

Phenothiazinyl-containing aromatic amines as novel amorphous molecular materials for optoelectronics

G. Blazys^a, S. Grigalevicius^a, J.V. Grazulevicius^{a,*}, V. Gaidelis^b,
V. Jankauskas^b, V. Kampars^c

^a Department of Organic Technology, Kaunas University of Technology, Radvilenu Plentas 19, LT 50254 Kaunas, Lithuania

^b Department of Solid State Electronics, Vilnius University, Sauletekio Aleja 9, LT 2040 Vilnius, Lithuania

^c Faculty of Material Science and Applied Chemistry, Riga Technical University, Azenes 14/24, Riga LV 1048, Latvia

Received 4 November 2004

Available online 25 March 2005

Abstract

Novel aromatic amines have been synthesized by the modified Ullmann reaction of 10H-phenothiazine and di(4-iodophenyl)ethylamine or 3,6-diiodo-9-hexylcarbazole. The full characterization of their structure is presented. The compounds possess high thermal stability with glass transition temperatures of 87–103 °C and onset decomposition temperatures of 346–377 °C. Room temperature hole drift mobilities in amorphous films of the materials were, respectively, 1.2×10^{-6} and 2×10^{-5} cm²/V s at an applied electric field of 3.6×10^5 V/cm. The electron photoemission spectra of the molecular glasses have been recorded and the ionisation potentials of 5.5–5.54 eV have been established. The values obtained have been compared with the values of ionisation potential of photoconductive oligomers containing unsubstituted carbazolyl or diphenylamino groups.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Amorphous material; π -Electron system; Hole drift mobility; Ionisation potential

1. Introduction

Low molecular weight organic compounds that readily form stable glasses are called molecular glasses or amorphous molecular materials. They show excellent processability, transparency, isotropic and homogeneous properties and receive growing attention both in terms of academic interest and technological applications. Aromatic amine based molecular glasses belong to the classes of light emitting and charge-transporting materials and are known for various applications such as displays, photovoltaic cells, photorefractive materials and organic photoreceptors [1–3].

For the purpose of developing electronically active molecular glasses, we have been studying the synthesis, properties and applications of novel molecules based on aromatic amines. We have reported previously on novel

families of hole-transporting amorphous materials based on carbazole and diphenylamine moieties [4] and 6,6'-di(*N*-diphenylamino)-9,9'-dialkyl-3,3'-bicarbazoles [5]. Hole mobilities in the amorphous films of the compounds approached 10^{-6} cm²/V s at an applied electric field of 3.6×10^5 V/cm. In the present study we report on the synthesis and properties of new glass-forming hole-transporting molecules in which phenothiazine species are attached to diphenylalkylamine or *N*-alkylcarbazole core.

2. Experimental

2.1. Instrumentation

¹H NMR spectra were recorded using a Bruker AC 250 (250 MHz) apparatus. Mass spectra were obtained on a Varian MAT-312 spectrometer. UV spectra were measured with a Specord M-40 spectrometer. Fluorescence spectra were

* Corresponding author. Tel.: +370 37 456 525; fax: +370 37 456 525.
E-mail address: Juozas.Grazulevicius@ktu.lt (J.V. Grazulevicius).

recorded with a Perkin-Elmer LS-5 spectrometer. Differential scanning calorimetry measurements were carried out using a Perkin-Elmer DSC-7 calorimeter. Thermogravimetric analysis was performed on a Perkin-Elmer Thermal Analysis System 409. The measurements were recorded in a nitrogen atmosphere at a heating rate of 10 °C/min.

The ionisation potentials of the layers of the compounds synthesized were measured by the electron photoemission method in air, which was described earlier [6]. The samples for the ionisation potential measurement were prepared as described previously [7].

Hole drift mobility was measured by the time of flight technique in electrophotographic regime [8]. The samples for the charge carrier mobility measurements were prepared by casting the solutions of the compounds and their molecular mixtures in weight proportion 1:1 with bisphenol Z polycarbonate (PC-Z) on glass plates with conductive SnO₂ layer or polyester films with Al layer. The thickness of the charge-transporting layer varied in the range of 3–5 μm.

2.2. Materials

9H-carbazole (**1**), diphenylamine (**5**), 10H-phenothiazine, potassium carbonate, 18-crown-6 and 1,2-dichlorobenzene were purchased from Aldrich and used as received.

