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Journal of Photochemistry and Photobiology A: Chemistry 157 (2003) 117–123

Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Cationic photopolymerization of carbazolyl-containing vinyl ethers

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Received 29 October 2002; received in revised form 27 January 2003; accepted 29 January 2003

Abstract

Photopolymerizations of 2-(9-carbazolyl) ethyl vinyl ether (CEVE) and (9-carbazolyl) methoxy ethyl vinyl ether (CMEVE) initiated with diphenyl iodonium tetrafluoroborate (DPIT), di(*tert*-butylphenyl)iodonium tetrafluoroborate (BPIT), cyclopropyldiphenylsulfonium tetrafluoroborate (CPS) and (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5,6-η)-(1-methyl ethyl) benzene]-iron (+)-hexafluorophosphate(-1) (I261) were studied. It was established that the efficiency of the iodonium salts and iron–arene complex is much higher in the cationic photopolymerization of the monomers than that of the sulfonium salt. CMEVE showed higher reactivity in cationic photopolymerization than CEVE. Higher degrees of polymerization were established for the products CEVE photopolymerization compared with those of the products of CMEVE reaction. The influence of the temperature on the rate of CEVE and CMEVE photopolymerization, molecular weight and conversion limit is discussed.

Keywords: Photopolymerization; Vinyl ether; Carbazole; Iodonium salt; Sulfonium salt; Iron–arene complex

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1. Introduction

Because of the development of efficient photoinitiators, cationic photopolymerization recently became a candidate of new UV curing system, which is available by the polymerization of epoxides or vinyl ether compounds. It was reported [1,2] that several onium compounds such as diaryliodonium and sulfonium salts, as well iron–arene complexes serve as highly efficient cationic photoinitiators. The mechanism of initiation through “onium” salt photolysis was first investigated by Crivello and Lam [3]. However the cationic photopolymerization of epoxy monomers initiated by these salts was found to occur slower than the radical photopolymerization of acrylates. On the other hand, vinyl ethers are among the most reactive monomers known readily to polymerize by cationic mechanism in the presence of suitable “onium” salts photoinitiators [4]. These systems were extensively studied by several authors [5,6].

Interest in vinyl polymers with pedant aromatic amino groups is high from both scientific and a technical point of view due to their photoconductive properties. The classical example of such polymers is poly(*N*-vinyl carbazole). Its synthesis and properties have been extensively studied [7]. Many other polymers containing carbazolyl groups as pendants have been widely used as organic photoconductors [8].

In our previous works [9,10], it was shown that carbazolyl-containing epoxides undergo facile photoinitiated cationic polymerization in the presence of onium salts and iron–arene complex.

In this paper, we report on the cationic photopolymerization of two carbazolyl-containing vinyl ether monomers: 2-(9-carbazolyl) ethyl vinyl ether (CEVE) and (9-carbazolyl) methoxy ethyl vinyl ether (CMEVE) initiated by diaryliodonium, sulfonium salts and iron–arene complex in solution.

2. Experimental

2.1. Materials

Paraformaldehyde and 2-chloroethylvinyl ether were used as received from Aldrich. 2-(9-Carbazolyl) ethyl vinyl ether (CEVE) was synthesized according to the reported procedure [11].

2.1.1. 2-(9-Carbazolyl) ethyl vinyl ether (CEVE)

About 0.04 mol (14.1 ml) of 2-chloroethylvinyl ether and 0.04 mol (6.72 g) KOH were added to 0.02 mol (10.02 g) of carbazole dissolved in 45 ml of ethyl methyl ketone. The reaction mixture was stirred and heated to reflux. 3.36 g of KOH was added to the reaction mixture after a period of 8 h. Then the mixture was stirred and heated to reflux for an additional 1 h.. After cooling, the inorganic residue was

