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Regioselective Polymerization of 3-(4-Octylphenyl)thiophene with $FeCl_3$

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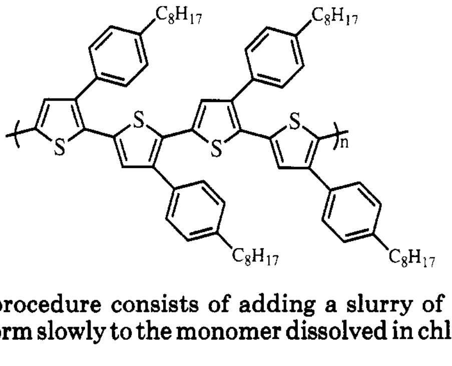
ABSTRACT: We have shown that it is possible to regioselectively polymerize 3-(4-octylphenyl)thiophene with $FeCl_3$. Adding $FeCl_3$ slowly to the monomer leads to a soft and therefore regioselective polymerization. The head-to-tail content was determined by ^1H NMR to be 94 ± 2%. Thin films of the polymer treated with chloroform vapor have an absorption maximum at 602 nm (2.06 eV) with clear vibronic fine structure. Free standing films have a conductivity of 4 S/cm, which is 100 times higher than for earlier prepared poly(3-(4-octylphenyl)thiophene). A mechanism for the regioregular polymerization is also proposed.

Introduction

Poly(3-alkylthiophenes) (P3AT) have received much attention as electrically conducting polymers with many potential applications.[1] During the study of the properties of these materials, it has become clear that it is important to investigate well-defined polymers or oligomers.[2] For example, the regioregularity plays a key role in achieving high conductivity in these materials.[3] Regioregularity is also critical for the color of the emitted light from a light-emitting diode made of the polymer.

McCullough et al. have prepared regioregular P3AT by a Grignard polymerization reaction.[4] Chen et al. have used zinc thiophene for the same purpose.[5] Both groups have shown that improved regularity results in enhanced conductivity of the doped polymers.[6,7] These types of polymerizations are rather sophisticated and require extremely pure monomers to give high molecular weight products. In contrast, polymerization of thiophenes with ferric(III) chloride ($FeCl_3$) is easy, is suitable for large scale production, and gives high molecular weight polymers. Polymerization with $FeCl_3$ has up to now been reported to produce irregular polymers only.[3] The standard procedure is to suspend $FeCl_3$ in chloroform and then add the thiophene monomer quickly.[8] We now report a method to prepare regioregular poly(3-(4-octylphenyl)thiophene)[9] (POPT) with $FeCl_3$ in chloroform.



Our procedure consists of adding a slurry of $FeCl_3$ in chloroform slowly to the monomer dissolved in chloroform. By this method the Fe^{3+}/Fe^{2+} ratio is low and thus also the oxidation potential is low during the whole polymerization process. Therefore, a more selective polymerization can occur and the produced polymer becomes more stereoregular. There is also less risk of mislinkages in the polymerization, e.g. coupling at the 4-position on the thiophene ring. Originally, this procedure was used for the polymerization of oligomers of alkylthiophenes to yield higher molecular weight polymers.[10]

Experimental Section

3-(4-Octylphenyl)thiophene was prepared according to the procedures described elsewhere.[9] Recrystallization in methanol produced isomerically pure 3-(4-octylphenyl)thiophene determined by GC. MP: 57–58 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, 2H, J = 8.3 Hz), 7.40 (dd, 1H, J = 1.8, 2.4 Hz), 7.37 (m, 2H), 7.21 (d, 2H, J = 8.3 Hz), 2.62 (t, 2H, J = 7.7 Hz), 1.63 (m, 2H), 1.3 (m, 10H), 0.88 (t, 3H, J = 6.9 Hz).

