

Photocalorimetric study on the photoinitiation activity of water soluble copolymers with pendent benzil moieties

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Abstract

The photopolymerisation rates of a series of water soluble polymeric benzil initiators have been compared and examined with model water soluble benzil initiators in acrylamide using photocalorimetry. Polymerisation rate dependencies of the polymeric benzil initiators are found to be significantly higher than those of model water soluble systems indicating a high degree of quenching reactions are occurring in the latter. Polymeric benzil chromophores are considered to be much less prone to quenching reactions such as radical termination. The coiling effect of the macromolecular chain initiator appears to protect the initiating radicals, the effect being enhanced as the polymerisation reaction progresses due to increasing viscosity. The identification of benzil terminal groups in the photopolymerised polymers confirms the active role of the benzil ketyl radical in the initiation and termination steps. ©2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

In order to circumvent some drawbacks, such as odour, yellowing and migration in post-cured materials, derived from conventional low molecular weight derivatives, the use of polymeric photoinitiators has been proposed. Polymeric photoinitiation systems are showing increasing interest for use in UV/visible curable formulations and in this regard numerous systems have been developed [1–3].

Our previous studies on polymeric [4,5] and water soluble [6,7] photoinitiators prompted us to prepare new water soluble polymeric photoinitiators bearing side-chain benzil moieties and to study their photochemical and photoinitiation activity [8]. We studied the photochemistry and photoinitiation activity of three water soluble copolymers with benzil pendant groups prepared by the copolymerisation of a benzil derivative monomer, 1-phenyl-2-[4-(2-methacroyloxyethoxy)phenylethanodione-1,2,(MBz)] and two commercial comonomers, acrylamide (AAm) and 2-acrylamido-2-methylpropanesulphonic acid (MSO₃H), and 2-acroyloxyethyl trimethylamonium iodide(MI).

The efficiency of a photoinitiator system of polymerisation is known to be dependent upon a number of fac-

tors, not simply related to its inherent structure, but more often to its environment. In this regard the nature of the amine co-synergistic is a major player operating as an initiator, oxygen scavenger and a chain transfer agent/terminator. Oil-soluble benzil derivatives have been used as photoinitiators in combination with amines for many years despite their known ability to undergo primary radical termination and degradative initiator chain transfer processes [9,10] decreasing their photoinitiation efficiency.

Another important factor is the photopolymerisable system itself where one variable is the viscosity of the resin/monomer used. Whilst the functional character of the resin is crucial, viscosity can drastically control the rate of conversion and termination through control of the radical mobility. In this investigation, we have determined photopolymerisation rates using water-soluble copolymers containing benzil as pendant groups as photoinitiators by photocalorimetry in order to examine radical rates. Hence, the aim of this paper is to gain a deeper understanding of the photoinitiation mechanism of free radical polymerisation using the novel water soluble polymers compared with a low molecular weight model compounds used previously and to determine, at least qualitatively, the influence of the polymer environment in the process. The structures and the names used for the water soluble low molecular weight model compound,

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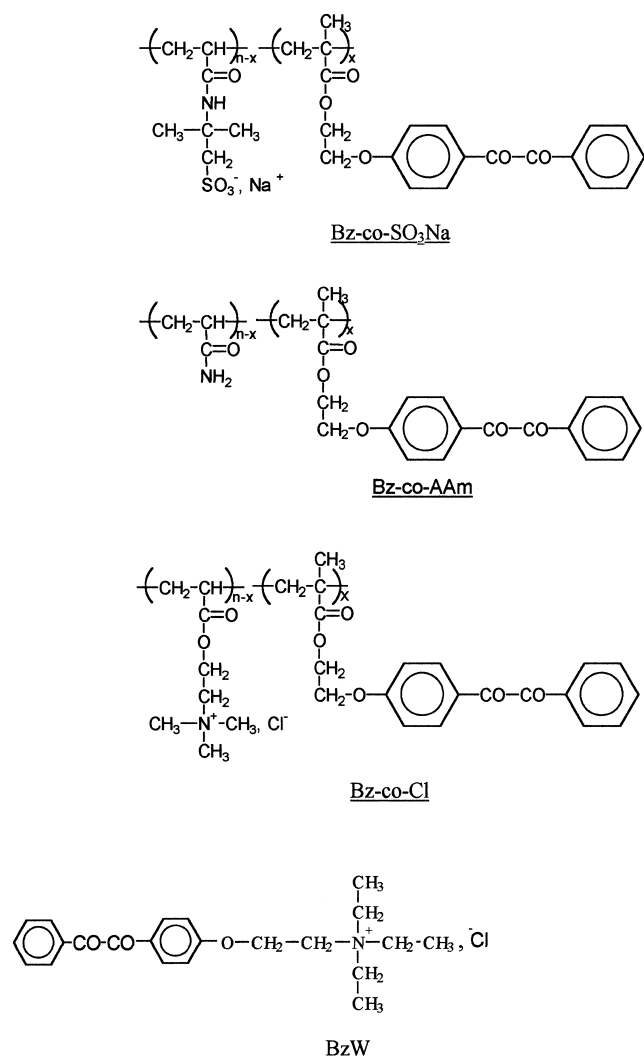


