

Synthesis, photochemical and photoinitiation activity of water-soluble copolymers with anthraquinone chromophores as side-chain groups

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Received 13 March 2000; received in revised form 16 April 2000; accepted 30 May 2000

Abstract

Novel water-soluble anthraquinone copolymers are synthesised by copolymerisation of 2-acryloxy and 2-acrylamido anthraquinone monomers at 1–2% w/w concentration with three water-soluble co-monomers: acrylamide, 2-acrylamido-2-methylpropane sulphonic acid and 2-acryloxyethyl trimethylammonium iodide. The proton and the iodide were replaced on the corresponding obtained copolymers by sodium and chloride using ionic exchange resins. The absorption, phosphorescence (in methanol), photoreduction and microsecond flash photolysis characteristics of the new copolymers are examined in aqueous solution and the results compared with those of a water-soluble low molecular weight anthraquinone, 2-(*N,N,N*-trimethylammoniumpropoxy) anthraquinone chloride, also synthesised in this work. The photoinduced polymerisation activities of the new products are evaluated by photodilatometry in the presence of triethanolamine as a hydrogen donor. The acrylate anthraquinone copolymers exhibit similar rates and quantum yields of polymerisation to those of the model, while lower values for the acrylamide anthraquinone copolymers are found. The polymerisation activity correlates well with their measured photoreduction quantum yields in water using triethanolamine as the cosynergist. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Water-soluble copolymers; Anthraquinone chromophores; Side-chain groups

1. Introduction

The applications of water-soluble formulations for the surface-coatings industry have been growing at a rapid rate in the last decade [1,2]. Research is continuing in the development of novel water-soluble photoinitiators and many academic studies are being carried out in this area, specially modifying well-known radical generator molecules to water-soluble structures. For most applications, the photosensitive component of the formulation, the photoinitiator system, must be compatible, easily soluble, have low steam volatility, be odourless, safe and non-toxic. In this context, polymeric photoinitiators [3,4], macromolecular systems bearing photoreactive groups in their structure, have gained a great deal of interest. In addition to the advantages derived from their higher molecular weight, which can meet the requirements indicated, there are other advantages inherent to their macromolecular nature and their structure–activity relationships, such as improved efficiency and possibility of novel designing.

In previous papers, we reported on the photochemistry and photopolymerisation activity of a series of water-soluble thioxanthenes [5,6], benzophenones [7] and benzil [8,9] derivatives. Generally, these structures are organic structures of well-known photoinitiation activity, which have been developed by introducing ionic groups in the oil-soluble structure as well as copolymers of the acrylic derivative of the chromophore with a water-soluble co-monomer. Also in earlier studies, we investigated the photochemistry and the photoinitiation activity of a wide series of anthraquinone derivatives [10–15] and oil-soluble copolymers having a low content of this chromophore in the macromolecular structure [16].

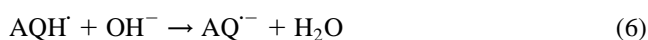
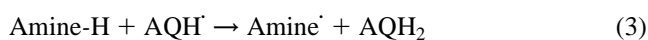
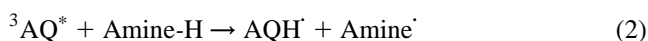
Water-soluble anthraquinone derivatives of sodium salts of mono- and disulphonic acids have been studied [17]; however, under irradiation, they give a dark-coloured species and this has severely limited their application. Their ability to photoreduce via electron transfer in the presence of hydrogen donors and to form radicals has, however, promoted their effective use as photoinitiators of polymerisation. Their mechanism is such that they fall into the category of Type II photoreducing chromophores. In general, anthraquinones exhibit a high reactivity when used in combination with tertiary amines as coinitiators as

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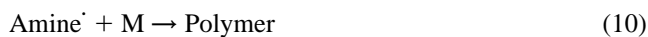
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we have stated on our earlier works [10–16]. The use of these coloured aromatic ketones as light-absorbing components in photoinitiator systems allows the initiation of the polymerisation reaction by means of visible light. Generally, such products are used in a low concentration since many of them exhibit high molar absorption coefficients at the near-UV or visible region of the electromagnetic spectrum. Their photoactivity seems to be dependent on the nature of the lowest triplet state and the photopolymerisation conditions [12–14]. For anthraquinones, the general mechanism proposed for the photogeneration of initiating radicals, in the presence of a tertiary amine, is shown below:

