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The effect of co-initiator structure on photoinitiating efficiency of photoredox couples composed of quinoline[2,3-b]-1H-imidazo[1,2-a]pyridinium bromide and phenoxyacetic acid or N,N-dimethylaniline derivatives

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Summary

Two groups of electron donors (phenoxyacetic acid derivatives, PAADs, and the family of N,N-dimethylaniline derivatives DMADs) in combination with quinoline[2,3-b]-1H-imidazo[1,2-a]pyridinium bromide (QIPB) were applied as photoinitiator for free radical polymerization induced with UV emission of an argon-ion laser (351 and 361 nm). Analysis of the data obtained for the initial time of photoinitiated polymerization indicates that both, the rate of electron transfer process between QIPB and tested co-initiators as well as the structure of obtained free radical can affect the overall photoinitiation ability of tested photoredox pairs.

Keywords: co-initiators; dyeing photoinitiator; kinetics of photoinitiated polymerization; photochemistry; photopolymerization

Introduction

Quinoline[2,3-b]-1H-imidazo[1,2-a]pyridinium bromide (QIPB) belongs to polycyclic aromatic heterocycles, often described in literature as potential visible light absorbing chromophores that can be applied for the preparation of a two component free radical photoinitiating system. This group of dyes includes the dyes first reported by Oster [1], the group of fluorone dyes [2], pyrene [3], or the dyes described by our group [4]. The dyes of this type usually weakly fluoresce. Because of their high intersystem crossing efficiencies giving a long-lived triplet states, they are considered as potential sensitizers for photoinitiated polymerization. For quinolineimidazopyridinium dyes group the quantum yield of intersystem crossing oscillates in the range between 0.08 and 0.45 [5]. Nevertheless, for a practical application the absorbing dye to be a good photoinitiator needs a partner that can transfer either hydrogen atom or electron to its excited state. Typically, as hydrogen atom donors the compounds such alcohols, THF or thiols are applied [6]. As electron transfer molecules, most commonly, tertiary

aromatic amines, a wide group of aminoacids, sulfur-containing aminoacids or aromatic carboxylic acids, borate anions and many other compounds are used [4d]. The rate of triplet state quenching can either be diffusion controlled or can be well bellow diffusion rate. When the intermolecular electron transfer rate is not diffusion controlled, the variation in polymerization rates observed for identical electron acceptor (light absorbing chromophore) and different electron donors can be explained as a effect of structure and reactivity of radicals obtained during the secondary reactions that follow electron transfer process. Thus, one can conclude that the overall efficiency of photoinitiation depends both on the light absorbing chromophore properties and on an electron donor molecule (co-initiator) photochemical properties.

The presented paper is a part of the studies that tries to explain an influence of a co-initiator structure on an overall initiation ability of the photoredox pair composed of electron acceptor molecule (QIPB) and various electron donors. The main goal of the study was an attempt of finding the classical photochemical and chemical correlations between the co-initiator structure and properties and observed efficiency of photoinitiated polymerization. The knowledge of such correlations might be very helpful during designing of a photoinitiating photoredox pairs that exhibit specific, required photoinitiation properties.

Experimental

Materials

Substrates used for the preparation of the dye and electron donors were purchased from Aldrich or Lancaster. Phenoxyacetic acid (PAA), (4-methylphenoxy)acetic acid (MPAA), (4-hydroxyphenoxy)acetic acid (HPAA), (4-acetylphenoxy)acetic acid (AcPAA), (4-chlorophenoxy)acetic acid (ClPAA), N,N-dimethylaniline (DMA), 4-bromo-N,N-dimethylaniline (BrDMA), 4-(dimethylamino)benzonitrile (DMABN), ethyl 4-dimethylaminobenzoate (EDAB), 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), 1-methyl-2-pyrrolidinone (MP) were purchased from Aldrich. (4-Methoxyphenoxy)acetic acid (MePAA) and N,N-dimethyl-p-toluidine (DMT) were obtained from Lancaster.

Quinoline[2,3-b]-1H-imidazo[1,2-a]pyridinium bromide dye (QIPB) was prepared using the procedure described elsewhere [5]. The final product was purified with the use of preparative thin–layer chromatography and identified by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy.

