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Free radical macrophotoinitiators: an overview on recent advances

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Abstract

This paper provides an overview of the recent advances on polymeric photoinitiators for UV curing. During the last decade, significant developments have been achieved in the synthesis of macrophotoinitiators, due to the advantages derived of their macromolecular nature, in comparison with their corresponding low molecular weight analogues. In particular, a variety of macromolecules containing the two main types of free radical photoinitiators: hydrogen-abstracting (thioxanthone, benzil, anthraquinone, camphorquinone) and photofragmenting chromophores (benzoin ether, acylphosphine oxides) are described. For hydrogen-abstracting photoinitiator, the photoinitiation activity have been examined in terms of volume and nature of substituent in the polymeric coil, and their influence to prevent the recombination of radicals favouring their reaction with the monomer. Also, copolymers bearing chromophore and amine groups with potential synergistic effects of activity are reported. It has been found that the approach of the tertiary amine to the chromophore to produce the corresponding exciplexes is dependent on both the monomeric or polymeric nature of chromophore and the tertiary amine. Type II polymeric photoinitiators, such as benzoin ether derivatives having the benzoin methyl ether moieties connected to the main chain through the benzyl aromatic are reported. And a fragmentation mechanism involving the formation of an stable quinoid structure and aliphatic acyl radical is proposed for the above copolymers, which would justified their lower initiating efficiency than the corresponding low molecular weight model. In addition, polymers bearing phosphine oxide moieties are described. The efficiency in the polymerisation of all photoinitiators was found to be similar and irrespective of the presence of flexible spacer in their structure. However, it was found that the flexible oligomethylene spacer enhanced the compatibility of the new polymeric photoinitiators in acrylic adhesive formulations. Finally, polysilanes as photoinitiators are reported. Under UV irradiation, polysilanes undergo main-chain scission leading to free silyl radicals capable of reacting with olefinic monomers. The silyl radicals generated by photolysis can be oxidised by appropriate onium salts to yield cationic initiating species (photoinitiated radical promoted cationic polymerisation). The photoinitiation efficiency of polysilanes having different aliphatic and aromatic side groups has been investigated and compared with commercial low molecular weight photoinitiators as benzoin.

Keywords: Macrophotoinitiators; Chromophore; Photoinitiation; Photopolymerisation; Water-soluble photoinitiators

1. Introduction

During the last 20 years, the fields of photopolymerisation and photoimaging science and technology have grown from subjects of esoteric research specialities into major industrial developments. They are now fields of central importance in polymer science and technology. Inherent to these technologies, is the use of a photoactivator system which is capable of absorbing the incident UV and/or visible radiation wavelengths used for converting a monomer or prepolymer system into a linear polymer or crosslinked network [1–5]. In recent years, there have been many new developments in the synthesis and photochemical studies of novel photoinitiator molecules. These have been designed to have desirable properties such as higher activity or greater curing speed coupled with lower migration rates and/or water solubility. Two areas of importance in this regard are the development of monomeric and polymeric photoinitiators with reactive functionalities [6].

Polymeric photoinitiators can be defined as macromolecular systems that contain pendant or in-chain chromophores which through a light absorption process can generate active species able to initiate the polymerisation and crosslinking of mono- and multi-functional monomers and oligomers. From an industrial point of view, their higher cost may be justified by the various advantages compared to their corresponding low molecular weight analogues. The presence of the polymer chain in many cases improves the compatibility in the formulation and reduces the migration onto the film surface. Thus, contributing to manufacturing low-odouring and non-toxic coatings.

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In addition, the photoinitiation activity can be improved as result of energy migration along the polymer chain, or intramolecular reactions responsible for the formation of more reactive species. The macromolecular chain can protect the active species, similar to a cage effect.

The incorporation of a photoinitiator moiety into a polymer may be accomplished by inclusion of the chromophore as a pendant or in terminal position in a polymer, or by copolymerising the chromophore so that it is present in the macromolecular backbone. The copolymerisation of photosensitive monomers with conventional co-monomers offer the possibility of macromolecular design, in the context of nature and distance from the backbone of the pendant photosensitive moieties and nature of the co-monomer. The synthesis of copolymers bearing different photosensitive groups may provide potential synergistic effects of activity, giving different properties to the polymeric photoinitiator.

A wide variety of macromolecules containing the two main types of free radical photoinitiators: photofragmenting (type I photoinitiators) and hydrogen-abstracting chromophores (type II photoinitiators) are described in the literature. Examples of type I photoinitiators are polymers bearing side-chain benzoin methyl ether moieties [7] and polymeric trichloro- and α-amino-acetophenone [8]. The hydroxyl group on substituted acetophenones or benzoins allows to attach polymerisable moieties, as acrylate or vinyl groups, and the polymerisable photoinitiators may be thermally or photochemically polymerised to give polymeric photoinitiators. Most of type II polymeric photoinitiators are based on benzophenone [9,10], probably because of its relatively low cost. However, in the last decade, new polymers bearing thioxanthone (TX), anthraquinone, camphorquinone or benzyl moieties have been synthesised.

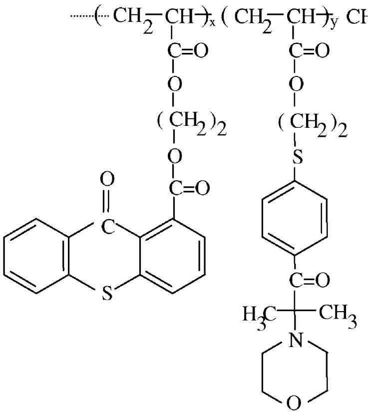
In this paper, we provide an overview of the recent advances on polymeric photoinitiators, with particular reference to the water-soluble macrophotoinitiators. Water-borne UV-curable formulations have resulted in an increase in industrial applications. Many academic studies are carried out in this area to develop novel water-soluble photoinitiators, specially modifying well-known radical generator molecules to water-soluble structures. In aqueous systems, problems such as low activity and poor solubility arise with polymeric photoinitiators.

