Macromolecules **1993**, *26*, 4560–4566

Photoinitiated Polymerization of Acrylates and Methacrylates with Decahydroacridine-1,8-dione/Onium Salt Initiator Systems

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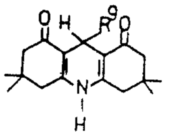
Received February 24, 1993; Revised Manuscript Received May 23, 1993

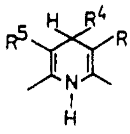
ABSTRACT: The utilization of a photoinitiator system for radical polymerization which is based on decahydroacridine-1,8-dione and iodonium salt is shown. Differences of the initiation mechanism in two monomer systems are discussed: (a) in a solution of methyl methacrylate in acetonitrile measured by means of dilatometry and (b) in a 20-μm film of a multi-acrylate system measured by means of IR spectroscopy. The quantum yields of polymerization, φ_p, and the maximum polymerization rates, r_p^{max}, are compared with those values of the well-known initiators working through α-cleavage.

1. Introduction

Diaryliodonium and triarylsulfonium salts can be used for the short-wavelength photoinitiation of the cationic polymerization.[1,2] Technological requirements referring to the widely applied light sources with emission wavelengths of λ_1 = 313 nm and λ_2 = 365 nm caused the investigation of the corresponding sensitized photopolymerization process.[3-8] In this way, it has been shown that onium salts also act in the initiation of radical polymerization. Aromatic hydrocarbons (e.g., anthracene), ketones (e.g., benzophenone, thioxanthone), and dyes (e.g., fluorescein, acridine yellow) are suitable as sensitizers.



1a: R^9 = Ph
1b: R^9 = Me



2a: $R^{3,5}$ = COOEt, R^4 = Ph
2b: $R^{3,5}$ = CONHPh, R^4 = Ph
2c: $R^{3,5}$ = tBu, R^4 = H

Very recently we reported the application of decahydroacridine-1,8-diones (1) as a new sensitizer for the decomposition of onium salts.[9,10] High quantum yields of the bleaching of 1, φ, and of the formation of radicals, φ_r, have been found. As a consequence, in this paper we describe the photopolymerization initiated by combinations of 1 with onium salts. This was done (a) in a 3.8 mol/L solution of methyl methacrylate (MMA) in acetonitrile (MeCN) as a widely used model system and (b) in an acrylic system, which is commonly used in UV-curing applications (Bisphenol A glycidyl ether diacrylate (EA)/hexanediol diacrylate (HDDA) = 3/2 (w/w)).

Kinetic features, such as the dependence of the polymerization quantum yield, φ_p, on the onium salt concentration, the monomer concentration, and the light intensity are measured and discussed. Furthermore, the consequences of the 2,3- and 5,6-bridging in the case of the 1,4-dihydropyridine derivatives 1 compared to the 2,3- and 5,6-nonbridged 1,4-dihydropyridine derivatives 2 are considered.

Finally, it was in our particular interest to compare this new photoinitiator system with other commercially available photoinitiators.

2. Experimental Section

Materials. The epoxyacrylate (Actilane 70, SNPE), the HDDA (Norsolor), and the MeCN (Merck, "zur UV-Spektroskopie") were used without further purification. Technical MMA was treated with a 5% aqueous NaOH solution and after washing dried and distilled in vacuum. Compounds 1 and the onium salts have been prepared as described previously.[9] The photoinitiators benzoin isopropyl ether (BIPE), 1-benzoylcyclohexanol-1 (Irgacure 184), and 2-(dimethylamino)-2-benzyl-1-(4-morpholinophenyl)butanone-1 (Irgacure 369) were used as received from Ciba-Geigy AG.

Photopolymerization. The solution experiments were carried out in an automatic photodilatometer.[11] The argon-bubbled solutions (10 mL of MMA and 15 mL of MeCN) were irradiated with monochromatic light of λ = 365 nm and 4.0×10^{-7} mol/L·s $< I_0 < 6.0 \times 10^{-7}$ mol/L·s. The concentrations of 1 and the other initiators were chosen to have an absorption of E = 5 with an optical length of d = 3.5 cm, e.g., [1] = 2.3×10^{-4} mol/L. To overcome the problems derived from the high absorbance inside the reaction vessel, the mixtures were intensively stirred by a magnetic stirrer.

The polymerization rates, r_p, were obtained from the slope of the linear part of the time–conversion curve measured by this setup. The quantum yield of polymerization, φ_p, is expressed as the ratio of r_p to the absorbed light intensity. The values r_p were measured below a conversion of 5%.

The photopolymerization of the bulk monomers EA/HDDA = 3/2 (w/w) was carried out on 20-μm-thick films placed between two polyethylene films. The reaction kinetics was monitored in real-time IR spectroscopy.[12,13] A high-pressure mercury lamp (HLS 210 UH, Hoya-Schott) was used for the irradiation. When working in a monochromatic mode of λ = 365 nm, the light intensity was measured by a radiometer to be $I_0^{365} = 1.3 \times 10^{-2}$ mol/L·s (7.5 mW/cm²).

