Notes

A Liquid Crystalline Polyketone Prepared from Allene Having an Azobenzene Substituent and Carbon Monoxide

Yasumasa Takenaka, Kohtaro Osakada,* Makoto Nakano, and Tomiki Ikeda

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Received June 18, 2002
Revised Manuscript Received December 4, 2002

Introduction

Progress for two or three decades in Pd complex-promoted alternating copolymerization of alkenes with carbon monoxide has enabled many polyketones to be synthesized with regulated structures and molecular weights.[1] Introduction of functional side chains would add new properties to the polymers, but this has attracted much less attention than studies of the polymerization reaction and structure of the products. Very recently, Nozaki,[2] Rieger,[3] and their respective co-workers reported that the Pd-catalyzed copolymerization of alkenes containing substituents composed of mesogen and spacer groups produced several new thermotropic liquid crystalline polyketones.

In our recent study of metal-complex-catalyzed polymerization,[4,5] we found that a Rh complex initiated the living copolymerization of arylallenes with carbon monoxide, and we obtained several polyketones with the unique enone structure shown in Chart 1 of the Supporting Information.

Since the C═C double bonds of the repeat unit are fixed in a *Z* configuration, all of the side chains of the polymer are oriented in the same direction along the polymer chain. The regulated molecular structure of the polyketones and the dependence of their glass transitions (30−120 °C) on the side chains[6] prompted us to investigate the preparation and anisotropic properties of polyketones with an azobenzene mesogen[7] and spacer in the side chain. In this paper, we report the copolymerization of an allene containing azobenzene-terminated long alkyl substituents with carbon monoxide and the physical properties of the product.

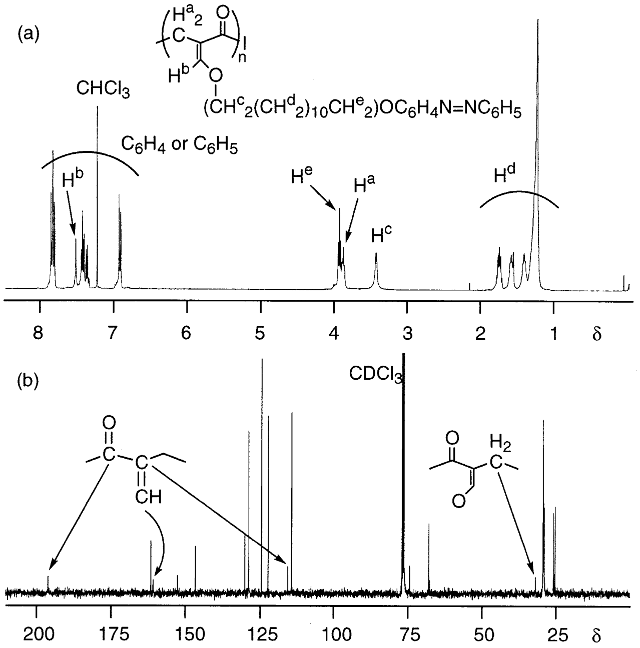
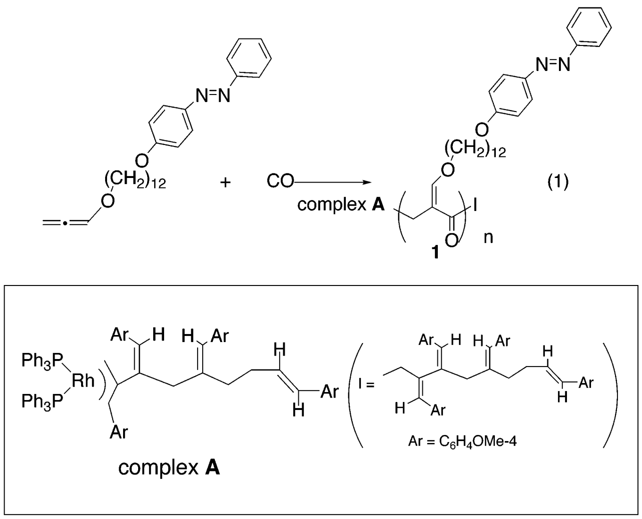


Figure 1. (a) ^{1}H and (b) ^{13}C{^{1}H} NMR spectra of polymer **1** in CDCl$_3$.

