

Glass-forming hole-transporting carbazole-based hydrazone monomers, polymers, and twin compounds

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ABSTRACT

The synthesis, optical, thermal, and photoelectrical properties of new carbazole-based hydrazone monomers, polymers, and twin compounds are reported. All the synthesized materials are capable of glass formation. Their glass transition temperatures range from 27 to 90 °C. The ionization potentials of the films of carbazole-based hydrazones measured by the electron photoemission technique range from 5.18 to 5.48 eV. Hole-drift mobilities in the amorphous films of the synthesized hydrazone monomers measured by the time-of-flight technique at room temperature reach 10^{-4} cm²/(V s) at high applied electric fields.

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1. Introduction

Hydrazones represent a big class of organic electronically active materials [1]. They are applied as organic semiconductors in optoelectronic devices, mainly in electro-photographic photoreceptors. Both polymeric and low-molar-mass organic semiconductors are used 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 [2]. Charge-transporting polymers have some important advantages with respect to their low-molar-mass counterparts and molecularly doped polymers. They usually possess good 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.

Among hole-transporting hydrazones low-molar-mass materials prevail [3–7]. Recently some hydrazone main chain polymers were described [8–10]. They were obtained by polyaddition reaction of diepoxy monomers containing hydrazone moieties with dithiols. These polymers have relatively high molecular weights. They exhibit relatively high glass transition temperatures, good

film-forming properties, and moderate charge transport properties.

Herewith we report on the design, synthesis and characterization of two new epoxy monomers containing hydrazone moieties, their polymers, and four twin compounds. The polymers were prepared by cationic polymerization. To our knowledge, this is the first report on cationic polymerization of the epoxy monomers containing hydrazone moieties. Our previous attempts to polymerize cationically hydrazones with the epoxy groups attached at the nitrogen atoms of hydrazone moieties failed. This was apparently because of the formation of stable cyclic complexes between the initiator and the monomer. The possibility of formation of such complexes was recently reported [11].

In order to enhance inclination to cationic polymerization we have synthesized epoxy monomers in which reactive functional groups are not directly attached to hydrazone moieties.

2. Experimental

2.1. Instrumentation

¹H NMR and ¹³C NMR spectra were recorded with a Bruker AC 250 (250 Hz) and Varian Unity Inova (300 Hz) spectrometers. All the data are given as chemical shifts δ (ppm) downfield from (CH₃)₄Si. IR-spectroscopy measurements were performed on a Perkin Elmer Spectrum GX spectrophotometer, using KBr pellets.

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UV/VIS spectra were recorded with Spectronic Unicam Genesys 8 spectrophotometer. Mass spectra were obtained on a Waters Micromass ZQ mass spectrometer. Thermogravimetry (TG) analysis was performed on a Perkin Elmer Thermal Analysis System 409 apparatus at a heating rate of 10 K/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer Pyris Diamond DSC apparatus at a 10 K/min heating rate under nitrogen atmosphere. Cyclic voltammetry (CV) measurements were performed with a glassy carbon working electrode in a three-electrode cell using μ -Autolab Type III (EcoChemie, Netherlands) potentiostat. The measurements were carried out in a solution of dry dichloromethane containing 0.05 M tetrabutylammonium perchlorate at 25 °C. The potentials were measured against Ag/AgNO₃ as reference electrode and each measurement was calibrated as with the standard ferrocene/ferrocenium (Fc) redox system [12]. The samples for ionization potential measurements were prepared as described previously [13]. The materials were dissolved in THF and were coated on Al plates pre-coated with ~0.5 μ m thick methylmethacrylate and methacrylic acid copolymer (MKM) adhesive layer. The function of this layer was not only to improve adhesion, but also to eliminate the electron photoemission from Al layer. In addition, the MKM layer is conductive enough to avoid charge accumulation on it during the measurements. The thickness of the layers was 0.5–1 μ m. The ionization potentials were measured by the electron photoemission in air method, as reported earlier [14]. The measurement method was, in principle, similar to that demonstrated by Miyamoto et al. [15]. Hole-drift mobilities were measured by a xerographic time-of-flight method [16]. The samples for the charge carrier mobility measurements were prepared by procedure, as we described earlier [17].

2.2. Materials

The starting compounds 9-(oxiranylmethyl)carbazole (Biolar, Latvia), *N*-methyl-*N*-phenylhydrazine (Acros Organics), *N,N*-diphenylhydrazine hydrochloride (Aldrich), 4,4'-thiobisbenzenethiol (Aldrich), 1,3-benzenedithiol (Aldrich), and the required chemicals, i.e. hydrochloric acid (Riedel-de Haen), sodium chloride (Fluka), anhydrous sodium sulfate (Fluka), copper sulfate (Reakhim), acetic anhydride (Aldrich), sodium carbonate (Aldrich), sodium acetate (Aldrich), tetrabutylammonium hydrosulphate (Aldrich), anhydrous magnesium sulfate (Aldrich), potassium hydroxide (Aldrich), phosphorus oxychloride (Riedel-de Haen), triethylamine (Aldrich), were purchased as reagent grade chemicals and used as received. Boron trifluoride diethyletherate (Aldrich) was distilled before use (m.p. 126 °C). The solvents, i.e. 1,4-dioxane (POCH), toluene (Aldrich), chloroform (Penta), dimethylformamide (Lachema), dichloromethane (POCH), ethylacetate (Penta), hexane (Penta), methanol (Penta), isopropanol, were purified and dried using the standard procedures [18].

2.2.1. 3-(Carbazol-9-yl)-2-chloropropan-1-ol (**1**)

Compound **1** was synthesized from 9-(oxiranylmethyl)carbazole as described in the literature [19].

