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Polymer 43 (2002) 2603–2608

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# Synthesis and properties of poly(3,9-carbazole) and low-molar-mass glass-forming carbazole compounds

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Received 19 August 2001; received in revised form 12 December 2001; accepted 13 January 2002

## Abstract

The novel $\pi$-conjugated polymer poly(3,9-carbazole) was prepared by Ullmann polycondensation reaction of 3-iodo-9*H*-carbazole. The polymer has a number-average molecular weight of ca. 2400 with a molecular weight distribution of 2.15. The dimer model compound and the carbazole trimer 3,6-di(carbazolyl)alkylcarbazole have been synthesized by stepwise reactions. All these compounds have been found to form glasses with glass transition temperatures in the range 35–157 °C as characterized by differential scanning calorimetry. The ionization potentials of these compounds range from 5.45 to 5.97 as determined by the electron photoemission method. Time of flight experiment showed that hole drift mobilities of the low-molar-mass glasses were in the range $10^{-5}$–$10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords*: Poly(3,9-carbazole); Low-molar-mass glasses; Hole drift mobility

## 1. Introduction

Hole transport organic amorphous materials with good film forming properties are known for various applications such as electrophotographic photoreceptors [1], displays [2,3], photovoltaic cells [4,5] and photorefractive materials [6]. Organic amorphous hole transport materials which are used in these devices are mainly of two kinds. One is low-molar mass material. Using this kind of materials the devices are generally fabricated by vacuum-deposition. The other kind is polymers. The devices from polymers are fabricated by casting or spin coating methods.

Polymers with carbazolyl groups have been extensively studied for the different applications due to their good hole transport and luminescent properties [7]. Recently in our laboratories, several carbazole derivatives have been synthesized and their charge transport properties have been studied [8]. Here, we report on the synthesis and properties of conjugated carbazole polymer and low-molar-mass glass-forming carbazole compounds.

## 2. Experimental

### 2.1. Instrumentation

FTIR spectra were recorded using a Bio-Rad Digilab FTS-40 spectrometer. $^1$H NMR spectra were recorded using a Bruker AC 250 (250 MHz) apparatus. UV–Vis spectra were recorded with a Hitachi U3000 spectrometer. Fluorescence emission and spectra were recorded with a Shimadzu RF 5301 PC spectrofluorophotometer. Differential scanning calorimetry (DSC) measurements were carried out using a Perkin Elmer DSC-7 calorimeter.

The molecular weight was determined by a Waters GPC system including a Waters 410 UV detector (254 nm) using THF as eluent and polystyrene standards.

The ionization potentials of poly(3,9-carbazole) and the low-molar-mass carbazole compounds were measured by the modified electron photoemission method in air [9]. The samples for the ionization potential measurement were prepared as follows. The 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 function of this layer is 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 layers was 0.5–1 μm.

The hole drift mobilities were measured by time of flight method (TOF) [10]. The samples for the charge carrier mobility measurements were prepared by casting the solutions of the title compounds or the solutions of the mixtures (1:1 by weight) of these compounds with

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PII: S0032-3861(02)00067-8

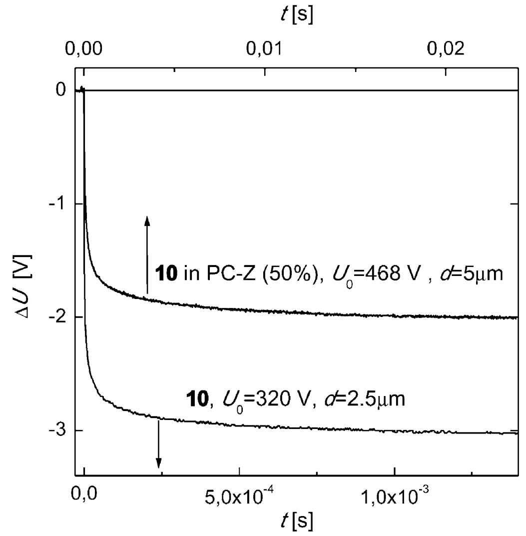


Fig. 1. The potential decay of **10** (lower time scale) and **10** doped in PC (50 wt%) (upper time scale) samples after illumination with 337 nm light pulse.

