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Luminescence studies of polymer matrices: 1. Phosphorescence of benzophenone dispersed in poly(methyl methacrylate)

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The photophysical behaviour of benzophenone (BP) in poly(methyl methacrylate) (PMMA) has been studied as a function of temperature. Time-resolved phosphorescence data reveal that at no temperature between 77 and 420 K can the decay behaviour of the triplet state of BP in PMMA be described adequately by a single exponential function. This contrasts with the phosphorescence behaviour of BP in low temperature, low molecular mass, glassy matrices and that reported previously for BP dissolved in PMMA at temperatures below the onset of the β relaxation of the polymer. The complexity of the phosphorescence decay kinetics of the BP/PMMA system increases at temperatures greater than that of the β transition of the polymer host. This has been rationalized in terms of the onset of enhanced energy transfer interactions between the BP triplet excited state and the PMMA solvent, as proposed earlier. However, the function derived previously on the basis of diffusion-controlled quenching of the triplet state of BP by the PMMA host, did not model, adequately, the time-resolved phosphorescence data obtained in the current study. In this respect, the form of the quenching influence exerted by the polymer matrix upon the photophysical behaviour of the BP solute remains to be explained. Notwithstanding the absence of a complete rationalization of the influence of the PMMA host upon the photophysical behaviour of the BP guest, it has been shown that both the intensity of phosphorescence emitted by the BP and its mean decay time provide means whereby transitions within the polymer matrix can be detected. In this respect the data are not equivalent: the lifetime data 'sense' the presence of the α' transition (at ~345 K) of the PMMA. This transition is not apparent in the temperature dependence of intensity data which, in common with the lifetime data, are sensitive to the onset of both the γ and β transitions of the polymer. The relevance of the data in respect of establishing phosphor/polymer combinations for application as phosphorescent coding media is discussed.

(Keywords: phosphorescence; benzophenone; poly(methyl methacrylate))

INTRODUCTION

Polymer matrices have been regarded, over many years, as 'ambient temperature alternatives' to low temperature organic glasses, as media for isolation of dispersed species for phosphorescence measurements[1–5]. In this context, the influence of oxygen diffusion within the polymer matrix was recognized as a key factor in determining the amount of phosphorescence observable from a given solute. It was also realized that physical transitions within the matrix[2,6,7] play a role in controlling the intensity of phosphorescence from dissolved triplet guests. Interactions, through energy transfer, between solute and polymer host were also cited[4] as being of importance in determining the thermal dependence of the luminescence of triplet guests.

Guillet and co-workers[8,9], studying a series of polymers containing both ketonic and naphthyl derivatives as phosphorescent species, further quantified the extents to which the rate of deactivation of excited triplet states is dependent upon the physical behaviour of the host matrix. 'Arrhenius' plots of $\ln I_p$ as a function of T^{-1} revealed the existence of transitions within the polymer matrix, the positions of which were independent of the chromophore employed. In such studies[6–9], increases in the rate of translational diffusion of O_2, as quencher of the triplet state, dominated the thermal dependence of I_p.

Rutherford and Soutar[10,11] have shown (in reports primarily directed towards the use of phosphorescence anisotropy measurements in studying macromolecular relaxation processes) that both phosphorescence intensity and lifetime data, whether from covalently bound labels or dispersed probes, can be used to detect transitions in solid polymers even in the absence of oxygen. It was noted, however, that the temperatures at which transitions became apparent were not readily predicted on the basis of an 'expected test frequency' as estimated from the lifetime of the excited state. (This observation is consistent with the fact that Guillet and co-workers[8,9] detected a given transition, in a particular polymer, in

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the same range of T, regardless of the interrogating chromophore used.) The limitations of phosphorescence intensity measurements in the study of solid-state transition phenomena were further demonstrated by Beavan and Phillips[12,13]. Using 'enone' phosphors, it was shown that, in addition to the transitions which might be revealed through oxygen diffusion, discontinuities appeared in the 'Arrhenius' plots for I_p, as a result of intramolecular relaxations within the conformational behaviour of the probes themselves[12,13].

If luminescence techniques are to be used in studies of relaxation phenomena in polymers, there is no doubt that the most powerful means of addressing the problem is that of luminescence anisotropy (depolarization)[10,11,14]. The fluorescence-based experiment yields information on polymer motions in the high frequency domain, characterized, typically, by motions occurring on a timescale of tens of nanoseconds[14,15]. The phosphorescence anisotropy experiment, although more difficult to perform, offers the opportunity to investigate, in a direct fashion, molecular mobilities and relaxation mechanisms extant at lower frequencies. The main advantage of the phosphorescence anisotropy approach is that it allows the investigator the opportunity to assess the importance of the various macromolecular motions, upon timescales which allow resolution of the different processes that contribute to the overall relaxation profile of a given polymer in the solid state[10,11,15,16]. On the other hand, if the primary objective is to study the diffusion of oxygen (or some other quencher) through a solid polymer, phosphorescence intensity studies are capable of providing such information[17].

Phosphorescence studies of the photophysical behaviour of certain solutes, dispersed in polymeric media, are of significance for different reasons. In such investigations, the possibility of energy transfer from the dispersed triplet state to the polymeric host has assumed a dominant role in the interpretation of the thermal dependence of the phosphorescence from the solute[4,18-24]. Studies of the phosphorescence behaviour of benzophenone (BP) have featured strongly in such investigations[18-27].