Fig. 1. Structures of the copolymers bearing benzil moieties as pendant groups and low molecular weight model (BzW).

1-phenyl-2-[4-(2-triethylaminoethoxy)phenyl]ethanodione-1,2-chloride (BzW) and copolymers are shown in Fig. 1.

2. Experimental

2.1. Materials

The 2-(*N,N*-diethylamino)ethanol was obtained from the Aldrich Chemical, UK and was purified by distillation before use. Acrylamide from Merck was purified by recrystallisation in acetone. In all the experiments, MiliQ grade water was used as the solvent.

2.2. Synthesis

The synthesis of the low molecular weight model compound and the copolymers bearing benzil moieties as

Table 1
Percentage of benzil chromophore in the copolymers

	Bz-co-Cl	Bz-co-AAm	Bz-co-SO ₃ Na
Bz (%)	2.3	2.7	2.3

pendant groups was carried out according to the synthetic route described previously [8].

The weight percentages of benzil chromophore in the copolymers were determined in aqueous solution by UV spectroscopy using the molar absorption coefficient of the model compound BzW in water, at 295 nm $\log \epsilon = 4.20$. The measured contents of benzil are illustrated in Table 1.

2.3. Apparatus

2.3.1. Spectroscopic measurements

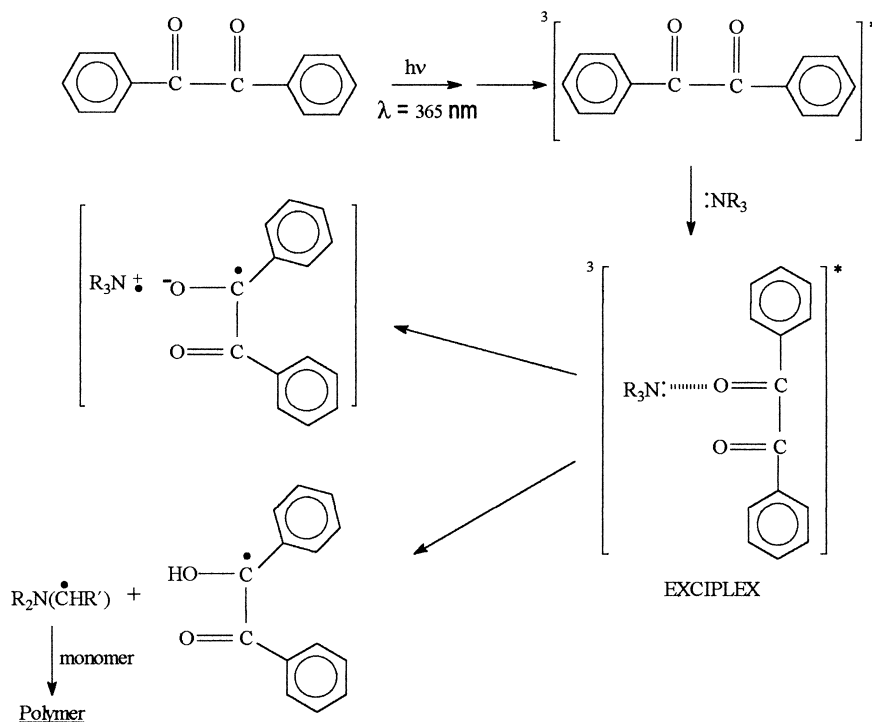
Absorption spectra were obtained using Shimadzu UV-265-FS spectrophotometer.

