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Preparation of poly(3,3′-dialkynyl-2,2′-bithiophene-5,5′-diyl) with high coplanarity and effective π-conjugation system

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Abstract

New head-to-head type polythiophenes with acetylenic –C≡CR side groups, HH-P3(C≡CR)Th (R = n-$C_{10}H_{21}$, n-C_6H_{13}, n-C_4H_9), were prepared by palladium-catalyzed polycondensation of the corresponding dibromo-monomers by using $Me_3SnSnMe_3$ as the polycondensing agent. The single crystal structure of the monomer revealed high coplanarity of the bithiophene unit, and the derived polymer showed a UV–vis absorption peak at approximately 520 nm. The λ_{max} position was red-shifted from those of regioregular poly(3-alkylthiophene)s (385 and 430 nm for HH- and HT-type polymers, respectively). These data indicate that the newly synthesized polythiophene with the –C≡CR group has a highly coplanar structure with a large effective π-conjugation system.

Keywords: Polythiophene; Stacking; Coplanar structure

1. Introduction

Polythiophenes is one of the most widely studied π-conjugated polymers [1–4]. For polythiophenes with an alkyl substituent at the 3-position, synthesis of head-to-tail (HT) type [5,6] and head-to-head (HH) type [7] polymers has been carried out. The HT type poly(3-alkylthiophene-2,5-diyl)s, HT-P3RTh, assumes a well stacked solid structure and shows interesting electronic and optical properties [5,6,8]. To the contrary, HH-P3RTh does not assume such a stacked solid structure due to steric repulsion between the R group and the thiophene ring (Chart 1).

By the way, π-conjugated polymers with acetylenic –C≡CR groups are the subject of recent interest [9,10]. The CPK molecular model of the HH-type polymer with the acetylenic –C≡CR group, HH-P3(C≡CR)Th (cf.chart1), reveals the absence of steric repulsion between the –C(5)–C(6)– carbons and the thiophene ring and suggests the possibility that above shown HH-P3(C≡CR)Th assumes a coplanar structure and form a stacked assembly in the solid, in contrast to the case of HH-P3RTh. The self-assembling force may be even stronger than that of HT-P3RTh, because some steric repulsion seems to be present between the R group and the thiophene ring in the regioregular HT-P3RTh.

In this paper, we report that HH-P3(C≡CR)Th can be synthesized from the corresponding coplanar dibromo monomer by Pd-catalyzed polycondensation and that the obtained polymer actually shows a strong tendency to form self-assembly. Obtaining such polythiophenes with the –C≡CR side groups may expand the scope of π-conjugated polymers.

2. Experimental

2.1. Synthesis of the monomers **2a–2c**, 5,5′-dibromo-3,3′-dialkynyl-2,2′-bithiophenes

To a mixture of 3,3′-dibromo-2,2′-bithiophene [11] (13.0 g, 40.1 mmol), [$Pd(PPh_3)_4$] (4.64 g, 4.02 mmol), CuI (0.76 g, 3.99 mmol), toluene (200 cm^3), and diisopropylamine (200 cm^3) was added 1-dodecyne (16.7 g, 100 mmol), and the mixture was stirred for 24 h at 135 °C. After an aqueous solution of NH_4Cl was added, the solvents were removed and the product was extracted with chloroform (three times). The extract was washed with an aqueous solution of NH_4Cl and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on SiO_2 (eluent = 20:1 mixture of hexane and chloroform). Removal of eluent under vacuum gave a yellow solid of **1a** (15.9 g, 79.6%

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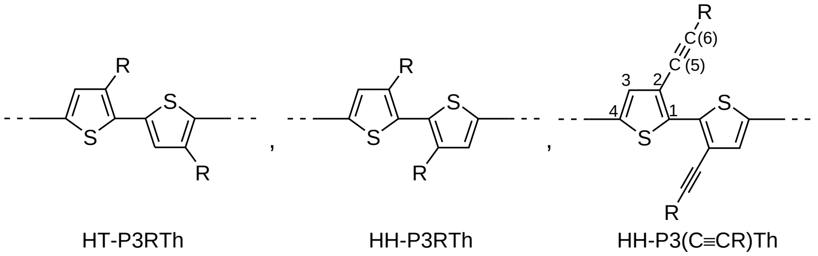