polycarbonate Z (PC-Z) on the substrates. The substrates were glass plates with conductive $SnO_2$ layer or polyester film with Al layer. The thickness of the transporting layer varied in the range 2.5–5 μm. The potential decay experiments showed that initial rapid potential decay is followed by the small and slow relaxation after the sample illumination with nanosecond light pulse (Fig. 1). This is characteristic both for the samples of pure **8** or **10** and their compositions (50 wt%) with PC-Z. This observation shows that well-defined drift speed is characteristic for the hole transport. In addition the residual potential of these layers, measured at illumination with strongly absorbed light, is low (7–15%). Consequently most of the holes are traversing the whole layer thickness. The TOF transients were of disperse character (Fig. 2). The TOF value was found by approximating the initial and end parts of the transient by straight lines and finding an interception point of these straight lines.

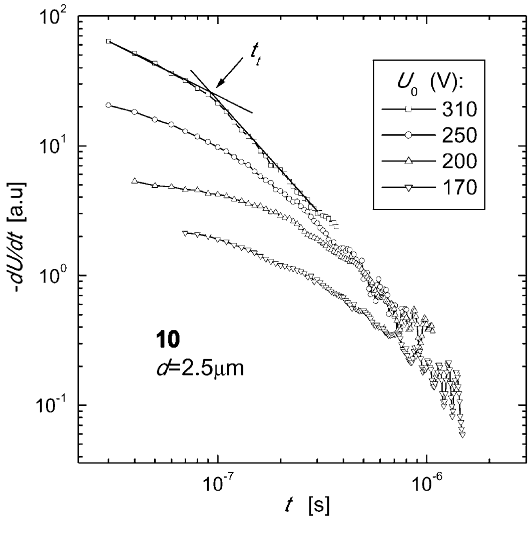


Fig. 2. Time of flight transients in amorphous films of **10**.

### 2.2. *Materials*

#### *2.2.1. 3-Iodo-9H-carbazole (**2**) and 3,6-diiodo-9H-carbazole (**3**)*

These compounds were obtained by a modified procedure of Tucker [11].

#### *2.2.2. 3-Iodo-9-hexylcarbazole (**4**) and 3,6-diiodo-9-alkylcarbazoles (**5–6**)*

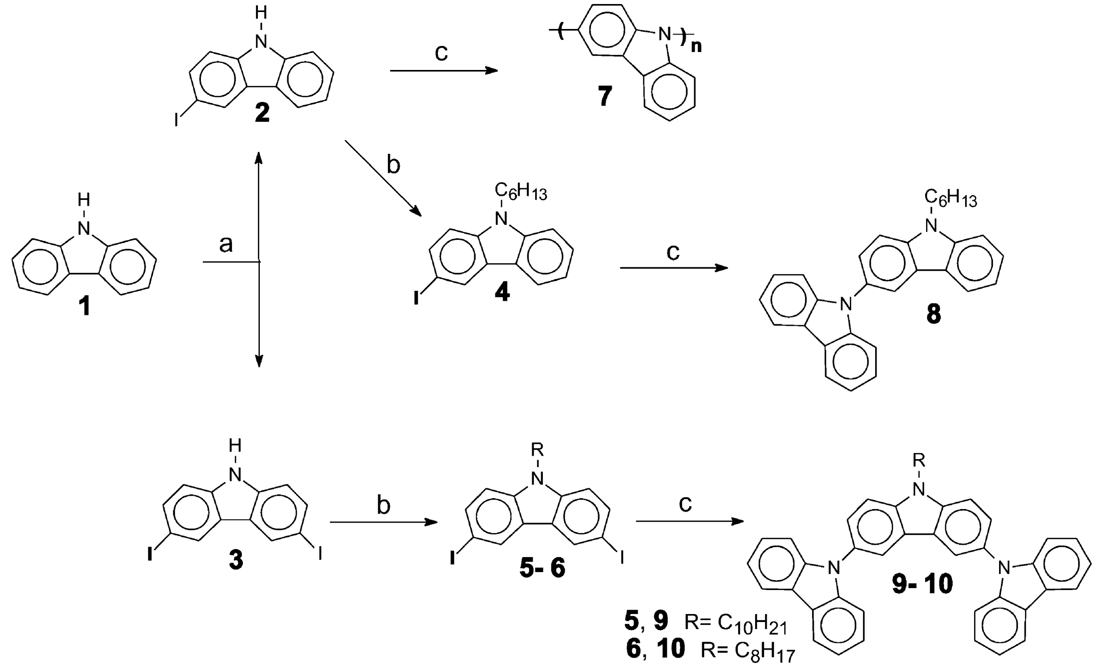
These compounds were prepared by alkylation of 3-iodo-9*H*-carbazole (**2**) and 3,6-diiodo-9*H*-carbazole (**3**), respectively, in the presence of a phase transfer catalyst [12].

