Synthesis and photoinitiation activity of macroinitiators comprising benzophenone derivatives

A.M. Rufs [a], A. Valdebenito [a], M.C. Rezende [a], S. Bertolotti [b], C. Previtali [b], M.V. Encinas [a,*]

[a] Facultad de Química y Biología, Universidad de Santiago de Chile, Departamento de Química, Casilla 307-2, Santiago, Chile
[b] Departamento de Química, Facultad de Ciencias Exactas, Físico-Químicas y Naturales, Universidad Nacional de Río Cuarto, Argentina

ARTICLE INFO

ABSTRACT

Macrophotoinitiators bearing 4-substituted benzophenones bound to an N-isopropylacrylamide chain were synthesized in one-step reaction. Triethanolamine was used as coinitiator. These systems were evaluated as photoinitiators of the N-isopropylacrylamide polymerization in different solvents. They present a high photoinitiation efficiency that depends on the structure of the initiator and on the medium properties. In all solvents, the macroinitiators were more efficient than the corresponding low-molecular-weight analog. The photophysics of ketones was studied in the different solvents. The triplet state of the ketone was deactivated by the amine with a diffusional controlled rate. The characterization of the transients produced in this process explained the influence of the 4-substituent and of the solvent on the yield of the active radical and the polymerization efficiency.

1. Introduction

Photoinitiated free-radical polymerizations have received increased interest because of their numerous applications. Recently, the development of novel photoinitiators incorporated in a polymeric chain, defined as macroinitiators, has received special attention [1–15]. The macromolecular nature of these compounds offers advantages compared with their corresponding low-molecular-weight analogs. Among these advantages are a higher activity, lower migration rate, improved solubility, and also the possibility of macromolecular design.

There are many studies concerning bimolecular macrophotoinitiators [2,8–12,15–18]. Many of these compounds consist of aromatic ketones bound to acrylic or methacrylic polymers, and they have been used for the polymerization of acrylate monomers. In these compounds the active radicals are produced from the interaction of the chromophore with tertiary amines which proceeds through a charge-transfer intermediate. An increase of the photoinitiation efficiency with respect to the low-molecular-weight model compound is frequently found when the photoinitiator is incorporated into a polymer backbone and the coinitiator is a low-molecular-weight amine [2,8,9,11,12,16,17]. Systems with the photoinitiator and the coinitiator bound to a polymer chain are less efficient [2,8,15,16]. This behaviour has been attributed to

a polymer effect. In spite of this extensive work, there are few systematic studies on the relation between the structure of these systems and their efficiency as photoinitiators, and the polymer effect is not well understood.

In this work we studied the efficiency of three benzophenones bearing different 4-substituents as photoinitiators in the N-isopropylacrylamide polymerization. The same 4-substituted ketones bound to a poly(N-isopropylacrylamide) chain were also synthesized. Triethanolamine (TEOHA) was used as coinitiator. In order to understand the effect of the chromophore microenvironment on the photoinitiation efficiency, we studied the photochemical behaviour of the model monomeric photoinitiator in several solvents. Poly(N-isopropylacrylamide) is a very suitable polymer for these studies since it presents a wide range of solubility. The polymer conformation in several solvents was analyzed.

2. Experimental

2.1. Material

Triethanolamine (TEOHA) (Aldrich) was purified by distillation under reduced pressure prior to use. Benzophenones (BP) obtained from Aldrich were recrystallized from ethanol. N-Isopropylacrylamide (NIPAM) from Aldrich (>97%) was used as-received. 2,2′-Azobis-(isobutyronitrile) (AIBN) was recrystallized from ethanol. Benzoyl chloride, 4-methoxybenzoyl chloride, 4-

cyanobenzoyl chloride and 2-phenoxyethyl methacrylate were purchased from Aldrich.

2.2. Measurements

NIPAM polymerization rates (R_p) were measured dilatometrically in oxygen-free solutions at 25 °C. The monomer concentration was 0.4 M. The samples were irradiated in a Rayonet photochemical reactor with 360 nm fluorescent lamps. Low absorbances (0.25) of BP, free or incorporated into the polymeric chain, were used to avoid the generation of an inhomogeneous free-radical distribution [19]. The polymerization times were chosen such that the conversion remained below 20%. The intrinsic viscosity of polymers was measured in several solvents using an Ubbelhode viscometer at 25 °C. Molecular weights were determined by size exclusion chromatography (SEC) on a HP Series 1100 apparatus on the basis of linear polyglycol standards using water as eluent.

Transient absorption measurements were made using a laser flash photolysis equipment. The third harmonic of a Nd:YAG laser (355 nm, 10 mJ/pulse, 20 ns) was employed for sample excitation. The signals from the monochromator/photomultiplier system were initially captured by a HP54504 digitizing oscilloscope and transferred to a computer for storage and analysis.

