



# Synthesis and cross-linking of bifunctional monomers containing carbazole moieties

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## ABSTRACT

New bifunctional carbazolyl-containing monomers were synthesized and their cationic photo-initiated polymerization investigated. The monomers containing two reactive groups such as epoxy, oxetanyl and vinyloxyethyl, were prepared from commercially available 9-(2,3-epoxypropyl)carbazole. The kinetics of UV curing of the monomers was monitored by real-time FT-IR technique. The type of functionality was found to have a considerable influence on the photo-curing rate, but has not an evident effect on the final reactive group conversion. The cross-linked systems were found to have low glass transition temperatures ranging from 7 to 10 °C. Electron photoemission spectroscopy revealed ionization potentials of 5.75–5.8 eV for the thin cross-linked layers of the monomers.

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## 1. Introduction

Polymers and low-molar-mass derivatives containing carbazolyl groups have been widely investigated for their interesting chemical and physical properties. Several reviews are published reporting synthesis, properties and applications of the materials in the field of optoelectronic devices [1–5].

Photo-initiated polymerization has obtained important applications in a number of industrial fields such as coatings, inks, adhesives and photolithography. The basic investigations on the photo-polymerization, either with the radical or with the cationic mechanism, have been reported in several reviews [6–8]. The cationic photo-polymerization involves some advantages with respect to the radical one, such as absence of oxygen inhibition, low shrinkage, good adhesion, low toxicity of the functional groups [9]. Several series of cationically photo-cross-linkable polymers [10] and monomers [11] were reported for the application in optoelectronic devices, e.g. organic light emitting diodes.

Previously we have studied cationic photo-polymerization of oxiranes and vinyl ethers containing different electro-active groups initiated with various photo-initiators in bulk and in solution [12,13]. We have also studied cationic photo-cross-linking of the bifunctional 1,3-di(carbazol-9-yl)-2-propanol-based epoxy, oxetanyl and vinyl ether monomers and obtained highly cross-

linked networks characterized by a high gel content and  $T_g$  values ranging from 40 to 20 °C [14].

In this paper we report the preparation of new monomers containing carbazolyl groups and their cationic photo-initiated polymerization. The kinetics of UV curing reaction was investigated by real-time FT-IR analysis for all the monomers following the decrease of the absorption bands of the functional groups present in the monomers under UV irradiation. The aim was to compare the reactivity of the different functional groups as well as the preparation of electro-active polymer networks.

## 2. Experimental

### 2.1. Materials

9-(2,3-Epoxypropyl)carbazole (**1**) was purchased from “Biolars” (Latvia) and purified by re-crystallization from ethyl alcohol. M.p.: 113–114 °C.

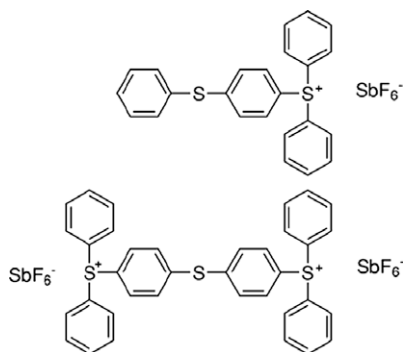
Tetraethylene glycol, epichlorohydrin, (2-chlorethyl)vinylether, potassium hydroxide, potassium carbonate, anhydrous sodium sulfate and tetrabutylammonium hydrogensulphate (TBAS) were purchased from Aldrich and used as received.

3-(Bromomethyl)-3-methyl oxetane was purchased from Chemada Fine Chemicals (Israel).

A mixture of triphenyl sulphonium hexafluoroantimonate salts (TSAS in Scheme 1) in propylene carbonate solution (50 wt%) was employed as photo-initiator (UVI6979 from Dow).

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Scheme 1. Structure of TSAS.

15-(Carbazol-9-yl)-3,6,9,12-tetraoxa-1,14-pentadecanediol (**2**): 15 g (70 mmol) of 9-(2,3-epoxypropyl)carbazole (**1**) and 130 g (700 mmol) of tetraethylene glycol were heated at 240 °C for 18 h under a nitrogen atmosphere. The reaction was stopped when no starting material **2** was left (TLC control). The reaction mixture was poured into water and the product was extracted with ethyl acetate. After washing with water the solution was dried over anhydrous sodium sulfate. Then the solvent was removed by evaporation and the product was purified by column chromatography using the mixture of *n*-hexane and ethyl acetate (vol. ratio 1:3) as an eluent. The yield of the product was 21.1 g (78%).