2.2.2. 3-(Carbazol-9-yl)-2-chloropropyl ethanoate (**2**)

The acetylation of compound **1** was done according to the procedure described in literature [20]. CuSO₄·5H₂O (0.85 g, 0.034 mol) was added to a solution of compound **1** (20 g, 0.077 mol) in 20 ml (0.21 mol) of acetic anhydride. The reaction mixture was kept at the room temperature for 43 h. The end of the reaction was detected by TLC (eluent chloroform). Acetic anhydride was neutralized with 130 ml of 10% Na₂CO₃ solution. The reaction mixture was extracted with dichloromethane. An organic fraction was twice washed with a saturated solution of NaCl, dried with Na₂SO₄,

and evaporated. The yield of resin **2** was 74.4% (19.66 g). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 1.99 (s, 3H, —CH₃), 3.54–3.71 (m, 2H, —CH₂—), 4.46–4.65 (m, 2H, —CH₂—), 5.41–5.49 (m, 1H, —CH—), 7.22–7.28 (m, 2H, —CH Ar.), 7.44–7.57 (m, 4H, —CH Ar.), 8.10 (d, —CH Ar., 2H, *J* = 7.7 Hz). IR (KBr), (cm⁻¹): 3047, 3028 ν (CH, Ar.); 2962, 2947 ν (CH, Aliph.); 1726 ν (C=O), 1484, 1462 ν (C=C, Ar.); 754, 725 γ (CH, Ar.). MS (APCI⁺, 20 V), *m/z* (%): 302 ([M + H]⁺, 100). Elemental analysis calculated for C₁₇H₁₆ClNO₂: C, 67.66%; H, 5.34%; N, 4.64%. Found: C, 67.74%; H, 5.28%; N, 4.61%.

2.2.3. 3-(3-Formylcarbazol-9-yl)-2-chloropropyl ethanoate (**3**)

Compound **3** was synthesized by the method of Vilsmeier [21]. A round bottom flask with DMF (13.6 ml, 3.5 mol) was placed in a bath with the mixture of crushed ice and NaCl and cooled down to 0 °C. POCl₃ (11.37 ml, 3.5 mol) was added drop-wise keeping the reaction mixture at 0 °C. When all POCl₃ was added the reaction mixture was let to warm up slowly to the room temperature. Then compound **2** (18.55 g, 0.062 mol) dissolved in 13.6 ml (3.5 mol) of DMF was added. The reaction was carried out at 90 °C for 72 h. The end of the reaction was detected by TLC (eluent: ethylacetate/hexane, 1:2). The hot reaction mixture was poured into water with crushed ice and neutralized with 51 g of sodium acetate. The mixture obtained was kept in the refrigerator for 12 h. The formed crystals were filtered off, recrystallized from methanol and dried. The yield of compound **3** was 30% (6.5 g). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 1.96 (s, 3H, —CH₃), 3.57–3.76 (m, 2H, —CH₂—), 4.53–4.73 (m, 2H, —CH₂—), 5.40–5.50 (m, 1H, —CH—), 7.2–7.6 (m, 4H, —CH Ar.), 8.02 (dd, 1H, 5-H_{HT}, (H_A), *J*_{AX} = 1.6 Hz, *J*_{AB} = 8.6 Hz), 8.14 (d, 1H, 4-H_{HT}, *J* = 7.7 Hz), 8.59 (s, 1H, —CH Ar.), 10.10 (s, 1H, CHO). IR (KBr), (cm⁻¹): 3053, 3018 ν (CH Ar.); 2815, 2743 ν (CH Aliph.); 1742, 1683 ν (C=O), 1595 ν (C=C Ar.); 750 γ (CH Ar.). MS (APCI⁺, 20 V), *m/z* (%): 330 ([M + H]⁺, 79). Elemental analysis calculated for C₁₈H₁₆ClNO₃: C, 65.56%; H, 4.89%; N, 4.25%. Found: C, 65.61%; H, 4.87%; N, 4.22%.

2.2.4. 9-(Oxiranylmethyl)carbazol-3-yl-carbaldehyde (**4**)

KOH (85%, 1.32 g, 34.8 mmol) and phase transfer catalyst tetrabutylammonium hydrosulphate were added to a solution of compound **3** (2 g, 5.8 mmol) in 20 ml of 1,4-dioxane. The reaction mixture was stirred for 48 h. The reaction was monitored by TLC (eluent: ethylacetate/hexane, 1:2). When the reaction was finished KOH was filtered off. The filtrate was extracted with ethylacetate until pH = 6–8, dried with anhydrous MgSO₄ and evaporated. The product was purified by column chromatography (eluent: ethylacetate/hexane, 1:2). The yield of the yellow resin **4** was 33% (0.5 g). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 2.59 (q, 1H, *J*_{AX} = 2.5 Hz, *J*_{AB} = 7 Hz, OCH₂), 2.87 (t, 1H, *J*_{AX} = 4.8 Hz, *J*_{AB} = 8.5 Hz, CH₂O), 3.41 (m, 1H, —CHO), 4.41 (dd, 1H, one proton of NCH₂, (H_A), *J*_{AX} = 5.1 Hz, *J*_{AB} = 16 Hz), 4.76 (dd, 1H, another proton of NCH₂, (H_B), *J*_{BX} = 2.8 Hz, *J*_{AB} = 13 Hz), 7.34–7.42 (m, 1H, CH Ar.), 7.54–7.62 (m, 3H, —CH Ar.), 8.05 (dd, 1H, 2-H_{HT}, (H_A), *J*_{AX} = 2 Hz, *J*_{AB} = 7 Hz), 8.2 (d, 1H, 5-H_{HT}, *J* = 7.8), 8.64 (s, 1H, 4-H_{HT}), 10.13 (1H, CHO). IR (KBr), (cm⁻¹): 3338, 3055 ν (CH, Ar.); 2801, 2722 ν (CH, Aliph.); 1682 ν (CHO); 1595 ν (C=C, Ar.); 744, 725 γ (CH, Ar.). MS (APCI⁺, 20 V), *m/z* (%): 252 ([M + H]⁺, 100). Elemental analysis calculated for C₁₆H₁₃NO₂: C, 76.48%; H, 5.21%; N, 5.57%. Found: C, 76.51%; H, 5.19%; N, 5.59%.

