Synthesis and Characterization of Monocarboxylated Poly(3-hexylthiophene)s via Quantitative End-Group Functionalization

Ruth H. Lohwasser and Mukundan Thelakkat*

Applied Functional Polymers, Department of Macromolecular Chemistry I, University of Bayreuth, Universitätsstrasse 30, 95444 Bayreuth, Germany

Received June 15, 2010; Revised Manuscript Received July 26, 2010

ABSTRACT: We report the quantitative conversion of bromine end groups in regioregular poly(3-hexylthiophene)s (P3HTs) and the characterization of the resulting monocarboxylated P3HTs (P3HT-COOHs) carrying one carboxylic acid group at their chain ends. The monocarboxylation for three different chain lengths is carried out, and the resulting P3HT-COOHs are characterized with size exclusion chromatography, matrix-assisted laser desorption ionization spectroscopy with time-of-flight detection mass spectroscopy, and UV−vis spectroscopy. The thermal properties and crystallinity in bulk and thin films were studied in a comparison between P3HT and P3HT-COOHs. Differential scanning calorimetry and wide-angle X-ray scattering support the increasing crystallinity for the higher molecular weight samples. Preliminary OFET measurements show a good charge carrier mobility in the range of 10^{-3} cm^2/(V s) for P3HT-COOHs with molecular weights of 5000 and 10 800 g/mol.

Introduction

In recent years organic electronics is gaining increasing attention, especially in the fields of organic light-emitting diods (OLEDs), organic field effect transistors (OFETs), and organic solar cells. A common hole conductor material used in these devices is regioregular poly(3-hexylthiophene) (P3HT).[1,2] After its invention in the 1980s, one major step in the synthetic development was the use of an asymmetric monomer to gain P3HT with a regioregularity around 98%.[3−5] Further, the invention of the Grignard metathesis polymerization (GRIM) by McCullough and Yokozawa allowed the control over molecular weight and narrow molecular weight distributions.[6,7] Apart from the use of new side chains bearing oxyethylene, amino, or carboxylic acid functions,[8,9] a lot of effort was put in the introduction of new polymer chain end groups via controlled ways. A good control of end groups and its functionalization is a prerequisite for e.g. the synthesis of block copolymers and for the anchoring onto surfaces.[10−12] Initial end-group functionalizations were often realized with multiple postpolymerization steps.[13,14] Later, the in situ end-group functionalization by McCullough enabled a simpler introduction of functional groups like e.g. amino, hydroxy, vinyl, or alkynyl groups.[15] Depending on the nature of the used end-capper, primarily mono- or difunctionalization was achieved. Despite the versatility of this method, one important end group for the coordination of nanoparticles or anchoring onto surfaces—the carboxylic acid group—was not yet reported. Recently, we showed a method for multifunctional carboxylation, where the functionalized P3HT showed good adsorption on TiO$_2$ and therefore could be used as a sensitizer in dye-sensitized solar cells. But a multicarboxylation resulted also in a complete loss of crystallinity.[11]

Here we introduce a more controlled method for the selective and quantitative monocarboxylation of P3HT at only one chain end, where the polymer maintains its semicrystallinity after carboxylation. Further, we investigate the influence of the COOH end groups on thermal, optical, and electronic properties, depending on the chain length of the carboxylated polymer.

Experimental Section

Materials and Characterization. ^{1}H NMR spectra were recorded in chloroform on a Bruker Avance 250 spectrometer at 300 MHz. Coupling constants are given in hertz. The spectra were calibrated according to solvent signal at 7.26 ppm. Size exclusion chromatography (SEC) measurements were carried out in THF using a UV detector from Waters and a mixed-C PL-Gel (PL) column. Polystyrene was used as external standard and 1,2-dichlorobenzene as an internal standard for calibration. FT-IR spectra were obtained from drop-cast films on the ATR unit with a Perkin-Elmer Spectrum 100 FT-IR spectrometer. UV−vis measurements were performed with a U-3000 spectrometer from Hitachi. Differential scanning calorimetry (DSC) measurements were done on a Perkin-Elmer Diamond DSC with a heating and cooling rate of 10 K/min. Matrix-assisted laser desorption ionization spectroscopy with time-of-flight detection mass spectroscopy (MALDI-TOF MS) measurements were performed on a Bruker Reflex I using dithranol as matrix and a mixture of 1000:1 (matrix:polymer). The laser intensity was set to around 70%. The reflection mode was calibrated with a fullerite mixture from Sigma-Aldrich (CAS 131159-39-2). WAXS measurements were performed at the beamline ID2 at the European Synchrotron Radiation Facility in Grenoble. The energy of the photons was 12.540 keV (λ~0.1 nm). The samples were prepared on Kapton foils, and all diffractograms were corrected with the diffractogram of a pure foil.