HT-P3RTh, HH-P3RTh, HH-P3(C≡CR)Th

Chart 1. Regioregular polythiophenes.

yield). ^{1}H NMR: (300 MHz, $CDCl_3$) δ: 7.01 (d, 2H, $J=5.1$ Hz), 7.14 (d, 2H, $J=5.1$ Hz), 2.48 (t, 4H, $J=7.1$ Hz), 1.69–1.60 (m, 4H), 1.51–1.27 (m, 28H), 0.88 (t, 6H, $J=6.7$ Hz). Anal. Calcd for $C_{32}H_{46}S_2$: C, 77.67%; H, 9.37%; S, 12.96%. Found: C, 77.88%; H, 9.44%; S, 12.65%.

An ether (50 cm^3) solution of **1a** (9.90 g, 20.0 mmol) was added to a hexane solution of butyllithium (80.0 mmol) at −40 °C. After the mixture was stirred for 4 h at r.t., an ether solution of CF_2BrCF_2Br (26.0 g, 100 mmol) was added at −40 °C. After stirring for 0.5 h, an aqueous solution of $Ns_2S_2O_3$ was added, and the products were extracted with ether (three times). The extract was washed with brine, and dried over $MgSO_4$. After removal of solvents, the crude product was purified with SiO_2 column chromatography (eluent = hexane). Removal of hexane under vacuum gave a yellow solid of **2a** (6.50 g, 49.8% yield). ^{1}H NMR: (300 MHz, $CDCl_3$) δ: 6.95 (s, 2H), 2.49 (t, 4H, $J=7.0$ Hz), 1.70–1.60 (m, 4H), 1.52–1.27 (m, 28H), 0.88 (t, 6H, $J=6.7$ Hz). Anal. Calcd for $C_{32}H_{44}Br_2S_2$: C, 58.89%; H, 6.80%; S, 9.83%; Br, 24.49%. Found: C, 58.66%; H, 6.73%; S, 9.57%; Br, 24.21%.

Monomers **2b** (yield = 69.7%) and **2c** (yield = 75.5%) were prepared analogously.

2b: ^{1}H NMR: (300 MHz, $CDCl_3$) δ: 6.95 (s, 2H), 2.50 (t, 4H, $J=7.0$ Hz), 1.70–1.60 (m, 4H), 1.53–1.26 (m, 12H), 0.90 (t, 6H, $J=6.9$ Hz). Anal. Calcd for $C_{24}H_{28}Br_2S_2$: C, 53.34%; H, 5.22%; S, 11.87%; Br, 29.57%. Found: C, 53.06%; H, 5.14%; S, 11.83%; Br, 29.49%.

2c: ^{1}H NMR: (300 MHz, $CDCl_3$) δ: 6.95 (s, 2H), 2.50 (t, 4H, $J=7.0$ Hz), 1.69–1.60 (m, 4H), 1.54–1.44 (m, 4H), 0.96 (t, 6H, $J=7.1$ Hz). Anal. Calcd for $C_{20}H_{20}Br_2S_2$: C, 49.60%; H, 4.16%; S, 13.24%; Br, 33.00%. Found: C, 49.32%; H, 4.14%; S, 13.04%; Br, 32.91%.

2.2. Synthesis of polymers 3a–3c

2a (0.653 g, 1.10 mmol), $Pd(PPh_3)_4$ (0.127 g, 0.11 mmol), CuI (0.013 g, 0.07 mmol), and $Me_3SnSnMe_3$ (0.360 g, 1.10 mmol) were added to a mixed solvent of dry THF (5 cm^3) and dry NMP (5 cm^3), and the mixture was stirred at 110 °C for 3 days. The reaction mixture was poured into an aqueous solution of KF and methanol. The precipitate was collected by filtration, washed with methanol twice, and dried under vacuum to obtain purplish-black polymer **3a** (98% yield). Polymerization at 95 °C for 46 h gave 97% yield.

Polymers **3b** (purplish-black powder; yield = 91% at 110 °C and 94% at 95 °C) and **3c** (brown powder) were prepared analogously. ^{1}H NMR spectra of **3a** and **3b** are disclosed in Fig. 2.

