

## Cross-linkable hydrazone-containing molecular glasses for electrophotography

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### Abstract

The novel family of the hydrazone based hole-transporting materials with two epoxypropyl groups were synthesized and investigated as potential new materials for electrophotography. The molecular structure of these dihydrazones ensures good compatibility with most commonly used binding materials (BM) and allows stable films to be prepared. These materials may be of particular interest for development of future electrophotographic photoreceptors as the epoxy groups allow for cross-linking of these transporting materials (TM) in the layer without significant decrease of charge carrier mobility. Obtained compounds were characterized by differential scanning calorimetry and time of flight method. The highest hole mobility, exceeding  $10^{-5}$  cm<sup>2</sup>/V s at  $6 \times 10^5$  V/cm electric field, was observed in the hydrazones with triphenylamine moieties.

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### 1. Introduction

Aromatic hydrazone molecules dispersed in a binder polymer are used as the main constituent of electrophotographic devices due to their excellent hole-transporting properties and relatively simple synthesis [1–4]. The presence of large proportion of BM in the electrophotographic layers (EPL), usually 50% of the total composition mass leads to considerable decrease of carrier mobility. Even in such compositions, the possibility of the TM crystallization remains and this causes problems during electro-photographic layer (EPL) preparation and extended printing. Another problem, which arises with preparation of the belt format EPL on flexible supports, is bending and stretching stability of the layers. This problem is especially acute in machines with liquid development, because liquid developer promotes crack formation. Another question is TM solubility in liquid developer, which leads to deterioration of both EPL and liquid developer during printing. Solving of these prob-

lems requires TM with special molecule design and improved properties.

It is of interest and significance to develop photo- and electroactive low-molecular-weight amorphous materials that form stable amorphous glasses having glass-transition temperatures above room temperature. These molecular glasses will form stable films without BM, and are expected to manifest properties and functions more effectively relative to molecularly doped polymer compositions. Molecular glasses are already used in technical applications and can be regarded as attractive candidates for some newly developing fields. They are used as charge-transporting and/or emitting materials in light-emitting diodes [5,6–9], electrophotographic materials [10,11], and photovoltaic devices [12,13]. As photoconductive or multifunctional materials they can be applied in photorefractive systems [14]. Molecular glasses are also candidates for the application as electrically conducting materials [15], photochromic materials [16,17], and resist materials for electron-beam lithography [18]. Among the great number of studies devoted to low-molar-mass aromatic hydrazones only few glass-forming compounds with hydrazone moiety are reported [19–24].

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In the present article, we report on the synthesis, characterization and photoconductive properties of molecular glasses **1–3** possessing hydrazone moieties as hole transporting materials. The molecules of these TM consist of two flexible 2,3-epoxypropyl groups attached to the large  $\pi$  electron system conjugated through nitrogen atoms. The molecular structure of these TM makes crystallization in solid state difficult, so these materials are low molecular glasses. Another peculiarity of these TM is presence of two 2,3-epoxypropyl groups in the molecule. This improves adhesion and compatibility with various BM, including polycarbonate (PC) and polyvinylbutyral (PVB). The investigated compounds contain two active groups, which make them cross-linkable using three functional compounds for example trithiocyanuric acid (TTA). Such cross-linked systems enable to prepare electrophotographic photoreceptors with high solvent resistance and good mechanical properties. Moreover, the investigated compounds **1–3** are precursors for synthesis of a novel class of hole transporting polymers containing hydrazone moieties [25].

## 2. Experimental details

### 2.1. Preparation of the hydrazone-containing cross-linkable TM

Synthesis of the corresponding dialdehydes and dihydrazones was carried out according to the known procedures [26].

#### 2.1.1. General synthetic method of bis(*N*-2,3-epoxypropyl-*N*-phenyl)hydrazones (**1–3**)

To the mixture of (1 mol) diphenylhydrazone of corresponding dialdehyde and (22.5 mol) of epichlorohydrin, (4.5 mol) of powdered 85% potassium hydroxide and (0.6 mol) of anhydrous  $\text{Na}_2\text{SO}_4$  were added in three portions with prior cooling of the reaction mixture to 20–25 °C (1st portion—1/2 of  $\text{Na}_2\text{SO}_4$  and 1/3 of KOH; 2nd portion—1/4 of  $\text{Na}_2\text{SO}_4$  and 1/3 of KOH after 1 h from the beginning of the reaction; 3rd portion—1/4 of  $\text{Na}_2\text{SO}_4$  and 1/3 of KOH after 2 h from the beginning of the reaction). The reaction mixture was stirred vigorously at 35–40 °C until the starting dihydrazone disappeared (7–8 h). After termination of the reaction, the mixture was cooled to RT and filtered off. The organic part was 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 excess of epichlorohydrin was removed. In the case of **1** and **2**, the obtained residue was dissolved in the toluene. The crystals formed upon standing were filtered off and washed with 2-propanol. Compound **3** was purified by column chromatography.

