1864 *Macromolecules* **2007,** *40,* 1864−1867

Chiral 1-Methylpropargyl Alcohol: A Simple and Powerful Helical Source for Substituted Polyacetylenes

Yuji Suzuki, Masashi Shiotsuki, Fumio Sanda,* and Toshio Masuda*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura Campus, Kyoto 615-8510, Japan

Received December 27, 2006; Revised Manuscript Received January 3, 2007

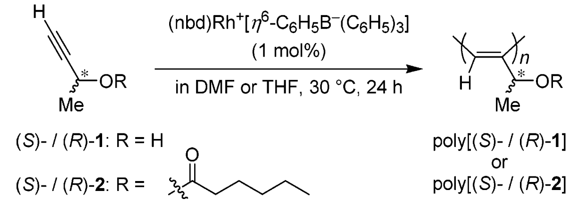
ABSTRACT: (*S*)- and (*R*)-1-methylpropargyl alcohols [(*S*)-**1** and (*R*)-**1**] and their ester derivatives (*S*)- and (*R*)-1-methylpropargyl hexanoates [(*S*)-**2** and (*R*)-**2**] were polymerized using (nbd)$Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ as catalyst to afford the corresponding substituted polyacetylenes with moderate molecular weights in good yields. The polymers possessed cis-stereoregular structures according to ^{1}H NMR. Large optical rotations and clear CD signals demonstrated that these polymers took a helical structure with predominantly one-handed screw sense, stabilized by steric repulsion between the side chains containing chiral groups adjacent to the main chain.

Introduction

Helix is the most common higher order structure of macromolecules, and many delicate functions and intricate biological activities of biomacromolecules such as DNA and proteins largely depend on their well-ordered helical structures. An in-depth understanding of the relationship between structure and functions of biomacromolecules is not only indispensable from the standpoint of fundamental study but also may lead to a huge array of applications in various scientific fields. Synthesis and properties of well-ordered artificial helical polymers have been extensively studied in parallel with the research on naturally occurring polymers. Various synthetic helical polymers have been reported so far, which include poly(alkyl methacrylates),[1] polychloral,[2] polyisocyanides,[3] polyisocyanates,[4] and polysilanes.[5] Monosubstituted acetylenes undergo polymerization with Rh catalysts to provide the corresponding polyacetylenes having a cis-stereoregular main chain.[6]

Substituted polyacetylenes form helical structures with predominantly one-handed screw sense by the introduction of chiral substituents into the side chains, wherein chiral carboxylic acids,[7] alcohols,[8] amino acids,[9] sugars,[10] terpenes,[11]and so forth have been employed as the helical sources. Propargyl alcohol is the simplest acetylene monomer having a hydroxy group, which undergoes polymerization with Pd and Ni catalysts.[12] 1-Methylpropargyl alcohol is a chiral derivative of propargyl alcohol and has found various applications in the field of organic chemistry; e.g., it has been utilized for regioselective carbometalation with Grignard reagents affording 2-substituted allylic alcohols,[13a] synthesis of 2-substituted indoles via Sonogashira coupling cyclization,[13b] as a precursor of chiral allenylzinc and indium reagents,[13c] and synthesis of phosphinoyl 1,3-diene.[13d] On the other hand, the polymerization of 1-methylpropargyl alcohol has not been reported so far. In the present article, we would like to report the polymerization of (*S*)- and (*R*)-1-methylpropargyl alcohols [(*S*)-**1** and (*R*)-**1**] with a Rh catalyst and the helix formation of the formed polymers (Scheme 1). We also describe the synthesis and polymerization of the ester derivatives, (*S*)- and (*R*)-1-methylpropargyl hexanoates [(*S*)-**2** and (*R*)-**2**], and the helical properties of the obtained polymers.