#### *2.2.3. Poly(3,9-carbazole) (**7**)*

1.64 g (5.58 mmol) of 3-iodo-9*H*-carbazole (**2**), 0.71 g (11.16 mmol) of copper powder, 3.08 g (22.32 mmol) of potassium carbonate and 0.15 g (0.56 mmol) of 18-crown-6 in 20 ml of 1,2-dichlorobenzene were refluxed for 36 h in a nitrogen atmosphere. The inorganic components were then filtered off while hot and the product was precipitated into hexane several times. The solid residue was extracted with hot ethanol to remove 18-crown-6. Yield: 0.8 g (87%) of a brown powder. Elemental analysis for $C_{12}H_7N$: %Calc. C 87.25, H 4.27, N 8.48; %Found C 86.91, H 4.47, N 8.62. $^1H$ NMR ($CDCl_3$): $\delta = 7.26–7.38$ (m, 1H), 7.43–7.56 (m, 2H), 7.57–7.71 (m, 2H), 8.07–8.23 (m, 1H), 8.32–8.44 (m, 1H). IR (KBr): $\nu = 3427$, 3049, 2898, 1626, 1600, 1577, 1493, 1461, 1325, 1314, 1272, 1232, 1108, 809, 746 $cm^{-1}$.

#### *2.2.4. 3-(9-Carbazolyl)-9-hexylcarbazole (**8**)*

0.84 g (5.0 mmol) of 9*H*-carbazole (**1**), 0.75 g (11.8 mmol) of copper powder, 3.23 g (23.7 mmol) of potassium carbonate and 0.15 g (0.55 mmol) of 18-crown-6 in 30 ml of 1,2-dichlorobenzene were heated to reflux. 1.3 g (3.56 mmol) of 3-iodo-9-hexylcarbazole (**4**) in 10 ml of 1,2-dichlorobenzene was added slowly and the mixture was refluxed for 36 h. The inorganic components were then removed by filtration of the hot reaction mixture. The solvent was distilled under reduced pressure and the crude product was purified by column chromatography with silicagel using hexane/chloroform (volume ratio 8:1) as eluent. Yield: 0.9 g (63%) of a white powder, mp: 146 °C. Elemental analysis for $C_{30}H_{28}N_2$: %Calc. C 86.50, H 6.77, N 6.72; %Found C 86.51, H 6.47, N 7.01. $^1H$ NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 6.6$ Hz, 3H), 1.06–1.52 (m, 6H), 1.81–2.05 (m, 2H), 4.3 (t, $J = 6.9$ Hz, 2H), 7.08–7.54 (m, 11H), 8.01 (d, $J = 7.9$ Hz, 1H), 8.07–8.23 (m, 3H). IR (KBr): $\nu = 3077$, 3035, 2947, 2929, 2850, 1626, 1596, 1573, 1497, 1471, 1450, 1333, 1316, 1285, 1238, 1143, 806, 754 $cm^{-1}$. MS: $m/z = 416$ ($M^+$), 345, 331, 208, 172, 166.



