Polymethacrylates with Pendant Oxadiazole Units Synthesis and Application in Organic LEDs

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ABSTRACT: In this paper we report an effective synthesis and the characterization of novel 1,3,4-oxadiazole monomers via tetrazole intermediates and their polymerization to side group polymers with laterally fixed charge transport units. The use of these polymers as electron transport layer in light emitting diodes (LED) together with poly (phenylene vinylene) (PPV) leads to improved device performance. The light intensity of our LEDs was increased by a factor of 100 compared to a PPV monolayer diode to 300 Cd/m^2 at 30 V. This corresponds to an external quantum yield of 0.1% using a silver electrode, as cathode.

1. Introduction

Since the discovery of electroluminescence (EL) in conjugated polymers a lot of efforts have been made to improve the efficiency of polymer light emitting diodes (LEDs). Typical LEDs fabricated from a single layer of the conjugated polymer poly(phenylene vinylene) (PPV) exhibit quantum yields of 0.001% with an Al cathode.[1]

Several ways to enhance the quantum efficiency in polymer LEDs are known. The first one is the use of low work function metals like Ca or Mg for electron injection. This leads to a tenfold increase of the efficiency in the case of a Ca-electrode.[2] The main disadvantage of this approach is the inherent instability of Ca-electrodes toward moisture.

Another possibility is to introduce an additional organic layer that acts as electron transport material, because hole transport is strongly favored compared to electrons in PPV. Such multilayer devices which have first been realized by Tang and VanSlyke in 1987 were a major breakthrough in organic electroluminescence.[3] Such multilayer LEDs were prepared by subsequent vacuum deposition of different low molar mass compounds. Each layer is responsible for another process, like charge carrier injection, transport, and emission.[4]

The low molar mass materials usually form amorphous films after vacuum deposition but have a strong tendency to recrystallize due to their low glass transition temperature. In addition diffusion between adjacent layers may occur during LED operation. These points are thought to be responsible for the limited lifetime of many organic LEDs .

Another method for the preparation of electron transport layers is the use of guest host systems in which low molar mass compounds are embedded in a polymer matrix, e.g., poly(methyl methacrylate). Such a system with 2-(biphenyl)-5-(*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) as electron transporting material was used to enhance the quantum yield of PPV-LEDs.[5a,b] Nevertheless the concentration of the transporting molecules in the polymer host is limited due to recrystallization of the guest molecules.

Recently a number of starburst compounds that form stable glasses have been reported.[6] But the choice of starburst molecules which act as electron transport materials is still rather small.[7a−c]

Therefore polymers in which the active units are covalently bound in the main chain or as side groups are excellent candidates to overcome the above mentioned difficulties and to achieve stable electron transport materials.

Stimulated by the work of Tsutsui and Saito on multilayer devices in the beginning of the 90's, we designed polymethacrylates with laterally fixed oxadiazole units. Up to now, only a few oxadiazole side group polymers and their use in polymer LEDs have been reported.[8a−c]

Recently the synthesis of some poly(methacrylates) with oxadiazole units has been described.[8a] The unsymmetrical monomers were prepared in an eight step reaction and subsequently polymerized to homopolymers with end-on fixed oxadiazole units.

In this paper we report an effective synthesis of novel side group polymers with laterally fixed 1,3,4-oxadiazole units and their application in bilayer LEDs with PPV.

2. Polymer Synthesis

The synthesis of the methacrylate monomers is outlined in Scheme 1. The central part of the monomers, 5-acetoxyisophthaloyl chloride, is prepared from 5-hydroxyisophthalic acid by protecting the hydroxy group with acetic anhydride and subsequent transformation to the acid chloride with $SOCl_2$.

The common route to oxadiazoles is the ring closure of bishydrazides with dehydrating agents like phosphorous oxychloride.[9] We used a different method: the reaction of the acid chloride **2** with substituted tetrazoles **3a**−**c** leads to the oxadiazoles **4a**−**c** by intramolecular ring transformation.[10]

The tetrazole intermediates **3a**−**c** which allow the facile introduction of a wide range of substituents were synthesized from the corresponding nitriles with sodium azide.[10] The tetrazole route has two major advantages compared to the ring closure with $POCl_3$. The first one is the high yield and the second is the facile workup

