moiety's microenvironment. The importance of accessing the time dependence of the formation of the *target* species (in this case, the excimer) cannot be overstated. The intensity–time profile of the receptor site in any energy transfer/channelling situation contains valuable (often vital) information pertinent to construction of an appropriate mechanistic scheme with which to model the physical behaviour.

Furthermore, as has been stressed by Zachariasse *et al.*[12], evolution of an 'all-encompassing' kinetic scheme requires sampling of the photophysical behaviour over as a broad a temperature range as possible. Allied to such considerations is the obvious requirement to use as high temporal resolution as is available. As described below, the combination of relative intensities and/or decay parameters involved in the deviations from dual-exponential behaviour in the αα-DNP/iso-octane study places severe limitations on the capabilities of a time-resolved system based upon a combination of flashlamp excitation and photomultiplier detection (despite the high-performance temporal characterization of both the 199F and XP2020Q components within such classes of instrumentation).

Given that *Scheme 1* is inappropriate for modelling of the photophysical behaviour of αα-DNP, an alternative must be sought. In the simplest approach, the decay complexity would be rationalized by invoking the presence of an excited-state species additional to those of the monomer and excimer adopted in *Scheme 1*. However, at no temperature is there *spectral* evidence for the existence of such a species. Even under time-resolved examination (cf. *Figure 2*), the only discernible emission bands are those conventionally ascribed to monomer and excimer[6]. Clearly, if a further excited state exists, it must be of similar energy to either M* or D*.

Alternatively, the assumption that the rate coefficients within *Scheme 1* (notably that for excimer formation, k_{DM}) may be properly regarded as time-independent (within the temporal resolution addressed) might be questioned. In the context of the latter consideration, it has been shown that time-dependent effects are manifest within nanosecond and subnanosecond time domains in *inter*molecular excimer formation between short-lived species such as diphenyloxazole (PPO)[13] (in which case the influence of diffusion-controlled terms is enhanced, within the decay profile, as a consequence of the brevity of the excited-state existence) or in relatively long-lived species such as pyrene[14–17]. In the latter case, the influence (and thence relative importance in kinetic analyses) of transient terms within the analytical evaluation may be enhanced by markedly increasing the viscosity of the medium in which the pyrene is dispersed, as in the case of a biological membrane[14]. More recently, Winnik *et al.*[15–17] have shown that distortions of the time profiles of pyrene-based chromophores by time-dependent diffusive terms are significant even in situations of relatively low local viscosities.

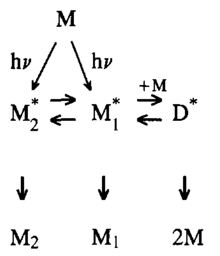
In the case of *intra*molecular excimer formation, two groups of workers[18,19] have drawn attention to the facts that both rotational[18] and energy-migrative[19] sampling of excimer trapping sites within the conformational ensemble might induce transient/diffusive effects, which could negate the assumption that the rate coefficients in adopted kinetic schemes might be regarded as rate 'constants'. In either instance, the simplest approach to the treatment of the effects of such transient processes results, in the absence of excimer dissociation, in a functional form for fluorescence decay, in the region of monomer emission, of the type:

$$i_m(t) = A\exp(-at - bt^{1/2}) \qquad (7)$$

where a and b are constants.

Fortunately, considerations of the effects of energy migration, while germane to those of polymer photophysics as addressed by Fredrickson and Frank[19], are not subject to accountability within the transient luminescence framework of bichromophoric systems. (The chromophores might well interact via energy exchange. However, in the *simplest* analysis such interactions would merely result in 'energy sharing' such as to broaden the 'pool' of chromophores to be accessed by rotational sampling. In a more complex situation, a (linear?) combination of $t^{1/2}$ effects might result from 'one-hop' Förster transfers and rotational sampling. If the combination proved other than linear, the situation would prove more difficult to access than can be accomplished with the present data. In addition, and *more* importantly, it would infer negation of *either* model in description of polymer photophysics since the probability exists for more extensive than intrabichromophoric 'box-type' interactions *in combination with* rotational-sampling effects.) In contrast, the potential for rotational-sampling terms to become manifest in distortion of decay profiles beyond the predictions of *n*-state models which invoke rate constants as interlocutors between states *must* be considered in any treatment of bichromophoric molecular systems. In turn, bichromophoric species should, in principle, provide ideal 'testing grounds' for the importance of rotational-sampling effects within overall photophysical behavioural patterns.

