End-Functionalization of Poly(2,7-fluorene): A Key Step toward Novel Luminescent Rod−Coil Block Copolymers

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Introduction. The academic as well as the industrial interest in semiconducting polymers such as poly(*p*-phenylene) (PPP),[1] poly(*p*-phenylenevinylene) (PPV),[2] and related materials is driven by their broad application potential[3,4] in combination with a low-cost production of processable materials. Especially polyfluorene (PF) and derivatives are very attractive as active components in light-emitting diodes (LEDs) or solid-state light-emitting cells (LECs) due to their thermal and chemical stability, their high fluorescence quantum yields in the solid state,[5] and the possibility to attach the solubilizing alkyl chains at the remote C-9 position without affecting the extended π-conjugation. The substitution can also be used to control interchain interactions like excimer formation, which has been reported for substituted polyfluorenes[6] as well as for several other planarized rigid-rod polymers.[7] Other strategies toward suppression of the often undesired aggregation involve the synthesis of statistical polyfluorene copolymers[8] or the attachment of sterically demanding dendritic end groups,[9] which act as spacers between the rigid polymer chains.

A novel concept toward controlling the self-assembly, film morphology, and hence the photoelectronic properties of conjugated polymers comprises the synthesis of luminescent rod−coil block copolymers.[4,10] The most interesting feature of rod−coil block copolymers is that even short block lengths lead to phase-separated structures in the nanometer regime.[10−13] The high immiscibility of the covalently connected rod and coil blocks drive the block copolymer into the so-called "nanophase separation", which can be controlled by varying the rod:coil volume fraction by synthesis. The block ratio of the luminescent rods and the nonemissive coils plays an important role, since on one hand the block lengths should be long enough to form nanophase separated structures and on the other the length of the flexible coil should be minimized to obtain a material with the highest possible concentration of optical active species. Because of the difficult synthetic access, only a few rod−coil block copolymers are known in the literature,[10−20] where the luminescent ones are in the minority.[14−20] Synthetic strategies toward rod−coil block copolymers involve either a condensation of two preformed blocks (grafting-onto process) or polymerization using a macroinitiator (grafting-from process). A perfect end-functionalization of the desired luminescent polymers is a necessary prerequisite for both approaches. The expansion of our previously reported concept[21,22] toward better emitters led us to the synthesis of perfectly mono-end-functionalized polyfluorenes, where the α-(phenyl)-ω-(benzyl alcohol)-poly(2,7-fluorene) (**6**) can be used as macroinitiator for the synthesis of poly(2,7-fluorene)-*b*-poly(ethylene oxide) (**9**).

Results and Discussion. In analogy to our previously reported strategy to control the termini of PPP chains,[19] we prepared the AB monomer (**2**) by monolithiation of 2,7-dibromo-9,9-dioctylfluorene (**1**) with 1.1 equiv of butyllithium followed by boronation with triisopropyl borate at −78 °C (see Scheme 1) in high purity and good yield (75%). Polymerization of **2** using a modified Suzuki coupling protocol[19] followed by endcapping with bromobenzene yielded α-bromo-ω-phenyl-poly(9,9-dioctylfluorene) (**3**) (Scheme 1). The FD mass spectrum of **3** exhibited two signals per degree of polymerization, which can be clearly assigned to H/Br and Ph/Br end groups and unequivocally proves the complete mono-end-functionalization (Figure 1). GPC analysis (THF, PPP calibration) revealed a M_n of 3380 g/mol, which corresponds to eight fluorene repeating units. The limitation of the molecular weight of the mono-end-functionalized polyfluorene **3** is due to precipitation of the unpolar polymer in the very polar solvent during polymerization. The use of dimethylacetamide as proton-free solvent, however, is a necessary prerequisite to achieve 100% bromine mono-end-functionalized rigid rods.[19] A second Suzuki reaction of **3** with an excess of 4-formylphenylboronic (**4**) acid (Scheme 1), now using the well-known toluene−soda two-phase system,[23] yielded almost quantitatively α-(4-formylphenyl)-ω-(phenyl)-poly(2,7-(9,9-dioctylfluorene)) (**5**). The FD mass spectrum of polymer **5** again showed two mass peaks per repeat unit with the corresponding shift to higher masses due to the 4-formylphenyl end groups without any signals for remaining bromo end groups. Comparison of the relative ^{1}H NMR signal intensities of the fluorene repeating units (δ = 7.47−7.83) and the signal for the benzaldehyde proton (δ = 9.8) offers the opportunity to determine the molecular weight of the polyfluorene. The molecular weight of 3500 g/mol determined by ^{1}H NMR is in good agreement with the value determined by GPC analysis (M_n = 3380 g/mol). Reduction of **5** with an excess of sodium borohydride in THF afforded α-(4-hydroxymethylphenyl)-ω-(phenyl)-poly(2,7-(9,9-dioctylfluorene)) (**6**) in excellent yield (93%), which is proven by the disappearance of the ^{1}H NMR benzaldehyde resonance at δ = 9.8 and the formation of a broad signal of the methylene protons at δ = 4.5.