2.2.5. 9-(Oxiranylmethyl)carbazol-3-yl-carbaldehyde *N,N*-diphenylhydrazone (**5a**)

A solution of *N,N*-diphenylhydrazine hydrochloride (0.66 g, 2.97 mmol) in 15 ml of methanol and sodium acetate (0.25 g, 2.98 mmol) were added slowly to a solution of compound **4** (0.5 g, 1.98 mmol) in 12 ml of methanol. The reaction mixture was stirred at 65 °C for 2 h. After the reaction the solvent was evaporated and the product was purified by column chromatography

(eluent:ethylacetate/hexane, 1:2). The yield of compound **5a** was 61% (0.5 g). $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 2.53 (q, 1H, OCH_2 , (H_A), $J_{AX} = 2.8$ Hz, $J_{AB} = 7.3$ Hz), 2.78 (t, 1H, CH_2O (H_A), $J_{AX} = 4.5$ Hz, $J_{AB} = 8.7$ Hz), 3.29–3.36 (m, 1H, $-\text{CHO}$), 4.35 (dd, 1H, one proton of NCH_2 , (H_A), $J_{AX} = 5$ Hz, $J_{AB} = 15.7$ Hz), 4.60 (dd, 1H, another proton of NCH_2 , (H_B), $J_{BX} = 3.3$ Hz, $J_{AB} = 15.3$ Hz), 7.8 (dd, 1H, 2- H_{HT} , $J_{AX} = 1.6$ Hz, $J_{AB} = 8.6$ Hz), 8.06 (d, 1H, 5- H_{HT} , $J = 7.7$ Hz), 8.2 (s, 1H, 4- H_{HT}), 7.1–7.5 (m, 15H, $-\text{CH Ar.}$). IR (KBr), (cm^{-1}): 3420, 3050 ν (CH Ar.); 2922 ν (CH Aliph.), 1589, 1493 ν (C=C Ar.), 747, 700 γ (CH Ar.). MS (APCI $^+$, 20 V), m/z (%): 418 ($[\text{M} + \text{H}]^+$, 100). Elemental analysis calculated for $\text{C}_{28}\text{H}_{23}\text{N}_3\text{O}$: C, 80.55%; H, 5.55%, N, 10.06%. Found: C, 80.56%; H, 5.54%, N, 10.03%.

2.2.6. 9-(Oxiranylmethyl)carbazol-3-yl-carbaldehyde *N*-methyl-*N*-phenylhydrazone (**5b**)

Compound **4** (0.5 g, 1.98 mmol) and *N*-methyl-*N*-phenylhydrazine (0.36 g, 2.98 mmol) were dissolved in 20 ml of methanol and stirred at 65 °C for 22 h. After the reaction the solvent was evaporated. The crude product was purified by column chromatography (eluent:ethylacetate/hexane, 1:2), crystallized from methanol, and dried. The yield of compound **5b** was 34% (0.5 g). M.p. 151 °C (DSC). $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 2.54 (q, 1H, one proton of OCH_2 , (H_A), $J_{AX} = 2.5$ Hz, $J_{AB} = 4.7$ Hz), 2.78 (t, 1H, another proton of CH_2O , $J_{BX} = 4.1$ Hz, $J_{AB} = 8.7$ Hz), 3.32 (m, 1H, $-\text{CHO}$), 3.44 (s, 3H, $-\text{CH}_3$), 4.35 (dd, 1H, one proton of NCH_2 , (H_A), $J_{AX} = 5$ Hz, $J_{AB} = 15.7$ Hz), 4.59 (dd, 1H, another proton of NCH_2 , (H_B), $J_{BX} = 3.3$ Hz, $J_{AB} = 15.7$ Hz), 7.9 (dd, 1H, 2- H_{HT} , $J_{AX} = 1.6$ Hz, $J_{AB} = 8.5$ Hz), 8.12 (d, 1H, 5- H_{HT} , $J = 7.3$ Hz), 8.3 (s, 1H, 4- H_{HT}), 6.7–7.7 (m, 10H, $-\text{CH Ar.}$). IR (KBr), (cm^{-1}): 3430, 3048 ν (CH, Ar.); 2993, 2922 ν (CH, Aliph.); 1589, 1499 ν (C=C, Ar.); 746 γ (CH Ar.). MS (APCI $^+$, 20 V), m/z (%): 356 ($[\text{M} + \text{H}]^+$, 100). Elemental analysis calculated for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}$: C, 77.72%; H, 5.96%, N, 11.82%. Found: C, 77.78%; H, 5.89%, N, 11.76%.

2.2.7. Poly[9-(oxiranylmethyl)carbazol-3-yl-carbaldehyde *N,N*-diphenylhydrazone] (**6a**)

Dry dichloromethane (0.28 ml) was added to a flask with compound **5a** (0.1 g, 0.28 mmol) under nitrogen. The flask was placed in the bath of dry ice with isopropanol and cooled down to -70 °C. Then 0.2 ml of 1 M solution of $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$ in dichloromethane were added. The reaction was carried out for 5 h. Then few drops of triethylamine (TEA) were added. The reaction mixture was concentrated and precipitated into methanol. The formed white precipitates were filtered, washed with methanol two times, and dried at room temperature. The yield of polymer **6a** was 50% (0.05 g). $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 3.3–4.5 (m, 5H), 7.8–8.2 (m, 3H, 2, 4, 5- H_{HT}), 6.9–7.5 (m, 15H, $-\text{CH Ar.}$). IR (KBr), (cm^{-1}): 3564 ν (OH), 3054 ν (CH Ar.); 2932, 2871 ν (CH Aliph.), 1590, 1493 ν (C=C Ar.), 747, γ (CH Ar.).

2.2.8. Poly[9-(oxiranylmethyl)carbazol-3-yl-carbaldehyde *N*-methyl-*N*-phenylhydrazone] (**6b**)

6b was synthesized from 9-(oxiranylmethyl)carbazol-3-yl-carbaldehyde *N*-methyl-*N*-phenylhydrazone **5b** (0.27 g, 0.76 mmol) using 0.2 ml of 1 M solution of $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$ in dichloromethane as initiator by the same way as polymer **6a**. The yield polymer **6b** was 26% (0.07 g). $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 3.0–4.5 (m, 5H), 7.8–8.5 (m, 3H, 2, 4, 5- H_{HT}), 6.7–7.8 (m, 10H, $-\text{CH Ar.}$). IR (KBr), (cm^{-1}): 3324 ν (OH), 3051 ν (CH, Ar.); 2972, 2933, 2877 ν (CH, Aliph.); 1597, 1493 ν (C=C, Ar.); 1111, 1084, 1062, 1030 ν (C–O); 749 γ (CH, Ar.).

