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Photochemistry and photopolymerization activity of monomers and copolymers of 2-substituted amidoanthraquinone and acryloxyanthraquinone with methyl methacrylate

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Abstract

The photophysical and photoinduced polymerization activities of the monomers 2-acrylamidoanthraquinone (2-AAAQ) and 2-acryloxyanthraquinone (2-AOAQ) were determined in solution, together with the corresponding properties of their copolymers with methyl methacrylate (MMA). Copolymers of 2-acrylamidoanthraquinone with a narrow polydispersity (1.8–2.5) were obtained with chromophore contents in the range 8.49–9.92 mol.% and a number average molecular weight which decreased from 89 937 to 35 624 g mol^{-1} depending on the irradiation time. Copolymers of 2-acryloxyanthraquinone with a broader polydispersity (2.9–5.6) were obtained with similar chromophore contents, but a lower number average molecular weight which decreased from 69 446 to 20 678 g mol^{-1} over an irradiation period of 840 min. Overall, low fluorescence quantum yields were obtained, with the values for the copolymers being higher than those for the monomers. This suggests a high rate of deactivation of the lowest excited singlet state via either internal conversion or intersystem crossing to the lowest excited triplet state. The latter appears to be highly favourable in the case of the 2-acryloxyanthraquinone copolymer where the phosphorescence quantum yields were enhanced markedly by two orders of magnitude (10^2). The photoreduction quantum yields in acetonitrile, although low, were enhanced in the presence of a tertiary amine. Higher values were obtained for the 2-acryloxyanthraquinone monomer and copolymer. Similar effects were observed in the photoinduced polymerization of methyl methacrylate. Higher rates were observed for the 2-acryloxyanthraquinone monomer and copolymer, and the rates for the two copolymers were higher than those of the corresponding monomers. These two notable effects are associated with the higher activity of the lowest excited triplet $n\pi^*$ state of the 2-acryloxyanthraquinone chromophore, and the greater rigidity of the chromophores in the copolymers which enhances the intersystem crossing rates and triplet state activity via hydrogen atom abstraction or electron transfer processes. © 1997 Elsevier Science S.A.

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1. Introduction

The field of radiation curing is a widely established area of industrial importance and academic interest. Applications continue to grow as new initiators, monomers and prepolymers are developed [1]. In earlier studies, we investigated the potential of 2-substituted anthraquinone chromophores as effective UV and visible photoinitiators. In this regard, we recently developed effective photoinitiators for the crosslinking of fibre-forming nylon 6,6 polymer based on 2-substituted amidoanthraquinones, where the addition of an acrylated monomer or prepolymer is unnecessary [2,3]. The polymeric form of the monomer, 2-acrylamidoanthraquinone, was also synthesized and, together with its monomeric form, was found to be more active as a photoinitiator than camphorquinone [4]. Owing to their extended absorption into the near UV–visible region of the electromagnetic spectrum, the activity of these compounds as visible photoinitiators would have important commercial implications. There is widespread interest in polymeric photoinitiators with near-UV and visible activity [5] and photopolymers of thioxanthone have been found to be useful in this regard [6]. Advantages can include higher photoactivity, improved solubility and reduced migration rates.

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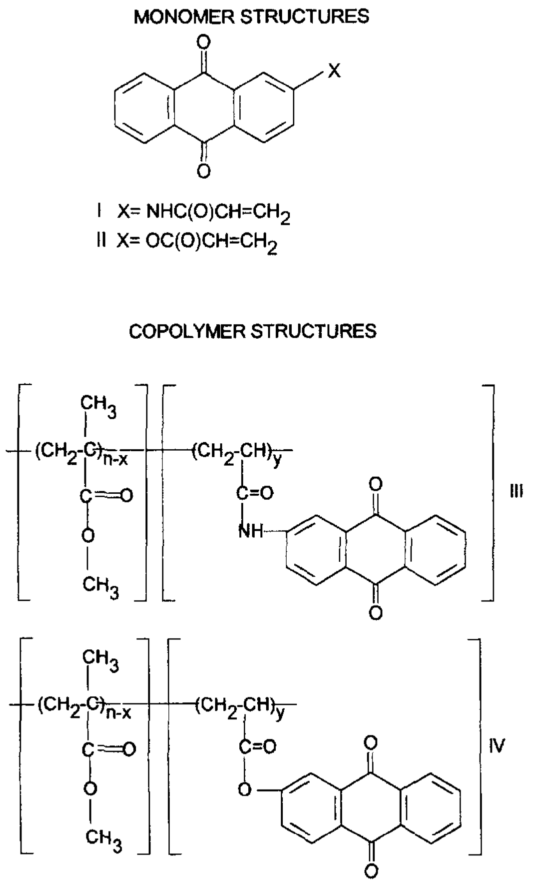

Scheme 1.