2.3. Measurements

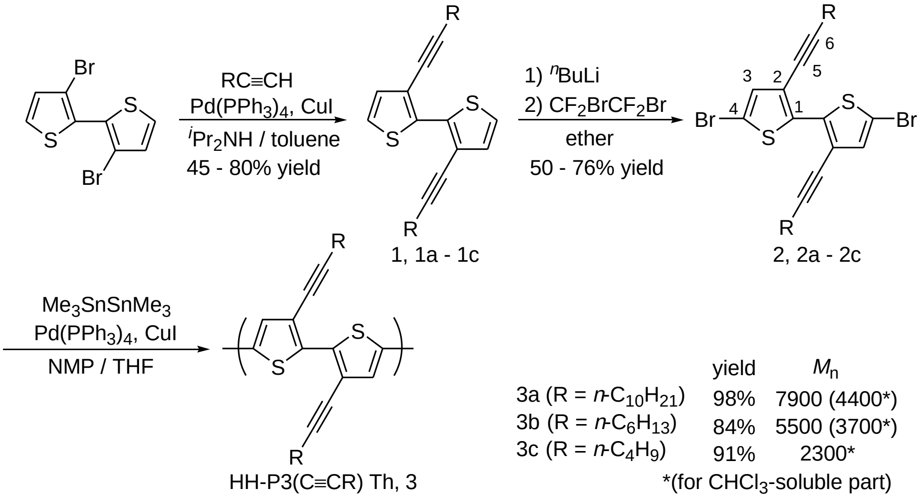
^{1}H NMR, CP-MAS ^{13}C NMR, and UV–vis spectra were obtained with JEOL Lambda 300, JEOL JNM-ECA 400, and Shimadzu UV-3100PC spectrometers, respectively. GPC analysis was carried out with Shimadzu LC-9A (eluent = chloroform at 40 °C) and Waters 150CV (eluent = 1,2-dichlorobenzene at 135 °C). Light scattering measurements of a chloroform solution of **3a** was carried out with Otsuka Electronics Photal DLS-7000 by using He–Ne laser (632.8 nm) .

3. Results and discussion

The monomer **2** was synthesized from 3,3′-dibromo-2,2′-bithiophene [11] according to the route shown in Scheme 1. Polymers **3a**–**3c** were prepared according to a Pd-catalyzed polycondensation using $Me_3SnSnMe_3$ as the condensing agent. Similar Pd-catalyzed polycondensation using $Bu_3SnSnBu_3$ (Bu = butyl) was reported for preparation of HH-P3RTh [12]; use of a diboronic compound was also reported [13]. However, our experiments indicated that $Me_3SnSnMe_3$ served as a better condensing agent than $Bu_3SnSnBu_3$.

Fig. 1 depicts the single crystal molecular structure of **2a**. **2a** forms a coplanar structure for the –C(6)≡C(5)–Th–Th–C(5′)≡C(6′)– unit, with a dihedral angle of 1° between the two thiophene rings. The structural data of **2a** reveals the absence of the steric repulsion between the –C≡CR group and the thiophene ring, and support the notion that HH-P3(C≡CR)Th **3** can form a coplanar structure. To the contrary, single crystal structures of alkylated oligothiophene usually show some torsion (e.g. by about 30°) of the thiophene ring [14,15]. The monomer **2a** was stable at room temperature under air, and obtaining of **2** and application of the Pd-catalyzed polycondensation using $Me_3SnSnMe_3$ made synthesis of the polymer **3** possible. Dehalogenative polycondensation of **2** with a zerovalent nickel complex [4] was not successful for the preparation of **3**.

The obtained polymers were partly (about 30% for **3a**) soluble in $CHCl_3$ and $CHCl_2CHCl_2$ at room temperature. The solubility was lower than that of HT-P3RTh and HH-P3RTh, suggesting a higher tendency to form the stacked assembly. The chloroform soluble part of **3a** and **3b** gave the



Scheme 1. Synthetic route of polymer **3**.

number average molecular weights (M_ns) of 4400 and 3700, respectively, in the GPC analysis using chloroform (vs. polystyrene standards). **3a** was almost completely soluble in 1, 2-dichlorobenzene at 120 °C and the M_n value of **3a** was determined as 7900 by using 1,2-dichlorobenzene at the elevated temperature. Most part of **3b** was soluble in 1,2-dichlorobenzene at 120 °C and the GPC analysis showed an M_n value of 5500. **3c** had lower solubility than **3a** and **3b**, presumably due to weaker solubilizing effect of the short side chain.

