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Journal of Photochemistry and Photobiology A: Chemistry 194 (2008) 206–211

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Chain transfer agents in vinyl polymerizations photoinduced by bimolecular photoinitiators

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Received 24 May 2007; received in revised form 10 August 2007; accepted 11 August 2007
Available online 17 August 2007

Abstract

The behavior of 2-mercaptoethanol and phenols as chain transfer agents in the polymerization of methyl methacrylate and acrylamide at 25 °C photoinitiated by bimolecular initiators based on xanthene dyes and aromatic ketones in the presence of amine was studied. Addition of millimolar concentrations of 2-mercaptoethanol or phenol to the methyl methacrylate polymerization reduced notably the polymer molecular weights, with minor changes of the polymerization rate. The photochemical behavior of the initiators in the polymerization media was analyzed. These studies allowed explaining the behavior of alkyl thiols and phenols as chain transfer agents in terms of the competition of the coinitiator and chain transfer agents to deactivate the triplet state of the photoinitiator, and the characteristics of the intermediates formed in the deactivation processes. Chain transfer constants were determined, and the values are similar to that obtained in the polymerization photoinduced by the α-cleavage of aliphatic azo compounds.

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Keywords: Photopolymerization; Photoinitiator quenching; Bimolecular photoinitiators; Chain transfer

1. Introduction

Photoinitiated free radical polymerization is a technologically important process involved in many applications that range from graphic arts to microelectronics [1,2]. In these systems the photoinitiator is the key to control the photopolymerization process. Free radical photoinitiators fall into two categories, namely Type I and Type II [3,4]. Unimolecular photoinitiators, Type I, form the active radicals through a photoinduced α-cleavage process. Bimolecular photoinitiators, Type II, are based on compounds whose triplet excited state abstracts a hydrogen atom from suitable donors (coinitiator) producing an initiating radical.

The molecular weight control of polymers is a subject of increasing interest since many of their properties depend on the chain length. In free radical polymerization the control of the polymer chain length is difficult to attain. For many industrially important systems, a chain transfer agent is added to the polymerization composition in order to lower the polymer molecular weight. A growing macroradical abstracts a hydrogen atom from the chain transfer agent giving a terminated polymer chain and a new initiating radical, which adds to the monomer giving a new propagating species. The chain transfer constant, C_{tr}, defined as the ratio of the rate constant for the chain transfer to the propagation rate constant, k_{tr}/k_p, is a measure of the reactivity of a chain transfer agent. Among the most employed chain transfer agents are thiols and phenols [5–9]. The high reactivity of these compounds has been attributed to their ability to scavenge radicals by H–atom abstraction. This behavior is expected in terms of the weakness of the S–H bond in thiols [10,11], and the O–H in phenols [11,12], and the high reactivity to the formed radicals [13–15]. Studies on the control of the molecular weight using thiols or phenols in photoinduced polymerizations employ as radical source the direct photocleavage of the initiator, unimolecular systems. While the use of this control based on a bimolecular reaction between initiator excited states and a coinitiator, is scarce. This contrasts with the growing interest of polymerizations photoinduced by bimolecular systems. However, to adequately utilize these chain transfer agents is necessary that they do not quench the excited states of the photoinitiator. Recently Fouassier et al. [16] have reported that the addition of phenols to the polymerization of acrylate resins photoinitiated by benzophenone/amine retards

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doi:10.1016/j.jphotochem.2007.08.012

and inhibits the polymerization. However, the kinetic behavior of these compounds as chain transfer agents was not quantified.

In the present communications we report the chain transfer properties of an aliphatic thiol, 2-mercaptoethanol, and phenols on the photopolymerization of methyl methacrylate (MMA), at 25 °C. Two compounds of very different structural and photophysical properties, Eosin and benzophenone, were used as photoinitiators. Xanthene dyes and aromatic ketones are among the most used bimolecular photoinitiators for free radical polymerization in the presence of tertiary amines [17–21]. Triethanol amine (TEOHA) was used as coinitiator. A detailed study on the photochemical behavior of the photoinitiators in the polymerization media was carried out. These studies allowed analyzing the chain transfer efficiency in terms of the photophysical behavior of the photoinitiator in the presence of the coinitiator and the chain transfer agents. Some experiments were also carried out with acrylamide in aqueous media.