The monomer 2,5-dibromo-3-hexylthiophene and the catalyst 1,3-bis(diphenylphosphino)propanenickel(II) chloride [Ni(dppp)-Cl$_2$] were synthesized according to the literature.[16] All glass apparatus for polymerization and polymer-analogous reactions were heated and cooled under argon. Dry THF was distilled over calcium hydride and potassium. *i*-PrMgCl (2 M in THF) and *t*-BuMgCl (1.7 M in THF) were purchased from Acros and titrated according to Krasovskiy and Knochel.[17] CO$_2$ gas (99.995%, <5 ppm of H$_2$O, Riessner Gase) and hexamethyldisilazane (HMDS) (99%, Aldrich) for the OFETs were used as

*Corresponding author. E-mail: mukundan.thelakkat@uni-bayreuth.de.

received. A commercial P3HT with a number-average molecular weight M_n of 19 400 g/mol was purchased from Rieke metals for comparative studies.

General Procedure for the Synthesis of P3HT-COOH. The regioregular P3HTs (P3HT1−5) were synthesized according to published procedures.[15] The polymers were used without any purification by fractionation. The procedure for the mono-carboxylation is explained below with P3HT2 as a typical example. P3HT2 (348 mg) was dried under vacuum and dissolved in dry THF (68 mL) in a Schlenk flask. The solution was degassed via three freeze−pump−thaw cycles and 14.5 mL of i-PrMgCl (1.3 M, 150−200 molar excess compared to the bromine end groups) were added with a syringe. The solution was stirred overnight, and CO_2 was bubbled into the solution at room temperature for 5 min and then 1 h at 0 °C. After 1 h additional stirring at 0 °C the reaction was terminated with 2 N HCl. The solution was con-centrated under reduced pressure; the polymer was dissolved in $CHCl_3$ and precipitated in methanol. The functional polymer was filtered, washed with methanol in a Soxhlet overnight, and extracted with chloroform. Pure P3HT2-COOH (340 mg) was isolated from the chloroform extract by precipitation into methanol, filtering, and drying under vacuum. The following spectroscopic analysis is valid for all three P3HT-COOHs. δ ^{1}H (300 MHz; $CDCl_3$): 7.03 (0.045 H, s, H_{ar} of end group unit with COOH), 6.98 (1 H, br s, H_{ar}), 3.01 (0.09 H, t, α-CH_2 of end group unit with COOH), 2.80 (2 H, br, α-CH_2), 1.85−1.50 (2 H, br m, β-CH_2), 1.50−1.10 (6 H, br m), 1.0−0.75(3 H, br m, CH_3). FT-IR ν_{max} (film)/cm^{-1}: 3055 w, 2957 s, 2928 s, 2857 s, 2644 b, 2542 b, 1665 s, 1526 w, 1457 s, 1439 s, 1378 w, 829 m, 724 w.

OFET Preparation and Measurements. OFET substrates were purchased from Frauenhofer IMPS, Dresden. The geometry of the device was a bottom gate top electrode type, with n-doped (doping at wafer surface: $n \approx 3^{17}$ cm^{-3}) silicon as gate electrode and a 230 nm SiO_2 layer as gate dielectric. The source and drain electrodes were ITO (indium tin oxide) (10 nm) as adhesion layer with high work function and gold (30 nm). The analyzed channel length was 20 μm and the width 10 mm. The substrates were cleaned with acetone, H_2O_2/H_2SO_4 15 min, VE-water, VE-water (ultrasonic bath 15 min), acetone (ultrasonic bath 15 min), and isopropanol (ultrasonic bath 15 min) and rinsed with hexane. The H_2O_2/H_2SO_4 solution should be handled with care because it is highly corrosive. After plasma etching for 15 min the substrates were hydrophobized with hexamethyldisilazane (HMDS) vapor for 3 h. Excess HMDS was washed off with hexane. All following steps were done under inert gas atmo-sphere in a glovebox. The active polymer layers were spin-coated at 2000 rpm from a 1 wt % solution in $CHCl_3$. Output and transfer characteristics were measured with a Hewlett-Packard 41555A semiconductor parameter analyzer. The hole transport mobilities were determined from the transfer characteristics according to eq 1.[18] Since the mobility did not reach a saturation regime for all devices, all the given mobilities are for a fixed gate voltage of −40 V.

$$\mu_{sat} = \left(\frac{\partial \sqrt{I_{SD}}}{\partial V_G}\right)^2 \frac{2L}{WC_i} \quad (1)$$

Results and Discussion

Synthesis and End-Group Analysis. First three regioregular poly(3-hexylthiophene)s (P3HT1−3) with defined molecular weights between 1000 and 10 000 g/mol were synthesized via the Grignard metathesis polymerization developed by McCullough and co-workers.[15] The number-average mole-cular weights (M_n) of these samples as determined according to size exclusion chromatography (SEC) are 1500 g/mol for P3HT1, 5000 g/mol for P3HT2, and 10 200 g/mol for P3HT3 (Table 1). The absolute molecular weights were determined with matrix-assisted laser desorption ionization spectroscopy with time-of-flight detection spectroscopy (MALDI-

Table 1. Molecular Weights and Molecular Weight Distributions (PDI) Determined with Size Exclusion Chromatography (SEC) and MALDI-ToF MS of Nonfunctionalized Poly(3-hexylthiophene)s (P3HTs) and Monocarboxylated Poly(3-hexylthiophene)s (P3HT-COOHs)^a

sample	M_n(SEC) [g/mol]	M_n(MALDI) [g/mol]	DP (MALDI)	PDI (SEC)
P3HT 1	1500	1400	8	1.11
P3HT 2	5000	3200	20	1.15
P3HT 3	10200	7000	42	1.15
P3HT 1-COOH	1800	1500	9	1.11
P3HT 2-COOH	5000	3200	20	1.17
P3HT 3-COOH	10800	7000	42	1.16

^{a} DP = degree of polymerization; M_n = number-average molecular weight.

