Photochemistry of Phenothiazine Sensitizers in Poly(methyl methacrylate) Films[1]

Mónica Barra,[2] Robert W. Redmond,[3] Mary Tedd Allen,[4] Gary S. Calabrese,*[,4] Roger Sinta,[4] and J. C. Scaiano*[,2,3]

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5, Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Ontario, Canada K1A 0R6, and Shipley Company, Inc., 455 Forest Street, Marlboro, Massachusetts 01752

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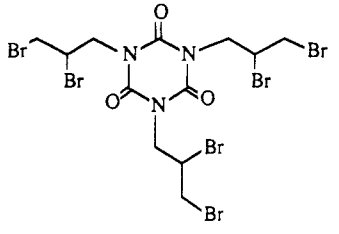
ABSTRACT: The photochemistry of phenothiazine (PH0) and 7*H*-benzo[*c*]phenothiazine (PH2) in poly(methyl methacrylate) (PMMA) films has been studied by using several time-resolved laser techniques. The luminescence properties of PH0 or PH2 used as dopants in PMMA films closely resemble those observed for the respective molecules in solution. Both PH0 and PH2 exhibit long-lived triplet–triplet absorptions; this behavior is shown to result from a very slow rate of oxygen diffusion within the polymer film. The occurrence of electron transfer to the photosensitive acid generator (PAG) 1,3,5-tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (1) was demonstrated through emission and transient absorption experiments involving PH0- or PH2-doped PMMA films; this reaction was conclusively demonstrated to involve only singlet processes.

Introduction

Over the years, a number of photoresist systems have been developed for the manufacture of microelectronics which rely on photochemically induced changes in the solubility of thin polymer films.[5,6] A new family of photoresists have recently been developed having the unusual property of being both negative-tone (irradiated regions become insoluble) and developable in aqueous media. These systems contain phenolic resins, thermally assisted acid-activated cross-linking agents, and a photosensitive acid generator (PAG). Non-metal-containing PAGs are preferred in the electronics industry due to the possibility of device contamination by metal ions. In this regard, some of the most effective are halogen-containing organic compounds, especially those that have halogen atoms bound to saturated carbon centers and which are essentially transparent at wavelengths >300 nm. An example of this type of PAG is 1,3,5-tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (compound 1).[7,8]



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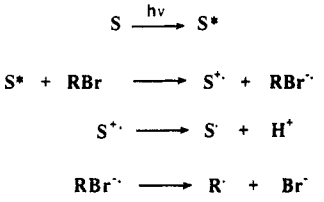
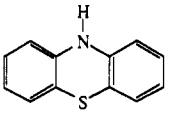
For certain applications, however, it would be advantageous to extend the photosensitivity of these systems to the 365- (i-line) and 436-nm (g-line) emissions from the mercury lamp. One approach would be to incorporate an appropriate chromophore into the structure of the PAG or, alternatively, to incorporate a photosensitizer in the photoresist which is capable of activating the PAG. The latter approach is currently being explored in formulations containing 1 as the PAG and that utilize phenothiazines as photosensitizers.[8] For this system the mechanism of sensitization is believed to be that of Scheme I. The acid that is generated from this sequence initiates the cross-linking reaction resulting in the insolubilization of the exposed areas of the resist, giving rise to a negative image after development.

Scheme I

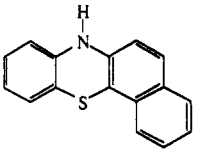


In a recent publication we examined the photophysical and photochemical properties of a range of phenothiazine derivatives in dilute diglyme solutions.[7] We concluded that under these experimental conditions the mechanism of sensitization for phenothiazines when used in conjunction with 1 involves electron transfer, mainly from the excited singlet state of the sensitizer; only in a few cases was a contribution from the excited triplet state observed.

Obviously, a photophysical study in dilute solution, while giving valuable fundamental information, does not correspond very well with the situation in polymer films. Technical applications frequently require resist films thicknesses of the order of a few micrometers, doped with concentrations of sensitizer which are orders of magnitude greater than those used in the solution experiments.[5] To gain more insight into the parameters that determine the usefulness of phenothiazines as photosensitizers in photoresist applications and to simulate more accurately the actual situation, the sensitization mechanism for phenothiazine (PH0), an efficient i-line photosensitizer, and 7*H*-



PH0



PH2

benzo[*c*]phenothiazine (PH2), a candidate for i- or g-line sensitization, has been investigated in polymer films by using several time-resolved laser techniques. The polymer of choice was poly(methyl methacrylate) (PMMA), which

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provides a reasonably inert polymer matrix in which the photoacid-generating system can be studied in the absence of significant chemical processes involving the matrix. The results of this exploratory study are presented here.

