ELSEVIER

Polymer 43 (2002) 665–669

polymer

www.elsevier.com/locate/polymer

Poly(phenylacetylene) with bulky chiral germyl groups: synthesis and effects of measuring solvents and temperature on chiroptical properties

Giseop Kwak, Toshio Masuda*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

Received 27 September 2001; received in revised form 3 October 2001; accepted 3 October 2001

Abstract

(+)-*p*-[{Methyl(1-naphthyl)phenyl}germyl]phenylacetylene, an acetylene with a bulky chiral germyl group, was polymerized with $[(nbd)RhCl]_2$–Et_3N to give a high-molecular-weight polymer in good yield. The CD spectrum of the polymer exhibited very large molar ellipticities $[\theta]$ in the UV region in non-aromatic solvents (e.g. THF and $CHCl_3$). In contrast, the CD signals of the polymer in aromatic solvents (e.g. toluene, tetralin, and benzene) became appreciably smaller: $[\theta]_{max} = 6.4 \times 10^4$ (330 nm) and $-4.7 \times 10^{4\circ}$ $cm^2\ dmol^{-1}$ (370 nm) in $CHCl_3$; $[\theta]_{max} = 1.1 \times 10^4$ (330 nm) and $-0.7 \times 10^{4\circ}$ $cm^2\ dmol^{-1}$ (370 nm) in toluene. The $[\theta]_{max}$ values of the polymer in aromatic solvents increased when the solutions were heated, which is attributed to decreased π–π interaction between the solvents and side groups. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(phenylacetylene); Chiral germyl group; Chiroptical property

1. Introduction

The π–π interaction between aromatic molecules helps to control molecular recognition and self-assembly phenomena. In the π-conjugated polymers containing aromatic rings in the main chain (e.g. poly(thiophene)s [1], poly(phenylenevinylene)s [1,2], and poly(phenyleneethynylene)s [3–6]), interchain π–π stacking induces the formation of aggregates in poor solvents, solvent/non-solvent mixtures, and the solid state. Their optical and chiroptical properties such as absorption, fluorescence, and circular dichroism (CD) effect remarkably change upon the formation of aggregates.

Some polyacetylenes with chiral subsutituents form helical conformations with an excess of one-handed screw sense in the main chain. Recently, we have synthesized helical poly(phenylacetylene) (Chart 1, poly(MeNpPhSi*PA)) containing chiral silicons in which the chirality is induced by three aromatic rings (i.e. a naphthyl, a phenyl, and the phenylene group bonded to the main chain) and a methyl group [7]. This polymer shows very large molar ellipticities, and its CD effects in toluene hardly change even at high temperature [8]. Germanium (Ge) belongs to group 14 along with carbon and silicon (Si) in the periodic table. The properties of Ge resemble those of Si, but the former possesses a larger relative electron density and a larger covalent radius than the latter. Thus, it is interesting to investigate chiroptical properties of chiral Ge-containing helical polyacetylene (Chart 1, poly(MeNpPhGe*PA)) in comparison with the corresponding chiral Si-containing one.

In the present study, we investigated the synthesis of chiral Ge-containing polyacetylene [poly(MeNpPhGe*PA)] for the first time and, further, the effects of solvent and temperature on both CD effect and UV absorption in solution. Eventually, we found that this polymer shows larger CD effects in non-aromatic solvents than in aromatic solvents, and that the CD effects in aromatic solvents increase with increasing temperature.

2. Experimental

2.1. Monomer synthesis (Scheme 1, synthesis of (+)-p-[{methyl (1-naphthyl)phenyl}germyl]phenylacetylene)

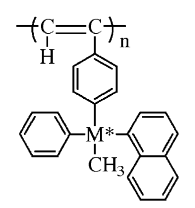
(−)-Methyl(1-naphthyl)phenylmenthoxygermanium (**1**). This compound was prepared according to the literature, using tetraphenylgermanium as a starting material [9]. Its optical purity was >99% de (by ^{1}H NMR), $[\alpha]_D = -49.8°$ (c 10 g dl^{-1}, in cyclohexane).

(+)-p-[Methyl(1-naphthyl)phenylgermyl]bromobenzene (**2**). A 100 ml round-bottomed flask was equipped with a

---

* Corresponding author. Tel.: +81-75-753-5613; fax: +81-75-753-5908.
E-mail address: masuda@adv.polym.kyoto-u.ac.jp (T. Masuda).

