

ADVANCES IN POLYMER SCIENCE

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Polyfluorenes



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Polyfluorenes

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Preface

With this collection of short review papers we would like to present a broad overview of research on polyfluorenes and related heteroanalogues over the last two decades. The collection begins with papers on the synthesis of polyfluorenes and related polyheteroarenes, then reports photophysical properties of this class of conjugated polymers both at the ensemble and the single chain level, continues with a discussion of the rich solid state structures of polyfluorenes, and finally switches to device applications (e.g. in OLEDs). In addition, two chapters are devoted to defined oligofluorenes as low molecular weight model systems for polyfluorenes and also to degradation studies.

We feel that this up-to-date collection will be very helpful to all polymer chemists and physicists, and will also aid graduate students interested in this fascinating and still growing area of research, since such a compact overview is only now available. All articles are presented by leading scientists in their fields, insuring state-of-the-art coverage of all relevant aspects. Together with the body of references this volume is meant to assist researchers in the daily lab routine. Moreover, *Advances in Polymer Science*, as an established series of high quality review papers, represents a very appropriate platform for our project. We hope that this short collection will be of great value both for beginners and established research scientists in the field of polyfluorene research.

Wuppertal und Potsdam, April 2008

Ullrich Scherf
und Dieter Neher

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Bridged Polyphenylenes – from Polyfluorenes to Ladder Polymers

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Abstract This chapter reviews the synthesis of polymers based on bridged phenylenes for use in electronic applications such as blue-light-emitting diodes and polymer lasers. We show how the optoelectronic properties may be tuned by varying the amount of bridging between one bridge per two phenylenes in polyfluorenes through to completely bridged ladder-type polyphenylenes, and by changing the nature of the substituents at the bridge-heads. Of particular importance is the suppression of undesirable long wavelength emission by controlling interchain interactions and choosing synthetic methods so as to hinder or prevent the formation of emissive defects. The electroluminescence efficiency of these materials

can also be enhanced by the use of charge-transporting substituents. Copolymerisation with lower band-gap units enables tuning of the emission colour across the entire visible range.

Keywords Electroluminescence · Ladder polymers · Lasing · Light-emitting diodes · Photoluminescence

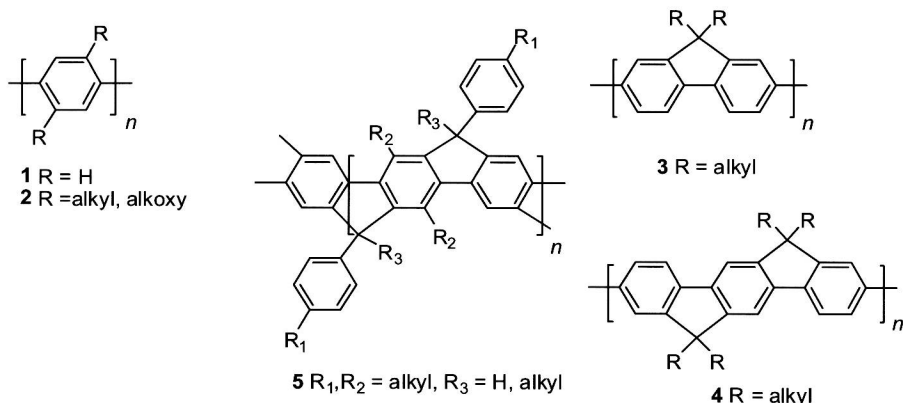
Abbreviations

^t Bu	<i>tert</i> -butyl
ECL	Effective conjugation length
EL	Electroluminescence
eV	Electron volt
HOMO	Highest occupied molecular orbital
IR	Infrared
ITO	Indium tin oxide
LEC	Light-emitting electrochemical cell
LED	Light-emitting diode
LPPP	Ladder-type poly(<i>para</i> -phenylene)
LUMO	Lowest unoccupied molecular orbital
Me	Methyl
Me-LPPP	Methyl-substituted LPPP
M_n	Number-averaged molecular weight
M_w	Weight-averaged molecular weight
NMR	Nuclear magnetic resonance
PDAF	Poly(dialkylfluorene)
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEO	Poly(ethylene oxide)
PF	Polyfluorene
Ph	Phenyl
Ph-LPPP	Phenyl-substituted LPPP
PIF	Polyindenofluorene
PSS	Poly(styrene sulfonate)
PVK	Poly(<i>N</i> -vinyl carbazole)
TGA	Thermal gravimetric analysis
UV-VIS	Ultraviolet-visible

