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Synthesis and Properties of Poly(*p*-fluoranthene vinylene): A Novel Conjugated Polymer with Nonalternant Repeating Units

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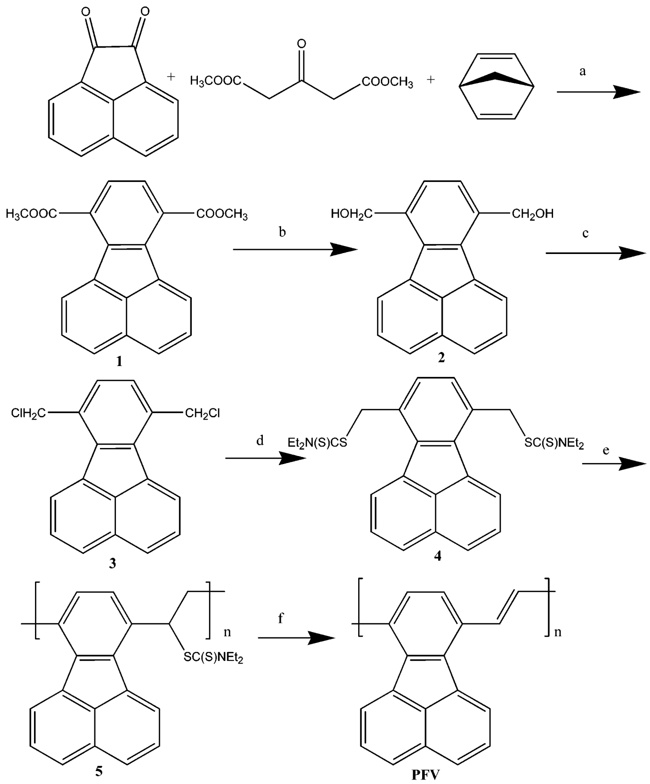
Conjugated polymers continue to attract increasing attention as a result of their promising properties for optoelectronic applications such as light-emitting diodes,[1] solar cells,[2] sensors,[3] and field effect transistors.[4] Whereas for selected applications suitable conjugated polymers are available, the quest for materials with improved properties continues. One method to achieve this objective is the introduction of functional groups. A more radical approach focuses on the design of hitherto unknown polymer backbone architectures. We have combined both tactics and prepared the novel poly(*p*-fluoranthene vinylene) (PFV) (Scheme 1), with a new backbone architecture containing nonalternant polycyclic aromatic hydrocarbon repeating units, in which the base structure of poly(*p*-phenylene vinylene) PPV remains readily recognizable.

Our search for novel materials was inspired by the field of organic solar cells. In such solar cells, which currently can already reach efficiencies as high as 5%,[5] a p-type conjugated polymer such as poly(3-hexylthiophene) (P3HT) or OC_1C_{10}-PPV is combined with a soluble derivative of C_{60}, PCBM, as the electron acceptor.[2,5] However, an n-type polymeric alternative for PCBM is of interest to facilitate the formation of an optimal morphology.[6] Whereas it is possible to incorporate C_{60} as the substituent in a polymer,[7] this approach is rather laborious and hence not necessarily cost-effective for future applications. Fortunately, remarkable progress has been made in the synthesis of functionalized substructures of C_{60} by researchers in the field of nonalternant hydrocarbons.[8] This prompted us to incorporate one of these substructures, i.e. fluoranthene, in the backbone of a conjugated polymer. The incorporation of such substructures can have a considerable impact on the electronic properties.[9] Furthermore, the use of cyclopenta-fused nonalternant hydrocarbons is expected to result in a significantly increased electron affinity of the resulting materials, which would render them possibly indeed n-type.[10] The novel conjugated polymer PFV described in this Communication is of particular interest since it is the first PPV-type polymer with nonalternant repeating units.

The synthesis of PFV starts with the straightforward one-step synthesis of dimethylfluoranthene-7,10-dicarboxylic ester (**1**) from acenaphtenequinone, acetone dicarboxylic ester, and norbornadiene followed by the conversion of the ester groups into the diol **2** by reduction with $LiAlH_4$ according to a literature procedure (Scheme 1).[8] Subsequently, 7,10-bis(chloromethyl)-fluoranthene (**3**) was obtained by reaction with thionyl chloride in THF solution. The rather limited solubility of **2** and **3** required the use of dilute solutions. After recrystallization from chloroform, pure **3** was obtained in 62% yield as light yellow crystals (melting point 232−234 °C).