2. Polymeric photoinitiators based on thioxanthone

Thioxanthones are among one of the most widely used bimolecular photoinitiators in vinyl polymerisations. They have been introduced in processes such as printing inks, surface coating, microelectronics, and photoresists [11], for particular applications in UV curing of heavily pigmented resins where the pigment (TiO_2) screens out much of the UV light from the irradiation source. Many studies have been devoted to gain an understanding of the initiation efficiency of these compounds and the nature of the mechanism involved [12]. The activity as photoinitiators of these compounds is based in the radical production from the interaction of the thioxanthone excited triplet state with tertiary amines which proceeds through a charge transfer intermediate (normally a triplet exciplex) [13,14]. Due to the charge transfer characteristics of this intermediate its decomposition steps are highly dependent on the donor–acceptor capability of the photoinitiator and the co-initiator. It has been seen that the radical production was markedly dependent on the substituents on the thioxanthone chromophore [15].

In previous work, photochemistry and photopolymerisation activity of free and polymer-bound 2-benzyloxy thioxanthone were studied. The polymeric photoinitiator was prepared by chemical modification of an atactic polystyrene [16]. The polymerisation and initiation quantum yields obtained for both photoinitiators, clearly showed that the bound chromophore operates in the same way and with similar polymerisation efficiency as the free photoinitiator.

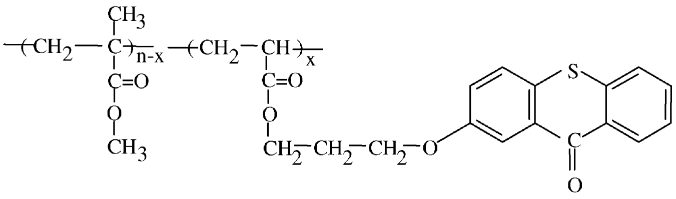
In order to prevent the screening effect of pigments in coatings, because of their strong absorption below 380 nm, an elegant design of a new polymeric photoinitiator was accomplished by combining two chromophores in the same polymeric chain [17]. The structure of the polymeric photoinitiator, based on side-chain thioxanthone and α-morpholino acetophenone moieties, ATX-co-AMMP, is shown:



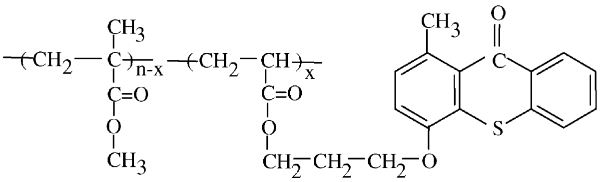
ATX-co-AMMP

It has been found that the photoinitiation activity of the polymeric photoinitiator was one order of magnitude higher than that of the mixture of the corresponding low molecular weight analogous. It was due to a very efficient sensitisation mechanism, which involves the excitation energy transfer from the thioxanthone triplet state to the ground state of adjacent α-morpholino acetophenone moieties. It was confirmed by time-resolved laser spectroscopy studies of copolymers with several content of thioxanthone. Rate constant (k_{tr}) and efficiency (ϕ_{tr}) of the excitation energy transfer from sensitiser to photoinitiator were found to be much higher in the copolymers than in a mixture system. Similar behaviour was found with other polymeric photoinitiators bearing side-chain thioxanthone and α-aminoacetophenone moieties [18].

Recently, new thioxanthone derivatives substituted with acrylic groups have been synthesised and have been examined in terms of their efficiency as photoinitiators to initiate radical polymerisation [14]. Polymeric photoinitiators have been obtained by copolymerisation of the thioxanthone acrylic derivatives with methyl methacrylate (MMA) [19]. The content of thioxanthone chromophore in the polymer was 2%, determined by UV spectroscopy. The structures of methyl methacrylate-co-2-(3′-acryloxy)propoxy thioxanthone (MMA-co-M2) and methyl methacrylate-co-1-methyl-4-(3′-acryloxy)propoxy thioxanthone (MMA-co-M4) are shown:



MMA-co-M2



MMA-co-M4

The photoinitiation activity of the polymeric photoinitiators was studied and compared to that of their corresponding low molecular weight structural models [20]. MMA polymerisation rates (R_p) were measured dilatometrically in MMA–acetonitrile (1:1 (v/v)) solutions, using the thioxanthones as photoinitiators, and several concentrations of 2-(N,N-diethylamino)ethanol (DEOHA) as co-initiator. R_p were obtained from the initial slope of the conversion versus time plots.

The macroinitiators were found to be more efficient, at all amine concentrations, than the corresponding low molecular weight analogues (M2 and M4). This polymer effect has been already reported for several bimolecular polymeric photoinitiators based on thioxanthone and benzophenone [10,21,22].

The chain transfer reactions and primary radical termination were checked to be negligible for the photoinitiator. Then, the photoinitiation efficiencies for the 2-substituted derivatives were evaluated with respect to that obtained with AIBN as photoinitiator, $\phi_{AIBN} = 0.4$, and using the following equation:

$$\frac{\phi_{TX}}{\phi_{AIBN}} = \frac{(R_p)^2_{TX}}{(R_p)^2_{AIBN}} \quad (1)$$

The photoinitiation quantum yield for the polymeric photoinitiator was found to be two times higher than that of the low molecular weight compound, $\phi_{TX} = 0.24$ and 0.11 for MMA-co-M2 and M2, respectively.

It is very well known that for amine–thioxanthone system, the alkylamino radicals originated from the decomposition of the charge transfer complex, are the effective initiating species. The active radical quantum yield is given by:

$$\Phi_{rad} = \Phi_{isc}\beta_T \frac{(^3k_q)_{Am}[Am]}{(^3k_q)_{Am}[Am] + (^3k_q)_{MMA}[MMA] + k_0} \quad (2)$$

where β_T is related to the fraction of radicals originated from the decomposition of the charge transfer intermediate. The polymerisation data obtained with the polymeric photoinitiators and their models can be fitted quite well with Eq. (2), as it is shown in Fig. 1. This result indicates that the radicals that lead to polymerisation are those originated from the interaction of the thioxanthone triplet with amine.

