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# Volatile Organic Compound Detection Using Nanostructured Copolymers

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## ABSTRACT

**Regioregular polythiophene-based conductive copolymers with highly crystalline nanostructures are shown to hold considerable promise as the active layer in volatile organic compound (VOC) chemresistor sensors. While the regioregular polythiophene polymer chain provides a charge conduction path, its chemical sensing selectivity and sensitivity can be altered either by incorporating a second polymer to form a block copolymer or by making a random copolymer of polythiophene with different alkyl side chains. The copolymers were exposed to a variety of VOC vapors, and the electrical conductivity of these copolymers increased or decreased depending upon the polymer composition and the specific analytes. Measurements were made at room temperature, and the responses were found to be fast and appeared to be completely reversible. Using various copolymers of polythiophene in a sensor array can provide much better discrimination to various analytes than existing solid state sensors. Our data strongly indicate that several sensing mechanisms are at play simultaneously, and we briefly discuss some of them.**

The demand for low-cost, low-power, and portable volatile organic compound (VOC) detection is increasing dramatically due to the need for environment monitoring, space exploration, homeland security, agriculture, and medical applications.[1−3] Sensing devices are needed for stand-alone operation as well as building blocks for sensor network systems. One of the most difficult challenges is to find specific materials that have both high sensitivity and good selectivity to the substances to be detected. An array of chemical sensors, where each array element is a different chemically selective material, can potentially provide a combinatorial response that can be used to not only detect but also identify specific analytes. While there has been a lot of success in sensor development for greenhouse gases ($CO_2$, $CH_4$, $N_2O$, NO, and CO), technology for detection of VOCs remains a weak point. Existing VOC-sensing materials includes semiconducting metal oxides,[3−6] conductive polymers (CPs),[7−12] and carbon black−polymer composites.[13,14] Metal oxide materials such as $SnO_2$ and ZnO, have been widely used in commercial chemical vapor sensors. A big drawback of these materials is limited selectivity to various VOCs and the required high operating temperature (200−500 °C).[3] Carbon black−polymer composites have also attracted a lot of research interest as a promising sensing material system. The different gas−solid partition coefficients of different polymers to various analytes are believed to generate swelling-induced conductivity changes between carbon black particles via a percolation concept.[13] Therefore, these materials generally show similar responses (increased resistance) to all tested analytes. Conductive polymers with alternating single and double carbon−carbon bonds have recently attracted extensive research interest for sensor applications.[15,16] Of the conductive polymers, regioregular poly(3-alkylthiophene)s are very promising due to their high electrical conductivity and their large number of possible chemical variants. Indeed, extended chemical selectivity may be achieved by molecular structure modification. Furthermore, their solution solubility enables the possibility of using ink-like printing as a batch process for electronic device fabrication.[17−19]

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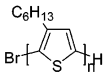
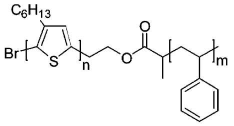
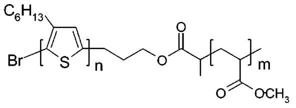
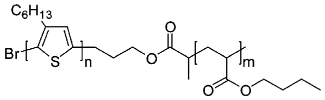
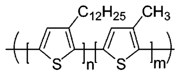
**Table 1.** Chemical Structures and Properties of Polythiophene-Based Copolymers: 1, Poly(3-hexylthiophene) (P3HT); 2, Poly(3-hexylthiophene)-*b*-polystyrene (PHT-*b*-PS); 3, Poly(3-hexylthiophene)-*b*-poly(methylacrylate) (PHT-*b*-PMA); 4, Poly(hexylthiophene)-*b*-poly(butylacrylate) (PHT-*b*-PBA); 5, Poly(3-dodecylthiophene-ran-3-methylthiophene) (PHT-*ran*-PMT)

| Polymer | Chemical structure | Composition[a] | Molecular Weight[b] | PDI[b] | Conductivity ($S\cdot cm^{-1}$)[c] |
|---|---|---|---|---|---|
| P3HT |  | 100 mol % PHT | 11600 | 1.17 | $3.0\times10^{-4}$ |
| PHT-*b*-PS |  | 65 mol % PHT | 16500 | 1.3 | $3.7\times10^{-6}$ |
| PHT-*b*-PMA |  | 80 mol % PHT | 14620 | 1.21 | $7.9\times10^{-5}$ |
| PHT-*b*-PBA |  | 82 mol % PHT | 16000 | 1.23 | $1.2\times10^{-5}$ |
| PDDT-*ran*-PMT |  | 50 mol % PDDT | 11950 | 1.2 | $4.5\times10^{-5}$ |