Scheme 1. Synthetic Scheme for Monocarboxylated Poly(3-hexylthiophene)s (P3HT-COOHs) via a Grignard Reaction at the Bromine Chain End with Gaseous CO_2^{a}
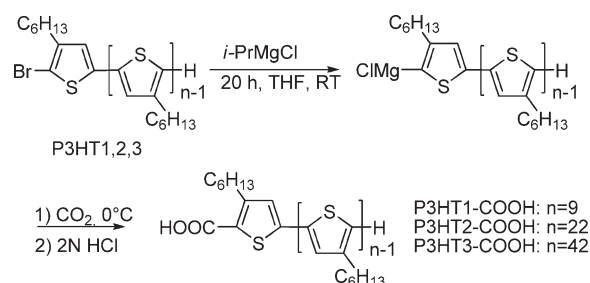
^{a} Degrees of polymerization n were calculated from MALDI-ToF MS.

ToF MS). The MALDI-ToF MS (M_n) values correspond to 1400, 3200, and 7000 g/mol. Thus, the degree of polymeriza-tion (as obtained by MALDI-ToF) corresponds to roughly 8 (P3HT1), 19 (P3HT2), and 42 repeating units (P3HT3). While the molecular weights determined with SEC and MALDI-ToF MS were nearly the same for P3HT1, the SEC molecular weights are usually overestimated for higher molecular weight P3HTs. This is expected if a rather stiff polymer like P3HT is measured with a column calibrated with a more flexible poly-styrene standard.[19] MALDI-ToF MS also indicates that the predominant end groups ($\geq$80%) after polymerization were a bromine arising from the starting unit and a hydrogen result-ing from quenching the active chain end with hydrochloric acid (Figure 2). Scheme 1 shows the synthetic procedure for the monocarboxylation of P3HTs via a Grignard reaction. The bromine end groups were selectively and quantitatively transformed into an active Grignard species via a metathesis reaction with i-PrMgCl. The introduction of gaseous CO_2 and quenching the reaction with hydrochloric acid resulted in a quantitative conversion of the Br chain ends to COOH groups.

The size exclusion chromatography traces of the mono-carboxylated P3HT-COOHs are shown in Figure 1, and the respective data as compared with nonfunctionalized P3HTs are given in Table 1. After monocarboxylation the poly-dispersity index of all polymers remained low, and there were only minor shifts in the number-average molecular weights. Thus, only negligible chain coupling occurred, and the modi-fication is well controlled. For the lowest molecular weight sample P3HT1-COOH, the M_n increased during functiona-lization by about 300 g/mol (SEC). This is due to the fact that carboxylation improves the polarity of the polymer, and thus shorter functionalized chains were removed during Soxhlet extraction with methanol.
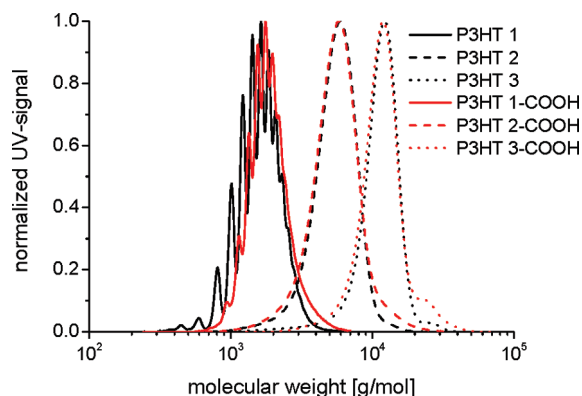
Figure 1. Size exclusion chromatography (SEC) traces of nonfunctionalized poly(3-hexylthiophene)s (P3HTs) and monocarboxylated poly(3-hexylthiophene)s (P3HT-COOHs) with different chain lengths. Number-average molecular weight M_n increases from 1500 to 10 200 g/mol for P3HT1 to P3HT3. After functionalization no serious changes in the molecular weight distributions are observed.
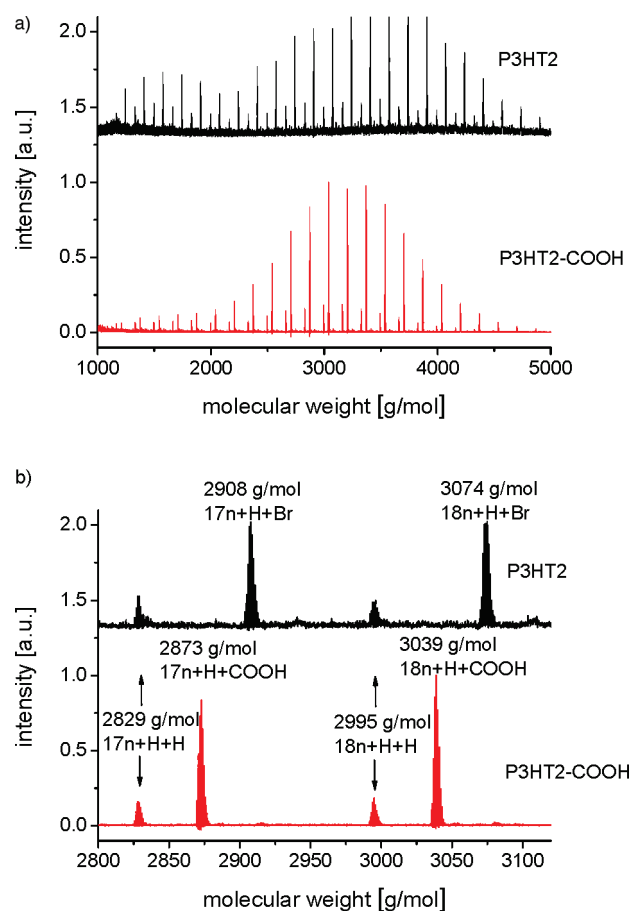

