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Photopolymerization of neopentyl glycol diglycidylether and its compositions with 9-(2-oxiranylmethyl) carbazole

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Abstract

Photopolymerization of neopentyl glycol diglycidylether (NPG) initiated with diphenyl iodonium tetrafluoroborate (TB) in bulk has been studied. The influence of concentration of the photoinitiator on the rate of polymerization and monomer conversion is discussed. The initiator exponent was established for the photopolymerization of NPG with TB. Photopolymerization of the compositions consisting of NPG and 9-(2-oxiranylmethyl) carbazole (OMC) initiated with TB has been studied. It was established that OMC undergoes both homopolymerization and copolymerization during the UV irradiation of the composition. The effect of the temperature on the rate and conversion of epoxy groups for the photopolymerization of NPG alone and in the presence of OMC has been examined. It was established that 9-vinylcarbazole (VCz) acts as synergist of NPG photopolymerization as well of photopolymerization of the composition of NPG and OMC. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photopolymerization; Photocrosslinking; Epoxide; Carbazole; Iodonium salts

1. Introduction

Photoinitiated cationic polymerization (photocrosslinking) is highly attractive technique for many applications due to its advantages: using photoinitiated cationic polymerization, it is possible to prepare crosslinked films from multifunctional monomers at high speed; cationic photopolymerization is not sensitive to oxygen inhibition; it can be carried out under ambient conditions; cationic photopolymerization of liquid monomers can proceed without the use of volatile, aggressive organic solvents [1].

Our previous investigations [2,3] have shown that carbazolyl-containing epoxy monomers undergo facile cationic photoinitiated polymerization in the presence of onium salts such as diphenyl iodonium tetrafluoroborate, di-(tert-butyl phenyl) iodonium tetrafluoroborate and cyclopropyldiphenyl sulfonium tetrafluoroborate.

Poly [9-(2,3-epoxypropyl) carbazole] as an organic photoconductor has been widely used in electrophotography [4]. It was shown earlier [5,6] that crosslinkable hole-transport materials are very attractive compounds for the preparation of multilayer devices by spin-coating. In order to make the spin-coating method suitable for the preparation of multilayer organic light emitting devices or electrophotographic photoreceptors, the solubility of the layers has to be reduced after their deposition [7]. One possibility to achieve this is to use multifunctional low-molecular weight molecules, which can be converted into durable network by crosslinking reactions.

With this in mind, we have started cationic photopolymerization of photocrosslinkable epoxy monomer and of the system containing bifunctional epoxy monomer and epoxy monomer with photoconductive group. In this paper, we report on photoinitiated cationic polymerization (photocrosslinking) of the bifunctional epoxy monomer, neopentyl glycol diglycidylether (NPG) and its compositions with 9-(2-oxiranylmethyl) carbazole (OMC) initiated with diphenyl iodonium tetrafluoroborate (TB) in bulk.

2. Experimental details

Neopentyl glycol diglycidylether (NPG) was used as received from (Aldrich). 9-(2-Oxiranylmethyl) carbazole (OMC) (Biolar, Latvija) was recrystallized twice from isopropanol, mp 111–112 °C. 9-Vinylcarbazole (VCz) was used as received from Fluka, m.p. −66 °C. Diphenyliodonium tetrafluoroborate (TB) was synthesized and purified as described before [8]. The structural formulas of the monomers and the photoinitiator employed in this investigation are shown in Scheme 1. The solvents, 1,2-dichloroethane,

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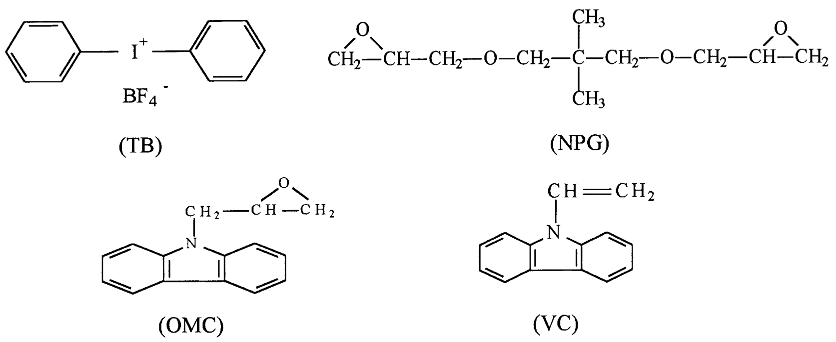


Scheme 1.