Experimental Section

Phenothiazine (PH0) was obtained from Aldrich, and 7*H*-benzo[*c*]phenothiazine (PH2) was synthesized according to literature procedures.[9] PH0 and PH2 were recrystallized from toluene; in the case of PH2 this was followed by purification on a spinning silica plate using a 1:1 ethyl acetate/hexane mixture as eluant. Diglyme [bis(2-methoxyethyl) ether], 1,3,5-tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (compound 1), medium molecular weight poly(methyl methacrylate) with a glass transition temperature (T_g) of 110 °C, and 2-acetonaphthone (2-AP) were all purchased from Aldrich and used as received. 2-AP was employed in some control experiments.

PMMA films of varying thickness and composition were prepared as follows. To a solution of PMMA in diglyme (25% w/w) was added solid PH0 or PH2 and 1 in the desired amounts (concentrations of sensitizer and compound 1 are given in terms of percent weight with respect to weight of PMMA). A few drops of these solutions were then added at one end of a 3 cm × 10 cm quartz plate and drawn out into a film by using a wet film, wire-wound applicator rod. Different film thicknesses were obtained by using Meier rods of different wire diameters purchased from the Paul N. Gardner Co. Inc., Pompano Beach, FL. The coated plates were then baked to dryness in an oven at 90 °C for 30 min.

For all spectroscopic measurements the film thicknesses (equivalent to optical path length) and sensitizer concentrations were selected to give sample absorbances in the 0.3–0.5 range at the laser excitation wavelength. Excitation was achieved by using either a Molectron UV-24 nitrogen laser (λ = 337 nm, ~10 ns, <10 mJ/pulse) or a frequency-tripled Lumonics Hyperyag 750 Nd/YAG laser (λ = 355 nm, ~8 ns, attenuated to ~10 mJ/pulse). The laser flash photolysis system with either photomultiplier[10,11] or optical multichannel analyzer (OMA) detection[12] has been described previously. The laser dose could be adjusted with a set of calibrated neutral density filters. For emission work the signals were collected and transmitted to the entrance slit of the spectrograph attached to the gated OMA by using a quartz fiber optic cable, as previously described.[13] Sample plates could be mounted in a stepper motor-driven holder which moved the plate a determined distance following each laser pulse, thus ensuring irradiation of a fresh portion of the film with each shot. Unless otherwise specified, all measurements were carried out on air-equilibrated films.

Ground-state absorption spectra of films were measured by using a Hewlett-Packard 8451A UV–visible diode array spectrophotometer.

Results

Sample Preparation and Absorption Properties. Using a constant sensitizer absorbance at wet film thicknesses from 20 to 350 μm allowed us to study concentration effects on the ground state of the sensitizer. On drying of the films, the thickness is decreased by a factor of ca. 4. This results in concentrations of sensitizer up to 0.3 M in the film which are as much as 3 orders of magnitude higher than in our previous solution study. Under such conditions we were concerned with possible phenomena due to ground-state aggregation of the sensitizers. However, even at the highest sensitizer loading, we observed no apparent change in the absorption spectrum, which proved to be identical with that observed in dilute solution. A Beer–Lambert behavior was observed on the basis of concentrations calculated according to film thickness and known sensitizer loadings. Therefore, no evidence for sensitizer aggregation or ground-state interaction was obtained from the UV–visible absorption measurements.

Emission Studies. The films were irradiated by 337-nm laser pulses, and the emission was monitored with the OMA detector. The duration of the detection gate can be varied from a minimum of 20 ns with the trigger of the opening gate being variable with respect to the laser pulse, in 10-ns steps. Unless otherwise stated, the minimum gate duration of 20 ns was employed. By integration of the emission spectra measured at different delay times the rate constant of the various emission processes could be estimated. The OMA lifetime measurements carry significant error when the excited-state lifetime and the detection gate are of comparable duration (vide infra).

