Comparative Study of the Field-Effect Mobility of a Copolymer and a Binary Blend Based on Poly(3-alkylthiophene)s

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Received July 29, 2004. Revised Manuscript Received October 19, 2004

The performance of highly soluble regioregular poly[(3-hexylthiophene)-*co*-(3-octylthiophene)] (P3HTOT) as a semiconducting material in organic field-effect transistors (OFETs) is presented in comparison to that of the corresponding homopolymers. Transistors made from as-prepared layers of P3HTOT exhibit a mobility of ca. 7×10^{-3} cm^2 $V^{-1}s^{-1}$, which is comparable to the performance of transistors made from as-prepared poly(3-hexylthiophene) (P3HT) and almost 6 times larger than the mobility of transistors prepared with poly(3-octylthiophene) (P3OT). On the other hand, the solubility parameter δ_p of P3HTOT is close to that of the highly soluble P3OT. Moreover, compared to a physical blend of poly(3-hexylthiophene) and poly(3-octylthiophene), the mobility of P3HTOT devices is almost twice as large and the performance does not degrade upon annealing at elevated temperatures. Therefore, the copolymer approach outlined here may be one promising step toward an optimum balance between a sufficient processability of the polymers from common organic solvents, a high solid state order, and applicable OFET performances.

1. Introduction

Poly(3-alkylthiophene)s (P3AT) are a class of polymers which are widely used for the preparation of semiconductor layers in organic field-effect transistors (OFETs). Although the first transistor fabricated from nonsubstituted polythiophene yielded a very low mobility of $\sim 10^{-5}$ $cm^2V^{-1}s^{-1}$,[1] mobilities of more than 0.1 $cm^2V^{-1}s^{-1}$ were reported for regioregular poly(3-hexylthiophene) (P3HT)[2,3] and poly(3,3‴-dialkyl-quaterthiophene) (PQT).[4] The much better performance of alkyl-substituted polythiophenes (PTs) compared to the nonsubstituted compound has several reasons. First, substituted PTs are soluble in selected organic solvents such as chloroform, and impurities and low-molecular-weight fractions (exhibiting low field-effect mobility) can be selectively removed. For example, it was recently shown that decreasing the average molecular weight of P3HT from ca. 37.000 g/mol to ca. 2.500 g/mol results in a drastic drop of the field effect mobility from ca. 10^{-2} cm^2/Vs down to 10^{-6} cm^2/Vs.[5,6] Second, the solid-state packing of regioregular P3AT favors the transport of charges between the PT backbones parallel to the substrate.[7] It is well-known that P3ATs exhibit a microphase-separated morphology in the solid state, in which layers consisting of the planar polythiophene main chains are separated by layers of the isolating alkyl chains.[8] For regioregular P3HT, these layers were found to be oriented preferentially parallel to the substrate.[3] As a result of such packing, the π-stacking direction lays in the plane of the substrate, allowing for rapid charge carrier motion along this direction. It was further reported that the chemical nature and the length of the alkyl side chains have a great effect on the charge carrier mobility in P3AT-based transistors.[9,10] In general, the attachment of branched, bulky side chains led to a low crystallinity of the solid layers. Also, the $\pi-\pi$ overlap distance between the conjugated backbones within the main chain layers was larger in these compounds, resulting in a low field-effect mobility.[9,11]

For linear alkyl chains, the mobility was shown to decrease with increasing chain length. This was attributed to the isolating nature of the alkyl substituents.[12] In fact, the largest mobility reported for poly(3-octylthiophene) is 2×10^{-3} cm^2/Vs,[13] approximately 1−2 orders of magnitude lower than

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10.1021/cm040183e CCC: $30.25
Published on Web 01/20/2005

the typical mobilities of P3HT layers. However, a critical length of the alkyls is needed for a sufficient solubility and processability of the polymer from solution. For example, high-molecular-weight batches of regioregular P3HT are well soluble in chlorinated solvents such as chloroform but only weakly soluble in non-chlorinated solvents such as toluene or xylene. On the other hand, P3OT dissolves quickly in toluene at RT. At the moment, P3HT is considered to present the best compromise with respect to solubility, layer formation, and overall transistor performance.