MS electron impact was obtained on a MAT 95XP, Thermo Finnigan spectrometer, using as reference perfluorokerosene. ^{1}H NMR spectra were recorded on a Bruker Avance-400 instrument, employing tetramethylsilane as internal reference.

2.3. Synthesis of monomers

2.3.1. 4-Benzoylphenoxyethyl methacrylate (1a)

To a cooled (0–5 °C), stirred solution of benzoyl chloride (53 mmol) and 2-phenoxyethyl methacrylate (53 mmol) in chloroform (50 mL) was added anhydrous AlCl$_3$ (53 mmol) in small portions. After the addition was complete, the solution was allowed to reach room temperature (25 °C) and stirred for 7 h. Water was added, and the organic phase was washed with a dilute solution of sodium bicarbonate, then with water, and dried over anhydrous CaCl$_2$. Evaporation of the solvent left an oily residue which was purified by flash chromatography (silicagel 60H) employing chloroform as eluent. The pure product **1a** was obtained as an oil in 62% yield. HRMS: found 310.1204, calculated for C$_{19}$H$_{18}$O$_4$ 310.1205. ^{1}H NMR (CDCl$_3$) δ 1.96 (3H, s, CH$_2$=CCH$_3$); 4.31 (2H, d, J = 4.4 Hz, PhOCH$_2$); 4.54 (2H, d, J = 4.5 Hz, PhOCH$_2$CH$_2$); 5.60 (1H, s, CH=C); 6.15 (1H, s, CH=C); 6.98 (2H, d, J = 8.8 Hz, OAr–H ortho to phenoxide O); 7.47 (2, t, J = 7.9 Hz, O=CAr–H meta to carbonyl); 7.57 (1H, t, J = 8.1 Hz, OCAr–H para to carbonyl); 7.75 (2H, d, J = 7.9 Hz, O=CAr–H ortho to carbonyl); 7.83 (2H, d, J = 8.8 Hz, OAr–H meta to phenoxide O). ^{13}C NMR (CDCl$_3$) δ 18.5, 63.0, 62.3, 114.4, 126.4, 128.4, 129.9, 130.8, 132.2, 132.8, 136.1, 138.4, 162.3, 167.5, 165.7.

2.3.2. 4-(4-Methoxybenzoyl)phenoxyethyl methacrylate (1b)

To a cooled (0–5 °C), stirred suspension of 2-phenoxyethyl methacrylate (7.5 mmol) and anhydrous aluminum chloride (7.5 mmol) in CS$_2$ (4 mL) was slowly added a solution of 4-methoxybenzoyl chloride (7.3 mmol) in CS$_2$ (8 mL). The resulting mixture was allowed to reach room temperature and was then stirred for other 22 h. Dilute HCl was then added, and the organic phase was washed with a dilute solution of sodium hydroxide, and then with water, and dried over anhydrous CaCl$_2$. Evaporation of the solvent left an oily residue which was purified by flash chromatography (silicagel 60H) employing hexane:ethyl acetate 4:1 as eluent. The pure product **1b** was obtained as a solid, mp 98 °C in 68% yield. HRMS: found 340.1312, calculated for C$_{20}$H$_{20}$O$_5$ 340.1311. ^{1}H NMR (CDCl$_3$) δ 1.96 (3H, s, CH$_2$=CCH$_3$); 4.31 (2H, d, J = 4.4 Hz, PhOCH$_2$); 4.54 (2H, d, J = 4.5 Hz, PhOCH$_2$CH$_2$); 5.60 (1H, s, CH=C); 6.15 (1H, s, CH=C); 6.96 (2H, d, J = 8.4 Hz, MeOAr–H ortho to OMe); 7.01 (2H, d, J = 8.4 Hz, –OAr–H ortho to OCH$_2$); 7.78 (4H, d, J = 8.4 Hz, O=CAr–H ortho to carbonyl). ^{13}C NMR (CDCl$_3$) δ 18.5, 55.7, 63.0, 66.3, 113.7, 114.3, 126.4, 128.7, 130.9, 131.4, 132.4, 136.1, 162.0, 163.1, 167.5, 194.6.

2.3.3. 4-(4-Cyanobenzoyl)phenoxyethyl methacrylate (1c)

