

# Monomers and oligomers with the pendent adducts of carbazole with 5*H*-dibenz(b,f)azepine and its 10,11-dihydro derivative

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## ABSTRACT

The synthesis of a series of carbazole-based monomers incorporating dibenzazepines at the 3 position is reported. Full characterization of their structures is presented. The monomers were subjected to cationic polymerization using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as an initiator. The synthesized low-molar-mass compounds and oligomers were examined by differential scanning calorimetry, UV spectrometry, electron photoemission and time of flight techniques. The electron photoemission spectra of the films of synthesized materials revealed the ionization potentials of 5.12–5.34 eV. Hole drift mobilities of low-molar-mass compounds molecularly dispersed in bisphenol Z polycarbonate range from  $2.6 \times 10^{-8}$  to  $1.7 \times 10^{-6} \text{ cm}^2/\text{V s}$  at high electric fields as it was established by xerographic time of flight technique.

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## 1. Introduction

Electroactive film-forming polymers and low-molar-mass glasses are known for various applications such as electrophotographic photoreceptors [1], light emitting diodes [2], photovoltaic cells [3]. In electrophotography low-molar-mass charge-transporting materials are usually used as components of molecular mixtures with inert polymers. Such systems are known as molecularly doped polymers [4]. Charge-transporting polymers have some important advantages with respect to their low-molar-mass counterparts and molecularly doped polymers. They usually possess better mechanical properties and high morphological stability. In addition no diffusion between layers is observed in the multilayer devices when polymers are used for the preparation of charge-transporting layers.

Polymers containing carbazolyl groups have been extensively studied for the different applications due to their good hole-transporting and luminescent properties [5]. In our laboratories, several families of new carbazole derivatives have been synthesized and their charge transport properties have been studied [6,7]. Carbazole derivatives having 9-carbazolyl substituents in the 3rd and 6th positions of carbazole ring have appeared to show high triplet energies and to be effective hosts of blue electrophosphorescent devices [8]. Carbazole derivatives having diphenylamino moieties in the 3rd position of carbazole ring showed

moderate hole-transporting properties [9,10]. One of the reasons of this observation could be non-planar structure of diphenylamino groups which apparently hinders  $\pi$ -stacking.  $\pi$ -Stacking, although not a guarantee of good wavefunction overlap [11], is a feature of many high mobility materials [12]. It was therefore of interest to compare the properties of diphenylamino-substituted derivatives with those of the analogous compounds containing the moieties of dibenz(b,f)azepine and its 10,11-dihydro derivative. The rotation of phenyl groups in the later moieties is expected to be restricted thus making more probable formation of the planar structures.

Herewith we report on the design, synthesis and characterization of new monomers and oligomers with electroactive pendants consisting of dibenzazepine- and dihydro dibenzazepine-substituted carbazole moieties.

## 2. Experimental

### 2.1. Instrumentation

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using Varrian Unity Inova (300 MHz ( $^1\text{H}$ ), 75.4 MHz ( $^{13}\text{C}$ )) apparatus. Infrared (IR) spectra were recorded using Perkin Elmer Spectrum GX spectrometer. The spectra of solid compounds were performed in KBr pellets. Mass (MS) spectra were obtained on a Waters ZQ 2000 (Waters, Milford, USA). Elemental analysis was performed with an Exeter Analytical CE-440 Elemental. Melting point (m.p.) of the material was determined using Electrothermal Mel-Temp apparatus.

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Ultraviolet (UV) absorption spectra were recorded with Hitachi U-3000 and Spectronic Unicam Genesys 8 spectrometers. Fluorescence (FL) emission spectra were recorded with a Hitachi MPF-4 (Japan) spectrometer and Shimadzu RF-5301PC. Dilute solutions of the materials in tetrahydrofuran (THF) were used for the UV absorption and FL measurements.

Different scanning calorimetry (DSC) measurements were carried out using Perkin-Elmer Diamond DSC apparatus. Thermogravimetric analysis (TGA) was performed on METTLER TOLEDO TGA/SDTA 851<sup>e</sup> and Netzsch STA 409 with a data acquisition system 414/1. The DSC and TGA experiments were performed in a nitrogen atmosphere at a heating rate of 10 °C/min.

The average molecular weights and the molecular weight distributions were estimated by size exclusion chromatography (SEC) using a system including Waters 515 pump, Waters 410 UV detector (254 nm), precolumn (SDV-Gel (PSS), *L*: 5 cm, *D*: 0.8 cm, particle size: 5 μm, pore size 100 Å) and analytical columns (mixed-C PL-Gel (PL), *L*: 2 × 30 cm; *D*: 0.8 cm, particle size 5 μm). THF was used as eluent at elution rate of 0.5 ml/min. Calibration was carried out using polystyrene standards.

MALDI-TOF spectra were recorded using a Shimadzu AXIMA Performance instrument. Dithranol (1,8-dihydroxy-9,10-dihydroanthracen-9-one) and Norharmane (9H-pyrido[3,4-b]indole) dissolved in tetrahydrofuran were used as matrices.

The ionization potentials ( $I_p$ ) of the films of the synthesized compounds were measured by the electron photoemission in air method as described before [13]. The samples for the measurements were prepared by dissolving materials in THF and by coating on Al plates pre-coated with ~0.5 μm thick methylmethacrylate and methacrylic acid copolymer adhesive layer [14]. The measurement method is, in principle, similar to the described in literature [15].

Hole drift mobility was measured by xerographic time of flight technique [16,17]. The samples for the charge carrier mobility measurements were prepared by procedure as described earlier [18].

## 2.2. Materials

9H-carbazole and 3-bromomethyl-3-methyloxetane were purchased from Reachim and Chemada, respectively. 5H-Dibenz(b,f)azepine (iminostilbene), 10,11-dihydro-5H-dibenz(b,f)azepine (iminodibenzyl), 2-ethylhexylbromide, 2-chloroethylvinylether, tris-(dibenzylideneacetone)dipalladium(0) (Pd<sub>2</sub>(dba)<sub>3</sub>), tri-*tert*-butylphosphine (1 M solution in toluene, (t-Bu)<sub>3</sub>P) were purchased from Aldrich and used as received. Boron trifluoride diethyl etherate [BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>] (Aldrich) was distilled before use (bp 125–126 °C). 3-Iodocarbazole (m.p.: 191–193 °C, lit.: 192–194 °C) was synthesized by the method of Tucker [19]. 3-Iodo-9-(2-ethylhexyl)carbazole was prepared by alkylation of 3-iodocarbazole in the presence of a phase transfer catalyst [20]. 3-Iodo-9-[(3-methyloxetane-3-yl)methyl]carbazole (m.p.: 111–112 °C, lit.: 115 °C) was prepared by the reported procedure [21].

