Induction of Screw-Sense in Poly(isocyanide)s by Random Copolymerization between Chiral and Achiral Isocyanides Using Pd-Pt μ -Ethyndiyl Dinuclear Complex as an Initiator

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 December 27, 1999)

KEY WORDS Poly(isocyanide)s / Helical Polymer / Random Copolymerization / Transition Metal Complex /

Atropisomerism in macromolecules due to a restricted rotation of C–C single bonds in a main chain gives rise to a helical structure, which is one of the most important and fundamental secondary structure of macromolecules and is closely related to their function characteristic to biomacromolecules.¹ However, such artificial polymers that maintain a stable helical structure in solution are still limited.^{2–4} Poly(isocyanide)s with bulky substituents adopt a stable helical structure and usually exist in a 1 : 1 mixture of two conformational isomers with right-handed (*P*) and left-handed (*M*) helices.^{5,6} Although it is well-known that optically active poly(isocyanide)s having a single-handed helical conformation predominantly may be obtained by polymerization of chiral isocyanides,⁷ some attempts to prepare single-handed helical polymers from achiral isocyanides have been made by a transition metal catalysis in recent years.^{8–11}

We have previously reported that dinuclear μ -ethyndiyl complex **1** is effective for the living polymerization of aryl isocyanides.¹² Recently, the living nature of this system was successfully applied to a novel screw-sense selective (SSS) polymerization of achiral isocyanides using a block copolymerization technique.¹³ Chiral oligomer complexes prepared from **1** and chiral isocyanides initiate the SSS polymerization of achiral isocyanides possessing a bulky substituent to give single-handed helical polymers predominantly. However, the SSS polymerization of achiral isocyanides with small substituents was not achieved by this block copolymerization method, since poly(isocyanide)s with small substituents do not keep a helical structure in solution. We present herein the SSS polymerization of achiral isocyanides having small substituents by random copolymerization with a chiral isocyanide to give a one-handed helical polymer predominantly. Although random copolymers of chiral and achiral isocyanides have been prepared by use of a Ni catalyst, the substituents on chiral and achiral isocyanides are quite different from each other.⁸ It may be difficult to estimate the selectivity of the helical structures of such random copolymers, since the optical rotations and the $\Delta\epsilon$ values in CD spectra are sensitive to the substituents on poly(isocyanide)s.^{13b} In this study, we used chiral and achiral aryl isocyanides

having alkoxy-carbonyl groups at *p*-position to exclude the effect of substituents on the optical rotations and the $\Delta\epsilon$ values.

RESULTS AND DISCUSSION

A THF solution of complex **1** was added to a THF solution containing 50 equivalents of *p*-(*l*)-menthoxy-carbonylphenyl isocyanide (*l*)-**2** and 50 equivalents of *p*-cyclohexyloxy-carbonylphenyl isocyanide (**3**). After reflux for 15 h, all isocyanide monomers were consumed to give copolymer (*l*)-**4**₅₀₋₅₀ (*n* = 50, *m* = 50, *M_n* = 12500, *M_w*/*M_n* = 1.14) quantitatively. The elemental analysis supported the composition of (*l*)-**2** and **3** in the resulting polymer (*l*)-**4**₅₀₋₅₀ to be 1 : 1. There was little difference in the rate of homopolymerization between (*l*)-**2** (*k* = $2.60 \times 10^{-5} \text{ s}^{-1}$, 338 K) and **3** (*k* = $1.99 \times 10^{-5} \text{ s}^{-1}$, 338 K) and the consumption rates of both isocyanide monomers were confirmed to be almost equal in this copolymerization, suggesting that (*l*)-**4**₅₀₋₅₀ is a random copolymer. As shown in Figure 1, the CD spectrum of (*l*)-**4**₅₀₋₅₀ exhibited a strong positive Cotton effect at 364 nm, which is characteristic to helical chiral poly(aryl isocyanide)s^{7,8} and is similarly observed for homopolymer (*l*)-**5**₁₀₀ prepared from (*l*)-**2** having a stable one-handed helical conformation predominantly.^{13b} The $\Delta\epsilon$ value of (*l*)-**4**₅₀₋₅₀ at 364 nm is smaller than that of homopolymer (*l*)-**5**₁₀₀, but larger than that of block copolymer (*l*)-**6**₅₀₋₅₀ between (*l*)-**2** and **3** with the same composition. Random copolymer (*l*)-**4**₅₀₋₅₀ showed a large positive optical rotation ($[\alpha]_D^{20} = +890^\circ$, *c* 0.1, CHCl₃), which is slightly smaller than that of homopolymer (*l*)-**5**₁₀₀ ($[\alpha]_D^{20} = +1079^\circ$, *c* 0.1, CHCl₃) with the same degree of polymerization, but higher than that of block copolymer (*l*)-**6**₅₀₋₅₀ ($[\alpha]_D^{20} = +599^\circ$, *c* 0.1, CHCl₃). These data clearly show that random copolymer (*l*)-**4**₅₀₋₅₀ maintains one-handed helical structure with the same screw-sense as (*l*)-**5**₁₀₀ in solution predominantly though the selectivity of screw-sense for (*l*)-**4**₅₀₋₅₀ is slightly lower than (*l*)-**5**₁₀₀. Copolymerization between 50 equivalents each of (*d*)-**2** and **3** by **1** also produced random copolymer (*d*)-**4**₅₀₋₅₀, which exhibited the CD spectrum with a symmetrical pattern to that of (*l*)-**4**₅₀₋₅₀ (Figure 1) and a large negative optical rotation ($[\alpha]_D^{20} = -909^\circ$, *c* 0.10, CHCl₃). It may be of interest that achiral isocyanide monomer **3** produce a one-handed helical

