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Photopolymerization of carbazolyloxiranes with sulphonium and tropylium salts

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Abstract

The photopolymerization of 1-allyloxa-3-(carbazol-9-yl)-2-propanol glycidyl ether (ACPGE) and 1-(carbazol-9-yl)-4-oxa-2-pentanol glycidyl ether (COPGE) with cyclopropyldiphenylsulphonium tetrafluoroborate and tropylium hexafluorophosphate is reported. Oligomers with a degree of polymerization of 9–19 were obtained in the photopolymerization of ACPGE with these salts. The photopolymerization of COPGE yielded oligomers with a degree of polymerization of 4–5. The behaviour of tropylium and sulphonium salts is discussed. Tropylium hexafluorophosphate initiates both the photopolymerization of carbazolyloxiranes and the cationic polymerization of unsaturated monomers. Cyclopropyldiphenylsulphonium tetrafluoroborate acts exclusively as a photoinitiator. © 1997 Elsevier Science S.A.

Keywords: Carbazolyloxiranes; Photopolymerization; Sulphonium salts; Tropylium salts

1. Introduction

Reactive oligomers are widely used in different technologies. Most photoconductive oligomers, e.g. poly(9-vinylcarbazole), have high glass transition temperatures and poor film-forming properties. However, carbazolyloxirane oligomers, a type of photoconductive oligomer, show good photoconductive and film-forming properties [1]. For this reason, they are indispensable in the production of electrophotographic microfilms and photothermoplastic layers. These oligomers are obtained by the ionic polymerization of the carbazolyloxiranes 9-(2,3-epoxypropyl)carbazole, 3,6-dibromo-9-carbazolyl)oxirane and (9-carbazolyl)-ethoxymethyloxirane [2–4].

Recently, we have investigated the cationic photopolymerization of carbazolyloxiranes [5]. Photopolymerization (photocrosslinking) of low-molecular-weight photoconductors containing functional groups is a powerful tool in the preparation of electrophotographic layers with good mechanical properties. Photopolymerization is especially useful in the case of liquid monomers. In such cases, the synthesis of photoconductive oligomers can be carried out without the use of organic solvents. In this paper, we report the photopolymerization of two new liquid carbazolyloxiranes, 1-allyloxa-3-(carbazol-9-yl)-2-propanol glycidyl ether (ACPGE) and 1-(carbazol-9-yl)-4-oxa-2-pentanol glycidyl ether (COPGE), initiated by sulphonium and tropylium salts.

2. Experimental details

2.1. Materials

9-(2,3-Epoxypropyl)carbazole (EPC) (Biolar, Latvia) was recrystallized from ethyl alcohol (m.p., 110–111 °C). 1,2-Epoxy-6-(9-carbazolyl)-4-oxahexane (ECOH) was synthesized by condensation of 9-(2-oxyethyl)carbazole with 1-chloro-2,3-epoxypropane in the presence of KOH [6]. It was purified by recrystallization from ethyl alcohol (m.p., 57.5–58 °C). 3-Methyl-9-(2,3-epoxypropyl)carbazole (MEPC) was synthesized by reaction of 3-methylcarbazole with 1-chloro-2,3-epoxypropane in the presence of KOH and dry K_2CO_3 [7]. 9-Vinylcarbazole from Aldrich was used as received.

2.1.1. 1-(Carbazol-9-yl)-4-oxa-2-pentanol (COP)

A mixture of 44.6 g (0.2 mol) of EPC, 10 g (0.25 mol) of NaOH and 13.8 g (0.1 mol) of dry K_2CO_3 was boiled in 250 ml of methyl alcohol for 2 h; the product was extracted

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with ether. After distillation, the resulting monomer was isolated by column chromatography (eluent, acetone–hexane 1 : 4); 44.7 g (87.6%) of monomer was obtained. COP was recrystallized from ethyl alcohol (m.p., 56.5–57.5 °C).

IR (KBr): 3420, 3048, 3017, 2976, 2928, 2888, 2816, 1132, 1122, 1107 cm^{-1}.

^{1}H nuclear magnetic resonance (NMR) ($CDCl_3$) δ: 2.57 (s), 2.83–3.24 (m), 3.78–4.22 (m), 6.82–7.42 (m), 7.87 (d) ppm.

Elemental analysis for $C_{16}H_{17}N_1O_2$ (255.32): calculated: C, 75.3%; H, 6.7%; N, 5.5%; found: C, 75.2%; H, 7.1%; N, 6.0%.

