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Symmetrical azine-based polymers possessing 1-phenyl-1,2,3,4-tetrahydroquinoline moieties as materials for optoelectronics

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ABSTRACT

Glycidyl-terminated 3-hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline-6-carbaldehyde azine and its 4,4'-thiobisbenzenethiol, 2,5-dimercapto-1,3,4-thiadiazole, and 1,3-benzenedithiol copolymers were synthesized by multi-step synthetic route. The materials were examined by various techniques including differential scanning calorimetry, UV and fluorescence spectrometry as well as xerographic time of flight technique. The ionization potentials of these materials are in the range of 5.40–5.61 eV as determined by the electron photoemission method. The hole mobility, reaching 10^{-6} cm²/V s at the 10^{6} V/cm electric field, was observed in the polymer obtained in the polyaddition reaction of the above mentioned monomer with 4,4'-thiobisbenzenethiol.

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1. Introduction

Aromatic carbonyl compounds react easily with hydrazine forming hydrazones, which could condense with a second molecule of the carbonyl compound to yield an azine [1]. Due to fascinating physical and chemical properties, azines and their derivatives have been extensively applied in such areas as dyes [2-11], aggregationinduced emission enhancement or nonlinear optical fluorophores [12,13], biological [2,5,11,14–16], and pharmaceutical [17,18] applications. Some of the azines have been also investigated as liquid crystal compounds [19-23]. They have been studied for the possible application in the twisted-nematic displays [24]. Furthermore, there are many papers on polyazines as highly conjugated polymers in electronic, optoelectronic, and photonic applications [25-29]. Additionally, a number of papers dedicated to the polyazines obtained by oxidative polymerization of various monomers with chromophores connected via the azine linkage have been published, and some of these polymers demonstrate high photoefficienty [30,31].

Recently, we have reported a new class of monomers [32] and polymers [33–36] based upon hydrazone moieties. The monomers were obtained in the reaction of various bifunctional hydrazones with epichlorohydrin. The hydrazone containing monomers were

* Corresponding author. E-mail address: vytautas.getautis@ktu.lt (V. Getautis). employed in the polyaddition reaction with bifunctional nucleophilic linking agents in the presence of triethylamine (TEA) to yield the polymeric hole transporting materials (HTM). These HTM are soluble in common organic solvents such as THF, chloroform, dioxane, and exhibit hole drift mobility of 10^{-5} cm²/V s at strong electric field [37,38].

Generally, symmetrical azines (Fig. 1a) are crystalline materials which make them quite easy to purify by recrystallization. This fact and one-step synthesis procedures, usually with quantitative yield of the desired product, are two main advantages of the symmetrical azines. However, this crystallinity is the key limiting factor for applying various chromophores connected *via* azine linkage in the optoelectronic devices. Unsymmetrical azines (Fig. 1b) prepared from two different carbonyl compounds are more promising from this point of view, as the tendency to crystallize is significantly reduced; however, they are much more difficult to synthesize compared to the symmetrical analogues. 3-Hydroxy-1,2,3,4-tetrahydroquinoline possesses flexible aliphatic chain and reactive hydroxyl group, which can be exploited to further modify the molecule in order to further enhance the solubility and decrease tendency to crystallize. All these findings prompted us to synthesize new symmetrical azine based polymers, containing phenyl-1,2,3,4-tetrahydroquinoline moieties, which could be used as HTM in optoelectronic devices.

In the light of these findings, we designed a synthesis route to azine chromophore-containing monomers and polymers with



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Fig. 1. Chemical structure of symmetrical (a) and unsymmetrical (b) azines.

charge transporting ability. To the best of our knowledge, the charge drift mobility of the azine polymers has not been yet investigated. In this paper, we report the synthesis and the characterization of new photoconductive polymers containing symmetrical azine moieties obtained by polyaddition of glycidyl-terminated 3-hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline-6-carbaldehyde azine and aromatic dimercapto compounds.

