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Cationic photopolymerization of 1,3-di(9-carbazolyl)-2-propanol glycidyl ether

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Abstract An absorbance probe method was used for the investigation of photolysis of cationic photoinitiators. The rates of the photolysis of diphenyliodonium hexafluorophosphate (*DPIH*), diphenyliodonium tetrafluoroborate (*DPIB*), di(*tert*-butylphenyl)iodonium tetrafluoroborate (*DTIB*), di(*tert*-butylphenyl)iodonium bromate (*DTIBr*), triphenylsulfonium hexafluorophosphate (*TPS*) and cyclopropyldiphenylsulfonium tetrafluoroborate (*CPS*) were studied in the presence of acid indicator quinaldine red (*QR*) in acetonitrile. Diphenyliodonium hexafluorophosphate and triphenylsulfonium hexafluorophosphate showed the highest photolysis rate. Photopolymerization of 1,3-di(9-carbazolyl)-2-propanol glycidyl ether (*DCPGE*) initiated with the iodonium and sulfonium salts in bulk and in solution was studied. It was established that the highest initial rate of polymerization is characteristic of *DCPGE* photopolymerization initiated with *DPIH* and *TPS* in bulk. The oligomers of *DCPGE* of number average molecular weight ($\overline{M_n}$) ranging from 710 to 1220 were obtained in these reactions in bulk and those with $\overline{M_n}$ ranging from 1300 to 1600 were obtained in solution.

Keywords Polymerizations; Photochemistry; Oligomers; Carbazole; Onium salts.

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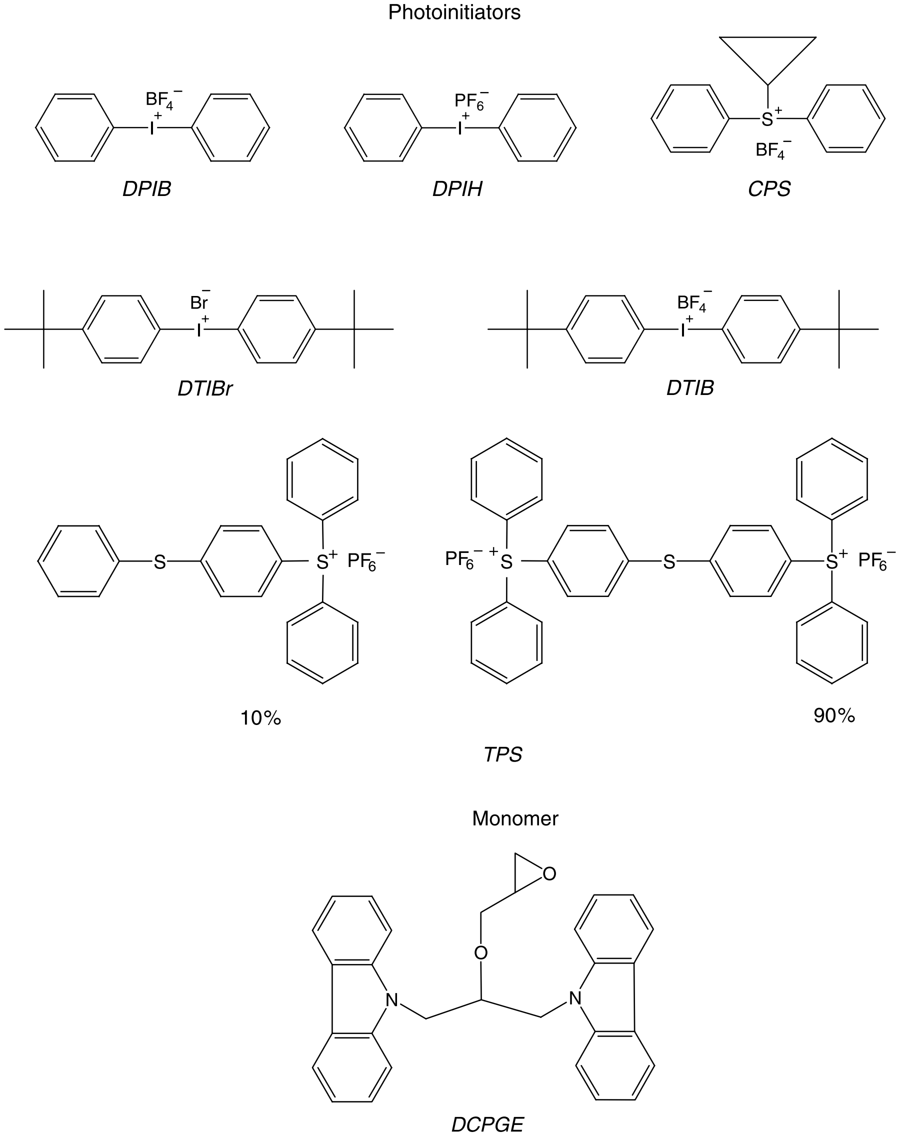
Introduction

