Synthesis of Regioregular π-Conjugated Poly(thienyleneethynylene) with a Hindered Phenolic Substituent

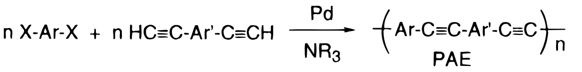
Hideki Hayashi and Takakazu Yamamoto*

Research Laboratory of Resources Utilization,
Tokyo Institute of Technology, 4259 Nagatsuta,
Midori-ku, Yokohama 226, Japan

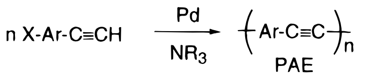
Received August 19, 1996
Revised Manuscript Received December 2, 1996

The preparation of regioregular π-conjugated polymers consisting of 3-substituted thiophene units has been a subject of recent interest, and the polymers have interesting electrical and optical properties.[1−4] Recently, Ni-promoted C−C coupling reactions[5] have been applied to the synthesis of regioregular poly(3-alkylthiophene-2,5-diyl)s (P3RTh) with a high (>98%) content of HT (head-to-tail) linkage.[1,2]

On the other hand, it has been reported that a Pd-catalyzed C−C coupling reaction between an acetylenic compound and aryl halide provides a useful route for preparation of poly(aryleneethynylene) (PAE) type polymers.[6−8]

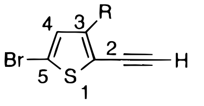


$$n\ \text{X-Ar-X} + n\ \text{HC}{\equiv}\text{C-Ar'-C}{\equiv}\text{CH} \xrightarrow[\text{NR}_3]{\text{Pd}} \underbrace{\left(\text{Ar-C}{\equiv}\text{C-Ar'-C}{\equiv}\text{C}\right)_n}_{\text{PAE}} \tag{1}$$



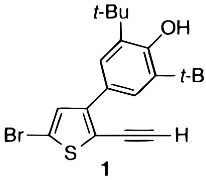
$$n\ \text{X-Ar-C}{\equiv}\text{CH} \xrightarrow[\text{NR}_3]{\text{Pd}} \underbrace{\left(\text{Ar-C}{\equiv}\text{C}\right)_n}_{\text{PAE}} \tag{2}$$

If one can obtain the following monomer, its polycondensation will give a new regioregular PAE type π-conjugated polymer with the 3RTh unit.



We have found that the above shown monomer can be prepared in a good yield from 3-substituted thiophene due to the difference in chemical reactivity between the 2- and 5-positions of 3-substituted thiophene, and the polycondensation actually gives the regioregular PAE type polymer. Tour and co-workers recently reported preparation of oligomeric model compounds for such a regioregular PAE type polymer.[9]

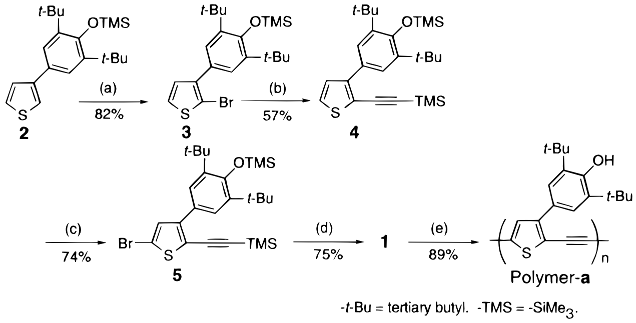
For the monomer, the following compound with a hindered phenolic substituent has been selected because of the interesting redox behavior of the hindered phenol, and here we report the preparation and properties of the polymer.



1

Monomer **1** is obtained starting from the corresponding 3-substituted thiophene and polymerized according to eq 2 (Scheme 1). Compounds **2** and **3** (solid) were prepared as previously reported.[10] Compounds **4**, **5**, and **1** are yellow liquids, and their ^{1}H-NMR data agree with their structures; the mass spectrum of **1** shows parent peaks at *m*/*e* 390 (from ^{79}Br species) and 392 (from ^{81}Br species) in almost equal intensity. Figure 1 exhibits the ^{1}H-NMR spectrum of polymer **a**, and comparison of the IR spectra of monomer **1** and polymer **a** is shown in Figure 2. As shown in these figures, signals originating from the C−Br and C≡CH groups of monomer **1** are not observable in the ^{1}H-NMR and IR spectra of polymer **a**. The ν(C≡C) absorption band of the C≡CH group is shifted to a higher frequency (Figure 2), where a ν(C≡C) absorption band of disubstituted acetylene appears.[11] The ^{1}H- and ^{13}C{^{1}H}-NMR spectra of polymer **a** agree with the molecular structure of polymer **a**.