Fig. 2 exhibits ^1H NMR spectra of **3a** and **3b** in $CDCl_2CDCl_2$ at room temperature. The thiophene-H peak appears at δ 7.03 (for both **3a** and **3b**), and aliphatic-H peaks, including C(6)–CH_2– peak at δ 2.49 (for both **3a** and **3b**), are observed at normal positions. Additional aromatic peaks are observed in a range from δ 7.25–7.66. The solution is considered to contain self-assembled colloidal particles of the polymer as discussed below, and the additional aromatic signals are tentatively assigned to aromatic-H in the colloidal particles. Since the polymer contains only a small amount of Br (0% for **3a** and 0.5% for **3b**) and the ^1H NMR signal of the $–SiMe_3$ group (δ 0.28) is unobservable in the ^1H NMR spectrum, the polymer is considered to have mainly a -H terminal group. The -H terminal group may be formed from polymer-Pd terminal propagating species during the work-up. It is reported that π-conjugated polymers prepared by organometallic polycondensation sometimes have such a -H terminal group as the main terminal group, and the terminal -H can be detected in the ^1H NMR spectrum [16]. However, for **3a** and **3b**, it was difficult to assign the terminal-H signal in the ^1H NMR signal. Fig. 3 shows CP-MAS solid ^{13}C NMR spectra of **3a** and **3b**. The –C≡C– signals of **3b** are observed as a sharp signal, however, those of **3a** are broadened suggesting the presence of plural phases such as an amorphous phase and stacked crystalline phase.

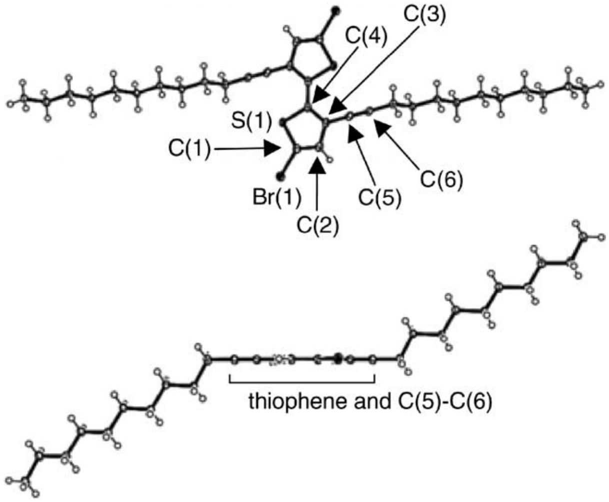


Fig. 1. Single crystal molecular structure of **2a**. Selected bond length (Å) and angle (°): S(1)–C(1) 1.721(3), C(1)–C(2) 1.357(3), C(2)–C(3) 1.422(3), C(3)–(C4) 1.392(3), S(1)–C(4) 1.740(2), C(3)–C(5) 1.436(3), C(5)–C(6) 1.188(3), C(1)–S(1)–C(4) 91.4(1).

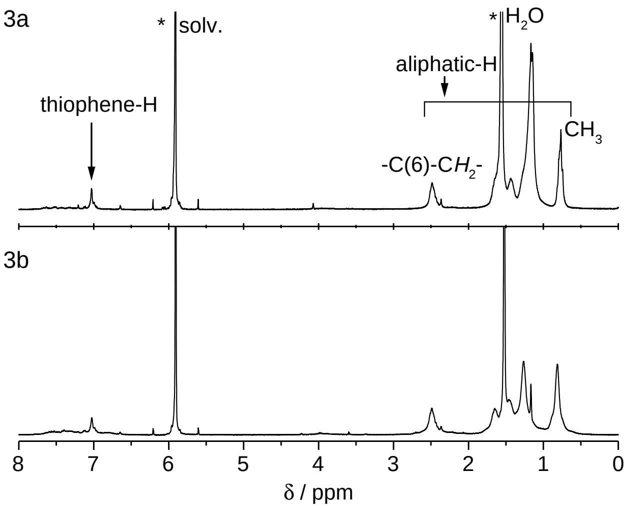


Fig. 2. ^1H NMR spectra of **3a** and **3b** in $CDCl_2CDCl_2$ at room temperature. The peaks with the (*) mark are due to the solvent impurity and H_2O. The H_2O peak disappears after addition of D_2O.

