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Synthesis and properties of the polymers containing 3,3′-dicarbazyl units in the main chain and their model compounds

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Abstract

The polymers containing 3,3′-dicarbazyl moieties in the main chain have been synthesized by dehalogenative condensation of 1,6-di(3-iodo-9-carbazolyl)alkanes. The number-average molecular weights of the polymers synthesized were in the range of 1900–6000 with a molecular weight distribution of 2.2–2.5. The model compounds of the polymers 9,9′-dialkyl-3,3′-bicarbazoles have been synthesized by stepwise reactions. All these compounds have been found to form glasses with glass transition temperatures in the range of 71–169 °C as characterised by differential scanning calorimetry. The electron photoemission spectra of the compounds have been recorded and the ionisation potentials of 5.46–5.57 eV have been established. Hole drift mobilities of 3.6×10^{-6} and 2.8×10^{-5} cm^2/V s were observed in the amorphous films of the polymer and of the dimer model compound, respectively, by the time of flight technique at an applied field of 6.4×10^5 V/cm. © 2002 Published by Elsevier Science Ltd.

Keywords: Dicarbazyl; Polymer; Model compound

1. Introduction

Hole transporting organic amorphous materials capable to form films 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 can be divided into two categories. One is low-molar mass molecules; the devices are generally fabricated by vacuum-deposition. The other is polymers; the devices are fabricated by the casting or spin-coating methods.

Carbazole-containing polymers have been extensively studied for the different applications due to their good hole transport and luminescent properties [7]. Most of these polymers contain carbazolyl groups as pendants. Much less presentations are reported on the polymers containing carbazole moieties in the main chain [8–11]. Here, we report on the synthesis and properties of polymers containing 3,3′-dicarbazyl units in the main chain and their glass-forming model compounds. One such model compound has already been reported. 9,9′-Diethyl-3,3′-dicarbazyl has appeared to be fairly effective charge transport material for the application in light-emitting diodes [12]. Similar polymers have been very recently described [13] when the present paper was already submitted. Hole drift mobilities in these compounds have not been measured yet. In this paper we concentrate our attention on the synthesis and properties of such hole transporting compounds, the amorphous films of which can be prepared by casting from solutions. This technique of the preparation of films is usually used in electrophotography.

2. Experimental

2.1. Instrumentation

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker AC 250 (250 MHz) apparatus.

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All data are given as chemical shifts δ (ppm) downfield from $(CH_3)_4Si$.

Mass spectra (MS) were obtained on a Finnigan MAT 8500 (70 eV) with a MAT 112 S Varian. Differential scanning calorimetry (DSC) measurements were carried out using a Perkin Elmer DSC-7 calorimeter. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TAS-409.

The molecular weight was determined by a Waters gel permeation chromatography system including a Waters 410 differential refractometer using THF as eluent and polystyrene standards.

The samples for the ionisation potential measurement were prepared as described previously [14]. The ionisation potentials of the layers of the compounds synthesized were measured by the electron photoemission method in air. The measurement method was, in principle, similar to that described by Miyamoto et al. [15].

The hole drift mobility was measured by time of flight technique in electrophotographic regime [16]. The samples for the charge carrier mobility measurements were prepared by casting the solutions of the compounds and their mixtures in weight proportion 1:1 with polycarbonate Z (PC-Z) on glass plates with conductive SnO_2 layer or polyester films with Al layer. The thickness of the transporting layer varied in the range of 3–5 μm.

2.2. Materials

9H-Carbazole (**1**), *zinc powder* and *triphenylphosphine* were purchased from Aldrich and used as received.

9-Alkylcarbazoles (**2** and **3**) were prepared by alkylation of 9*H*-carbazole (**1**) with bromoalkanes in the presence of a phase transfer catalyst [11].

9,9′-Dialkyl-3,3′-dicarbazyls (**4** and **5**) were obtained by chemical oxidation of the corresponding 9-alkylcarbazoles (**2** and **3**) in the presence of $FeCl_3$ [17]. To a solution of the corresponding 9-alkylcarbazole in chloroform anhydrous $FeCl_3$ was added. The mixture was stirred at ambient temperature for 30 min and poured into methyl alcohol. The precipitated material was recovered by filtration and the crude product was purified by column chromatography.