Scheme 1



Results and Discussion

The reaction of 4-{12-(allenyloxy)dodecyloxy}azobenzene with carbon monoxide (1 atm) in the presence of a catalytic amount of π-allylrhodium complex (**A**) proceeds smoothly at room temperature to produce the alternating copolymer **1** with 78−82% yield (Scheme 1). The reaction is completed within 21 h and proceeds faster than the recently reported copolymerization of a monoalkylallene with a shorter substituent, (3-phenylpropyl)allene, with carbon monoxide giving the corresponding polyketone.[8] The alkyl substituent bonded to the allene monomer enhances the growth of the polymer, similar to other monomers with bulky substituents.[8] The monomer with 12 methylene groups between the azobenzene group and allene group was used in this study because it is long enough as the spacer and because of the facility of the preparation of the monomer. The structure of **1** was confirmed by the ^{1}H and ^{13}C{^{1}H} NMR spectra shown in Figure 1. The ^{1}H NMR signals of the CH$_2$ hydrogens of the polymer chain and the vinylidene hydrogen are observed at δ 3.91 and 7.55,

10.1021/ma020958+ CCC: $25.00

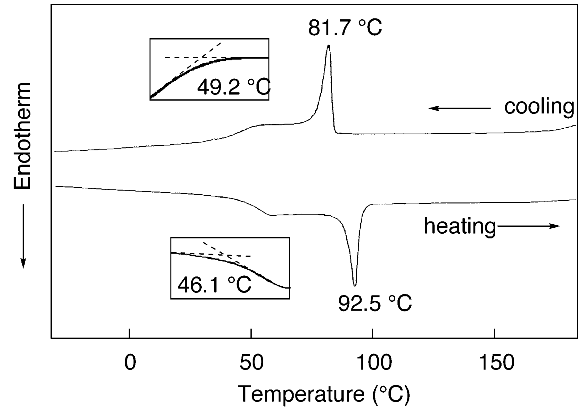


Figure 2. DSC traces of **1** (second scan). Expanded traces around the T_g are shown in the inset. Heating and cooling rate, 10 °C min^{-1}.

respectively. The spectrum also contains the signals of the side chain including OCH_2 (δ 3.96 and 3.55), CH_2 (δ 1.8−1.2), and phenyl (δ 7.87, 7.84, 7.46, 7.40, and 6.94) hydrogens. The $^{13}C\{^1H\}$ NMR spectrum exhibits the signals of the main chain carbons at reasonable positions as suggested in Figure 1b. These NMR data indicate that the polymer forms via alternating insertion of the allene monomer and carbon monoxide into the growing polymer end.

The presence of an absorption band at 348 nm in the electronic spectrum is assigned to the $\pi-\pi^*$ transition of the azobenzene groups. Irradiation at 350 nm causes isomerization of the trans structure of the polymer to the cis structrue that shows the $n-\pi^*$ transition at 448 nm. Conversion of this photoisomerization seems to be high because the $\pi-\pi^*$ absorption of the trans isomer decreases almost completely by the reaction. Thermal isomerization of the cis polymer to trans isomer shows the growth of the peak at 348 nm, which obeys first-order kinetics in the range 40−70 °C. The kinetic parameters, $E_a = 94$ kJ mol^{-1}, $\Delta H° = 93$ kJ mol^{-1}, and $\Delta S° = -34$ J mol^{-1} deg^{-1}, are similar to the isomerization of the monomer, $E_a = 87$ kJ mol^{-1}, $\Delta H° = 84$ kJ mol^{-1}, and $\Delta S° = -59$ J mol^{-1} deg^{-1}.

