

Photoinitiator systems for concurrent radical and cationic polymerization

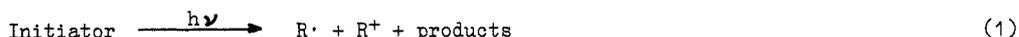
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Abstract - In this report a classification of the known photoinitiator systems for concurrent radical and cationic polymerization is given. Mainly by experimental results received in the group of the author the general mechanism and the effectivities of such photoinitiator systems will be discussed. Also a short discussion of the complex influences of several system parameters is included.

INTRODUCTION

For photoinitiation of radical or ionic polymerization numerous initiators or initiator systems are established (ref. 1). Recently, photoinitiators were designed which can initiate both radical and ionic (mostly cationic) polymerization (ref. 2 & 3). The basic reaction of those initiators is according to Eq. (1) in the course of which radicals and ionic species

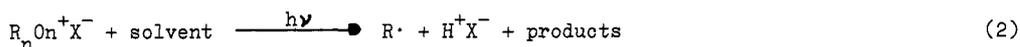


are obtained simultaneously.

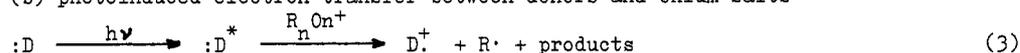
In general, the concurrent initiation of radical and cationic polymerization may combine the specific advantages of both reaction pathways. The radical polymerization is characterized by a high rate, but will be influenced by oxygen. On the other hand, there is only little influence of oxygen on the cationic polymerization. Thus, photocurable compositions which contain these photoinitiators and functionality for both polymerization processes may provide an enhanced curing rate even in presence of oxygen.

The known concurrent radical-cationic photoinitiators can be classified by the following principles:

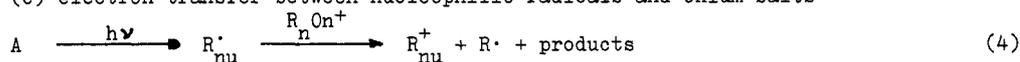
(a) direct photolysis of onium salts



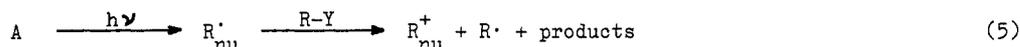
(b) photoinduced electron transfer between donors and onium salts



(c) electron transfer between nucleophilic radicals and onium salts



(d) electron transfer between nucleophilic radicals and organic halogen compounds



It is the aim of this paper to present some results of the photochemical aspects of the systems (b) to (d) obtained in the authors laboratory. Reactions of type (a) are reviewed in ref. 4 and 5.

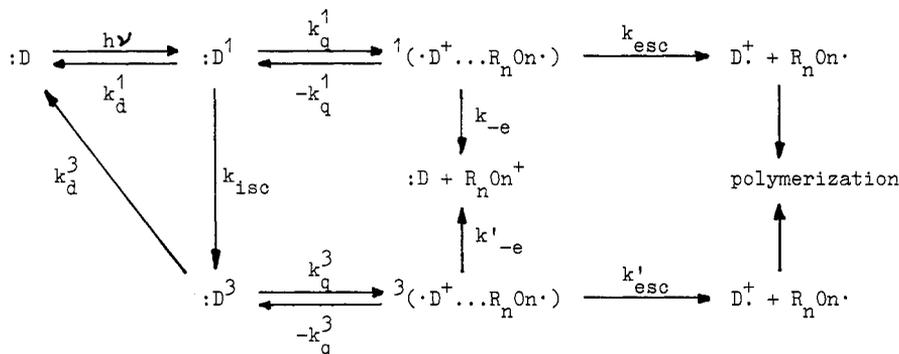
PHOTOINDUCED ELECTRON TRANSFER BETWEEN DONORS AND ONIUM SALTS

A simplified mechanism for the electron transfer between excited donors and onium salts (further informations in ref. 6) is shown in Scheme 1. Both excited singlet and triplet states can be involved in this process. The application of those systems as photoinitiators predicts two fundamental conditions: (1) The quenching reaction with the onium salts must be proceed faster than the monomolecular deactivation and the bimolecular quenching with oxygen