To a cooled (0–5 °C), stirred suspension of 4-cyanobenzoyl chloride (3.0 mmol) and anhydrous aluminum chloride (4.6 mmol) in CH$_2$Cl$_2$ (30 mL) was slowly added 2-phenoxyethyl methacrylate (1.4 mmol). The resulting mixture was stirred under nitrogen and allowed to reach room temperature. It was then stirred for other 21 h. After this time a second portion of anhydrous aluminum chloride (4.6 mmol) was added, and the mixture was allowed to react with stirring for further 10 h. Dilute HCl was then added, and the organic phase was washed with a dilute solution of sodium hydroxide, and then with water, and dried over anhydrous CaCl$_2$. Evaporation of the solvent left an oily residue which was purified by flash chromatography (silicagel 60H) employing CH$_2$Cl$_2$:ethyl acetate 99:1 as eluent. The pure product **1c** was obtained as a solid, mp 118 °C in 59% yield. HRMS: found 335.1130, calculated for C$_{20}$H$_{17}$NO$_4$ 335.1158. ^{1}H NMR (CDCl$_3$) δ 1.96 (3H, s, CH$_2$=CCH$_3$); 4.31 (2H, d, J = 4.4 Hz, PhOCH$_2$); 4.54 (2H, d, J = 4.5 Hz, PhOCH$_2$CH$_2$); 5.60 (1H, s, CH=C); 6.15 (1H, s, CH=C); 7.00 (2H, d, J = 8.8 Hz, OAr–H ortho to OCH$_2$); 7.77–7.83 (6H, Ar–H). ^{13}C NMR (CDCl$_3$) δ 18.5, 62.9, 66.4, 114.7, 115.5, 118.3, 126.4, 129.6, 130.1, 132.3, 132.8, 136.1, 142.2, 163.0, 193.9.

2.4. Copolymerization procedure

Copolymers **2** were obtained by heating under nitrogen at 60 °C, for 1 h, a mixture of 1 equiv of the substituted benzophenone **1** with 10 equiv of *N*-isopropylacrylamide in dimethylformamide, in the presence of 2,2′-azobis-(isobutyronitrile) (AIBN) (0.3 equiv%). The product was precipitated by the addition of diethylether. ^{1}H NMR spectra of copolymers **2** exhibited a conspicuous doublet at δ 2.93, which corresponded to the two-methyl protons of the isopropyl group, and a broad signal near 4.0 ppm, that was assigned to the CHMe$_2$ proton. The degree of incorporation of the benzophenone fragment into the copolymer was estimated by the relative integration of any of these isopropyl signals and the benzoyl signals ortho to the carbonyl group. In all cases, the resulting percentage of incorporation was estimated to be 4%. Molecular weights of the copolymers were in the range of 44,000–50,000.

3. Results and discussion

3.1. Synthesis of polymeric photoinitiators

All photoinitiators were prepared by Friedel–Crafts benzoylation of 2-phenoxyethyl methacrylate, to form the corresponding substituted benzophenones **1**, which reacted with *N*-isopropylacrylamide in the presence of 2,2′-azobis-(isobutyronitrile) (AIBN) to give copolymers **2**.

3.2. Polymerization studies

The polymerization of *N*-isopropylacrylamide was carried out in several solvents using as photoinitiator 4-substituted BPs incorporated in a poly(*N*-isopropylacrylamide) (PNIPAM) chain. For the sake of comparison, the low-molecular-weight analogs were also employed as photoinitiators. In all cases the coinitiator was TEOHA 0.1 M. At this amine concentration a maximum value of polymerization rate (R_p) was reached. Further amine addition did not change the R_p. The polymerizations were carried out at low conversion (<20%). Under these conditions the polymerization
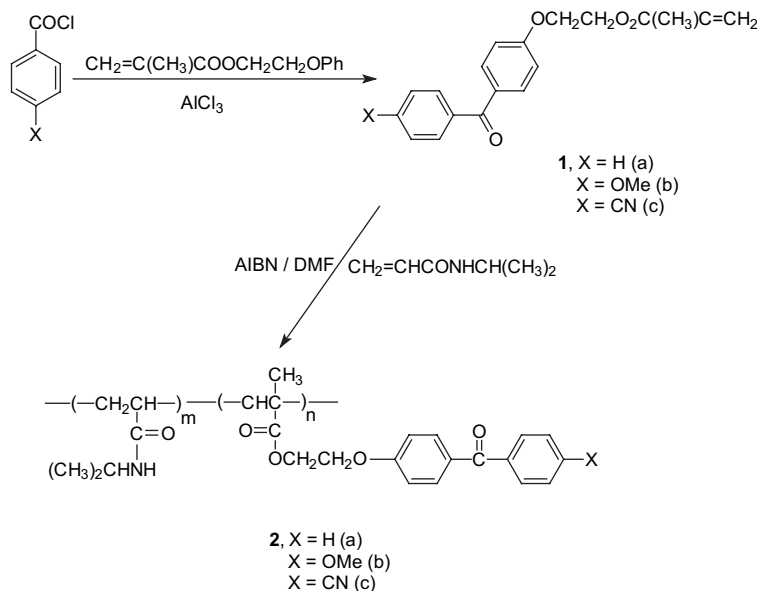
remained homogeneous due to the solubility of the polymer in all the employed solvents. R_ps were obtained from the initial slope of plots of the conversion versus time. Polymerization rates are given in Table 1.