Recently, Babel and Jenekhe presented binary blends of semiconducting polymers as a novel approach to tune the properties of polymer FETs.[14,15] In the first set of experiments, a series of 10 binary blends of regioregular poly(3-hexylthiophene)s and poly(3-decylthiophene)s was prepared and the dependence of the charge carrier mobility on the blend composition was determined.[14] They found that the field-effect mobility of these blends was relatively high (2×10^{-3} cm^2/Vs) and constant over a broad composition range (5−80 wt % of poly(3-decylthiophene)). On the basis of atomic force microscope studies, the authors concluded that phase separation does not take place during preparation and storage at room temperature. This result is surprising as polymer blends are generally immiscible due to the reduced combinatorial entropy of mixing.[16] In their second investigation,[15] a series of 10 binary blends of regioregular poly(3-hexylthiophene) and poly(9,9-dioctylfluorene) (PFO) were investigated. However, in these blends, phase separation was found at room temperature, which might explain the rather low field-effect mobilities (below 10^{-3} cm^2/Vs) at PFO weight fractions larger than 20%.

An alternative approach to combine desirable properties of two polymers is by copolymerization of the respective monomer units. In fact, for random copolymers, phase separation in the bulk is highly unlikely. Here, we report on the performance of highly soluble regioregular poly[(3-hexylthiophene)-*co*-(3-octylthiophene)] (P3HTOT) as semiconducting material in OFETs. P3HTOT is a statistical copolymer of 3-hexylthiophene and 3-octylthiophene with a molar ratio of 50:50. For comparison, we investigated the corresponding homopolymers P3HT and poly(3-octylthiophene) (P3OT) as well as a binary blend of P3HT and P3OT with a 50:50 molar ratio. The degree of ordering in the solid state was related to the occurrence of long wavelength absorption bands which reflect the presence of planarized P3AT chains. The solubility parameter δ_p, which is a useful measure for the miscibility of a polymer with a solvent (or another polymer), was determined analytically for all polymers using the titration method. The report shows a way toward a suitable compromise between sufficient solubility of the polythiophenes (allowing solution processing) and a high solid state order (guaranteeing good OFET performance).

2. Results and Discussion

Synthesis. The homopolymers poly(3-hexylthiophene) (P3HT), poly(3-octylthiophene) (P3OT), and the statistical copolymer poly[(3-hexylthiophene)-*co*-(3-octylthiophene)] (P3HTOT) were synthesized using the nickel-catalyzed Grignard metathesis coupling according to McCullough.[17,18] This method is known to yield highly regioregular polymers. The monomer feed ratio in the copolymer was 50:50. After polymerization, the isolated polymer powders were extracted in a Soxhlet apparatus using hexane to remove short chain oligomers. Values for the molecular weight (M_w) and the polydispersity index (PDI) of the different polymers as measured by gel permeation chromatography (GPC, versus a polystyrene standard) are as follows: 25 650 g/mol and 1.35 for P3HT, 46 000 g/mol and 1.27 for P3HTOT, and 69 400 g/mol and 1.76 for P3OT, respectively.

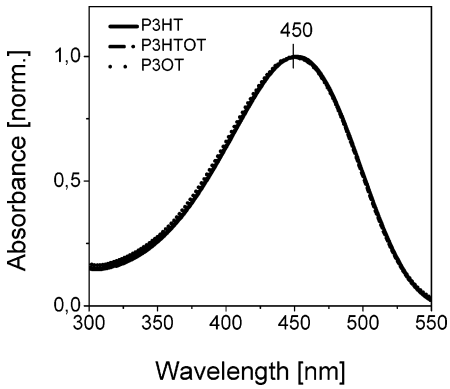

Figure 1. Normalized optical absorption spectra of P3HT, P3HTOT, and P3OT dissolved in chloroform.

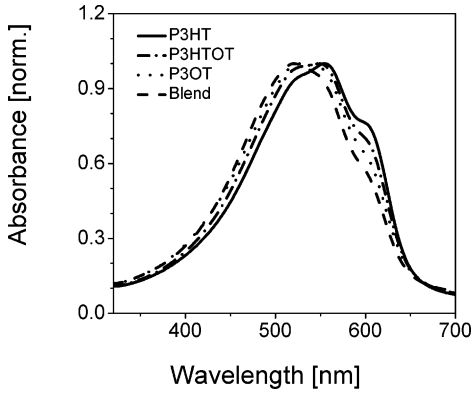

Figure 2. Normalized thin film optical absorption spectra of P3HT, P3HTOT, P3OT, and a blend of P3HT + P3OT (50:50 in molar ratio).

