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Triplet state energy and electron transfer in coronene-doped polymethylmethacrylate

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Abstract

The phosphorescence yield and decay kinetics of coronene in deoxygenated polymethylmethacrylate (PMMA) have been determined over the temperature range 77–300 K. At temperatures below ∼200 K the decays were close to single exponential (lifetime = 9.3 s at 77 K). However, at higher temperatures the decays were best fitted by the function $I(t) = I_0 \exp(at + bt^n)$, where $0.3 < n < 0.4$. This kinetic behaviour is attributed to long range energy transfer via a number of steps following a quasi-one-dimensional random walk from the coronene triplet state to trap sites.

Discontinuities were observed in the temperature dependence of the phosphorescence yield of coronene in polymethylmethacrylate at temperatures of 175 and 255 K, corresponding to the onset of rotations within the polymer molecule.

Keywords: Polymethylmethacrylate; Coronene; Triplet state; Energy transfer; Electron transfer

1. Introduction

With the growth in optical communications and the promise of optical computers there is considerable interest in fabricating optically-active devices from synthetic polymers doped with suitable chromophores. Optical modulators, switches and holographic data recording materials with extremely high data storage capacities have been produced [1–3]. While these devices are mechanically robust and relatively inexpensive, a major impediment to the use of optically-active polymers is their photoinstability which limits operational lifetimes [4]. Valuable studies of the photophysics and photochemistry of the triplet states of some aromatic molecules dispersed in transparent polymers were undertaken some years ago [5–8] and this area merits re-examining in order to understand the processes that contribute to the photodegradation of these polymer systems.

Because the electronic transition from the excited triplet state to the ground singlet state is spin forbidden, the intrinsic lifetimes of the triplet states of aromatic hydrocarbons are as long as several seconds in some cases [9]. However, they are highly reactive species and consequently, in fluid solution they are rapidly quenched, frequently by diffusion-controlled reaction with dissolved oxygen [10].

By contrast, in low-temperature glasses where quenching reactions are restricted by the rigid matrix, the triplet states of many aromatic hydrocarbons are long-lived and the relaxation of the excited triplet to the ground state is apparent as phosphorescence decaying with pure first-order kinetics. Early studies of the triplet state decay kinetics of a number of aromatic hydrocarbons dispersed in solid polymethylmethacrylate (PMMA) at ambient temperature also displayed single exponential decays indicative of true, or pseudo, first-order deactivation processes [5,6]. However, in the less rigid polystyrene matrix, some deviation from a single exponential decay was observed [7,8]. There have also been more recent reports of deviations from single exponential phosphorescence decay kinetics in PMMA. In some cases, the triplet states were present at relatively high concentrations and the faster decaying component was attributed to triplet–triplet annihilation [11–13]. In other cases, the short-lived, non-exponential component in the decays of some triplet states with high energies was explained in terms of endothermic energy transfer to a triplet electronic level [14–16] associated with PMMA and/or residual

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methylmethacrylate (MMA) monomer [17]. For the benzophenone triplet state in PMMA, however, Ebdon et al. [18] reported that quenching by the host did not adequately describe the phosphorescence decay kinetics they observed.

Coronene, which has a triplet state energy lying well below the putative triplet energy of PMMA, has been reported previously to exhibit single exponential phosphorescence decays in PMMA at temperatures ranging from 77 to 300 K [11,12]. However, in the work presented in this paper, the phosphorescence decay of coronene in PMMA was found to deviate from an exponential decay above ∼200 K, close to the T_γ transition temperature of 175 K associated with the onset of α-methyl group rotation [19]. Energy and/or electron transfer is invoked to explain the kinetics of this triplet state relaxation.

2. Experimental details

2.1. Sample preparation

Methylmethacrylate monomer supplied by Nuplex Industries was freed from inhibitor by extraction with 5% NaOH, 20% NaCl solution and dried over magnesium sulfate. Coronene was dissolved in the methylmethacrylate monomer at concentrations of 1.2×10^{-4}, and 3×10^{-5} mol/l.

The solutions were expressed through a 0.2 μm PTFE Millipore filter into glass cuvettes with parallel windows where they were deoxygenated by purging with a gentle stream of argon gas and then sealed. Polymerisation was initiated using 0.1% w/w AIBN and completed with thermal treatment at 40 °C for 48 h followed by a further 12 h at 100 °C.