This alcohol-terminated poly(2,7-fluorene) **6** appeared to be the ideal substrate to serve as macroinitiator since it is known that potassium alcoholates are capable of starting the anionic polymerization of ethylene oxide.[24] To generate the required potassium poly(2,7-fluorenolate) (**8**), we utilized a dark green potassium naphthalenide (**7**) solution in THF and titrated the slightly yellow solution of **6** until a light green color remained. An appropriate amount of ethylene oxide to afford a rod−coil block copolymer with the theoretical composition n:m = 1:1 (n = 8) was added. After 24 h at 35 °C the reaction was finally quenched by the addition of 1 mL of methanol. GPC analysis (PPP calibration) of the precipitated material using UV as well as RI detection, however, revealed the presence of the desired block copolymer **9** as well as a small amount of poly(ethylene oxide) homopolymer. This is due to the somehow trouble-

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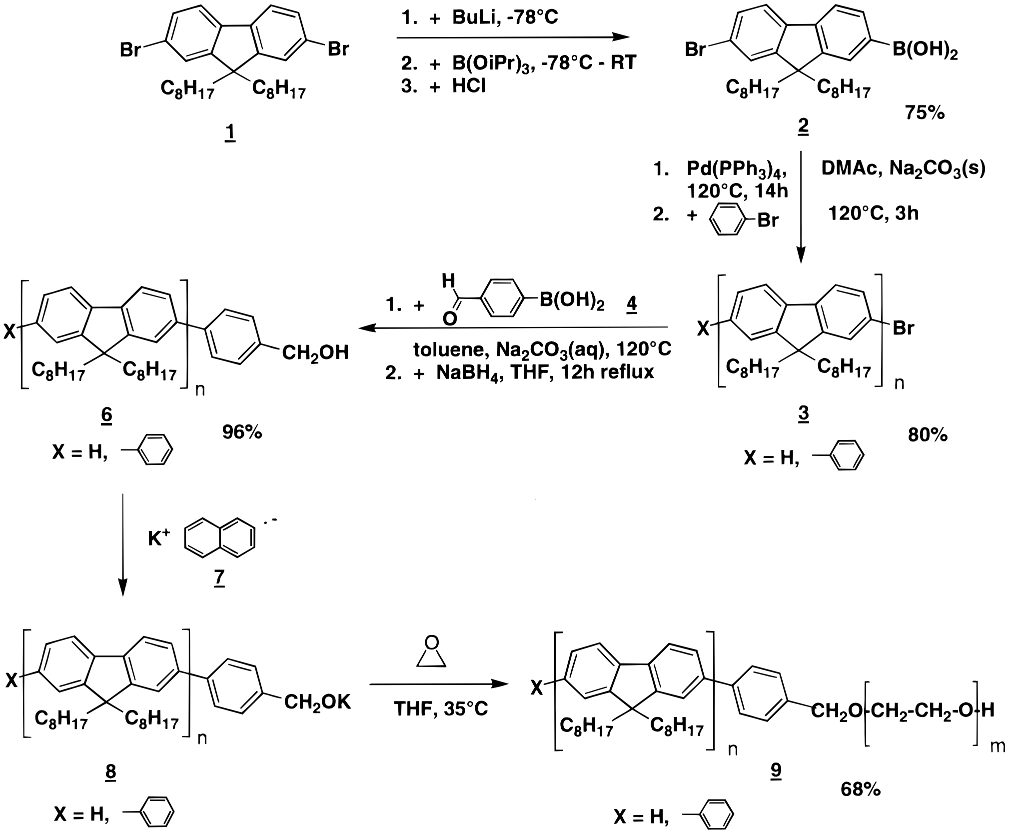
Scheme 1. Synthesis of Poly(2,7-(di-*n*-octylfluorene))-*b*-poly(ethylene oxide) (9)



