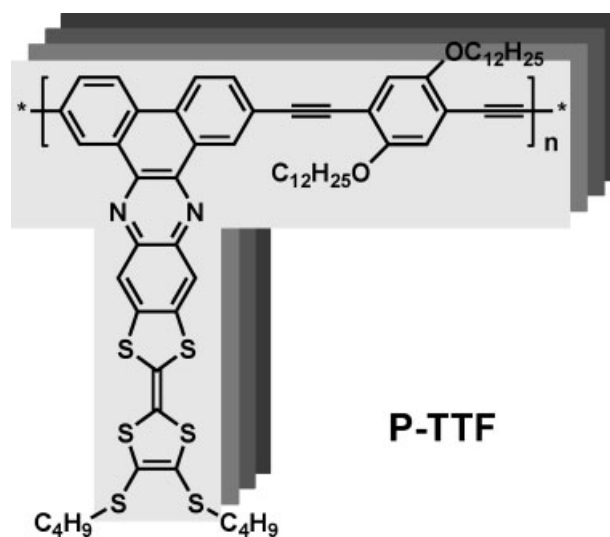


# A Novel Poly(aryleneethynylene) with Tetrathiafulvalene (TTF) Side Chains: Synthesis, Self-Assembly, and Electroactive Property<sup>a</sup>

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A novel poly(aryleneethynylene), in which the main chain and the tetrathiafulvalene (TTF) side chains are coplanar, has been prepared and characterized. The polymer can self-assemble in tetrahydrofuran (THF) and the  $\pi$ -extended coplanar backbones adopt good face-to-face stacking, which is confirmed by X-ray diffraction (XRD) analysis. Cyclic voltammetry has revealed that the polymer has reversible electroactive properties. The optical bandgap deduced by UV-vis absorption spectroscopy and the electrochemical bandgap are 2.03 and 2.14 eV. The conductivities of the powder and the realigning solid of the polymer are  $6 \times 10^{-8}$  and  $4 \times 10^{-6}$  S cm<sup>-1</sup>.



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<sup>a</sup> Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mrc-journal.de>, or from the author.

## Introduction

Tetrathiafulvalene (TTF) and its derivatives have attracted intensive research interest since the discovery of the first metallic charge-transfer (CT) complex, TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane).<sup>[1]</sup> The progress in the synthesis of TTF derivatives<sup>[2]</sup> has been closely related to the discovery of new conducting or superconducting materials.<sup>[3]</sup> Despite many inherent electronic advantages of TTF derivatives, their CT complexes have two serious problems.<sup>[4]</sup> The first is that the CT complexes are unprocessable because of their brittleness. The second

is that the CT complexes only behave as quasi one-dimensional metals and conduct along their highly ordered stacks. Combining TTF-based molecules with linear  $\pi$ -conjugated polymers might be an exciting idea to develop organic conducting materials. From the viewpoint of polymer physical properties, polymers are well known for their good film-forming property. The incorporation of TTF units into a polymer would improve the processability of the conducting material. Moreover, for the conjugated polymer with TTF units, charge conduction will not only be along the stacking direction through  $\pi$ -orbital overlap, the polymer backbone will also provide a conducting pathway through  $\pi$ -conjugation.<sup>[4,5]</sup> As such, the incorporation of donor TTF units into a conjugated polymer could increase the dimensionality of the conduction process.

There have been some attempts to prepare conjugated polymers with TTF units either in the main chain or in side chains.<sup>[4,6]</sup> For the conjugated polymers with TTF in the main chain, the strong propensity of TTFs to self-assemble into regular  $\pi$ -stacking is an interesting approach to indirectly control the long-range order of the conjugated chains. However, for most of the reported polymers with TTF side chains, the TTF units and the polymer skeletons might give rise to many possible conformations. They could only undergo partial stacking of the TTF moieties,<sup>[4a]</sup> rather than continuous stacking of the whole molecules.<sup>[6a]</sup> The main reason for this is that it is difficult to achieve coplanarity between the main chain and the TTF side chains. Herein, we report a novel poly(*p*-aryleneethynylene) with TTF side chains. The  $\pi$ -conjugated TTF units attach to the planar main chain by phenazine rings. So the main chain and the TTF side chains are coplanar. In order to increase the solubility of the polymer, flexible alkyl chains are grafted onto the TTF units and the main chain. As expected, the polymer could adopt good continuous stacking that consisted of both the  $\pi$ -extended coplanar backbones and the crystallinity of the long alkyl chains by realignment in tetrahydrofuran (THF).

