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Dichroic photo- and electroluminescence of oligo *p*-(phenylene vinylene) derivatives

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Abstract

The synthesis and characterization of all *trans*-configured, monodisperse 2-ethylhexyloxy-substituted PV-oligomers (OPVs) are presented. The synthetic route is based on a step-wise synthesis using the Horner–Wadsworth–Emmons reaction. Bright fluorescence of the OPVs makes them suitable for the use in organic light emitting diodes (OLEDs). Due to the anisotropy of shape, the oligomers can be aligned which leads to linear polarized photoluminescence and electroluminescence. Different alignment layers were tested. The best results were achieved by using poly(tetrafluoroethylene) (PTFE) as alignment layer. The pentamer shows dichroic ratios of 17.1 for fluorescence and 8.5 for electroluminescence, respectively.

Keywords: Oligo *p*-(phenylene vinylene); Polarized electroluminescence; Liquid crystals; Organic ligth emitting diodes; Dichroism

1. Introduction

Organic light emitting devices (OLEDs) based on low molar mass organic semiconductors [1] or polymers [2] have been extensively studied during the last decade [3] and developed to give excellent performance. Additional improvements may be achieved by orientational order of the semiconducting molecules or chromophores which can lead to high charge carrier mobility [4,5] and polarized emission, respectively. Consequently, the electroluminescence of systems containing columnar liquid crystals [6,7] or calamitic liquid crystals [8] has been studied. The quality of polarized emission can be described by the dichroic ratio $D:=I_{\parallel}/I_{\perp}$, where $I_{\parallel}$ and $I_{\perp}$ correspond to the fluorescence intensities measured with a linear polarizer aligned parallel and perpendicular to the preferred plane of polarization of the emitted light, respectively. Polarized electroluminescence with dichroic ratios up to 15 has been reported, so far [9–24] (Table 1). The best results are reported for liquid crystalline polymers which were uniaxally aligned by means of an additional alignment layer [23,24].

2. Experiment and results

Continuing our investigations on the synthesis and characterization of all *trans*-configured, monodisperse alkyl- and alkyloxy-substituted PV-oligomers (OPVs) [25–28] we have been recently focussing on liquid crystalline materials that are suitable for the preparation of highly oriented layers. Varying the kind and shape of side chains and endgroups numerous homologous series of monodisperse OPVs were synthesized. While in our former works the metathesis polycondensation was used for the chain growth reaction, our new method is based on step-wise synthesis strategy using organic coupling reactions. The present paper describes a study on liquid crystalline and easily soluble di-2,5-[(2-ethylhexyl)-oxy]-substituted PV-oligomers with *p*-(decyloxy)-phenyl end-groups where the degree of polymerization and the preparation of the alignment layer were varied systematically. The backbone of the OPV derivatives contains four ($n=2$) to seven ($n=5$) benzene rings. Corresponding monodisperse OPV dialdehyds were obtained by controlled growth synthesis strategy, where the main chain elongation is accomplished via consecutive coupling and deprotection steps. From these monodisperse PV-dialdehydes, the *p*-decyloxy-phenyl-terminated OPVs were obtained via Horner–Wadsworth–Emmons reaction in 80% yield (Fig. 1).

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Table 1
Dichroic ratio D_{EL} of the electroluminescence reported for different systems

Emitter	Alignment technique	D_{EL}	Reference
p-Hexaphenyl	Epitaxial growth on rubbed *p*-hexaphenyl	5	[10]
Smectic oxadiazole derivative	Rubbed ITO on glass	2.4	[11]
Nematic oxadiazole derivative	Rubbed PSS/PEDOT	2.8	[12]
Columnar perylene derivatives	Friction-deposited PTFE	3.2	[13]
Smectic main chain polymer	Rubbed PI	6.3	[14]
Heterocyclic rigid rod polymer	Mechanical shearing	1.6	[15]
Poly(silane)	Friction-transferred poly(diethylsilane)	1.6–2	[16]
LC side chain polyacrylate	PEDOT layer	6.1	[17]
Thiophene-based polymers	Rubbed emitting layer	3	[18]
PPV derivative	Rubbed emitting layer	4.5	[19]
Amphiphilic polymers/oligomers	Rubbed emiting layer	8	[20]
Freestanding PPV films	Tensile drawing	8	[21]
PPV	Rubbing of the PPV precursor polymer	12	[22]
Nematic poly(fluorene)	LPP	13	[23]
Nematic poly(fluorene)	PI/rubbed PPV/LPP	14–15	[24]

PI: alignment layer made of rubbed polyimide; PPV: poly(*p*-phenylenevinylene); LPP: alignment layer made by polymerization with linearly polarized UV radiation; PTFE: poly(tetrafluoroethylene).

