

Cationic Photopolymerization of 1,2-Epoxy-6-(9-carbazolyl)-4-oxahexane Initiated by Sulfonium Salt and Iron Arene Complex

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Abstract. The photopolymerization of 1,2-epoxy-6-(9-carbazolyl)-4-oxahexane (ECOH) initiated with dual function sulfonium salt bis [4(diphenylsulfonio)-phenyl] sulfide-bis-hexafluoroantimonate (Cyracure® UVI 6974) and (η^5 -2,4-cyclopentadien-1-yl) [(1,2,3,4,5,6- η)-(1-methylethyl)benzene]-iron (+)-hexafluorophosphate (–1) (Irgacure® 261) has been studied. Higher rate constant values and degrees of polymeri-

zation are established for the ECOH photopolymerization initiated with Cyracure® compared with those obtained using Irgacure®. The influence of temperature on the rate of ECOH photopolymerization, molecular weight and conversion limit is discussed. The activation energy for the photopolymerization of ECOH with the sulfonium salt has been established.

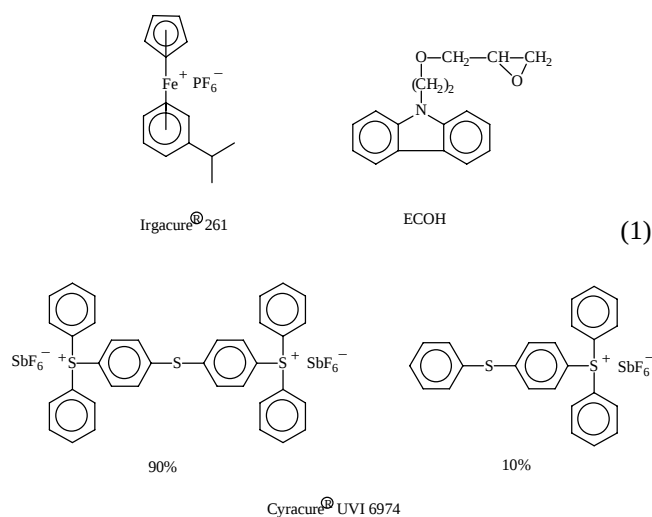
Due to their good photoconductive and film-forming properties carbazolyl-containing oligoethers have found use in the production of electrophotographic microfilms and photothermoplastic layers [1]. Carbazolyl-containing oligoethers are prepared by anionic [2, 3] and cationic [4] polymerization of the corresponding epoxy monomers.

Over the past several years cationic photopolymerization has developed due to its advantages of high reactivity, a lack of oxygen inhibition and efficiency. Photopolymerization (photocrosslinking) of low-molecular compounds containing functional groups can become an attractive alternative to the widely utilized method of preparation of electrophotographic layers.

Several studies conducted earlier in our laboratory have shown that carbazolyl-containing epoxides undergo facile photoinitiated cationic ring-opening polymerization to give oligomers in the presence of onium salts (diaryliodonium and triarylsulfonium salts containing BF_4^- anion were used) [5, 6].

The aim of the present work was to determine the efficiency of some new initiator systems: bis [4(diphenylsulfonio)-phenyl] sulfide-bis-hexafluoroantimonate (Cyracure® UVI 6974) and (η^5 -2,4-cyclopentadien-1-yl) [(1,2,3,4,5,6- η)-(1-methylethyl)benzene]-iron (+)-hexafluorophosphate (–1) (Irgacure® 261) in the photopolymerization reaction of ECOH in bulk. The structure of the photoinitiators and the monomer used are shown in the scheme 1. Iron arene complexes have been demonstrated to be a novel class of cationic photoinitiators [7]. The mechanism of initiation of cationic photopolymerization of oxiranes with the iron arene com-

plexes has been reported [7]. Being stable enough in the amorphous solid state ECOH is very convenient monomer for the photopolymerization studies since the reaction can be carried out in bulk at the temperatures lower than the melting point of the monomer.