Scheme 1. (a) KI, $KIO_3$, $CH_3COOH$; (b), KOH, tetrabutylammonium hydrogen sulfate, acetone, 1-bromoheksane for **4**, 1-bromooctane for **6** and 1-bromodecane for **5**; (c) Cu, $K_2CO_3$, 18-crown-6, 1,2-dichlorobenzene, 9*H*-carbazole for **8**–**10**.

### *2.2.5. 3,6-Di(9-carbazolyl)-9-decylcarbazole (**9**)*

1.14 g (6.8 mmol) of 9*H*-carbazole (**1**), 1.7 g (27 mmol) of copper powder, 7.5 g (54 mmol) of potassium carbonate and 0.3 g (1.1 mmol) of 18-crown-6 in 10 ml of 1,2-dichlorobenzene were heated to reflux. 0.9 g (2.26 mmol) of 3,6-diiodo-9-decylcarbazole (**5**) in 10 ml of 1,2-dichlorobenzene were added slowly and the mixture was refluxed for 36 h. The inorganic components were then removed by filtration of the hot reaction mixture. The solvent was distilled under reduced pressure and the crude product was purified by column chromatography with silicagel using hexane/chloroform (volume ratio 3:1) as eluent. Yield: 0.62 g (63%). Recrystallization from acetone yielded 0.45 g of white crystals, mp: 200 °C. Elemental analysis for $C_{46}H_{43}N_3$: %Calc. C 86.62, H 6.79, N 6.59; % Found C 86.51, H 6.86, N 6.53. $^1$H NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 6.6$ Hz, 3H), 1.16–1.62 (m, 14H), 1.85–2.15 (m, 2H), 4.3 (t, $J = 7.3$ Hz, 2H), 7.15–7.64 (m, 18H), 8.05–8.2 (m, 6H). IR (KBr): $\nu = 3077$, 3035, 2947, 2929, 2850, 1626, 1596, 1573, 1497, 1471, 1450, 1333, 1316, 1285, 1238, 1143, 806, 754 cm$^{-1}$. MS: $m/z = 637$ ($M^+$), 552, 510, 496, 319, 166.

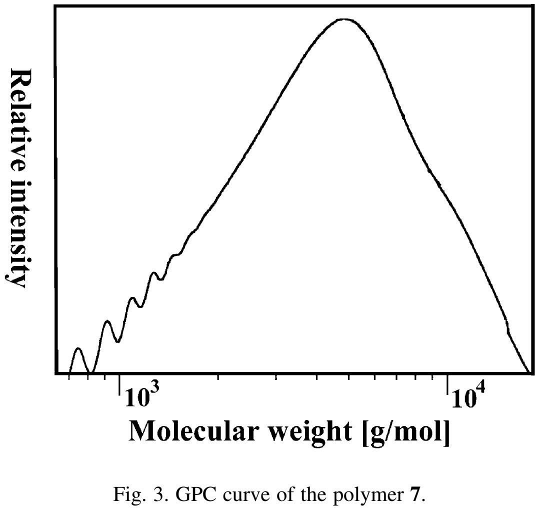


Fig. 3. GPC curve of the polymer **7**.

### *2.2.6. 3,6-Di(9-carbazolyl)-9-octylcarbazole (**10**)*

This compound was prepared from 1.25 g (2.28 mmol) of 3,6-diiodo-9-octylcarbazole (**6**) and 1.14 g (6.8 mmol) of 9*H*-carbazole (**1**) in the same way as product **9** and purified by column chromatography with silica gel using hexane/chloroform (volume ratio 6:1) as eluent. Yield: 1.05 g (77%). Recrystallization from mixture of hexane/chloroform (volume ratio 9:1) yielded 0.7 g of white crystals, mp: 218 °C. Elemental analysis for $C_{44}H_{39}N_3$: %Calc. C 86.66, H 6.45, N 6.89; %Found C 86.51, H 6.49, N 6.99. $^1$H NMR ($CDCl_3$): $\delta = 0.91$ (t, $J = 7.3$ Hz, 3H), 1.52–1.26 (m, 10H), 2.13–1.96 (m, 2H), 4.46 (t, $J = 7.1$ Hz, 3H), 7.29–7.15 (m, 4H), 7.44–7.32 (m, 8H), 7.65–7.63 (m, 4H), 8.16–8.13 (m, 6H). IR (KBr): $\nu = 2950$, 2930, 2850, 1625, 1590, 1565, 1495, 1475, 1450, 1335, 1315, 1285, 1230, 1150, 815 cm$^{-1}$. MS: $m/z = 609$ ($M^+$), 510, 496, 344, 304, 166.