## Experimental Part

Measurements and procedures for the synthesis and characterization of monomers are provided in the Supporting Information.

### Synthesis of Polymer P-TTF

Diisopropylamine (2 mL) was added to a mixture of monomers **6** (0.177 g, 0.2 mmol), **7** (0.099 g, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.012 g, 0.01 mmol), and CuI (0.002 g, 0.01 mmol) in 30 mL of THF under an argon atmosphere. The mixture was refluxed for 48 h. After the reaction, the resulting solution was poured into *N,N*-dimethylformamide (DMF). The precipitated solid was twice

re-dissolved in THF and re-precipitated into DMF. The product P-TTF was separated by filtration, washed with excess methanol, and dried under vacuum (0.082 g, 71%).

FT-IR (KBr): 2 918, 2 850, 2 206, 1 595, 1 460, 1 430, 1 203, 1 090, 775 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.32 (s, 2H), 9.06 (d,  $J$  = 8.2 Hz, 2H), 8.33 (d,  $J$  = 8.2 Hz, 2H), 8.04 (s, 2H), 6.98 (s, 2H), 2.81 (m, 8H), 1.66 (br, 8H), 1.26 (br, 40H), 0.88 (m, 12H).

GPC (THF):  $\bar{M}_n$  = 13 000, DP = 12, PDI = 1.6.

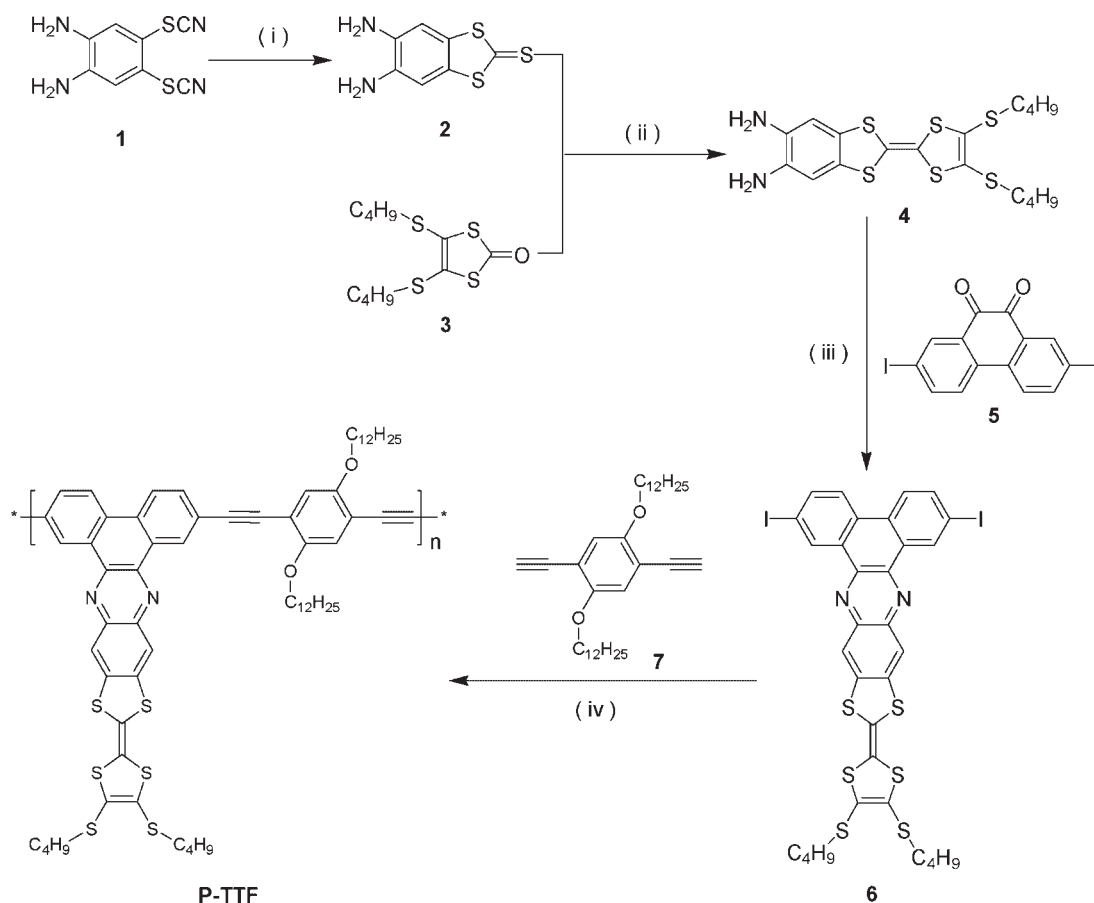
(C<sub>66</sub>H<sub>78</sub>N<sub>2</sub>O<sub>2</sub>S<sub>6</sub>)<sub>n</sub> (1122.5)<sub>n</sub>: Calcd. C 70.54, H 7.00, N 2.49, S 17.12; Found C 69.93, H 6.89, N 2.96, S 17.75.

