Novel Families of Hole-Transporting Monomers and Polymers

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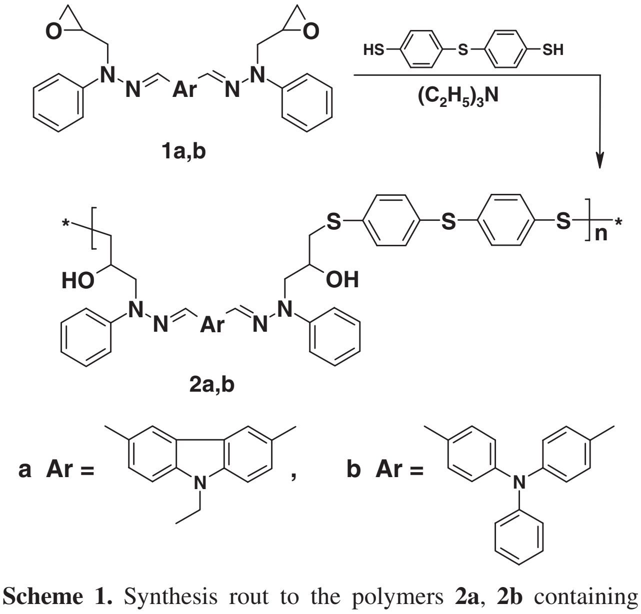
The novel families of hole transporting monomers and polymers containing hydrazone moieties are reported. The polymers were prepared in polyaddition reaction of hydrazone-containing diepoxides with 4,4′-thiobisbenzenethiol. The hole drift mobilities in the newly synthesized polymers exceed 10^{-4} cm^2 V^{-1}s^{-1} and in the compositions of the monomers with polymeric binder exceed 10^{-6} cm^2 V^{-1}s^{-1} at an electric field of 10^6 V cm^{-1} as characterized by the xerographic time of flight technique.

Organic charge-transporting materials are used in electrophotographic photoreceptors, light-emitting diodes, photovoltaic devices, and other optoelectronic devices.[1] Rapid charge transporting ability, high photosensitivity, simple synthesis, and low price are the advantages of the hydrazones against others charge transporting materials (TM).[2] Low molecular weight TM containing hydrazone moieties are usually crystalline materials, are not capable of forming thin neat homogenous layers, and must be used in combination with polymeric hosts. The presence of a large proportion of polymer host in the compositions, usually reaching 50% of the total composition mass, leads to the considerable decrease of charge carrier mobility. Even in such compositions, the possibility of the TM crystallization remains and this causes problems during electrophotographic layer preparation and extended printing. From this point of view the photoconducting polymers or oligomers are superior to crystalline materials.



Scheme 1. Synthesis rout to the polymers **2a**, **2b** containing hydrazone moieties from monomers **1a**, **1b**.

In this work we briefly report on the synthesis, characterization and photoconductive properties of novel photoconductive monomers and polymers containing hydrazone moiety. The newly synthesized polymers exhibit high hole drift mobilities and excellent film-forming properties.

Synthesis of the monomers containing hydrazone moieties was carried out by three step reaction. The first step was Vilsmeyer formylation of 9-ethylcarbazole or triphenylamine using $POCl_3/DMF$ complex to get diformyl compounds. The second step was the condensation of the diformyl compounds with phenylhydrazine to obtain dihydrazones of diformyl compounds. By interaction of the dihydrazones with epichlorohydrin in the presence of KOH 9-ethylcarbazole-3,6-dicarbaldehyde bis(*N*-2,3-epoxypropyl-*N*-phenylhydrazone) (**1a**) and triphenylamine-4,4′-dicarbaldehyde bis(*N*-2,3-epoxypropyl-*N*-phenylhydrazone) (**1b**) were obtained. The synthesized diepoxides **1a**, **1b** were purified by column chromatography followed by crystallisation from toluene to obtain pure and well defined compounds. **1a**, **1b** were characterized by ^{1}H NMR, IR and elemental analysis.[3,4] In the additional step, polyaddition of diepoxypropylhydrazones **1a**, **1b** with 4,4′-thiobisbenzenethiol in THF was carried out in the presence of triethylamine at the reflux temperature of THF (Scheme 1). Polymers **2a**, **2b** possessing hydrazone moieties were isolated with 50–80% yield.