1,4-dioxan, tetrahydrofuran were purified by standard procedures [9].

Photopolymerizations were monitored by IR spectroscopy using Specord 75 IR spectrometer. Photopolymerizations were carried out at room or 50 °C temperature in 10–15 μm film of the bifunctional monomer (or the composition of the monomer with OMC) containing various amounts of the photoinitiator. Irradiation was carried out with a 240 W medium pressure mercury lamp (Model DRT 240, Russia) set at the distance of 7 cm. The monomer/photoinitiator solution was coated onto a glass or silicon plate and dried in vacuum. The kinetics of photopolymerization (photocrosslinking) of the monomers or their compositions was studied by IR spectroscopy [10,11]. The decrease upon UV exposure of the IR absorption bands characteristic of the epoxy groups at 3005 cm^{-1} and 3060 cm^{-1} was recorded. The degree of conversion of the epoxy groups at any time during the UV irradiation was established by measuring the peak height under the specific absorption band according to Eq. (1). Here A_0 and A_t are the absorbency levels of the epoxy groups in the photopolymerizable film before and after UV irradiation during a certain period of time, respectively.

$$\text{Degree of conversion (\%)} = \frac{A_0 - A}{A_0} \times 100 \qquad (1)$$

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). Insoluble fraction was estimated by the method of gravimetry.

3. Results and discussion

Fig. 1 shows conversion versus time curves for photopolymerization of NPG with the different amounts of the photoinitiator. It is evident that high initial rate of

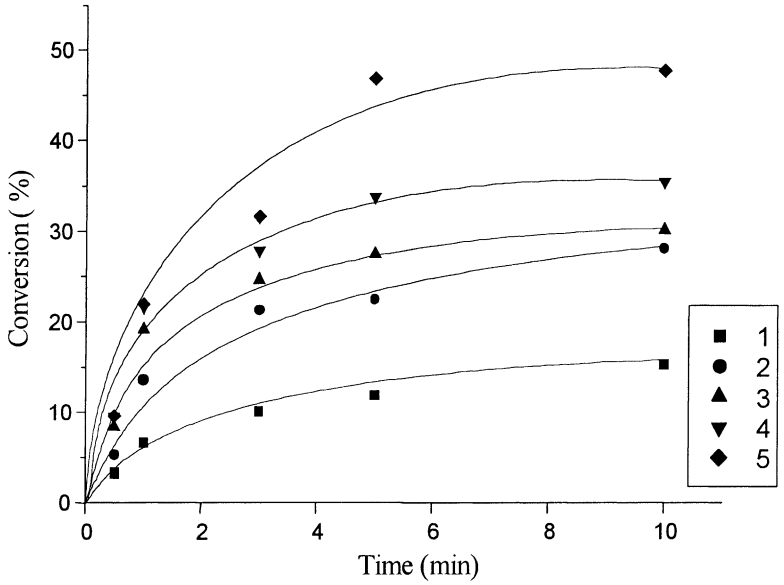


Fig. 1. Conversion vs. time curves for the photopolymerization of NPG initiated with TB: (1) 0.5 mol%; (2) 1 mol%; (3) 1.5 mol%; (4) 2 mol%; (5) 3 mol%/monomer (at 20 °C).

photopolymerization, which slows down markedly after reaching certain degree of conversion, is characteristic of this reaction. It is also evident that the degree of conversion and the initial photopolymerization rate increases with the increase in the concentration of TB. For the NPG photopolymerization initiated with 0.5 mol% TB, only ca. 15% monomer conversion is observed after 10 min irradiation. At 3 mol% initial concentration of TB, ca. 50 % degree of conversion is achieved in the photopolymerization after the same period of time. At 0.5 mol% concentration of TB, the photopolymerization rate (R) of NPG is slow with a R_p value of 0.54×10^{-2} mol/l s. Increasing the TB concentration up to 3 mol% markedly increases the R_p value to 1.54×10^{-2} mol/l s.