2.4. Photocalorimetry

The set-up for photocalorimetry was described previously [10] using a modification, designed in the CSIC laboratory, with the aid of a modified Perkin–Elmer differential scanning calorimeter. The sample and reference are irradiated by way of two fibre optic cables carrying the light energy from a high pressure 100 W Hanovia mercury lamp and then by a monochromator for isolation of the 365 nm line. Heat evolution with time of irradiation is measured by maintaining the sample chamber at 40°C. The exotherm curve for each experiment is integrated to calculate the area under the curve at given time intervals. Corrections are then made for reaction times and sample weights. Hence, the kinetics of the photoinitiated polymerisations of acrylamide, used as monomer, were monitored using 20 μ l of water solution (1.5 mol dm⁻³) in each case and the benzil derivatives (10⁻³ mol dm⁻³) and 2-(*N,N*-diethylamino)ethanol (10 mol dm⁻³) as photoinitiator system. Benzil concentration (10⁻³ mol dm⁻³) was chosen to ensure total light absorption at 365 nm. Plots of percentage conversion with time were obtained from which seconds plots of mol dm⁻³ versus time in seconds were calculated. From the initial slopes of the second plots, photopolymerisation rates, R_p (mol dm⁻³ s⁻¹) were calculated. This general method has been described previously [12].

3. Results and discussion

The mechanism of the photopolymerisation of vinyl monomers by a benzil-amine photoinitiator system is dependent on the employed irradiation wavelength. Hence, upon irradiating at $\lambda > 330$ nm, the general accepted mechanism [8,10,11] involves the complexation of one of the



carbonyl groups by the excited triplet state of the benzil derivative with the amine. The generation of ion radicals by deactivation of this triplet-exciplex in water can compete with the formation of the ketyl and alkylamino radicals, the last being responsible for the initiation of the free radical polymerisation, when a monomer is present in the medium. The general mechanism is shown in Scheme 1. Also, the secondary reactions of the ketyl radical can influence the photoinitiation activity of the system by a termination reaction with growing macromolecular radicals.

The kinetics and detailed aspects of the photopolymerisation of acrylamide in water solution under an atmosphere of air, irradiating at 365 nm, using polymeric and monomeric benzil derivatives as photoinitiators and a tertiary amine, 2-(*N,N*-diethylamino)ethanol, (DEAOH) as coinitiator have been studied by photocalorimetry. The data are shown in Table 2.

Table 2

Polymerisation rates R_p , of acrylamide (2.8 mol dm^{-3}) in water photoinitiated by benzil derivatives ($0.008 \text{ mol dm}^{-3}$) and 2-(*N,N*-diethylamino)ethanol (0.08 mol dm^{-3}) and photoreduction quantum yields, ϕ_r^a

Compound	$R_p \times 10^3 \text{ (mol dm}^{-3} \text{ s}^{-1})$	$(\phi_r \times 10^3)^b$
BzW	3.2	0.2
Bz-co-Cl	2.2	23
Bz-co-AAm	2.1	0.6
Bz-co-SO ₃ Na	2.2	2.7

^a $\lambda_{\text{irr}} = 365 \text{ nm}$, $I_0 = 2.7 \times 10^{-9} \text{ Einstein s}^{-1}$, air atmosphere.

^b [8], under nitrogen atmosphere.

Under the experimental conditions (aerobic media, high viscosity increase, ...) polymerisation rates are influenced by factors, such as oxygen quenching rate constants and monomer quenching rate constants, so that these obtained figures are valuable from an applied point of view regarding the industrial procedures.

In general, we can state that polymerisation rates of acrylamide photoinitiated by the copolymers with benzil moieties are similar to those photoinitiated by the low molecular weight model, BzW, under an atmosphere of air. However, the differences, shown in Table 2, between photoreduction behaviour, measured under nitrogen conditions (where MBz-co-Cl shows the highest photoreduction quantum yield) point to the importance of quenching reactions.

Polymerisation rate dependencies with benzil and amine concentrations are summarised in Table 3. From these values, the reaction order with respect to components of the photoinitiator system can be calculated. In our case, we have found a value of 0.1 for the water soluble benzil WBz and an apparent value of 0.37 for DEAOH. These low values for a radical photoinitiated polymerisation can be explained by quenching reactions involving the photoinitiator system which must decrease its global efficiency [13,14]. However, the initiator order for the water soluble polymeric photoinitiator Bz-co-SO₃Na is 0.47, close to the expected theoretical value of 0.5, indicating that quenching reactions are prevented by the macromolecular chain coil in water solution.