In the absence of solute–polymer interactions, the phosphorescence of BP would be characterized by a first-order decay law. MacCallum and co-workers[18-20] and Horie *et al.*[21-24] have noted that the phosphorescence decay of BP dispersed in poly(methyl methacrylate) (PMMA) follows such a single exponential decay law both below the onset temperature of the β relaxation of the polymer and above its glass transition temperature (T_g). At intermediate temperatures, marked deviations from single exponential decay behaviour were observed[18-24]. Similar temperature dependences of the phosphorescence decay profile of BP dispersed in other acrylic polymers[24] and in both polystyrene[25] and polycarbonate[25] have been reported.

The complexities of the phosphorescence decay of BP in PMMA have attracted a variety of interpretations. MacCallum and co-workers[18-20] invoked involvement of a triplet–triplet (T–T) annihilation mechanism, in which the polymer matrix itself participated both as an acceptor of energy from the benzophenone triplet and as a medium for the triplet energy migration, to account for the non-exponential behaviour at room temperature. On the other hand, Horie *et al.*[21-24] attributed the non-exponential decay to a single photon process whereby intermolecular dynamic quenching of the benzophenone triplet by ester groups in the side chain of the PMMA occurs. They reasoned that non-exponential behaviour was not observed above T_g since a steady state of quenching moieties became available to the chromophore above this relaxation temperature. Horie and Mita[23] excluded the occurrence of T–T annihilation on the grounds that the non-exponential decay profile at 20°C was independent of irradiation intensity.

Salmassi and Schnabel[26] measured the decay of phosphorescence and triplet absorption of benzophenone in PMMA under the high intensity irradiation from a frequency doubled ruby laser pulse at 347 nm. The initial triplet concentration, $[T]_0$, amounted to 6×10^{-4} M, compared with $<6 \times 10^{-6}$ M achieved by Horie *et al.*[21-24] using a nitrogen laser pulse. Under these high intensity conditions, a single triplet decay mode, following first-order kinetics, was observed[26] at $T < 150$ K and at $T > 410$ K. Two distinct modes of triplet decay were observed[26] in the intermediate temperature range: a fast first-order process, the lifetime (4 μs at 295 K) being independent of the initial triplet concentration, and a slow second-order process, the first half-lifetime being proportional to $[T]_0^{-1}$. It was concluded from these results that T–T annihilation is an important deactivation route under high intensity irradiation at temperatures between T_g and T_γ, where the rotation of the α-methyl groups of the PMMA commences.

Of relevance to the current study are a number of other investigations of the photophysical behaviour of BP in polymer matrices. Morantz and Wigley[27,28] reported non-exponential decay behaviour from various aromatic ketone triplet states dispersed in PMMA at room temperature. It was suggested that the quenching process might include physical and chemical mechanisms. Whilst the importance of triplet energy transfer processes was not excluded, it was considered that hydrogen abstraction played an important role in the deactivation. Horie and co-workers[29,30] have also observed non-exponential decay behaviour in the phosphorescence of benzophenone dispersed in poly(vinyl alcohol) (PVA) within a temperature range between T_γ (-100°C) and T_g (85°C). Below T_γ and above T_g the decays were adequately described by a single exponential function. The origin of the non-exponential decay was attributed to diffusion-controlled hydrogen abstraction by the benzophenone triplet from the polymer matrix with a time-dependent rate coefficient. It was argued that the occurrence of non-exponential decays in PVA, where there is no possibility of triplet energy migration, is further evidence for the absence of the T–T annihilation mechanism in the phosphorescence decay of benzophenone in polymer matrices.

Given the uncertainties apparent in the interpretation of the triplet photophysics of BP in polymeric hosts, it was considered appropriate that the excited-state behaviour of this species in PMMA be examined further under lower levels of incident excitation flux than those employed in previous studies using pulsed laser radiation sources[18-24,26]. The importance of phosphorescent bis-arylketone derivatives in postal coding applications (see, for example, ref. 31) added a technological perspective to the work. The results of our recent investigations in this area are discussed below.

EXPERIMENTAL

Materials

BP (BDH) was purified by multiple recrystallization from ethanol, followed by sublimation under high vacuum.

Ethanol, methanol, methylcyclohexane and n-pentane (all Aldrich spectrophotometric grades) were used as supplied in making mixed solvent matrices for spectroscopy.

PMMA, used as the polymeric solvent for BP in spectroscopic studies, was prepared by free radical solution (50 wt% in monomer) polymerization of methyl methacrylate (MMA) (Aldrich) in benzene (Aldrich) at 60°C under high vacuum, using 2,2'-azobisisobutyronitrile (AIBN) as initiator. Degrees of conversion were limited to less than 10%. Prior to polymerization, the MMA monomer was treated (several applications) with 5% NaOH to remove inhibitor, washed with distilled water until the washings were neutral to litmus, and fractionally distilled under high vacuum. The resultant PMMA ($\bar{M}_n = 490\,000$; $PD = 1.9$ as estimated by size exclusion chromatography) was purified by multiple reprecipitation from dichloromethane (Aldrich spectrophotometric grade) into rapidly stirred methanol.

Mixed solvent systems, used as low temperature glasses for phosphorescence spectroscopy, were thoroughly degassed by repeated 'freeze–pump–thaw' cycles, prior to sealing in quartz tubes under high vacuum. PMMA films for spectroscopy, containing BP, were cast from dichloromethane (Aldrich spectrophotometric grade). Traces of solvent were removed, following drying at reduced pressure at room temperature, by heating *in vacuo* at steadily increased temperatures to a final temperature of 120°C, over a period of several days. The films were subsequently sealed under high vacuum for spectroscopic analysis.