2.2.9. 4,4'-Di({3-[(2,2-diphenylhydrazine-1-ylidene)methyl]carbazole-9-yl}-2-hydroxypropylsulfanyl)diphenylsulfane (**7a**)

Compound **5a** (0.52 g, 1.24 mmol), 4,4'-thiobisbenzenethiol (0.14 g, 0.6 mmol), triethylamine (0.2 ml), and 2-butanone (7 ml)

were added to the reaction flask. The reaction mixture was refluxed for 24 h. When the reaction was finished, the solvent was evaporated, and the crude product was purified by column chromatography (eluent:ethylacetate/hexane, 1:2). The yield of compound **7a** was 29% (0.4 g). $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 3.09–3.26 (m, 4H, SCH_2), 3.3 (s, 2H, OH), 3.69–3.76 (m, 2H, $-\text{CH}$), 4.37 (dd, 2H, one proton of NCH_2 , (H_A), $J_{AX} = 4.6$ Hz, $J_{AB} = 15.7$ Hz), 4.6 (dd, 2H, another proton of NCH_2 , (H_B), $J_{BX} = 2.8$ Hz, $J_{AB} = 15.8$ Hz), 7.80 (d, 2H, 2- H_{HT} , $J = 8.6$ Hz), 8.07 (d, 2H, 5- H_{HT} , $J = 7.8$ Hz), 8.23 (s, 2H, 4- H_{HT}), 6.81–8.45 (m, 38H, $-\text{CH Ar.}$). IR (KBr), (cm^{-1}): 3550, 3341 ν (OH), 3049 ν (CH Ar.); 1588, 1493, 1475 ν (C=C Ar.); 746, γ (CH Ar.). MS (APCI $^+$, 20 V), m/z (%): 1088 ($[\text{M} + \text{H}]^+$, 10). Elemental analysis calculated for $\text{C}_{68}\text{H}_{58}\text{N}_6\text{O}_2\text{S}_3$: C, 75.11%; H, 5.38%, N, 7.73%. Found: C, 75.22%; H, 5.32%, N, 7.65%.

2.2.10. 1,3-Di({3-[(2,2-diphenylhydrazine-1-ylidene)methyl]carbazole-9-yl}-2-hydroxypropylsulfanyl)benzene (**7b**)

Compound **7b** was synthesized by the similar procedure as compound **7a**, only 1,3-benzenedithiol was used instead of 4,4'-thiobisbenzenethiol and the reaction time was 5 h. The yield of compound **7b** was 42%. $^1\text{H NMR}$ (300 MHz, DMSO), δ (ppm): 3.05–3.24 (m, 4H, SCH_2), 3.99–4.14 (m, 2H, $-\text{CH}$), 4.3 (dd, 2H, one proton of NCH_2 , (H_A), $J_{AX} = 6$ Hz, $J_{AB} = 14$ Hz), 4.5 (dd, 2H, another proton of NCH_2 , (H_B), $J_{BX} = 4.4$ Hz, $J_{AB} = 14$ Hz), 5.49 (d, 2H, $J = 5.1$ Hz, OH), 7.85 (d, 2H, 2- H_{HT} , $J = 7.4$ Hz), 8.17 (d, 2H, 5- H_{HT} , $J = 7.7$ Hz), 8.27 (s, 2H, 4- H_{HT}), 7.01–7.64 (m, 38H, $-\text{CH Ar.}$). IR (KBr), (cm^{-1}): 3428 ν (OH), 3049 ν (CH, Ar.); 1589, 1493, 1463 ν (C=C, Ar.); 746 γ (CH, Ar.). MS (APCI $^+$, 20 V), m/z (%): 980 ($[\text{M} + \text{H}]^+$, 10). Elemental analysis calculated for $\text{C}_{62}\text{H}_{54}\text{N}_6\text{O}_2\text{S}_2$: C, 76.04%; H, 5.56%, N, 8.58%. Found: C, 76.13%; H, 5.62%, N, 8.49%.

2.2.11. 4,4'-Di({3-[(2-methyl-2-phenylhydrazine-1-ylidene)methyl]carbazole-9-yl}-2-hydroxypropylsulfanyl)diphenylsulfane (**8a**)

Compound **8a** was synthesized by the same procedure as compound **7a**, only compound **5b** was used instead of compound **5a**. The yield of compound **8a** was 19.6%. $^1\text{H NMR}$ (300 MHz, DMSO), δ (ppm): 3.09–3.26 (m, 4H, SCH_2), 3.40 (s, 6H, CH_3), 4.09 (m, 2H, $-\text{CH}$), 4.41 (dd, 2H, one proton of NCH_2 , (H_A), $J_{AX} = 7.4$ Hz, $J_{AB} = 15.4$ Hz), 4.55 (dd, 2H, another proton of NCH_2 , (H_B), $J_{BX} = 5$ Hz, $J_{AB} = 15$ Hz), 5.52 (d, 2H, $J_{AX} = 5.5$ Hz, OH), 7.87 (d, 2H, 2- H_{HT} , $J = 7.32$ Hz), 8.18 (d, 2H, 5- H_{HT} , $J = 7.7$ Hz), 8.4 (s, 2H, 4- H_{HT}), 6.85–7.61 (m, 28H, $-\text{CH Ar.}$). IR (KBr), (cm^{-1}): 3340 ν (OH), 3048 ν (CH, Ar.); 2963, 2923 ν (CH, Aliph.); 1596, 1492, 1465 ν (C=C, Ar.); 746 γ (CH, Ar.). MS (APCI $^+$, 20 V), m/z (%): 964 ($[\text{M} + \text{H}]^+$, 10). Elemental analysis calculated for $\text{C}_{58}\text{H}_{54}\text{N}_6\text{O}_2\text{S}_2$: C, 72.32%; H, 5.65%, N, 8.72%. Found: C, 72.41%; H, 5.58%, N, 8.67%.

2.2.12. 1,3-Di({3-[(2-methyl-2-phenylhydrazine-1-ylidene)methyl]carbazole-9-yl}-2-hydroxypropylsulfanyl)benzene (**8b**)