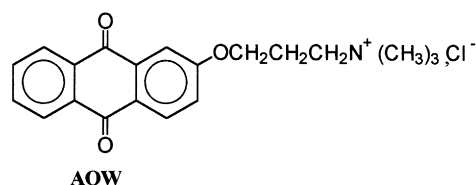


In the first step (Eq. (1)) anthraquinones after absorption yield efficiently a triplet reactive state, which in the presence of a hydrogen donor, tertiary amine, leads to the semi-quinone radical AQH $^\cdot$ (Eq. (2)), which can further react in the same way (Eq. (3)) producing the dihydroquinone AQH $_2$. These species have the possibility of reoxidation, hence the semi-reduced ketone and the 9,10-dihydroxyanthracene derivatives can regenerate the starting anthraquinone [1,18] (Eqs. (4) and (5)). These reactions deplete oxygen concentration dissolved in the formulation and revert back to the original photoinitiator. Hence, anthraquinones, as different from other aromatic ketones, exhibit an interesting initiation efficiency, from the application point of view, under aerobic conditions [13,15]. As we published before [15], an anthraquinone radical anion, AQ $^{\cdot-}$, can be produced from the semi-quinone radical (Eq. (6)) or from the triplet state (Eq. (7)) in basic media. This radical anion exists in equilibrium with the semi-quinone radical (Eq. (8)) and can disappear by disproportion (Eq. (9)). The alkylamino radical, Amine $^\cdot$, produced in reactions (2) and (3) is the true initiating species, and can react with the monomer giving the corresponding polymer.



In this paper we have extended the utilisation range of the anthraquinone chromophore preparing a new water-soluble

anthraquinone of low molecular weight and six new water-soluble copolymers. We have used, 2-(3-*N,N,N*-trimethylammoniumpropoxy) anthraquinone chloride salt, AQW, as a model compound. These copolymers have been prepared using the 2-acrylamidoanthraquinone (AAAQ) or 2-acryloxyanthraquinone (AOAQ), by copolymerisation with three water-soluble co-monomers. Two of them are commercial products, acrylamide (AAm) and 2-acrylamido-2-methylpropanesulphonic acid (MSO $_3$ H) and a previously synthesised monomer [8], 2-acryloxyethyl trimethylammonium iodide (MI). The proton and iodide were replaced in the corresponding polymer structures by sodium and chloride by the use of ionic exchange resins. The structures of AQW and the new water-soluble copolymers are shown below with their corresponding reference abbreviation:



Also, in this work, we describe the photophysical and photochemical activities of these novel water-soluble anthraquinone derivatives including their efficiency as photoinitiator of polymerisation of a homogeneous aqueous system, acrylamide/water. The data obtained with the new copolymers were compared with those of the low molecular weight model compound AQW. Owing to the cumbersome names of the products and frequent reference, they will be referred to throughout the text by their reference abbreviation.

2. Experimental

2.1. Materials

Monomers containing anthraquinone, AAAQ and AOAQ were prepared as described previously [19]. The water-soluble co-monomer, MI, was synthesised and characterised as reported before [8]. AAm was obtained from Merck and was purified by recrystallisation in acetone. MSO $_3$ H was purchased from Kodak and used as received. Anionic exchange resin, Amberlite IRA 400, was used to substitute iodide anion by chloride in the copolymers with MI. Also, a cationic exchange resin, Amberlite IR 120, was employed to change the proton of the acid groups by sodium-yielding sulphonate salts in the copolymers with MSO $_3$ H. The solvent used in the copolymerisation, *N,N*-dimethylformamide was obtained from Aldrich Chemical Co. and distilled under reduced pressure (47°C/15–20 mmHg). 2,2'-Azo-bis-isobutyronitrile (AIBN), from Aldrich Chemical Co., was purified by crystallisation from ethyl ether prior to use.

Table 1
Ultraviolet absorption in water and percentage of anthraquinone in the water-soluble copolymers

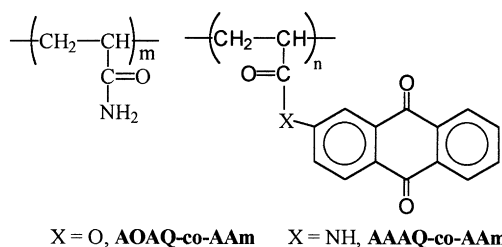
Sample	λ_{\max} (nm) in H ₂ O	Anthraquinone (%)
AQW ^a	337	–
AOAQ-co-AAm	333	1
AOAQ-co-MCl	329	1
AOAQ-co-MSO ₃ Na	332	2
AAAQ-co-AAm	338	1
AAAQ-co-MCl	339	1
AAAQ-co-MSO ₃ Na	337	1

^a $\log \epsilon_{\max} = 3.82$.