Using the data presented in Figs. 1 and 2 the initiator exponent was calculated. TB exponent of 0.8 for the NPG photopolymerization was obtained.

It was of interest to study the influence of temperature on photopolymerization of NPG. The results are presented in Fig. 3 and Table 1. For the photopolymerization of NPG conducted at 20 °C the decrease in the reaction rate is observed above 40% conversion (Fig. 3, curve 1). This apparently occurs due to immobilization of residual functional groups in the glassy crosslinked product formed. It was shown earlier that the rate of polymerization of epoxy monomer slows down above 30% conversion as the irradiated polymer hardens and become glassy [12]. The final product contains a large amount of unreacted epoxy groups. The increase of the temperature upto 50 °C considerably increases the rate of reaction and conversion of the monomer. At 50 °C, 90% conversion of NPG was observed after 90 min irradiation, meanwhile, ca. 70% conversion of the monomer was reached at 20 °C after the same period of exposure. The increased chain mobility at higher temperature apparently allows to polymerize some of the remaining monomer. At higher temperature, the decrease of the polymerization rate is observed at higher conversion of the epoxy groups.

It is known [13] that carbazole compounds (including *N*-vinylcarbazole) act as synergists of cationic

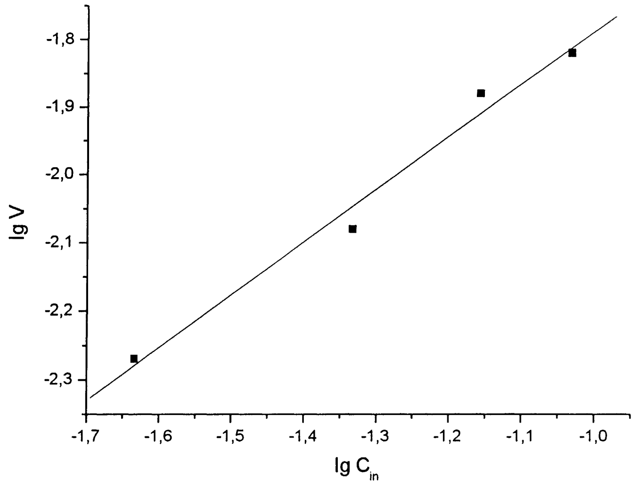


Fig. 2. lg V vs. lg C_{in} plot for the photopolymerization of NPG initiated with TB. (V—polymerization rate; C_{in}—concentration of initiator).

Table 1
Photopolymerization of NPG initiated with TB (3 mol%/monomer)[a]

Photopolymerization of NPG[a]	Temperature (°C)	Rate × 10^{-2} (mol/l s)	Conversion (%)[a]
Without the use of VCz	20	154	9.5
	50	2.84	17.7
In the presence of 2 mol% VCz	20	6.03	37.6
In the presence of 10 mol% VCz	20	7.52	46.9

[a] Measured after 30 s UV irradiation.

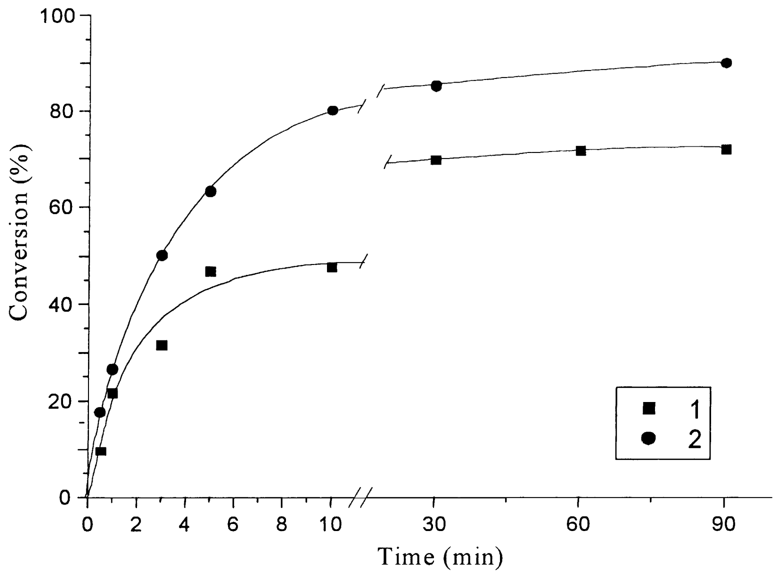
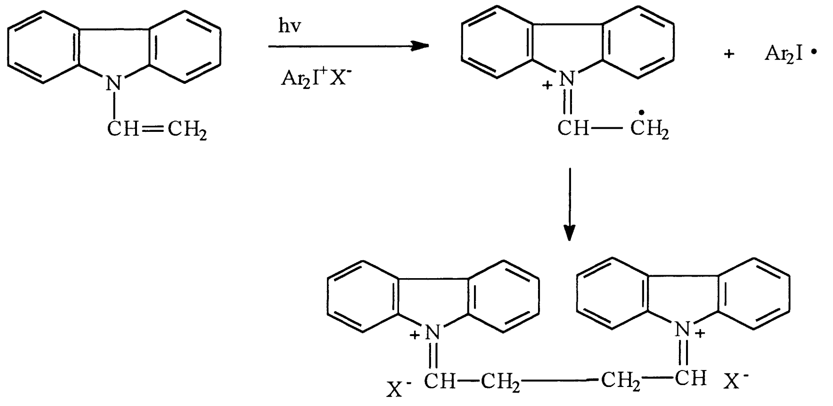