On the other hand, the data obtained at high amine concentration, where it can be considered that >90% of the triplets are deactivated, show that the macroinitiators exhibit higher efficiency than the corresponding low molecular weight models. This could be the consequence of an increased production of active radicals and/or higher reactivity of the formed radicals towards the monomer double bond. The absorbancies measured for the ketyl radicals derived from

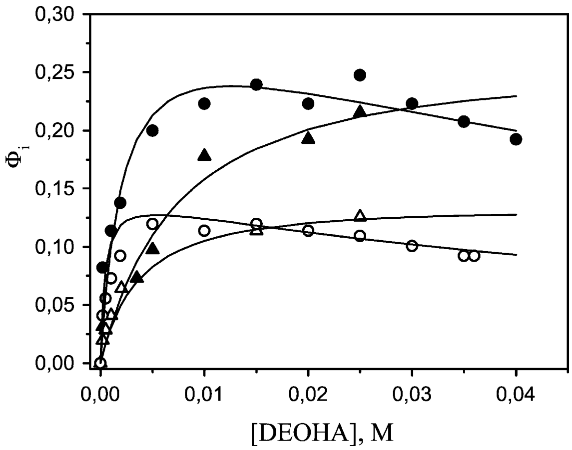


Fig. 1. Photoinitiation quantum yield as function of the amine concentration. Photoinitiators: (●) MMA-co-M2; (○) M2; (▲) MMA-co-M4; (△) M4.

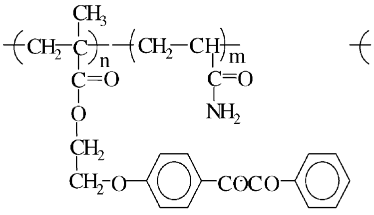
the 2-propoxy thioxanthone derivatives show that the ketyl radical formation and then the amine radical formation, for the thioxanthone bound to the polymer is only 1.2 times higher than that of the free thioxanthone. This indicates that the higher photoinitiation activity of the macroinitiator is due to a higher reactivity for the radicals produced in the macroinitiator system. Polymer chain could prevent the recombination of radicals favouring their reaction with the monomer and could explain the enhanced activity of the macroinitiators. Also, a high monomer concentration on the locus, macromolecular coil, where the radicals are formed could lead to a high initiation activity of the systems comprising a polymeric initiator and a low molecular weight co-initiator.

3. Polymeric photoinitiators based on benzil

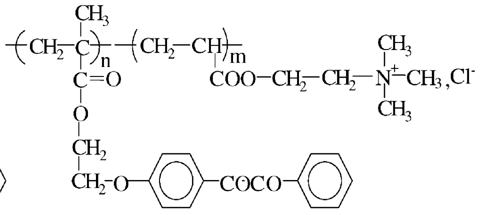
Benzil derivatives are well-known type II photoinitiators and benzil–amine systems have been used as photoinitiators for vinyl free radical polymerisation for many years exhibiting low rates of cure. The mechanism for the photopolymerisation of vinyl monomers by benzil–amine photoinitiator system is dependent of the employed irradiation wavelength. At short wavelengths ($\lambda < 330$ nm) benzoyl radicals are produced by a Norrish type I cleavage, which then abstract hydrogen atoms from the amine. However, irradiating at $\lambda > 330$ nm, hydrogen atom abstraction of the amine by the lowest excited triplet state of benzil takes place [23]. The generation of ion radicals by deactivation of this exciplex in water can compete with the formation of the ketyl and alkylamino radicals, the last being responsible of the initiation of the free radical polymerisation, when a monomer is present in the medium. Also, the secondary reactions of the ketyl radical can influence the photoinitiation activity of the system by termination reaction with growing macromolecular radicals.

The benzil–amine–vinyl monomer system has been extensively studied [24,25]. It has been found that the photoinitiation activity is enhanced by the introduction of electron donating substituents, as the methacryloxyethoxy group, in the *para*-position of the benzil structure. A similar effect can be expected by incorporating the benzil moiety into the backbone of a polymeric system. Oil-soluble polymers containing benzil moieties, as pendant groups in the main chain and as terminal groups have been previously studied [26,27].

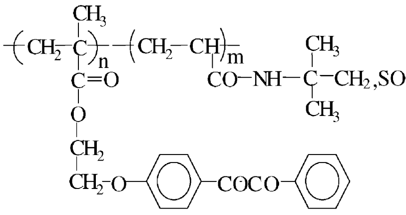
Recently, new water-soluble polymeric photoinitiators based on benzil, containing water-soluble monomer structures in the main chain of the polymer as hydrophilic segments, have been synthesised [28]. The new macroinitiators have been prepared by copolymerisation of a benzil derivative monomer (MBz) and three water-soluble co-monomers, acrylamide (AAm), 2-acrylamido-2-methylpropanesulphonic acid (MSO_3H), and 2-acryloxyethyltrimethylammonium iodide (MI). The proton of the acidic co-monomer (MSO_3H), and the iodine on MI 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 corresponding copolymers are shown:



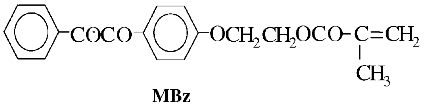
MBz-co-AAm



MBz-co-Cl



MBz-co-SO₃Na



MBz

The photoinitiation activity of the new polymeric photoinitiators were studied and compared with a synthesised model compound, 1-phenyl-2-[4-(2-triethylaminoethoxy)-phenyl]ethandione-1,2-chloride (BzW).