Instruments

The oxidation potentials of the electron donors were measured by cyclic voltammetry using Electroanalytical Cypress System Model CS-1090 with Ag-AgCl electrode serving as a reference electrode. The supporting electrolyte was 0.5 M tetrabutyl-ammonium perchlorate.

The kinetics of free radical polymerization was studied using a polymerization solution composed of 1 mL of MP and 9 mL of TMPTA. Dye concentration was 1.8×10^{-3} M. The concentration of electron donors was 0.1 M. The polymerizing formulations were not deoxygenated. The kinetics measurements were carried out using the methodology described earlier [7]. For further discussion, only the data for the initial times of polymerization were used for the calculation of the polymerization

rates in order to avoid the possibility of non-isothermal reaction conditions. Irradiation of the polymerization mixture was carried out with the UV emission of Innova 90-4 argon-ion laser (351 and 361 nm lines). The incident light intensity at the sample surface position was measured with Coherent Model Fieldmaster power meter.

Nanosecond laser flash photolysis experiments were performed using LKS.60 Laser Flash Photolysis apparatus (Applied Photophysics). Laser irradiation at 355 nm from the third harmonic of the Q-switched Nd:YAG laser from Lambda Physic/model LPY 150 operating at 65 mJ/pulse (pulse width about 4-5 ns) was used for the excitation.

Results and Discussion

The structure of the dye used as absorbing chromophore, quinoline[2,3-b]-1H-imidazo[1,2-a]pyridinium bromide (**QIPB**), is presented below. Its spectroscopic and photochemical properties were presented in our earlier paper [5], and in part, are summarized in Table 1.
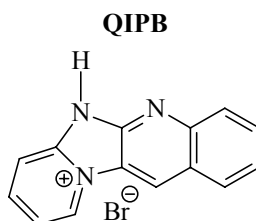
QIPB

Table 1. Spectroscopic properties, quantum yield of singlet oxygen (Φ^1O_2), and the triplet state (Φ_T) formation, lifetime of triplet state (τ_T), the triplet state quenching rate constant (k_q) and thermodynamical characteristics of QIPB.

Abs. [a]λ_{max} [nm]	ε_{max} [$M^{-1}cm^{-1}$]	Fl. [b]λ_{max} [nm]	Φ_{Fl}	E_T^{00} [eV]	E_{red} [mV]	[c]ΔG^0 [eV]	[d]Φ^1O_2	[e]Φ_T	τ_T [μs]	[f]k_q [$M^{-1}s^{-1}$]
387	2610	447								
408	3040	477	0.23	2.28	-1054	-0.591	0.31	0.29	1.01	3.44×10^8
432	2360	511								

[a] measured in ethyl acetate, [b] measured in 2-methyltetrahydrofuran, [c] calculated for N-(4-acetyl-phenyl)glycine (E_{ox}=635 mV), [d] measured using Schaap's methodology [8], [e] measured with the use of method given by Lament et.al. [9], [f] N-(4-acetyl-phenyl)glycine (APG) was used as the triplet state quencher. Note: viscosity of monomeric formulation equals η = 37.7 mPas that yields k_{diff} = 1.61×10^8 $M^{-1}s^{-1}$.
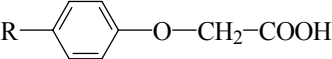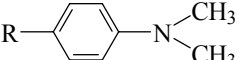
For the illustration of the electron donor (ED) structure on photoinitiation ability of QIPB-ED photoredox couple, two different groups of electron donating compounds were selected. Their structures and basic photochemical properties are compiled in Table 2.

The first group of electron donor compounds belongs to the phenoxyacetic acid derivatives (PAADs), the second is the family of N,N-dimethylaniline derivatives (DMADs).

Figure 1 and Figure 2 show the kinetic curves recorded during the polymerization photoinitiated by QIPB in the presence of electron donors under the study. From the

slopes of a linear part of the kinetic curves the relative rates of polymerization, R_p, were evaluated. They are presented in Table 2.

Table 2. Electron donors tested: structures, rates of photoinitiated polymerization (R_p), oxidation potentials (E_{ox}), thermodynamic characteristics (ΔG_{el}), quenching rate constants (k_q) of QIPB.