Sengupta et al. [9,10] have found primary radical termination and degradative initiator transfer for the photopolymeri-

Table 3

Polymerisation rates of acrylamide (1.5 mol dm^{-3}) in water photoinitiated by BzW and Bz-co-SO₃Na, using DEAOH as coinitiator, at 40°C at different photoinitiator or amine concentrations^a

Compound	[Bz] × 10 ⁵ mol dm ⁻³	[DEAOH] × 10 ⁴ mol dm ⁻³	R _p × 10 ⁴ mol dm ⁻³ s ⁻¹
Model BzW, I ₀ = 2.7 × 10 ⁻⁹ Einstein dm ⁻³ s ⁻¹	40	8	9.3
	24		8.6
	8		8
	4		7.1
	1		6.5
	80	80	4.7
		8	3.3
Bz-co-SO ₃ Na, I ₀ = 4.2 × 10 ⁻⁹ Einstein dm ⁻³ s ⁻¹		4	2.5
		2.4	1.6
	8	8	4.3
	6		3.8
	4		3.2
	2		2.3
	1		1.6

^a λ_{irr} = 365 nm.

sation of methyl methacrylate using benzil-dimethylaniline or triethylamine as initiator systems. In view of this fact, initiator-dependent termination for our novel water-soluble benzil derivatives combined with a tertiary amine (DEAOH) has been studied. Acrylamide polymerisation rates using different benzil concentrations for a fixed amine concentration have been determined by photocalorimetry and the result compiled in Table 3.

The primary radical termination and degradative initiator transfer reactions have been determined for the low molecular weight model, BzW, and the copolymer Bz-co-SO₃Na.

The analysis of primary radical termination has been carried out by using the equation derived by Deb and Meyerhoff for this purpose, which is as follows:

$$\log \frac{R_p^2}{[\text{Bz}][\text{DEAOH}][\text{M}]^2} = \log \frac{fk_d k_p^2}{k_t} - 0.8684 \frac{k_{\text{prt}}}{k_i k_p} \frac{R_p}{[\text{M}]^2}$$

where k_{prt} is the primary radical termination rate constant [15].

The plot of the left-hand side of the equation against $R_p/[\text{M}]^2$ for BzW (Fig. 2) gives a straight line with a negative slope and a value of $1.1 \times 10^4 \text{ mol dm}^{-3} \text{ s}$ for the rate constant ratio $k_{\text{prt}}/k_i k_p$, indicating primary radical termination occurs also for water soluble benzil derivatives. However, the efficiency of this process is lower than in organic solvents where a value of $2 \times 10^6 \text{ mol dm}^{-3} \text{ s}$ has been determined [10]. The proposal that the ketyl radical is responsible for the termination by primary radicals is in accordance with our lower $k_{\text{prt}}/k_i k_p$ value found in water solution where the formation of ion-radicals competes with the ketyl radicals.

The analysis of primary radical termination for the polymeric photoinitiator Bz-co-SO₃Na is shown in Fig. 3. The rate constant ratio $k_{\text{prt}}/k_i k_p$ gives a value of $7.7 \times 10^2 \text{ mol dm}^{-3} \text{ s}$, indicating the lower importance of this reaction when the benzil is attached to a macromolecular chain. In the case of polymeric benzil photoinitiators, the chain terminator ketyl radical is polymer bound and

therefore, as the polymerisation progresses the medium viscosity increases restricting its reactions due to a higher steric hindrance.

The evaluation of initiator chain transfer has been carried out by the rate constant for this process k'_t , determined by using the following equation:

$$2 \frac{k_t}{k_p^2} \frac{R_p^2}{[\text{Bz}][\text{DEAOH}][\text{M}]^2} = 2\phi\epsilon I_0 - \frac{k'_t}{k_p} \frac{R_p}{k_p [\text{M}]}$$

where k_t/k_p^2 for acrylamide in water [16] has the value ($8.2 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}$).

