Macromolecules **2005,** *38,* 1513−1516 **1513**

Thermally Induced Helical Conformational Change in Poly(aryl isocyanide)s with Optically Active Ester Groups

Fumie Takei, Kiyotaka Onitsuka,* and Shigetoshi Takahashi

The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

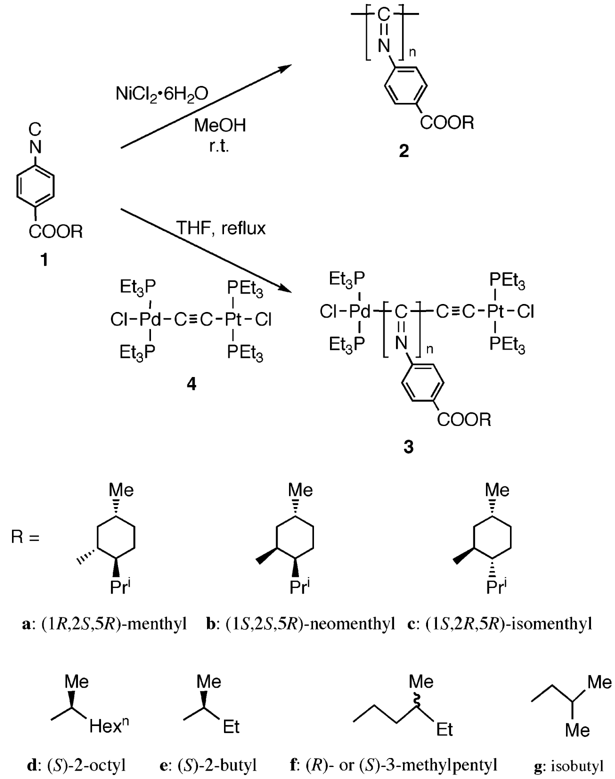
Received October 13, 2004
Revised Manuscript Received November 10, 2004

Introduction

Increasing attention has been paid to helical polymers because of their unique optical properties and molecular-recognition ability, which may be applicable to the development of novel functional materials.[1] Polyisocyanides with bulky substituents are an example of artificial polymers that maintain stable helical conformation in solution.[2] Although the conformation of polyisocyanides having less bulky substituents has been a subject of controversy based on theoretical and experimental studies,[3,4] it has been shown that polyisocyanides with appropriate chiral substituents have predominantly a one-handed helical conformation.[5] As the main chain consists of imino groups, polyisocyanides exhibit stereoregularity that is likely to be dependent on the polymerization conditions due to the configuration around the C═N double bonds (syn and anti forms). To the best of our knowledge, however, the influence of stereoregularity on helical conformation has been scarcely studied so far.

Previously, we showed that Pd−Pt μ-ethynediyl complexes efficiently initiated the living polymerization of aryl isocyanides[6] and that polyisocyanides having predominantly one-handed helical structures were produced by the polymerization of isocyanide monomers with chiral ester groups.[7] Because a polymerization catalyst or an initiator is expected to influence the stereoregularity of polyisocyanides, the comparison of the chiroptical properties of the polymers prepared from the same chiral isocyanide monomers using various catalysts or initiators is of interest. Thus, we prepared polyisocyanides from chiral monomers by using $NiCl_2$, which is a common polymerization catalyst for isocyanides,[2] and examined their chiroptical properties. We present herein the selectivity for and the irreversible change of the one-handed helical conformation of the polyisocyanides prepared with the $NiCl_2$ catalyst. We found that the conformational change in ^{13}C-labeled polyisocyanides was detectable by ^{13}C NMR spectroscopy and discussed the origin of the change.

