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Ladder-type materials

Ullrich Scherf

Max-Planck-Institut für Polymerforschung, Ackermanweg 10, D-55128 Mainz, Germany. E-mail: scherf@mpip-mainz.mpg.de

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Materials with a ribbon- or ladder-type framework possess a two-dimensional geometry and are thus intermediate between linear and three-dimensional systems. The limited conformational freedom of ladder polymers is particularly relevant in the case of conjugated ladder-type materials since the steric inhibition of electron delocalization is drastically reduced.

Up until today two general routes have been used to prepare ladder-type materials: (1) the polymerisation of multifunctional monomers, in which both strands of the ladder structure are generated in a single reaction; and (2) the cyclisation of suitably functionalized open-chain (single-stranded) precursor polymers in a polymer-analogous process. Both strategies pre-suppose certain essentials to arrive at structurally defined ladder polymers, especially the exclusion of side-reactions and an almost quantitative conversion of the starting materials.

The main attention of this article is focused on an active physical function of ladder-type materials. Among others, ladder-type poly(*p*-phenylene)s (LPPPs) represent an outstanding class of ladder-type materials. They are characterized by an extraordinarily low concentration of active traps (topological defects, impurities) and display a set of attractive electronic properties (very intensive photo- and electroluminescence, high charge carrier mobilities). This unique performance has established the solution processable LPPPs as standard materials for organic polymer based light emitting diodes (LEDs) and optically pumped solid state lasers.

1 Introduction

Considerable progress has been made in the synthesis of double-stranded or ladder polymers during the last decade. Today, the synthetic polymer chemist has access to a variety of efficient synthetic strategies for the preparation of ladder polymers that are structurally accurate and largely defect-free. Depending on the target structure, two principal methods are of choice for the synthesis:[1–3]

1. A stepwise formation of the double strand by polymer-analogous conversion of a functionalized, single-stranded precursor polymer;

2. The synchronous, concerted construction of the ladder structure by way of suitable multi-center reactions (*e.g.*, repetitive [4+2]- or [2+2+2]-cycloaddition steps).

The first, 'classical' synthetic variant is the method of choice: it is suitable in particular for the synthesis of highly unsaturated, aromatic ladder polymers with π-conjugation throughout the main chain. By optimization of the substitution pattern and the reaction conditions it was possible to control the final, polymer-analogous reaction step so that it took place quantitatively and with complete regioselectivity (intramolecular). The latter is essential for the synthesis of structurally defined ladder polymers.[1,2] The second, concerted reaction variant was successfully applied to the synthesis of band polymers, which contain saturated, sp^3-carbon centers in the main chain. The Diels–Alder cycloaddition in particular has been used for the simultaneous connection of both strands of the ladder polymer.[4] Depending on the structure of the monomers, the resulting band polymers contain additional functional groups, for example, keto groups, or double bond and –O– bridges. Extensive attempts to convert the initially formed polymer adducts into unsaturated, π-conjugated band structures by polymer-analogous reactions were only partially successful.

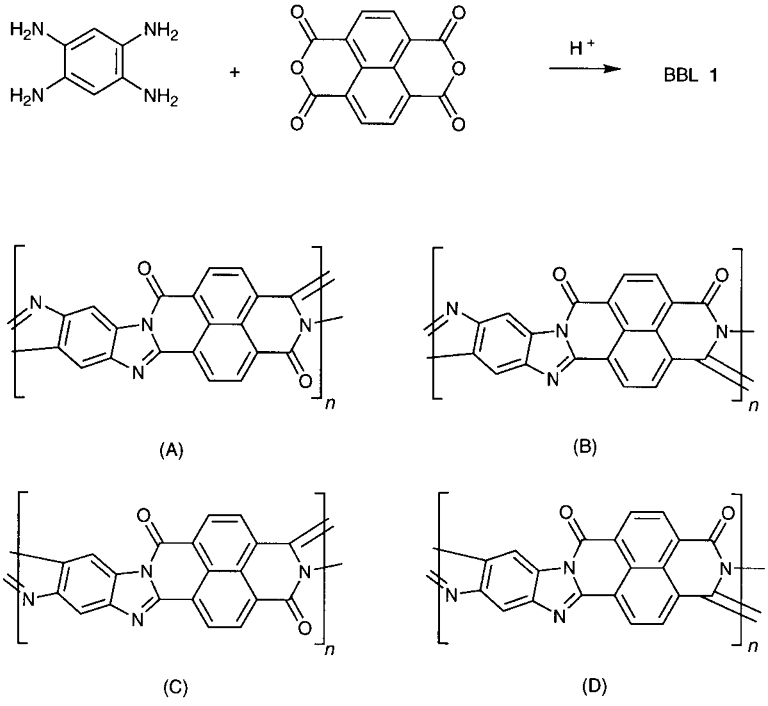
The reaction steps required often cannot be carried out quantitatively and lead to polymers with structural defects. Nevertheless, very promising results on the way to selective, polymer-analogous conversions have recently been published.[5]

For the step from pure polymer synthesis to investigations into the function of materials, from polymer chemistry aimed at the individual structure, to materials science directed at assemblies of molecules in the solid state, the question of structural homogeneity gains considerable, additional significance. Structure defects possess enormous influence for many fixed material properties, such as thermal stability, photo- and electroluminescence, electrical and photoconductivity, *etc.*, that are the focus of interest; frequently, these material parameters are completely controlled by defects, or the presence of defects completely alters the properties. However, in order to derive reliable and applicable structure–property relationships, the availability of structurally defined materials with reproducible property profiles is a conditional prerequisite and of utmost importance. A guaranteed structure–property relationship of this type is in turn the basis for the bespoke synthesis of polymers with optimized material properties.

The emphasis of the following article will therefore be to consider the fruitful interaction between polymer synthesis and the optimization of important material properties using the examples of some selected ladder polymers. The main focus on the one hand will be the modern synthetic strategies for the generation of highly-defined, molecular architectures with a high degree of homogeneity, and on the other the intimate relation between active physical function and molecular or supramolecular structure in the solid state. The central focus is on the execution of the synthesis, characterization, and application of aromatic, conjugated ladder polymers of the poly(*p*-phenylene) type (LPPP), hitherto the most intensively examined group of organic band polymers.[1,2,6] LPPP materials of this type were first described in 1991; since then over 100 publications have appeared, dealing with their synthesis, physical properties, and their application in photonics and optics. In addition, an overview of further classes of important ladder structures, which are attractive or potentially attractive from the materials science perspective, will also be given.

2 Heteroaromatic ladder polymers by multifunctional polycondensation

Up to the beginning of the sixties, the only synthetic approaches described in the polymer chemistry literature were those that led to incompletely formed double strands or to partially cross-linked ladder structures rich in defects.[5,7]



Scheme 1 Synthesis of BBL **1** according to Arnold and vanDeussen; BBL **1** consists of the two *m*-phenylene structural units (A) and (B) and the *p*-phenylene structural units (C) and (D); relative to the tetraamino building block.

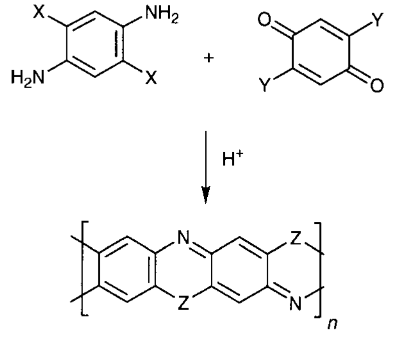
Incompletely formed ladder polymers result, for example, from the polymer-analogous aldol condensation (dehydration) of poly(vinyl methyl ketone);[8,9] cross-linked, insoluble structures rich in defects are formed by the thermal or thermo-oxidative conversion of polyacrylonitrile (PAN).[10–12] The latter process is, however, of considerable importance for the preparation of precursor materials for carbon fibers.[13]

A breakthrough to structurally defined, processable band polymers was achieved by the synthesis of poly(benzimidazobenzophenanthroline) (BBL) **1** by Arnold and vanDeussen in 1966 (Scheme 1).[14–17] The central principle of the synthesis was the condensation of tetrafunctional monomers, in this case an aromatic tetraamine (1,2,4,5-tetraaminobenzene) with naphthalene-1,4,5,8-tetracarboxylic anhydride in a protic medium such as polyphosphoric or sulfuric acid. In order to largely avoid the undesired formation of branched and cross-linked structures, special reaction conditions were introduced, for example, a preliminary condensation to give single-stranded intermediates at 180 °C, followed by a subsequent polymer-analogous condensation at elevated temperature (350 °C). By using such optimized reaction conditions it is possible to generate completely soluble, essentially linear and unbranched products. The heteroaromatic ladder polymer can be processed from solution into high quality films and layers, for example, by casting or by spin coating. However, in this way one is forced into the use of protic solvents that are quite aggressive and difficult to handle, for example, concentrated sulfuric acid, polyphosphoric acid (PPA), or methanesulfonic acid, or, alternatively, mixtures of nitromethane with Lewis acids such as aluminum trichloride, iron trichloride, or magnesium chloride.[18,19] As an electron-poor, heteroaromatic ladder polymer BBL **1** has been intensively investigated in terms of its optical and electronic properties, such as the electrical and photo conductivity in both the neutral state and after so-called doping.[20]

The BBL band gap energy was estimated to be *ca.* 2.0–2.2 eV;[21] the band gap can be reduced by doping (with electron donors like alkali metals or by ion implantation).[3,20] Solution cast BBL films exhibit a layer-like structure, with the BBL molecules in the plane of the film surface.[22] However, the ribbon-like molecular plane of the ladder molecules orients perpendicular to the film surface. The cast BBL films exhibit an electrical conductivity of up to 0.01 S cm^{-1}.[23] Photoconductivity of BBL cast films was also observed, within the delocalized absorption band as well as in a region of *ca.* 1.6 eV, well below the interband transition. This low energy photoconductivity peak suggests the presence of electronic (defect) states within the gap.[24]