[†]To whom correspondence should be addressed.

Scheme 1.

Table I. Copolymerization of chiral (Ar^{*}NC) and achiral isocyanides (ArNC) using complex **1** as an initiator

Entry no.	Ar [*] NC	<i>n</i>	ArNC	<i>m</i>	Random copolymer (Homopolymer)					Block copolymer				
					Polymer	$M_n \times 10^{-3}$ ^a	M_w/M_n	$[\alpha]_D^{20}$ ^b deg	$\Delta\epsilon_{364}$ ^c dm ³ cm ⁻¹ mol ⁻¹	Polymer	$M_n \times 10^{-3}$ ^a	M_w/M_n	$[\alpha]_D^{20}$ ^b deg	$\Delta\epsilon_{364}$ ^c dm ³ cm ⁻¹ mol ⁻¹
1			3	100	7₁₀₀	13.3	1.13	0	0	— ^d	— ^d	— ^d	— ^d	— ^d
2	(<i>l</i>)- 2	30	3	70	(<i>l</i>)- 4₃₀₋₇₀	12.0	1.15	582	5.12	(<i>l</i>)- 6₃₀₋₇₀	13.0	1.15	393	3.46
3	(<i>l</i>)- 2	50	3	50	(<i>l</i>)- 4₅₀₋₅₀	12.5	1.14	890	9.40	(<i>l</i>)- 6₅₀₋₅₀	12.7	1.13	599	6.70
4	(<i>l</i>)- 2	70	3	30	(<i>l</i>)- 4₇₀₋₃₀	12.5	1.12	1054	11.58	(<i>l</i>)- 6₇₀₋₃₀	12.9	1.13	832	9.86
5	(<i>l</i>)- 2	100			(<i>l</i>)- 5₁₀₀	12.9	1.12	1079	13.01	— ^d	— ^d	— ^d	— ^d	— ^d
6			8	100	11₁₀₀	— ^e	— ^e	— ^e	— ^e	— ^d	— ^d	— ^d	— ^d	— ^d
7	(<i>l</i>)- 2	30	8	70	(<i>l</i>)- 9₃₀₋₇₀	12.9	1.13	565	4.51	(<i>l</i>)- 10₃₀₋₇₀	13.1	1.15	441	3.58
8	(<i>l</i>)- 2	50	8	50	(<i>l</i>)- 9₅₀₋₅₀	13.1	1.12	855	7.55	(<i>l</i>)- 10₅₀₋₅₀	13.0	1.14	685	5.95
9	(<i>l</i>)- 2	70	8	30	(<i>l</i>)- 9₇₀₋₃₀	12.9	1.11	1083	10.13	(<i>l</i>)- 10₇₀₋₃₀	13.6	1.12	885	8.29
10	(<i>d</i>)- 2	30	3	70	(<i>d</i>)- 4₃₀₋₇₀	12.6	1.13	-552	-5.92	(<i>d</i>)- 6₃₀₋₇₀	12.8	1.12	-393	-3.65
11	(<i>d</i>)- 2	50	3	50	(<i>d</i>)- 4₅₀₋₅₀	12.7	1.13	-909	-9.07	(<i>d</i>)- 6₅₀₋₅₀	13.1	1.12	-629	-5.93
12	(<i>d</i>)- 2	70	3	30	(<i>d</i>)- 4₇₀₋₃₀	12.0	1.15	-1014	-12.24	(<i>d</i>)- 6₇₀₋₃₀	13.6	1.12	-878	-9.28
13	(<i>d</i>)- 2	100			(<i>d</i>)- 5₁₀₀	13.4	1.12	-1054	-12.59	— ^d	— ^d	— ^d	— ^d	— ^d