Scheme 1



Experimental Section

Measurements. Specific rotations ($[\alpha]_D$) were measured with a JASCO DIP-1000 digital polarimeter. IR spectra were obtained with a JASCO FTIR-4100 spectrophotometer. NMR (^{1}H: 400 MHz; ^{13}C: 100 MHz) spectra were recorded on a JEOL EX-400 spectrometer. Elemental analyses were conducted at the Kyoto University Elemental Analysis Center. Number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymers were estimated by GPC (Shodex columns K803, K804, K805) eluted with $CHCl_3$ and GPC (TOSOH columns α-M, GMH_{XL}) eluted with a solution of LiBr (10 mM) in DMF calibrated by polystyrene standards. CD and UV−vis spectra were recorded on a JASCO J-820 spectropolarimeter.

Materials. Unless stated otherwise, reagents were used as received including (*S*)-**1** {$[\alpha]_D = -7.30°$ ($c = 0.29$ g/dL in DMF)} and (*R*)-**1** {$[\alpha]_D = +7.05°$ ($c = 0.16$ g/dL in DMF)}. (nbd)$Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ was prepared according to the literature.[14] THF and DMF used for polymerization were distilled prior to use.

Monomer Synthesis. (*S*)-1-Methylpropargyl hexanoate [(*S*)-**2**] was prepared by applying the literature method, as follows:[15] 4-(Dimethylamino)pyridine (0.170 g, 1.43 mmol) and 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (2.73 g, 14.3 mmol) were sequentially added to a solution of (*S*)-**1** (1.0 g, 14.3 mmol) and hexanoic acid (1.66 g, 14.3 mmol) in CH_2Cl_2 (100 mL), and the resulting mixture was stirred at room temperature overnight. The reaction mixture was washed with 2 M HCl and saturated aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$, and concentrated on a rotary evaporator. The residual mass was purified by flash column chromatography on silica gel eluted with hexane/ethyl acetate = 9/1 (v/v) to obtain (*S*)-**2** as a colorless liquid in 52% yield. $[\alpha]_D = -96.9°$ ($c = 0.10$ g/dL in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.90 (CH_2CH_3, t, $J = 6.8$ Hz, 3H), 1.30−1.33 ($CH_2CH_2CH_3$, m, 4H), 1.50 ($CHCH_3$, d, $J = 6.8$ Hz, 3H), 1.60−1.68 ($COCH_2CH_2$, m, 2H), 2.32 ($COCH_2$, t, $J = 7.6$ Hz, 2H), 2.45 ($C{\equiv}CH$, d, $J = 2.0$ Hz, 1H), 5.44 ($CHCH_3$, q, $J = 4.8$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 13.83, 22.16, 22.23, 24.47, 31.15, 34.15, 59.67, 72.64, 82.22, 172.57. IR (neat): 3294, 2959, 2936, 1742, 1170,

---

* To whom all correspondence should be addressed. E-mail: sanda@adv.polym.kyoto-u.ac.jp, masuda@adv.polym.kyoto-u.ac.jp.

10.1021/ma0629642 CCC: $37.00

Table 1. Polymerization of (*S*)-/(*R*)-1 and (*S*)-/(*R*)-2[a]

		polymer								
					$[\alpha]_D$[e] (deg)					
monomer	solvent	yield[c] (%)	M_n[d]	M_w/M_n[d]	MeOH	DMF	DMSO	toluene	$CHCl_3$	THF
(*S*)-**1**	DMF[b]	79	19 000	2.03	+1187	+1413	+1534	–[f]	–[f]	–[f]
(*R*)-**1**	DMF[b]	77	21 000	1.70	−1214	−1512	−1529	–[f]	–[f]	–[f]
(*S*)-**2**	THF	88	34 000	3.38	–[f]	–[f]	–[f]	+840	+766	+600
(*R*)-**2**	THF	79	32 000	3.16	–[f]	–[f]	–[f]	−873	−702	−654