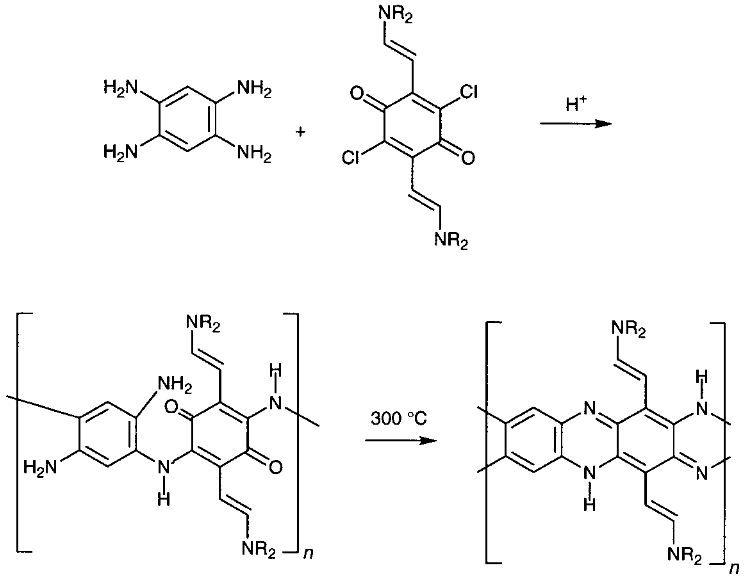
BBL films can be doped by ion implantation to high electrical conductivities of up to 100 S cm^{-1}.[25,26] The doped samples display a high atmospheric stability over hundreds of hours, also at elevated temperatures (250 °C).

The principle of the polycondensation of tetrafunctional monomers used for the synthesis of BBL was extended to other combinations of tetrafunctional monomers in synthetic work published in parallel at the end of the sixties, in particular by Stille *et al.* and by Marvel *et al.* They condensed 2,5-dihydroxy-, 2,5-diacetoxy-, or 2,5-dichlorobenzo-1,4-quinone with 2,5-dihydroxy-, 2,5-dithio-, or 2,5-dichlorophenylene-1,4-diamine or 1,2,4,5-tetraaminobenzene, respectively, to give linear, heteroaromatic ladder polymers, which contained phenoxazine, phenothiazine, or quinoxaline structural elements (Scheme 2).[27–33] Unfortunately, the resulting polymers are only slightly soluble or even insoluble, rendering detailed



X: -NH$_2$, -OH, -SH, -Cl
Y: -OH, -Cl, -CO$_2$CH$_3$
Z: -NH-, -O-, -S-

Scheme 2 Synthesis of heteroaromatic ladder polymers: poly(quinoxaline)s, poly(phenoxazine)s, poly(phenothiazine)s.



2

R: $-C_2H_5$, $-CH(CH_3)_2$, $-C_6H_{13}$

Scheme 3 Synthesis of soluble poly(quinoxaline)s **2** according to Yu and Dalton.

characterization impossible. One possibility of attaining soluble, easily processed materials is the introduction of solubilizing, flexible side groups into the rigid polymer backbone. This procedure was adopted by Yu, Dalton *et al.* in the case of the polyquinoxaline derivative **2** (Scheme 3), in which they introduced dialkylaminovinyl side groups into the 3,6-positions of the 2,5-dichlorobenzo-1,4-quinone building block.[34,35] The resulting ladder polymers are soluble and could be characterized using IR and NMR spectroscopy. The resulting ladder polymers were intensively investigated by Yu, Dalton, and their co-workers, especially for their non-linear optical properties.

3 Conjugated ladder polymers by polymer-analogous cyclization of single-stranded precursor polymers

3.1 Ladder-type polyphenylenes

The optical and electronic properties of conjugated polymers frequently depend markedly on the conformation of the main chain. Twisting of the conjugated main chain, for example, induced by bulky substituents, leads in polyacetylenes, poly(*p*-phenylene)s, and polythiophenes to a reduction in the conjugative interaction, coupled with drastic changes in the optical properties (hypsochromic shift of the longest wavelength absorption maximum λ_{max}, reduction of the photoluminescence quantum yield ϕ) and the electronic properties (reduced charge transfer mobility).[36–40] On the other hand, the introduction of solubilizing side chains is often necessary to guarantee that the material is sufficiently processable. An ideal case for such materials would be the combination of a maximum π-conjugation in the main chain (lowest possible conformational twisting) with an optimal processability from solution. One strategy with this aim in mind is the incorporation of a π-conjugated backbone into the rigid, planar structure skeleton of a ladder polymer in which additional, peripheral substituents provide the desired degree of solubility and processability. The execution of such a strategy in 1991 resulted in the preparation of the first conjugated ladder polymer (LPPP) **3** by Scherf and Müllen (Scheme 4).[6] The transition from the insoluble and infusible poly(*p*-phenylene) (PPP) root system to PPP ladder polymers LPPP **3** that could be easily processed from solution represented an enormous step forward, from the perspective of both synthetic methodology and materials science. The incorporation of the basic PPP structure into the rigid and planar, double-stranded ladder allows a maximum π-conjugation of the aromatic sub-units. The synthesis of LPPP type ladder polymers **3** resulted from a ‘classical’ multi-step process:

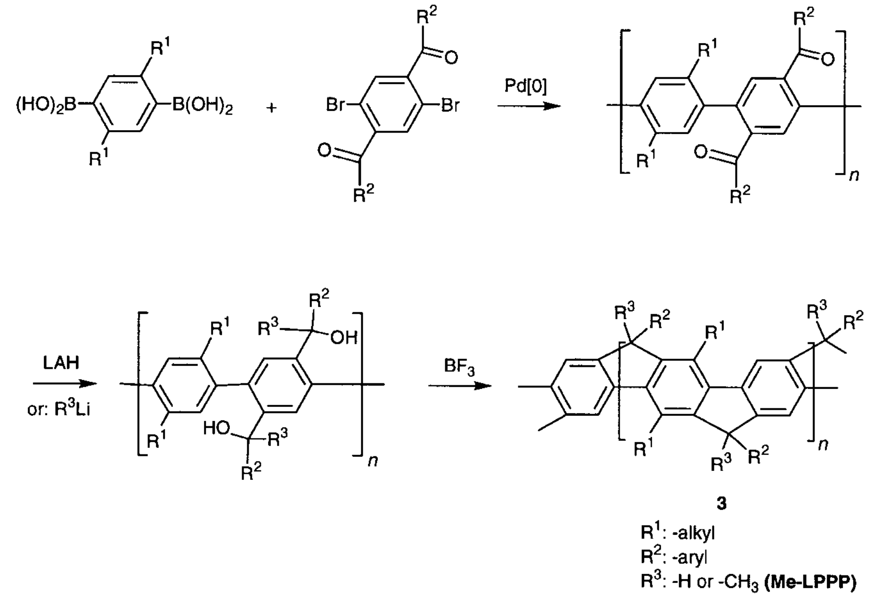
1. First, a keto-functionalized, single-stranded precursor polymer was prepared using a Pd(0)-catalyzed Suzuki coupling;

2. The double strand of the ladder polymer was then generated in two, polymer-analogous reaction steps: (i) the keto group was reduced with lithium aluminum hydride; or, alternatively, the >C=O groups alkylated with alkyllithium or an alkylmagnesium halide followed by (ii) ring closure in a polymer-analogous Friedel–Crafts alkylation.

Here, the substitution pattern at the methylene bridge is decisive for the desired, quantitative, completely intramolecular cyclization. If the reaction center $-CR^2R^3OH$ is not protected by bulky substituents ($-CH_2OH$), an intermolecular Friedel–Crafts reaction takes place that leads to the formation of branched, cross-linked, and insoluble products. On the other hand, if the reaction center is too strongly shielded by bulky aryl substituents ($-C(C_6H_5)_2OH$), the cyclization is incomplete, the result of which is that the ladder structure is not fully formed.[1,2] An optimal substitution pattern for the generation of a defect-free, double strand is the combination R^2=aryl, R^3=H, and R^2=aryl, R^3=alkyl at the methylene center $-CR^2R^3OH$. In these cases the ring closure is quantitative: no structure defects could be detected (incomplete cyclization, branching) by NMR spectroscopy and MALDI-TOF mass spectrometry.

LPPP derivatives **3** are accessible with number average molecular mass M_n of up to *ca.* 50 000 (M_w/M_n *ca.* 2), which corresponds to a linear coupling of up to 150 phenylene rings in the main chain of the double-stranded polymers. Using X-ray or small angle neutron scattering (SAXS/SANS)[41] or viscometry[42] a persistence length of *ca.* 8–10 nm was calculated for the ladder polymers of the LPPP type, a value that corresponds to that in other, single-stranded, stiff-chain polymers (aromatic polyesters, polyaryls).[43,44]

In the transition from the conformationally strongly twisted, single-stranded precursor structures to the double-stranded



Scheme 4 Synthesis of poly(*p*-phenylene) ladder polymers (LPPP) **3** according to Scherf.

ladder polymer in the key step of the LPPP synthesis, a drastic change occurs in the optical properties of the conjugated polymer, as shown by a marked red shift of the long wavelength absorption peak λ_{max} and the appearance of a very intense, blue photoluminescence (PL). The deep yellow colored ladder polymer **3** of the LPPP type (λ_{max} *ca.* 450 nm) possess the typical absorption spectrum of a delocalized, one-dimensional π-electron system with a very steep absorption edge and a pronounced vibrational fine structure. This absorption characteristic is thus a further indication for the existence of a highly defined electronic structure that is extremely low in defects. The photoluminescence of LPPP **3** derivatives in dilute solution is characterized by the appearance of a mirror-plane symmetrical photoluminescence (PL) spectrum, whereby a very small Stokes shift of less than 150 cm^{-1} is observed.[45] A Stokes shift of this magnitude can be interpreted as a consequence of the geometrically constrained, rigid π-electron system, which permits no major changes in geometry in the transition from the ground to the excited state. Connected with the planar construction of the conjugated main chain in LPPP, unusually high PL quantum yields of over 90% are observed in dilute solution, as few routes exist for non-radiative deactivation.