Scheme 1. Synthesis of PFV[a]



[a] a: glycine; b: $LiAlH_4$; c: $SOCl_2$, pyridine; d: $NaSC(S)NEt_2{\cdot}3H_2O$; e: LHMDS; f: thermal treatment.

For the polymerization, the dithiocarbamate (DTC) precursor route[11,12] was chosen. The DTC precursor route was previously developed in our laboratory and offers not only a straightforward monomer synthesis but also a precursor polymer of higher quality than most other available precursor routes.[12] The monomer for the DTC precursor route was synthesized from **3** by reaction with sodium diethyldithiocarbamate trihydrate, giving the monomer 7,10-bis((*N*,*N*-diethyldithiocarbamate)-methyl)fluoranthene (**4**) in an excellent yield. The introduction of the dithiocarbamate groups substantially increases the solubility of the fluoranthene monomers. Hence, a polymerization can be accomplished in a straightforward manner. Polymerization of **4** was carried out with lithium bis(trimethylsilyl)amide (LHMDS) as the base in dry THF under an inert atmosphere (Scheme 1). After polymerization for 3 h at ambient temperature, the reaction was terminated by the addition of ice water followed by neutralization with hydrochloric acid. After extraction the precursor polymer **5** was isolated by preparative SEC. In this way low-molecular-weight contaminants can be removed in an uncomplicated manner. After purification, precursor polymer **5** was obtained in 82% yield as a yellow solid. The observed molecular-weight distribution is monomodal, with $M_w = 5.9 \times 10^4$ and PD $= M_w/M_n = 1.6$ (Analytical SEC, solvent DMF). This is in the same order of magnitude as previously found for typical polymerizations of dithiocarbamate monomers.[12] However, it should be noted that since these molecular weights are referenced to polystyrene standards, the actual value for M_w will differ from the apparent M_w observed with analytical SEC.

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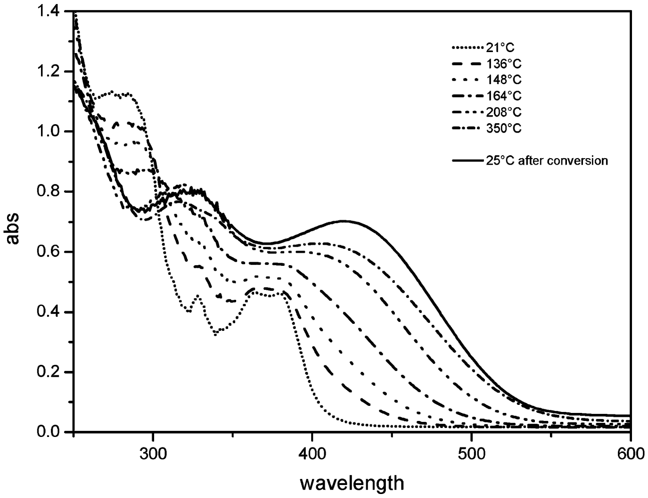

Figure 1. UV−vis spectra at selected temperatures during the conversion of precursor polymer **5** to PFV. The precursor polymer was heated from ambient temperature to 350 °C at 1 °C/min.

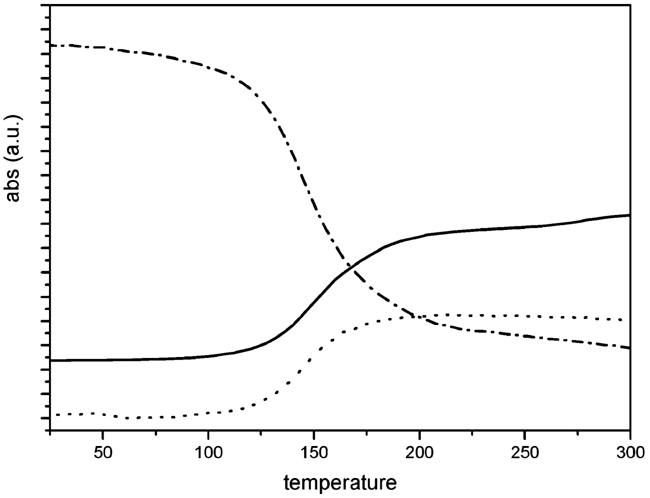

Figure 2. UV−vis profile at 420 nm (solid) and FT-IR profiles at 954 cm^{-1} (dotted) and 1266 cm^{-1} (dashed−dotted) as a function of temperature during the conversion process of precursor polymer **5** to PFV.