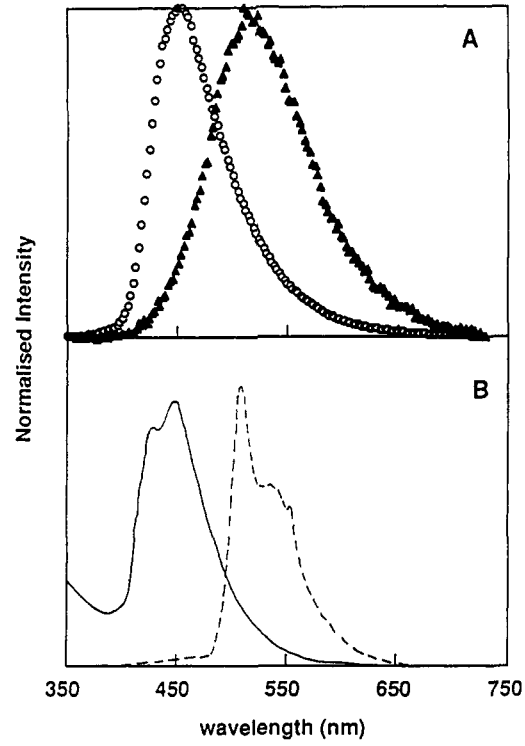

Figure 1. (A) Gated emission spectra of 0.32% PH0 in PMMA film at delays of 10 (○) and 50 ns (▲) following the 337-nm laser pulse. (B) Steady-state emission spectra of PH0 in diglyme at room temperature (solid line) and in ethanol glass at 77 K (broken line, 20-μs delay between excitation pulse and detection in fluorometer).

In the case of PH0 the emission observed following laser excitation was dependent on the delay of the detection gate with respect to the laser, the concentration of PH0, and the presence of added 1. In the absence of 1 the time dependence of the emission spectrum can be illustrated in Figure 1A. Immediately following the laser pulse, a very short-lived blue emission was observed with λ_{max} = 450 nm, in good agreement with the fluorescence in solution, as shown in Figure 1B. After 50 ns, the fluorescence has virtually disappeared and a weaker green emission with λ_{max} = 520 nm is observed. This "green" emission shows a two-component decay with intense fast (nanosecond) and very weak slow (microsecond) contributions. The emission spectrum appears to be similar for both fast and slow components. The slow component agrees well with the low-temperature phosphorescence of PH0 (cf. Figure 1B) and with the lifetime determined from laser flash photolysis (vide infra).

The lifetime of the "fast" green emission obtained from OMA measurements was shown to be dependent on the concentration of PH0, as shown in Table I. The plot of k_{obs} against [PH0], depicted in Figure 2, shows a nonlinear behavior at higher [PH0]; this nonlinearity can be, at least partly, explained by the inaccuracy in determining the values of k_{obs} at high concentrations of PH0. These values are based on a plot of the log of the integrated

Table I
Dependence of Fast Green Emission on the Concentration of PH0

% PH0	k_{obs}, 10^7 s^{-1}	% PH0	k_{obs}, 10^7 s^{-1}
0.31	6.97	1.18	13.3
0.59	7.43	5.97	23.5
0.79	8.88		

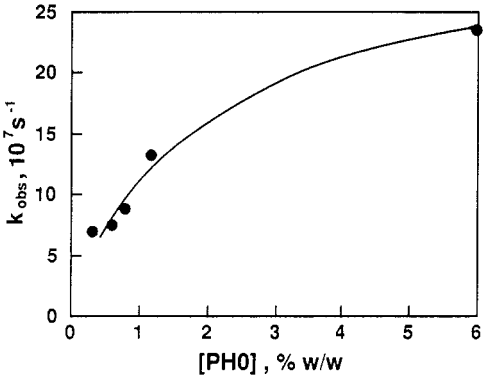

Figure 2. Dependence of observed decay rate constant (k_{obs}) for fast green emission of PH0 on the PH0 concentration in PMMA films.