2.1.2. *1-(Carbazol-9-yl)-4-oxa-2-pentanol glycidyl ether (COPGE)*

1-Chloro-2,3-epoxypropane (47.3 ml, 0.6 mol), 6.9 g (0.05 mol) of dry K_2CO_3 and 19.8 g (0.3 mol) of 85% KOH were added to 25.5 g (0.1 mol) of COP dissolved in ethyl methyl ketone. The reaction mixture was stirred for 40 h at room temperature. After extraction with toluene, COPGE was isolated by column chromatography (eluent, acetone–hexane 1 : 4); 20.3 g (65.2%) of COPGE was obtained.

IR (film): 3048, 3018, 2983, 2928, 2878, 2828, 2808, 1252, 906, 854, 1135, 1120, 1105 cm^{-1}.

^{1}H NMR ($CDCl_3$) δ: 1.98–2.44 (m), 2.51–2.78 (m), 2.96–3.33 (m), 3.56–3.87 (m), 4.11–4.33 (m), 6.91–7.44 (m), 7.86 (d) ppm.

Elemental analysis for $C_{19}H_{21}N_1O_3$ (311.38): calculated: C, 73.3%; H, 6.8%; N, 4.5%; found: C, 73.0%; H, 6.5%; N, 4.7%.

2.1.3. *1-Allyloxa-3-(carbazol-9-yl)-2-propanol (ACP)*

A mixture of 44.6 g (0.2 mol) of EPC, 10 g (0.25 mol) of NaOH and 13.8 g (0.1 mol) of dry K_2CO_3 was boiled in 200 ml of allyl alcohol for 1 h. After extraction with toluene, the resulting resin was isolated by column chromatography (eluent, acetone–hexane 1 : 4). ACP was recrystallized from ethyl alcohol (m.p., 52.5–54.0 °C).

IR (KBr): 3440, 3095, 3060, 3025, 3020, 2925, 2915, 2910, 2880, 2810, 1130, 1115 cm^{-1}.

^{1}H NMR ($CDCl_3$) δ: 2.61 (s), 3.05–3.38 (m), 3.63–4.60 (m), 4.98–5.40 (m), 5.50–6.10 (m), 6.68–7.83 (m), 7.95 (d) ppm.

Elemental analysis for $C_{18}H_{19}N_1O_2$ (281.25): calculated: C, 76.9%; H, 6.8%; N, 5.0%; found: C, 76.7%; H, 6.9%; N, 5.1%.

2.1.4. *1-Allyloxa-3-(carbazol-9-yl)-2-propanol glycidyl ether (ACPGE)*

1-Chloro-2,3-epoxypropane (47.3 ml, 0.6 mol), 6.9 g (0.05 mol) of dry K_2CO_3 and 19.8 g (0.3 mol) of 85% KOH were added to 28.1 g (0.1 mol) of ACP dissolved in 200 ml of ethyl methyl ketone. The reaction mixture was stirred for 60 h at room temperature. The product was extracted with toluene and isolated by column chromatography (eluent, acetone–hexane 1 : 4); 24.4 g (72.4%) of ACPGE was obtained.

IR (film): 3052, 3002, 2923, 2868, 1252, 928, 854, 1154, 1124, 1104 cm^{-1}.

^{1}H NMR ($CDCl_3$) δ: 2.03–2.58 (m), 2.58–2.85 (m), 2.93–3.73 (m), 3.73–4.13 (m), 4.13–4.48 (m), 5.03–5.48 (m), 5.60–6.15 (m), 7.00–7.83 (m), 7.96 (d) ppm.

Elemental analysis for $C_{21}H_{23}N_1O_3$ (337.42): calculated: C, 74.8%; H, 6.9%; N, 4.2%; found: C, 74.3%; H, 6.6%; N, 4.4%.

2.1.5. *Other materials*

The solvents 1,2-dichloroethane and 1,4-dioxane were purified by standard procedures [8]. Cyclopropyldiphenylsulphonium tetrafluoroborate and tropylium hexafluorophosphate were used as received from Aldrich.

2.2. *Polymerization*

The polymerization of carbazolyloxiranes was carried out in the form of thin (20–30 μm) films in the presence of air. Solutions of monomer, photoinitiator and solvent were poured onto a glass plate and irradiated. The conversion of monomers was measured after irradiation of the coatings for various periods of time by gel permeation chromatography (GPC). The UV light source was a 240 W medium pressure mercury arc lamp (model DRT-240) set at a distance of 6 cm. Racemic mixtures of both ACPGE and COPGE were used for polymerization.

2.3. *Measurements*

GPC was carried out using a modified liquid chromatograph "Milichrom" (Chernogolovka, Russia) with a special column packed with Silasorb [9]. 1,4-Dioxane was used as eluent. ^{1}H NMR spectra were recorded on a Hitachi R-22 (90 MHz) or Tesla BS-487C (80 MHz) spectrometer. IR data were obtained on a Specord M 80 spectrophotometer. Column chromatography was carried out on silica gel L 100/160 (Chemapol).