The tertiary amine, triethanolamine (TEOA), from Merck was used as received. In all the experiments, MiliQ grade water was used and the other solvents were Analar or spectroscopic grades from Aldrich Chemical Co. Ltd. For the synthesis of the model compound AQW, 2-hydroxyanthraquinone was obtained from Merck and the reactives, 1-bromo-3-chloropropane and triethylamine were purchased from Aldrich Chemical Co.

2.2. Synthesis of 2-(3-*N,N,N*-trimethylammoniumpropoxy) anthraquinone chloride

The synthesis of the new water-soluble model compound, AQW, was carried out by the procedure shown below:



A propoxy spacer between the anthraquinone chromophore and the ammonium group was chosen in order to minimise the hypsochromic effect in the absorbance that the polar group should induce in the anthraquinone derivatives.

2-Hydroxyanthraquinone (8.96 g, 0.04 mmol) and potassium hydroxide (20 g) were dissolved in a solvent mixture of water (125 cm⁻³) and dioxane (25 cm⁻³). A change from yellow to red was detected when the potassium salt of the 2-hydroxyanthraquinone is formed. The reaction temperature was maintained at 0°C by refrigeration with an external ice/water bath and under these conditions 3-bromo-1-chloropropane (7.25 g, 46 mmol) was added under stirring. The temperature was increased and after 6 h of refluxing, a mixture of 2-(3'-chloropropoxy) and 2-(3'-bromopropoxy) anthraquinones was separated and purified from 2-hydroxyanthraquinone by flash column chromatography (silica-gel) using chloroform as eluent (yield 70%).

In a second step reaction, as indicated in the above procedure, 1 g of the obtained 2-halopropoxyanthraquinone

mixture was dissolved in 100 cm⁻³ of ethanol and under stirring trimethylamine in excess (0.59 g, 0.01 mmol) was added and then left under reflux for 20 h. Vacuum-evaporation of the solvent yielded a yellow solid, which was characterised by ¹H NMR (D₂O): δ (ppm), 2.9 (9H, CH₃); 3–4 (6H, CH₂); 7.95 (2H, ar.); 8.20 (4H, ar.); 8.55 (1H, ar.) and UV (H₂O) $\lambda_{\max} = 337$ nm, $\log \epsilon_{\max} = 3.82$.

2.3. Synthesis of the acrylate and acrylamide anthraquinone copolymers

Six copolymer samples of 2-AOAQ and 2-AAAQ, each with three water-soluble co-monomers: AAm, MSO₃H and MI, were prepared by radical copolymerisation using AIBN as the thermal initiator. The copolymerisation reactions were carried out in six identical Pyrex ampoules (20 cm large, 2 cm diameter) under nitrogen at 70°C for 40 min. A mixture of DMF/water (8:2, v/v) was used as monomer solvent. Molar fraction in the feed was chosen to yield, in all the cases, a low content of the chromophore in the copolymers; f_{AOAQ} or f_{AAAQ} in each case (was fixed at a value of 0.017 and, hence the remaining co-monomers had a molar fraction $f = 0.983$). The AIBN concentration was 0.3% in w/v. After the reaction time, when total conversion was reached, the copolymers were precipitated in acetone and then purified by two repeated precipitations from water to acetone.

The obtained copolymers AOAQ-co-MI and AAAQ-co-MI, following the general procedure, were precipitated in ethanol, filtered, dissolved in water and then passed through an anionic exchange resin *Amberlite IRA 400* to give the corresponding chloride copolymers, AOAQ-co-MCl and AAAQ-co-MCl. All attempts using an anionic change in the monomer structures gave rise to unstable solid products. The solvent was removed by evaporation and then the copolymers dried to constant weight. Hence, with this anion change we avoid the possible heavy atom effect in their photochemical behaviour.

Moreover, the copolymers AOAQ-co-MSO₃H and AAAQ-co-MSO₃H were treated in the same way by changing the acid proton of the sulphonic acid by a sodium cation, in this case using the cationic exchange resin *Amberlite IR 120*. The sodium salt copolymers, AOAQ-co-MSO₃Na and AAAQ-co-MSO₃Na are more stable polymers and their photochemistry is not so pH dependent as might be expected for the copolymers containing the sulphonic acid group.

The weight percentages of anthraquinone chromophore in the copolymers were determined in water by UV spectroscopy using the molar absorption coefficient of the model compound AQW in the same solvent at the maximum wavelength. The data are collected in Table 1.

