

# Synthesis, photochemical and photoinitiation activity of water soluble copolymers with pendent benzil chromophores

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In the present paper the synthesis of three novel water soluble copolymers with benzil pendant groups are described. The new polymers have been prepared by copolymerization of the obtained benzil acrylate, 1-phenyl-2-[4-(2-methacroyloxyethoxy)phenyl]ethandione-1,2 (MBz) with three water soluble comonomers: acrylamide, 2-acrylamido-2-methylpropane sulphonic acid and 2-acryloxyethyl trimethylammonio iodine. The absorption, luminescence, photoreduction and microsecond flash photolysis characteristics of the new copolymers were examined in water and methanol and the results compared to the corresponding low molecular weight compound. The photoinduced polymerization activities of the new products have been determined by photodilatometry in the presence of a tertiary amine. The copolymers exhibit polymerization rates and quantum yields similar to those of the low molecular weight model compounds. © 1998 Published by Elsevier Science Ltd. All rights reserved.

## INTRODUCTION

Polymeric photoinitiators can be defined as a macromolecular system that contains pendant or in-chain chromophores which through a light absorption process can generate initiating primary radicals capable of initiating polymerization reactions. Macromolecules containing photofragmenting (Type I photoinitiators) and photoreducing chromophores (Type II photoinitiators) have been prepared and studied in the last decade<sup>1,2</sup> due to various advantages compared to their corresponding low molecular weight analogues. Their macromolecular nature offers reduced migration and improved solubility characteristics. In previous articles we reported on the preparation and characterization of new polymerizable and polymeric photoinitiators containing thioxanthone functional groups able to initiate the polymerization of vinyl monomers in oil<sup>3,4</sup> and aqueous systems<sup>5,6</sup>.

From a reactivity point of view this can often be improved because of the influence of the macromolecular microenvironment on lower recombination processes, local concentration control and synergistic effects with others groups present in the same polymer chain. One other attractive possibility is the specific design of the polymeric photoinitiator which can provide versatility in the synthesis through the copolymerization of photosensitive monomers.

Water-borne UV-curable formulations have resulted in an increase in industrial applications and are nowadays readily available systems that can be successfully used in many applications. In aqueous systems problems such as low activity and poor solubility arise with polymeric

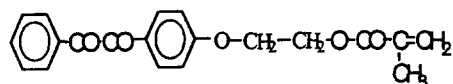
photoinitiators. This paper is concerned with the synthesis of new water soluble polymeric photoinitiators based on benzil containing water soluble monomer structures in the main chain of the polymer as hydrophilic segments. Also, a water soluble model has been synthesized by the substitution of an ammonium group onto the oil soluble benzil chromophore. The synthesized new polymeric photoinitiators are compared with a model compound in terms of their general photochemistry in an aqueous system and related to the corresponding photoinitiation activity.

Benzil derivatives are well-known Type II photoinitiators<sup>7,8</sup> and benzil/amine systems have been used as photoinitiators for vinyl free radical polymerization for many years<sup>9,10</sup> exhibiting low rates of cure. The photoinitiation activity is enhanced by the introduction of electron donating substituents in the *para* position of the benzil structure. Consequently, in this work, we have synthesized a benzil chromophore substituted with a methacryloxyethoxy group in position 4. A similar improvement in reactivity can be expected by incorporating the benzil moiety into the backbone of a polymeric system. Oil soluble polymers containing benzil moieties as pendant groups<sup>11</sup> in the main chain and as terminal groups have been studied previously<sup>12–14</sup>.

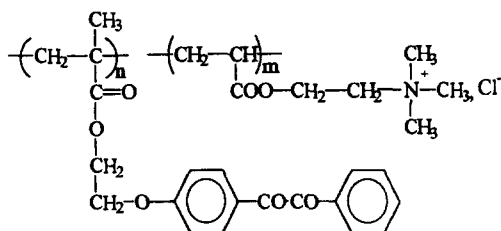
In this paper, three new water soluble copolymers with benzil pendant groups have been prepared by copolymerization of a benzil derivative monomer (MBz) and two commercial water soluble comonomers, acrylamide (AAM), 2-acrylamido-2-methylpropanesulphonic acid (MSO<sub>3</sub>H), and a previously synthesized monomer, 2-acryloxyethyl trimethylammonio iodide (MI). The proton and the iodine can be replaced by sodium and chlorine, respectively, on the obtained polymers by the use of ionic exchange resins. The structures of MBz and the

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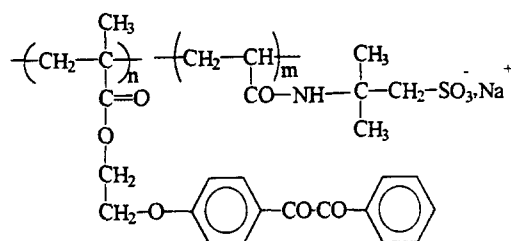
corresponding copolymers are shown below:



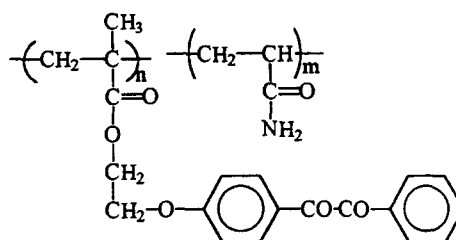
MBz



Bz-co-Cl

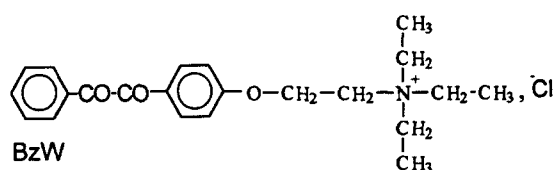


Bz-co-SO<sub>3</sub>Na



Bz-co-AAm

For comparison we have synthesized a water soluble benzil to use as a low molecular weight model compound, 1-phenyl-2-[4-(2-triethylaminoethoxy)phenyl]ethandione-1,2 chloride (BzW).



BzW

This paper describes the study of these novel water soluble benzil derivatives as photoinitiators of an aqueous system, acrylamide/water. The aim was to correlate photochemical behaviour with efficiency as radical photoinitiators. A detailed kinetic study has been undertaken for the polymerization of acrylamide photoinitiated by the benzil-bound copolymers including the determination of polymerization rates and quantum yields. The data were compared with those of the low molecular weight model compound BzW.

## EXPERIMENTAL

### Synthesis details

1-Phenyl-2-[4-(2-hydroxyethoxy)phenyl]ethandione-1,2 (I) was prepared following the method described previously by Lukáč *et al.*<sup>11</sup>.