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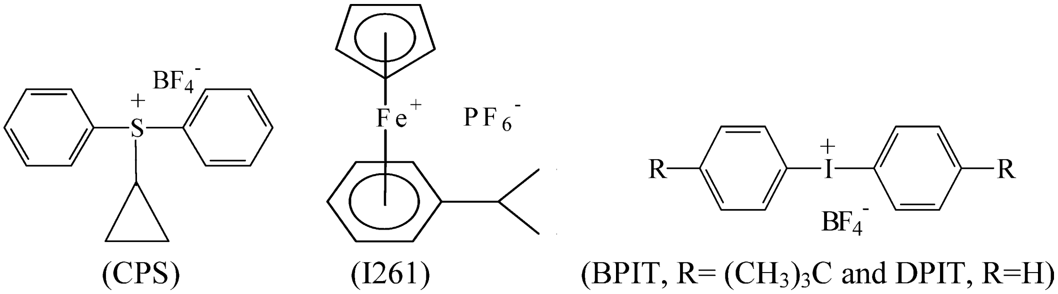
doi:10.1016/S1010-6030(03)00076-5



Scheme 1.

filtered off. The product was re-crystallized from isopropyl alcohol. Yield of CEVE 79.89%; mp 89 °C.

^{1}H NMR = 3.9–4.1 (m, 4H, CH_2=, –OCH_2–), 4.4–4.6 (t, 2H, –CH_2N), 6.35–6.45 (quart, 1H, –CH=), 7.1–7.3 (m, 2H, carbazole), 7.32–7.51 (m, 4H, carbazole), 7.98–8.17 (d, 2H, carbazole).

Elemental analysis for $C_{16}H_{15}N_1O_1$ (248): calculated: C 77.42%; H 6.04%; N 5.64%; O 6.45%; found: C 76.7%; H 5.7%; N 5.57%.

2.1.2. *9-Hydroxymethyl carbazole (HMC)*

Carbazole (0.1 mol) dissolved in 50 ml of ethyl alcohol was treated with 0.2 mol of paraformaldehyde and 9 g of KOH. The reaction mixture was stirred for 6 h at 80 °C. After cooling, the precipitate was filtered off. The product was re-crystallized twice from benzene. Yield of HMC 56.1%; mp 129 °C.

2.1.3. *(9-Carbazolyl) methoxy ethyl vinyl ether (CMEVE)*

About 0.015 mol of 2-chloroethylvinyl ether, 0.3 g K_2CO_3 and 1.4 g KOH were added to 0.015 mol of HMC dissolved in 5 ml of ethyl methyl ketone. The reaction mixture was stirred and heated to reflux. A 1.4 g of KOH was added to the reaction mixture after 1.5 h. Then the mixture was stirred and heated to reflux for an additional 1 h. The reaction mixture was separated by column chromatography using the mixture of dichloromethane and n-hexane (1:1) as an eluent. The product was re-crystallized from diethyl ether. Yield of CMEVE 41.2%, mp 83 °C.

^{1}H NMR ($CDCl_3$, δ, ppm): 3.9–4.13 (m, 6H, CH_2=, –OCH_2–, CH_2O–); 4.49–4.53 (t, 2H, O–CH_2–N); 6.32–6.40 (quart, 1H, –CH=); 7.19–7.25 (m, 4H, carbazole); 7.41–7.47 (m, 2H, carbazole); 8.05–8.08 (d, 2H, carbazole).

Elemental analysis for C_{17} H_{17} N_1 O_2 (267.26): calculated: C 76.37%; H 6.42%; N 5.24%; O 11.97%; found: C 76.61%; H 6.37%; N 5.40%.

Diphenyl iodonium tetrafluoroborate (DPIT), di(*tert*-butylphenyl)iodonium tetrafluoroborate (BPIT) were synthesized and purified as described elsewhere [12]. Cyclopropyldiphenylsulfonium tetrafluoroborate (CPS) and (η^5-2, 4-cyclopentadien-1-yl)[1,2,3,4,5,6-η)-(1-methyl ethyl)benzene]-iron (+)-hexafluorophosphate(-1) (I261) were purchased from Aldrich and used without further purification. The formulas of the iodonium salts, the sulfonium salt and the iron–arene complex used as photoinitiators are presented in Scheme 1.

The solvents: 1,2-dichloroethane, toluene, tetrahydrofuran and 1,4-dioxan were purified by the standard procedures [13]. Ethyl methyl ketone (“Lachema”) was used as received.