PII: S0032-3861(01)00659-0



M = Ge: poly(MeNpPhGe*PA)
M = Si: poly(MeNpPhSi*PA)

Chart 1. Structures of chiral germyl- and silyl-containing poly(phenylacetylene)s.

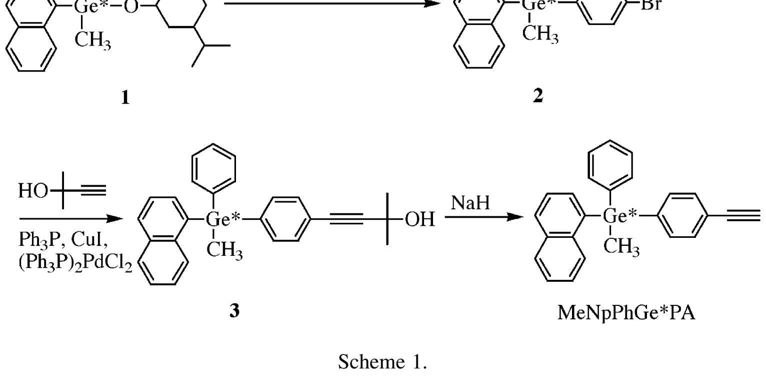
three-way stopcock, a dropping funnel, and a magnetic stirring bar. After the flask was flushed with nitrogen, *p*-dibromobenzene (2.62 g, 11.0 mmol) and diethyl ether (40 ml) were placed in the flask at 0°C. At the same temperature, a hexane solution of *n*-butyllithium (7.2 ml, 1.5 M, 11.0 mmol) was added dropwise, and the reaction mixture was stirred for 2 h. A solution of compound **1** (3.0 g, 6.7 mmol) in diethyl ether (10 ml) was added dropwise, and stirring was continued for 24 h. After removal of insoluble salts by filtration, the product was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate. Diethyl ether was evaporated, and the crude product was purified by flash column chromatography (Nakarai Tesque, silica gel 60; eluent, hexane/benzene 5:1) to give the desired product (yield 2.4 g, 80%) as a colorless solid. $[\alpha]_{\mathrm{D}} = 2.03^{\circ}$ (c 16 g dl^{-1}, in cyclohexane), ^{1}H NMR (CDCl$_3$): δ 7.91–7.29 (16H, aromatic) and 1.02 (3H) ppm.

(+)-4-p-[{Methyl(1-naphthyl)phenyl}germyl]phenyl-2-methyl-3-butyn-2-ol (**3**). A 100 ml round-bottomed flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar, and flushed with dry nitrogen. Triethylamine (30 ml), (Ph$_3$P)$_2$PdCl$_2$ (10 mg, 14 μmol), CuI (15.4 mg, 81 μmol), PPh$_3$ (14.2 mg, 54 μmol), 2-methyl-3-butyn-2-ol (0.6 ml, 6.0 mmol) and compound **2** (2.3 g, 5.3 mmol) were placed in the flask, and the mixture was stirred for 3 h at 80°C. After the completion of reaction had been confirmed by thin layer chromatography (TLC), triethylamine was evaporated. Diethyl ether (ca. 200 ml) was added, and insoluble salts were removed by filtration. The solution was washed with 2N hydrochloric acid and then with water. The organic phase was dried over anhydrous sodium sulfate, and diethyl ether was evaporated. The crude product was purified by flash column chromatography (eluent, hexane/ethyl acetate 5:1) to give the desired product (yield 1.7 g, 72%) as a pale yellow liquid. $[\alpha]_{\mathrm{D}} = 2.40^{\circ}$ (c 16 g dl^{-1}, in cyclohexane), ^{1}H NMR (CDCl$_3$): δ 7.94–7.30 (16H, aromatic), 1.99 (1H), 1.62 (6H), and 1.02 (3H) ppm.

