Soluble Mainchain Polyoxadiazoles as Electron Transport Materials

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In recent years much progress has been made toward the development of polymer based Light Emission Diodes (LEDs).^{1,2} For such LEDs polymers are required that are either selective hole or electron conductor. Mainchain polyoxadiazoles have been proposed as electron transport materials,^{3–8} but often suffer from low solubility in organic solvent. We therefore started to study polyoxadiazoles containing an indane ring in the backbone. The indane ring is bulky and leads to a twisting of the structure. Both factors are well known to increase the solubility of polymers. The polymers are obtained by reaction of 1,1,3-trimethyl-3-phenylindane-4',5-dicarboxylic acid **1** with aromatic hydrazides **2** under acidic conditions similar to those described by Ueda *et al.* (Figure 1).^{9,10}

Mulder *et al.* reported a polyoxadiazole obtained by condensation of **1** with hydrazine for gas separation membranes.^{11,12} That polymer has much smaller π systems and shows therefore not sufficient electron affinity and electron mobility for application as electron transport material. Polymers with the structure shown in Figure 1 are to the best of our knowledge new.

EXPERIMENTAL

Materials and Apparatus

Polymers were characterized by glass transition temperature T_g (using DuPont 2000), the temperature of 5% weight loss T_{d5} (using Seiko SCC-5200, heating rate 10 °C min⁻¹ under nitrogen), ¹H NMR spectroscopy (using JEOL JNM-EX-90), IR-spectroscopy (using JEOL JIR-5500), fluorescence spectroscopy (of polymer films using JASCO F 5-777) and inherent viscosity η_{inh} (at 30 °C, 50 mg mL⁻¹ in 97% H₂SO₄). All starting materials are commercially available. With the exception of the methane-

sulfonic acid, they were used as received. Methanesulfonic acid was distilled under reduced pressure and stored under argon.

Semi-empirical calculations of the repeating unit were made with MOPAC 6.0 using AM1 hamiltonians.¹³ Only ground-state calculations have been performed.

Typical Procedure for the Preparation of Polyoxadiazoles

3 g Phosphorus pentoxide were dissolved at 100 °C in 20 mL of a mixture of methanesulfonic acid and methanesulfonic acid anhydride (about 1 : 1 weight ratio) under argon. The temperature was lowered to 70 °C, 1.59 g (8.20 mmol) terephthalic dihydrazide **2b** and 2.66 g (8.20 mmol) 1,1,3-trimethyl-3-phenylindane-4',5-dicarboxylic acid **1** were added and the mixture stirred for 3 h at 70 °C. The resulting viscous solution was poured into about 200 mL ice/water and the obtained polymer washed with water, aqueous NaHCO₃, water and methanol and dried under reduced pressure, yielding 3.3 g (90%) of a slightly yellow polymer **3b** with an inherent viscosity of 0.64 dL g⁻¹. Samples used for evaluation in LEDs have been redissolved in tetrachloroethane and precipitated in methanol.

LED Fabrication

LEDs have been prepared by first spincoating of the sulfonium precursor polymer of poly(phenylene vinylene) (precursor PPV, 50 nm thickness) onto cleaned indium tin oxide (ITO) coated glass, thermal conversion of the polymer to PPV according to a published procedure,¹⁴ followed by casting the polyoxadiazole (50 nm thickness) and evaporation of aluminum on top. The LEDs have not been encapsulated and been operated under air.

Figure 1. Preparation of polyoxadiazoles.

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RESULTS AND DISCUSSION

The procedure for the one step polymerization of hydrazides with acids in a mixture of methanesulfonic acid and phosphorous pentoxide reported by Ueda^{9,10} has been modified. We found that the addition of methanesulfonic anhydride allows to reduce reaction time and temperature. Shorter reaction time and lower temperature should help to avoid possible degradation reactions during the polymerization, that would lead to inferior, darkened polymers. Consequently, our polymers were usually almost colorless. Complete cyclization from the intermediate polyhydrazide to the polyoxadiazole was confirmed by IR spectroscopy (absence of bands due to the hydrazide group at 3250 and 1650 cm⁻¹) and TGA (no weight loss below 300 °C).

The polymers show glass transition temperatures T_g of more than 300 °C and high decomposition temperatures T_{d5} of more than 440 °C (Table I), as expected for polyoxadiazoles. The thermal properties do not depend significantly on the type of aromatic group Ar in the backbone. Selfstanding films can be prepared that exhibit blue fluorescence. With the exception of the naphthalene containing polymer, all polymers are soluble in organic solvents such as *N*-methylpyrrolidone (NMP), chloroform or tetrachloroethane. The solubility reflects the stiffness of the polymer backbone. The *m*-linkage in the *m*-phenylene and 2,6-pyridine polymer **3c** and **3d** leads to a twisting of the backbone and therefore a much better solubility than the corresponding *p*-phenylene polymer **3b**. The large aromatic system of the naphthalene polymer **3a** is reducing the solubility so far, that the polymer is no longer soluble in the tested organic solvents.