2.2. *Photopolymerization*

The photopolymerization of the monomers was carried out in air atmosphere in 1,2-dichloroethane solution in the presence of various photoinitiators in quartz tube at different temperatures. The initial concentration of a monomer was 1 mol/l. The UV source was a 240 W medium pressure mercury lamp (Model DRT-240, Russia) set at a distance of 6 cm.

2.3. *Measurements*

Conversion of the monomers, 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. GPC was carried out on the liquid chromatograph “Milichrom” (Chernogolovka, Russia) using a special column packed with Silasorb. 1,4-Dioxan was used as eluent.

The parameter $R_p/[M_o]$ was determined from the slope of the conversion versus exposure time curves according to equation:

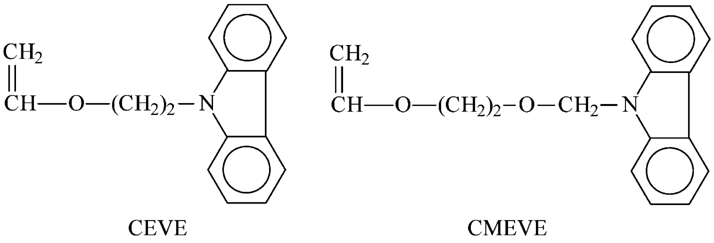
$$\frac{R_p}{[M_o]} = \frac{[\text{conversion}]_{t_2} - [\text{conversion}]_{t_1}}{t_2 - t_1}$$

where R_p and $[M_o]$ are the rate of polymerization and the initial concentration of a monomer, respectively. The conversions were determined directly from the curves at the exposure times t_1 and t_2.

3. Results and discussion

3.1. *Synthesis*

The structures of the monomers studied are shown in Scheme 2. CEVE was synthesized by the earlier described procedure [11].



Scheme 2. Vinyl ethers used as monomers.

3.2. *CEVE CMEVE*

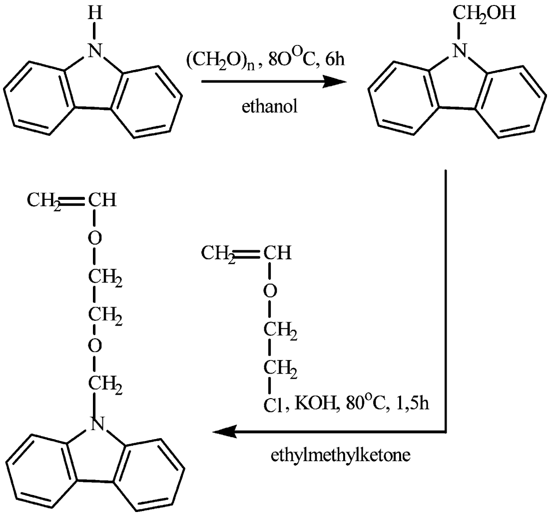
CMEVE was prepared by the synthetic route involving the hydroxyalkylation of carbazole and subsequent nucleophilic substitution reaction of obtained 9-hydroxymethyl carbazole with 2-chloroethylvinyl ether (Scheme 3).

3.3. *Photopolymerization*

The carbazolyl-containing vinyl ether monomers were polymerized using iodonium, sulfonium salts and iron–arene complex.

The results for CEVE photopolymerization initiated with DPIT, BPIT, CPS and I261 are plotted as irradiation time versus conversion curves in Fig. 1 and the data are summarized in Table 1. The induction period is characteristic of CEVE photopolymerization at the conditions described in the legend of Fig. 1. The longest induction period, which lasts ca. 40 min, was observed for the photopolymerization of CEVE initiated with CPS. CEVE photopolymerizations initiated with the diaryliodonium salts and the iron–arene complex start after 5–10 min irradiation.

Table 1 presents $R_p/[M_o]$ values which were obtained from the slopes of the individual curves. It is evident that the highest rate is characteristic of CEVE photopolymerization initiated with DPIT. Slightly lower polymerization rate is observed for the photopolymerization of CEVE with BPIT, however the highest degree of conversion ca. 75% is reached in this case (Fig. 1, curve 1). When the sulfonium salt is used as a photoinitiator CEVE photopolymerization occurs with the lowest polymerization rate, however after longer irradiation almost the same degree of conversion is reached (Fig. 1, curve 4).