1-phenyl-2-[4-(2-tosylethoxy)phenyl]ethandione-1,2 (II). 0.78 g of compound I (2.9 mmol) and 0.40 g of p-toluensulfonyl chloride (3.2 mmol) were placed in a flask and dissolved in dichloromethane with continuous stirring. The mixture was cooled to 0°C in an ice bath followed by the addition of triethylamine (2 ml), previously distilled. After 1 h the colour of the solution changed to dark yellow. The mixture was then stirred at room temperature for 25 h and then poured into a

mixture of ice and hydrochloric acid (35%) in water. The product of the reaction was then extracted with dichloromethane. The organic phase was washed with water and dried over anhydrous magnesium sulphate, filtered and concentrated to a lower volume under reduced pressure. Purification through flash chromatography on a silica gel column was carried out using dichloromethane as eluent phase and a yellow product, compound II (m.p. = 107°C), was obtained (yield = 65%).

|  |  |
|--|--|
| Elemental analysis:                              | 64.88% C, 4.65% H, 7.26% S<br>(calculated: 65.09% C, 4.70% H, 7.5% S)  |
| <sup>1</sup> H NMR (CDCl <sub>3</sub> ): δ(ppm): | 2.3(3H, CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> ); 4.3(m, 4H, OCH <sub>2</sub> CH <sub>2</sub> O); 6.8-7.9 (13H ar) |

1-phenyl-2-[4-(2-triethylaminoethoxy)phenyl]ethandione-1,2 tosylate (III). A mixture of 0.8 g (0.56 mmol) of 1-phenyl-2-[4-(2-tosylethoxy)phenyl]ethandione 1,2 (II) and 0.5 ml of triethylamine was dissolved in 20 ml *N,N*-dimethylformamide (DMF) by stirring at room temperature until total dissolution and then heated at 65°C for 48 h. The solvent was then removed under reduced pressure using a rotary evaporator. The residue was solved in dichloromethane and extracted with water. The aqueous portion was concentrated to give an orange viscous liquid, compound III (yield = 55%).

|  |   |
|--|---|
| Elemental analysis:                            | 66% C, 6.5% H, 2.8% N, 5.88% S<br>(calculated: 66.28% C, 6.60% H, 2.6% N, 6.09% S)  |
| <sup>1</sup> H NMR (D <sub>2</sub> O): δ(ppm): | 1.3 (t, 9H, CH <sub>3</sub> -CH <sub>2</sub> ); 2.4 (3H, CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> ); 3.3 (6H, CH <sub>3</sub> -CH <sub>2</sub> ); 3.8 (2H, CH <sub>2</sub> -N); 4.5 (2H, OCH <sub>2</sub> ); 7.1-8 (13H ar) |

1-Phenyl-2-[4-(2-triethylaminoethoxy)phenyl]ethandione-1,2 chloride (BzW). Compound III was passed through a column with an anionic exchange resin: Dowex 1 × 8 (3.5 milliequiv. per g of dried resin) and then developed with water. The water was removed under reduced pressure to give a yellow solid, identified as compound BzW

(yield = 70%).

IR (KBr),  $\nu_{\max}$  (cm<sup>-1</sup>): 1670 (C=O st); 1600, 1570, 1510, 1475 (arC-H  $\delta$  ip); 1390 (-CH<sub>3</sub>,  $\delta$  si); 1220 (arC-O-Cal, st as); 1030 (C-O-C, st si)

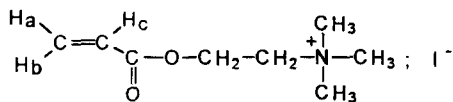
UV (H<sub>2</sub>O);  $\lambda_{\max}$  (nm): 295 (log  $\epsilon$  = 4.19)

<sup>1</sup>H NMR (D<sub>2</sub>O);  $\delta$  (ppm): 1.3 (9H, CH<sub>3</sub>-CH<sub>2</sub>); 3.3 (6H, CH<sub>3</sub>-CH<sub>2</sub>-N<sup>+</sup>); 3.7 (2H, CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>); 4.5 (2H, OCH<sub>2</sub>); 7.1-8.2 (m, 9H ar)

### Synthesis of monomers

**1-Phenyl-2-[4-(2-methacroyloxyethoxy)phenylethane-dione-1,2 (MBz)].** This was prepared by esterification of compound I with methacrylic acid following the method described previously<sup>11</sup>.

**2-Acryloxyethyltrimethylamonio iodide (MI).** 20 ml of 2-(dimethylamino)ethyl acrylate (0.13 mmol) were dissolved at room temperature in 50 ml of acetone, and then 9 ml of methyl iodide (0.14 mmol) was added slowly. The precipitate was filtered, washed with diethyl ether and dried to give the monomer MI (yield = 95%)



Elemental analysis: 36.2% C, 4.7% N, 7.0% H, 44% I (calculated: 33.70% C, 4.91% N, 5.62% H, 44.54% I)

IR (KBr),  $\nu_{\max}$  (cm<sup>-1</sup>): 3100,  $\nu_s$ (C-H); 1730,  $\nu_s$ (C=O); 1650,  $\nu_s$ (C=C); 1460, 1380  $\delta_{as}$ ,  $\delta_s$ (CH<sub>3</sub>); 1200,  $\nu_s$ (O-C); 990, 890  $\delta_{oop}$ (=CH<sub>2</sub>)

<sup>1</sup>H NMR (D<sub>2</sub>O);  $\delta$ (ppm), J(Hz): 6.12 (H<sub>c</sub>, J<sub>c,b</sub> = 6.2); 5.93 (H<sub>a</sub>, J<sub>a,b</sub> = 6.2); 6.24 (H<sub>b</sub>, J<sub>a,b</sub> = 6.2, J<sub>b,c</sub> = 6.2); 4.55 (O-CH<sub>2</sub>); 3.69 (CH<sub>2</sub>-N<sup>+</sup>); 3.13 (CH<sub>3</sub>)

### Copolymerization procedure

Three new copolymers were obtained by copolymerization of MBz with acrylamide (AAm), 2-acryloxyethyl trimethylamonio iodide (MI) and 2-acrylamido-2-methyl propane sulfonic acid (MSO<sub>3</sub>H). The copolymerization reactions were carried out in Pyrex ampoules under the same conditions under nitrogen at 70°C for 40 min using *N,N*-dimethylformamide/water (8/2, v/v) as solvent and azo-bis-isobutironitrile (AIBN) as initiator (0.3% w/v).

Molar fractions in the feed were chosen to yield a low content of the chromophore in the copolymers such as  $f_{MBz} = 0.017$  and 0.983 for the remaining comonomers.

The copolymer Bz-co-MI was precipitated in methanol, filtered, dissolved in water and then passed through an anionic exchange resin AMBERLITE IRA 400 to give the corresponding chloride copolymer Bz-co-Cl. The solvent was removed by evaporation and then the copolymer dried to constant weight.