Optical, Thermal, and Structural Properties in Solution and in Thin Layers. Dissolved in chloroform, P3HT, P3OT, and P3HTOT exhibit broad and featureless UV−Vis absorption spectra with one maximum located at 450 nm (Figure 1). In contrast, the absorption spectra of the thin films prepared from these polymers are significantly red shifted (Figure 2). It has been reported that P3ATs adopt a twisted backbone conformation in good solvents, causing a featureless and broad absorption spectrum. Upon the transition into the solid state, the polymer backbone planarizes, resulting in a well-structured and red-shifted absorption.[19,20] In our case, the strongest red-shift was observed for P3HT, and the

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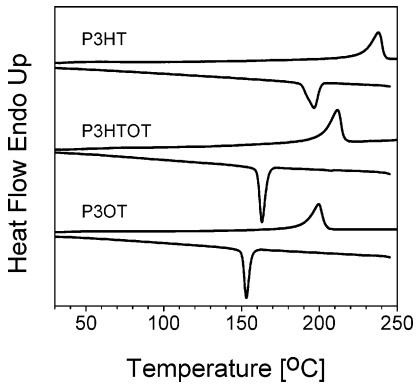

Figure 3. Differential scanning calorimetry (DSC) thermograms of P3HT, P3HTOT, and P3OT.

Table 1. Melting Points (T_m) and Melting Enthalpies (ΔH_m) Measured Using DSC

polymer	T_m (endothermic) [°C]	T_m (exothermic) [°C]	ΔH_m [J/g]
P3HT	237.8	196.5	21.900
P3HTOT	211.6	163.1	19.400
P3OT	199.5	153.0	19.000

smallest was observed for P3OT, with that of the copolymer between. This result indicates the highest degree of main chain planarization and interchain ordering in P3HT with the shortest side chains. Compared to the homo- and copolymers, the absorption spectrum of the P3HT/P3OT blend in the solid state shows an even smaller red-shift, indicative of an even lower degree of interchain ordering in the blend. In line with the optical data, X-ray diffraction (XRD) measurements show the occurrence of a sharp first order Bragg peak only for P3HT (not shown here).

Differential scanning calorimetry (DSC) measurements for all polymers are shown in Figure 3 and the extracted melting points and transition enthalpies are listed in Table 1. The melting point decreases systematically with increasing side chain length (237.8 °C for P3HT, 211.6 °C for P3HTOT, and 199.5 °C for P3OT). The single melting point of P3HTOT, between that of P3HT and P3OT, confirms the statistical assembly of the 3-hexylthiophene and 3-octylthiophene building blocks. Interestingly, the melting enthalpies of the three derivatives are quite similar, between 21.900 J/g for P3HT and 19.000 J/g for P3OT. This indicates that the degree of crystallinity in the solid powder is not very different among all three polymers. Thus, the absence of a diffraction peak in solid layers of P3HTOT and P3OT might be related to a small domain size rather than to a highly amorphous structure.

Determination of Solubility Parameters. To achieve a sufficient solubility of a polymer in a suitable solvent, its solubility parameter (δ_p) should be close enough to the solubility parameter of the solvent (δ_s). It is frequently found that polymers dissolve only in solvents having solubility parameters which differ by less than 1 $cal^{1/2}cm^{3/2}$.[16] The δ_p parameter can be determined experimentally, e.g. by solvent−nonsolvent titration, inverse gas chromatography, etc.; or calculated theoretically from chemical structure data of the polymer. Unfortunately, we could not calculate the δ_p values of our polymers due to the lack of knowledge about the structural parameters. Therefore, we used the solvent−nonsolvent titration method for the determination of the solubility parameters δ_p of the two homo- and the copolymers.

