ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 154 (2003) 161–167

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photoconductive molecular glasses consisting of twin molecules

S. Grigalevicius [a], G. Blazys [a], J. Ostrauskaite [a], J.V. Grazulevicius [a,*],
V. Gaidelis [b], V. Jankauskas [b]

[a] *Department of Organic Technology, Kaunas University of Technology, Radvilenu Plentas 19, LT 3028 Kaunas, Lithuania*
[b] *Department of Solid State Electronics, Vilnius University, Sauletekio Aleja 9, LT 2040 Vilnius, Lithuania*

Received 20 July 2002; received in revised form 20 July 2002; accepted 29 August 2002

Abstract

Synthesis and properties of photoconductive low-molar-mass glass-forming compounds consisting of twin molecules in which two bulky groups, i.e. 3-(9-carbazolyl)carbazole, 3-(*N*-diphenylamino)carbazole, 3-(10-phenothiazinyl)carbazole and 3,6-di(9-carbazolyl)carbazole are linked by flexible aliphatic units are reported. These compounds are found to form stable glasses with glass-transition temperatures in the range of 94–179 °C as characterised by differential scanning calorimetry (DSC). The electron photoemission spectra of the molecular glasses synthesised have been recorded and the ionisation potentials have been established. The lowest value of ionisation potential (5.32 eV) was observed for the molecular glass containing 3-(*N*-diphenylamino)carbazole moieties. The molecular glass containing 3-(9-carbazolyl)carbazole moieties exhibited ionisation potential of 5.80 eV, which is close to that of the polymer containing electronically isolated carbazole chromophores. Hole drift mobilities of the synthesised materials measured by the time of flight method are in the range of 10^{-4} to 10^{-7} cm^2 V^{-1} s^{-1} at an applied electric field of 3.6×10^5 V cm^{-1}.

Keywords: Photoconductivity; Low-molar-mass glasses; Ionisation potentials

1. Introduction

Low-molar-mass organic compounds that readily form stable glasses are called amorphous molecular materials or molecular glasses. They receive growing attention both in terms of academic interest and technological applications [1,2]. Some of these materials exhibit charge-transporting properties and are known for various applications such as light-emitting diodes, photovoltaic cells, electrophotographic and photorefractive materials [3–5]. Amorphous low-molar-mass materials have been known for a long time, especially those of the natural origin such as colophony, however, they did not receive much attention until the work of Tang and Van Slyke was reported [6]. These researchers used vapour deposited amorphous molecular materials for organic electroluminescent displays. Recently, a lot of new charge-transporting molecular glasses have been reported. They are reviewed in the recent review articles [1,7,8]. Unfortunately, many of molecular glasses exhibit poor morphological stability. They tend to crystallise. Morphological stability of molecular glasses can be increased and their brittleness can be reduced by introducing flexible groups or linkages [9]. However, introduction of flexible aliphatic groups decrease the glass-transition temperature (T_g) of amorphous molecular materials which is not desirable, especially when they are applied in organic light-emitting diodes. Increasing molecular weight of the molecules and especially their rigidity can increase T_g of molecular glasses. The aim of this work was investigation of the synthesis and properties of hole-transporting molecular glasses combining high morphological stability high T_g and good film-forming properties allowing preparation of thin films on a substrate by the simple casting technique. For the achievement of such an object, we have designed and synthesised novel molecules containing both very bulky heteroaromatic groups and aliphatic flexible linkages.

2. Experimental

2.1. Instrumentation

FTIR spectra were measured using a Bio-Rad Digilab FTS-40 spectrometer. ^{1}H NMR spectra were recorded using a Bruker AC 250 (250 MHz) apparatus. UV spectra were measured with a Hitachi U3000 spectrometer. Fluorescence (FL) emission and excitation spectra were recorded with a

---

* Corresponding author. Tel.: +370-745-6525; fax: +370-745-6525.
E-mail address: juorgra@ctf.ktu.lt (J.V. Grazulevicius).

1010-6030/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
PII: S1010-6030(02)00326-X

Shimadzu RF 5301 PC spectrofluorophotometer. DSC measurements were carried out using a Perkin-Elmer DSC-7 calorimeter.

The samples for the charge carrier mobility and electrophotographic measurements were prepared by casting films on the substrates from the solutions of the title compounds or the solutions of the mixtures (1:1 by weight) of these compounds with polycarbonate Z (PC-Z). The substrates were glass plates with conductive SnO_2 layer or polyester film with Al layer. In some cases, charge generation layer was coated on the substrate before the coating of the transporting layer. The dispersion, consisting of Y form of titanyl phthalocyanine and polyvinylbutyral in 2:1 mass proportion in tetrahydrofurane was used for this purpose. After coating the samples were heated at 80 °C for 1 h, thus, the transporting layers of the samples were formed. In some cases, in order to avoid crystallisation, the layers were dried at room temperature for several hours. The thickness of the transporting layer varied in the range 1.5–5 μm.