UV:  $\lambda_{\max}$  (H<sub>2</sub>O) = 295 nm

IR (KBr),  $\nu_{\max}$  (cm<sup>-1</sup>): 1730,  $\nu_s$ (C=O); 1670,  $\nu_s$ (C=O); 1580, 1560, 1500, 1440,  $\nu$ (C-C<sub>aromatic</sub>), 1460, 1380  $\delta_{as}$ ,  $\delta_s$ (CH<sub>3</sub>); 1200,  $\nu_s$ (O-C); 990, 890  $\delta_{oop}$ (=CH<sub>2</sub>)

The copolymer Bz-co-AAm was purified by successive precipitations from aqueous solutions into methanol and acetone.

UV:  $\lambda_{\max}$  (H<sub>2</sub>O) = 298 nm

IR (KBr),  $\nu_{\max}$  (cm<sup>-1</sup>): 3200 (N-H); 1730, O<sub>s</sub>(C=O); 1700 O<sub>s</sub>(C=O) 1670,  $\nu_s$ (C=O)<sub>Bz</sub>; 1580, 1560, 1500, 1440,  $\nu$ (C-C<sub>aromatic</sub>), 1460, 1380  $\delta_{as}$ ,  $\delta_s$ (CH<sub>3</sub>)

The copolymer Bz-co-SO<sub>3</sub>H was purified by precipitation in acetone. Due to the high reactivity of the polyacids, copolymer Bz-co-SO<sub>3</sub>H was transformed into the corresponding sodium salt to obtain a more stable polymeric photoinitiator using a cationic exchange resin AMBERLITE IR 120. The solution was concentrated by evaporation to obtain Bz-co-SO<sub>3</sub>Na.

UV:  $\lambda_{\max}$  (H<sub>2</sub>O) = 299 nm

The content as percentage in weight of the benzil chromophore in the copolymers were determined in water by UV spectroscopy using the molar absorption coefficient of the model compound BzW in water, at 295 nm log  $\epsilon$  = 4.20. The obtained contents of benzil are collected in Table 1.

### Steady-state irradiation

Quantum yields of photoreduction,  $\phi_r$ , were determined in aqueous solution (chromophore concentration, 10<sup>-3</sup> M) in the presence and absence of 2-diethylaminoethanol (2 × 10<sup>-2</sup> M) as hydrogen donor, irradiating under nitrogen at a wavelength of 365 nm. The irradiation system and the experimental procedure have been described in an earlier paper<sup>3</sup>.

### Microsecond flash photolysis

End-of pulse transient absorption spectra on the microsecond time scale were obtained using a kinetic flash photolysis apparatus equipped with two xenon-filled flash lamps (pulse duration 10  $\mu$ 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<sup>-4</sup> M) were degassed using white spot nitrogen gas (<5 ppm O<sub>2</sub>). Flash photolysis measurements were also carried out in the presence of triethanolamine at 10<sup>-3</sup> M concentration.

### Photodilatometry

Acrylamide photopolymerizations were carried out in water:acetonitrile solution (5:2, v:v) at 0.78 M, using benzil copolymers and water soluble model compound (benzil concentration: 3.17 × 10<sup>-5</sup> M) together with 2-(*N,N*-diethylamino)ethanol ([DEA] = 3 × 10<sup>-4</sup> M) as a photoinitiator system. Nitrogen was pumped through the dilatometer, filled with such photopolymerizable solutions, and then irradiated at 365 nm. A detailed description of the dilatometer and irradiation system employed, experimental procedure and determination of polymerization rates,  $R_p$ , was published earlier<sup>3</sup>.

### Materials

*p*-Toluenesulfonyl chloride (Panreac), triethylamine (Scharlau), methacrylic acid (Merck), methyl iodide (Aldrich), dichloromethane (Quimicen), *N,N*-dimethylformamide (Scharlau) were used as received. Anionic exchange resin: Dowex 1 × 8, anionic exchange resin AMBERLITE IRA 400. Cationic exchange resin: AMBERLITE IR 120. In all experiments, MilliQ grade water was used.

**Table 1** Percentage of benzil chromophore in the copolymers

| Bz-co-Cl | Bz-co-AAm | Bz-co-SO <sub>3</sub> Na |
|----------|-----------|--------------------------|
| 2.3      | 2.7/9.5   | 2.3                      |
| ± 0.1    |           |                          |

2-(*N,N*-diethylamino)ethanol was obtained from Aldrich Chemical Co. Ltd. and was purified by vacuum distillation. Acrylamide from Merck was purified by recrystallization in acetone. The monomers, 2-(dimethylamino)ethyl acrylate from Tecal and 2-acrylamido-2-methyl propane sulfonic acid from Kodak, were used as received.

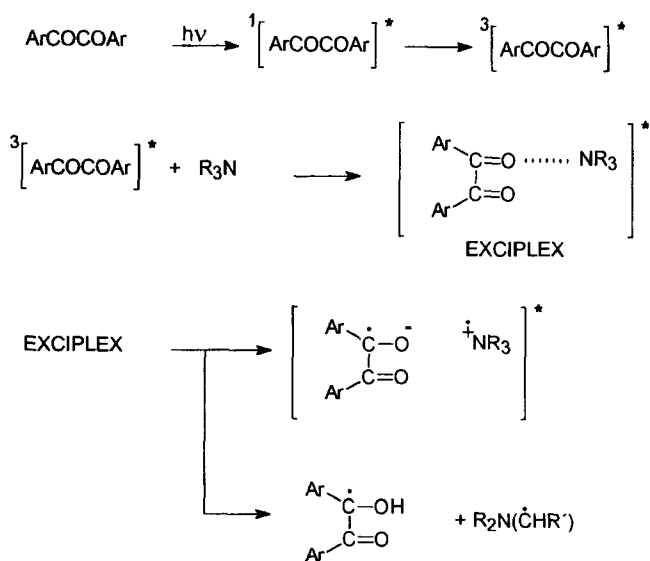
#### Apparatus

IR and <sup>1</sup>H-NMR spectra were recorded on a Perkin Elmer model 783 and on a Bruker model AM operating at 200 MHz, respectively.

**Spectroscopic measurement.** UV spectra were recorded by means of a Shimadzu UV-265-FS spectrophotometer. Fluorescence and phosphorescence emission spectra were obtained using a Perkin-Elmer LS-50B luminescence spectrophotometer. Phosphorescence quantum yields were determined using the relative method with benzophenone as a standard assuming a quantum yield of 0.74 in ethanol glass at 77 K<sup>15</sup>. Clear glasses were obtained under these conditions. Emission triplet lifetimes were calculated from the phosphorescence decays at 77 K.