2.2. Phosphorescence measurements

Coronene phosphorescence was excited with UV radiation from a xenon arc lamp at 325 mm with bandpasses of 20, 10 and 5 nm and a corresponding range of intensities selected by the monochromator of a Hitachi 3010 spectrofluorimeter. This excitation could be interrupted in less than 3×10^{-2} s with a mechanical shutter. The phosphorescence intensity at wavelengths longer than 495 nm, selected by passage through a Schott GG 495 glass filter, was detected by a silicon photodiode and the signal amplified by a Stanford Research Systems SR570 preamplifier and stored using a Hewlett-Packard HP34970A multiplexer. The “half-life” response time of the detection system was $<1 \times 10^{-2}$ s with a sampling rate of 20 Hz and the decays were recorded over periods of 120 s at temperatures between 300 and 77 K. The sample temperatures were monitored with a thermocouple in contact with the sample, and maintained to better than ±1 K using an Oxford Instruments DN1704 cryostat and ITC4 temperature controller. The sample was allowed to come to thermal equilibrium for 20 min before each phosphorescence decay measurement.

2.3. Data analysis

The phosphorescence decays were fitted to a number of functions, including a single exponential, multiple exponentials, and the so-called “stretched” exponential:

$$I(t) = I_0 \exp(-at - bt^n), \quad \text{where } 0 < n < 1 \qquad (1)$$

The suitability of the fit was determined from both the magnitude and distribution of the residuals. The relative total phosphorescence intensities, I_{tot}, were determined by integration of the intensities of each decay from time $t = 0.5$ to 60 s.

3. Results

3.1. Decay kinetics

Between 300 and ∼200 K a single exponential did not adequately describe the decay data. Rather, the most appropriate function was that given in Eq. (1); the parameters obtained for these fits are given in Table 1. Below ∼200 K, the phosphorescence decay was most successfully fitted by a single exponential with a rate coefficient similar to that of the longer-lived component observed at 300 K. While the residuals are not evenly distributed about zero for these single exponentials, the fits were not improved by the introduction of a greater number of adjustable parameters, either as a sum of two exponentials or as a fractional exponent. Typical fits at temperatures of 300 and 100 K, and the associated distributions of residuals are shown in Figs. 1 and 2, respectively.

As seen in Table 1, the phosphorescence decay kinetics were essentially independent of coronene concentration from 0.3×10^{-4} to 1.2×10^{-4} mol/l. The decay kinetics were also independent of the excitation intensity corresponding to 20, 10 and 5 nm slit widths.

3.2. Phosphorescence intensity temperature dependence

Fig. 3 shows the dependence of coronene phosphorescence intensity on temperature. Three linear segments in the

Table 1
The best-fit values of parameters in Eq. (1) for the phosphorescence decay kinetics of coronene in PMMA

Concentration (mol/l)	Temperature (K)	a	b	n
1.2×10^{-4}	301	0.135	0.26	0.38
	277	0.131	0.17	0.34
	243	0.124	0.10	0.31
	221	0.121	0.09	0.22
	122	0.109	0	0
	101	0.108	0	0
	79	0.109	0	0
3×10^{-5}	296	0.133	0.27	0.40
	79	0.110	0	0
Representative variation	±1	±2	±10	±20

