

Oxadiazole Containing Polymers and their Use in Polymer LEDs

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ABSTRACT

Synthetic aspects and a detailed investigation of the properties of new polymethacrylates with oxadiazole side groups and aromatic polyethers with oxadiazole units in the main chain are described. The application of these oxadiazole polymers in bilayer devices with PPV as hole injection and transport layer is demonstrated. The electron withdrawing oxadiazole units facilitate electron injection and transport and lead to an increase of the external quantum efficiency.

INTRODUCTION

Poly (1,4-phenylene vinylene) (PPV) was the polymer, in which electroluminescence was discovered by R.H. Friend in 1990¹. Due to the excellent thermal and chemical stability PPV is an attractive material for polymer light emitting diodes (LEDs), which are today developed and improved in many laboratories all over the world.

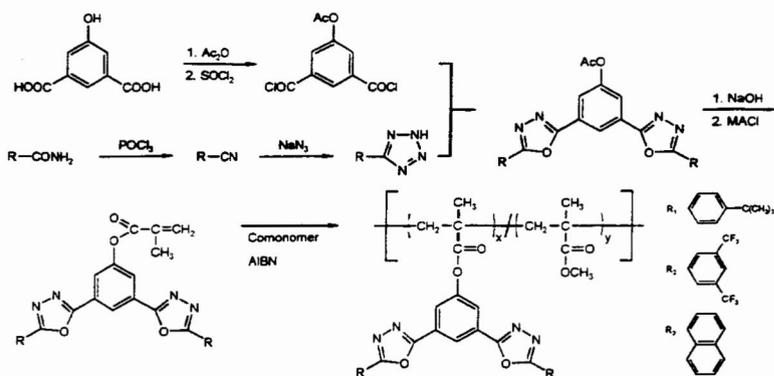
Monolayer devices from PPV with an active area up to 50 cm² and a lifetime of more than four weeks in an inert atmosphere have been made in our group². Such devices have an onset voltage of electroluminescence of about 2V. One disadvantage of PPV-LEDs is the unbalanced carrier injection, which leads to low quantum efficiencies. The injection and the transport of holes is strongly favoured compared to electrons in PPV. One possibility to enhance the quantum efficiency is the use of an additional electron transport layer³.

Within the last years we have synthesized a number of polymers with oxadiazole units as side groups or as part of the main chain and low molecular weight oxadiazole glasses^{4,5}. The oxadiazole group has been chosen for several reasons. Due to the three electronegative heteroatoms the aromatic oxadiazole ring facilitates the injection and the transport of electrons. Besides, oxadiazoles are known as building blocks for thermostable polymers⁶ and a large number of oxadiazoles exhibit strong fluorescence.

SIDE GROUP POLYMERS

The synthesis of a number of polymethacrylates with pendent oxadiazole units⁵ is outlined in scheme 1. The crucial step is the intermolecular formation of the oxadiazole unit from an isophthaloyl chloride derivate and tetrazoles with different substituents. Finally, side group polymers were prepared by free radical polymerisation with AIBN in solution. We have synthesized the homopolymers 1-3 and the copolymers 4-6 with methyl methacrylate and 7-8 with a second oxadiazole monomer.

The properties of the side group polymers are summarized in table 1. The absorption maxima are between 278 to 333 nm. The fluorescence maxima of the side group polymers with bisphenyloxadiazole units are in the ultraviolet range, whereas homopolymer 3 with bisnaphthyloxadiazole units exhibits blue fluorescence with a maximum at 418 nm.