The molecular weights of **1** are influenced by the molar ratio of the allene monomer to the Rh complex; the reactions with 100:1 and 50:1 molar ratios give products with $M_n = 35\,000$ (GPC vs polystyrene standards, $M_w/M_n = 1.12$) and with $M_n = 20\,000$ ($M_w/M_n = 1.10$), respectively. An increase in the molecular weight of the polymer by increasing the monomer/initiator ratio as well as the narrow polydispersity of the product suggests the polymerization is living.

The DSC trace of polymer **1** in Figure 2 shows reversible and reproducible glass transitions at 49.2 °C (cooling) and 46.1 °C (heating) and isotropization at 81.7 °C (cooling) and 92.5 °C (heating). The exotherm at 81.7 °C on cooling has a change of enthalpy of $\Delta H = 1.63$ kJ mol^{-1}. The textures observed during the cooling of the polymer from the isotropic state (120 °C) are shown in Figure 3 and indicate that a smectic liquid crystalline phase forms between T_g and T_i. Figure 4 shows the X-ray diffraction pattern of a cast film heated at 80 °C and cooled quickly to room temperature prior to the measurement. Two sharp diffractions at $2\theta = 5.2°$ (Cu Kα, $d = 17.0$ Å) and 7.9° ($d = 11.2$ Å) are assigned to the ordered arrangement of the mesogen groups. The distance of the former diffraction is close to half (= sin 60°) the length of the side chain (approximately 30 Å). At present, we tentatively assign the state of polymer **1** between T_g and T_i as a smectic C phase based on the above results.

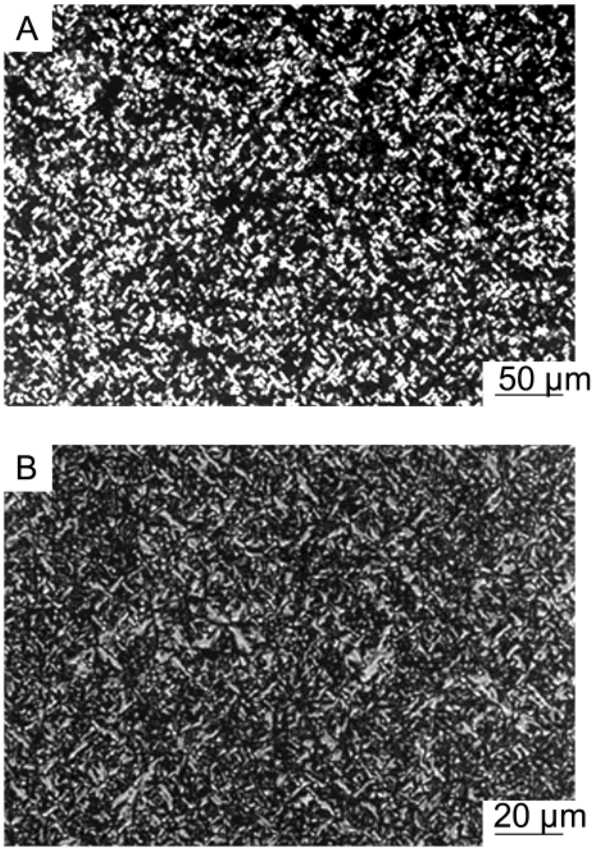


Figure 3. Texture of the liquid crystalline state of **1**. (A) and (B) show the textures of the same samples with different scales. The measurement was made of the sample which was cooled at 3 °C min^{-1} from 120 °C.

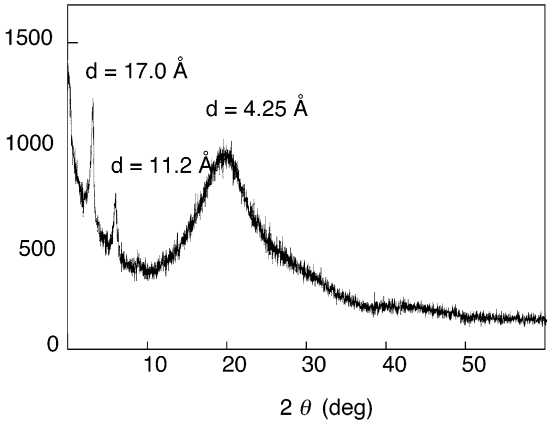


Figure 4. X-ray diffraction pattern of **1** at room temperature. The polymer was made as a cast film on a glass plate and measured after heating at 80 °C and quickly cooling to room temperature.