3. Results and Discussion

Photopolymerization of MMA in Solution. Kinetics of Initiation and Polymerization. The exposure of combinations $1/Ph_2IBF_4$ in solutions of MMA in MeCN

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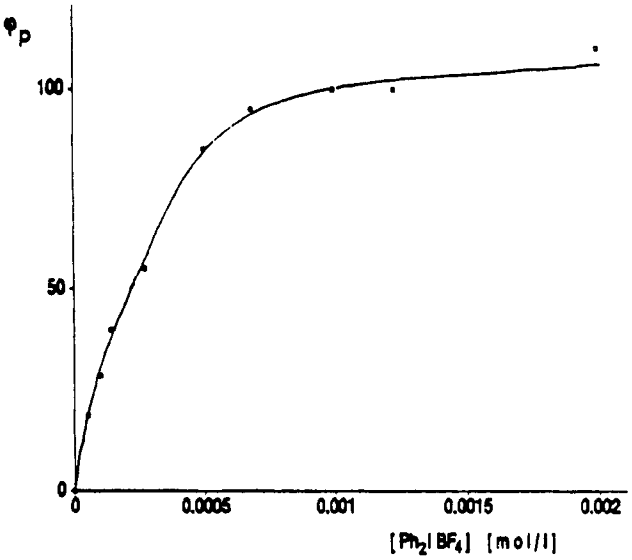


Figure 1. Dependence of the polymerization quantum yield φ_p on the iodonium salt concentration, in MeCN; [**1a**] = 2.3×10^{-4} mol/L, [MMA] = 3.8 mol/L, $I_a = 4.2 \times 10^{-7}$ mol/L·s, λ = 365 nm, O_2-free.

gives rise to polymer formation. The viscosity-average molecular weight of the poly(methyl methacrylate) (PMMA) is $\bar{M}_\eta = 1.4 \times 10^6$ ([Ph_2IBF_4] = 0.001 mol/L, $I_a = 4.2 \times 10^{-7}$ mol/L·s). The dependence of the quantum yield of the polymerization on the concentration of the coinitiator is shown in Figure 1. As can be seen, high values of φ_p are obtained already at a low [Ph_2IBF_4] = 0.001 mol/L.

The polymerization of MMA with the above-mentioned photoinitiator system is initiated by phenyl radicals produced in an electron-transfer process from the T_1 state of **1** to the onium salt.[9] Furthermore, the use of the nonprotic and polar medium mixture MeCN/MMA favors the intersystem crossing process of the S_1 state compared to the electron transfer also possible from this state. MMA influences both excited states; quenching constants of $k_m^s = 4.2 \times 10^7$ L/mol·s and $k_m^t = 1.3 \times 10^6$ L/mol·s have been determined. With this information the kinetic situation can be expressed by Scheme I.

This scheme represents a very complex kinetic system. The most important pathway for the polymerization initiation is the formation of the triplet radical pair, ^{3}RP. In the course of phenyl radical generation from ^{3}RP, a radical-consuming reaction takes place in a secondary radical pair.[10] By means of spin-trapping experiments it was evaluated that the efficiency of this reaction is $\eta^h = 0.3$. To get more information about the initiation process, eq 1 has been derived from the kinetic model in Scheme I.

$$\varphi_r = \left[\frac{k_{isc}}{k_{isc} + k_f + k_m{}^s[\mathrm{MMA}] + k_q{}^s[\mathrm{Ph_2IBF_4}]}\right] \times \left[\frac{2(0.86)(1-\eta_h)k_q{}^t[\mathrm{Ph_2IBF_4}]}{k_q{}^t[\mathrm{Ph_2IBF_4}] + k_m{}^t[\mathrm{MMA}] + k_d{}^t}\right] + \frac{2(0.86)(1-\eta_h)k_q{}^s[\mathrm{Ph_2IBF_4}]}{k_{isc} + k_f + k_q{}^s[\mathrm{Ph_2IBF_4}] + k_m{}^s[\mathrm{MMA}]} \quad (1)$$

Together with the above k_m^s and k_m^t, the following data are known:[9] (1) $k_q^s = 7.2 \times 10^9$ L/mol·s and $k_q^t = 8.8 \times 10^8$ L/mol·s (fitted according to the solvent dependence of these constants); (2) $\tau_0^s = 1.4$ ns, $k_{isc} = 6.8 \times 10^8$ s^{-1} (fitted according to the solvent dependence of τ_0^s); (3) $k_f = 6.7 \times 10^7$ s^{-1}, $k_d^t = 3.3 \times 10^4$ s^{-1}; (4) $k_{34}/(k_{34} + k_{30}) = 0.86$ (taken from the intercept of the $1/\varphi$ vs $1/[\mathrm{Ph_2IBF_4}]$ correlation in ref 9).

Scheme I

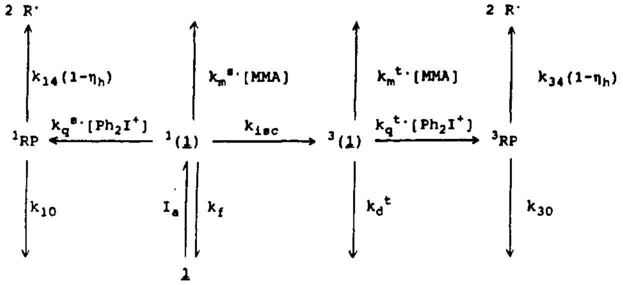


Table I. Calculated Quantum Yields of Radical Formation φ_r, the Efficiency of the T_1 State η_r^t, the Efficiency of the Monomer Quenching η_m^{s+t}, and the Experimental Quantum Yields of the Bleaching of 1a φ and Polymerization φ_p in Dependence on the Iodonium Salt Concentration (in MMA/MeCN = 2/3 (v/v), Argon-Bubbled, λ = 365 nm, [1a] = 2.3×10^{-4} mol/L)

[Ph_2IBF_4] (mol/L)	φ_r	η_r^t	η_m^{s+t}	φ	φ_p
0	0		0.91	0.035	0
0.00005	0.008	0.950	0.91	0.06	19
0.0001	0.016	0.949	0.90	0.085	29
0.00014	0.023	0.945	0.89	0.10	40
0.00027	0.043	0.940	0.88	0.16	55
0.0005	0.077	0.936	0.85		85
0.00068	0.100	0.935	0.83	0.31	95
0.001	0.14	0.930	0.80		100
0.0012	0.17	0.929	0.78	0.37	100
0.002	0.25	0.920	0.71		110

The data, calculated with eq 1, for the quantum yields of the radical formation φ_r, the efficiencies of the triplet pathway η_r^t on this process, and the efficiencies of the monomer quenching $\eta_m^{s,t}$ are summarized in Table I. For comparison, experimental data of φ and φ_p measured under identical experimental conditions are given.