2. Experimental

2.1. Materials

Hydrazine hydrate, 4,4-thiobisbenzenethiol (TBBT), 2,5-dimercapto-1,3,4-thiadiazole (DMTD), and 1,3-benzenedithiol (BDT) were purchased from Aldrich and used as received. 3-Hydroxy-1phenyl-1,2,3,4-tetrahydroquinoline (1), 3-acetyl-1-phenyl-1,2,3, 4-tetrahydroquinoline (2), and 3-acetyl-1-phenyl-1,2,3,4-tetrahydroquinoline-6-carbaldehyde (3) were synthesized according to procedures described previously [39]. 3-Hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline-6-carbaldehyde (4) was prepared according to the published procedure [40].

2.2. Synthesis

2.2.1. 1,2-Bis(3-hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline-6ylmethylene)azine (5)

Aldehyde **4** (9.5 g, 0.04 mol) was dissolved in 10 ml of hot THF. The solution was cooled to room temperature, hydrazine hydrate (1 ml, 0.02 mol) was added and the reaction mixture was refluxed for 1 h. The crystalline product formed during the reaction (TLC, THF:*n*-hexane = 1:4) was filtered off and washed with 2-propanol. Yield: 8 g (85%); mp: 224–226 °C (recrystallized from THF).

¹H NMR (300 MHz, DMSO- d_6 , δ , ppm): 8.45 (s, 2H, CH=N), 7.50– 7.17 (m, 14H, Ar), 6.54 (d, J = 8.6 Hz, 2H, 8-H of Ht), 5.12 (d, J = 3.9 Hz, 2H, OH), 4.21–4.10 (m, 2H, CH of Ht), 3.68 (dd, J_{AB} = 11.7 Hz, J_{AX} = 2.2 Hz, 2H, one of NCH₂ protons, H_A), 3.44 (dd, J_{BA} = 11.7 Hz, J_{BX} = 6.6 Hz, 2H, another of NCH₂ protons, H_B), 3.05 (dd, J_{AB} = 15.7 Hz, J_{AX} = 4.1 Hz, 2H, one of CH₂Ar protons, H_A), 2.76 (dd, J_{BA} = 15.7 Hz, J_{BX} = 7.2 Hz, 2H, another of CH₂Ar protons, H_B). IR selected bonds (KBr, v, cm⁻¹): 3600–3200 (OH), 3058, 3033 (aromatic CH), 2930, 2865 (aliphatic CH), 1606 (CH=N), 824, 795 (CH=CH of 1,2,4-trisubstituted benzene), 765, 701 (CH=CH of monosubstituted benzene). ¹³C NMR (75 MHz, DMSO- d_6 , δ , ppm): 159.78, 146.46, 146.08, 130.18, 129.68, 126.96, 125.50, 125.39, 124.89, 123.46, 121.61, 113.21, 66.96, 62.00, 56.72, 35.76, 25.08. ESI-MS (20 V, m/z,%): 503 [M + 1]⁺ (1 0 0). Anal. calcd for C₃₂H₃₀N₄O₂: C, 76.47; H, 6.02; N, 11.15. Found: C, 76.59; H, 5.91; N, 11.28.

2.2.2. 1,2-Bis(3-oxiranylmethoxy-1-phenyl-1,2,3,4tetrahydroquinoline-6-ylmethylene)azine (6)

A mixture of **5** (2.8 g, 0.0045 mol) and epichlorohydrin (25 ml, 0.3 mol) was stirred vigorously for 5 h at 35–40 °C. During the course of the reaction anhydrous Na_2SO_4 (3 g, 0.02 mol) and 85% powdered KOH (6.7 g, 0.1 mol) were added in six equal portions every hour with prior cooling of the reaction mixture to 30 °C. After termination of the reaction (TLC, THF:*n*-hexane = 1:4), the mixture was extracted with ethyl acetate, the organic layer was dried over

anhydrous magnesium sulfate and filtered off. Ethyl acetate and excess of epichlorohydrin were removed. The residue was dissolved in methanol:THF = 3:1 and crystals formed when kept at -5 °C. The crystalline product was filtered off and washed with diethyl ether. Yield: 2.0 g (59%); mp: 132–134 °C (recrystallized from ethyl acetate:2-propanol = 2:1).

¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.51 (s, 2H, CH=N), 7.58 (s, 2H, 5-H of Ht), 7.47-7.14 (m, 12H, Ar), 6.67, 6.66 (2 d, J = 8.6 Hz, 2H, diastereomeric 8-H of Ht), 4.14-4.01 (m, 2H, CH of Ht), 3.94-3.40 (m, 8H, NCH₂ and OCH₂), 3.27-3.09 (m, 4H, CH₂Ar), 3.05-2.90 (m, 2H, CH of epoxy gr.), 2.83-2.76 (m, 2H, one of CH2CH protons from epoxy gr., H_A), 2.61 (dd, J_{AB} = 4.7 Hz, J_{BX} = 2.7 Hz, 1H, H_B of one diastereomer of CH2CH from epoxy gr.), 2.56 (dd, $J_{A'B'}$ = 4.7 Hz, $J_{B'X'}$ = 2.4 Hz, 1H, $H_{B'}$ of other diastereomer of CH_2CH from epoxy gr.). IR selected bonds (KBr, v, cm⁻¹): 3060, 3032 (aromatic CH), 2943, 2864 (aliphatic CH); 1608 (CH=N), 1091 (C-O-C): 698 (CH=CH of monosubstituted benzene). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 160.74, 146.73, 146.62, 146.47, 146.40, 129.93, 129.80, 129.66, 127.99, 127.86, 125.54, 125.43, 125.08, 125.01, 124.38, 124.28, 121.08, 121.01, 114.38, 114.25, 71.52, 71.39, 69.43, 69.22, 54.09, 53.55, 50.97, 50.90, 44.32, 33.83, 33.52. ESI-MS (20 V, m/z,%): 615 $[M + 1]^+$ (95) Anal. calcd for C₃₈H₃₈N₄O₄: C, 74.25; H, 6.23; N, 9.11. Found: C, 74.37; H, 6.38; N. 8.92.

2.2.3. General procedure for synthesis of polymers P1-P3

The polymers **P1–P3** were prepared according to the general procedure described below: monomer **6** (1.3 mmol), corresponding dimercapto linking agent (1.3 mmol), and TEA (2.6 mmol) were refluxed in THF (10 ml) under argon atmosphere for 45 h (TLC, THF:*n*-hexane = 3:2). The reaction mixture was cooled to room temperature and filtered through the 3–4 cm layer of silica gel and the silica gel was washed with THF. Obtained solution was concentrated to 10–15 ml by evaporation and then poured into 20-fold excess of *n*-hexane with intensive stirring. The resulting precipitate was filtered off and washed repeatedly with *n*-hexane and dried under vacuum at 40 °C.

2.2.3.1. Poly[1,2-bis(3-oxiranylmethoxy-1-phenyl-1,2,3,4-tetrahydroquinoline-6-yl-methylene)azine-alt-4,4'-thiobisbenzenethiol]

(*P1*). Polymer **P1** was prepared according to the same procedure as described above, except that 1.3 mmol of 4,4'-thiobisbenzenethiol was used. Yield: 0.65 g (56%).

¹H NMR (300 MHz, CDCl₃, *δ*, ppm): 8.48 (s, 2H, CH=N), 7.53 (s, 2H, 5-H of Ht), 7.45–6.98 (m, 20H, Ar), 6.63 (d, *J* = 8.4 Hz, 2H, 8-H of Ht); 4.01–3.35 (m, 12H, NCH₂CH and OCH₂CH); 3.17–2.69 (m, 8H, CH₂Ar and SCH₂), 2.10–1.51 (m, 2H, OH). IR selected bonds (KBr, *ν*, cm⁻¹): 3600–3200 (OH), 3035 (aromatic CH), 2864 (aliphatic CH), 1608 (CH=N); 1268 (C–N), 1114 (C–O–C), 813, 698 (CH=CH of 1,4-disubstituted benzene, 1,2,4-trisubstituted benzenes and monosubstituted benzenes). ¹³C NMR (CDCl₃, 75 MHz, *δ*, ppm): 160.69, 146.59, 146.55, 146.41, 135.06, 133.24, 131.40, 129.97, 129.69, 127.92, 125.41, 125.34, 125.11, 124.20, 120.88, 120.83, 114.40, 114.34, 75.06, 71.36, 70.62, 70.48, 68.89, 53.55, 36.87, 33.40.

