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The Effect of Epoxy Resin and Polyamine Hardener on the Photo-Fading of 2-Piperidinoanthraquinone in Solution: A Flash Photolysis Study

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ABSTRACT

The triplet state of 2-piperidinoanthraquinone has been generated in toluene solutions using nanosecond laser flash photolysis. The effect of epoxy resin and polyamine hardener on the yield and lifetimes of the dye triplet state and the dye semiquinone species has been studied. For both resin and hardener, dye semiquinone species are produced which subsequently disproportionate to yield the hydroquinone and so cause photo-fading. The mechanisms by which these free radicals are formed and their relevance to the photo-fading of dyed epoxy resin are discussed in detail.

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INTRODUCTION

The instability of dyed epoxy resin systems to prolonged exposure to sunlight is an important technological problem; for example, in the conservation of museum exhibits.[1,2] Both the resin and dyes undergo changes. In particular, epoxy resins suffer extensive chain scission, cross-linking and yellowing[3-6] while the dyes photo-fade.[2] In a recent paper, the photo-fading of anthraquinone dyes in cured epoxy resins was investigated.[7] Compared with a relatively inactive polymer system such as cellulose triacetate, epoxy resins were found to accelerate photo-fading through a dye reduction mechanism in which the polyamine hardeners played a significant part. The dye, 2-piperidinoanthraquinone, was selected for this study because of its easily identifiable excited states and because its basic photo-chemical free radical chemistry is reasonably well established.[8-13] The purpose of the present investigation is, therefore, to study the effect of epoxy resin and hardener on the excited states of 2-piperidinoanthraquinone in toluene solutions.

EXPERIMENTAL

The epoxy resins used in this study are all based on the Bisphenol A diglycidyl ether unit. In particular, Araldite (AY105 and MY790) (Ciba-Geigy Ltd, Great Britain) and Thermoset (TS600) (Thermoset Plastics Inc., Indiana, USA) resins were employed. The hardeners were polymeric amines which contained either the polyoxypropylene diamine (AB-B) (Ablestick Laboratories) or polyoxypropylene triamine (XD716) (Ciba-Geigy Ltd, Great Britain)[7] units. Spectroscopic grade toluene was used to prepare all solutions. Degassing of solutions was achieved by purging with 'white spot' nitrogen.

The laser flash photolysis experiments were carried out using a Neodymium laser which produced approximately 100 mJ, 15 ns pulses of 355 nm light. Transient absorption changes were measured by illuminating the 1 cm path length quartz reaction cell with light from a pulsed Xenon lamp. Selection of wavelength was achieved with a diffraction grating monochromator set at 5 nm bandwidth. The kinetics changes in the light signal at these selected wavelengths were detected and amplified by an appropriate photomultiplier prior to collection by a storage oscilloscope. In the conventional flash photolysis experiments, polychromatic excitation was employed. A similar detection system to that described above was used except that pulsing of the analytical light source was not necessary. The path length of the reaction cell in this case was 10 cm.

RESULTS AND DISCUSSION

Using the nanosecond laser flash photolysis technique (excitation at 355 nm), a transient species was observed immediately after the laser pulse. Its difference absorption spectrum (Fig. 1) has maxima at 400 nm and 560 nm. First-order decay kinetics were observed at all wavelengths yielding an average value for the decay constant of $6{\cdot}5 \times 10^4\,s^{-1}$. Saturation of the solution with oxygen resulted in an increased rate of decay consistent with a bimolecular oxygen quenching rate constant of $2{\cdot}0 \times 10^9\,M^{-1}\,s^{-1}$. All this data indicates the production of the triplet state of 2-piperidinoanthraquinone, particularly when comparison is made with data from pulse radiolysis experiments where the triplet state was generated by reaction with excited states of benzene.[12] Figure 1 also shows that the decay reaction of the triplet state produces no other transient absorbing species.

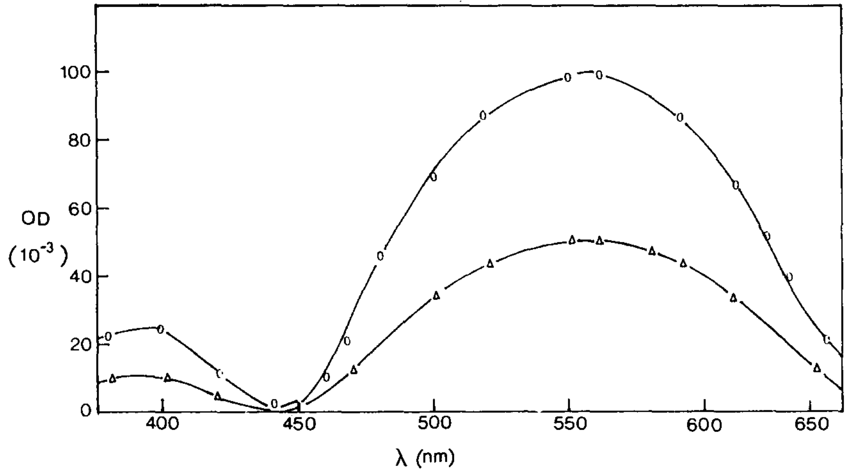

Fig. 1. Difference absorption spectra observed at 0·2 μs (⊙) and 4 μs (△) after giving a 15 ns pulse of 355 nm laser radiation to a de-aerated solution of 10^{-4} M 2-piperidino-anthraquinone in toluene.