Table II
Dependence of Emission Yields and Lifetime on [1]

% 1 (w/w)	A_0/A (PH0, 450 nm)	A_0/A (PH0, 520 nm)	k_{obs}/k^0_{obs} (PH0, 520 nm)	A_0/A (PH2, 505 nm)
0	1	1	1	1
2.6	1.53	10.4	1.32	1.06
5.2	1.70	18.9	1.48	1.20
10.3	2.37	20.3	not measd	1.42
14.6				1.67
16.5	3.83	24.3	1.64	

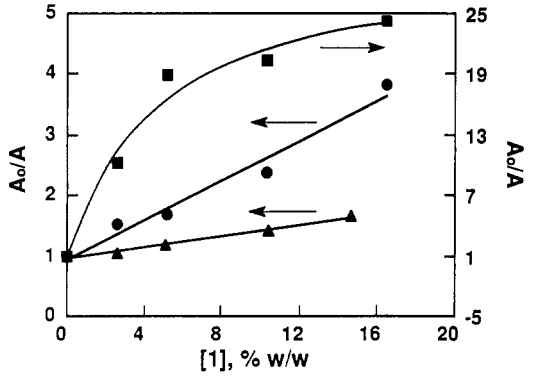

Figure 3. Dependence of emission yields on concentration of 1 in PMMA films: (●) PH0 fluorescence; (■) PH0 fast green emission; (▲) PH2 fluorescence.

intensity as a function of the delay between the laser and the detection gate; significant error is introduced when these two values are comparable, as is the case for a significant part of the data in Figure 2. The lifetime of the fast green emission was also found to decrease in the presence of added 1 (see Table II). Figure 3 shows the reduction of the fluorescence and fast green emission as a function of increasing concentration of 1. Nonlinear behavior is again seen for the fast green emission, and a comparison in Table II of the relative changes in yield and rate constant of emission demonstrates that a major proportion of the quenching of emission must be due to a static mechanism. The fluorescence quenching, monitored at 450 nm, follows linear Stern–Volmer kinetics.

The intensity of the fast green emission was studied as a function of the laser dose to determine whether monophotonic or biphotonic processes were responsible for this emission. The resulting plot (not shown) of emission intensity was a linear function of pulse energy, suggesting that transient–transient interactions or biphotonic processes are not responsible for this emission.

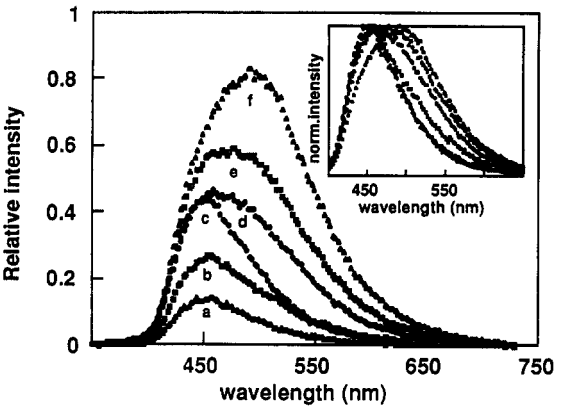

Figure 4. Emission spectra arising from 337-nm excitation of the same area of a 0.31% PH0 in PMMA film as a function of the number of irradiation pulses: (a) 1 pulse; (b) 20 pulses; (c) 50 pulses; (d) 100 pulses; (e) 200 pulses; (f) 300 pulses. Inset shows the same spectra normalized to maximum emission.

Repetitive irradiation of the same portion of the film led to a drastic increase in the emission intensity, measured at a delay of 10 ns, accompanied by a shift in λ_{max} from 450 to 510 nm (see Figure 4). This effect proved to be largely reversible; for example, a sample irradiated with multiple laser shots and then left for 60 min exhibited a reduction in emission intensity with a blue-shifted spectrum in comparison to the spectrum arising from the same area at the end of the irradiation cycle. This is likely the result of the local accumulation of unstable products.

The long-lived weak green emission was unaffected with respect to intensity or rate of decay by the concentration of either PH0 or compound 1. This emission was so weak in intensity that it required the use of a gate duration of 100 μs to collect sufficient emission for a reasonable spectrum. This may be contrasted with the fluorescence and fast green emission where 20-ns gates resulted in emission intensities which were orders of magnitude greater than that for the weak emission. On repeated pulsing of the film, the intensity of the weak green emission also increased, as demonstrated by a 2-fold rise in the integrated intensity of emission detected with a gate of 100 μs at a delay of 50 μs following the laser pulse. Other experiments reported below suggest that this emission is phosphorescence and that this emission enhancement results from local photoinduced oxygen depletion.