Neglecting, in the first instance, the influence of rotational-sampling perturbations upon the photophysical behaviour of αα-DNP, we may address the possibility of adopting a three-state model in description of the kinetic behaviour observed across the temperature range accessed in the current study. The findings of time-resolved spectroscopy (*vide supra*) would suggest consideration of models involving the interconversion either of two *kinetically* distinct excited monomeric configurations with a single excimer (*Scheme 2*) or of a single monomeric entity with two energetically equivalent excimer states. The existence of two energetically equivalent excimer conformations (*endo* and *exo*) as invoked in explanation of the fluorescence decay complexities apparent in the photophysical 'make-up' of di(1-naphthylmethyl) ether[20] (DNME) is deemed unlikely in the case of αα-DNP as a consequence of the additional steric restraints imposed by the central methylene link in the αα-DNP compared to those induced by the ether linkage of DNME[20]. This argument is reinforced by the observations that photochemical conversions in DNME result in cyclomers of *endo* and *exo* origin[20] whereas αα-DNP produces the *endo* cyclomer in exclusion[21]. On the basis of these premises, it is attractive to test a kinetic model based upon the existence of *two* kinetically distinguishable excited-state monomeric species and *one* excimer (as in *Scheme 2*) against the observed fluorescence decay characteristics. That such a decay model might be invoked is supported by the suggestions of Morawetz *et al.*[22] that the excimer configuration, accessible in the $g^{\pm}g^{\mp}$ conformation, can only be attained from one of the ground-state conformations ($tg^{\pm}$) via a single rotation. Consequently, it is to be assumed that, in general, provided circumstances controlled by temperature and/or solvent interactions do not result in rapid (relative to the lifetime of the electronically excited monomeric states) interconversions between the *monomeric* conformational precursors (tt and $tg^{\pm}$) of the excimer, a three-state situation corresponding to *Scheme 2 should* exist. This, in turn, will produce decay kinetics more complex than those for which dual-exponential modelling would prove adequate.



Scheme 2

Photophysical modelling using *Scheme 2* would predict evolution of decay profiles for monomer, $i_m(t)$, and excimer, $i_d(t)$, of the form:

$$i_m(t) = A_{1M}\exp(-\lambda_1 t) + A_{2M}\exp(-\lambda_2 t) + A_{3M}\exp(-\lambda_3 t) \qquad (8)$$

and

$$i_d(t) = A_{1E}\exp(-\lambda_1 t) + A_{2E}\exp(-\lambda_2 t) + A_{3E}\exp(-\lambda_3 t) \qquad (9)$$

wherein

$$\sum_{i=1}^{3} A_{iE} = 0$$

These equations make provision for extremely rigorous testing of the viability of *Scheme 2*. Not only should the fluorescence decays accumulated in both the regions of monomer and excimer be expected, in general, to require three exponential terms for adequate description; it is required that the decay parameters λ_{iM} should equal their λ_{iE} counterparts. Attempts to test the quality of *Scheme 2* in respect of the low-temperature data met with little success. Although application of three exponential terms improved the statistical quality of the resultant fits over those obtained using dual-exponential models, the kinetic parameters, λ_i, when allowed to vary without constraint (along with the pre-exponential terms A_i) were not concordant between monomer and excimer. At one or two temperatures a 'semi-global' fitting procedure was adopted. In analysis of a 'monomer' decay, one of the decay parameters is constrained to equal that of the most abundant component resolved in 'excimer' decays. A similar approach was adopted in analysis of excimer decays applying constraints according to data retrieved from the region of monomeric emission. Fits, of reasonable quality, were obtained, to which agreement between the λ_i values of the next most prominent component of both monomer and excimer was achieved. Rarely could the λ_i of the minority components of each decay be matched. However, these observations do not automatically infer that triple-exponential fits are inappropriate (which in turn would render *Scheme 2* inapplicable). Two possibilities might exist:

(i) Within *Scheme 2*, 'rotational-sampling' effects might be evident such that the restriction of kinetic analysis to the application of rate *constants* would not be valid[18]. In this instance, the *minimum* complexity that would be encountered in generation of a suitable model function might involve 'expansion' of at least one of the exponential terms to incorporate diffusional terms (of '$t^{1/2}$' or some other dimensionality). The data are simply not of sufficient quality to test such a complexity.

(ii) The resolution within the data may not be sufficient to support the testing of *Scheme 2* in totally unrestrained fits. We believe this to be the case. At most temperatures, the minor component of monomer or excimer decay is of such insignificance (compared to the contributions made by the other two components) as to guarantee that independent recovery of all six λ_i decay components (with sufficient precision to allow strict comparison) would prove difficult. In a similar manner, it would then be logical to assume that the quality of data would be insufficient to allow for the testing of the distortions from double-exponential fitting that diffusional effects would induce.

Since *Scheme 2* seems a logical general mechanistic standpoint in setting the basis for expectation, there is a reason to attempt to determine whether or not its predictions in terms of minimal modelling requirements are observed in the low-temperature region. In order to do this, higher-resolution data than those reported herein are necessary. To this end we intend to re-examine the photophysical behaviour of this system using picosecond laser excitation and microchannel plate detection. The results will be published elsewhere in a manner more concerned with the photophysical characteristics of the problem[23]. However, the current results are of *particular* interest with respect to polymer science:

(i) Intramolecular excimer formation has proven a useful probe of macromolecular dynamics within the polymeric solid state (for reviews, see refs. 1b and 24). In such applications it is common to adopt probes that have been shown to adhere, *strictly*, to Birks[9] kinetics and to base all subsequent analyses on dual-exponential fitting of 'monomer decays'[1b,24]. The key parameter to be extracted from the fluorescence decay data is k_{DM}, the rate parameter governing excimer formation: k_{DM} is, in turn, related to a correlation time τ_c $(=k_{DM}^{-1})$, assumed to be characteristic of the motions of the polymer segments, the *effects* of which are reflected in the probe's dynamics[1b,24]. The validity of such an approach is crucially dependent upon the applicability of the Birks[9] scheme to the photophysical behaviour of the bichromophoric probe *within the matrix of interest*. In applications concerning the use of intramolecular excimer formation to interrogate the local viscosity of microenvironments, it is necessary to employ a bichromophoric probe, the conformational dynamics, and associated photophysics, of which are well understood. (As an example, the *meso* isomers of the diarylpentanes appear to conform to Birks' kinetics in a variety of media[1b,24].) In the instance whereby the probe is to be applied under conditions of viscosity and/or temperature that are markedly different from those in which the photophysical behaviour has been assessed, it is imperative to confirm that the kinetics continue to conform to the Birks' (or other assumed) format. This is especially important at high local viscosities, where it might be expected that transient kinetic terms will become manifest in the conformational behaviour of the molecular probe.

(ii) Since αα-DNP constitutes the simplest possible system for the modelling of the photophysics of naphthalene-containing polymers (being devoid of tacticity and energy-migrative complications), and since it displays complex kinetics (compared to the Birks scheme) over much of the temperature range examined here, it is little wonder that the time-resolved fluorescence behaviour of dilute solutions of polymers containing 1-vinylnaphthalene is as complex as has been reported[4].

CONCLUSIONS

The photophysical behaviour of the model compound αα-DNP is more complex than implied by the Birks[9] scheme. The observed complexity of the fluorescence behaviour of macromolecules in which intramolecular excimer formation is encountered is not, then, surprising.

Great care should be exercised in the use of bichromophoric probes of macromolecular dynamics. The suitability of the kinetic model (e.g. that of Birks[9]) on the basis of which the dynamic information is to be derived should be rigorously tested under the conditions of polymer relaxation to be studied.