3-Iodo-9-[2-(vinylxy)ethyl]carbazole was prepared by the reaction of 3-iodocarbazole with an excess of 2-chloroethylvinylether under basic conditions in the presence of a phase transfer catalyst. 3-Iodocarbazole (3 g, 10 mmol), 2-chloroethylvinylether (5.43 g, 51 mmol), sodium sulfate (2.84 g, 20 mmol), potassium hydroxide (3.34 g, 60 mmol) and tetrabutylammonium hydrogensulfate (TBAHS) (0.07 g, 0.2 mmol) were stirred in ethylmethylketone (10 ml) at 60 °C for 3 h. The crude product was extracted with ethylacetate and crystallized from methanol. The yield was 95% of white crystals (FW = 363 g/mol, m.p.: 119–120 °C).

<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>, δ, ppm): 4.00–4.04 (m, 3H, CH=CH<sub>2</sub>, NCH<sub>2</sub>), 4.18 (dd, *J*<sub>1</sub> = 14.3 Hz, *J*<sub>2</sub> = 2.2 Hz, 1H, CH=CH<sub>2</sub>), 4.50 (t, *J* = 6.1 Hz, 2H, OCH<sub>2</sub>), 6.45 (dd, *J*<sub>1</sub> = 14.6 Hz, *J*<sub>2</sub> = 7.0 Hz, 1H, O—CH=), 7.34–7.65 (m, 3H, Ar), 8.16 (d, *J* = 7.8 Hz, 1H, Ar), 8.34 (s, 1H, Ar).

IR (KBr, cm<sup>-1</sup>): 3043 (C—H, Ar); 2926, 2870 (C—H); 1612, 1606 (C=C), 1452, 1469 (C—C, Ar); 1316 (C—N); 1012 (C—O—C); 818, 795 (C—H, Ar).

MS (APCI<sup>+</sup>, 20 V, *m/z*): 364 ([M+H]<sup>+</sup>, 45%).

3-[Dibenz(b,f)azepinyl]-9-(2-ethylhexyl)carbazole (**1a**) was obtained by Ullmann coupling reaction. 3-Iodo-9-(2-ethylhexyl)carbazole (1.57 g, 3.8 mmol), 5H-dibenz(b,f)azepine (0.5 g, 2.5 mmol), powdered anhydrous potassium carbonate (2.79 g, 20 mmol), copper powder (0.635 g, 10 mmol) and 18-crown-6 (0.3 g, 1 mmol) were refluxed in *o*-dichlorobenzene (5 ml) under nitrogen for 24 h. Then copper and inorganic salts were removed by filtration of the hot reaction mixture. The solvent was distilled under reduced pressure. The crude product was purified by column chromatography using an eluent mixture of hexane and acetone in a volume ratio of 10:1. The yield was 22% (0.4 g) of yellow crystals (FW = 470 g/mol, m.p.: 166–167 °C).

<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>, δ, ppm): 0.92 (t, *J* = 7.3 Hz, 6H, CH<sub>3</sub>), 1.30–1.42 (m, 8H, CH<sub>2</sub>), 2.00–2.07 (m, 1H, CH), 4.07 (q, 2H, NCH<sub>2</sub>), 6.55 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.2 Hz, 1H, Ar), 6.89 (s, 2H, Ar), 6.97 (d, *J* = 2.2 Hz, 1H, Ar), 7.10 (t, *J* = 8.1 Hz, 2H, Ar), 7.30–7.68 (m, 10H, Ar), 7.84 (d, *J* = 8.1 Hz, 1H, Ar).

<sup>13</sup>C NMR spectrum (75.4 MHz, CDCl<sub>3</sub>, δ, ppm): 11.2 (CH<sub>3</sub>), 14.4 (CH<sub>3</sub>), 23.4 (CH<sub>2</sub>), 24.6 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 31.3 (CH<sub>2</sub>), 39.8 (CH), 47.7 (NCH<sub>2</sub>), 102.9, 108.9, 112.4, 117.9, 120.5, 122.7, 123.1, 123.4, 127.2, 130.2, 130.9, 131.4, 135.3, 137.2, 141.7, 143.0, 144.6.

IR (KBr, cm<sup>-1</sup>): 3042 (C—H, Ar); 2950, 2925, 2875 (C—H); 1459, 1441 (C—C, Ar); 1320 (C—N); 796, 745 (C—H, Ar).

MS (APCI<sup>+</sup>, 20 V, *m/z*): 471 ([M+H]<sup>+</sup>, 100%).

Elemental analysis. Calcd for C<sub>34</sub>H<sub>34</sub>N<sub>2</sub> (%): C 86.77, H 7.28, N 5.95; found (%): C 84.61, H 7.63, N 5.57.

3-[Dibenz(b,f)azepinyl]-9-[(3-methyloxetane-3-yl)methyl]carbazole (**1b**) was obtained by the similar procedure as described [22]. Pd<sub>2</sub>(dba)<sub>3</sub> (0.12 g, 0.13 mmol) and (t-Bu)<sub>3</sub>P (0.02 g, 0.13 mmol) were dissolved under argon in 23 ml of dry toluene and stirred for 10 min at room temperature (preformation of the catalyst). Then the mixture of 3-iodo-9-[(3-methyloxetane-3-yl)methyl]carbazole (2 g, 5.3 mmol), 5H-dibenz(b,f)azepine (1.33 g, 6.8 mmol) and sodium *tert*-butoxide (3.05 g, 31.8 mmol) in 65 ml of dry toluene were added. The reaction mixture was heated at 90 °C for 2 h. After cooling, the reaction mixture was diluted with ethyl acetate and the organic phase was washed with water and brine. After being dried over Na<sub>2</sub>SO<sub>4</sub> and filtered, the solvent was removed and the residue was purified by column chromatography using an eluent mixture of hexane and acetone in volume ratio of 20:1. The yield was 57% (1.32 g) of yellow crystals (FW = 442 g/mol, m.p.: 200–201 °C).

<sup>1</sup>H NMR spectrum (300 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 1.28 (s, 3H, CH<sub>3</sub>), 4.12 (d, *J* = 5.9 Hz, 2H, OCH<sub>2</sub>), 4.33 (s, 2H, NCH<sub>2</sub>), 4.55 (d, *J* = 5.9 Hz, 2H, OCH<sub>2</sub>), 6.36 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.2 Hz, 1H, Ar), 6.78 (d, *J* = 2.2 Hz, 1H, Ar), 6.91 (s, 2H, Ar), 7.02 (t, *J* = 7.7 Hz, 1H, Ar), 7.25 (d, *J* = 9.2 Hz, 1H, Ar), 7.34 (t, *J* = 8.0 Hz, 1H, Ar), 7.44–7.51 (m, 3H, Ar), 7.57–7.63 (m, 6H, Ar), 7.67 (d, *J* = 8.1 Hz, 1H, Ar).