PH2 exhibits a strong emission with λ_{max} = 505 nm. Unlike PH0, there is no spectral change with time and its intensity is not reduced by increasing the concentration of PH2. The spectrum is identical with the fluorescence detected in solution at room temperature, as shown in Figure 5 (spectrum a). The fluorescence lifetime was determined to be 36 ns (see inset in Figure 5) by flash photolysis measurements which may be compared to values of 20 and 41 ns in nitrogen- and air-saturated diglyme, respectively. No other emission processes were detected, and no effect of repeated irradiation of the same area of the film surface was observed. Compound 1 quenched the fluorescence emission from PH2, as shown in Figure 5 (see Table II). The quenching of the fluorescence of PH2 was much less efficient than that for PH0 as demonstrated by the respective slopes in Figure 3, particularly considering that the slopes are proportional

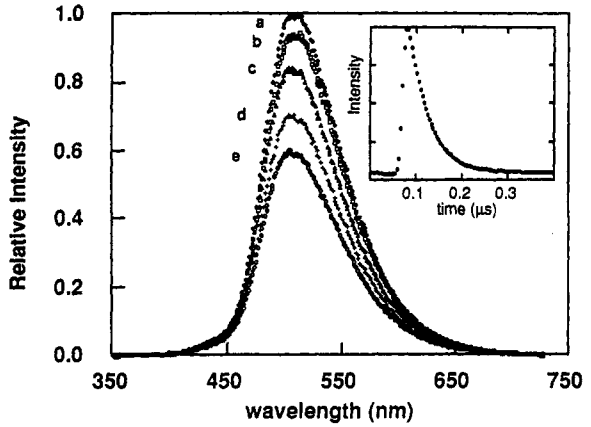

Figure 5. Dependence of fluorescence emission intensity from PH2 (0.42%) on concentration of 1 in PMMA film: (a) 0%, (b) 2.6%, (c) 5.1%, (d) 10.4%, and (e) 14.6% 1 in film. Inset shows time-resolved fluorescence decay at 510 nm.

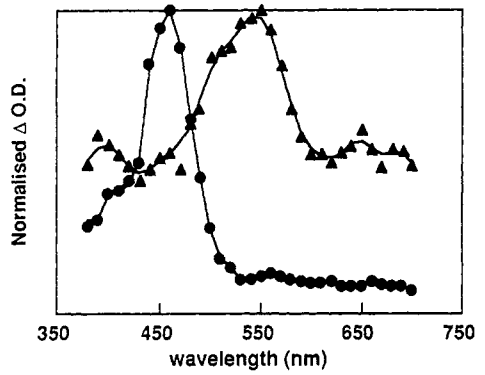

Figure 6. Transient absorption spectra measured immediately following 337-nm laser irradiation of 0.43% PH0 (●) and 0.45% PH2 (▲) in PMMA films.

to $k_q\tau$ (where k_q is the quenching rate constant and τ is the fluorescence lifetime) and that τ for PH2 is 36 ns compared to a value of <1 ns for PH0; i.e., k_q for quenching of PH2 by 1 is at least 100 times lower than for PH0. This quenching is of a static nature as no decrease in fluorescence lifetime is observed when the concentration of 1 is increased.

Transient Absorption Studies. Transient absorption studies were carried out on PMMA films identical with those used in emission studies. Transient absorption spectra for PH0 and PH2 were essentially identical with the triplet–triplet absorption spectra observed in solution, as shown in Figure 6. No effect of sensitizer or compound 1 concentration was observed on the decay kinetics of transients from PH0 or PH2 when the sample was moved between shots to ensure irradiation of a fresh portion of the film surface. The transient decay was remarkably long-lived in air-equilibrated films (Figure 7, trace c) which caused us some concern considering that in degassed diglyme solution a maximum lifetime of ~3.5 μs for triplet PH0 was measured.[7]