The photophysical behaviour of αα-DNP in iso-octane at temperatures less than 30°C is more complex than that which can be accommodated using the Birks[9] scheme. Higher-resolution data than are currently available are required to determine the source of such complexity. Work to achieve this end is currently in progress.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge support by the SERC in the form of equipment grants and a studentship (to TA). The manuscript for this paper was completed when IS was on a brief period of study leave in Melbourne. IS wishes to thank The Royal Society for funding the visit (in part) and Dr K. P. Ghiggino and the University of Melbourne for affording him the facilities and conditions in which to write.

REFERENCES

1 Winnik, M. A. (Ed.) 'Photophysical and Photochemical Tools in Polymer Science' *NATO ASI Ser. C* 1985, **182** and contributions therein from: (a) Vandendriessche, J., Goedeweeck, R., Collart, P. and De Schryver, F. C., p. 225; (b) Bokobza, L. and Monnerie, L., p. 449; and (c) Soutar, I. and Phillips, D., p. 97

2 Hoyle, C. E. and Torkelson, J. M. (Eds.) 'Photophysics of Polymers' *ACS Symp. Ser.* 1987, **358**

3 De Schryver, F. C., Demeyer, K., Van der Auweraer, M. and Quanten, E. *Ann. NY Acad. Sci.* 1981, **366**, 93

4 Roberts, A. J. and Soutar, I. in 'Polymer Photophysics' (Ed. D. Phillips), Chapman and Hall, London, 1985

5 Zachariasse, K. A., Busse, R., Duveneck, G., Macanita, A. and Kühnle, W. reported in ref. 12 as data to be published

6 Chandross, E. A. and Dempster, C. J. *J. Am. Chem. Soc.* 1970, **92**, 3856

7 (a) Durbin, J. and Watson, G. S. *Biometrika* 1950, **37**, 409; (b) Durbin, J. and Watson, G. S. *Biometrika* 1951, **38**, 159

8 Knutson, J. R., Beecham, J. M. and Brand, L. *Chem. Phys. Lett.* 1983, **102**, 501

9 Birks, J. B. 'Photophysics of Aromatic Molecules', Wiley, Chichester, 1970, Ch. 7

10 (a) Rumbles, G. PhD Thesis, University of London, 1984; (b) Annable, T. PhD Thesis, Lancaster University, 1989

11 Stevens, B. and Ban, M. J. *Trans. Faraday. Soc.* 1964, **60**, 1515

12 Zachariasse, K. A., Busse, R., Duveneck, G. and Kühawe, W. *J. Photochem.* 1985, **28**, 237

13 Birch, D. J. S., Dutch, A. D., Imhof, R. E., Nadolski, B. and Soutar, I. *J. Photochem.* 1987, **88**, 239

14 Vanderkooi, J. M. and Callis, J. B. *Biochemistry* 1974, **13**, 4000

15 Martinho, J. M. G. and Winnik, M. A. *J. Phys. Chem.* 1987, **91**, 3640

16 Martinho, J. M. G., Tencer, M., Campos, M. and Winnik, M. A. *Macromolecules* 1989, **22**, 322

17 Martinho, J. M. G., Campos, M., Tencer, M. and Winnik, M. A. *Macromolecules* 1987, **20**, 1582

18 Itagaki, H., Horie, J. and Mita, I. *Macromolecules* 1983, **16**, 1395

19 Fredrickson, G. H. and Frank, C. W. *Macromolecules* 1983, **16**, 572

20 Todesco, R., Gelan, J., Martens, H., Put, J. and De Schryver, F. C. *J. Am. Chem. Soc.* 1981, **103**, 7304

21 Chandross, E. A. and Dempster, C. J. *J. Am. Chem. Soc.* 1970, **92**, 703

22 Goldenberg, M., Emert, J. and Morawetz, H. *J. Am. Chem. Soc.* 1978, **100**, 7171

23 Annable, T., Phillips, D., Rumbles, G. and Soutar, I. work in progress and to be published

24 Bokobza, L. *Prog. Polym. Sci.* 1990, **15**, 337