*Materials Science-Poland*, *Vol. 27*, *No. 1*, *2009*

# Methacryloyl functionalized hydrazones as hole-transporting materials for electrophotography

R. BUDRECKIENE[1*] V. ANDRULEVICIUTE[1], G. BUIKA[1],
J.V. GRAZULEVICIUS[1**], V. JANKAUSKAS[2], V. GRAZULEVICIENE[3]

[1]Department of Organic Technology, Kaunas University of Technology,
Radvilėnų pl. 19, LT-50254 Kaunas, Lithuania

[2]Department of Solid State Electronics, Vilnius University,
Sauletekio al. 9, LT-10222, Vilnius, Lithuania

[3]Department of Chemistry, Lithuanian University of Agriculture,
Studentu g. 11, LT-4324, Akademija, Kauno r. Lithuania

Syntheses and thermal, optical as well as photoelectrical properties of carbazolyl-, triphenylamino- and 2-hydroxy-4-diethylaminophenyl-based hydrazones with reactive methacryloyl groups have been reported. All the synthesized materials form glasses with glass transition temperatures ranging from 9 to 50 °C. They absorb electromagnetic radiation in the 250–440 nm range. Ionization potentials of the amorphous films of the synthesized materials, established by electron photoemission technique range from 5.20 to 5.71 eV. The lowest ionization potential and the best charge transport properties were observed for 2-(methacryloyl)oxy-4-diethylaminophenyl-1-carbaldehyde *N*,*N*-diphenylhydrazone. Time-of-flight hole mobilities in its 50% solid solution in bisphenol Z polycarbonate reach $10^{-5}$ cm$^2$/(V·s) at high electric fields.

Key words: *reactive hydrazone; glass; ionization potential; charge mobility*

## 1. Introduction

Materials accepting charges generated in adjacent materials and transporting them towards appropriate electrodes are called charge transport materials or semiconductors [1]. Most of known charge transport materials are photoconductive in UV light, and conversely, all truly photoconductive materials can act as transporting media for

[*]Present address: Department of Biological Chemistry, Lithuanian Veterinary Academy, Tilzes str. 18, LT-47181, Kaunas, Lithuania.
[**] Corresponding author, e-mail: Juozas.Grazulevicius@ktu.lt

charges generated extrinsically. Organic photoconductors or charge transport materials are used in photoreceptors of most modern copying machines, laser printers, and fax machines. They are also used in commercial organic light emitting diodes. The forthcoming fields of application of organic semiconductors are solar cells and field effect transistors. Most of the practical electrophotographic photoreceptors are multilayer devices in which every layer has its own function. Organic semiconductors are used for the fabrication of charge transport layers of devices usually several micrometers thick and represent so called molecularly doped polymers, i.e. solid solutions of low-molar-mass organic semiconductors in inert polymers such as polycarbonates [2].

One of the frequent requirements for charge transport layers of electrophotographic photoreceptors is that they be resistant to organic solvents. This requirement is particularly important if liquid developers are used in electrophotographic processes. Solvent resistant charge transport layers can be prepared by (photo)crosslinking. For this, charge transporting materials with reactive functional groups are required. The aim of this work was to synthesize and study methacryloyl functionalized hydrazones as hole transport materials for electrophotographic photoreceptors. Hydrazones are very effective hole transport materials widely used in electrophotography [3–5]. Earlier, hydrazones containing reactive epoxy- [4, 6] and vinyloxyethyl- [7, 8] groups were reported. However the reactivity of epoxy- and vinyloxyethyl-substituted hydrazones has appeared to be not too high, particularly in cationic polymerization reactions. Therefore it was of interest to synthesize methacryloyl-substituted hydrazones as radically (photo)polymerizable or (photo)crosslinkable compounds, which can be used for the preparation of solvent resistant charge transport layers.

## 2. Experimental

*Materials*. All required chemicals: N-phenylhydrazine, 97% (Aldrich), potassium carbonate, 99% (Aldrich), potassium hydroxide, 86% (Lachema), phosphorus oxychloride, 99% (Aldrich), triethylamine, 99% (Acros), sodium chloride, 99% (Lachema), magnesium sulphate, 97% (Aldrich), sodium sulphate, 98% (Aldrich) were used as received without further purification. Methacryloylchloride, 97% (Fluka) was distilled (water pump vacuum) before use collecting the fraction with the boiling point 92 °C. Organic solvents were purified and dried by the standard methods [9]. 4-(Diphenylamino)benzaldehyde (**4**) (yield of $C_{19}H_{15}N_1O_1$ (*FW* = 273.26) was 72% (5.57 g of yellowish crystals); m.p. 126–126.5 °C)) [10]; di(4-formylphenyl)phenylamine (**4a**) (yield of $C_{20}H_{15}N_1O_2$ (*FW* = 301.26) was 44% (8.2 g of yellow-orange crystals); m.p. 126–126.5 °C)) [10], 9-ethylcarbazole-3-carbaldehyde (**1**) (yield of the product $C_{15}H_{15}N_1O_1$ (*FW* = 223.21) was 80% (4.57g of grey crystals); m.p. 84.5–85 °C)) [11], 9-ethylcarbazole-3,6-dicarbaldehyde (**1a**) (yield of $C_{16}H_{15}N_1O_2$ (*FW* = 251.22) was 60% (11.5 g of brown crystals); m.p. 146.5–148 °C)) [11], were prepared by the known procedures.