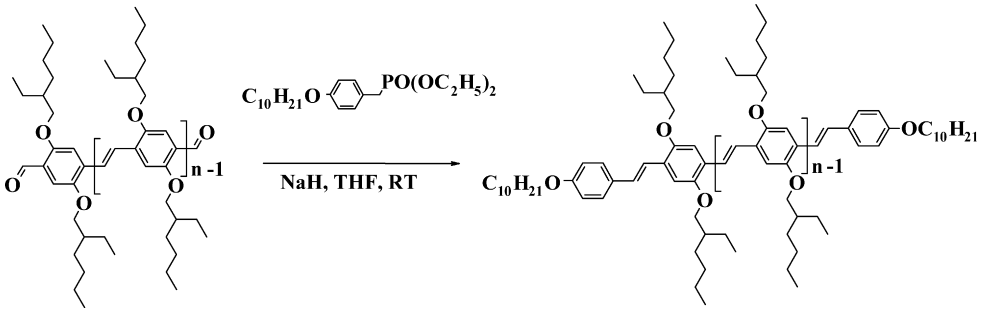

Fig. 1. Introduction of the *p*-(decyloxy)-phenyl end-groups via Horner–Wadsworth–Emmons reaction; $n = 2–5$.

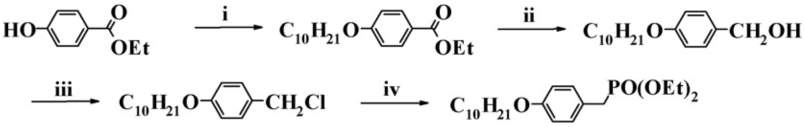

Fig. 2. Synthesis of diethyloxy-[4-(decyloxy)phenyl]-methyl-phosphonate; reaction conditions: (i) bromodecane, K_2CO_3, DMF, 120 °C, 2 h; (ii) $LiAlH_4$, Et_2O, room temp., 4 h; (iii) $SOCl_2$, CH_2Cl_2, pyridine, room temp., 30 min; (iv) $P(OEt)_3$, 140 °C, 24 h.

The diethyloxy-[4-(decyloxy)phenyl]-methyl-phosphonate was synthesized from ethyl-4-hydroxybenzene-carboxylate in 40% overall yield (Fig. 2).

The monodispersity and the chemical structure were verified by means of MALDI TOF mass spectrometry (Fig. 3) and NMR spectroscopy. The ^{1}H- and ^{13}C-NMR data are given in the appendix. The liquid crystallinity was proven via DSC and polarization microscopy indicating the appearance of nematic phases in these compounds (Table 2).

Contact preparations with a typical calamitic nematic liquid crystal (PCH7) show complete miscibility, which indicates that the thermotropic nematic phase of the OPV derivatives is a classical calamitic nematic phase, as opposed to discotic nematic phases. It is interesting to note that mixtures of these compounds with toluene show also a lyotropic nematic phase, which is stable above 60 °C and metastable even at room temperature. This property might play a role in obtaining a uniform alignment when the compounds are deposited on a substrate by spin coating.

The photoluminescence spectra of OPVs ($n = 2–5$) show as expected shifts towards higher wavelengths for increasing oligomer chain lengths (Fig. 4). The color of the emitted luminescence varies from green ($n = 2$) to orange-red ($n = 5$). For comparison, a polymer containing similar monomer units

Table 2
Phases and phase transition temperatures of the *p*-(phenylene vinylene) oligomers (Cr: crystalline, N: nematic, is: isotropic liquid)

n	Transition temperatures
2	Cr 87.5 °C N 73.6 °C is
3	Cr 95 °C N 135 °C is
4	Cr 112 °C N 184 °C is
5	Cr 165 °C N 230 °C is