Photopolymerisation of acrylamide using the polymeric photoinitiator in a solvent mixture of water–acetonitrile (5:2 (v/v)) was followed by a photodilatometric technique, and compared to that using the low molecular weight model. In Fig. 2, polymerised monomer concentration is plotted versus absorbed energy. Polymerisation quantum yields from the slope of the plots indicated a higher photoinitiation efficiency of the copolymers Bz-co-AAm and Bz-co-SO_3Na than that of the model compound. However, the copolymer Bz-co-Cl showed a lower photopolymeri-

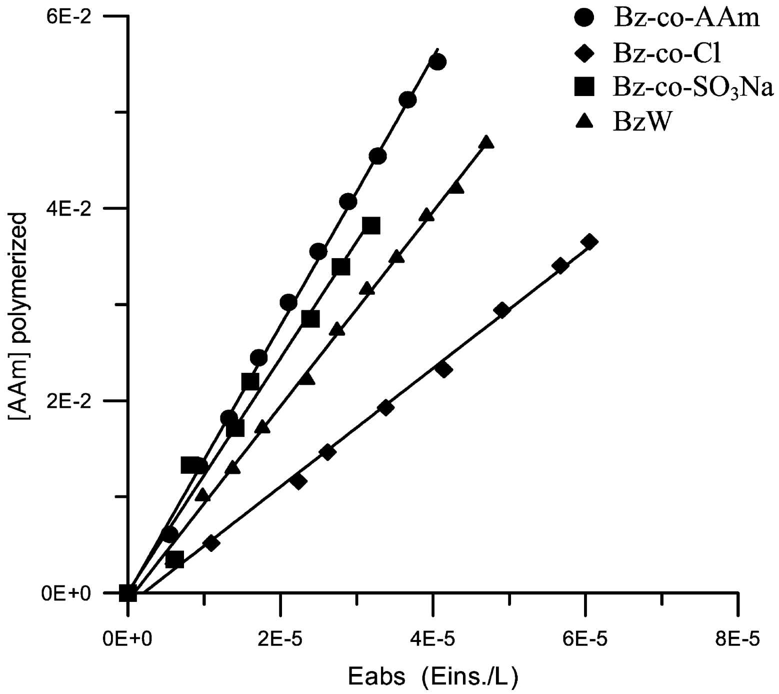


Fig. 2. Plot of the concentration of polymerised acrylamide [AAm] against absorbed energy (einstein l^{-1}) using 2-(*N*,*N*-diethylamino)ethanol (DEOHA, 3×10^{-4} M)/various benzil-bound copolymers and the low molecular weight model as photoinitiators, [benzil] = 3.17×10^{-5} M, at 30 °C in water–acetonitrile (5:2 (v/v)) solutions ($\lambda_{irr} = 365$ nm).

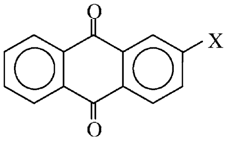
sation quantum yield. This behaviour was suggested to be related to the different conformations that these copolymers can adopt in water–acetonitrile solution depending on their total ionic charge density. The mechanism of the reaction occurs through hydrogen atom abstraction of the benzil triplet excited state from the amine to produce alkylamino radicals and mainly ketyl and ion radicals. The approach of the tertiary amine to the benzil chromophore to produce the corresponding exciplexes can be sterically hindered in the bulky polymer coils.

The influence of the microenvironment corresponding to the polymeric coil on the hydrogen atom abstraction process was also studied by means of microsecond flash photolysis. Essentially, two main absorption bands were observed in the region 300–400 and 450–700 nm associated to the ketyl radical and radical anion, respectively. It was found that the absorbance for the ketyl radical band centred at 360–370 nm for the copolymers decreased respect to the water-soluble model. 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 [29] for benzil in 2-propanol in the presence and absence of a 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.

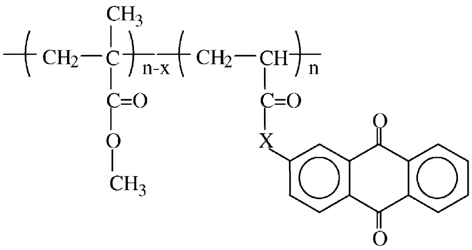
4. Polymeric photoinitiators based on anthraquinone

In general, anthraquinones exhibit a high reactivity when used in combination with tertiary amines as co-initiators [30,31]. Their ability to photoreduce via electron transfer in the presence of hydrogen donors and to form radicals has promoted their effective use as photoinitiators of polymerisation. Their mechanism is such that they are included into the type II photoreducing chromophores [32]. The reactions involved in the photogeneration of initiating radicals, deplete oxygen concentration dissolved in the formulation and revert back to the original photoinitiator. Hence, anthraquinones, unlike other aromatic ketones, exhibit an interesting initiation efficiency, in the application point of view, under aerobic conditions [30,33].

A wide series of anthraquinone derivatives [34–39] and oil-soluble copolymers having a low content of this chromophore in the macromolecular structure [40] have been synthesised. Copolymers of 2-substituted acrylamidoanthraquinone (AAAQ) and acryloxyanthraquinone (AOAQ) with methyl methacrylate have been prepared. Their photochemistry and the photoinitiation activity have been examined, and compared with the corresponding anthraquinone monomers. The structures are shown:



X = $OC(O)CH{=}CH_2$ **AOAQ**
X = $NHC(O)CH{=}CH_2$ **AAAQ**

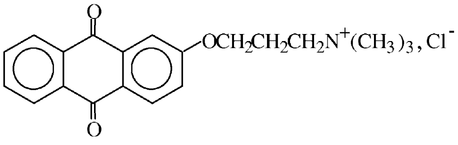


X = O, **AOAQ-co-MMA**
X = NH, **AAAQ-co-MMA**

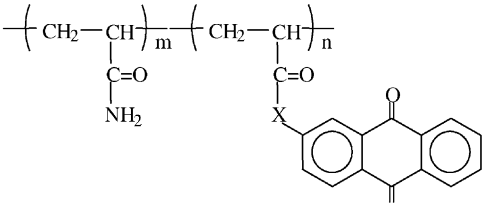
It was found that in the copolymers the phosphorescence quantum yields at 77 K increased markedly ($\phi_p = 9.4 \times 10^{-2}$ and 0.61 in 2-AAAQ-co-MMA and 2-AOAQ-co-MMA, respectively, in CH_2Cl_2) respect to the low molecular weight anthraquinones (no phosphorescence detected). It would indicate that the molecular rigidity of the chromophore on the polymer backbone exhibits an important effect in the rate of singlet–triplet intersystem crossing, but also in the deactivation of the lowest triplet excited state by intersystem crossing.