9,9′-Diethyl-3,3′dicarbazyl (**4**). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 8.40 (s, 2H (H_4)), 8.18 (d, 2H (H_5)), 7.83 (d, 2H (H_2)), 7.52–7.21 (m, 8H (H_1, H_6, H_7 and H_8)), 4.46–4.36 (m, 4H ($-N-CH_2-$)), 1.48 (t, 6H ($-CH_3$)). MS (70 eV): $m/z = 388$ (M^+), 194.

9,9′-Dibutyl-3,3′-dicarbazyl (**5**). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 8.31 (d, 2H (H_4), $^4J = 1.07$ Hz), 8.09 (d, 2H (H_5), $^3J = 7.69$ Hz), 7.72 (dd, 2H (H_2), $^4J = 1.70$ Hz, $^3J = 8.48$ Hz), 7.41–7.10 (m, 8H (H_1, H_6, H_7 and H_8)), 4.21 (t, 4H ($-N-CH_2-$), $^3J = 7.06$ Hz), 1.84–1.72 (m, 4H ($-N-CH_2-CH_2-$)), 1.39–1.24 (m, 4H ($-CH_2-CH_3$)), 0.85 (t, 6H ($-CH_3$), $^3J = 7.26$ Hz). ^{13}C NMR (250 MHz, $CDCl_3$) δ (ppm): 141.37 and 139.99 (C_{10} and C_{13}), 133.81 (C_3), 126.09, 125.98, 120.90 and 119.18 (C_2, C_4, C_6 and C_7), 123.85 and 123.51 (C_{11} and C_{12}), 119.38 (C_5), 109.33 and 109.23 (C_1 and C_8), 43.38 ($-N-CH_2-$), 31.65 ($-N-CH_2-CH_2-$), 21.06 ($-N-CH_2-CH_2-CH_2-$), 14.38 ($-CH_3$). MS: $m/z = 444$ (M^+), 414.

3-Iodo-9H-carbazole (**6**) was obtained by a modified procedure of Tucker [18].

1,6-Di(3-iodo-9-carbazolyl)hexane (**7**). Four grams (13.65 mmol) of 3-iodo-9*H*-carbazole, 1.33 g (5.46 mmol) of 1,6-dibromohexane and 0.139 g (0.41 mmol) of tetrabutylammonium hydrogensulfate were refluxed in 20 ml of acetone and 0.765 g (13.36 mmol) of potassium hydroxide was added. After stirring for 4 h acetone was removed, and the reaction product was dissolved in chloroform. The suspension obtained was filtered, and the solution was washed with water and dried over magnesium sulfate. The solvent was removed, and the crude product was purified by two crystallization from acetone to provide 1.65 g (45%) of white crystals. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 8.27 (d, 2H (H_4), $^4J = 1.56$ Hz), 7.90 (d, 2H (H_5), $^3J = 7.74$ Hz), 7.53 (dd, 2H (H_2), $^4J = 1.57$ Hz, $^3J = 8.56$ Hz), 7.37–6.91 (m, 8H (H_1, H_6, H_7 and H_8)), 4.03 (t, 4H ($-N-CH_2-$), $^3J = 6.91$ Hz), 1.66–1.61 (m, 4H ($-N-CH_2-CH_2-$)), 1.20–1.10 (m, 4H ($-N-CH_2-CH_2-CH_2-$)). ^{13}C NMR (250 MHz, $CDCl_3$) δ (ppm): 140.67 and 139.85 (C_{10} and C_{13}), 134.18 (C_2), 129.59 (C_4), 126.76 (C_7), 125.70 and 121.92 (C_{11} and C_{12}), 120.95 (C_5), 119.76 (C_6), 111.04 and 109.18 (C_1 and C_8), 81.65 (C_3), 43.20 ($-N-CH_2-$), 29.09 ($-N-CH_2-CH_2-$), 27.37 ($-N-CH_2-CH_2-CH_2-$).