Scheme 1 The structure of the photoinitiators and the monomer used on photopolymerization reaction

Results and Discussion

Typical exotherm plots of ECOH photopolymerization initiated with Cyracure and Irgacure are presented in Fig. 1 and 2. Using differential scanning photocalorimetry (DSP) the evolution of the heat of polymerization

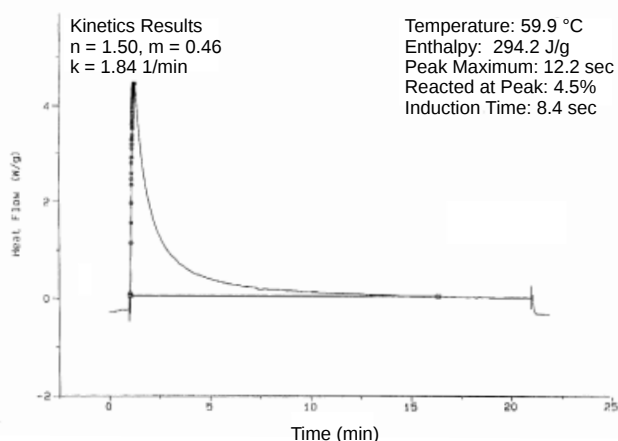


Fig. 1 Exotherm plot of the photopolymerization of ECOH initiated with Cyracure® UVI 6974

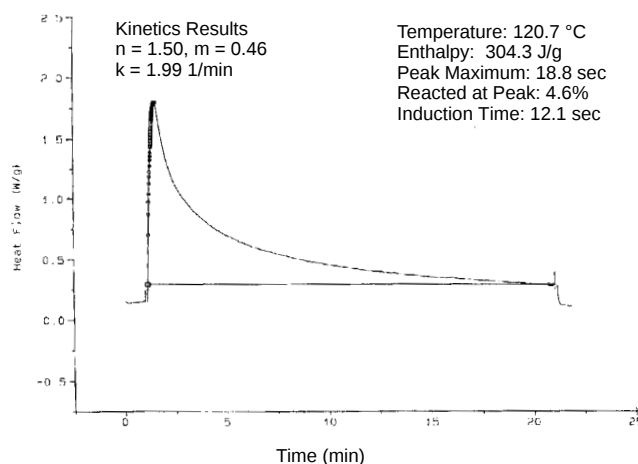


Fig. 2 Exotherm plot of the photopolymerization of ECOH initiated with Irgacure® 261

can be followed as a function of polymerization time. The heat of polymerization reflected by the area underneath the DSP curve is directly related to the conversion. Thus one can directly draw conclusions about the reactivity of a monomer based on the onset and sharpness of the exothermic DSP peak. DSP curves obtained for cationic photopolymerization of ECOH show quite high reactivity of the monomer with both initiators, Cyracure® and Irgacure®. The photopolymerizations were almost complete after 5–15 min of irradiation. The induction period, polymerization enthalpy, degree of conversion and rate constant have been calculated from the recorded exotherms.

It is known that glycidylethers are less reactive than cycloaliphatic epoxides [8]. The photopolymerization of glycidylethers initiated with iron arene complexes has to be carried out in the temperature range of 50–150 °C. If the photopolymerization occurs at lower temperature oxidizing agents or sensibilizers are indispensable for these reactions [8].

With this in mind we have studied cationic photopolymerization of ECOH initiated with Irgacure® at 60 °C and at higher temperatures. Fig. 3 illustrates the

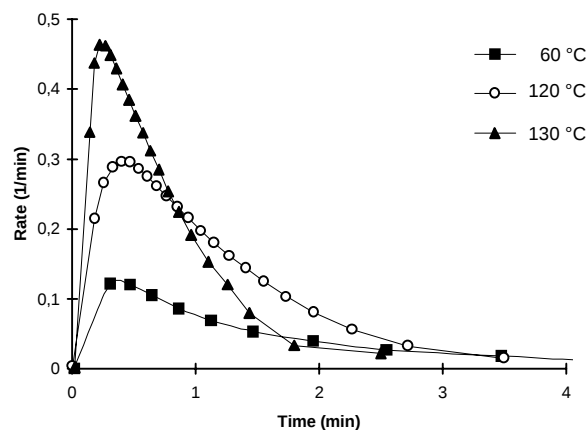


Fig. 3 Rate versus time curves for the photopolymerization of ECOH initiated with Irgacure® 261

dependence of the rate of the reaction on temperature. The rate maximum of ECOH photopolymerization with Irgacure is reached in ca. 20 s. This is followed by a period in which the rate of polymerizations slows down considerably. At this stage of the reaction, the higher the temperature, the faster decrease of polymerization rate is observed. After ca. 3 min of irradiation a very similar rate of polymerization is observed at the different temperatures.