## Results and Discussion

The synthetic route for monomer **6** is shown in Scheme 1. The starting materials, **1**, **3**, **5**, and another monomer **7** were synthesized according to the literature.<sup>[7–10]</sup> Compound **2** was obtained by modifying the reported procedure (yield 48%).<sup>[8]</sup> By a phosphite-mediated cross-coupling reaction of **2** with **3**, the diamine TTF **4** could be obtained (yield 35%).<sup>[11]</sup> Monomer **6** was easily obtained by direct condensation of **4** with **5** (yield 70%). All compounds were purified and fully characterized.

The polymer, P-TTF, was synthesized by a Pd–Cu-catalyzed Sonogashira–Hagihara coupling reaction between the monomers **6** and **7** as described in Scheme 1. Because of the long flexible alkyl chains, the obtained brown-colored P-TTF dissolved well in common solvents (THF, CHCl<sub>3</sub>, *o*-dichlorobenzene, 1,2,4-trichlorobenzene, etc.). However, when the THF solution was left standing for five days, solid appeared in the solution. <sup>1</sup>H NMR spectroscopy confirmed that the precipitated solid was still P-TTF, and it could be re-dissolved in THF by ultrasonification. Since the main chain and TTF side chains are coplanar, it is assumed that the molecules of P-TTF realign in the solution and the  $\pi$ -extended coplanar backbones form continuous stacking, which results in the precipitation of P-TTF (this was confirmed by XRD patterns of P-TTF shown below). The number-average molecular weight, polydispersity index, and the degree of polymerization of the polymer powder are  $\bar{M}_n$  = 13 000, PDI = 1.6, and DP = 12, respectively, as determined by gel permeation chromatography (GPC) calibrated relative to polystyrene standards. By realigning in THF solution, the polydispersity of P-TTF becomes narrow (PDI = 1.4), and the average molecular weight becomes higher ( $\bar{M}_n$  = 16 000 and DP = 15). This indicates that the polymer with a relatively small molecular weight did not precipitate in THF solution. As such, the realigning not only purifies the polymer, but also makes the polymer form a structure with better continuous  $\pi$ -stacking.

The thermogravimetric analysis (TGA) in an inert nitrogen atmosphere revealed that the onset temperature of weight loss of P-TTF was about 230 °C (see Supporting Information). Differential scanning calorimetry (DSC)



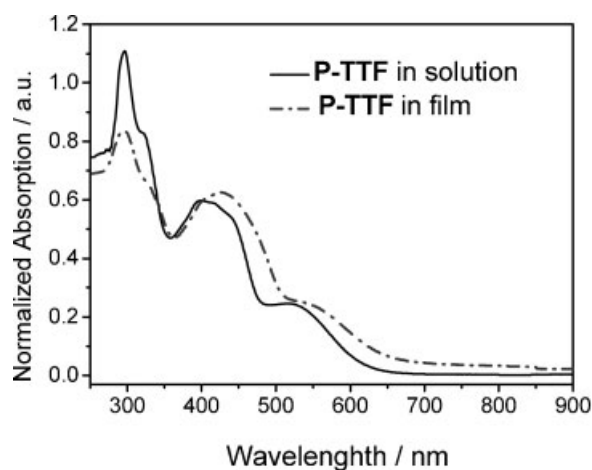
**Scheme 1.** Synthetic route for P-TTF. (i)  $\text{Na}_2\text{S}_2$ ,  $\text{H}_2\text{O}$ ,  $70^\circ\text{C}$ , 1 h;  $\text{CS}_2$ ,  $45^\circ\text{C}$ , 2 h; (ii)  $\text{P}(\text{OEt})_3$ , toluene,  $120^\circ\text{C}$ , 3 h; (iii) ethanol, reflux, 3 h; (iv)  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{CuI}$ ,  $i\text{-Pr}_2\text{NH}$ , THF, reflux, 48 h.

measurement of the polymer was also conducted in an inert nitrogen atmosphere. There was no thermal transition observed below  $230^\circ\text{C}$ , which indicates that the polymer chain is so rigid that the  $T_g$  may be higher than the decomposition temperature.