Scheme 1. Polymerization of Aryl Isocyanides



Results and Discussion

The polymerization of chiral isocyanide (**1a**) with $NiCl_2$ catalyst in methanol at room temperature produced yellow polymer (**2a**) with $M_w = 22\,700$ and $M_w/M_n = 2.00$ (Scheme 1).[8] Although the IR, NMR, and UV−vis spectra of **2a** were similar to those of an analogous polymer (**3a**: $M_w = 15\,000$ and $M_w/M_n = 1.13$) prepared with Pd−Pt μ-ethynediyl complex (**4**), its chiroptical properties were very different from those of **3a**.[7d] The specific rotation of **2a** was $[\alpha]_D^{20} = +354$, whereas that of **3a** was $[\alpha]_D^{20} = +1070$. The value of the Cotton effect in the CD spectrum of **2a** ($\Delta\epsilon_{364} = +3.9$), which was characteristic of helical poly(aryl isocyanide)s due to the n−π^* transition of the imino group, was also smaller than that of **3a** ($\Delta\epsilon_{364} = +13.0$). Because we have experimental evidence that the chiroptical values of **3a** are increased with an increase in molecular weight of up to approximately $M_w = 15\,000$ and remain constant in a region of higher molecular weight,[7c] the difference in chiroptical properties between **2a** and **3a** is due not to the difference in molecular weight, but to the difference in selectivity for the one-handed helical structure.

To our surprise, the chiroptical values were slightly increased when a solution of **2a** was left at room temperature for a long time. Thus, we monitored the change by measuring the CD spectra. As shown in Figure 1, the CD intensity was gradually increased with time at 80 °C in $CHCl_3$ and reached a constant value of $\Delta\epsilon_{364} = +8.3$. This phenomenon sharply contrasted the CD spectra of **3a** that showed no significant change even at higher temperatures.[7c] Whereas the transition rate of the CD intensity was low at low temperature, the convergent CD intensities were slightly increased as the temperature was decreased (Figure 2). When the solutions of **2a** were cooled to room temperature, the measured CD spectra were identical with each other regardless of the annealing temperature, suggesting that the transition was irreversible and that the increase in the convergent CD intensities was simply due to the temperature dependence of the CD spectrum of the resulting polymer. A similar transition was observed in other organic solvents such as toluene, THF, and dioxane. For example, the specific rotation and the CD intensity were $[\alpha]_D^{20}] = +1038$ and $\Delta\epsilon_{364} = +11.6$, re-

10.1021/ma047883p CCC: $30.25

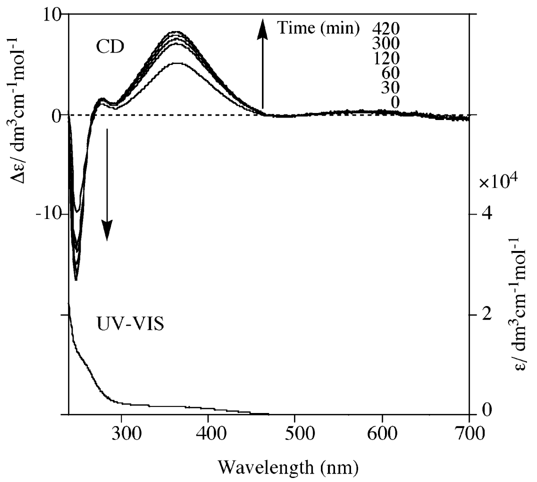


Figure 1. Time-dependent CD spectral changes (in $CHCl_3$, at 80 °C) and the UV−vis spectrum (in $CHCl_3$, at room temperature, before annealing) of polymer **2a**.

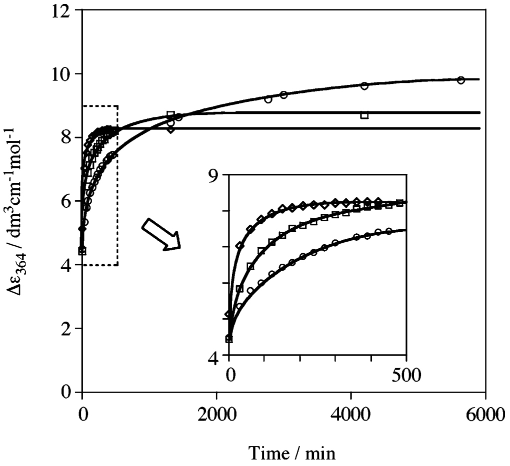


Figure 2. Plots of time-dependent changes of the CD intensity at 364 nm for polymer **2a** (in $CHCl_3$) at 80 (◇), 60 (□), and 40 °C (○). The inset indicates the expansion at the early stages.

spectively, after **2a** was annealed in refluxing THF for 15 h. Because no significant differences were detected in the results of GPC analysis and conventional spectral measurements except for the CD spectra compared to those before annealing, the enhancement of the chiroptical properties must be due to the increase in selectivity for the one-handed helical conformation.