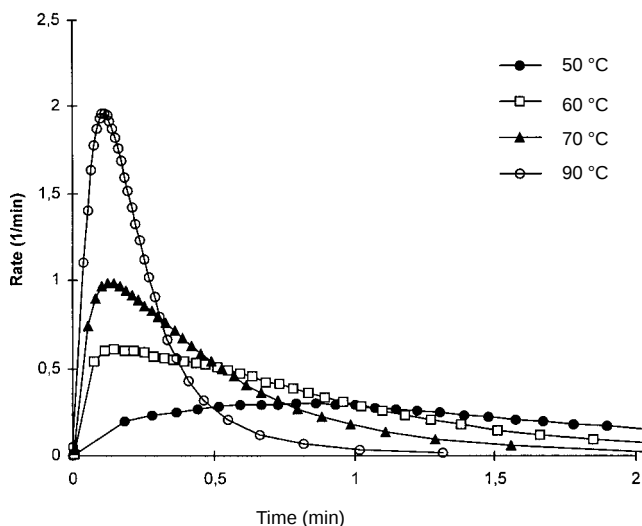
The results of the photopolymerization of ECOH with Irgacure® at various temperatures are presented in Table 1. It is evident that ECOH photopolymerization initiated with the iron arene complex leads to high conversions of the monomer. At 130 °C temperature after 20 min irradiation ca. 90% conversion is reached. The molecular weight and the polydispersity index of the oligomers increase with increasing temperature. Photopolymerization of ECOH initiated with Irgacure® at 130 °C leads to the highest values of the molecular weight and polydispersity index. Degree of polymerization (DP) ca. 30 is reached in this case.

In order to compare the results of ECOH photopolymerization initiated by the iron arene complex with those observed for photopolymerization induced by a sulfonium salt the photopolymerization of ECOH initiated with a difunctional sulfonium salt, Cyracure® UVI 6974, was investigated. The rate vs. time curves of the ECOH photopolymerization with Cyracure® conducted at various temperatures are presented in Fig. 4. It is evident that the rate of the ECOH photopolymerization increases with increasing temperature. At 60 °C the maximum rate is reached after ca. 7 s from the beginning of irradiation. The data presented in Fig. 3 and Fig. 4 show that

Table 1 Photopolymerization of ECOH in melt with Irgacure® 261 and Cyracure® UVI 6974. Initial concentration of initiator 5wt%/monomer

Initiator	Time (min)	Temperature (°C)	M _n	M _w	M _w /M _n	DP	Conversion (%)
Irgacure® 261	20	60	2511	4216	1.67	9.4	61.5
		120	7465	13807	1.85	27.9	86.0
		130	7908	14744	1.86	29.6	88.1
Cyracure® UVI 6974	20	50	4328	7301	1.68	16.2	82.1
		60	4851	8456	1.74	18.2	83.0
		70	5476	10045	1.83	20.5	83.6
		80	6663	12216	1.83	24.9	84.7
		90	9260	16946	1.83	34.7	85.1

ECOH photopolymerization initiated with Cyracure® is much faster at the initial stage than that initiated with Irgacure®. This observation can be explained by the faster photolysis of the sulfonium salt one molecule of which gives two active centers.

**Fig. 4** Rate versus time curves for the photopolymerization of ECOH initiated with Cyracure® UVI 6974

The data presented in Table 1 show that the photopolymerizations of ECOH initiated with the sulfonium salt

yields oligomers of higher DP compared to the reactions initiated by the iron arene complex.