DTC precursor polymers can be readily transformed into the corresponding conjugated polymers by thermal treatment either in solution or in a thin film.[11,12] During this treatment the dithiocarbamate group is eliminated from the precursor polymer. Since it appeared that the conjugated PFV was insoluble in all common organic solvents tested, the thermal conversion of **5** into PFV was only performed in a thin film. Otherwise, an intractable solid would have been obtained. For the conversion, precursor polymer **5** was spin-coated from a $CHCl_3$ solution (10 mg/mL) onto NaCl or quartz disks. Subsequently, the disks were placed in a controlled temperature cell. A dynamic heating rate of 1 °C/min from ambient temperatures up to a temperature sufficiently high to have full conversion (vide infra) under a continuous flow of N_2 was used for the conversion process.

It is noteworthy that in the thin film processes the thermal elimination reaction can be followed by means of in situ UV−vis and FT-IR spectroscopy. Indeed, upon heating a thin film of **5** the formation of the conjugated structure of PFV is readily observed (Figure 1). In the precursor polymer, the long wavelength side of the UV−vis absorption spectrum is dominated by the typical HOMO−LUMO absorption bands of the substituted fluoranthene at 359 and 380 nm, which are also present in monomer **4**. Upon heating, these “monomeric” bands disappear and two new absorption bands develop ($\lambda_{max} = 320$ and 420 nm at 25 °C) which originate from the conjugated structure. This is in contrast to unsubstituted PPV which exhibits at ambient temperatures only a single band at ca. 420 nm in the UV−vis absorption spectrum.[12] The additional band at 320 nm is a result of the more extended conjugated system in PFV.[13]

The optical band gap can be derived from the low-energy side tangent to the $\pi-\pi^*$ transition. A value for the band gap of 2.34 eV is obtained, which is only slightly smaller than the reported band gap of PPV (ca. 2.4 eV).[12,14] From the absorption profile at 420 nm it is evident that conversion of **5** to PFV starts around 100 °C and is virtually complete at 200 °C (Figure 2). The apparent minor decrease in absorption at temperatures above 200 °C is a result of a reversible thermochromic effect. Furthermore, the UV−vis analysis indicates that no substantial degradation of the conjugated structure is observed in the entire temperature range up to 300 °C. It has been previously observed that unsubstituted PPV is stable until 350 °C,[12] which indicates that the extension of the conjugated structure does not impact the thermal stability of the conjugated system to a significant extent. For comparison, the thermal stability of PFV was also measured with TGA, although this does not directly give information about the thermal stability of the conjugated backbone.[15] From these measurements it is evident that the complete degradation of PFV as observed with TGA does not commence until 325 °C. Since PFV is insoluble, no molecular weight could be determined. However, it can be expected that the molecular weight will not substantially deviate from the one observed for the precursor polymer **5** (vide supra).

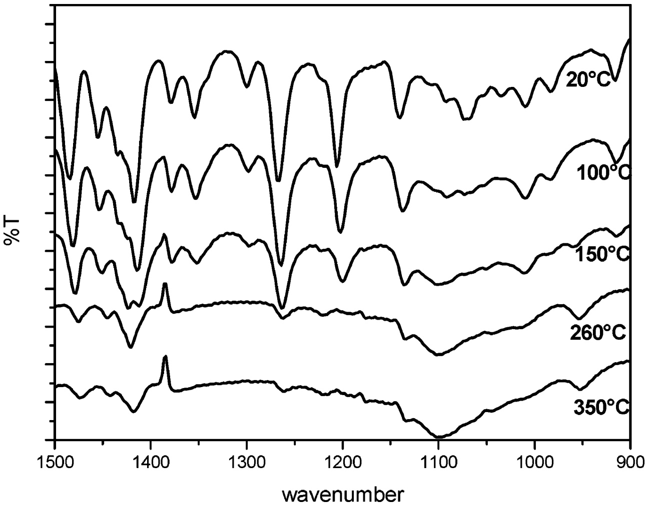

Figure 3. FT-IR spectra at selected temperatures during the conversion of precursor polymer **5** to PFV. The precursor polymer was heated from ambient temperature to 350 °C at 1 °C/min.