<sup>1</sup>H NMR spectrum (300 MHz, DMSO,  $\delta$ , ppm): 8.14 (d,  $J = 7.7$  Hz, 2H, 4,5-H Ht), 7.63 (d,  $J = 7.7$  Hz, 2H, 1,8-H Ht), 7.45 (m, 2H, 2,7-H Ht), 7.2 (m, 2H, 3,6-H Ht), 5.19 (d,  $J = 5.3$  Hz, 1H, CHOH), 4.61 (t,  $J = 5.5$  Hz, 1H, CH<sub>2</sub>OH), 4.47 (dd,  $J = 14.7$  Hz,  $J = 4.8$  Hz 1H, one proton NCH<sub>2</sub>), 4.31 (dd,  $J = 14.7$  Hz,  $J = 6.6$  Hz 1H, other proton NCH<sub>2</sub>), 4.13–4.01 (m, 1H, CH), 3.65–3.37 (m, 18H, CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>-CH<sub>2</sub>CH<sub>2</sub>).

MS(APCI<sup>+</sup>, 20 V),  $m/z$  (%): 418 ([M+H]<sup>+</sup>, 100).

IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3325 (OH), 3049 (C–H in Ar), 2934 (C–H), 1485, 1460 (C–N in Ar), 1048 (C–O–C), 747, 723 (Ar).

15-(Carbazol-9-yl)-3,6,9,12-tetraoxa-1,14-pentadecanediol diglycidyl ether (**3**): 4.8 mmol (2 g) of 15-(carbazol-9-yl)-3,6,9,12-tetraoxa-1,14-pentadecanediol (**2**) was dissolved in 1.3 g (14.1 mmol) of epichlorohydrin. After adding 14.1 mmol (1.98 g) of potassium carbonate and 14.1 mmol (0.8 g) of potassium hydroxide, the reaction mixture was stirred for 12 h at 25 °C. When the reaction was finished (TLC control), the reaction mixture was poured into water. The product was extracted with ethyl acetate. The organic fraction was dried over anhydrous sodium sulfate and the solvent was evaporated. The product was purified by column chromatography using the mixture of *n*-hexane and acetone (vol. ratio 1:1) as an eluent. The yield of the product was 1.8 g (74%).

<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.10 (d,  $J = 7.7$  Hz, 2H, 4,5-H, Ht), 7.48 (d,  $J = 7.7$  Hz, 2H, 1,8-H Ht), 7.47–7.35 (m, 2H, 2,7-H Ht), 7.23–7.10 (m, 2H, 3,6-H Ht), 4.53–4.26 (m, 2H NCH<sub>2</sub>), 3.98–3.84 (m, 1H, NCH<sub>2</sub>CH), 3.77–3.18 (m, 22H, CHOCH<sub>2</sub>, CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>4</sub>CH<sub>2</sub>), 3.11–3.01 (m, 1H, CH of oxirane), 2.85–2.72 (m, 1H, CH of other oxirane), 2.68 (dd,  $J = 5.0$  Hz,  $J = 4.2$  Hz 1H, one proton CH<sub>2</sub> of oxirane); 2.57–2.41 (m, 2H, other proton CH<sub>2</sub> of oxirane and one proton CH<sub>2</sub> of other oxirane), 2.36 (dd,  $J = 5.0$  Hz,  $J = 2.7$  Hz, 0.5H, one proton CH<sub>2</sub> of other oxirane), 2.20 (dd,  $J = 5.0$  Hz,  $J = 2.7$  Hz, 0.5H, one proton CH<sub>2</sub> of other oxirane).

MS(APCI<sup>+</sup>, 20 V),  $m/z$  (%): 530 ([M+H]<sup>+</sup>, 100).

IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3051C–H, in Ar), 2873C–H), 1484; 1460C–N, in Ar), 1107C–O–C of epoxy group), 754, 725Ar).

15-(Carbazol-9-yl)-1,14-di(vinyloxyethoxy)-3,6,9,12-tetraoxapentadecane (**4**): 4.8 mmol (2 g) of 15-(carbazol-9-yl)-3,6,9,12-tetraoxa-1,14-pentadecanediol (**2**) and 14.1 mmol (1.45 ml) of 2-chlorethylvinyl ether was dissolved in 20 ml of ethyl methyl

ketone. 14.1 mmol (1.98 g) of potassium carbonate, 14.1 mmol (0.8 g) of potassium hydroxide and catalytic amount of TBAS were added to the solution. The mixture was stirred for 28 h at 25 °C. When the reaction was finished (TLC control), the reaction mixture was poured into water. The product was extracted with ethyl acetate. The organic fraction was dried over anhydrous sodium sulfate and the solvent was evaporated. The product was purified by column chromatography using the mixture of *n*-hexane and acetone (vol. ratio 1:1) as an eluent. The yield of the product was 0.26 g (10%).