The UV-vis absorption spectra of P-TTF in  $\text{CH}_2\text{Cl}_2$  solution and as a film on a quartz plate are shown in Figure 1. There are three absorption peaks at around 300, 400, and 520 nm. In comparison with the absorption spectrum of the polymer solution, that of the film in the visible region becomes bathochromically shifted by about 20 nm, which indicates that in the solid film the interchain interactions make the main chains undergo  $\pi$ -stacking (also see the XRD below). This phenomenon has been observed in other similar conjugated polymers.<sup>[12]</sup> The optical bandgap ( $E_g^{\text{opt}}$ ) of P-TTF was estimated to be 2.03 eV from its absorption edge.

The electroactive property of the polymer was investigated by cyclic voltammetry (CV). Figure 2 shows the cyclic voltammogram of its thin-film on a Pt electrode in a 0.1 M  $\text{Bu}_4\text{NPF}_6$  acetonitrile solution. The polymer shows two reversible single electron oxidation waves at about

$E_{\text{ox}1} = 0.50$  and  $E_{\text{ox}2} = 0.77$  V, which correspond to the typical redox peaks of the TTF units.<sup>[11,13]</sup> The first oxidation should be attributed to the bis(thioether)-substituted half-unit, whilst the second should arise from



**Figure 1.** UV-vis absorption spectra of P-TTF in  $\text{CH}_2\text{Cl}_2$  solution and a P-TTF film on quartz plates.

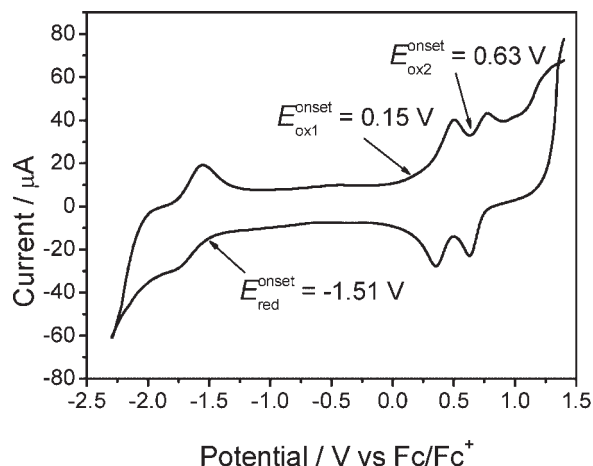


Figure 2. Cyclic voltammograms of a P-TTF film on platinum plates in an acetonitrile solution of 0.1 M  $\text{Bu}_4\text{NPF}_6$  with a potential scanning rate of  $0.1 \text{ V} \cdot \text{s}^{-1}$  at room temperature and potential vs  $\text{Fc}/\text{Fc}^+$ .

the phenazinedithiol moieties. This assignment is justified by the strong electron withdrawing effect of the phenazine moieties.<sup>[14]</sup> Moreover, the polymer has a quasi-reversible reduction process at about  $-1.76 \text{ V}$ , which could be assigned to the reduction of the acceptor phenazine moieties. The redox property of P-TTF is similar to that of other similar TTF-fused donor-acceptor (D-A) ensembles.<sup>[11,13]</sup>

For simple conjugated polymers, the difference between the onset of the first oxidation peak and the reduction peak corresponds to be the electrochemical bandgap. Using the first oxidation process for P-TTF, this bandgap value might be approximately  $1.66 \text{ eV}$ , which is less than that determined by UV-vis absorption spectroscopy. Skabara et al. thought that this redox event, which evolved from the first oxidation (attributed to the bis(thioether)-substituted dithiol unit), was independent of the conjugated main chain,<sup>[14]</sup> and they suggested that the onset of the second oxidation peak should be used in the determination of the bandgap value.<sup>[14]</sup> As such, using the onset of the second oxidation peak to obtain the bandgap value of P-TTF gives  $2.14 \text{ eV}$ , which is close to that determined by the UV-vis absorption spectroscopy results above.