Polymer	X				Polymer	Y			
	R ₁ (%)	R ₂ (%)	R ₃ (%)	MMA (%)		R ₁ (%)	R ₂ (%)	R ₃ (%)	MMA (%)
1	100	0	0	0	5	0	50	0	50
2	0	100	0	0	6	0	25	0	75
3	0	0	100	0	7	75	25	0	0
4	0	75	0	25	8	25	75	0	0

Scheme 1: Synthesis of the polymethacrylates 1-8 with oxadiazole side groups

Table 1: Properties of the polymethacrylates with oxadiazole side groups

Polymer	M _n ¹ (g/mol)	T _g (°C) ²	T _{dec} (°C) ³	ABS ⁴ λ _{max} (nm)	FL ⁴ λ _{max} (nm)
1	72000	208	318	294	375
2	36000	185	314	284	365
3	18000	198	335	333	418
4	24000	181	256	278	362
5	56000	177	281	278	360
6	23000	160	263	278	362
7	21000	187	275	286	368
8	16000	204	294	281	368

1) determined by GPC, eluent THF or CHCl₃, polystyrene calibration

2) glass transition temperature determined by DSC, second heating, 20 °C/min

3) thermogravimetric analysis, onset of the decomposition in N₂, 10 °C/min

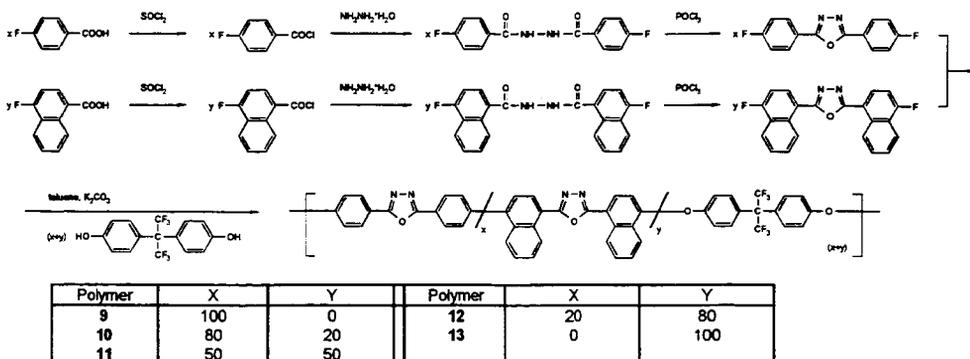
4) films on quartz substrates, absorption (ABS), fluorescence (FL)

MAIN CHAIN POLYMERS

The synthesis of the main chain polyethers⁴ requires bifunctional oxadiazole monomers (scheme 2). They were prepared by intramolecular ring closure of the bisacylhydrazides with POCl₃. The oxadiazole polyethers **9-13** were synthesized from difluoroxadiazole monomers with hexafluorobisphenol A via nucleophilic displacement of the fluorine atoms.

The conditions for the polycondensation have been optimized. The substitution of N-methylpyrrolidone (NMP) and 1,3-dimethyltetrahydro-2(-1H)pyrimidone (DMPU), which we have used as solvents before⁴, by diphenylsulfone leads to an improvement of the polymers. Using NMP or DMPU the polymers are still slightly coloured, whereas colourless polymers are achieved if the reaction is carried out in diphenylsulfone.

The properties of the aromatic polyethers **9-13** are summarized in table 2. The polyethers with bisphenyloxadiazole units show an absorption maximum at 299 nm, whereas the substitution of bisphenyloxadiazole by bisnaphthyloxadiazole leads to a bathochromic shift of the absorption to 345 nm. The fluorescence spectra exhibit the same trend. Polyethers with bisnaphthyloxadiazole units show a blue fluorescence with a maximum at 430 nm.

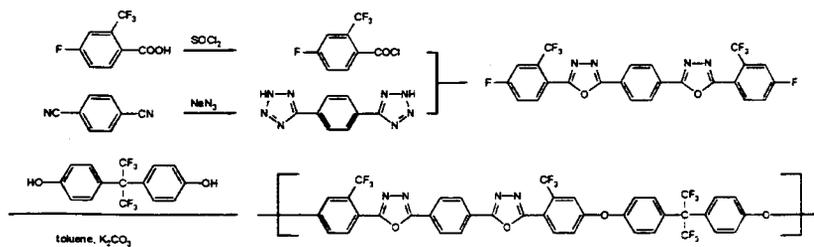


Scheme 2: Synthesis of aromatic polyethers 9-13 with oxadiazole units in the main chain