<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.07 (d,  $J = 7.7$  Hz, 2H, 4,5-H, Ht), 7.53 (d,  $J = 7.7$  Hz, 2H, 1,8-H Ht), 7.48–7.40 (m, 2H, 2,7-H Ht), 7.26–7.18 (m, 2H, 3,6-H Ht), 6.48 (dd,  $J = 14.3$  Hz,  $J = 6.8$  Hz, H, CH = CH<sub>2</sub>), 6.33 (dd,  $J = 14.3$  Hz,  $J = 6.8$  Hz, H, CH = CH<sub>2</sub>), 4.54 (dd,  $J = 15.0$  Hz,  $J = 5.2$  Hz 1H, one proton NCH<sub>2</sub>), 4.39 (dd,  $J = 15.0$  Hz,  $J = 6.9$  Hz 1H, other proton NCH<sub>2</sub>), 4.21–3.41 (m, 31H, CH(OCH<sub>2</sub>CH<sub>2</sub>O)CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>5</sub>, 2xCH = CH<sub>2</sub>).

MS(APCI<sup>+</sup>, 20 V),  $m/z$  (%): 558 ([M+H]<sup>+</sup>, 100).

IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3050(C–H in Ar), 2873 (C–H), 1620 (C = C), 1484, 1460; 1121 (C–N and C = C in Ar), 754, 725 (Ar).

15-(Carbazol-9-yl)-1,14-di(3-methyloxetan-3-ylmethoxy)-3,6,9,12-tetraoxapentadecane (**5**): 4.8 mmol (2 g) of 15-(carbazol-9-yl)-3,6,9,12-tetraoxa-1,14-pentadecanediol (**2**) were dissolved in 7.7 g (47 mmol) of 3-(bromomethyl)-3-methyl oxetane and 14.1 mmol (2 g) of potassium carbonate and 14.1 mmol (0.8 g) of potassium hydroxide were added. The reaction mixture was stirred for 2 h at room temperature. When the reaction was finished (TLC control), the reaction mixture was poured into water. The product was extracted with ethyl acetate. The organic fraction was dried over anhydrous sodium sulfate and the solvent was evaporated. The product was purified by column chromatography using the mixture of *n*-hexane and acetone (vol. ratio 1:1) as an eluent. The yield of the product was 1.76 g (64%).

<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.03 (d,  $J = 7.7$  Hz, 2H, 4,5-H, Ht), 7.49–7.35 (m, 4H, 1,2,7,8-H, Ht), 7.23–7.14 (m, 2H, 3,6-H, Ht), 4.56–3.40 (m, 32H, CH, CH<sub>2</sub> except one proton of oxetanyl group), 3.09 (d,  $J = 8.9$  Hz, one proton of oxetanyl group), 1.23 (s, 3H, CH<sub>3</sub>), 0.98 (s, 3H, CH<sub>3</sub>).

MS(APCI<sup>+</sup>, 20 V),  $m/z$  (%): 586 ([M+H]<sup>+</sup>, 100).

IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3051C–H in Ar), 2955, 2930C–H), 1485, 1461C–N in Ar), 1219, 1326C–CH<sub>3</sub>), 1110C–O–C), 754, 725Ar).

## 2.2. Procedures

Cationic photo-initiated cross-linking of the monomers **3–5** was carried out as follows. 4 wt% of the photo-initiator were added to the different monomers and the mixtures obtained were coated onto glass substrates by means of a wire wound applicator and irradiated by means of a medium pressure Hg lamp (Italquartz, Milano, Italy). The light intensity at the film surface was 20 mW/cm<sup>2</sup>.

The kinetics of the photo-polymerization were monitored by real-time FT-IR spectroscopy, employing a Thermo-Nicolet 5700 instrument provided with a low temperature detector. The products were coated onto a silicon wafer. The sample was exposed simultaneously to the UV beam and to the IR beam, which analyzes in situ the extent of the reaction. Since the IR absorbance is proportional to the monomer concentration, conversion versus irradiation time profiles can be obtained. Reactive group conversions were followed by monitoring the decrease of the area in the region of 760–780 cm<sup>-1</sup> due to epoxy groups, in the region of 873–808 cm<sup>-1</sup> due to oxetanyl groups and in the region of 1560–1640 cm<sup>-1</sup> due to vinyl ether double bonds. A medium pressure mercury lamp equipped with an optical waveguide was used to induce the photo-polymerization (light intensity on the surface of the sample was of ca 3 mW/cm<sup>2</sup>). For avoiding differences in the kinetic curves

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