Scheme 3.

The data presented in Table 1 show that CEVE photopolymerization with BPIT gives the highest degree of polymerization ($\overline{DP}$) of the resulting products ($\overline{DP} \sim 43$). It can be assumed that the diaryliodonium salts are the most effective photoinitiators for CEVE photopolymerization among those studied in this work.

In order to examine the influence of initiator concentration on the polymerization rate and the monomer conversion reached photopolymerizations of CEVE initiated with various amounts of BPIT were carried out (Fig. 2). As it is seen from Fig. 2 the rate of the reaction in the initial stage slightly increases with the increase of BPIT concentration. However the complete termination after reaching ca. 70% conversion is observed in all the photopolymerizations. The value of the initiator exponent was calculated using these data. The BPIT exponent of 0.62 was established.

Conversion versus time curves for CMEVE photopolymerization initiated with various initiators are presented in Fig. 3.

It is evident that all the initiators used, iodonium, sulfonium salts and iron–arene complex, initiate photopolymerization of CMEVE. BPIT, DPIT and I261 act as efficient cationic photoinitiators of CMEVE photopolymerization. CMEVE photopolymerization initiated with I261 showed the highest initial rate of polymerization. However, the degree of the monomer conversion (ca. 60%) observed for CMEVE photopolymerization with I261 was slightly lower than that reached in CMEVE photopolymerization with diaryliodonium salts. The limit conversion of approximately 70% was observed for these photopolymerizations. The induction period, which lasts 40 min, the lowest polymerization rate and low limit conversion of 45% are the characteristics of CMEVE photopolymerization initiated with the sulfonium salt. The data presented above show the different reactivities of iodonium and sulfonium salts containing the same borate anion in the photopolymerization reaction of CMEVE. The differences in polymerization

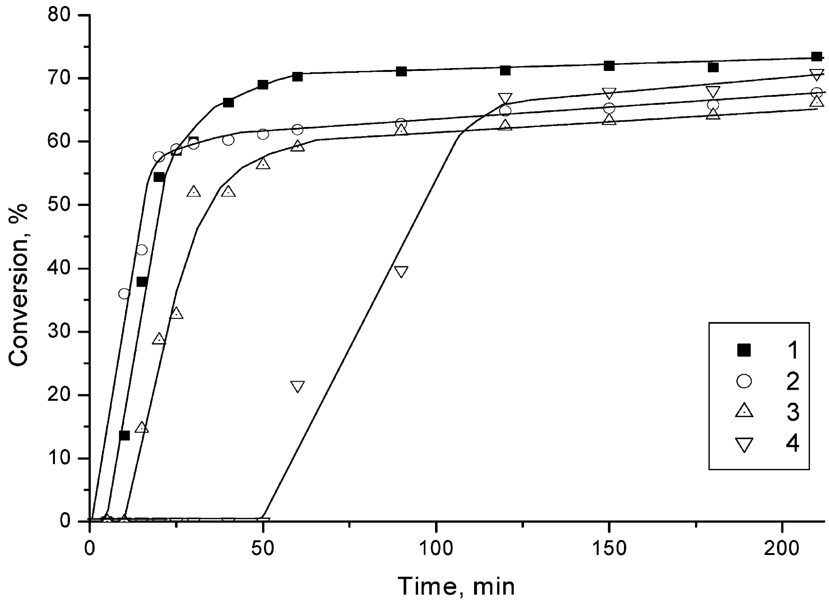


Fig. 1. Conversion vs. time curves for the photopolymerization of CEVE initiated with: 1, DPIT; 2, BPIT; 3, I261; 4, CPS at 30 °C. Initial concentration of initiator, 1 mol%/monomer, $[CEVE]_o = 1$ mol/l.