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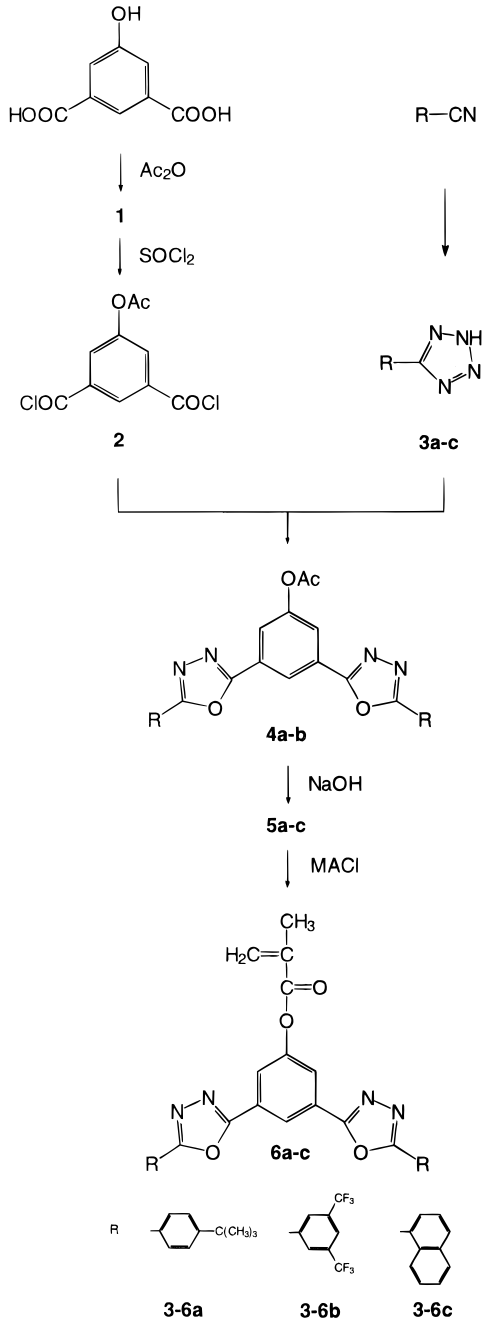
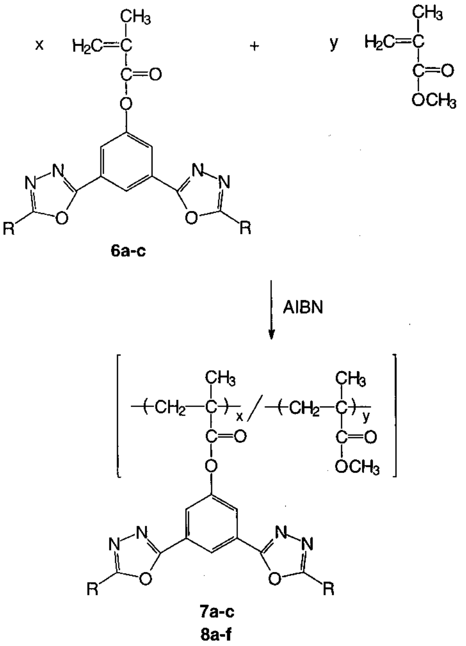
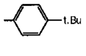
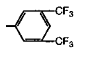
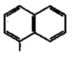
Scheme 1. Synthesis of 1,3,4-Oxadiazole Methacrylates with Different Substituents



Scheme 2. Synthesis and Composition of the Polymethacrylates 7a–c and 8a–f with Oxadiazole Side Groups



	6a (%) 	6b (%) 	6c (%) 	MMA (%)
7a	100	0	0	0
7b	0	100	0	0
7c	0	0	100	0
8a	0	75	0	25
8b	0	50	0	50
8c	0	25	0	75
8d	25	75	0	0
8e	75	25	0	0
8f	25	0	75	0

procedure which leads to pure oxadiazole derivatives without any chromatographic step.

The next steps involve the cleavage of the acetyl group and subsequent esterification with methacryloyl chloride to the methacrylates **6a**–**c**.

The methacrylate monomers were polymerized by free radical polymerization in chlorobenzene with AIBN as initiator. Polymer **7a** with *tert*-butyl substituents kept in solution during the polymerization. Polymer **7a** is well soluble in $CHCl_3$ and in THF. In contrast, homopolymer **7b** with trifluoromethyl groups precipitated during polymerization and is poorly soluble in THF and insoluble in $CHCl_3$.