1

Introduction

Phenylene-based polymers are one of the most important classes of conjugated polymers, and have been the subject of extensive research, in particular as the active materials in light-emitting diodes (LEDs) [1, 2] and polymer lasers [3]. These materials have been of particular interest as potential blue emitters in such devices [4]. The discovery of stable blue-light emitting materials is a major goal of research into luminescent polymers [5]. Poly(*para*-phenylene) (PPP, Scheme 1, 1) is a blue emitter [6], but it is insoluble and so films of PPP have to be prepared via precursor routes [7]. Substitution with long alkyl



Scheme 1 Unbridged and bridged phenylene polymers

or alkoxy groups as in **2** induces solubility [8], but the steric repulsion between the sidechains causes a marked twisting of the polymer backbone [9], leading to very short conjugation lengths and a corresponding shifting of the emission into the ultraviolet. In order to obtain solubility and thus processability without undesired blue-shifting of the absorption and emission bands the substituents can be attached to short carbon bridges between some or all of the benzene rings. Some types of bridged phenylene materials that will be covered in this review are shown in Scheme 1. These range from polydialkylfluorenes (PDAFs, **3**) with a unit of two bridged benzene rings, through polymers with longer bridged units, e.g., polyindenofluorenes (PIFs, **4**) to fully bridged ladder-type polyphenylenes (LPPPs, **5**). In this introduction we present an overview of the important properties of these materials that need to be controlled in order to obtain efficient LEDs, of the general principles of how these properties may be controlled by synthetic or physical methods, and of the general synthetic methods available for the preparation of these polymers. We will then present a more detailed discussion of the synthesis and optimisation of polymer properties for each class of material.

There are several properties of luminescent materials that need to be controlled in order to make efficient LEDs and lasers. The first is the colour of the emission, which is primarily determined by the energy difference (band-gap) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), but in the solid state is also affected by interactions between the molecules or polymer chains which can lead to red-shifts in the emission due to formation of aggregates. This can be controlled by manipulating both the polymer backbone and the substituents. Polyphenylenes are intrinsically blue-emitting materials with large HOMO-LUMO gaps, but as we will show, by copolymerisation with other materials it is possible to tune the emission colour across the entire visible spectrum. Even without the incorporation of comonomers it is possible to tune the

emission colour over a substantial range by controlling the conjugation length through restriction of the torsion of adjacent phenylene rings. Thus, as mentioned above, substitution of PPP (1) with solubilising groups to give soluble PPPs (2) causes a blue-shift in the emission as the steric interactions between the side-chains induce increased out-of-plane twisting of the phenylene units, while the enforced coplanarity produced by the methine bridges in LPPP (5) results in a marked red-shift in the emission. The “stepladder” polymers such as PDAFs (3) and PIFs (4) produce emission spectra intermediate between those of 2 and 5. As already mentioned, solid-state interactions between polymer chains can cause red-shifts in the emission of these materials, which can be suppressed by a suitable choice of substituents. This can, however, adversely affect the charge transporting properties of the material (see below).

The second critical property to be tuned is the efficiency of the charge injection, which is determined by the energy barrier between the HOMO and the anode (for hole injection) and between the LUMO and the cathode (for electron injection), and of charge transport which is controlled by intermolecular or interchain interactions. Polyphenylenes are materials with intrinsically low-lying HOMOs (typically 5.8–6.0 eV) which create a large barrier to hole injection from the most widely used anode material, indium tin oxide (ITO), which has a work function of 4.8–5.0 eV. The LUMO values are typically around 2.2–2.5 eV, which makes electron injection from air-stable metals such as aluminium (work function 4.3 eV) difficult, thus requiring the use of more electropositive metals such as calcium (work function 2.9 eV) as cathodes. Obviously one can improve the charge injection by raising the HOMO and/or lowering the LUMO energy of the polymer, but in doing so, one reduces the size of the energy gap and so induces a red-shift in the emission colour. As a result, obtaining efficient blue emission is a particular problem.