The samples for the ionisation potential measurement were prepared as follows. The transporting materials were dissolved in THF and were coated on Al plates pre-coated with ∼0.5 μm thick methylmethacrylate and methacrylic acid copolymer (MKM) adhesive layer. The 0.3% solution of MKM in 1:1 acetone and water mixture was used for coating. The function of this layer is not only to improve adhesion, but also to eliminate the electron photoemission from Al layer. No photoemission was detected from Al layer over-coated with MKM at illumination with up to 6.25 eV quanta energy light. In addition, the MKM layer is conductive enough to avoid charge accumulation on it during measurements. The thickness of the charge-transporting layer was 0.5–1.5 μm.

The ionisation potential of the charge-transporting layer I_p was measured by the electron photoemission method in air. Usually, the photoemission experiments with metal or inorganic semiconductor samples are carried out in vacuum and high vacuum is one of the main requirements for these measurements [10,11]. If vacuum is not high enough, the sample surface oxidation and gas adsorption are influencing the measurement results. In our case, however, the organic materials investigated are resistant enough with respect of oxygen. The samples are prepared from solutions in organic solvents in air, so oxygen and other air gases may be not only adsorbed on the surface, but they saturate the volume of the samples. These organic layers are also used in practice, e.g. in electrophotography, in air, so we believe that this justifies measurement of the characteristics of these materials in air.

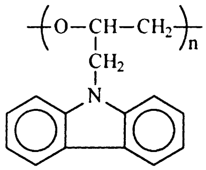
The measurement method is, in principle, similar to that described in [12]. The samples were illuminated with monochromatic light from the quartz monochromator with deuterium lamp. The power of the incident light beam was $(2–5) \times 10^{-8}$ W. The negative voltage of −300 V was supplied to the sample substrate. The counter-electrode with the 4.5 mm × 15 mm slit for illumination was placed at 8 mm distance from the sample surface. The counter-electrode was connected to the input of the BK2-16 type electrometer, working in the open impute regime, for the photocurrent measurement. The 10^{-15} to 10^{-12} A strong photocurrent was flowing in the circuit under illumination. The photocurrent I is strongly dependent on the incident light photon energy $h\nu$. The $I^{0.5} = f(h\nu)$ dependence was plotted. Usually the dependence of the photocurrent on incident light quanta energy is well described by this relationship near the threshold [10–12]. The linear part of this dependence was extrapolated to the $h\nu$ axis and I_p value was determined as the photon energy at the interception point. We evaluate the ionisation potential measurement error as ±0.03 eV.

The hole drift mobility was measured by time of flight method in electrophotographic regime [13]. Electric field was created by positive corona charging. The charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration was 2 ns, wavelength 337 nm). The layer surface potential decrease as a result of pulse illumination was up to 1–5% of initial potential before illumination. The capacitance probe that was connected to the wide frequency band electrometer measured the rate of the surface potential decrease dU/dt. The transit time t_t for the samples with the transporting material was determined by the kink on the curve of the dU/dt transient in double logarithmic scale. Because of the transient current dispersion log–log scale was used. The drift mobility was calculated by the formula $\mu = d^2/U_0 t_t$, where d is the layer thickness, U_0 is the surface potential at the moment of illumination.

The electrophotographic parameters of the samples were measured using conventional methods [14]. Photosensitivity was evaluated from the potential half decay exposure $Lt_{1/2}$ at the light intensity 10^{17} quanta $m^{-2}\,s^{-1}$ and calculated by the formula $S_{1/2} = 1/Lt_{1/2}$. The residual potential U_R was evaluated as a layer surface potential after injection of all the surface charge into the layer bulk.

2.2. Materials

Poly[9-(2,3-epoxypropyl)carbazole] (PEPK) was received from Biolar (Latvia). It was prepared by the anionic polymerisation of 9-(2,3-epoxypropyl)carbazole and purified by adsorption chromatography [15]. The number average molar-mass of PEPK was 1200 g mol^{-1}, polydispersity index M_w/M_n was 1.15.



PEPK

3-Iodo-9H-carbazole (**2**) and 3,6-diiodo-9H-carbazole (**3**) were obtained by a procedure of Tucker [16].

1,6-Di(3-iodo-9-carbazolyl)hexane (**5**): 6 g (20.48 mmol) of 3-iodo-9H-carbazole (**2**), 1.94 g (8 mmol) of 1,6-dibromohexane and 0.2 g (0.6 mmol) of tetrabutylammonium hydrogen sulphate were heated to reflux in 30 ml of acetone and then 0.9 g (16 mmol) of powdered potassium hydroxide was added. After refluxing for 6 h, during which time a white precipitate formed, acetone was removed and the reaction product was dissolved in chloroform. The suspension obtained was filtered and solution was washed with water. After removal of the solvent, the product was purified by two crystallisations from acetone to yield 2.36 g (44.5%) of white crystals. Elemental analysis for $C_{30}H_{26}N_2I_2$: %Calc. C 53.91, H 3.92, N 4.19, I 37.28; %Found C 53.93, H 3.96, N 4.11. ^{1}H NMR ($CDCl_3$): $\delta = 1.24$–1.31 (m, 4H), 1.67–1.82 (m, 4H), 4.15 (t, $J = 6.93$ Hz, 4H), 7.04 (d, $J = 8.78$ Hz, 2H), 7.16–7.64 (m, 8H), 7.99 (d, $J = 7.85$ Hz, 2H), 8.35 (s, 2H). MS: $m/z = 669$, 668, 542, 414, 306, 179.