[a] Mole percentage of PHT composition was determined by $^1$H NMR spectroscopy. [b] Number average molecular weight and polydispersity were determined by gel permeation chromatography with polystyrene as standard. [c] The conductivity measurements were performed on ink jet printed thin films deposited on Au spiral electrodes with 0.5 V dc voltage applied. Upon the basis of polymer-to-solvent ratios of the jetted solution, the dried film thickness was estimated to be about 50 nm.

While it has been demonstrated that these materials have good sensitivity to polar VOCs, such as alcohols and acetone,[11,12] their rather poor response to nonpolar analytes has been viewed as a major drawback. In this report, we explored two ways to improve the sensor performance of regioregular polythiophene. The first approach is to add a second polymer at the end of the polythiophene chain to form a block copolymer. This second polymer interacts with the analytes in different ways, thus adding another dimensionality to the sensing response of the material. The second approach is to make a random copolymer of polythiophene with various side chains. Having a mixture of side chains along the polythiophene backbone, for example, may enable new polymer conformational changes induced by interactions between the analytes and side chains. We present new sensing results for conductive copolymers based on the polythiophene structure, and we show that the copolymer structures allow for good sensitivity and selectivity to both polar and nonpolar VOCs.

The copolymers of regioregular poly(3-hexylthiophene) (rr-P3HT) were prepared using procedures described elsewhere.[20−22] The chemical structures and properties of the polymers discussed in this work are shown in Table 1. The regioregular P3HT homopolymer is included in this study for comparison. PHT-*b*-PS, PHT-*b*-PMA, and PHT-*b*-PBA are block copolymers of P3HT with different second blocks: polystyrene, poly(methylacrylate), and poly(*n*-butylacrylate). PHT-*ran*-PMT is a copolymer of 3-methylthiophene and 3-dodecylhiophene, where the methyl and dodecyl side chains are randomly distributed throughout the polymer chain. Atomic force microscopy (AFM) has been used to characterize the morphology of these polymers when cast from a slowly evaporating solvent onto an oxidized silicon substrate. The AFM image for rr-P3HT (Figure 1a) shows the nanowire morphology. These nanowires were shown to be one polymer wide, stacked sheets of rr-P3HT with the polymer backbone aligned perpendicular to the nanowire axis.[18−19,23] These nanowires were also shown to be highly crystalline by X-ray crystallography.[23] Nanowire morphologies were also observed for the block copolymers, where the nanowire core consists of the rr-P3HT block and the darker (softer) surrounding region consists of the second amorphous block. While the images of the rougher surfaces of our more rapidly dried sensor polymers, prepared by ink jetting, are not so well defined, it is conjectured that ordering may exist at least over shorter distances. The presence of these crystalline nanostructures may help improve sensitivity and response time in our sensors.

To evaluate the chemical-sensing properties of these polymers, chemresistors with 200 $\mu$m diameter spiral gold electrodes were fabricated by standard photolithography processes. The overall length of the gold electrodes is approximately 4000 $\mu$m and the electrode spacing is 3 $\mu$m. The polymers were dissolved in trichlorobenzene at 5 mg/ml and deposited on the fabricated gold electrodes by an automated ink-jet system.[24] Advantages of using the high precision ink-jet printing system include precise control of localized spot positioning and good repeatability of the polymer film deposition process. The sensor repeatability from device to device prepared at the same time appears to be reasonably good. However, only very limited repeatability studies have been performed. The polymers were used in