[a] Conditions: catalyst (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$], nbd = norbornadiene, $[M]_0$ = 1.0 M, $[M]_0/[Rh]$ = 100, 30 °C, 24 h. [b] $[M]_0$ = 3.0 M. [c] Insoluble part in Et_2O {poly[(*S*)-**1**] and poly[(*R*)-**1**]} and MeOH {poly[(*S*)-**2**] and poly[(*R*)-**2**]}. [d] Determined by GPC eluted with DMF {poly[(*S*)-**1**] and poly[(*R*)-**1**]} and $CHCl_3$ {poly[(*S*)-**2**] and poly[(*R*)-**2**]}. [e] Determined by polarimetery at room temperature, *c* = 0.063−0.604 g/dL. [f] Not determined because the polymer was insoluble.

664 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.49; H, 9.76.

(*R*)-1-Methylpropargyl hexanoate [(*R*)-**2**] was synthesized from (*R*)-**1** in a manner similar to (*S*)-**2**. Yield 48%; $[\alpha]_D$ = +86.7° (*c* = 0.25 g/dL in $CHCl_3$). Anal. Calcd for $C_{10}H_{16}O_2$: 71.39; H, 9.59. Found: C, 71.47; H, 9.71.

Polymerization. A solution of (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] (5.1 mg, 0.01 mmol) in a distilled solvent (0.5 mL) was added to a solution of a monomer (1.0 mmol) in a distilled solvent (0.5 mL) under dry nitrogen, and the resulting solution was kept at 30 °C for 24 h. The reaction mixture was poured into Et_2O or MeOH to precipitate a polymer. It was separated by filtration and dried under reduced pressure.

Spectroscopic Data of the Polymers. Poly[(*S*)-**1**]. ^{1}H NMR (DMSO-d_6): δ 1.09 (CH_3, br, 3H), 4.48 (C*H*, br, 1H), 4.52 (O*H*, br, 1H,), 6.27 (C=C*H*, br, 1H). IR (KBr disk): 3428, 2943, 1461, 1063, 654 cm^{-1}. Poly[(*R*)-**1**]. ^{1}H NMR (DMSO-d_6): δ 1.09 (CH_3, br, 3H), 4.47 (C*H*, br, 1H), 4.52 (O*H*, br, 1H,), 6.27 (C=C*H*, br, 1H). IR (KBr disk): 3426, 2943, 1462, 1063, 655 cm^{-1}. Poly[(*S*)-**2**]. ^{1}H NMR ($CDCl_3$): δ 0.88 (CH_2CH_3, br, 3H), 1.30 ($CH_2CH_2CH_2$-CH_3, br, 6H), 1.60 ($CHCH_3$, br, 3H), 2.27 ($COCH_2$, br, 2H), 5.62 (C*H*CH$_3$, br, 1H), 6.38 (C=C*H*, br, 1H). IR (KBr disk): 3453, 2861, 1730, 1634, 1418, 786 cm^{-1}. Poly[(*R*)-**2**]. ^{1}H NMR ($CDCl_3$): δ 0.87 (CH_2CH_3, br, 3H), 1.29 ($CH_2CH_2CH_2CH_3$, br, 6H), 1.60 ($CHCH_3$, br, 3H), 2.29 ($COCH_2$, br, 2H), 5.64 (C*H*CH$_3$, br, 1H), 6.41 (C=C*H*, br, 1H). IR (KBr disk): 3453, 2859, 1731, 1634, 1417, 786 cm^{-1}.