1,6-Di(3,6-diiodo-9-carbazolyl)hexane (**4**) was synthesised from 3,6-diiodo-9H-carbazole (**4**) and 1,6-dibromohexane by a similar procedure as **5**.

1,6-Di[3-(9-carbazolyl)-9-carbazolyl]hexane (**6a**): 0.81 g (4.8 mmol) of 9H-carbazole, 0.45 g (6.4 mmol) of copper powder, 1.9 g (12.8 mmol) of potassium carbonate and 0.13 g (0.5 mmol) of 18-crown-6 in 10 ml of 1,2-dichlorobenzene were heated to reflux. One gram (1.55 mmol) of 1,6-di(3-iodo-9-carbazolyl)hexane (**5**) in 10 ml of 1,2-dichlorobenzene were added slowly and the mixture was refluxed for 24 h. The inorganic components were filtered of while hot and the product was precipitated into hexane and further purified by column chromatography with silica gel using hexane: chloroform (volume ratio 3:2) as eluent. Yield: 0.78 g (70%) of a white powder. Elemental analysis for $C_{54}H_{42}N_4$: %Calc. C 86.83, H 5.67, N 7.50; %Found C 86.76, H 5.71, N 7.53. ^{1}H NMR ($CDCl_3$): $\delta = 1.44$–1.61 (m, 4H), 1.87–2.02 (m, 4H), 4.35 (t, $J = 6.93$ Hz, 4H), 7.19–7.56 (m, 22H), 8.04 (d, $J = 7.85$ Hz, 2H), 8.17 (d, $J = 7.45$ Hz, 4H), 8.22 (s, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 27.16$, 28.95, 43.08, 108.92, 109.5, 109.79, 119.31, 119.52, 120.23, 120.64, 122.41, 123.04, 123.73, 125.18, 125.79, 126.34, 128.85, 139.43, 140.99, 141.91. IR (KBr): $\nu = 3045$, 2930, 1630, 1595, 1490, 1470, 1455, 1335, 1315, 1280, 1235, 1115, 815, 755 cm^{-1}. MS: $m/z = 747$ (M^+), 746, 581, 373, 345, 331 179, 166.