TABLE 1. Free reaction enthalpies (ΔG_{et}) and rate constants (k_q) for electron transfer between excited singlet or triplet state of donor and onium salt (measured in acetonitrile/water 90 vol%)

Donor	Onium salt	ΔG_{et}^1 (eV mol ⁻¹)	$k_q^1 \times 10^{-9}$ (M ⁻¹ s ⁻¹)	ΔG_{et}^3 (eV mol ⁻¹)	$k_q^3 \times 10^{-7}$ (M ⁻¹ s ⁻¹)
Anthracene	(Ph) ₂ I ⁺	-2.0	16	-0.6	0.7
	(Ph) ₃ S ⁺	-1.1	15	+0.4	< 0.01
	(NCCH ₂)(Ph) ₃ P ⁺	-1.5	17		
9.10-Diphenylanthracene	(Ph) ₂ I ⁺	-1.1	18		
	(Ph) ₃ S ⁺	-0.6	11		
2.4.5-Triphenyloxazole	(Ph) ₂ I ⁺		4.5		
	(Ph) ₃ S ⁺		2.8		
10-Methylacridone	(Ph) ₂ I ⁺		8.4		0.1
Benzophenone	(Ph) ₂ I ⁺			-0.3	2.0
Thioxanthone	(Ph) ₂ I ⁺	-1.2	4.9	-0.9	
Thiopyronine	(Ph) ₂ I ⁺	-0.9	18	-0.6	1.0
Fluorescein	(Ph) ₂ I ⁺	-1.0	19	-0.5	

Scheme 1



or monomers. (2) Because the polymerization is initiated normally by uncorrelated radicals, the efficiency of the formation of free $R_n On \cdot$ and $D^{\cdot+}$ may approach nearly one.

In order to select those systems, which possess high values of free reaction enthalpy (ΔG_{et}), a necessary condition for high quenching constants k_q^1 and k_q^3 , the Weller-Eq. (6) can be employed.

$$\Delta G_{et} = E_{1/2}^{ox}(:D/D^{\cdot+}) - E_{1/2}^{red}(R_n On^+/R_n On \cdot) - E_{0,0}^D - e^2/\epsilon a \quad (6)$$

Typical examples for such systems are listed in Table 1. Polynuclear aromatics, heteroaromatics, dyes, ketones and quinones are usable as donors due to their favorable spectral properties and oxidation potentials. Diaryliodonium salts, triarylsulfonium salts, phosphonium salts, pyrylium and thiapyrylium salts possess enough thermal stability and corresponding reduction potentials to function as electron acceptors.

As predicted by the theory, the quenching constants of singlet states of various systems measured by life time experiments are nearly diffusion controlled. Evidence in support of the electron transfer mechanism has been obtained by the detection of $D^{\cdot+}$ -species of some donors using their typical absorption data. Additionally, the isolation of the expected fragmentation products of the $R_n On$ -radicals points to this mechanism.



Since various $:D/R_n On^+$ combinations exhibit a high value of k_q^1 , at concentrations of onium salts $> 5 \times 10^{-2}$ M competitive bimolecular quenching reactions of the S_1 are suppressed, the isc-process is still possible. The efficiencies of isc (η_{isc}) by $R_n On^+$ -concentrations of 10^{-2} M calculated by Eq. (8) are outlined in Table 2. In contrast to the S_1 reaction, the

$$\eta_{isc} = k_{isc}/k_q^1 [R_n On^+] + k_d^1 + k_{isc} \quad (8)$$

TABLE 2. Efficiencies of isc-process of the donor in presence of onium salt (η_{isc}), quantum yields of onium salt decomposition (Φ_{in}) and of polymerization (Φ_p) of methylmethacrylate with the donor/onium salt system (measured in acetonitrile/water 90 vol%, $\lambda = 365$ nm, absence of oxygen, concentration of donor and onium salt (1×10^{-2} M)