Scheme 1. Synthesis of Polymer a[a]



[a] (a) NBS, room temperature. (b) TMSC≡CH, Pd(PPh$_3$)$_4$, CuI, NEt$_3$, 50 °C. (c) (i) *n*-BuLi, −70 °C. (ii) CF$_2$BrCF$_2$Br, room temperature. (d) KOH, room temperature. (e) Pd(PPh$_3$)$_4$, CuI, NEt$_3$, 60 °C.

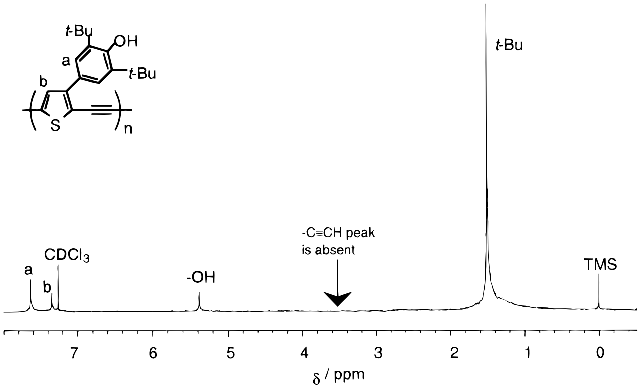


Figure 1. ^{1}H-NMR spectrum of polymer **a** in CDCl$_3$ at 20 °C.

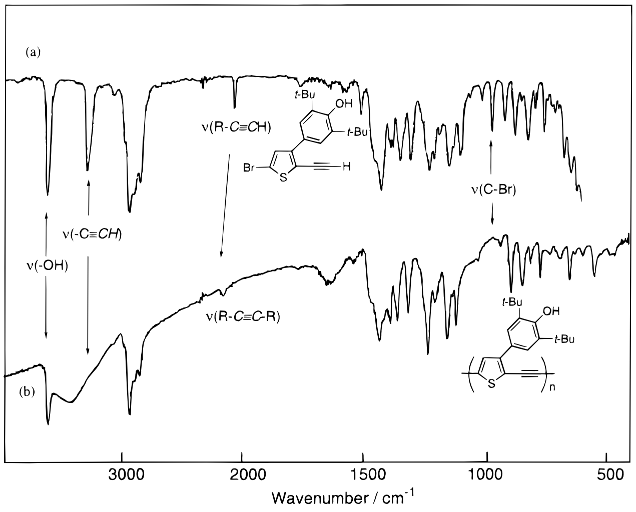


Figure 2. IR spectra of (a) monomer **1** (liquid, on a NaCl plate) and (b) polymer **a** (in a KBr disk).

Sharp signals in the ^{1}H- and ^{13}C{^{1}H}-NMR spectra clearly indicate that polymer **a** has the expected stereoregular structure. Polymer **a** has an [η] value of 0.15

S0024-9297(96)01246-6 CCC: $14.00

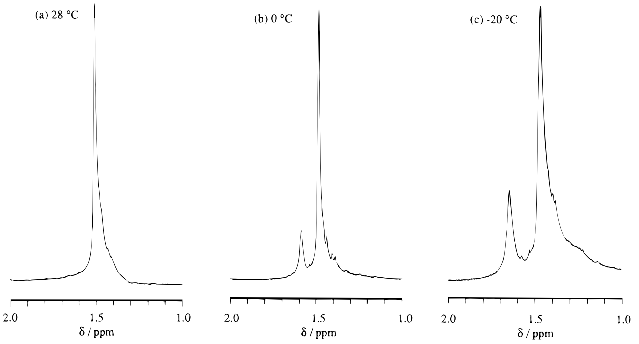
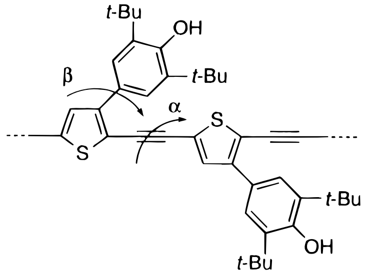


Figure 3. Variable-temperature ^{1}H-NMR spectra of polymer **a** in CD_2Cl_2 at (a) +28, (b) 0, and (b) −20 °C. The CH_3 signals of the *t*-Bu group are shown.