2. Experimental

Methyl methacrylate (MMA, Merck) was purified by distillation under reduced pressure. Acrylamide from Aldrich (>99%) was used as received. Eosin Y (Aldrich) was used without purification. 2,2′-Azobisisobutyronitrile (AIBN) and benzophenone were from Aldrich and used after crystallization. Triethanolamine (TEOHA) was distilled before its use. Phenol and 4-methoxyphenol (Aldrich) were either sublimed or recrystallized.

UV measurements were performed using a HP8453 diode array spectrophotometer. The fluorescence measurements were carried out on Spex Fluorolog spectrofluorometer in air-equilibrated solutions at 20 °C. Time resolved fluorescence studies were carried out with an Edinburg Instrument OB-900 (Edinburgh, Scotland) time-correlated single-photon-counting fluorimeter. H_2 gas was used in the flash lamp. Analysis of the fluorescence decays were done by a least squares iterative convolution method based on the Marquardt algorithm by using the analysis routine provided by Edinburgh Instrument (Edinburgh, Scotland). The quality of the fit was examined by the χ^2-value together with the distribution of the residuals. The laser flash photolysis setup has been described elsewhere [22]. The samples were excited with of a Nd:YAG laser using 355 or 532 nm.

Polymerization rates (R_p) were measured dilatometrically in oxygen free solutions at 25 °C. The polymerization times were chosen such that conversion remained below 20%. The MMA polymerization was carried out in monomer/acetonitrile (1:1). Eosin Y in the presence of TEOHA, benzophenone with TEOHA as coinitiator, and AIBN were used as photoinitiators. Acrylamide polymerizations were carried out in aqueous solutions at pH 9.5. The acrylamide concentration was 0.8 M. The samples were irradiated in a Rayonet photochemical reactor with 525 or 360 nm lamps. Polymers were precipitated in methanol. The molecular weights of the polymers were determined by gel permeation chromatography at 30 °C using a HP 1100 Liquid Chromatograph equipped with Waters Ultrastragel columns of pore size 10^5, 10^4 and 10^3 and 500 Å. MMA standards were used for calibration, and tetrahydrofuran as the mobile phase with a flow rate of 1 mL/min.

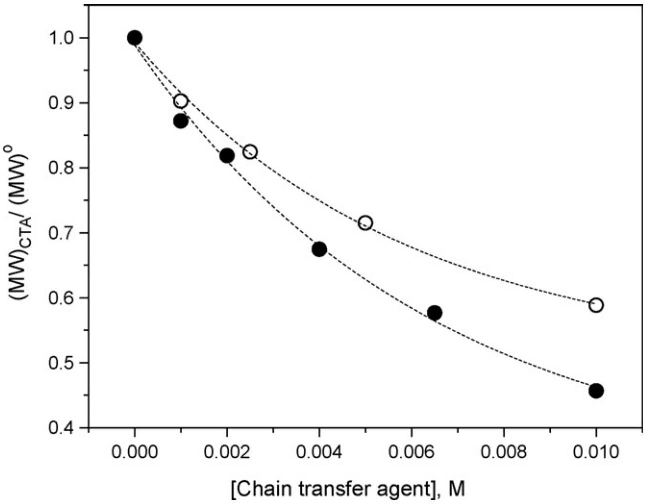

Fig. 1. Effect of the 2-mercaptoethanol and phenol concentration on the ratio of molecular weights of poly(methyl methacrylate) obtained in the presence $(MW)_{CTA}$ and absence $(MW)_0$ of chain transfer agents: (●) 2-mercaptoethanol; (○) phenol. Phenol concentrations are multiplied by 10. Photoinitiator: Eosin/TEOHA (50 mM). Monomer/acetonitrile (1:1), at 25 °C.