In order to obtain processable polymers with trifluoromethyl substituents two possibilities exist. The copolymerization with methylmethacrylate (MMA) leads to polymers **8a**–**c**, which are soluble in $CHCl_3$. A more elegant method is the incorporation of the well-soluble monomer **6a** with *tert*-butyl groups. This leads to soluble copolymers **8d**–**f**, which are fully substituted with oxadiazole units.

All polymer structures were confirmed by NMR and FTIR spectroscopy.

3. Properties

In most cases, high molecular weight polymers are obtained in the free radical polymerization of the methacrylates **6a**–**c**. The molecular weights (M_n) were determined by gel permetation chromatography (GPC) and are listed in Table 1. The M_n values are in the range 9 000–62 000. Polymer **7a** has the highest M_w value of 490 000 and exhibits a broad weight distribution, which is typical for most of the polymers.

The thermal properties of the polymethacrylates were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). All polymers are amorphous and have high glass transition temperatures (Table 1). The homopolymers with oxadiazole groups (**7a**–**c**) and the copolymers of different oxadiazole methacrylates exhibit T_gs between 185 and 210 °C. This is attributed to the bulky, laterally fixed oxadiazole side groups. The incorporation of flexible MMA units leads to a decrease of the T_g. So the glass transition

Table 1. Molecular Weights and Thermal and Optical Properties of the Oxadiazole Polymers

polymer	M_n,[a] g/mol	T_g,[b] °C	$T_{-5\%}$ decomp,[c] °C	ABS,[d] nm	PL,[d] nm
7a	47 000	208	372	288	377
7b	35 000[e]	185	350	284	365
7c	18 000	198	387	333	418
8a	9 000	181	333	278	362
8b	62 000	177	341	278	360
8c	24 000	160	304	278	362
8d	16 000[e]	187	341	286	368
8e	23 000	204	354	281	368
8f	23 000	209	382	331	425

[a] Determined by GPC, $CHCl_3$, or THF. [b] Glass transition temperature determined by DSC, 20 °C/min. [c] Thermogravimetric analysis, N_2, 10 °C/min. [d] Film on quartz substrate, absorption (ABS) and photoluminescence (PL). [e] Polystyrene standards.

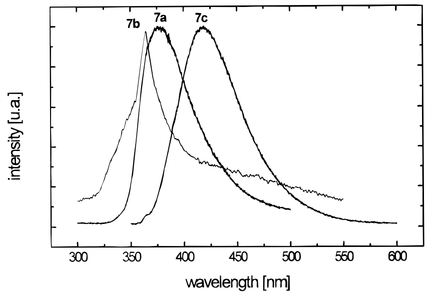


Figure 1. Normalized photoluminescence spectra of the homopolymers **7a**−**c**.

temperature drops to 160 °C for polymer **8c** with the highest amount of MMA. No polymer sample showed any evidence for crystallization in the DSC experiment.

TGA measurements reveal that the 5% weight loss values of the homopolymers are between 350 °C for polymer **7b** with trifluoromethyl groups and 387 °C for polymer **7c** with naphthyl substituents. The incorporation of MMA units decreases the decomposition temperatures to 304 °C for polymer **8c**. The copolymers **8d**−**f** with two oxadiazole monomers have decomposition temperatures from 341 °C for polymer **8d** to 382 °C for polymer **8f** with naphthyl groups (Table 1).

The absorbance maxima of the polymers are between 278 and 288 nm in the solid state. Substitution of the phenyl group by a naphthyl group leads to a bathochromic shift of the maximum to 333 nm. The same trend is observed in the fluorescence experiment, which is shown in Figure 1. The polymers with phenyl substituents emit in the UV region with maxima at about 370 nm, whereas the polymers **7c** and **8f** exhibit strong blue fluorescence with a maxima at 418 and 425 nm (Table 1).

4. Application in Organic Light Emitting Diodes

In order to test the polymers in LED applications, different bilayer devices with PPV as hole transport and emitting layer and the oxadiazole polymers as electron transport layer have been fabricated. For that purpose a thin layer of PPV precursor was cast from solution onto a pattered indium tin oxide (ITO) coated glass substrate. This film was converted to PPV by annealing at 160 °C in an argon atmosphere for 2 h. Oxadiazole polymer films were spin coated from chloroform or THF solution (0.25 wt %) on top of the PPV layer to give a transparent film. A silver electrode was vacuum deposited at pressures below 10^{-6} mbar.