At the molecular level, an optimally suitable, tailor-made system is available for applications as polymeric emitter, for example, in light-emitting diodes (LEDs) based on organic luminophores. Complications, typical for the use of organic materials in electronic elements, nevertheless appear in the changeover from the isolated molecule in (dilute) solution to molecular assemblies in the solid state. Here, cooperative phenomena become of decisive importance and can lead to a drastic change in the property spectrum. This was also seen in the case of the new ladder polymers of LPPP **3** type, the PL properties of which change dramatically (*e.g.*, for R^2 = aryl, R^3 = H) in the transition to the solid state (film, layer; see Fig. 1). These changes are expressed in an emission spectrum that is dominated by a red-shifted, unstructured broad emission band in the yellow region.[45] In addition, the PL quantum yield is reduced (*ca.* 10%).[46] This characteristic of the PL in the solid state could be definitively characterized as aggregate emission, *e.g.* by means of 'site'-selective PL spectroscopy[45] and by time-resolved monitoring of the growth and decay of the PL in the fs and ps range.[47] However, the dominance of the red-shifted aggregate emission, undesired in terms of the target of a blue, efficient PL, can be effectively suppressed by a minor change of the substitution pattern at the methylene bridge (*e.g.*, in the transition from an LPPP derivative with R^2 = aryl, R^3 = H to a new one with R^2 = aryl, R^3 = CH_3 (so-called Me-LPPP).[48] In the latter case (Me-LPPP) the PL properties in dilute solution and in the solid state are largely identical (Fig. 2). Moreover, there is very

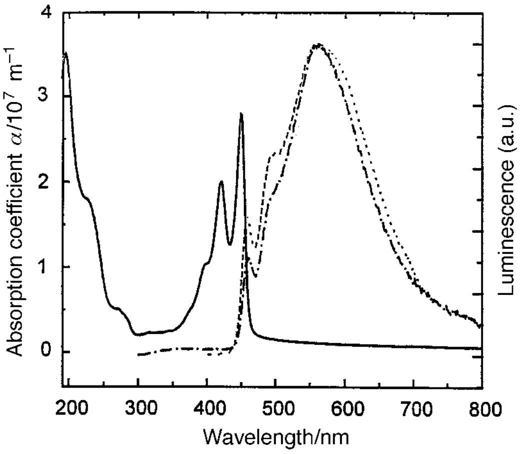


Fig. 1 Absorption (—) and photoluminescence (----) spectra of a thin film of LPPP **3** (R^2 = aryl, R^3 = H) and electroluminescence (–·–·) spectrum of an ITO–LPPP **3** (60 nm)–Al device.

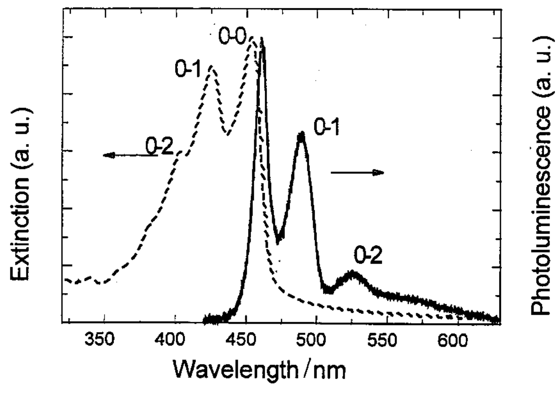


Fig. 2 Absorption (----) and photoluminescence (—) spectra of the Me-LPPP **3** (R^2 = aryl, R^3 = CH_3) ladder polymer synthesized according to Scherf and Müllen.

satisfactory, marked increase in the solid state PL quantum yield for Me-LPPP to a value of *ca.* 40%, which represents a peak value for organic, polymeric emitters in the solid state.[46,49,50] Thus, the resulting property spectrum of Me-LPPP shows: (i) excellent solubility and high molecular weight, with M_n up to *ca.* 50 000, which permits processing from solution into layers and films with high optical quality (film thickness: 20–2000 nm); (ii) high solid state PL-quantum yield of up to 40%; and (iii) high thermo-oxidative and photochemical stability; and represents an optimum and very promising basis for the application of Me-LPPP and derivatives as emitter and photoactive material in electronic devices. In addition, the completely amorphous ladder polymer materials of the LPPP **3** type show unusually high charge carrier mobilities with a surprisingly low temperature and field dependence. A value of more then $10^{-3}\ \mathrm{cm^2\,(Vs)^{-1}}$ was measured for the hole mobility μ at room temperature and an applied external field E of $4–6\times10^6\ \mathrm{V\,cm^{-1}}$ using time-of-flight (TOF) measurements of the photoconductivity.[51] This hole mobility is significantly above that of other conjugated polymers (for example, PPV and PPV derivatives) and is only two orders of magnitude below that of (crystalline) anthracene.[51] A theoretical explanation for this unusually high charge carrier mobility in a completely amorphous polymer, which is of considerable advantage for application in electronic devices, has not yet been found.

Within the last five or six years LPPP **3** materials have been intensively tested for potential application in electronic devices, especially light emitting devices.[90] In the next section a short overview will be given of the results obtained thereby.

As mentioned above, the PL characteristics described represent an excellent basis for experiments on the use of LPPP **3** materials in light-emitting diodes (LEDs) that contain organic emitters as active components. The application of an LPPP **3** with R^2 = aryl, R^3 = H in a single-layer construction ITO–LPPP–Ca leads to a yellow-emitting LED at a service potential of 5–7 V and a film thickness of the active layer of about 100 nm. The yellow color of the emission results from the aggregation of individual LPPP molecules (Fig. 1). The external quantum efficiency of the electroluminescence has been measured as about 1%,[52] whereby the overall characteristic of these light diodes is generally comparable with that of other yellow or orange LEDs based on organic emitter polymers (for example, PPV or MEH-PPV). However, LPPP materials are potential blue emitters because of their absorption and emission energy in the range 2.5–2.8 eV, if it is possible to effectively suppress the yellow aggregate emission. Blue emitter materials are particularly attractive at the moment, as blue LEDs from inorganic semiconductors (amorphous silicon, gallium nitride) are not readily accessible. As already described in the case of the PL properties, it was possible to largely suppress the aggregation and to achieve a blue electroluminescence with the methyl derivative Me-LPPP (R^2 = aryl, R^3 = CH_3) obtained by the exchange of a hydrogen atom with a methyl group as substituent on the methylene bridge. In single-layer construction ITO–Me-LPPP–Ca blue LEDs of this type show an astonishingly high EL quantum efficiency of up to 4%, representing a peak value for blue emitters in the organic class, at a relatively low field strength of *ca.* 0.5 MV $\mathrm{cm^{-1}}$.[50]

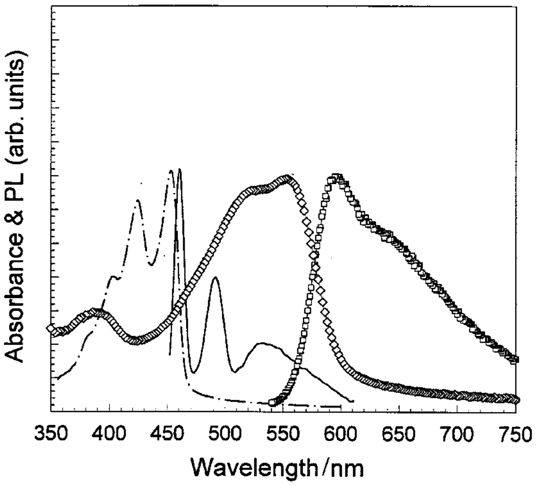
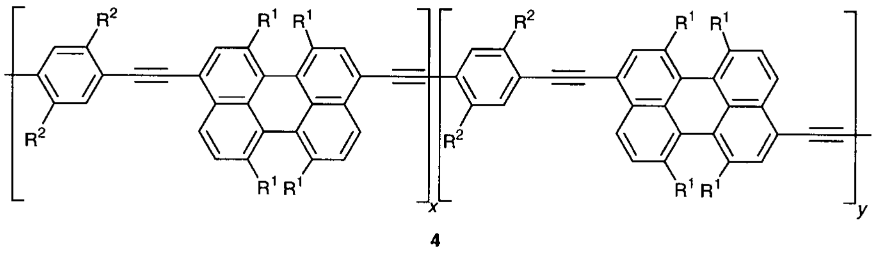


Fig. 3 Absorbance and photoluminescence (PL) spectra of Me-LPPP **3** (R^2 = aryl, R^3 = CH_3) acting as matrix polymer (absorbance: –·–·–; PL: —) and of PPDB **4** acting as orange–red luminescent dopant (absorbance: ◇◇◇; PL: □□□).

An alternative way of suppressing the undesired aggregate emission is to dilute aggregating LPPP luminophores in a suitable matrix polymer. In this manner, blends of 10% LPPP **3** (R^2 = aryl, R^3 = H) in poly(vinylcarbazole) show a drastic reduction in the (yellow) aggregate emission, which leads to a pure blue emission of the light-emitting diode.[52]

As a result of their absorption energy at the 'high-energy' edge of the visible spectrum blue LEDs of this type in turn form an appropriate basis for tailor-making all other ('low energy') colors of the visible spectrum (green, yellow, red) through energy transfer to lower emission energies.