some titration step, where the color change between yellow and green is difficult to recognize. Repeated washing with methanol led to the isolation of the pure poly(2,7-(9,9′-bisoctylfluorene))-*b*-poly(ethylene oxide) (**9**) as proven by ^{1}H NMR and FD mass analysis. Comparison of the signal intensities of the polyfluorene repeating units ($\delta = 7.58-7.84$) with the poly(ethylene oxide) repeating units ($\delta = 3.89$) showed a block ratio of 1.42:1, which corresponds to a degree of polymerization of 5–6 for the poly(ethylene oxide) coil. The GPC results (PPP calibration) also indicate the formation of the desired rod–coil block copolymer, although the determined M_n of 4000 g/mol corresponds to 10 poly(ethylene oxide) repeating units. The FD mass spectrum of **9** exhibited seven major peak series (polyfluorene chains with phenyl terminus) and seven minor peak series (polyfluorene chains with H-terminus), where every peak in both series is surrounded by 5–7 peaks (Figure 1). This is due to the overlap of the two polydispersities of poly(2,7-fluorene) (H and phenylene termini) and the polydispersity of the oligomeric poly(ethylene oxide).

The UV/vis spectrum in solution (THF) of block copolymer **9** revealed a slightly hypsochromic shift ($\lambda_{max} = 360$ nm) of 8 nm compared to the poly(2,7-fluorene) homopolymer **6** in combination with a sharper absorption edge. The fluorescence spectrum of **9** in THF solution ($\lambda_{exc} = 360$ nm) remains unchanged compared to the homopolymer **6** but displays a more detailed vibronic fine structure. Investigation of the optical properties in the solid state, however, revealed some interesting features: the films of both the homo-poly(2,7-fluorene) and the block copolymer **9** were prepared identically by drop-casting from equally concentrated THF-solutions followed by slow solvent evaporation in a closed chamber. The absorption maximum of **6** is located at $\lambda_{max} = 369$ nm with a shoulder at 432 nm while the absorption maximum of **9** is slightly bathochromically shifted ($\lambda_{max} = 377$ nm) with an additional peak at 428 nm (see Figure 2). The shoulder and the additional peaks at longer wavelengths have been assigned by Bradley et al.[25] to order phenomena (aggregation), and it seems that the pronounciation of this peak in the rod–coil block copolymer **9** compared to the homopolymer **6** points to the enhanced order of the luminescent rods in the block copolymer. The fluorescence spectrum of **6** displays a vibronic fine structure with maxima located at 420, 437, and 460 nm in combination with two shoulders at 495 and 536 nm (see Figure 3). The fluorescence spectrum of **9**, however, exhibits some major changes: the maxima are located at 437, 464, and 495 nm combined with two shoulders at 420 and 536 nm (Figure 3). The fluorescence maxima appear much more detailed and better resolved. These features again point to an enhanced number of well-ordered luminescent rods in the block copolymer **9** compared to the homo-poly(2,7-fluorene) **6** in the bulk.

The thermal properties of the polymers were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA measurement (10 °C/min, N_2) of **9** revealed a two-step degradation process with the first level at 112 °C (≈15% weight loss) and the second level at 420 °C. DSC analysis of **9** showed a phase transition at −53 °C (second heating scan) and two endothermic peaks at 55 and 81 °C (first heating scan). The decomposition of the corresponding homopolyfluorene polymer **6** starts at 445 °C as determined by TGA; DSC measurements show no glass transition or sign of any phase transition, which may be due to the low degree of polymerization of **6** (high molecular weight poly(2,7-(9,9-di-*n*-octylfluorene)) exhibits a T_g of 47 °C).[26]