In this work, we have prepared novel copolymers of 2-acrylamidoanthraquinone (2-AAAQ) and 2-acryloxyanthraquinone (2-AOAQ) with methyl methacrylate (MMA) (structures **I–IV**, Scheme 1). The photophysical and photochemical activities of the copolymers are compared with the corresponding properties of the anthraquinone monomers. This comparative study will enable the influence of the methacrylated cofunctionality to be determined in terms of the photochemical activity of the anthraquinone chromophore. Photoinduced polymerization studies were undertaken in MMA monomer. The properties of the copolymers were established by gel permeation chromatography (GPC) and UV absorption/luminescence spectroscopy.

2. Experimental details

2.1. Materials

2-AOAQ and 2-AAAQ were prepared as described previously [2–4]. All solvents used in this study were obtained as Analar or spectroscopic grades from Aldrich Chemical Company (UK) and were used as supplied after storage over molecular sieves (MS4A). MMA, triethylamine, *N*,*N*-diethylaminoethanol and 2,2′-azobisisobutyronitrile (AIBN) were obtained from the same company.

2.2. Synthesis of the copolymers

Six copolymer samples of 2-AOAQ and 2-AAAQ, each with MMA, were prepared by radical copolymerization using AIBN as initiator. Six identical ampoules were prepared for each anthraquinone monomer according to the following concentrations (DMF, *N*,*N*-dimethylformamide): [MMA], 1 cm^3 in 9 cm^3 DMF = 0.935 M; [2-AOAQ]/[2-AAAQ], 90/100 mg in 9 cm^3 DMF = 0.032 M; [AIBN], 30 mg in 9 cm^3. This gave initial monomer ratios of $f_{MMA} = 0.967$ and $f_{AOAQ} = 0.033$ and $f_{MMA} = 0.963$ and $f_{AAAQ} = 0.037$.

The reaction temperature was chosen to be 80 °C as this gave the most suitable reaction times for practical use. The solutions were measured into glass tubes with a "quick-fit" socket and tapered neck. The solutions were then degassed on a high vacuum line by the freeze–thaw method until a constant vacuum of 1.8×10^{-3} mbar was attained. After degassing, the ampoule was heat sealed. Copolymerizations were undertaken at 80 °C for various periods of time in order to obtain a variety of conversions. The copolymers were then purified by three repeat precipitations from chloroform into methanol, with filtering and drying after each stage.

The chromophore content in each copolymer was measured by UV spectroscopy by comparison with the molar extinction coefficients of the model compounds 2-acetoxyanthraquinone and 2-acetylamidoanthraquinone reported recently [7].

2.3. Spectroscopic measurements

Absorption spectra were obtained using a Perkin–Elmer Lambda 7 absorption spectrometer. Fluorescence and phosphorescence excitation and emission spectra were obtained using a Perkin–Elmer LS-50B luminescence spectrometer. Fluorescence quantum yields were obtained by the relative method using quinine sulphate in 0.05 M sulphuric acid as a standard [8]. The quantum yield of quinine sulphate was assumed to be 0.55. Phosphorescence quantum yields were obtained in ethanol at 77 K using the relative method with benzophenone as a standard assuming a quantum yield of 0.74 in ethanol [8].

2.4. Rates of photopolymerization

Solutions of the photoinitiators (2×10^{-3} M) in MMA monomer in tetrahydrofuran (50 : 50 v/v) were irradiated on an optical bench set-up utilizing a 100 W high-pressure Hg/W lamp (full wavelength spectrum) (Phillips Laboratory Equipment, UK) at a distance of 10 cm in a quartz tube. Triethylamine was used at 7×10^{-3} M and the monomer was treated with sodium hydroxide solution (2 M) to remove the inhibitor, followed by drying with anhydrous magnesium sulphate overnight. Aliquots of the irradiated monomer were added to methanol, and the precipitated polymer was repeat precipitated from chloroform, filtered off, washed and dried. The rates of polymerization were obtained from plots of the percentage conversion vs. the irradiation time as described previously [9].

2.5. *GPC*

The weight and number average molecular weights of the polymethyl methacrylate samples were analysed by the UK Science and Engineering Research Council RAPRA service in Shrewsbury. The GPC/viscosity and conventional GPC (using polystyrene equivalents) methods were used. Sample solutions were prepared by dissolving 20 mg of sample in 10 cm^3 of dichloromethane, together with a trace of 1,2-dichlorobenzene as an internal marker. After dissolving overnight, the solutions were filtered through a 0.2 μm polyamide membrane. Each sample was run in duplicate on a PLgel 2×mixed bed-B (30 cm, 10 μm) at ambient temperature at a flow rate of 1.0 cm^3 min^{-1} using UV/refractive index detectors.