Photopolymerisation of methyl methacrylate using the polymeric and monomeric photoinitiators in tetrahydrofuran (50:50 (v/v)) were carried out and the rates of polymerisation were obtained from plots of conversion versus irradiation time (Table 1). In the case of the two copolymers, the R_p values increased significantly in the presence of amine as co-initiator. It clearly showed that the nature of the lowest excited state and its ability to form an exciplex plays a crucial role in determining the photoinduced polymerisation activity.

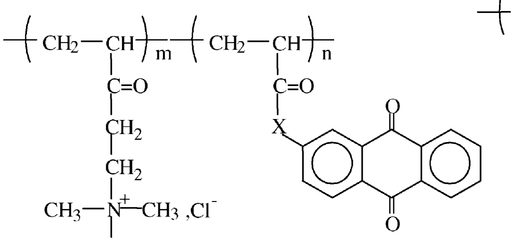
In order to extend the utilisation range of the anthraquinone, water-soluble polymeric anthraquinones have been synthesised. Generally, these structures are organic structures of well-known photoinitiation activity, which have been developed by introducing ionic groups in the oil-soluble structure as well as copolymers of the acrylic derivative of the chromophore with a water-soluble co-monomer. New copolymers have been prepared using AAAQ and AOAQ, by copolymerisation with three water-soluble monomers, acrylamide and 2-acrylamido-2-methylpropanesulphonic acid, and 2-acryloxyethyltrimethylammonium iodide [32]. The structures of the anthraquinone derivatives are shown:



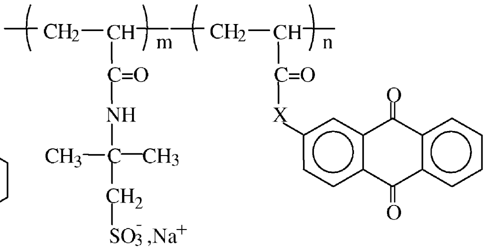
AQW



X = O, **AOAQ-co-AAm**
X = NH, **AAAQ-co-AAm**



X = O, **AOAQ-co-MCl**
X = NH, **AAAQ-co-MCl**



X = O, **AOAQ-co-MSO$_3$Na**
X = NH, **AAAQ-co-MSO$_3$Na**

The absorption, phosphorescence, photoreduction and microsecond flash photolysis characteristics of the new copolymers have been examined. Their efficiency as photoinitiators of polymerisation of an homogeneous aqueous system, acrylamide–water has been studied by photodilatometry, and compared with that of the low molecular weight model compound, AQW.

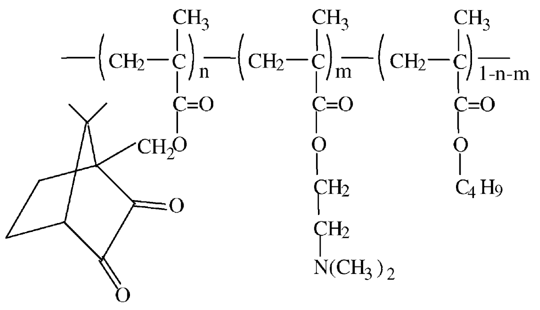
Table 1
Rates of photoinduced polymerisation of MMA by the monomers and copolymers of 2-AOAQ and 2-AAAQ with MMA in tetrahydrofuran (50:50 (v/v))

Sample	R_p ($\times 10^{-4}$ M s^{-1})	
	No amine	Amine[a]
2-AAAQ	1.34	1.66
2-AOAQ	2.28	2.70
2-AAAQ-co-MMA	2.04	2.98
2-AOAQ-co-MMA	2.84	4.08

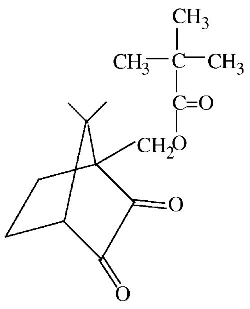
[a] Triethylamine at 7×10^{-3} M.

In general, low photoreduction quantum yields were found for the model and copolymers anthraquinones. Acryloxy copolymers exhibited higher photoreduction quantum yields than those of acrylamide anthraquinones. It seems to be associated with the differences in the nature of the excited state induced by 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 [36–38].

In the absence of amine, no microsecond transient absorption was detected by means of microsecond flash photolysis. It confirms that intramolecular hydrogen abstraction does not occur. In the presence of triethanolamine, all the products displayed similar spectra but with very different relative intensities. The absorption band observed in the region 340–450 nm can be assigned to the semi-anthraquinone radicals (AQH$^{\bullet}$) and the absorption band in the 500–600 nm is due to the radical anions (AQ$^{\bullet -}$) transients, as it is very well established [39,41]. In general a decrease in absorbance of the semi-quinone radical, as well as much shorter semi-quinone radical lifetime was observed in the copolymers (Table 2). It was probably due to the influence of the microenvironment corresponding to the polymeric coil on the disproportionation termination process.



Poly(MCQ) (n=1,m=0)
Poly(MCQ-co-BM) (m=0)
Poly(DMAEM) (m=1,n=0)
Poly(MCQ-co-DMAEM) (n+m=1)
Poly(MCQ-co-DMAEM-co-BM) (n+m<1)



PCQ

Photopolymerisation of acrylamide in a solvent mixture of water–acetonitrile (5:2 (v/v)) was carried out in a photodilatometer, using the new water-soluble products and triethanolamine as a hydrogen donor. In the absence of amine, no photopolymerisation was observed in accordance with neither detectable transient nor intramolecular photoreduction. In general, the acrylate anthraquinone copolymers show similar photoinitiation efficiency than that of the low molecular weight product when used in combination with triethanolamine, whereas the acrylamide derivatives have lower efficiency in agreement with their lower photoreduction quantum yields.