## 3. Results and discussion

The classical method for the preparation of the aromatic

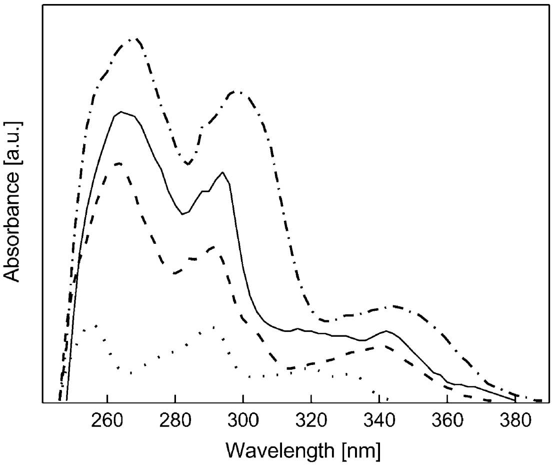


Fig. 4. UV absorption spectra of dilute chloroform solutions ($10^{-5}$ mol l$^{-1}$) of 9-ethylcarbazole (dotted line), **8** (dashed line), **9** (solid line) and **7** (dash dotted line).

amine-based big conjugated molecules is the Ullmann coupling reaction. Poly(3,9-carbazole) (**7**) was prepared from 3-iodo-9*H*-carbazole (**2**) with a copper catalyst in the presence of 18-crown-6 (Scheme 1) and purified by reprecipitation from chloroform solution into hexane followed by extraction of the solid residue with hot ethanol. The polymer **7** was identified by elemental analysis, IR and electronic absorption, as well as $^1$H NMR spectroscopy. The gel permeation chromatography (GPC) curve of the polymer **7** is shown in Fig. 3.

The GPC revealed number average molecular weight ($M_n$) of around 2360 with a molecular weight distribution of 2.15. The number average degree of polymerization for this value of molecular weight is ca. 14. Some lower individual oligomerhomologues are reflected in the GPC curve.

3-(9-Carbazolyl)-9-hexylcarbazole (**8**) and 3,6-di(9-carbazolyl)-9-alkylcarbazoles (**9** and **10**) were prepared as described in Scheme 1 by the Ullmann coupling reaction of 3-iodo-9-hexylcarbazole (**4**) and 3,6-diiodo-9-alkylcarbazoles (**5** and **6**), respectively, with an excess of 9*H*-carbazole. The starting compounds **4–6** were synthesized by a two-step reaction involving iodination of 9*H*-carbazole (**1**) and alkylation of iodocompounds (**2** and **3**) with 1-bromoalkanes. The compounds **8–10** were purified by column chromatography and identified by elemental analysis, mass spectrometry, IR absorption, electronic absorption, and $^1$H NMR spectroscopy.

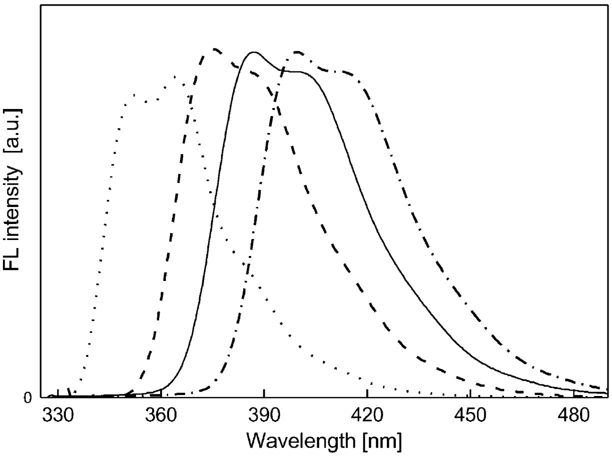


Fig. 5. Fluorescence emission (normalized) spectra of 9-ethylcarbazole (dotted line), dimer **8** (dashed line), trimer **9** (solid line) and polymer **7** (dash dotted line) in THF solutions ($10^{-5}$ mol l$^{-1}$). Exciting wavelength: 290 nm.