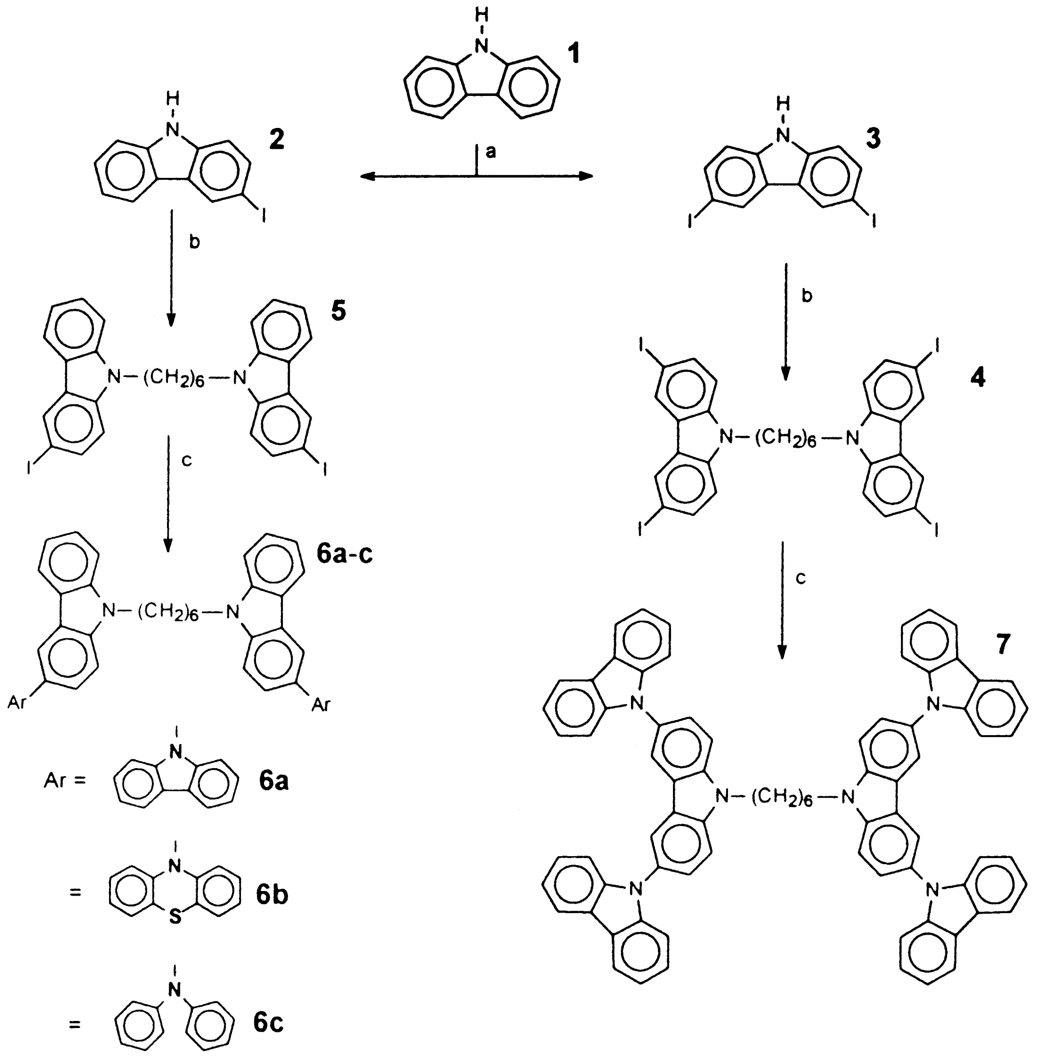
1,6-Di[3-(10-phenothiazinyl)-9-carbazolyl]hexane (**6b**) was prepared from 0.7 g (1.05 mmol) of 1,6-di(3-iodo-9-carbazolyl)hexane (**5**), 0.27 g (4.2 mmol) of copper powder, 1.16 g (8.4 mmol) of potassium carbonate and 0.06 g (0.21 mmol) of 18-crown-6 in the same way as product **6a**, using 0.54 g (2.9 mmol) of 10-phenothiazine as secondary amine, and purified by column chromatography with silica gel using hexane: chloroform (volume ratio 1:40) as eluent. Yield: 0.43 g (51%). Recrystallisation from mixture of hexane: chloroform (volume ratio 1:15) yielded 0.29 g of white crystals, mp: 276 °C. Elemental analysis for $C_{54}H_{42}N_4S_2$: %Calc. C 79.97, H 5.22, S 7.91, N 6.91; %Found C 79.84, H 5.34, N 6.79. ^{1}H NMR ($CDCl_3$): $\delta = 1.34$–1.61 (m, 4H), 1.89–2.12 (m, 4H), 4.34 (t, $J = 6.93$ Hz, 4H), 6.09–6.21 (m, 4H), 6.61–6.72 (m, 8H), 6.96–7.08 (m, 4H), 7.14–7.52 (m, 6H), 8.08 (d, $J = 12.45$ Hz, 4H), 8.11 (s, 2H). IR (KBr): $\nu = 3056$, 2930, 1595, 1571, 1491, 1461, 1441, 1351, 1307, 1237, 1169, 1122, 1043, 923 cm^{-1}. MS: $m/z = 811$ (M^+), 810, 613, 548, 405, 377 198, 179.

1,6-Di[3-(N-diphenylamino)-9-carbazolyl]hexane (**6c**) was prepared from 1.2 g (1.8 mmol) of 1,6-di(3-iodo-9-carbazolyl)hexane (**5**), 0.46 g (7.2 mmol) of copper powder, 1.99 g (14.4 mmol) of potassium carbonate and 0.095 g (0.36 mmol) of 18-crown-6 in the analogous way as product **6a**, using 0.84 g (4.95 mmol) of diphenylamine as secondary amine, and purified by column chromatography with silica gel using hexane: chloroform (volume ratio 3:1) as eluent. Yield: 0.66 g (49%). Recrystallisation from mixture of hexane: chloroform (volume ratio 6:1) yielded 0.53 g of white crystals, mp: 180 °C. Elemental analysis for $C_{54}H_{46}N_4$: %Calc. C 86.37, H 6.17, N 7.46; %Found C 86.41, H 6.26, N 7.59. ^{1}H NMR ($CDCl_3$): $\delta = 1.37$–1.49 (m, 4H), 1.79–1.92 (m, 4H), 4.22 (t, $J = 6.75$ Hz, 4H), 6.85–7.42 (m, 40H), 7.81–7.94 (m, 4H). IR (KBr): $\nu = 3057$, 2931, 1595, 1712, 1586, 1487, 1467, 1374, 1349, 1310, 1277, 1233, 1151, 1124, 1076, 1027 cm^{-1}. MS: $m/z = 750$ (M^+), 347, 333 269, 168.