Fig. 3. Conversion vs. time curves for the photopolymerization of NPG initiated with TB (3 mol%/monomer) at: (1) 20 °C, (2) 50 °C.

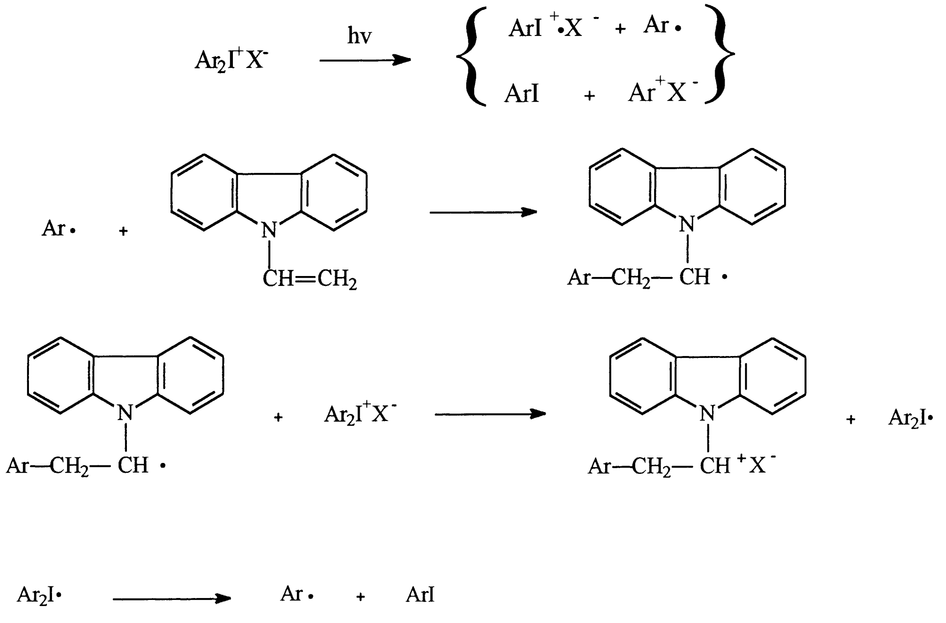


Scheme 2.

photopolymerization of epoxides. Electron-transfer photosensitization, which involves a redox reaction, takes place when excited carbazole interacts with the onium salt. A different mechanism is involved during the reaction of *N*-vinylcarbazole (VCz) with the onium salts. The Schemes 2 and 3 show that photolysis of onium salts in the presence of VCz leads to the generation of additional active cationic centres. Higher amount of cationic centres leads to higher rate of the process.