Polyaddition reaction was carried out for 4 and 60 h, and the polymers with different molecular weight were isolated. The average molecular weights and their distribution of the polymers **2a**, **2b** detected by GPC are presented in Table 1. Longer duration of the reaction obviously increases molecular weight of the polymers. DSC results show a slight increase in glass transition temperature (T_g), from 127 to 131 °C for polymer **2a** and from 122 to 125 °C for polymer **2b**, with increasing molecular weight. A change of chromophore, from carbazole to triphenylamine, leads to the decrease of T_g by ca. 5–6 degrees. This is apparently due to less tight packing of the polymer chains in the compound **2b**.

The absorption spectra of the monomers **1a**, **1b** and polymers **2a**, **2b** are given in Figure 1. The absorption spectrum of the polymer **2b** is bathochromically shifted with respect to the

Table 1. Molecular mass and DSC data of polymers

Polymer	M_n	M_w	M_w /M_n	T_g, /°C	Reaction time,/h	Yield, /%
2a	6700	26000	3.9	127	4	52
	8500	74000	8.7	131	60	82
2b	7100	29000	4.1	122	4	50
	9100	63000	6.9	125	60	77

spectrum of polymer **2a** this is the consequence of the increased conjugated π-electron system of the triphenylamine in comparison with carbazolyl chromophore. On the other hand difference in π-electron conjugation between corresponding monomers and polymers is not significant which proves that conjugated π-electron systems remain intact during polyaddition reaction.

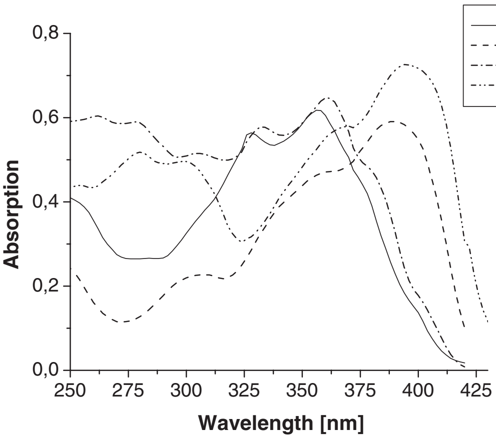


Figure 1. UV absorption spectra of the monomers **1a**, **1b** and polymers **2a**, **2b** in THF solutions.

The ionization potential (I_p) was measured by electron photoemission in air, similar to the method described.[5] The I_p value of 5.37 eV is for monomer **1a** and 5.40 eV for polymer **2a**. Replacement of the 9-ethylcarbazolyl group by the triphenylamino group leads to the decrease of I_p to 5.34 eV for monomer **1b** and 5.30 eV for polymer **2b** accordingly.

Polymers **2a**, **2b** are soluble in common organic solvents such as chloroform, THF, dioxane etc. This really good solubility is mainly due to the flexible linking fragments between chromophores. Clear, transparent and homogeneous films of polymers **2a**, **2b** were obtained by the casting technique. The hole-drift mobility for synthesized monomers **1a**, **1b** polymers **2a**, **2b** was measured by time of flight technique.[6,7] Positive corona charging created electric field inside the TM layer. 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 speed of the surface potential decrease dU/dt. The transit time t_t was determined by the kink on the curve of the dU/dt transient in linear or double logarithmic scale. The drift mobility was calculated by the formula ($\mu = d^2/U_0t_t$, where d is the layer thickness and U_0 is the surface potential at the moment of illumination. Figure 2 shows the room temperature dependencies of hole-drift mobility on electric field in monomers **1a**, **1b** with polymeric binding material polyvinylbutiral (PVB) and polymers **2a**, **2b**. The hole-drift mobilities in amorphous films of **2a**, **2b** exceeds $10^{-4}\,\mathrm{cm^2\,V^{-1}s^{-1}}$ at an electric field of $10^6\,\mathrm{V\,cm^{-1}}$. This is a rather high mobility as for amorphous polymeric TM, it is by ca. one order of magnitude higher than in the compositions of **1a**, **1b** with PVB. This improvement in results over monomers is mainly due to the elimination of polymeric binding material from the composition. The hole-drift mobilities in amorphous films of **2a**, **2b** is by ca. three orders of magnitude higher than in a classical polymeric photoconductor poly(*N*-vinylcarbazole).[8] In addition, the hole mobility in polymer **2b** containing triphenylamine moiety is by ca. one order of magnitude higher than in polymer **2a** containing carbazolyl group.

