7752 *Macromolecules* **2008**, *41*, 7752−7754

Notes

Anomalous Stiff Backbones of Helical Poly(phenyl isocyanide) Derivatives

Kento Okoshi,*[,†,‡] Kanji Nagai,[†,§] Takashi Kajitani,[†] Shin-ichiro Sakurai,[†] and Eiji Yashima*[,†,§]

Yashima Super-structured Helix Project, Exploratory Research for Advanced Technology, Japan Science and Technology Agency, Japan, and Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan

Received July 16, 2008
Revised Manuscript Received August 8, 2008

Introduction

Fully synthetic helical polymers with an excess one-handed helical sense have recently drawn much attention because of implications for biological helices and functions as well as their possible applications as chiral materials.[1] Rodlike synthetic helical polymers are particularly interesting, since they often form chiral liquid crystals (LCs) in concentrated solutions or in a melt,[2] as observed in biological polymers, such as DNA,[3] polysaccharides,[4] and polypeptides,[5] which adopt a stiff rodlike structure with a controlled helix-sense stabilized by intra- and/or intermolecular hydrogen-bonding networks. Such intramolecular hydrogen bonds have been utilized in constructing biomimetic helical polymers, such as polyisocyanopeptides,[1d,2c,6] amino acid-bound polyacetylenes,[7,8] and foldamers.[9]

Recently, we reported a unique polyisocyanide (poly-**1** in Chart 1) prepared by the polymerization of an enantiomerically pure phenyl isocyanide bearing an L- or D-alanine pendant with a long *n*-decyl chain with an achiral $NiCl_2$ catalyst, whose helical sense (right- or left-handed helix) could be controlled by the polymerization solvent and temperature. The resulting diastereomeric poly-**1**s showing intense first Cotton effects ($\Delta\varepsilon_{1st} = -11.0$ to $+8.14$) at the imino chromophore regions of the polymer backbones (ca. 360 nm) formed lyotropic cholesteric LCs with opposite twist senses in concentrated solutions due to their main-chain stiffness arising from the intramolecular hydrogen-bonding between the pendant amide groups.[10]

In order to explore the effect of the chiral pendant structure on the chiroptical properties of the polyisocyanide, a series of optically active polyisocyanides bearing different optically active functional groups, such as L-lactic acid (poly-**2**), L-phenylalanine (poly-**3**), and L-alaninol (poly-**4**) residues, with the same *n*-decyl chain as the pendants were prepared in various solvents at different temperatures.[11] In sharp contrast to poly-**1**, poly-**2** and poly-**4** exhibited weak Cotton effects, while poly-**3** showed rather intense positive Cotton effects, independent of the polymerization conditions. We then concluded that the helical senses and the excess of one helical sense of the polyisocyanides were governed by specific interactions (intermolecular hydrogen-bonding and steric effect) occurring between the pendant residues of the growing chain end and monomers during the propagation reaction, which might be influenced by the solvent polarity and temperature of the polymerization process.

Table 1. Chiroptical Properties of Helical Polyisocyanides[a]

polymer	$M_n \times 10^{-4}$ [b]	M_w/M_n [b]	$[\alpha]^{25}_D$ [c]	$\Delta\varepsilon_{1st}$ [c]	q (nm)[d]
poly-**1**[e]	19.0	1.92	−814	−11.0	220
poly-**2**	17.3	2.17	−243	−3.21	30.8
poly-**3**	19.8	2.08	+688	+8.94	103
poly-**4**	20.8	1.53	−273	−1.28	81.8

[a] Obtained by polymerization with $NiCl_2 \cdot 6H_2O$ in toluene at 100 °C (cited from ref 11). [b] Determined by SEC-MALS measurements with THF containing TBAB (0.1 wt %) as the eluent. [c] Measured in chloroform at 25 °C. [d] Estimated by SEC-MALS measurements with the wormlike chain model. [e] Obtained by annealing a toluene solution of the polymer at 100 °C for 6 days.[10]