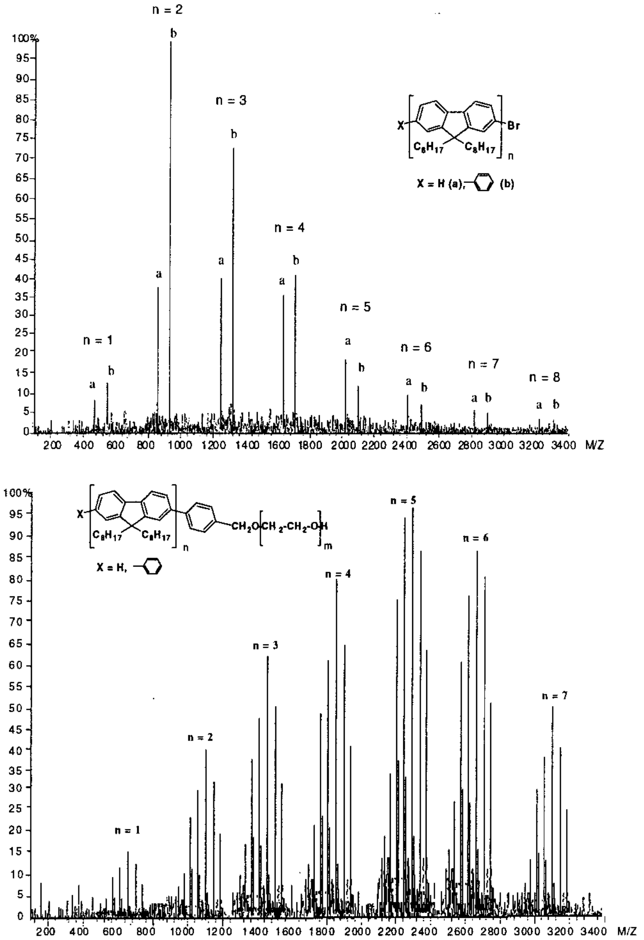


Figure 1. Characterization of the end-functionalized 2,7-PF **3** and the therefrom-derived block copolymer **9** by FD (VG ZAB 2-SE-FPD, acceleration voltage 8 kV).

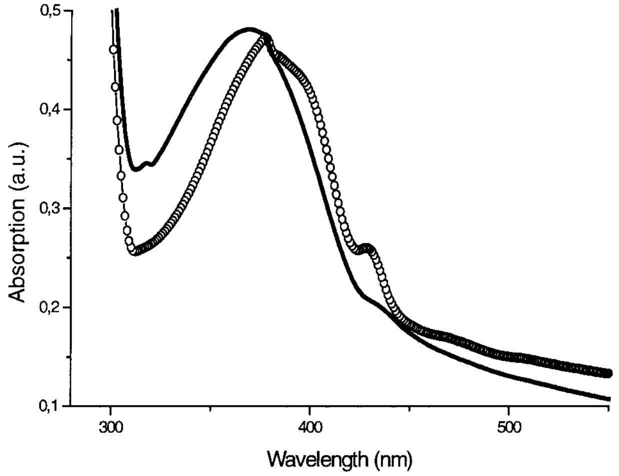


Figure 2. Film absorption spectra of block copolymer **9** (○) and poly(2,7-fluorene) **6** (—). The large apparent baseline absorbance arises from light scattering within the film.

Summary. In summary, we have presented the perfect mono-end-functionalization of poly(2,7-(9,9-dioctylfluorene)), which enabled us to synthesize the novel luminescent rod−coil block copolymer **9** via a grafting-from procedure. The absorption and fluorescence measurements of films of the block copolymer **9** reveal an influence of the coil blocks on the optoelectronic properties of the rods; the origin of this effect and especially the determination of the morphology of **9**, however, require further investigation.

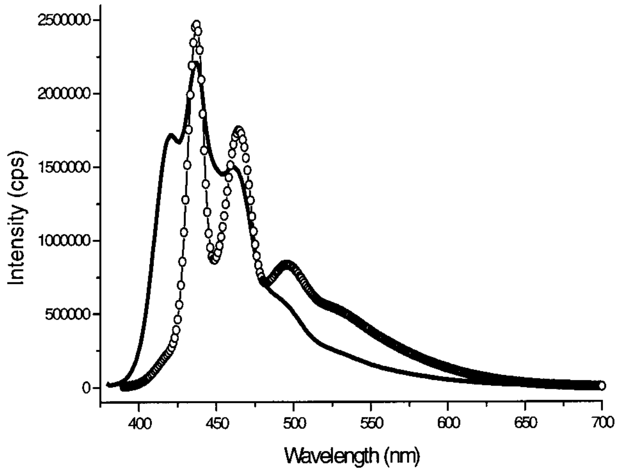


Figure 3. Film fluorescence ($\lambda_{exc} = 360$ nm) spectra of block copolymer **9** (○) and poly(2,7-fluorene) **6** (—).

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Supporting Information Available: Experimental section describing syntheses of compounds **2**, **3**, **5**, **6**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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