Carbazole moiety is widely used as a building block in the design and synthesis of electroactive polymers and low molecular mass compounds. Some of carbazole-containing polymers and oligomers, like poly(9-vinylcarbazole), poly[9-(2,3-epoxypropylcarbazole)] have been widely studied as organic photoconductors [1]. Low-molar-mass carbazole compounds, which are stable in amorphous phase, are used in light-emitting diodes [2].

Cationic photopolymerization is a relatively new technique, which has attracted increasing attention in recent years due to the growth of applications, associated with synthesis of diaryliodonium, triarylsulfonium, and ferrocenium salts [3]. The photoinitiated cationic polymerization of epoxy monomers is currently of considerable scientific and commercial interest [4]. Preparation of the multilayer electrophotographic photoreceptors and electroluminescent devices is one of the potential fields of application of this method [5].

Recently the reaction between the *Brønsted* acid generated from photolysis of onium salt and the acid indicator quinaldine red was reported as a new method for the investigation of the rates of photoacid generation and their preliminary activity in the photopolymerization of epoxy monomers [6, 7].

In our previous papers we have reported the synthesis and cationic photopolymerization of epoxy

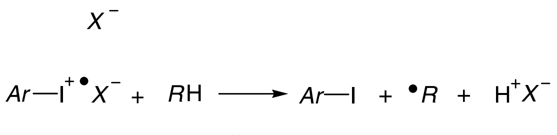


Scheme 1

monomers containing carbazole moiety [8, 9]. In this paper we report on the photolysis studies of photoinitiators, such as diphenyliodonium hexafluorophosphate (*DPIH*), diphenyliodonium tetrafluoroborate (*DPIB*), di(*tert*-butylphenyl)iodonium tetrafluoroborate (*DTIB*), di(*tert*-butylphenyl)iodonium bromate (*DTIBr*), triphenylsulfonium hexafluorophosphate (*TPS*) and cyclopropyldiphenylsulfonium tetrafluoroborate (*CPS*) (Scheme 1) in the presence of the acid indicator quinaldine red (*QR*) in acetonitrile. We also report on the cationic photopolymerization of 1,3-di(9-carbazolyl)-2-propanol glycidyl ether initiated with these initiators in bulk and in solution.

Results and discussion

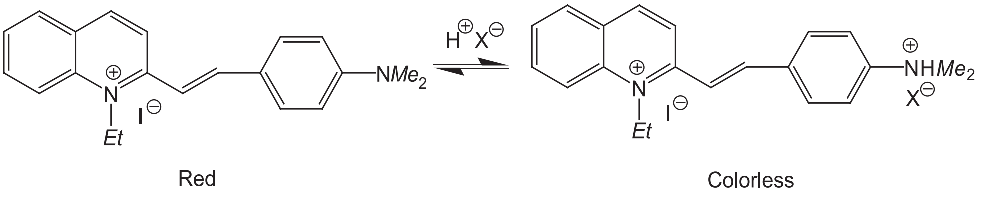
Among several very sensitive analytical methods to determine the rate of *Brønsted* acid generation on photolysis of iodonium salts (Scheme 2), investigation of the reactions, which occur in the system iodonium salt – quinaldine red (*QR*) under irradiation in