Figure 2. (a) MALDI-ToF MS spectra of nonfunctionalized poly(3-hexylthiophene) with a size exclusion molecular weight of 5000 g/mol (P3HT2) and the respective monocarboxylated poly(3-hexylthiophene) (P3HT2-COOH.) (b) Magnified section of the MALDI-ToF MS spectra for 17 and 18 repeating units with the molecular weights and end groups for all peak series. A high (>80%) content of H/Br chain ends for P3HT2 is obtained, which are quantitatively transformed into H/COOH end groups for P3HT2-COOH.

MALDI-TOF MS additionally allows an analysis of the end groups before and after carboxylation. Figure 2 shows the spectra of P3HT2 and P3HT2-COOH as a representative example (for others see Supporting Information). All the P3HTs exhibit ≥80% H/Br end groups. While the

minor molecular weight peak series (≤20%) with hydrogen/hydrogen end groups remained unchanged during functionalization, a quantitative conversion of the bromine end groups in the hydrogen/bromine series is observed. The peaks are shifted by 35 g/mol (2908 g/mol − 2873 g/mol = 35 g/mol), which is equivalent to the mass difference between a bromine atom (79.9 g/mol) and a carboxylic acid group (45 g/mol). The intensity ratio between H/H end groups and H/COOH end groups in P3HT2-COOH is nearly the same as the ratio between H/H and H/Br end groups in P3HT2, which also indicates the quantitative transformation. However, this assumption has to be taken with caution since it is only true if the desorption behaviors of P3HTs with bromine and carboxylic acid end groups are the same. But the quantitative transformation is further confirmed by ^{1}H NMR analysis. The α-CH$_2$ signal of the end group unit with bromine at 2.57 ppm vanishes, and a new signal for the α-CH$_2$ signal of the COOH-terminated end group unit appears at 3.01 ppm. These signals have the same integral ratio in comparison to the α-CH$_2$ signal of the repeating units at 2.80 ppm

Optical Characterization. It is interesting to study the influence of one carboxylic end group on the thermal and optical properties in solution, bulk, and thin films, depending on the chain length of the monocarboxylated polymers. This is of utmost importance if these polymers are to be used as electronic materials in devices. While bromine end groups may have only sterical effects on the packing of P3HT, COOH groups have the ability to form hydrogen bonds and thus may behave different toward molecular packing. The existence of hydrogen bonds can be evidenced in the FT-IR spectra of the P3HT-COOHs (see Supporting Information). The C=O vibration of the carboxylic acid groups in P3HT-COOHs occur at 1665 cm^{-1} and the O−H overtone vibrations at 2542 and 2644 cm^{-1}, corresponding to characteristic hydrogen-bonded acid groups.[11] The usual O−H stretching vibrations between 3000 and 3500 cm^{-1} overlap with the C−H vibrations.

The three functionalized P3HT-COOHs were further characterized with UV−vis spectroscopy in THF solution (concentration 0.02 mg/mL) and thin films (thickness ca. 100 nm on quartz by spin-coating from 1 wt % solution in CHCl$_3$). The respective data for thin films are shown in Figure 3 and that for solutions in the Supporting Information. Generally, the solution spectra for all P3HT-COOHs are comparable to the respective nonfunctionalized P3HTs. The λ_{max} values in solution vary from 415 to 443 nm for P3HT1-COOH to P3HT3-COOH. The spectrum of P3HT1-COOH is hypsochromically shifted, and a loss of optical density can be observed in comparison to P3HT2-COOH and P3HT3-COOH. This is not unexpected since the maximum conjugation length is not yet reached for a polymer with ca. 9 repeating units. For the two higher molecular weight samples P3HT2-COOH and P3HT3-COOH (for spectra see Supporting Information) the optical density and the maximum absorption wavelength λ_{max} are almost the same. A maximum conjugation seems reached.