Although the fact that poly-**1** formed a cholesteric LC in concentrated solutions, which indicated its rigid rodlike feature of the main chain, the persistence length *q*, a useful measure to evaluate the stiffness of rodlike polymers, has not been estimated. We now show the persistence lengths of a series of helical polyisocyanides bearing different optically active pendant groups (poly-**1**−poly-**4**) and describe the effect of the chiral pendant structures on their main-chain stiffness. We found that poly-**1** possesses an extremely long *q* value of 220 nm, which is the highest among all synthetic helical polymers reported so far.[12]

Results and Discussion

Poly-**1**−poly-**4** were prepared according to previously reported methods by the polymerization of the corresponding monomers with an achiral $NiCl_2$ catalyst under the experimental conditions that yielded helical polyisocyanides with high molecular weights ($M_n = 17.3{-}20.8 \times 10^4$) showing almost the highest Cotton effect intensities (Table 1),[10,11] although the $\Delta\varepsilon_{1st}$ values reflecting the excess of one helical sense were different from each other.[11]

The *q* values of poly-**1**−poly-**4** were then estimated on the basis of the wormlike chain model,[16] which can be described as an analytical function of the molecular weight (M_w) and the radius of gyration (S) if the *q* values and the molar mass per unit contour length (M_L), which eventually leads to the monomer unit height (h), are given. The radii of gyration (S) of (poly-**1**−poly-**4**) in tetrahydrofuran (THF) containing 0.1 wt % tetra-*n*-butylammonium bromide (TBAB) were measured as a function of M_w using size exclusion chromatography (SEC) equipped with multiangle laser light scattering (MALS) and refractive index detectors in series (Figure 1).

The solid curves in the plots were calculated using the parameters determined from the fits of the unperturbed wormlike chain model over the entire M_w studied range, and are represented by the theoretical values of $\langle S^2\rangle^{0.5}$. The calculated *h* values of poly-**1**−poly-**4** are in agreement with the reported value (0.087 nm) of poly-**1** determined by X-ray structural analysis,[17] indicating that these polymers appear to take a similar helical conformation irrespective of the structures of the chiral pendant groups.

The calculated *q* value of poly-**1** is 220 nm, which is unprecedentedly long and the highest value among all synthetic

---

* To whom correspondence should be addressed. E-mail: kokoshi@polymer.titech.ac.jp; yashima@apchem.nagoya-u.ac.jp.
[†] Japan Science and Technology Agency.
[‡] Present address: Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8552, Japan.
[§] Nagoya University.

10.1021/ma8015954 CCC: $40.75

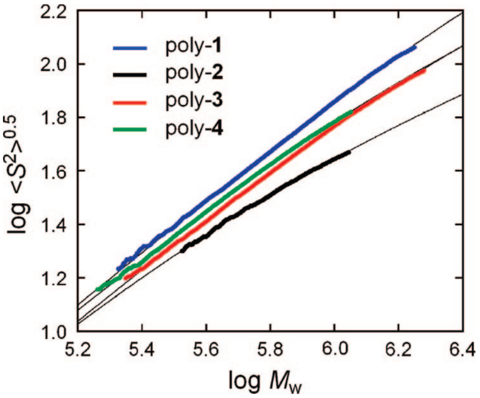


Figure 1. Double-logarithmic plots of the radius of gyration versus the molecular weight of poly-**1** (blue points), poly-**2** (black points), poly-**3** (red points), and poly-**4** (green points) in THF containing TBAB (0.1 wt %) obtained by SEC-MALS measurements at 40 °C. Solid curves (black lines) were obtained on the basis of the wormlike chain theory and fit well with the experimental data. The evaluated parameters are as follows: $q = 220$ nm, $M_{\mathrm{L}} = 3577$, $h = 0.10$ nm for poly-**1**; $q = 30.8$ nm, $M_{\mathrm{L}} = 3796$, $h = 0.094$ nm for poly-**2**; $q = 103$ nm, $M_{\mathrm{L}} = 4041$, $h = 0.11$ nm for poly-**3**; $q = 81.8$ nm, $M_{\mathrm{L}} = 3625$, $h = 0.095$ nm for poly-**4**.