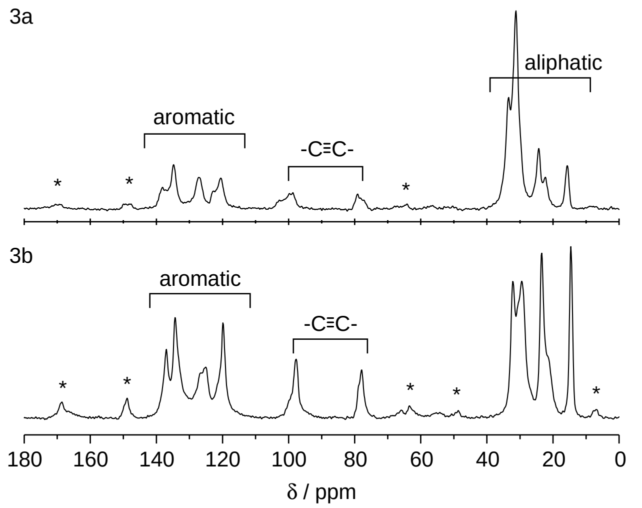


Fig. 3. CP-MAS solid ^{13}C NMR spectra of **3a** and **3b**. The peak with the (*) mark is assigned to spinning side band. The sp^2 carbons usually give a stronger side band because of the magnetic anisotropy around the carbon.

Fig. 4 shows UV–vis spectra of **3a** in chloroform and in a cast film. **3a** in chloroform gives a UV–vis peak at 520 nm which locates at a longer wavelength by 90 nm and by 130 nm than the UV–vis peaks of HT-P3RTh ($\lambda_{max}=430$ nm [5,6]) and HH-P3RTh ($\lambda_{max}=390$ nm [7]), respectively. This shift to a longer wavelength is considered to originate from the higher coplanarity of HH-P3(C≡CR)Th and/or partial expansion of the π-conjugation to the side chain. In the film, the UV–vis peak is shifted to a longer wavelength, and a new peak is observed at 546 nm, with shoulder peaks characteristics of the UV–vis spectrum of π-conjugated polymers in the solid [1–8]. Such a red shift in film suggests that **3a** molecules have an intermolecular electronic interaction in the stacked solid. The shoulder peak at 548 nm, observed with the solution of **3a** (cf. Fig. 4(a)), suggests the presence of some aggregated particles in the solution. However, estimation of the aggregation by a light scattering method using He–Ne laser (632.8 nm) [8] was not possible because of absorption of the laser at 632.8 nm by the solution (cf. Fig. 4) and photoluminescent (emission peak = 583 nm with a quantum yield of 14%) properties of the polymer in the chloroform solution. The excitation spectrum for photoluminescence exhibits a peak at 518 nm for **3a**, agreeing with the UV–vis data. Powder XRD patterns of **3a** and **3b** exhibited in Fig. 5 show distinct peaks, supporting formation of an ordered structure in the solid. Similar XRD patterns have been reported for HT-P3RTh [5,6,8]. The d_1 (24.3 and 15.1 Å for **3a** and **3b**, respectively) and d_2 (3.8 Å) distances shown in Fig. 5 seem to be assignable to a distance between the polythiophene main chains separated by the –C≡CR side chains and a face-to-face stacking distance of layered polymer molecules, respectively, similar to the case of HT-P3RTh [5,6,8]. The peak at approximately $d = 4.5$ Å is assigned to a side-to-side distance between loosely packed alkyl chains [17]. As described above, the polymer was photoluminescent in the solution, however, the polymer did not show light emission in the solid (spincoat film), probably due to the presence of quenching process(es) according to π-stacking of the polymer molecules in the solid.

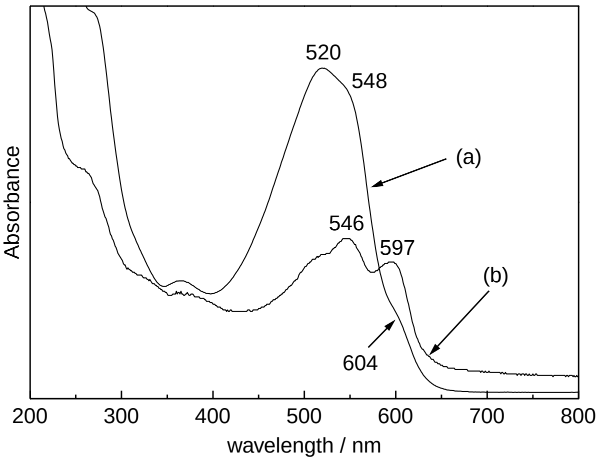


Fig. 4. UV–vis spectra of (a) a chloroform solution and (b) film of **3a**.