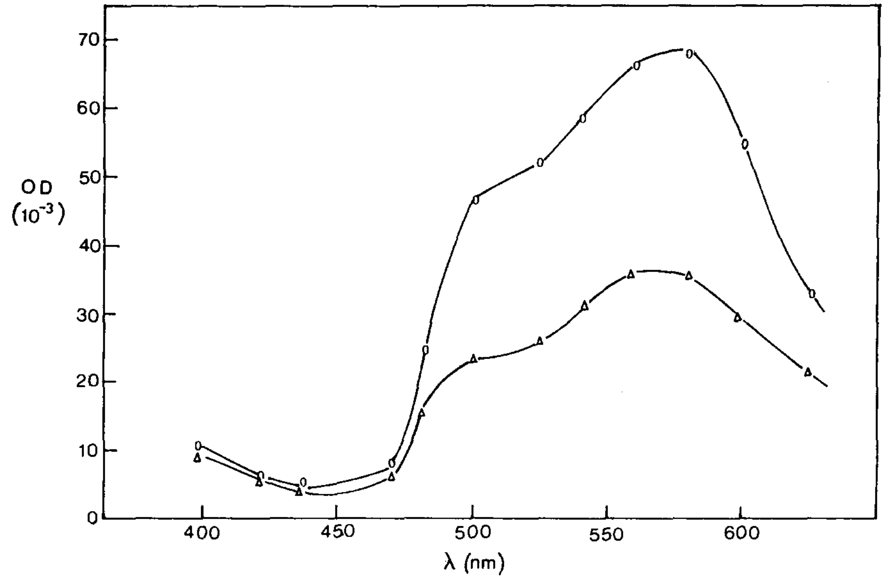

Fig. 2. Difference absorption spectra observed at 0·2 μs (⊙) and 8 μs (△) after giving a 15 ns pulse of 355 nm laser radiation to a de-aerated solution of 10^{-4} M 2-piperidinoanthraquinone and 4% w/v XD716 hardener in toluene.

In the presence of the polyoxypropylenetriamine hardener XD716, the difference spectrum observed immediately after the laser flash (Fig. 2) is significantly different to that in Fig. 1. In addition to maxima at 400 nm and 560 nm, there is a shoulder about 490–500 nm. The effect of hardener concentration on the decay kinetics of this spectrum depends on the wavelength. This is detailed in Table 1.

On the assumption that the principal species absorbing at 600 nm is the triplet state of the dye, it is apparent that there is no bimolecular reaction between the hardener and the triplet state. It is equally clear, however, that the longer half-life of the transient absorption at 400 nm indicates the presence of another species in addition to the dye triplet state. It is well known that amines efficiently quench the first excited singlet state of 2-piperidinoanthraquinone in solution, probably by electron transfer to the quinone.[13] It is to be expected, therefore, that, in addition to the dye triplet state, some semiquinone free radicals will be produced within the lifetime of the laser flash. These free radicals are probably in the radical anion form in view of the inferred preference of the 2-piperidinoanthraquinone triplet state to react by electron transfer rather than by hydrogen abstraction.[10] In methanolic solutions, these radical anions are known to

TABLE 1

Effect of XD716 Concentration on the Half-Lives of the Transient Absorptions Measured at 400 nm and 600 nm After Giving a Laser Flash (355 nm) to Deaerated Solutions of 2-Piperidinoanthraquinone in Toluene

[XD716] (% *w/v*)	*400 nm*	*600 nm*
0	6·8 μs	7·0 μs
0·56	9·0 μs	7·5 μs
1·0	12·0 μs	7·5 μs
1·6	13·0 μs	7·6 μs
2·2	12·0 μs	7·6 μs

absorb in the range 350 nm–550 nm with maxima at 390 nm and 470 nm.[3] The addition of such a spectrum to that of the dye triplet state would yield spectra similar to those shown in Fig. 2.

In de-aerated toluene solutions containing only dye and uncured resin, spectral changes observed immediately (0·2 μs) after the laser flash could only be attributed to the triplet state of the dye. No absorption could be attributed to the semiquinone free radical species. However, as with hardener, the decay kinetics of the transient absorptions varied with wavelength. Table 2 shows details of this effect.