3. Results and discussion

3.1. Polymerization studies

The irradiation of Eosin did not lead to the MMA polymerization. However, it was efficiently activated in the presence of aliphatic tertiary amines. The addition of millimolar concentrations of 2-mercaptoethanol to the polymerization mixture at constant TEOHA concentration reduced markedly the molecular weight of the polymer, Fig. 1, with negligible decrease of the polymerization rate. A decrease of the molecular weight of polymers was also found when 2-mercaptoethanol was added to the polymerization of MMA carried out using the photoinitiator system based on aromatic carbonyl-amine (benzophenone–TEOHA). Furthermore, the irradiation of Eosin or benzophenone in the presence of thiol and in the absence of amine did not lead to polymer formation. This suggests that the thiol does not act as coinitiator, at least at concentrations up to 50 mM, as described for some aromatic thiols [8,23–26]. The decrease of the polymer molecular weight by the addition of the alkyl thiol to the polymerization mixture can be explained in terms of the simple mechanism reaction scheme, where Pi stands for the photoinitiator and Am for the amine:

$$\mathrm{Pi} + h\nu \rightarrow \mathrm{Pi}{*} \tag{1}$$

$$\mathrm{Pi}{*} + \mathrm{Am} \rightarrow \mathrm{Pi}^{\bullet -} + \mathrm{Am}^{\bullet +} \tag{2}$$

$$\mathrm{Pi}^{\bullet -} + \mathrm{Am}^{\bullet +} \rightarrow \mathrm{Pi}^{\bullet} + \mathrm{Am}^{\bullet} \tag{3}$$

$$\mathrm{Am}^{\bullet} + \mathrm{M} \rightarrow \mathrm{M}_n{}^{\bullet} \tag{4}$$

$$\mathrm{M}_n{}^{\bullet} + \text{R-SH} \rightarrow \mathrm{M}_n\mathrm{H} + \mathrm{RS}^{\bullet} \tag{5}$$

$$\mathrm{RS}^{\bullet} + \mathrm{M}_n{}^{\bullet} \rightarrow \mathrm{M}_n\mathrm{SR} \tag{6}$$

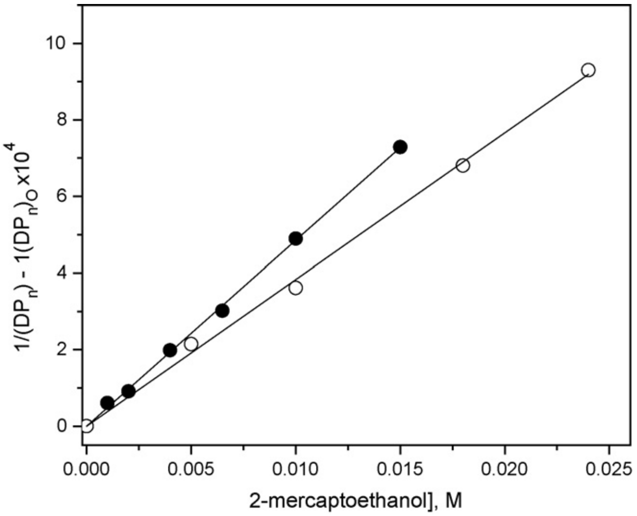

Fig. 2. Mayo plot (Eq. (9)) for the determination of the chain transfer constant of 2-mercaptoethanol in the polymerization of methyl methacrylate at 25 °C photoinitiated by (○) benzophenone/TEOHA (50 mM) and (●) Eosin/TEOHA (50 mM).