These results show that R_p is higher for the polymeric photoinitiator, a common observation for the three 4-substituted ketones, in all solvents employed in this study. This increased activity has been described for several bimolecular photoinitiators comprising a free amine as coinitiator and macroinitiators based on thioxanthone, camphorquinone and benzophenones [2,5,8,16,17]. On the other hand, data of Table 1 show that R_p is highly dependent on the solvent employed. Furthermore, in the same solvent, R_p values depend on the 4-substituent in the BP ring. Thus, in highly polar solvents (MeOH, DMSO, and acetonitrile) the polymerization rate depends on the electron-donating ability of the group at the 4-position. The electron-donating OCH_3 group increases the polymerization rate, whereas the strong electron-withdrawing CN substituent decreases it.

As described for the free-radical polymerization of vinyl monomers photoinitiated by aromatic ketone–amine, the R_p can be expressed by the classical kinetic law [8,20], given by

$$R_p = \left(\frac{k_P}{k_t^{1/2}}\right)\Phi_i^{1/2}I_a^{1/2}[M] \tag{1}$$

where I_a is the intensity of the absorbed light by the photoinitiator, and Φ_i is the initiation quantum yield. From Eq. (1) it can be deduced that for the same monomer concentration and identical I_a, the dependence of R_p on the nature of the photoinitiator will be a consequence only of the initiation quantum yield. Similarly, Eq. (1) implies that the variation of the R_p with the solvent is due to changes in both the ratio $k_P/k_t^{1/2}$ and Φ_i. In order to avoid changes in k_p or k_t with the solvent, in this study we compared the R_p values of the polymerization photoinitiated by the macroinitiator and the monomeric compound in the same solvent.

The photoinitiation efficiencies were evaluated with respect to that obtained with the classical unimolecular photoinitiator, AIBN. Under the same absorption condition, and at the same monomer concentration Eq. (1) leads to Eq. (2)

$$\frac{\Phi_{BP}}{\Phi_{AIBN}} = \frac{(R_p)_{BP}^2}{(R_p)_{AIBN}^2} \tag{2}$$

The values of the photoinitiation quantum yield for the polymerization initiated by BP in the presence of 0.1 M TEOHA, relative to those obtained using AIBN, are shown in Table 2.

It is interesting to note that the polymerization efficiency of BP in the presence of amine is markedly higher than that obtained with the classical unimolecular photoinitiator (AIBN). Some experiments carried out with 2-chlorothioxantone (TX) as photoinitiator show the same pathway. This is contrary with what was reported for the polymerization of methyl methacrylate, where the polymerization is more efficient for the azo compound [8,21]. The difference in polymerization efficiency can be explained in terms of the different reactivity of active radicals towards the electron-

Table 1
N-Isopropylacrylamide polymerization rates in different solvents, photoinitiated by 4-substituted benzophenones in the presence of TEOHA 0.1 M

4-Substituent	Solvent	R_p (a.u.)	
		Monomeric photoinitiator	Polymeric photoinitiator
–OCH$_3$	Methanol	0.54	0.67
	DMSO	0.46	0.77
	Acetonitrile	0.49	0.83
	Dioxane	1.9	3.2
	Benzene	2.9	–
–H	Methanol	0.43	0.52
	DMSO	0.15	0.38
	Acetonitrile	0.44	0.60
	Dioxane	1.6	2.23
	Benzene	2.7	–
–CN	Methanol	0.12	0.65
	DMSO	Np[a]	0.07
	Acetonitrile	0.18	0.40
	Dioxane	2.0	2.6
	Benzene	3.13	–

[a] No polymer is formed.

Table 2
Photoinitiation quantum yields using benzophenone as photoinitiator relative to AIBN in different solvents

Solvent	Φ_{BP}/Φ_{AIBN}
Benzene	5.2
Acetonitrile	4.0
Methanol	4.7

Table 3
N-Isopropylacrylamide polymerization rates in different solvents photoinitiated by 4-substituted benzophenones in the absence of amine

4-Substituent	Solvent	R_p (a.u.)	
		Monomeric photoinitiator	Polymeric photoinitiator
–OCH$_3$	Methanol	0.21	0.14
	DMSO	Np[a]	Np[a]
	Acetonitrile	0.02	0.03
	Dioxane	1.25	1.64
	Benzene	0.17	–
–H	Methanol	0.37	–
	DMSO	Np[a]	Np[a]
	Acetonitrile	0.08	0.02
	Dioxane	1.0	1.32
	Benzene	0.27	–
–CN	Methanol	0.75	0.70
	DMSO	Np[a]	Np[a]
	Acetonitrile	0.04	0.07
	Dioxane	1.6	1.6
	Benzene	0.20	–

[a] No polymer is formed.