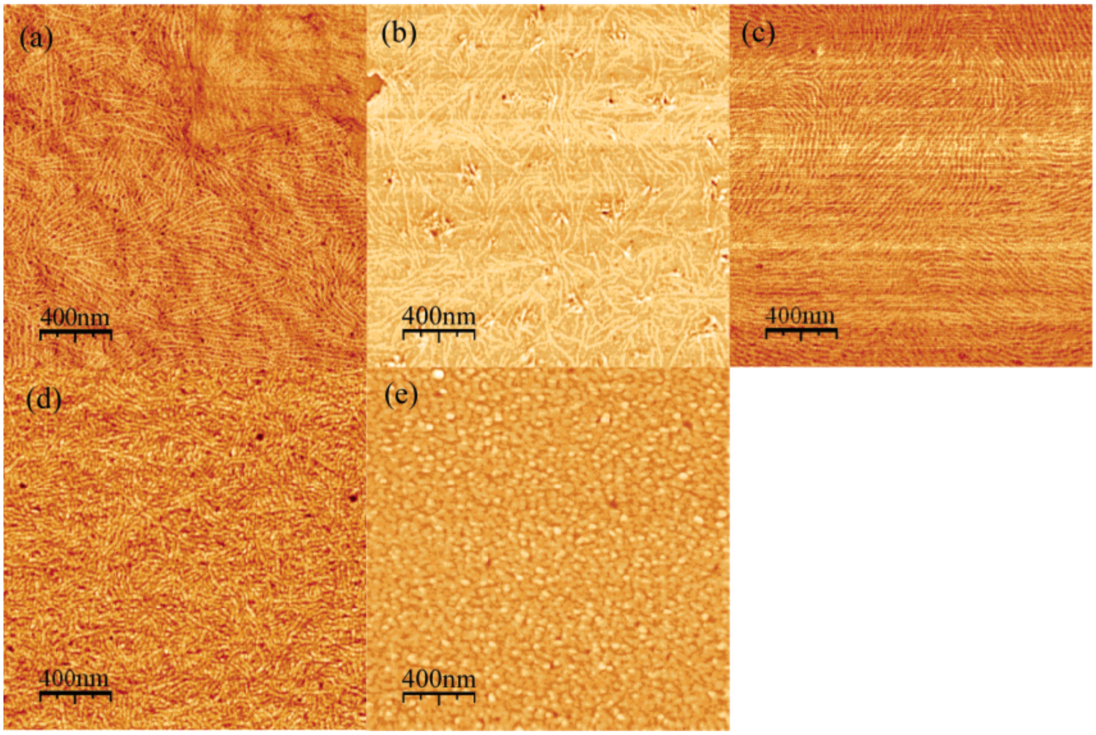


**Figure 1.** Tapping mode AFM phase images of polymer thin films: (a) poly(3-hexylthiophene); (b) poly(3-hexylthiophene)-*b*-polystyrene; (c) poly(hexylthiophene)-*b*-poly(butylacrylate); (d) poly(3-hexylthiophene)-*b*-poly(methylacrylate); (e) poly(3-dodecylthiophene-*ran*-3-methylthiophene).

their pristine stage without any intentional doping process and via FET device characterization the materials were found to be p-type semiconductors.[23] The conductivities of the ink-jetted polymer thin films are shown in Table 1. The sensors were then tested at room temperature for their chemical sensing responses to various VOC vapors using 1 L/min pure nitrogen as a carrier gas. Analyte concentrations ranging from 10 to 3500 ppm (depending on the vapor pressure of the compound) were introduced into the sensor chamber at 10 min intervals with 10 min exposure times. As examples of the exposure response, Figure 2 shows the normalized conductance changes of the polymers for exposure to acetone and toluene. For acetone exposure, P3HT and PHT-*b*-PBA showed a positive response, indicating that the conductivity increases. PHT-*b*-PMA and PDDT-*ran*-PMT showed a negative response, indicating that the conductivity decreases. For toluene exposure, P3HT, PHT-*b*-PBA, and PDDT-*ran*-PMT showed a negative response, while PHT-*b*-PS and PHT-*b*-PMA showed positive responses. The sensors demonstrated a fast, reasonably linear, response and recovered completely to their original baseline when the analyte vapor was turned off. Unlike most conductive polymer-based chemical sensors reported before,[7,12,13] the samples studied here show both negative and positive response patterns, which enables a much better VOC vapor discrimination. Table 2 lists the sensor array responses to 10 different VOC vapors: methanol, ethanol, 2-propanol, acetone, *n*-hexane, cyclohexane, methylene chloride, acetonitrile, toluene, and benzene. Different VOC vapors clearly have different response patterns.