*9-Ethylcarbazole-3-carbaldehyde N-phenylhydrazone (**2**).* 9-Ethylcarbazole-3-carbaldehyde (**1**) (10.0 g, 0.045 mol) was dissolved in 300 ml of methanol under mild heating. Then a solution of 7.25 g (0.067 mol) of N-phenylhydrazine in methanol was added. The reaction mixture was refluxed for 2 h and stopped when no starting materials were left (TLC control). After recooling, yellow-grey crystals were separated by filtration, washed with a large amount of methanol and dried. The yield of $C_{21}H_{19}N_3$ (*FW* = 313.32) was 92% (13.12 g); m.p. 136–137 °C. IR (KBr) (in $cm^{-1}$): $\nu$(N–H) 3306, $\nu$(C–H in Ar) 3051, $\nu$(C–H) 2972, $\nu$(C=C, C–N in Ar) 1602; 1494; 1475; 1237, $\nu$(C–N) 1256, $\gamma$(Ar) 815; 747; 731. MS (APCI$^+$, 20 V), *m*/*z* = 314 ([M + H]$^+$); 222. $^1$H NMR (100 MHz, $CDCl_3$, δ, ppm): 1.34 (*t*, *J* = 7.0 Hz, 3H, $CH_3$); 4.23 (*q*, *J* = 7.0 Hz, 2H, $CH_2$); 6.90–7.64 (*m*, 8H, Ar); 7.60 (*s*, 1H, Ar); 7.81 (*d*, 1H, Ar); 8.08 (*d*, 2H, Ar); 8.15(*d*, 1H, =CH).

*9-Ethylcarbazole-3-carbaldehyde-N-(methacryloyl)-N-phenylhydrazone (**3**).* 9-Ethylcarbazole-3-carbaldehyde-N-phenylhydrazone (**2**) (5.0 g, 0.0157 mol) was dissolved in 40 ml of dry dichloromethane under nitrogen atmosphere and 2.61 ml (0.0188 mol) of triethylamine and 1.82 ml (0.0188 mol) of freshly distilled methacryloylchloride was added dropwise. The reaction mixture was stirred and heated at ca. 40 °C for 10 h and cooled down. Then the product was extracted using chloroform and distilled water. The organic layer was dried using anhydrous sodium sulphate and filtered. The solvent was removed from the filtrate with a rotary evaporator. The product was purified by column chromatography using an eluent mixture of hexane and ethyl acetate in the volume ratio of 3:1. The solvents were rotary evaporated and the product was washed with a large amount of benzene, filtered and dried. Yield of the product was 23.45% (1.4 g of brownish powder). IR (KBr) (in $cm^{-1}$): (C–H in Ar) 3062, 3033, $\nu$(C–H) 2970, $\nu$(C=O) 1671, $\nu$(C=C in Ar) 1598, 1491, $\nu$(C–N) 1238, 1202, $\gamma$(Ar) 747, 679. MS (APCI$^+$, 20 V), *m*/*z* = 382.37 ([M+H]$^+$), 288.36, 260.39, 221.40, 149.16. $^1$H NMR (100 MHz, $CDCl_3$, $\delta$, ppm): 3.50 (*s*, 3H, $CH_3$–C); 4.19–4.27 (*q*, *J* = 6.5 Hz, 1H, $CH_2$= ), 5.40–5.54 (*q*, *J* = 6.0 Hz, 1H, $CH_2$= ), 7.19–8.15 (*m*, 13H, Ar, –CH=). Elemental analysis for $C_{25}H_{23}N_3O_1$ (*FW* = 381.38): calculated: C 78.71%; H 6.08%; N 11.02%; O 4.20%; found: C 78.87%; H 6.52%; N 10.92%.

*4-(Diphenylamino)benzaldehyde N-phenylhydrazone (**5**).* 4-(Diphenylamino)benzaldehyde (**4**) (10.0 g, 0.037 mol) was dissolved in 300 ml of methanol under mild heating. Then, a solution of 5.94 g (0.055 mol) of N-phenylhydrazine in 5 ml of methanol was added. The reaction mixture was refluxed for 0.5 h until no starting materials were observed (TLC control). After recooling and crystallisation, yellowish crystals were filtered, washed with a large amount of methanol and dried. The yield of $C_{25}H_{21}N_3$ (*FW* = 363.36) was 86.7% (11.7 g); m.p. 168–169 °C. IR (KBr) (in $cm^{-1}$): $\nu$(N–H) 3294, $\nu$(C–H in Ar) 3026, $\nu$(C=C in Ar) 1595; 1489, $\nu$(C–N) 1282; 1257, $\gamma$(Ar) 750; 731. MS (APCI$^+$, 20 V), *m*/*z* = 364 ([M+H]$^+$), 314, 223, 159. $^1$H NMR (100 MHz, $CDCl_3$, δ, ppm): 6.55–7.64 (m, 21H, Ar, = CH, –NH).