$$Ar-\underset{X^-}{\overset{+}{I}}-Ar' \xrightarrow{h\nu} Ar-I^{+\bullet}X^- + {}^{\bullet}Ar'$$

$$Ar-I^{+\bullet}X^- + RH \longrightarrow Ar-I + {}^{\bullet}R + H^+X^-$$

Scheme 2



Scheme 3

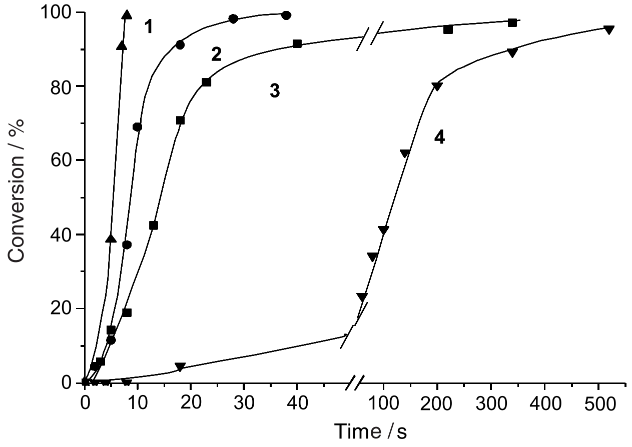


Fig. 1 *QR* conversion *versus* time curves for the photolysis of: *DPIH* (▲), *DTIB* (●), *DPIB* (■), DTIBr (▼) in acetonitrile

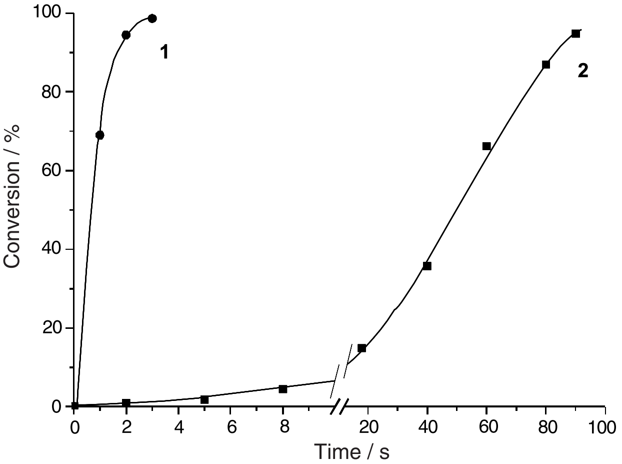


Fig. 2 *QR* conversion *versus* time curves for the photolysis of: *TPS* (●) and *CPS* (■) in acetonitrile

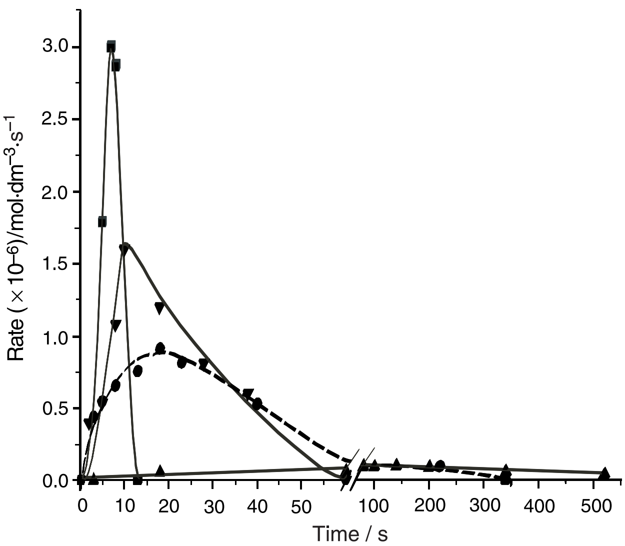


Fig. 3 Rate of acid generation *versus* irradiation time curves for the photolysis of *DPIH* (■), *DTIB* (▼), *DPIB* (●), and *DTIBr* (▲)

acetonitrile or ethanol is reported as the most effective one (Scheme 3) [7].