We have studied the photopolymerization of NPG initiated with TB in the presence of 2 mol% VCz (Fig. 4, curve 2 and Table 1). For comparison, the conversion versus time curve for the NPG photopolymerization without the use of VCz is presented in Fig. 4 (curve 1). When small amount (2 mol%) of VCz is added to the reaction mixture, acceleration of the rate of cationic photopolymerization of NPG occurs. In addition, NPG conversion is also enhanced in the presence of VCz. For the NPG photopolymerization, in the presence of VCz the degree of conversion of ca. 100% after 30 min irradiation is observed. Meanwhile, only 70% conversion is reached during the same period of exposure in the case of the photopolymerization of NPG in the absence of VCz. The increase of the concentration of VCz enhances the rate of photopolymerization. The photopolymerization of NPG in the presence of 2 mol% VCz occurs with the R_p value of 6.03×102 mol/1 s, while the R_p value of 7.52×10^{-2} mol/l s is observed in the presence of 10 mol% of VCz.

The soluble fraction versus time curve for the photopolymerization of NPG with 2 mol% VCz is shown in Fig. 4 (curve 4). It is evident that crosslinking process of the sample occurs very fast at the initial stage of the photopolymerization (ca. 75% insoluble fraction are obtained after 1 min exposure). However, after formation of ca. 80% of insoluble fraction, a marked slowing down of the process is



Scheme 3.

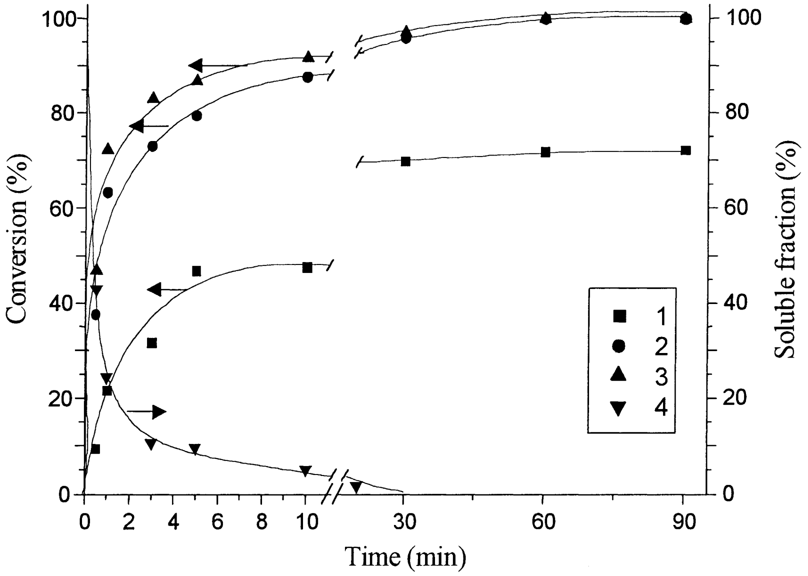


Fig. 4. Conversion vs. time curves for the photopolymerization of NPG: (1) in the absence of VCz; presence of VCz: (2) 2 mol%, (3) 10 mol%/ NPG monomer; (4) soluble fraction vs. time curve for the photopolymerization of NPG in the presence of 2 mol% VCz; $[TB]_0 = 3$ mol%/NPG monomer; temperature: 20 °C.

observed. For the photopolymerization of NPG with 2 mol% VCz complete depletion of the soluble fraction was established after 20 min of irradiation.

It was of interest to study photopolymerization of NPG in the presence of various amounts of OMC initiated with TB. The plots and the data obtained in these experiments are presented in Figs. 5 and 6, Table 2. It is evident that the high consumption rate of epoxy groups is the characteristic of photopolymerization of the system NPG:OMC (weight parts 10:1) (Fig. 5, curve 1). However, after reaching ca. 50% conversion of epoxy groups, the photopolymerization of the system NPG:OMC (10:1) slows down considerably and finally ca. 80% conversion of epoxy groups is reached after 150 min exposure. The decrease of the rate of the reaction occurs apparently due to gelation and vitrification of the samples which cause the chain mobility restrictions.