## RESULTS AND DISCUSSION

Benzil chromophore photochemistry is dependant on the irradiation wavelength. Although not unanimously agreed, our earlier work indicated that at short wavelengths ( $\lambda < 330$  nm) benzoyl radicals are produced by a Norrish I cleavage, which then abstract hydrogen atoms from the amine<sup>16</sup>. However, at long-wavelengths hydrogen atom abstraction of the amine by the lowest excited triplet state of benzil takes place. The Benzil-amine-vinyl monomer system has been extensively studied<sup>8,9,17,18</sup>. There are some conflicting statements regarding whether the benzil-amine system follows the general mechanism of reaction in which just one carbonyl group is excited or in contrast, if during this process both carbonyl groups of the benzil are excited. This second mechanism has been evidenced by different authors<sup>9,17,18</sup>. The proposed mechanism for the photopolymerization of vinyl monomers ( $\lambda_{irr} > 330$  nm) by benzil-amine photoinitiator system considering the complexation of just one of its carbonyl groups is shown in *Scheme 1*.



Scheme 1

The decomposition of the exciplex can lead to free radicals and/or ion radical formation depending on the acid-base conditions of the system. In general, free radical formation is favoured in nonpolar solvents, while ion radical formation becomes an important pathway of exciplex deactivation in a polar solvent. The efficiency of the initiation process in water<sup>19</sup> depends mainly of the ability of the charge transfer complex, formed with the amine, to undergo proton transfer. Hence, the generation of the ion radicals stabilized by resonance could compete very well with the proton transfer between the two ion radicals of the exciplex which gives finally a ketyl radical and the corresponding alkylamino radical. The alkylaminoradical can initiate the polymerization and also, when the benzil concentration is high, can react with the benzil to produce an unwanted ketyl radical causing a decrease in the efficiency of the initiating system<sup>7,20</sup>.

The aim of this paper is to carry out a study to determine the mechanism and to evaluate the efficiency of the novel water soluble monomeric and polymeric benzil derivatives as photoinitiators of free radical polymerization as well as to understand, at least qualitatively, the influence of the polymer environment in the process.

#### Synthesis

The synthesis of the low molecular weight model compound was carried out according to *Scheme 2*.

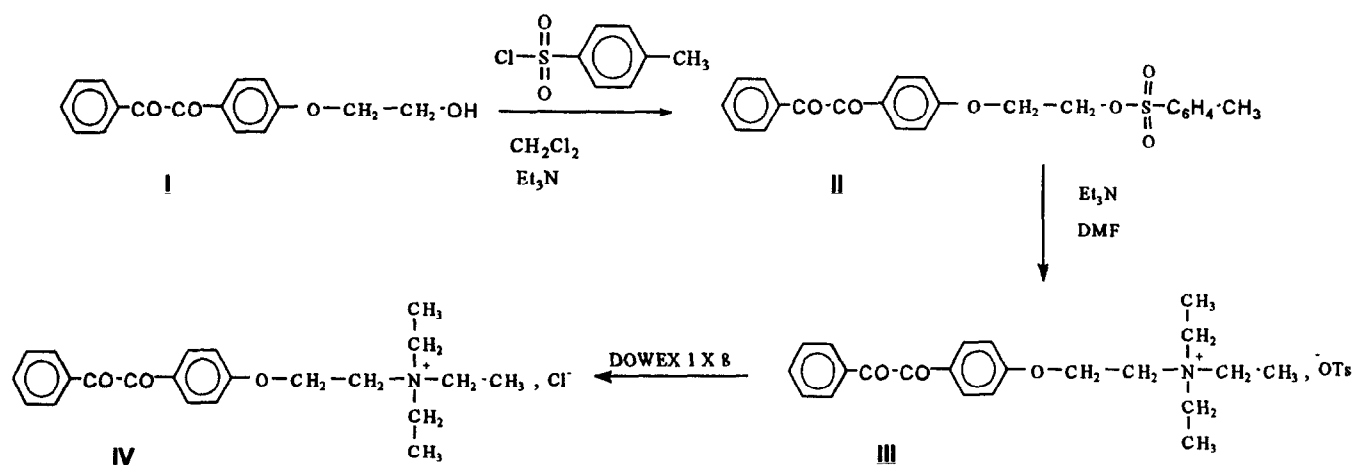
Compound II was prepared with good yield by reaction of compound I with *p*-toluensulfonyl chloride in the presence of triethylamine in dichloromethane solvent. Formation of the tosylate salt was carried out by reaction of compound II with triethylamine in DMF solution with 55% yield. Then, tosylate anion exchange by the chloride was accomplished by passing a water solution of compound III through an anionic exchange resin saturated in chloride anions to yield our low weight model compound, BzW.

Water soluble monomers: acrylamide (AAM), 2-acrylamido-2-methylpropanesulphonic acid (MSO<sub>3</sub>H), and 2-acryloxyethyl trimethylammonio iodide (MI) were copolymerized with the oil-soluble benzil derivative monomer (MBz) to obtain new water soluble copolymers with benzil pendants groups. Monomer, MBz, was synthesized by reaction of compound I with methacrylic acid and 2-acryloxyethyltrimethylammonio iodide, MI, by reacting 2-(dimethylamino)ethyl acrylate with methyl iodide with quantitative yield.

The copolymerization reactions were carried out by a free radical polymerization using AIBN as thermal photoinitiator in DMF/water (8:2, v:v) as solvent. Ratios of comonomer feed were 0.983/0.017; where the lower feed was chosen in all the polymerizations for the monomer bearing the benzil chromophore to assure homogeneity in chromophore distribution along the copolymer chains.

The exchange of iodide anion by chloride in the copolymer was carried out to avoid the heavy atom effect in its photochemical behaviour. Attempts to carry out the anionic exchange in the comonomer structure, prior to copolymerization, yields an unstable solid. However, passing an aqueous solution of copolymer with iodide counterions through an anionic exchange resin gives the corresponding chloride copolymer with quantitative yield.

The copolymer obtained with the commercial comonomer, 2-acrylamido-2-methylpropanesulphonic acid, shows a very high reactivity due to the sulphonic acid moieties. This copolymer was modified by changing the acid groups by sodium sulphate salts to obtain a more stable polymer.



### BzW

Scheme 2

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

| COMPOUND                 | Absorption in Water<br>$\lambda_{\text{max}}$ (nm) | Absorption in Methanol<br>$\lambda_{\text{max}}$ (nm) | Phosphorescence (77 K)      |                         |                                  |
|--------------------------|--|---|-----------------------------|-------------------------|----------------------------------|
|                          |  |   | $\lambda_{\text{max}}$ (nm) | $\phi_{\text{p}}^{(a)}$ | $\tau_{1/2}$ (ms) <sup>(b)</sup> |
| Benzil                   | —  | 266   | 514                         | 0.79                    | 5                                |
| MBz                      | —  | 291   | 500                         | 0.79                    | 3                                |
| BzW                      | 295<br>(log $\epsilon = 4.20$ )                    | 291   | 512, 502, 495               | 0.75                    | 3                                |
| Bz-co-Cl                 | 295  | —   | 510, 498, 490               | 0.72                    | 3                                |
| Bz-co-AAm                | 298  | —   | —                           | —                       | —                                |
| Bz-co-SO <sub>3</sub> Na | 299  | —   | 512, 500, 487               | 0.52                    | 3                                |

- not soluble

(a)  $\pm 0.02$

(b)  $\pm 0.2$

The weight percentages of benzil chromophore in the copolymers were determined in water by UV spectroscopy using the extinction molar coefficient of the model compound BzW in the same solvent. The data are collected in Table 1.