<sup>13</sup>C NMR spectrum (75.4 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 23.5 (CH<sub>3</sub>), 43.0 (CH), 48.6 (NCH<sub>2</sub>), 80.1 (OCH<sub>2</sub> in oxetane ring), 102.3, 110.3, 110.4, 112.7, 118.9, 120.4, 122.2, 126.2, 127.9, 130.9, 131.1, 131.6, 135.6, 137.1, 142.1, 143.4, 144.3.

IR (KBr, cm<sup>-1</sup>): 3049 (C—H, Ar); 2964, 2944, 2872 (C—H); 1486, 1463 (C—C, Ar); 1317 (C—N); 1156 (C—O—C); 805, 795, 744 (C—H, Ar).

MS (APCI<sup>+</sup>, 20 V, *m/z*): 443 ([M+H]<sup>+</sup>, 100%).

Elemental analysis. Calcd for C<sub>31</sub>H<sub>26</sub>N<sub>2</sub>O (%): C 84.13, H 5.92, N 6.33; found (%): C 84.59, H 6.24, N 6.73.

3-[Dibenz(b,f)azepinyl]-9-[2-(vinylxy)ethyl]carbazole (**1c**) was synthesized by similar procedure as compound **1b**. 3-Iodo-9-(2-(vinylxy)ethyl)carbazole (1 g, 4.7 mmol), 5H-dibenz(b,f)azepine (1.3 g, 6.09 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.1 g, 1.2 mmol), (t-Bu)<sub>3</sub>P (0.02 g,

1.2 mmol), sodium *tert*-butoxide (2.7 g, 28.2 mmol) and dry toluene (40 ml) were used. The crude product was purified by column chromatography using an eluent mixture of hexane and acetone in volume ratio of 5:1. The yield was 49% (0.9 g) of yellow crystals (FW = 428 g/mol, m.p.: 162–163 °C).

<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>, δ, ppm): 4.01–4.04 (m, 3H, CH = CH<sub>2</sub>, NCH<sub>2</sub>), 4.18 (dd, *J*<sub>1</sub> = 14.3 Hz, *J*<sub>2</sub> = 2.2 Hz, 1H, CH = CH<sub>2</sub>), 4.48 (t, *J* = 6.2 Hz, 2H, OCH<sub>2</sub>), 6.45 (dd, *J*<sub>1</sub> = 14.6 Hz, *J*<sub>2</sub> = 7.0 Hz, 1H, O–CH=), 6.57 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.6 Hz, 1H, Ar), 6.90 (s, 2H, Ar), 6.98 (d, *J* = 2.6 Hz, 1H, Ar), 7.12–7.17 (m, 2H, Ar), 7.36–7.69 (m, 10H, Ar), 7.86 (d, *J* = 7.7 Hz, 1H, Ar).

<sup>13</sup>C NMR spectrum (75.4 MHz, CDCl<sub>3</sub>, δ, ppm): 42.4 (NCH<sub>2</sub>), 65.9 (CH=CH<sub>2</sub>), 87.2 (OCH<sub>2</sub>), 103.0 (CH=CH<sub>2</sub>), 108.7, 112.5, 118.5, 120.7, 123.06, 123.4, 125.7, 127.3, 130.2, 130.9, 131.4, 134.8, 137.2, 141.3, 143.4, 144.6, 151.6.

IR (KBr, cm<sup>-1</sup>): 3049 (C–H, Ar); 2921, 2868 (C–H); 1610 (C=C), 1485, 1461 (C–C, Ar); 1307 (C–N); 1095 (C–O–C); 800, 736 (C–H, Ar).

MS (APCI<sup>+</sup>, 20 V, *m/z*): 429 ([M+H]<sup>+</sup>, 35%).

Elemental analysis. Calcd for C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>O (%): C 84.08, H 5.65, N 6.54; found (%): C 86.99, H 6.19, N 6.92.

3-[10,11-Dihydrodibenz(b,f)azepinyl]-9-(2-ethylhexyl)carbazole (**2a**) was prepared according to the same procedure as described for **1a**, using 10,11-dihydro-5*H*-dibenz(b,f)azepine as secondary amine, and purified by column chromatography using an eluent mixture of hexane and acetone in volume ratio of 10:1. The yield was 37% of compound **2a** (FW = 472 g/mol, m.p.: 94–95 °C).

<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>, δ, ppm): 0.96 (t, *J* = 7.3 Hz, 6H, CH<sub>3</sub>), 1.31–1.50 (m, 8H, CH<sub>2</sub>), 2.07–2.02 (m, 1H, CH), 3.11 (s, 4H, CH<sub>2</sub>–CH<sub>2</sub>), 4.20 (q, 2H, NCH<sub>2</sub>), 6.96 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 2.0 Hz, 1H, Ar), 7.15 (t, *J* = 7.3 Hz, 1H, Ar), 7.26–7.59 (m, 12H, Ar), 7.94 (d, *J* = 7.7 Hz, 1H, Ar).

<sup>13</sup>C NMR spectrum (75.4 MHz, CDCl<sub>3</sub>, δ, ppm): 11.2 (CH<sub>3</sub>), 14.4 (CH<sub>3</sub>), 23.4 (CH<sub>2</sub>), 24.7 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 31.3 (CH<sub>2</sub>), 31.65 (2CH<sub>2</sub>), 39.8 (CH), 47.7 (NCH<sub>2</sub>), 105.0, 109.0, 109.3, 114.4, 118.1, 120.6, 122.8, 123.5, 125.6, 126.7, 127.3, 130.6, 131.2, 135.2, 138.8.

IR (KBr, cm<sup>-1</sup>): 3048 (C–H, Ar); 2953, 2930, 2870 (C–H); 1485, 1459, 1440 (C–C, Ar); 1321 (C–N); 774, 744 (C–H, Ar).

MS (APCI<sup>+</sup>, 20 V, *m/z*): 473 ([M+H]<sup>+</sup>, 100%).

Elemental analysis. Calcd for C<sub>34</sub>H<sub>36</sub>N<sub>2</sub> (%): C 86.40, H 7.68, N 5.93; found (%): C 86.34, H 8.12, N 5.82.