LEDs were prepared with a PPV layer thickness of 200 nm and oxadiazole polymer films of 50 nm on top.

Table 2. Typical External Quantum Yields and Threshold Voltages of Monolayer and Heterolayer LEDs

device configuration[a]	η_{ex}, %	threshold voltage for EL, V
ITO/PPV/Ag	0.0001	5.0
ITO/PPV/**7a**/Ag	0.05	8.5
ITO/PPV/**7c**/Ag	0.04	8.0
ITO/PPV/**8e**/Ag	0.10	8.5
ITO/PPV/**8f**/Ag	0.10	6.5

[a] Layer thickness: 200-nm PPV and 50-nm oxadiazole polymers **7a**, **7c**, **8e**, and **8f**.

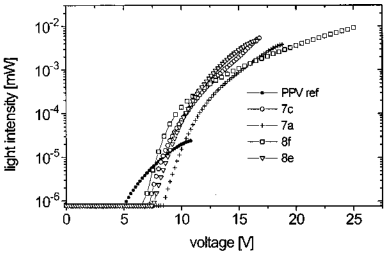


Figure 2. Plot of light intensities vs bias between monolayer and heterolayer devices.

The active area of the devices was 25 mm^2. To enable a direct comparison of the experimental data the devices were prepared under identical conditions and a PPV monolayer LED was made for comparison. All measurements were carried out under ambient conditions.

The current−voltage (I−V) characteristics and light intensities were simultaneously measured with a Keithley 237 source measure unit and a Bentham silicon photodiode (DH-Si) in a calibrated integrating sphere. The experimental setup for the measurements of the light intensities has a detection limit of 8×10^{-7} mW. This corresponds for the emission spectrum of PPV to a brightness of 3×10^{-3} Cd/m^2.

The brightness normal to the film plane was determined with a Minolta chroma meter CS-100. Due to the viewing angle dependence of the emitted light intensities the values measured by the Minolta chroma meter are higher than those obtained with the integrating sphere.

Bilayer devices with PPV and the homopolymers **7a**−**c** and copolymers **8d,f** were prepared to investigate the oxadiazole polymers as electron transporting materials (ETL). The external quantum efficiencies η_{ex} and typical threshold voltages for EL of the monolayer and bilayer diodes are summarized in Table 2. In comparison to the monolayer LEDs the heterolayer structures exhibit an enhanced external quantum efficiency accompanied by a slight increase of the onset voltage.

The EL intensity as a function of bias is shown in Figure 2. The PPV monolayer (200 nm) reference LED starts to emit light at a voltage of 5 V, which is slightly higher compared to an Al reference diode.[1]

The threshold voltages of the heterolayer devices were between 6.5 and 8.5 V (PPV monolayer: 5 V), which corresponds to a field between 2.4 and 3.2×10^5 V/cm.

The electroluminescence characteristics of heterolayer devices exhibit a sharper rise than the monolayer reference diode, indicating enhanced electron injection. This leads to increased external efficiencies which are between 0.04% (homopolymer **7c**) and 0.1% (copolymer **8f**). An increase of light intensities by more than 2 orders of magnitude was achieved compared to PPV monolayer LEDs. Our best heterolayer diode with copolymer **8f** as ETL has a brightness of 300 cd/m^2 at

30 V. These data are to our knowledge the best values for bilayer LEDs made from PPV and oxadiazole side group polymers.[8a,b]

All LEDs were prepared and tested under ambient conditions. A comparison between bilayer diodes with the oxadiazole polymer **7a** and diodes with an evaporated layer of a corresponding oxadiazole model compound[8c] showed that the polymer LEDs exhibit lifetimes of 30 h, whereas the LEDs with the evaporated electron transport layer decomposed within minutes.

Nevertheless these experiments are only of priliminary nature since it is well-known that LEDs have to be manufacturated and chiefly operated under inert conditions in order to obtain long lifetimes.