Results and Discussion

Polymerization. In general, Rh catalysts tolerate a wide variety of functional groups,[16] and the polymerization of monosubstituted acetylenes thereby gives corresponding polyacetylenes with a cis-stereoregular main chain.[6] Thus, the polymerization of (*S*)-**1**, (*R*)-**1**, (*S*)-**2**, and (*R*)-**2** was carried out using (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] as catalyst in DMF and THF at 30 °C for 24 h (Table 1). Monomers (*S*)-**1** and (*R*)-**1** having a hydroxy group successfully underwent polymerization to give the polymers {poly[(*S*)-**1**] and poly[(*R*)-**1**]} with moderate molecular weights in good yields, which were isolated by precipitation with Et_2O. The ester counterparts, poly[(*S*)-**2**] and poly[(*R*)-**2**], were obtained as MeOH-insoluble parts. Poly[(*S*)-**1**] and poly[(*R*)-**1**] were soluble in highly polar solvents such as MeOH, DMF, and DMSO but insoluble in toluene, $CHCl_3$, and THF, whereas poly[(*S*)-**2**] and poly[(*R*)-**2**] displayed a totally opposite tendency; i.e., they were insoluble in the former three solvents but soluble in the latter three solvents. All the polymers exhibited no ^{1}H NMR signal assignable to ethynyl proton but a signal due to the olefinic proton of the *cis*-polyacetylene main chain. The integration ratios of the signals confirmed that the cis contents of the polymers were quantitative. The IR spectroscopic data of the polymers also supported the formation of substituted polyacetylenes.

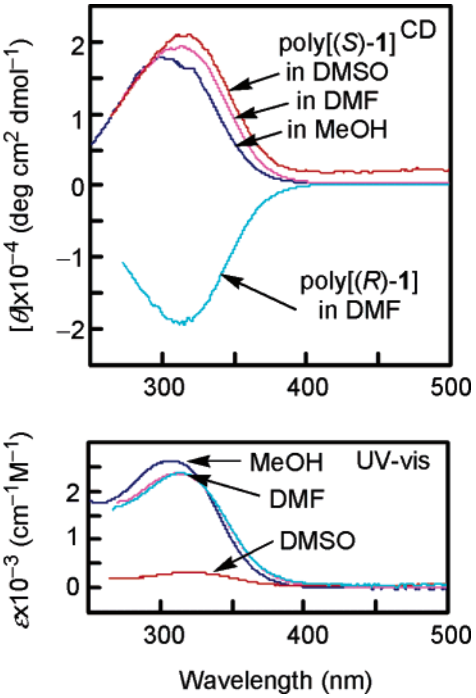


Figure 1. CD and UV−vis spectra of poly[(*S*)-**1**] and poly[(*R*)-**1**] measured in MeOH, DMF, and DMSO (*c* = 0.11−1.0 mM) at 20 °C.

Secondary Structure. As summarized in Table 1, the polymers displayed extremely large optical rotations, which were opposite in sign to those of the corresponding monomers irrespective of the kind of solvent. As depicted in Figures 1 and 2, all the polymers showed intense CD signals in the absorption region of the main-chain chromophore in solvents with different polarities and hydrogen-bonding abilities. The large optical rotations and CD signals are attributable to the helicity of the polyacetylene main chains with predominantly one-handed screw sense. The finding that the wavelengths of CD and UV−vis peaks coincide with each other implies that the CD signals originate directly from the main-chain structure. The fact that the CD signals are hardly affected by the solvents unlike the case of poly(*N*-propargylamides) implies the formation of helices due to steric effect rather than hydrogen bonding.[7] The behavior of poly[(*S*)-**2**] and poly[(*R*)-**2**] to form a stable helix lies in stark contrast to those of poly(propargyl esters) carrying chiral centers at the α-position of the acyl groups, which do not form a helix.[7f] This conspicuous difference is attributable to a remote location of the chiral center from the main chain in poly(propargyl esters). It is noteworthy that the very small chiral units, especially in the cases of poly[(*S*)-**1**] and poly[(*R*)-**1**], efficiently induce helicity. The remarkable ability of such a small chiral moiety to induce helicity is probably due to location of the chiral group adjacent to the main chain. In other words, the presence of a chiral group in a close proximity to the main chain is quite effective to induce a helix stabilized by steric repulsion between the side chains. The sterically induced helix in the