2.2.3.2. Poly[1,2-bis(3-oxiranylmethoxy-1-phenyl-1,2,3,4-tetrahydroquinoline-6-yl-methylene)azine-alt-2,5-dimercapto-1,3,4-thiadiazole] (P2). Polymer **P2** was prepared according to the same procedure as described above, except that 1.3 mmol of 2,5-dimercapto-1,3,4thiadiazole was used. Yield: 0.33 g (32%).

¹H NMR (300 MHz, DMSO, δ, ppm): 8.42 (s, 2H, CH=N), 7.60– 7.12 (m, 14H, Ar), 6.52 (d, 2H, J = 8.4 Hz, 8-H of Ht), 5.42–5.33 (m, 2H, OH), 4.21–2.72 (m, 20H, NCH₂CH, OCH₂CH, CH₂Ar and SCH₂). IR selected bonds (KBr, v, cm⁻¹): 3600–3200 (OH), 2969, 2868 (aliphatic CH), 1608 (CH=N), 1270 (C-N), 1112 (C-O-C), 699 (monosubstituted benzene).

2.2.3.3. Poly[1,2-bis(3-oxiranylmethoxy-1-phenyl-1,2,3,4-tetrahydroquinoline-6-yl-methylene)azine-alt-1,3-benzenedithiol] (P3). Polymer **P3** was prepared according to the same procedure as described above, except that 1.3 mmol of 1,3-benzenedithiol were used. Yield: 0.88 g (86%).

¹H NMR (300 MHz, CDCl₃, *δ*, ppm): 8.51 (s, 2H, CH=N), 7.56 (s, 2H, 5-H of Ht), 7.46–7.07 (m, 16H, Ar), 6.67 (d, *J* = 8.6 Hz, 2H, 8-H of Ht), 4.03–3.39 (m, 12H, NCH₂CH and OCH₂CH), 3.20–2.80 (m, 8H, CH₂Ar and SCH₂), 1.80–1.60 (m, 2H, OH). IR (KBr, *ν*, cm⁻¹): 3600–3200 (OH); 3057, 3036 (aromatic CH); 2897, 2864 (aliphatic CH); 1608 (CH=N); 1268 (C–N); 1114 (C–O–C); 698 (monosubstituted benzene). ¹³C NMR (CDCl₃, 75 MHz, *δ*, ppm): 160.74, 146.61, 146.42, 136.90, 129.98, 129.69, 129.34, 127.93, 126.52, 125.41, 125.35, 125.08, 124.22, 120.97, 120.92, 114.41, 114.37, 71.43, 71.40, 70.66, 70.50, 69.03, 68.98, 53.59, 36.74, 33.46.

2.3. Measurement

The ¹H NMR spectra were taken on a Varian Unity Inova (300 MHz for ¹H and 75 Hz for ¹³C) spectrometer. Elemental analyses were performed with an Exeter Analytical CE-440 Elemental Analyzer. The UV spectra were recorded on a PerkinElmer Lambda 35 UV/VIS spectrometer in THF. Solution (10^{-4} M) of investigated HTM and microcell with an internal width of 1 mm were used. IR-spectroscopy was performed on Perkin Elmer Spectrum BX II FT-IR System using KBr pellets. Fluorescence emission and excitation spectra were recorded with a Hitachi MPF-4 luminescence spectrometer in THF. Solution (10^{-4} M) of investigated HTM and microcell with an internal width of 1 cm were used. 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 . 10⁵, 10⁴ and 5000 nm) using THF as eluant. Polystyrene standards were used for column system calibration.