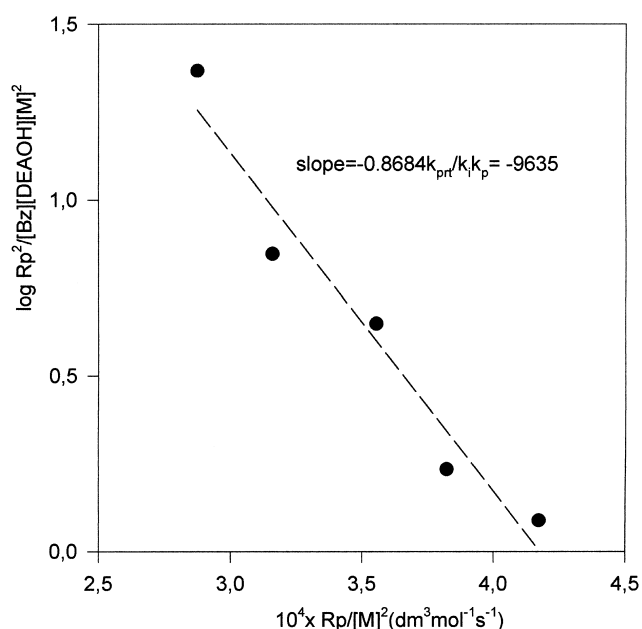


Fig. 2. Analysis of termination by primary radicals in the polymerisation of acrylamide photoinitiated by DEAOH/BzW at 40°C in water. Plot of $\log \{R_p^2/[\text{Bz}][\text{DEAOH}][\text{M}]^2\}$ vs. $R_p/[\text{M}]^2$ at a fixed amine concentration $[\text{DEAOH}] = 8 \times 10^{-4} \text{ mol dm}^{-3}$.

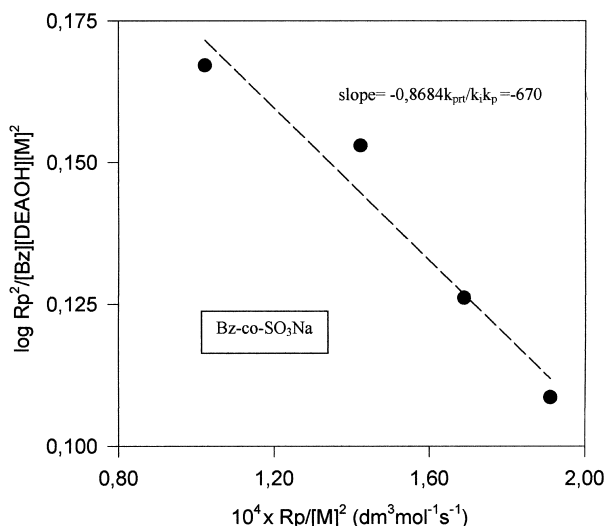


Fig. 3. Analysis of termination by primary radicals in the polymerisation of acrylamide photoinitiated by DEAOH/Bz-co-SO₃Na at 40°C in water. Plot of $\log \{R_p^2/[Bz][DEAOH][M]^2\}$ vs. $R_p/[M]^2$ at a fixed amine concentration $[DEAOH] = 8 \times 10^{-4} \text{ mol dm}^{-3}$.

From the slope of the plot in Fig. 4, the value of k_t'/k_p for BzW obtained is 6.6×10^3 . This higher value in comparison with that of the Bz/TEA/MMA in benzene [10] (1.4×10^3) indicates a higher degradative chain transfer, caused by the formation of amine cation radicals, more favoured in polar media such as water. Water-soluble benzil BzW acts as an inifer (initiatortransfer agent) causing degradative chain transfer.

In Fig. 5 the analysis of initiator chain transfer for the copolymer Bz-co-SO₃Na is shown. The lower value of k_t'/k_p