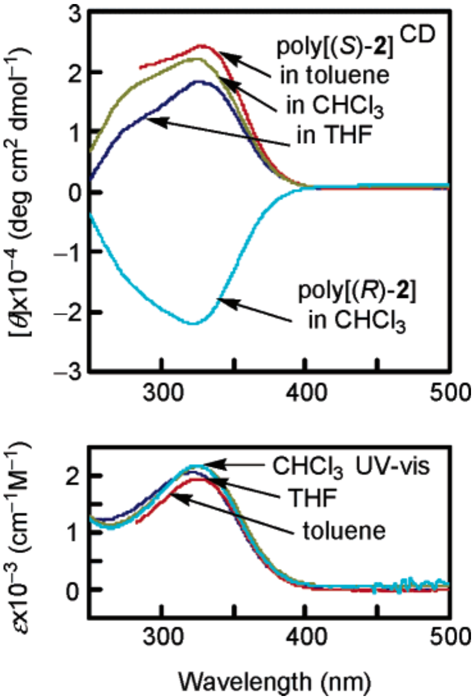


Figure 2. CD and UV−vis spectra of poly[(*S*)-**2**] and poly[(*R*)-**2**] measured in toluene, $CHCl_3$, and THF (c = 0.22−0.67 mM) at 20 °C.

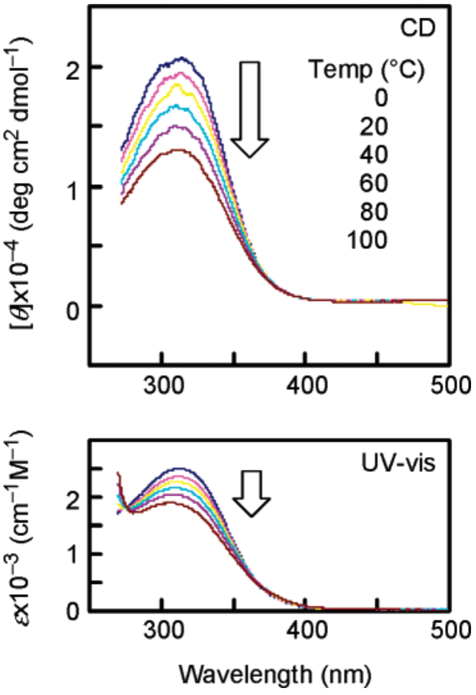


Figure 3. CD and UV−vis spectra of poly[(*S*)-**1**] measured in DMF (c = 0.90 mM) at various temperatures.

present polymers are more or less similar to those of poly(3-methyl-1-pentyne)[17] and poly(propiolic esters),[8] whereas it is different from those of poly(*N*-propargylamides)[7] and poly[(4-dodecyloxy-3,5-dihydroxyphenyl)acetylene][18] which are mainly generated by hydrogen bonding.

The (*S*)- and (*R*)-polymers having side chains with different absolute configuration exhibited oppositely signed optical rotations and mirror-image CD signals to each other. This result indicates that these polymers take helical structures with opposite screw sense mutually and that the helix sense of the polymers is controlled by the absolute configuration of the chiral group adjacent to the main chain. The UV−vis absorption maxima

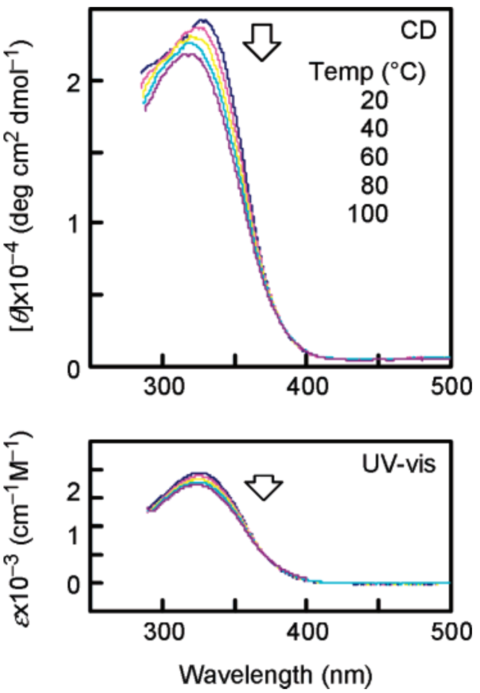


Figure 4. CD and UV−vis spectra of poly[(*S*)-**2**] measured in toluene (c = 0.54 mM) at various temperatures.