Electron donor	R	[a]R_p [μmol/s]	E_{ox} [V]	[b]ΔG_{el} [eV]	k_q [$M^{-1}s^{-1}$]
		R—〈benzene〉—O—CH_2—COOH			
MePAA	-OCH_3	81.45	1.170	-0.056	1.25×10^9
MPAA	-CH_3	66.10	1.310	0.084	7.02×10^8
PAA	-H	35.40	1.450	0.216	2.52×10^8
ClPAA	-Cl	26.10	1.320	0.085	2.30×10^8
AcPAA	-C(O)CH_3	15.12	1.600	0.374	1.39×10^8
HPAA	-OH	11.80	0.800	-0.426	2.60×10^9
		R—〈benzene〉—N(—CH_3)(CH_3)			
DMT	-CH_3	82.39	0.785	-0.441	5.62×10^8
DMA	-H	72.01	0.805	-0.421	5.00×10^8
BrDMA	-Br	53.35	0.890	-0.336	4.40×10^8
EDAB	-C(O)OC_2H_5	30.92	1.320	0.094	3.08×10^8
DMABN	-CN	21.74	1.435	0.209	2.46×10^8

[a] visible-light intensity: 50 mW/0.785cm^2

[b] calculated for QIPB as electron acceptor: E_{red} = 1.054 V, E_T^{00} = 2.28 eV [5].

The data in Figure 1 and 2 clearly show that the photoinitiation efficiency of the QIPB – PAAD and QIPB – DMAD photoredox couples and their polymerization inhibition time depends on the structure of both phenoxyacetic acid or N,N-dimethylaniline derivatives.

Since the polymerizing formulations were not deoxygenated the observed inhibition is probably caused by typical oxygen inhibition. The differences observed are probably cased by the competition between the reaction of dye triplet quenching by oxygen and by co-initiators, structure of which differ.

The mechanism involved in free radical production is different for both groups of electron donors. Both reactions appear to go by electron transfer from either phenoxyacetic acid or N,N-dimethylaniline derivative to the triplet state of QIPB. The photochemistry of the radical generation for QIPB – PAADs photoredox couples can be compared to the photochemistry of benzophenone – thiophenoxyacetic acid, whose mechanistic aspect was clarified by Marciniak and Wrzyszczyński [10]. According to this mechanism, after an initial formation of a radical-ion pair, there are three main channels of its decay. First is back electron transfer that regenerates substrates in their ground state. Second is proton transfer within the radical-ion pair involving the deprotonation from a carbon adjacent to the sulfur-centered radical cation. The third pathway is a separation of radical ions to form the free sulfur–centered radical cation

that decarboxylates yielding stable Ph-S-CH$_2^\bullet$ radical. It appeared that this radical is responsible for free radical polymerization photoinitiation process.
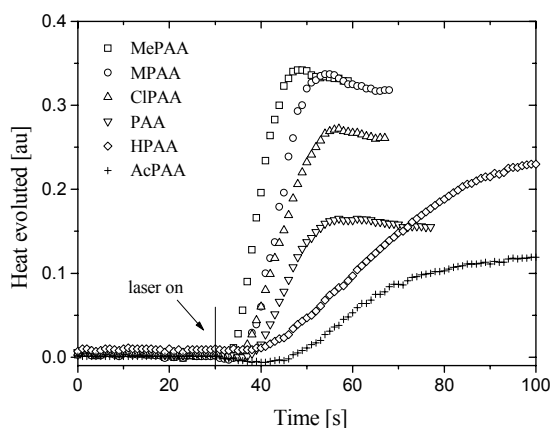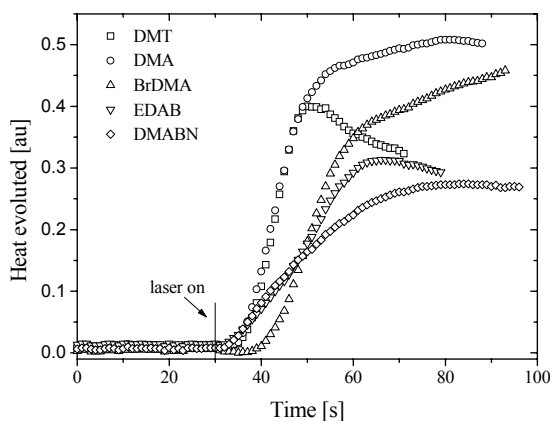

Fig. 1. Photopolymerization kinetic curves recorded for QIPB in the presence of electron donors marked in Figure. Monomer formulation: 1 mL of MP and 9 mL of TMPTA. Electron donors, phenoxyacetic acid derivatives (0.1 M). Light intensity of an argon-ion laser irradiation equal 50 mW/0.785cm^2.