Also shown in Table 2 is the effect of resin concentration on the initial yield of the 2-piperidinoanthraquinone triplet state. It is apparent from

TABLE 2

Effect of Epoxy Resin (AY105) Concentration on the Half-Lives and Initial Optical Density (0·2 μs) of the Transient Absorptions Measured at 400 nm and 600 nm After Giving a Laser Flash (355 nm) to De-aerated Solutions of 2-Piperidinoanthraquinone in Toluene

[AY105]	*400 nm*		*600 nm*	
(% *w/v*)	$t^{1/2}$ *μs*	*OD* (10^{-3})	$t^{1/2}$ *μs*	*OD* (10^{-3})
0	8·5	26·6	8·5	72·5
1	50	18·2	2·3	49·2
2	50	15·4	1·8	33·0
3	50	13·3	1·5	28·3
4	50	12·2	1·5	27·0

the data at 600 nm that not only is the triplet lifetime reduced by a factor of five but its yield is also reduced by a factor of three. At 400 nm, however, although the apparent yield of species is reduced by a factor of about two, the lifetime *increases* by a factor of six. All this data therefore indicates that: (i) the dye triplet state is quenched by the resin in a bimolecular reaction to produce semiquinone free radical species, probably in the form of the radical anion; (ii) the resin effectively quenches the first excited singlet state of the dye so as to reduce singlet–triplet crossover—this quenching apparently does not lead to a chemical change; (iii) the long-lived absorption at 400 nm is attributable to the semiquinone form of the dye produced in the reaction of dye triplet state and resin. The quenching of the first excited state of the dye by the resin may occur through the formation of a ground state complex between 2-piperidinoanthraquinone and resin as found in earlier studies of the fluorescence quenching of this dye by alcohols.[13] The structure of the epoxy resin, AY105, as described earlier, contains both hydroxy groups and aromatic rings to aid such complex formation.

The results detailed above for experiments with either dye/hardener or dye/epoxy resin systems can therefore be summarised in the following reaction scheme:

$$\mathrm{2PAQ} + \mathrm{resin} \rightleftharpoons [\mathrm{2PAQ{:}resin}] \tag{1}$$

$$\mathrm{2PAQ} \xrightarrow{h\nu} {}^{1*}(\mathrm{2PAQ}) \tag{2}$$

$$[\mathrm{2PAQ{:}resin}] \xrightarrow{h\nu} {}^{1*}([\mathrm{2PAQ{:}resin}]) \tag{3}$$

$${}^{1*}\mathrm{2PAQ} \overset{h\nu'}{\rightsquigarrow} \mathrm{2PAQ} \tag{4}$$

$${}^{1*}([\mathrm{2PAQ{:}resin}]) \overset{h\nu''}{\rightsquigarrow} [\mathrm{2PAQ{:}resin}] \tag{5}$$

$${}^{1*}(\mathrm{2PAQ}) \xrightarrow{\mathrm{I.S.C.}} {}^{3*}(\mathrm{2PAQ}) \tag{6}$$

$${}^{1*}([\mathrm{2PAQ{:}resin}]) \xrightarrow{\mathrm{I.S.C.}} {}^{3*}([\mathrm{2PAQ{:}resin}]) \tag{7}$$

$${}^{1*}(\mathrm{2PAQ}) + \mathrm{hardener} \longrightarrow \mathrm{2PAQ}^{\cdot -} \quad (\text{or } \mathrm{2PAQH}\cdot) \tag{8}$$

$${}^{3*}(\mathrm{2PAQ}) + \mathrm{resin} \longrightarrow \mathrm{2PAQ}^{\cdot -} \quad (\text{or } \mathrm{2PAQH}\cdot) \tag{9}$$

$${}^{3*}(\mathrm{2PAQ}) + \mathrm{hardener} \longrightarrow \text{no reaction} \tag{10}$$

In nanosecond laser flash photolysis experiments where both hardener and resin were present in addition to 2-piperidinoanthraquinone, it was clear that the system responded in a similar way to the dye/resin solution, i.e. the hardener exerted no effect in that there was no immediate (0·2 μs) production of semiquinone species. It would appear, therefore, that the proposed complex formation between resin and dye severely reduces the possibility of fluorescence quenching of the dye by an electron transfer through reaction with the amine hardener.