^a By GPC analyses using polystyrene standard. ^b CHCl₃, *c* 0.1. ^c CD spectra were measured in CHCl₃ at ambient temperature. The $\Delta\epsilon$ values are based on the molecular mass of an isocyanide monomer unit. ^d See the column of random copolymer. ^e Molecular weight and specific rotation could not be measured due to low solubility.

polymer predominantly by random copolymerization with (*l*)-**2** though the homopolymer of **3** do not keep a helical structure.^{13b} Nolte and Drenth have already reported that copolymerization between chiral and achiral isocyanides by a Ni catalyst gives one-handed helical poly(isocyanide)s.⁸ The helical sense of the resulting polymer in their system, however, is opposite to that preferred by the homopolymer of chiral isocyanides since the chiral isocyanides having a low polymerization rate depress the growth of helix with the same screw sense as that of the homopolymer of chiral isocyanide. On the other hand, the copolymer prepared in this study has the same screw sense as that of the chiral homopolymer because the screw-sense of the main chain is governed by thermodynamic control.^{13b}

The random copolymerization between chiral and achiral isocyanides in several molar ratios was performed and the results are summarized in Table I along with the results of block copolymerization.^{13b} In all cases

Figure 1. CD spectra of random and block copolymers, and chiral homopolymers.

Figure 2. Plots of optical rotation vs. content of chiral isocyanides (*l*- and *d*-)**2** in random copolymers (*l*- and *d*-)**4_{n-m}** (□, ■), and block copolymers (*l*- and *d*-)**6_{n-m}** (○, ●).

the polymerization proceeded smoothly to give random copolymers **4** and **9** quantitatively, of which the molecular weights are almost same since all chiral and achiral isocyanide monomers employed here have an almost same molecular weight. The incorporation of chiral isocyanides (*l*- and *d*-)**2** in the resulting polymers depends on the initial molar ratio of isocyanide monomers. It is noteworthy that all the random copolymers show a large optical rotation than the corresponding block copolymers (Figure 2). The optical rotation of the random and block copolymers prepared in this study is represented as a function of the molar incorporation ratio of the chiral monomers. In block copolymers the polymer block composed of chiral isocyanides (*l*- and *d*-)**2** maintain a one-handed helix predominantly, while the block of achiral isocyanides **3** and **8** does not keep the regular helical structure due to small substituents.^{13b} Therefore, the $[\alpha]_D$ value of block copolymers proportionally increases with increase in the molar ratio of the chiral monomers. In contrast, optical rotation of random polymers are out of proportion to the molar ratio of chiral/achiral isocyanides with a convex deviation from the linearity. Typically, random copolymers prepared from chiral and achiral isocyanides in a molar ratio of 70 : 30 show the almost same optical rotation as the homopolymer of chiral isocyanides. A positive nonlinear effect was also observed for the Cotton effect at 364 nm in the CD spectra of random copolymers. Similar phenomena have been observed in random copolymerization between chiral and achiral isocyanates.¹⁴ Recently we also found the positive nonproportional relationship between the optical rotations of resulting polymers and the optical purity of monomers in the polymerization of **2**.¹⁵

A living nature enables to control the incorporation of a chiral monomer as well as the molecular weight of resulting polymers. Our system may be, therefore, suitable to investigate the induction of screw-sense in random copolymers between chiral and achiral isocyanides, and may provide a convenient method for the synthesis of a variety of helical chiral poly(isocyanide)s which have potentials to serve as unique functional materials.

Acknowledgments. This work was supported by Grant-in-Aid for Scientific Research on Priority Areas, "New Polymers and Their Nano-Organized Systems" (No. 277/08246103) from the Ministry of Education, Science, Sports and Culture.