(+)-p-[{Methyl(1-naphthyl)phenyl}germyl]phenylacetylene (MeNpPhGe*PA). A 50 ml round-bottomed flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar and flushed with dry nitrogen. Toluene (30 ml), NaH (11 mg, 0.46 mmol), and compound **3** (1.6 g, 3.7 mmol) were placed in the flask, and the mixture was stirred for 3 h at 80°C. After the completion of reaction had been confirmed by TLC, insoluble salts were removed by filtration, and toluene was evaporated. The crude product was purified by flash column chromatography (eluent, hexane/benzene 10:1) to give the desired product (yield 0.8 g, 75%) as a white solid. Mp 60–62°C, $[\alpha]_{\mathrm{D}} = 4.00^{\circ}$ (c 4.0 g dl^{-1}, in cyclohexane), IR (KBr): 3280, 1506, 1430, 1380, 1258, 1143, 1100, 977, 824, 796, 785, 731, 713, 700, 661 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.92–7.20 (16H, aromatic), 3.10 (1H), and 1.05 (3H) ppm. ^{13}C NMR (CDCl$_3$): δ 137.0, 136.9, 136.6, 135.9, 135.2, 135.0, 133.2, 131.4, 130.7, 130.4, 129.4, 128.8, 128.1, 127.8, 125.5, 125.3, 124.9, 122.8, 83.9, 77.9, −2.6 ppm. The attempt to determine the optical purity of this compound by HPLC and ^{1}H NMR using NMR shift reagent was unsuccessful.

2.2. Polymerization with Rh, Mo and W catalysts

Polymerizations were carried out under dry nitrogen. A detailed procedure of the polymerization has been described elsewhere [8,10]. Polymers were isolated by precipitation into a large amount of methanol, and polymer yields were determined by gravimetry.



Scheme 1.

Table 1
Polymerization of MeNpPhGe*PA

No.	Catalyst	Temperature (°C)	Polymer		
			Yield (%)	10^{-3} M_w (M_w/M_n)[a]	$[\alpha]_D$[b] (°)
1[c]	$[(nbd)RhCl]_2$–Et_3N	25	90	2100 (2.7)	−148
2[d]	WCl_6–Et_3SiH	30	52	62 (3.6)	−30
3[d]	WCl_6–Et_3SiH	80	85	720 (5.1)	−19
4[e]	$MoCl_5$–Et_3SiH	30	37	180 (4.6)	−29
5[e]	$MoCl_5$–Et_3SiH	80	52	48 (2.4)	−20

[a] Determined by GPC.
[b] In chloroform, $c = 0.11$ gdl^{-1}.
[c] Polymerized with $[(nbd)RhCl]_2$–Et_3N in toluene for 1 h; $[M]_0 = 0.50$ M, [cat] = 1.0 mM, [cocat] = 2.0 mM.
[d] Polymerized with WCl_6–Et_3SiH in toluene for 3 h; $[M]_0 = 1.0$ M, [cat] = 10 mM, [cocat] = 10 mM.
[e] Polymerized with $MoCl_5$–Et_3SiH in toluene for 3 h; $[M]_0 = 1.0$ M, [cat] = 10 mM, [cocat] = 10 mM.

2.3. Measurements

The weight- and number-average molecular weights (M_w and M_n, respectively) of polymers were determined by gel permeation chromatography (GPC); eluent $CHCl_3$, Shodex K-805, K-806, and K-807 polystyrene gel columns (Showa Denco, Japan), polystyrene calibration. ^{1}H NMR spectra were measured in $CDCl_3$ and toluene-d_8 solution at 25°C on a JEOL EX-400 spectrometer. The optical purities of monomer were examined by HPLC equipped with an optically active stationary phase (cellulose carbamates, Daicel Chem. Ind., CHIRALCEL OD) and ^{1}H NMR spectroscopy using NMR shift reagent [europium tris(heptafluorobutanoylpivaloylmethanate) (Eu-FOD)]. IR and UV–visible spectra were measured on Shimadzu FTIR-8100 and Shimadzu UV-2200 spectrophotometers (KBr pellet and $CHCl_3$ solution), respectively. CD spectra and specific rotations were recorded with Jasco J600 (a quartz cell, thickness 1 cm) and Jasco DIP-1000 spectropolarimeters, respectively.

3. Results and discussion

3.1. Polymerization

Table 1 shows the results for the polymerization of MeNpPhGe*PA with several transition-metal catalysts. The polymerization with $[(nbd)RhCl]_2$–Et_3N provided a polymer having very high molecular weight (M_w) over 2×10^6 in high yield up to 90%. The polymerizations with WCl_6–Et_3SiH and $MoCl_5$–Et_3SiH also yielded polymers in good yields of ca. 30–85%. The M_w values of the polymers were ca. 720×10^3 and 48×10^3 at 80°C, respectively, and lower than that with $[(nbd)RhCl]_2$–Et_3N.

3.2. Structure, solubility, and thermal properties of polymer

General properties of poly(MeNpPhGe*PA) were examined using the Rh-based sample (Table 1, No 1). The IR spectrum of the present polymer exhibited no absorption around 3200 cm^{-1} ($\nu_{H-C\equiv}$) that was seen in the monomer. Anal. poly(MeNpPhGe*PA) Calcd for $(C_{25}H_{20}Ge)_n$: C, 76.40; H, 5.09. Found: C, 76.47; H, 5.03.