To establish if long triplet lifetimes were common under these conditions, we carried out several experiments using a PMMA film doped with 0.7% (w/w) 2-acetonaphthone (2-AP), a ketone that normally displays a triplet lifetime of >20 μs in degassed solution under identical irradiation conditions. The transient absorption spectrum of 2-AP in PMMA film shows λ_{max} at 430 nm and is identical with the triplet–triplet spectrum observed in solution. The decay of the triplet absorption of 2-AP was also observed to be long-lived in air-equilibrated PMMA film, thus supporting the assignment of triplet character to the signals

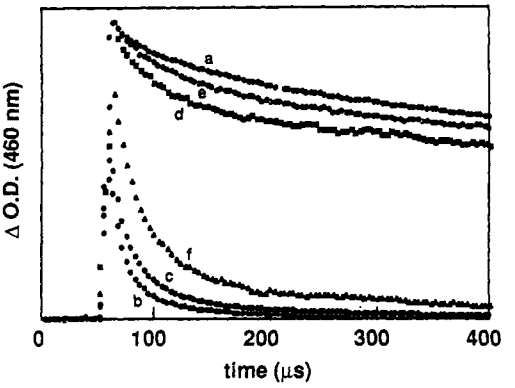

Figure 7. Transient decays measured at 460 nm from 355-nm irradiation of 0.35% PH0 in PMMA films: (a) N_2 equilibrated, fresh area each shot; (b) O_2 equilibrated, fresh area each shot; (c) air equilibrated, fresh area each shot; (d) air equilibrated after 10 shots of irradiation; (e) O_2 equilibrated after 10 shots of irradiation; (f) O_2 equilibrated after 10 shots of irradiation followed recovery time of 10 min.

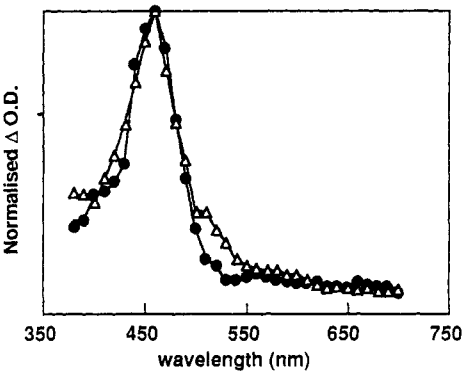

Figure 8. Transient absorption spectra measured immediately following 337-nm laser irradiation of 0.5% in PH0 in the absence (●) and presence (△) of 15% 1 in PMMA films.

from PH0 and PH2.

An interesting observation was the severe dependence of the transient decay rate on the number of pulses used to irradiate the area of the film probed by the analyzing light. Figure 7 shows the transient decay observed on irradiation of a previously air equilibrated film of PH0 when either the film was moved between shots or the same area was irradiated. We can see that on using a fresh portion of the film for each shot (Figure 7, trace c) a triplet lifetime of ca. 20 μs was determined in contrast to the extremely long-lived signal obtained following irradiation of the sample with 10 laser shots at 355 nm followed by only 1 shot for the signal acquisition (Figure 7, trace d). The absorption spectrum observed under repeated irradiation was identical with that for the triplet. Thus, we interpret this dependence of the transient decay rate as being due to a photochemical removal of oxygen from the film which leads to an increase of the triplet lifetime (see Discussion). The presence of 1 up to a concentration of 15% (w/w) did not appear to affect either the maximum absorbance of the triplet at 460 nm or the triplet decay kinetics. However, on comparison of the transient spectra a shoulder at 510–520 nm is suggested, which would be in agreement with the radical cation of PH0 observed in solution at 520 nm.[7] This absorption was not observed in the absence of 1, as shown in Figure 8. The relative proportion of radical cation formed is much lower than observed in solution.

PH2 also shows the "degassing" effect of increased triplet lifetime on irradiation of the same surface area of the film but is totally unaffected by the presence of up to 16% 1.

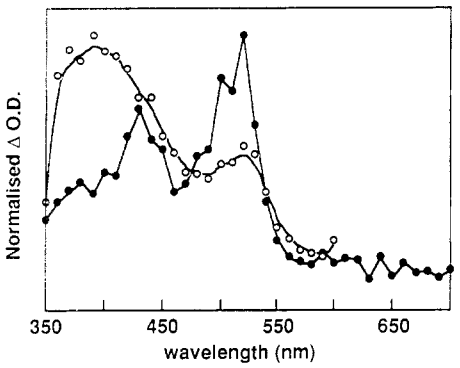

Figure 9. Residual absorption spectra (after triplet decay) for PH0 in (●) diglyme + 0.1 M 1 and for (○) solution of PMMA/diglyme (25% w/w) + 15% w/w 1.