REFERENCES

- (a) O. Vogl and G. D. Jaycox, *CHEMTECH*, **16**, 698 (1986). (b) G. Wulff, *Angew. Chem., Int. Ed. Engl.*, **28**, 21 (1989). (c) Y. Okamoto and T. Nakano, *Chem. Rev.*, **94**, 349 (1994). (d) A. E. Rowan and R. J. M. Nolte, *Angew. Chem., Int. Ed. Engl.*, **37**, 63 (1998).
- (a) T. Nakano, Y. Okamoto, and K. Hatada, *J. Am. Chem. Soc.*, **114**, 1318 (1992). (b) Y. Okamoto, M. Nishikawa, T. Nakano, E. Yashima, and K. Hatada, *Macromolecules*, **28**, 5135 (1995).
- (a) M. Goodman and S.-c. Chen, *Macromolecules*, **3**, 398 (1970). (b) A. J. Bur and L. J. Fetters, *Chem. Rev.*, **76**, 727 (1976). (c) M. M. Green, N. C. Peterson, T. Sato, A. Teramoto, R. Cook, and S. Lifson, *Science*, **268**, 1860 (1995).
- (a) M. Fujiki, *J. Am. Chem. Soc.*, **116**, 6017 (1994). (b) K. Obata, C. Kakuto, and M. Kira, *J. Am. Chem. Soc.*, **119**, 11345 (1997).
- (a) F. Millich, *Chem. Rev.*, **72**, 101 (1972). (b) F. Millich, *Adv. Polym. Sci.*, **19**, 117 (1975). (c) W. Drenth and R. J. M. Nolte, *Acc. Chem. Res.*, **12**, 30 (1979). (d) R. J. M. Nolte, *Chem. Soc. Rev.*, **23**, 11 (1994).
- (a) M. M. Green, R. A. Gross, F. C. Schilling, K. Zero, and C. Crosby III, *Macromolecules*, **21**, 1839 (1988). (b) C. Kollmar and R. Hoffman, *J. Am. Chem. Soc.*, **112**, 8230 (1990). (c) M. Clericuzio, G. Alagona, C. Ghio, and P. Salvadori, *J. Am. Chem. Soc.*, **119**, 1059 (1997).
- (a) F. Millich and G. K. Baker, *Macromolecules*, **2**, 122 (1969). (b) A. J. M. van Beijnen, R. J. M. Nolte, W. Drenth, and A. M. F. Hezemans, *Tetrahedron*, **32**, 2017 (1976). (c) A. J. M. van Beijnen, R. J. M. Nolte, W. Drenth, A. M. F. Hezemans, and P. J. F. M. van de Coolwijk, *Macromolecules*, **13**, 1386 (1980). (d) A. J. M. van Beijnen, R. J. M. Nolte, A. J. Naaktgeboren, J. M. Zwikker, W. Drenth, and A. M. F. Hezemans, *Macromolecules*, **16**, 1679 (1983). (e) D. Pini, A. Iuliano, and P. Salvadori, *Macromolecules*, **25**, 6059 (1992). (f) D. B. Amabilino, E. Ramos, J.-L. Serrano, T. Sierra, and J. Veciana, *J. Am. Chem. Soc.*, **120**, 9126 (1998).
- P. C. J. Kamer, M. C. Cleij, R. J. M. Nolte, T. Harada, A. M. F. Hezemans, and W. Drenth, *J. Am. Chem. Soc.*, **110**, 1581 (1988).
- P. C. J. Kamer, R. J. M. Nolte, and W. Drenth, *J. Am. Chem. Soc.*, **110**, 6818 (1988).
- (a) Y. Ito, E. Ihara, and M. Murakami, *Angew. Chem., Int. Ed. Engl.*, **31**, 1509 (1992). (b) Y. Ito, E. Ihara, M. Murakami, and M. Sisido, *Macromolecules*, **25**, 6810 (1992). (c) Y. Ito, T. Miyake, S. Hatano, R. Shima, T. Ohara, and M. Sugimoto, *J. Am. Chem. Soc.*, **120**, 11880 (1998).
- T. J. Deming and B. M. Novak, *J. Am. Chem. Soc.*, **114**, 7926 (1992).
- (a) K. Onitsuka, T. Joh, and S. Takahashi, *Angew. Chem., Int. Ed. Engl.*, **31**, 851 (1992). (b) K. Onitsuka, K. Yanai, F. Takei, T. Joh, and S. Takahashi, *Organometallics*, **13**, 3862 (1994).
- (a) F. Takei, K. Yanai, K. Onitsuka, and S. Takahashi, *Angew. Chem., Int. Ed. Engl.*, **35**, 1554 (1996). (b) F. Takei, K. Yanai, K. Onitsuka, and S. Takahashi, *Chem. Eur. J.*, **6**, 983 (2000).
- (a) M. M. Green, M. P. Reidy, R. J. Johnson, G. Darling D. J. O'Leary, and G. Willson, *J. Am. Chem. Soc.*, **111**, 6452 (1989). (b) K. Maeda and Y. Okamoto, *Macromolecules*, **31**, 1046 (1998).
- F. Takei, K. Onitsuka, and S. Takahashi, *Polym. J.*, **31**, 1029 (1999).