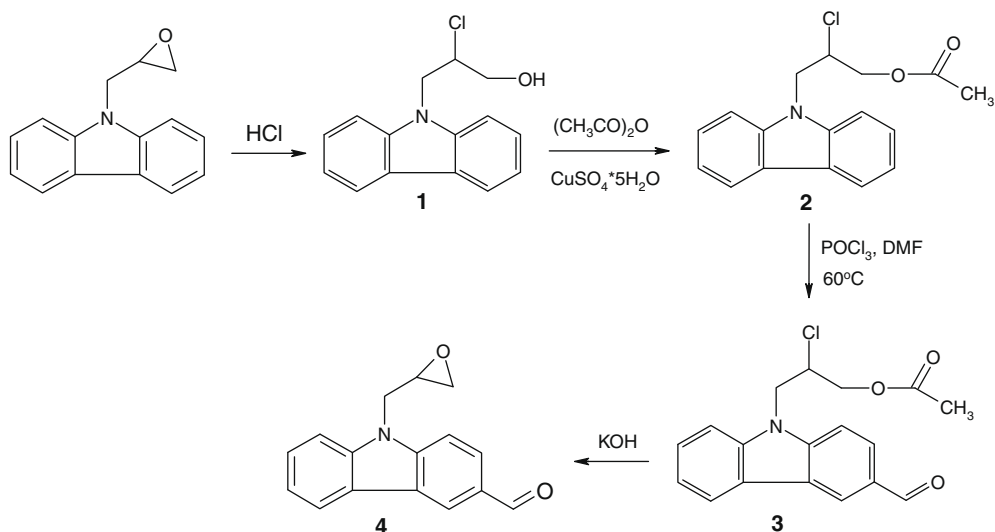
Compound **8b** was synthesized by the same procedure as compound **7a**, only compound **5b** was used instead of compound **5a** and 1,3-benzenedithiol was used instead of 4,4'-thiobisbenzenethiol. The yield of compound **8b** was 24%. $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 2.78–3.06 (m, 4H, SCH_2), 3.37 (s, 6H, $-\text{CH}_3$), 3.70–3.74 (m, 2H, $-\text{CH}$), 4.25–4.30 (m, 4H, NCH_2), 6.81–8.30 (m, 30H, $-\text{CH Ar.}$). IR (KBr), (cm^{-1}): 3380 ν (OH), 3048 ν (CH, Ar.); 2960, 2926 ν (CH, Aliph.); 1596, 1568, 1491, 1462 ν (C=C, Ar.); 746 γ (CH, Ar.). MS (APCI $^+$, 20 V), m/z (%): 856 ($[\text{M} + \text{H}]^+$, 10). Elemental analysis calculated for $\text{C}_{52}\text{H}_{50}\text{N}_6\text{O}_2\text{S}_2$: C, 73.04%; H, 5.89%, N, 9.83%. Found: C, 73.18%; H, 5.81%, N, 9.76%.

3. Results and discussion

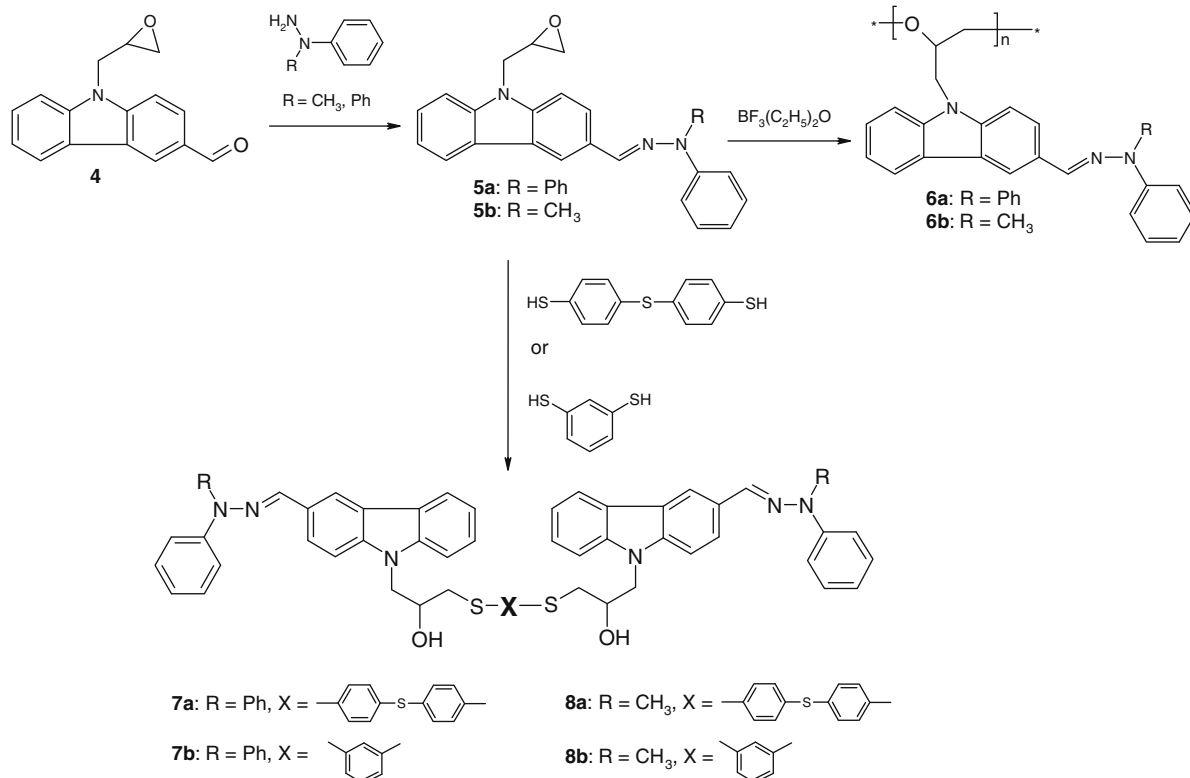
The starting compound **4** required for the synthesis of epoxy monomers **5a** and **5b** was prepared by the synthetic route shown in **Scheme 1**. The protection of the oxirane ring of 9-(oxiranylmethyl)carbazole is necessary for the synthesis of 9-(oxiranylmethyl)carbazol-3-yl-carbaldehyde (**4**). For this purpose 9-(oxiranylmethyl)carbazole was treated with HCl to get 2-chloro-3-hydroxypropyl derivative **1**. Then the hydroxy group of compound **1** was blocked using acetic anhydride and copper sulfate and 3-(carbazol-9-yl)-2-chloropropyl ethanoate (**2**) was formed. In the next step the formylation of compound **2**

was carried out with the complex of POCl_3 and DMF by the method of Vilsmeier. In the last step the aldehyde **3** was treated with an excess of KOH to close the oxirane ring and to give 9-(oxiranylmethyl)carbazol-3-yl-carbaldehyde (**4**).

The synthetic routes to the new carbazole-based hydrazone compounds are shown in **Scheme 2**. The epoxy monomer **5a** was obtained in the reaction of compound **4** and *N,N*-diphenylhydrazine hydrochloride. The epoxy monomer **5b** was obtained in the analogous reaction of aldehyde **4** and *N*-methyl-*N*-phenylhydrazine. The cationic ring opening polymerization of oxirane monomers **5a** and **5b** using $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$ as initiator resulted in



Scheme 1. Synthetic route to 9-(oxiranylmethyl)carbazol-3-yl-carbaldehyde (**4**).