1,6-Di[3,6-di(9-carbazolyl)-9-carbazolyl]hexane (**7**) was prepared from 1.1 g (1.2 mmol) of 1,6-di(3,6-diiodo-9-carbazolyl)hexane (**4**), 0.64 g (10 mmol) of copper powder, 2.76 g (20 mmol) of potassium carbonate, 0.19 g (0.7 mmol) of 18-crown-6 and 1.18 g (7 mmol) of 9H-carbazole in the analogous way as compounds **6a**–**c**, and purified by column chromatography with silica gel using hexane: chloroform (volume ratio 1:3) as eluent. Yield: 0.84 g (65%) of a white powder. Elemental analysis for $C_{78}H_{56}N_6$: %Calc. C 86.96, H 5.24, N 7.8; %Found C 86,51, H 5.47, N 8.02. ^{1}H NMR ($CDCl_3$): $\delta = 1.48$–1.64 (m, 4H), 1.97–2.14 (m, 4H), 4.47 (t, $J = 6.58$ Hz, 4H), 7.21–7.74 (m, 32H), 8.03–8.15 (m, 12H). IR (KBr): $\nu = 3049$, 2929, 1625, 1595, 1496, 1479, 1452, 1335, 1315, 1286, 1231, 1106, 962, 807, 749 cm^{-1}. MS: $m/z = 1077$ (M^+), 1076, 911, 746, 605, 579, 497, 389, 332, 249, 217, 173, 155.

3. Results and discussion

1,6-Di[3-(9-carbazolyl)-9-carbazolyl]hexane (**6a**), 1,6-di-[3-(10-phenothiazinyl)-9-carbazolyl]hexane (**6b**), 1,6-di[3-(*N*-diphenylamino)-9-carbazolyl]hexane (**6c**) and 1,6-di[3,6-di(9-carbazolyl)-9-carbazolyl]hexane (**7**) were prepared as described in Scheme 1 via the Ullmann coupling reaction of 1,6-di(3-iodo-9-carbazolyl)hexane (**5**) or 1,6-di(3,6-diiodo-9-carbazolyl)hexane (**4**) with an excess of secondary amine. The key starting materials **4** and **5** were synthesised by alkyltion of 3,6-diiodo-9H-carbazole (**3**) and 3-iodo-9H-carbazole (**2**), respectively, with 1,6-dibromohexane. Mass spectrometry, IR absorption, electronic absorption, elemental analysis and ^{1}H NMR spectroscopy methods were used to identify all these materials. The compounds **6a**–**c** are soluble in common organic solvents. Poor solubility of the compound



Scheme 1. (a) KI, KIO_3, CH_3COOH; (b) 1,6-dibromohexane, KOH, tetrabutylammonium hydrogen sulphate, acetone; (c) Cu, K_2CO_3, 18-crown-6, 1,2-dichlorobenzene, 9H-carbazole (for **6a** and **7**), 10H-phenothiazine (for **6b**) or diphenylamine (for **6c**).

7 did not allow to prepare the films and to measure its photoelectric characteristics.

Table 1 lists the UV absorption (in CH_2Cl_2 solutions) and photoluminescense (PL) emission (in tetrahydrofuran solutions) maxima of the compounds **6a–c** and **7**.

The comparison of the UV absorption (Fig. 1a) and PL emission (Fig. 1b) spectra of **6a** and **7** with that 9-ethylcarbazole shows that the bulky groups (i.e. 3-(9-carbazolyl)carbazole, 3-(*N*-diphenylamino)carbazole, 3-(10-phenothiazinyl)carbazole and 3,6-di(9-carbazolyl) carbazole) of the compounds **6a–c** and **7** are significantly π-conjugated through the lone electron pair at the nitrogen atom and that π-electrons are de-localised over these groups.

The electron photoemission spectra of the compounds **6a–c** are presented on Fig. 2. For the comparison the

Table 1
UV absorption (in CH_2Cl_2 solutions[a]) and PL emission (in tetrahydrofuran solutions[a]) maxima of the compounds **6a–c** and **7**

Compound	UV		PL: λ_{max} (nm)
	λ_{max} (nm)	ε ($\times 10^{-5}$, mol^{-1} dm^3 cm^{-1})	
6a	263, 291, 339	1.63, 1.06, 0.37	375, 387
6b	273, 296, 348	1.82, 1.23, 0.54	407
6c	272, 297, 360	1.65, 1.48, 0.36	418
7	267, 294, 342	1.87, 1.47, 0.45	386, 401

[a] 10^{-5} mol l^{-1}.

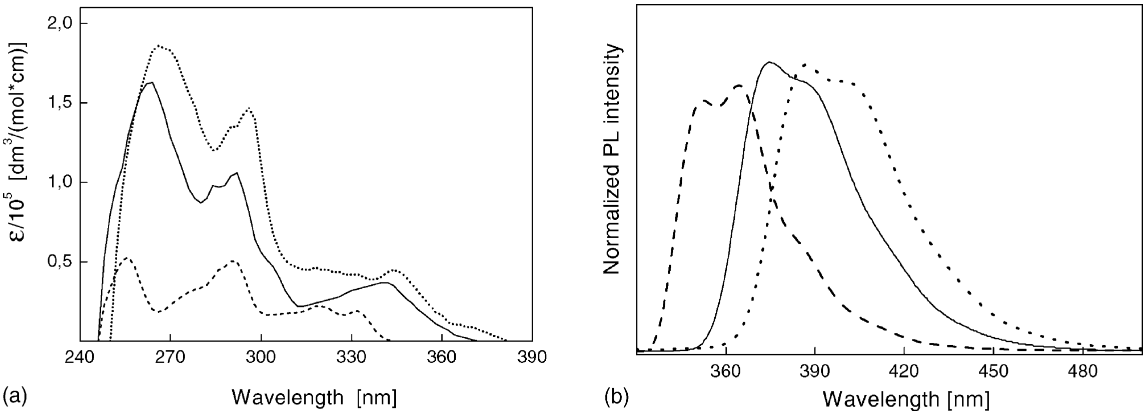


Fig. 1. UV absorption (a) and normalised PL emission (b) spectra of **6a** (solid line), **7** (dotted line) and 9-ethylcarbazole (dashed line) dilute solutions (10^{-5} mol l^{-1}). Excitation wavelength 290 nm.