Instrumentation

Phosphorescence spectra and intensity measurements were recorded using Perkin–Elmer MPF-3L and LS50 spectrometers. Time-resolved phosphorescence measurements were made using a specially constructed spectrometer, based upon an earlier design, which has been previously described[16,32]: the instrument incorporated an optics and monochromation system commissioned from Edinburgh Instruments, and conventional MCA (Inotech 5300) and NIM (Ortec) unit technology. The excitation source was a pulsed Xe arc lamp (Chelsea Instruments W3101) triggered using a Lyons pulse generator (type PG71N) which sends a synchronized, delayed signal to initiate a scaling sweep in the MCA. An EMI 7863 (D307) red-sensitive, low noise photomultiplier tube was used as detector. Temperature control of samples was achieved using an Oxford Instruments Cryostat (DN 1754 and ITC 4 controller). The sample temperature was allowed to stabilize for a minimum of 20 min (dependent upon the difference in temperature increments) prior to each phosphorescence measurement.

RESULTS AND DISCUSSION

Dependence of phosphorescence intensity of BP, dispersed in PMMA, on temperature

The temperature dependence of the intensity of phosphorescence (I_p) from BP dispersed in PMMA (1.7 wt% with respect to polymer) is shown in *Figure 1*, in the form of a plot of $\ln I_p$ as a function of T^{-1}. In the fashion adopted by previous workers[8–11], the onset temperatures of enhanced deactivation of the triplet state of BP are conveniently revealed by approximation of the dependences of $\ln I_p$ upon T^{-1}, in the various polymer host-controlled regions of behaviour, to linear trends. The 'transition temperatures' of ~170 and 240 K agree, within experimental error, with those estimated by Rutherford and Soutar[11] from phosphorescence intensity data for naphthalene species both simply dispersed in the PMMA matrix and covalently bound, at low concentrations, as phosphorescent 'ester group' or 'main chain' labels. These discontinuities in observed phosphorescence behaviour correspond to the β and γ transitions of PMMA[11].

The observation above reinforces previous assertions[10,11,16] that the realization of increased deactivation of the phosphorescent 'reporting chromophore' is controlled solely by the polymer matrix and its inherent relaxation mechanisms, regardless of the lifetime of the phosphorescent species used to interrogate the polymer system: the excited-state lifetime of the BP 'probe', used in the current work, differs by almost three orders of magnitude from that of the naphthyl species previously[11] adopted (see below). The absence of a shift in transition temperature that might have been expected on the basis of 'time–temperature equivalence' is significant, and emphasizes the essentially vicarious nature of the sampling of polymer relaxation effects by emission intensity measurements[11,16]. Further evidence for this 'dominance of matrix control' is to be found in a previous report[11] in which it was demonstrated that the marked reductions in phosphorescence lifetime which could be induced, at elevated temperatures, in an acenaphthyl-labelled sample of PMMA by the introduction of O_2, as quencher, did *not* affect the observed sub-glass transition temperatures of the matrix.

In the absence of bimolecular quenching the quantum yield of phosphorescence, ϕ_p, may be written as

$$\phi_p = \phi_{TM}(k_{PT}/k_{PT} + k_{IT}) \qquad (1)$$

where ϕ_{TM} is the quantum yield of intersystem crossing, k_{PT} is the rate constant governing the phosphorescence of

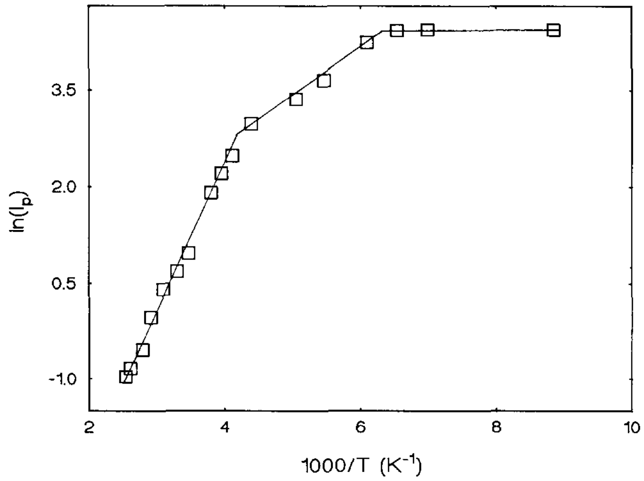

Figure 1 'Arrhenius' presentation of BP phosphorescence intensity data

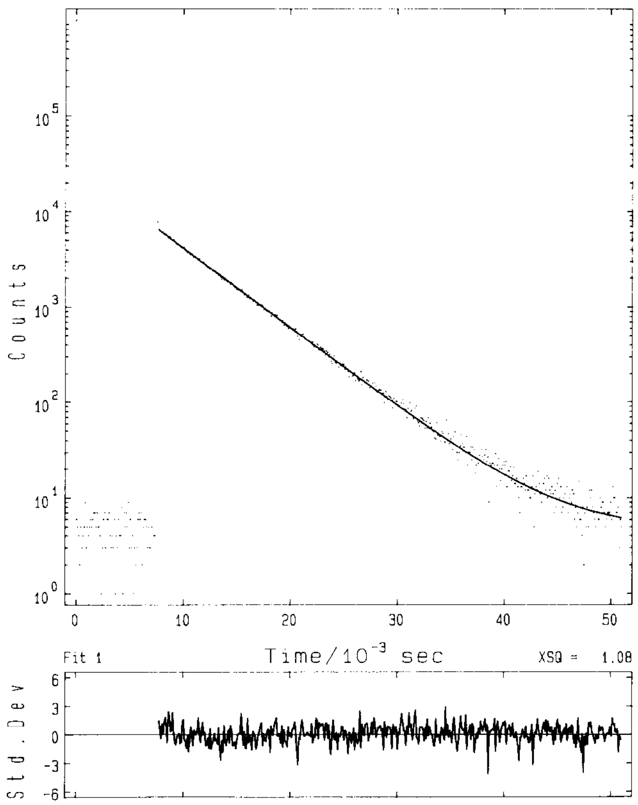

Figure 2 Decay of phosphorescence from BP dispersed in methylcyclohexane/n-pentane (4:1 v/v) glass at 77 K

