

Communications

Soluble Segmented Stepladder Poly(*p*-phenylenes) for Blue-Light-Emitting Diodes

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Introduction

The synthesis of structurally defined ladder-type poly(phenylene)s **1** (Figure 1) in 1991¹ has initiated a lot of activities to (re)investigate so-called "classical" (stepwise) routes to generate ribbon structures. Thus, this approach has been favored recently in the case of several target structures.² Electroluminescence devices based on polyconjugated materials are currently investigated worldwide (see refs 3 and 4 and references therein). Different polymers were used to achieve blue-light emission. Beside the "wide-bandgap" polymers such as poly(alkylfluorene)⁵ and poly(paraphenylene),⁶ more sophisticated approaches like copolymers and blends⁷⁻⁹ are used.

We have shown recently that the bandgap and hence the luminescence emission color of poly(phenylene) can be influenced by chemical means.¹⁰ In the ladder-type poly(phenylene)s **1**, the photo- and electroluminescence behavior is determined by the formation of aggregates (excimers). There is a distinct Stokes shift between absorption and emission, which results in the generation of yellow-colored light. We show that the synthesis of a segmented so-called stepladder structure **2** results in a pure blue-light emission in highly efficient light-emitting diodes.

Synthesis

The "classical" synthesis to ladder polymers proceeds in two main steps: the chain formation via polymeri-

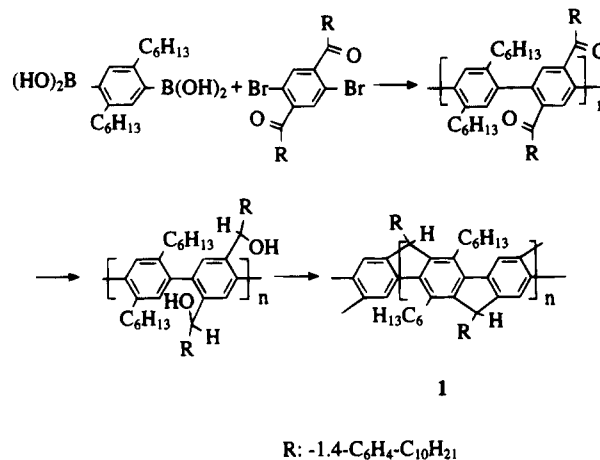


Figure 1. Synthesis of a structurally defined ladder-type poly(phenylene).

zation or polycondensation of suitable monomers is followed by a polymer-analogous cyclization under generation of the double-stranded macromolecules.¹¹ Adapting such a synthetic process, the demands upon the second step to generate structures free of defects are a quantitative cyclization coupled with chemo- and regioselectivity of the ring-closure reaction. In the case of the soluble ladder-type poly(phenylene)s **1** it is possible to generate structurally well-defined ribbons with number-average molecular weights up to 20 000 (about 50 1,4-phenylene subunits).

The chain formation step is a SUZUKI-type¹² cross-coupling reaction of a 2,5-dialkyl-1,4-phenylenediboronic acid with 4,4'-dialkyl-2',5'-dibromoterephthalophenone. To guarantee a sufficient solubility of the coupling products, solubilizing alkyl chains were introduced into both coupling monomers used. The benzoyl-substituted polyketone formed is then reduced with lithium aluminum hydride to the corresponding polyalcoholic species. The key step toward **1**, a polymer-analogous (Friedel-Crafts type) cyclization to the desired ribbon structures, proceeds completely and regioselectively. No indications for defects such as incomplete cyclization or cross-linking were found (according to ¹H or ¹³C NMR spectroscopy and gel-permeation chromatography; see ref 1). The ladder-type poly(phenylene)s **1**, consisting of alternating five- and six-membered rings, form very stable doped species by chemical or electrochemical oxidation.¹³ Because there is an outstanding interest in blue-light-emitting materials, we have searched for structurally related materials unable to form excimers. The means of success was the synthesis of statistical copolymers **2** possessing ladder-type oligo(phenylene) subunits connected by spacer units causing a distinct distortion of the rigid ladder-type oligo(phenylene) units

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subunits each to another.¹⁴ Using, e.g., 2,5-dialkyl-1,4-phenylene subunits as spacer units, the formation of excimers is suppressed very efficiently.