spectrum of the oligomeric photoconductor PEPK with the pendant carbazolyl chromophores is shown.

The photoemission spectra are dependent on the groups connected to the 3rd and 6th positions of carbazole ring. This indicates to the electronic interaction between the carbazole ring and the pendant groups. The values of the ionisation potential I_p in eV are: 5.80 for **6a**, 5.50 for **6b**, 5.32 for **6c** and 5.86 for PEPK. It is evident that the I_p the compound **6a** containing double carbazole rings is about of the same value as that of PEPK containing lone carbazole rings as chromophores. This means that the highest occupied orbital for the two-cargazole rings, connected in the manner as it is in the compound **6a**, is near to that of the lone carbazole ring. However, the edge of electron absorption spectrum of **6a** is significantly shifted to the read as compared with that of 9-ethylcarbazole (Fig. 1). This shift is to be ascribed to the different positions of the excited states of the molecules. The attachment of the phenothiazine (**6b**) and especially of diphenylamine (**6c**) moieties to the carbazolyl group leads to the significant decrease of I_p, making these materials interesting from the practical point of view.

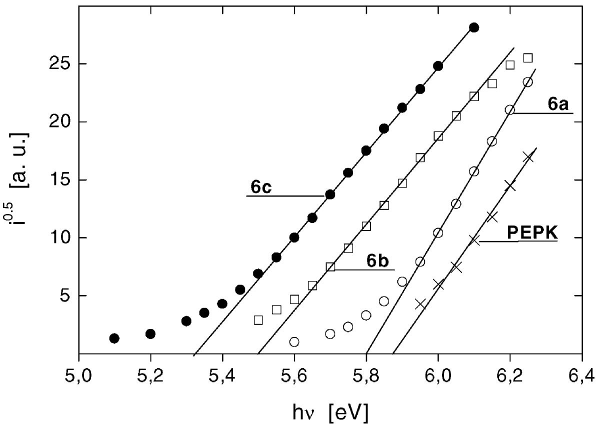


Fig. 2. The photoemission spectra of the compounds **6a–c** and PEPK.

The thermal properties of all the materials were examined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under a nitrogen atmosphere. The glass-transition temperatures (T_g), melting temperatures (T_m), temperatures at which initial loss of mass was observed (T_{ID}), and changes in heat capacity at T_g (ΔC_p) are summarised in Table 2.

The compound **7** was obtained as amorphous glass as confirmed by DSC. When the samples of this compound were heated the glass-transition was observed at 179.2 °C, and no peaks due to crystallisation and melting appeared. All the attempts to crystallise this compound in different solvents failed. The compounds **6a–c** melt only on first heating and form glasses upon cooling from the melt. As an example, the DSC curves of **6c** are shown in Fig. 3.

When the crystalline sample of **6c** prepared by recrystallisation from the mixture of hexane and chloroform, was heated, the endothermic peak due to melting was observed at 180 °C. When the melt sample was cooled down either rapidly with liquid nitrogen or slowly at room conditions, it readily formed a stable glass. When the amorphous glassy sample was heated again, the glass-transition phenomenon was observed at 93.7 °C and no peaks due to crystallisation and melting appeared on further heating. No differences were observed comparing the DSC curves of the second, third and the following heating. The casting or doctor blade techniques allows to prepare the films of the compounds **6a–c** and **7** on the substrates. No any signs of crystallisation were observed in these films after several months of

Table 2
Thermal characteristics of the compounds **6a–c** and **7**

Compound	T_g (°C)	ΔC_p (J g^{-1} (°C)$^{-1}$)	T_m (°C)	T_{ID} (°C)
6a	102.6	0.601	245	312
6b	124.8	0.358	276	383
6c	93.7	0.634	180	396
7	179.2	0.321	–[a]	400

[a] Obtained as glass.