Simultaneous thermogravimetric analysis and differential scanning calorimetry (TGA–DSC) was performed with a Netzch STA 409 PC Luxx. Samples of 5–8 mg were heated in aluminium pans at a scan rate 10 K/min under a nitrogen flow. During the first heating the melting point was determined for the monomer. The glass transition temperatures (T_g) for all investigated compounds were determined during the second run.

The samples for the ionization potential measurement were prepared by dissolving materials in THF and were coated on Al plates pre-coated with ~0.5 μ m thick methylmethacrylate and methacrylic acid copolymer adhesive layer. The thickness of the transporting material layer was 0.5–1 μ m. The ionization potential (I_p) was measured by the photoemission in air method [41], similar to the one used in [42]. Usually, photoemission experiments are carried out in vacuum and high vacuum is one of the main requirements for these measurements. If vacuum is not high enough, the sample surface oxidation and gas adsorption are influencing the measurement results. In our case, however, the organic materials investigated are stable enough towards oxygen and the measurements may be carried out in the air.

The samples were illuminated with monochromatic light from the quartz monochromator with deuterium lamp. The power of the incident light beam was $(2-5) \cdot 10^{-8}$ W. The negative voltage of -300 V was supplied to the sample substrate. The counter-electrode with the 4.5×15 mm² slit for illumination was placed at 8 mm distance from the sample surface. The counter-electrode was connected to the input of the BK2–16 type electrometer, working in the open input regime, for the photocurrent measurement. The strong $(10^{-15}-10^{-12} \text{ A})$ photocurrent was flowing in the circuit under illumination. Photocurrent *I* is strongly dependent on the incident light photon energy *hv*. The $I^{0.5} = f(hv)$ dependence was plotted. Usually the dependence of photocurrent on incident light quanta energy is well described by the linear relationship between $I^{0.5}$ and *hv* near the threshold [42,43]. The linear part of this dependence was extrapolated to the *hv* axis and I_p value was determined as the photon energy at the interception point.

The hole drift mobility was measured by the XTOF technique [43–45]. The samples for mobility measurements were prepared from solutions in THF of neat HTM. The layer thickness was in the range of $1.5-2 \,\mu\text{m}$. The sample substrate was polyester film with a conductive Al layer. Positive corona charging created an electric field inside the HTM layer. Charge carriers were generated at the laver surface by illumination with pulses of a xenon flash (pulse duration 1 us, used UV filter). The laver surface potential decrease as a result of pulse illumination was up to 5–10% 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 in a 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. XTOF integral transients are measured with charge integrator connected to the capacitance probe.

3. Results and discussion

The key monomer 1,2-bis(3-oxiranylmethoxy-1-phenyl-1,2,3,4-tetrahydroquinolin-6-ylmethylene)azine (**6**) was synthesized according to the Scheme 1. 3-Hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline (**1**) was obtained by a one-pot reaction of diphenylamine with epichlorohydrin. In order to protect hydroxyl group, **1** was converted to the acetyl derivative **2**, which in turn was formylated and the hydroxyl group was deprotected to yield 3-hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline-6-carbaldehyde (**4**). The reaction between **4** and hydrazine hydrate yielded a symmetrical azine **5**, which was then alkylated with epichlorohydrin, and the glycidyl-terminated 3-hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline-6-carbaldehyde azine **6** was isolated.

In the ¹H NMR spectra (Fig. 2a) of **6**, the epoxy groups give a double set of signals of the AB part of an ABX system at 2.85–2.50 ppm, indicating that due to the presence of two stereogenic centers, the monomer was isolated as a mixture of diastereomers.

Finally, the symmetrical azine based polymers **P1–P3**, containing 1-phenyl-1,2,3,4-tetrahydroquinoline moieties, were synthesized by the nucleophilic oxirane ring opening reaction of monomer **6** with 4,4-thiobisbenzenethiol (TBBT), 2,5-dimercapto-1,3,4-thiadiazole (DMTD), or 1,3-benzenedithiol (BDT), respectively, in the presence of a catalyst TEA (Scheme 2).