$$RS^\bullet + RS^\bullet \rightarrow Q \tag{7}$$

$$RS^\bullet + M \rightarrow RSM^\bullet \tag{8}$$

The decrease of the molecular weight by the addition of a chain transfer agent is quantitatively given by the Mayo equation [27], which expresses the reciprocal of the polymerization degree (DP_n) as a function of the rate of the chain growth and the chain stopping, Eq. (9):

$$\frac{1}{DP_n} = \frac{1+\alpha}{(DP_n)_0} + C_{tr}\frac{[CTA]}{[M]} \tag{9}$$

where $(DP_n)_0$ is the polymerization degree in the absence of chain transfer agent, [CTA] the concentration of the chain transfer agent, [M] the monomer concentration, and α is the fraction of termination by disproportionation. The value of α can be considered as 0 for the polymerization of MMA at 25 °C [28]. Fig. 2 shows the experimental data according to Eq. (9). Since, thiols decreases the molecular weights with negligible changes of the polymerization rate ($v_8 \gg v_6$), the chain transfer constant (C_{tr}) is given by the ratio of the chain transfer rate constant (k_{tr}) to the propagation rate constant (k_p), Eq. (10):

$$C_{tr} = \frac{k_{tr}}{k_p} \tag{10}$$

The C_{tr} values for the two studied photoinitiators (Table 1) are in the range to that recently reported for aliphatic thiols as chain transfer agents of the MMA polymerization initiated by radicals produced through the unimolecular cleavage of azo compounds [29,30]. These results show that aliphatic thiols behavior as efficient chain transfer agent of the MMA polymerization photoinitiated by both bimolecular systems. Also, it is interesting to note that this behavior is hold for photoinitiators of very different structural and photophysical properties, such as xanthene derivatives and aromatic ketones.

Table 1
Chain transfer constants for the polymerization of MMA

Chain transfer agent	Photoinitiator		
	Eosin/TEOHA	Benzophenone/ TEOHA	AIBN
2-Mercaptoethanol	0.27	0.22	0.6 [29,30]
Phenol	0.016	0.027	0.022
4-Methoxyphenol	[a]	–	0.03

[a] No polymer is observed.

Similar experiments to that described for 2-mercaptoethanol were carried out using phenol and 4-methoxyphenol as chain transfer agents. The addition of phenol to the MMA polymerization photoinitiated by Eosin or benzophenone in the presence of TEOHA (50 mM) decreased the molecular weight of the polymers (Fig. 1) with minor changes in the polymerization rate. The irradiation of the photoinitiators in the absence of amine and with 100 mM phenol did not lead to the MMA polymerization, indicating that the presence of the amine is important for effective photopolymerization. The decrease of the molecular weights using both photoinitiators was well fitted to the classical Mayo equation and gives C_{tr} values similar to that we obtained using the unimolecular photoinitiator 2,2′-azobis(isobutyronitrile) (Table 1). The similarity between the C_{tr} values obtained for the unimolecular and bimolecular photoinitiation systems indicates that phenol acts as a chain transfer agent of the MMA polymerization photoinitiated by both bimolecular photoinitiating systems.

On the other hand, when 4-methoxyphenol was added to the polymerization photoinitiated by Eosin/amine, at the same concentrations used with phenol, it was not observed polymerization. This result is opposite to that expected from the high electron donor ability of the 4-methoxy substituent that was found to be more efficient chain transfer agent than the unsubstituted compound [31]. With benzophenone/amine as photoinitiator system, the polymerization efficiency was very low.

The addition of phenol and 2-mercaptoethanol also was assessed in the polymerization of acrylamide photoinitiated by Eosin/TEOHA in aqueous medium. The polymerization rate of acrylamide increases with the TEOHA concentration reaching a constant value at 10 mM of amine. Higher amine concentrations do not seem to affect the polymerization rate. On the other hand, the addition of TEOHA up to 50 mM did not modify the polymerization rate or the molecular weights of the acrylamide photoinitiated by 2′,2′-azobis(2-amidinopropane). This indicates that the amine does not modify the kinetic parameters of the acrylamide polymerization in aqueous media. When the polymerization was done using the Eosin as photoinitiator, the addition of phenol (10–100 mM) or thiol (up to 20 mM) did not show appreciable variations of the polymerization rates or the molecular weights. In the presence of 20 mM 4-methoxyphenol no polymer formation was observed. However, these compounds were efficient chain transfer agents when the polymerization of acrylamide was photoinitiated by the azo compound. These results show that the alkyl thiol and the phenols do not act as chain transfer agents for the polymerization of acrylamide in aqueous medium photoinitiated by the xanthene–amine system.