3,6-Diiodo-9H-carbazole (**2**) and di(4-iodophenyl)amine (**6**) were obtained by a modified procedure of Tucker [9].

3,6-Diiodo-9-hexylcarbazole (**3**) was prepared by alkylation of 3,6-diiodo-9H-carbazole (**2**) in the presence of a phase transfer catalyst [10].

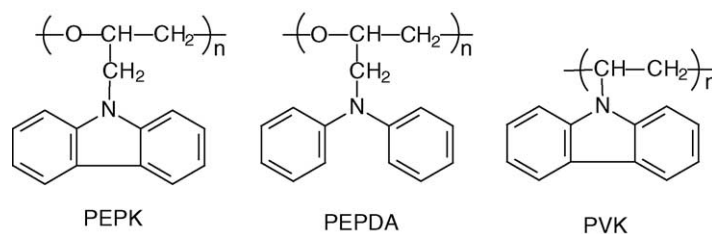
Di(4-iodophenyl)ethylamine (**7**) was prepared by alkylation of di(4-iodophenyl)amine (**6**) in the presence of a phase transfer catalyst [11]. 1.78 g (4.22 mmol) of di(4-iodophenyl)amine (**6**), 1 g (6.5 mmol) of ethyl iodide and 0.1 g (0.3 mmol) of tetrabutylammonium hydrogen sulfate (TBAS) were dissolved in 20 ml of acetone in 100 ml round bottom flask equipped with a magnetic stirrer and a reflux condenser. The mixture was heated to reflux and 0.4 g (7 mmol) of powdered potassium hydroxide was added. After refluxing for 8 h acetone was removed and the reaction product was dissolved in 60 ml of diethyl ether. The suspension obtained was filtered and solution was washed with water. After removal of the solvent the product was purified by two crystallisations from a methanol to yield 1.2 g (63%) of brownish crystals. ¹H NMR (CDCl₃): δ = 7.51(d, *J* = 8.85 Hz, 4H), 6.73(d,

J = 8.85 Hz, 4H), 3.74–3.65(m, 2H), 1.17(t, *J* = 7.05 Hz, 3H). IR (KBr): ν = 3059, 3034, 2854, 1587, 1486, 1311, 1274, 1226, 1175, 750 cm⁻¹. MS: *m/z* = 449(*M*⁺), 433, 307, 166.

3,6-Di(10-phenothiazinyl)-9-hexylcarbazole (**4**), 1.75 g (8.8 mmol) of 10H-phenothiazine, 0.81 g (12.8 mmol) of copper powder, 3.54 g (25.6 mmol) of potassium carbonate and 0.17 g (0.64 mmol) of 18-crown-6 in 10 ml of 1,2-dichlorobenzene were heated to reflux. 1.6 g (3.2 mmol) of 3,6-diiodo-9-hexylcarbazole (**3**) in 5 ml of 1,2-dichlorobenzene was added slowly and the mixture was refluxed for 46 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 silicagel column chromatography with an eluent mixture of hexane and chloroform in a volume ratio of 6:1. Yield: 1.2 g (56%). Recrystallisation from acetone yielded 0.99 g of greenish crystals, mp: 263 °C. ¹H NMR (CDCl₃): δ = 8.17–8.03 (m, 2H), 7.64–7.57 (m, 2H), 7.55–7.43 (m, 2H), 7.41–7.32 (m, 4H), 7.05–6.12 (m, 12H), 4.44(t, *J* = 7.4 Hz, 2H), 2.09–1.97 (m, 2H), 1.64–1.37 (m, 6H), 0.94 (t, *J* = 6.95 Hz, 3H). IR (KBr): ν = 3067, 2929, 2854, 1591, 1567, 1466, 1314, 1289, 813, 743, 684 cm⁻¹. MS: *m/z* = 645 (*M*⁺), 574, 560, 376, 322, 198. Elemental analysis for C₄₂H₃₅N₃S₂: % Calcd. C, 78.1; H, 5.46; N, 6.51; % found C, 78.31; H, 5.26; N, 6.59.