These results indicate that the composition of the copolymers is basically controlled by the monomer feed ratios. With their low anthraquinone content we can avoid possible problems derived from high local concentration in the

Table 2
Absorption in water and phosphorescence properties in methanol solution at 77 K

Sample	λ_{\max} (nm) in H ₂ O	Phosphorescence in methanol (77 K)		
		λ_{\max} (nm)	ϕ_p	τ (ms)
AQW	337	485, 492, 530	0.26	4.5
AOAQ-co-Aam	333	512	0.20	3.6
AOAQ-co-MCl	329	496	0.25	3.4
AOAQ-co-MSO ₃ Na	332	501	0.21	3.7
AAAQ-co-Aam	338	523	0.31	2.6
AAAQ-co-MCl	339	507	0.32	2.7
AAAQ-co-MSO ₃ Na	337	515	0.28	2.6

solution macromolecular coil and the consequent inhomogeneous distribution of the chromophore in the irradiation volume.

All the new water-soluble copolymers obtained were characterised by ¹H NMR. Owing to the low anthraquinone content in the copolymers, NMR proton signals are below the normal detection levels and, hence, only characteristic data are summarised below.

- AOAQ-co-AAm — ¹H NMR (D₂O): δ (ppm), 5.6 (NH); 1.9 (HC-CON); 1.2 (C-CH₂-C).
- AOAQ-co-MCl — ¹H NMR (D₂O): δ (ppm), 4.7 (O-CH₂); 3.6 (CH₂-N⁺); 2.1 (HC-COO); 1.3 (C-CH₂-C).
- AOAQ-co-MSO₃Na — ¹H NMR (D₂O): δ (ppm), 1.4 (2H, C-CH₂-C); 1.6 (1H, HC-CON); 2.1 (6H, CH₃); 5.0 (2H, CH₂-SO₃⁻Na⁺).
- AAAQ-co-AAm — ¹H NMR (D₂O): δ (ppm), 5.4 (NH); 1.8 (HC-CON); 1.2 (C-CH₂-C).
- AAAQ-co-MCl — ¹H NMR (D₂O): δ (ppm), 4.7 (O-CH₂); 3.6 (CH₂-N⁺); 3.1 (CH₃-N⁺); 2.1 (HC-COO); 1.3 (C-CH₂-C).
- AAAQ-co-MSO₃Na — ¹H NMR (D₂O): δ (ppm), 1.5 (C-CH₂-C); 1.8 (CH-CON); 2.1 (CH₃); 4.8 (CH₂-SO₃⁻Na⁺).

2.4. Spectroscopic measurements

Absorption spectra were obtained using a Shimadzu UV-265-FS spectrophotometer. Luminiscence spectra, excitation and emission, were recorded by means of a Perkin-Elmer LS-50B luminescence spectrometer. Phosphorescence quantum yields were determined by the relative method using benzophenone in ethanol glass at 77 K as standard and assuming a quantum yield [20] of 0.74. Clear glasses were obtained under these conditions. Emission triplet lifetimes were calculated from the phosphorescence decay at 77 K.

2.5. Photoreduction quantum yields

The absolute quantum yields of photoreduction (ϕ_r)

were determined for all the products in aqueous solution at an anthraquinone chromophore concentration of 10⁻⁵ mol dm⁻³ in the presence and absence of triethanolamine (10⁻⁴ mol dm⁻³) as hydrogen donor. An irradiation wavelength of 365 nm was selected using a Phillips high-pressure Hg lamp (HB-CS 500W) and a Kratos GM252 monochromator. The quartz sample cell was thermostatically controlled at 20°C and the solution was saturated by nitrogen (<5 ppm O₂ content). The photolysis of the anthraquinone chromophore was monitored by measuring the change in the UV absorption of the maximum in the same quartz cuvettes. The absorbed light intensity was measured using an International Light model 700 radiometer previously calibrated by the Aberchrome 540 actinometer [21].

2.6. Microsecond flash photolysis

Transient absorption spectra recorded immediately after the lamp flash on the microsecond time scale were obtained using a kinetic flash photolysis apparatus equipped with two xenon-filled flash lamps (pulse duration 10 μ s at 10 kV) and 150 W tungsten-halogen monitoring source. Transient decay profiles were stored using a Gould model 1425 storage oscilloscope. Water solutions of the studied compounds (10⁻⁵ mol dm⁻³) were degassed using white spot nitrogen gas (<5 ppm O₂ content). Flash photolysis measurements were also carried out in the presence of triethanolamine at 10⁻⁴ mol dm⁻³ concentration.