The efficiency of devices can be increased by the incorporation of layers of charge injecting (or level-matching) materials which have energy levels intermediate between that of the emissive layer and the work function of the electrode, but the use of such layers has the disadvantages of increasing the device thickness which increases the driving voltage, and also complicates device fabrication as successive layers have to be deposited in ways such that the lower layers are not disturbed by deposition of the upper ones. Blending charge transporting materials into the emissive layer leads to problems with phase separation, giving unstable device performance. The incorporation of charge accepting units into the polymer backbone or onto the side-chains avoids both these problems. This approach has been used to successfully improve both the hole and electron accepting properties of phenylene-based polymers. Good charge transport in the solid state requires close packing of polymer chains, permitting rapid and efficient hopping of charges between chains. As mentioned above, strong inter-chain interactions can cause undesirable red-shifts in the emission bands, so that it is sometimes necessary to compromise the charge transport properties of the material to obtain the desired emission colour.

Other desirable properties are the ability to form defect-free films, preferably by solution-processing techniques, a high solid-state photoluminescence (PL) quantum efficiency, and good stability towards oxygen and light. For some applications the ability to obtain polarised light is also desirable. All of these properties are to some extent controllable by the design of the structure and the synthetic pathway. The formation of a thick, uniform, defect-free film by spin-coating or similar solution-processing methods is dependent upon many factors. The first is the molecular mass of the compound, as low molar mass materials tend to be crystalline and so do not form high-quality amorphous films, while very high molar mass polymers are difficult to dissolve. The second is the solubility. To get a good film, the material must be reasonably soluble as too dilute solutions give too thin films, and must not form aggregates in solution as these will tend to lower the film quality (uneven morphology) and may produce red-shifts in the emission. The exact PL efficiency of a given material is as yet not predictable, but the removal of fluorescence quenching defects such as halide atoms or carbonyl groups, and the suppression of inter-chain interactions leading to non-radiative decay pathways are known to assist in improving the solid state quantum efficiency of materials. The stability of a polymer towards photo-oxidation can be improved by avoiding susceptible functional groups, e.g., benzyl protons. Polarised emission is obtained by alignment of the polymer chains, which seems to be easiest for polymers which possess a liquid crystalline mesophase [10]. Circularly polarised emission has been obtained by using chiral side-chains.

There exist two general methods for the synthesis of bridged phenylene-based materials: (a) oxidative coupling of monomers, which is of strictly limited synthetic utility as only low molecular-mass materials are obtained from such methods; and (b) transition mediated polycondensations of substituted aromatic compounds and/or aryl organometallic compounds. The latter is the main method for preparing bridged phenylene-based polymers. The two main polycondensation methods used are the Suzuki polycondensation of arylhalides with arylboronic acids or esters [11], and the Yamamoto polymerisation of aryl dihalides using nickel(0) reagents [12]. Generally speaking the Suzuki method gives higher molecular masses than the Yamamoto procedure, but is synthetically more demanding. A more detailed comparison of the relative merits of the two methods will be given in the discussion of the synthesis of PDAFs (Sect. 2.1 below).

2

Polyfluorenes

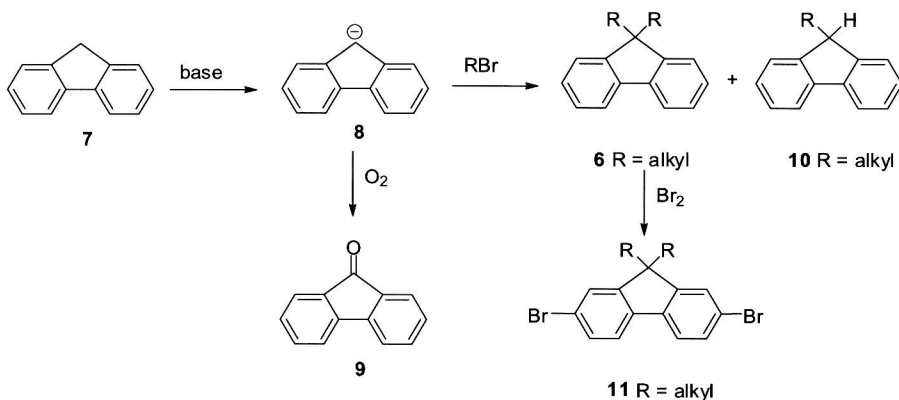
Polyfluorenes (PFs), the simplest regular stepladder-type polyphenylenes, in which only every second ring is bridged, have been much studied in recent years due to their large PL quantum efficiencies and excellent chemical and

thermal stability, as evidenced by the number of recent reviews [4, 13–15]. A further attractive feature of poly(9,9-dialkylfluorene)s (PDAFs) is the ready synthetic accessibility of the monomers as the alkylation and halogenation of fluorene proceed smoothly and in high yields.