These results indicate that the composition of the copolymers is basically controlled by the monomer feed ratios.

The proton nuclear magnetic resonance of the copolymers does not show any peak at 6.15 and 5.75 ppm, indicating that no residual monomer was present in the copolymers. FTIR spectra also confirms this feature.

#### Spectroscopic measurements

The first interesting feature of the spectroscopic properties is the bathochromic effect observed with the introduction of the ethoxy segment in position 4 compared to the benzil structure. Also, the spacer avoids the hypsochromic effect of the polar group in the benzil ring and absorption bands in water of the three copolymers are identical to those of the model BzW as shown by the absorption data in Table 2.

Fluorescence emission from these compounds was not detected. Similar results to the absorption data have been found for the phosphorescence characteristics of the copolymers in methanol compared to the model BzW. This photochemical behaviour seems to indicate that there is no interaction between neighbouring benzil groups in the

macromolecular chain both in the ground and triplet states. The equal values of phosphorescence lifetimes are indicative of the fact that the self-quenching of benzil excited states does not occur in the copolymers, at least for these low chromophore contents. Also, the high phosphorescence quantum yields and short phosphorescence lifetimes measured in a polar solvent such as methanol are indicative of a lowest lying triplet  $n-\pi^*$  state. However, due to substitution effects in the copolymers some mixing with a close lying triplet  $\pi-\pi^*$  state.

#### Steady-state photolysis

Photoreduction quantum yields for the new benzil derivatives were determined in water solution in the absence and presence of a hydrogen donor, 2-(*N,N*-diethylamino)ethanol. Table 3 summarizes the quantum yields obtained under a nitrogen atmosphere.

Photoreduction quantum yields are low in the absence of amine but increase in its presence confirming a hydrogen atom abstraction mechanism. However, photoreduction quantum yields are lower than that expected for aromatic ketones in the presence of amine, due to the absorption by the photoreduction products (benzoin structures) at the analysis wavelength 295 nm. In this case UV spectroscopy as detection method to follow the photoreduction of benzil does not provide absolute quantum yields. However, interesting information is obtained regarding the effect of the percentage of chromophore in the polymer as well as the

**Table 3** Photoreduction quantum yields of benzil photoinitiators. [Bz] =  $10^{-5}$  M, DEA: 2-(*N,N*-diethylamino)ethanol, under  $N_2$ ;  $\lambda_{ir} = 365$  nm,  $I_0 = 8 \times 10^{-6}$  Eins/L.s

| Compound                        | $\phi_r^{(a)} \times 10^3$ | $\phi_r^{(b)} \times 10^3$ |
|---------------------------------|----------------------------|----------------------------|
| BzW                             | —                          | 0.2                        |
| Bz-co-Cl (2.3%)                 | 4.7                        | 20                         |
| Bz-co-AAm (2.7%)                | —                          | 0.6                        |
| Bz-co-AAm (9.5%)                | 3.8                        | 4.5                        |
| Bz-co-SO <sub>3</sub> Na (2.3%) | 1.8                        | 2.7                        |

— Not observed

± 0.1

(a) absence of amine (DEA)

(b) presence of DEA ( $2 \times 10^{-3}$  M)

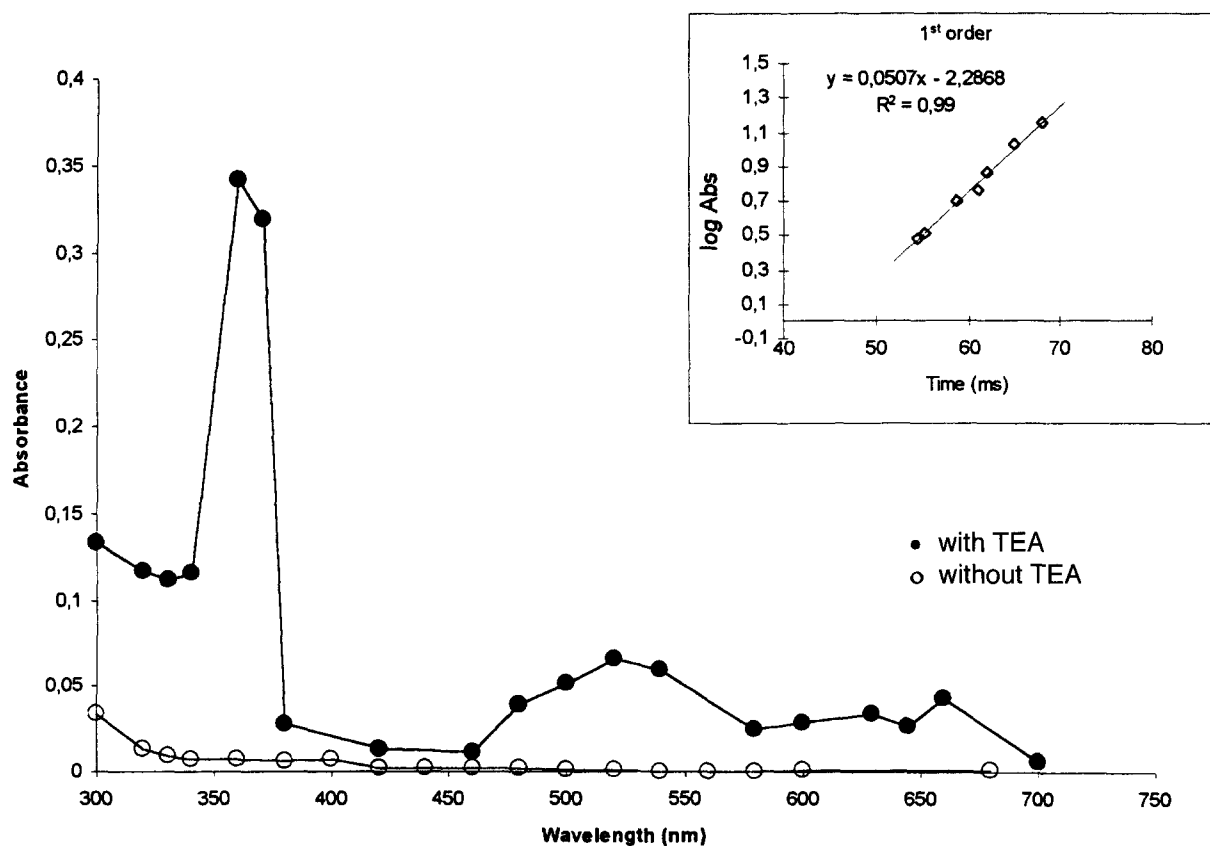
nature of the polymer on their photochemical behaviour. In the case of Bz-co-Cl the presence of amine leads to a higher increase of the photoreduction quantum yield than the rest of the copolymers. The macromolecular conformation in solution plays an important role favouring the exciplex formation (*Scheme 2*) between the benzil chromophore and the amine for Bz-co-Cl. However, in MBz-co-AAm and MBz-co-SO<sub>3</sub>Na exciplex interaction between the benzil chromophore and the amine seems to be more restricted and only a slight increase in the quantum yield is observed due to the presence of the amine.