Over a wide range of [Ph_2IBF_4] the portion of the T_1 state to the production of free radicals is more than 90%. However, the high potential for the bimolecular reaction pathway with the iodonium salt is greatly lowered by the competing monomer quenching. Even at the high concentration [Ph_2IBF_4] = 0.01 mol/L about 40% of the excited states deactivate by this process. Notice that this reaction does not contribute to the polymerization initiation (at [Ph_2IBF_4] = 0, φ_p equals 0). This is in contrast to the findings for 1-benzyl-1,4-dihydronicotinamide (BNAH)/MMA in CH_2Cl_2.[14] There should be a different mechanism based on the lower oxidation potential of BNAH and the electron acceptor properties of CH_2Cl_2.

If the ideal polymerization kinetics are obeyed for the system investigated, then eq 2 describes the correlation between the rate constants of polymerization (k_p) and termination (k_t), the absorbed light intensity (I_a), the monomer concentration ([MMA]), and φ_r (f represents a factor for the amount of radical addition onto the C=C double bond).

$$\varphi_p = \frac{k_p}{(k_t I_a)^{1/2}}[\mathrm{MMA}](f\varphi_r)^{1/2} \quad (2)$$

According to eq 2 the dependence $\varphi_p = f(\varphi_r^{1/2})$ gives a straight line (Figure 2). The slope of this relationship yields $k_p/k_t^{1/2} = 0.041$. The deviation from the literature data (0.057,[15] 0.067[16]) could be explained by three models: (1) $f < 1$ (Initiator radicals are consumed also by the solvent or the initiator itself. But this is less for the phenyl radical presumably, because of the unfavorable ratio of the rate constants[17] and the very low initiator concentration.); (2)

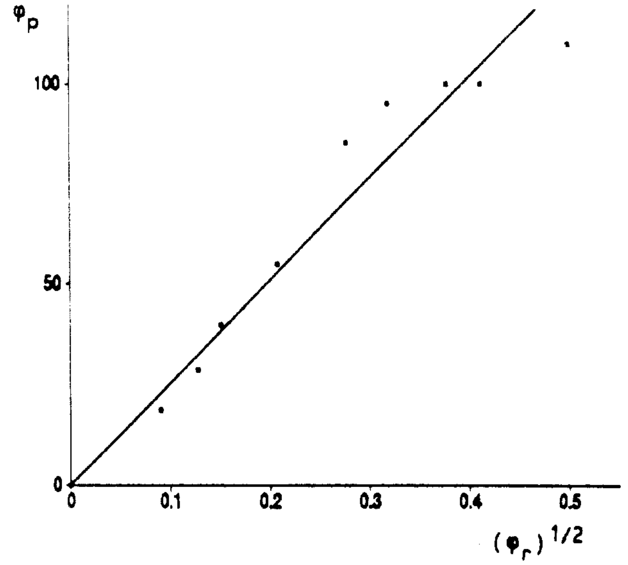


Figure 2. Dependence of the polymerization quantum yield φ_p on the square root of the calculated quantum yield of radical formation φ_r. Experimental conditions are as in Figure 1.

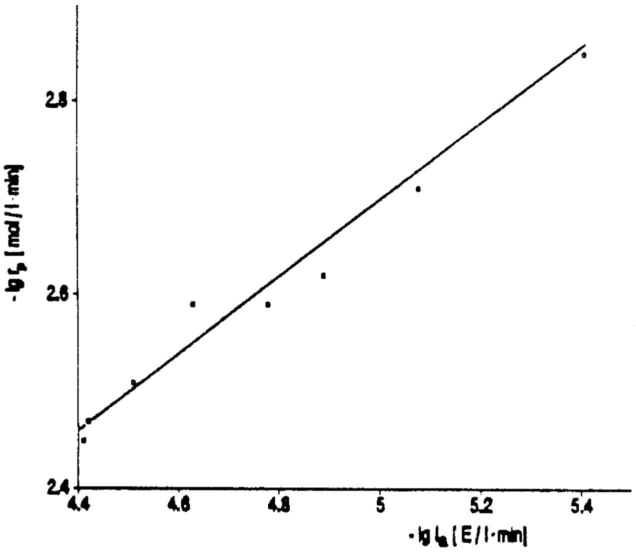


Figure 3. Dependence of the polymerization rate r_p on the light intensity I_a, in MeCN; [MMA] = 3.8 mol/L, [**1a**] = 2.3 × 10^{-4} mol/L, [Ph_2IBF_4] = 0.001 mol/L, λ = 365 nm, O_2-free.

processes which lower φ_r but are not taken into account in the above model; (3) no ideal polymerization kinetics, but participation of initiator radicals in the termination step.

To support the last argument, the exponent β of the light intensity (Figure 3) and the monomer exponent α (Figure 4) were determined. Using the experimental data, the former can be calculated to be $\beta = 0.37$ and the monomer exponent to be $\alpha = 1.0$. Due to the β-value it seems that a primary radical termination process participates in the overall termination. Owing to the nontrivial influence of MMA on the pathways in Scheme I and the kinetics of the polymerization, the α-value cannot give information concerning the primary radical termination.