Di[4-(10-phenothiazinyl)phenyl]ethylamine (**8**) was prepared from 0.8 g (4 mmol) of 10H-phenothiazine, 0.37 g (5.8 mmol) of copper powder, 1.6 g (11.6 mmol) of potassium carbonate and 0.08 g (0.29 mmol) of 18-crown-6 in the same way as 3,6-di(10-phenothiazinyl)-9-hexylcarbazole, using 0.65 g (1.45 mmol) of di(4-iodophenyl)ethylamine (**7**) as diiodocompound and purified by silicagel column chromatography with an eluent mixture of cyclohexane and ethylacetate in a volume ratio of 22:1. Yield: 0.63 g (74%), mp: 217 °C. ¹H NMR (CDCl₃): δ = 7.36–7.28 (m, 8H), 7.03 (d, *J* = 7.4 Hz, 4H), 6.92–6.77 (m, 8H), 6.32 (d, *J* = 8.3 Hz, 4H), 3.92 (q, *J* = 6.93 Hz, 2H), 1.36 (t, *J* = 6.93 Hz, 3H). IR (KBr): ν = 3052, 2932, 2865, 1469, 1314, 1293, 814 cm⁻¹. MS: *m/z* = 591 (*M*⁺), 548, 393, 295, 198. Elemental analysis for C₃₈H₂₉N₃S₂: % Calcd. C, 77.13; H, 4.94; N, 7.1; % found C, 77.41; H, 4.86; N 7.39.

Poly[9-(2,3-epoxypropyl)carbazole] (PEPK) was received from Biolar (Latvia) and used after purification by column chromatography [12]. Poly[*N*-(2,3-epoxypropyl)diphenylamine] (PEPDA) was prepared by



Scheme 1.

ionic polymerization of the corresponding epoxy monomer [13]. Polyvinylcarbazole (PVK) was used as received from BASF. The structures of PEPK, PEPDA and PVK are given in Scheme 1.

3. Results and discussion

3,6-Di(10-phenothiazinyl)-9-hexylcarbazole (**4**) and di[4-(10-phenothiazinyl)phenyl]ethylamine (**8**) were synthesised as shown in Scheme 2 by the modified Ullmann coupling reaction [14] of 3,6-diiodo-9-hexylcarbazole (**3**) and di(4-iodophenyl)ethylamine (**7**), respectively, with an excess of secondary amine 10H-phenothiazine. The key starting materials **3** and **7** were synthesised by two step synthetic routes involving iodination of 9H-carbazole (**1**) and diphenylamine (**5**), respectively, followed by an alkylation of diiodocompounds **2** and **6**. All these materials were identified by mass spectrometry, IR absorption, electronic absorption spectroscopy, elemental analysis and ^1H NMR spectroscopy.

Thermal properties of all the materials were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under a nitrogen atmosphere. Compounds **4** and **8** demonstrated high thermal stability. The temperature at which initial loss of mass (1%) was observed is 346°C for **4** and 377°C for **8** with a heating rate of $10^\circ\text{C}/\text{min}$, as confirmed by TGA. Compounds **4** and **8** were found to form glasses when the melt samples were cooled either rapidly with liquid nitrogen or slowly at room conditions. The amorphous films of these materials can also be prepared by casting or spin coating from the solutions.

The DSC thermograms of **8** are shown in Fig. 1. When the crystalline sample of **8** was heated, the endothermic peak due to melting was observed at 217°C . When the melt sample was cooled down, it formed glass. When the amorphous sample was heated again, the glass-transition phenomenon

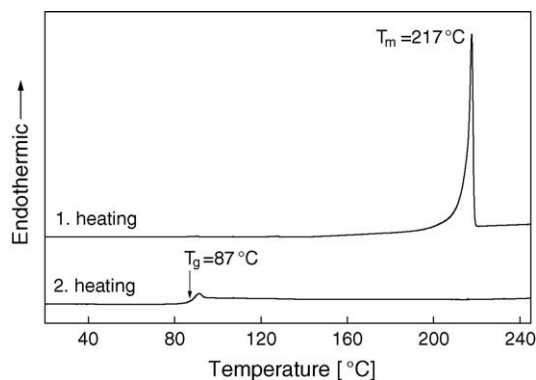


Fig. 1. DSC curves of compound **8**. Heating rate: $10^\circ\text{C}/\text{min}$.