Fluorescence measurements further confirm the successful formation of the conjugated structure. Whereas precursor polymer **5** has a fluorescence emission at $\lambda_{em} = 475$ nm (excitation at $\lambda_{exc} = 380$ nm),[16] this fluorescence is no longer present in the conjugated structure. Instead, for PFV a distinct emission is found at $\lambda_{em} = 545$ nm (excitation at $\lambda_{exc} = 412$ nm),[16] which originates from the conjugated structure.

The conversion process is also readily observed using temperature-dependent FT-IR spectroscopy (Figure 3). Upon heating, the vibrations at 1485, 1415, 1266, and 1204 cm^{-1}, which are associated with the dithiocarbamate group, decrease in intensity. At the same time a new vibration develops at 954 cm^{-1}, which arises from the double bonds in the conjugated backbone. This vibration is typical for PPV-type polymers and

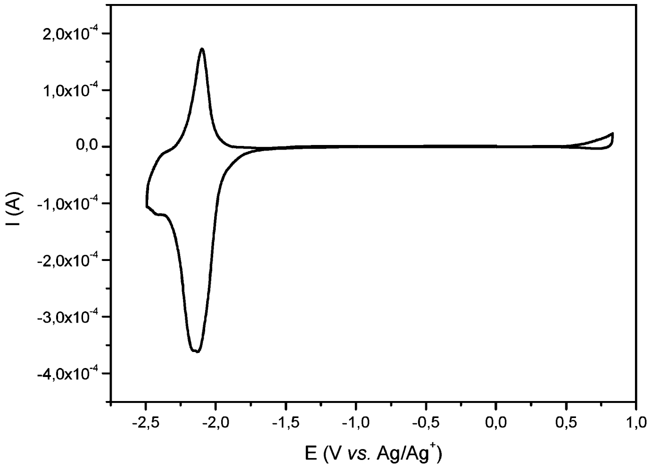

Figure 4. Cyclic voltammogram of the oxidation and reduction behavior of a thin film of PFV on ITO.

originates from the *trans*-vinylene double bond.[12,17,18] The FT-IR measurements confirm that the formation of double bonds starts at 100 °C and is virtually complete around 180 °C (Figure 2), with only minimal intensities of the dithiocarbamate groups remaining.

Thin-film cyclic voltammetry (CV) was employed to investigate the electrochemical behavior of PFV and to estimate the position of its lowest unoccupied molecular orbital (LUMO) energy level. The cyclic voltammogram of PFV displays a distinct reduction process (Figure 4), i.e., n-doping. In contrast, the current density associated with the p-doping, viz. the oxidation process, is very small. This suggests that this new polymer under the applied electrochemical conditions acts as an n-type conjugated polymer. Such polymers are quite rare and highly desired for applications.[19] The observed unusual n-type behavior originates from the nonalternant polycyclic aromatic hydrocarbon units in the backbone. The conduction band edge energy level is accurately determined from the onset of reduction at −1.82 V vs Ag/AgNO$_3$, which corresponds to a LUMO energy level of −3.10 eV.[20] This is significantly lower than the LUMO energy level observed for PPV (−2.7 eV) reported in the literature.[21] However, this apparent difference is a result of differences in the electrochemical procedures and reference system, and in reality no significant difference between the LUMO values of PFV and PPV exists.[22] Although the HOMO energy level of PFV is more difficult to estimate, based on the electrochemical measurements a value of −5.6 eV can be derived, which indicates that the electrochemical band gap of PFV is ca. 2.5 eV. This is in the same order of magnitude as PPV.[22]

In conclusion, recent progress in the synthesis of substructures of C$_{60}$ has provided us with an opportunity to create a new conjugated polymer with a hitherto unknown backbone structure containing nonalternant polycyclic aromatic hydrocarbon repeating units. While many properties of PFV are similar to those of its "parent" polymer PPV, PFV exhibits unusual n-type behavior, which is likely associated with the nonalternant character of its backbone. The straightforward synthesis toward this novel polymer as developed in our laboratory provides the opportunity to use PFV as a platform for further functionalization, thus allowing for a further adjustment of the optoelectronic properties.

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Supporting Information Available: Synthetic details and spectroscopic characterization of all intermediates, monomers, and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) We have measured thin films of unsubstituted PPV with the same electrochemical measurement setup and reference system as employed for PFV. In this way a LUMO energy level of −3.11 eV has been found for PPV, which is virtually identical to the LUMO of PFV (−3.10 eV). Furthermore, we estimate that the electrochemical band gap of PPV is 2.47 eV.

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