the triplet state and k_{IT} is that of its 'internal deactivation'. (The nomenclature is that of Birks[33].) In the absence of spectral changes, the temperature dependence of ϕ_p may be monitored through phosphorescence intensity, I_p, measurements. Separation of the non-radiative deactivation rate constant, k_{IT}, into temperature-independent and thermally activated components furnishes the expression[7,8]

$$1/I_p - 1/I_0 = A\exp(-E/RT) \qquad (2)$$

where I_0 is the limiting intensity of phosphorescence as $T \to 0$ (effectively, that obtained at 77 K for most chromophore/polymer combinations). In the instance whereby I_p is negligible compared with I_0, 'Arrhenius' plots of $\ln I_p$ *versus* T^{-1} (as applied, for example, by Somersall *et al.*[8]) would yield an 'activation parameter' characteristic of the temperature dependence of the phosphorescence behaviour. Reference to *Figure 1* reveals that such a condition does not apply in the current work. Meaningful estimation of the 'activation parameter', E, of equation (2) would require that we plot $\ln(I_p^{-1} - I_0^{-1})$ as a function of T^{-1}. We have not adopted such an approach here since we have shown earlier[10,11,16] that the resultant E data are *not* related directly to the relaxation characteristics of the matrix (but reflect merely the effects of the macromolecular relaxations upon the stability of the excited triplet states dispersed in the polymer glass).

From a technological viewpoint, wherein the interest might lie in achieving as much intensity as possible from organic phosphors dispersed in thin polymer films, the implications of *Figure 1* are clear: even under the optimized conditions in which the polymer film is sealed under high vacuum, the onset of the secondary (β and γ) relaxations of the polymer produces a net reduction in phosphorescence intensity of almost two orders of magnitude when comparing I_p at ambient temperature with that obtained below T_γ ($\sim$160 K). The magnitude of the thermal dependence of I_p at temperatures around and below ambient would be enhanced in the presence of a diffusive triplet quencher such as oxygen.

Time-resolved phosphorescence data

The phosphorescence decays of BP dissolved (10^{-4} M) in either of the two low molar mass glasses used in this work are well described, at 77 K, by a single exponential decay law ($\chi^2 < 1.3$; residuals randomly distributed about zero; etc.). *Figure 2* shows a typical example of a phosphorescence decay, single exponential 'best fit' to the data, and the associated distribution of residuals. The decay profiles (and thence resultant lifetime, τ_p) were invariant with the wavelengths of both BP excitation and emission. For the methylcyclohexane/n-pentane (4:1 by volume) glass at 77 K, τ_p was estimated as 5.18 ± 0.05 ms. In the more polar ethanol/methanol (9:1 by volume) glass at 77 K, τ_p increased to 5.66 ± 0.05 ms. These values are in reasonable agreement with those reported by Porter and Suppan[34] for the lifetime of the BP triplet state in cyclohexane and isopropanol glasses at 77 K.

In contrast, at no temperature in the range studied (77–420 K) could the phosphorescence decays of BP in PMMA be regarded as strictly mono-exponential according to the criteria that we have adopted (see above) in gauging adequacy of fit to the decay data. *Figure 3a* shows the best fit achievable using a single exponential function to describe the decay of phosphorescence at 77 K. Compared with decays of BP phosphorescence in low molar mass glasses at this temperature, the value of χ^2 increases (to 2.2) and a non-random distribution of the residuals results. A marked improvement in the 'goodness of fit', to an acceptable level, is obtained when the data are modelled using a double exponential function (as illustrated in *Figure 3b*): $\chi^2 = 1.2$ and the residuals are randomly distributed. In view of this observation, all BP phosphorescences were analysed in terms of multi-exponential functions of the form

$$i_p(t) = \sum_{i=1}^{n} A_i \exp(-t/\tau_i) \qquad (3)$$

Such fitting procedures have been adopted to parameterize the decay data and to reveal the temperature ranges in which the complexity of the photophysical behaviour of the BP changes: it is not implied that the resultant 'lifetimes', τ_i, have any physical association with the existence of distinct emitting species within the distribution of BP excited states that exists within the matrix.

Double exponential functions provide statistically adequate fits to the BP phosphorescences observed in the temperature range 77–220 K (see *Table 1*). At temperatures between $\sim$250 and 390 K, the decay behaviour (as judged by the value of χ^2) becomes more complex. A minimum of three exponential terms must be applied, in equation (3), to model adequately the 'true' time dependence, $i_p(t)$, of the observed phosphorescence intensity, $I_p(t)$. This increase in complexity of the decay characteristics is also evident in the increasing curvature of plots of $\ln I_p$ as a function of time (*Figure 4*) as the