and CD signals of (*S*)-/(*R*)-poly(**1**)s and (*S*)-/(*R*)-poly(**2**)s were located at 305−315 and 323−328 nm, respectively, thus indicating that (*S*)-/(*R*)-poly(**2**)s have a conjugation longer than that of (*S*)-/(*R*)-poly(**1**)s and form a looser helix[19] presumably due to the larger substituent.

We further examined the thermal stability of helical conformation of the polymers. As depicted in Figure 3, poly[(*S*)-**1**] gradually decreased the CD intensity in DMF upon raising temperature from 0 to 100 °C. The simultaneous decrease of the UV−vis absorption indicates the occurrence of transformation from helix into random coil in accordance with temperature rise as commonly observed in the heat response of dynamic helical polymers.[17,20] On the other hand, the helical conformation of poly[(*S*)-**2**] was thermally quite stable compared to that of poly[(*S*)-**1**]. It is likely that the hydroxy groups of poly[(*S*)-**1**] interact with the solvent strongly, while the ester groups of poly[(*S*)-**2**] do not so much. The bulkier side chains of poly[(*S*)-**2**] than those of poly[(*S*)-**1**] may also effectively maintain the helical structure owing to steric effects, resulting in the larger stability of the helical structure.

Conclusion

In the present study, we have demonstrated that the polymerization of (*S*)- and (*R*)-1-methylpropargyl alcohols and the ester derivatives successfully proceeded in the presence of a Rh catalyst to give the corresponding substituted polyacetylenes, which took a helical structure with predominantly one-handed screw sense in solution based on steric repulsion between the side chains. The helical conformation of the polymer carrying ester groups was thermally more stable than that of the one with free hydroxy groups. As far as we know, this is the first finding that polymers from (*S*)- and (*R*)-1-methylpropargyl alcohols and the ester derivatives adopt a helical conformation. The present study has revealed that chiral 1-methylpropargyl alcohol is a simple but very powerful and useful helical source for substituted polyacetylenes.

Acknowledgment. This research was partly supported by a Grant-in-Aid for Science Research in a Priority Area "Super-

Hierarchical Structures (No. 446)" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

(1) (a) Yamamoto, C.; Okamoto, Y. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 227−257. (b) Habaue, S.; Okamoto, Y. *Chem. Rec.* **2001**, *1*, 46−52. (c) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013−4038. (d) Okamoto, Y.; Suzuki, K.; Ohta, K.; Hatada, K.; Yuki, H. *J. Am. Chem. Soc.* **1979**, *101*, 4763−4765.

(2) (a) Ute, K.; Hirose, K.; Kashimoto, H.; Hatada, K.; Vogl, O. *J. Am. Chem. Soc.* **1991**, *113*, 6305−6306. (b) Corley, L. S.; Vogl, O. *Polym. Bull. (Berlin)* **1980**, *3*, 211−217.

(3) (a) Onitsuka, K.; Mori, T.; Yamamoto, M.; Takei, F.; Takahashi, S. *Macromolecules* **2006**, *39*, 7224−7231. (b) Cornelissen, J. J. L. M.; Graswinckel, W. S.; Rowan, A. E.; Sommerdijk, N. A. J. M.; Nolte, R. J. M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1725−1736. (c) Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1993**, *115*, 9101−9111. (d) Kamer, P. C. J.; Nolte, R. J. M.; Drenth, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4063−4065.