The synthetic scheme to the statistical copolymer **2** is closely related to the generation of the homopolymer **1**. Hereby, a part (40–80%) of the 4,4''-dialkyl-2',5'-dibromoterephthalophenone is replaced by a 2,5-dialkyl-1,4-dibromobenzene, which is unable to form the methylene bridges in the following polymer-analogous reaction steps. In addition, investigations of Schlüter and Wegner¹⁵ have shown, that 2,5-dialkyl-1,4-phenylene units act as efficient conjugation barriers when incorporated in PPP-type polymers. The result is a segmented ladder structure, a so-called stepladder polymer. The defined structure of **2** was proven using NMR spectroscopy, no defects are detectable. Especially the three signals of benzylic hydrogens of **2** (¹H NMR spectroscopy) belonging to the main-chain hexyl substituents (two signals; ladder segment –2.85 ppm respectively 2,5-dialkyl-1,4-phenylene units –2.28 ppm) and the side-chain decyl substituents (one signal; ladder segments –2.53 ppm) verify the formation of statistical copolymers and allow for an analysis of the copolymer composition. Hereby, the ratio of the monomer concentrations is quantitatively reproduced in the resulting copolymers **2**. Unfortunately, an estimation of the distribution of the segment lengths is not possible by means of NMR spectroscopy.

Experimental Part

The homopolymer **1** and two different copolymers **2** (ratio x/y of the dibromomonomers 50/50 (I) and 60/40 (II) respectively Figure 2) of the 2,5-dialkyl-1,4-dibromobenzene are studied concerning of their optical properties.

The absorption of the homopolymer **1** is characterized by a sharp longest wavelength absorption maximum centered at ca. 440 nm (2.8 eV) as a consequence of the planar structure of the macromolecules (Figure 3). The absorption spectra of both copolymers **2** (I and II as shown in Figure 4) have the same structure reflecting the presence of planarized oligo(phenylene) units of different length in the macromolecules. Hereby, the structured absorption feature with λ_{\max} : 347 nm represents planar terphenyl ($n = 0$), the following two peaks with λ_{\max} : 373/395 nm planar pentaphenyl ($n = 1$) and the absorption centered at λ_{\max} : 419 nm planar heptaphenyl ($n = 2$) subunits as shown in model studies.¹⁶ The absorption peaks of the longer subunits ($n \geq 3$) form an unstructured absorption edge (up to ca. 450 nm) similar to the homopolymer **1**. In the view of the absorption behavior, the ladder-type subunits in **2** act as nearly independent chromophors. This is a further argument for the statistical course of the copolymerization during the synthesis of **2**.

The solubility of the PPP-type ladder polymer **1** and the stepladder copolymers **2** in common organic solvents allows for the generation of high-quality thin films (spin coating, casting), hence **1** was successfully used as the active layer in electroluminescence (EL) devices (LEDs).¹⁷ A typical polymer EL device is based on an ITO (indium–tin–oxide) coated glass substrate, which is covered with the active polymer layer and an evaporated top metal contact. The color of the luminescence emission is determined by the electronic structure of the polymer. There is a good agreement between the photoluminescence (PL) and EL spectra of these polymers, so we suggest that the EL occurs from the same process as the PL. After

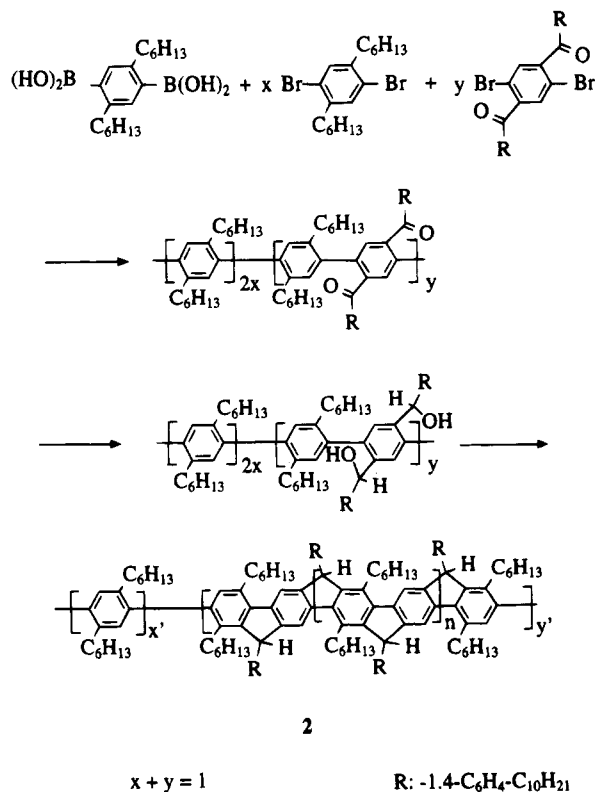


Figure 2. Synthesis of a segmented ladder-polymer, a so-called stepladder structure.