The titration started from a polymer solution in a "good" solvent (solvent), to which two pre-selected "bad" solvents (nonsolvents) are added. One of the nonsolvents possesses a higher, the other a lower, solubility parameter than the good solvent. In this work, chloroform ($\delta_s = 9.3$ $cal^{1/2}cm^{3/2}$) was used as the solvent, and hexane ($\delta_s = 7.3$ $cal^{1/2}cm^{3/2}$) and methanol ($\delta_s = 14.5$ $cal^{1/2}cm^{3/2}$) were used as the nonsolvents.[21] During titration, the nonsolvent is added gradually to the polymer solution. At a certain concentration of the nonsolvent, polymer aggregation is induced and an additional red-shifted absorption band appears in the spectrum of the solution.[19]

Figure 4 shows the result of titration with hexane for all three polymers. The absorption spectra recorded during the titration process are spectrally similar for both homopolymers and the copolymer. However, the amount of nonsolvent necessary to induce aggregation differs from polymer to polymer. Also, as expected, a smaller amount of methanol (compared to hexane) was needed to induce aggregation (Figure 5 compared to Figure 4). This is related to the quite similar solubility parameters of the nonpolar solvents hexane and chloroform, and the distinctly different δ_s parameter of the more polar methanol.

We have calculated the solubility parameter of the homo- and copolymers using the formalism proposed by Suh and Clarke.[22] In this formalism, the solubility parameter of the polymer is determined by

$$\delta_p = \frac{\sqrt{V_{12}}\,\delta_{12} + \sqrt{V_{13}}\,\delta_{13}}{\sqrt{V_{12}} + \sqrt{V_{13}}} \tag{1}$$

where

$$\boldsymbol{V}_{1i} = \frac{V_1 V_i}{\phi_1 V_i + \phi_i V_1};\ i = 2,3 \tag{2}$$

$$\delta_{1i} = \phi_1\delta_1 + \phi_i\delta_i;\ i = 2,3 \tag{3}$$

with

$$\phi_i = 1 - \phi_1 = \frac{v_i}{v_1 + v_i};\ i = 2,3 \tag{4}$$

Here, V_i is the molar volume, ϕ_i is the volume fraction, and v_i is the volume of the nonsolvent added to the polymer solution to induce polymer aggregation. The subscript 1 refers to the solvent and subscripts 2 and 3 refer to the nonsolvent with the lower and higher solubility parameter, respectively.

Table 2 lists solubility parameters of two homopolymers and the copolymer calculated from the results of the titration

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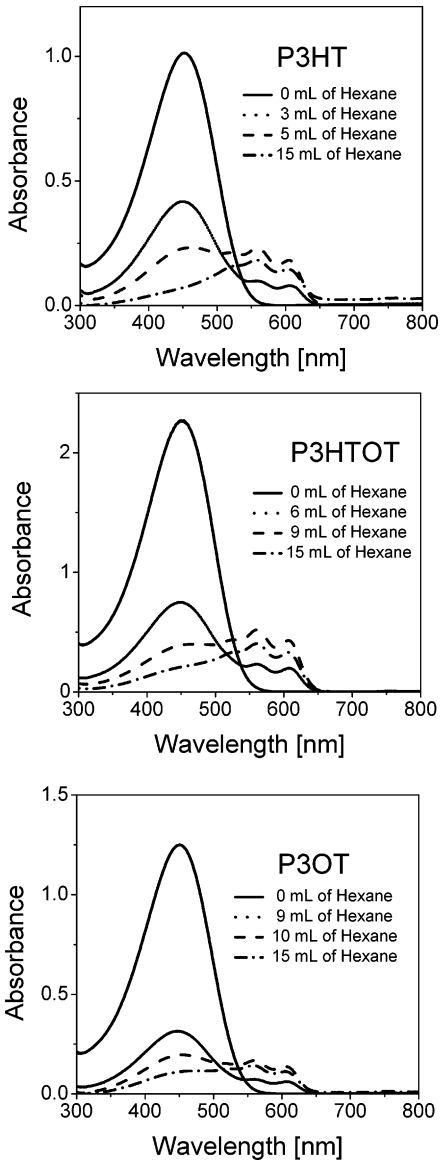

Figure 4. UV-Vis absorption spectra of P3HT, P3HTOT, and P3OT dissolved in 3 mL of chloroform with a concentration of 10^{-4} M and titrated with hexane.