Table 4
Rate constants for the 4-substituted benzophenone triplet in acetonitrile

4-R	Quencher	k_q, M^{-1} s^{-1}
OCH$_3$	TEOHA	5.6×10^8
	N-Isopropylacrylamine	8×10^6
H	TEOHA	2×10^9
	N-Isopropylacrylamine	7.6×10^6
CN	TEOHA	4.1×19^9
	N-Isopropylacrylamine	7×10^6

deficient double bond in the NIPAM. This reactivity will be conditioned by the nucleophilicity of the active radicals. Thus, the higher photoinitiaton efficiency of the system ketone–amine is in agreement with the high nucleophilic character of the aminoalkyl radicals [22,23]. On the other hand, the CN group adjacent to the carbon-centered radicals formed from the cleavage of AIBN makes them electrophilic, and less reactive towards the monomer.

Polymerization rates were also measured in the absence of amine. These values are given in Table 3.

These studies show that the polymerization is almost negligible in acetonitrile and DMSO, whereas significant polymerization is observed in methanol and dioxane.

In order to understand the effect of solvent and the structure of the photoinitiators on the polymerization efficiencies, the photochemical behaviour of these compounds, under the polymerization conditions, was studied.

3.3. Photochemical studies

Similarly to the low-molecular-weight benzophenones, the copolymers bearing 4-substituted benzophenones exhibit a weak absorption in the region 320–370 nm due to the n → π* transition. As expected for these transitions, the absorption band in polar media is slightly shifted to shorter wavelengths. The deactivation of the BP triplet excited state in the polymerization medium can be represented by the following reactions,

$$BP + h\nu \rightarrow {}^1B^* \rightarrow {}^3BP^* \tag{3}$$

$$^3BP^* \rightarrow BP \tag{4}$$

$$^3BP^* + \text{solvent} \rightarrow P_4 \tag{5}$$

$$^3BP^* + \text{monomer} \rightarrow P_5 \tag{6}$$

$$^3BP^* + \text{amine} \rightarrow P_6 \tag{7}$$

To understand the different efficiencies of the photoinitiators it is necessary to know the rate constants of all steps that deactivate the BP triplet state. With this aim, we studied the photochemical behaviour of the monomeric ketones.

The photochemical behaviour of the excited states of the unsubstituted benzophenone has been widely studied, whereas less is known about the photochemistry of the substituted compounds. Since, the rate constant of the intersystem crossing from the lowest singlet excited state of BP and derivatives is very large (ca. 10^{11} s^{-1}), the photochemistry occurs from the lowest triplet excited state. The triplet absorption spectrum of the BPs is well known [24,25]. It presents an absorption band in the region 440–620 nm with a maximum at 520–545 nm. The pseudo-first-order rate constants of the triplet decay, k_{obs}, are related to the quenching rate constant (k_q) by Eq. (8).

$$k_{obs} = k_o + k_q[Q] \tag{8}$$

Values of the k_q for TEOHA and NIPAM, determined from the slope of the linear relation of k_{obs} at 600 nm as a function of the quencher concentration, are shown in Table 4.

The amine k_q values increase with increasing electrophilicity of the 4-susbtituent at the BP ring. This trend is similar to that found for 4-susbtituted BPs by triethylamine [26]. Quenching rate constants are almost independent of the solvent; only a small decrease was observed in methanol [27]. The BP triplet also abstracts a H-atom from moderate hydrogen donors by a simple bimolecular step. As expected for these reactions, the rate depends on the energy of the broken bond, and it is almost independent of the solvent. Rate constant values of 9.4×10^5 M^{-1} s^{-1} and 2×10^5 M^{-1} s^{-1} have been reported for the hydrogen abstraction from dioxane and methanol, respectively [28]. This reaction is negligible for acetonitrile or benzene [29,30].

The quenching of BP triplets by amines is a well-known process which has been extensively investigated [31–34]. It is due to the electron transfer from the amine to the ketone giving the contact radical ion pair (CRIP). One of the decay processes of this intermediate is the proton transfer from the amine radical cation to the benzophenone radical anion forming the radical pair, Scheme 1.
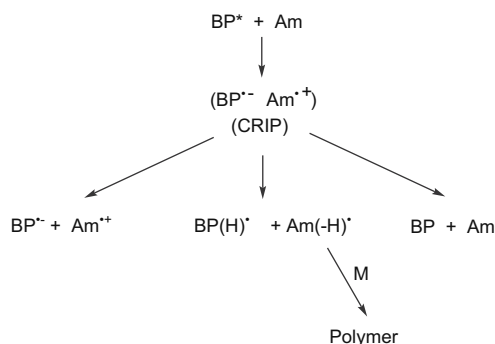
Scheme 1.