3-[10,11-Dihydrodibenz(b,f)azepinyl]-9-[(3-methyloxetane-3-yl)methyl]carbazole (**2b**) was synthesized according to the same procedure as described for **1b**, using 10,11-dihydro-5*H*-dibenz(b,f)azepine as secondary amine, and purified by column chromatography using using an eluent mixture of hexane and acetone in volume ratio of 20:1. The yield was 67% of yellow crystals (FW = 444 g/mol, m.p.: 208–209 °C).

<sup>1</sup>H NMR spectrum (300 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 1.33 (s, 3H, CH<sub>3</sub>), 2.97 (s, 4H, CH<sub>2</sub>–CH<sub>2</sub>), 4.16 (d, *J* = 5.9 Hz, 2H, OCH<sub>2</sub>), 4.40 (s, 2H, NCH<sub>2</sub>), 4.59 (d, *J* = 5.9 Hz, 2H, OCH<sub>2</sub>), 6.79 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.2 Hz, 1H, Ar), 7.07 (t, *J* = 7.7 Hz, 1H, Ar), 7.22–7.55 (m, 12H, Ar), 7.81 (d, *J* = 7.7 Hz, 1H, Ar).

<sup>13</sup>C NMR spectrum (75.4 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 23.5 (CH<sub>3</sub>), 31.4 (2CH<sub>2</sub>), 43.1 (CH), 48.6 (NCH<sub>2</sub>), 80.1 (OCH<sub>2</sub> in oxetane ring), 105.1, 110.3, 110.9, 115.1, 119.0, 120.7, 122.4, 123.3, 126.3, 127.2, 127.9, 130.3, 131.7, 135.7, 138.5.

IR (KBr, cm<sup>-1</sup>): 3053 (C–H, Ar); 2954, 2925, 2874 (C–H); 1488, 1466, 1456 (C–C, Ar); 1317 (C–N); 1062 (C–O–C); 781, 751 (C–H, Ar).

MS (APCI<sup>+</sup>, 20 V, *m/z*): 445 ([M+H]<sup>+</sup>, 100%).

Elemental analysis. Calcd for C<sub>31</sub>H<sub>28</sub>N<sub>2</sub>O (%): C 83.75, H 6.35, N 6.30; found (%): C 82.52, H 6.41, N 6.27.

3-[10,11-Dihydrodibenz(b,f)azepinyl]-9-[2-(vinyl-oxy)ethyl]carbazole (**2c**) was synthesized according to the same procedure as described for **1c**, using 10,11-dihydro-5*H*-dibenz(b,f)azepine as

secondary amine, and purified by column chromatography using an eluent mixture of hexane and acetone in volume ratio of 20:1. The yield was 53% of compound **2c** (FW = 430 g/mol, m.p.: 132–133 °C).

<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>, δ, ppm): 3.10 (s, 4H, CH<sub>2</sub>–CH<sub>2</sub>), 4.03–4.10 (m, 3H, CH=CH<sub>2</sub>, NCH<sub>2</sub>), 4.18 (dd, *J*<sub>1</sub> = 14.3 Hz, *J*<sub>2</sub> = 2.6 Hz, 1H, CH=CH<sub>2</sub>), 4.54 (t, *J* = 5.9 Hz, 2H, OCH<sub>2</sub>), 6.45 (dd, *J*<sub>1</sub> = 14.3 Hz, *J*<sub>2</sub> = 7.0 Hz, 1H, O–CH=), 6.94 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.6 Hz, 1H, Ar), 7.14–7.58 (m, 13H, Ar), 7.93 (d, *J* = 7.7 Hz, 1H, Ar).

<sup>13</sup>C NMR spectrum (75.4 MHz, CDCl<sub>3</sub>, δ, ppm): 31.6 (2CH<sub>2</sub>), 42.5 (NCH<sub>2</sub>), 66.0 (CH=CH<sub>2</sub>), 87.2 (OCH<sub>2</sub>), 104.9 (CH=CH<sub>2</sub>), 108.8, 109.1, 114.4, 118.6, 120.7, 123.1, 123.8, 125.8, 126.8, 127.4, 130.6, 131.2, 134.7, 138.8, 141.6.

IR (KBr, cm<sup>-1</sup>): 3048 (C–H, Ar); 2936, 2916, 2870 (C–H); 1612, 1606 (C=C), 1488, 1467 (C–C, Ar); 1321 (C–N); 1148 (C–O–C); 811, 778, 744 (C–H, Ar).

MS (APCI<sup>+</sup>, 20 V, *m/z*): 431 ([M+H]<sup>+</sup>, 100%).

Elemental analysis. Calcd for C<sub>30</sub>H<sub>26</sub>N<sub>2</sub>O (%): C 83.69, H 6.09, N 6.51; found (%): C 83.30, H 6.41, N 6.37.

Poly{3-[dibenz(b,f)azepinyl]-9-[(3-methyloxetane-3-yl)methyl]carbazole} (**3**) 3-[Dibenz(b,f)azepinyl]-9-[(3-methyloxetane-3-yl)methyl]carbazole (**1b**, 0.5 g, 1.1 mmol) was dissolved in 2 ml of dichloroethane under nitrogen. Then BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (0.055 mmol, 6.4 μl) was added to the solution and the reaction mixture was stirred for 24 h at 60 °C under argon. After the reaction the initiator was neutralized by ammonia solution. Then the solvent was removed by evaporation. The product was dissolved in a small amount of THF and precipitated into methanol. After Soxhlet extraction (24 h) by methanol and re-precipitation, the yield of polymer **3** was 89% (0.45 g).

<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>, δ, ppm): 0.61–1.09 (m, 3H, CH<sub>3</sub>), 2.93–3.41 (m, 4H, OCH<sub>2</sub>, NCH<sub>2</sub>), 3.91–4.28 (m, 2H, OCH<sub>2</sub>), 6.28–7.85 (m, 17H, Ar).

IR (KBr, cm<sup>-1</sup>): 3049 (C–H, Ar); 2871 (C–H); 1488, 1464 (C–C, Ar); 1319 (C–N); 1119 (C–O–C); 795, 743 (C–H, Ar).

Poly{3-[10,11-dihydrodibenz(b,f)azepinyl]-9-[(3-methyloxetane-3-yl)methyl]carbazole} (**4**) was prepared using 3-[10,11-dihydrodibenz(b,f)azepinyl]-9-[(3-methyloxetane-3-yl)methyl]carbazole (**2b**) (0.4 g, 0.9 mmol) and cationic initiator BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (5.2 μl, 0.045 mmol) by the same procedure as described for polymer **3**. After Soxhlet extraction (24 h) by methanol and re-precipitation, the yield of polymer **4** was 55% (0.22 g).