Table I. Properties of homopolymers **3a–d**

Polymer	$T_g/^\circ\text{C}$	$T_{d5}/^\circ\text{C}$	$\eta/\text{dL g}^{-1}$	λ_{fl}/nm^a	NMP ^b	CHCl ₃ ^b	C ₂ H ₂ Cl ₄ ^b
3a	353	456	0.37	436	–	–	o
3b	336	443	0.64	418	o	–	+
3c	318	459	1.11	380	+	+	+
3d	332	442	0.39	383	+	+	+

^a Fluorescence maximum, upon excitation at 250 nm. ^b +: > 5% soluble, o: partial soluble, –: insoluble.

The fluorescence emission of the *m*-phenylene and 2,6-pyridine polymer **3c** and **3d** (about 380 nm) polymers are at significantly smaller wavelength than that of the *p*-phenylene polymer **3b** (418 nm) due to the higher resonance stabilization of the latter. The naphthalene polymer **3a** shows an even higher emission wavelength (436 nm) due to the increase of the size of the π -system. The emission is in this case almost completely in the visible region.

Copolymers have been prepared by reaction of the acid **1** with two types of hydrazides (**2a–d**), as well as with hydrazides and hydrazine. For example, the reaction of **1** with naphthalene-2,6-dicarboxylic acid dihydrazide **2a** and hydrazine (molar ratio: 1 : 0.5 : 0.5) yields a polymer that shows similar optical and thermal properties as the homopolymer **3a**, but significantly improved solubility. This copolymer is readily soluble in NMP, chloroform and tetrachloroethane, whereas the homopolymer is only partially soluble in tetrachloroethane and insoluble in NMP and chloroform (first entry in Table I).

Further development of such polymers would be much faster, if the properties of the polymers would be “predictable”. Semi-empirical calculations are an easy and

Figure 2. Correlation between fluorescence wavelength λ and calculated inverse HOMO-LUMO gap $1/E$ ($\lambda = 5831/E - 367$, $r = 0.948$; for labels see Figure 3).

Figure 3. Polymers studied by fluorescence spectroscopy.

fast tool to achieve such predictions. The geometry of the oxadiazole ring is known to be calculated systematically inaccurate (N–N bond too short, C–N too long)¹⁵ using AM1 and other semi-empirical parameter sets such as PM3 and MNDO, however, such systematic effects should cancel out if correlation between experimental and calculated values are used for “normalization”. For the calculation of frontier orbitals it was sufficient to calculate only the repeating unit, since these orbitals are dominated by π states and the indane ring is interrupting the π -conjugation along the back bone. In order to broaden the data set, we also prepared polyoxadiazoles containing ether and hexafluoroisopropylidene units in the back-bone (structures shown Figure 3). A plot of the fluorescence emission wavelength *versus* the inverse value of the calculated HOMO-LUMO gap yields indeed a reasonable linear correlation (Figure 2). A similar linear correlation (Figure 4) has been found between the calculated and experimental LUMO energy of oxadiazoles^{16,17} and polyoxadiazoles¹⁸ (Figure 5). Experimental values taken from the literature^{16–18} are based on electrochemical measurements. The LUMO energy level is

Figure 4. Plot of experimental *vs.* calculated LUMO energy for a variety of oxadiazoles and polyoxadiazoles (Exp = 1.01 * Calc – 1.39, $r = 0.974$, experimental data from ref 16–18).

an important factor for the ease of electron injection from the cathode into electron transporting material, and is therefore significantly influencing the driving voltage of the LED. For the application of polymer LEDs, a low driving voltage is a vital requirement.

Although not very accurate, correlation such as those shown in Figures 2 and 4 can be used as an easy and fast guidance for the optimization of the electronic properties of polyoxadiazoles.

Preliminary tests as electron transport materials have been made with bilayer LEDs using poly(phenylene vinylene) (PPV) as hole transport material, indium tin oxide (ITO) coated glass as transparent anode and aluminum as cathode. In such an LED holes are injected from the ITO into the PPV, and electrons from the aluminum into the polyoxadiazole. Holes and electrons combine at the polymer-polymer interface under emission of light. In our case the visible green emission is derived from the PPV. Using **3b** as electron transport material a maximum luminance of about 200 cd m^{-2} at 29 V with a maximum efficiency of 0.3 cd A^{-1} (at 18 cd m^{-2}) was achieved (Figure 6), compared to values below 5 cd m^{-2}

Figure 6. Typical example for the current-voltage and brightness/voltage of an LED based on **3b** [ITO/PPV (50 nm)/**3b** (50 nm)/Al].

Figure 5. Structure of oxadiazoles with experimentally determined LUMO energy.^{16–18}

for the maximum luminance and $10^{-2} - 10^{-3} \text{ cd A}^{-1}$ for maximum efficiency typically obtained without an electron transport layer.

The new soluble polyoxadiazoles are obviously good candidates as electron transporting materials in polymer LEDs.

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