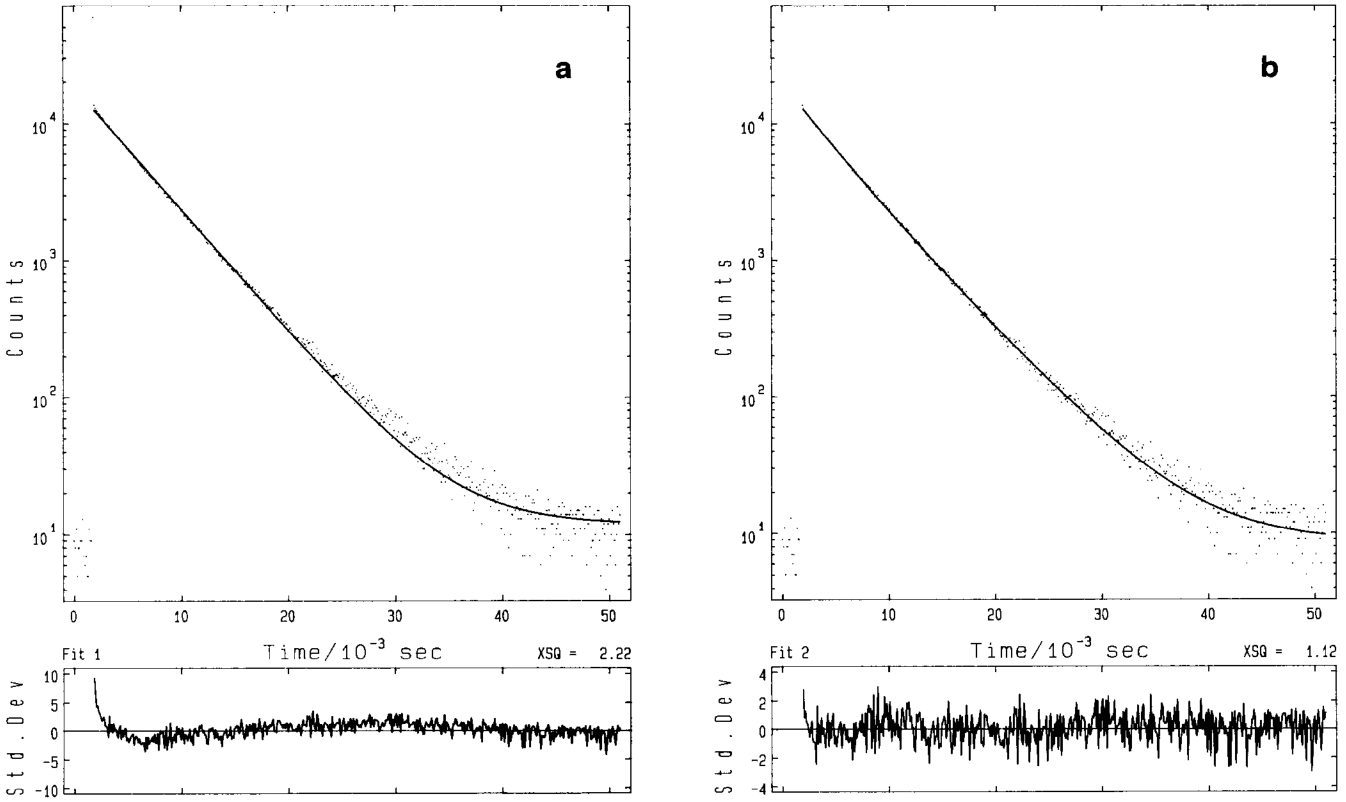

Figure 3 Decay of phosphorescence from BP dispersed in PMMA at 77 K, fitted using single exponential (a) and double exponential (b) model functions

Table 1 Variations in the complexity of the decay kinetics of BP phosphorescence in PMMA with change in temperature

Temp. (K)	τ_1 (ms)[a]	τ_2 (ms)[a,b]	τ_3 (ms)[b]	χ^2
77	5.4 (75.3%)	3.3		1.1
100	5.3 (79.4%)	3.1		1.1
120	5.2 (77.1%)	3.1		1.2
150	5.0 (82.2%)	2.7		1.2
170	4.7 (87.3%)	2.0		1.2
190	4.5 (82.0%)	2.1		1.1
220	4.1 (80.4%)	1.5		1.3
220	4.4 (58.4%)	2.6 (36.4%)	0.8	1.2
250	3.5 (70.9%)	1.2		1.8
250	4.0 (46%)	2.1 (46%)	0.6	1.2
270	2.9 (66%)	0.8		2.0
270	3.4 (42.3%)	1.6 (47.5%)	0.4	1.0
295	1.9 (63%)	0.4		5.4
295	2.2 (46.3%)	0.7 (43.8%)	0.2	1.4
310	1.5 (55%)	0.3		2.9
310	2.0 (31.5%)	0.7 (51%)	0.2	1.1
340	0.8 (45.8%)	0.2		2.1
340	1.1 (21.8%)	0.4 (52.9%)	[0.01]	1.2
370	0.2 (48.4%)	0.1		2.0
370	0.6 (11.8%)	0.1 (63.4%)	[0.04]	1.4
390	0.1 (70.4%)	[0.03]		1.4
390	0.3 (25.2%)	[0.08] (61.2%)	[0.02]	0.9
410	0.1 (88%)	[0.02]		1.3
420	0.1 (93%)	[0.02]		1.0

[a] Figures in parentheses indicate relative contributions to the overall phosphorescence intensity

[b] Figures in square brackets indicate the 'nominal' value for τ_i which results from analysis using the minimum of exponential terms in order to achieve an acceptable value for χ^2. Quotation to two decimal places does not indicate an implied accuracy for these lifetimes (the lifetimes are essentially 'zero' within experimental error)

temperature is increased. The temperature (~250 K) at which this increase in the complexity of decay of BP phosphorescence occurs, corresponds well with that marking the onset of the β relaxation in PMMA, as revealed in the thermal dependence of the steady-state I_p (as discussed in the previous section). In this region, in which motion of the ester group of the polymer becomes activated on the timescale of the experiment, Horie *et al.*[21,22] have reported that the BP phosphorescence exhibits deviations from mono-exponential behaviour. Therefore, the current data are in broad agreement with those of both Horie *et al.*[21,22] and MacCallum and co-workers[20] in that changes in decay complexity occur.