In films, P3HTs exhibit more pronounced vibronic fine structure than the P3HT-COOHs. Generally, all maxima are shifted batochromically in comparison to the solution spectra and vary between 447 and 510 nm with increasing chain length (Figure 3c). Similar to the solution spectra both P3HT1 and P3HT1-COOH show low λ_{max} values and no vibronic fine structure in thin films as well. The bathochromic shift from solution to film is only 32 nm, and the optical density is lower than for the higher molecular weight samples. Low molecular weight P3HT1 or P3HT1-COOH
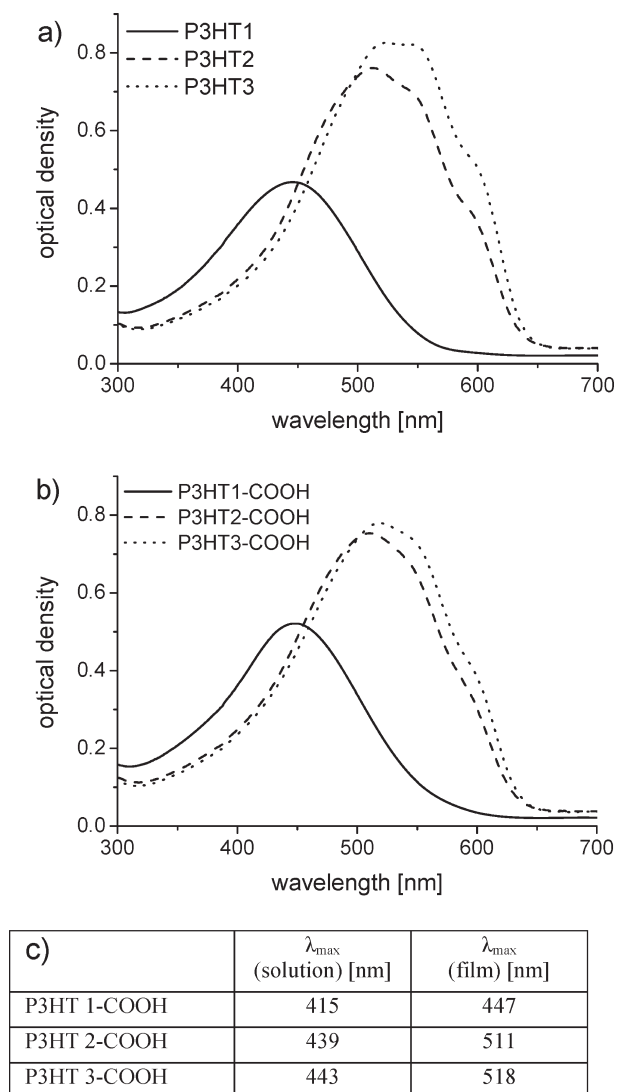
a)

b)

c)

	λ_{max} (solution) [nm]	λ_{max} (film) [nm]
P3HT 1-COOH	415	447
P3HT 2-COOH	439	511
P3HT 3-COOH	443	518

Figure 3. UV−vis spectra of (a) nonfunctionalized poly(3-hexylthiophene)s (P3HTs) and (b) monocarboxylated poly(3-hexylthiophene)s (P3HT-COOHs) measured on thin films on quartz (thickness ca. 100 nm spin-coated from 1 wt % solution in CHCl₃). (c) Maximum absorption wavelength λ_{max} of the P3HT-COOHs in solution (0.02 mg/mL in THF) and in ca. 100 nm thick films on quartz. P3HT2-COOH and P3HT3-COOH show a vibronic fine structure in thin film, which is only little less pronounced than for P3HT2 and P3HT3. This indicates that both carboxylated P3HT-COOHs crystallize in thin films. For solution spectra, see the Supporting Information.

do not crystallize in thin films, which is explained in detail in thermal characterization (see Table 2). Thus, for P3HT1 and P3HT1-COOH the bathochromic shift is only caused by a change of the polarity in film compared to the THF solution.[20] For the higher molecular weight samples (P3HT2-COOH, P3HT3-COOH), the λ_{max} shift from solution to film spectra is around 70 nm (e.g., 439 to 511 nm; see Figure 3c). Additionally, a vibronic fine structure is observed as seen in the corresponding P3HTs. The fine structure is less pronounced than in the nonfunctionalized homologues shown in Figure 3a. This fine structure is typical for polymers with π−π-stacking and is more pronounced for the higher molecular weight sample P3HT3-COOH. It is obvious that unlike the earlier reported multicarboxylation method, where the functionalized P3HT completely loses its crystallinity, the controlled monocarboxylation leads to P3HT-COOHs with sufficient crystallization and π−π-stacking.[11]