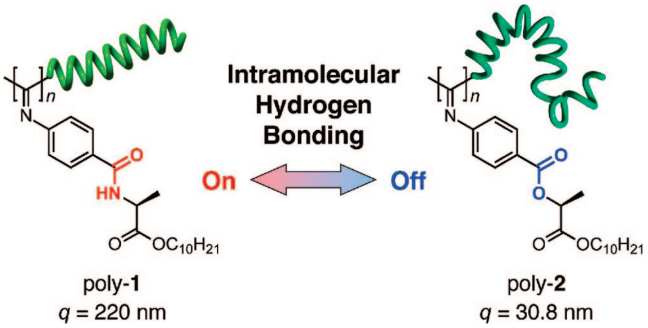


Figure 2. Schematic illustration of the extremely different main-chain stiffness of poly-**1** and poly-**2** resulting from the "on and off" of the intramolecular hydrogen-bonding networks.

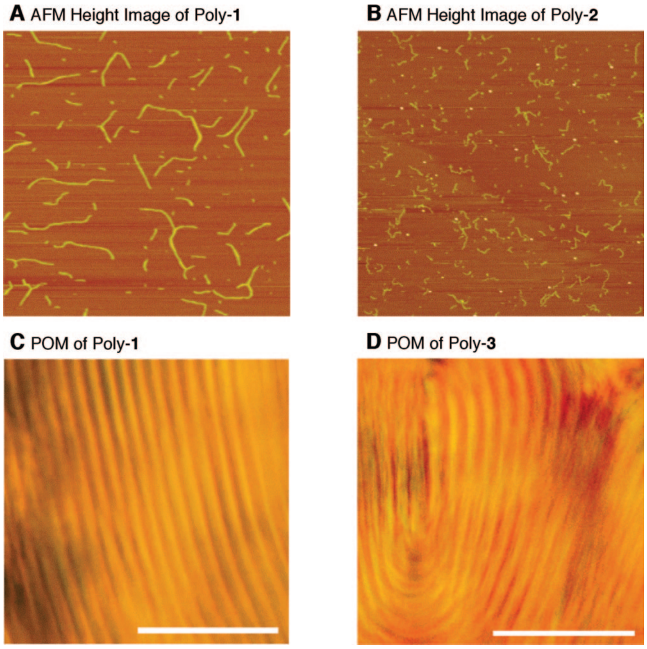


Figure 3. AFM height images (2 × 2 μm^2) of poly-**1** (A) and poly-**2** (B) cast from a dilute solution of chloroform (2.5 μg/mL) on mica modified with trimethoxypropylsilane. Polarized optical micrographs (POM) of poly-**1** (C) and poly-**3** (D) in 15 wt % chloroform solutions in glass capillary tubes taken at ambient temperature (20−25 °C). Scale bars: 50 μm.

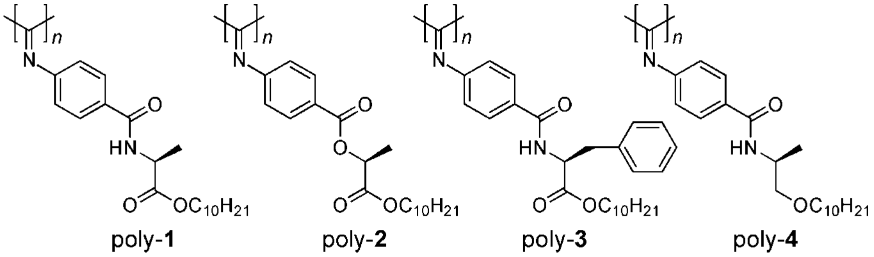
helical polymers reported so far,[12,18] including polyisocyanates,[13] polyguanidines,[14] polyisocyanides,[6b] polysilanes,[15] and polyacetylenes,[8d] and is comparable to those of biological, multistranded helical polymers, such as the triple-stranded helical collagen (160−180 nm)[19] and schizophyllan (150−200 nm),[20] and even stiffer than the double-stranded helical DNA (60 nm)[21] and xanthan (120 nm).[22] In contrast, poly-**2**, in which the amide linkage of poly-**1** was replaced by an ester, showed a dramatic decrease in its persistence length to 30.8 nm, indicating a rather semirigid polymer. This change in the q value clearly demonstrates that the main-chain stiffness of poly-**1** can be dictated by intramolecular hydrogen-bonding networks of the pendant amide groups (Figure 2).[17]