(4) (a) Muellers, B. T.; Park, J. W.; Brookhart, M. S.; Green, M. M. *Macromolecules* **2001**, *34*, 572−581. (b) Green, M. M.; Park, J.; Sato, T.; Teramoto, A.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3139−3154. (c) Green, M. M.; Andreola, C.; Muñoz, B.; Reidy, M. P.; Zero, K. *J. Am. Chem. Soc.* **1988**, *110*, 4063−4065. (d) Goodman, M.; Chen, S. *Macromolecules* **1970**, *4*, 398−402.

(5) (a) Saxena, A.; Rai, R.; Kim, S. Y.; Fujiki, M. Naito, M.; Okoshi, K.; Kwak, G. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *44*, 5060−5075. (b) Sato, T.; Terao, K.; Teramoto, A.; Fujiki, M. *Polymer* **2003**, *44*, 5477−5495. (c) Fujiki, M. *J. Am. Chem. Soc.* **1994**, *116*, 6017−6018. (d) Fujiki, M. *J. Am. Chem. Soc.* **1994**, *116*, 11976−11981.

(6) (a) Sedláček, J.; Vohlídal, J. *Collect. Czech. Chem. Commun.* **2003**, *68*, 1745−1790. (b) Tabata, M.; Sone, T.; Sadahiro, Y. *Macromol. Chem. Phys.* **1999**, *200*, 265−282. (c) Kishimoto, Y.; Itou, M.; Miyake, T.; Ikariya, T.; Noyori, R. *Macromolecules* **1995**, *28*, 6662−6666. (d) Furlani, A.; Napoletano, C.; Russo, M. V.; Camus, A.; Marsich, N. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 75−86. (e) Forlani, A.; Napoletano, C.; Russo, M. V.; Feast, W. J. *Polym. Bull. (Berlin)* **1986**, *16*, 311−317.

(7) (a) Tabei, J.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Macromolecules* **2005**, *38*, 5860−5867. (b) Tabei, J.; Nomura, R.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Macromol. Chem. Phys.* **2005**, *206*, 323−332. (c) Deng, J.; Tabei, J.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Macromolecules* **2004**, *37*, 7156−7162. (d) Deng, J.; Tabei, J.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Macromolecules* **2004**, *37*, 5149−5154. (e) Tabei, J.; Nomura, R.; Masuda, T. *Macromolecules* **2002**, *35*, 5404−5409. (f) Nomura, R.; Tabei, J.; Masuda, T. *J. Am. Chem. Soc.* **2001**, *123*, 8430−8431.

(8) (a) Nakako, H.; Nomura, R.; Masuda, T. *Macromolecules* **2001**, *34*, 1496−1502. (b) Nakako, H.; Mayahara, Y.; Nomura, R.; Tabata, M.; Masuda, T. *Macromolecules* **2000**, *33*, 3978−3982. (c) Nomura, R.; Fukushima, H.; Nakako, H.; Masuda, T. *J. Am. Chem. Soc.* **2000**, *122*, 8830−8836. (d) Nakako, H.; Nomura, R.; Tabata, M.; Masuda, T. *Macromolecules* **1999**, *32*, 2861−2864.

(9) (a) Onouchi, H.; Hasegawa, T.; Kashiwagi, D.; Ishiguro, H.; Maeda, K.; Yashima, E. *Macromolecules* **2005**, *38*, 8625−8633. (b) Morino, K.; Oobo, M.; Yashima, E. *Macromolecules* **2005**, *38*, 3461−3468. (c) Zhao, H.; Sanda, F.; Masuda, T. *Polymer* **2005**, *46*, 2841−2846. (d) Sanda, F.; Terada, K.; Masuda, T. *Macromolecules* **2005**, *38*, 8149−8154. (e) Lam, J. W. Y.; Tang, B. Z. *Acc. Chem. Res.* **2005**, *38*, 745−754. (f) Gao, G.; Sanda, F.; Masuda, T. *Macromolecules* **2003**, *36*, 3932−3937. (g) Li, B. S.; Cheuk, K. K. L.; Ling, L. S.; Chen, J. W.; Xiao, X. D.; Bai, C. L.; Tang, B. Z. *Macromolecules* **2003**, *36*, 77−85.