Another important question is the stability of the oxadiazole itself. We have started to investigate the stability of a number of low molar mass oxadiazoles and oxadiazole polymers. These measurements include thermostability and photostability, which has been tested by irradiation under ambient conditions and in different atmospheres, as well as investigations of the electrochemical stability. The results of these investigations show that all of the oxadiazole compounds exhibit sufficient thermal stability. In the absence of oxygen the oxadiazole compounds are photostable. The weak point seems to be a limited electrochemical stability, since a number of oxadiazole model compounds show an irreversible reduction in cyclic voltammetry experiments.[11]

5. Experimental Section

5-Acetoxyisophthalic Acid (1). 5-Hydroxyisophthalic acid, 15.18 g (83.35 mmol), is dissolved in 50 mL of acetic anhydride and 10 drops of concentrated H_2SO_4 are added. After refluxing for 5 h, the solution is allowed to cool to room temperature and is poured into 500 mL of water. The product is filtered off and purified by recrystallization from a water/acetone mixture (9/1).

Yield: 11.74 g (63%); T_m = 230−232 °C. IR (KBr): 3082; 2991; 1774 (CO_2CH_3); 1700 (COOH); 1280; 1212 cm^{-1}. ^1H NMR (DMSO-d_6): 2.30 (COC**H**$_3$, s, 3 H); 7.90 (C_{Ar}**H**, s, 2 H); 8.35 ppm (C_{Ar}**H**, s, 1 H).

5-Acetoxyisophthaloyl Chloride (2). 5-Acetoxyisophthalic acid, 6.4 g (26.93 mmol), and 75 mL of thionyl chloride are refluxed under argon for 4 h. The excess of $SOCl_2$ is evaporated and the residue is purified by recrystallization from dry hexane.

Yield: 3.34 g (52%). IR (KBr): 3090; 1771 (CO_2CH_3); 1764 (COCl); 1282; 1190 cm^{-1}. ^1H NMR ($CDCl_3$): 2.35 (COC**H**$_3$, s, 3 H); 8.15 (C_{Ar}**H**, s, 2 H); 8.70 ppm (C_{Ar}**H**, s, 1 H).

4-*tert*-Butylphenyltetrazole (3a).[12] 4-*tert*-Butyl benzonitrile, 5.00 g (31.40 mmol), 2.52 g (47.10 mmol) of ammonium chloride, and 3.06 g (47.10 mmol) of sodium azide in 50 mL of dry DMF are stirred overnight at a 100 °C in argon atmosphere. After cooling, the reaction mixture is poured into 500 mL of water and subsequently acidified with dilute HCl. The white precipitate is filtered off, washed with water, and dried over P_2O_5 .

Yield: 5.58 g (88%); T_m = 186−192 °C. IR (KBr): 3076 (NH); 2963; 2867; 2740; 2651; 1629; 1438; 835 cm^{-1}. ^1H NMR (DMSO-d_6): 1.75 (C(C**H**$_3$)$_3$, s, 9 H); 8.05 (C_{Ar}**H**, d, 2 H); 8.40 ppm (C_{Ar}**H**, d, 2 H).

3,5-Bistrifluoromethylphenyltetrazole (3b) was prepared from 3,5-bistrifluoromethylbenzonitrile and sodium azide in analogy to **3a**.

Yield: 94%; T_m= 160−166 °C. IR (KBr): 3073 (NH); 2921; 1628; 1562; 1279; 1140 cm^{-1}. ^1H NMR ($CDCl_3$): 8.40 (C_{Ar}**H**, s, 1 H); 8.60 ppm (C_{Ar}**H**, s, 2 H).

1-Napthyltetrazole (3c). 1-Napthonitrile, 5.16 g (33.70 mmol), 2.81 g (65.80 mmol) of lithium chloride, and 4.29 g (65.90 mmol) of sodium azide in 50 mL of 2-methoxyethanol are refluxed for 7 days in argon atmosphere. After cooling, 150 mL of aqueous sodium hydroxide solution are added to the reaction mixture. The filtered solution is acidified with dilute HCl and the white precipitate is filtered off, washed with water, and dried over P_2O_5.

Yield: 4.30 g (65%); T_m= 184−188 °C. IR (KBr): 3073 (NH); 2600; 1831; 1588; 1569; 1512; 1052; 773 cm^{-1}. ^1H NMR (DMSO-d_6): 7.60−7.65 (C_{Ar}**H**, m, 3 H); 7.95 (C_{Ar}**H**, d, 1 H); 8.05−8.10 (C_{Ar}**H**, m, 1 H); 8.20 (C_{Ar}**H**, d, 1 H); 8.50−8.60 ppm (C_{Ar}**H**, m, 1 H).