#### Microsecond flash photolysis

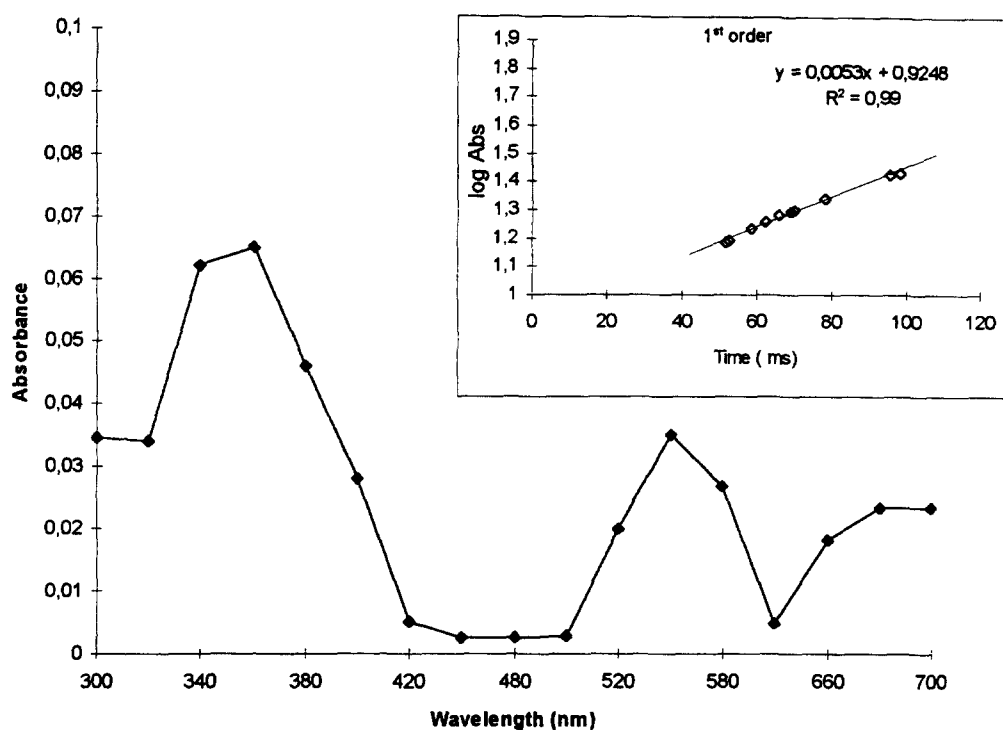
End of pulse transient absorption spectra for the aqueous solution of the new water soluble benzil, BzW, and the copolymers in the presence of triethanolamine are shown in *Figures 1–4*. In *Figure 1*, the spectra in the absence of amine does not show significant bands due to the very poor hydrogen atom donor behaviour of the water but the

presence of amine induces transient absorption bands confirming its role as a hydrogen atom donor. All the products displayed similar spectra but with different relative intensities of the transients from the model to the copolymers in the region 300–700 nm. Essentially, two main absorption bands were observed in the region 300–400 and 450–700 nm. In our earlier work<sup>16</sup> on benzil, we found a unique band with an absorption maximum at 340 nm and this was assigned to a benzoyl type radical structure by photofragmentation since we irradiated with white light. In that case the addition of a tertiary amine to the 2-propanol solution of benzil gave a reduction of transient formation by up 50% since the amine had a strong influence on the triplet state precursor to fragmentation. In water, the band with a maximum at 360 nm is enhanced by the addition of amine and this effect is normally associated with the formation of the ketyl radical produced by the triplet state of the benzil abstracting a hydrogen atom from the amine. The longest wavelength absorption band at 450–700 nm is associated with the radical anion formation. This band was not observed, in our earlier work<sup>16</sup>, for benzil in 2-propanol. These results indicate that aqueous media favours the ion radical formation process and from the anion radical the ketyl radical can be produced by proton abstraction, in agreement with other authors<sup>19</sup>. In the presence of oxygen, transient absorptions are negligible confirming the effective quenching of the benzil triplet state being responsible for the radical formation in accordance with the proposed *Scheme 1*. In *Table 4*, the obtained data are summarized.

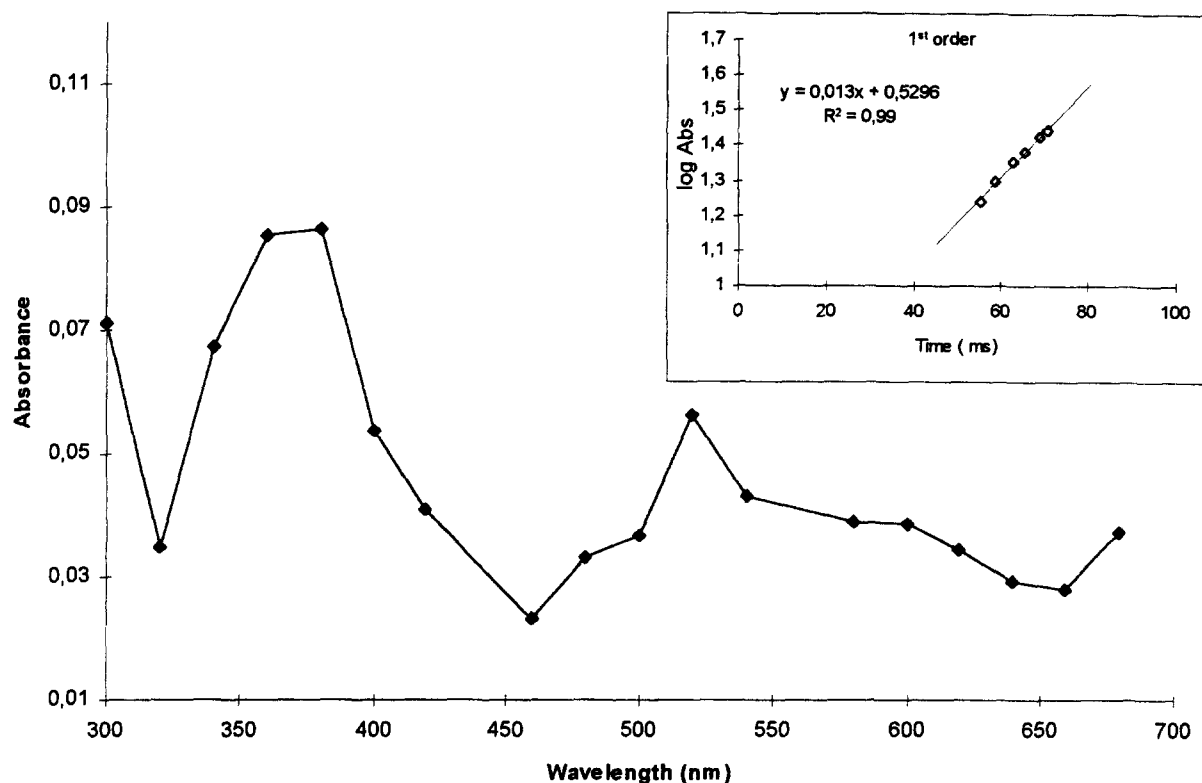
One interesting feature is the decrease in the measured absorbance for the ketyl radical band centred at 360–370 nm in the copolymers indicating the influence of the microenvironment corresponding to the polymeric coil on