2.7. Photopolymerisation study by photodilatometry

Acrylamide photopolymerisations were carried out in water/acetonitrile solution (5:2, v/v) at 0.78 mol dm⁻³, using the new anthraquinone copolymers and the water-soluble model compound (anthraquinone concentration: 10⁻⁵ mol dm⁻³), together with triethanolamine ([TEOA]) = 10⁻⁴ mol dm⁻³) as photoinitiator system. Nitrogen was pumped through the dilatometer, filled with such photopolymerisable solutions, and then irradiated at 365 nm. A detailed description of the dilatometer and irradiation system employed, experimental procedure and determination of polymerisation rates (R_p), was published earlier [22].

3. Results and discussion

3.1. Spectroscopic measurements

As we found before [16], 2-substituted anthraquinones exhibit low fluorescence emission yields. For example, 2-acryloxy and 2-acrilamido anthraquinones have fluorescence quantum yield in the order of 10⁻⁴ in ethanol. In this case, the new water-soluble model and the copolymers do not exhibit any fluorescence emission, which is associated with a high rate of intersystem crossing to the triplet

Table 3

Photoreduction quantum yields of the water-soluble anthraquinones, model and copolymers. [anthraquinone] = 10^{-5} mol dm $^{-3}$ in water; [TEOA] = 10^{-4} mol dm $^{-3}$; under N $_2$; λ_{irr} = 365 nm; I_0 = 8×10^{-6} Einstein dm $^{-3}$ s $^{-1}$

Sample	$\phi_r \times 10^3$
AQW	4.5
AOAQ-co-AAm	9.6
AOAQ-co-MCl	6.1
AOAQ-co-MSO $_3$ Na	8.8
AAAQ-co-AAm	2.5
AAAQ-co-MCl	0.3
AAAQ-co-MSO $_3$ Na	0.4

state. The absorption and phosphorescence emission properties of the model and copolymers of anthraquinone are shown by the data given in Table 2.

The absorption properties of the acryloxy anthraquinone copolymers are blue-shifted by 5–10 nm compared with the absorption maximum of the low molecular weight compound owing to the hypsochromic effect of the ester group with respect to the propoxy substituent in the 2-position of AQW. Also, in water there is a red shift from the acryloxy structures compared to the acrylamide anthraquinone copolymers. This effect is lower than that of our earlier findings [11,16] where the absorption maximum in organic solvents of the amide structure was associated with an $n\pi^*$ transition whereas that for the acryloxy derivatives was associated with an $\pi\pi^*$. In water this difference in transition nature is not so clear. The phosphorescence spectra of the model and the water-soluble copolymers are illustrated by the data given in Table 2.

Similar results to the absorption data have been found for the phosphorescence characteristics of the copolymers in methanol compared to that for the model. The phosphorescence spectrum of AQW exhibits vibrational structure with bands at 485, 492 and 530 nm whereas the emission bands

of the copolymers are broad and structureless. In water, all the products have similar phosphorescence quantum yields and lifetimes indicating that there is no interaction between neighbouring groups in the triplet state. The triplet lifetimes are certainly indicative of a lowest lying triplet $n\pi^*$ state. We can conclude that, in water, the polymer chain has no significant influence on the absorption and phosphorescence emission of the anthraquinone chromophores.

3.2. Photoreduction quantum yields

Photoreduction quantum yields for the new water-soluble anthraquinone derivatives were determined in water solution in the presence and absence of TEOA used as hydrogen donor. In the presence of oxygen no photoreduction of the anthraquinone has been detected confirming the effective quenching of the triplet state by oxygen. Under nitrogen atmosphere, the photoreduction was observed only in the presence of an amine as might be expected because of the poor hydrogen donor character of water. The data also show that the macromolecular chain of the copolymers does not have any hydrogen donor role in the photoreaction. Table 3 summarises the photoreduction data obtained under nitrogen and in the presence of triethanolamine.

The photoreduction quantum yields of the model and copolymers in water are all relatively low. The restricted solubility of the products did not allow a wider evaluation. Acryloxy copolymers exhibit higher photoreduction quantum yields than that of the model, which is an indication that the polymer chain does not impair any restriction in the approach of the amine to the excited triplet state of the pendant anthraquinone. In contrast, acrylamide anthraquinone copolymers have lower values of the quantum yield than that of the low molecular weight anthraquinone. These differences are evidently associated with the differences in the nature of the excited state induced by the substitution. Thus, the triplet excited states of the ester structures are more reactive with the amine, probably because of their ability to form a more stable triplet-exciplex as was found previously [12–14].