5. Polymeric photoinitiators based on camphorquinone

Camphorquinone is a very well-known photoinitiator, which is widely employed for the photocuring of restorative dental composite resins [42]. Camphorquinone acts in combination with hydrogen donors as tertiary amines, to generate radicals according to a mechanism involving excitation of the ketone to the triplet excited state, followed by electron and proton transfer through a charge transfer intermediate.

Polymethacrylic derivatives bearing camphorquinone and camphorquinone–tertiary amino groups have been synthesised, and their photoinitiation activity in the polymerisation of a mixture of hexanediol diacrylate (HDDA) and *n*-butyl acrylate (BA) evaluated by microwave dielectrometry [43].

It was found that the photoinitiating activity of polymeric radical initiators based on camphorquinone is dependent on both the monomeric or polymeric nature of camphorquinone and the tertiary amine. Polymerisation rate determined by the slope of the conversion versus time curve are showed in Table 3.

In general, higher efficiency was found for systems based on both low molecular weight components, PCQ–DMAEP, or constituted by combinations of low and high molecular weight components, such as PCQ–poly(DMAEM) and poly(MCQ-co-BM)–DMAEP, compared to the system based on all polymeric components. It was probably due to the steric hindrance for exciplex formation when the

Table 2
Transient absorption data obtained immediately after the flash lamp on microsecond flash photolysis of the water-soluble anthraquinone model and copolymers

Sample	Semi-anthraquinone radical ($AQH^{\bullet}$)			Radical anion ($AQ^{\bullet -}$)	
	λ_{max} (nm)	Absorbance	τ (μs)[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_3Na	380	0.15	4	450	0.09
AAAQ-co-AAm	380	0.40	2	460	0.13
AAAO-co-MCl	375	0.50	2	455	0.15
AAAQ-co-MSO_3Na	340	0.30	2	480	0.11

[Anthraquinone] = 10^{-5} M; [TEOA] = 10^{-4} M in water, under N_2 atmosphere.

[a] Second-order kinetic decay.

Table 3
Polymerisation of HDDA–BA mixture (1:1) photoinitiated by polymeric and low molecular weight systems based on camphorquinone ($\lambda_{irr} > 400$ nm, under nitrogen)

Photoinitiator	$R_{p,50}$ ($\times 10^{-3}$ s^{-1})[a]	$R_{p,max}$ ($\times 10^{-3}$ s^{-1})[b]	Conversion (%)[c]
CQ	1.5	1.6	60.1
PCQ–DMAEP	7.7	9.3	86.3
PCQ–poly(DMAEM)	6.4	9.6	84.2
Poly(MCQ-co-BM)–DMAEP	13.5	15.7	85.2
Poly(MCQ-co-BM)–poly(DMAEM)	5.7	6.7	85.4
Poly(MCQ-co-DMAEM-co-BM)	4.1	6.3	87.0

[a] Polymerisation rate at 50% conversion.

[b] Maximum polymerisation rate.

[c] Double bound conversion after 600 s irradiation time.

camphorquinone and amine were both macromolecular. Poly(MCQ-co-BM)–DMAEP exhibited the highest value of polymerisation rate. It could be related to the macromolecular nature of the camphorquinone, and the possibility of intramolecular hydrogen abstraction from the BM units and/or energy migration between excited and ground state neighbouring camphorquinone groups located along the polymeric chain.

The lowest activity was found for the terpolymeric system poly(MCQ-co-BM-co-DMAEM). In the copolymeric photoinitiator, due to the close vicinity between amine and camphorquinone moieties along the macromolecular backbone, their mobility is more restricted and the recombination between radicals is favoured, and the concentration of initiating active species is lower.

6. Polymeric photoinitiators based on benzoin ether

Benzoin ether derivatives are well known type I photofragmenting photoinitators, which under irradiation produce benzoyl and α-alkoxybenzyl primary radicals [44,45]. It has been suggested that benzoyl radicals are more active as initiating species than the alkoxybenzyl radicals, which are involved in the termination reaction [46].

Polymeric photoinitiators based on side-chain benzoin methyl ether were synthesised by copolymerisation with methacrylic monomers, and also the insertion of amine moieties into the macromolecular backbone was carried out [47]. Higher efficiency was found for polymeric photoinitiators with respect to low molecular weight model. It was attributed to a reduced mobility of the radicals anchored to the polymer to give coupling reactions, and as a consequence a much higher concentration of initiating radical.

Recently, polymeric photoinitiators having benzoin methyl ether moieties connected to the main chain through the benzyl aromatic ring, poly(MHBM) and poly(MMBM) have been synthesised by radical homopolymerisation [48]. The activity of these systems as photoinitiators was

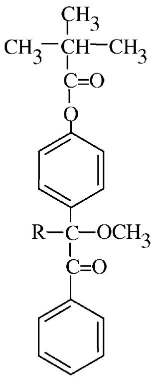
Table 4
Kinetic parameters determined by microwave dielectrometry from the UV curing of HDDA–BA (1:1) by polymeric and low molecular weight systems based on benzoin methyl ether

Photoinitiator	$R_{c,1/2}$ (s^{-1})[a]	t_0 (s)[b]
Poly(MHBM)	9.2	3.6
PHBM	11.0	3.6
Poly(MMBM)	5.5	4.0
PMBM	10.2	3.6
Poly(ABME)	9.8	2.9
Poly(AMBE)	7.8	3.3

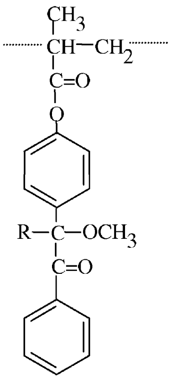
[a] Polymerisation rate expressed as percent conversion of monomers to polymers per second, determined at half-time of the process.

[b] Induction period of the polymerisation process.