This study describes a new liquid crystalline polymer composed of regulated enone structure of polymer chain and side chains containing an azobenzene mesogen.

Experimental Section

General, Measurement, and Materials. Manipulations of Rh complex and polymerization were carried out under nitrogen or argon using standard Schlenk techniques. THF was dried over Na/K and distilled prior to use. NMR spectra (^1H and ^{13}C) were recorded on Varian MERCURY 300 or JEOL

EX-400 spectrometers. GPC was performed at 40 °C on a JASCO high-speed liquid chromatograph system equipped with a differential refractometer detector and a variable-wavelength UV−vis detector, using THF as eluent at a flow rate of 1.0 mL min^{-1} with a Shodex-806L column. HPLC analyses was carried out at 40 °C on a Japan Analytical Industry LC-908 using hexane−ethanol as eluent at a flow rate of 1.0 mL min^{-1} with a YMC pack ODS-A column. DSC measurement was carried out by using on a Seiko DSC220C instrument at a heating rate of 10 °C min^{-1}. Three scans were performed to check the reproducibility. Complex **A** (Scheme 1) was prepared as analytically pure red crystals according to the literature.[4]

Preparation of Monomer. We added acetone (200 mL) to a mixture of 4-hydroxyazobenzene (5.00 g, 25.2 mmol), 12-bromododecanol (6.69 g, 25.2 mmol), and K_2CO_3 (5.00 g, 36.2 mmol) to dissolve the organic substrates. The mixture was heated at reflux for 60 h. After removal of the resulting salt by filtration, the product was purified by column chromatography (silica gel, hexane) to give 4-{(12-hydroxy)dodecyloxy}-azobenzene as a yellow solid (7.00 g, 73%). ^{1}H NMR (300 MHz in $CDCl_3$ at 25 °C): δ 7.91 (d, 2H, $\mathrm{OC_6H_2}H_2$, $J = 9$ Hz), 7.87 (d, 2H, $\mathrm{C_6H_3}H_2$ (ortho), $J = 8$ Hz), 7.49 (dd, 2H, $\mathrm{C_6H_3}H_2$ (meta), $J = 7, 8$ Hz), 7.43 (d, 1H, $\mathrm{C_6\ H_4}H$ (para), $J = 7$ Hz) 7.00 (d, 2H, $\mathrm{OC_6H_2}H_2$, $J = 9$ Hz), 4.04 (t, 2H, $\mathrm{C_6H_4OC}H_2$, $J = 7$ Hz), 3.63 (t, 2H, $\mathrm{HOC}H_2$, $J = 7$ Hz), and 1.86−1.29 (m, 20H, $\mathrm{C}H_2$). ^{13}C{^{1}H} NMR (75 MHz in $CDCl_3$ at 25): δ 161.7 ($\mathrm{OC_5}C\mathrm{H_4}$ (ipso)), 152.8 ($\mathrm{C_5}C\mathrm{H_5}$, (ipso)), 146.8 ($\mathrm{C_5}C\mathrm{H_4N}{=}$ (ipso)), 130.3 ($\mathrm{C_5}C\mathrm{H_5}$ (para)), 129.0 ($\mathrm{C_4}C_2\mathrm{H_5}$ (meta)), 124.7 ($\mathrm{O\ C_4}C_2\mathrm{H_4}$ (meta)), 122.5 (${=}\mathrm{NC_4}C_2\mathrm{H_5}$ (ortho)), 114.7 ($\mathrm{OC_4}C_2\mathrm{H_4}$ (ortho)), 68.3 ($\mathrm{C_6H_4O}C\mathrm{H_2}$), 63.1 ($\mathrm{HO}C\mathrm{H_2}$), 32.8 ($C\mathrm{H_2}$), 29.6 ($C\mathrm{H_2}$), 29.5 ($C\mathrm{H_2}$), 29.4 ($C\mathrm{H_2}$), 29.2 ($C\mathrm{H_2}$), 26.0 ($C\mathrm{H_2}$), and 25.7 ($C\mathrm{H_2}$).