Comparison with Other Photoinitiators. In Table II are compared the polymerization quantum yields of different initiators which have been measured under almost the same conditions. The system $1/R_nX^+$ works worse with the sulfonium salt because of its lower reduction potential compared to the iodonium salt. A change of the substituent in the 9-position of 1 (methyl, **1b**, instead of phenyl, **1a**) also lowers φ_p. This is due to a less efficient intersystem crossing, which causes finally lower φ_r values.[9] In spite of a 10 times higher iodonium salt concentration, an unfavorable kinetic situation appears with 1,4-dihydropyridine derivatives having nonbridged 2,3- and 5,6-substituents. No triplet excited state but a very short-lived singlet excited state is incorporated in the initiation mechanism.

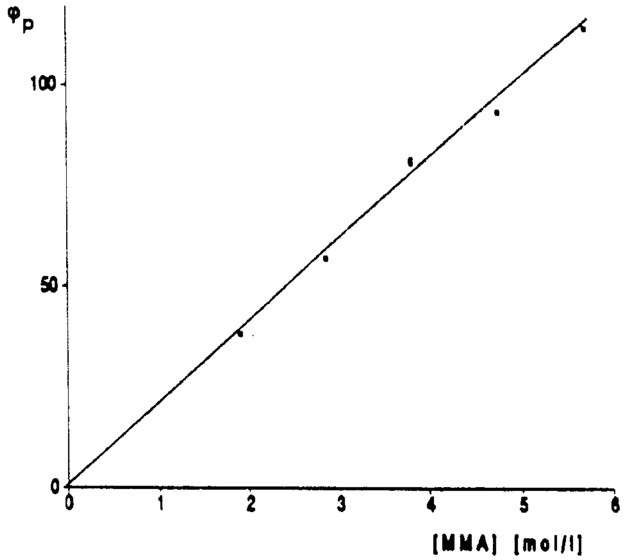


Figure 4. Dependence of the polymerization quantum yield φ_p on the monomer concentration [MMA], in MeCN; [**1a**] = 2.3 × 10^{-4} mol/L, [Ph_2IBF_4] = 0.001 mol/L, I_a = 6.3 × 10^{-7} mol/L·s, λ = 365 nm, O_2-free.

Table II. Comparison of the Polymerization Quantum Yield φ_p of Different Photoinitiators (in MeCN, [MMA] = 3.8 mol/L, λ = 365 nm, Argon-Bubbled, Conversion Below 5%)

initiator	I_a (×10^{-7} mol/L·s)	φ_p
1a/Ph_2IBF_4 (0.001 M)	4.2	100
1a/Ph_3SBF_4 (0.001 M)	6.0	15
1b/Ph_2IBF_4 (0.001 M)	4.2	72
2a/Ph_2IBF_4 (0.01 M)	4.2	26
2b/Ph_3SBF_4 (0.01 M)	4.2	32
anthracene/Ph_2IBF_4 (0.01 M)	4.7	36
thioxanthone/Ph_2IBF_4 (0.01 M)	4.3	42[15]
benzoin isopropyl ether	3.0	40[18]
IRGACURE 184	4.2	106
IRGACURE 369	4.2	63

However, also other initiator systems based on an electron transfer to onium salts are less efficient even at high concentrations of the coinitiator. To explain this behavior, the thioxanthone (TX)/Ph_2IBF_4 combination can be selected. Two reasons should be regarded to cause the lower φ_r in this case: (1) a more unfavored separation of the radical pair $TX^{\bullet+}Ph_2I^{\bullet}$ (The value $\varphi_{max} = 0.27$[18] is equal the ratio $k_{34}/(k_{34} + k_{30})$. With eq 1 $\varphi_r = 0.067$ was calculated for TX/Ph_2IBF_4 (0.01 mol/L). This value agrees quite well with that of $\varphi_r = 0.06$ determined by means of spin-trapping experiments.[10]); (2) a more efficient quenching of the excited triplet state of TX by the monomer (A rate constant $k_m^t = 1.5 \times 10^7$ L/mol·s is reported for this process.[19]).

Finally, the well-known photoinitiators functioning through α-cleavage exhibit lower φ_p than the decahydroacridine-1,8-dione/iodonium salt combination. This astonishing fact can be explained at best by taking into account the rate constants of the addition of the radicals formed to MMA. A much higher value $k_{add} = 1.8 \times 10^8$ L/mol·s[17] is known for the phenyl radical compared to $k_{add} = 10^5$ L/mol·s[20] for the benzoyl radical. Therefore,

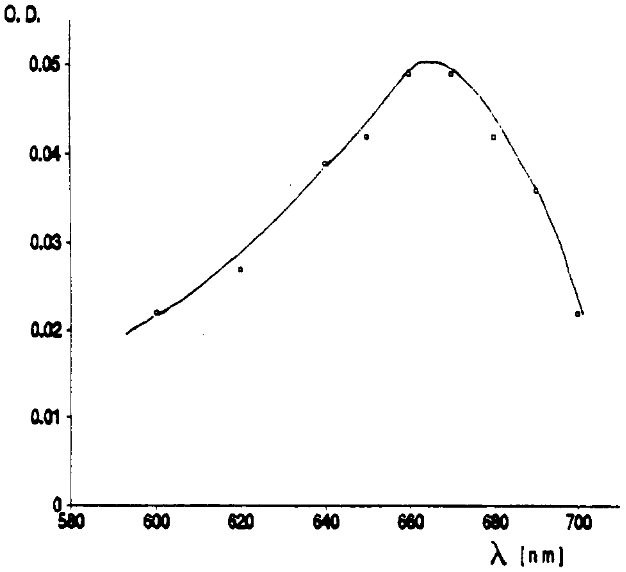
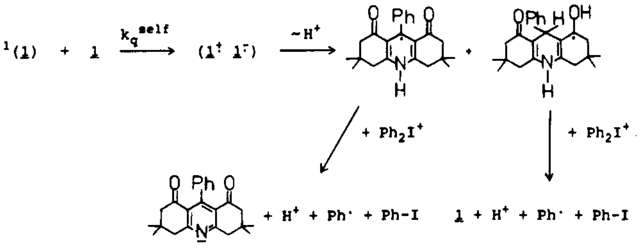


Figure 5. T–T absorption spectra of **1a** in the multi-acrylate monomer system EA/HDDA = 3/2 (w/w); [**1a**] = 1×10^{-4} mol/L, λ_{exc} = 355 nm, air.