Other chiral poly(aryl isocyanide)s **2b**−**2f** having chiral ester pendants were also prepared by the polymerization with $NiCl_2$ catalyst, and the results are summarized in Table 1.[7e] Although the initial chiroptical values of **2b**−**2e** were smaller than those of analogous polymers **3b**−**3e**, a similar enhancement was observed in these polymers. In contrast, **2f** showed a small specific rotation ($[\alpha]_D^{20} = +11$) and no Cotton effect ($\Delta\epsilon_{364} = \sim 0$), which did not change even after annealing. This observation was consistent with the fact that polymer **3f** also showed small chiroptical values due to its nonhelical structure.

To obtain information on the conformational changes of **2**, we prepared ^{13}C-labeled polymers and examined them by means of ^{13}C NMR spectroscopy. A rather broad signal assignable to the imino carbon of the main chain was observed at δ 161.4 in the ^{13}C NMR spectrum of **2a′** (Figure 3a). Green et al. reported broad and complicated signals of the imino carbons of poly(alkyl isocyanide)s due to the stereoirregularity of the main chain.[4a] The sealed sample tube containing the $C_6D_5CD_3$ solution of **2a′** was heated at 80 °C for 15 h, and then the ^{13}C NMR spectrum was measured under the same conditions after cooling. The signal was slightly shifted to the lower magnetic field (δ 161.8), and the half-width was changed from 208 to 124 Hz (Figure 3b), which was similar to that observed for **3a′** (Figure 3c). Similar changes were observed in the ^{13}C NMR spectra of ^{13}C-labeled polymers **2b′** and **2c′** that showed resonances at approximately δ 162. These results suggested that the conformational change was detectable by ^{13}C NMR spectroscopy using the ^{13}C-labeled polymers.

In the ^{13}C NMR spectrum of **2f ′**, a rather sharp signal due to the imino carbon was observed at δ 163.2 along with two shoulder signals at approximately δ 162 and 161 (Figure 4a). After annealing (80 °C, 15 h), the main signal was slightly increased and the shoulder signals were decreased, as found in Figure 4b, similar to those of **3f′** (Figure 4c). Similar changes were found in the ^{13}C NMR spectrum of achiral polyisocyanide **2g′** with isobutoxycarbonyl groups ($M_w = 24\,700$, $M_w/M_n = 2.52$). Because **2f** and **2g** as well as **3f** and **3g** did not have the one-handed helical structure, the spectral change should be derived from the configurational change of the main chain (syn−anti isomerization of the imino groups), as shown in Scheme 2;[9] that is to say, stereoirregular polyisocyanides were produced with $NiCl_2$ catalyst, and these were isomerized to the thermodynamically stable stereoregular polyisocyanides at high temperature. Recently, Yashima et al. reported that the ^{13}C resonances of the imino carbon in achiral poly[(4-ethoxycarbonyl)phenyl isocyanide] that adopted a nonhelical conformation became sharp when the solution was left to stand at 30 °C for 28 days.[10] On the other hand, the polymerization by using **4** gave stereoregular polymers **3** because the reaction was performed in refluxing THF. Although we have no experimental evidence to indicate whether isotactic or syndiotactic polyisocyanides have been produced, the isotactic polymer seems to be reasonable as the thermodynamically stable form to reduce the steric repulsion among the side groups.

The conformational change in **2a**−**2e** may also be explained from the viewpoint of stereoregularity. The initial selectivity for the one-handed helical structure in **2a**−**2e** is not as high as that in **3a**−**3e** due to their low stereoregularity. The isomerization of the imino group at high temperature, which increased the stereoregularity, led to the increase in the selectivity for the one-handed helical structure. Similar conformational changes, including the isomerization of the imino groups, were also suggested in the induction of the helical structure in poly(4-carboxyphenyl isocyanide)s by chiral amines.[10,11]

In conclusion, we have shown that the selectivity for the one-handed helical structure of polyisocyanides depends on the conditions for the polymerization and reaches similar values by isomerization of the imino groups through annealing. This is the first example showing that the stereoregularity of polyisocyanides has a significant influence on the selectivity for the helical conformation. The results reported herein may be useful for the precise synthesis of helical polyisocyanides.

