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Novel hydrazone based polymers as hole transporting materials

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Abstract

The novel family of hole transporting polymers containing hydrazone moieties is reported. The polymers were prepared in polyaddition reaction of hydrazone-containing diepoxydes with 4,4′-thiobisbenzenethiol in the presence of catalyst triethylamine (TEA). Obtained polymers were found to constitute novel polymeric hole transporting materials (TM) characterized by differential scanning calorimetry and time of flight method. The highest hole drift mobility in the newly synthesized polymers exceed 10^{-4} cm^2 V^{-1} s^{-1} at an electric field of 10^6 V cm^{-1} was observed in the TM with triphenylamine moieties.

Keywords: Polymers; Polyaddition; Hydrazones

1. Introduction

Organic charge-transporting materials are used in electrophotographic photoreceptors, light-emitting diodes, photovoltaic devices and other optoelectronic devices [1]. Recently, a variety of TM's, involving hydrazone, stilbene, pyrazoline, arylalkane, arylamine, oxadiazole or benztriazole moiety have been generated [2]. Rapid charge transporting ability, high photosensitivity, simple synthesis and low price are the advantages of the hydrazones against others hole transporting materials. 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. Aromatic hydrazone molecules dispersed in a binder polymer are used as the main constituent of electrophotographic devices due to their excellent hole-transporting property [3]. 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.

In this work we report on the synthesis, characterization and photoconductive properties of novel photoconductive polymers containing hydrazone moiety. The newly synthesized polymers exhibit high hole drift mobilities and excellent film-forming properties and can be chemically crosslinked in the layer by reaction of the hydroxyl groups with polyisocyanates [4,5].

2. Experimental details

2.1. Preparation of the polymeric TM (Scheme 1)

Synthesis of monomers **1a–c** was carried out according to the following procedure.

To a 1000 ml 3-neck round bottom flask equipped with reflux condenser, thermometer and mechanical stirrer were added 0.19 mol of bis(*N*-phenyl)hydrazone of

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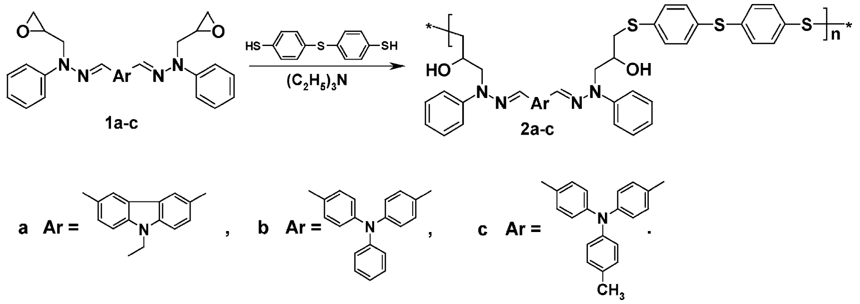

Scheme 1. Synthesis rout to polymers **2a–c** containing hydrazone moieties from monomers **1a–c**.

corresponding dicarbaldehyde and 328 ml (4.2 mol) of epichlorohydrin. The reaction mixture was stirred vigorously at 35–40 °C during 7 h, during which 92 g (1.4 mol) of powdered 85% potassium hydroxide and 21 g (0.17 mol) of anhydrous Na_2SO_4 were added in three portions with prior cooling of the reaction mixture to 20–25 °C. After termination of the reaction, the mixture was cooled to room temperature and filtered off. The organic part was treated with ethyl acetate and washed with distilled water until the wash water was neutral. The organic layer was dried over anhydrous magnesium sulfate, treated with activated charcoal, filtered and solvents were removed. The residue was dissolved in 120 ml of toluene. The crystals formed upon standing were filtered off and washed with 2-propanol to give monomers **1a**,**b**. The monomer **1c** was purified by column chromatography.