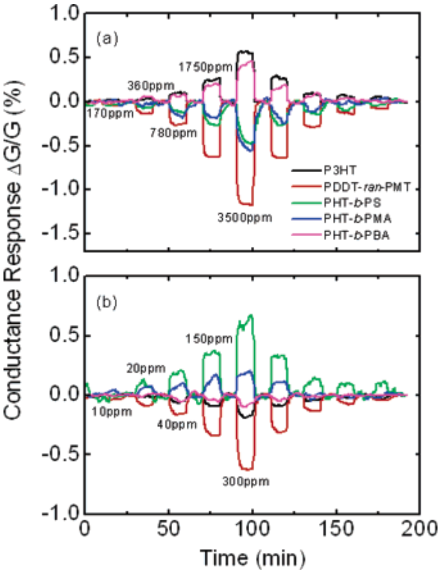


**Figure 2.** Chemresistor normalized conductivity responses to tested analytes as a function of time: (a) acetone; (b) toluene. 1 L/min $N_2$ was used as carrier gas. Analytes were introduced at 10 min intervals.

To better understand the sensor responses, conduction mechanisms of the polymers must be conceived, and then reviewed as to the role of the analytes, as mechanisms that would induce changes in the conductivity. In the room temperature regime, polaron hopping conduction is generally believed to be the charge transportation mechanism inside the primary, conjugated, polythiophene polymer.[25,26] Meanwhile, according to the morphology shown in Figure 1, there are two other physical regions, corresponding to conduction between polymer molecules: (1) conduction within a nanostructure, such as along the nanowire length and (2)

**Table 2.** Conductance Response of Copolymers to Various Chemical Vapors[a]

| chemical vapor | $\mu$ (D) | $\Delta G/G \times 10^{-6}$ P3HT | PDDT-*ran*-PMT | PHT-*b*-PS | PHT-*b*-PMA | PHT-*b*-PBA |
|---|---|---|---|---|---|---|
| methanol | 1.70 | 6.39 | −1.75 | 4.45 | −1.25 | 1.76 |
| ethanol | 1.69 | 10.5 | −8.05 | 13.84 | −3.72 | 4.53 |
| 2-propanol | 1.58 | 2.79 | −5.67 | 5.79 | 0.00 | 1.79 |
| acetone | 2.88 | 1.25 | −3.12 | −0.76 | −1.45 | 1.04 |
| methylene chloride | 1.60 | 9.25 | 6.64 | 4.65 | 2.36 | 8.27 |
| acetonitile | 3.93 | 2.48 | −2.86 | −3.67 | −4.02 | 2.69 |
| toluene | 0.38 | −1.43 | −19.6 | 20.5 | 14.6 | 0.00 |
| benzene | 0.00 | −1.11 | −8.42 | 5.91 | 2.45 | 0.00 |
| hexane | 0.00 | −1.77 | −3.86 | 0.00 | 0.00 | −1.28 |
| cylcohexane | 0.00 | −1.94 | −4.24 | −1.05 | 0.00 | −1.38 |

[a] Listed are measured values of $\Delta G/G$ normalized to 1 ppm of each vapor. $\mu$ is the dipole moment values of the chemical vapors.

conduction between nanostrucutres, such as, at the nanowire boundaries. Therefore, overall conductivity could be strongly influenced by the degree of crystalline order and by the nanostructure boundaries. Furthermore, characteristics such as the planarity (largely affected by the regioregularity) of the conjugate polymer chain, the length of the polymer chain, and the side chain composition will influence the overall conductivity.[18,22,27−32] For a material, for which the conductivity is limited by the boundary regions, the boundary material properties such as barrier potential, electronic state density, and physical length will be of significance.[33] Hence, for a copolymer, the secondary polymer chemistry plays an important role. For a chemresistor device, analyte sensitivity represents a modulation in one, or several, of these conduction mechanisms. Hence, we can see that there are multiple possible conduction limiting mechanisms, while physical insight about the actual sensing mechanisms is still very limited. In general, from our data we suspect that multiple mechanisms exist and that multiple mechanisms may occur simultaneously during an analyte exposure.