POPT was prepared as follows. The monomer, 3-(4-octylphenyl)thiophene was dissolved in chloroform. A suspension of $FeCl_3$ in chloroform of equal volume was added to the monomer solution for 6 h while it was being stirred at room temperature under an argon atmosphere. The final concentration for the monomer and $FeCl_3$ was 0.05 and 0.2 M, respectively. When the addition was complete, the mixture was stirred for an additional 1 h. The reaction mixture was poured into methanol, and a precipitate formed. This was filtered off and washed with methanol. The resulting polymer was then completely dedoped by stirring the polymer, chloroform, and concentrated ammonia while the mixture was being boiled for 30 min. The water phase was separated, and fresh ammonia was added. This procedure was repeated four times, and then the chloroform solution was washed twice with ethylenediaminetetraacetic acid (EDTA) dissolved in water (0.05 M). The chloroform solution was finally washed with water and then filtrated. The amount of chloroform was reduced, and then the residue was poured into methanol and the polymer precipitated. The low molecular weight and irregular part of the polymer (5%) was removed by Soxhlet extraction with diethyl ether. The yield of regular polymer was 80%, and the molecular weight was determined to be $\bar{M}_n$ = 23 000 and $\bar{M}_w$ = 52 000 by SEC in THF with polystyrene standards.

Results and Discussion

It is possible to determine the head-to-tail (HT) and head-to-head (HH) ratio for P3AT by ^1H NMR.[3,11] The two peaks around δ 2.7 ppm come from the $-CH_2-$ group next to the thiophene ring. The ratio between these two peaks corresponds to the relative amounts (1 HT and 2 HH) of the diads. The four signals around δ 7.0 ppm come

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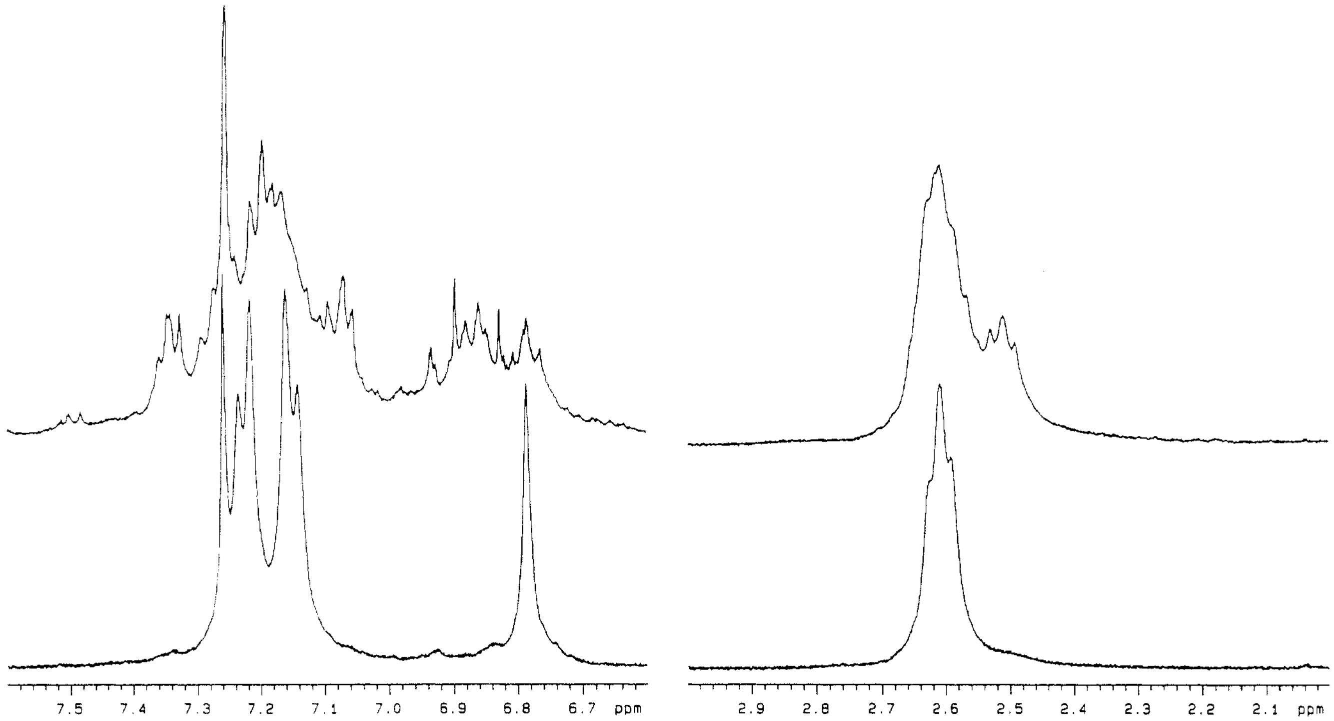


Figure 1. Selected parts of ^1H NMR (400 MHz, CDU_3) spectra of regioregular POPT (lower lines) and of the ether soluble fraction from the workup (upper lines). The HT content was calculated to be 94 ± 2% for POPT and 77 ± 2% for the ether soluble fraction from the peak areas at δ 2.61 and 2.51 ppm.

from the proton in the 4-position on the thiophene ring and represent the four possible triads. The density of the triads can be determined from these signals.[11] Selected parts of the ^1H NMR spectra of POPT and of the ether soluble fraction from the workup are shown in Figure 1.