QR is an indicator with an absorption band maximum at 520 nm that is not observed for the protonated form (Scheme 3). When used in low concentrations, *QR* is essentially transparent below 350 nm where the iodonium salts absorb [10]. Several iodonium salts shown in Scheme 1 differing in anion were irradiated in acetonitrile and the bleaching of *QR* was observed measuring the absorption spectra after the different irradiation time. The results obtained are presented in Fig. 1.

It has been shown earlier that *QR* bleaching (conversion) rate depends on the dissociation constant of the acid released [10]. In comparison to BF_4^- anion of *DTIB* bromide anion of *DTIBr* is much more basic anion, therefore the acid release is a much slower in the presence of *DTIBr* salt (Fig. 1, curve 4). PF_6^- anion of *DPIH* is the least basic anion thus the corresponding acid is the strongest one (Fig. 1, curve 1).

Figure 2 shows *QR* bleaching results in the presence of the sulfonium salts. It is evident that *TPS* generates much stronger acid compared with *CPS*.

The data presented in Figs. 3 and 4 allow to compare the rates of acid release in the photolysis process of the different iodonium and sulfonium salts used in this work. The highest rate of acid release is characteristic of the photolysis of sulfonium salt *TPS*, while the lowest rate of acid release is observed for *CPS* and *DTIBr*.

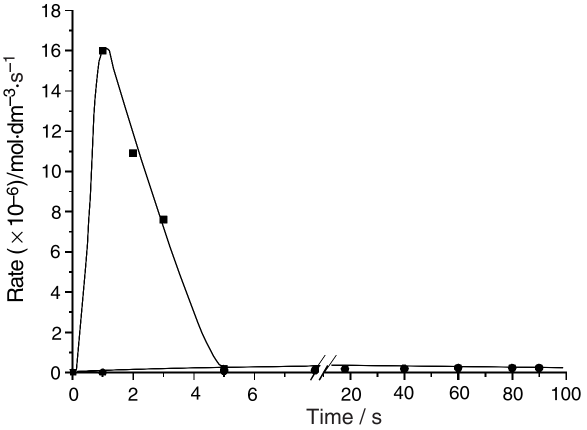


Fig. 4 Rate of acid generation *versus* irradiation time curves for the photolysis of *TPS* (■) and *CPS* (●)

DCPGE the structure of which is shown in Scheme 1 was chosen as a monomer in order to examine the activity of these photoinitiators in photopolymerization. We succeeded to prepare stable enough solid amorphous films of *DCPGE* pouring 15–20% solution of the monomer in dichloromethane onto a glass slide and drying the obtained layers first at the normal pressure then in vacuum.

The results of the cationic photopolymerization of *DCPGE* initiated with the different iodonium salts in bulk at room temperature are presented in Fig. 5 and summarized in Table 1. The highest initial rate of polymerization (R_p) with the value of $R_p = 19.2 \times 10^{-3}\,\mathrm{mol \cdot dm^{-3}\,s^{-1}}$ was observed for the photopolymerization of the monomer initiated with *DPIH* (Fig. 5, curve 1). *DTIB* initiated photopolymerization of *DCPGE* showed the lowest $R_p = 4.9 \times 10^{-3}\,\mathrm{mol \cdot dm^{-3}\,s^{-1}}$. However in all three cases very similar limit monomer conversion of 70–75% was reached. The results presented in Fig. 5 revealed different reactivity of the iodonium salts bearing the same cation and different anions. The efficiency of *DPIH* is higher than that of *DPIB* in these reactions. This indicates that the larger size and nucleophilicity of $\mathrm{PF_6}^-$ anion renders the iodonium cation more photosensitive [6].