Below we attempt to discuss qualitatively different hypotheses to represent some sensing mechanisms resulting from our data. Since all the measurements are at room temperature and all sensor responses are fully recoverable, the possibility of chemical reactions between polymer and analyte molecules can be excluded. First, we notice that P3HT had positive responses to all polar analytes. The adsorption of polar analyte on a polymer molecule can generate a sufficient induced dipole moment to enhance the electrostatic interaction of the polymer molecules.[34] Thus, a plausible explanation for the conductivity increasing is that the induced dipole moment will reduce the average polymer molecule spacing distance, namely, increasing the density of states for interchain polaron hopping, resulting in a higher conductivity.[26] For PHT-*b*-PS, the responses to acetone and acetonitrile were negative, and for PHT-*b*-PMA, the responses to all polar analytes are negative except for methylene chloride. This illustrates that adding the second block introduced other mechanisms that override those of the homopolymer. For example, acetone is not a solvent for P3HT, but a solvent for PS and PMA. Hence, the conductivity decrease of PHT-*b*-PS and PHT-*b*-PMA to acetone vapor is most likely due to the swelling by absorption of acetone into the PS and PMA block. The decrease in conductivity for P3HT upon exposure to nonpolar analytes, hexane, cyclohexane, toluene, and benzene, is most likely due to the swelling effect. Perhaps the analyte molecules dissolve into the polymer film and enlarge the spacing between polymer molecules, resulting in a lower conductivity. Contrary to the P3HT behavior, we notice that exposure of PHT-*b*-PS and PHT-*b*-PMA by toluene and benzene caused a strong increase in conductivity. In these cases, toluene and benzene may interact more strongly with the PS and PMA block than with the P3HT block, but the mechanism for increased conductivity is unclear. Meanwhile, the effects of hexane and cyclohexane are minimal.

In the case of the random copolymer, PDDT-*ran*-PMT, the responses were negative for all the vapors except for methylene chloride. The presence of the shorter methyl side chains may introduce some space where the analytes can penetrate and cause a conformational change in the polymer backbone. Here, most of the analytes have negative responses, which imply that the polymer backbone twists out of conjugation with a torsion angle formed between monomer units, thus reducing electronic coupling between monomers and the overall conductivity.[32] However, we also notice, from Figure 1e, that this polymer film has more grain boundaries. This means that a grain boundary effect can also play a role to cause a conductivity decrease.[33] Although a conductivity decrease seems to be the dominant response of PDDT-*ran*-PMT, the positive response to methylene chloride further indicates that multiple mechanism occurs simultaneously upon analyte exposure. It is clear from these discussions that film morphology, and, hence, film preparation techniques, can play a very important role in sensitivity. For this reason, future sensing studies will involve variations in micro- and nanostructures.

In summary, we have demonstrated that copolymers of polythiophene are promising materials for use in VOC vapor sensors. The sensing results showed new response patterns, which can greatly enhance the discrimination of VOCs. Multiple sensing mechanisms involving various physical interactions between the polymers and analytes are most likely at play simultaneously, and further experiments are underway to better identify and understand those mechanisms. Hopefully this work and future studies will illuminate new design dimensions for conductive polymer based chemical-sensing materials.