From Figure 1, it can be seen that signals from the $-CH_2-$ group next to the phenyl ring at δ 2.61 ppm appear as an almost resolved triplet for POPT. The ether soluble fraction shows a multiplet at 2.61 ppm, and this is probably due to different triads. It can also be seen that the HH dyad gives signals at δ 2.51 ppm as a resolved triplet. We assume that there is no significant difference in the interpretation of the ^1H NMR signals for the $-CH_2-$ group in P3AT compared to that of POPT. This supports the assignment that these peaks correspond to the HT and HH diads for P3AT. The HT density of POPT is 94 ± 2% and for the ether soluble fraction 77 ± 2%, calculated from the peaks at δ 2.61 and 2.51 ppm in Figure 1. McCullough reports 91–96% HT for P3AT with different alkyl chain lengths using their method. Chen claims to have 98.5 ± 1.5% HT in poly(3-hexylthiophene). POPT prepared with our polymerization procedure seems to be as regular a polymer as that obtained from the Grignard polymerization method. ^{13}C NMR spectra show high regularity of POPT, and no extra set of signals due to irregularities was detected as for poly(3-(4-(octyloxy)-phenyl)thiophene).[12]

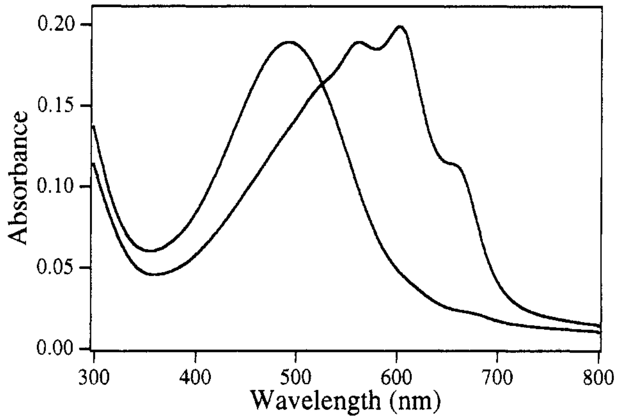


Figure 2. UV–Vis absorption spectra of a spin-coated film of POPT on glass (λ_{max} = 493 nm) and the same film treated with chloroform vapor (λ_{max} = 602 nm).

Table 1. UV–Vis Data for Solution and Films of POPT

POPT	λ_{max}, nm (E, eV)	ΔE, eV
$CHCl_3$	467 (2.66)	
film (pristine)	493 (2.68)	
film ($CHCl_3$ treated)	ca. 518 (2.40)	
		0.19
	562 (2.21)	
		0.15
	602 (2.06)	
		0.19
	664 (1.87)	

UV–Vis spectra of the polymers also show the regioregularity. In chloroform solution, the maximal absorption occurs at 467 nm for POPT at room temperature. Heating is needed to dissolve the polymer in chloroform. The shift of the maxima for the spin-coated film on glass of the same polymer is only 26 nm. However, after a treatment of the same film with saturated chloroform vapor at room temperature, the maximum is shifted to 602 nm; see Figure 2. The shift after the vapor treatment is due to solvent-induced ordering giving a more planar conformation. This conversion can also be made almost completely by heating the film. The ordered film also shows a very clear vibronic fine structure. The location of the vibronic peaks was determined from the second derivative of the spectra; see Table 1. ΔE is the difference between the vibronic peaks and should be of equal energy. The more ordered the polymer is the closer the absorption maximum (λ_{max}) is to the 0–0 absorption line (E_{0-0}).[13] Thus the energy difference ($\lambda_{max} - E_{0-0}$) can be used as a measure of the order in the film.[14] In our case the difference is 0.19 eV for the chloroform treated film and 0.81 eV for the pristine film. Slow evaporation of the solvent results in purple transparent films or copper–bronze luster for thick films.[7]