**Figure 1** End-of pulse transient absorption spectra produced on the  $\mu$ s flash photolysis of the water soluble benzil model BzW ( $5 \times 10^{-5}$  M in water) in the absence and presence of triethanol amine TEA ( $10^{-3}$  M). The insertion shows the first order kinetic plot obtained from the transient decay at 360 nm



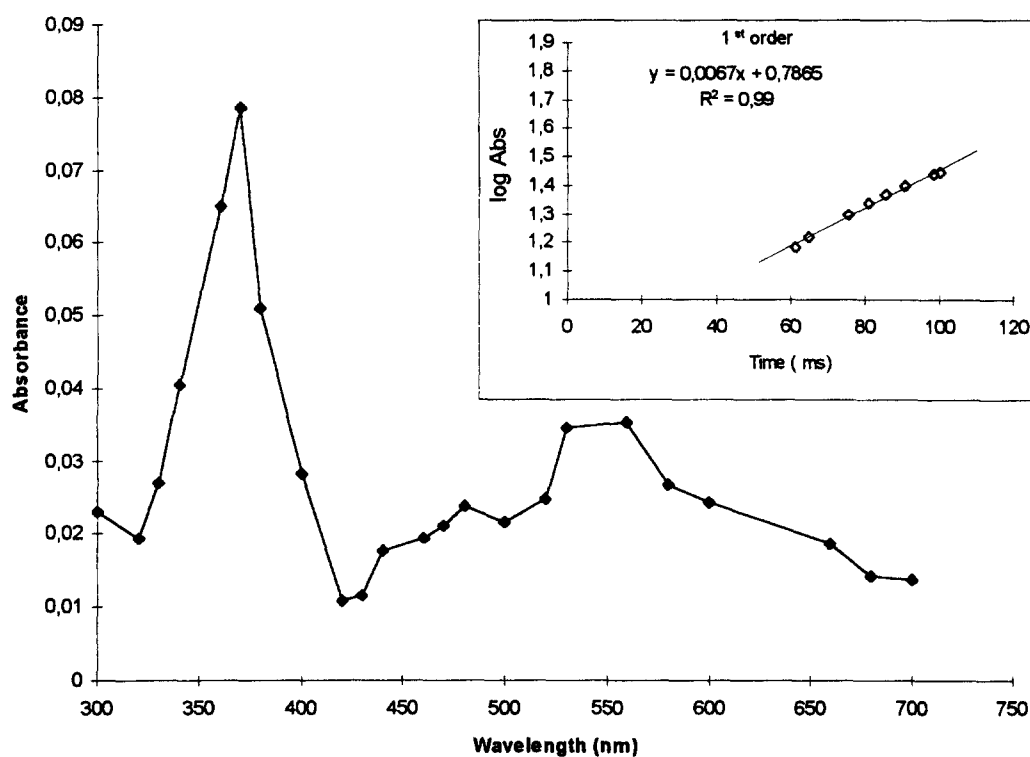
**Figure 2** End-of pulse transient absorption spectra produced on the  $\mu$ s flash photolysis of the water soluble copolymer Bz-co-Cl (concentration of benzil  $10^{-4}$  M in water) in the presence of triethanol amine TEA ( $10^{-3}$  M). The insertion shows the first order kinetic plot obtained from the transient decay at 360 nm



**Figure 3** End-of pulse transient absorption spectra produced on the ns flash photolysis of the water soluble copolymer Bz-co-AAm (concentration of benzil  $10^{-4}$  M in water) in the presence of triethanol amine TEA ( $10^{-3}$  M). The insertion shows the first order kinetic plot obtained from the transient decay at 370 nm

the hydrogen atom abstraction process. Both bands are similar in intensity for the copolymers which can be related to the impediment for the proton transfer process to give a ketyl radical from the radical anion. Another important observation is the longer measured ketyl radical lifetime on the copolymers compared to the model compound, which

can be associated with a less effective quenching process of the ketyl structure due to the macromolecular coil in solution. The decay profile for all the studied new products appears to fit more accurate with a first-order kinetic decay, in contrast with that of second-order kinetics found earlier<sup>16</sup> for benzil in 2-propanol in the presence and absence of a



**Figure 4** End-of-pulse transient absorption spectra produced on the ms flash photolysis of the water soluble copolymer Bz-co-SO<sub>3</sub>Na (concentration of benzil 10<sup>-4</sup> M in water) in the presence of triethanol amine TEA (10<sup>-3</sup> M). The insertion shows the first order kinetic plot obtained from the transient decay at 360 nm

**Table 4** End-of-pulse transient absorption data produced on microsecond flash photolysis of the water soluble model compound and the water soluble copolymers (benzil chromophore concentration 5 × 10<sup>-5</sup> M) in the presence of triethanolamine (TEA) (10<sup>-3</sup> M)

|                          | Transient maxima and lifetimes |                           |                            |                       |                           |
|--------------------------|--------------------------------|---------------------------|----------------------------|-----------------------|---------------------------|
|                          | $\lambda_{\max}$ (nm)          | Ketyl radical             |                            | Radical anion         |                           |
|                          |                                | Absorbance <sup>(a)</sup> | $\tau$ (ms) <sup>(b)</sup> | $\lambda_{\max}$ (nm) | Absorbance <sup>(a)</sup> |
| BzW                      | 360                            | 0.340                     | 20                         | 520                   | 0.066                     |
| Bz-co-Cl                 | 360                            | 0.065                     | 190                        | 560                   | 0.035                     |
| Bz-co-AAm                | 370                            | 0.078                     | 80                         | 530                   | 0.034                     |
| Bz-co-SO <sub>3</sub> Na | 370                            | 0.085                     | 150                        | 520                   | 0.050                     |

(a) ± 0.002

(b) ± 2 ms

tertiary amine. This fact suggests that the volume of the substituent in the model and the polymer chain in the copolymers decreases significantly or eliminates totally the self termination to produce a radical coupling reaction. Lifetimes and kinetics of decay of the radical anion region were difficult to assess on a quantitative basis due to the complexities of contributions from the ketyl radical itself<sup>21</sup>.