<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>, δ, ppm): 0.84–1.20 (m, 3H, CH<sub>3</sub>), 2.80–3.10 (m, 4H, CH<sub>2</sub>–CH<sub>2</sub>), 3.14–3.59 (m, 4H, OCH<sub>2</sub>, NCH<sub>2</sub>), 4.00–4.49 (m, 2H, OCH<sub>2</sub>), 6.59–7.96 (m, 15H, Ar).

IR (KBr, cm<sup>-1</sup>): 3049 (C–H, Ar); 2925, 2873 (C–H); 1487, 1464, 1448 (C–C, Ar); 1320 (C–N); 1110 (C–O–C); 774, 744 (C–H, Ar).

Poly{3-[dibenz(b,f)azepinyl]-9-[2-(vinyl-oxy)ethyl]carbazole} (**5**) was prepared using 3-[Dibenz(b,f)azepinyl]-9-[2-(vinyl-oxy)ethyl]carbazole (**1c**) (0.3 g, 0.7 mmol) and BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (4 μl, 0.035 mmol) by the same procedure as described for polymer **3**. After Soxhlet extraction (24 h) by methanol and re-precipitation, the yield of polymer **5** was 30% (0.12 g).

<sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>, δ, ppm): 1.54–1.81 (m, 2H, CH<sub>2</sub>), 3.65–4.54 (m, 4H, OCH<sub>2</sub>, NCH<sub>2</sub>), 4.98–5.02 (m, 1H, OCH), 6.27–8.27 (m, 17H, Ar).

IR (KBr, cm<sup>-1</sup>): 3051, 3021 (C–H, Ar); 2927 (C–H); 1488 (C–C, Ar); 1319 (C–N); 1115 (C–O–C); 797, 763, 746 (C–H, Ar).

Poly{3-[10,11-dihydrodibenz(b,f)azepinyl]-9-[2-(vinyl-oxy)ethyl]carbazole} (**6**) was prepared using 3-[10,11-Dihydrodibenz(b,f)azepinyl]-9-[2-(vinyl-oxy)ethyl]carbazole (**2c**) (0.35 g, 0.81 mmol) and BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (4.7 μl, 0.04 mmol) by the same procedure as described for polymer **3**. After Soxhlet extraction (24 h) by methanol and re-precipitation, the yield of polymer **6** was 67% (0.23 g).

$^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 1.34–2.00 (m, 2H,  $\text{CH}_2$ ), 2.65–3.25 (m, 4H,  $\text{CH}_2\text{—CH}_2$ ), 3.66–4.02 (m, 4H,  $\text{OCH}_2$ ,  $\text{NCH}_2$ ), 4.98–5.10 (m, 1H,  $\text{OCH}$ ), 6.71–8.12 (m, 15H, Ar).

IR (KBr,  $\text{cm}^{-1}$ ): 3020 (C—H, Ar); 2925 (C—H); 1488, 1466 (C—C, Ar); 1318 (C—N); 1111 (C—O—C); 796, 775, 745 (C—H, Ar).

### 3. Results and discussion

3-Substituted carbazole monomers **1b–c**, **2b–c** and glass-forming model compounds **1a**, **2a** were synthesized by three-step synthetic route involving iodination and the reactions of 3-iodocarbazole with 3-bromomethyl-3-methyloxetane, 2-chloroethylvinyl ether or 2-ethylhexylbromide, followed by aromatic C—N coupling reactions of 3-iodo-9-alkylcarbazoles with an excess of different dibenzazepines (Scheme 1).

The oxetanyl- and vinyloxyethyl-functionalized monomers (**1b**, **1c**, **2b** and **2c**) were used for the synthesis of oligomers **3–6** by cationic polymerization (Scheme 2). The monomers were subjected to polymerization in 1,2-dichloroethane solutions using  $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$  as an initiator. Low-molar-mass fractions were removed by Soxhlet extraction with methanol.

The structures of all derivatives were confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectrometries. Low-molar-mass compounds were also characterized by mass spectrometry and elemental analysis. The data were found to be in good agreement with the proposed structures. The number average ( $M_n$ ) and weight average ( $M_w$ ) molecular weights of the products of polymerization (**3–6**) were estimated by SEC using polystyrene standards. The SEC results (Table 1) indicate that the cationic polymerizations yield polymers of rather low molecular weights with  $M_w$  ranging from 2630 to 5740 and relatively broad molecular weight distribution. This observation can apparently be explained by chain transfer reactions which can occur during cationic polymerization [23].

MALDI-TOF measurements were also used to estimate the molecular weights and the molecular weights distribution of the synthesized oligomers **3–6**. The MALDI-TOF results, given in Table 1, show that  $M_n$  and  $M_w$  values of compounds **3–6** differ from the corresponding molecular weights estimated by SEC. It could be explained by the relatively broad molecular weight distribution of compounds **3–6** [24].

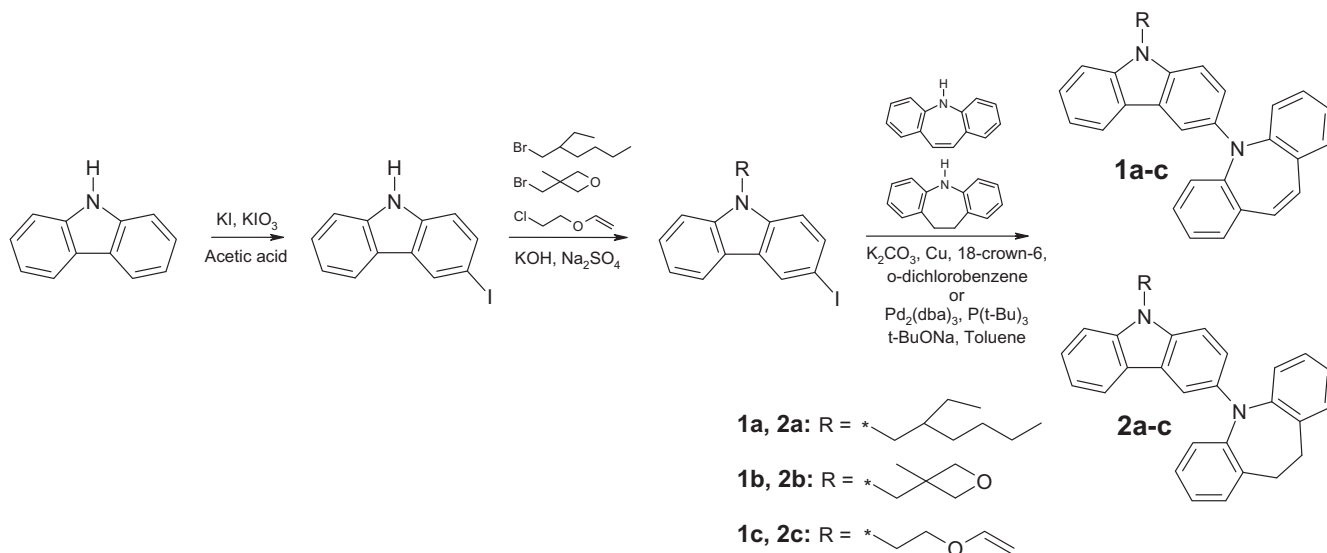
The behavior under heating of the low-molar-mass compounds and oligomers was studied by DSC and TGA under nitrogen