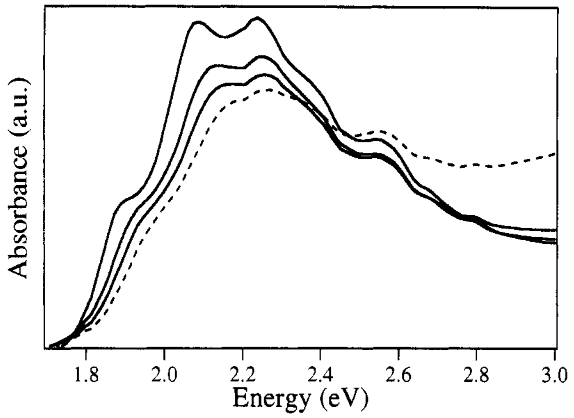


Figure 3. Optical absorption spectra of POPT films treated with chloroform vapor at room temperature, 150 °C, 200 °C, and 250 °C (dashed), inside a vacuum cell.

Light-emitting diodes prepared of spin-coated POPT show red electroluminescence. If the diode is heated, the emission is shifted continuously with the heating time. When the diode is heated for a long time, the POPT film is converted to the ordered form, and the emission is shifted to near infrared.[15]

In ref 12 it was observed that poly(3-(2-(octyloxy)-phenyl)thiophene) showed thermochromic behavior. The vibronic fine structure disappeared when the film was heated from 40 to 160 °C. We have measured the thermochromic behavior of a spin-coated film of POPT converted with chloroform vapor; see Figure 3. The absorbance was normalized at 1.7 eV. When heating from room temperature to 250 °C, only minor thermochromic shifts of optical absorption were observed. This is probably due to a very regular and stiff polymer backbone in the thermodynamically stable form of the film. This is also seen in the fact that when POPT is heated in a melting point microscope, no melting could be observed below 300 °C.

Enhanced regioregularity and therefore higher structural order in the material give higher conductivity. Free standing films were prepared by slow evaporation of a filtered chloroform solution of the polymers on a glass substrate. The films were removed from the substrate with methanol. Doping with $FeCl_3$ was done by treating the films with 1 M $FeCl_3 \cdot 6H_2O$[16] in acetonitrile for 24 h. The doped films (ca. 20 μm) were washed with acetonitrile and dried in vacuum. The conductivity was measured with the four-probe method with pressure contacts. POPT prepared in our way showed a mean conductivity of 4 S/cm at room temperature. The free-standing films are rather flexible in both the undoped and the doped states. Films prepared as described here of POPT[9] had a mean conductivity of 0.04 S/cm when doped in the same way with $FeCl_3$. Doping the films with solid iodine in a closed container for 24 h gave the same conductivity as for $FeCl_3$ doping for both types of POPT. The increased regularity and more well-defined polymer gave 100 times higher conductivity for our POPT than for the earlier reported POPT[9].

The molecular weight of the polymer prepared by our procedure can be increased by using a higher ratio of $FeCl_3$ to monomer or using a longer polymerization time after the addition of $FeCl_3$, possibly due to cross-linking. When the molecular weight increases, the solubility decreases. However, ^1H NMR peaks become broader and it is no longer possible to determine the exact HT content. This is the reason why we have chosen to describe the polymerization procedure for a somewhat lower molecular weight polymer.

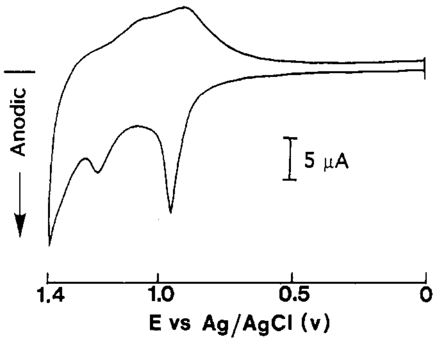


Figure 4. Cyclic voltammogram of a POPT film on a Pt electrode in 0.5 M $LiClO_4$ solution in acetonitrile.