*2.1.1. 9-Ethyl-3,6-carbazoledicarbaldehyde bis(N-2,3-epoxypropyl-N-phenyl)hydrazone (**1a**)*

The yield of **1a** 63%, mp 119–120 °C (recrystallized from toluene). ^1H NMR spectrum ($CDCl_3$), ppm: 8.38 (split s, 2H, 4-H_{Ht}); 7.9–7.88 (m, 4H, Ar, CH=N); 7.49–7.43 (m, 4H, Ar); 7.40–7.32 (m, 6H, Ar); 6.96 (t, 2H, $J=7.2$ Hz, 4-H_{Ph}); 4.42–4.29 (m, 4H, $\mathit{CH_2}CH_3$, one of NCH_2 protons); 4.06–3.97 (dd, 2H, (H_A), $J_{AX}=4.5$ Hz, $J_{AB}=16.4$ Hz, another of NCH_2 protons); 3.31 (m, 2H, CHO); 2.90–2.85 (dd, 2H, (H_A), $J_{AX}=3.9$ Hz, one of CH_2O protons); 2.70–2.65 (dd, 2H, (H_B), $J_{BX}=2.7$ Hz; $J_{AB}=5.1$ Hz, another of CH_2O protons); 1.43 (t, 3H, $J=7.2$ Hz, CH_3). Anal. Calcd for $C_{34}H_{33}N_5O_2$ %: C 75.11; H 6.12; N 12.88. Found, %: C 75.16; H 6.09; N 12.81.

*2.1.2. 4-(4-Formyldiphenylamino)benzaldehyde bis(N-2,3-epoxypropyl-N-phenyl)hydrazone (**1b**)*

The yield of **1b** was 52%, mp 163.5–165 °C (recrystallized from toluene). ^1H NMR spectrum ($CDCl_3$), ppm: 7.63 (s, 2H, CH=N); 7.62–7.56 (m, 4H, Ar); 7.43–7.02 (m, 17H, Ar); 6.94 (t, 2H, $J=7.1$ Hz, 4-H_{Ph}); 4.40–4.30 (dd, 2H, (H_A), $J_{AX}=2.1$ Hz, $J_{AB}=16.5$ Hz, one of NCH_2 protons); 4.02–3.92 (dd, 2H, (H_B), $J_{BX}=4.2$ Hz another of NCH_2 protons); 3.26 (m, 2H, CHO); 2.84 (dd, 2H, (H_A), $J_{AX}=4.2$ Hz, $J_{AB}=5.1$ Hz, one of CH_2O protons); 2.65–2.60 (dd, (H_B), $J_{BX}=2.7$ Hz, another of CH_2O protons). 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.

*2.1.3. 4-(4-Formyl-4′methyldiphenylamino)benzaldehyde bis(N-2,3-epoxypropyl-N-phenyl)hydrazone (**1c**)*

The yield of **1c** (amorphous substance) 55%. ^1H NMR spectrum ($CDCl_3$), ppm: 7.63 (s, 2H, CH=N); 7.61–7.54 (m, 4H, Ar); 7.42–7.02 (m, 16H, Ar); 6.94 (t, 2H, $J=7.2$ Hz, 4-H_{Ph}); 4.40–4.28 (dd, 2H, (H_A), $J_{AX}=2.1$ Hz, $J_{AB}=16.5$ Hz, one of NCH_2 protons); 4.02–3.90 (dd, 2H, (H_B), $J_{BX}=4.2$ Hz, another of NCH_2 protons); 3.26 (m, 2H, CHO); 2.84 (dd, 2H, (H_A), $J_{AX}=4.2$ Hz, $J_{AB}=4.8$ Hz, one of CH_2O protons); 2.66–2.60 (dd, (H_B), $J_{BX}=2.7$ Hz, another of CH_2O protons); 2.33 (s, 3H, CH_3). Anal. Calcd for $C_{39}H_{37}N_5O_2$ %: C 77.08; H 6.14; N 11.52. Found, %: C 77.14; H 6.10; N 11.58.