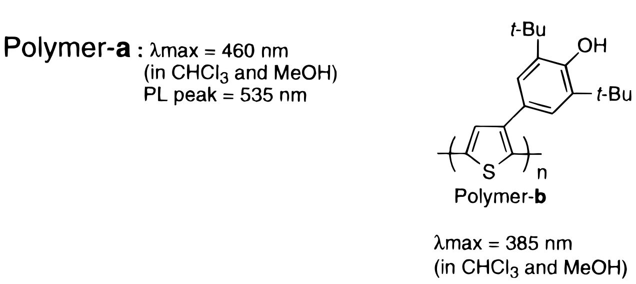
dL g^{-1} in $CHCl_3$ at 30 °C and an M_n value of 7700 as estimated from GPC (in $CHCl_3$, polystyrene standard). The relation between the obtained [η] and M_n values deviates somewhat from the viscosity equation[12] observed with poly(3-hexylthiophene-2,5-diyl) (P3HexTh).

One of the interesting findings about polymer **a** is that the CH_3 signal of the *t*-Bu group appears as a singlet both in the ^{1}H-NMR and in the $^{13}C\{^1H\}$-NMR spectra, which suggests free rotation of the hindered phenolic group on the NMR time scale. Lowering the temperature makes the rotation slower, thus giving rise to several ^{1}H-NMR peaks for the *t*-Bu protons at the low temperature as shown in Figure 3. The $^{13}C\{^1H\}$-NMR signals of the *t*-Bu group are broadened at −20 °C.

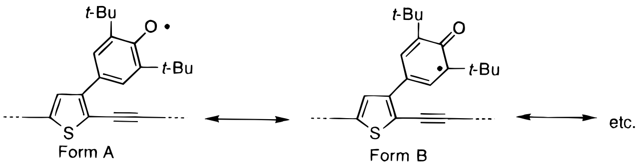
However, the complicated absorption pattern shown in Figures 3b and 3c indicates that not only the rotation of the hindered phenoxy group (β-rotation) but also a rotation around the polymer main chain (α-rotation) takes place at 20 °C and the rotations are frozen at the low temperature.



Polymer **a** is highly soluble in organic solvents such as $CHCl_3$ and benzene. The polymer exhibits a $\pi-\pi^*$ absorption peak at 460 nm in both $CHCl_3$ solution and cast film. The peak is located at a longer wavelength compared with that of polymer **b** shown below,[10] indicating that polymer **a** has a longer effective π-conjugation system due to negligible steric repulsion between the substituents in the neighboring units. The bulky substituents of the thiophene decrease the degree of the effective π-conjugation.[13]

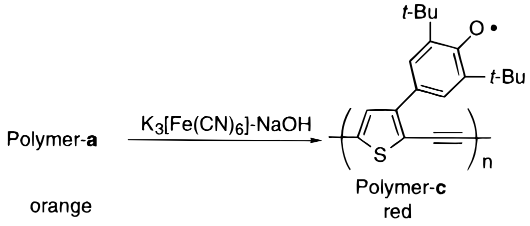


Scheme 2



Polymer **a** shows a photoluminescence (PL) peak at 535 nm, which agrees with the onset position of the $\pi-\pi^*$ absorption band.

Since the hindered phenolic group often generates a stable radical,[10,14] oxidation of polymer **a** is intriguing. It is known that a mixture of $K_3[Fe(CN)_6]$ and NaOH oxidizes such a hindered phenol to generate a stable radical,[15] and application of this oxidation method to polymer **a** gives a new polymer, polymer **c**.



The sharp ν(OH) absorption band of polymer **a** at 3630 cm^{-1} (Figure 1) completely disappears after the oxidation, and a new strong absorption band at 1730 cm^{-1} appears in the region of ν(C=O). The appearance of the new absorption band at 1730 cm^{-1} suggests contribution from the resonance forms shown in Scheme 2. Such resonance forms containing the C=O group have also been proposed for low-molecular-weight hindered phenoxides,[14] and in the present polymer, the main-chain π-conjugation system will also participate in the resonance. Due to stabilization of the C=O bond by contribution of the various resonance forms, the ν(C=O) band of polymer **c** appears at a higher wavenumber (1730 cm^{-1}) than those of 4-Ph-2,6-*t*-BuPhO$^\bullet$ (1650 cm^{-1}),[14] PbO_2-oxidized polymer **b** (1680 cm^{-1}),[10] and a previously reported polyacetylene with the same hindered phenoxy radical (1660 and 1610 cm^{-1}).[14c] Due to the stabilization discussed above, polymer **c** is inert, even to reduction with $N_2H_4 \cdot H_2O$ as proven by IR and UV−visible spectroscopy.