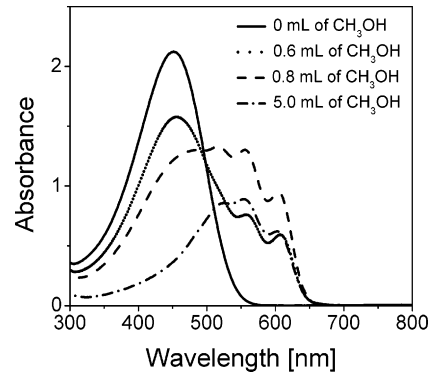

Figure 5. UV-Vis absorption spectra of P3HTOT dissolved in 3 mL of chloroform with a concentration of 10^{-4} M and titrated with methanol.

experiments using eqs 1−4. All polymers show solubility parameters within the range of 0.2−0.4 $cal^{1/2}cm^{3/2}$ to that of chloroform, which indicates that all of them are highly soluble in this solvent. Further, it was found that P3HTOT has a solubility parameter close to that of P3OT and that

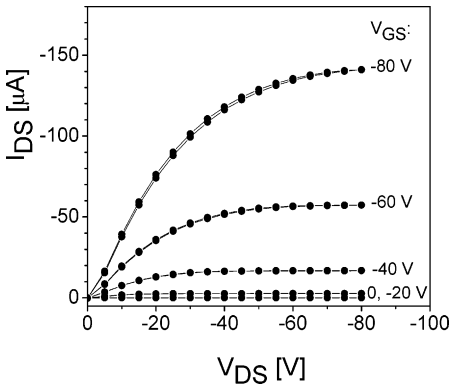

Figure 6. Output characteristic of an OFET consisting of an as-prepared P3HTOT layer.

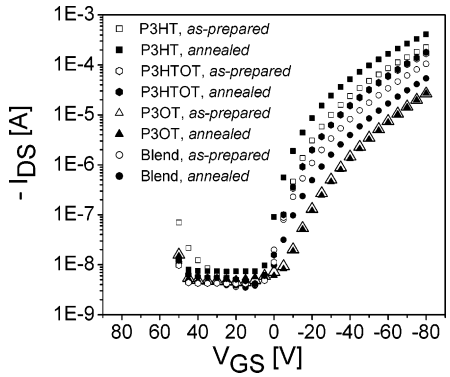

Figure 7. Transfer characteristic of OFETs (taken at $V_{DS} = -80$ V), prepared from P3HT, P3HTOT, P3OT, and a blends of P3HT and P3OT (50:50 in molar ratio).

Table 2. Solubility Parameters Deduced from the Experimental Titration Experiments with Hexane and Methanol

polymer	δ_p $(cal/cm^3)^{1/2}$
P3HT	9.1 ± 0.01
P3HTOT	8.9 ± 0.02
P3OT	8.9 ± 0.02

this value is similar to the solubility parameter of toluene ($\delta_s = 8.9$ $cal^{1/2}cm^{3/2}$).

Transistor Properties. Regioregular P3HT, P3OT, P3HTOT, and the P3HT/P3OT blend (molar ratio 50:50) were used as the semiconducting layers in OFETs. The output characteristics of transistors based on these different polymers show well-resolved linear and saturation regions (see, e.g., Figure 6 for a transistor prepared from P3HTOT). The field-effect mobility was determined from the transfer characteristics measured at $V_{DS} = -80$ V. In this case, the square-root of the drain current at saturation $I_{DS,sat}^{1/2}$ versus gate voltage should follow the relation

$$I_{DS,sat} = \frac{WC_i}{2L}\mu_{sat}(V_{GS} - V_o)^2 \qquad (5)$$

Here, W and L are the channel width and length, respectively, C_i is the capacitance per unit area of the SiO_2-insulator, and V_o is the onset-voltage. Figure 7 shows the transfer characteristics of the devices. Also, the on/off ratio was determined as the ratio of the drain currents at saturation measured for $V_{DS} = -80$ and 20 V. The field-effect mobility and the on/

Table 3. Field-effect Mobilities Calculated from the Square Root of the Drain Current in the Saturation Region, $I_{DS,Sat}^{1/2}$ versus Gate Bias, V_{GS} and the On/off Ratios Measured at $V_{DS} = -80$ V

material and treatment	mobility [$cm^2V^{-1}s^{-1}$]	on/off
P3HT, as-prepared	8.6×10^{-3}	5.6×10^4
P3HT, annealed	1.4×10^{-2}	5.3×10^4
P3HTOT, as-prepared	6.7×10^{-3}	4.2×10^4
P3HTOT, annealed	7.2×10^{-3}	4.3×10^4
P3OT, as-prepared	1.3×10^{-3}	5.7×10^3
P3OT, annealed	1.3×10^{-3}	5.7×10^3
blend P3HT + P3OT, as-prepared	4.4×10^{-3}	2.9×10^4
blend P3HT + P3OT, annealed	2.4×10^{-3}	1.5×10^4

off ratio measured at $V_{DS} = -80$ V are summarized in Table 3.