1,6-Di(3-iodo-9-carbazolyl) dodecane (**8**) was synthesized by the similar procedure as **7**. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 8.29 (d, 2H (H_4), $^4J = 1.62$ Hz), 7.92 (d, 2H (H_5), $^3J = 7.77$ Hz), 7.58 (dd, 2H (H_2), $^4J = 1.65$ Hz, $^3J = 8.57$ Hz), 7.41–7.04 (m, 8H (H_1, H_6, H_7 and H_8)), 4.12 (t, 4H ($-N-CH_2-$), $^3J = 7.12$ Hz), 1.77–1.66 (m, 4H ($-N-CH_2-CH_2-$)), 1.18–1.08 (m, 8H ($-N-CH_2-CH_2-(CH_2)_4-$)). ^{13}C NMR (250 MHz, $CDCl_3$) δ (ppm): 140.78 and 139.96 (C_{10} and C_{13}), 134.14 (C_2), 129.57 (C_4), 126.70 (C_7), 125.74 and 121.95 (C_{11} and C_{12}), 120.91 (C_5), 119.66 (C_6), 111.15 and 109.27 (C_1 and C_8), 81.54 (C_3), 43.54 ($-N-CH_2-$), 29.83 ($-N-CH_2-CH_2-$), 29.79 ($-N-CH_2-CH_2-CH_2-$), 29.74 ($-N-CH_2-CH_2-CH_2-CH_2-$), 29.28 ($-N-CH_2-CH_2-CH_2-CH_2-CH_2-$), 27,64 ($-N-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$).

The catalytic precursor *NiBr₂/bipy* (bipy = 2,2′-bipyridine) was prepared as follows. To a solution of 5.5 g (0.252 mol) of nickel(II) bromide hydrate in 50 ml of ethyl alcohol 3.15 g (0.02 mol) of 2,2′-bipyridine in 25 ml of ethyl alcohol were added dropwise at 60 °C. The mixture was stirred for 12 h and the precipitated catalyst was filtered, washed with ethanol and dried under vacuum.

The polymer **9**. Activated zinc powder (0.76 g, 11.62 mmol), $NiBr_2$/bipy (0.0713 g, 0.191 mmol), triphenylphosphine (0.590 g, 2.25 mmol) and 1,6-di (3-iodo-9-carbazolyl) hexane (2.5 g, 3.744 mmol) were dissolved in 5.05 ml of dimethylacetamide (DMA) under an argon atmosphere. The solution was stirred at 95 °C for 4 h and into poured into 200 ml (5 wt%) of sulphuric acid. The precipitated polymer was filtered, washed with ether and methanol, and dried under vacuum. Yield: 1.0 g (65%) of white powder. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 8.37 (2H (H_4)), 8.12 (2H (H_5)), 7.67 (2H (H_2)), 7.40–7.20 (8H (H_1, H_6, H_7 and H_8)), 4.15 (4H ($-N-\mathit{CH}_2-$)), 1.75 (4H ($-N-CH_2-\mathit{CH}_2-$)), 1.30 (4H ($-N-CH_2-CH_2-\mathit{CH}_2-$)).

The polymer **10** was synthesized by the similar procedure as **9**. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 8.31 (2H (H_4)), 8.09 (2H (H_5)), 7.71 (2H (H_2)), 7.36–7.15 (8H (H_1, H_6, H_7 and H_8)), 4.19 (4H ($-N-\mathit{CH}_2-$)), 1.78 (4H ($-N-CH_2-\mathit{CH}_2-$)), 1.12 (8H ($-N-CH_2-CH_2-(\mathit{CH}_2)_4-$)).

3. Results and discussion

Polymers containing 3,3′-dicarbazyl in the main chain **9** and **10** were generally synthesized as described in Scheme 1 by dehalogenative condensation of 1,6-di(3-iodo-9-carbazolyl)hexane (**7**) and 1,12-di(3-iodo-9-carbazolyl)dodecane (**8**), respectively, which were prepared by alkylation of 3-iodo-9*H*-carbazole (**6**) with dibromoalkanes.

The model compounds of the polymers 9,9′-diethyl-3,3′-dicarbazyl (**4**) and 9,9′-dibutyl-3,3′-dicarbazyl (**5**) were synthesized as described in Scheme 1 by chemical oxidation of the corresponding 9-alkylcarbazoles (**2**, **3**), which were prepared by alkylation of 9H-carbazole (**1**), in the presence of $FeCl_3$. Both polymers and the models were soluble in chlorinated hydrocarbons, *N*,*N*-dimethylacetamide and tetrahydrofuran (THF) however the solubility of polymer **9** in THF was limited.