The data presented in Table 2 enable the comparison of some selected kinetic parameters of ECOH photopolymerization initiated by Irgacure® with those obtained using Cyracure® as a photoinitiator. It is evident that a longer induction period is observed with Irgacure®. Using this photoinitiator an induction period lasts 9–18 s. When Cyracure® is used as a photoinitiator an induction period of 3–12 s is observed. It should be noted that much higher rate constant values are obtained with Cyracure® compared to those obtained for the reactions with Irgacure®. Cationic photoinitiators with hexafluoroantimonate anions usually give higher photopolymerization rate compared to the reactions with the photoinitiators containing the other anions [9].

The time from the start of the irradiation to the maximum of the exothermic effect gives us a measure of peak maximum. Table 2 presents peak maximum and monomer reacted at peak values obtained on the photopolymerizations of ECOH initiated with Irgacure® and Cyracure®. These values can be taken as parameters for comparison of the efficiency of initiator systems. It is evident that the maximum of the exothermic effect is reached faster when the photopolymerization of ECOH initiated with Cyracure® (12.2 sec at 60 °C) compared the reaction initiated with Irgacure® (30.2 sec at 60 °C). Table 2 also shows that the photopolymerization of

Table 2 Kinetic results for the photopolymerization of ECOH in melt initiated with Cyracure® UVI 6974 and Irgacure® 261. Initial concentration of initiator is 5 wt%/monomer.

Initiator	Temperature (°C)	Induction time (s)	Rate constant (min ⁻¹)	Peak maximum ^{a)} (s)	Monomer reacted at peak (%)
Cyracure® UVI 6974	50	12.4	0.97	53.4	3.1
	60	8.4	1.84	12.2	4.5
	70	5.2	3.35	9.8	9.3
	80	3.6	4.95	9.2	11.4
	90	3.4	6.65	8.6	14.6
Irgacure® 261	60	18.5	0.75	30.2	2.7
	120	12.1	1.99	18.8	4.6
	130	9.3	2.21	18.5	7.4

^{a)} The time from the start of the irradiation to the maximum of the exothermic effect.

ECOH initiated with the sulfonium salt leads to higher monomer fraction reacted at peak values compared to those established for the reaction with the iron arene complex. From the data presented above it can be assumed that Cyracure® UVI 6974 is more effective photoinitiator for the polymerization of ECOH than Irgacure® 261.

In our previous work [6] the bulk photopolymerization of ECOH initiated with diphenyl iodonium tetrafluoroborate was investigated. The comparison of the obtained results shows that rate of the ECOH reaction initiated by the iodonium salt is very similar to that when Cyracure® is used as initiator. However, the oligomers of lower degree of polymerization (ca. 4) are obtained when diphenyl iodonium tetrafluoroborate is used as a photoinitiator.

In order to establish the activation energy value the photopolymerizations of ECOH with Cyracure® UVI 6974 were conducted at various temperatures. After measuring the rate constants the plot of $\ln k$ versus $1/T$ was obtained (Fig. 5). The activation energy of 47.5 kJ/mol for the photopolymerization of ECOH initiated with Cyracure® at light intensity 4 mW/cm² was established.

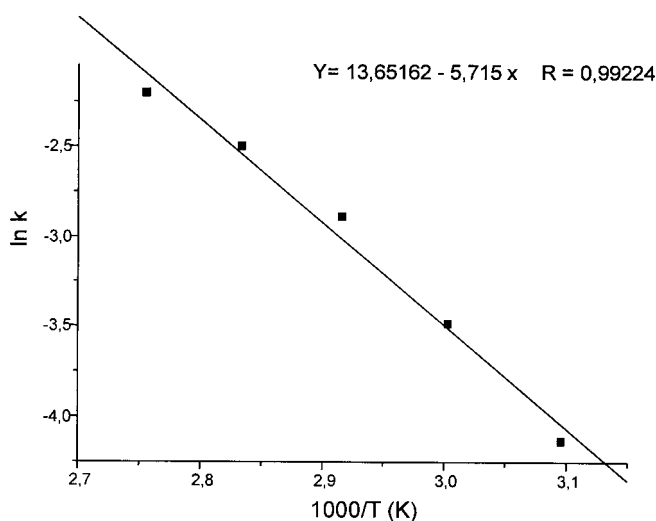


Fig. 5 $\ln k$ versus $1/T$ plot for the ECOH photopolymerization initiated with Cyracure® UVI 6974 at light intensity – 4 mW/cm²