All transistors had an onset-voltage close to zero. For transistors with as-prepared layers, the highest field-effect mobility of 8.6×10^{-3} cm^2 $V^{-1}s^{-1}$ and a large on/off ratio of 5.6×10^4 was found for P3HT. As reported earlier, the performance of transistors made from P3HT could be further improved by annealing the layer at a sufficiently high temperature.[6] Transistors with P3OT exhibited a mobility of only 1.3×10^{-3} $cm^2V^{-1}s^{-1}$ for both the as-prepared and the annealed samples. This is ca. 1 order of magnitude lower than the mobility of 1.4×10^{-2} $cm^2V^{-1}s^{-1}$ for annealed P3HT. Remarkably, the transistors based on the copolymer P3HTOT show a reasonably high field-effect mobilities of ca. 7.2×10^{-3} $cm^2V^{-1}s^{-1}$ and large on/off ratio of 4.3×10^4. These values are comparable with those of the transistors based on as-prepared P3HT.

At this point the question arises regarding which mechanism predominately controls the mobility of the charges in the polymer samples. As mentioned in the Introduction, it has been argued that the smaller mobility of charges in P3OT compared to those in P3HT is due to the isolating nature of the side chain layers.[12] Thus, it is expected that the mobility of P3HTOT will be intermediate between the values for the two homopolymers. Alternatively, one might argue that the purity of the polymer samples plays the dominant role. Because the solubility of P3OT is better than that of P3HT, removal of, e.g., low-molecular-weight components is more difficult. In fact, the polydispersity index is larger for P3OT (1.76) than for P3HT (1.35). It has further been shown that P3HT fractions with low molecular weight have a much smaller mobility.[5,6] This suggests that short chains in the P3OT sample could be responsible for its lower mobility. On the other hand, the average molecular weight of the P3OT is a factor of almost 3 larger than that of P3HT, so the number of short chains in the P3OT sample should be very small. Finally, we point out that there is a direct correlation between the mobility and the absorption properties. Most remarkably the intensity of the shoulder at 600 nm drops substantially when going from P3HT to P3HTOT to P3OT. Recently, the 600 nm shoulder has been assigned to an interchain excitation.[23] We, therefore, propose that besides the thickness of the isolating side chain layers, the packing of the polymer chains in the main chain layers significantly controls the mobility of the homo- and copolymers studied here.

For the device based on the as-prepared P3HT/P3OT blend, the field-effect mobility is approximately the average of the mobility measured for as-prepared P3HT and P3OT layers. Recent work by S. Pal and A. K. Nandi has shown that regioregular P3HT and P3OT cocrystallizes at a weight fraction of 0.5:0.5 as indicated by a single DSC melting peak and a single (100) Bragg peak in the X-ray diffraction pattern of the blend.[24] Also note that the investigation using blends of regioregular poly(3-hexylthiophene) and poly(3-decylthiophene) did not reveal any evidence for phase separation (see Introduction) and the interlayer spacing was intermediate between those of the two homopolymers.[14] This suggests that as-prepared layers of P3HT and P3OT have perfect blend morphology with intermediate layer spacing.