#### Photopolymerization

In order to evaluate the efficiency of these novel benzil derivatives as photoinitiators of polymerization we studied the photopolymerization of acrylamide in water solution by photodilatometry.

Photopolymerization of acrylamide followed by a photodilatometric technique was carried out using the copolymers bearing the benzil group as photoinitiators in a solvent mixture of water:acetonitrile (5:2, v:v) and compared to that using the low molecular weight model. Polymerization rates,  $R_p$ , and photopolymerization quantum yields,  $\phi_m$ , of acrylamide in water:acetonitrile (5:2, v:v) solutions at 30°C are summarized in Table 5. In Figure 5, polymerized

**Table 5** Polymerization rates,  $R_p$ , and photopolymerization quantum yields,  $\phi_m$ , of acrylamide (0.78 M) in water:acetonitrile (5:2, v:v) at 30°C under argon atmosphere.  $\lambda_{\text{irr}} = 365 \text{ nm}$ ,  $I_0 = 8.5 \times 10^{-7} \text{ Eins/L}\cdot\text{s}$

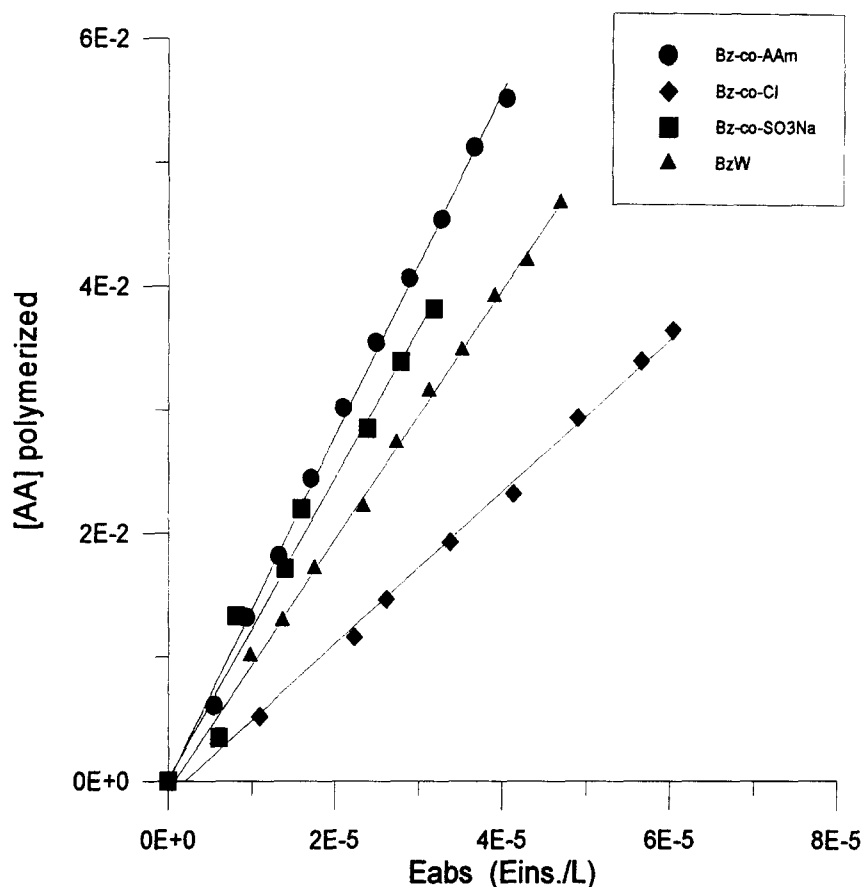
| Photoinitiator           | $R_p \times 10^3 \text{ (Ms}^{-1}\text{)}$ <sup>(a)</sup> | $\phi_m^{(b)}$ |
|--------------------------|---|----------------|
| BzW                      | 3.3   | 1010           |
| Bz-co-Cl                 | 2.0   | 590            |
| Bz-co-AAm                | 4.5   | 1390           |
| Bz-co-SO <sub>3</sub> Na | 4.0   | 1230           |

(a) ± 0.1

(b) ± 20

monomer concentration is plotted versus absorbed energy. Polymerization quantum yields from the slope of the plots indicate a higher photoinitiation efficiency of the copolymers Bz-co-AAm and Bz-co-SO<sub>3</sub>Na than the model compound. However, the copolymer Bz-co-Cl shows a lower photopolymerization quantum yield. This behaviour can be related to the different conformations that these copolymers can adopt in water:acetonitrile solution depending on their total ionic charge density. The approach





**Figure 5** Plot of the concentration of polymerized acrylamide [AA] against absorbed energy ( $\text{Eins}\cdot\text{L}^{-1}$ ) using 2-(*N,N*-diethylamino)ethanol, DEA,  $3 \times 10^{-4}$  M/various benzil-bound-copolymers and the low molecular weight model as photoinitiators,  $[\text{benzil}] = 3.17 \times 10^{-5}$  M, at  $30^\circ\text{C}$  in water/acetonitrile (5/2 in volume) solutions.  $\lambda_{\text{irr}} = 365$  nm

of the tertiary amine to the benzil chromophore to produce the corresponding exciplexes can be sterically hindered in the bulky polymer coils.

The obtained polymerization rates and quantum yields of acrylamide photoinitiated by the copolymers with benzil moieties are similar to those photoinitiated by the water soluble model. These results clearly show that the benzil chromophore when included as pendant group in the water soluble polymers (2.3% benzil) seems to operate in the same way and with similar photoinitiation efficiency as the free water soluble benzil in conditions of dilute chromophore concentration. The mechanism of the reaction occurs through hydrogen atom abstraction of the benzil triplet excited state from the amine to produce alkylamino radicals and mainly ketyl and ion radicals.

## CONCLUSION

This paper contributes to an improvement in photoinitiator design by preparing macromolecular photoinitiators which are as efficient and effective as their low molecular weight counterparts but with the associated advantages derived from their macromolecular nature. In the presence of an amine cosynergist electron abstraction via a triplet exciplex with the benzil chromophore appears to be the primary mode of action of the initiator.

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