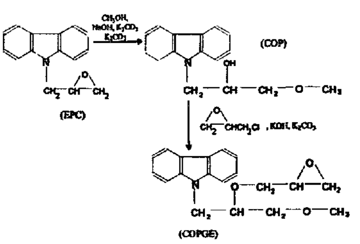
3. Results and discussion

3.1. *Synthesis of carbazolyloxiranes*

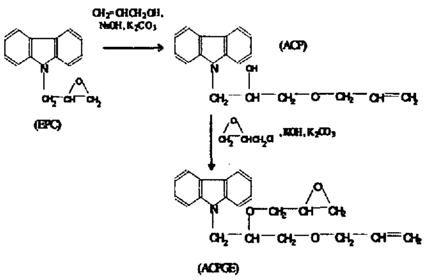
COPGE was prepared by the reaction of EPC with methyl alcohol, followed by the reaction of the product obtained (COP) with 1-chloro-2,3-epoxypropane (Scheme 1). ACPGE was synthesized by the reaction of EPC with allyl alcohol, followed by the reaction of the product obtained (ACP) with 1-chloro-2,3-epoxypropane (Scheme 2).

3.2. *Photopolymerization*

Conversion vs. time curves for the photopolymerization of COPGE with tropylium and sulphonium salts are presented in Fig. 1. Polymerization photoinitiated by tropylium hexa-



Scheme 1.



Scheme 2.

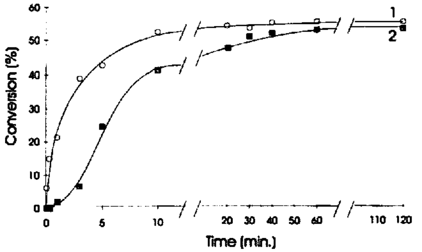


Fig. 1. Photopolymerization of COPGE with initiators (3%/monomer): 1, sulphonium salt; 2, tropylium salt. Initial concentration of monomer, 25%. Solvent, 1,2-dichloroethane.

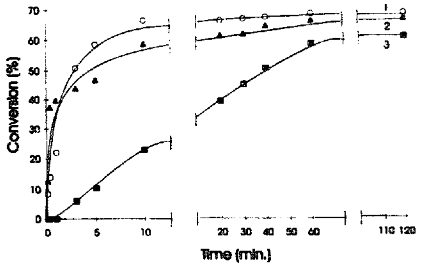


Fig. 2. Conversion vs. time curves for the photopolymerization of ACPGE with sulphonium salt (1) and tropylium salt (2) and the dark polymerization of ACPGE with tropylium salt (3). Concentration of initiator, 3%/monomer. Initial concentration of monomer, 25%. Solvent, 1,2-dichloroethane.

fluorophosphate is considerably slower initially than that photoinitiated by cyclopropyldiphenylsulphonium tetrafluoroborate. The initial phase of this reaction shows an inhibition period. This is followed by a period in which rapid conversion to monomer occurs and, finally, a very similar degree of conversion is achieved as in the photopolymerization with cyclopropyldiphenylsulphonium tetrafluoroborate. The limiting conversion is approximately 55%–57%.

Fig. 2 (curves 1 and 2) illustrates the photopolymerization of ACPGE with tropylium and sulphonium salts. A rapid, nearly explosive rate is observed initially for the photoinitiation with tropylium hexafluorophosphate. However, after a certain time, the photopolymerization slows down and a limiting degree of conversion of approximately 64% is achieved. A much lower initial rate is observed for the photopolymerization of ACPGE with cyclopropyldiphenylsulphonium tetrafluoroborate.

A comparison of the data obtained with the results reported recently shows that the efficiencies of tropylium hexafluorophosphate and cyclopropyldiphenylsulphonium tetrafluoroborate in the cationic photopolymerization of carbazolyloxiranes are very similar to that of diaryliodonium salts. However, polymerization with tropylium and sulphonium salts as photoinitiators gives ACPGE oligomers with a higher degree of polymerization (DP). The DP of ACPGE oligomers obtained with tropylium salt is approximately 9 and that of oligomers obtained with sulphonium salt is approximately 19. The photopolymerization of ACPGE with di-(tert-butylphenyl)iodonium tetrafluoroborate yields an oligomer with DP ≈ 6. The DP of COPGE oligomers obtained with tropylium salt as photoinitiator is approximately 4, with sulphonium salt approximately 5 and with di-(tert-butylphenyl)iodonium tetrafluoroborate approximately 4.

It is evident from the data presented above that tropylium hexafluorophosphate is an effective catalyst for the cationic photopolymerization of the monomers studied. For comparison, data on the dark polymerization of ACPGE induced by tropylium hexafluorophosphate are presented in Fig. 2 (curve 3). The initial polymerization rate in the dark is much lower than that on irradiation; however, after 2 h, a fairly high conversion of approximately 58% is achieved. The photopolymerization of ACPGE yields oligomers of much higher molecular weight than dark polymerization under the same conditions (Table 1).