Upon annealing, the mobility of the blend layer decreases to 2.4×10^{-3} $cm^2V^{-1}s^{-1}$. This value is close to that measured for P3OT in the as-prepared or annealed devices. Interestingly, this value can be explained under the assumption that the two compounds phase-separate and they occupy approximately the same area at the interface to the SiO_2 insulator. In this case, the charges travel the same distance $L/2$ (with L the channel length) in both components. Assuming further that the electric field is the same in both phases, the carriers need a total time

$$\tau_{drift} = \frac{L/2}{\mu_{P3HT}E} + \frac{L/2}{\mu_{P3OT}E} = \frac{L}{\bar{\mu}E} \tag{6}$$

to drift through the channel. Thus, the average mobility $\bar{\mu}$ is given by

$$\frac{1}{\bar{\mu}} = \frac{1}{2}\left[\frac{1}{\mu_{P3HT}} + \frac{1}{\mu_{P3OT}}\right] \tag{7}$$

With $\mu_{P3HT} = 1.4 \times 10^{-2}$ $cm^2V^{-1}s^{-1}$ and $\mu_{P3OT} = 1.3 \times 10^{-3}$ $cm^2V^{-1}s^{-1}$, the average mobility $\bar{\mu}$ is predicted to be 2.4×10^{-3} $cm^2V^{-1}s^{-1}$, which is close to the measured mobility. This result suggests that the P3HT/P3OT blend morphology is not stable at elevated temperatures.

3. Conclusions

We have shown that a statistical polythiophene copolymer, regioregular poly[(3-hexylthiophene)-*co*-(3-octylthiophene)] (P3HTOT), is a highly soluble semiconductor with good electrical properties. Transistors made from as-prepared layers of P3HTOT exhibit a mobility of ca. 7.2×10^{-3} cm $V^{-1}s^{-1}$, which is comparable to the performance of transistors made from as-prepared P3HT and almost 6 times larger than the mobility of transistors prepared with P3OT. Moreover, compared to a physical blend of poly(3-hexylthiophene) and poly(3-octylthiophene), the mobility of P3HTOT devices is almost twice as large and the performance does not degrade upon annealing at elevated temperatures. Therefore, the copolymer approach outlined here may be one promising step toward an optimum balance between a sufficient

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processability of the polymers from common organic solvents, a high solid state order, and applicable OFET performances. In future work, we plan to investigate the performance of transistors made from the same polymers but dissolved in less polar non-chlorinated solvents such as toluene as our calculations predict that these solvents should be more suitable to dissolve the copolymer.

4. Experimental Section

All synthesis reactions were carried out in argon atmosphere, and solvents with a pure analysis quality were used. The synthetic procedures were similar to those reported in the literature.[17,18] The polymer fractions were extracted in a Soxhlet apparatus to remove short chain oligomers from the precipitate.

UV−Vis absorption spectra were measured with a Perkin-Elmer Lambda 19 spectrometer. DSC thermograms were measured using Perkin-Elmer Thermal Analysis DSC-7 calibrated with Indium (99.99% pure). The measurements were carried out under Argon atmosphere with heating and cooling rates of 10 °C/minute.

A highly doped Si substrate was used as the transistor substrate as well as the gate electrode. A thermally grown silicon dioxide layer of 300 nm acted as the gate dielectric with a unit area capacitance of 11 nF/cm^2. Prior to the deposition of polymers, the surface of the silicon dioxide layer was cleaned with several common solvents, exposed to oxygen plasma (P = 200 W for 5 min) and silanized in hot hexamethyldisilazane vapor (26 h at 60 °C). The polymers were dissolved in chloroform with similar amount of 0.03 mole for each polymer and spin-coated from solution with 1200 rpm for 60 s at room temperature, resulting in a layer thickness of ca. 30−70 nm (because they have different M_w, therefore, although the amounts of moles were similar, their thicknesses are still varied). All solutions were filtered through a 0.20-μm pore size PTFE membrane syringe filter before use. In some cases, the polymer-covered SiO_2/Si samples were annealed for 5 min at 150 °C prior to the deposition of the source and drain electrodes. Interdigitating Au electrodes with a thickness of 100 nm functioning as source and drain electrodes (channel length 100 μm and total channel width 148.5 mm) were evaporated on top of the polymers. The output and transfer characteristics of these devices were measured using two Keithley 2400 source meters. All preparation processes and the characterization of the OFETs were performed inside the N_2-filled glovebox.

Acknowledgment. We thank Dr. J. Pflaum and S. Hirschmann (University of Stuttgart) for the XRD measurements. We also acknowledge fruitful discussions with Dr. H. Sirringhaus (University of Cambridge). The financial support from German Science Foundation and *Fond der Chemischen Industrie* are gratefully acknowledged.

CM040183E