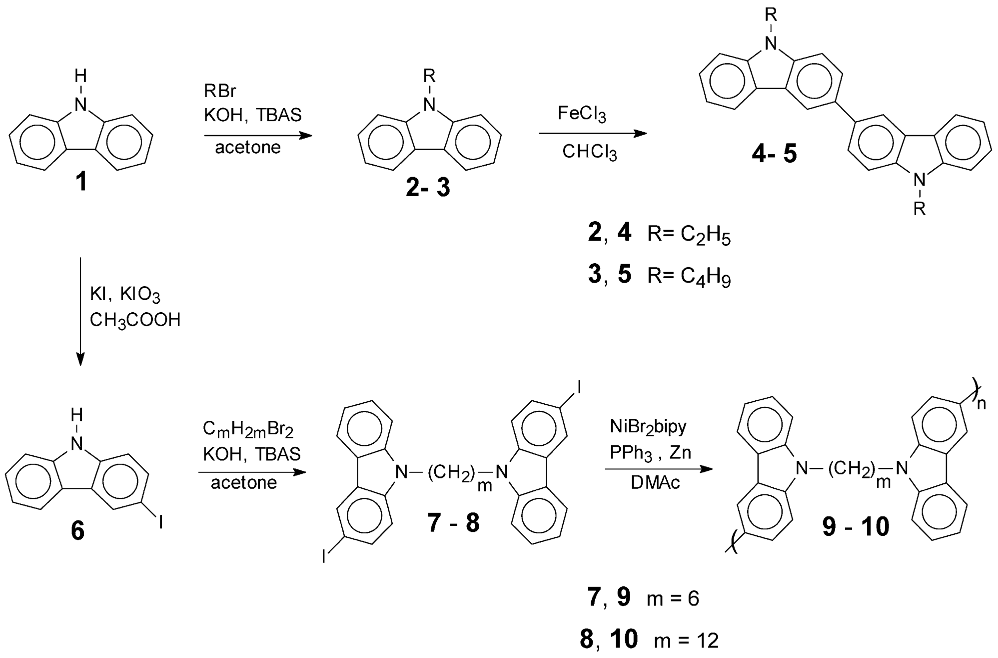
The molecular weight distribution curve of the polymer **10** is shown in Fig. 1. It is evident that bimodal molecular weight distribution is characteristic of this polymer. The GPC results indicated number average molecular weight (M_n) of around 6000 with a molecular weight distribution of 2.5. The number-average degree of polymerization for this value of the molecular weight is ca. 15. The soluble in THF fraction of polymer **9** has M_n of around 1900 with a molecular weight distribution of 2.2.

The thermal properties of the polymers **9**, **10** and the model compounds **4**, **5** were examined by DSC and TGA techniques under a nitrogen atmosphere.

The DSC thermograms of **4** are shown in Fig. 2. When the crystalline sample of **4**, prepared by recrystallization from acetone, was heated, the endothermic peak due to melting was observed at 193 °C. When the melt sample was cooled down at the cooling rate of 10 °C/min it formed glass. When the amorphous sample was heated again, the glass transition was observed at 79 °C and on further heating no peaks due to crystallisation and melting appeared. The crystalline sample of compound **5** also melts only on first heating at 118 °C and forms glass ($T_g = 71$ °C) upon cooling from the melt. The polymer **9** showed glass transition at 169 °C. The polymer **10** forms amorphous films, but the DSC apparatus used did not detect T_g.

All the materials **4**, **5**, **9** and **10** demonstrated a high thermal stability, up to 340 °C with a heating rate of 10 °C/min, as confirmed by TGA.

The amorphous films of the polymers and the model compounds for the measurements of ionisation potentials and for the time of flight measurements we prepared by casting from the solutions in chloroform. The morphological stability of the thin films (0.5–1 μm) of low molar mass compounds **4** and **5** was good enough for the recording of



Scheme 1.