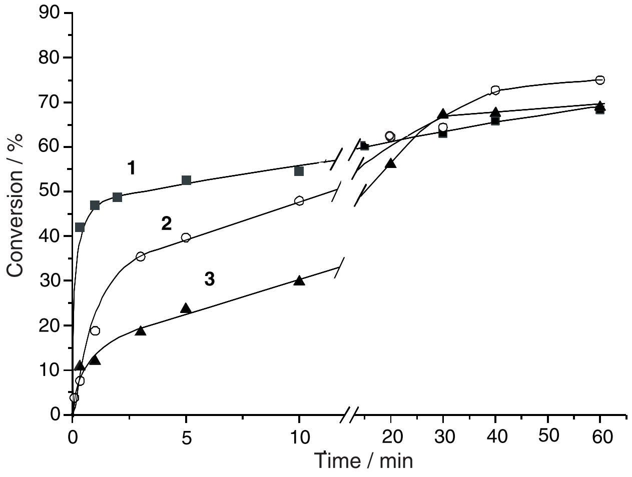


Fig. 5 Conversion *versus* time curves for the *DCPGE* photopolymerization in bulk initiated with: *DPIH* (■), *DPIB* (○), 3 – *DTIB* (▲). $[DPIH]_o = [DPIB]_o = [DTIB]_o = 3$ mol% monomer

Table 1 The data of *DCPGE* photopolymerization in bulk. $[\mathrm{I}]_o = 3$ mol% monomer

Photo-initiator	R_p[a] ($\times 10^{-3}$)/ $\mathrm{mol \cdot dm^{-3} \cdot s^{-1}}$	$\overline{M_n}$ / $\mathrm{g \cdot mol^{-1}}$	$\overline{M_w}$ / $\mathrm{g \cdot mol^{-1}}$	$\overline{M_w}/\overline{M_n}$
DPIH	19.2	711	1332	1.87
DPIB	7.7	1217	1276	1.05
DTIB	4.9	1212	1310	1.08
TPS	15.1	608	908	1.49
CPS	2.7	1205	1264	1.05

[a] After 60 s irradiation

The effect of the concentration of *DPIH* on the monomer conversion and the rate of photopolymerization of *DCPGE* is characterized by the data presented in Fig. 6. The increase of concentration of the photoinitiator leads to the increase of the rate of the photopolymerization and the degree of conversion. High initial reaction rate and monomer conversion of 60–70% (after 30 min irradiation) are observed for these photopolymerizations at high initial concentra-

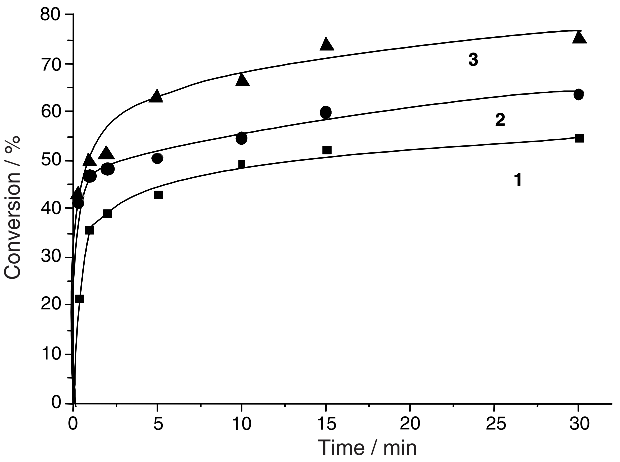


Fig. 6 Conversion *versus* time curves for *DCPGE* photopolymerization intiated with *DPIH* in bulk: 1 mol% (■); 3 mol% (●); 5 mol% monomer (▲)

tions of initiator (3–5 mol% monomer). When low initial initiator concentration is used the rate of polymerization is slightly lower and the termination of the reaction occurs at *ca.* 50% conversion of the monomer (Fig. 6, curve 1).

Using the data presented in Fig. 6 the initiator exponent was calculated. *DPIH* exponent of 1.6 for *DCPGE* photopolymerization was obtained.

Photopolymerization of *DCPGE* intiated with the different sulfonium salts in bulk was also studied. The results obtained are presented in Fig. 8 and Table 1. The rate of *DCPGE* photopolymerization initiated with *TPS* is much higher than that of photopolymerization initiated with *CPS*. Photopolymerization of *DCPGE* with *TPS* occurs explosively and after 10 min irradiation *ca.* 100% conversion of the monomer is reached. Only 48% degree of conversion after 60 min irradiation is achieved in the *DCPGE* photopolymerization using *CPS* as an initiator.