3.4. Photoinitiation efficiency

It is well known that aminoalkyl radicals (Am(−H)•) are the species that add to the monomer. Ketyl radicals are not reactive towards vinyl monomers due to the steric hindrance and the delocalization of the unpaired electron. Thus, the photoinitiation quantum yield is related to the competition of the deactivation by the amine (Eq. (7)) with all the deactivation steps of the ketone triplets. According to Eqs. (4)–(7), the photoinitiation quantum yield is given by Eq. (9)

$$\Phi_i = \alpha\beta \frac{k_7\,[Am]}{k_7[Am] + k_6[M] + k_5[S] + k_4} \qquad (9)$$

where α is the fraction of neutral aminoalkyl radicals that are formed from the decomposition of the CRIP, and β is the fraction of neutral amine radicals that adds to the monomer. The reported value of the quantum yield of ketyl radical of BP is 1, that is $\alpha = 1$, in acetonitrile and benzene [32]. Taking the values of k_6 and k_7 given in Table 4 (k_q) and the reported values of k_5, Eq. (9) predicts that at the TEOHA concentration used in our experiments (0.1 M), in all studied solvents, more than 90% of the BP triplet are quenched by the amine.

Data of Table 1 show high polymerization efficiencies in the weak polar solvents (benzene and dioxane), and are almost independent of the 4-substituents. The higher values of R_p for the macroinitiator in 1,4-dioxane suggest a polymer effect on the photoinitiation efficiency. Unfortunately, we could not compare the macroinitiators with the monomeric photoinitiators in benzene because of the low solubility of the polymer in this solvent. On the other hand, a different behaviour can be observed for the polar solvents (methanol, acetonitrile, and DMSO). In these media, R_p decreases from 4-methoxybenzophenone to 4-cyanobenzophenone. This trend is much lower when the macroinitiator is used, and is more important in the most polar solvents, DMSO and acetonitrile. Considering that more than 90% of ketone triplets are quenched by the amine, the low value of R_p when is used the CN-substituted compound suggests a lower formation of neutral ketyl and amine radicals.

Flash photolysis experiments were performed in order to characterize the transients formed by the interaction of 4-cyanobenzophenone with the amine in different solvents. The transient absorption spectra in acetonitrile at different times can be seen in Fig. 1A. In the absence of amine, immediately after the excitation, a peak is observed with a maximum at 553 nm. This absorption may be ascribed to the 4-cyanobenzophenone triplet by comparing with the triplet–triplet absorption of the unsubstituted benzophenone [32]. In the presence of the amine, the triplet is quenched and new intermediates are formed. At 100 ns the spectrum exhibits a maximum at 570 nm. This spectrum corresponds to the ketyl radical. The red shift of these peaks with respect to the unsubstituted ketone is similar to that reported for benzophenones with electron-withdrawing substituents on the aromatic ring [25,35]. The radical decays within a few nanoseconds and a new long-lived absorption appears in the region 550–750 nm (inset Fig. 1A). This absorption is attributed to the radical anion by comparison with the spectra of the radical anions of various benzophenones [26,27,31]. Similar experiments were also carried out in benzene. In the presence of the amine, the absorption spectrum showed only the presence of the neutral ketyl radicals (Fig. 1B).

These results can be explained in terms of a fast deprotonation of the ketyl radical (BP(H)•) produced from the interaction of ketone triplets with the amine. This process leads to the radical ion pair (Scheme 2) [26], and is inhibited in benzene. The fast deprotonation of the ketyl radicals derived from BPs with electron-withdrawing substituents, is in agreement with a lower pK_a due to
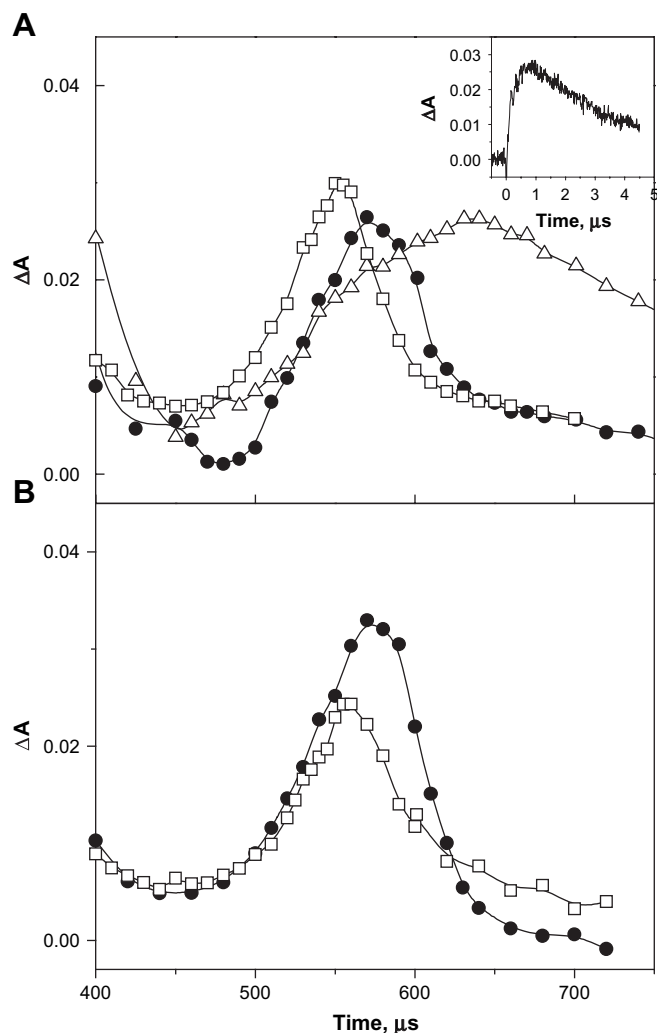