Table 2: Properties of aromatic polyethers with oxadiazole units in the main chain

Polymer	M_n^1 (g/mol)	T_g ($^{\circ}\text{C}$) ²	T_{dec} ($^{\circ}\text{C}$) ³	ABS ⁴		FL ⁵	
				λ_{max} (nm)	λ_{max} (nm)		
9	54000	202	446	299	360		
10	106000	214	438	299	419		
11	73000	219	434	303	423		
12	59000	225	431	347	425		
13	53000	229	436	345	427		
14	58000	179	431	316	395,412		

- 1) determined by GPC, eluent THF, polystyrene calibration
- 2) glass transition temperature determined by DSC, second heating, 10 $^{\circ}\text{C}/\text{min}$
- 3) thermogravimetric analysis, onset of the decomposition in N_2 , 10 $^{\circ}\text{C}/\text{min}$
- 4) films on quartz substrates, absorption (ABS), fluorescence (FL)



Scheme 3: Synthesis of aromatic polyether 14 with oxadiazole units in the main chain

Using a similar synthetic pathway we prepared polyethers with a larger number of oxadiazole units. The synthesis is shown in scheme 3. Due to the simultaneous formation of two oxadiazole rings the monomers were synthesized via tetrazole intermediates. The comparison of polyether 14 with polyether 9 shows that the increase in the oxadiazole content leads to a bathochromic shift in the absorption maximum as well as in the fluorescence maximum (table 2).

PROPERTIES OF THE POLYMER LEDS

Due to the good solubility of most polymers in organic solvents like CHCl_3 , THF or NMP and the excellent film forming properties homogeneous transparent films could easily be fabricated by spin-coating. Bilayer devices with PPV and the polymers 1, 3 and 7 were prepared. The onset of electroluminescence slightly increased to 4-8V compared to PPV monolayer devices^{4,6}. The brightness has been improved and is two orders of magnitude higher than that for monolayer devices.

The best results were obtained with polymer 7 with two additional strongly electron withdrawing CF_3 groups per oxadiazole unit. Compared to the homopolymer 2, which contains only trifluoromethylsubstituted units, copolymer 7 has the advantage of a better solubility and better film forming properties.

Table 3: External quantum yields and typical threshold voltages of oxadiazole heterolayer LEDs

Device Configuration ¹⁾	Threshold Voltage for EL (V)	η_{ext} (%)
ITO/PPV/1/Ag	8	0.05
ITO/PPV/3/Ag	5.5	0.04
ITO/PPV/7/Ag	4	0.10

1) layer thickness: PPV 580nm, oxadiazole polymer 50nm

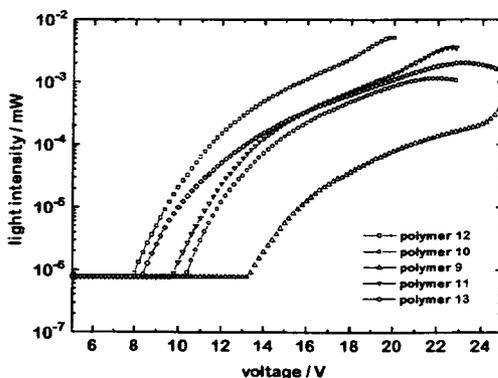


Figure 1: Light intensity vs voltage in bilayer devices with the polyether 9-13 and PPV (device configuration: ITO/PPV 150nm/polyether 30nm/Al)

In figure 1 the light intensity as a function of the bias voltage is displayed for bilayer devices with the polyethers 9-13 and PPV. All polyethers containing bisnaphthyloxadiazole units 10-13 show a similar behavior. The threshold voltage for EL is in the same range (8-10V) just as the brightness and the quantum efficiencies (0.01-0.1%). A significant difference is observed in the polyether 10 containing only bisphenyloxadiazole units. The threshold voltage is increased to 13V and brightness reduced for an order of magnitude.

We have reported a number of new polymers in which oxadiazole units are incorporated either as side groups or as part of the main chain and demonstrated their application as efficient electron injection and transport material in bilayer devices with PPV.

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