Table 1
Photopolymerization of CMEVE and CEVE initiated with different initiators

Monomer	Initiator	Temperature (°C)	Slope ($R_p/[M_o]$) (s^{-1})	$\overline{M_n}$	$\overline{M_w}$	$\overline{M_w}/\overline{M_n}$	$\overline{DP}$	Conversion (%)
CMEVE	BPIT	30	0.115	1475	4573	3.10	5	73.8
	DPIT	30	0.268	1285	4424	3.44	5	71.0
	I261	30	0.277	1075	1461	1.36	4	64.5
		60	0.006	592	649	1.09	2	45.4
	CPS	30	0.065	665	430	1.24	3	45.3
CEVE	BPIT	30	0.032	10186	17577	1.73	43	73.5
	DPIT	30	0.064	6513	12682	1.95	27	67.7
	I261	30	0.023	4876	9017	1.85	20	66.2
	CPS	30	0.016	5228	9111	1.74	22	70.8

$[CMEVE]_o = [CEVE]_o$=1 mol/l. Initial concentration of initiator—1 mol%/monomer. Irradiation time—210 min.

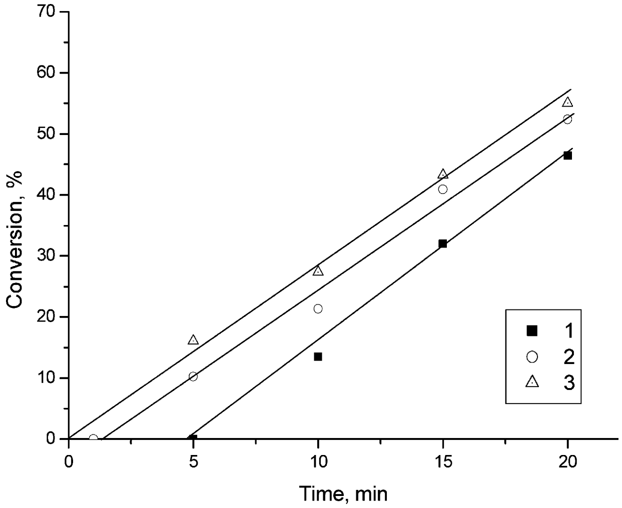


Fig. 2. Conversion vs. time curves for the photopolymerization of CEVE initiated with different amounts of BPIT at 30 °C. $[CEVE]_o = 1$ mol/l. The initial concentration of BPIT: 1–1; 2–2; 3–3 mol%/monomer.

rate and conversion values can be attributed to the different spectral sensitivity of onium salts and different quantum yield of acid generation [14].

Some characteristics of the polymers obtained by CMEVE photopolymerization initiated with various initiators are presented in Table 1. CMEVE photopolymerization initiated with diaryliodonium salts yields oligomers with the highest $\overline{M_n}$ and $\overline{DP}$. $\overline{DP}$ of CMEVE oligomers obtained with BPIT and DPIT is approximately 5. The highest polydispersity index was also established for these products.

Fig. 4 and Table 1 enable the comparison of the results of the photopolymerizations of CMEVE and CEVE monomers initiated with the iodonium, sulfonium salts and iron–arene complex. The comparison of the data obtained for both photopolymerizations revealed the higher reactivity of CMEVE in cationic photopolymerization. Much longer induction period, which lasts 10–40 min is characteristic of CEVE photopolymerization. The rate of CMEVE photopolymerization is higher than that of CEVE monomer. However very similar limit conversions of 65–70% are reached in the