Scheme II



the initiation efficiency *f* is lower than in the onium salt systems.

As an exception, the α-(hydroxyalkyl)aryl ketone derivative IRGACURE 184 exhibits a high value of $\varphi_p = 106$. In contrast to benzoin isopropyl ether the second radical formed in the α-cleavage is more reactive, $k_{add} = 5 \times 10^5$ L/mol·s.[20]

Polymerization in Bulk Monomer. General Remarks. The initiation mechanism of the system 1/Ph_2IBF_4 in the bulk monomer is different from that operating in solution. The epoxyacrylate contains hydroxylic groups. This structural feature of the monomer causes a significant lowering of k_{isc}. This is confirmed by the following experiments:

(1) Addition of the monomer to a nonpolar solution of **1a** does not quench the fluorescence but increases the fluorescence intensity. In spite of the significant quenching by the monomer (the concentration of acrylate units is about 6 mol/L), the fluorescence lifetime of **1a** increases to $\tau_0{}^s$ = 4.0 ns in the pure acrylate compared to that in benzene/MeCN = 3/1 ($\tau_0{}^s$ = 1.0 ns[9]).

(2) The triplet–triplet absorption spectrum (Figure 5) is closer to the spectrum in MeCN/H_2O = 2/1 than to that in benzene/MeCN = 3/1 both in its optical density and in its maximum absorption wavelength.

Therefore, in contrast to the situation in MMA/MeCN the triplet excited state of **1a** contributes only in a minor extent to the formation of radicals. Because of the greatly increased concentration of **1a** ([**1a**] = 0.015 mol/L) the self-quenching mechanism of **1** can compete with the electron transfer to the onium salt even at 0.01 mol/L < [Ph_2IBF_4] < 0.05 mol/L. Therefore, besides the general reactions in Scheme I the reaction pathways shown in Scheme II must take place. Since the rate constant $k_q{}^{self}$ = 4×10^9 L/mol·s is comparable to $k_q{}^s$ = 3.3×10^9 L/mol·s (in protic solvents), at [Ph_2IBF_4] = 0.01 mol/L these reaction pathways contribute to the initiation more than 50%.

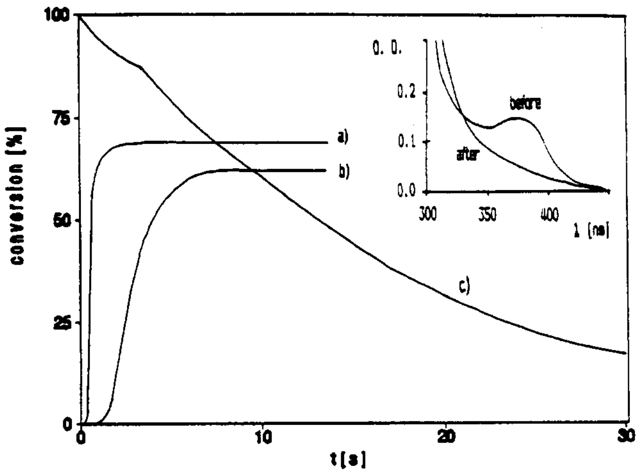


Figure 6. Photopolymerization profiles recorded by real-time IR spectroscopy in a 20-μm laminate of epoxyacrylate/HDDA = 3/2 (w/w): (a) IRGACURE 369 (2%) as the initiator, I_a/I_0 = 0.42; (b) **1a** (0.015 mol/L)/Ph_2IBF_4 (0.05 mol/L) (2.3%) as the initiator, I_a/I_0 = 0.26; (c) decay of **1a** during the polymerization recorded by UV spectroscopy, high-pressure mercury lamp HLS 210 UH (Hoya-Schott), λ = 365 nm, I_0 = 0.013 mol/L·s (7.5 mJ/cm²). The inset shows UV spectra of the laminate before and after prolonged irradiation.

Table III. Dependence of the Inhibition Time t_i, the Maximum Conversion U_{max}, and the Maximum Polymerization Rate $r_p{}^{max}$ on the Iodonium Salt Concentration (Epoxyacrylate/HDDA = 3/2 (w/w), Laminate, d = 20 μm, λ = 365 nm, I_0 = 0.007 mol/L·s)

[Ph_2IBF_4] (mol/L)	t_i (s)	U_{max} (%)	$r_p{}^{max}$ (mol/L·s)
0.02	2.3	59	0.14
0.03	1.6		0.47
0.04	1.8	55	0.73
0.05	1.3		0.84
0.057	2.0	58	0.76
0.06	0.9		0.81
0.10	0.8	61	1.54

Another important feature of the initiation mechanism in the multi-acrylate system is that the monomer quenches the S_1 state more efficiently than methacrylates; e.g., $k_m{}^s$ = 8.3×10^7 L/mol·s (ethyl acrylate) and $k_m{}^s$ = 9.5×10^7 L/mol·s (EA/HDDA, calculated per mole of acrylate) have been measured. No significant differences were found for the T_1 state quenching; e.g., $k_m{}^t$ = 1.1×10^6 L/mol·s (ethyl acrylate).

Altogether, it can be concluded that the efficiency of the initiator 1/Ph_2IBF_4, at a certain onium salt concentration, is lower in the bulk monomer EA/HDDA than in MMA/MeCN. The reasons are the lowering of φ_{isc} and an increased competition of the monomer quenching.