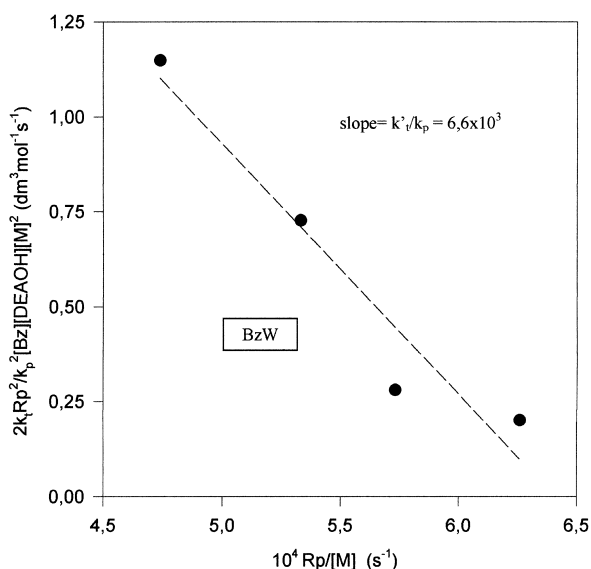


Fig. 4. Initiator chain transfer in the polymerisation of acrylamide (1.5 mol l^{-1}) photoinitiated by BzW/DEAOH at 40°C in water. Plot of $\{2k_t R_p^2/k_p^2 [Bz][DEAOH][M]^2\}$ vs. $R_p/[M]$ at a fixed amine concentration $[DEAOH] = 8 \times 10^{-4} \text{ mol dm}^{-3}$.

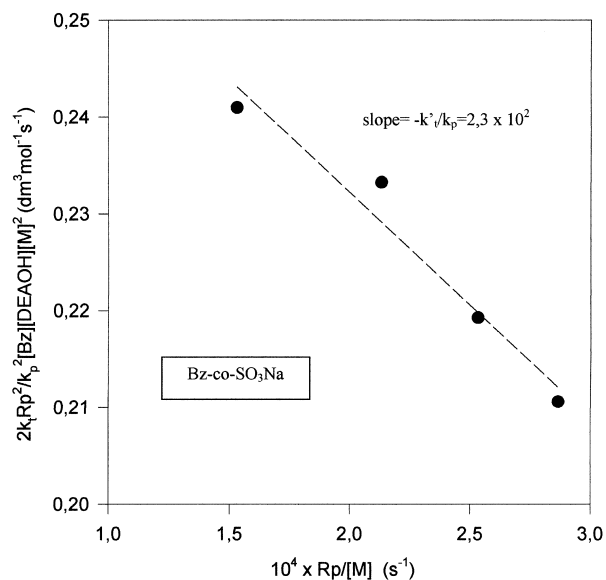


Fig. 5. Initiator chain transfer in the polymerisation of acrylamide (1.5 mol dm^{-3}) photoinitiated by Bz-co-SO₃Na/DEAOH at 40°C in water. Plot of $\{2k_t R_p^2/k_p^2 [Bz][DEAOH][M]^2\}$ vs. $R_p/[M]$ at a fixed amine concentration $[DEAOH] = 8 \times 10^{-4} \text{ mol dm}^{-3}$.

(2.3×10^2) compared with that of the low molecular weight model indicates the impediment of this reaction when benzil is a pendant group in a polymeric backbone. In this case, the order of reaction with the initiator concentration is close to the 0.5 expected value in the absence of quenching reactions.

The participation of benzil radicals in the primary radical termination step is shown in Fig. 6 where the UV spectra of polyacrylamide photoinitiated by BzW/DEAOH is compared with that of a polyacrylamide initiated by AIBN. The presence of benzil end-groups in the polyacrylamide initiated by benzil confirms the participation of the benzil radical, produced in the photoinitiation mechanism, as the effective species in the termination process.

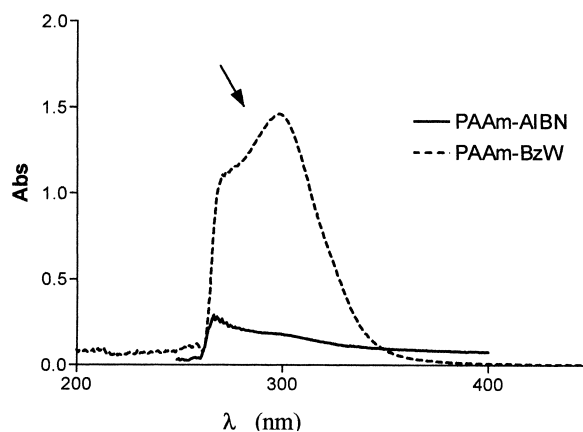


Fig. 6. UV spectra of polyacrylamide polymerised using BzW/DEAOH as photoinitiator (---) and thermally polymerised using AIBN as initiator (—). The arrow shows the absorbance due to the benzil chromophore.

4. Conclusions

It is evident from the kinetic analysis of the photopolymerisation rates that the attachment of benzil moieties to macromolecular chains prevents secondary reactions (primary radical termination and initiator chain transfer reactions) with respect to those of a low molecular weight model benzil derivative. Also, in the presence of oxygen, similar activities of the benzil, model and polymers, are found.

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