Purity and structure of the synthesized polymers **P1–P3** were confirmed by IR, UV, and ¹H NMR spectroscopy. ¹H NMR spectra (Fig. 2b) show the characteristic signals associated with the resonance of the hydrogen atoms of phenyl-1,2,3,4-tetrahydroquinoline core and confirm the molecular structure. Additionally, some individual downfield peaks have been assigned to characteristic protons: a singlet of protons of CH=N group appears in the region of 8.51–8.42 ppm, as well as a singlet and a doublet of 5-H and 8-H of tetrahydroquinoline in the regions of 7.56–7.53 ppm and 6.67–6.52 ppm, respectively. In the FTIR spectra of the azine-based compounds the imine vibration at about 1606 cm⁻¹ was recorded (Fig. 3). Furthermore, IR and NMR analyses have indicated that polymers **P1–P3** do not possess thiol end groups as characteristic signals attributed to these groups are absent. The IR spectra exhibit



Scheme 1. Synthesis route to the symmetrical azine based monomer 6.



Fig. 2. ¹H NMR spectra (CDCl₃) of the monomer 6 (a) and polymer P3 (b).



Scheme 2. Synthesis route to the azine-based polymers P1-P3.



Fig. 3. FTIR absorption spectra of monomer 6 and polymer P2.

a broad absorption band in 3600–3200 cm⁻¹, which demonstrates strong hydrogen bonding in the target polymers **P1–P3**.

The average molecular weights and their distribution of the synthesized polymers **P1–P3** were detected by GPC and are presented in the Table 1. As seen from the GPC results, the relatively high molecular weight polymers **P1** and **P3** were obtained using TBBT and BDT as linking agents. On the other hand, low molecular weight of oligomer **P2** most likely could be explained by unfavorable conformation of resulting oligomeric chains, which, in turn, inhibit further reaction between these segments.

Thermal stability of the investigated compounds was examined by TGA under the nitrogen atmosphere. The data obtained is presented in Table 1. The 5% weight loss temperatures ($T_{dec-5\%}$) for polymers **PI–P3** are close to that obsorved for monomer **6** (314 °C) and are in the range of 305–310 °C. The thermal degradation of these compounds proceeds, apparently, by the breakage of azo bond of azine moiety. Formation of the glassy state of monomer **6** and azine-based **P1–P3** was confirmed by DSC analysis. These investigations (Fig. 4) have revealed that monomer **6** can exist both in crystalline and amorphous phase. The DSC first heating

Table 1		
Characteristics	of polymers	P1-P3.



Fig. 4. DSC first heating, cooling, and second heating curves for monomer 6.

curve of **6** reveals melting at 115 °C, no crystallization takes place during cooling, and only glass transition at 57 °C is registered during the second heating. The material remains in glassy state after melting, therefore, compound **6** can be considered as a molecular glass. Formation of the glassy state in azine-based polymers **P1**, **P2** and **P3** was observed at 114 °C, 120 °C and 94 °C, respectively (Table 1 and Fig. 5). Influence of varying flexible spacers and molecular weight is clearly noticeable. Although **P2** is just an olygomer, its T_g is similar to that of **P1**. On the other hand, **P3** and **P1** possess somewhat similar molecular weights, but their T_g differ by 20 °C. This difference could be attributed to more loose packing of the polymeric chains in case of **P3**, as *metha*-substituted linking agent BDT clearly introduces more structural disorder compared with more symmetrical *para*-substituted TBBT.

The UV absorption spectra of aldehyde **4**, monomer **6**, and target polymers **P1–P3** are presented in Fig. 6. The absorption spectrum of the **6** is batochromically (\approx 55 nm) and hyperchromically shifted with respect to the spectrum of aldehyde **4** as a consequence of the increased conjugated π -electron system of azinebased monomer **6**. On the other hand, difference in π -electron conjugation between monomer **6** and corresponding polymers is not significant (\approx 2 nm) what proves that conjugated π -electron

Compound	\overline{M}_n , (g mol ⁻¹)	\overline{M}_w , (g mol ⁻¹)	$\overline{M}_w/\overline{M}_w$	T_{g} (°C)	$T_{dec-5\%}$ (°C)	Reaction time (h)	Yield (%)	$I_{\rm p} ({\rm eV})$
P1	11,716	65,205	5.6	114	305	45	56	5.61
P2	5842	16,280	2.8	120	304	45	32	5.40
P3	12,768	38,658	3.0	94	310	45	86	5.42



Fig. 5. DSC second heating curves for polymers P1-P3.