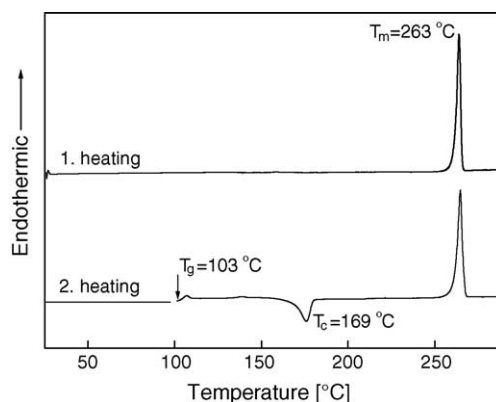
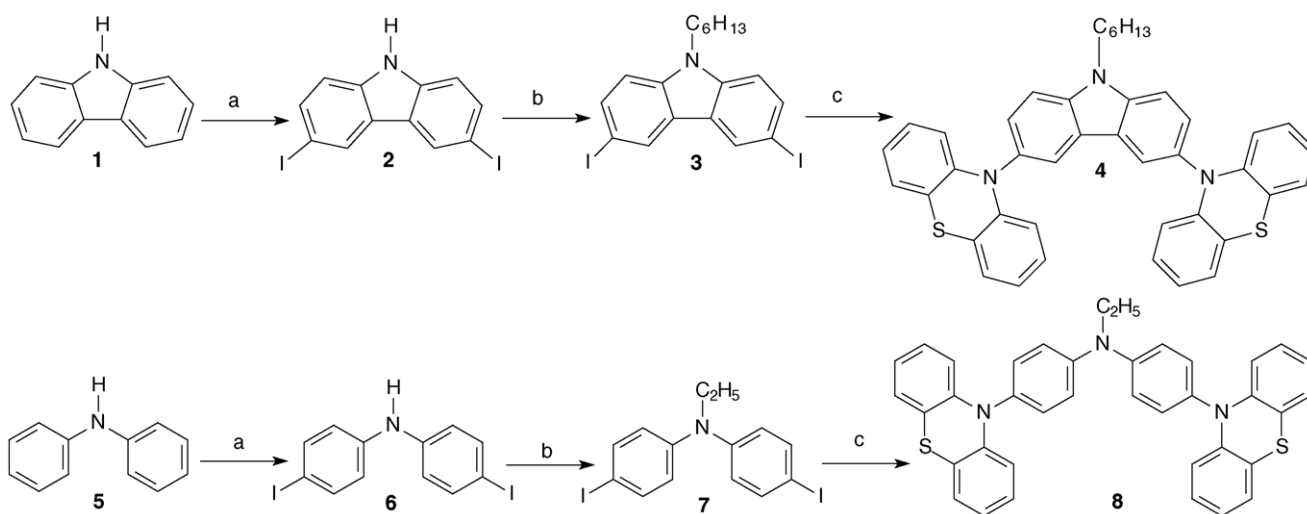


Fig. 2. DSC curves of compound **4**. Heating rate: $10^\circ\text{C}/\text{min}$.

was observed at 87°C and on further heating no peaks due to crystallisation and melting appeared. The same DSC curves were reproduced repeatedly.

Fig. 2 shows the DSC curves of compound **4**. The crystalline sample of **4** obtained by recrystallisation from acetone melted at 264°C on first heating and formed glass upon



Scheme 2. (a) KI, KIO_3 , CH_3COOH ; (b) KOH, TBAS, acetone, $\text{C}_6\text{H}_{13}\text{Br}$ for **3** and $\text{C}_2\text{H}_5\text{I}$ for **7**; (c) 10H-phenothiazine, Cu, K_2CO_3 , 18-crown-6, 1,2-dichlorobenzene.

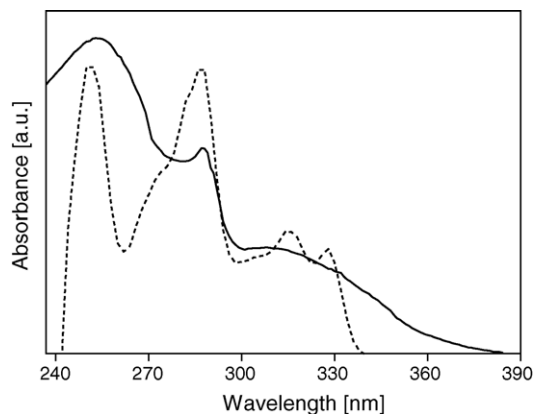


Fig. 3. UV absorption spectra of dilute solutions compound **4** (solid line) and 9-ethylcarbazole (dotted line) in chloroform. Concentration: 10^{-5} mol/l.