Donor	Onium salt	η_{isc}	Φ_{in}	Φ_p^a
Anthracene	$(Ph)_2I^+$	0.47	0.22	36
	$(Ph)_3S^+$	0.51	0.20	41
	$(NCCH_2)(Ph)_3P^+$	0.54	0.40	93
9.10-Diphenylanthracene	$(Ph)_2I^+$		0.21	38
	$(Ph)_3S^+$		0.27	42
2.4.5-Triphenyloxazole	$(Ph)_2I^+$		0.03 ^b	26
	$(Ph)_3S^+$		<0.01 ^b	42
Benzophenone	$(Ph)_2I^+$	~ 1	0.06	
	$(Ph)_3S^+$	~ 1	0.015	
Thioxanthone	$(Ph)_2I^+$	0.95	0.27	43
Fluorescein	$(Ph)_2I^+$		0.55	

^a Incident light intensity $4.7-5.1 \times 10^{-7}$ einstein min^{-1} , concentration of methylmethacrylate 3.8 M.

^b Measured by $\lambda = 313$ nm.

constants of the triplet quenching by R_nOn^+ are only in the order of $10^7 M^{-1}s^{-1}$. That is surprising, because the calculated ΔG_{et}^{\ddagger} -values predict diffusion controlled reactions in some cases. Direct evidence for the electron transfer has been obtained from laser flash photolysis studies, CIDNP measurements as well as from the isolation of corresponding reaction products. Therefore, the T_1 yields polymerization initiating species by the pathways outlined in Scheme 1 too.

As expected, the quantum yields of the onium salt decomposition as well as of the donor decrease (Φ_{in}) depend on the R_nOn^+ -concentration. Assuming, that only one excited state is involved in the electron transfer, a correlation corresponding to Eq. (9) can be deduced (τ^0 : life time in absence of onium salts). Indeed, the experimental data obey this relationship. Values for Φ_{in} measured under identical conditions are listed in Table 2.

$$\frac{1}{\Phi_{in}} = \frac{k_{sep} + k_{-e}}{k_q \tau^0 k_{sep}} \frac{1}{[R_nOn^+]} + \frac{k_{sep} + k_q}{k_{sep}} \quad (9)$$

Irradiation of some D/R_nOn^+ systems results in formation of reactive radicals and cations (or radical cations) in quantum yields, which are comparable to those of photoinitiators, based on homolytic cleavage.

The aforementioned systems are able to start both radical and cationic polymerization processes. Quantum yields of polymerization (Φ_p) of model monomers methylmethacrylate and 2.3-epoxypropyl phenyl ether received under similar experimental conditions are presented in Table 2 and 3. It is obvious, that a variety of parameters acts on this value. This situation is still more complicated since also some exciplexes $^*(D...R_nOn^+)$ initiate the radical polymerization, as it was shown recently by us.

ELECTRON TRANSFER BETWEEN NUCLEOPHILIC RADICALS AND ONIUM SALTS

Corresponding to Eq. (4), nucleophilic radicals (R_{nu}^{\cdot}) may reduce onium salts in a dark reaction, if the thermodynamic conditions are so, that electron transfer is allowed. The only way to utilize the complete system as photoinitiator for concurrent radical and cationic polymerization is the photochemical formation of those radicals. The following photoreactions can be used:

- α -cleavage of benzoin derivatives, benzil ketals, 2-alkoxyacetophenones and related compounds
- hydrogen abstraction reactions of ketones and quinones
- decay of exciplexes of benzophenones and aminosubstituted aromatic ketones (e.g. Michler ketone, acridone, 10-methylacridone)
- redox reactions of coordination compounds (e.g. formation of $CO_2^{\cdot-}$)

TABLE 3. Quantum yields (Φ_p) and rates (v_p) of the polymerization of 2,3-epoxypropyl phenyl ether with diphenyliodoniumhexafluorophosphate coinitiator systems (measured in bulk, $\lambda = 365$ nm, absorbed light intensity 2.8×10^{-6} einstein min^{-1})