Both Horie *et al.*[21,22] and MacCallum and co-workers[20] ascribe the observed deviations from exponential behaviour to a quenching of the triplet excited state of the BP, $^3B^*$, by the PMMA, P, as depicted in equation (4):

$$^3B^* + P \rightarrow B + {}^3P^* \qquad (4)$$

The major difference in the interpretations of the observed decay behaviour proposed by these two groups concerns the relative importance of the nature of the quenching process, represented by equation (4), and the role played by the polymer-borne triplet, $^3P^*$. Horie *et al.*[21,22] have invoked the ester groups of the polymer as diffusive quenchers of $^3B^*$. On the basis of the theory of time-dependent diffusion-controlled kinetics, they have

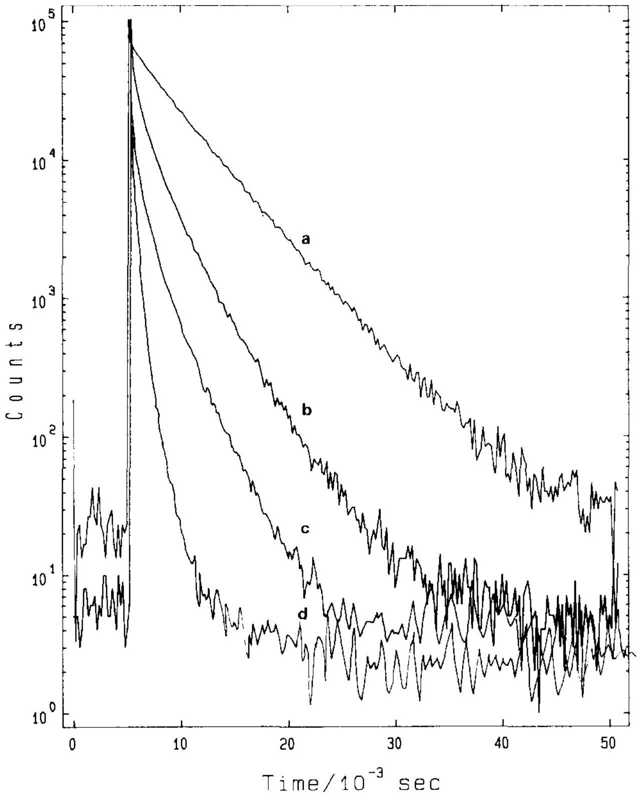

Figure 4 Dependence of decays of phosphorescence from BP dispersed in PMMA on temperature: (a) 150 K; (b) 270 K; (c) 295 K; (d) 340 K

derived a function of the form

$$i_p(t) = B\exp[-t/\tau - C(-t/\tau)^{1/2}] \qquad (5)$$

to describe the kinetics of the decay of $^3B^*$. MacCallum and co-workers[20], on the other hand, have proposed that, following the quenching step, energy may migrate within the polymer matrix as depicted in equation (6):

$$^3P^* + P \rightarrow P + {}^3P^* \qquad (6)$$

It was argued that, at high triplet concentrations, T–T annihilation would be possible if the mobile triplet, $^3P^*$, were to encounter a benzophenone triplet, $^3B^*$. Thus,

$$^3P^* + {}^3B^* \rightarrow P + {}^1B^* \qquad (7)$$

The decay kinetics of $^3B^*$ would consequently be complicated by the influence of this biphotonic quenching step.

In the current work we have established that the decay behaviour of the BP/PMMA system is independent of the photon flux incident upon the sample under the conditions of excitation employed here. Consequently, the 'MacCallum[18,20] mechanism' does not play a significant role, in this instance, in determining the complexities apparent in the decay kinetics of the BP phosphorescence. Clearly, T–T annihilation might provide an important route to deactivation of $^3B^*$ at the higher excited state concentrations achieved using a laser as excitation source.

Attempts to model the phosphorescence decay behaviour of BP in PMMA in the higher temperature region (e.g. between 25 and 350 K) using the functional form of equation (5) as proposed by Horie *et al.*[21,22] met with little success. Using equation (5) and allowing the fitting parameters B, C and τ unconstrained variation, does generate fits of good 'statistical quality' to the decay data. However, the question must be asked as to whether the resultant fitting parameters have any physical significance, or whether they merely serve to parameterize the decay in a fashion similar to the application of dual- and triple-exponential models. As an example, application of this model function 'fitting the BP phosphorescence decay obtained at 290 K' produced an estimate for τ of 42 ms. Since τ represents the lifetime of $^3B^*$ in the absence of the energy transfer processes leading to evolution of equation (5), it is not reasonable to suppose that retrieval of a value for τ which is an order of magnitude greater than the lifetime observed for the BP excited state in PMMA at 77 K (see below) is meaningful.