Nevertheless, an effective photopolymerization is detectable by means of real-time IR measurements (Figure 6). After the inhibition period t_i = 1.3 s an increasing consumption of the acrylic C=C double bonds occurs. Maximum rates $r_p{}^{max}$ = 1.4 moL/l·s in the monochromatic mode (λ = 365 nm) and even $r_p{}^{max}$ = 6.3 mol/L·s in the polychromatic mode are reached. Because of gelation only 63% of the acrylic functions are consumed. As a typical sign for the good hardening, the polyethylene film of the laminate can be peeled off very easily after the exposure.

The dependence of the kinetic values t_i, $r_p{}^{max}$, and U_{max} on the concentration of the coinitiator is given in Table III. As in the case of the MMA solution in the absence of the coinitiator, no polymerization occurs at all. The

Table IV. Dependence of the Half-Life $t_{1/2}$ and the Quantum Yield of the Decay of 1a φ on the Iodonium Salt Concentration (Epoxyacrylate/HDDA = 3/2 (w/w), Laminate, d = 20 μm, λ = 365 nm, I_a = 0.003 mol/L·s)

$[Ph_2IBF_4]$ (mol/L)	0.00	0.02	0.03	0.04	0.05	0.06
$t_{1/2}$ (s)	26.4	24.8	18.4	17.5	14.8	13.4
φ	0.12	0.13	0.17	0.18	0.21	0.23

values r_p^{max} increase linearly up to the maximum oniun salt concentration $[Ph_2IBF_4]$ = 0.1 mol/L. Furthermore, because of the increasing φ_r, the time t_i necessary for the consumption of the oxygen is shortened.

Decay of the Sensitizer. No significant dependence of the maximum conversion of double bonds U_{max} was found for iodonium salt concentrations between 0.02 and 0.1 mol/L. Therefore, there is no complete consumption of both the sensitizer and the coinitiator until the polymerization has been finished. The decay of the sensitizer during the irradiation was followed UV-spectroscopically at λ = 370 nm close to the absorption maximum of **1a** (Figure 6). To get the maximum conversion of double bonds, only a portion of about 40% of the whole sensitizer is needed. Importantly, the bleaching of the sensitizer is continued in the polymer. All the photoproducts absorb at shorter wavelengths (Figure 6, inset). In this way, a polymerization in thicker films should also be possible. The dependence of the half-life $t_{1/2}$ of the sensitizer on the coinitiator concentration is given in Table IV. To have an idea on the efficiency of the bleaching of the decahydroacridine-1,8-dione, the integral quantum yield φ was calculated using eq 3 ($I_a^{t=0}$ = 0.0032 mol/L·s, c_0 = 0.015 mol/L).

$$\varphi = \frac{c_0/2}{0.75 I_a^{t=0} t_{1/2}} \tag{3}$$

The value at $[Ph_2IBF_4]$ = 0 should be mainly due to the self-reaction of **1**. This is in good agreement with a calculation using eq 4 and the rate constants measured in solution.

$$\eta_{self} = \frac{k_{self}[\mathbf{1a}]}{k_{self}[\mathbf{1a}] + k_m^s[\text{acrylate}] + k_f} = 0.1 \tag{4}$$

In a similar manner, at $[Ph_2IBF_4]$ = 0.05 mol/L, η_{self} = 0.08, η_{salt} = 0.2, and η_m = 0.63 are obtained. Taking into account the ratios $k_{14}/(k_{14} + k_{10})$ and $k_{34}/(k_{34} + k_{30})$ (not every quenching step gives a product), the experimental φ = 0.21 is also in good agreement with the sum $\eta_{self} + \eta_{salt}$ = 0.28. Because of the special behavior of the secondary radical pair which is expressed by η_h[10] ($\varphi_r < 2\varphi$), a value $0.2 < \varphi_r < 0.4$ at $[Ph_2IBF_4]$ = 0.05 mol/L can be expected. Therefore, in the bulk monomer at high concentrations $[Ph_2IBF_4] > 0.01$ mol/L similar values as in the MMA solution are achieved at $[Ph_2IBF_4]$ = 0.001 mol/L.

Influence of the Light Intensity. In contrast to the situation in the MMA solution at low light intensities, in the bulk monomer the polymerization efficiency is not decreased by increasing I_a. Between $I_a = 4.4 \times 10^{-4}$ and 3.2×10^{-3} mol/L·s the light intensity coefficient is constantly β = 1.13.

Comparison with Other Photoinitiators. A comparison of different photoinitiators is given in Tables V and VI. Notice that the calculation of φ_p was made from the actual maximum polymerization rate r_p^{max} without taking into account the dark polymerization. Therefore, the interruption of the irradiation after a conversion of about 10% would lead to much higher values.

The results of the measurements in solution concerning φ_p are confirmed in the case of the donor/R_nX^+ systems. The combination **1a**/Ph_2IBF_4 exhibits the highest φ_p. **1b**/Ph_2IBF_4 is less efficient, but this is compensated by a better solubility. Combinations with sulfonium salt coinitiators and combinations with 2,3- and 5,6-nonbridged 1,4-dihydropyridine derivatives or anthracene (An) as the electron donor have very low polymerization quantum yields because of significant drawbacks in the initiation mechanism.

In contrast to the results with MMA, using the acrylic monomer the combination with thioxanthone is more efficient than the decahydroacridine-1,8-dione. This is caused by a change of the hydrogen donor properties of the monomer. Actilane 70 contains H atoms which can very easily be abstracted by the T_1 state of thioxanthone. Therefore, the polymerization is initiated even in the absence of the iodonium salt, because substructures of the monomer itself can function as a coinitiator. Then, the addition of the iodonium salt opens two new pathways capable of generating radicals. The direct photooxidation of the excited TX by the iodonium salt is less efficient as has been shown in MMA. However, the TX ketyl radicals formed as a result of the H abstraction are able to reduce Ph_2IBF_4, giving phenyl radicals.[15] The accompanying radical from the H donor may also participate in this manner. Altogether, an increased concentration of initiating radicals results.