One possibility of realizing this is the admixture of suitable green, yellow, or red fluorescence dyes to the blue-emitting Me-LPPP matrix. Thus, monomeric as well as polymeric dyes could be employed as emissive dopant. If one admixes, for example, increasing amounts of the red-emitting poly(peryleneethynylene-alt-phenyleneethynylene) copolymer **4** (Scheme 5, Fig. 3) to Me-LPPP as matrix polymer, the blue matrix emission is completely suppressed when one reaches a fraction of *ca.* 1.5–2% of the red-emitting perylene chromophore (Fig. 4).[53] Hereby, a complete energy transfer (Förster transfer) to the red polymer dye occurs. This method of adjusting the color of polymer LEDs, given here only by way of example, can be extended to any desired color within the visible spectrum; it is limited only by the availability of suitable fluorescence dyes that can be mixed into the matrix. If the dye is employed in only small quantities, an emission characteristic, which is composed of two EL components (matrix–monomeric or polymeric dye) is also adjustable; this can result, for



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R^1: -4-*t*-butylphenyloxy
R^2: -*n*-hexyloxy

Scheme 5 Structure of a red-emitting polyaryleneethynylene copolymer **4** containing perylene moieties.

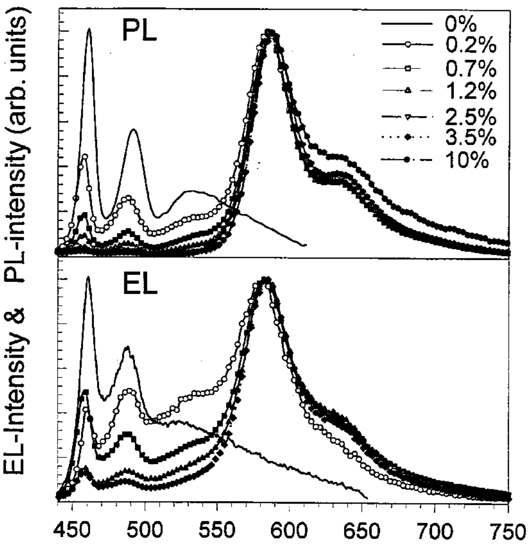


Fig. 4 Photoluminescence (PL) and electroluminescence (EL) spectra of Me-LPPP **3** (R^2=aryl, R^3=CH_3)–PPDB **4** films and devices (configuration ITO–Me-LPPP 3–PPDB 4–Al) containing increasing amounts of the PPDB **4** dopant (0–10%).

example, in a white total emission.[54] White light sources of this type are, for example, of considerable interest for background illumination (backlighting).

In addition to the intensively used, spontaneous emission of conjugated polymer materials, described above for LEDs, the ability for stimulated emission has recently also been the focus of research interests. The excellent suitability of LPPP **3** derivatives such as Me-LPPP (**3**, R^2=aryl, R^3=CH_3) for stimulated emission was demonstrated in 'pump and probe' experiments, first carried out in 1995 by two research groups.[55–57] Building on this, a cooperative, so-called amplified spontaneous emission (ASE) could be observed in PL studies with a continuous increase in the excitation energy in the simple configuration quartz substrate/'spin-coated' Me-LPPP.[58–61] If an Me-LPPP film is pumped with fs laser pulses at 400 nm, a marked change of the PL spectrum can be observed above a threshold energy of *ca.* 25 μJ cm^{-2}, whereby the first vibrational side band experiences a resonant amplification. This leads to a characteristic reduction of the linewidth of this PL band. By means of time-resolved PL spectroscopy and by variation of the excitation geometry, this behavior could be characterized unambiguously as amplified spontaneous emission (ASE), based on a 'four-level system' with population inversion.[58,62,63] For the realization of a genuine laser emission it is necessary to couple this ASE effect with an appropriate resonator geometry. That could be impressively demonstrated for Me-LPPP independently using two resonator geometries. On the one hand, a blue Me-LPPP solid state laser could be realized in an open-cavity configuration, whereby the polymer film was spin coated onto one of the two mirrors. With an optimally adjusted mirror distance a single-mode laser emission at *ca.* 585 nm resulted which is characterized by a linewidth of less than 1 nm.[64] In the second case a flexible, blue Me-LPPP solid-state laser could be demonstrated for the first time in the so-called 'distributed feedback' (DFB) configuration, whereby a microstructured, high modulated poly(ethylene terephthalate) (PET) film (periodicity: *ca.* 300 nm) acted as resonator onto which the active Me-LPPP layer was spin coated (Fig. 5). For this arrangement an unusually low threshold energy of about 1.5 nJ pulse^{-1} was measured in attaining the single-mode laser emission.[65] The laser emission in the blue is centered at *ca.* 487 nm and possesses a typical linewidth of less than 0.4 nm (Fig. 6). The emission is thereby strongly oriented in the lattice direction and is highly polarized (see Fig. 7). Further experiments should now answer the question of whether electrically pumped solid-state lasers (laser diodes) can also be realized. A combination of the typical LED arrangement with an appropriate resonator geometry is necessary for this, in order to generate a population inversion at the necessarily high current and excitation densities, leading to a laser emission of the electronic device.

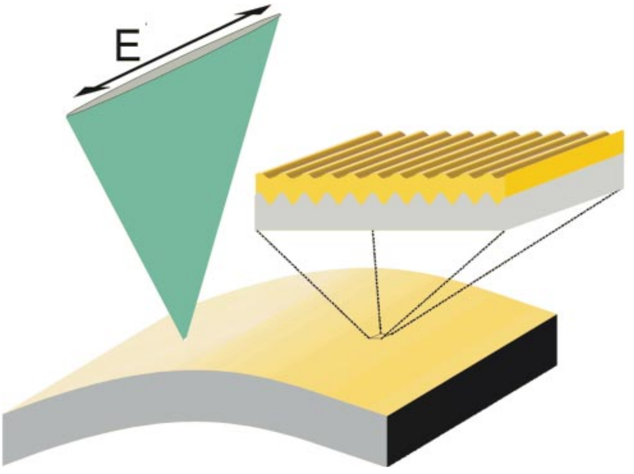


Fig. 5 Schematic sketch of the flexible polymer laser device based on an emitting Me-LPPP **3** (R^2=aryl, R^3=CH_3) film spin coated on a microstructured PET foil acting as distributed feedback (DFB) reflector.

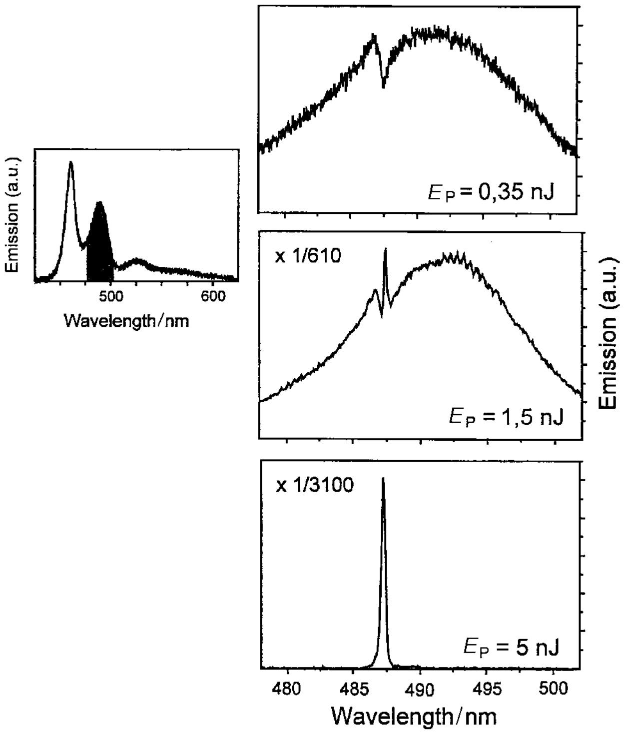


Fig. 6 Emission spectra of the flexible DFB polymer laser based on Me-LPPP **3** (R^2=aryl, R^3=CH_3) at wavelengths between 480 and 500 nm (inset of the PL overview spectrum) at different energies of the pumping pulses (0.35, 1.5, and 5.0 nJ).