The present polymer showed excellent solubility to various organic solvents such as $CHCl_3$, THF, benzene, toluene, tetralin, cyclohexane, and *o*-dichlorobenzene, but was insoluble in hexane, anisole, DMF, decalin, and alcohols such as methanol, ethanol, and 2-propanol. No difference of solubility between poly(MeNpPhGe*PA) and poly(MeNpPhSi*PA) was found.

The thermal stability of the present polymer was examined by the thermogravimetric analysis (TGA) in air (Fig. 1). The weight loss began at ca. 300°C, which is similar to that of poly(MeNpPhSi*PA), and higher than the temperature (ca. 200°C) for poly(phenylacetylene), and its weight residue was more in quantity than that of poly(phenylacetylene) at any temperature. At 700°C, the weight residue of the present polymer was about 19% which is about the same as that of poly(MeNpPhSi*PA). Thus, the present polymer was fairly thermally stable in air at high temperature.

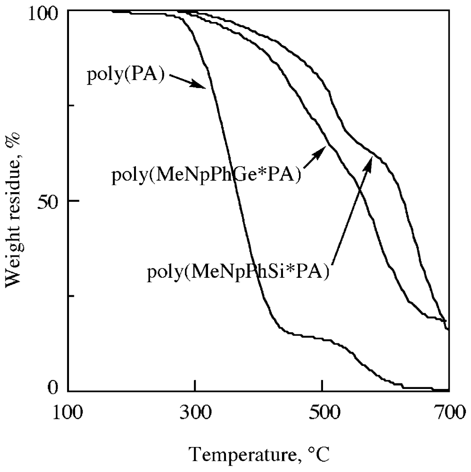


Fig. 1. TGA curves of poly(MeNpPhGe*PA) (sample from Table 1, run 1), poly(MeNpPhSi*PA), and poly(phenylacetylene) [poly(PA)] (heating rate 10°C min^{-1}, in air).

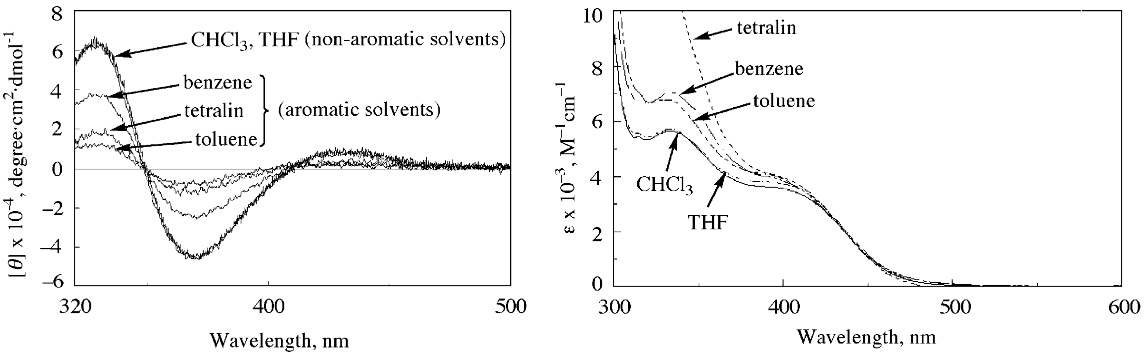


Fig. 2. CD and UV–visible spectra of poly(MeNpPhGe*PA) in various solvents (25°C, 5.0×10^{-5} mol l^{-1}).

3.3. Chiroptical properties

In general, Rh catalysts give stereoregular poly(phenylacetylene) [11], which is advantageous to induce helical conformation of one-handed screw sense in the presence of chiral substituents. Quite interestingly, the CD spectrum of the Rh-based poly(MeNpPhGe*PA) exhibited very large molar ellipticities $[\theta]$ in the UV region in $CHCl_3$; $[\theta]_{max} = 6.4 \times 10^{4°}$ cm^2 $dmol^{-1}$ at 330 nm and -4.7×10^4 at 370 nm (Fig. 2). The optical rotation ($[\alpha]_D$) of the Rh-based poly(MeNpPhGe*PA) in chloroform was −148°, which is similar to that (−150°) of poly(MeNpPhSi*PA) (see Table 1). On the other hand, the W- and Mo-based poly(MeNpPhGe*-PA)s (Table 1, Nos. 2–5) showed much smaller $[\alpha]_D$ values and no CD signals.