*4-(Diphenylamino)benzaldehyde N-(methacryloyl)-N-phenylhydrazone (**6**).* 4-(Diphenylamino) benzaldehyde N-phenylhydrazone (**5**) (5.0 g, 0.0135 mol) was dissolved

in 40 ml of dry dichloromethane in a nitrogen atmosphere, and 2.26 ml (0.0163 mol) of triethylamine was added. The reaction mixture was cooled down to 0 °C. Then 1.58 ml (0.0163 mol) of freshly distilled methacryloylchloride was added dropwise into the reaction mixture. The reaction mixture was stirred for 3 h and the second portion of methacryloylchloride (1.58 ml) and TEA (2.26 ml) was added. After 4 h the reaction was terminated when no starting materials were left (TLC control). The product was extracted using chloroform and distilled water. The organic layer was dried using anhydrous sodium sulphate and filtered. The solvent was removed from the filtrate with a rotary evaporator. The product was purified by the column chromatography using an eluent mixture of hexane and ethyl acetate in the volume ratio of 3:1. Finally, the solvent was rotary evaporated and the product was freeze dried. The product yield was 22.77% (1.33 g of yellowish brown powder). IR (KBr) (in $cm^{-1}$): $\nu$(C–H in Ar) 3036, $\nu$(C–H) 2829, 2742, $\nu$(C=O) 1689, $\nu$(C=C in Ar) 1585, 1489, $\nu$(C–N) 1287, 1220, 1155, $\gamma$(Ar) 757, 696. MS (APCI$^+$, 20 V), *m*/*z* = 432.25 ([M+H]$^+$), 162.22. $^1$H NMR (100 MHz, $CDCl_3$, δ, ppm): 2.2 (s, 3H, $CH_3$–C); 5.39–5.57 (m, 2H, $CH_2$= ), 6.79–7.81 (*m*, 20H, Ar, –CH= ). Elemental analysis for $C_{29}H_{25}N_3O_1$ (*FW* = 431.42): calculated: C 80.71%; H 5.48%; N 9.74%; O 3.71%; found: C 80.91%; H 6.02%; N 9.16%.

*Di{4-[(N-phenylamino)iminomethyl]phenyl}phenylamine (7)*. Di(4-formylphenyl)-phenylamine (**4a**) (7.6 g, 0.025 mol) was dissolved in 150 ml of methanol under mild heating. Then, a solution of 6.75 g (0.0625 mol) of N-phenylhydrazine in 5 ml of methanol was added. The reaction mixture was refluxed for 2 h and stopped when no starting materials were observed (TLC control). After recooling and crystallisation, yellow-orange crystals were filtered off, washed with a large amount of methanol and dried. The yield of $C_{32}H_{27}N_5$ (*FW* = 481,48) was 84.1% (10.21 g); m.p. 131.5–132 °C. IR (KBr) (in $cm^{-1}$): $\nu$(N–H) 3295, $\nu$(C–H in Ar) 3027, $\nu$(C=C in Ar) 1597; 1499, $\nu$(C–N) 1287; 1253, $\gamma$(Ar) 749; 723. MS (APCI$^+$, 20 V), *m*/*z* = 482.24 ([M+H]$^+$), 392.28, 180.24, 112.99. $^1$H NMR (100 MHz, $CDCl_3$, $\delta$, ppm): 3.34 (*s*, 2H, –NH), 6.72–7.84 (*m*, 25H, Ar, =CH).

*Di(4-{[(N-methacryloyl)-N-phenylamino]iminomethyl}phenyl)phenylamine (8)*. Di{4-[(N-phenylamino)iminomethyl]phenyl}phenylamine (**7**) (5.0 g, 0.0104 mol) was mixed with 50 ml of dry dichloromethane ($CH_2Cl_2$) in a nitrogen atmosphere. 3.48 ml (0.025 mol) of triethylamine was added and the heterogeneous reaction mixture was cooled to 0 °C. Then 2.42 ml (0.025 mol) of freshly distilled methacryloylchloride was dropped into the reaction mixture. The reaction mixture was stirred at 40 °C and stopped after 18 h when no starting materials were left in the reaction mixture (TLC control). After recooling, the product was extracted using chloroform and distilled water. The organic layer was dried using anhydrous sodium sulphate and filtered. The solvent was removed from the filtrate with a rotary evaporator. The product was purified by the column chromatography using an eluent mixture of hexane and acetone in the volume ratio of 6:1. Finally, the solvent was rotary evaporated and the product was freeze dried. Yield: 23% (1.7 g of yellowish powder). IR (KBr) (in $cm^{-1}$): $\nu$(arene C –H) 3284, 3063, $\nu$(C–H) 3008, 2973; 2924; $\nu$(C=O) 1673, $\nu$(C=C, in Ar) 1594; 1509;

1490, $\nu$(C–N) 1283; 1233, 1183, $\gamma$(Ar) 755; 696. MS (APCI$^+$, 20 V), *m*/*z* = 618.17 ([M+H]$^+$), 458.25, 298.36, 297.35, 134.14. $^1$H NMR (100 MHz, $CDCl_3$, $\delta$, ppm): 2.20 (*s*, 6H, $CH_3$), 5.35–5.44 (*m*, 2H, $CH_2$= ); 5.48–5.59 (*m*, 2H, $CH_2$= ), 7.03 (s, 2H, –CH=); 7.1–7.6 (*m*, 23H, Ar). Elemental analysis for $C_{40}H_{35}N_5O_2$ (*FW* = 617.59): calculated: C 77.77%; H 5.71%; N 11.34%; O 5.18%; found: C 78.29%15.0 g (0.0776 mol); H 4.92%; N 10.96%.