Scheme 2. Synthetic routes to epoxy monomers **5a** and **5b**, oligomers **6a** and **6b**, and twin compounds **7a**, **7b**, **8a**, and **8b**.

polymers **6a** and **6b** respectively. The twin compounds **7a**, **7b**, **8a**, and **8b** were obtained in the reaction of epoxy compounds **5a** and **5b** with different dithiols in the presence of triethylamine (TEA).

The newly synthesized compounds were characterized by IR, ^1H NMR, and mass spectrometry as described in Experimental section. The monomers **5a** and **5b** were found to be readily soluble in common organic solvents like chloroform, acetone, and tetrahydrofuran at room temperature.

The following average molecular weights were detected by gel permeation chromatography (GPC) for the polymers: for polymer **6a** $\bar{M}_n = 3040$, $\bar{M}_w = 4080$, $\bar{M}_n/\bar{M}_w = 1.3$ and for polymer **6b** $\bar{M}_n = 1050$, $\bar{M}_w = 1870$, $\bar{M}_n/\bar{M}_w = 1.8$. Both polymers were found to be soluble in common organic solvents like chloroform, acetone, tetrahydrofuran.

UV spectra of the synthesized monomers, polymers, and twin compounds are presented in Fig. 1. The synthesized carbazole-based hydrazone compounds absorb in the region of 225–400 nm. The spectra of the monomers (**5a**, **5b**), polymers (**6a**, **6b**), and twin compounds (**7a**, **7b**, **8a**, **8b**) are similar to the spectra of the corresponding 9-alkylcarbazolyl hydrazones [22]. They exhibit strong K bands attributed to $\pi \rightarrow \pi^*$ transitions in the region of 341–346 nm. The absorption edges of the compounds having diphenyl substituted hydrazone moieties (**5a**, **6a**, **7a**, and **7b**) are red shifted by few nm with respect to the absorption edges of the compounds with methyl phenyl substituted hydrazone moieties (**5b**, **6b**, **8a**, and **8b**). The absorption edges of the polymers (**6a**, **6b**) show only very small bathochromic shifts with respect to those of the corresponding monomers (**5a**, **5b**).

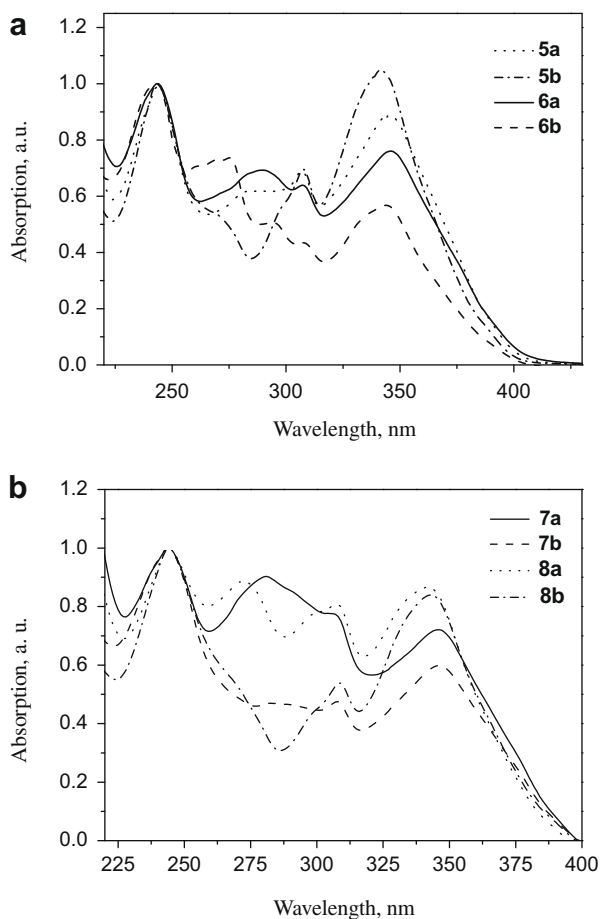


Fig. 1. Normalized UV/VIS absorption spectra of the dilute solutions (10^{-5} mol l^{-1} in THF) of compounds **5a**, **5b**, **6a**, and **6b** (a), and **7a**, **7b**, **8a**, and **8b** (b).

The behaviour under heating of the synthesized carbazole-based hydrazone monomers, polymers and twin compounds was studied by DSC and TGA under the nitrogen atmosphere. The epoxy monomers **5a** and **5b** exhibited moderate thermal stability. The 5% weight loss temperature was detected at 261 °C for compound **5a** and at 298 °C for **5b**. Thermogravimetric curves of compounds **5a** and **5b** are shown in Fig. 2. The thermal degradation of these compounds proceeds in two stages. The first step is apparently due to the break of azo bond of hydrazone moiety.

Monomers **5a** and **5b** were obtained as crystalline materials after the synthesis. However they could be transformed into the solid amorphous materials (molecular glasses) either by cooling from the melt or casting from solutions. DSC curves of compound **5b** are presented in Fig. 3. It showed the melting peak in the first DSC scan at 151 °C. Only the glass transition was observed at 29 °C for compound **5b** in the second and the following DSC scans. The similar behaviour was observed for compound **5a**. It showed the glass transition at 64 °C.

Twin compounds **7a**, **7b**, **8a**, and **8b** were obtained as amorphous materials after the synthesis. Only the glass transition signals were observed in the curves of repeated DSC heating–cooling scans of compounds **7b**, **8a**, and **8b** at 58 °C, 90 °C, and 27 °C respectively. The glass transition of compound **7a** was not detected in the DSC curves, apparently because of the insufficient sensitivity of the apparatus used. However neither the signals of melting or the signals of crystallization were observed in the DSC

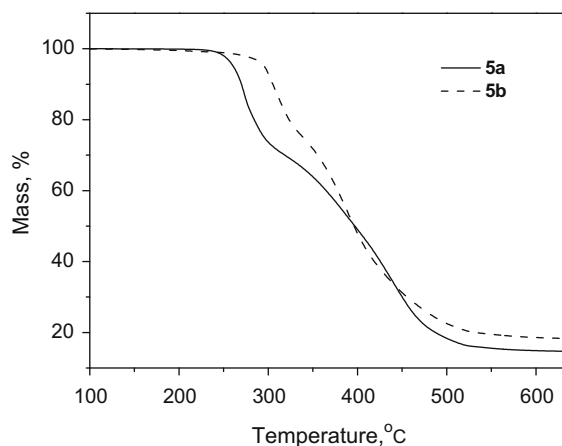


Fig. 2. TGA curves of the compounds **5a** and **5b**.