3,5-Bis[5-(4-*tert*-butylphenyl)-2-oxadiazolyl]phenyl Acetate (4a). 5-Acetoxyisophthaloyl chloride (**2**), 1.79 g (6.86 mmol), and 2.78 g (13.72 mmol) of 4-*tert*-butylphenyltetrazole (**3a**) are dissolved in 40 mL of dry pyridine. After refluxing for 2 h under argon atmosphere, the solution is cooled down and poured into a mixture of 350 mL of water and 50 mL of concentrated HCl. The precipitate is filtered off, washed with water, and dried over P_2O_5.

Yield: 2.57 g (78%); T_m = 179−182 °C. IR (KBr): 2962; 1773 (CO_2CH_3); 1616 (oxa); 1548; 1495; 1197; 842 cm^{-1}. ^1H NMR ($CDCl_3$): 1.35 (C(C**H**$_3$)$_3$, s, 18 H); 2.40 (COC**H**$_3$, s, 3 H); 7.55 (C_{Ar}**H**, d, 4 H); 8.05 (C_{Ar}**H**, s, 2 H); 8.15 (C_{Ar}**H**, d, 4 H); 8.75 ppm (C_{Ar}**H**, s, 1 H).

3,5-Bis[5-(3,5-bistrifluoromethylphenyl)-2-oxadiazolyl]phenyl Acetate (4b). 5-Acetoxyisophthaloyl chloride, 1.87 g (7.17 mmol), and 4.05 g (14.35 mmol) of 3,5-bistrifluoromethylphenyltetrazole (**3b**) are suspended in 80 mL of xylene. The reaction mixture is refluxed for 8 h with a slight argon current to remove the HCl gas. The solution was cooled and the precipitated product filtered off and dried.

Yield: 4.59 g (92%); T_m = 240−243 °C. IR (KBr): 1767 (CO_2CH_3); 1548; 1280; 1185; 1129 cm^{-1}. ^1H NMR (DMSO-d_6): 2.35 (COC**H**$_3$, s, 3 H); 8.20 (C_{Ar}**H**, s, 2 H); 8.30 (C_{Ar}**H**, s, 2 H); 8.75 (C_{Ar}**H**, s, 4 H); 8.90 ppm (C_{Ar}**H**, s, 1 H).

3,5-Bis[5-(4-*tert*-butylphenyl)-2-oxadiazolyl]phenol (5a). 4a, 3.29 g (6.13 mmol), is dissolved in 130 mL of THF and 368 mg (9.20 mmol) NaOH dissolved in 5 mL of water are added. After refluxing for 1 h the reaction mixture is cooled and acidified with concentrated HCl. The solvent is evaporated and 100 mL of water are added to the crude product. After stirring for 1 h, the white precipitate is filtered off, washed with water, and dried.

Yield: 2.98 g (98%); T_m = >300 °C. IR (KBr): 3423 (OH); 2964; 1616 (oxa); 1552; 1496; 842 cm^{-1}. ^1H NMR (THF-d_8): 1.35 (C(C**H**$_3$)$_3$, s, 18 H); 7.60 (C_{Ar}**H**, d, 4 H); 7.75 (C_{Ar}**H**, s, 2 H); 8.10 (C_{Ar}**H**, d, 4 H); 8.30 (C_{Ar}**H**, s, 1 H); 9.40 ppm (O**H**, s, 1 H).

3,5-Bis[5-(3,5-bistrifluoromethylphenyl)-2-oxadiazolyl]phenol (5b) was prepared in analogy to **5a**. Yield: 94%; T_m = >300 °C. IR (KBr): 3500−3000 (OH); 1558; 1387; 1280; 1180; 1139; 907 cm^{-1}. ^1H NMR (THF-d_8): 7.85 (C_{Ar}**H**, s, 2 H); 8.30 (C_{Ar}**H**, s, 2 H); 8.45 (C_{Ar}**H**, s, 4 H); 8.75 (C_{Ar}**H**, s, 1 H); 10.65 ppm (O**H**, s, 1 H).

3,5-Bis(5-naphthyl-2-oxadiazolyl)phenol (5c). 5-Acetoxyisophthaloyl chloride, 1.00 g (3.83 mmol), and 1.46 g (7.66 mmol) of 1-naphthyltetrazole (**3c**) are suspended in 30 mL of xylene. The reaction mixture is refluxed for 20 h with a slight argon current to remove the HCl gas. The solution is cooled and the precipitate filtered off. The product is stirred in aqueous sodium hydroxide solution for 2 h to yield the phenol **5c** directly. It is further purified by recrystallization from DMF/water (7/1).