To investigate the crystallinity of the polymer in the solid state, X-ray diffraction (XRD) patterns were collected on a powder sample of P-TTF and the realigned solid of P-TTF that had slowly precipitated from the THF solution (Figure 3). Upon realignment in THF solution, the diffraction peaks become sharper, and the amorphous phase of P-TTF obviously diminishes. The diffraction peak at  $2\theta = 2.3^\circ$ , which corresponds to the spacing  $d_1 = 38.38 \text{ \AA}$ , is assigned to the distance between the conjugated main chains separated by the long side chains, as reported for other similar  $\pi$ -conjugated polymers with long side chains.<sup>[15]</sup> The  $d_2$  peak is assigned to the second-order

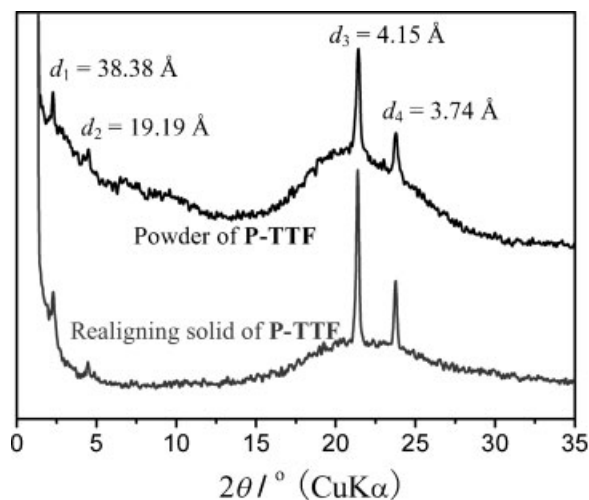


Figure 3. X-ray diffraction patterns of a powder sample of P-TTF and the realigned solid of P-TTF which slowly precipitated from the THF solution. Peaks are labeled with  $d$ -spacings in angstroms.

peak of  $d_1$  ( $d_2 = d_1/2$ ). The effective cross section of the alkyl chains is about  $S = 20 \text{ \AA}$  and their hexagonal-like aggregation gives about  $d = 4.2 \text{ \AA}$ .<sup>[15]</sup> This value is in agreement with what we observed for the peak at  $d_3$  ( $4.15 \text{ \AA}$ ) from the polymer. The value of  $d_4$  is close to the  $\pi$ -stacking distances reported for TTF-fused D-A organic compounds, which were observed from their single crystal structures.<sup>[11,16]</sup> Therefore,  $d_4$  is considered to be the layer-to-layer  $\pi$ -stacking distance between the coplanar backbones. Based on these results, it is believed that by realigning in the THF solution, P-TTF adopts good continuous stacking that consists of the  $\pi$ -extended coplanar backbones. The  $\pi$ -stacking of the coplanar backbones could also influence the long alkyl chains to array in order.

Because of the good continuous stacking of P-TTF, conductivity measurements by four-probe methods were performed on compressed pellets of the powder and the realigned solid of P-TTF at room temperature. The conductivities of the powder and the realigned solid of the polymer are  $6 \times 10^{-8}$  and  $4 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ . From a crystal engineering point of view, the re-precipitated sample should have a more ordered structure, as such it is expected that it shows better conductivity.

## Conclusion

In summary, we have prepared a novel tetrathiafulvalene (TTF)-fused poly(aryleneethynylene) with coplanarity of the main chain and the TTF side chains. The polymer reveals good reversible electroactivity. The coplanarity of the main chain and the donor TTF side chains ensures that the polymer can adopt good  $\pi$ -stacking in the solid state. The self-assembly and reversible electroactive properties

indicate that this kind of TTF-fused polymer may become a promising active material for organic electronic applications. Further studies are in progress to optimize the polymer with the coplanarity of the main chain and the TTF side chains for better electronic properties.