A mixture of *t*-BuOK (4.10 g, 36.6 mmol) and 4-{(12-allenyloxy)dodecyloxy}azobenzene (7.00 g, 18.3 mmol) was dissolved in THF (150 mL) in a three-necked flask equipped with a condenser and a nitrogen inlet under nitrogen stream. Propargyl bromide (3.30 g, 27.5 mmol) in THF (50 mL) was added to the above solution over 1 h at reflux. The reaction mixture was then heated for 3 days with stirring and quenched by a saturated NH_4Cl aqueous solution (200 mL). Organic products were extracted with CH_2Cl_2 and dried over $MgSO_4$. Purification by column chromatography (silica gel, hexane) and HPLC gave 4-{(12-allenyloxy)dodecyloxy}azobenzene (1.17 g, 15%). ^{1}H NMR (400 MHz in $CDCl_3$ at 25 °C): δ 7.91 (d, 2H, $\mathrm{OC_6H_2}H_2$, $J = 9$ Hz), 7.87 (d, 2H, $\mathrm{C_6H_3}H_2$ (ortho), $J = 8$ Hz), 7.49 (dd, 2H, $\mathrm{C_6H_3}H_2$ (meta), $J = 7, 8$ Hz), 7.43 (d, 1H, $\mathrm{C_6H_4}H$ (para), $J = 7$ Hz) 7.00 (d, 2H, $\mathrm{OC_6H_2}H_2$, $J = 9$ Hz), 6.72 (t, 1H, $\mathrm{C{=}C{=}C}H$, $J = 6$ Hz), 5.42 (d, 2H, $H_2\mathrm{C{=}C{=}C}$, $J = 6$ Hz), 4.04 (t, 2H, $\mathrm{C_6H_4OC}H_2$, $J = 7$ Hz), 3.55 (t, 2H, $\mathrm{HOC}H_2$, $J = 7$ Hz), 1.85−1.29 (m, 20H, $\mathrm{C}H_2$). ^{13}C{^{1}H} NMR (100 MHz in $CDCl_3$ at 25 °C): δ 201.4 (${=}C{=}$), 161.7 ($\mathrm{OC_5}C\mathrm{H_4}$, (ipso)), 152.8 (${=}\mathrm{NC_5}C\mathrm{H_5}$ (ipso)), 146.9 ($\mathrm{C_5}C\mathrm{H_4N}$ (ipso)), 130.2 (${=}\mathrm{NC_5}C\mathrm{H_5}$ (para)), 129.0 (${=}\mathrm{NC_4}C_2\mathrm{H_5}$ (meta)), 124.7 ($\mathrm{O\ C_4}C_2\mathrm{H_4}$ (meta)), 122.5 (${=}\mathrm{NC_4}C_2\mathrm{H_5}$ (ortho)), 121.6 ($\mathrm{C{=}C{=}}C\mathrm{H}$), 114.7 ($\mathrm{OC_4}C_2\mathrm{H_4}$ (ortho)), 90.3 ($\mathrm{H_2}C\mathrm{{=}C{=}C}$), 68.9($\mathrm{C{=}CH{-}O}C\mathrm{H_2}$), 68.4 ($\mathrm{C_6H_4\text{-}O}C\mathrm{H_2}$), 29.5 ($C\mathrm{H_2}$), 29.4 ($C\mathrm{H_2}$), 29.2 ($C\mathrm{H_2}$), and 26.0 ($C\mathrm{H_2}$).