3.2. Photochemical studies

To understand the role of thiols and phenols on the chain length of polymers in the polymerization initiated by the bimolecular photoinitiators, the photochemical behavior of the photoinitiator under the polymerization conditions must be analyzed. It is well known that excited states of xanthene dyes [32,33] and aromatic ketones [34,35] are quenched by amines through a mechanism that involves electron transfer from the amine to the excited state forming a charge transfer intermediate. Rapid proton transfer from the amine radical cation to the radical anion leads to the α-amino neutral radicals:

$$\begin{tikzcd}
\mathrm{Pi}^* + \mathrm{Am} \arrow[r] & (\mathrm{Pi}^{\bullet -} + \mathrm{Am}^{\bullet +}) \arrow[dl] \arrow[dr] & \\
\text{Deactivation} & & \mathrm{Pi(H)}^{\bullet} + \mathrm{Am(\text{-}H)}^{\bullet}
\end{tikzcd} \qquad (11)$$

It is widely accepted that the α-amino radicals originating from the interaction between triplet excited states and amines are the species that initiate the polymerization of vinyl monomers. The triplet of xanthenes dyes [36] and aromatic ketones [37,38] are deactivated by phenols through an electron transfer process:

$$\begin{tikzcd}
\mathrm{Pi}^* + \mathrm{PhOH} \arrow[r] & (\mathrm{Pi}^{\bullet -} + \mathrm{PhO}^{\bullet +}) \arrow[dl] \arrow[dr] & \\
\text{Deactivation} & & \mathrm{Pi(H)}^{\bullet} + \mathrm{PhO}^{\bullet}
\end{tikzcd} \qquad (12)$$

The presence of phenoxy radicals has been showed in the deactivation of the triplet of Eosin [36] and benzophenone [37]. The fact that we did not observed polymerization when both photoinitiators were irradiated only in the presence of phenols indicates a low addition rate of the phenoxy radicals to the monomer double bond. Thus, we did not detect changes in the decay of phenoxy radicals (measured at 400 nm) when they were generated by the irradiation of the benzophenone in acetonitrile and in the acetonitrile/MMA mixture. This is in agreement with the rather low chain transfer constant of phenol (Table 1). Aliphatic thiols are also relatively good quenchers of the triplet states of xanthene dyes [39] and benzophenone [40,41] following a charge transfer process. However, in the absence of the coinitiator at the concentrations of the chain transfer agents used in these studies was not observed polymerization.

On the other hand, the deactivation of the excited states by the chain transfer agents will compete with the deactivation by the amine (reaction (11)). The fraction of photoinitiator triplet states quenched by the amine in the presence of the chain transfer agent can be evaluated by the following equation:

$$f_{\mathrm{T}} = \frac{(k_{\mathrm{q}})_{\mathrm{Am}}[\mathrm{Am}]}{(k_{\mathrm{q}})_{\mathrm{Am}}[\mathrm{Am}] + (k_{\mathrm{q}})_{\mathrm{CTA}}[\mathrm{CTA}] + (k_{\mathrm{q}})_{\mathrm{MMA}}[\mathrm{MMA}] + k_{\mathrm{D}}} \qquad (13)$$