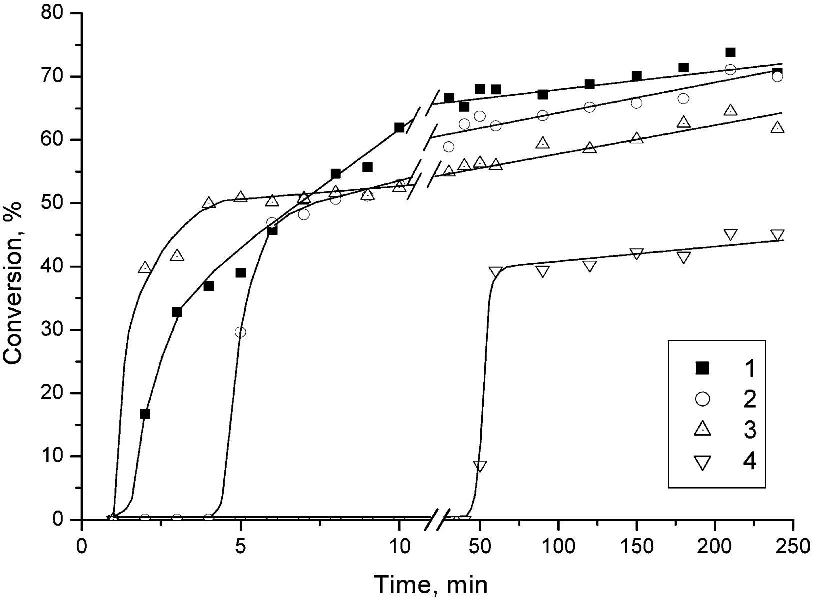


Fig. 3. Conversion vs. time curves for the photopolymerization of CMEVE in 1,2-dichloroethane solution initiated with: 1, BPIT; 2, DPIT; 3, I261; 4, CPS at 30 °C. $[\text{CMEVE}]_o = 1$ mol/l. Initial concentration of the initiators, 1 mol%/monomer.

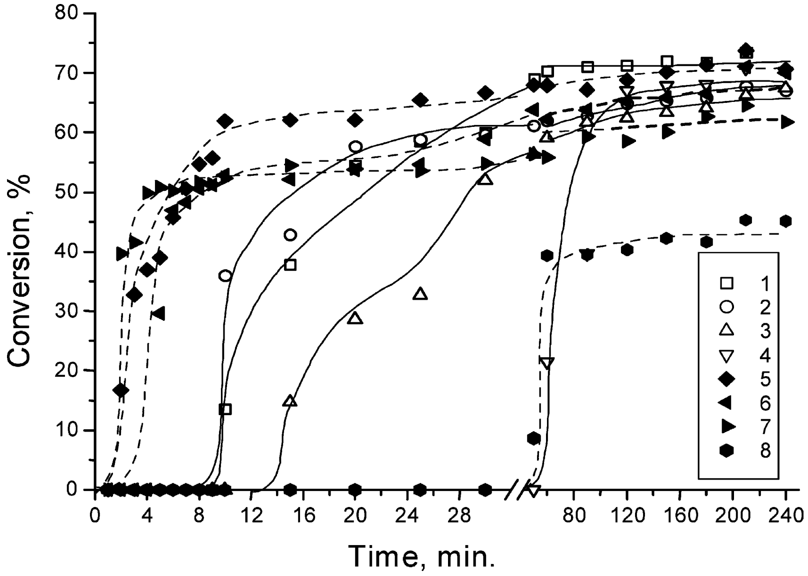


Fig. 4. Conversion vs. time curves for the photopolymerization of CMEVE (- - -) and CEVE (—) initiated with: 1,5: BPIT; 2,6: DPIT; 3,7: I261; 4,8: CPS at 30 °C. $[\text{CMEVE}]_o = [\text{CEVE}]_o = 1$ mol/l. Initial concentration of initiator, 1 mol%/monomer.

both CMEVE and CEVE photopolymerizations initiated with iodoniums salt and iron–arene complex. Higher reactivity of CMEVE can apparently be explained by the longer distance between carbazole and vinyl group. The increase of the length of the spacer increases both the flexibility of the monomer and freedom of motion in the reaction medium.

The effect of temperature was further investigated to determine its influence on the rate of reaction and the conversion of a monomer for both CEVE and CMEVE photopolymerizations as well on the molar mass of the oligomers obtained.

Table 2
Photopolymerization of CEVE in 1,2-dichloroethane solution initiated with BPIT (1 mol%/monomer) at the different temperatures

Temperature (°C)	Slope $(R_p/[M_o])$ (s^{-1})	$\overline{M_w}$	$\overline{M_w}/\overline{M_n}$	$\overline{DP}$	Conversion (%)
20	0.076	16147	1.68	40	69.13
30	0.057	17826	1.97	38	71.71
40	0.051	14196	1.75	34	70.12
50	0.037	9697	1.63	25	53.22

Initial concentration of the monomer 1 mol/l.