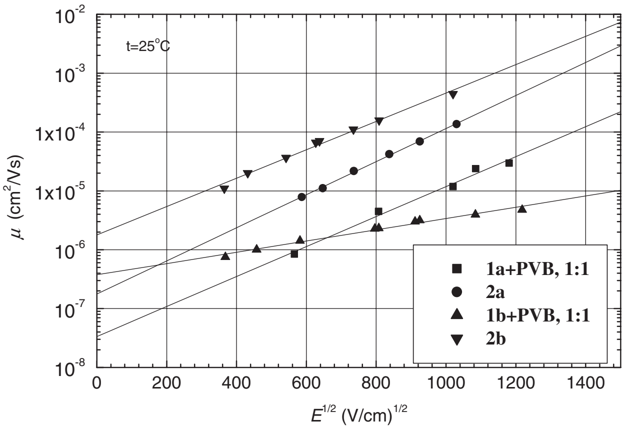


Figure 2. Field dependencies of the hole-drift mobilities.

More representatives of this family of hole-transporting polymers will be described in our following publications.

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References and Notes

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3 **1a**: mp 119–120 °C (from toluene) ^{1}H NMR (300 MHz, CDCl$_3$), δ: 8.38 (split s, 2H); 7.9–7.88 (m, 4H); 7.49–7.43 (m, 4H); 7.40–7.32 (m, 6H); 6.96 (t, 2H, $J = 7.2$ Hz); 4.42–4.29 (m, 6H); 4.06–3.97 (dd, 2H, (H$_A$), $J_{AX} = 4.5$ Hz, $J_{AB} = 16.4$ Hz); 3.31 (m, 2H); 2.90–2.85 (dd, 2H, (H$_A$), $J_{AX} = 3.9$ Hz); 2.70–2.65 (dd, 2H, (H$_B$), $J_{BX} = 2.7$ Hz; $J_{AB} = 5.1$ Hz); 1.43 (t, $J = 7.2$ Hz). Anal. Calcd for $C_{41}H_{46}N_6O_2$: C 75.20; H 7.08; N 12.83%. Found, C 75.01; H 6.91; N 12.68%.

4 **1b**: mp 163.5–165 °C (from toluene) ^{1}H NMR (300 MHz, CDCl$_3$), δ: 7.63 (s, 2H); 7.62–7.56 (m, 4H); 7.43–7.02 (m, 17H); 6.94 (t, 2H, $J = 7.1$ Hz); 4.40–4.30 (dd, 2H, (H$_A$), $J_{AX} = 2.1$ Hz, $J_{AB} = 16.5$ Hz); 4.02–3.92 (dd, 2H, (H$_B$), $J_{BX} = 4.2$ Hz); 3.26 (m, 2H); 2.84 (dd, 2H, (H$_A$), $J_{AX} = 4.2$ Hz, $J_{AB} = 5.1$ Hz); 2.65–2.60 (dd, (H$_B$), $J_{BX} = 2.7$ Hz). Anal. Calcd for $C_{38}H_{35}N_5O_2$: C 76.87; H 5.94; N 11.80%. Found, C 76.71; H 5.91; N 11.70%.

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