atmosphere. The values of glass transition temperatures ( $T_g$ ), melting points ( $T_m$ ) and of 5% weight loss temperatures ( $T_{10}$ ) are summarized in Table 2. The synthesized materials demonstrate relatively high thermal stability. Their  $T_{10}$  values of range from 320 to 410 °C. The oligomers exhibit higher  $T_{10}$  than the corresponding monomers (Table 2). Among low-molar-mass compounds the highest  $T_{10}$  values were observed for oxetanes **1b** and **2b**, while vinyl ethers **1c** and **2c** demonstrated the lowest thermal stabilities. It seems that the nature of pendants does not have any substantial effect on the thermal stability of the compounds synthesized.

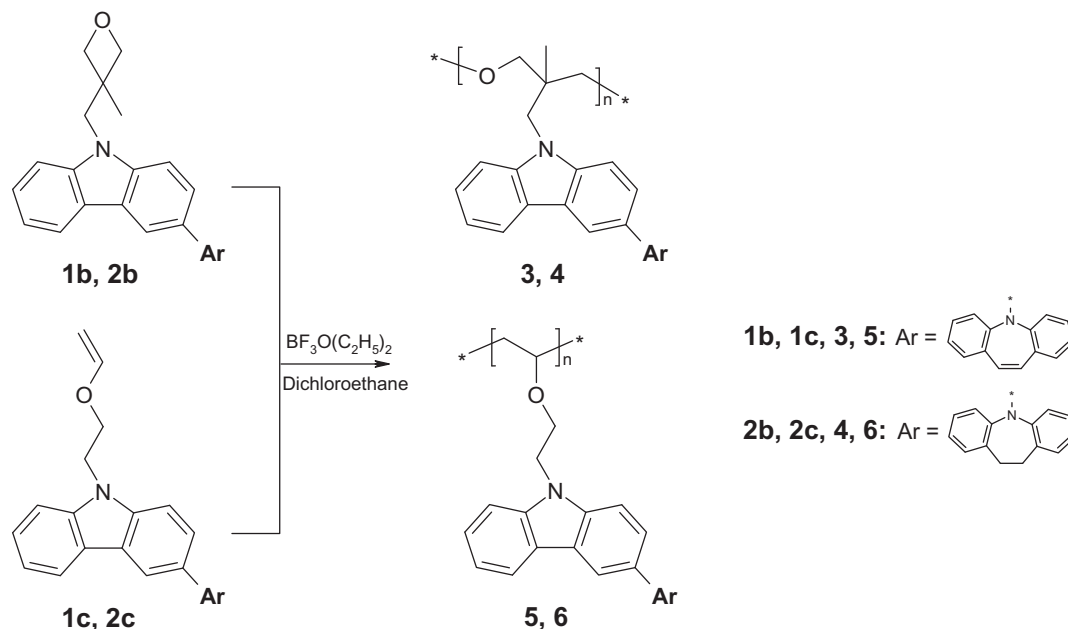
The monomers **1a–c** and **2a–c** were obtained as crystalline materials however they readily formed glasses when their melt samples were cooled down. DSC thermograms of **2a** are shown in Fig. 1. When the crystalline sample was heated, the endothermic polymorphic peaks due to melting were observed at 86 °C and 96 °C. When the melt sample was cooled down and heated again, the glass transition was observed at 26 °C and on further heating no peaks due to crystallization and melting appeared. Oligomers **3–6** were obtained as amorphous materials with high glass transition temperatures. When samples of oligomers were heated during the DSC experiments glass transitions were observed in the region from 187 to 205 °C and no peaks due to crystallization and melting appeared. Cooling down and repeated heating revealed only the glass transitions again.

The values of  $T_g$  of low-molar-mass glasses are affected by the nature of substituents at 9 position of carbazole ring and increase in the order 2-ethylhexyl (**1a**, **2a**) < vinyloxyethyl (**1c**, **2c**) < oxetanyl (**1b**, **2b**). The compounds having iminostilbene moieties (**1a–c**, **3** and **5**) have higher  $T_g$  values than the corresponding derivatives containing iminodibenzyl groups (**2a–c**, **4** and **6**). This is apparently to more rigid structure of iminostilbene derivatives.

The optical and photophysical properties of dilute solutions of the synthesized compounds were investigated by UV and FL spectrometries. Fig. 2a shows UV spectra of iminostilbenyl-containing compounds **1c** and **5**, while Fig. 2b shows the spectra of iminodibenzyl-containing derivatives **2c** and **6**. For the comparison the UV spectra of the unsubstituted 5*H*-dibenz(b,f)azepine (ISB), 10,11-dihydro-5*H*-dibenz(b,f)azepine (IDB) and 9-ethylcarbazole (EtCz) are given. UV spectra of oligomers are very similar to those of the corresponding monomers. The lowest energy absorption bands of all the newly synthesized compounds show maxima at ca. 380 nm. They are significantly red-shifted in comparison with the those of EtCz, ISB and IDB.



Scheme 1. Synthesis of 3-substituted carbazole based compounds **1a–c** and **2a–c**.



**Table 1**  
Molecular weights and polydispersity indexes of oligomers 3–6.

Compound	SEC <sup>a</sup>			MALDI-TOF <sup>b</sup>		
	$M_w$	$M_n$	$M_w/M_n$	$M_w$	$M_n$	$M_w/M_n$
3	5740	2550	2.2	3550	2980	1.2
4	4380	2480	1.7	3270	2870	1.1
5	2630	1750	1.5	1870	1470	1.3
6	4550	2350	1.9	2540	2090	1.2

<sup>a</sup> Calculated from the SEC curve using the formulas  $M_n = (\sum M_i N_i) / (\sum N_i)$ ,  $M_w = (\sum M_i^2 N_i) / (\sum M_i N_i)$ .