where $(k_{\mathrm{q}})_{\mathrm{Am}}$ is the rate constant of quenching by the amine, $(k_{\mathrm{q}})_{\mathrm{CTA}}$ the rate constant of quenching by the chain transfer agent, $(k_{\mathrm{q}})_{\mathrm{MMA}}$ the rate constant of quenching by the monomer, and k_{D} is the rate constant for the triplet decay in the absence of additives. Since, the quenching rate constant for charge transfer processes is strongly dependent on medium properties, we measured these values in ethyl acetate/acetonitrile (1:1), a solvent mixture that mimics the polymerization medium (MMA/acetonitrile, 1:1). In order to get information on the effect of the chain transfer agent on the aqueous polymerization of acrylamide, the quenching rate constants for Eosin were also measured in water at pH 9.5. Bimolecular rate constants for the quenching of Eosin singlet were determined from the Stern–Volmer plots of the decrease of the singlet lifetime as function of the quencher concentration. The values obtained are collected in Table 2. The data in the aqueous medium, with the exception of thiol, can be considered to be within the diffusional limit, and are one order of magnitude lower than in the organic solvent mixture. The fraction of Eosin singlet excited states quenched by the amine (50 mM) in ethyl acetate/acetonitrile is 0.19, and is almost unchanged by the addition of the thiol or phenol. Triplet quenching rate constants were obtained from the decay of the triplet at 580 and 600 nm for Eosin and benzophenone, respectively. These values are included in Table 2. Benzophenone triplet decay also was shortened by the addition of MMA with a bimolecular rate constant of $7 \times 10^{7}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. This result indicates that in the absence of amine 99% of the benzophenone triplet states are quenched by the monomer; however this process does not lead to polymerization as evidenced by the lack of polymer in the absence of additive. Eosin triplet lifetime was similar in the acetonitrile/ethyl acetate or in the mixture

Table 2
Rate constants for the Eosin and benzophenone triplet quenching

Quencher	k ($\times 10^{-8}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$)				
	Eosin				Benzophenone
	Singlet		Triplet		Triplet
	EtAc/AN[a]	Water[b]	EtAc/AN[a]	Water[b]	EtAc/AN[a]
Triethanolamine	12	21	0.17	1.8	40
Phenol	4	21	0.04	0.3	3
4-Methoxyphenol	25	33	2.1	40	40
2-Mercaptoethanol	< 0.5	–	0.02	0.05	0.3

[a] Ethyl acetate/acetonitrile (1:1).
[b] Water pH 9.5.

containing the monomer. This shows that the quenching of the Eosin triplet by the MMA is negligible.

The rate constant values, for all quenchers, are in agreement with those expected for an electron transfer mechanism. The triplet k_q values are more than one order the magnitude lower than the singlet quenching. The introduction of an electron donor group (4-methoxy) into the benzene ring of phenol increases the quenching efficiency. The values obtained for Eosin show an important dependence on the medium properties, as expected for a charge transfer process. The high increase observed for the triplet quenching by phenolic compounds in the aqueous medium reflects the contribution of the quenching by the phenolate anion. The low rate constant values for the quenching by 2-mercaptoethanol is in agreement with the high oxidation potential of aliphatic thiols. A much lower value for quenching rate constant by alkyl thiols with respect to amines also have been reported for photoinitiators based on the thioxanthone chromophore [26,42].

From Eq. (13) at 50 mM TEOHA and 100 mM phenol, the highest phenol concentration used in the polymerization experiments, it can be estimated that the fraction of Eosin triplets quenched by the amine is 0.67. Under the same conditions, 36% of the benzophenone triplet is quenched by the amine. This lower value is consequence of the high quenching rate by the monomer. In the absence of phenol, only the 38% of benzophenone triplets are quenched by the amine. The decrease of the polymer molecular weight by the phenol addition and the lack of polymerization when the photoinitiators were irradiated in the presence of phenol and absence of amine show that the α-amino radicals are the main initiating species, and the phenol acts as a chain transfer agent. Furthermore, the fact that similar C_{tr} values were obtained using the bimolecular photoinitiators or AIBN confirms that phenol behavior as a simple chain transfer agent of the polymerization of MMA photoinitiated by the bimolecular systems.