(10) (a) Kadokawa, J.; Tawa, K.; Suenaga, M.; Kaneko, Y.; Tabata, M. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2006**, *43*, 1179−1187. (b) Otsuka, I.; Sakai, R.; Satoh, T.; Kakuchi, R.; Kaga, H.; Kakuchi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5855−5863. (c) Matuura, K.; Furuno, S.; Kobayashi, K. *Chem. Lett.* **1998**, 847−848.

(11) Aoki, T.; Shinohara, K.-i.; Kaneko, T.; Oikawa, E. *Macromolecules* **1996**, *29*, 4192−4198.

(12) (a) Zhan, X.; Yang, M.; Sun, H. *Macromol. Rapid Commun.* **2001**, *22*, 530−534. (b) Zhan, X.; Yang, M.; Sun, H. *Catal. Lett.* **2000**, *70*, 79−82. (c) Russo, M. V.; Furlani. A.; Altamura, P.; Fratoddi, I. *Polymer* **1997**, *38*, 3677−3690. (d) Furlani, A.; Russo, M. V.; Longo, A. *Polymer* **1997**, *38*, 183−189. (e) Yang, M.; Zheng, M.; Furlani, A.; Russo, M. V. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2709−2713.

(13) (a) Lu, Z.; Ma, S. *J. Org. Chem.* **2006**, *71*, 2655−2660. (b) Palimkar, S. S.; Kumer, P. H.; Lahoti, R. J.; Srinivasan, K. V. *Tetrahedron* **2006**, *62*, 5109−5115. (c) Marshall, J. M.; Eidam, P.; Eidam, H. S. *J. Org. Chem.* **2006**, *71*, 4840−4844. (d) Han, L. B.; Ono, Y.; Yazawa, H. *Org. Lett.* **2005**, *7*, 2909−2911.

(14) Schrock, R. R.; Osborn, J. A. *Inorg. Chem.* **1970**, *9*, 2339−2343.

(15) Dhaon, M. K.; Olsen, R. K.; Ramasamy, K. *J. Org. Chem.* **1982**, *47*, 1962−1965.

(16) (a) Maeda, K.; Goto, H.; Yashima, E. *Macromolecules* **2001**, *34*, 1160−1164. (b) Mitsuyama, M.; Ishii, R.; Kondo, K. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3419−3427. (c) Russo, M. V.; Furlani, A.; D'Amoto, R. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 93−102. (d) D'Amoto, R.; Sone, T.; Tabata, M.; Sadahiro, Y.; Russo, M. V.; Furlani, A. *Macromolecules* **1998**, *31*, 8660−8665.

(17) (a) Ciardelli, F.; Lanzillo, S.; Pieroni, O. *Macromolecules* **1974**, *7*, 174−179. (b) Pieroni, O.; Matera, F.; Ciardelli, F. *Tetrahedron Lett.* **1972**, *7*, 597−600.

(18) Aoki, T.; Kaneko, T.; Maruyama, N.; Sumi, A.; Takahashi, M.; Sato, T.; Teraguchi, M. *J. Am. Chem. Soc.* **2003**, *125*, 6346−6347.

(19) Percec, V.; Obata, M.; Rudick, J. G.; De, B. B.; Glodde, M.; Bera, T. K.; Magonov, S. N.; Balagurusamy, V. S. K.; Heiney, P. A. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3509−3533.

(20) (a) Moore, J. S.; Gorman, C. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 1704−1712. (b) Aoki, T.; Kokai, M.; Shinohara, K.; Oikawa, E. *Chem. Lett.* **1993**, 2009−2012.

MA0629642