Surprisingly, the 3,5-dianilido-substituted 1,4-dihydropyridine derivative **2b** is in combination with Ph_3SBF_4 almost as efficient as the decahydroacridine-1,8-diones. Although there is a lack of a complete explanation, it can be assumed that this compound works through a com-

Table V. Comparison of the Photopolymerization of Epoxyacrylate/HDDA = 3/2 (w/w) Initiated by Different Photoinitiators at Monochromatic Exposure (Laminate, d = 20 μm, λ = 365 nm, $I_0 = 1.3 \times 10^{-2}$ mol/L·s, $[R_nXBF_4]$ = 0.05 mol/L)

initiator	m_i[a] (%)	t_i (s)	U_{max} (%)	r_p^{max} (mol/L·s)	I_a/I_0	$r_{p,rel}^{max}$	φ_p
Ph_2IBF_4	1.8		0	0	0	0	
1a/Ph_2IBF_4	2.3	1.3	63	1.4	0.26	0.14	430
1b/Ph_2IBF_4	2.9	0.9	64	2.2	0.6	0.22	282
1a/Ph_3SBF_4	2.3	3.0		0.08	0.26	0.01	24
2a/Ph_2IBF_4	2.3	3.3	68	0.23	0.26	0.02	71
2b/Ph_3SBF_4	2.5	1.1	55	1.67	0.32	0.17	405
2c/Ph_3SBF_4	2.4		0	0	0.35	0	0
An/Ph_2IBF_4	2.6	16.2	58	0.15	0.34	0.01	34
TX	0.5	0.5	59	0.7	0.34	0.07	380
TX/Ph_2IBF_4	2.3	0.2	67	4.6	0.34	0.46	1080
IRGACURE 369	2.0	0.3	69	10.0	0.42	1.00	1850
IRGACURE 184	2.0	3.2	67	0.5	0.01	0.05	3800
BIPE	2.0	2.9	61	1.2	0.04	0.12	2400
BP	2.0	14.0		0.01	0.04	0.001	20
BP/DEOMA (3%)	5.0	0.3	60	0.7	0.04	0.07	1400

[a] Mass of initiator.

Table VI. Comparison of the Photopolymerization of Epoxyacrylate/HDDA = 3/2 (w/w) Initiated by Different Photoinitiators at Polychromatic Exposure (Laminate, d = 20 μm, HLS 210 UH Hoya-Schott, $[R_nXBF_4]$ = 0.05 mol/L)

initiator	m_i[a] (%)	t_i (s)	U_{max} (%)	r_p^{max} (mol/L·s)	$r_{p,rel}^{max}$
Ph_2IBF_4	1.8	0.5	57	2.2	0.09
1a/Ph_2IBF_4	2.3	0.2	64	6.3	0.28
2a/Ph_2IBF_4	2.3	0.4	61	3.1	0.12
2b/Ph_3SBF_4	2.5	0.3	67	6.0	0.24
TX	0.5	0.2	62	1.7	0.07
TX/Ph_2IBF_4	2.3	0.2	70	12.0	0.48
IRGACURE 369	2.0	0.1	72	25.0	1.00
IRGACURE 184	2.0	0.3	67	8.3	0.33
BP	2.0	1.6	67	0.6	0.02
BP/DEOMA (3%)	5.0	0.2	67	4.4	0.18

[a] Mass of initiator.

pletely different reaction pathway from the bimolecular electron transfer which is known for the other 1,4-dihydropyridine compounds.[10] As a hint, such types of 1,4-dihydropyridine derivatives (also with a substituent in the 4-position) are the only ones which are unstable in the presence of iodonium salt in the dark. Therefore, we assume the formation of a complex of **2b** with onium salts, as it is also known as an intermediate product for the thermal reaction of onium salts with amines. In the case of the iodonium salt this complex is very reactive. Due to its lower reduction potential and/or a sterical hindrance (three phenyl groups instead of two), in the case of the sulfonium salt the formation of products is very slow. This complex is stable in the dark but appears to be very reactive toward a photochemical redox reaction. Therefore, the bimolecular photoelectron transfer is bypassed by a more effective monomolecular reaction pathway.

In contrast to the MMA solution, the initiators based on α-cleavage are significantly more efficient than 1/Ph_2IBF_4 combinations. But because of the unfavorable absorption of IRGACURE 184 and BIPE with respect to the irradiation mode, only IRGACURE 369 having a sufficiently long wavelength absorption at λ = 365 nm can transform this advantage in a high polymerization rate r_p.

There is no change in the general conclusions if polychromatic light is used (Table VI). It is a matter of course that the relative polymerization rate of IRGACURE 184 compared to IRGACURE 369 is increased, because of its higher absorption at the emission line λ = 313 nm. The relative value $r_{p,rel}^{max}$ of **1a**/Ph_2IBF_4 is also increased to almost 30% of IRGACURE 369. This is due to the direct photolysis of the iodonium salt at λ = 313 nm where **1a** possesses an absorption gap.

Influence of Oxygen. In contrast to the initiators functioning through α-cleavage, it is an important feature of the 1/onium salt systems that there is no polymerization in the presence of oxygen, i.e., in the absence of a second polyethylene film. This is an astonishing fact, because in the laminate the inhibition time t_i necessary for the consumption of the oxygen is lower or almost the same compared to some other initiators which work in the presence of air (e.g., compare the values for 1/Ph_2IBF_4 in Table VI with the values of IRGACURE 369 or benzophenone (BP)/diethanolmethylamine (DEOMA) in Table V).