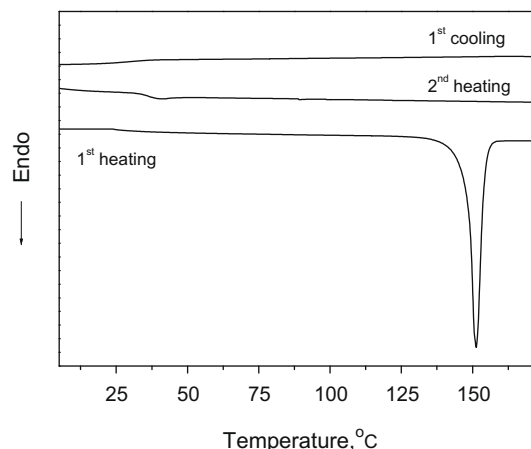


Fig. 3. DSC curves of the compound **5b**.

curves of compound **7a** either. This observation allows us to conclude that compound **7a** is an amorphous material.

The electrochemical stability and the reversibility of the redox processes of compounds were studied by cyclic voltammetry. The electrochemical coupling reactions were observed for all the newly synthesized carbazole-based hydrazones. The epoxy monomer with two phenyl substituents at hydrazine moiety (**5a**) exhibited two steps reversible oxidation in all repeated cycles of redox process (the first cycle E_{ox1} vs. $Ag/Ag^+ = 0.64$ V, E_{ox2} vs. $Ag/Ag^+ = 1.14$ V) (Fig. 4a). The oxidation of the new cation radical formed in the first cycle of redox process was observed in the second and the following cycles of redox process in the cyclic voltammogram of epoxy monomer **5b** (the second cycle E_{ox2} vs. $Ag/$

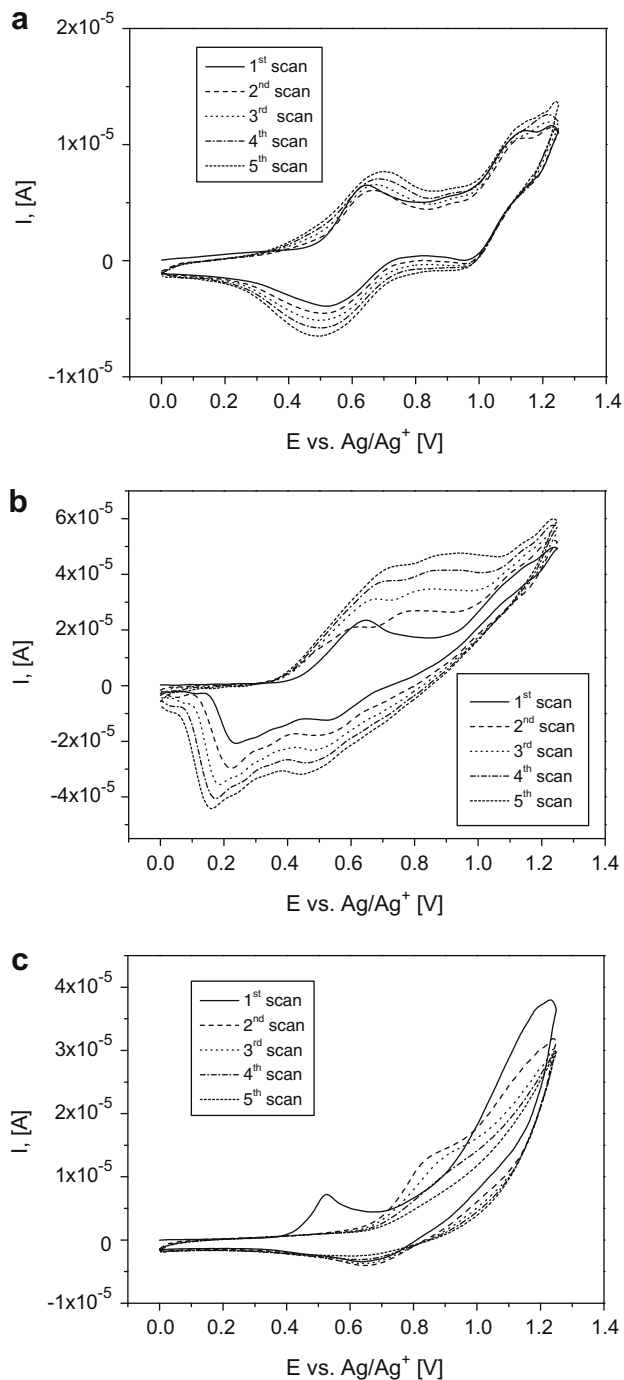


Fig. 4. Cyclic voltammograms of epoxy monomers **5a** (a), **5b** (b), and twin compound **8a** (c) measured in dichloromethane at 25 °C at a sweep rate of 0.1 V/s.

$Ag^+ = 0.78$ V) (Fig. 4b). The formation of the new cation radicals was observed in the cyclic voltammograms of all the studied twin compounds and oligomers. As an example, the cyclic voltammogram of the twin compound **8a** is shown in Fig. 4c (the first cycle E_{ox1} vs. $Ag/Ag^+ = 0.52$ V, the second cycle E_{ox1} vs. $Ag/Ag^+ = 0.85$ V). The studied compounds do not show any reduction behaviour in the measurement range from (+)1.3 V to (–)1.0 V with respect to Ag/Ag^+ .

The values of the ionization potentials (I_p) established from the electron photoemission spectra of the amorphous films of compounds **5a**, **5b**, **6a**, and **6b** are 5.48, 5.43, 5.39, and 5.18 eV respectively. Polymers **6a** and **6b** showed slightly lower ionization potentials than epoxy monomers **5a** and **5b**. This observation is in agreement with the UV spectrometry data. As an example, the electron photoemission spectra of the amorphous films of the compounds **5a** and **6a** are presented in Fig. 5a.

The values of the ionization potentials of the twin compounds **7a**, **7b**, **8a**, and **8b** are comparable: 5.41, 5.42, 5.34, and 5.38 eV respectively (Fig. 5b). Hydrazones **5b**, **6b**, **8a**, and **8b** with methyl groups showed somewhat lower ionization potentials than their counterparts with diphenyl substituents (**5a**, **6a**, **7a**, and **7b**).