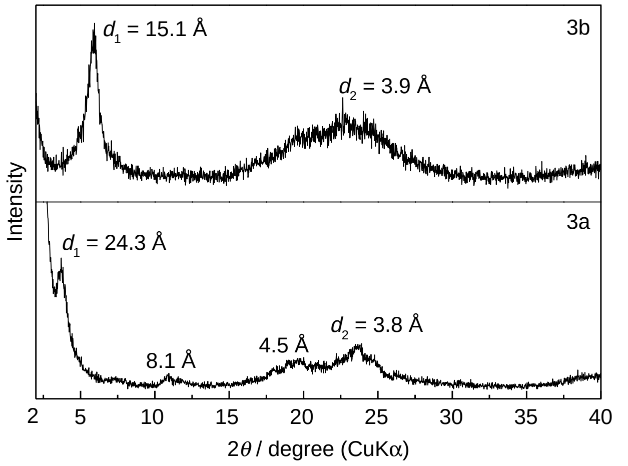


Fig. 5. Powder XRD patterns of **3a** and **3b**. The peak of **3a** at 8.1 Å is assigned to the third order (300) peak of the d_1 peak.

As described above, the new –C≡CR substituted polythiophenes were obtained for the first time by using $Me_3SnSnMe_3$ as the condensing agent. The polymer is considered to have a coplanar structure and a highly π-conjugated electronic system. Obtaining such new polythiophenes is expected to expand the scope of π-conjugated polymers.

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References

[1] Nolwa HS. Handbook of organic conductive molecules and polymers. Chichester: Wiley; 1997.

[2] Skotheim TA, Elsenbaumer RL, Reynolds JR. Handbook of conducting polymers. 2nd ed. New York: Wiley; 1977.

[3] Fichou D. Handbook of oligo- and polythiophenes. Weinheim: Wiley-VCH; 1999.
[4] Yamamoto T. Synlett 2003;425.
[5] McCullough RD, Tristram-Nagle S, Williams SP, Lowe RD, Jayaraman M. J Am Chem Soc 1993;115:4910.
[6] Chen TA, Wu X, Rieke RD. J Am Chem Soc 1995;117:233.
[7] Maior RMS, Hinkelmann K, Eckert H, Wudl F. Macromolecules 1990;23:1268.
[8] Yamamoto T, Komarudin D, Arai M, Lee BL, Suganuma H, Asakawa N, et al. J Am Chem Soc 1998;120:2047.
[9] (a) Hayashi H, Yamamoto T. Kobunshi Ronbunsyu 2001;58:221.
(b) Hayashi H, Yamamoto T. Chem Abstr 2001;135:153–78.
[10] Yamamoto T, Mahmut A, Abe M, Kuroda S, Imase T, Sasaki S. J Polym Sci, Part B: Polym Phys 2005;43:2219.
[11] (a) Khor E, Ng SC, Li HC, Chai S. Heterocycles 1991;32:1805.
(b) Yu WL, Meng H, Pei J, Huang W, Li Y, Heeger AJ. Macromolecules 1998;31:4838.
[12] Xu J, Ng SC, Chan HSO. Tetrahedron Lett 2001;42:5327.
[13] Izumi A, Nomura R, Masuda T. Macromolecules 2000;33:8918.
[14] Graf DD, Duan RG, Campbell JP, Miller LL, Mann KR. J Am Chem Soc 1997;119:5888.
[15] Barbarella G, Zambianchi M, Antolini L, Ostoja P, Maccagnani P, Bongini A, et al. J Am Chem Soc 1999;121:8920.
[16] Yamamoto T, Saitoh Y, Anzai K, Fukumoto H, Yasuda T, Fujiwara Y, et al. Macromolecues 2003;36:6722.
[17] (a) Jordan Jr EF, Feldeisen DW, Wrigley AN. J Polym Sci, Part A-1 1971;9:1835.
(b) Swan PR. J Polym Sci 1962;56:403.