Table 1
Thermal characteristics of the compounds **7–10**

| Compound | $T_g$ (°C) | $T_{cr}$ (°C) | $T_m$ (° C) | $T_{ID}$[a] (°C) |
|---|---|---|---|---|
| **7** | 157 | – | –[b] | 321 |
| **8** | 35 | – | 146 | 305 |
| **9** | 119 | 111 | 200 | 367 |
| **10** | 134 | 118 | 218 | 375 |

[a] $T_{ID}$ is the temperature at which initial loss of mass (1%) was observed.
[b] Obtained as an amorphous substance.

The electronic absorption and fluorescence emission spectra of the polymer **7**, the dimer **8**, and the trimer **9** are shown in Figs. 4 and 5. For the comparison the corresponding spectra of 9-ethylcarbazole are given in these figures. All the compounds synthesized exhibit a broad absorption. The absorption maximums show a bathochromic shift with increasing size of the molecule. This shift is relatively small compared to the shift observed in conjugated polyenes and apparently converges towards an upper limit with increasing chain length like it was observed in model compounds of poly(phenylene sulfide) [13] and poly(phenylenevinylene) [14].

Dilute solutions of both the polymer **7** and those of carbazole dimer and trimer compounds exhibit intensive fluorescence. The structure of the fluorescence bands is similar to that of other carbazole-containing compounds [15]. The different structure of fluorescence spectra as compared to that of absorption spectra can be apparently explained by the solvation effect as well as by conformational changes in the excited state. The fluorescence spectra of the compounds **8** and **9**, and polymer **7** are considerably shifted towards long wavelength region with respect of the spectrum of 9-ethylcarbazole. The extent of the shift increases with increasing size of the molecule. These results confirm that the **7–10** molecules are π-conjugated through the lone electron pair at the nitrogen atom and that π-electrons are delocalised over these molecules.

The behavior under heating of the polymer **7** and the low-molar-mass compounds was studied by DSC and thermogravimetric analysis under a nitrogen atmosphere. The values of glass transition temperatures ($T_g$), melting points ($T_m$), crystallization temperatures ($T_{cr}$) and temperatures at which initial loss (1%) of mass was observed ($T_{ID}$) are summarized in Table 1. All these materials demonstrate high thermal stability. The mass loss occurs at the temperatures

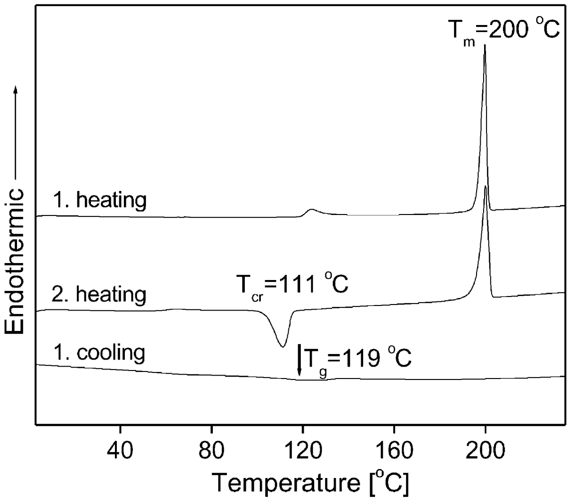


Fig. 6. DSC curves of **9**. Heating rate: 10 °C min$^{-1}$.

higher than 300 °C, as confirmed by TGA with a heating rate of 10 °C min$^{-1}$.