The polymers **2a–c** were prepared according to the general procedure described below: 1.84 mmol of the monomer **1a–c**, 0.461 g (1.84 mmol) of 4,4′-thiobis-benzenethiol and 0.26 ml (1.8 mmol) of TEA were refluxed in 15 ml of THF under argon for 4 and 60 h. The reaction mixture was cooled to the room temperature and filtered through the 3–4 cm layer of silica gel (grade 62, 60–200 mesh, 150 Å) and the silica gel was washed with THF. Obtained solution was concentrated to 15–20 ml by evaporation and then poured into 20-fold excess of methanol with intensive stirring. The resulting precipitate of polymers **2a–c** was filtered and washed repeatedly with methanol and dried under vacuum at 50 °C. The yields of **2a–c** and determined molecular mass data are presented in the Table 1.

*2.1.4. Polymer (**2a**)*

^1H NMR spectrum (DMSO-d_6), ppm: 8.35–8.25 (m, 2H, 4-H_{Ht}); 8.06–7.91 (m, 2H, CH=N); 7.85–7.73 (m, 2H, 1-H_{Ht}); 7.61–7.00 (m, 18H, Ar); 6.88–6.75 (m, 2H, 4-H_{Ph}); 5.62–5.52 (m, 2H, OH); 4.47–4.25 (m, 2H, $\mathit{CH_2}CH_3$); 4.23–3.93 (m, 6H, NCH_2CH); 3.25–3.04 (m, 4H, CH_2S); 1.36–1.18 (m, 3H, CH_3). IR (KBr): 3340 cm^{-1} (OH, broad); 3053, 3039 cm^{-1} (aromatic CH); 2971, 2914 cm^{-1} (aliphatic CH); 807 cm^{-1} (CH=CH of 1,4-disubstituted benzene); 748, 692 cm^{-1} (CH=CH of monosubstituted benzene); 649, 625 cm^{-1} (C–S).

Table 1
Characteristics of polymers **2a–c**

Polymer	M_n	M_w	M_w/M_n	T_g (°C)	Reaction time (h)	Yield (%)
2a	6700	26,000	3.9	127	4	52
	8500	74,000	8.7	131	60	82
2b	7100	29,000	4.1	122	4	50
	9100	63,000	6.9	125	60	77
2c	7800	19,700	2.6	104	60	80

2.1.5. Polymer (**2b**)

^{1}H NMR spectrum (DMSO-d$_6$), ppm: 7.76–7.58 (m, 2H, CH=N); 7.52–6.85 (m, 29H, Ar); 6.83–6.67 (m, 2H, 4-H$_{Ph}$); 5.58–5.45 (m, 2H, OH); 4.18–3.86 (m, 6H, NCH$_2$CH); 3.23–3.01 (m, 4H, CH$_2$S). IR (KBr): 3352 cm^{-1} (OH, broad); 3057, 3030 cm^{-1} (aromatic CH); 2960, 2914 cm^{-1} (aliphatic CH); 812 cm^{-1} (CH=CH of 1,4-disubstituted benzene); 750, 694 cm^{-1} (CH=CH of monosubstituted benzene); 645, 628 cm^{-1} (C–S).

2.1.6. Polymer (**2c**)

^{1}H NMR spectrum (DMSO-d$_6$), ppm: 7.77–7.59 (m, 2H, CH=N); 7.57–6.69 (m, 30H, Ar); 5.59–5.45 (m, 2H, OH); 4.22–3.88 (m, 6H, NCH$_2$CH); 3.25–3.01 (m, 4H, CH$_2$S); 2.33–2.15 (m, 3H, CH$_3$). IR (KBr): 3352 cm^{-1} (OH, broad); 3051, 3025 cm^{-1} (aromatic CH); 2953, 2916 cm^{-1} (aliphatic CH); 812 cm^{-1} (CH=CH of 1,4-disubstituted benzene); 749, 691 cm^{-1} (CH=CH of monosubstituted benzene); 640, 615 cm^{-1} (C–S).