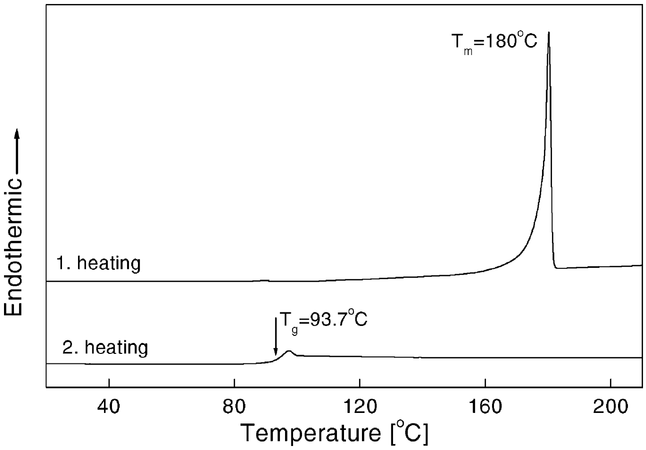


Fig. 3. DSC curves of **6c**. Heating rate: 10 °C min^{-1}.

storage. T_g of the compounds synthesised in this work range from 94 to 179 °C. The values of T_g of the compounds synthesised correlate with the values T_m, however, they do not observe strictly the rule $T_g/T_m = 2/3$ [17]. For all the compounds this ratio is lower than 2/3. In the series **6a–c** the highest T_g was observed for the compound containing phenothiazinyl groups while the compound containing diphenyl amino groups exhibited the lowest T_g. The value of T_g can certainly also be varied varying the length of the alkyl spacer.

All the materials demonstrated a high thermal stability, up to 300 °C with a heating rate of 10 °C min^{-1}, as confirmed by TGA.

The typical time of flight transients are presented on Fig. 4. The small charge time of flight transient decrease is of hyperbolic type in the materials investigated, which indicates the dispersive transport [18]. In double log–log scale the transients can be approximated by two straight lines: ($\mathrm{d}U/\mathrm{d}t \sim I \sim t^{-1+\alpha}$) at initial stage and ($\mathrm{d}U/\mathrm{d}t \sim I \sim t^{-1-\alpha}$) in final stage, where α is the dispersion parameter. The straight lines interception point gives the transit time t_t.

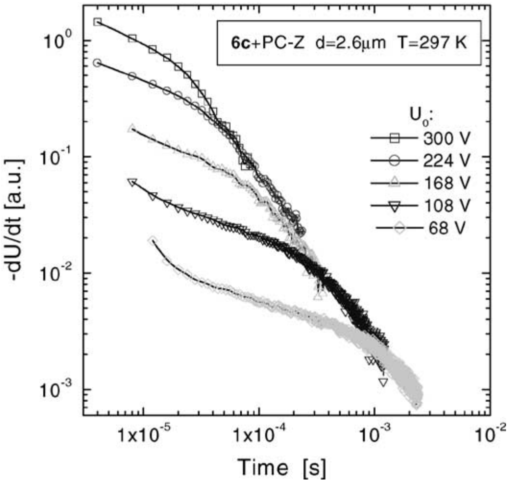


Fig. 4. Typical time-of-flight transients in **6c** + PC-Z at various surface potentials U_0.

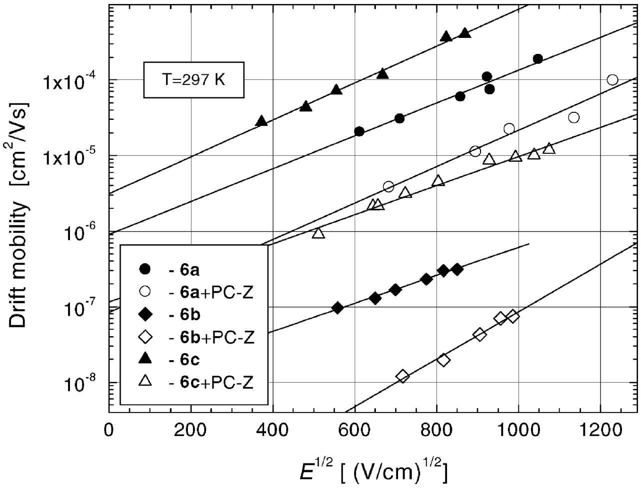


Fig. 5. The field dependencies of the hole drift mobilities in the layers of the compounds **6a–c** and of their solid solutions in PC-Z.

The room temperature dependences of hole drift mobility (μ) values on an applied electric field are given in Fig. 5. The highest mobilities at high electric field considerably exceeding 10^{-4} cm^2 V^{-1} s^{-1} have been observed in the film of molecular glass, containing 3-(*N*-diphenylamino)carbazole moieties (**6c**), while the molecular glass containing 3-(10-phenothiazinyl)carbazole moieties (**6b**) exhibited the lowest hole mobilities. Amorphous molecular material **6c** possesses low enough ionisation potential, good film-forming properties and T_g approaching 100 °C. For these reasons compound **6c** can be interesting for practical application. The hole drift mobilities in the solid solutions of **6a–c** in polycarbonate are lower than in pure molecular glasses. However, the extent to which the mobilities decrease after introduction of the binder material is different for the different systems. The hole mobilities in the solid solutions of **6a** in polycarbonate are only by about one order of magnitude lower than those in neat **6a**, while the system **6b** + PC-Z exhibited the mobilities almost by two orders lower than in pure molecular glass **6b**.