Fig. 2. Photopolymerization kinetic curves recorded for QIPB in the presence of electron donors marked in Figure. Monomer formulation: 1 mL of MP and 9 mL of TMPTA. Electron donors, N,N-dimethylaniline derivatives (0.1M). Light intensity of an argon-ion laser irradiation equal 50 mW/0.785cm^2.

The mechanism of free radical generation for QIPB-DMADs resulted from a fundamental contribution by Cohen *et al.* who studied the photochemistry of bezophenone-sensitized oxidation of tertiary aromatic amines [11]. The process initially generates ion radical pair, followed by rapid deprotonation of α-aminyl or α-amino radical-cation (depends on the structure of amine) that yields corresponding radical. The rate constant for proton transfer depends on the nature of amine and is close to a diffusion limit [12].

An important issue relevant to the present study is whether the photoinitiation ability of tested photoredox pairs follows typical relationships observed for photoinduced electron transfer reaction. The relationship between the logarithm of measured relative rates of polymerization as a function of free energy change for electron transfer reaction calculated using the Rehm-Weller equation (Eq. 2) [13] is such relation. Figures 3a and 3b demonstrate this type of behavior .
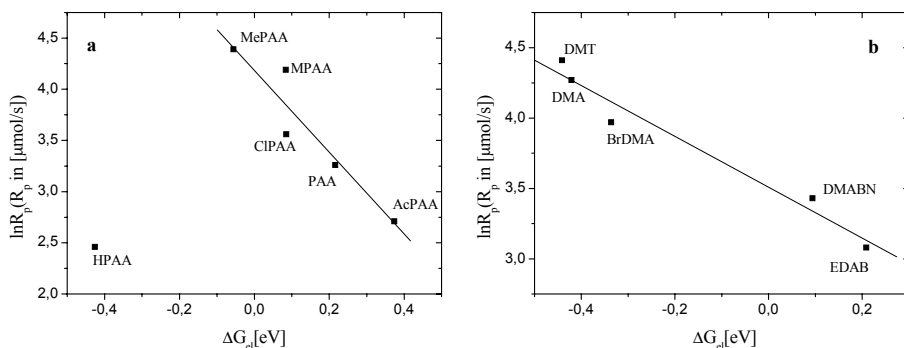

Fig. 3. Relationship between the rate of polymerization and the free energy change associated with electron transfer for tested photoredox pairs. Electron acceptor QIPB; electron donors: (a) phenoxyacetic acid derivatives (PAADs), (b) N,N-dimethylaniline derivatives (DMADs).

As observed in Figure 3 the relationship is roughly linear (with exception of the point for HPAA in Figure 3a). Similar in character relations (Figure 4) are observed between the logarithm of rates of polymerization and Hammett's constants. In the footnote of it is indicated that k_{diff} in polymerizing formulation is ca. 1.61×10^8 $M^{-1}s^{-1}$. The analysis of the QIPB triplet state quenching by applied electron donors, as shown in Table 2, are the same order, e.g. their values might be only in part controlled by diffusion. Thus, the observed in Figure 3a phenomena can be explain assuming that the rate of polymerization (measured at initial time of reaction) is controlled by the electron transfer reaction. It should be noted that the electron transfer rate constant essentially does not depends on solvent viscosity, as long as its k_{diff} is higher or equal to electron transfer rate constant.

However, it should be emphasize that the linear dependencies observed in Figures 3 and 4 describe the linear free energy relationships observed for different type of reactions. The first is connected with the electron transfer rate being a function of free energy change related with electron transfer reaction (calculated using the Rehm-Weller equation, Eq. 2). The second (Figure 4) is associated with the free energy activation for the addition reaction between the monomer and free radical being a result of the secondary reactions that follow electron transfer process. The first relationship deals with primary photochemical reaction, while the second one is related with secondary processes (dark reactions).

The main question that derives from above analysis is, which process is crucial for an overall observed rate of photoinitiation.