Fig. 1. (A) Transient absorption spectra of 4-cyanobenzophenone in acetonitrile: (□) in the absence of amine, taken immediately after the laser pulse, and in the presence of 0.1 M TEOHA at (●) 100 ns and (△) 3 μs. Inset: time profile of the absorption at 650 nm in the presence of 0.1 M TEOHA. (B) Transient absorption spectra of 4-cyanobenzophenone in benzene. (□) in the absence of amine at 1 μs; (●) in the presence of 1 M TEOHA at 2 μs after the laser pulse.

the decrease of the charge density on the oxygen atom. This is further corroborated by the transient absorption spectra of 4-methoxybenzophenone in the presence of amine in acetonitrile. In this case only the formation of the neutral radical is observed.

The transient spectroscopic behaviour of the benzophenones reported here is in excellent agreement with that we found for their efficiency as photoinitiators of the NIPAM polymerization. The reduced R_p value in acetonitrile using 4-cyanobenzophenone as photoinitiator is consistent with the deprotonation of the ketyl radicals. Since this process does not lead to the Am(−H)• active radicals (Scheme 2), the polymerization will be inhibited. In nonpolar solvents and/or with 4-methoxybenzophenone, where the
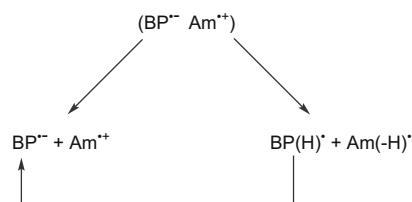
Scheme 2.

deprotonation of the ketyl radicals is a slow process, the addition of the amine neutral radicals to the monomer is an important process as demonstrated by the high R_p value (Table 1). Furthermore, the fact that the decrease of R_p in polar solvents with increasing electron-withdrawing ability of the 4-susbtituent is diminished in the macroinitiator indicates a lower polarity of the ketone microenvironment due to the protection offered by the polymer chain.

Data of R_p for the irradiation of the BP photoinitiators in the absence of amine, Table 3, show that the polymerization of the NIPAM is important only in dioxane and methanol. The fact that in the relatively inert solvents, acetonitrile or DMSO, polymerization is not observed indicates that the interaction of the BP with the monomer does not lead to polymerization. Then, the polymerization in methanol and in 1,4-dioxane shows that the active radicals come from the deactivation of the BP triplet by these solvents. The ketyl radical yield arising from the H-atom from both solvents is reported to be 1 [28]. Taking $k_q = 2 \times 10^5 \, M^{-1} \, s^{-1}$, Eq. (9) predicts that 61% of the triplets are deactivated by methanol. This is in agreement with the relatively high polymerization rate observed. In dioxane, the triplets are quenched by 80%. The photoreduction of the BP can be represented by Eq. (10)

$$BP^* \; + \; \text{(dioxane)} \; \longrightarrow \; BP(H)^\bullet \; + \; \text{(dioxanyl radical)}^\bullet \qquad (10)$$
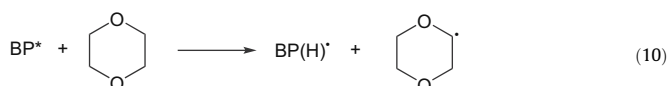
The high R_p value in dioxane shows that the carbonyl-centered radicals derived from dioxane add efficiently to the monomer double bond. Interestingly, the polymer effect in this case also increases R_p, an evidence of the importance of the radical stabilization in nonpolar media like that offered by the polymer chain.

On the other hand, the fact that the photoinitiation efficiency with all macroinitiators and in all solvents is higher than that of the corresponding low-molecular-weight analogs could also indicate a higher reactivity of the active radicals. The polymer chain could prevent the recombination of the radicals favouring their reaction with the monomer. Furthermore, a higher concentration in the molecular coil, where the radicals are formed, could lead to an enhanced activity. The fact that the polymer efficiency is lower when methanol is used as solvent (Table 1) could imply a high local concentration of the amine around the BP moiety in the polymeric system. Measurements of the intrinsic viscosity of NIPAM in the solvents employed in this study showed that methanol is the best thermodynamic solvent for the polymer. An extended chain would decrease the concentration effect of the coinitiator.