In addition to the extensive investigations on the use of LPPP materials as polymeric emitters described hitherto, experiments on a potential application in photovoltaic elements[66–68] and as photoconductors[51,69,70] have also been carried out. Within the scope of this article we can only mention a few results and publications. These concern, for example, the charge generation and the charge carrier transport in Me-LPPP layers, which are doped with fullerene derivatives as electron acceptors[67,68] or with dye-sensitized titanium dioxide particles.[69] Further investigations, for example, on appli-

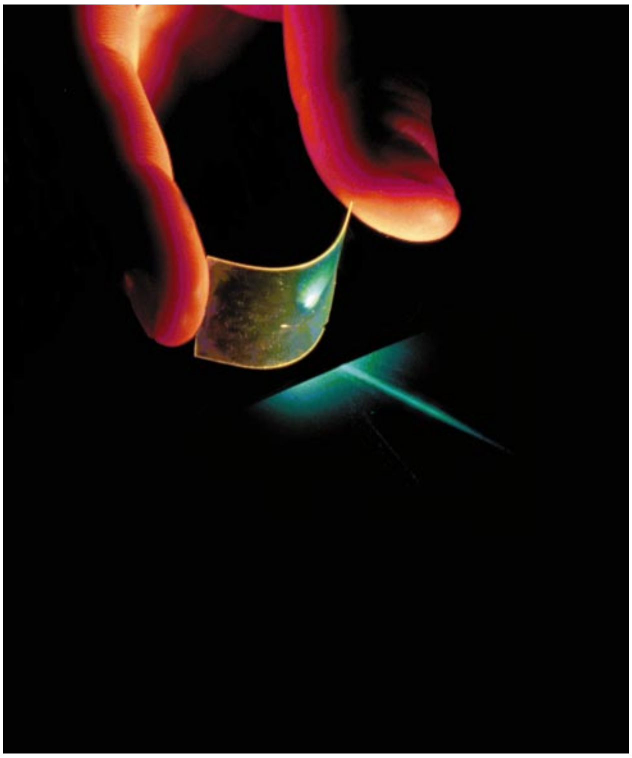
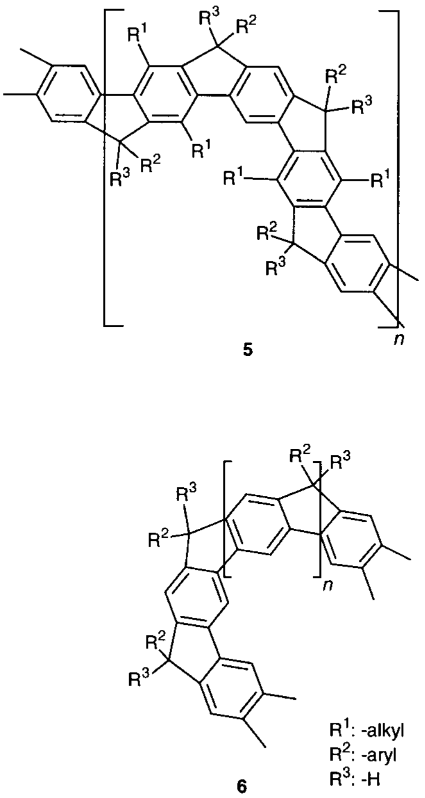


Fig. 7 Photograph of a blue, flexible polymer laser: Me-LPPP **3** (R^2 = aryl, $R^3 = CH_3$) on a microstructured poly(ethylene terephthalate) substrate.

cation of the high photoconductivity and high charge carrier mobility[51] in arrangements for electrophotography, are underway at the moment.

In the area of synthesis of ladder polymers of the LPPP **3** type new research into further structure modification has been reported recently. Thus, it was possible to shift the absorption and emission of the polymer, both further into the UV range (hypsochromic shift) and also into the red part of the visible spectrum (bathochromic shift) by chemical modification of the LPPP skeleton. The former can be effected by the incorporation of *m*-phenylene units (Scheme 6), which leads to an interruption of the conjugation in the main chain.[71] Thus, for polyphenylene ladder polymers LPPMP **5** with alternating *p*- and *m*-phenylene units the long wavelength absorption maximum λ_{max} is shifted hypsochromically by about 60 nm from 450 to 389 nm;[71] the all-*meta* ladder polymer LPMP **6** shows an absorption maximum λ_{max} in the UV at about 356 nm (Fig. 8).[49] On the other hand, the long wavelength absorption maximum λ_{max} is shifted bathochromically (red shifted), if *p*-phenylene units in the main polymer chain are replaced with 2,5-thienylene units.[72] Thus, the red emitting ladder polymer LPPPT **7** (Scheme 7), composed of alternating *p*-phenylene and 2,5-thienylene blocks, shows a value for λ_{max} of *ca.* 530 nm (Fig. 8), which is red-shifted by *ca.* 80 nm when compared with the parent poly(*p*-phenylene) system LPPP **3** (λ_{max}: *ca.* 450 nm).

A further structure modification was published by Freund *et al.* in 1994.[73] They replaced the aryl–aryl linkages of LPPP **3** by aryl–S–aryl linkages. The first step in this synthesis was a nucleophilic coupling of aromatic dichloro diketo monomers and aromatic bisthiols. The single-stranded precursors of the poly(phenylene sulfide) type were then cyclized in a polymer-analogous fashion (Scheme 8). The resulting sulfur-containing ladder polymers **8** could be obtained with high number average molecular weights M_n of up to 150 000. The ladder polymers **8** possess a heteropoly[*n*]acene perimeter and can be oxidized to fully conjugated polycations which are isoelectronic with the corresponding poly[*n*]acenes.[74]



Scheme 6 Structures of PPP-ladder polymers containing *m*-phenylene building blocks: LPPMP **5** and LPMP **6**.

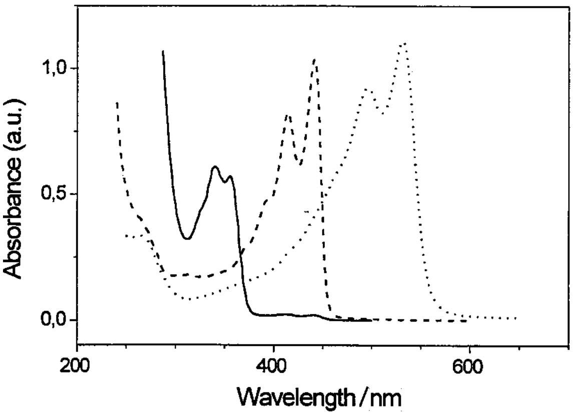
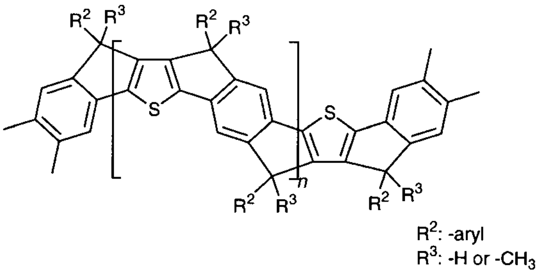
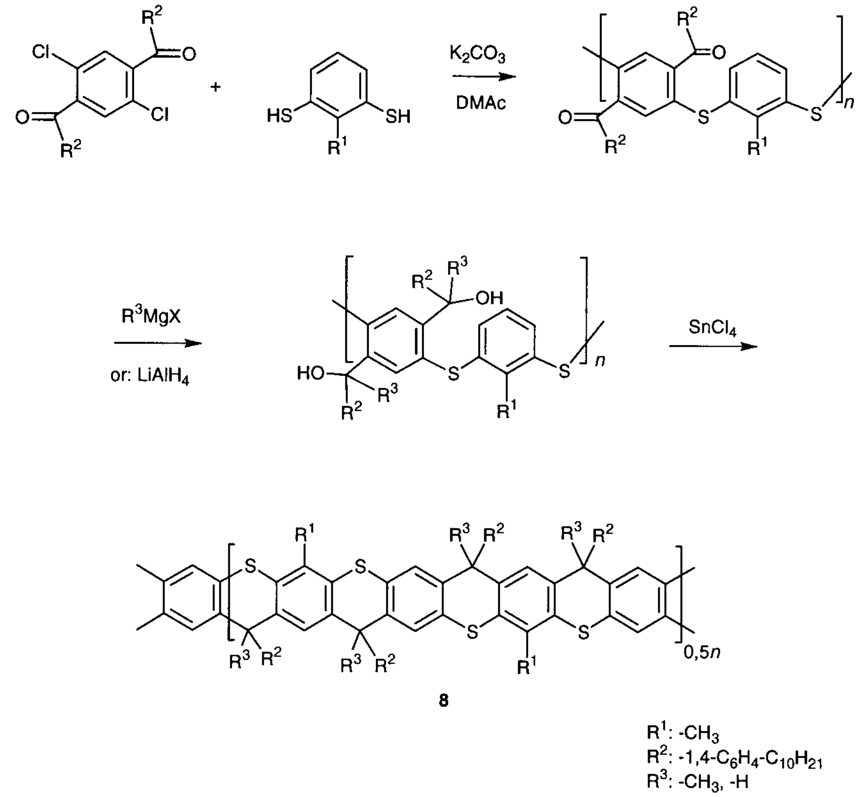


Fig. 8 Absorption spectra of polyarylene ladder polymers: LPPPT **7** (·····) composed of alternating *p*-phenylene and 2,5-thienylene units, LPPP **3** (----) composed of *p*-phenylene units, and LPMP **6** (—) composed of *m*-phenylene units.



7

Scheme 7 Structure of the heteroaromatic ladder polymer LPPPT **7** containing alternating *p*-phenylene and 2,5-thienylene building blocks.



8

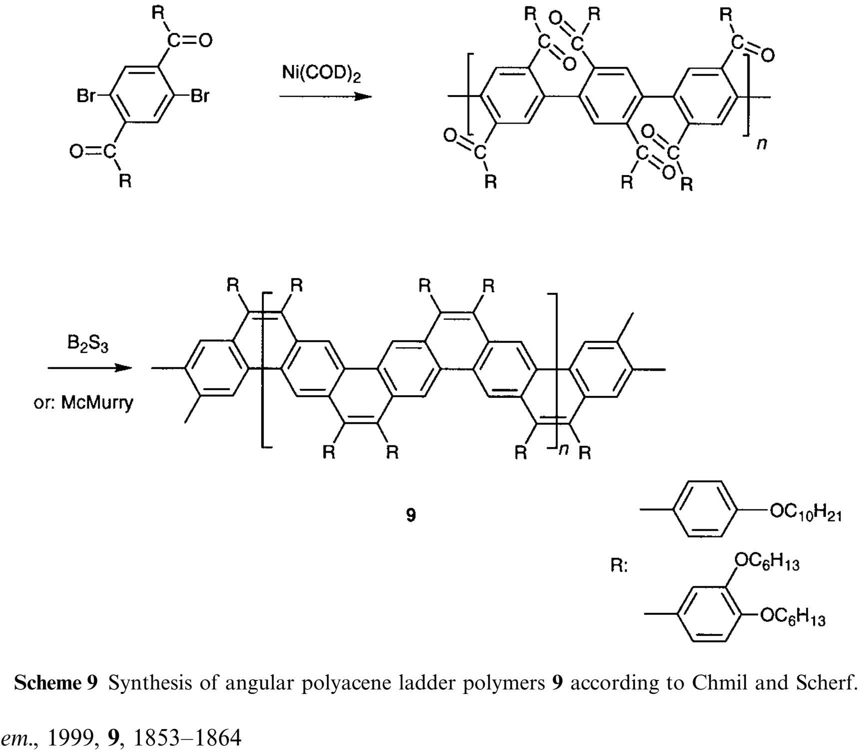
R^1: $-CH_3$
R^2: $-1,4-C_6H_4-C_{10}H_{21}$
R^3: $-CH_3$, $-H$

Scheme 8 Synthesis of sulfur-containing ladder polymers **8** containing a heteropoly[*n*]acene perimeter according to Freund, Scherf and Müllen.