Experimental Section

All reactions were carried out under an argon atmosphere. All chemicals commercially available were used without

Table 1. Poly(aryl isocyanide)s Having Chiral Alkoxycarbonyl Groups

	polymer	M_w[a]	M_w/M_n[a]	$[\alpha]_D^{20}$ [b]	$\Delta\epsilon_{364}$/dm^3 cm^{-1} mol^{-1} [c]	after annealing[d] $[\alpha]_D^{20}$ [b]	after annealing[d] $\Delta\epsilon_{364}$/dm^3 cm^{-1} mol^{-1} [c]
2a	R = (1*R*,2*S*,5*R*)-menthyl	22 700	2.00	+354	+3.9	+1038	+11.6
2b	R = (1*S*,2*S*,5*R*)-neomenthyl	26 300	2.13	−234	−3.0	−963	−9.9
2c	R = (1*S*,2*R*,5*R*)-isomenthyl	20 000	1.83	−174	−3.0	−948	−10.1
2d	R = (S)-2-octyl	25 500	1.98	−355	−4.0	−886	−8.2
2e	R = (*S*)-2-butyl	27 600	1.74	−376	−4.0	−1038	−8.9
2f	R = (*R*)-3-methylpentyl	67 000	1.62	+11	~0	+8	~0
3a	R = (1*R*,2*S*,5*R*)-menthyl	15 000	1.13	+1070	+13.0	*e*	*e*
3b	R = (1*S*,2*S*,5*R*)-neomenthyl	15 400	1.18	−1280	−12.8	*e*	*e*
3c	R = (1*S*,2*R*,5*R*)-isomenthyl	14 200	1.09	−1060	−13.2	*e*	*e*
3d	R = (*S*)-2-octyl	18 200	1.11	−860	−9.7	*e*	*e*
3e	R = (*S*)-2-butyl	18 100	1.13	−1030	−8.5	*e*	*e*
3f	R = (*S*)-3-methylpentyl	15 700	1.17	−19	~0	*e*	*e*

[a] M_w and M_w/M_n were determined by GPC analysis based on polystyrene standards. [b] $c = 0.1$ in $CHCl_3$. [c] CD spectra were measured in $CHCl_3$ at ambient temperature. [d] Polymers were refluxed in THF for 15 h. [e] The values were not changed by annealing.