2.2. Measurement

The ^{1}H NMR spectra were taken on a Gemini-2000 (300 MHz) spectrometer. The IR spectra were taken in KBr pellets on a Perkin–Elmer Spectrum GX FT-IR spectrometer. The UV spectra were recorded on a Spectronic Genesys 8 spectrometer in THF. 10^{-4} M solution of investigated TM and microcell with an internal width of 1 mm was used. The course of the reactions products were monitored by thin-layer chromatography on Silufol UV-254 plates using diethylether-hexane (2:1) as the eluent and development with iodine vapour or UV light. Silica gel (grade 62, 60–200 mesh, 150 Å, Aldrich) was used for column chromatography.

Thermal transition data for synthesized polymers possessing hydrazone moieties was collected using a TA Instruments Model 2929 differential scanning calorimeter (New Castle, DE) equipped with a DSC refrigerated cooling system (−70 °C minimum temperature limit), and dry helium and nitrogen exchange gases. The calorimeter ran on a Thermal Analyst 2100 workstation with version 8.10B software. An empty aluminums pan was used as the reference. Samples of 5–8 mg as obtained from the synthesis were heated in aluminums pans at a scan rate 10 K/min under a nitrogen flow. The glass transition temperatures (T_g) were determined from the second heating.

The average molecular weight and the molecular weight distribution were estimated by gel permeation chromatography (GPC) using a Waters GPC system including a Waters 410 UV detector (254 nm), four columns (300 × 7.5 mm) filled with PL-Gel absorbent (pore sizes: 10^6, 10^5, 10^4 and 5000 nm) using THF as eluant. Polystyrene standards were used for column system calibration.

Ionization potential was measured by the photo-emission in air method similar to the used in Ref. [6] and described in Ref. [7].

The monomeric structures are able to form homogenous layers only with polymeric binder, so sample for mobility measurements were prepared from 1:1 mass proportion composition of **1a** with polyvinylbutyral (PVB): PVB from Aldrich with average $M_w = 70{,}000$–$100{,}000$ was used. In the case of film forming polymers **2a–c** the samples for mobility measurements were prepared from solutions of neat materials using THF as the solvent. The sample substrate was polyester film with conductive Al layer. The layer thickness was in the range 5–10 μm.

The hole drift mobility was measured by xerographic time of flight (XTOF) technique [8–10]. 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 the initial potential before illumination. The capacitance probe that was connected to the wide frequency band electrometer measured the rate 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 double logarithmic scale. The drift mobility was calculated by the formula $\mu = d^2/U_0 t_t$, where d is the layer thickness and U_0 is the surface potential at the moment of illumination.

3. Results and discussion

Synthesis of the polymers **2a–c** containing hydrazone moieties was carried out by multi-step reaction. The first step was Vilsmeyer formylation of 9-ethylcarbazole, triphenylamine or 4-methyltriphenylamine 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 obtained dihydrazones with epichlorohydrin in the presence of KOH monomers

9-ethyl-3-carbazolecarboxaldehyde-*N*-2,3-epoxypropyl-*N*-phenylhydrazone (**1a**), 4-(diphenylamino)benzaldehyde-*N*-2,3-epoxypropyl-*N*-phenylhydrazone (**1b**) and 4-(4-formyl-4′methyldiphenylamino)benzaldehyde bis(*N*-2,3-epoxy-propyl-*N*-phenyl)hydrazone (**1c**) were obtained (Scheme 1). Finally, the polyaddition of the monomers **1a–c** with 4,4′-thiobisbenzenethiol in THF was carried out in the presence of TEA at the reflux temperature of THF. The polymers **2a–c** possessing hydrazone moieties were isolated with 50–80% yield.

The 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 were 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°. This is apparently due to the less tight packing of the polymer chains in the compound **2b**. Introduction of methyl group into the triphenylamine chromophore of the polymer **2c** reduces T_g by ca. 21° compared with polymer **2b**. Lower molecular mass of the obtained polymer **2c** and addition of alkyl group are the main causes for such decrease in the T_g temperature.