Yield: 1.20 g (65%); T_m = >300 °C. IR (KBr): 3154 (OH); 3052; 1608; 1531; 1474; 1211; 772 cm^{-1}. ^1H NMR (DMF-d_7): 7.60−7.80 (C_{Ar}**H**, m, 6 H); 7.90 (C_{Ar}**H**, s, 2 H); 8.15 (C_{Ar}**H**, d, 2 H); 8.30 (C_{Ar}**H**, d, 2 H); 8.40−8.60 (C_{Ar}**H**, m, 3 H); 9.35 (C_{Ar}**H**, d, 2 H); 10.95 ppm (O**H**, br s, 1 H).

3,5-Bis[5-(4-*tert*-butylphenyl)-2-oxadiazolyl]phenyl Methacrylate (6a). Methacryloyl chloride, 0.69 mL (7.10 mmol), is slowly added to a solution of 2.70 g (5.46 mmol) of **5a**, 1.14 mL (8.19 mmol) of triethylamine, and 100 mg of hydrochinone in 250 mL of dry THF. The reaction mixture is stirred for 36 h at room temperature. The hydrochloride is filtered off and the solvent is evaporated. The residue is washed with water and further purified by column chromatography on silica gel with chloroform as eluent.

Yield: 2.30 g (76%); T_m = 209−212 °C. IR (KBr): 2964; 1740 (CO_2C); 1614 (oxa); 1494; 1184; 1110; 722 cm^{-1}. ^{1}H NMR ($CDCl_3$): 1.40 ($C(C\mathbf{H}_3)_3$, s, 18 H); 2.15 ($COC\mathbf{H}_3$, s, 3 H); 5.85 ($C{=}C\mathbf{H}_2$, s, 1 H); 6.45 ($C{=}C\mathbf{H}_2$, s, 1 H); 7.55 ($C_{Ar}\mathbf{H}$, d, 4 H); 8.10 ($C_{Ar}\mathbf{H}$, s, 2 H); 8.15 ($C_{Ar}\mathbf{H}$, d, 4 H); 8.75 ppm ($C_{Ar}\mathbf{H}$, s, 1 H). ^{13}C-NMR ($CDCl_3$): 18.3 ($CO\mathbf{C}H_3$); 31.1 ($C(\mathbf{C}H_3)_3$); 35.1 ($\mathbf{C}(CH_3)_3$); 120.8; 122.1; 123.0; 126.0; 126.5; 126.9; 135.2 ($\mathbf{C}{=}CH_2$); 152.0 ($\mathbf{C}_{Ar}O$); 155.8 ($\mathbf{C}_{Ar}C(CH_3)_3$); 162.8 ($\mathbf{C}_{oxa}$); 165.2 ($\mathbf{C}O$); 165.3 ppm ($\mathbf{C}_{oxa}$).

3,5-Bis[5-(3,5-bistrifluoromethylphenyl)-2-oxadiazolyl]phenyl methacrylate (6b) was prepared like **6a** and purified by recrystallization from ethyl acetate.

Yield: 80%; T_m = 192−196 °C. IR (KBr): 3083; 1740 (CO_2C); 1553; 1386; 1282; 1188; 1140; 906 cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.10 ($COC\mathbf{H}_3$, s, 1 H); 5.90 ($C{=}C\mathbf{H}_2$, s, 1 H); 6.50 ($C{=}C\mathbf{H}_2$, s, 1 H); 8.10 ($C_{Ar}\mathbf{H}$, s, 2 H); 8.15 ($C_{Ar}\mathbf{H}$, s, 2 H); 8.60 ($C_{Ar}\mathbf{H}$, s, 4 H); 8.85 ppm ($C_{Ar}\mathbf{H}$, s, 1 H). ^{13}C NMR ($CDCl_3$): 18.2 ($CO\mathbf{C}H_3$); 122.6; 123.6 (^1J $\mathbf{C}F_3$, 271 Hz); 124.0; 125.5; 125.8; 127.1; 128.8; 132.5 (^2J $\mathbf{C}_{Ar}CF_3$, 34 Hz); 135.0 ($\mathbf{C}{=}CH_2$); 152.2 ($\mathbf{C}_{Ar}O$); 162.9 ($\mathbf{C}_{oxa}$); 163.7 ($\mathbf{C}_{oxa}$); 165.1 ppm ($\mathbf{C}O$).