*2-Hydroxy-4-diethylaminophenyl-1-carbaldehyde N,N-diphenylhydrazone (**9**).* 2-Hydroxy-4-diethylaminophenyl-1-carbaldehyde (15.0 g, 0.0776 mol) was dissolved in 50 ml of methanol under mild heating. Then a solution of 25.69 g (0.1164 mol) of *N*,*N*-diphenylhydrazine hydrochloride dissolved in ca. 50 ml of methanol was added. The reaction mixture was stirred at ca. 30 °C for 2 h and cooled down. Then the reaction product was extracted and shaken in a separatory funnel with diethyl ether and distilled water. The organic layer was dried using anhydrous sodium sulphate and filtered. The solvent was removed by rotary evaporation. The product was purified by the column chromatography using an eluent mixture of hexane and chloroform in the volume ratio of 1:1 and crystallized from the eluent. The yield of $C_{23}H_{25}N_3O_1$ (*FW* = 359.38) was 74.73% (20.85 g of grey crystals); m.p. 100.5–101 °C. IR (KBr) (in cm$^{-1}$): $\nu$(O–H) 3218, $\nu$(C–H in Ar) 3057, $\nu$(C–H) 2971; 2932; 2894, $\nu$(C=C in Ar) 1633, 1596, 1495, $\nu$(C–N) 1298, 1245, $\gamma$(Ar) 751, 700. MS (APCI$^+$, 20 V), *m*/*z* = 360.4 ([M+H]$^+$), 206.4, 120.1. $^1$H NMR (100 MHz, $CDCl_3$, δ, ppm): 1.15 (*t*, *J* = 7.0 Hz, 6H, $CH_3$); 3.33 (*q*, *J* = 7.0 Hz, 4H, $CH_2$); 6.73 (*d*, *J* = 9.0 Hz, 1H, =CH); 7.05–7.45 (*m*, 13H, Ar), 11.25 (*s*, 1H, –OH).

*2-(Methacryloyl)oxy-4-diethylaminophenyl-1-carbaldehyde N,N-diphenylhydrazone (**10**).* 2-Hydroxy-4-diethylaminophenyl-1-carbaldehyde-*N*,*N*-diphenylhydrazone (**9**) (7.0 g, 0.019 mol) was dissolved in 10 ml of dry dichloromethane in a nitrogen atmosphere and 3.2 ml (0.023 mol) of triethylamine was added. The reaction mixture was cooled down to 0 °C. Then 2.22 ml (0.023 mol) of freshly distilled methacryloylchloride was added dropwise. The reaction mixture was stirred for 10 min and terminated, since no starting materials were left (TLC control). The product was extracted using chloroform and distilled water. The organic layer was dried with anhydrous sodium sulphate and filtered. The solvent was removed by rotary evaporation. The product was purified by column chromatography using diethyl ether as an eluent. Finally, the solvent was rotary evaporated and the product was freeze dried. The yield of the product was 89.54% (7.45 g of yellowish brown resin). IR (KBr) (in cm$^{-1}$): $\nu$(C–H in Ar) 3061, 3023, $\nu$(C–H) 2973, 2929, 2895, $\nu$(C=C in Ar) 1783, $\nu$(C=O) 1736, $\nu$(C–O) 1319, 1290, 1273, $\gamma$(Ar) 749, 701. MS (APCI$^+$, 20 V), *m*/*z* = 428.4 ([M+H]$^+$). $^1$H NMR (100 MHz, $CDCl_3$, $\delta$, ppm): 1.2 (*t*, *J* = 7.0 Hz, 6H, $CH_3$);1.8 (*s*, 3H, $CH_3$–C=), 3.23 (*q*, *J* = 7.0 Hz, 4H, $CH_2$); 5.49 (s, 1H, $H_2C$=), 5.98 (*s*, 1H, $H_2C$=), 6.99–7.42 (m, 13H, Ar), 7.9(*d*, *J* = 9.0 Hz, 1H, –CH=). Elemental analysis for $C_{27}H_{29}N_3O_2$ (*FW* = 427.44): calculated: C 75.84%; H 6.84%; N 9.83%; O 7.49%; found: C 75.43%; H 7.24%; N 9.59%.

### 2.2. Measurements

IR spectra were recorded with Bio-Rad Digilab FTS-40 and Perkin Elmer Spectrum GX spectrophotometers. The spectra were obtained from KBr pellets. UV/VIS spectra were recorded with a Spectronic Unicam Genesys$^{TM}$ 8 spectrophotometer. Fluorescence emission spectra were recorded with a Hitachi MPF-4 luminescence spectrometer. $^1$H NMR spectra were obtained using a Bruker AC 250 (250 MHz), Varian Unity Inova (300 MHz) and JOEL FX 100 (100 MHz) apparatus. All the data are given as chemical shifts in $\delta$ (ppm), multiplicity, integration downfield from $(CH_3)_4Si$. Electron impact mass spectra were obtained on a Waters 2Q 2000. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409. Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer DSC-7 calorimeter.