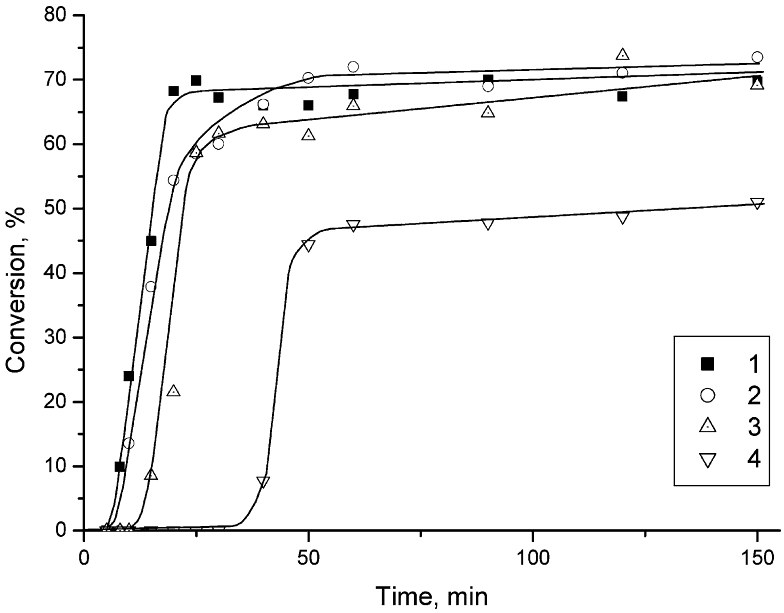


Fig. 5. Conversion vs. time curves for the photopolymerization of CEVE initiated with BPIT (1 mol%/monomer) in 1,2-dichloroethane at different temperatures: (1) 20 °C, (2) 40 °C, (3) 50 °C. Initial concentration of CEVE, 1 mol/l.

Fig. 5 shows kinetic curves of CEVE photopolymerizations conducted at the different temperatures. Table 2 presents the $R_p/[M_o]$ values for these reactions. The $R_p/[M_o]$ value established for CEVE photopolymerization at 20 °C is much higher than that obtained at 50 °C. At the same time increase of the temperature increases the duration of induction period of the reaction and decreases the limit conversion of the monomer. The CEVE photopolymerization initiated with BPIT at 50 °C shows induction period of ca. 30 min (Fig. 5, curve 4), while induction period of 5–15 min is characteristic of CEVE photopolymerizations conducted at lower temperatures (Fig. 5, curves 1–3). The limit conversion of 50% was observed for CEVE photopolymerization at 50 °C while the limit conversion of ca. 70% was established for the photopolymerization carried out at 20 °C.

It is known that the rate of cationic polymerization of various vinyl ethers is markedly dependent on temperature, being very much greater at lower temperatures. These reactions have a negative temperature coefficient [16].

The effect of temperature on molar mass of poly (CEVE) has been studied (Fig. 6). It is evident that $\overline{M_n}$ of the obtained oligomers increases with decreasing temperature and