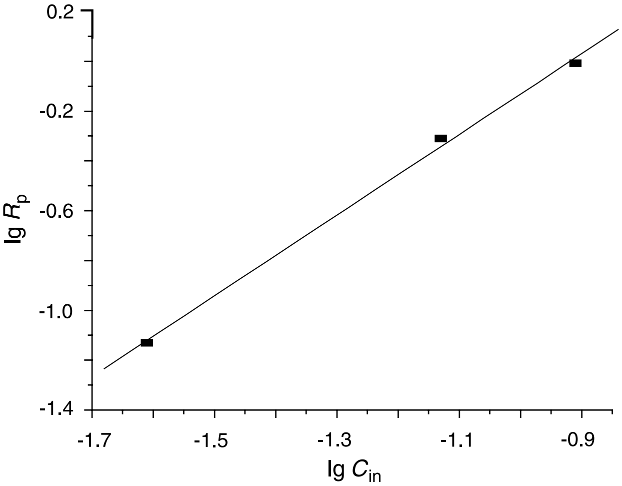


Fig. 7 lg R_p *versus lg* C_{in} plot for the photopolymerization of *DCPGE* initiated with *DPIH*. (C_{in} – concentration of initiator)

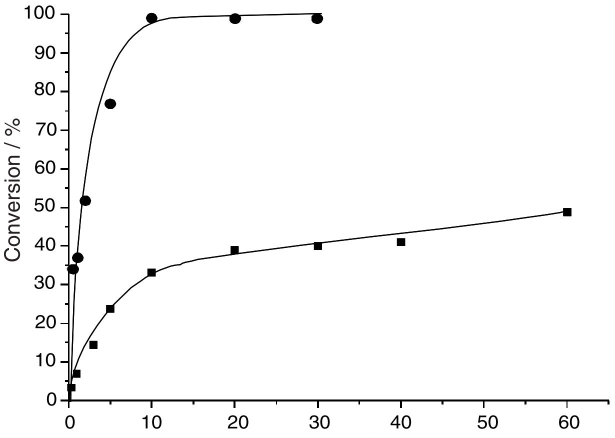


Fig. 8 Conversion *versus* time curves for *DCPGE* photopolymerization intiated with: *CPS* (■), *TPS* (●). $[CPS]_o = [TPS]_o = 3$ mol% monomer

Table 1 summarizes the characteristics of the oligomers obtained in the photopolymerizations of *DCPGE* with the different photoinitiators in bulk. The number average molecular weights of the products of photopolymerization range from 710 to 1220. The oligomers of narrow polidispersity index are obtained in these reactions.

The comparison of the results of *DCPGE* photopolymerizations initiated with various iodonium and sulfonium salts revealed that *TPS* and *DPIH* are the most effective photoinitiators for these reactions (Table 1). The rate of photopolymerization of *DCPGE* initiated with *DPIH* in the initial period is very high ($R_p = 19.2 \times 10^{-3}\,\mathrm{mol \cdot dm^{-3}\,s^{-1}}$), however after some time *DCPGE* photopolymerization slows down considerably and finally only *ca.* 70% monomer conversion is reached after 60 min irradiation. In case of *TPS ca.* 100% limit conversion is achieved. However when *TPS* is used as a photoinitiator the oligomers of the lowest degree of polymerization are obtained.

We have also studied *DCPGE* photopolymerization in 1,2-dichloroethane solution initiated with different initiators. The data obtained are presented in Fig. 9 and Table 2. The highest initial rate ($R_p = 2.22 \times 10^{-3}\,\mathrm{mol \cdot dm^{-3} \cdot s^{-1}}$) and the