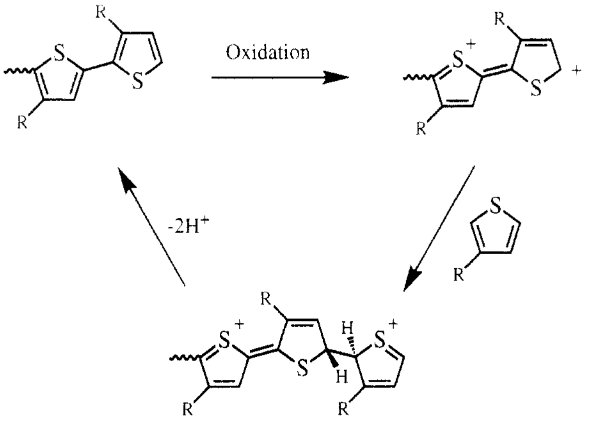
The cyclic voltammogram of a POPT-coated Pt wire was measured in a one-compartment three-electrode cell with a Pt wire counter electrode and an Ag/AgCl reference. The electrolyte was 0.5 M $LiClO_4$ in acetonitrile, and the cell was purged with argon. Two distinct oxidation peaks at 0.95 and 1.2 V were observed; see Figure 4. Two oxidation peaks in polythiophene voltammograms have been reported earlier. They were explained as due to two distinct electrochemical processes.[17] Regular P3AT also shows two peaks,[18] and they seem to be more distinct when the polymer is well-defined.

Regioregular POPT could also be prepared by using the standard polymerization procedure.[8] After dedoping, the polymer contained both regular and irregular parts. Soxhlet extraction of the polymer with ether removed the irregular part. The regular polymer had the same regularity as described earlier, determined by ^1H NMR. The ether soluble part (48%) contained polymer of the same molecular weight as the regular part. This was determined by SEC and can be explained by the fact that the irregular polymer is more soluble than the regular polymer. The yield of regular polymer was 46%. When we terminated the standard polymerization method of POPT at a very early stage, we could observe that most of the irregular polymer is formed in the beginning of the polymerization reaction. This is consistent with an oxidation potential which decreases with polymerization time.

We consider it convenient to describe the $FeCl_3$ oxidation as a redox process with a varying ratio of Fe^{3+}/Fe^{2+}. When the standard procedure for polymerizing the monomers is used, the ratio of Fe^{3+}/Fe^{2+}, and thus the oxidation potential in the $FeCl_3$/chloroform slurry, changes with time after the addition of the monomer, simply because Fe^{3+} is consumed and Fe^{2+} is formed. In the beginning of the polymerization, the Fe^{3+}/Fe^{2+} ratio is high, and thus the oxidation potential is high. This results in monomer oxidation and unselective coupling reactions, and an irregular polymer is formed. After some time the Fe^{3+}/Fe^{2+} ratio and potential decrease. The polymerization reaction proceeds more selectively, and a more stereoregular polymer is formed. Our polymerization procedure to add the Fe^{3+} slowly gives a low and more even oxidation potential of the slurry and therefore a more selective polymerization reaction during the whole polymerization process.

If the origin of the regioregularity was only due to a steric effect, 3-cyclohexylthiophene[19] should also form a regular polymer by our method of oxidation, but this is not observed experimentally. When using our polymerization method on 3-octylthiophene, no significant difference at room temperature was observed. However, when the reaction temperature is lowered, the regularity of the polymer increases. These results show that the

Scheme 1. Proposed Propagation Mechanism for the Regioselective Polymerization of POPT by $FeCl_3$ via a Carbocation Mechanism



regularity obtained for POPT is due to the phenyl ring in the 3-position, which activates the thiophene ring more than an alkyl side chain in the same position. The activating effect of the phenyl ring is also seen in the cyclic voltammogram of the monomers. The onset of oxidation is 0.3 V lower for 3-(4-octylphenyl)thiophene than for 3-octylthiophene against Ag/AgCl in acetonitrile.

The earlier proposed mechanism for the polymerization of thiophene with $FeCl_3$ involves a radical reaction.[20] We believe the propagation occurs via a cation or a radical cation because the growing polymer chain cannot be neutral under the strong oxidizing condition. The high selectivity in the polymerization supports a mechanism via a cation. Therefore, we propose an alternative mechanism, as shown in Scheme 1. We believe that the initiation species is a thiophene radical cation. As soon as oligomers are formed, the propagation proceeds through a carbocation, as shown above.

The growing polymer chain is fully oxidized by $FeCl_3$, and positively charged bipolarons are formed. Polythiophene which is fully oxidized is known to contain mainly bipolarons.[21] The bipolarons in Scheme 1 are shown for convenience with two positive charges on adjacent thiophene rings, but the actual charges are probably more separated. The positively charged polymer chain then acts as an electrophile and reacts with the monomer in a normal electrophilic aromatic substitution reaction. The attack of the electrophile on the monomer is regioselective at the 2-position and then the two hydrogens at the newly formed carbon–carbon bond leave as protons. The new extended polymer chain can then be reoxidized. This simple mechanism is consistent with our observations of regioselective polymerization in the presence of both Fe^{3+} and Fe^{2+}.