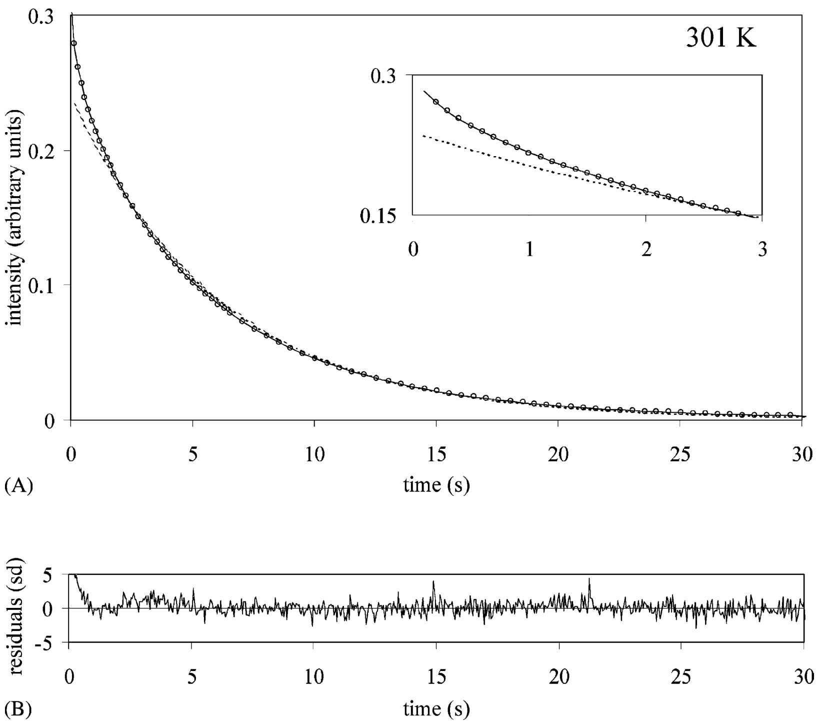

Fig. 1. (A) Fits to the phosphorescence decay of coronene in PMMA at 301 K. ○, Experimental data (number of points reduced for clarity); ——, fit to a "stretched exponential"; dotted line, fit to a single exponential. Inset: expended view of the first 3 s of decay. (B) Distribution of residuals for the "stretched" exponential fit (in units of standard deviation).

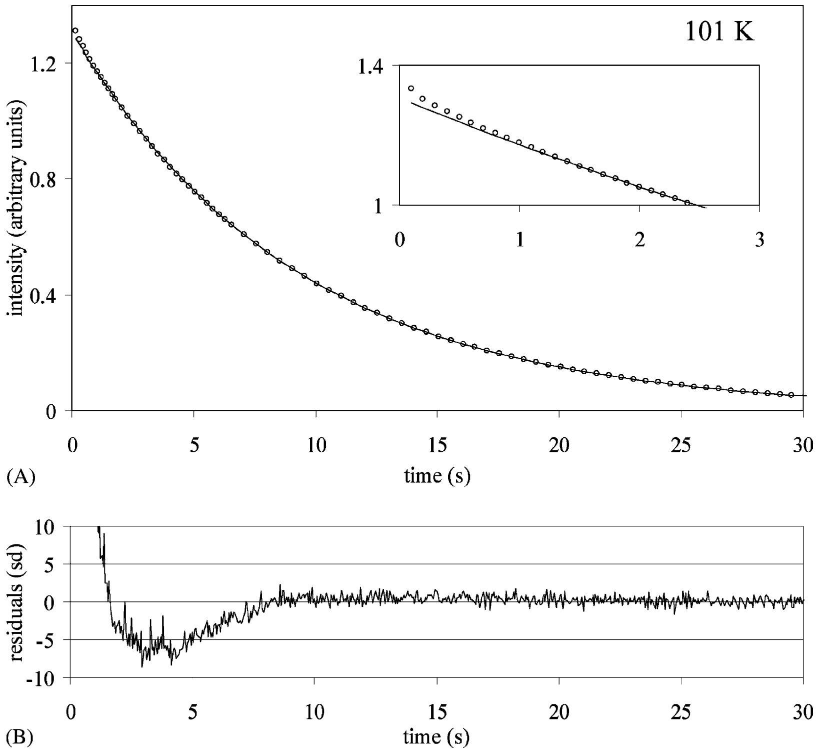

Fig. 2. (A) Fits to the phosphorescence decay of coronene in PMMA at 101 K. ○, Experimental data (number of points reduced for clarity); ——, fit to a single exponential. Inset: expended view of the first 3 s of decay. (B) Distribution of residuals for the single exponential fit (in units of standard deviation).