Polymerization. A THF (1 mL) solution of Rh complex **A** (Scheme 1) (2.9 mg, 2.4 μmol) was prepared in a Schlenk flask (ca. 25 mL volume) equipped with a stopcock that is connected to a rubber balloon (ca. 2 L) filled with carbon monoxide (ca. 1.05 atm). After addition of 4-{(12-allenyloxy)dodecyloxy}-azobenzene (100 mg, 0.24 mmol) to the solution, the system was degassed by repeated freeze-and-thaw cycles. Carbon monoxide was introduced to the flask, and the reaction mixture was allowed to warm to room temperature with stirring. The solution changed color from orange to pale yellow. The reaction mixture was stirred for 21 h at that temperature. Pouring the reaction mixture into MeOH (200 mL) precipitated an orange solid, which was then collected by filtration, washed repeatedly with MeOH, and dried in vacuo to give **1** as an orange solid (85 mg, 82%). ^{1}H NMR (400 MHz in $CDCl_3$ at 25 °C): δ 7.87 (d, 2H, $\mathrm{C_6H_3}H_2$ (ortho), $J = 8$ Hz), 7.84 (d, 2H, $\mathrm{OC_6H_2}H_2$, $J = 9$ Hz), 7.55 (s, 1H, $\mathrm{C(O)C{=}C}H$), 7.46 (dd, 2H, $\mathrm{C_6H_3}H_2$ (meta), $J = 7, 8$ Hz), 7.40 (d, 1H, $\mathrm{C_6H_3}H_2$ (para), $J = 7$ Hz) 6.94 (d, 2H, $\mathrm{OC_6H_2}H_2$, $J = 9$ Hz), 3.96 (t, 2H, $\mathrm{C_6H_4OC}H_2$, $J = 7$ Hz), 3.91 (br, 2H, $\mathrm{HOC}H_2$, 3.55 (br, 2H, ${=}\mathrm{CHOC}H_2$), 1.80−1.25 (m, 20H, $\mathrm{C}H_2$). ^{13}C{^{1}H} NMR (100 MHz in $CDCl_3$ at 25 °C): δ 195.6 ($C\mathrm{O}$), 161.7 ($\mathrm{OC_5}C\mathrm{H_4}$, (ipso)), 160.8 ($\mathrm{C{=}}C\mathrm{HOCH_2}$), 152.7 ($\mathrm{NC_5}C\mathrm{H_5}$ (ipso)), 146.8 ($\mathrm{OC_5}C\mathrm{H_4}$ (ipso)), 130.3 ($\mathrm{C_5}C\mathrm{H_5}$ (para)), 129.0 ($\mathrm{C_4}C_2\mathrm{H_5}$ (meta)), 124.7 ($\mathrm{OC_4}C_2\mathrm{H_4}$ (meta)), 122.5 ($\mathrm{C_4}C_2\mathrm{H_5}$ (ortho)), 115.8 ($\mathrm{C(O)}C\mathrm{{=}CH}$), 114.6 ($\mathrm{OC_4}C_2\mathrm{H_4}$ (ortho)), 74.8 ($\mathrm{C_6H_4O}C\mathrm{H_2}$), 68.3 ($\mathrm{C{=}C(H)O}C\mathrm{H_2}$), 32.2 ($\mathrm{C(O)}C\mathrm{H_2}$) 29.8 ($C\mathrm{H_2}$), 29.6 ($C\mathrm{H_2}$), 29.4 ($C\mathrm{H_2}$), 29.3 ($C\mathrm{H_2}$), 29.2 ($C\mathrm{H_2}$), 26.0 ($C\mathrm{H_2}$) and 25.5 ($C\mathrm{H_2}$). GPC (polystyrene standards, eluent: THF): $M_\mathrm{n} = 35.0 \times 10^3$, $M_\mathrm{w}/M_\mathrm{n} = 1.12$.

The reaction with the monomer/Rh ratio of 50 produced **1** with $M_\mathrm{n} = 20\,000$ ($M_\mathrm{w}/M_\mathrm{n} = 1.10$).

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from Ministry of Education, Science, Culture, and Sports, Japan (11166221). Authors are grateful to Prof. Kyoko Nozaki of Tokyo University for her helpful suggestions.