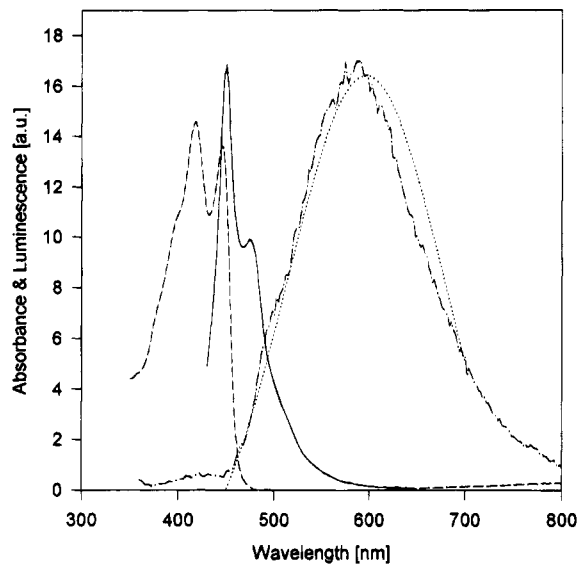


Figure 3. Absorption (---) and photoluminescence (– · –) spectra of a thin film of the ladder-type poly(phenylene) **1**, photoluminescence (–) spectrum of a solution (**1** in toluene) and electroluminescence emission spectrum (···) of an ITO/**1**/Al device.

the creation of an electron–hole pair in valence band and conduction band (negatively and positively charged polaron pair) the oppositely charged carriers combine and form a so-called exciton. The energy (color) of the luminescence emission E_L is determined by the bandgap energy E_g and the binding energy δE_{SE} of the singlet exciton ($E_L = E_g - \delta E_{SE}$).

The bandgap energy of both polymers **1** and **2** is about 2.6 eV. Therefore one would expect a blue emission color. Both PL and EL spectra of **1** show a significant Stokes shift, the emission color is yellow, and the broad emission peak is

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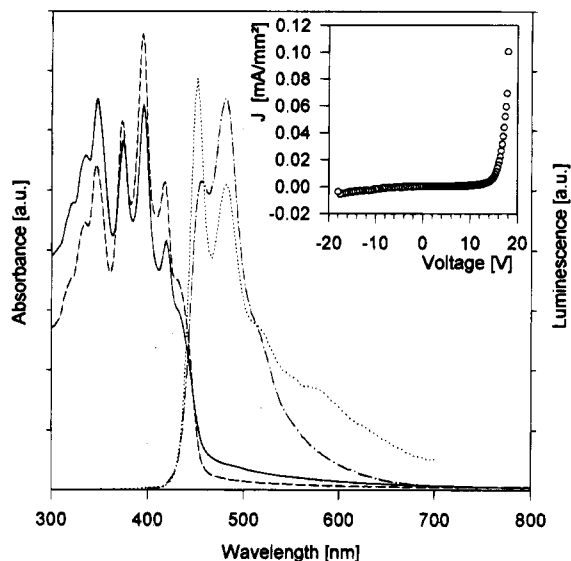


Figure 4. Absorption spectra of the two different segmented ladder-type poly(phenylenes) **2** I (---) and II (—), photoluminescence (— · —) and electroluminescence emission spectra (···) of II. The insert shows the I - V characteristics of an ITO/II/Al device.

centered at about 600 nm.¹⁸ We propose that this broad emission is due not to singlet excitons but to the formation of self-trapped excitons (excimers), which is a commonly observed relaxation or trapping process in organic molecular crystals.¹⁹ Besides this, blue emission can be achieved with a special morphology of the polymer layer.²⁰ This statement is confirmed by the fluorescence excitation and emission spectra of

1 in dilute solution, that reveals only a small Stokes shift attributed to singlet excitons.

In contrast, both PL and EL spectra of **2** does not show this broad Stokes shift, the excimer formation is suppressed by the distorted structure of the copolymers **2**. Interestingly, the shortest wavelength emission maxima and the structure of the PL spectra are nearly independent relative to the chemical composition of **2** (ratio x/y ; see Figure 2). There is an efficient intermolecular relaxation during the excitation process, the final light emission exclusively originates from the longest planar ladder-type subunits ($n \geq 3$). The result is a pure blue-light emission both in solution (PL) and in the solid state (PL and EL; see Figure 4).

The PL quantum yield is strongly enhanced for the segmented copolymer. While the homopolymer **1** yields only 61%, the stepladder polymer **2** has 84% quantum yield in toluene solution with respect to coumarin 102. In the solid state the quantum yield of the step-ladder polymer **2** is reduced to only about 20%. This behavior cannot be explained by the reduction of multiphonon emission processes for polymers with higher gap energies. The copolymer forms "quantum well" structures along the polymer chain, and this is known to enhance the electroluminescence yield.²¹ We propose that the local potential minima of the quantum well structure trap the excitons and limit the possibility for nonradiative decay.

The insert in Figure 4 shows the typical I - V characteristics of an ITO/2/Al device. The threshold voltage of the electroluminescence depends on the thickness of the active layer, whereas the field strength is on the order of 10^6 V/cm. The average quantum efficiency of the device yields 0.2% at 0.5 mA current in forward bias.

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