Light absorbing component	Φ_p	$v_p(N_2)/v_p(O_2)$
Anthracene ^a	53	1.13
9.10-Phenanthrenequinone ^a	55	1.17
Benzophenone ^b	21	0.99
Benzoin isopropyl ether ^a	42	0.70
2-Phenylbenzoin ^c	30	0.71
Benzil dimethylketal ^a	170	

^a Concentration of $(\text{Ph})_2\text{I}^+\text{PF}_6^-$ 2×10^{-2} M.

^b Concentration of $(\text{Ph})_2\text{I}^+\text{PF}_6^-$ 5×10^{-2} M.

^c Concentration of $(\text{Ph})_2\text{I}^+\text{PF}_6^-$ 4×10^{-2} M.

TABLE 4. Rate constants of the electron transfer (k_e) between nucleophilic radicals and onium salts (measured in acetonitrile/water 90 vol%, T = 20 °C, absence of oxygen)

Nucleophilic radical	$R_n\text{On}^+$	$k_e \times 10^{-6}$ $\text{M}^{-1} \text{s}^{-1}$
Diphenylketyl radical	$(\text{Ph})_2\text{I}^+$	30
	$(\text{Ph})_3\text{S}^+$	0.1
CO_2^-	$(\text{Ph})_2\text{I}^+$	5
	$(\text{Ph})_3\text{S}^+$	0.005
9.10-Phenanthrenesemiquinone	$(\text{Ph})_2\text{I}^+$	0.1
	$(\text{Ph})_3\text{S}^+$	0.07
Michlers aminyl radical	$(\text{Ph})_2\text{I}^+$	36
	$(\text{Ph})_3\text{S}^+$	16
1-Naphthylphenylketyl radical	$(\text{Ph})_2\text{I}^+$	62
	$(\text{Ph})_3\text{S}^+$	0.1

Key features for the action of such systems are: (1) The photochemical formation of R_{nu}^{\cdot} must be initiated with light of wavelenghts out of the spectral response of onium salts, to prevent inner filter effects. (2) The photoreaction forming R_{nu}^{\cdot} should proceed very efficient. (3) Compared to other reactions, the electron transfer between R_{nu}^{\cdot} and $R_n\text{On}^+$ has to be favored thermodynamically and kinetically.

Because the oxidation potentials of R_{nu}^{\cdot} are mostly unknown, the calculation of ΔG_{et} by Eq. (10) normally failed. Some k_e -values obtained by flash photolysis studies are summarized in Table 4. The main conclusion from these results is, that fast electron transfer occurs

$$\Delta G_{\text{et}} = E_{1/2}^{\text{ox}}(R_{\text{nu}}^{\cdot}/R_{\text{nu}}^+) - E_{1/2}^{\text{red}}(R_n\text{On}^+/R_n\text{On}\cdot) - e_2^0/\epsilon a \quad (10)$$

even if the $R_n\text{On}^+$ -concentration is in the order of 10^{-2} M. The effectivity of onium compounds is related to their electron acceptability. Evidence is given from CIDNP studies, spin trapping experiments as well as from isolation of corresponding reaction products that the discussed process is really an electron transfer. This process is outlined for benzoin ether/onium salt systems in Scheme 2. All expected products have been found. The quantitative formation of diketones also in presence of onium salts indicates, that the electrophilic benzoyl radical does not efficient react with $R_n\text{On}^+$. In consequence of the recombination of acyl and ether radical ($k_{-\alpha}$) CIDNP signals of the initial benzoin ethers were found. In presence of $R_n\text{On}^+$ the intensity of signals may approach zero. Both acyl and ether radicals formed by the α -cleavage of the benzoin derivatives were detected by means of ESR spin trapping on benzylidene-tert-butylamine-N-oxide in absence of onium salt. In their presence only the signals of acyl radicals and R-radicals could be found.