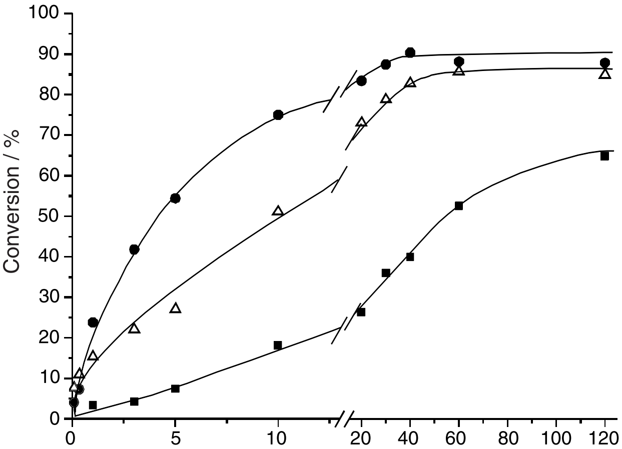


Fig. 9 Conversion *versus* time curves for *DCPGE* photopolymerization in 1,2-dichloroethane at 25°C initiated with: *CPS* (■); *DPIB* (△); *DTIB* (●). $[CPS]_o = [DPIB]_o = [DTIB]_o = 3$ mol% monomer

Table 2 Photopolymerization of *DCPGE* in solution

Solvent	Initiator	Temperature/°C	R_p[a] ($\times 10^{-3}$)/ $\mathrm{mol \cdot dm^{-3} \cdot s^{-1}}$	$\overline{M_n}$ / $\mathrm{g \cdot mol^{-1}}$	$\overline{M_w}$ / $\mathrm{g \cdot mol^{-1}}$	$\overline{M_w}/\overline{M_n}$
1,2-Dichloroetane	CPS	25	0.32	1261	1257	1.02
	DTIB	25	2.22	1360	1516	1.11
	DPIB	25	1.43	1458	1662	1.14
Toluene	*DTIB*	50	0.69	1590	1921	1.21
	DTIB	75	2.03	1551	1833	1.18

[a] After 60 s irradiation

highest degree of conversion of *ca.* 87% were observed for *DCPGE* photopolymerization initiated with *DTIB*. *DCPGE* photopolymerization with *CPS* showed the lowest polymerization rate ($R_p = 0.32 \times 10^{-3}\,\mathrm{mol \cdot dm^{-3} \cdot s^{-1}}$) and the lowest monomer conversion. Inhibition period of 30 s and 65% degree of conversion (after 120 min irradiation) were observed for photopolymerization of *DCPGE* with *CPS*.

It was of interest to study the effect of solvent nature on *DCPGE* photopolymerization. For this reason we have also studied *DCPGE* photopolymerization in toluene. Since the system showed poor solubility in toluene at room temperature, the *DCPGE* photopolymerization in toluene was carried out at 50 and 75°C (Fig. 10 and Table 2). The increase of the temperature increased the rate of photopolymerization of the monomer and the limit degree of conversion. The initial rate of $0.69 \times 10^{-3}\,\mathrm{mol \cdot dm^{-3} \cdot s^{-1}}$ was observed for the photopolymerization of *DCPGE* at 50°C, while $R_p = 2.03 \times 10^{-3}\,\mathrm{mol \cdot dm^{-3} \cdot s^{-1}}$ was characteristic of photopolymerization of the monomer at 75°C. The degree of conversion of 93% was reached in the reaction of *DCPGE* in toluene at 75°C. Table 2 also shows that oligomers of the highest degree of polymerization of 4–5 are obtained in *DCPGE* photopolymerization in toluene.

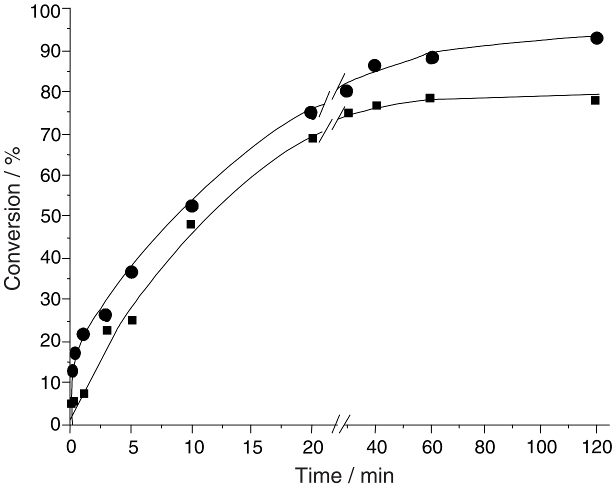


Fig. 10 Conversion *versus* time curves for the photopolymerization of *DCPGE* in toluene at the different temperatures: 50°C (■); 75°C (●). $[DTIB]_o = 3$ mol% monomer