In attempts to test further the applicability of equation (5) in description of the decay kinetics of BP phosphorescence in PMMA, we tried to aid convergence, during fitting, to a unique solution through setting τ to a predetermined 'fixed' value: cross-correlations between the fitting parameters B, C and τ will hinder generation of a unique solution if all are freely varied. Since τ is unique to the system under investigation at any given temperature, independent estimation of its value is difficult. In the present study, an estimated value for τ was obtained as follows. It was assumed that the temperature dependence of the excited-state lifetime of BP/PMMA observed at temperatures below 200 K would be maintained if quenching induced by the motion of ester groups in the matrix did not occur following the onset of the β relaxation of the polymer. Accordingly, a plot of $\ln(1/\langle\tau\rangle)$ *versus* T^{-1} was extrapolated from $T < T_\beta$ to the temperature (e.g. 290 K) at which the phosphorescence data to be analysed were accumulated. [$\langle\tau\rangle$ is the average lifetime of phosphorescence and can be estimated either from 'forced' fits to an exponential decay law at $T < T_\beta$ or from dual-exponential fits using equation (8)

$$\langle\tau\rangle = \frac{\sum A_i\tau_i^2}{\sum A_i\tau_i} \qquad (8)$$

(Concordant estimates of $\langle\tau\rangle$ were achieved in these approaches.)] The value of the 'unquenched lifetime' obtained at 290 K, for example, was 4.5 ns. When the phosphorescence data at 290 K were re-analysed varying the parameters B and C in equation (5) whilst 'fixing' the value of τ to 4.5 ms, the model function failed to produce a fit of adequate quality, as illustrated in *Figure 5*. Consequently, it has to be concluded that, as far as the current work is concerned, the model of Horie *et al.*[20,21] does not help promote understanding of the complexities of the phosphorescence of BP in PMMA.

Consideration of the transient phosphorescence data obtained for the BP/PMMA system in the current work reveals that the photophysical behaviour has yet to be satisfactorily interpreted: our results indicate that under the scrutiny afforded by modern statistical analysis techniques, the time-resolved phosphorescence of BP dispersed in PMMA is not described properly by a simple first-order decay law even at temperatures below T_β. (It has to be noted, however, that this observation, which appears to be at variance with earlier reports[18-24], is based upon application of extremely rigorous criteria of adequacy of fit: the deviations from single exponential behaviour in the lowest temperature range accessed are

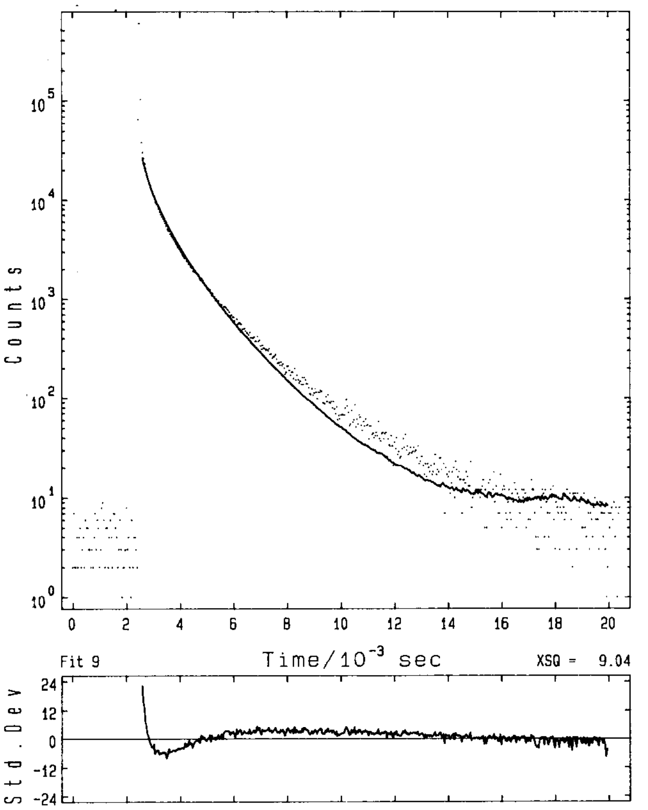

Figure 5 Decay of phosphorescence from BP dispersed in PMMA at 340 K and 'best fit' obtained using equation (5) (see text)

small, but significant, compared with the decay characteristics of BP in low molar mass glasses at 77 K.) Clearly, the onset of the β relaxation of the PMMA solvent promotes deactivation of the triplet excited state of BP. This is likely to result (as noted by both MacCallum and co-workers[18-20] and Horie *et al.*[21,22]) from energy transfer interactions with the polymeric host. Although the functional form evolved by Horie *et al.*[21,22] does not provide adequate descriptions of the decay data obtained in the current work, this does not imply that the suggested *molecular* mechanism for the interaction lacks substance: it implies merely that proper mathematical modelling of the quenching of $^3B^*$ by the polymer has yet to be achieved. Considering the complexity of the system, it may be that the latter is an unattainable goal using a function from which useful parameters can be extracted in matching to empirical photophysical data.

Temperature dependence of $\langle\tau\rangle$

The temperature dependence of $\langle\tau\rangle$ [calculated using equation (8)] is governed by the physical nature of the host matrix and complements the use of phosphorescence intensity data in revealing transitions within the PMMA glass. Following the approach of Rutherford and Soutar[10,11], $\ln\langle\tau\rangle^{-1}$ is plotted as a function of T^{-1} in *Figure 6*. Changes in the temperature dependence of $\langle\tau\rangle$ are apparent in this plot at ~160 and 245 K, in good agreement with the transition temperatures derived using I_p data and which we ascribed to the onset of the γ and β relaxations of the matrix, respectively (as described above). These estimates of T_γ and T_β are in agreement also with those made by Rutherford and Soutar[11] using phosphorescence lifetime data for a series of naphthalene species either dispersed as probes or incorporated as covalently bound labels in PMMA matrices.

As shown in *Figure 6*, $\langle\tau\rangle$ for BP displays a measurable temperature dependence below T_β and shows a slight dependence upon T even below T_γ. These observations contrast with those of Horie *et al.*[21,22], who reported no lifetime dependence on temperature of the BP triplet state at temperatures below T_β. The current data indicate that the decays of BP phosphorescence are not strictly exponential below T_β and imply that some form of interaction occurs with the polymer matrix even at the lowest temperatures accessed. In this respect, the data differ from those obtained when benzoyl naphthalene is used as a phosphorescent probe of the PMMA system[35]. The value of 4.9 ms obtained for $\langle\tau\rangle$ at 77 K in PMMA is comparable with published values of 4.6 ms (ref. 36), 4.8 ms (ref. 20) and 5.0 ms (refs 21, 22), and approaches that of 5.2 ms observed in the less polar of the two low molar mass glasses employed in this work.