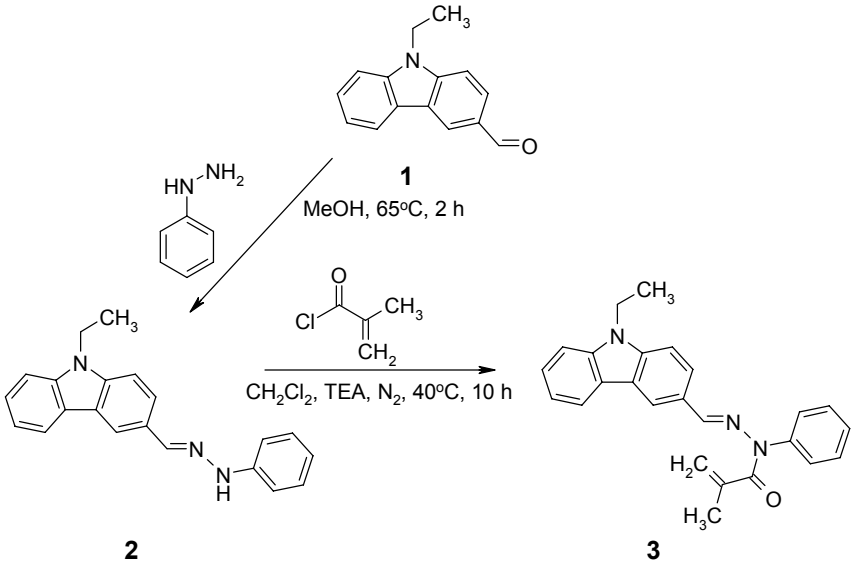
Ionization potential ($I_p$) was measured by the electron photoemission in air method as described earlier [12]. The samples for the measurements were prepared by casting the solutions of the compounds on Al plates pre-coated with methylmethacrylate and methacrylic acid copolymer as adhesive layer.

Charge carrier mobility ($\mu$) was measured by the xerographic time of flight method [13, 14]. The samples for the measurements were prepared by casting the solutions of the compounds or solutions of the mixtures of these compounds with the polymer host, i.e. bisphenol Z polycarbonate (PC-Z) at the mass proportion 1:1 in THF. The substrate was polyester film with an Al layer. The thickness of the charge-transporting layer varied in the range of 3–10 μm.

## 3. Results and discussion

New charge transport compounds bearing methacryloyl function groups **3**, **6**, **8**, **10** have been synthesized by the procedures described in Schemes 1–3**.** These procedures are similar to that reported earlier by Strohriegl [15]. The key starting materials aldehyde N-phenylhydrazones **2**, **5**, **7** and **9** were synthesized by multi-step synthesis, as described in previous works [7, 8, 16].

The first step was the formylation of arylamine, using $POCl_3$/DMF complex as a catalyst, by the Vilsmeier method [17] to get mono- and diformyl compounds **1**, **1a**, **4** and **4a**. The second step was condensation of aldehydes with N-phenylhydrazine, and the third step was the nucleophilic substitution reactions of 9-ethylcarbazole-3-carbaldehyde-N-phenylhydrazone (**2**), 4-(diphenylamino)benzaldehyde N-phenylhydrazone (**5**) and di{4-[(N-phenylamino)iminomethyl]phenyl}phenylamine (**7**) with methacryloylchloride in the presence of triethylamine in nitrogen atmosphere.




Scheme 1. Synthesis of 9-ethylcarbazole-3-carbaldehyde-N-(methacryloyl)-N-phenylhydrazone (**3**)

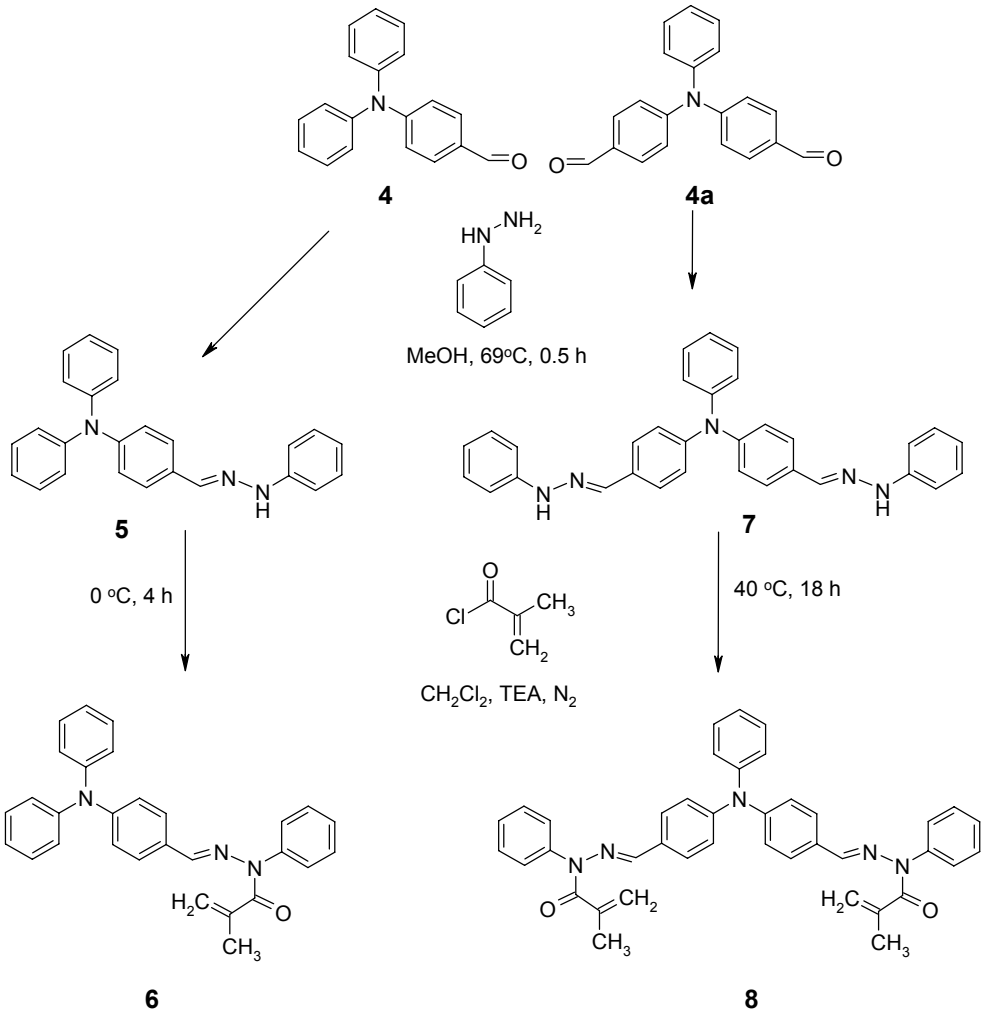
2-(Methacryloyl)oxy-4-diethylaminophenyl-1-carbaldehyde *N*,*N*-diphenylhydrazone (**10**) was synthesized by a two-step procedure as shown in Scheme 3. The first step was condensation of 2-hydroxy-4-diethylaminophenyl-1-carbaldehyde with *N*,*N*-diphenylhydrazine hydrochloride and the second step was alkylation of 2-hydroxy-4 -diethylaminophenyl-1-carbaldehyde *N*,*N*-diphenylhydrazone (**9**) with methacryloyl-chloride in the presence of triethylamine in a nitrogen atmosphere.