In conclusion, we used an absorbance probe method for the investigation of photolysis of a series of cationic photoinitiators employing quinaldine red as an acid indicator and acetonitrile as a solvent. *TPS* and *DPIH* showed the highest rate of acid release in the group of photoinitiators used in this work. The rate of photopolymerization of *DCPGE* initiated with *TPS* and *DPIH* in bulk was found to be much higher as compared to that initiated with *DPIB*, *DTIB*, or *CPS*. The data of reactivity of the iodonium and sulfonium salts used as initiators for *DCPGE* photopolymerization in solution correspond to those established in the photolysis studies of the salts. It can be concluded that the method used for the investigation of rates of photoacid generation enables to predict the activity of the photoinitiator. The photopolymerizations of *DCPGE* proceeds rapidly, affording oligomers of number average molecular weight from 710 to 1220 for the reactions in bulk and that from 1300 to 1600 for the polymerizations in solution. The nature of solvent as well as the temperature influence the results of *DCPGE* photopolymerization. Oligomers of the highest degree of polymerization were obtained using toluene as a solvent.

Experimental

Quinaldine red (*QR*) was used as received from "Aldrich". Initiators: diphenyliodonium tetrafluoroborate (*DPIB*), di(*tert*-butylphenyl)iodonium tetrafluoroborate (*DTIB*), and di(*tert*-butylphenyl)iodonium bromate (*DTIBr*) were synthesized and purified as described before [11]. Diphenyliodonium hexafluorophosphate (*DPIH*), triphenylsulfonium hexafluorophosphate (*TPS*), and cyclopropyldiphenylsulfonium tetrafluoroborate (*CPS*) were used as received from "Aldrich". 1,3-Di(9-carbazolyl)-2-propanol glycidyl ether (*DCPGE*) was synthesized according to Ref. [12]. The solvents were purified by the standard procedures [13].

Photopolymerization

The photopolymerizations of *DCPGE* were carried out in air atmosphere either in solution (concentration of the monomer was 25%) containing initiator at different temperatures in quartz tubes or in bulk *i.e.*, in thin films (thickness 10–15 μm). For the preparation of thin film solutions of monomer, initiator, and solvent (dichloromethane) were poured on a glass slide and dried. Initial concentration of the monomer was 20%. Irradiation of the sample was carried out with a 240 W medium pressure mercury lamp (Model DRT – 240, Russia) set at a distance of 6 cm. The light intensity on the sample was about 15 mW cm^{-2} (measured with a NEO-Lab UV measuring units). Conversion of the monomer, number average molecular weight, polydispersity index, and number average degree of polymerization of the obtained oligomers were measured by GPC after irradiation of the samples for various periods of time. All experiments were repeated three times and average values for the obtained results were calculated.

Measurements

The rate of acid release was measured by the following procedure. Solutions of iodonium and sulfonium salts containing ~10 ppm of quinaldine red (*QR*) in acetonitrile were prepared ($7.8 \times 10^{-3}\,M$). The solutions were irradiated and the absorbance of *QR* at 520 nm was measured using spectrophotometer "Cary 19". Conversion was calculated from the following Eq. (1), where A_o was the absorbance at the beginning and A_n was the absorbance after irradiation time t [6]:

$$\text{Conversion} = (1 - A_n/A_o) \times 100\% \qquad (1)$$

All experiments were repeated three times and average values for the obtained results were calculated.

Gel permeation chromatography (GPC) was carried out on the modified liquid chromatograph Milichrom (Chernogolovka, Russia) using a special column packed with "Lichrispher Si 100" (1,4-dioxan was used as an eluent at flow rate $200\,\text{mm}^3 \cdot \text{min}^{-1}$). All data are referenced to narrow polystyrene standards.

Acknowledgements

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