Scheme 2

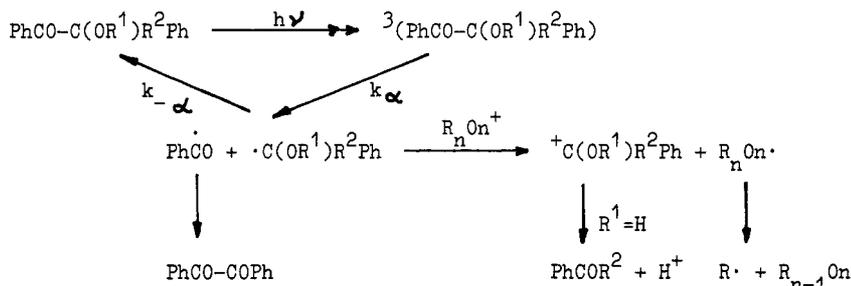


TABLE 5. Photoinduced decomposition of onium salts by $\text{PhCO-C(OR}^1\text{)R}^2\text{Ph}$: quantum yields of α -cleavage (Φ_α), quantum yields of onium salt decomposition (Φ_{in}), quantum yields of polymerization of methylmethacrylate (Φ_p) and the ratio of polymerization rate in presence (v_p) and absence (v_p^0) (measured in acetonitrile/water 90 vol%, $\lambda = 365$ nm, absence of oxygen, concentration of onium salt 1×10^{-2} M)

R^1	R^2	Φ_α^a	$R_n\text{On}^+$	Φ_{in}	Φ_p^a	v_p/v_p^0 ^b
$(\text{CH}_3)_2\text{CH}$	H	0.39	$(\text{Ph})_2\text{I}^+$	0.12	53	1.2
			$(\text{Ph})_3\text{S}^+$	0.019		
CH_3CO	H	0.33	$(\text{Ph})_2\text{I}^+$	0.044	30	1.6
			$(\text{Ph})_3\text{S}^+$	0.037		
H	Ph	0.10	$(\text{Ph})_2\text{I}^+$	0.032	26	1.9
			$(\text{Ph})_3\text{S}^+$	0.016		
CH_3	OCH_3	0.50	$(\text{Ph})_2\text{I}^+$	0.22	60	1.0
			$(\text{Ph})_3\text{S}^+$	0.18		

^a Measured in presence of oxygen.

^b Concentration of methylmethacrylate 3.8 M, absorbed light intensity 3.1×10^{-7} einstein min^{-1} .

The quantum yields of onium salt decomposition (Φ_{in}) give important hints on the effectivity of such systems. For some combinations the Φ_{in} are listed in Table 5. It is indicated again that the different reduction potentials of the onium salts influence on Φ_{in} -data. Various systems exist, in which almost all photochemically formed nucleophilic radicals are consumed by the $R_n\text{On}^+$ (see the small differences in Φ_α and Φ_{in}). Data of the action of these photoinitiators in cationic polymerization of 2,3-epoxypropyl phenyl ether and in radical polymerization of methylmethacrylate are given in Tables 3 and 5, respectively. In order to discuss the dependence of the Φ_{in} -values it must be kept in mind, that in the case of radical polymerization electrophilic radicals are produced simultaneously with R_{nu} (see Scheme 2). But, as can be seen from Table 5, the decomposition of $R_n\text{On}^+$ by R_{nu} increases the Φ_p -values indicated by the ratio of polymerization rates in presence (v_p) and in absence of onium salts (v_p^0).

ELECTRON TRANSFER BETWEEN NUCLEOPHILIC RADICALS AND ORGANIC HALOGEN COMPOUNDS

Nucleophilic radicals are able to transfer their odd electron to further electron acceptors. Those electron transfer to halogen compounds creates new photoinitiator systems for concurrent radical and cationic polymerization. This possibility is outlined in Scheme 3 for benzyl ether radicals, which are formed via photolysis of benzoin ethers. Some chlorine- or bromine-containing compounds (e.g. mono- or polyhalogen alkanes, benzylhalogenides, α - or β -substituted esters) have been found to exhibit the best acceptor properties, whereas C-F-bond in analogous fluorine-containing compounds reacts only very inefficiently.