An electric field well exceeding 10^6 V cm^{-1} can be reached in the layers of the pure materials investigated of their blends with PC-Z when charged with corona. The value of the residual potential U_R, measured in 10–15 s after exposure with strongly absorbed light, makes up about 15% of the U_0 in the case of the material **6a**, it decreases down to 1.5–1.6% for **6c** (see Table 3).

This indicates that the deep traps concentration is low in this material. The double layer system with the titanyl phthalocyanine charge generation layer below the transporting layer was tested. The system can be charged up to 10^6 V cm^{-1}. The layers posses high photosensitivity to the read light. The decrease of the residual potential with the shift from **6a** to **6c** may be caused by lowering of the deep traps concentration and improved hole injection from charge generation layer into transporting layer (Table 4).

Table 3
Electrophotographic parameters of the layers of compounds **6a–c** and of their solid solutions in PC-Z at illumination with 10^{17} quanta $m^{-2}\,s^{-1}$ and 260 nm light

Transport material	d (μm)	U_0 (V)	$S_{1/2}$ ($m^2\,J^{-1}$)	U_R/U_0
6a	1.3	264	10	0.15
6a + PC-Z	1.8	440	3.7	0.11
6b	1.8	268	32	0.045
6b + PC-Z	2.1	332	11	0.060
6c	1.3	204	21	0.015
6c + PC-Z	2.4	364	9.4	0.016

Table 4
Electrophotographic parameters of the samples **6a–c** and of their solid solutions in PC-Z with titanyl phthalocyanine charge generation layer at illumination with 10^{17} quanta $m^{-2}\,s^{-1}$ and 780 nm light

Transport material	d (μm)	U_0 (V)	$S_{1/2}$ ($m^2\,J^{-1}$)	U_R/U_0
6a	1.6	−104	115	0.12
6a + PC-Z	2.5	−200	119	0.18
6b	1.8	−128	123	0.063
6b + PC-Z	2.1	−188	89	0.17
6c	1.6	−144	178	0.028
6c + PC-Z	2.6	−196	187	0.02

Among the materials investigated the amorphous molecular material **6c** possesses low enough ionisation potential, good film-forming properties and T_g approaching 100 °C. For these reasons, this compound can be interesting for practical application.

Acknowledgements

The Kaunas group is indebted to Prof. H.-W. Schmidt in whose laboratories at the Department of Macromolecular Chemistry I (University of Bayreuth, Germany) the characterisation of the compounds was carried out.

References

[1] Y. Shirota, J. Mater. Chem. 10 (2000) 1.
[2] C.-W. Ko, Y.-T. Tao, J.T. Lin, K.R. Justin Thomas, Chem. Mater. 14 (2002) 357.
[3] T. Ohara, K. Okumoto, H. Inada, T. Noda, Y. Shirota, M. Kinoshita, J. Am. Chem. Soc. 122 (2000) 11021.
[4] Y. Haga, Y. Harada, Jpn. J. Appl. Phys. 140 (2001) 855.
[5] C. Hohle, P. Strohriegl, S. Schloter, U. Hofmann, D. Haarer, Xerographic photoreceptors and organic photorefractive materials IV, in: Proceedings of the SPIE-International Society for Optical Engineering, vol. 3471, San Diego, CA, 22–23 July 1998, p. 29.
[6] C.W. Tang, S.A. Van Slyke, Appl. Phys. Lett. 51 (1987) 913.
[7] J.V. Grazulevicius, P. Strohriegl, Light emitting diodes, lithium batteries and polymer devices, in: H.S. Nalwa (Ed.), Handbook of Advanced Electronic and Photonic Materials and Devices, vol. 10, Academic Press, London, 2000, p. 258.
[8] M. Thelekkat, H.-W. Schmidt, Polym. Adv. Technol. 9 (1998) 429.
[9] H.O. Wirth, Angew. Macromol. Chem. 185–186 (1991) 329.
[10] M. Cordona, L. Ley, Top. Appl. Phys. 26 (1978) 13.
[11] V.S. Fomenko, I.A. Podchernyaeva, Emission and Adsorption Properties of Compounds and Materials, Atomizdat, Moscow, 1975 (in Russian).
[12] E. Miyamoto, Y. Yamaguchi, M. Yokoyama, Electrophotography 28 (1989) 364.
[13] J. Kalade, E. Montrimas, V. Jankauskas, in: Proceedings of the ICPS'94 on the Physics and Chemistry of Imaging Systems, Rochester, 1994, p. 747.
[14] R.M. Schaffert, Electrophotography, The Focal Press, London, 1965, pp. 175–203.
[15] J.V. Grazulevicius, R. Kavaliunas, A. Undzenas, V.G. Uss, N. Kreiveniene, Zh. Nauch. Prikl. Fotogr. 32 (1987) 22 (in Russian).
[16] S.H. Tucker, J. Chem. Soc. (1926) 546.
[17] K. Naito, A. Miuara, J. Phys. Chem. 97 (1993) 6240.
[18] H. Scher, E.W. Montroll, Phys. Rev. B 12 (1975) 2455.