3.4. Solvent effect on chiroptical properties

Fig. 2 shows the effect of measuring solvents on chiroptical properties of poly(MeNpPhGe*PA). Poly(MeNpPhGe*PA) displayed very large CD signals in chloroform and THF. In contrast, the CD signals of poly(MeNpPhGe*PA) in aromatic solvents (e.g. toluene, tetralin, and benzene) became appreciably smaller. For instance, the values of $[\theta]_{max}$ in toluene were 1.1×10^4 and $-0.7 \times 10^{4°}$ cm^2 $dmol^{-1}$ at 330 and 370 nm, respectively, which were about one-sixth of those in the non-aromatic solvents. Generally, π-conjugated polymers show hypochromic effects upon the formation of aggregates [1–6]. In the present polymer, the molar absorptivities (ε_{max}) around 330 nm in chloroform and THF were about 5600 $M^{-1}cm^{-1}$, which were smaller than those (>7000 $M^{-1}cm^{-1}$) in aromatic solvents. These results suggest that the present polymer forms aggregates more readily in non-aromatic solvents than in aromatic solvents. In other words, it can be said that aromatic solvents interact with aromatic side groups of the present polymer to prevent interchain π–π interaction.

Unfortunately, no information was available regarding aggregation because the resolution of the ^1H and ^{13}C NMR spectra of the present polymer was very poor owing to high molecular weight and high viscosity. However, the ^1H NMR spectrum of the monomer showed obviously different chemical shifts between $CDCl_3$ and toluene-d_8 solutions: Two singlet signals due to the methyl and acetylenic protons of the monomer showed upfield shifts (0.89 and 2.69 ppm, respectively) in toluene-d_8, as compared to those in $CDCl_3$ solution (1.05 and 3.10 ppm, respectively). The signals due to aromatic (one naphthyl and two phenyl) protons of the monomer in toluene-d_8 were more complicated than those in $CDCl_3$ solution. Thus, these spectral data support the idea that the aromatic solvents interact with the aromatic side groups of the present polymer to interrupt the aggregation of polymer molecules.

3.5. Effect of temperature on chiroptical properties

Fig. 3 shows the effect of temperature on chiroptical properties of poly(MeNpPhGe*PA) in aromatic solvents. In tetralin, the values of $[\theta]_{max}$ of the present polymer increased with increasing temperature. The values at 90°C were 3.7×10^4 and $-3.4 \times 10^{4°}$ cm^2 $dmol^{-1}$ at 330 and 370 nm, respectively, which were about twice of those at 25°C. The magnitude of the values no more changed above 90°C. It has been reported that conventional helical polyacetylenes have short persistence lengths of helical domain and that their helical conformation is thermally rather unstable, so that their CD effects readily decrease when they are heated in solution [12,13]. As shown in Fig. 3, however, the present polymer in aromatic solvents showed very unique thermal behavior unlike the conventional polymers. Furthermore, the variation of the CD effects with temperature was reversible. This suggests that the π–π interaction between aromatic solvents and aromatic side groups in the polymer solution at low temperature is large enough to prevent the interchain π–π interaction, whereas the interaction decreases with increasing temperature, so that the interchain π–π interaction partially resumes, resulting in the formation of aggregates. This consideration is supported by the following UV spectral results (Fig. 3(b)); i.e. the band at 380 nm decreases with increasing temperature, a new band around 460 nm, which is assignable to the aggregate band, appears with increasing temperature, and an isosbestic point is seen at 425 nm.