cooling. No crystallisation peak was observed in the cooling scan. When the glassy sample was heated again, the glass-transition was observed at 103°C , and on further heating an exothermic peak due to crystallisation at 169°C and an endothermic peak due to melting at 263°C were observed. The enthalpy changes for melting were 55.1 J/g (the first heating scan) and 54.6 J/g (the second heating scan) and -28.2 J/g for crystallisation (the second heating scan). Such a difference in the absolute values of the enthalpy changes of melting and crystallisation is often observed by DSC for low-molar-mass glass-forming compounds [15,16]. Such compounds often do not readily (fully) crystallise neither from the melt nor from the solution. It is evident that the replacement of diphenylamine fragment by a more bulky carbazole core enables considerably to increase T_g . The values of T_g of the compound synthesized could also be varied by changing the length of the alkyl chain at the nitrogen atom of the central core. The higher morphological stability of the glass of compound **8** can be apparently explained by its not planar molecular structure, which prevents easy packing and hence ready crystallisation.

The electronic absorption spectra of dilute solutions of compounds **4** and **8** in chloroform show bands with λ_{max} at 254, 290 and 308 nm for **4**, and at 258 and 316 nm for **8**. The dilute solutions of these compounds in THF exhibit intensive fluorescence with λ_{max} at 466 nm for **4** and at 460 nm for **8**. The comparison of the UV absorption spectrum of **4** with that of 9-ethylcarbazole (Fig. 3) or 10-methylphenothiazine (λ_{max} at 249 and 298 nm), and the spectrum of **8** with that of diphenylamine (λ_{max} at 296 nm) or 10-methylphenothiazine indicates that molecules of compounds **4** and **8** are π -conjugated through the lone electron pairs at the nitrogen atoms and that π -electrons are delocalised over these molecules. The bands of fluorescence spectra of **4** and **8** are also considerably shifted towards longer wavelength region relative to those of 9-ethylcarbazole, diphenylamine or 10-methylphenothiazine (Fig. 4). In the same manner with the red shift of UV absorption, which is interpreted as the extended conjugation, stabilizing the oxidized state of the

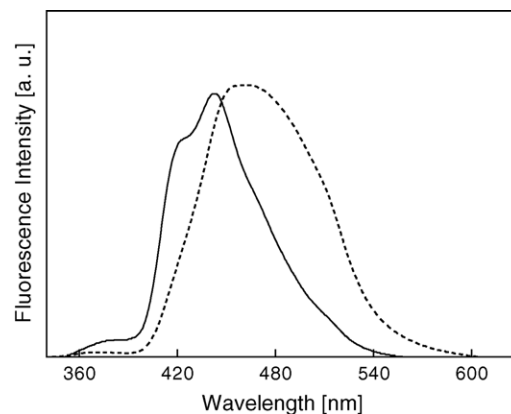


Fig. 4. Normalized fluorescence spectra of dilute solutions in THF of **4** (dotted line) and 10-methylphenothiazine (solid line) THF. Excitation wavelength: 290 nm.

compounds, they are expected to demonstrate lower values of ionisation potentials (I_p) than compounds containing unsubstituted carbazole rings or diphenylamino groups as chromophores.

The photoemission spectra of compounds **4** and **8** are presented in Fig. 5. For the comparison the spectra of the materials, containing unsubstituted carbazole rings as chromophores (PEPK and PVK) and unsubstituted diphenylamino groups (PEPDA) are shown.

The values of I_p in eV are 5.50 for **4**, 5.54 for **8**, 5.76 for PEPDA, 5.77 for PVK and 5.86 for PEPK. As it could be expected, the values of I_p of the newly synthesized compounds **4** and **8** are lower than those of the oligomers having unsubstituted electrophores. Comparison of the I_p values for **4** and PEPK shows that the attachment of two phenothiazine rings to the carbazole moiety leads to the decrease of I_p by 0.36 eV. On the other hand, it is evident from Fig. 3 that the edge of the electronic absorption spectra for compound **4** is at 375 nm, or 3.31 eV, while for the model compound 9-ethylcarbazole it is at 339 nm, or 3.66 eV. So the difference between the absorption edges of lone 9-ethylcarbazole and compound **4** is of 0.35 eV, i.e. of about the same value as the difference be-