In the Fig. 1 there are presented DSC second heating curves for the polymers **2a–c** (reaction time 60 h). The structure of the charge transporting chromophores has a significant influence on glass transition points of the presented compounds. These temperatures are lower for the polymer with triphenylamine chromophore **2b** as compared with carbazolyl **2a** and the lowest T_g is observed for the compound **2c** with 4-methyltripenylamine chromophore.

The absorption spectra of the monomers **1a–c** and polymers **2a–c** are given in Fig. 2. The absorption spectrum of the polymer **2b** is bathochromically shifted with respect to the 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 introduction of the methyl group into the triphenylamine chromophore of the monomer **1c** has minor positive effect (≈2 nm) on the π-electron conjugation compared with the compound **1b**. 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.

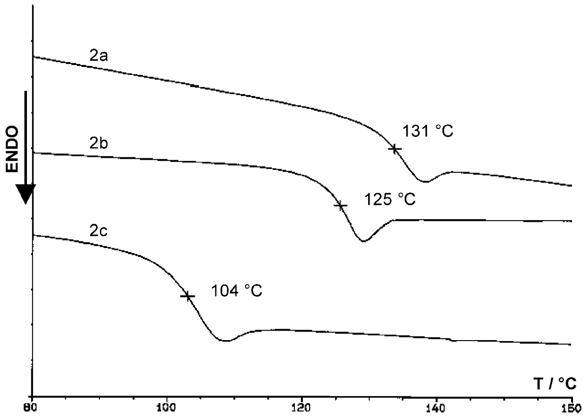

Fig. 1. DSC second heating curves of polymers **2a–c** (heating rate 10 K/min).

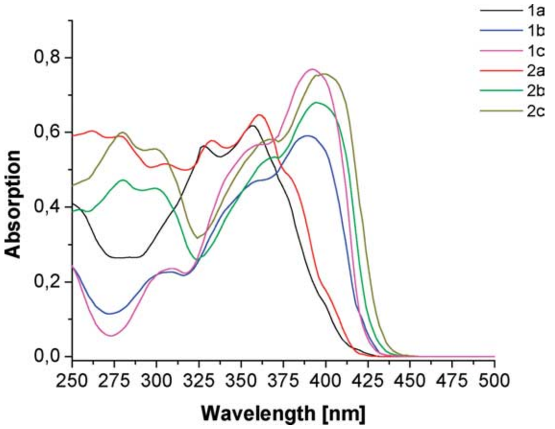

Fig. 2. UV absorption spectra of monomers **1a–c** and polymers **2a–c** in THF solutions.

The ionization potential (I_p) value for polymeric TM **2a** is 5.40 eV. Replacement of the 9-ethylcarbazolyl group by the triphenylamino group leads to the decrease of I_p to 5. 33 eV for polymer **2b** and 5.32 eV for polymer **2c** accordingly (Fig. 3).

Polymers **2a–c** 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–c** were obtained by the casting technique. The hole drift mobility for synthesized

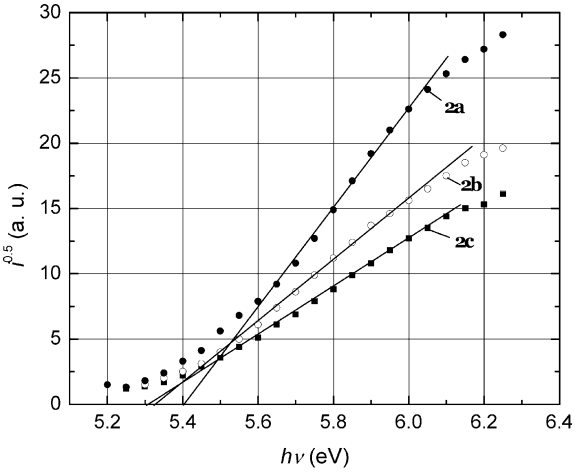

Fig. 3. Photoemission in air spectra of the polymers investigated.