2.6. *Photoreduction quantum yields*

The absolute quantum yields of photolysis (Φ_r) of the initiators were determined in acetonitrile at 10^{-5} M using an irradiation wavelength of 365 nm, selected using a Philips high-pressure Hg lamp (HB-CS 500 W) and a Kratos GM252 monochromator. Sample cells were thermostatically controlled at 30 °C and the solutions were saturated with oxygen or nitrogen (much less than 5 ppm O_2). The absorbed light intensity was measured using an International Light model 700 radiometer previously calibrated by the Aberchrome 540 actinometer [10,11].

3. Results and discussion

3.1. *Copolymerization*

The ratios of the anthraquinone chromophores to MMA in the copolymers are shown by the chromophore contents in Tables 1 and 2. Depending on the reaction time, they vary from 8.49 to 9.92 mol.% and 6.95 to 9.0 mol.% for the 2-acrylamido and 2-acryloxy copolymers respectively. Our kinetic studies suggest that the anthraquinone monomers have a higher rate of addition to the MMA radical than that of the MMA radical to its own monomer. This aspect of the work will be reported on separately. Molecular weight distributions obtained by UV and refractive index detection were comparable to within ±2%, indicating that the chromophores are randomly distributed along the polymer chain. Therefore only the UV data are shown for comparison. If the anthraquinone monomers were acting as effective chain terminators, the molecular weight values would be higher by UV analysis. The polydispersities are narrower for the 2-AAAQ monomer than for 2-AOAQ. As can be seen from the molecular weight values, the 2-AOAQ copolymer (Table 2) contains a higher degree of lower molecular weight fragments than the 2-AAAQ copolymer.

3.2. *Spectroscopic properties*

The absorption properties of the monomers and copolymers of anthraquinone are shown by the data given in Table 3. The absorption maximum of 2-AAAQ is significantly red shifted from that of 2-AOAQ and this is also reflected in the copolymer spectra. The polymer chain has no significant influence on the absorption maxima of the chromophores. As

Table 1
Properties of copolymers of 2-AAAQ with MMA in DMF

Reaction time (min)	Yield (%)	Polydispersity (UV)	M_n (UV) (g mol^{-1})	λ_{max}	Chromophore content (mol.%)
10	3.4	2.52	89937	367	9.92
15	9.5	2.11	81944	368	9.78
20	19	2.19	65812	366	9.84
30	45.5	1.88	35624	368	8.83
60	69.9	2.19	38321	368	8.49
360	73.1	2.16	39269	366	8.62

Table 2
Properties of copolymers of 2-AOAQ with MMA in DMF

Reaction time (min)	Yield (%)	Polydispersity (UV)	M_n (UV) (g mol^{-1})	λ_{max}	Chromophore content (mol.%)
10	3.3	–	–	–	Insoluble
20	12.8	4.22	69446	326	8.56
30	30.8	3.12	62785	325	8.55
60	53.3	4.45	52186	325	7.63
90	53.9	2.99	34841	326	6.95
840	55.4	5.62	20678	326	9

Table 3
Absorption properties of monomers and copolymers of 2-AOAQ and 2-AAAQ with MMA

Sample	Toluene		Ethyl acetate	
	λ_{max}	log ϵ_{max}	λ_{max}	log ϵ_{max}
2-AAAQ	364	3.65	368	3.75
2-AOAQ	326	3.66	322	3.68
2-AAAQ-co-MMA	364	–	366	–
2-AOAQ-co-MMA	327	–	325	–

Table 4
Fluorescence properties of monomers and copolymers of 2-AOAQ and 2-AAAQ with MMA

Sample	Benzene		Dichloromethane		Ethanol	
	λ_{max}	Φ_f	λ_{max}	Φ_f	λ_{max}	Φ_f
2-AAAQ	517	1.4×10^{-3}	–	–	515	2.3×10^{-4}
2-AOAQ	414	1.8×10^{-4}	–	–	414	3.9×10^{-4}
2-AAAQ-co-MMA	517	6.9×10^{-4}	530	1.4×10^{-3}	–	–
2-AOAQ-co-MMA	419	7.8×10^{-3}	437	2.1×10^{-3}	–	–

Table 5
Phosphorescence properties of monomers and copolymers of 2-AOAQ and 2-AAAQ with MMA

Sample	Benzene		Dichloromethane	
	λ_{max}	Φ_p	λ_{max}	Φ_p
2-AAAQ	513	9.7×10^{-3}	–	–
2-AOAQ	460, 498, 522	3.0×10^{-2}	–	–
2-AAAQ-co-MMA	518	5.3×10^{-2}	519	9.4×10^{-2}
2-AOAQ-co-MMA	459, 492, 528	0.48	449, 492, 529	0.61

indicated previously, 2-AAAQ has a long-wavelength absorption maximum associated with a $\pi\pi^*$ transition, whereas that for 2-AOAQ is associated with an $n\pi^*$ transition. The corresponding spectral shifts in Table 3, although only for toluene and ethyl acetate, confirm our earlier findings [2,3,9].