Supporting Information Available: Schematic drawing of orientation of the side chain of the polyketone. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Reviews and recent references: (a) Sen, A. *Adv. Polym. Sci.* **1986**, *73/74*, 125. (b) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303. (c) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663. (d) Drent, E.; van Broekhoven, J. A. M.; Budzelaar, P. H. M. *Pays-Bas.* **1996**, *115*, 263. (e) Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641. (f) Brookhart, M.; Wagner, M. I. *J. Am. Chem. Soc.* **1996**, *118*, 7219. (g) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746. (h) Jiang, Z.; Sen, A. *J. Am. Chem. Soc.* **1995**, *117*, 4455. (i) Bronco, S.; Consiglio, G.; Di Benedetto, S.; Fehr, M.; Spindler, F.; Togni, A. *Helv. Chim. Acta* **1995**, *78*, 883. (j) Nozaki, K.; Sato, N.; Takaya, H. *J. Am. Chem. Soc.* **1995**, *117*, 9911. (k) Nozaki, K.; Kawashima, Y.; Nakamoto, K.; Hiyama, T. *Macromolecules* **1999**, *32*, 5168. (l) De Rosa, C. *Macromolecules* **1997**, *30*, 5495. (m) Carfagna, C.; Formica, M.; Gatti, G.; Musco, A.; Pierleoni, A. *Chem. Commun.* **1998**, 1113. (n) Zhang, S. A.; Kaneko, S.; Takahashi, S. *Macromolecules* **2000**, *33*, 6930. See also: Kim, S.-W.; Takeuchi, D.; Osakada, K. *J. Am. Chem. Soc.* **2002**, *124*, 762.

(2) Nozaki, K.; Kawashima, Y.; Oda, T.; Hiyama, T.; Kanie, K.; Kato, T. *Macromolecules* **2002**, *35*, 1140.

(3) Nieuwhof, R. P.; Marcelis, A. T. M.; Sudhölter, E. J. R.; Wursche, R.; Rieger, B. *Macromol. Chem. Phys.* **2000**, *201*, 2484.

(4) Osakada, K.; Choi, J. C.; Yamamoto, T. *J. Am. Chem. Soc.* **1997**, *119*, 12390. (b) Choi, J. C.; Yamaguchi, I.; Osakada, K.; Yamamoto, T. *Macromolecules* **1998**, *31*, 8731.

(5) Reports of alternating copolymerization of allene with carbon monoxide catalyzed by Pd complexes. See: Maatschappij, B. V. *Neth. Appl.* **1988**, 88 01168; *Chem. Abstr.* **1990**, *113*, 24686f. Kacker, S.; Sen, A. *J. Am. Chem. Soc.* **1997**, *119*, 10028.

(6) Takenaka, Y.; Yamaguchi, I.; Osakada, K.; Yamamoto, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1505.

(7) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817. (b) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847. (c) Ikeda, T.; Tsutsumi, O. *Science* **1995**, *268*, 1873. (d) Wu, Y.; Ikeda, T.; Zhang, Q. *Adv. Mater.* **1999**, *11*, 300. (e) Yamamoto, T.; Hasegawa, M.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Phys. Chem. B* **1999**, *103*, 9873. (f) Yamamoto, T.; Ohashi, A.; Yoneyama, S.; Hasegawa, M.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Phys. Chem. B* **2001**, *105*, 2308. (g) Ikeda, T.; Kanazawa, A. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1715. (h) Natansohn, A.; Rochon, P.; Gosselin, J.; Xie, S. *Macromolecules* **1992**, *25*, 2268. (i) Iftime, G.; Labarthet, F. L.; Natansohn, A.; Rochon, P. *J. Am. Chem. Soc.* **2000**, *122*, 12646. (j) Iftime, G.; Natansohn, A.; Rochon, P. *Macromolecules* **2002**, *35*, 365. (k) Lévesque, I.; Leclerc, M. *Macromolecules* **1997**, *30*, 4347. (l) Teraguchi, M.; Masuda, T. *Macromolecules* **2000**, *33*, 240. (m) Izumi, A.; Teraguchi, M.; Nomura, R.; Masuda, T. *Macromolecules* **2000**, *33*, 5347.

(8) Takenaka, Y.; Osakada, K. *Macromol. Chem. Phys.* **2001**, *202*, 3571.

MA020958+