3.2 Ladder polymers of polyacene type

The previous section was dedicated to the hitherto most intensively investigated class of conjugated ladder materials, ladder polymers of poly(*p*-phenylene) type (LPPPs). Their electronic properties have permitted LPPP and its structural derivatives to be established as standard materials for research in the area of organic semiconductors. In addition to the ladder polymers of LPPP type, in 1993 representatives of a second class of aromatic, conjugated ladder polymers were first described by Chmil and Scherf.[75,76] While LPPP is constructed of an alternating series of six- and five-membered rings, the representatives of the second class are composed solely of condensed six-membered rings, hence the description polyacenes. The angular construction of the main chain thus leads to the description angular polyacenes.

Ladder polymers of this type can also be constructed using a classical multi-step mechanism, whereby once again single-stranded, substituted precursor polymers are cyclized in the key step to form the ladder polymer. In this case, a 2,5-diketo-substituted poly(*p*-phenylene) derivative is first generated from an aromatic dibromo diketo monomer (a 2,5-dibromo-1,4-dibenzoylbenzene derivative) by aryl–aryl homocoupling with the $Ni(COD)_2$ reagent. In turn, this precursor polymer is



9

Scheme 9 Synthesis of angular polyacene ladder polymers **9** according to Chmil and Scherf.

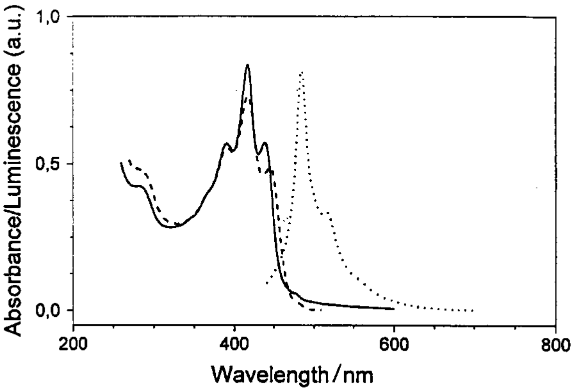


Fig. 9 Absorption (—), photoluminescence (·····) and PL excitation (----) spectra of a polyacene ladder polymer **9** synthesized according to Chmil and Scherf.

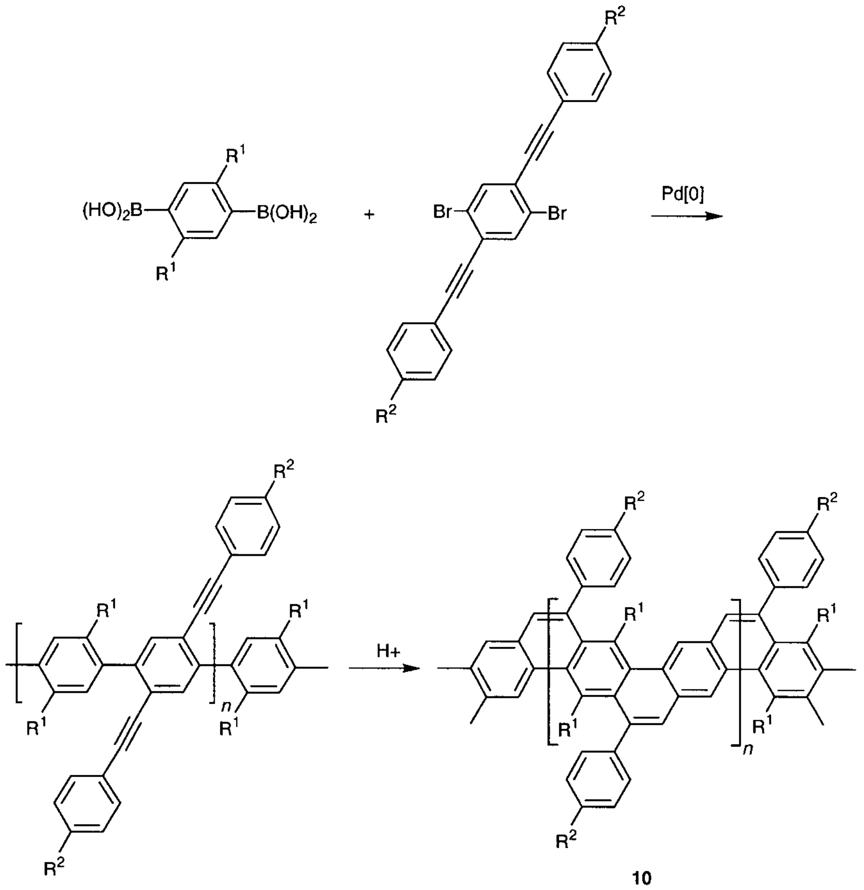
converted in a subsequent polymer-analogous cyclization step into the final angular polyacene ladder polymer, whereby planarization of the strongly twisted, single-stranded precursor again takes place. The McMurry reagent showed itself to be an excellent reagent to guarantee a selective and complete carbonyl olefination of neighboring keto functions under formation of the target ladder structure.[2,75,76] The soluble polyacene ladder polymers **9** (Scheme 9) can be prepared with a number average molecular weight of up to 25 000, which corresponds to a coupling of more than 25 phenylene building blocks.[76] The angular polyacene ladder polymers **9** are yellow colored and show a long wavelength absorption maximum λ_{max} at *ca.* 440 nm. The ladder polymers **9** are characterized by a very steep absorption edge and the appearance of a pronounced vibrational fine structure (Fig. 9), which suggests the existence of a geometrically intact, planar π-electron system (see also the chapter on LPPP type ladder polymers **3**).

The angular polyacenes **9** show an intense blue–green photoluminescence (Fig. 9) and could be used as active emitter materials in blue–green LEDs based on polymeric organic emitters.[77]

Ladder polymers **10** of a very similar structure were described by Goldfinger and Swager in 1994, whereby the synthesis of **10** also involved the polymer-analogous cyclization of suitably substituted single-stranded poly(*p*-phenylene) precursor polymers (Scheme 10).[78] However, the electronic properties (*e.g.* photo- and electroluminescence) of their ladder materials **10** have not been investigated in much detail to date. The synthesis of hetero analogues **11** (aza-analogues) of angular polyacenes was described in 1994 by Tour and Lamba (Scheme 11).[79,80] Unfortunately, their 'aza'-ladder polymers **11**, also prepared *via* the classical route which uses a polymer-analogous cyclization of appropriately substituted precursors, are almost completely insoluble in common organic solvents. They can only be brought into solution in strongly protic solvents, for example, in trifluoroacetic acid, which leads to protonation of the nitrogen centers. The poor solubility has so far hindered a comprehensive spectroscopic characterization of these products.

4 Ladder polymers by repetitive Diels–Alder cycloaddition

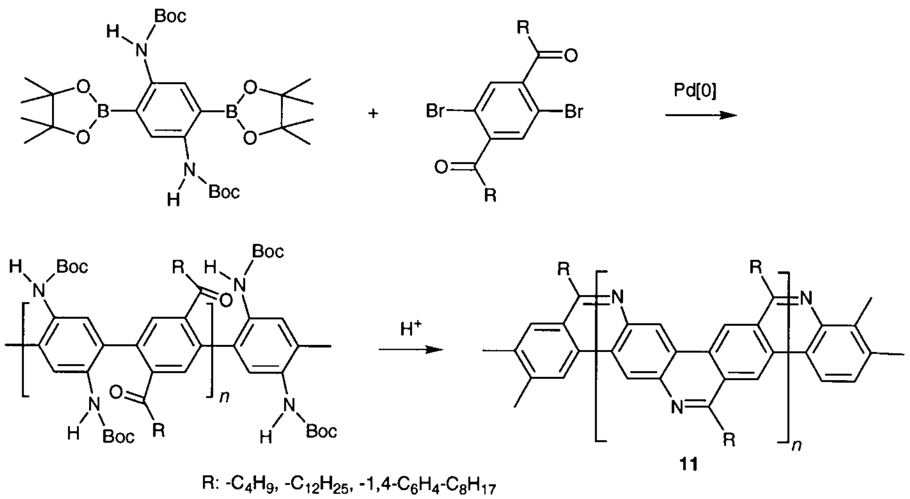
The fundamental work on the synthesis of ladder polymers by synchronous construction of both strands using Diels–Alder polyaddition was published at the beginning of the sixties by