<sup>b</sup> Calculated from the MALDI-TOF MS using the formulas  $M_n = (\sum M_i N_i) / (\sum N_i)$ ,  $M_w = (\sum M_i^2 N_i) / (\sum M_i N_i)$ .

The FL spectra of dilute THF solutions of compounds **1c**, **2c** and oligomers **5**, **6** are shown in Fig. 3. Wide fluorescence spectra of iminostilbenyl-containing compounds **1c** and **5** are nearly identical with only of about 4 nm red shift of the spectrum of polymer **5** relative that of monomer **1c**. The spectra of **1c** and **5** show large Stokes shift of about 170 nm. A large Stokes shift and a wide fluorescence spectrum are typical features of the charge transfer states [25]. Charge transfer is much less expressed in case iminodibenzyl-substituted compounds **2c** and **6**. Dilute solutions of compounds **2c** and **6** in THF show much lower fluorescence emission bands with peaks at 410 nm and 416 nm. The Stokes shifts (ca 25 nm) of these compounds are considerably lower than those of iminostilbenyl-substituted compounds (**1c** and **5**).

The similar UV spectra of iminostilbenyl compounds (**1c** and **5**) to those of iminodibenzyl substituted derivatives (**2c** and **6**) show

**Table 2**  
Thermal characteristics of compounds 1–6.

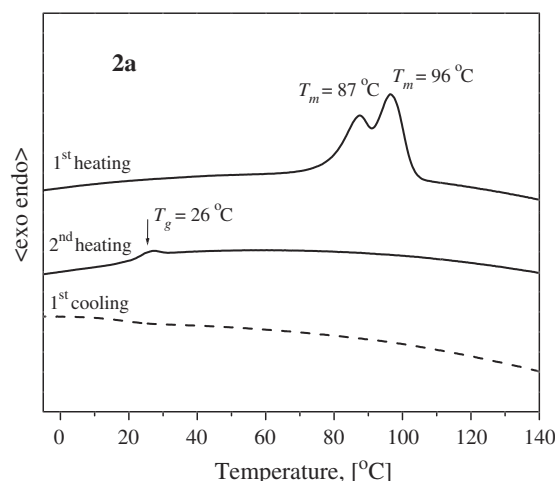
Compound	1a	1b	1c	2a	2b	2c	3	4	5	6
$T_g^a$ (°C)	32	97	52	23	88	41	203	187	217	205
$T_m^a$ (°C)	167 <sup>c</sup>	200 <sup>c</sup>	160 <sup>c</sup>	87, 96 <sup>c</sup>	208 <sup>c</sup>	136 <sup>c</sup>	– <sup>d</sup>	– <sup>d</sup>	– <sup>d</sup>	– <sup>d</sup>
$T_{10}^b$ (°C)	335	368	325	338	348	320	410	390	390	390

<sup>a</sup> Determined by DSC, scan rate 10 °C/min, N<sub>2</sub> atmosphere.

<sup>b</sup> 5% weight loss determined by TGA, heating rate 10 °C/min, N<sub>2</sub> atmosphere.

<sup>c</sup> 1st heating only.

<sup>d</sup> Obtained as an amorphous material.



**Fig. 1.** DSC curves of **2a**. Heating rate 10 °C/min, N<sub>2</sub> atmosphere.

that for absorption the similar fragments are responsible. The very different fluorescence spectra show that the different moieties are responsible for the emission. Apparently intramolecular twisting is characteristic of the molecules of **1c** and **5**. They are probably more twisted in the ground state and more planar in the excited state.

An important characteristic of electronically active compounds used in optoelectronic devices is ionization potential ( $I_p$ ), which characterizes the electron releasing work under illumination. The

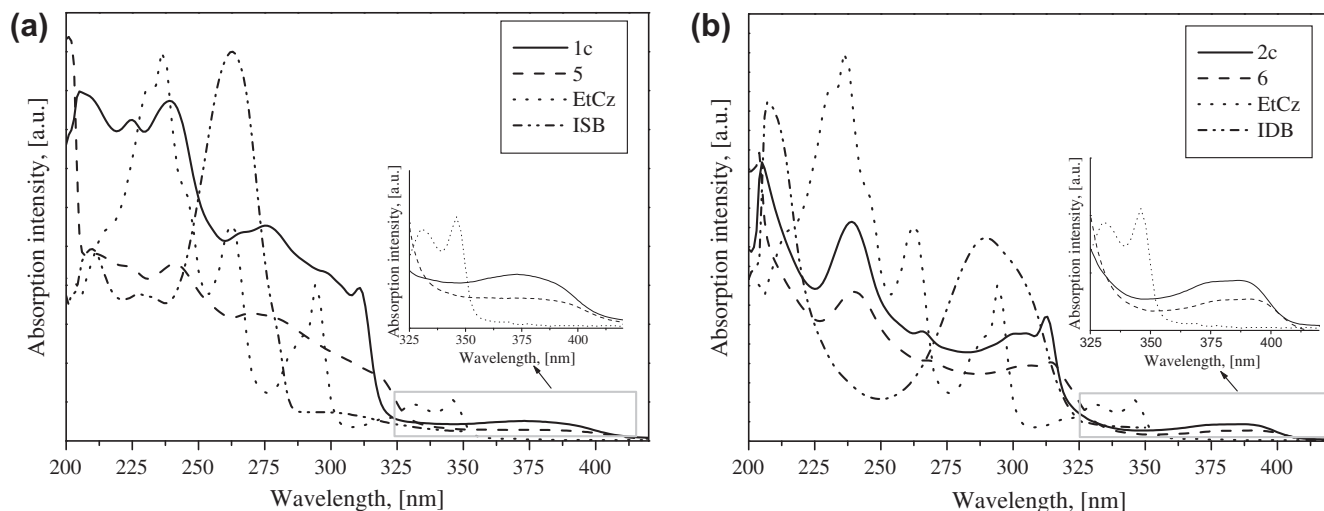


Fig. 2. UV spectra of the dilute THF solutions ( $10^{-5}$  M) of compounds **1c**, **5** (a) and **2c**, **6** (b).