All the products were purified by the column chromatography to obtain pure and well defined compounds. All the synthesized materials were characterised by IR, $^1$H NMR spectroscopy, mass spectrometry and elemental analysis.

IR spectra of compounds **3**, **6**, **8**, **10** have characteristic absorption of C=O groups at ca. 1725 cm$^{-1}$.

The signals in $^1$H NMR spectra of all the newly synthesized hydrazone compounds can be exactly assigned to the characteristic hydrogen atoms of these compounds. The well distinguished signals of $CH_3$–C protons are at 1.8–3.5 ppm in the spectra of all methacryloyl substituted hydrazones. Characteristic signals of the protons of $CH_2$= group of methacryloyl group are observed at 4.19–4.27 and 5.26–5.98 ppm in the spectra of compounds **3**, **6**, **8**, **10**. The signals at 6.99–8.15 ppm can be assigned to the aromatic and heterocyclic protons.

Mass spectra of all the synthesized hydrazones show the corresponding molecular ion peaks and peaks due to alkyl and respective aryl fragments.




Scheme 2. Synthesis of triphenylamine-based hydrazones containing methacryloyl functional groups

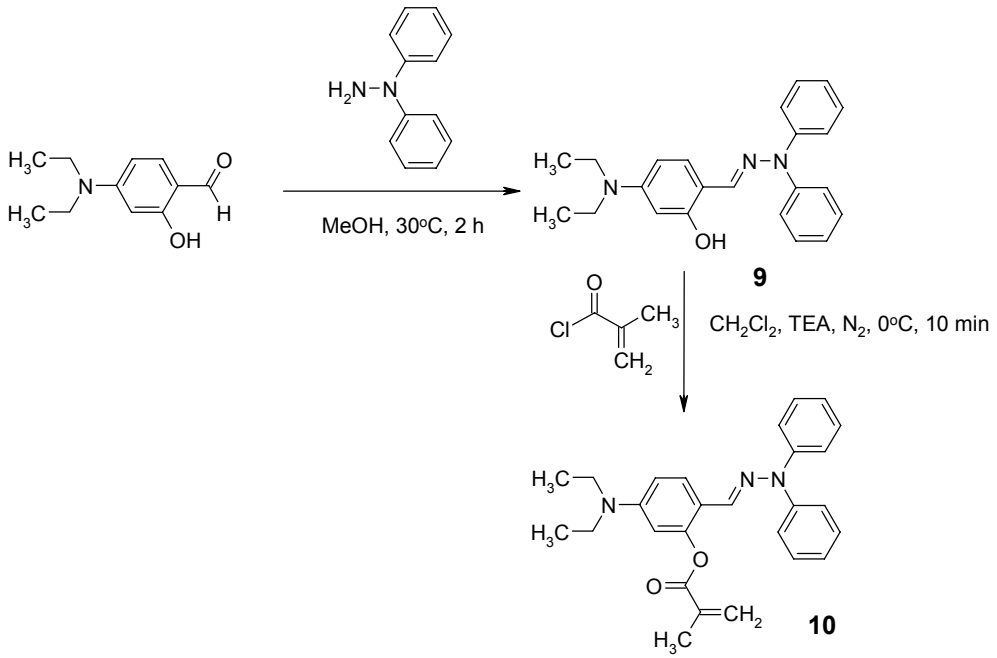
Compounds **3**, **6**, **8**, **10** were studied by UV/VIS spectrometry. They absorb electromagnetic radiation in the region of 200–420 nm. The wavelengths of the absorption maxima for methacryloyl-substituted hydrazones are given in Table 1.

Table 1. Wavelengths of absorption maxima for compounds **3**, **6**, **8** and **10** [nm]

| Compound | **3 (2)** | **6 (5)** | **8 (7)** | **10 (9)** |
|---|---|---|---|---|
| $\lambda$ | 298, 326 (348) | 354 (376) | 381 (394) | 368 (370) |

Methacryloyl-substituted hydrazones **3**, **6**, **8**, **10**, owing to the electron withdrawal effect of the carbonyl group, exhibit hypsochromic shift (up to 22 nm) with respect to

the corresponding nonsubstituted hydrazones. In the case of the substitution of one hydrazone group (**3** and **6** compounds), the shift is the same, i.e., is 22 nm. Substitution of two hydrazone groups results in a smaller hypsochromic shift of 13 nm. This indicates stronger electron withdrawal into delocalization when a chromophore contains two hydrazone groups. In the case of the substitution of the OH group, the spectrum exhibits 2 nm hypsochromic shift of the longwave peak, that means only negligible distortion of the system in hydrazone **10** conjugated by the methacryloyl group.