10

R^1: $-OC_8H_{17}$
R^2: $-OC_{10}H_{21}$

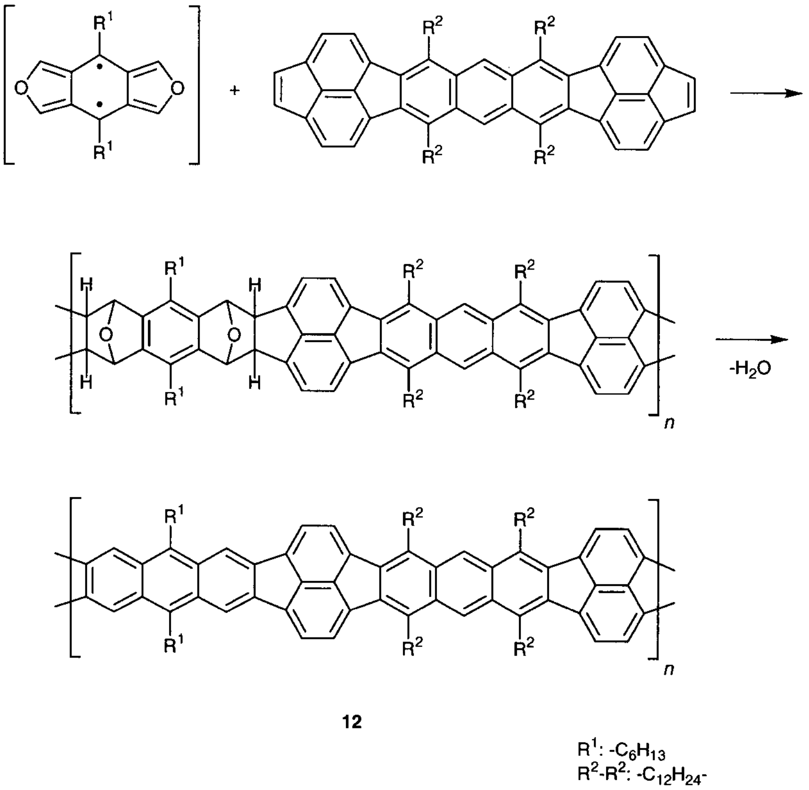
Scheme 10 Synthesis of angular polyacene ladder polymers **10** according to Goldfinger and Swager.



Scheme 11 Synthesis of aza-polyacene ladder polymers **11** according to Tour and Lamba.

Bailey *et al.* (for a review see ref. 81) and in the following decades taken up by numerous research groups.[4,82–88] In particular, the solubility of the products could be decisively improved by the introduction of solubilizing substituents, which then allowed comprehensive characterization for the first time. Investigations from the materials science perspective, however, did not follow. It was not possible to convert the heavily coiled double strands containing saturated sp^3 centers in a polymer-analogous conversion into stiff chain, fully aromatic ladder polymers.[86,88] All attempts to remove the functional groups still present after the first Diels–Alder cycloaddition step (keto groups, exocyclic bridges) in polymer-analogous fashion led to unsatisfactory results.

Schlüter *et al.*, in the middle of the nineties, were first able to present fully aromatic ladder polymers **12**, which they prepared using a synchronous route (repetitive Diels–Alder cycloaddition; Scheme 12). They condensed a bis-furan monomer, generated *in situ*, with a bifunctional pyracyclene dienophile in an AA/BB-type polyaddition to give soluble Diels–Alder polyadducts with number average molecular weight M_n of 5000–10 000.[5] The exocyclic –O– bridges of the primary, folded polyadducts could be eliminated by polymer-analogous dehydration. The resulting planar (unfolded) ladder polymers **12** are red colored, but unfortunately largely insoluble. The complete aromatization could be confirmed by means of solid state ^{13}C NMR spectroscopy. The resulting ladder polymer possesses a long wavelength absorption maximum λ_{max} at *ca.* 585 nm corresponding to an absorption energy (band gap) of *ca.* 2.1 eV. Initial investigations into the electrical conductivity of neutral and doped samples were published recently, whereby the conductivity increased by several orders of magnitude on reductive doping with alkali metals (Rb, K) or oxidative doping with arsenic pentafluoride.[89]



12

Scheme 12 Synthesis of conjugated ladder polymers **12** containing pyracyclene moieties according to Löffler, Schlüter *et al.*

5 Conclusion

The wealth of results from the last few years presented in this article impressively demonstrate the advance and the enormous dynamism of polymer research in the area of (conjugated) ladder polymers. Generally, a definite trend toward structurally well defined and easily processable materials can be ascertained. A particularly high level of interest is apparent in potential applications (*e.g.*, use as the emitter layer in polymer LEDs), from a direction in which structural accuracy, a minimum number of structure defects, and the purity of the substances are absolute requirements for attaining an optimal device performance. Apart from this, the availability of several powerful synthetic strategies for conjugated ladder polymers was and will be extremely promising for the developments achieved hitherto and those anticipated in the future.

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6 References

1 U. Scherf and K. Müllen, *The Synthesis of Ladder Polymers*, in: *Adv. Polym. Sci.*, Vol. **123**, 1995, p. 1.
2 U. Scherf, *Conjugated Ladder-Type Structures*, in: *Handbook of Conducting Polymers, Second Edition*, eds. T. Skotheim, R. L. Elsenbaumer and J. R. Reynolds, Marcel Dekker, New York, Basel, Hong Kong, 1998, Chapter 14, p. 363.
3 C.-S. Wang, *Trends Polym. Sci. (TRIP)*, 1997, **5**, 138.
4 A.-D. Schlüter, *Adv. Mater.*, 1991, **3**, 282.
5 M. Löffler, A.-D. Schlüter, K. Gessner, W. Saenger, J.-M. Toussaint and J.-L. Bredas, *Angew. Chem.*, 1994, **106**, 2281; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2209.
6 U. Scherf and K. Müllen, *Makromol. Chem. Rapid Commun.*, 1991, **12**, 489.
7 C. G. Overberger and J. A. Moore, *Ladder Polymers*, in: *Adv. Polym. Sci.*, Vol. 7, 1970, p. 113.
8 C. S. Marvel and C. L. Levesque, *J. Am. Chem. Soc.*, 1938, **60**, 280.
9 C. S. Marvel, J. O. Cormer and E. H. Riddle, *J. Am. Chem. Soc.*, 1942, **64**, 92.
10 M. Grassie and I. C. McNeil, *J. Chem. Soc.*, 1956, 3929; *J. Polym. Sci.*, 1958, **27**, 207; 1958, **33**, 171; 1959, **39**, 211.
11 P. J. Goodhew, A. J. Clarke and W. J. Bailey, *J. Mater. Sci. Eng.*, 1975, **17**, 3.
12 G. Arey, S. K. Chadda and R. Poller, *Eur. Polym. J.*, 1983, **19**, 313; *J. Polym. Sci. Chem. Ed.*, 1982, **20**, 2249.
13 C. L. Renschler and A. P. Sylwester, *Appl. Phys. Lett.*, 1987, **50**, 1420.
14 R. L. vanDeussen, *J. Polym. Sci. B*, 1966, **4**, 211.
15 R. L. vanDeussen, O. K. Goins and A. J. Sicree, *J. Polym. Sci. A1*, 1968, **6**, 1777.
16 F. E. Arnold and R. L. vanDeussen, *Macromolecules*, 1969, **2**, 479.
17 F. E. Arnold and R. L. vanDeussen, *J. Appl. Polym. Sci.*, 1971, **15**, 2035.
18 S. A. Jenekhe, P. O. Johnson and A. K. Agrawal, *Macromolecules*, 1989, **22**, 3216.
19 S. A. Jenekhe and P. O. Johnson, *Macromolecules*, 1990, **23**, 4419.
20 N. Yu, M. Chen and L. R. Dalton, *Chem. Mater.*, 1990, **2**, 649.
21 S. Y. Hong, M. Kertesz, Y. S. Lee and O. K. Kim, *Macromolecules*, 1992, **25**, 5424.
22 H. H. Song, *Synth. Met.*, 1995, **69**, 533.
23 A. K. Agrawal, C.-S. Wang and H. H. Song, *Mater. Res. Soc. Symp. Proc.*, 1994, **328**, 279.
24 K. S. Narayan, B. E. Taylor, R. S. Spry and J. B. Ferguson, *J. Lumin.*, 1994, **60**, 482.
25 D. J. Leopold, I. M. Brown and T. C. Sandreczki, *Synth. Met.*, 1996, **78**, 67.
26 S. A. Jenekhe and S. J. Tibbets, *J. Polym. Sci., Polym. Phys.*, 1988, **26**, 201.
27 J. K. Stille, E. L. Mainen, M. E. Freeburger and F. W. Harris, *Polym. Prep.*, 1967, **8**, 244.
28 J. K. Stille and M. E. Freeburger, *J. Polym. Sci. A1*, 1968, **6**, 161.
29 J. K. Stille and E. L. Mainen, *Macromolecules*, 1968, **1**, 36.
30 J. K. Stille and E. L. Mainen, *J. Polym. Sci. B*, 1966, **5**, 39, 665.
31 M. Okada and C. S. Marvel, *J. Polym. Sci. A1*, 1968, **6**, 1259.
32 R. Wolf, M. Okada and C. S. Marvel, *J. Polym. Sci. A1*, 1968, **6**, 1503.
33 H. Jadamus, F. DeSchryver, W. DeWinter and C. S. Marvel, *J. Polym. Sci. A1*, 1966, **4**, 2831.
34 L. Yu and L. R. Dalton, *Synth. Met.*, 1989, **29**, E463.
35 L. Yu and L. R. Dalton, *Macromolecules*, 1990, **23**, 3439.
36 R. D. McCullough, *Adv. Mater.*, 1998, **10**, 93.
37 A.-D. Schlüter, *Synthesis of Poly(p-phenylene)s*, in: *Handbook of Conducting Polymers, Second Edition*, eds. T. Skotheim, R. L. Elsenbaumer and J. R. Reynolds, Marcel Dekker, New York, Basel, Hong Kong, 1998, Chapter 8, p. 209.
38 A.-D. Schlüter, *Acta Polym.*, 1993, **44**, 59.
39 U. Scherf and K. Müllen, *Novel Conjugated Polymers—Tuning Optical Properties by Synthesis and Processing*, in: *ACS Symposium Series*, Vol. 672: *Photonic and Optoelectronic Polymers*, eds. S. A. Jenekhe and K. J. Wynne, ACS, Washington, DC, 1997, Chapter 24, p. 358.
40 J. C. W. Chien, *Polyacetylene: Chemistry, Physics and Materials Science*, Academic, Orlando, 1984.
41 P. Hickl, M. Ballauf, U. Scherf, K. Müllen and P. Lindner, *Macromolecules*, 1997, **30**, 273.
42 C. Gans, J. Schnee, U. Scherf, G. Staikos, E. Pierri and A. Dondos, *Polymer*, 1998, **39**, 4155.
43 P. Galda, D. Kirstner, A. Martin and M. Ballauf, *Macromolecules*, 1993, **26**, 1595.
44 L. Schmitz and M. Ballauf, *Polymer*, 1995, **36**, 879.
45 U. Lemmer, S. Heun, R. F. Mahrt, U. Scherf, M. Hopmeier, U. Siegner, E. O. Göbel, K. Müllen and H. Bässler, *Chem. Phys. Lett.*, 1995, **240**, 373.
46 W. Graupner, S. Eder, S. Tasch, G. Leising, G. Lanzani, M. Nisoli, S. de Silvestri and U. Scherf, *J. Fluorescence*, 1995, **7**, 195s.
47 R. F. Mahrt, T. Pauck, U. Lemmer, U. Siegner, M. Hopmeier, R. Hennig, H. Bässler, E. O. Göbel, P. Haring Bolivar, G. Wegmann, H. Kurz, U. Scherf and K. Müllen, *Phys. Rev. B*, 1996, **54**, 1759.
48 U. Scherf, A. Bohnen and K. Müllen, *Makromol. Chem.*, 1992, **193**, 1127.
49 J. Stampfl, W. Graupner, G. Leising and U. Scherf, *J. Lumin.*, 1995, **63**, 117.
50 S. Tasch, A. Niko, G. Leising and U. Scherf, *Appl. Phys. Lett.*, 1996, **68**, 1090.
51 D. Hertel, H. Bässler and U. Scherf, *Adv. Mater.*, 1998, **10**, 1119.
52 J. Grüner, H. F. Wittmann, P. J. Hamer, R. H. Friend, J. Huber, U. Scherf, K. Müllen, S. C. Moratti and A. B. Holmes, *Synth. Met.*, 1994, **67**, 181.
53 S. Tasch, C. Hochfilzer, J. W. E. List, G. Leising, H. Quante, Y. Geerts, P. Schlichting, U. Rohr, U. Scherf and K. Müllen, *Phys. Rev. B*, 1997, **56**, 4479.
54 S. Tasch, J. W. E. List, O. Ekström, G. Leising, H. Quante, Y. Geerts, U. Scherf and K. Müllen, *Appl. Phys. Lett.*, 1997, **71**, 2883.
55 W. Graupner, G. Leising, G. Lanzani, M. Nisoli, S. de Silvestri and U. Scherf, *Phys. Rev. Lett.*, 1996, **76**, 847.
56 W. Graupner, G. Leising, G. Lanzani, M. Nisoli, S. de Silvestri and U. Scherf, *Chem. Phys. Lett.*, 1995, **246**, 95.
57 T. Pauck, R. Hennig, M. Perner, U. Lemmer, U. Siegner, R. F. Mahrt, U. Scherf, K. Müllen, H. Bässler and E. O. Göbel, *Chem. Phys. Lett.*, 1995, **244**, 171.
58 C. Zenz, W. Graupner, S. Tasch, G. Leising, K. Müllen and U. Scherf, *Appl. Phys. Lett.*, 1997, **71**, 2566.
59 G. Kranzelbinder, M. Nisoli, S. Stagira, S. de Sivestri, G. Lanzani, K. Müllen, U. Scherf, W. Graupner and G. Leising, *Appl. Phys. Lett.*, 1997, **71**, 2725.
60 A. Haugeneder, M. Hilmer, C. Kallinger, M. Perner, W. Spirkl, U. Lemmer, J. Feldmann and U. Scherf, *Appl. Phys. B*, 1998, **66**, 389.
61 A. Haugeneder, M. Neges, C. Kallinger, W. Spirkl, U. Lemmer, J. Feldmann and U. Scherf, *J. Appl. Phys.*, 1999, **85**, 1124.