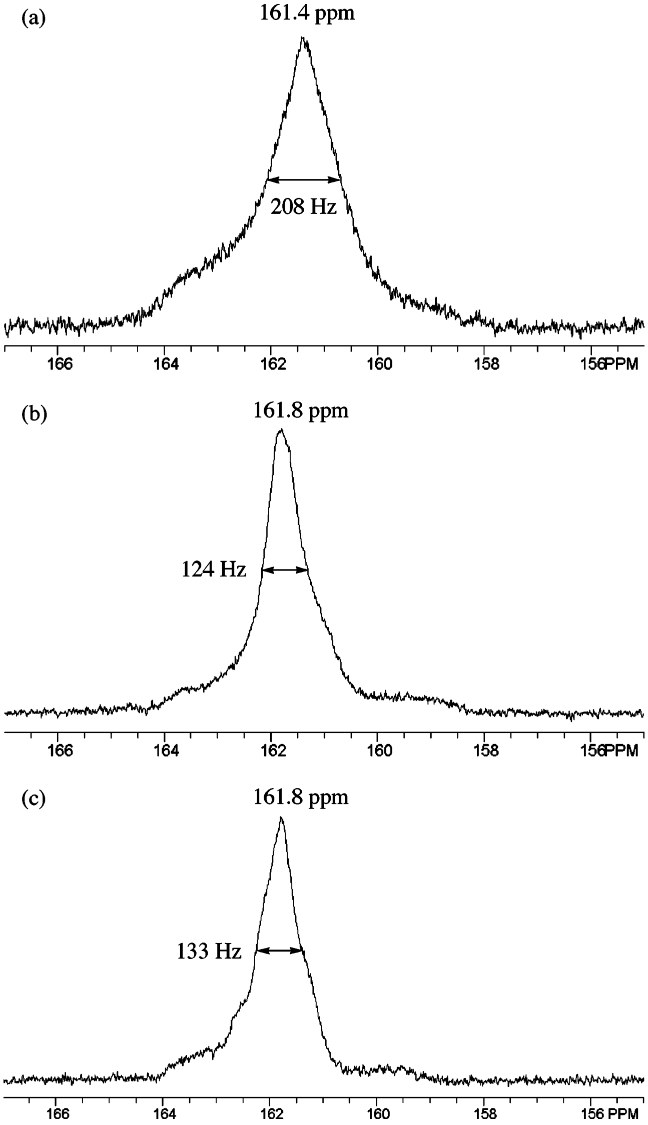


Figure 3. ^{13}C NMR (150.80 MHz, in $C_6D_5CD_3$) spectra of **2a′** and **3a′**. (a) **2a′** before annealing, (b) **2a′** after annealing (80 °C, 15 h), and (c) **3a′**.

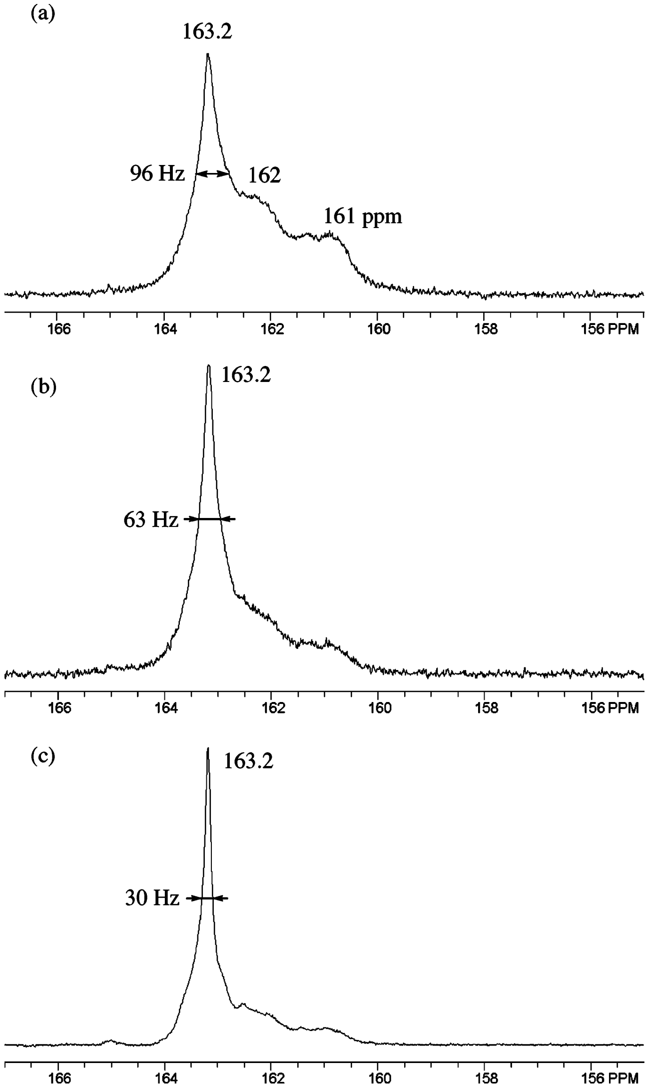
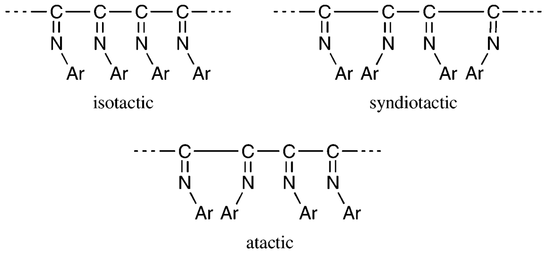


Figure 4. ^{13}C NMR (150.80 MHz, in $C_6D_5CD_3$) spectra of **2f′** and **3f′**. (a) **2f′** before annealing, (b) **2f′** after annealing (80 °C, 15 h), and (c) **3f′**.

further purification. Chiral isocyanide monomer **1a** was prepared as reported previously,[7c] and the other monomers were obtained by a similar method using the corresponding chiral alcohols instead of (1*R*,2*S*,5*R*)-menthol (L-menthol).[7e] ^{13}C atoms were introduced into the isocyanide monomers by using $H^{13}COOH$.