To investigate the fate of the dye semiquinone species produced in reactions (8) and (9), it was necessary to extend the time scale of the experiments so that transient absorptions could be monitored up to several milliseconds after the flash. Using the conventional flash photolysis apparatus described in the 'Experimental' section, therefore, it was possible to monitor the production of transient species at 4·5 ms after the flash. This does mean that there is a gap between these observations and those made on the nanosecond laser flash photolysis apparatus (up to 100 μs). However, in practice, the large yields of transient species produced using the polychromatic excitation on the conventional apparatus mean that there can still be substantial absorption changes attributable to a species whose concentration has decreased by up to 90 % of its initial value. With this in mind, Fig. 3 shows a typical difference absorption spectrum of transient species produced 4·5 ms after initially

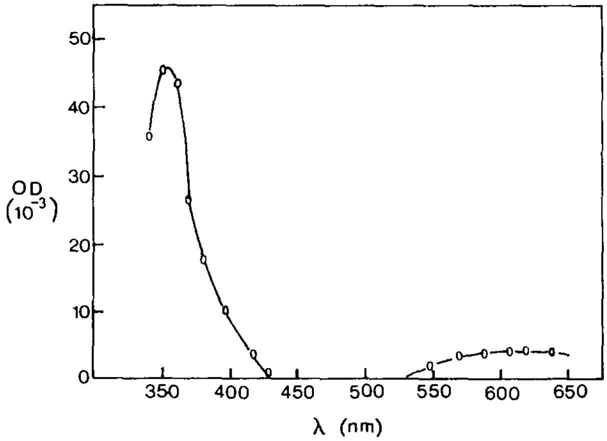

Fig. 3. A typical difference absorption spectrum observed 4·5 ms after initial polychromatic excitation of a de-aerated solution of 2-piperidinoanthraquinone in toluene containing either amine hardener or epoxy resin.

exciting (with polychromatic light) 2-piperidinoanthraquinone in de-aerated toluene solutions containing either resin or hardener. This spectrum can be divided into three parts: (i) a sharp peak at 355 nm, (ii) a region between 430 nm and 530 nm where the major change is one of fluorescence emission and (iii) a region between 530 nm and 640 nm where there is a relatively small amount of absorption. At 4·5 ms after the initial excitation it is clear from the laser flash photolysis experiments that most of the dye semiquinone species will have disappeared, presumably in a disproportionation reaction to yield the hydroquinone, e.g.:

$$2[2PAQH\cdot] \longrightarrow 2PAQH_2 + 2PAQ \qquad (11)$$

The peak at 355 nm may therefore be due to the difference spectrum of the hydroquinone which would also fluoresce weakly in the region between 430 nm and 530 nm.[10] The relatively small absorption in the region 530 nm–640 nm may be attributed to the tail-end of the absorption due to the semiquinone radical anion which has maxima at 390 and 470 nm.[12] This latter assignment must, of course, be speculative in view of the interference from fluorescence at shorter wavelengths. These experiments also show that the hydroquinone is unstable ($t^{1/2} \approx 60$ ms) and probably reacts to yield the anthrone, as suggested earlier.[10]

Table 3 shows the optical densities at 355 nm and 590 nm measured 4·5 ms after the flash in 2-piperidinoanthraquinone solutions containing a range of hardeners or resins.

Only with resin AY105 is there significant increase in the yield of the semiquinone radical ion with increase of resin concentration. It would

TABLE 3
The Effect of Hardener or Resin Concentration on the Optical Densities at 355 nm and 590 nm Measured 4·5 ms after Giving a Polychromatic Flash to De-aerated 2-piperidinoanthraquinone Solutions in Toluene

	OD (10^{-3})									
	AY105		*MY790*		*TS600*		*XD716*		*AB-B*	
Concentration	*λ/nm*		*λ/nm*		*λ/nm*		*λ/nm*		*λ/nm*	
(% w/v)	*355*	*590*	*355*	*590*	*355*	*590*	*355*	*590*	*355*	*590*
0·1	13·6	0·1	8·2	1·7	21·4	3·3	12·5	2·2	7·3	1·7
0·5	20·0	3·4	11·3	1·9	24·4	3·4	20·5	1·9	11·0	1·7
1·0	25·2	4·8	12·7	2·1	28·9	2·9	29·4	1·9	14·0	2·1
3·0	20·0	6·6	9·9	1·4	35·3	3·2	22·0	2·1	15·6	1·6

seem that electron transfer to the dye triplet state is more facile with this resin. The disproportionation reaction of the semiquinone species to yield the hydroquinone (reaction (11)) may involve both the neutral and radical ion forms. The correlation of radical anion yield with the hydroquinone yield is therefore not straightforward and not attempted here.

In conclusion, it has been found that epoxy resins and amine hardeners both contribute, albeit by different mechanisms, to the production of the hydroquinone via semiquinone formations. The excited states of 2-piperidinoanthraquinone probably react via electron transfer to yield radical anions; the involvement of neutral semiquinone species cannot however be ruled out. Although the present study was carried out in the solution phase, the same mechanism can be expected to prevail in dyed, cured epoxy resins.

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