No evidence for the radical cation of PH2 was observed (vide infra).

To ascertain that the different effects seen in PMMA films compared to those in solution were not due to sensitizer–PMMA interactions, the transient absorption following excitation of a sensitizer solution containing 25% (w/w) PMMA in diglyme was investigated. No difference in absorption spectrum of PH0 was seen in the absence or presence of the PMMA. In the same solution but containing 16% (w/w) 1 the absorption of the radical cation of PH0 was clearly observed, as shown in Figure 9. The presence of PMMA does not seem to affect the photochemistry of PH0 at all. However, in the absence and presence of 1 significant differences in the absorption spectrum measured after complete triplet decay are observed.

Discussion

The luminescence properties of PMMA films doped with either PH0 or PH2 are dominated by some of the same features that are observed in solution and in low-temperature glasses.[7] Thus, the most intense component in the emission spectra is the fluorescence, which closely resembles that in solution. In steady-state emission spectra and in gated measurements where the detection gate includes prompt emission, all other features of the luminescence (vide supra) are effectively negligible. PH0 phosphorescence emission spectra, detected only after relatively long delay times, are similar to those in solution and in glasses, although somewhat broader than the latter. No phosphorescence was detected for PH2.

In the case of PH0 we have also detected a green emission, spectrally very similar to the phosphorescence but with a short lifetime and an emission yield intermediate between those for fluorescence and phosphorescence. While we have been unable to characterize conclusively the origin of this luminescence, we hypothesize as to its origin.

Both PH0 and PH2, as well as 2-AP (used as a control), exhibit very long-lived triplet–triplet absorptions on irradiation in aerated PMMA films; we attribute this seemingly general behavior to a very slow rate of oxygen diffusion within the polymer film. PMMA even when loaded with 5% PH0 and 15% 1 (percent of PMMA by weight) at room temperature is well below its glass transition temperature of 86 °C and is thus in a rigid state in which molecular diffusion would be expected to be retarded with respect to more fluid media. Compared with solution, the lifetimes are much longer, both in aerated and deaerated media, this serving as an indication of the vast difference in the rate constants for diffusion control in these systems. In accordance with the long-lived transient absorption of PH0, a concurrent weak phosphorescence emission is observed. The absence of phosphorescence from PH2 is similar to its behavior in solution. Transient absorption decay kinetics and the yield of these transients were unaffected by additions of various concentrations of 1 or by changes in concentration of the ground-state sensitizer. In the case of PH0 this contrasts with our previous work in dilute solution where an efficient self-quenching process was observed ($k_{sq} = 2.4 \times 10^8$ M^{-1} s^{-1}).[7] Again, the lack of dynamic triplet self-quenching may be ascribed to the slow rate of molecular diffusion in the polymer film.

The transient absorption spectrum for PH0-doped PMMA films in the presence of 1 exhibits a small shoulder at 510 nm, suggesting the formation of PH0 radical cations, although in much lower yields than in solution. These species must arise from singlet–singlet electron transfer between PH0 and 1 as no dynamic triplet quenching is observed and no radical cation is observed in the absence of 1, thus precluding a photoionization mechanism. In accordance with a singlet–singlet electron-transfer mechanism, PH0 fluorescence emission is found to be quenched by 1. PH2 fluorescence emission is also quenched by 1 (mechanism proved to be static in nature), but no evidence for PH2 radical cation is observed, although we note that the overlap of triplet and radical absorption which is seen in solution would tend to make resolution of the radical cation difficult in the presence of the long-lived triplet state. Besides, in view of (a) the reduced radical cation yield from PH0 in film with respect to solution, (b) an increase in the relative efficiency PH0/PH2 for fluorescence quenching by 1 in film with respect to solution, and (c) the fact that PH2 in solution appears less efficient than PH0 in radical cation formation, the failure to detect the PH2 radical cation is perhaps not surprising.