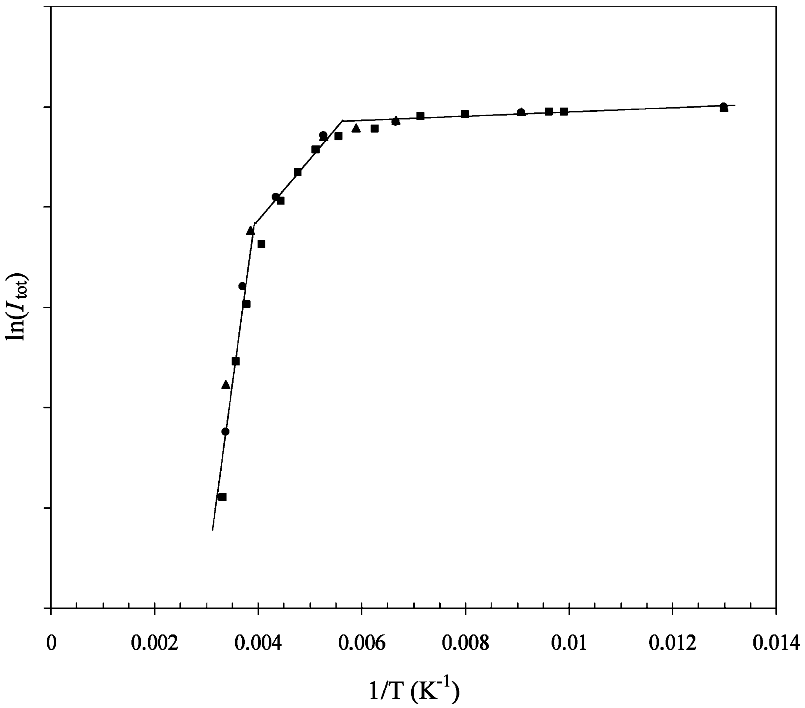

Fig. 3. The temperature dependence of the coronene phosphorescence intensity in PMMA. The different symbols represent data from different samples. The lines represent linear fits to subsets of the data.

plot of ln(I_{tot}) versus T^{-1} are evident, with discontinuities in slope occurring at ∼175 and ∼255 K.

4. Discussion

4.1. Phosphorescence decay kinetics

Horie and Mita interpret the decay of the triplet state phosphorescence of benzophenone in PMMA at temperatures above ∼240 K in terms of a quenching reactions between the triplet state and polymer ester groups that undergo diffusion-controlled encounters [14,15]. Based on the Smoluchowski theory of diffusion-controlled reactions, a decay law for emission from an excited state quenched by such a process is

$$I(t) = I_0 \exp\left[-\left(\frac{t}{\tau_0}\right) - B\left(\frac{t}{\tau_0}\right)^{1/2}\right] \qquad (2)$$

where τ_0 is the intrinsic lifetime of the excited state and I_0 and B are adjustable parameters [20]. Ebdon et al. [18] found that the phosphorescence of benzophenone in PMMA above 250 K could only be satisfactorily fitted to Eq. (2), if all three parameters I_0, B and τ_0 were varied. They argued that such a fit was over-parameterized because τ_0, being the intrinsic lifetime, should be invariant. Similarly, in the present work, the phosphorescence decay of coronene in PMMA at temperatures above ∼200 K could not be fitted adequately by Eq. (2). The decay could only be fitted with the fractional exponent varying between 0.3 and 0.4 rather than set at 0.5. This is interpreted as indicating that diffusion-controlled collisional quenching by an element of the PMMA polymer is not responsible for the time-dependent rate coefficient of the decay of coronene phosphorescence in this matrix.

In addition to the diffusion-controlled quenching of electronic excited states, which requires molecular encounters, deactivation can also occur by energy and electron transfer over distances greater than the sum of the encounter radii in rigid matrices [21]. An alternative explanation of the time-dependent rate coefficient proposed by MacCallum's group for the observed decay of benzophenone phosphorescence in PMMA was triplet–triplet annihilation with the triplet exciton migrating through the polymer chain by way of intermediary polymer triplet states [11,12], e.g.

$$^3\mathrm{B}_1^* + \mathrm{P}_1 \rightarrow {}^3\mathrm{P}_1^* + \mathrm{B}_1 \rightarrow {}^3\mathrm{P}_2^* \rightarrow {}^3\mathrm{P}_3^* + {}^3\mathrm{B}_2^* \rightarrow \mathrm{P}_3 + {}^1\mathrm{B}_2^*$$

where P represents the polymer, and B represents benzophenone. However, in the measurements reported here, the rate coefficient did not exhibit the square dependence on exciting intensity expected of triplet–triplet annihilation. This mechanism for coronene triplet state quenching can also be dismissed on thermodynamic grounds because the energy of the coronene triplet state, 229 kJ/mol, is substantially lower than that of the PMMA triplet state, $^3\mathrm{P}^*$, estimated to be 297 kJ/mol [17].