^{13}C NMR spectra were measured on JEOL JNM-LA400 and LA-600 spectrometers using $SiMe_4$ as the internal standard. IR and electronic spectra were recorded on a Perkin-Elmer System 2000 FT-IR and JASCO V-560, respectively. Gel permeation chromatography was performed with a Shimadzu LC-3A and 840 liquid chromatograph using a Shimadzu GPC-8025 column for oligomers and Shimadzu LC-6AD and SPD-

Scheme 2. Stereoregularity in Polyisocyanide



10A using Shimadzu GPC-805, -804, and -8025 columns for high-molecular-weight polymers. Specific rotation and CD spectra were measured with JASCO DIP-1000 and JASCO J-725 equipped with high-temperature cell JASCO TC-700, respectively. Elemental analyses were performed at The Material Analysis Center, ISIR, Osaka University.

Polymerization of *p*-(1*R*,2*S*,5*R*)-Menthyloxycarbonylphenyl Isocyanide (1a). To a solution of *p*-(1*R*,2*S*,5*R*)-menthyloxycarbonylphenyl isocyanide **(1a)** (650 mg, 2.3 mmol) in methanol (15 mL) was added $NiCl_2·6H_2O$ (5.4 mg, 0.023 mmol) at room temperature. The reaction mixture was stirred for 20 h, and the resulting precipitate was collected and washed with methanol to give a yellow solid (**2a**) (397 mg, 61%). IR (cm^{-1}, KBr): 1719 ($\nu_{C=O}$), 1651 ($\nu_{C=N}$), 1269 (ν_{C-O}). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.5 (*C*OOC), 160.5 (*C*N), 150.7 (Ar−*C*), 129.7 (Ar−*C*), 128.0 (Ar−*C*), 119.1(Ar−*C*), 117.4 (Ar−*C*), 74.4 (menthyl−*C*H), 47.0 (menthyl−*C*H), 40.6 (menthyl−*C*H_2), 34.3 (menthyl−*C*H_2), 31.5 (menthyl−*C*H), 26.5 (menthyl−*C*H), 23.7 (menthyl−*C*H_2), 22.1 (menthyl−*C*H_3), 20.7 (menthyl−*C*H_3), 16.9 (menthyl−*C*H_3). Anal. Calcd for $[C_{18}H_{23}NO_2]_n$: C, 75.76; H, 8.12; N 4.91. Found: C, 75.51; H, 8.11; N, 4.86.

Polymerization of *p*-(1*S*,2*S*,5*R*)-Neomenthyloxycarbonylphenyl Isocyanide (1b), *p*-(1*S*,2*R*,5*R*)-Isomenthlyoxycarbonylphenyl Isocyanide (1c), *p*-(*S*)-2-Octyloxycarbonylphenyl Isocyanide (1d), *p*-(*S*)-2-Butoxycarbonylphenyl Isocyanide (1e), *p*-(*R*)-3-Methylpentyloxycarbonylphenyl Isocyanide (1f), and *p*-Isobutoxycarbonylphenyl Isocyanide (1g). These reactions were performed by a method similar to that for **1a** to give yellow solids.

2b: 40% yield. IR (cm^{-1}, KBr): 1715 ($\nu_{C=O}$), 1651 ($\nu_{C=N}$), 1269 (ν_{C-O}). ^{13}C NMR ($CDCl_3$,100 MHz): δ 164.6 (*C*OOC), 161.0 (*C*N), 151.2 (Ar−*C*), 129.8 (Ar−*C*), 128.5 (Ar−*C*), 118.3 (Ar−*C*), 71.6 (neomenthyl−*C*H), 47.1 (neomenthyl−*C*H), 39.6 (neomenthyl−*C*H_2), 34.7 (neomenthyl−*C*H_2), 30.5 (neomenthyl−*C*H), 29.1 (neomenthyl−*C*H), 27.3 (neomenthyl−*C*H_2), 25.6 (neomenthyl−*C*H_3), 22.4 (neomenthyl−*C*H_3), 20.9 (neomenthyl−*C*H_3). Anal. Calcd for $[C_{18}H_{23}NO_2]_n$: C, 75.76; H, 8.12; N, 4.91. Found: C, 74.38; H, 8.22; N, 5.32.