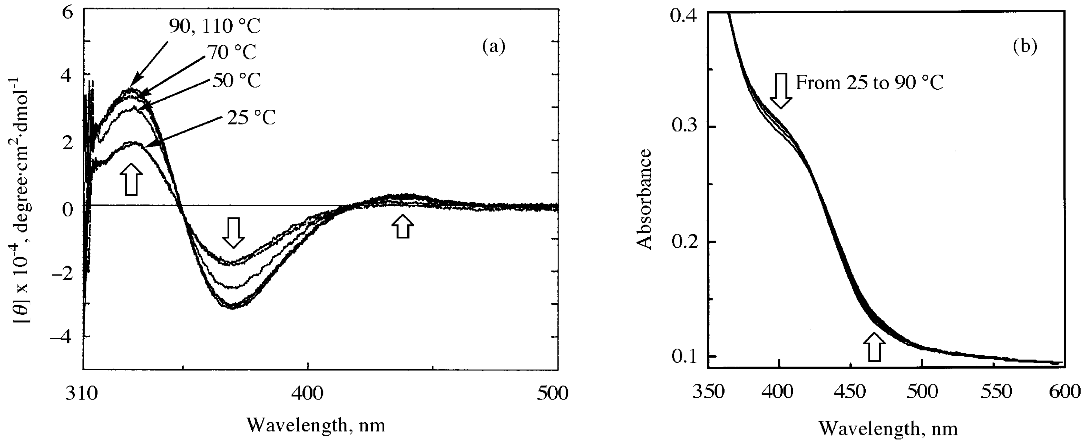


Fig. 3. Variation of (a) CD and (b) UV–visible spectra of poly(MeNpPhGe*PA) with temperature (in tetralin, 5.0×10^{-5} mol l^{-1}).

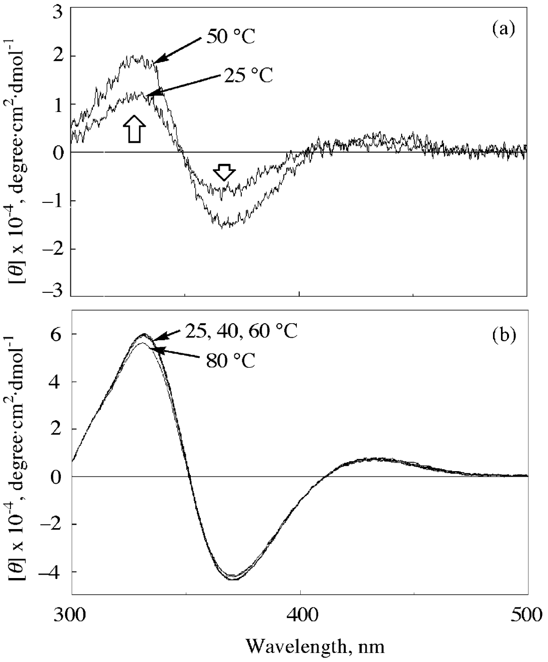


Fig. 4. Variation of the CD spectra of: (a) poly(MeNpPhGe*PA) and (b) poly(MeNpPhGe*PA) with temperature (in toluene, 5.0×10^{-5} mol l^{-1}).

Like the case of tetralin solution, the CD effect of the present polymer in toluene increased with increasing temperature (Fig. 4(a)). In contrast, the CD effect of the corresponding chiral silicon-containing polymer in toluene hardly changes in the temperature range 25–80°C (Fig. 4(b)). It is not clear at present why only the present polymer shows the temperature dependence of CD effect.

Acknowledgements

The authors thank Professor S. Kimura, Professor S. Ito, and Associate Professor M. Suginome for the permission of the use of a CD spectropolarimeter and a UV spectrophotometer. This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Culture, and Sports, Japan. The authors are also grateful to Dr R. Nomura and Dr H. Ohkita for technical assistance.

References

[1] Yue S, Berry GC, McCullough RD. Macromolecules 1996;29:933.
[2] Langeveld-voss BMW, Peeters E, Janssen RAJ, Meijer EW. Synth Met 1997;84:611.
[3] Fiesel R, Scherf U. Macromol Rapid Commun 1998;19:427.
[4] Halkyard CE, Rampey ME, Kloppenburg L, Studer-Martinez SL, Bunz UHF. Macromolecules 1998;31:8655.
[5] Fiesel R, Halkyard CE, Rampey ME, Kloppenburg L, Studer-Martinez SL, Scherf U, Bunz UHF. Macromol Rapid Commun 1999;20:107.
[6] Miteva T, Palmer L, Kloppenburg L, Neher D, Bunz UHF. Macromolecules 2000;33:652.
[7] Kwak G, Masuda T. Macromolecules 2000;33:6633.
[8] Kwak G, Masuda T. J Polym Sci Part A: Polym Chem 2001;39:71.
[9] Brook AG, Peddle GJD. J Am Chem Soc 1963;85:1869.
[10] Masuda T, Hamano T, Tsuchihara K, Higashimura T. Macromolecules 1990;23:1374.
[11] Tabata M, Inaba Y, Yokota K, Nozaki Y. J Macromol Sci Pure Appl Chem 1994;A31:465.
[12] Aoki T, Kokai M, Shinohara K, Oikawa E. Chem Lett 1993:2009.
[13] Ciardelli V, Lanzillo S, Pieroni O. Macromolecules 1974;7:174.