62 B. Schweitzer, G. Wegmann, D. Hertel, H. Giessen, U. Scherf, K. Müllen, W. W. Rühle, H. Bäßler and R. F. Mahrt, *Appl. Phys. Lett.*, 1998, **72**, 2933.
63 B. Schweitzer, G. Wegmann, R. F. Mahrt, H. Bäßler, F. Uckert, U. Scherf and K. Müllen, *Phys. Rev. B*, 1999, **59**, 4112.
64 C. Zenz, W. Graupner, S. Tasch, G. Leising and U. Scherf, *J. Appl. Phys.*, 1999, in the press.
65 C. Kallinger, M. Hilmer, A. Haugeneder, M. Perner, W. Spirkl, U. Lemmer, J. Feldmann, U. Scherf, K. Müllen, A. Gombert and V. Wittwer, *Adv. Mater.*, 1998, **10**, 920.
66 A. Köhler, J. Grüner, R. H. Friend, K. Müllen and U. Scherf, *Chem. Phys. Lett.*, 1995, **243**, 456.
67 C. Kallinger, A. Haugeneder, U. Lemmer, J. Feldmann, H. Hong, M. Tarabia, D. Davidov, E. Harth, M. Walter, U. Scherf, A. Gügel and K. Müllen, *Self-Assembly of Fullerene Monolayers for Optoelectronic Applications*, in: *Molecular Nanostructures*, eds. H. Kuzmany, J. Fink, M. Mehring and S. Roth, World Scientific Publishing Company, 1998, p. 515.
68 C. Waldauf, W. Graupner, S. Tasch, G. Leising, A. Gügel, U. Scherf, A. Kraus, M. Walter and K. Müllen, *Opt. Mater.*, 1998, **9**, 449.
69 M. Kocher, T. K. Däubler, E. Harth, U. Scherf, A. Gügel and D. Neher, *Appl. Phys. Lett.*, 1997, **72**, 650.
70 S. Barth, H. Bäßler, U. Scherf and K. Müllen, *Chem. Phys. Lett.*, 1998, **288**, 147.
71 U. Scherf and K. Müllen, *Polymer Commun.*, 1992, **33**, 2443.
72 M. Forster and U. Scherf, *Macromolecules*, in the press.
73 T. Freund, U. Scherf and K. Müllen, *Macromolecules*, 1995, **28**, 547.
74 T. Freund, U. Scherf and K. Müllen, *Angew. Chem.*, 1994, **106**, 2547; *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 2424.
75 K. Chmil and U. Scherf, *Makromol. Chem. Rapid Commun.*, 1993, **14**, 217.
76 K. Chmil and U. Scherf, *Acta Polym.*, 1997, **48**, 208.
77 S. Kirstein, G. Cohen, D. Davidov, K. Chmil, U. Scherf, M. Klapper and K. Müllen, *Synth. Met.*, 1995, **69**, 415.
78 M. B. Goldfinger and T. M. Swager, *J. Am. Chem. Soc.*, 1994, **116**, 7895.
79 J. M. Tour and J. S. S. Lamba, *J. Am. Chem. Soc.*, 1993, **115**, 4935.
80 J. M. Tour and J. S. S. Lamba, *J. Am. Chem. Soc.*, 1994, **116**, 11723.
81 W. J. Bailey, *Diels-Alder-Polymerization*, in: *Step growth polymerization*, ed. D. H. Solomon, Marcel Dekker, New York, 1972, p. 279.
82 F. H. Kohnke, A. M. Z. Slawin, J. F. Stoddart and D. J. Williams, *Angew. Chem*, 1987, **99**, 941; *Angew. Chem.*, *Int. Ed. Engl.*, 1987, **26**, 892.
83 P. R. Ashton, N. S. Isaacs, F. H. Kohnke, A. M. Z. Slawin, C. M. Spencer, J. F. Stoddart and D. J. Williams, *Angew. Chem.*, 1988, **100**, 981; *Angew. Chem.*, *Int. Ed. Engl.*, 1988, **27**, 966.
84 P. R. Ashton, N. S. Isaacs, F. H. Kohnke, J. P. Mathias and J. F. Stoddart, *Angew. Chem.*, 1989, **101**, 1266; *Angew. Chem.*, *Int. Ed. Engl.*, 1989, **28**, 1258.
85 A. Godt and A.-D. Schlüter, *Chem. Ber.*, 1991, **124**, 149.
86 M. Löffler and A.-D. Schlüter, *GIT Fachz. Lab.*, 1992, 1101.
87 S. Wegener and K. Müllen, *Chem. Ber.*, 1991, **124**, 2101.
88 U. Scherf and K. Müllen, *Synthesis*, 1992, 23.
89 B. Waage, A.-D. Schlüter and G. Leising, *Synth. Met.*, 1997, **84**(1–3), 933.
90 For two recent review articles on organic electroluminescent polymers including LPPP materials see: A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem.*, *Int. Ed. Engl.*, 1998, **37**, 402; R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. dos Santos, J. L. Bredas, M. Löglund and W. R. Salaneck, *Nature*, 1999, **397**, 121.

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