Conclusions

We have shown that it is possible to polymerize 3-(4-octylphenyl)thiophene regioselectively with $FeCl_3$. The HT content was determined by ^1H NMR to be 94 ± 2%, and that is as regular as P3AT prepared by a Grignard polymerization reaction. The absorption maximum of thin films of POPT is red shifted 109 nm when the films are treated with chloroform vapor due to ordering of the polymer. Ordered thin films show a clear vibronic fine structure and an absorption maximum at 602 nm. Free standing films show a conductivity which is 100 times higher than for earlier prepared POPT. We believe that the propagation of the polymerization of POPT occurs via a cation mechanism but chain initiation starts by the formation of a radical cation.

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References and Notes

(1) Bredas, J. L.; Silbey, R. *Conjugated Polymers*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.
(2) (a) Xu, B.; Holdcroft, S. *Macromolecules* **1993**, *26*, 4457. (b) Bäuerle, P.; Götz, G.; Segelbacher, U.; Huttenlocher, D.; Mehring, M. *Synth. Met.* **1993**, *57*, 4768.
(3) Leclerc, M.; Dias, F. M.; Wegner, G. *Makromol. Chem.* **1989**, *190*, 3105.
(4) McCullough, R. D.; Lowe, D. R. *J. Chem. Soc., Chem. Commun.* **1992**, 70.
(5) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087.
(6) McCullough, R. D.; Lowe, D. R.; Jayaraman, M.; Ewbank, P. C.; Anderson, D. L. *Synth. Met.* **1993**, *55*, 1198.
(7) Chen, T.-A.; Rieke, R. D. *Synth. Met.* **1993**, *60*, 175.
(8) Sugimoto, R.; Takeda, S.; Gu, H. B.; Yoshino, K. *Chem. Exp.* **1986**, *1*, 635.
(9) (a) Pei, Q.; Järvinen, H.; Österholm, J. E.; Inganäs, O.; Laakso, J. *Macromolecules* **1992**, *25*, 4297. (b) Järvinen, H.; Laakso, J.; Taka, T.; Österholm, J. E.; Pei, Q.; Inganäs, O. *Synth. Met.* **1993**, *55*, 1260.
(10) Andersson, M. R.; Pei, Q.; Hjertberg, T.; Inganäs, O.; Wennerström, O.; Österholm, J. E. *Synth. Met.* **1993**, *55*, 1227.
(11) Sato, M.; Morii, H. *Macromolecules* **1991**, *24*, 1196.
(12) Robitaille, L.; Leclerc, M.; Callender, C. L. *Chem. Mater.* **1993**, *5*, 1755.
(13) Hagler, T. W.; Pakbaz, K.; Voss, K. F.; Heeger, A. J. *Phys. Rev. B* **1991**, *44*, 8652.
(14) Ahlskog, M.; Paloheimo, J.; Stubb, H.; Dyrklev, P.; Fahlman, M.; Inganäs, O.; Andersson, M. R. *J. Appl. Phys.* **1994**, *76*, 893.
(15) Berggren, M.; Gustafsson, G.; Inganäs, O.; Andersson, M. R.; Wennerström, O.; Hjertberg, T. *Appl. Phys. Lett.*, in press.
(16) Väkiparta, K.; Moulton, J.; Heeger, A. J.; Smith, P.; Isotalo, H.; Stubb, H.; Loponen, M. *Synth. Met.* **1991**, *41*, 903.
(17) Guay, J.; Diaz, A. F.; Bergon, J.-Y.; Leclerc, M. *J. Electroan. Chem. Interfacial Electrochem.* **1993**, *361*, 85.
(18) McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910.
(19) Goedel, W. A.; Somanathan, N. S.; Enkelmann, V.; Wegner, G. *Makromol. Chem.* **1992**, *193*, 1195.
(20) Niemi, V. M.; Knuuttila, P.; Österholm, J.-E.; Korvola, J. *Polymer* **1992**, *33*, 1559.
(21) Nowak, M. J.; Spiegel, D.; Hotta, S.; Heeger, A. J.; Pincus, P. A. *Synth. Met.* **1989**, *28*, 399.