Atomic force microscopy (AFM) images of the isolated poly-**1** and poly-**2** chains were then measured on mica modified with trimethoxypropylsilane, which also support the change in their main-chain stiffness (A and B in Figure 3, respectively). Individual polymer chains with extended and tangled structures for poly-**1** and poly-**2**, respectively, can be directly visualized on the mica, indicating the stiff and flexible main-chain conformations, respectively. Helical poly(isocyanopeptide)s developed by Nolte, Rowan, and co-workers are also stabilized by well-defined arrays of intramolecular hydrogen bonds as supported by their characteristic IR spectra, thus showing a relatively high q value of 76 nm,[6b] being shorter than that of poly-**1**. Therefore, an extremely long q value (220 nm) of an analogous helical polyisocyanide poly-**1** may be ascribed to the phenyl substituents as the pendant groups, which may contribute more or less to its rigidity of the poly-**1** main chain.

We note that the persistence length of poly-**1** was measured by an SEC-MALS system using THF containing 0.1 wt % TBAB as the eluent,[23] which does not diminish the intramolecular hydrogen bonds of poly-**1** as observed in the IR and CD spectra (see Figure S1 in the Supporting Information).

Poly-**3**, whose structural characteristics are similar to those of poly-**1** except for its bulky phenylalanine residue, and poly-**4**, in which the ester linkage of poly-**1** was replaced by an ether, also maintained the main-chain stiffness, but exhibited relatively shorter persistence lengths of 103 and 81.8 nm, respectively. These results indicated that the appropriate bulkiness as well as the ester carbonyl groups at the pendant groups plays some roles in the stiffness of the polymer main chain. In other words,

Chart 1. Structures of Helical Polyisocyanides



the pendant groups of the polyisocyanides require an appropriate bulkiness to be packed in the preferable helical structure so that the amide groups as well as the ester carbonyl groups can participate in the formation of the intramolecular hydrogen-bonding networks,[11] resulting in stiff, rodlike polyisocyanides.[24]

As expected from the rodlike features of poly-**1** and poly-**3** together with their optical activity derived from a preferred-handed helical structure, these polymers formed lyotropic cholesteric LCs in a concentrated chloroform solution, thus showing a fingerprint texture (C and D in Figure 3, respectively). Poly-**2** and poly-**4** appear to be stiff enough to show a liquid crystallinity. However, they exhibited a nematic-like birefringence due to their low optical activity, that is, low one-handedness excesses on the basis of their $\Delta\varepsilon_{1st}$ values (Table 1).

In summary, we have estimated the persistence lengths of a series of optically active helical poly(phenyl isocyanide)s and investigated the effect of the chiral pendant structures on their stiffness. A helical poly(phenyl isocyanide) bearing L-alanine *n*-decyl esters as the pendants was found to possess an unprecedentedly long persistence length of 220 nm stabilized by intramolecular hydrogen-bonding networks. To the best of our knowledge, this is the highest persistence length among the synthetic helical polymers prepared so far. The present results may contribute to the design and synthesis of new rodlike helical polyisocyanides with a controlled helical sense. In addition, helical polyisocyanides with an extremely stiff polymer backbone together with a large electric dipole moment of the pendant amide residues[8e,17] may be used as a novel scaffold to build up uniformly aligned, supramolecular helical arrays, which will be further applicable to optoelectrical devices due to its polar structure.