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## References

(1) Ampuero, S.; Bosset, J. O. *Sens. Actuators, B* **2003**, *94*, 1−12.
(2) Snow, E. S.; Perkins, F. K.; Houser, E. J.; Badescu, S. C.; Reinecke, T. L. *Science* **2005**, *307*, 1942−1945.
(3) Srivastava, A. K. *Sens. Actuators, B* **2003**, *96*, 24−37.
(4) Tomchenko, A. A.; Harmer, G. P.; Marquis, B. T.; Allen, J. W. *Sens. Actuators, B* **2003**, *93*, 126−134.
(5) Afridi, M. Y.; Suehle, J. S.; Zaghloul, M. E.; Berning, D. W.; Hefner, A. R.; Cavicchi, R. E.; Semancik, S.; Montgomery, C. B.; Taylor, C. J. *IEEE Sens. J.* **2002**, *2*, 644−655.
(6) Pasini, P.; Powar, N.; Gutierrez-Osuna, R.; Daunert, S.; Roda, A. *Anal. Bioanal. Chem.* **2004**, *378*, 76−83.
(7) Hamilton, S.; Hepher, M. J.; Sommerville, J. *Sens. Actuators, B* **2005**, *107*, 424−432.
(8) Crone, B.; Dodabalapur, A.; Gelperin, A.; Torsi, L.; Katz, H. E.; Lovinger, A. J.; Bao, Z. *Appl. Phys. Lett.* **2001**, *78*, 2229−2231.
(9) Janata, J.; Josowicz, M. *Nat. Mater.* **2003**, *2*, 19−23.
(10) McCullough, R. D.; Sauvé, G.; Li, B.; Jeffries-EL, M.; Santhanam, S.; Schultz, L.; Zhang, R.; Iovu, M. C.; Cooper, J.; Sreedharan, P.; Revelli, J. C.; Kusne, A. G.; Kowalewski, T.; Snyder, J. L.; Weiss, L. E.; Lambeth, D. N.; Fedder, G. K. *Proc. SPIE* **2005**, *5940*, 28−34.
(11) Sakurai, Y.; Jung, H.-S.; Shimanouchi, T.; Inoguchi, T.; Morita, S.; Kuboi, R.; Natsukawa, K. *Sens. Actuators, B* **2002**, *83*, 270−275.
(12) Torsi, L.; Tafuri, A.; Cioffi, N.; Gallazzi, M. C.; Sassella, A.; Sabbatini, L.; Zambonin, P. G. *Sens. Actuators, B* **2003**, *93*, 257−262.
(13) Lonergan, M. C.; Severin, E. J.; Doleman, B. J.; Beaber, S. A.; Grubbs, R. H.; Lewis, N. S. *Chem. Mater.* **1996**, *8*, 2298−2312.
(14) Ha, S.-C.; Kim, Y. S.; Yang, Y.; Kim, Y. J.; Cho, S.-M.; Yang, H.; Kim, Y. T. *Sens. Actuators, B* **2005**, *105*, 549−555.
(15) Dai, L.; Soundarrajan, P.; Kim, T. *Pure Appl. Chem.* **2002**, *74*, 1753−1772.
(16) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537−2574.
(17) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93−116.
(18) Bao, Z.; Dodabalapur, A.; Lovinger, A. J. *Appl. Phys. Lett.* **1996**, *69*, 4108−4110.
(19) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741−1744.
(20) Iovu, M. C.; Jeffries-EL, M.; Sheina, E. E.; Cooper, J. R.; McCullough, R. D. *Polymer* **2005**, *46*, 8582−8586.
(21) Iovu, M. C.; Sheina, E. E.; Sauvé, G.; Jeffries-El, M.; Cooper, J. R.; McCullough, R. D. *Polym. Prepr.* **2004**, *45*, 278−279.
(22) McCullough, R. D.; Jayaraman, M. *J. Chem. Soc., Chem. Commun.* **1995**, *2*, 135−136.
(23) Zhang, R.; Li, B.; Iovu, M. C.; Jeffries-EL, M.; Sauvé, G.; Copper, J.; Jia, S.; Tristram-Nagle, S.; Smilgies, D. M.; Lambeth, D. N.; McCullough, R. D.; Kowalewski, T. *J. Am. Chem. Soc.* **2006**, *128*, 3480−3481.
(24) Weiss, L. E.; Schultz, L.; Miller, E. *Carnegie Mellon University Tech. Rep.* **2006**, *CMU-RI-TR-06-15*.
(25) Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 2339−2350.
(26) Johansson, E.; Larsson, S. *Synth. Met*. **2004**, *144*, 183−191.
(27) Sirringhaus, S.; Brown, P. J.; Friend, R. H.; Nieisen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwigand, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685−688.
(28) Babel, A.; Jenekhe, S. A. *Synth. Met.* **2005**, *148*, 169−173.
(29) Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J.; Fréchet, J. M. J.; Toney, M. F. *Macromolecules* **2005**, *38*, 3312−3319.
(30) Ewbank, P. C.; Loewe, R. S.; Zhai, L.; Reddinger, J.; Sauvé, G.; McCullough, R. D. *Tetrahedron* **2004**, *60*, 11269−11275.
(31) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608−11609.
(32) Grozema, F. C.; Duijnen, P. T. V.; Berlin, Y. A.; Ratner, M. A.; Siebbeles, L. D. A. *J. Phys. Chem. B* **2002**, *106*, 7791−7795.
(33) Someya, T.; Katz, H. E.; Gelperin, A.; Lovinger, A. J.; Dodabalapur, A. *Appl. Phys. Lett.* **2002**, *16*, 3079−3081.
(34) Hutchison, G. R.; Ratner, M. A.; Naaman, R.; Marks, T. J. *J. Phys. Chem. B* **2001**, *105*, 2881−2884.

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