Conclusion

Cationic photopolymerization of 1,2-epoxy-6-(9-carbazolyl)-4-oxahexane (ECOH) in bulk has been studied by differential scanning photocalorimetry and GPC. Bis [4(diphenylsulfonio)-phenyl] sulfide-bis-hexafluoroantimonate (Cyracure® UVI 6974) and (η^5 -2,4-cyclopentadien-1-yl) [(1,2,3,4,5,6- η)-(1-methylethyl)benzene]-iron (+)-hexafluorophosphate (–1) (Irgacure® 261) have been used as photoinitiators. Both initiators

initiate photopolymerization of the epoxy monomer. Higher reaction rate and higher degree of polymerization was observed in the reactions with bis [4(diphenylsulfonio)-phenyl] sulfide-bis-hexafluoroantimonate. It was found that the rate of the ECOH photopolymerization, molecular weight and polydispersity index of the obtained oligomers increase with increasing temperature. The activation energy of 47.5 kJ/mol for the photopolymerization of ECOH initiated with bis [4(diphenylsulfonio)-phenyl] sulfide-bis-hexafluoroantimonate at light intensity 4 mW/cm² has been established.

Experimental

Chemicals

1,2-Epoxy-6-(9-carbazolyl)-4-oxahexane (ECOH) was synthesized by the condensation of 9-(2-hydroxyethyl) carbazole with 1-chloro-2,3-epoxypropane in the presence of KOH [10]. It was purified by recrystallization from diethyl ether, *m.p.* 57 °C. The photoinitiators: bis [4(diphenylsulfonio)-phenyl] sulfide-bis-hexafluoroantimonate 50% solution in propylene carbonate supplied as Cyracure® UVI 6974 (Union Carbide) was dried over calcium hydride before use, (η^5 -2,4-cyclopentadien-1-yl) [(1,2,3,4,5,6- η)-(1-methylethyl)benzene]-iron (+)-hexafluorophosphate (–1) supplied as Irgacure® 261 was used as received from Ciba-Geigy.

Instrumentation

Differential scanning photocalorimetric (DPC) studies of the cationic photopolymerization of carbazolyepoxide were carried out using a DuPont 2100 photocalorimeter equipped with a standard high pressure Hg arc lamp (the 4 mW/cm² light intensity was used for irradiation of the samples). Photopolymerizations were conducted using computer controlled isothermal methods in air atmosphere in the temperature range of 40–130 °C. Irradiation was switched on after an initial equilibration period of 1 min. The exposure was carried out using the DSC DuPont standard pans containing 1.0–2.0 mg of the melted epoxy monomer with dissolved photoinitiator (5 wt%/monomer) covered with 2.5 mm PET film.

The autocatalytic model [equation (1)] has been used to calculate the kinetic parameters of the reactions [11].

$$dC/dt = k(T) C^m (1-C)^n \quad (1)$$

were: dC/dt – reaction rate (s^{–1}; C – the fractional conversion after time t ; $k(T)$ – rate constant at temperature T (min^{–1}; n and m – orders of reaction.

The reaction constant $k(T)$ can be expressed by equation 2:

$$k(T) = Ae^{-E/RT} \quad (2)$$

The parameters dC/dt and C can be obtained from the DPC exotherm:

$$dC/dt = (dH/dt)\Delta H_o \text{ and } C = \Delta H_p/\Delta H_o \quad (3)$$

The theoretical enthalpy of 353.9 J/g calculated for ECOH polymerization was established to be very close to the experimental enthalpy values (ca. 360.2 J/g) earlier estimated at our laboratory [12].

The number average molecular weight and polydispersity index of the obtained oligomers were determined by GPC after irradiation of samples for 20 min. GPC was carried out on the modified liquid chromatograph "Milichrom" (Chernogolovka, Russia) using a special column packed with Silasorb [13]. 1,4-Dioxane was used as eluent.

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