2c: 43% yield. IR (cm^{-1}, KBr): 1715 ($\nu_{C=O}$), 1651 ($\nu_{C=N}$), 1276 (ν_{C-O}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.3 (*C*OOC), 160.3 (*C*N), 150.8 (Ar−*C*), 130.8 (Ar−*C*), 129.9 (Ar−*C*), 117.2 (Ar−*C*), 72.4 (isomenthyl−*C*H), 45.6 (isomenthyl−*C*H), 35.6 (isomenthyl−*C*H_2), 29.9 (isomenthyl−*C*H_2), 27.7 (isomenthyl−*C*H), 26.4 (isomenthyl−*C*H), 21.0 (isomenthyl−*C*H_2), 20.7 (isomenthyl−*C*H_2), 20.3 (isomenthyl−*C*H_3), 19.4 (isomenthyl−*C*H_3). Anal. Calcd for $C_{18}H_{23}$ NO_2: C, 75.76; H, 8.12; N, 4.91. Found: C, 75.53; H, 8.28; N, 5.14.

2d: 68% yield. IR (cm^{-1}, KBr): 1716 ($\nu_{C=O}$), 1653 ($\nu_{C=N}$), 1275 (ν_{C-O}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.6 (*C*OOC), 161.9 (*C*N), 150.5 (Ar−*C*), 129.8 (Ar−*C*), 128.2 (Ar−*C*), 117.0 (Ar−*C*), 71.7 (octyl−*C*H), 35.8 (octyl−*C*H_2), 31.7 (octyl−*C*H_2), 29.2 (octyl−*C*H_2), 25.4 (octyl−*C*H_2), 22.6 (octyl−*C*H_2), 19.8 (octyl−*C*H_3), 14.0 (octyl−*C*H_3). Anal. Calcd for $[C_{18}H_{21}NO_2]_n$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.13; H, 8.22; N 5.67.

2e: 52% yield. IR (cm^{-1}, KBr): 1715 ($\nu_{C=O}$), 1620 ($\nu_{C=N}$), 1276 (ν_{C-O}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.8 (*C*OOC), 161.9 (*C*N), 150.5 (Ar−*C*), 129.9 (Ar−*C*), 128.1 (Ar−*C*), 117.1 (Ar−*C*), 72.7 (butyl−*C*H), 28.9 (butyl−*C*H_2), 19.4 (butyl−*C*H_3), 9.7 (butyl−*C*H_3). Anal. Calcd for $[C_{12}H_{13}NO_2]_n$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.26; H, 6.29; N, 6.90.

2f′: 64% yield. IR (cm^{-1}, KBr): 1720 ($\nu_{C=O}$), 1604 ($\nu_{C=N}$), 1270 (ν_{C-O}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.8 (*C*OOC), 162.3 (*C*N), 150.2 (Ar−*C*), 129.7 (Ar−*C*), 127.3 (Ar−*C*), 117.0 (Ar−*C*), 63.4 (methylpentyl−*C*H), 35.2 (methylpentyl−*C*H_3), 31.4 (methylpentyl−*C*H_2), 29.4 (methylpentyl−*C*H_2), 19.3 (methylpentyl−*C*H_3), 11.2 (methylpentyl−*C*H_3). Anal. Calcd for $[C_{11}{}^{13}CH_{13}NO_2]_n$: C, 72.81; H, 7.38; N, 6.03. Found: C, 72.88; H, 7.41; N, 6.11.