The polymer **7** was obtained as an amorphous substance. When the sample of the polymer was heated the glass transition was observed at 157 °C and no peaks due to crystallization and melting appeared. The dimer **8** shows melting at 146 °C only in first heating run and form stable glass upon cooling from the melt. The crystalline trimers **9** and **10** show melting in the first heating run and form glasses upon cooling. When the amorphous samples were heated again, exothermic peaks due to crystallization were observed at 111 °C for **9** and 118 for **10** to give the same crystals as obtained by recrystallization from solution. As an example, the DSC curves of **9** are shown in Fig. 6. Despite of the inclination towards crystallization of the glasses of the trimer compounds when they are heated above $T_g$ the amorphous films of these compounds can be prepared by casting from solutions. Such films were used for the recording of photoemission spectra and for the TOF experiments.

The values ionization potentials ($I_p$) of the polymer **7** and the compounds **8**–**10** measured by the electron photoemission method are shown in Table 2. It is evident that the $I_p$ of the compounds **7**–**10** decreases with increasing size of the molecule. The polymer **7** and the trimers **9**–**10** can be interesting from the practical point of view. The materials with $I_p$ of 4.8–5.8 can be used as hole transport materials in the multilayer electroluminescent devices using 8-hydroxyquinoline aluminum ($Alq_3$) (5.8 eV) as emitting and electron transporting layer [16]. The injection barrier of holes from electrode into hole transport layer of **9**–**10** can be decreased by using copper phthalocyanine layer (5.3 eV) [17].

Table 2
Ionization potentials of the materials **7**–**10**

| Material | $I_p$ (eV) |
|---|---|
| **7** | 5.45 |
| **8** | 5.97 |
| **9** | 5.80 |
| **10** | 5.81 |

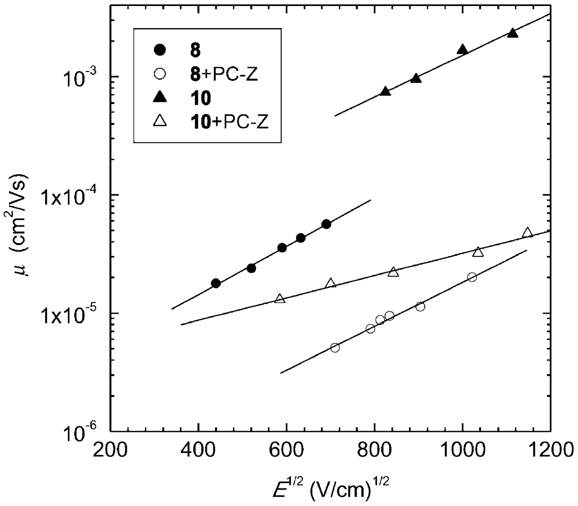


Fig. 7. The electric field dependencies of the hole drift mobility in the amorphous films of compounds **8** and **10** and their 50% solid solutions in PC-Z.

The electric field dependencies of hole mobilities for compounds **8** and **10** and their 50% solid solutions in PK-Z are shown in Fig. 7. The hole drift mobility of $7 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ was observed for the trimer **10** at an electric field of $6.4 \times 10^5$ V cm$^{-1}$ at 293 K. At higher electric fields the hole mobilities in this compound exceed $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$. These values are among the highest for carbazole based compounds and comparable those of *N*,*N′*-diphenyl-*N*,*N′*-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD) which is known as one of the most effective organic hole transport material [18]. Compound **8** the molecules of which are smaller shows lower hole mobilities. The mobility of ca. $5 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ was observed in the amorphous film of this compound at an electric field $3.6 \times 10^5$ V cm$^{-1}$. The hole drift mobilities of **8** and **10** dispersed in PC (50 wt%) are by one order of magnitude lower than those of the neat amorphous films of **8** and **10**. Unfortunately the quality of the films of the polymer **7** was not sufficient for the TOF measurements.

## Acknowledgements

Financial support of this research by the Lithuanian Science and Studies Foundation is gratefully acknowledged. S.G. is indebted to Prof. H.-W. Schmidt in whose laboratories at the Department of Macromolecular Chemistry I (University of Bayreuth, Germany) the characterization of the compounds was carried out.

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