It should be noted that only ACPGE, with both epoxy and allyl groups, is polymerized in the dark by tropylium hexafluorophosphate. COPGE shows no dark polymerization with tropylium hexafluorophosphate. It is of interest to establish whether tropylium hexafluorophosphate initiates the photopolymerization of other epoxy monomers. The data in Table 1 show that the photopolymerization of MEPC and ECOH occur in the presence of this salt, and a fairly high conversion

Table 1
Polymerization of carbazolyloxiranes with tropylium hexafluorophosphate

Monomer	Photopolymerization (60 min)				Dark polymerization (60 min)			
	M_n	M_w	M_w/M	Conversion (%)	M_n	M_w	M_w/M_n	Conversion (%)
COPGE	1063	1330	1.25	51.76	–	–	–	0
ACPGE	3268	1128	3.45	62.05	971	1215	1.25	52.83
ECOH	1392	2245	1.61	70.70	–	–	–	0
MEPC	820	987	1.20	40.04	–	–	–	0

Initial concentration of photoinitiator, 3 wt.% / monomer. Solvent, 1,2-dichloroethane. $[\text{ACPGE}]_0 = [\text{COPGE}]_0 = [\text{ECOH}]_0 = [\text{MEPC}]_0 = 25\%$.

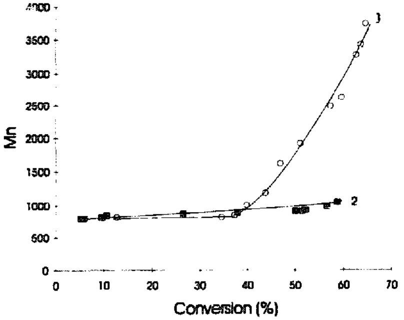


Fig. 3. M_n vs. conversion curves for the photopolymerization of ACPGE (1) and dark polymerization of ACPGE (2) with tropylium hexafluorophosphate (3%/monomer). Initial concentration of monomer, 25%. Solvent, 1,2-dichloroethane.

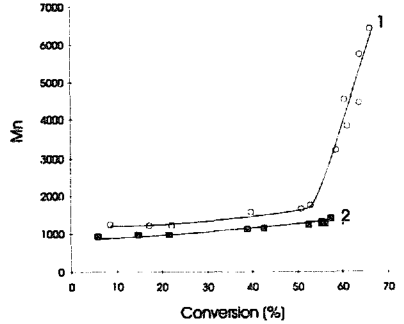


Fig. 4. M_n vs. conversion curves for the photopolymerization of ACPGE (1) and COPGE (2) with cyclopropyldiphenylsulphonium tetrafluoroborate (3%/monomer). Initial concentration of monomer, 25%. Solvent, 1,2-dichloroethane.

is observed within a short period of time. Fig. 3 shows that the photopolymerization of ACPGE with tropylium salt exhibits an increase in M_n when approximately 40% conversion is reached. In contrast, a sudden increase in M_n is not observed in the dark polymerization of ACPGE. It is evident that the mechanism of ACPGE polymerization on irradiation differs from that in the dark. It can be assumed that only the allyl group takes part in the dark polymerization of ACPGE with the tropylium salt. It was established that the absorption band of the allyl group at 1664 cm^{-1} disappears as a function of the time of dark polymerization of ACPGE. The results for the dark polymerization of 9-vinylcarbazole also confirm indirectly this assumption. In the same conditions, rapid, nearly explosive polymerization of 9-vinylcarbazole is observed. After 20 s, 90% conversion of the monomer is obtained.

It is evident from the data presented above that both cationic photopolymerization of epoxides and polymerization of unsaturated monomers can occur in the presence of tropylium salt. The polymerization of unsaturated monomers with tropylium hexafluorophosphate in the dark occurs by a cationic mechanism.

The data presented in Figs. 1 and 2 reveal different reactivities of ACPGE and COPGE. The initial rate of ACPGE photopolymerization with tropylium and sulphonium salts is much higher than that observed for COPGE photopolymerization. The dependence of the molecular weight of the products of ACPGE and COPGE photopolymerization in the presence of cyclopropyldiphenylsulphonium tetrafluoroborate on the conversion is shown in Fig. 4. Much higher values of M_n are achieved for the photopolymerization of ACPGE. After reaching approximately 60% conversion of the monomer, a sudden increase in the molecular weight of poly(ACPGE) is observed. This observation, as well as the decrease in the absorption band of the allyl group during photopolymerization, suggests that, at a certain degree of conversion, the allyl groups start to play a dominant role in the photopolymerization of ACPGE.

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