Within the limitations of an approach in which the various regions of an Arrhenius presentation of the $\langle\tau\rangle$ data are divided into a series of linear sections, a further 'transition' is apparent above T_β, at ~313 K. In a similar treatment of the temperature dependence of the lifetime of the phosphorescence from an acenaphthylene-labelled PMMA[11], an analogous transition was observed at ~345 K. This transition temperature corresponded to that at which motion of the polymer backbone, as sensed by the acenaphthylene label, first became evident in phosphorescence depolarization measurements[11] and was ascribed[11] to the onset of the α' transition[37,38] of the PMMA. Interestingly, the phosphorescence intensity of the BP does not reveal the existence of this transition (cf. *Figure 1*).

Finally, it can be noted that neither the I_p nor the $\langle\tau\rangle$ data obtained from BP reveal the existence of the glass (α) transition of the PMMA host, in the temperature range (up to ~420 K) accessed in the current work. Horie *et al.*[22], using BP as the phosphorescent probe, reported changes in the photophysical behaviour of the solute at ~380 K, promoted by the onset of the glass transition at this temperature. In other phosphorescence studies using benzoyl naphthalene[35] as the phosphorescent solute, T_g was also detectable at ~380 K. Using both copolymerized 1-vinylnaphthalene and acenaphthylene

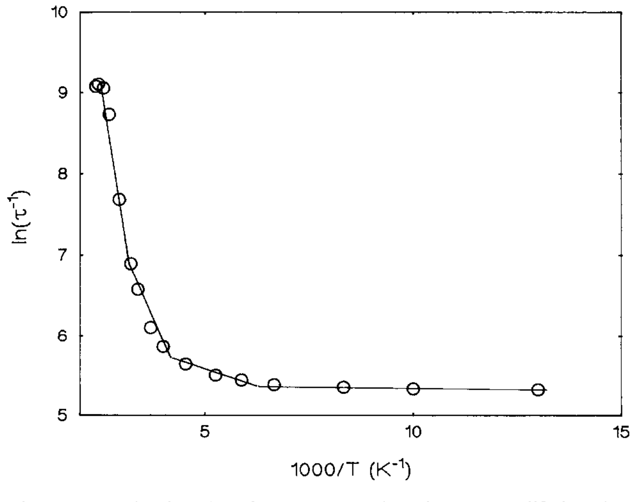

Figure 6 Arrhenius plot of BP/PMMA phosphorescence lifetime data

labels, Rutherford and Soutar[11] also detected the glass transition of PMMA in the temperature range 365–380 K in phosphorescence depolarization experiments. The reasons for the insensitivity of the I_p data, in the current work, to the onset of the α relaxation of the polymer are not clear, but do not affect the primary objective of this work, i.e. to investigate the factors which govern the phosphorescence of BP (and, therefore, of related chromophores) in PMMA (and, thence, in other polymer matrices) at temperatures close to ambient. In the case of our $\langle\tau\rangle$ data, it is less surprising that T_α is not apparent: the limit of temporal resolution of our current phosphorescence apparatus is $\sim$0.1 ms. The 'plateau' which occurs in the $\langle\tau\rangle$ data at around 420 K (and above) (cf. *Figure 6*) results from the lifetime of the BP triplet state attaining this value. The data of Horie and Mita[21] would indicate that the lifetime of the BP triplet state should be below that of our limit of temporal resolution at temperatures in excess of $\sim$400 K. However, were our transient data to have been sensitive to a transition at 380–400 K, we should have expected to observe limitations imposed by the time resolution of our experiments at temperatures lower than those evident from *Figure 6*.

CONCLUSIONS

The photophysical behaviour of the triplet state of BP, in the BP/PMMA system, is markedly dependent upon the physical behaviour of the PMMA matrix.

Both phosphorescence intensity and lifetime information can be used to detect transitions in a polymeric host: in the case of BP the temperature dependences of I_p and 'τ_p' provide complementary (but not equivalent) means of probing the relaxation behaviour of the polymeric host.

Interactions between the PMMA matrix and the BP solute are evident at all temperatures greater than 77 K.

1. At no temperature can the phosphorescence decay of the BP be regarded as truly exponential.
2. Deviations from mono-exponential decay behaviour increase as the T of the matrix is increased.
3. The complexities in the observed phosphorescence decays might originate in processes involving energy transfer from the BP to its polymeric host. If this is the case, it is apparent that the dominant mechanism of the transfer has yet to be understood and/or modelled. The function proposed by Horie *et al.*[21,22] and based upon time-dependent diffusional control was not capable of describing the observed luminescence behaviour of the BP/PMMA system, in an adequate fashion.
4. PMMA might be an adequate matrix for studying the triplet-state spectroscopies of dissolved chromophores: it *cannot* be regarded as an inert matrix in this respect (and, therefore, cannot be regarded as a simple alternative to low T, low molar mass glasses for phosphorescence spectroscopy).

Phosphorescent solute/polymer combinations are used as 'coding' materials in a broad range of applications. Optimization of performance at ambient temperature requires selection of a solute/polymer combination in which interactions between the luminescent state of the solute and its polymeric host, and the solubility and/or diffusion of adventitious quenchers such as oxygen, are minimized. Studies of these factors constitute part of a continuing research programme, the results of which will be reported in some of the future publications in this series.

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