The first possibility considers the effect of primary photochemical reaction on observed rate of photoinitiation. In order to clarify such relationship, the rate of QIPB triplet state quenching by electron donors under the study was measured.
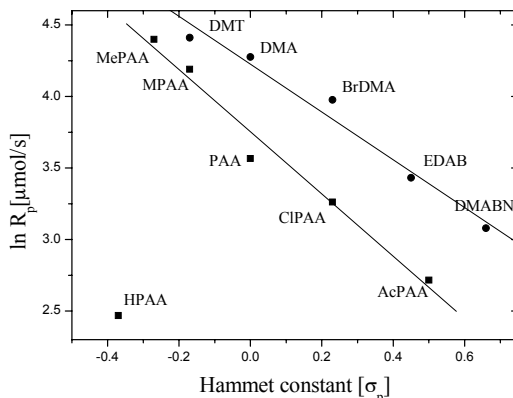
Fig. 4. Relationship between the logarithm of polymerization rates and the Hammett`s constants for the: phenoxyacetic acid derivatives (PAADs) and N,N-dimethylaniline derivatives (DMADs) in the presence of QIPB.

The quenching rate constants, k_q, were obtained by monitoring the triplet-triplet absorption decays of QIPB at fixed wavelengths for various quencher concentrations and by employing the classical Stern-Volmer relation.

$$k_{obs} = \tau_T^{-1} + k_q[ED] \tag{1}$$

where τ_T is the lifetime of the QIPB excited triplet state in the absence of an electron donor (ED). Typical plots based on Eq. (1) are presented in Figure 5a and 5b and the quenching rate constants established from the data shown in these Figures are summarized in Table 2.

The k_q values can be correlated to the standard free energy change for electron transfer. The free energy change (ΔG_{el}) associated with a single electron transfer from electron donors to the excited triplet state of the chromophore was calculated using the Rehm-Weller equation (2) [13].

$$\Delta G_{el} = E_{ox}(D/D^{\bullet+}) - E_{red}(A^{\bullet-}/A) - Ze^2/\varepsilon a - E_{00} \tag{2}$$

where $E_{ox} = (D/D^{\bullet+})$ is the oxidation potential of the electron donor, $E_{red} = (A^{\bullet-}/A)$ is the reduction potential of the electron acceptor, E_{00} is the excited state energy, and $Ze^2/\varepsilon a$ is the Coulombic energy, which is considered negligible with respect to the overall magnitude of the ΔG_{el} in the present system.

The obtained ΔG_{el} values for entire series of the electron donors are compiled in Table 2. The dependence of the quenching rate constant, k_q, on ΔG_{el} is presented in Figure 6. It is well known that the rate of the electron transfer is related to the free energy of the reaction through the classical Marcus equation [14]. The data presented in Figure 6 behave as predicted by this theory. For the tested photoredox pairs typical "normal region" of Marcus plot is observed, strongly supporting the electron-transfer mechanism in the quenching of the dye triplet by tested electron donors.

In our earlier papers we have documented that the rate of photoinitiated polymerization recorded at its initial time is proportional to the square root of the electron transfer rate constant between the partners of photoredox couple applied as photoinitiating system [7a,b]. Figure 7a and 7b illustrate such relationship.
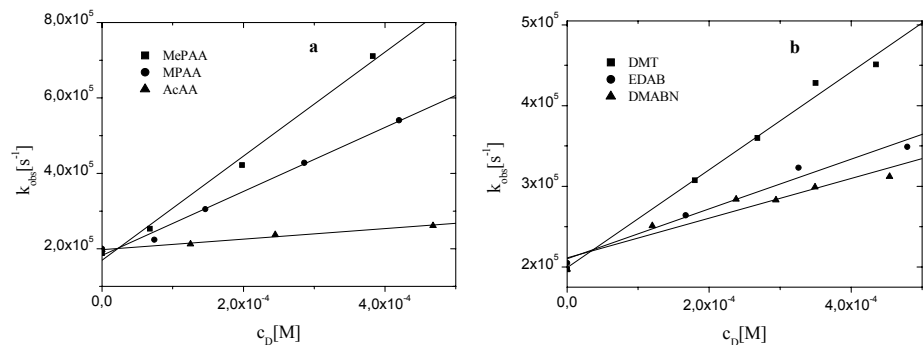
Fig. 5. Plot according to Eq. (1) for electron donors under the study: (a) PAADs, (b) DMADs.
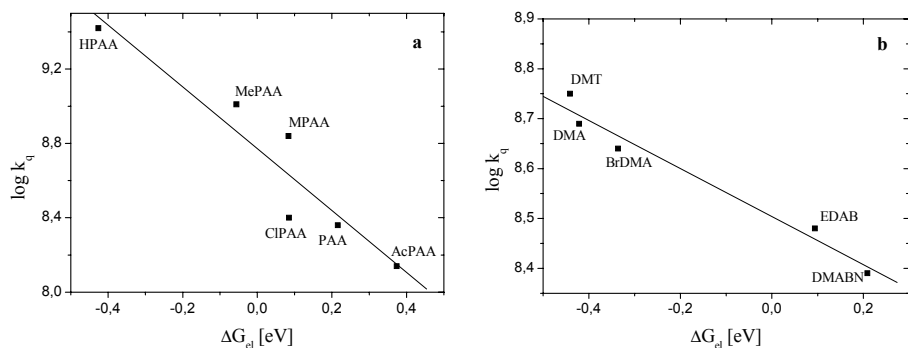