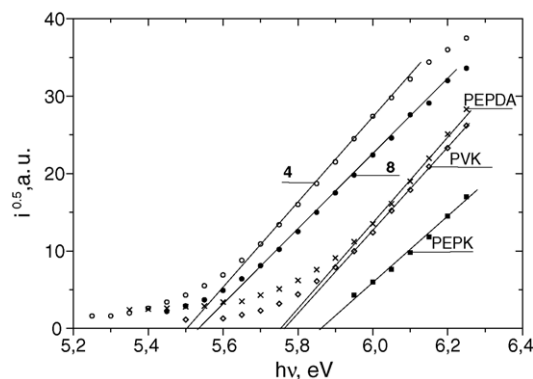


Fig. 5. The electron photoemission spectra in air of the compounds **4** and **8**. The spectra of PVK, PEPK and PEPDA are presented for the comparison.

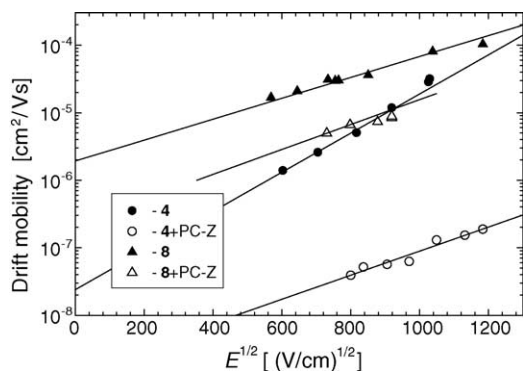


Fig. 6. Electric field dependencies of hole drift mobility in the layers of compounds **4** and **8** and their solid solutions in PC-Z.

tween the I_p values of PEPK and compound **4**. This can be interpreted as the shift of the position of the highest occupied orbital energy with the addition of the side phenothiazine rings.

Holes would be injected easily into layers of compounds **4** and **8** from the charge generation layer or conductive anode with I_p or work function close to 5.5 eV. The I_p values for charge generation materials, including those widely used in electrophotographic photoreceptors, such as titanil phthalocyanines [17,18], perylene pigments [19] and bisazo pigments [20] are in the range of 5.1–5.6 eV. The I_p values of the reported compounds are higher than that of indium–tin oxide (4.8 eV), which is widely used as an anode in electroluminescent devices [21]. However, the injection barriers of holes from electrode into the layers of **4** and **8** are not very high and could be reduced by using a thin layer of copper phthalocyanine [22]. This observation shows that the phenothiazine derivatives reported here can be used as hole-transporting layers in multilayer electroluminescent devices.

Time of flight measurements were used to characterise the magnitude of the hole drift mobility (μ_h) for the amorphous films of compounds **4** and **8**, and those doped in PC-Z (50 wt.%). The results are presented in Fig. 6. The room temperature μ_h shows a linear dependence on the square root of the electric field. This characteristic dependence is observed for the majority of non-crystalline organic semiconductors and can be attributed to the effects of disorder on charge transport [23].

The glass of **8** exhibits hole drift mobility of $2 \times 10^{-5} \text{ cm}^2/\text{V s}$ at an electric field of $3.6 \times 10^5 \text{ V/cm}$ at the room temperature. The value of μ_h for the glass of **4** is more than by one order of magnitude lower. The major properties of molecularly doped polymers directly depend on the amount of the transporting material doped in the polymeric binder. However it is evident from the data presented in Fig. 6 that the decrease in hole mobility observed comparing μ_h of pure amorphous compounds and molecularly doped polymers depend on the nature of the charge transporting compound. The value μ_h of **4** dispersed in PC-Z is by almost two orders of magnitude lower than that in pure amorphous films of **4**. Hole

drift mobility in the solid PC-Z solution of the same concentration of compound **8** is lower than that in pure amorphous film of **8** only by less than one order of magnitude. This may be so because the molecules of the compound **4** are more rigid as compared to the molecules of **8** (cf. the T_g values in Figs. 1 and 2). The more rigid molecules apparently cause higher energetic or positional disorder in the compositions with polymer host.