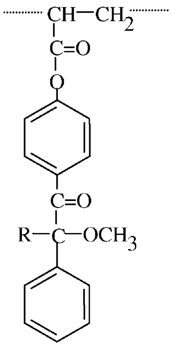
measured by microwave dielectrometry, and compared to low molecular weight models PHBM and PMBM, and homopolymers poly(AMBE) and poly(ABME) previously synthesised. The structures of monomeric and polymeric photoinitiators are shown:



PHBM (R=H)
PMBM (R=CH_3)



Poly (MHBM) (R=H)
Poly (MMBM) (R=CH_3)



Poly (ABME) (R=H)
Poly (AMBE) (R=CH_3)

The experimental kinetic parameters obtained in the polymerisation of a mixture hexanediol diacrylate and *n*-butyl acrylate (HDDA–BA (1:1)) using the polymeric and low molecular weight photoinitiators are compiled in Table 4.

It was observed a higher efficiency for model compounds than the corresponding polymers. It was proposed that the photoinitiators with ester groups in the para position of the benzyl group under irradiation produce benzyl and benzoyl primary radical, the former could evolve by further fragmentation to an stable quinoid structure and an aliphatic acyl radical (Scheme 1). The lower initiating activity of polymers would be justified by the lower activity of polymer-bound benzyl radicals due to steric hindrance of the polymer coil.

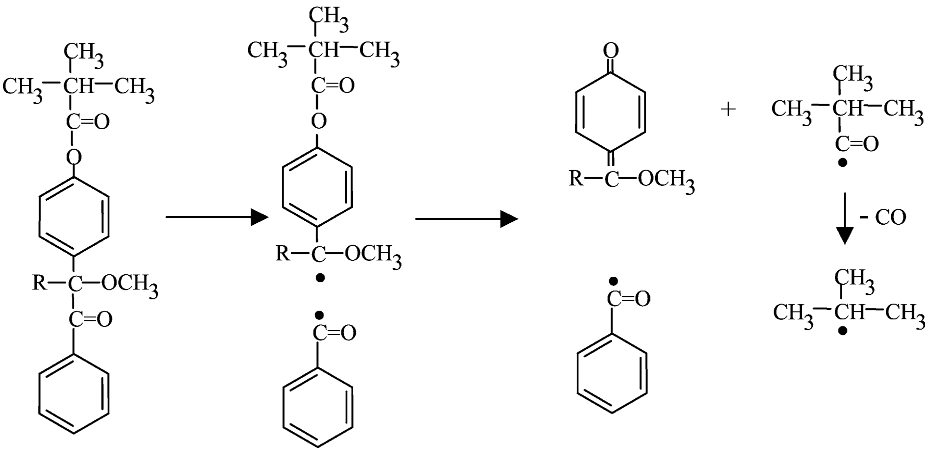
In general, all the α-methylated derivatives display lower activity than the unmethylated photoinitiators. It was due to the lower absorptivity of light at the irradiation wavelength, as it was already reported [49].

7. Polymeric photoinitiators based on acylphosphine oxides

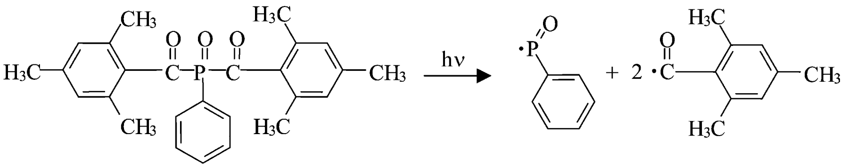
Under irradiation, acylphosphine oxides exhibited direct fragmentation at the carbonyl–phosphorous bond, with generation of two free radical, both capable of initiating the polymerisation [50] (Scheme 2). They are included into Norrish type I photofragmenting photoinitators. Acylphosphine oxides exhibit an absorption band centred around 380 nm and are particularly suitable for UV cure of TiO_2 pigmented coating. However, the use of these photoinitiators is restricted to the most applications due to their light sensitivity and relatively high cost.

Polymeric photoinitiators bearing 2,6-dimethylbenzoylphosphine oxide moiety (BPO) pendant from flexible tetramethylene oxide chains have been synthesised to be applied in photocurable adhesives [51].

The homopolymers of 4-(4′-acryloyloxy-1′-butoxy)-2,6-dimethylbenzoylphosphine oxide, poly(ABDBPO), and copolymer with butyl acrylate, poly(ABDBPO-co-BA) obtained, were evaluated as photoinitiators by microwave dielectrometry in the polymerisation of HDDA–BA and adhesive acrylic formulations. The results obtained were



Scheme 1.



TMBAPO

Scheme 2.

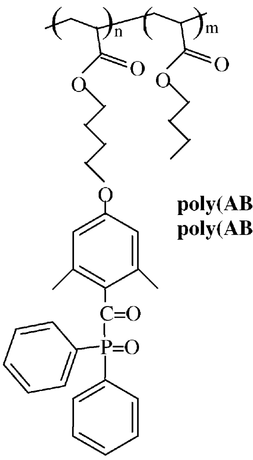
Table 5
Kinetic data of photoinitiated polymerisation of HDDA–BA (1:1) liquid films containing 0.5 mol% BPO moieties

Photoinitiator	Photoreactive unit (mmol g^{-1})	t_0 (s)[a]	$R_{c,\max}$ (s^{-1})[b]
TMBPO	2.87	0.1	20.9
Poly(ABDBPO)	2.09	0.2	11.1
Poly(ABDBPO-co-BA)	1.07	0.1	11.0
Poly(ADBPO-co-BA)	1.03	0.4	17.1

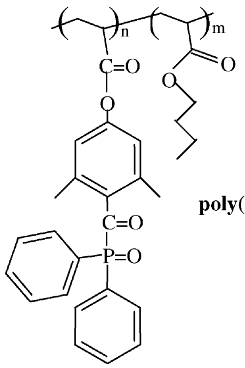
[a] Induction time of polymerisation.