The fluorescence and phosphorescence spectra of the monomers and copolymers are illustrated by the data given in Tables 4 and 5 respectively. Both anthraquinone monomers exhibit low fluorescence quantum yields, as found previously [2,3,9], which are associated with a high rate of intersystem crossing to the triplet state. These quantum yields increase when the chromophores are part of the copolymer, possibly due to molecular rigidity effects reducing the rate of internal conversion via vibrational relaxation. However, the wavelength maxima remain unaffected.

The phosphorescence spectra are significantly different. The phosphorescence emission spectrum of 2-AOAQ is an order of magnitude greater than that of 2-AAAQ and exhibits typical carbonyl symmetry associated with a lowest lying triplet $n\pi^*$ state. In the case of the copolymers, whilst the wavelength maxima remain unaffected, the quantum yields increase markedly. This is notable in the case of the 2-acryloxy copolymer where phosphorescence quantum yields of 0.48–0.61 are observed. Thus there is not only a significant increase in the rate of singlet–triplet intersystem crossing, but also a marked reduction in the rate of deactivation of the lowest excited triplet state by intersystem crossing. The molecular rigidity of the chromophore on the polymer backbone is obviously an essential feature in this regard.

3.3. Photoreduction and photopolymerization activity

The photoreduction quantum yields of the monomers and copolymers in acetonitrile are all relatively low (Table 6)

Table 6
Photoreduction quantum yields of the monomers and copolymers of 2-AOAQ and 2-AAAQ in acetonitrile

Sample	Φ_r	
	No amine	Amine [a]
2-AAAQ	0.0013	0.027
2-AOAQ	0.0058	0.16
2-AAAQ-co-MMA	0.0	0.024
2-AOAQ-co-MMA	0.026	0.091

[a] *N,N*-Diethylaminoethanol (10^{-4} M).

Table 7
Rates of photoinduced polymerization of MMA by the monomers and copolymers of 2-AOAQ and 2-AAAQ with MMA in tetrahydrofuran (50 : 50 v/v)

Sample	No amine, R_p (mol dm^{-3} s^{-1})	Amine [a], R_p (mol dm^{-3} s^{-1})
2-AAAQ	1.34×10^{-4}	1.66×10^{-4}
2-AOAQ	2.28×10^{-4}	2.70×10^{-4}
2-AOAQ-co-MMA	2.04×10^{-4}	2.98×10^{-4}
2-AOAQ-co-MMA	2.84×10^{-4}	4.08×10^{-4}

[a] Triethylamine at 7×10^{-3} M.

and only marginally enhanced by the addition of a tertiary amine. The restricted solubility of the copolymers did not allow a wider based study to be evaluated. In 2-propanol, 2-AOAQ exhibits a quantum yield of 0.37 [2,3,9], whereas that of 2-AAAQ is zero. These differences are evidently associated with the differences in the nature of the excited states of the two types of chromophore, 2-AOAQ with a lowest lying triplet $n\pi^*$ state being more reactive.

In terms of the photoinduced polymerization activity, it is the nature of the lowest excited triplet state and its ability to form an excited exciplex which play a crucial role in determining the activity. The data in Table 7 compare the photoinitiation activities of the two AQ monomers and copolymers in the polymerization of MMA monomer. The R_p values for 2-AOAQ are higher than those for 2-AAAQ in the absence and presence of a tertiary amine cosynergist. In the case of the two copolymers, the R_p values increase significantly, especially in the presence of an amine cosynergist. In the latter case, the rates almost double.

4. Conclusions

Novel copolymers of 2-AOAQ and 2-AAAQ with MMA were synthesized and characterized and their photochemical activities were evaluated. The quantum yields of triplet formation of the anthraquinone chromophores are significantly enhanced in the copolymer and this appears to be reflected in their ability to exhibit increased activity as photopolymerization initiators. The molecular rigidity of the anthraquinone chromophores on the polymer backbone is evidently responsible for this enhanced activity.

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