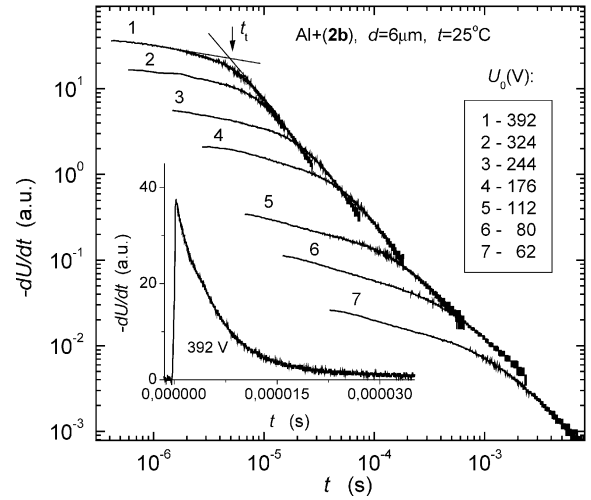

Fig. 4. XTOF transients for polymer **2b**. Insert shows the one transient curve in linear plot.

polymers **2a–c** was measured by xerographic time of flight technique.

XTOF measurements reveal that small charge transport transients are with well-defined transit time on log–log plots in all the investigated cases (Fig. 4). Fig. 5 shows the room temperature dependencies of hole-drift mobility on electric field in neat polymers **2a–c**. The composition of monomer **1a** with PVB was prepared for comparison of drift mobility data. The hole drift mobilities in amorphous films of **2a–c** exceeds 10^{-4} cm^2 V^{-1} s^{-1} at an electric field of 10^6 V cm^{-1}. This is a rather high mobility as for amorphous polymeric TM, it is by ca. two orders of magnitude higher than in the compositions of **1a** with PVB. This improvement in results over monomers is mainly due to the elimination of polymeric binding material from the composition. Moreover, the hole mobility in polymers **2b**,**c** containing triphenylamine moietie is by ca. one order of magnitude higher than in polymer **2a** containing carbazolyl group. In addition, the hole drift mobilities in amorphous films of **2a–c** is by ca. three orders of magnitude higher than in a classical polymeric photoconductor poly(*N*-vinylcarbazole) [2].

4. Conclusions

Polymeric hydrazone based hole transporting materials were synthesized and investigated as potential new

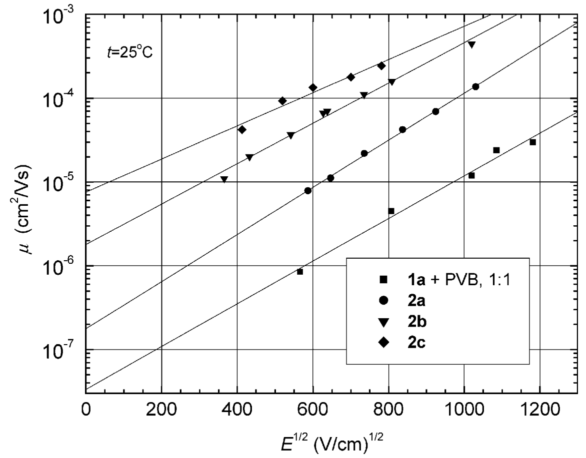

Fig. 5. Field dependencies of the hole drift mobilities of polymers **2a–c** and monomer **1a**.

materials for electrophotography. These polymer materials may be of particular interest for development of future electrophotographic photoreceptors and the hydroxyl groups allow for cross-linking of these transporting materials in the layer. The molecular structure of these polymeric hydrazones allows stable films to be prepared without binder material. The highest hole mobility, exceed 10^{-4} cm^2/Vs at 6×10^5 V/cm electric field, was observed in the polymer with triphenylamine moieties.

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