In conclusion, we have synthesized phenothiazinyl-containing aromatic amines which exhibit high thermal stability and form amorphous films with glass transition temperatures in the range of 87–103 °C. The values of ionisation potential (5.5–5.54 eV) and the hole drift mobility studies show that these compounds could be used as hole-transport materials in electrophotographic photoreceptors and electroluminescent devices.

Acknowledgements

This research was conducted in the frame of the joint research programme of Latvia, Lithuania and Taiwan. Financial support from the National Science Council of Taiwan and from the Lithuanian Ministry of Education and Science is gratefully acknowledged. Dr. Jolita Ostrauskaite is thanked for the help in TG and DSC measurements.

References

- [1] P. Stroehriegl, J.V. Grazulevicius, *Adv. Mater.* 14 (2002) 1439.
- [2] Y. Shirota, *J. Mater. Chem.* 10 (2000) 1.
- [3] M. Thelakkat, *Macromol. Mater. Eng.* 287 (2002) 442.
- [4] S. Grigalevicius, V. Getautis, J.V. Grazulevicius, V. Gaidelis, V. Jankauskas, E. Montrimas, *Mater. Chem. Phys.* 72 (2001) 395.
- [5] A. Balionyte, E. Lideikis, S. Grigalevicius, E. Burbulis, J. Ostrauskaite, J.V. Grazulevicius, E. Montrimas, V. Jankauskas, *J. Photochem. Photobiol. A: Chem.* 162 (2004) 187.
- [6] S. Grigalevicius, G. Blazys, J. Ostrauskaite, J.V. Grazulevicius, V. Gaidelis, V. Jankauskas, E. Montrimas, *Synth. Met.* 128 (2002) 127.
- [7] S. Grigalevicius, J.V. Grazulevicius, V. Gaidelis, V. Jankauskas, *Polymer* 43 (2002) 2603.
- [8] J. Kalade, E. Montrimas, V. Jankauskas, *Proceedings ICPS'94: The Physics and Chemistry of Imaging Systems*, Rochester, 1994, pp. 747–752.
- [9] S.H. Tucker, *J. Chem. Soc.* 1 (1926) 548.
- [10] J.M. Rodriguez-Parada, Percec K.F K., *Macromolecules* 19 (1986) 55.
- [11] C. Beginn, P. Stroehriegl, J. Simmerer, J.V. Grazulevicius, D. Haarer, *Macromol. Chem. Phys.* 195 (1994) 2353.
- [12] J.V. Grazulevicius, R. Kavaliunas, A. Undzenas, V.G. Uss, N. Kreivieniene, *Zh. Nauch. Prikl. Fotogr. Kinematogr.* 32 (1987) 22 (in Russian).
- [13] J. Adamonytė, V. Gaidelis, A. Girdzius, A. Undzenas, *Zh. Nauch. Prikl. Fotogr. Kinematogr.* 23 (1978) 59 (in Russian).
- [14] S. Gauthier, J.M.J. Frechet, *Synthesis* 1 (1987) 383.
- [15] D. Katsis, Y.H. Geng, J.J. Ou, S.W. Culligan, A. Trajkowska, S.H. Chen, L.J. Rothberg, *Chem. Mater.* 14 (2002) 1332.
- [16] Y. Geng, D. Katsis, S.W. Culligan, J.J. Ou, S.H. Chen, L.J. Rothberg, *Chem. Mater.* 14 (2002) 463.

- [17] Y. Oda, T. Homma, Y. Fujimaki, *Electrophotography* 29 (1990) 250.
- [18] Y. Chigono, T. Kitamura, *Electrophotography* 32 (1993) 7.
- [19] T. Nakazawa, A. Kawahara, Y. Mizuta, E. Miyamoto, *Electrophotography* 33 (1994) 127.
- [20] D. Aoki, M. Kashiwabara, M. Okabe, S. Hikosaka, E. Inoe, *J. Imaging Sci. Technol.* 44 (2000) 179.
- [21] X.T. Tao, Y.D. Zhang, T. Wada, H. Sasabe, H. Suzuki, T. Watanabe, S. Miyata, *Adv. Mater.* 10 (1998) 226.
- [22] Q. Wu, Y. Tao, J.A. Lavigne, M. D'Iorio, S. Wang, *Chem. Mater.* 13 (2001) 71.
- [23] P.M. Borsenberger, D.S. Weiss, *Photoreceptors for Imaging Systems*, Marcel Dekker, New York, 1993.