Scheme 3. Synthesis of 2-(methacryloyl)oxy-4-diethylaminophenyl -1-carbaldehyde *N*,*N*-diphenylhydrazone (**10**)

Fluorescence emission spectra of dilute solutions of compounds **3**, **6**, **8**, **10** are presented in Fig. 1. The wavelengths of the maximum fluorescence intensities are 382 nm for carbazole containing compound **3**, 475 nm and 448 nm for triphenylamine bearing compounds **6** and **8**, 425 nm for 2-hydroxy-4-diethylaminophenyl-1-carbaldehyde moiety containing compound **10**. The large Stokes shifts of 112 nm for **3**, 185 nm for **6**, 68 nm for **8**, and 85 nm for **10** can be explained by vibrational relaxation and internal conversion in excited state of these compounds.

The thermal stability of the synthesized materials was estimated by TGA. The temperatures of their initial thermal degradation are given in Table 2. The initial mass loss temperatures ($T_{ID}$) for these materials range from 260 to 280 °C. The highest thermal stability was observed for triphenylamine based compound **6**. Its $T_{ID}$ is 280 °C.

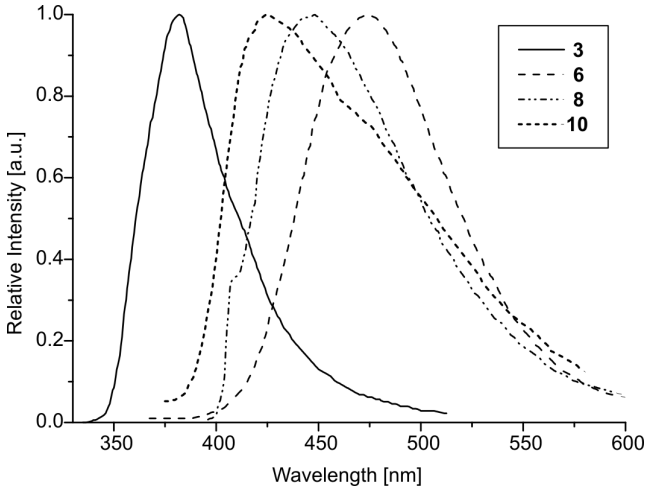



Fig. 1. Fluorescence spectra of diluted THF solutions ($10^{-5}$ M) of hydrazones **3** ($\lambda_{ex}$ = 270 nm), **6** ($\lambda_{ex}$ = 290 nm), **8** ($\lambda_{ex}$ = 380 nm) and **10** ($\lambda_{ex}$ = 340 nm)

Table 2. Thermal characteristics of compounds **3**, **6**, **8** and **10**

| Compound | $T_g$ [ °C] | $T_m$ [ °C] | $T_{ID}$ [ °C] |
|---|---|---|---|
| **3** | 43 | 84 | 260 |
| **6** | 41 | 128 | 280 |
| **8** | 50 | 85 | 260 |
| **10** | 9 | – | 260 |

Compounds **3, 6** and **8** were isolated as crystalline materials. The first DSC heating scans of these compounds revealed endothermic melting signals with the maxima at 84 °C for **3**, 124 °C for **6**, and at 85 °C for **8**. Cooling did no reveal any crystallization peaks and only glass-transitions were observed in the DSC second heating scans of these compounds at 43 °C, 41 °C and 50 °C respectively. Compound **10** was isolated as a viscous resin. It showed only glass transition in all DSC heating and cooling scans. Comparison of glass transition temperatures ($T_g$) of methacryloyl substituted hydrazones with their vinyloxyethyl substituted analogues reported earlier [7, 8, 16] show that metacrylolyl substituted hydrazones display higher glass transition temperatures from 9 °C to 23 °C. This observation can be explained by the presence of more polar methacryloyl groups in these compounds which predetermines stronger intermolecular interaction. All materials reported in this paper are soluble in common organic solvents such as acetone, chloroform, THF, etc. The values of $I_p$ are given in Table 3. They range from 5.20 eV to 5.70 eV. The lowest value of $I_p$ was observed for 2-methacryloyloxy-4-diethylaminophenyl-1-carbaldehyde hydrazone **10**. It was of interest to compare $I_p$ of methacroyl substituted hydrazones with those of their corresponding vinyloxyethyl substituted analogues reported earlier [7, 8, 16]. In all cases methacryloyl substituted hydrazones exhibit slightly higher $I_p$ values.

Table 3. Ionisation potentials of the amorphous films of compounds **3**, **6**, **8** and **10**

| Compound | **3** | **6** | **8** | **10** |
|---|---|---|---|---|
| $I_p$ [eV] | 5.70 | 5.60 | 5.70 | 5.20 |

Figure 2 shows electric field dependences of hole drift mobilities of solid solutions of methacryloyl substituted hydrazones **6**, **8**, **10** in PC-Z. The linear dependences of holes drift mobility on the square root of the electric field are observed for all the systems.