The I_p values of the amorphous layers of epoxy monomers **5a** and **5b**, polymers **6a** and **6b**, and the twin compounds **7a**, **7b**, **8a**, and **8b** are rather close to that of indium-tin oxide (ITO), which is widely used as anode in electroluminescent devices [23]. The injection barrier of holes from the electrode into the layers would be ca. 0.3 eV. The materials could also be applied for electro-photographic photoreceptors. Holes would be easily injected into charge transport layers of the compounds **5a**, **5b**, **6a**, and **6b** from charge generation layers with I_p close to 5.2–5.5 eV. The I_p values of

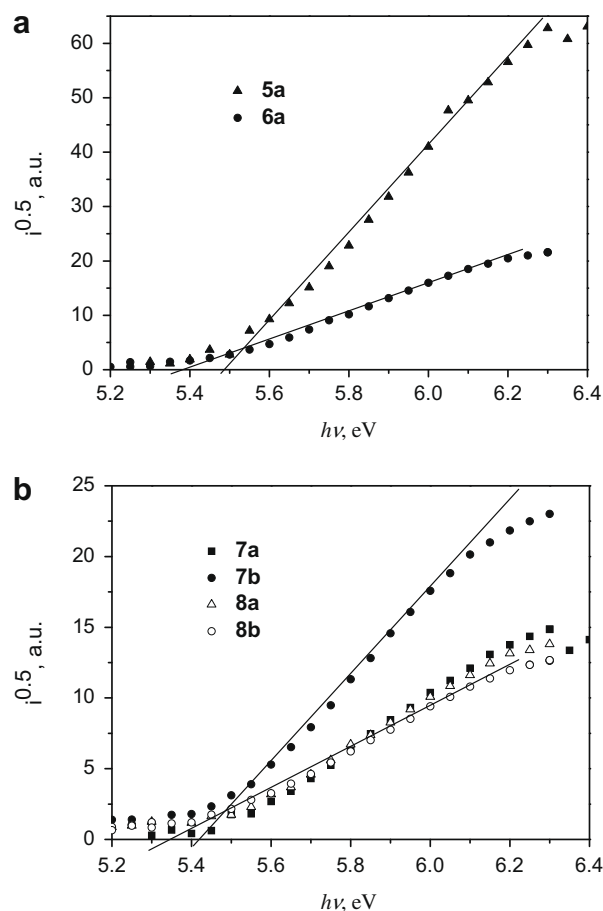


Fig. 5. Electron photoemission spectra of monomer **5a**, polymer **6a** (a), and twin compounds **7a**, **7b**, **8a**, and **8b** (b).

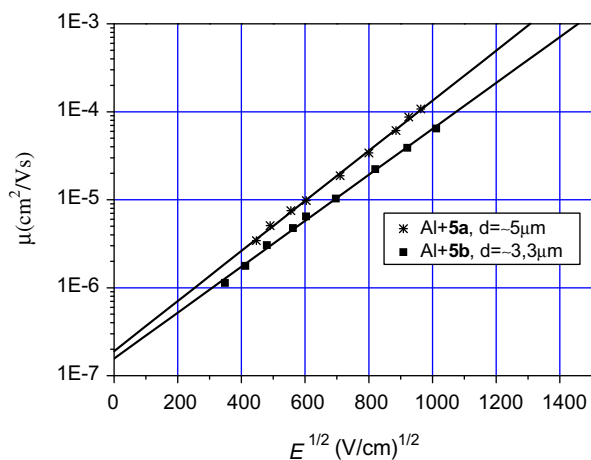


Fig. 6. Electric field dependencies of hole-drift mobilities in the amorphous layers of compounds **5a** and **5b**.

Table 1

Charge transport characteristics of hydrazones **5a**, **5b** and of the molecular mixtures of twin compounds **7a**, **8b** with bisphenol Z polycarbonate.

Composition	Thickness <i>d</i> , μm	μ_0^a , cm ² /(V s)	μ^b , cm ² /(V s)
Al + 5a	~5	$2 \cdot 10^{-7}$	$3.6 \cdot 10^{-5}$
Al + 5b	3.3	$1.6 \cdot 10^{-7}$	$1.9 \cdot 10^{-5}$
7a +(PC-Z), 1:1	8	$5.6 \cdot 10^{-9}$	$1.7 \cdot 10^{-6}$
8b +(PC-Z), 1:1	12	$4.5 \cdot 10^{-8}$	$1.4 \cdot 10^{-6}$

^a μ_0 – zero field mobility.

charge generation materials, widely used in electro-photographic photoreceptors pigments, such as titanil phthalocyanines [24,25], perylene pigments [26] and bisazo pigments [27] are in the same range of 5.1–5.6 eV.

Xerographic time-of-flight technique was used to characterize charge transport properties of the selected hydrazones **5a**, **5b**, **7a**, and **8b**. Hole-drift mobilities in the amorphous layers of hydrazones **5a** and **5b** (Fig. 6), and in the layers of the twin compounds (**7a** and **8b**) molecularly doped in polymer host bisphenol Z polycarbonate PC-Z (50 wt.%) were estimated at different electric fields at the room temperature. The results are summarized in Table 1.

The room temperature hole-drift mobilities in these materials showed linear dependencies on the square root of the electric field. This observation is characteristic of the majority of non-crystalline organic semiconductors and is attributed to the effects of disorder on charge transport [2]. The hole-drift mobilities observed in the amorphous layers of monomers **5a** and **5b** were similar and reached 10^{-4} cm²/(V s) at high electric fields. Hole-drift mobilities observed in the layers containing twin compounds **7a** and **8b** were lower due to the lower concentration of the charge-transporting species in the systems.

4. Conclusions

Hole-transporting carbazole-based hydrazone monomers, polymers, and twin compounds were synthesized and their optical,

thermal, and photoelectrical properties were studied. The synthesized carbazole-based hydrazone compounds absorb in the range of 225–400 nm. The thermal decomposition of the epoxy monomers starts above 240 °C. All the synthesized carbazole-based hydrazone compounds form glasses with the glass transition temperatures ranging from 27 °C to 90 °C. The ionization potentials of the films of carbazole-based hydrazones measured by the electron photoemission technique range from 5.18 to 5.48 eV. The hole-drift mobilities of the amorphous films of the synthesized hydrazone monomers measured by the time-of-flight technique reached 10^{-4} cm²/(V s) at high applied electric fields at the room temperature.

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