The rate constant for the quenching of the Eosin triplets by 4-methoxyphenol is over one order of magnitude higher than the rate constant by the amine. This explains the lack of MMA polymerization in the presence of the substituted phenol. At 4-methoxyphenol 50 mM, a concentration where the molecular weight of the polymer decrease 40% in the polymerization photoinitiated by the unimolecular photoinitiator AIBN, Eq. (13) indicates that only 7% of Eosin triplet are quenched by the amine. The similar values of the rate constants for the benzophenone triplet quenching by TEOHA and 4-methoxyphenol (Table 2) also explain the low polymerization efficiency observed.

The efficient behavior of 2-mercaptoethanol as chain transfer agent of MMA polymerization also can be explained by the relative quenching efficiency of the photoinitiator triplets by the amine and the thiol. The low value of quenching rate constants measured for 2-mercaptoethanol, Table 2, and the low concentration necessary to decrease the molecular weight of the poly(MMA) make that the triplet quenching by the thiol does not compete with the amine quenching. Thus, the thiol behaves as an ideal chain transfer agent to control the molecular weight of polymers obtained in the polymerization photoinitiated by both bimolecular systems.

It is also worth mentioning the lack of polymerization when the photoinitiators are irradiated in the presence of 2-mercaptoethanol without amine. Taking the measured value for the quenching rate constant of Eosin triplet (Table 2) and the triplet decay in the presence of monomer as 100 μs, Eq. (13) predicts that 66% of Eosin triplets are quenched by 0.01 mM thiol. However, under these conditions we did not observed polymerization. This result contrasts with that expected considering that thiols quench the triplet state of xanthene dyes with subsequent formation of thiyl radicals, which are highly reactive to double bonds [14]. The lack of photoinitiation by aliphatic thiols was also reported for the polymerization using camphorquinone as photoinitiator [26]. These results suggest that the quantum yield of radical formation is very low. A value of 0.05 has been reported for the decomposition of the charge transfer intermediate into radicals for the triplet quenching of rose bengal by alkyl thiols [39]. The high quenching rate constant of benzophenone triplet by MMA and the high concentration of monomer used in the polymerization experiments predicts (Eq. (13)) that the triplets are quenched by the thiol in less 1%. This avoids any possibility of initiating radical formation from the quenching process. In addition, a low value of radical quantum yield also has been reported for the decomposition of the charge transfer intermediate in the benzophenone triplet quenching by pentanethiol [40].

The deactivation rate constants of the Eosin triplet state by phenols and TEOHA are higher in aqueous solution than in organic medium. The addition of 2-mercaptoethanol or phenol to the acrylamide photopolymerization, at concentrations where Eq. (13) indicates that α-amino radicals are formed, shows that the effect on the polymer molecular weight is almost negligible. However, in aqueous polymerizations is necessary to consider the different ionization states of the species involved in the polymerization medium. Due to the high basicity of the polymerization mixture by the presence of the amine, phenol and thiol are mainly in their deprotonated form. The lack of chain transfer capacity of phenols and thiols is in agreement with that previously found that phenol and thiols act as chain transfer by the hydrogen abstraction from the O–H or S–H by the macroradicals, the phenolate and the thiol anion do not act as chain transfer agents [43,44].

In conclusion, the control of the molecular weight of polymers obtained by free radical polymerization photoinitiated by bimolecular systems in organic media can be achieved employing aliphatic thiols and phenol as chain transfer agents. The selection of the chain transfer agent depends on the competition of the photoinitiator excited state quenching by the coinitiator and the chain transfer agent. The low quenching rate constant for the triplet quenching of xanthene dyes and aromatic ketones by 2-mercaptoethanol avoids the competition of the excited state quenching by the amine. This makes alkyl thiols as ideal chain transfer agents for free radical polymerization. Since, low values of quenching rate constants are expected from the high oxidation potential of thiols, the use of these compounds as suitable chain transfer agents can be extended to several photoinitiators.

Acknowledgement

The financial support was provided by FONDECYT (grant 1030003).

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