3.3. Microsecond flash photolysis

Transient absorption spectra recorded immediately after the lamp flash for the aqueous solution of the new water-soluble anthraquinones, model and copolymers in the presence of triethanolamine are shown in Figs. 1–3.

In Fig. 1, the spectrum of the model, in the absence of amine, does not show any absorbance owing to the poor hydrogen atom donor behaviour of water. This is in marked contrast with other solvents such as alcohols where transient absorbances were detected in the absence of amines. The presence of an amine induces a strong transient absorption band confirming its hydrogen atom donor ability in the photoreaction. Figs. 2 and 3 represent the corresponding spectra obtained with the water-soluble anthraquinone copolymers, acrylates and acrylamides, respectively. In

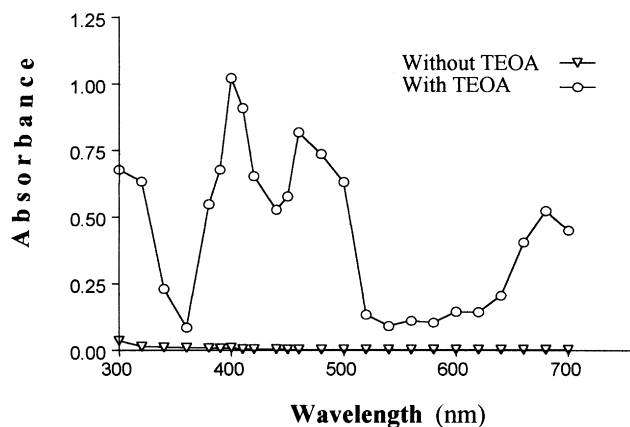


Fig. 1. Transient absorption spectra recorded immediately after the lamp flash on the microsecond flash photolysis of the water-soluble anthraquinone model AQW (10^{-5} mol dm $^{-3}$) in the presence and absence of triethanolamine (TEOA), 10^{-4} mol dm $^{-3}$.

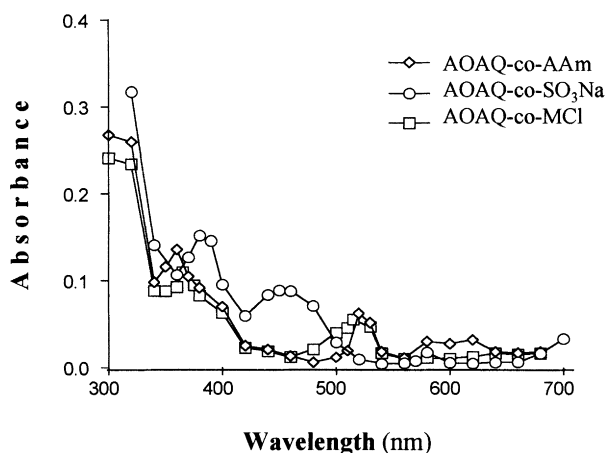


Fig. 2. Transient absorption spectra recorded immediately after the lamp flash on the microsecond flash photolysis of the water-soluble anthraquinone acrylate anthraquinone copolymers in the presence of triethanolamine. [anthraquinone] = 10^{-5} mol dm $^{-3}$; [TEOA] = 10^{-4} mol dm $^{-3}$.

the absence of triethanolamine no transient absorption was detected. This is a confirmation that the macromolecular copolymer chain does not participate in the photoreaction and, hence, does not give hydrogen atoms to the excited triplet state via an intramolecular photoreduction. In the presence of oxygen, transient absorptions are negligible confirming the effective quenching of the anthraquinone triplet state as being responsible for the radical formation. All the products displayed similar spectra but with very different relative intensities. The absorption bands can be assigned to one of two structures namely the semi-anthraquinone radical (AQH \cdot) and the radical anion (AQ \cdot^-), the nature of these transients has been well established [15,23]. The absorption band observed in the region 340–450 nm is assigned to the semi-quinone radical and the absorption band in the 500–600-nm region is due to the radical anion