3,5-Bis[5-naphthyl-2-oxadiazolyl]phenyl methacrylate (6c) was prepared like **6a** and purified by column chromatography on silica gel with chloroform as eluent.

Yield: 69%; T_m = 226−228 °C. IR (KBr): 3053; 1738 (CO_2C); 1604 (oxa); 1528; 1120; 805; 773 cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.15 ($COC\mathbf{H}_3$, s, 3 H); 5.85 ($C{=}C\mathbf{H}_2$, s, 1 H,); 6.45 ($C{=}C\mathbf{H}_2$, s, 1 H); 7.40−7.80 ($C_{Ar}\mathbf{H}$, m, 6 H); 7.90 ($C_{Ar}\mathbf{H}$, d, 2 H); 8.05 ($C_{Ar}\mathbf{H}$, d, 2 H); 8.15 ($C_{Ar}\mathbf{H}$, s, 2 H); 8.30 ($C_{Ar}\mathbf{H}$, d, 2 H); 8.80 ($C_{Ar}\mathbf{H}$, s, 1 H); 9.30 ppm ($C_{Ar}\mathbf{H}$, d, 2 H). ^{13}C NMR ($CDCl_3$): 18.3 ($CO\mathbf{C}H_3$); 119.8; 122.1; 123.0; 124.8; 126.1; 126.7; 128.2; 128.5; 128.6; 128.7; 129.7; 132.9; 133.7; 135.2 ($\mathbf{C}{=}CH_2$); 151.8 ($\mathbf{C}_{Ar}O$); 162.2 ($\mathbf{C}_{oxa}$); 165.0 ($\mathbf{C}_{oxa}$); 165.1 ppm ($\mathbf{C}O$).

Polymerization Procedure. The polymerization of **6a** is described as a typical example. All other homo- and copolymerizations were carried out in an analogous manner.

Poly(3,5-bis [5-(4-*tert*-buylphenyl)-2-oxadiazolyl]phenyl methacrylate) (7a). Monomer **6a**, 1.0 g (1.78 mmol), and 9.7 mg (3 mol %) of AIBN are dissolved in 15 mL of dry chlorobenzene. The flask is degassed by three freeze−thaw cycles. The solution is stirred for 48 h at 60 °C and then poured into an excess of cold methanol. The polymer is further purified by two reprecipitations from chloroform solution into methanol.[13]

Yield: 670 mg (67%). Found: C, 71.19; H, 5.82; N, 10.70; O, 11.60%. Calcd: C, 72.58; H, 6.09; N, 9.96; O, 11.37%. T_g = 208 °C. IR (KBr): 2950; 1756 (CO_2C); 1615 (oxa); 1494; 1267; 1494; 1267; 1253; 1185; 1104; 842; 752 cm^{-1}. ^{1}H NMR ($CDCl_3$): 0.80−1.50 ($C(C\mathbf{H}_3)_3$); 1.70−2.30 ($C(CH_3)CH_2$); 6.90−7.40 ($C_{Ar}\mathbf{H}$); 7.40−7.80 ($C_{Ar}\mathbf{H}$); 7.80−8.20 ppm($C_{Ar}\mathbf{H}$) (all signals are broad). ^{13}C NMR ($CDCl_3$): 21−22 ($\mathbf{C}H_3$ backbone); 29−30 ($C(\mathbf{C}H_3)_3$); 34.8 ($\mathbf{C}(CH_3)_3$); 46.6 ($\mathbf{C}H_2$ backbone); 120.1; 122−123; 124−128; 151.4 ($\mathbf{C}_{Ar}O$); 155.2 ($\mathbf{C}_{Ar}C(CH_3)_3$); 161.8 ($\mathbf{C}_{oxa}$); 164.4 ($\mathbf{C}_{oxa}$); 174−176 ($\mathbf{C}O$) ppm.

References and Notes

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(12) Sodium azide is thermally stable up to 350 °C. Tetrazoles are stable compounds which have to be heated up to 70−130 °C together with acyl chlorides before evolution of nitrogen starts.

(13) A slightly modified workup procedure was used for polymer **7c** and **8f**. Since the monomer **6c** is not soluble in methanol, it has been removed from the polymer by extraction with boiling acetone.

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