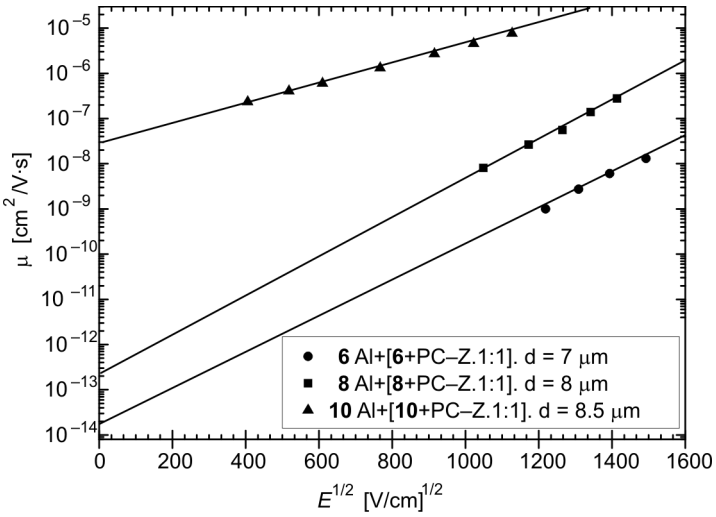



Fig. 2. Electric field dependences of holes drift mobilities of the solid solutions of compounds **6**, **8**, **10** in PC-Z

The highest hole drift mobilities were observed for the solid solution of compound **10** in PC-Z. At high electric fields, they reach $10^{-5}$ cm$^2$/(V·s). Hole drift mobilities in PC-Z doped with compound **10** are close to those observed in PC-Z doped with the vinyloxyethyl substituted analogue of **10** [16]. In other cases the systems containing methacryloyl substituted hydrazones show lower charge mobilities than the systems containing vinyloxyethyl substituted hydrazones [8].

## 4. Conclusions

We have synthesized hydrazones containing carbazole, triphenylamino and 2-hydroxy-4-diethylaminophenyl moieties with reactive methacryloyl groups as polymerizable or cross-linkable hole transport materials for electrophotographic photoreceptors. We have also studied thermal, optical and photoelectrical properties of the synthesized materials. All the materials form glasses with glass transition temperatures ranging from 9 °C to 50 °C. They absorb electromagnetic radiation in the 250–440 nm

range. Ionization potentials of the amorphous films of the synthesized materials, established by electron photoemission technique, range from 5.20 to 5.71 eV. The lowest ionization potential and the best charge transport properties were observed for 2-(methacryloyl)oxy-4-diethylaminophenyl-1-carbaldehyde *N*,*N*-diphenylhydrazone. Time of flight hole mobilities in its 50% solid solution in bisphenol Z polycarbonate reach $10^{-5}$ $cm^2/(V \cdot s)$ in high electric fields.

**Acknowledgements**

This research was supported by the Lithuanian Science and Studies Foundation. Habil. Dr. Valentas Gaidelis from the Department of Solid State Electronics, Vilnius University is thanked for the ionisation potential measurements.

## References

1] STOLKA M., [in:] *Special Polymers for Electronics and Optoelectronics*, J.A. Chilton, M.T. Goosey (Eds.), Chapman and Hall, London, 1995, p. 284.
[2] BORSENBERGER P.M., WEISS D.S, *Organic Photoreceptors for Xerography*, M. Dekker, New York, 1998, p. 768.
[3] JIANG K.J., SUN Y.L., SHAO K.F, YANG L.M., Chem. Lett., 33 (2004), 50.
[4] GETAUTIS V., STANISAUSKAITE A., MALINAUSKAS T., STUMBRAITE J., GAIDELIS V., JANKAUSKAS V., Monatsh. Chem., 137 (2006), 1401.
[5] GETAUTIS V., DASKEVICIENE M., MALINAUSKAS T., GAIDELIS V., JANKAUSKAS V., TOKARSKI Z., Synth. Met., 155 (2005), 599.
[6] GETAUTIS V., DASKEVICIENE M., MALINAUSKAS T., STANISAUSKAITE A., STUMBRAITE J., Molecules, 11 (2006), 64.
[7] BUDRECKIENE R., BUIKA G., GRAZULEVICIUS J.V., JANKAUSKAS V., STANISKIENE B., J. Photochem. Photobiol. A. Chem., 181 (2006), 257.
[8] BUDRECKIENE R., BUIKA G., GRAZULEVICIUS J.V., JANKAUSKAS V., TOKARSKI Z., Synth. Met., 156 (2006), 677.
[9] LIDLE D.R., *Handbook for Organic Solvents*, CRC Press, Boca Raton, 1995.
[10] LEE H.J., SOHN J., HWANG J., PARK S.Y., CHOI H., CHA M., Chem. Mater., 16 (2004), 456.
[11] OSTRAUSKAITE J., VOSKA V., ANTULIS J., GAIDELIS V., JANKAUSKAS V., GRAZULEVICIUS J.V., J. Mater. Chem., 12 (2002), 3469.
[12] MIYAMOTO E., YAMAGUCHI Y., YOKOYAMA M., Electrophotography, 28 (1989), 364.
[13] MONTRIMAS E., GAIDELIS V., PAZERA A., Lithuanian Journal of Physics, 6 (1966), 569.
[14] VAEZI-NEJAD S.M., Int. J. Electronics, 62, (1987) 361.
[15] STROHRIEGL P., Mol. Cryst. Liq. Cryst. 183, (1990), 261.
[16] BUDRECKIENE R., GRAZULEVICIUS J.V., JANKAUSKAS V., VEDEGYTE J., SIDARAVICIUS J., J. Optoelectronics Adv. Mater., 8 (2006), 1533.
[17] VILSMEIER A., HACK A., Ber. 60 (1927) 119.

*Received 23 October 2007*
*Revised 8 July 2008*