Table 2. Melting Temperature T_m in Second Heating Cycle, Recrystallization Temperature T_c, and Melting Enthalpy ΔH_m of Monocarboxylated Poly(3-hexylthiophene)s (P3HT-COOHs) and Nonfunctionalized Poly(3-hexylthiophene)s (P3HTs)[a]

	T_{m1}/T_{c1} [°C]	T_{m2}/T_{c2} [°C]	ΔH_{m2} [J/g]
P3HT 1	23/−9		
P3HT 1-COOH	53/−		
P3HT 2	64/57	183/165	10
P3HT 2-COOH	59/−	183/164	9
P3HT 3		225/195	22
P3HT 3-COOH		219/191	11

[a] T_{m2} is the melting point of the lamellar main chain stacking, and T_{m1} is the melting point observed in low molecular weight P3HTs which cannot be assigned to a lamellar main chain packing.

Table 3. Main Chain Melting Points T_{m2} of Different Poly(3-hexylthiophene)s along with the Respective Degree of Polymerization (DP) As Determined by MALDI-ToF MS

	T_{m2} [°C]	DP = n [MALDI]
P3HT 1	117[a]	8
P3HT 2	183	20
P3HT 3	225	42
P3HT 4	237	56
P3HT 5	244	65

[a] Calculated from eq 2 and linear fit of $1/T_{m2}$ against $2/n$ from Figure 4. P3HT 4 and P3HT 5 samples were additionally used to plot eq 2.

Thermal Characterization. More information about the crystallization behavior of the P3HT-COOHs can be gained from the thermal analysis. In general, all P3HT-COOHs showed a little lower degradation temperature (e.g., P3HT3-COOH onset 230 °C) than the nonfunctionalized P3HTs (P3HT3 onset 250 °C). This is expected due to the thermal instability of the carboxylic acid group. The differential scanning calorimetery (DSC) analysis showed that the COOH end groups also influence the melting behavior of the P3HT-COOHs as discussed below (Table 2).

The low-molecular-weight samples P3HT1 and P3HT1-COOH show a melting transition (T_{m1}) at 23 and 53 °C, respectively (Table 2). While P3HT1 shows a recrystallization at −9 °C, the recrystallization is kinetically hindered for P3HT1-COOH. Only in the first heating cycle a melting transition is seen at 53 °C. No recrystallization is observed during cooling under DSC scan rates of 10 K/min. But after a few days storing at room temperature, the melting transition is recovered during the next heating cycle. These transitions are not at typical temperatures for main chain crystallization, which should have a transition at higher temperatures according to theoretical calculations. The main chain melting temperature T_{m2} can be calculated with eq 2, which shows the melting point depression of polymers and has been adapted to P3HT by Wegner et al.[22,23]

$$\frac{1}{T_{m2}} - \frac{1}{T_{m2}^0} = \frac{R}{\Delta H_{m2}^0} \frac{2}{n} \quad (2)$$

In this equation, T_{m2}^0 is the melting temperature of a perfect crystal, ΔH_{m2}^0 the heat of fusion per mole of crystalline monomers, n the degree of polymerization (DP), and R the ideal gas constant. To calculate T_{m2}^0 and ΔH_{m2}^0, DSC data from two additional polymer samples P3HT4 and P3HT5 (Table 3) were used, and $1/T_{m2}$ was plotted against $2/n$ (Figure 4). T_{m2}^0 and ΔH_{m2}^0 were calculated from the linear fit to be 273 °C and 13 J/g. Using these parameters, the theoretical main chain melting point (T_{m2}) of P3HT1 could be calculated to be 117 °C. We have recently shown that in low-molecular-weight P3HT with M_n = 5000 g/mol an additional
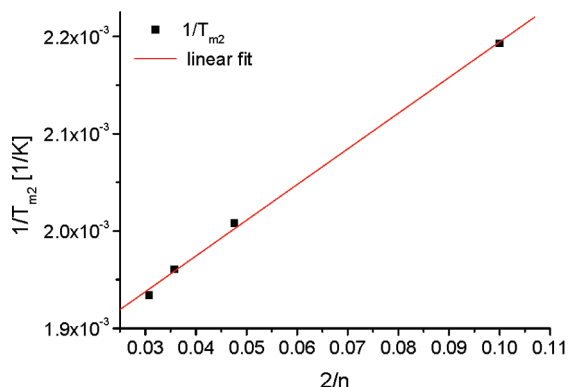
Figure 4. Plot of $1/T_{m2}$ against $2/n$ with a linear fit for the calculation of T_{m2}^0 and ΔH_{m2}^0. T_{m2}^0 is the melting temperature of a perfect crystal, and ΔH_{m2}^0 is the heat of fusion per mole of crystalline monomers.
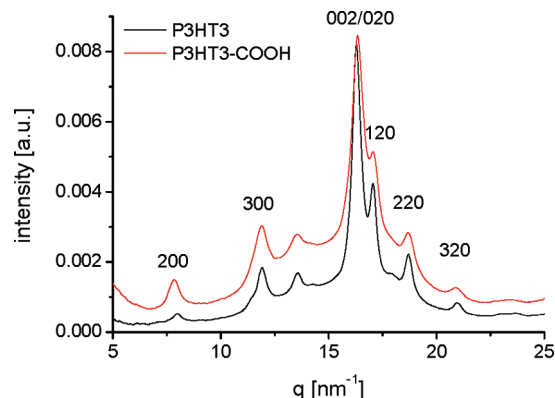