A single step Förster resonance energy transfer with three degrees of spatial freedom is inversely proportional to separation distance, r^6, and has been shown to have a rate coefficient of the same form as Eq. (2), [22]. Theoretical treatments by Kauffmann et al. [23] and others provide for a number of energy-transfer jumps down through successively lower sites via a quasi-one-dimensional pathway until it reaches a trap site. According to this model the fractional time dependence of the rate coefficient, $\exp(-t/\tau_0)^n$ has values $0 < n < 1$. Although originally derived to deal with singlet excitation migration, it has also been applied to triplet–triplet energy transport [24]. The dispersion parameter, n, is largely a phenomenological quantity and assumes a value near 0.5 when the exciton migration is considered to be a random walk along a one-dimensional pathway between an energetically random set of hopping sites with a Gaussian distribution which in turn is a result of the spatial disorder of the sites. The separation between the hopping sites, again dependent on their spatial arrangement, also impacts on the dispersion parameter [24,25]. Thus, statistical fluctuations and other irregularities in the spatial arrangement of the exciton transit sites affect the value of n. It is these irregularities in the dynamics of exciton migration that can account for values of $0.3 < n < 0.4$ observed for the time dependant decay rate coefficient for the triplet state of coronene in PMMA observed in this work.

The period over which the t^n component dominates the decay of the triplet state of coronene is a consequence of, and comparable with, the rate of transfer of triplet state energy from one site to the next. Dexter triplet state energy transfer is a concerted electron exchange between a triplet donor, and acceptor [26]. Examples of such electron transfer over long distances are well known in molecular systems with donors and acceptors linked by sigma bonds. This electron transport, although substantially slower than when there is orbital overlap between the donor acceptor, occurs by quantum mechanical tunneling through the linking sigma bonds which, in effect, “stretch” the molecular orbitals of the donor and acceptor [21,27–29]. As such, the rate of electron transfer decreases exponentially with increasing donor–acceptor separation. Compared with other triplet-state non-single exponential decays in polymers that have been reported previously [5–8,13–18], the t^n character of the rate coefficient persists for a long period at 300 K, and is only apparent because the coronene triplet state is so long-lived, i.e. a nominal lifetime of 7.4 s. Because of this, the time-dependant, polymer-mediated dissipation of excitation energy can compete with the intrinsic radiative and non-radiative relaxation of this triplet state. The rate of long range electron transfer is also dependent on the free energy difference between the electron donor and acceptor and it therefore decreases exponentially with temperature. As a consequence of this, at low temperatures the rate of exciton hopping will be too slow to make a significant contribution to triplet state relaxation and the decay rate coefficient for coronene phosphorescence is then dominated by the triplet state’s intrinsic relaxation, i.e. the decay is essentially first order.

4.2. *Temperature dependence of phosphorescence intensity*

The integrated phosphorescence intensity, I_{tot}, is directly proportional to the ratio of the radiative rate constant for triplet state deactivation to the sum of the radiative and non-radiative rate constants. Since the radiative relaxation is independent of temperature, a plot of $\ln I_{\text{tot}}$ against $1/T$ is effectively an Arrhenius plot for non-radiative relaxation and the activation energies associated with the gradients of such plots are for non-radiative processes.

A number of workers have reported discontinuities in the Arrhenius plots of phosphorescence intensity against reciprocal temperature for a number of different triplet states dispersed in PMMA [16,19,30]. In each case, the discontinuities occurred at approximately the same temperatures, an observation also supported by the results presented here. It is concluded therefore, that these discontinuities are inherent properties of the host PMMA matrix rather than of the solute triplet states. The discontinuity at 255 K is attributed to the onset of PMMA ester group rotation (T_β) while that at 175 K (T_γ) is associated with rotation of the α-methyl group of the polymer chain [19]. Such movements of the host polymer can accommodate the changes in triplet states geometry/vibrations that are required for non-radiative relaxation to their ground states, which is consistent with the observation that the coronene phosphorescence decays are only non-single exponential at temperatures above T_γ.

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