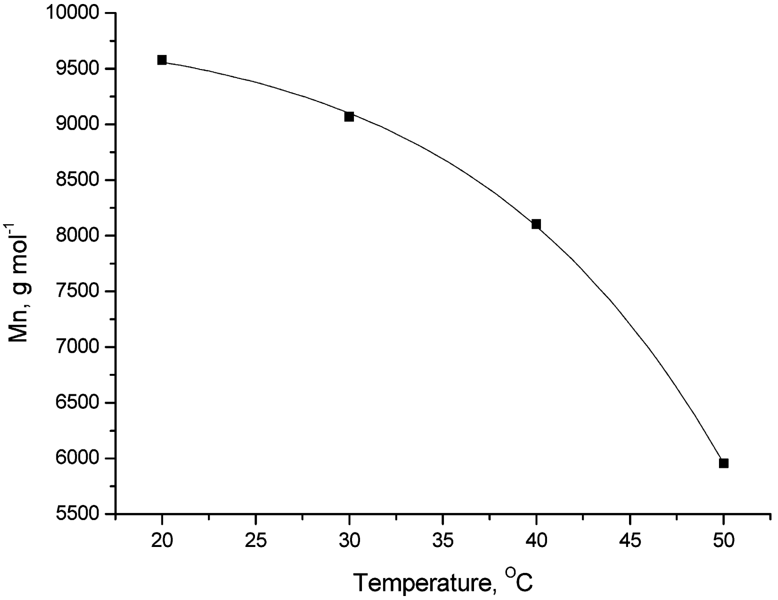


Fig. 6. The $\overline{M_n}$ vs. temperature curve for the photopolymerization of CEVE. $[CEVE]_o = 1$ mol/l. The initial concentration BPIT is 1 mol%. Irradiation time, 210 min.

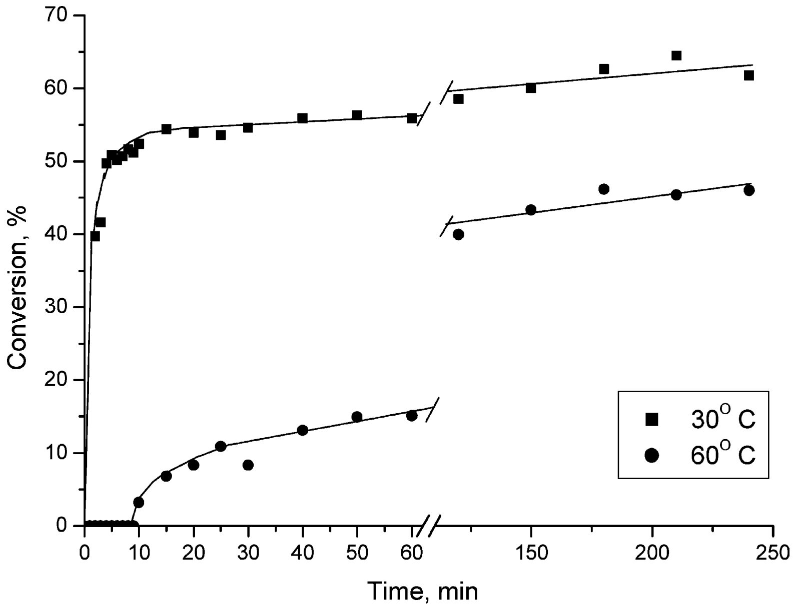


Fig. 7. Conversion vs. time curves for photopolymerization of CMEVE initiated with I261 at different temperatures. $[\mathrm{CMEVE}]_o = 1$ mol/l. Initial concentration of initiator, 1 mol%/monomer.

reaches ca 9500 at 20 °C. Polymers of $\overline{\mathrm{DP}}$ 40 are obtained by CEVE photopolymerization at 20 °C, while the photopolymerization of CEVE at 50 °C gives polymers of $\overline{\mathrm{DP}}$ ca. 25.

Relatively broad molecular weight distribution observed for poly (CEVE) obtained in these reactions (Table 2) may be due to the occurrence of chain transfer reactions [17].

Fig. 7 shows conversion versus time curves for CMEVE photopolymerizations with I261 carried out at various temperatures. The rate of CMEVE photopolymerization (Table 1) and degree of conversion considerably decreases with increase of the temperature. The increase of the temperature increases the duration of induction period of the reaction. The CMEVE photopolymerization initiated with I261 at 60 °C shows induction period of ca. 10 min. while induction period of 2 min is characteristic of the CMEVE photopolymerizations conducted at 30 °C. The limit conversion of CMEVE hotopolymerization also depends on the temperature. The limit monomer conversion value of ca. 40% was observed for CMEVE photopolymerization at 60 °C while 60% limit conversion was established for the photopolymerization carried out at 30 °C.

The decrease of $\overline{M_n}$ and $\overline{\mathrm{DP}}$ with increase of the temperature observed for both poly (CEVE) and poly (CMEVE) can be explained by the fact that decrease of the temperature leads to decrease of the rates of chain transfer and termination reactions, which apparently require higher activation energy compared to propagation. Thus propagation remains unaffected and the molecular weight increases. These observations do not contradict with experimental results of other authors established for cationic polymerization of vinyl ethers [18].

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