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- [1] J. Ferraris, D. O. Cowan, V. Walatka, J. H. Perlstein, *J. Am. Chem. Soc.* **1973**, *95*, 948.
- [2] [2a] M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891; [2b] M. Iyoda, M. Hasegawa, Y. Miyake, *Chem. Rev.* **2004**, *104*, 5085; [2c] A. Gorgues, P. Hudhomme, M. Sallé, *Chem. Rev.* **2004**, *104*, 5151.
- [3] [3a] J. Yamada, H. Akutsu, H. Nishikawa, K. Kikuchi, *Chem. Rev.* **2004**, *104*, 5057; [3b] T. Mori, *Chem. Rev.* **2004**, *104*, 4947; [3c] M. Fourmigué, P. Batail, *Chem. Rev.* **2004**, *104*, 5379; [3d] H. Seo, C. Hotta, H. Fukuyama, *Chem. Rev.* **2004**, *104*, 5005.
- [4] [4a] S. Inagi, K. Naka, Y. Chujo, *J. Mater. Chem.* **2007**, *17*, 4122; [4b] T. Uemura, K. Naka, Y. Chujo, *Adv. Polym. Sci.* **2004**, *167*, 81.
- [5] [5a] M. Adam, K. Müllen, *Adv. Mater.* **1994**, *6*, 439; [5b] M. R. Bryce, *J. Mater. Chem.* **2000**, *10*, 589; [5c] J. Roncali, *J. Mater. Chem.* **1997**, *7*, 2307.
- [6] [6a] E. Gomar-Nadal, L. Mugica, J. Vidal-Gancedo, J. Casado, J. T. L. Navarrete, J. Veciana, C. Rovira, D. B. Amabilino, *Macromolecules* **2007**, *40*, 7521; [6b] E. Wang, H. Li, W. Hu, D. Zhu, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2707; [6c] S. Shimada, A. Masaki, K. Hayamizu, H. Matsuda, S. Okada, H. Nakanishi, *Chem. Commun.* **1997**, 1421; [6d] T. Shimizu, T. Yamamoto, *Chem. Commun.* **1999**, 515.
- [7] J. L. Brusso, O. P. Clements, R. C. Haddon, M. E. Itkis, A. A. Leitch, R. T. Oakely, R. W. Reed, J. F. Richardson, *J. Am. Chem. Soc.* **2004**, *126*, 8256.
- [8] M. Frei, F. Diederich, R. Tremont, T. Rodriguez, L. Echegoyen, *Helv. Chim. Acta* **2006**, *89*, 2040.
- [9] P. Luliński, L. Skulski, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 115.
- [10] Q. Fang, S. Ren, B. Xu, J. Du, A. Cao, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3797.
- [11] C. Jia, S. X. Liu, C. Tanner, C. Leiggenger, A. Neels, L. Sanguinet, E. Levillain, S. Leutwyler, A. Hauser, S. Decurtins, *Chem. Eur. J.* **2007**, *13*, 3804.
- [12] [12a] E. Zhou, C. He, Z. Tan, C. Yang, Y. Li, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4916; [12b] R. S. Ashraf, M. Shahid, E. Klemm, M. Al-Ibrahim, S. Sensfuss, *Macromol. Rapid Commun.* **2006**, *27*, 1454.
- [13] C. Jia, S. X. Liu, C. Tanner, C. Leiggenger, L. Sanguinet, E. Levillain, S. Leutwyler, A. Hauser, S. Decurtins, *Chem. Commun.* **2006**, 1878.
- [14] [14a] P. J. Skabara, R. Berridge, E. J. L. McInnes, D. P. West, S. J. Coles, M. B. Hursthouse, K. Müllen, *J. Mater. Chem.* **2004**, *14*, 1964; [14b] R. Berridge, P. J. Skabara, C. Pozo-Gonzalo, A. Kanibolotsky, J. Lohr, J. J. W. McDouall, E. J. L. McInnes, J. Wolowska, C. Winder, N. S. Sariciftci, R. W. Harrington, W. Clegg, *J. Phys. Chem. B* **2006**, *110*, 3140.
- [15] [15a] T. Yamamoto, H. Ootsuka, T. Iijima, *Macromol. Rapid Commun.* **2007**, *28*, 1786; [15b] T. Yamamoto, B. L. Lee, *Macromolecules* **2002**, *35*, 2993; [15c] T. Vahlenkamp, G. Wegner, *Macromol. Chem. Phys.* **1994**, *195*, 1933.
- [16] [16a] Naraso, J. Nishida, D. Kumaki, S. Tokito, Y. Yamashita, *J. Am. Chem. Soc.* **2006**, *128*, 9598; [16b] Naraso, J. Nishida, S. Ando, J. Yamaguchi, K. Itaka, H. Koinuma, H. Tada, S. Tokito, Y. Yamashita, *J. Am. Chem. Soc.* **2005**, *127*, 10142.