The effect of the temperature on the photopolymerization of the system NPG:OMC (10:1) has been studied. Fig. 5 (curves 1 and 2) shows that the increase in temperature upto 50 °C leads to the increase of the rate of consumption of

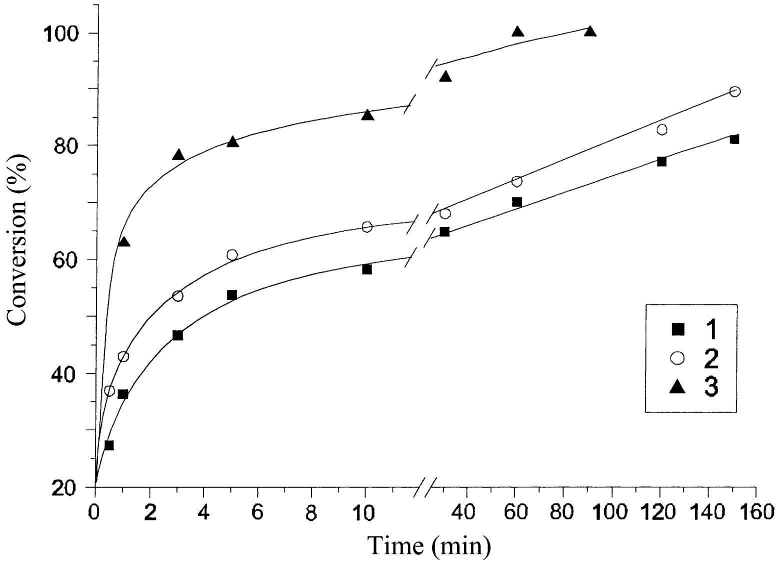


Fig. 5. Conversion vs. time curves for the photopolymerization of the composition NPG:OMC (10:1) in the absence (1, 2) and presence (3) of 2 mol% VCz. Temperature: 20 °C (1, 3); 50 °C (2). $[TB]_0 = 3$ mol%/monomers.

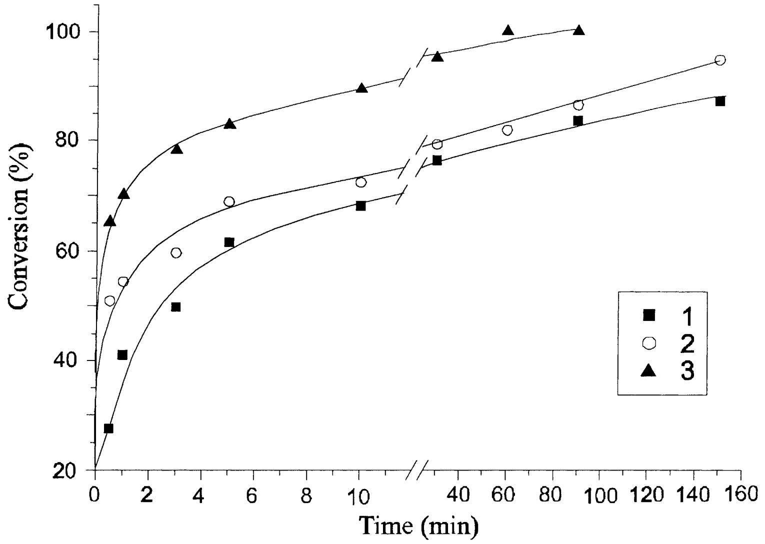


Fig. 6. Conversion vs. time curves for the photopolymerization of the composition NPG:OMC (8:1) in the absence (1, 2) and presence (3) of 2 mol% VCz. Temperature: 20 °C (1, 3); 50 °C (2). $[TB]_0 = 3$ mol%/monomers.

Table 2
Photopolymerization of the system NPG:OMC initiated with TB (3 mol%/ monomers)

Photopolymerization of composition NPG:OMC	Content of composition NPG:OMC (weight parts)	Temperature (°C)	Consumption rate of epoxygroups (%/s)[a]	Conversion of epoxygroups (%)[a]
Without the use of VCz	10:1	20	0.60	36.9
		50	0.72	42.9
	8:1	20	0.69	41.1
		50	0.91	54.4
In the presence of 2 mol%VCz	10:1	20	1.05	62.8
	8:1	20	1.16	70.1

[a] Measured after 1 min UV irradiation.

epoxy groups during the photopolymerization of the composition NPG:OMC (10:1). In addition, increase of the temperature enables to reach higher conversion of epoxy groups. Photopolymerization of the system NPG:OMC (10:1) conducted at 20 °C leads to 80% conversion of epoxy groups after 150 min irradiation, while ca. 90% conversion of epoxy groups is observed at 50 °C after the same period of time. The similar effect of the temperature was observed for the photopolymerization of the composition of NPG with OMC (8:1). The results obtained are shown in Fig. 6 (curves 1 and 2).