Scheme 3

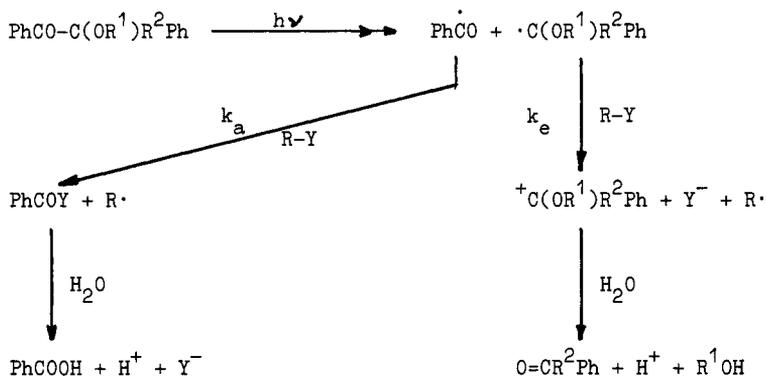


TABLE 6. Rate constants of electron transfer between diphenylketyl radical and halogen compounds (k_e), quantum yields of acid formation (Φ_{in}) and of polymerization (Φ_p) of methylmethacrylate with the halogen compound/2-phenylbenzoin system, ratio of quantum yields of polymerization in presence and absence (Φ_p^0) of halogen compound

Halogen compound	$k_e \times 10^{-4}$ ^a $M^{-1} s^{-1}$	Φ_{in} ^b	Φ_p ^c	Φ_p / Φ_p^0
CBr_4	34	0.58	44	1.8
$CHBr_3$	9.2	0.10	39	1.6
CCl_4	2.9	0.015	35	1.5
$CCl_3COOC_2H_5$	0.95	0.025	36	1.5
$CHCl_2COOC_2H_5$	0.20	0.014	31	1.3
CH_2Cl_2	0.01	0.008	24	1.0

^a Measured in acetonitrile in absence of oxygen.

^b Measured in acetonitrile/Water 66 vol%, in presence of oxygen, $\lambda = 365$ nm, concentration of halogen compound 1×10^{-2} M.

^c Measured in acetonitrile, in absence of oxygen, $\lambda = 365$ nm, concentration of halogen compound 1×10^{-2} M, concentration of methylmethacrylate 3.8 M, absorbed light intensity 4.4×10^{-7} einstein min^{-1} .

With iodo compounds the electron transfer leads to a product mixture. k_e -Values of the reaction between diphenylketyl radical and halogen compounds determined by means of flash photolysis studies are listed in Table 6. Evidence in support of the electron transfer is given by a correlation of $\log k_e$ versus reduction potentials, which holds for other electron acceptors too.

So far, only nucleophilic radicals formed by α -cleavage of benzoin derivatives and H-abstraction of excited ketones have been used for electron transfer to halogen compounds. In the former case there is a speciality—the electrophilic acyl radical is able to abstract halogen atom (see Scheme 3). High rate constants of this reaction (k_a) have been obtained, sometimes; thus, for the reaction between PhCO-radical and CBr_4 $k_a = 8.5 \times 10^6 M^{-1} s^{-1}$. When the reaction is carried out in aqueous solutions, it can be used for formation of protic acids due to the hydrolysis of acyl halides.

The quantum yield of protic acid formation can serve as a measure of the effectivity of both processes. Typical experimental results are shown in Table 6. In some cases high values were obtained, which are in the same order as those obtained for efficient photoinitiators. Indeed, the determined quantum yields of radical polymerization of methylmethacrylate are considerable with those of other systems. In contrast, due to the basicity of halide ions these systems are less suitable for cationic polymerizations. But, they may serve as photoinitiators for concurrent radical crosslinking and cationic condensation reactions of silicones in bulk phases.

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