[b] Maximum polymerisation rate (normalised as percent conversion over time).

compared with those of poly(ADBPO-co-BA), which have the BPO group directly attached to the main chain, and with those of a low molecular weight model photoinitiator, diphenyl-(2,4,6-trimethylbenzoyl)phosphine oxide (TMBPO). The structures of the new polymeric photoinitiator are shown below, and the kinetic data obtained are summarised in Table 5.



poly(ABDBPO) (m=0)
poly(ABDBPO-co-BA)

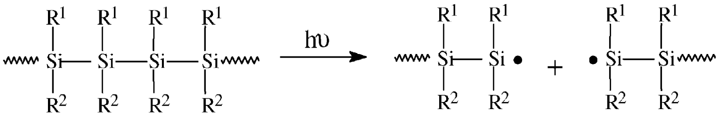


poly(ADBPO-co-BA)

Higher photoinitiating activity was found for the low molecular weight model, TMBPO. In general, all polymeric photoinitiators exhibited similar efficiency in the polymerisation of HDDA–BA, irrespective of the presence of flexible spacer in the structure. It seems that the effect of the flexible spacer on the mobility of radicals is comparable with that provided by electronic and steric factor. Acrylic adhesive formulations were employed to test the compatibility of the new polymeric photoinitiators and it was found that the flexible spacer introduced in the structure improved the solubility of the photoinitiators, and higher concentration of BPO (0.5 mol%) could be employed in the polymerisation processes, in contrast to that of most polymeric bearing acylphosphine oxide (0.1 mol%).

8. Polysilanes as photoinitiators

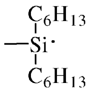
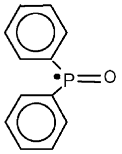
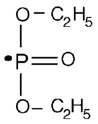
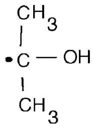
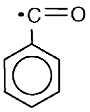
West et al. [52] investigated the possibility of using polysilanes as a source of silyl radicals for initiate polymerisation. Actually, polymers were formed when formulations containing a vinyl monomer and a polysilane, such as poly(methyl phenyl silane) and poly(di-*n*-hexyl silane), were exposed to UV light. Polysilanes undergo main-chain scission upon photolysis [53] a process essentially involving the homolytic cleavage of Si–Si bonds and thus leading to free silyl radicals as depicted by reaction (3):



$$\sim\sim\underset{R^2}{\overset{R^1}{\mathrm{Si}}}-\underset{R^2}{\overset{R^1}{\mathrm{Si}}}-\underset{R^2}{\overset{R^1}{\mathrm{Si}}}-\underset{R^2}{\overset{R^1}{\mathrm{Si}}}\sim\sim \xrightarrow{h\upsilon} \sim\sim\underset{R^2}{\overset{R^1}{\mathrm{Si}}}-\underset{R^2}{\overset{R^1}{\mathrm{Si}}}\bullet + \bullet\underset{R^2}{\overset{R^1}{\mathrm{Si}}}-\underset{R^2}{\overset{R^1}{\mathrm{Si}}}\sim\sim \quad (3)$$

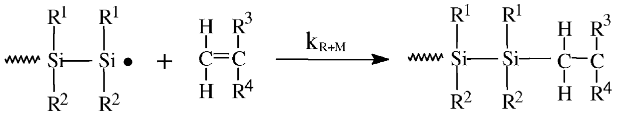
Silyl radicals generated according to reaction (3) are capable of reacting with olefinic monomers and in this way of

Table 6
Kinetic rate constants of some radicals towards vinyl monomers at room temperature (in $l\,mol^{-1}\,s^{-1}$)

Monomer	 $(C_6H_{13})_2Si^{\bullet}$	$(C_2H_5)_3Si^{\bullet}$				
St	1.6×10^8	2.2×10^8	6.0×10^7	2.5×10^8	3.5×10^5	1.2×10^5
MMA	7.6×10^7	4.6×10^8	8.0×10^7	5.3×10^7	5.4×10^5	0.9×10^5
AN	1.0×10^8	–	2.0×10^7	2.6×10^6	1.6×10^5	0.2×10^5
MAN	7.3×10^6	–	5.0×10^7	1.1×10^8	–	–
BVE	$<5.5 \times 10^5$	–	5.0×10^6	–	–	–

St: styrene; MMA: methyl methacrylate; AN: acrylonitrile; MAN: methacrylonitrile; BVE: butyl vinyl ether.

initiating their free radical polymerisation (4):



(4)

Polysilanes have a rather large quantum yield of main-chain scission and a very high reactivity of silyl radicals towards many olefinic monomers. Indicative of the high reactivity of silyl radicals are the values of the rate constant k_{R+M} determined by some of the present authors [54,55], which are one or two orders of magnitude larger than that of carbon-centred radicals. Typical are shown in Table 6. On the other hand, polysilanes appeared to be of unique advantage because of their low susceptibility to inhibition by molecular oxygen [56].

Kminek et al. [57] prepared a water-soluble derivative of PMPSi and used it as photoinitiator of the free radical polymerisation of hydrophilic monomers such as acrylamide and vinyl pyrrolidone. However, the photoinitiation efficiency was not determined in this case. Peinado et al. [58] demonstrated that regarding the free radical polymerisation of methyl methacrylate and styrene the photoinitiation efficiency of polysilanes having different aliphatic and aromatic side groups is in the order of 0.1 kinetic chains started per photon and thus compared with commercial low molecular weight photoinitiators as benzoin. Moreover, polysilanes have been employed as efficient photoinitators of commercial silicon-based formulations bearing pendant acrylate groups [59] and, in conjunction with onium salts, as photoinitiators of cationic monomers, such as cyclic ethers and *N*-vinylcarbazol. The silyl radicals generated by photolysis can be oxidised by appropriate onium salts to yield cationic initiating species (photoinitiated radical promoted cationic polymerisation) [60].

Finally, it is noteworthy that polysilanes are unique as type I polymeric photoinitiators that photofragment by main-chain scission to give the initiating radicals. Polymers obtained by using polysilanes as photoinitiators contain fragments of polysilane chains that can be further photolysed to yield new macroradicals which can react with a second co-monomer. Therefore, using polysilanes as multi-functional initiators provides a novel route for synthesising block copolymers [61] or interpenetrating networks with the prospect of improving material properties [59].

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