Neither PH0 or PH2 showed any significant dependence of the amplitude of triplet–triplet absorbance on concentration of 1. This is rather surprising since quenching of the fluorescence does indeed take place (see Figure 3). Given that singlet quenching does not lead to a significant change in triplet–triplet absorption, we reason that the nature of this process cannot be solely ascribed to electron transfer. The measurements indicate the operation of a parallel quenching mechanism which we ascribe to an enhancement of intersystem crossing in PH0 or PH2 induced by 1 (heavy-atom effect). The latter process, at least under our experimental conditions, appears to compensate for the anticipated reduction in triplet yield due to quenching of its precursor.

As already mentioned, the increase in triplet lifetime when the same area of an air-equilibrated film is irradiated by multiple laser shots can be interpreted as a consequence of a photochemical removal of available oxygen. To support this interpretation, the dependence of transient decay signals from identical films kept in an oxygen atmosphere prior to the experiment or under nitrogen on the number of pulses was analyzed. When the film was moved between shots, even in the O_2-equilibrated film, a relatively long lifetime was observed (Figure 7, trace b), which increases significantly in the N_2-equilibrated film (Figure 7, trace a). In the case of the oxygen-equilibrated film the transient lifetime increases rapidly with irradiation of the same film area (Figure 7, trace e). These "degassing" effects are reversible on a relatively long time scale; i.e., 10 min following repeated irradiation of the same spot the signal obtained on the first laser pulse following the delay was again approaching that obtained under air-equilibrated conditions (Figure 7, trace f). This obser-

vation rationalizes the lack of oxygen quenching as being due to a slow diffusion of oxygen through the film to replenish the amount removed, the phenomenon already suggested as responsible for the long triplet lifetimes and the lack of PH0 self-quenching observed in films. The longer lived triplet lifetimes in irradiated films explain the 2-fold increase in the weak phosphorescence emission observed by using gated detection (vide supra) under the same conditions.

The green emission from PH0 exhibits a two-component decay, the long-lived weak component being due to phosphorescence emission. To ascertain the origin of the faster component, the dependence of its intensity on the pulse energy was analyzed. As a linear process dependence was observed, the emission must arise from a monophotonic process. Biphotonic processes can be dismissed as the origin of this emission. On the other hand, no evidence for ground-state aggregation could be obtained by UV spectroscopy. One possible explanation for the fast green emission could be the existence of some kind of complex between the ground and the excited singlet states. Since the intensity of this emission decreases as PH0 concentration increases, we tentatively suggest that the emitting complex is formed by few sensitizer molecules, perhaps just two (i.e., an excimer). As the ground-state concentration increases, the number of molecules within the interaction sphere of the absorbing chromophore will also increase and nonradiative excitonic processes could then predominate. Complex formation is envisaged to be simply a result of the enforced close physical proximity of sensitizer molecules at the high loadings in the film which are frequently employed in the microelectronics industry. Consistent with the idea that the higher aggregates may not emit, only a weak fluorescence emission was recorded from crystalline PH0 and no green emission was observed.

The fast green emission is also quenched by 1, the intensity being much more sensitive than its decay kinetics to concentration of 1. Some dynamic quenching is observed, but the effect is predominantly static, as demonstrated in Table II. In fact, the incorporation of 1 in large concentrations may be expected to reduce the occurrence of excimer formation by acting as a "spacer" to reduce sensitizer–sensitizer interactions. Since no effect of ground state or 1 concentration on the maximum triplet–triplet absorbance could be observed, any complexation phenomena under these conditions did not affect the triplet yield to a detectable extent.

Finally, the emission spectral changes (increase in intensity and red shift in λ_{max}) observed on repeated irradiation at a delay of 10 ns could be attributed to the formation of an emitting photoproduct, which would compete with the sensitizer for photons and would accumulate during exposure. Photoproduct formation does in fact occur as one can see a change in color of the film where the irradiation has been performed. The absorption spectrum recorded after 500 shots on the same area shows, when compared with that prior to irradiation, a decrease in intensity ($\Delta A < 10\%$) in the range 300–350 nm and an absorption tail toward the visible region, a result that would support our interpretation. This process, however, was not studied in further detail. The apparent reversibility of the emission changes (vide supra) can also be rationalized by unstable photoproduct formation as the color in the film fades after irradiation.

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