It is evident from the data presented in Figs. 5 and 6 and Table 2 that the rate of photopolymerization and total conversion of epoxy groups increase with the increase in amount of OMC in the composition. This observation can be ascribed to the electron-transfer photosensitization effect of the carbazolyl group of OMC monomer.

In order to establish the amount of OMC bonded into the crosslinked product, the samples after photopolymerization were extracted with THF for 7 h. The amount of OMC crosslinked was established by UV spectroscopy. The data obtained are presented in Table 3. The increase in the amount of OMC in the composition leads to the increase of OMC content in the crosslinked product and insoluble fraction. It was determined by GPC that the extract of the photocrosslinked composition of NPG and OMC (weight parts 10:1) consists of both fraction of poly(OMC) and OMC monomer (9.5 and 90.5%, respectively). The degree of polymerization of poly(OMC) is ca. 6. It is evident that both homopolymerization and copolymerization of OMC with NPG occur during UV irradiation of the system.

Table 3
Photopolymerization of the system NPG:OMC initiated with TB (3 mol%/monomers)[a]

NPG:OMC composition (weight parts)	Conversion of epoxygroups (%)	Insoluble fraction (%)	OMC bonded into the crosslinked product (%)
8:1	87.2	94.1	95.0
10:1	81.7	92.4	92.9

[a] Irradiation time is 150 min

The influence of VCz on the photopolymerization process of the system NPG:OMC (10:1) has been examined.

Fig. 5 (curves 1 and 3) enables to compare the results obtained in the photopolymerization of the system NPG:OMC without the use of VCz with those observed in the presence of VCz. The marked acceleration of the consumption rate of epoxy groups occurs in this photopolymerization, when the small amount of VCz (2 mol%) is added to the reaction mixture. The consumption rate of epoxy groups with the $R_p = 0.6\%/\mathrm{s}$ is observed for the photopolymerization of the composition NPG:OMC (10:1). Meanwhile, the addition of 2 mol% VCz leads to the increase of the value to 1.05%/s. Very similar synergistic effect of VCz on the photopolymerization of NPG in the presence of the higher amount of OMC was observed (Fig. 6, curves 1 and 3).

4. Conclusions

Photoinitiated cationic polymerization (photocrosslinking) of the bifunctional epoxy monomer, neopentyl glycol diglycidylether and its compositions with 9-(2-oxiranylmethyl) carbazole initiated with diphenyl iodonium tetrafluoroborate in bulk has been studied. The initiator exponent of 0.8 was obtained for the photopolymerization of neopentyl glycol diglycidylether initiated with diphenyliodonium tetrafluoroborate. It was established that temperature influences the rate of photopolymerization of neopentyl glycol diglycidylether as well as the consumption rate of epoxy groups in the photopolymerization of the composition of neopentyl glycol diglycidylether with 9-(2-oxiranylmethyl) carbazole. The increase in the temperature increases the rate of the reaction and the limit degree of conversion.

The synergistic effect of 9-vinylcarbazole on the photopolymerization of neopentyl glycol diglycidylether alone and in the presence of 9-(2-oxiranylmethyl) carbazole has been examined. The addition of small amount of 9-vinylcarbazole leads to marked acceleration in the rate of photopolymerization of neopentyl glycol diglycidylether and the increase of the consumption rate of epoxy groups in the photopolymerization of the composition of neopentyl glycol diglycidylether with 9-(2-oxiranylmethyl) carbazole. The increase in the concentration of 9-vinylcarbazole enhances the rate of the photopolymerizations. This effect has been attributed to the presence of a photoinitiated free-radical chain reaction when a large amount of cationic species capable to initiate epoxide ring opening polymerization is generated.

It was established that the increase in the amount of 9-(2-oxiranylmethyl) carbazole in the composition of neopentyl glycol diglycidylether and 9-(2-oxiranylmethyl) carbazole increases the consumption rate and total conversion of epoxy groups. It is suggested that 9-(2-oxiranylmethyl) carbazole acts as photosensitizer of diaryl iodonium salts when electron-transfer photosensitization mechanism is involved.

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