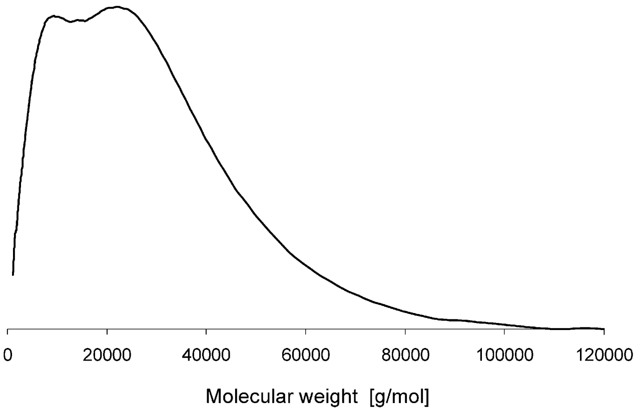


Fig. 1. Molecular weight distribution curve of the polymer **10**.

photoemission spectra. However the morphological stability of the thicker films of compound **4** was too low for the time of flight measurements and the solid solution of **4** in PC-Z were prepared.

The electron photoemission spectra of the polymers **9** and **10** and the dimer **4** are presented in Fig. 3. The ionisation potentials (I_p) of 5.46 eV for **4** and 5.55–5.57 eV for the polymers **9** and **10** have been observed. For poly(*N*-vinylcarbazole) (PVK) 5.8 eV ionization potential value was reported [19]. The similar value was found for oligoether with carbazolyl pendants poly[*N*-(2,3-epoxypropyl)carbazole] [20]. Holes would be injected easily from charge generation layer or conductive anode with I_p or work function close to these values. The ionisation potential values for charge generation materials, including those widely used in electrophotographic photoreceptors, such as as titanyl pthalocyanines [21,22], perylene pigments [23] and bisazo pigments [24] are in the range of 5.1–5.6 eV.

I_p of the reported compounds are higher than that of indium–tin oxide (4.8 eV) which is used as anode in electroluminescent devices [25]. However the injection barriers of holes from electrode into the layers of 3,3′-bicarbazoles are not very high and ranges from 0.66 to 0.77 eV. This observation show, that the polymers **9**, **10** and low molar mass compounds **4**, **5** can be used for hole transport layers in the multilayer electroluminescent devices.

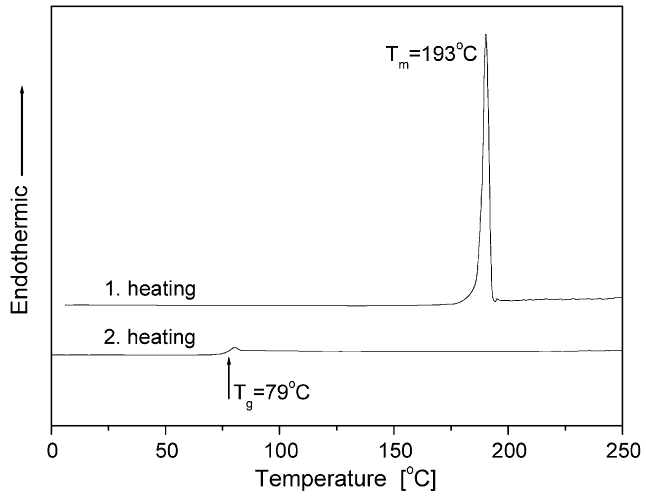


Fig. 2. DSC curves of **4**. Heating rate: 10 °C/min.

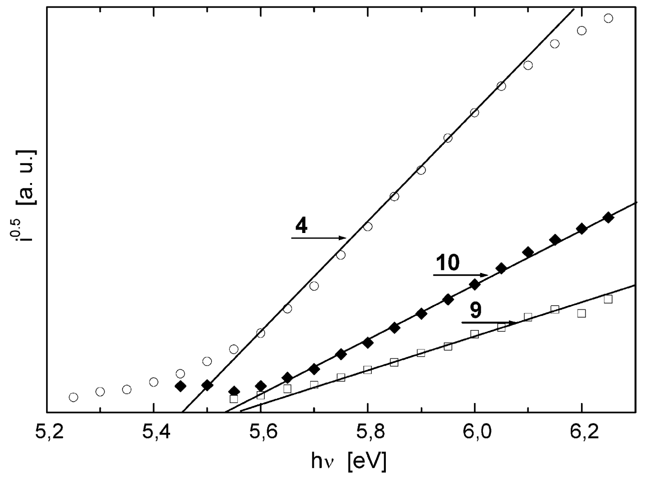


Fig. 3. The electron photoemission spectra of the compounds **4**, **9** and **10**.