Figure 5. Wide-angle X-ray diffractograms in bulk samples for non-functionalized poly(3-hexylthiophene) (P3HT3) and monocarboxyl-tated poly(3-hexylthiophene) (P3HT3-COOH). Both polymers show $h00$ reflection for lamellar stacking of main and side chain, a $0k0$ reflection for the $\pi-\pi$-stacking, and $00l$ reflections for the order along the chain. The mixed $hk0$ indices at high q values indicate additional side chain order.

melting point for the side chains is observed around 60 °C; the side-chain crystallization being kinetically hindered for higher molecular weight samples.[21] Thus, the observed transitions T_{m1} in P3HT1 and P3HT1-COOH might be arising from side chain melting. An exact crystalline structure elucidation requires detailed SAXS/WAXS measurements.

For P3HT2-COOH there is only a little influence of the COOH group on the thermal properties in comparison to P3HT2, bearing the bromine end group. Both polymers show a melting point of the main chain (T_{m2}) at 183 °C and a recrystallization at ca. 165 °C. Also, the melting enthalpies of the polymers are similar in the range of 9 J/g (P3HT2-COOH) and 10 J/g (P3HT2). The only difference is that P3HT2 exhibits a reversible side chain melting at 64 °C with a recrystallization at 54 °C. For P3HT2-COOH the side chains melt at 59 °C, but the recrystallization is again kineti-cally hindered, as in P3HT1-COOH. With a further increase in molecular weight from P3HT2-COOH to P3HT3-COOH, T_{m2}, T_{c2}, and ΔH_{m2} increase, but the shift in ΔH_{m2} is only small (2 J/g). A comparison with the nonfunctionalized P3HT3 ($\Delta H_{m2} = 22$ J/g) shows that the crystallinty of P3HT3-COOH ($\Delta H_{m2} = 11$ J/g) is lower. A maximum value of ΔH_{m2} seems to be reached for P3HT3-COOH with 11 J/g. As explained above, carboxylic acid groups can affect the crystallization by their capability to form hydrogen bonds. Hydrogen bonds are thermally stable interactions which may hinder the comparatively weaker $\pi-\pi$-interactions and thus lower the maximum ΔH_m. On comparison, the commercial P3HT sample with $M_n = 19400$ g/mol exhibits a ΔH_{m2} of 13 J/g. This indicates that the crystallinity of P3HT3-COOH is similar to that of the commercial sample. As expected for high molecular weight P3HTs, no side chain melting was observed for these P3HT3, P3HT3-COOH, and the com-mercial sample. It is interesting to note that the multi-carboxylated P3HT reported earlier was amorphous.[11]

WAXS Analysis in Bulk. To gain more information about the crystal structure in bulk, wide-angle X-ray measurements (WAXS) were performed.

Figure 5 shows the X-ray diffractograms of P3HT3-COOH and P3HT3 as a representative example (diffracto-gram of P3HT2-COOH and P3HT2 is given in the Support-ing Information). DSC analysis shows that the crystallinity of the carboxylated P3HT3-COOH is lower than for P3HT3. Still both polymers show a well-defined X-ray pattern typical for highly regioregular P3HT: $h00$ reflections for the lamellar packing between main and side chains at q values of 7.9 (200) and 11.9 nm^{-1}(300); a $0k0$ reflection for the distance of the $\pi-\pi$-stacking and $00l$ reflections for the distance of the

thiophene units along the chain at 16.3 nm^{-1}. Additionally mixed indices 120, 220, and 320 are observed at higher q values as shown in Figure 5, which indicate the order of the side chains as reported previously.[21] This confirms a highly ordered structure even for the carboxylated P3HT3-COOH.