Fig. 6. Dependence of the quenching rate constant on ΔG_{el} for quenching of QIPB triplet by tested electron donors (type marked in Figures).

The data shown in 7 suggest that the electron transfer reaction probably affect the rate of photoinitiation process. The specific properties observed for HPAA ((4-hydroxy-phenoxy)acetic acid) can be explained considering well known inhibiting effect typical for phenols [15].
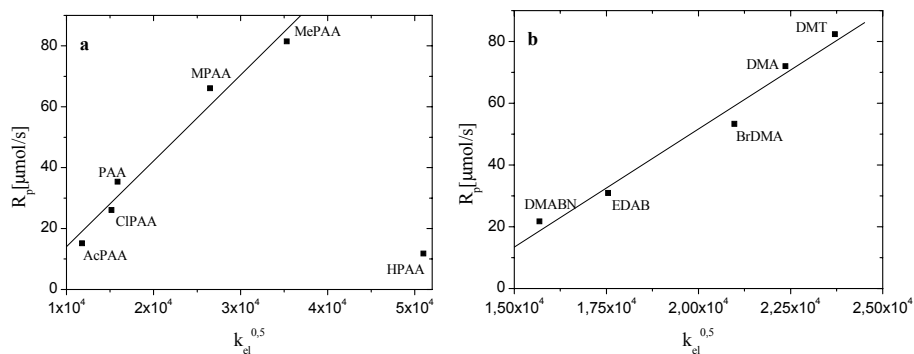

Fig. 7. Relationship between the rate of photoinitiated polymerization and square root of rate constant of electron transfer process for the QIPB- tested electron donors photoredox pairs.

On the other hand, one should take into account fact that the reactions that follow electron transfer process for each photoredox pair produce different radicals. There are two major factors that can affect the initiation efficiency in present system. The first is related with the reactivity of the free radicals that are formed as the result of PET. According to recent work of Fischer et al. [16] an analysis of many experimental absolute rate constants clearly exhibits the interplay of the reaction enthalpy effects, polar charge-transfer contribution and substituent effects on the free radical-monomer addition reaction activation energy barrier. Such conclusion allows one to assume that the observed initial rates of polymerization are controlled by the rate of free radical-monomer addition reaction. The change of the quantum yield of free radicals formation for different substituents, is the second variable that can affect the initial rate of photoinitiated polymerization. However, the precise determination of the quantum yield of the free radicals formation is experimentally very complex and the values of the quantum yield for the corresponding radicals formation are not available now.

Conclusion

This paper comprises two groups of the co-initiator being electron donors of photoredox couples that act as photoinitiating systems of free radical polymerization. The influence of the co-initiator structure on photoinitiation ability is clearly visible for both groups. The data suggest that both, the rate of an electron transfer between members of photoredox couples, as well as the reactivity of obtained free radicals can affect the overall efficiency of photoinitiation. The properties of co-initiators is of great interest for understanding the mechanisms leading to the free radicals formation and can help to design of suitable photoinitiators of free radical polymerization.

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