#### 2.1.2. 9-Ethyl-3,6-carbazoledicarbaldehyde bis(*N*-2,3-epoxypropyl-*N*-phenyl)hydrazone (**1**)

The yield of **1** was 63%, mp 119–120 °C (recrystallized from toluene).  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ ) (ppm): 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, ( $\text{H}_A$ ),  $J_{AX} = 4.5$  Hz,  $J_{AB} = 16.4$  Hz); 3.31 (m, 2H);

2.90–2.85 (dd, 2H, ( $\text{H}_A$ ),  $J_{AX} = 3.9$  Hz); 2.70–2.65 (dd, 2H, ( $\text{H}_B$ ),  $J_{BX} = 2.7$  Hz;  $J_{AB} = 5.1$  Hz); 1.43 (t,  $J = 7.2$  Hz). IR spectrum (KBr, selected bonds),  $\nu$  ( $\text{cm}^{-1}$ ): 3054 (aromatic CH); 2976, 2932, 2893 (aliphatic CH); 939 (epoxy group); 811, 750, 692 (CH=CH of carbazole, monosubstituted benzene). Anal. Calcd for  $\text{C}_{34}\text{H}_{33}\text{N}_5\text{O}_2$  (%): C 75.11; H 6.12; N 12.88. Found (%): C 75.16; H 6.09; N 12.81.

#### 2.1.3. 4-(4-Formyldiphenylamino)benzaldehyde bis(*N*-2,3-epoxypropyl-*N*-phenyl)hydrazone (**2**)

The yield of **2** was 52%, mp 163.5–165 °C (recrystallized from toluene).  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ ) (ppm): 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, ( $\text{H}_A$ ),  $J_{AX} = 2.1$  Hz,  $J_{AB} = 16.5$  Hz); 4.02–3.92 (dd, 2H, ( $\text{H}_B$ ),  $J_{BX} = 4.2$  Hz); 3.26 (m, 2H); 2.84 (dd, 2H, ( $\text{H}_A$ ),  $J_{AX} = 4.2$  Hz,  $J_{AB} = 5.1$  Hz); 2.65–2.60 (dd, ( $\text{H}_B$ ),  $J_{BX} = 2.7$  Hz). IR spectrum (KBr, selected bonds),  $\nu$  ( $\text{cm}^{-1}$ ): 3061, 3029 (aromatic CH); 2989, 2966, 2876 (aliphatic CH); 942 (epoxy group); 828, 754, 695 (CH=CH of 1,4-disubstituted and monosubstituted benzene). Anal. Calcd for  $\text{C}_{38}\text{H}_{35}\text{N}_5\text{O}_2$  (%): C 76.87; H 5.94; N 11.80. Found (%): C 76.71; H 5.91; N 11.70.

#### 2.1.4. 4-(4-Formyl-4'-methyl-diphenylamino)benzaldehyde bis(*N*-2,3-epoxypropyl-*N*-phenyl)hydrazone (**3**)

The yield of **3** (amorphous substance) was 55%.  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ ) (ppm): 7.63 (s, 2H); 7.61–7.54 (m, 4H); 7.42–7.02 (m, 17H); 6.94 (t, 2H,  $J = 7.2$  Hz); 4.40–4.28 (dd, 2H, ( $\text{H}_A$ ),  $J_{AX} = 2.1$  Hz,  $J_{AB} = 16.5$  Hz); 4.02–3.90 (dd, 2H, ( $\text{H}_B$ ),  $J_{BX} = 4.2$  Hz); 3.26 (m, 2H); 2.84 (dd, 2H, ( $\text{H}_A$ ),  $J_{AX} = 4.2$  Hz,  $J_{AB} = 4.8$  Hz); 2.66–2.60 (dd, ( $\text{H}_B$ ),  $J_{BX} = 2.7$  Hz); 2.33 (s, 3H). IR spectrum (KBr, selected bonds),  $\nu$  ( $\text{cm}^{-1}$ ): 3025 (aromatic CH); 2992, 2917 (aliphatic CH); 939 (epoxy group); 825, 751, 692 (CH=CH of 1,4-disubstituted and monosubstituted benzene). Anal. Calcd for  $\text{C}_{39}\text{H}_{37}\text{N}_5\text{O}_2$  (%): C 77.08; H 6.14; N 11.52. Found (%): C 77.14; H 6.10; N 11.58.

### 2.2. Cross-linking experiments with **2** and trithiocyanuric acid

A 20 mg of diepoxide **2** and 4 mg of TTA (received from Aldrich) were dissolved in 0.4 ml of THF. Some catalyst was added with help of glass baton, dipped into triethylamine (TEA). Small layer samples were coated on Al, after this the samples were heated. Cross-linking in layer takes place in about 1 h at 80 °C.

A control sample was made without the catalyst. A 24 mg of diepoxide **2** and 5 mg of TTA were dissolved in 0.4 ml of THF and coated on Al. The layer sample was heated up to 120 °C. Solubility of the cross-linked layers and the control sample was tested.

### 2.3. Measurement

The  $^1\text{H}$  NMR spectra were taken on a Gemini-2000 (300 MHz) NMR spectrometer. The IR spectra were taken in

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