2.1

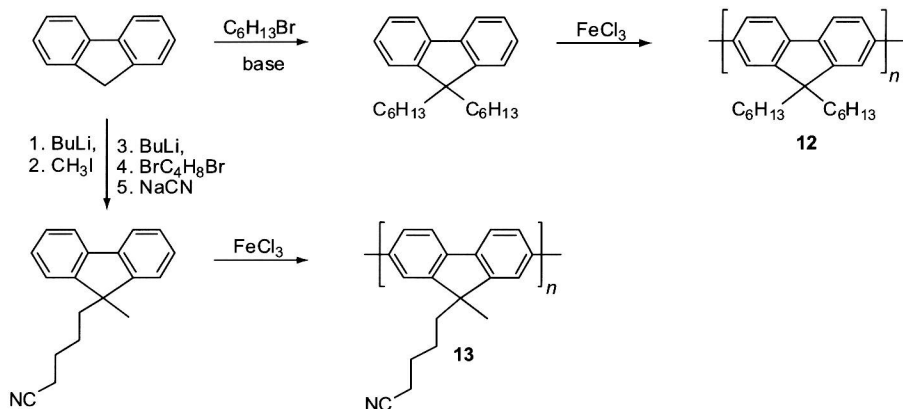
Poly(dialkylfluorene)s

The acidity of the bridgehead (C9) protons in fluorene makes the alkylation at this position extremely facile, with 9,9-dialkylfluorenes **6** being obtainable in high yield by treatment of fluorene **7** with an alkyl halide and base, usually under phase transfer catalysis conditions (Scheme 2). Some care is required to keep oxygen away as otherwise oxidation of the fluorenyl anion intermediate **8** leads to formation of fluorenone **9** as a byproduct. Another problem with this reaction is that the product may contain traces of the monoalkylfluorene **10**, which are difficult to detect and remove, and which as will be discussed in Sect. 2.3 can cause problems with the emission colour stability. Bromination of a dialkylfluorene **6** efficiently produces a 2,7-dibromo-9,9-dialkylfluorene **11**, which can also be made in a high yield by alkylation of 2,7-dibromofluorene. Both **6** and **11** can be used as monomers to make PDAFs.



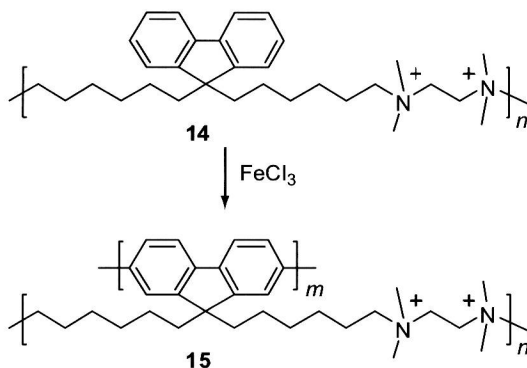
Scheme 2 Alkylation of fluorene to produce monomers for PDAFs

This ready accessibility of dialkylfluorene monomers is one of the major reasons for the extensive investigation of poly(dialkylfluorene)s. Three main methods have been used for the synthesis of the polymers. PDAFs can be made by oxidative coupling of the monomer **6** with iron(III) chloride. Poly(9,9-dihexyl-2,7-fluorene) (**12**) with a molecular mass of 5000 ($n = \text{ca. } 20$) was made in this way by Yoshino and co-workers (Scheme 3) [16, 17], and used to make low-efficiency blue-emitting ($\lambda_{\text{max}} = 470 \text{ nm}$) devices [18–20].



Scheme 3 Synthesis of polyfluorenes by oxidative polymerisation

These were the first blue-emitting LEDs reported using a phenylene-based polymer. The disadvantages of this method are that the degree of polymerisation is low, and the high level of defects produced due to coupling other than at the 2 and 7 positions. As a result this method is generally not used to make PDAFs. A recent exception is the synthesis of the polymer 13 with a cyanoalkyl substituent (Scheme 4) [21]. Here transition-metal mediated coupling methods such as Suzuki or Yamamoto polycondensation could not be used as the nitrile deactivates the metal catalysts by binding to the metal.



Scheme 4 Synthesis of a polyfluorene network by oxidative coupling

Oxidation of the polyionene 14 with iron(III) chloride to obtain an insoluble polyfluorene network 15 (Scheme 4) [22]. This shows violet PL (λ_{\max} = ca. 410 nm), suggesting that the polyfluorene segments are rather short. Due to its insolubility this material cannot be used to make good quality films for use in LEDs, but the incorporation of a conjugated backbone within a net-