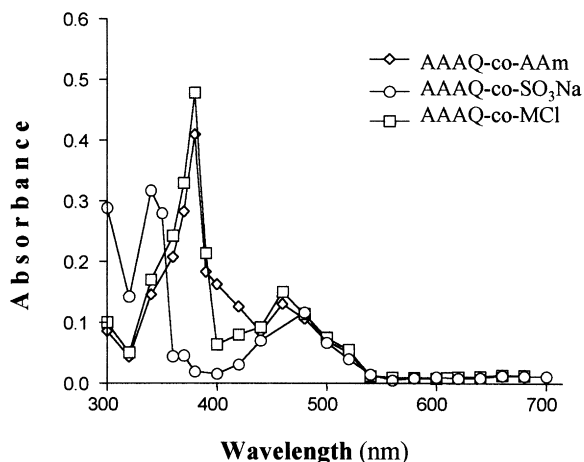


Fig. 3. Transient absorption spectra recorded immediately after the lamp flash on the microsecond flash photolysis of the water-soluble anthraquinone acrylamide anthraquinone copolymers in the presence of triethanolamine. [anthraquinone] = 10^{-5} mol dm $^{-3}$; [TEOA] = 10^{-4} mol dm $^{-3}$.

and are produced under this experimental condition by the routes indicated in Eqs. (2), (3), (6) and (7). The semi-anthraquinone absorption is particularly well defined for the model AQW and the amide anthraquinone copolymers in contrast with that for the acrylate anthraquinone copolymers where the differences with the radical anion band are not so clear. Table 4 summarises the flash photolysis data obtained.

For the model AQW the detected absorptions are much higher than those obtained for the copolymers and, in their turn, amide anthraquinone copolymers exhibit higher absorptions corresponding to the semi-anthraquinone radicals. This decrease in absorbance of the semi-quinone radical in the copolymers may possibly be due to the influence of the microenvironment corresponding to the polymeric coil on the disproportionation termination process. The absorbances of the radical anion exhibit the same behaviour in intensity commented on for the semi-anthraquinone radicals but, in this case, there is a general increase of these absorbances compared with those found previously [15] for the oil-soluble model and copolymers of anthraquinone. This higher production of radical anions under our conditions, compared with organic solvents, is due to the water polarity, which allows a better separation of the ion pair. As expressed in Eqs. (6) and (8), the radical anion is in equilibrium with the semi-quinone radical, such equilibrium and associated structures are shown in Fig. 4.

The measured lifetimes of semi-anthraquinone radicals by decay profile appear to fit more accurately with a second-order kinetic indicating the importance of the disproportionation mechanism of the semi-quinone radical termination as was expressed in Eq. (5). This kinetic order confirms that the polymer chain, in the copolymers, does not influence the bimolecular termination of the radicals and is consistent with the poor hydrogen donor character of water. Another important observation is the much longer measured semi-quinone radical lifetime on the low molecular weight model anthraquinone, AQW, compared to that for the copolymers, which can be associated with an efficient quenching process owing to the macromolecular coil in solution. Radical anion kinetic profiles were difficult to assess accurately because of the complexities of contribution from the semi-quinone radical [23]. The detection of these intermediates provides evidence for the mechanism of the photoreduction to produce reactive radicals by the anthraquinones in their use as photoinitiator of polymerisation, an aspect that will be considered in the next section.

3.4. Photopolymerisation study by photodilatometry

Photopolymerisations of acrylamide in a solvent mixture of water and acetonitrile, 5:2, were carried out in a photodilatometer as described in Section 2. The polyacrylamide conversion versus irradiation time was obtained using all the new water-soluble products and triethanolamine as a hydrogen donor. From conversion-time profiles, the rate

Table 4

Transient absorption data obtained immediately after the flash lamp on microsecond flash photolysis of the water-soluble anthraquinone model and copolymers. [anthraquinone] = 10^{-5} mol dm $^{-3}$; [TEOA] = 10^{-4} mol dm $^{-3}$ in water, under N $_2$

Sample	Semi-anthraquinone radical AQH \cdot			> Radical anion AQ $^{\cdot-}$	
	λ_{\max} (nm)	Absorbance	τ (ms) ^a	λ_{\max} (nm)	Absorbance
AQW	400	1.02	156	460	0.81
AOAQ-co-AAm	360	0.13	4	520	0.06
AOAQ-co-MCl	365	0.11	4	510	0.06
AOAQ-co-MSO $_3$ Na	380	0.15	4	450	0.09
AAAQ-co-AAm	380	0.40	2	460	0.13
AAAQ-co-MCl	375	0.50	2	455	0.15
AAAQ-co-MSO $_3$ Na	340	0.30	2	480	0.11

^a Second-order kinetic decay.

of polymerisation (R_p) was calculated using conversions lower than 10%. Using the general equation of the photo-initiated polymerisation shown below, the photoinitiation quantum yield (ϕ_i) and the photoinitiation rate (R_i) were calculated.

$$R_p = \frac{k_p}{k_t^{1/2}} [M] R_i^{1/2} = \frac{k_p}{k_t^{1/2}} [M] \phi_i^{1/2} I_a^{1/2}$$

where k_p and k_t are the propagation and termination rate constants and, for acrylamide at 19°C have the values [24] $k_p = 8.2 \times 10^3$ dm 3 mol $^{-1}$ s $^{-1}$ and $k_t = 5.5 \times 10^6$ dm 3 mol $^{-1}$ s $^{-1}$, I_a is the absorbed intensity and $[M]$ is the monomer concentration. The obtained data are compiled in Table 5.