Fig. 6. UV absorption and fluorescence spectra (λ_{ex} = 330 nm) of **4**, **6** and **P1–P3** in THF solutions.

system remains intact during polyaddition reaction. Moreover, the presence of the linking fragment TBBT in the molecule of polymer **P1** can be observed in 270 nm region of the UV spectrum due to the lone electron pairs of the sulfur atoms between phenyls.

The electron photoemission spectra of the films of polymers **P1–P3** are shown in Fig. 7 and Table 1. The I_p for **P1** is 5.6 eV, the I_p values for polymeric TM **P2** and **P3** are 5.4 and 5.42 eV, respectively. The I_p values of these compounds indicate that they are suitable for the application in electrographic photoreceptors, as it is widely known that holes are easily injected into the charge transport layer from the charge generation layer with I_p close to I_p



Fig. 7. Photoemission in air spectra of the polymers P1-P3.

of charge transport layer. The I_p values for charge transporting materials, including those widely used with pigments in electrophotographic photoreceptors, such as titanyl phthalocyanines, are in the range of 5.1–5.7 eV [46].

The important advantage of **P1–P3** is the lack of excimer forming sites in these polymers. Fig. 6 shows normalized fluorescence spectra of dilute THF solutions of azine-based polymers **P1–P3**. For comparison, the spectrum of a dilute solution of monomer **6** is presented. The spectra of **P1–P3** are almost identical to that of monomer **6** and only the structureless monomer fluorescence with a blue luminescence peaking at 460 nm is observed.

Clear, transparent, and homogeneous films of **P1** and **P3** were obtained by the casting technique, while in the case of **P2** the obtained film was mat. For the sample of **P1**, XTOF measurements have revealed that small charge transport is not Gaussian (*stochastic*), however well-defined transit time is seen on log–log plots (Fig. 8). The mobility field dependence is presented in Fig. 9. Investigated mobility μ may be well approximated by the formula

$$\mu = \mu_0 \exp(\alpha \sqrt{E}) \tag{1}$$

Here, μ_0 is the zero field mobility, α is Pool–Frenkel parameter, and *E* is electric field strength. Such mobility dependence is explainable by terms of the Borsenberger and Weiss [47] and Borsenberger et al. [48] disorder formalism.

Unfortunately, we were unable to measure the charge drift mobility of **P3** because of too dispersive charge carrier transport. However, XTOF integral transients (Fig. 10) indicate a rapid charge transfer of holes through the sample thickness at positive surface charging; practically all charge is transferred in \sim 0.02 s. It should



Fig. 8. XTOF transients for P1. Insert shows the one transient curve in linear plot.



Fig. 9. Field dependence of the hole drift mobility of P1.



Fig. 10. XTOF integral transients of P3.

be noted that the measured mobility of **P1** is high enough for many practical applications.

4. Conclusions

In conclusion, the symmetrical azine based polymers, obtained by the polyaddition reaction of glycidyl-terminated 3-hydroxy-1phenyl-1,2,3,4-tetrahydroquinoline-6-carbaldehyde azine with aromatic dimercapto compounds TBBT, DMTD, and BDT, were synthesized and their thermal, optical, and photoelectrical properties were studied. It is evident that structure of the linking fragments influences the speed of the polyaddition reaction as well as packing of the polymeric chains, which in turn, affect the glass transition temperature. Additionally, presence of the numerous aliphatic fragments significantly reduces the tendency of these symmetrical azines to crystallize. This fact as well as good ionization potential and adequate charge drift mobility makes them suitable for application as hole transporting materials in optoelectronic devices.

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