Because the lifetime of the T_1 state of **1a** in the bulk monomer is only little influenced by air (τ_0^t = 480 ns (air), τ_0^t = 580 ns (N_2)), the oxygen quenching of the T_1 state cannot be responsible for this behavior. Besides, as discussed above, the T_1 state contributes to the initiation mechanism to a smaller extent.

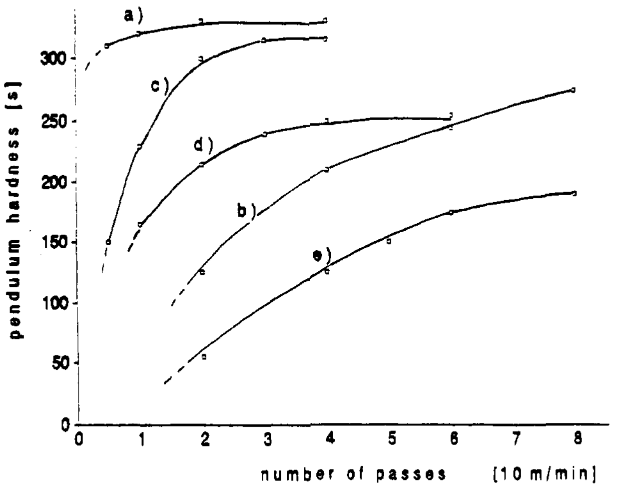


Figure 7. Dependence of the pendulum hardness on the number of passes through a UV-curing line (IST Strahlentechnik GmbH, Nürtingen), 80 W/cm², 10 m/min, photopolymer film (d=50μm) epoxyacrylate/HDDA = 3/2 (w/w) and different initiators: (a) IRGACURE 369 2% (air), (b) benzophenone/methyldiethanolamine 5% (air), (c–e) **1a** (0.015 mol/L)/Ph_2IBF with (c) 0.07, (d) 0.03, and (e) 0.007 mol/L, exclusion of air by a polyethylene film.

Although there is no complete explanation for the strong influence of oxygen on the onium salt systems, the following significant differences to the initiators based on α-cleavage should be taken into account:

(1) Oxygen is consumed by noninitiating radicals derived from 1 (Scheme II) already within the initiation mechanism.

(2) The phenyl radical gives no direct reaction with oxygen because of the high rate constant of the addition to the monomer k_{add} = 1.8 × 10⁸ L/mol·s (eq 7).

(3) It is well-known that oxidizable compounds, such as tertiary amines, undergo an effective chain process to consume oxygen (eqs 5 and 6). On the contrary, the highly reducible iodonium salt should interrupt such a radical chain reaction by the oxidation of the intermediate radicals (eq 7). The phenyl radical generated can enter the chain

$$ROO^{\bullet} + R'H \rightarrow ROOH + R'^{\bullet} \tag{5}$$

$$R'^{\bullet} + O_2 \rightarrow R'OO^{\bullet} \tag{6}$$

$$R'^{\bullet} + Ph_2I^+ \rightarrow R'^+ + PhI + Ph^{\bullet} \tag{7}$$

mechanism again only after two slow diffusion steps in the bulk monomer (eqs 8 and 9). The experimental results

$$Ph^{\bullet} + M \rightarrow PhM^{\bullet} \tag{8}$$

$$PhM^{\bullet} + O_2 \rightarrow PhMOO^{\bullet} \tag{9}$$

show that this more complex chain reaction can be as fast as the direct one to consume the oxygen dissolved within the monomer of the laminate. But this mechanism cannot compete with the diffusion of oxygen. Then, the lowering of the initial oxygen concentration $[O_2]_0 \simeq 0.001$ mol/L to the stationary oxygen concentration of $[O_2]_{st} \simeq 5 \times 10^{-6}$ mol/L[21] necessary for the polymerization is not achieved.

Hardness Measurements. Hardening data determined by exposure in an industrial curing line for 50-μm films of the above-discussed photopolymers are given in Figure 7. In all cases the wavelength emitted at λ = 313 nm, which would cause an efficient direct photolysis of the iodonium salt, has been excluded by a glass filter. Thus, the polymerization will be initiated only by radicals resulting from the electron transfer between the decahydroacridine-1,8-dione (1) and the onium salt.

As can be seen from Figure 7, the results in the industrial line correspond to that of the real-time IR measurements. With 1/Ph_2IBF_4 combinations the hardening time strongly depends on the coinitiator concentration. At high concentrations near the maximum solubility, the hardening efficiency becomes close to that of the initiator IRGACURE 369, which has been found to be the best initiator for this purpose.[22] Again, the above combinations with iodonium salt do not harden the multifunctional acrylates in the presence of air. Then, the hardness of the waxlike films are not measurable by the pendulum equipment.

4. Conclusions

Combinations of decahydroacridine-1,8-diones and diaryliodonium salts are effective photoinitiators for the radical polymerization. Because of changes in the initiation mechanism, the choice of the monomer and the initiator concentrations strongly influences the relative efficiency if compared with other photoinitiators. The decahydroacridine-1,8-dione/onium salt system works best in nonpolar methacrylic monomers. But importantly, in the commonly used multifunctional acrylic monomers the initiator IRGACURE 369 and the combination thioxanthone/iodonium salt have significant higher polymerization rates. Additional drawbacks of the combination decahydroacridine-1,8-dione/iodonium salt are the strong influence of oxygen and the low solubility of the sensitizer (maximum concentration of about 0.015 mol/L, 0.5%).

Acknowledgment. S.U. is thankful for a grant from the Foundation pour l'École Nationale Supérieure de Chimie, Mulhouse, France.

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