The typical time of flight transients of the compound **5** are presented in Fig. 4. The small charge time of flight transient decreasing is of hyperbolic type in the investigated materials which indicates that transport of holes is dispersive [26].

The plots of hole drift mobilities versus electric field for the amorphous films of the polymer **9**, model compound **5** and the solid solution of **4** in PC-Z are shown in Fig. 5. For all the samples the increase in charge mobilities with the increase of electric field is observed. Such dependencies of charge mobilities on electrical field are characteristic of many organic photoconductors [27]. At an electric field of $6.4 \times 10^5\ \mathrm{V\ cm^{-1}}$ at 293 K hole drift mobility of $3.6 \times 10^{-6}\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$ was observed for polymer **9**. This value is comparable to hole mobilities in carbazolyl-containing poly(meth)acrylates and polysiloxanes but

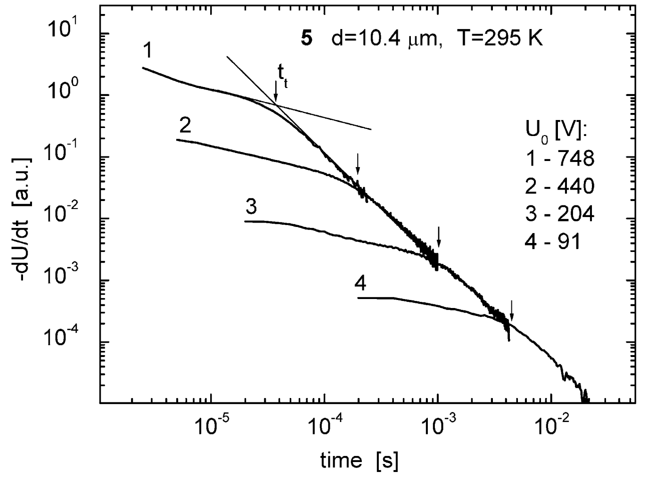


Fig. 4. The rates of the surface potential decrease d*U*/d*t* versus time curves for amorphous layer of **5** at various surface potentials U_0. Arrows mark the transit time (t_t).

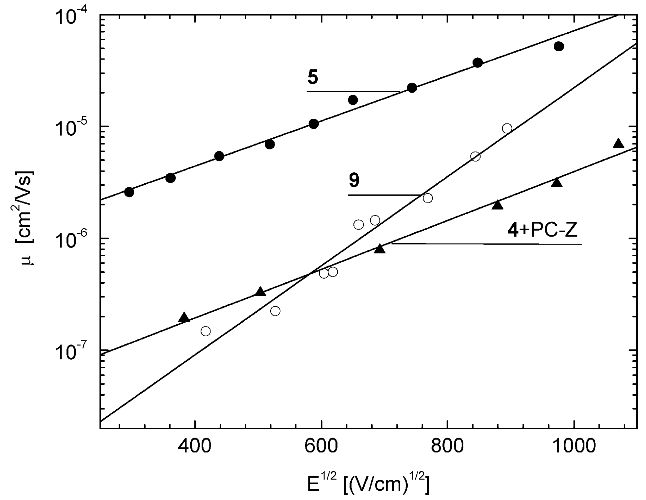


Fig. 5. The electric field dependencies of the hole drift mobilities for the amorphous layers of **5** and **9** and for the layer of **4** dispersed in PC-Z (the weight proportion is 1:1).

higher than that observed in PVK [7]. Amorphous film of **5** exhibited by about one order of magnitude higher hole drift mobilities than polymer **9** in almost all range of electric fields studied ($\mu = 2.8. \times 10^{-5}$ cm^2 V^{-1} s^{-1} at an electric field of 6.4×10^5 V cm^{-1}). This is apparently due to the higher purity of the low molar mass compound, since the chromophore concentration in compound **5** is even slightly lower than that in polymer **9**. The model compounds **4** and **5** were purified by column chromatography which is not possible in the case of the polymer. The charge mobilities observed in the film of the solid solution of **4** in PC-Z are by more than one order of magnitude lower than those observed in the amorphous film of pure **5**. Based on the studies of drift mobility dependence on the concentration of charge transport compounds in molecularly doped polymers [28] one can expect that the drift mobility for pure **4** would be similar to that observed in **5**.

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