In conclusion we synthesized in a one-step reaction novel macrophotoinitiators which incorporated 4-substituted benzophenone chromophores. These macroinitiators, as well as the monomeric analogs, are very efficient photoinitiators of the NIPAM polymerization using tertiary aliphatic amines as coinitiators. The photoinitiation efficiency is dependent on the nature of the 4-substituent and on the solvent where the polymerization is carried out. Benzophenones substituted with electron-donors present higher photopolymerization efficiencies than with electron-withdrawing substituents. Nonpolar media appear as more suitable to obtain high polymerization efficiencies. These results are in excellent agreement with the time-resolved spectroscopy experiments. A clear correlation was obtained between the decrease of the polymerization efficiency and the lack of active radical formation.

Acknowledgements

References

[1] Davidson RS. J Photochem Photobiol A Chem 1993;69:263–75.
[2] Pouliquen L, Coqueret X, Morlet-Savary F, Fouassier JP. Macromolecules 1995; 28:8028–34.
[3] Carlini C, Angiolini L, Caretti D, Corelli E. Polym Adv Technol 1996;7:379–84.
[4] Angiolini L, Caretti D, Carlini C, Corelli E, Salatelli E. Polymer 1999;40:7197–207.
[5] Angiolini L, Caretti D, Salatelli E. Macromol Chem Phys 2000;201:2646–53.
[6] Allonas X, Fouassier JP, Angiolini L, Caretti D. Helv Chim Acta 2001;84:2577–88.
[7] Degirmenci M, Hizal G, Yagci Y. Macromolecules 2002;35:8265–70.
[8] Corrales T, Catalina F, Peinado C, Allen NS, Rufs AM, Bueno C, et al. Polymer 2002;43:4591–7.
[9] Corrales T, Catalina F, Peinado C, Allen NS. J Photochem Photobiol A Chem 2003;159:103–14.
[10] Jiang X, Yin J. Polymer 2004;45:5057–63.
[11] Jiang X, Yin J. Macromolecules 2004;37:7850–3.
[12] Wang H, Wei J, Jiang X, Yin J. Macromol Chem Phys 2006;207:1080–6.
[13] Ullrich G, Ganster B, Salz U, Moszner N, Liska R. J Polym Sci Part A Polym Chem 2006;44:1686–700.
[14] Chen Y, Loccufier J, Vanmaele L, Barriau E, Frey H. Macromol Chem Phys 2007; 208:1694–706.
[15] Wei J, Wang H, Jiang X, Yin J. Macromolecules 2007;40:2344–51.
[16] Du FS, Zhang P, Li FM. J Appl Polym Sci 1994;51:2139–44.
[17] Pouliquen L, Coqueret X. Macromol Chem Phys 1996;197:4045–60.
[18] Jiang X, Luo X, Yin J. J Photochem Photobiol A Chem 2005;174:165–70.
[19] Lissi EA, Zanocco A. J Polym Sci Polym Chem Ed 1983;21:2197–202.
[20] Valderas C, Bertolotti S, Previtali CM, Encinas MV. J Polym Sci Part A Polym Chem 2002;40:2883–93.
[21] Encinas MV, Rufs AM, Corrales T, Catalina F, Peinado C, Schmith K, et al. Polymer 2002;43:3909–13.
[22] Burkey TJ, Castelhano AL, Griller D, Lossing FP. J Am Chem Soc 1983;105:4701–3.
[23] Lalevée J, Allonas X, Fouassier JP. J Org Chem 2005;70:814–9.
[24] Porter G, Topp MR. Proc R Soc London Ser A 1970;315:163–84.
[25] Baral-Tosh S, Chattopadhyay SK, Das PK. J Phys Chem 1984;88:1404–8.
[26] Bhattacharyya K, Das PK. J Phys Chem 1986;90:3987–93.
[27] Devadoss C, Fessenden RW. J Phys Chem 1991;95:7253–60.
[28] Kluge T, Brede O. Chem Phys Lett 1998;289:319–23.
[29] Naguib YMA, Steel C, Cohen SG. J Phys Chem 1987;9:3033–6.
[30] Du Y, Ma C, Knok WM, Xue J, Phillips DL. J Org Chem 2007;72:7148–56.
[31] Schaefer CG, Peters KS. J Am Chem Soc 1980;102:7566–7.
[32] Inbar S, Linschitz H, Cohen SG. J Am Chem Soc 1981;103:1048–54.
[33] Von Raumer M, Suppan P, Haselbach E. Helv Chim Acta 1997;80:719–24.
[34] Heeb LR, Peters KS. J Phys Chem B 2008;112:219–26.
[35] Sakamoto M, Cai X, Hara M, Tojo S, Fujitsuka M, Majima T. J Phys Chem A 2004;108:8147–50.