First, in the absence of amine no photopolymerisation was observed in accordance with the absence of any detectable photoreduction and the absence of transient absorption when triethanolamine is not added to the water solution. Slightly lower photopolymerisation rates and photoinitiation quantum yields were found for the acrylate anthraquinone copolymers compared with the obtained values for the model AQW. Only one of the copolymers, AOAQ-co-MCl, exhibits identi-

Table 5

Photopolymerisations of acrylamide, 0.78 mol dm $^{-3}$, photoinitiated by the new water-soluble anthraquinones, model and copolymers. [AQ] = 10^{-5} mol dm $^{-3}$, in the presence of triethanolamine, [TEOA] = 10^{-4} mol dm $^{-3}$ in H $_2$ O/ACN (5:2, v/v), $\lambda_{\text{irr}} = 365$ nm, under N $_2$ atmosphere

Sample	$R_p \times 10^5$ ^a	$R_i \times 10^{10}$ ^a	$\phi_i \times 10^3$
AQW	6.3	6	25
AOAQ-co-AAm	5.1	4	16
AOAQ-co-MCl	6.9	7.2	30
AOAQ-co-MSO $_3$ Na	4	2.4	10
AAAQ-co-AAm	3.4	1.7	7
AAAQ-co-MCl	2.1	0.6	2.5
AAAQ-co-MSO $_3$ Na	1.5	0.3	1.2

^a Measured in mol dm $^{-3}$ s $^{-1}$.

cal photopolymerisation activity to that of the low molecular weight product. This fact is in accordance with the same nature of the ionic group of the structures. Also, this is an indication that the polymer chain of the copolymers does not have a significant influence on the photoinitiation mechanism. The lower rates and quantum yields of photopolymerisations determined for the acrylamide anthraquinone copolymers are in agreement with the lower photoreduction quantum yields shown in Table 3. This general correlation of photopolymerisation activity with photoreduction confirms that the reaction occurs just through hydrogen abstraction by the triplet state of the anthraquinone only from the amine since water is a very poor hydrogen atom donor. This photoreaction leads to alkylamino radicals, which can initiate efficiently the polymerisation.

4. Conclusions

Novel water-soluble anthraquinones, model and copolymers have been synthesised in this work contributing to an improvement in photoinitiator design. In water, no photoreduction was observed as well as no microsecond transient absorption in the absence of triethanolamine. In the

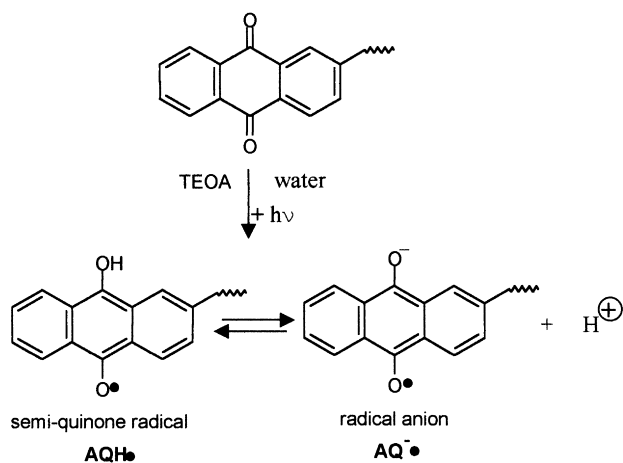


Fig. 4. Scheme of the water soluble anthraquinone photoreduction by triethanolamine showing the radical equilibrium present in water.

presence of the amine, semi-anthraquinone radicals and radical anions are produced and the latter is specially favoured by the polarity of water. The acrylate anthraquinone copolymers are similar in efficiency to that of the low molecular weight product in the photoinitiation of polymerisation when used in combination with triethanolamine. Acrylamide anthraquinone copolymers have lower efficiency in agreement with their lower photoreduction quantum yields.

Acknowledgements

We thank the Comisión Interministerial de Ciencia y Tecnología (CICYT) for financial support, MAT 97-0727.

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