The ESR spectrum of polymer **a** exhibits only a weak signal at $g = 2.0068$. On the other hand, the oxidized polymer **c** gives rise to a strong and somewhat broad (peak width = ~40 G) symmetrical ESR signal at $g = 2.0079$ and with ΔH_{pp} of 5.0 G. The broad signal suggests extensive delocalization of the radical to be coupled with many H nuclei.

References and Notes

(1) (a) McCullough, R. D.; Tristran-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910. (b) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70. (c) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904.
(2) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.
(3) Anderson, M. R.; Selse, D.; Berggeren, M.; Järvinen, H.; Hiertberg, T.; Inganäs, O.; Wennersröm, O.; Österholm, J.-E. *Macromolecules* **1994**, *27*, 6503.
(4) Arroyo-Villian, M. I.; Diaz-Quijada, G. A.; Abdou, M. S. A.; Holdcroft, S. *Macromolecules* **1995**, *28*, 975.
(5) (a) Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1977**, 353. (b) Yamamoto, T.; Hayashi, Y.; Yamamoto, A. *Bull. Chem. Soc.*

Jpn. **1978**, *51*, 2091. (c) Sanechika, K.; Yamamoto, T.; Yamamoto, A. *J. Polym. Sci., Polym. Lett. Ed*. **1980**, *18*, 9. (d) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *Chem. Ind. (London)* **1982**, 301.

(6) (a) Yamamoto, T. *Prog. Polym. Sci*. **1992**, *17*, 1153; *J. Synth. Org. Chem. Jpn*. **1995**, *53*, 999. (b) Sanechika, K.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn*. **1984**, *57*, 752. (c) Sanechika, K.; Yamamoto, T.; Yamamoto, A. *Polym. Prepr. Jpn*. **1981**, *30*, 160. (d) Yamamoto, T.; Takagi, M.; Kizu, K.; Maruyama, T.; Kubota, K. *J. Chem. Soc., Chem. Commun*. **1993**, 797. (e) Yamamoto, T.; Yamada, W.; Takagi, M.; Kizu, K.; Maruyama, T.; Ooba, N.; Tomaru, S.; Kaino, T.; Kubota, K. *Macromolecules* **1994**, *27*, 6620.

(7) Trumbo, D. L.; Marvel, C. S. *J. Polym. Sci., Part A: Polym. Chem*. **1986**, *24*, 2311.

(8) Havens, S. J.; Hergenrother, P. M. *J. Polym. Sci., Polym. Lett. Ed*. **1985**, *23*, 587.

(9) (a) Tour, J. M. *Chem. Rev*. **1996**, *96*, 537. (b) Pearson, D. L.; Schumm, J. S.; Tour, J. M. *Macromolecules* **1994**, *27*, 2348.

(10) (a) Yamamoto, T.; Hayashi, H. *J. Polym. Sci., Part A: Polym. Chem*., in press. (b) Hayashi, H.; Kanbara, T.; Yamamoto, T. *Polym. Prepr. Jpn*. **1995**, *44*, 374.

(11) Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*; Wiley: New York, 1954; p 59.

(12) Yamamoto, T.; Oguro, D.; Kubota, K. *Macromolecules* **1996**, *29*, 1833.

(13) Goedel, W. A.; Somanathan, N. S.; Enkelmann, V.; Wegner, G. *Makromol. Chem*. **1992**, *193*, 1195.

(14) (a) Müller, E.; Schick, A.; Scheffer, K. *Chem. Ber*. **1959**, *92*, 474. (b) Mukai, K.; Inagaki, N. *Bull. Chem. Soc. Jpn*. **1980**, *53*, 2695. (c) Nishide, H.; Yoshioka, N.; Inagaki, K.; Tsuchida, E. *Macromolecules* **1988**, *21*, 3119.

(15) (a) Nishide, H.; Yoshioka, N.; Kaneko, T.; Tsuchida, E. *Macromolecules* **1990**, *23*, 4487. (b) Nishide, H.; Yoshioka, N.; Inagaki, K.; Kaku, T.; Tsuchida, E. *Macromolecules* **1992**, *25*, 569.

MA961246K