2g′: 86% yield. IR (cm^{-1}, KBr): 1715 ($\nu_{C=O}$), 1650 ($\nu_{C=N}$), 1269 (ν_{C-O}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.9 (*C*OOC), 162.3 (*C*N), 150.4 (Ar−*C*), 129.6 (Ar−*C*), 127.3 (Ar−*C*), 117.0 (Ar−*C*), 70.6 (isobutyl−*C*H_2), 27.8 (isobutyl−*C*H), 19.1 (isobutyl−*C*H_3). Anal. Calcd for $[C_{11}{}^{13}CH_{13}NO_2]_n$: C, 71.05; H, 6.42; N, 6.85. Found: C, 70.49; H, 6.55; N, 6.69.

Acknowledgment. This work was supported by a Grand-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology. We thank the members of the Material Analysis Center, ISIR, Osaka University, for spectral measurements and microanalyses.

References and Notes

(1) For recent reviews, see: (a) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893. (b) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013. (c) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039. (d) Green, M. M.; Cheon, K.-S.; Yang, S.-Y.; Park, J.-W.; Swansburg, S.; Liu, W. *Acc. Chem. Res.* **2001**, *34*, 672. (e) Yashima, E.; Maeda, K.; Nishimura, T. *Chem.—Eur. J.* **2004**, *10*, 42.

(2) For reviews, see: (a) Millich, F. *Chem. Rev.* **1972**, *72*, 101. (b) Drenth, W.; Nolte, R. J. M. *Acc. Chem. Res.* **1979**, *12*, 30. (c) Nolte, R. J. M. *Chem. Soc. Rev.* **1994**, *23*, 11.

(3) (a) Kollmar, C.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 8230. (b) Clericuzio, M.; Alagona, G.; Ghio, C.; Salvadori, P. *J. Am. Chem. Soc.* **1997**, *119*, 1059.

(4) (a) Green, M. M.; Gross, R. A.; Schilling, F. C.; Zero, K.; Crosby, C., III. *Macromolecules* **1988**, *21*, 1839. (b) Pini, D.; Iuliano, A.; Salvadori, P. *Macromolecules* **1992**, *25*, 6059.

(5) (a) van Beijnen, A. J. M.; Nolte, R. J. M.; Drenth, W.; Hezemans, A. M. F.; van de Coolwijk, P. J. F. M. *Macromolecules* **1980**, *13*, 1386. (b) van Beijnen, A. J. M.; Nolte, R. J. M.; Naaktgeboren, A. J.; Zwikker, J. W.; Drenth, W.; Hezemans, A. M. F. *Macromolecules* **1983**, *16*, 1679. (c) Amabilino, D. B.; Ramos, E.; Serrano, J.-L.; Sierra, T.; Veciana, J. *J. Am. Chem. Soc.* **1998**, *120*, 9126.

(6) (a) Onitsuka, K.; Joh, T.; Takahashi, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 851. (b) Onitsuka, K.; Yanai, K.; Takei, F.; Joh, T.; Takahashi, S. *Organometallics* **1994**, *13*, 3862.

(7) (a) Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1554. (b) Takei, F.; Onitsuka, K.; Takahashi, S. *Polym. J.* **1999**, *31*, 1029. (c) Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. *Chem.—Eur. J.* **2000**, *6*, 983. (d) Takei, F.; Onitsuka, K.; Takahashi, S. *Polym. J.* **2000**, *32*, 524. (e) Takei, F.; Hayashi, H.; Onitsuka, K.; Takahashi, S. *Polym. J.* **2001**, *33*, 310. (f) Takei, F.; Hayashi, H.; Onitsuka, K.; Kobayashi, N.; Takahashi, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 4092. (g) Hida, N.; Takei, F.; Onitsuka, K.; Shiga, K.; Asaoka, S.; Iyoda, T.; Takahashi, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 4349.

(8) (a) Nolte, R. J. M.; Stephany, R. W.; Drenth, W. *Pays-Bas* **1973**, *92*, 83. (b) King, R. B.; Greene, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 907.

(9) Curtin, D. Y.; Grubbs, E. J.; McCarty, C. G. *J. Am. Chem. Soc.* **1966**, *88*, 2775.

(10) Ishikawa, M.; Maeda, K.; Yashima, E. *J. Am. Chem. Soc.* **2002**, *124*, 7448.

(11) Ishikawa, M.; Maeda, K.; Mitsutsuji, Y.; Yashima, E. *J. Am. Chem. Soc.* **2004**, *126*, 732.

MA047883P