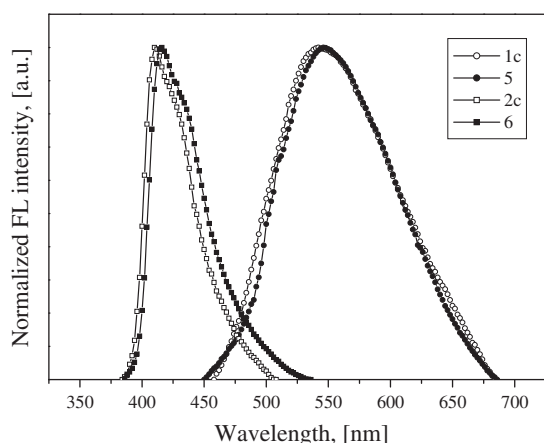


Fig. 3. The normalized FL spectra of the dilute THF solutions of compounds **1c**, **2c**, **5** and **6** ( $\lambda_{\text{ex}} = 310$  nm).

**Table 3**  
 $I_p$  and LUMO values of compounds **1–6**.

Compound		<b>1a</b>	<b>1b</b>	<b>1c</b>	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
Energy (eV)	$I_p$	5.2	5.2	5.3	5.2	5.2	5.3	5.2	5.2	5.1	5.1
	LUMO	2.2	2.2	2.3	2.2	2.2	2.3	2.3	2.2	2.2	2.1

$I_p$  of the solid samples was measured by electron photoemission in air technique. The values of  $I_p$ , which correspond the HOMO values, are presented in Table 3. They are in the range of 5.1–5.3 eV. Using the values of optical band gap ( $\Delta E$ ) which can be estimated from the absorption spectroscopy data, the LUMO values were calculated [26]. They are also given in Table 2. As it could be expected from the UV absorption spectrometry data, the  $I_p$  values of the monomers and their polymers are rather close. The  $I_p$  values of the synthesized compounds are considerably lower than those of the materials containing electronically isolated carbazolyl groups [9]. They are also a little lower than that of carbazole derivatives having diphenylamino moieties in the 3rd position of cabazole ring [10].

The xerographic time-of-flight (TOF) measurements were used to characterize the charge transport properties of the compounds synthesized. The measurements confirmed that amorphous layers

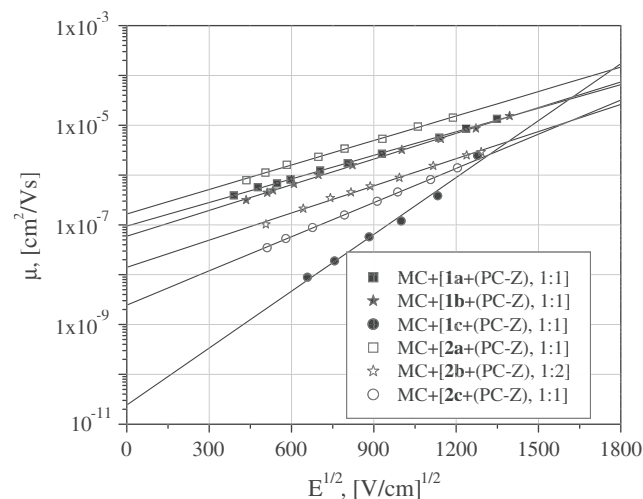


Fig. 4. Electric field dependencies of the hole drift mobilities ( $\mu$ ) in charge transport layers of compounds **1a–c** and **2a–c** doped in PC-Z.

**Table 4**  
Hole mobility data for molecular dispersions of **1a–c**, **2a–c** in PC-Z.

Layer composition	$d$ ( $\mu\text{m}$ )	$\mu_0$ ( $\text{cm}^2/\text{V s}$ )	$\mu^a$ ( $\text{cm}^2/\text{V s}$ )
<b>1a</b> + PC-Z, 1:1	5	$9.0 \times 10^{-8}$	$1.7 \times 10^{-6}$
<b>1b</b> + PC-Z, 1:1	5.5	$6.0 \times 10^{-8}$	$1.4 \times 10^{-6}$
<b>1c</b> + PC-Z, 1:1	6	$2.0 \times 10^{-11}$	$2.6 \times 10^{-8}$
<b>2a</b> + PC-Z, 1:1	8	$1.7 \times 10^{-7}$	$3.4 \times 10^{-6}$
<b>2b</b> + PC-Z, 1:2	6	$1.4 \times 10^{-8}$	$4.0 \times 10^{-7}$
<b>2c</b> + PC-Z, 1:1	6.2	$2.5 \times 10^{-9}$	$1.6 \times 10^{-7}$

<sup>a</sup> At  $6.4 \times 10^5$  V/cm.

of the oligomers **3–6** transport holes, however exact hole drift mobility values were not determined due to dispersive transport of the charges. For the molecular dispersions of compounds **1a–c** or **2a–c** in bisphenol Z polycarbonate (PC-Z) the room temperature hole drift mobilities show the linear dependencies on the square root of the electric field (Fig. 4). Such dependencies of charge mobility on electrical field are characteristic for many organic photoconductors and are predicted by the Bässler-Borsenberger model [1]. The solid solutions of compounds **1a–c** and **2a–c** in PC-Z (mass proportion 1:1 or 1:2) demonstrated hole drift mobility

values in a range from  $2.6 \times 10^{-8}$  to  $3.4 \times 10^{-6}$   $\text{cm}^2/\text{V s}$  at electric field  $E = 6.4 \times 10^5$   $\text{V/cm}$ , at room temperature (Table 4). Compounds **1a** and **2a** showed the best hole-transporting properties. They are comparable with those of carbazole derivatives having diphenylamino moieties in the 3rd position of carbazole ring [10].

In conclusion, we have synthesized low-molar-mass glass-forming compounds and oligomers with the pendent adducts of carbazole with 5*H*-dibenz(b,f)azepine and its 10,11-dihydro derivative. Polymerization of oxetanes and vinyl ethers bearing the corresponding electroactive substituents with cationic initiator  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  yielded oligomers with weight average molecular weights ranging from 2630 to 5740. The monomers and oligomers exhibit relatively high thermal stability with 5% weight loss temperatures ranging from 325 to 410 °C. The monomers can be transformed into the glassy state with the glass transition temperatures ranging from 23 to 97 °C. The oligomers show glass transition temperatures in the range of 187–217 °C. The values of ionization potentials established by electron photoemission technique of the solid samples of the synthesized derivatives are in the range of 5.12–5.34 eV. The molecular mixture of 3-[10,11-dihydrodibenz(b,f)azepinyl]-9-(2-ethylhexyl)carbazole (**2a**) with bisphenol Z polycarbonate (1:1 by weight) show hole mobility of  $3.4 \times 10^{-6}$   $\text{cm}^2/\text{V s}$  at an electric field of  $6.4 \times 10^5$   $\text{V/cm}$ . This value is comparable to the hole-mobility value of analogous system containing carbazole derivative with diphenylamino moiety in the 3rd position of carbazole ring.

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