Charge Carrier Mobility Measurements in OFET Devices. For the use in organic electronic devices, it is important to study the influence of the COOH group on the charge carrier mobility of the polymer. Usually the charge carrier mobility of P3HT, as measured in organic field effect transistors (OFETs), increases with molecular weight.[24] Only the two higher molecular weight samples P3HT2-COOH and P3HT3-COOH were studied in OFETs and compared with the re-spective P3HTs. Both polymers crystallize in thin films and thus are promising candidates for application in devices. Preliminary mobility measurements were preformed in or-ganic field effect transistors with the output characteristics shown in the Supporting Information. For P3HT2 and P3HT2-COOH the mobilities were determined to be 2×10^{-3} and 1×10^{-3} cm^2/(V s). Since both polymers have simi-lar melting enthalpies (9 and 10 J/g) and thus similar crystal-linies, no influence of the COOH group on the mobility was observed. For P3HT3-COOH, the hole mobility was 2×10^{-3} cm^2/(V s). This is again conclusive with the thermal analysis which showed a melting enthalpy of P3HT3-COOH (11 J/g) in the same range as for P3HT2 and P3HT2-COOH. For the uncarboxylated P3HT3 with a high melting enthalpy of 22 J/g the mobility was 1 order of magnitude higher with a value of 1×10^{-2} cm^2/(V s). Thus, all measured mobilities could be correlated with crystallinity of the respective poly-mers. Despite the decrease in mobility of P3HT3-COOH com-pared to P3HT3, values in the range of 10^{-3} cm^2/(V s) are still high and good enough for the application as a hole con-ductor dye in hybrid solar cells. This becomes clear by looking at the mobility of a regioregular commercial P3HT with a M_n of 19 400 g/mol, which also showed a mobility in the range of 10^{-3} cm^2/(V s) under the same conditions of device preparation and measurement. Thus, P3HT-COOHs are materials with a reasonable high mobility, depending on their molecular weight. Additionally, they carry an-choring groups for the coordination of nanoparticles or for the chemiesorption on semiconductor metal oxides such as titanium dioxide. A qualitative proof of the anchoring of P3HT-COOH to TiO$_2$ is given in the Sup-porting Information.

Lohwasser and Thelakkat

Conclusion

In conclusion, three P3HT-COOHs bearing single carboxylic acid groups at the chain ends were synthesized. The successful and very selective functionalization was confirmed with MALDI-ToF MS. Optical analysis revealed that the higher molecular weight samples P3HT2-COOH and P3HT3-COOH are crystalline in thin films. Thermal analysis supports that the functional polymers still crystallize, but a maximum melting enthalpy seems reached for P3HT3-COOH with a molecular weight of 10 800 g/mol and 42 repeating units. WAXS analysis shows that the crystals are highly ordered. The mobility of P3HT2-COOH and P3HT3-COOH is in the order of 10^{-3} cm^2/(V s). This high mobility and the carboxylic acid anchoring group make them very promising candidates for the application in hybrid devices.

Supporting Information Available: Figures showing FT-IR spectra, UV−vis spectra in solution, X-ray diffractograms, and output characteristics of OFET. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* 1998, *280*, 1744.
(2) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. *Adv. Funct. Mater.* **2005**, *15*, 1617–1622.
(3) Jen, K.-Y.; Miller, G. G.; Elsenbaumer, R. L. *Chem. Commun.* **1986**, 1346–1347.
(4) Chen, T.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087–10088.
(5) McCullough, R. D.; Lowe, R. D. *Chem. Commun.* **1992**, 70–72.
(6) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542–17547.
(7) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526–3528.
(8) Adachi, I.; Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Macromolecules* **2006**, *39*, 7793–7795.
(9) McCullough, R. D.; Zhai, L. *Adv. Mater.* **2002**, *14*, 901–905.
(10) Iovu, M. C.; Craley, C. R.; Jeffries-El, M.; Krankowski, A. B.; Zhang, R.; Kowalewski, T.; McCullough, R. D. *Macromolecules* **2007**, *40*, 4733–4735.
(11) Lohwasser, R.; Bandara, J.; Thelakkat, M. *J. Mater. Chem.* **2009**, *19*, 4126–4130.
(12) Sommer, M.; Lang, A. S.; Thelakkat, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7901–7904.
(13) Liu, J.; McCullough, R. D. *Macromolecules* **2002**, *35*, 9882–9889.
(14) Liu, J.; Tanaka, T.; Sivula, K.; Alivisatos, A. P.; Frechet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 6550–6551.
(15) Jeffries-El, M.; Sauve, G.; McCullough, R. D. *Macromolecules* **2005**, *38*, 10346–10352.
(16) Van Hecke, G. R.; Horrocks, W. *Inorg. Chem.* **1966**, *5*, 1968–1974.
(17) Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, *5*, 890–891.
(18) Sze, S. M.; Ng, K. K. In *Physics of Semiconductor Devices*; Wiley-Interscience: Hoboken, NJ, 2007.
(19) Liu, J.; Loewe, R. S.; McCullough, R. D. *Macromolecules* **1999**, *32*, 5777–5785.
(20) Trznadel, M.; Pron, A.; Zagorska, M.; Chrzaszcz, R.; Pielichowski, J. *Macromolecules* **1998**, *31*, 5051–5058.
(21) Wu, Z.; Petzold, A.; Henze, T.; Thurn-Albrecht, T.; Lohwasser, R. H.; Sommer, M.; Thelakkat, M. *Macromolecules* **2010**, *43*, 4646–4653.
(22) Sperling, L. H. In *Introduction to Physical Polymer Science*, 4th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2006; p 301.
(23) Zen, A.; Saphiannikova, M.; Neher, D.; Grenzer, J.; Grigorian, S.; Pietsch, U.; Asawapirom, U.; Janietz, S.; Scherf, U.; Lieberwirth, I.; Wegner, G. *Macromolecules* **2006**, *39*, 2162–2171.
(24) Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J.; Frechet, J. M. J. *Adv. Mater.* **2003**, *15*, 1519–1522.