Acknowledgment. K.N. expresses his thanks for the JSPS Research Fellowship for Young Scientists (No. 6683).

Supporting Information Available: Details on the SEC-MALS and AFM measurements, and CD, absorption, and IR spectra of poly-**1** in toluene, THF, and THF containing TBAB. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860–1865. (b) Okamoto, Y.; Yashima, E. *Angew. Chem., Int. Ed.* **1998**, *37*, 1020–1043. (c) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013–4038. (d) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039–4070. (e) Fujiki, M.; Koe, J. R.; Terao, K.; Sato, T.; Teramoto, A.; Watanabe, J. *Polym. J.* **2003**, *35*, 297–344. (f) Reggelin, M.; Doerr, S.; Klussmann, M.; Schultz, M.; Holbach, M. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5461–5466. (g) Yashima, E.; Maeda, K.; Nishimura, T. *Chem.—Eur. J.* **2004**, *10*, 42–51. (h) Amabilino, D. B.; Serrano, J.-L.; Sierra, T.; Veciana, J. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3161–3174. (i) Maeda, K.; Yashima, E. *Top. Curr. Chem.* **2006**, *265*, 47–88. (j) Yashima, E.; Maeda, K. *Macromolecules* **2008**, *41*, 3–12.

(2) (a) Sato, T.; Sato, Y.; Umemura, Y.; Teramoto, A.; Nagamura, Y.; Wagner, J.; Weng, D.; Okamoto, Y.; Hatada, K.; Green, M. M. *Macromolecules* **1993**, *26*, 4551–4559. (b) Okoshi, K.; Kamee, H.; Suzaki, G.; Tokita, M.; Fujiki, M.; Watanabe, J. *Macromolecules* **2002**, *35*, 4556–4559. (c) Cornelissen, J. J. L. M.; Granswinckel, 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. (d) Kim, J.; Novak, B. M.; Wadden, A. J. *Macromolecules* **2004**, *37*, 8286–8292.

(3) (a) Strzelecka, T. E.; Davidson, M. W.; Rill, R. L. *Nature* **1988**, *331*, 457–460. (b) Livolant, F.; Levelut, A. M.; Doucet, J.; Benoit, J. P. *Nature* **1989**, *339*, 724–726.

(4) (a) Fortin, S.; Charlet, G. *Macromolecules* **1989**, *22*, 2286–2292. (b) Inatomi, S.-i.; Jinbo, Y.; Sato, T.; Teramoto, A. *Macromolecules* **1992**, *25*, 5013–5019.

(5) (a) Robinson, C.; Ward, J. C. *Nature* **1957**, *180*, 1183–1184. (b) Tsujita, Y.; Yamanaka, I.; Takizawa, A. *Polym. J.* **1979**, *11*, 749–754. (c) Yu, S. M.; Conticello, V. P.; Zhang, G.; Kayser, C.; Fournier, M. J.; Mason, T. L.; Tirrel, D. A. *Nature* **1997**, *389*, 167–170.

(6) (a) Cornelissen, J. J. L. M.; Donners, J. J. J. M.; de Gelder, R.; Graswinckel, W. S.; Metselaar, G. A.; Rowan, A. E.; Sommerdijk, N. A. J. M.; Nolte, R. J. M. *Science* **2001**, *293*, 676–680. (b) Samorí, P.; Ecker, C.; Gösell, I.; de Witte, P. A. J.; Cornelissen, J. J. L. M.; Metselaar, G. A.; Otten, M. B. J.; Rowan, A. E.; Nolte, R. J. M.; Rabe, J. P. *Macromolecules* **2002**, *35*, 5290–5294. (c) Metselaar, G. A.; Adams, P. J. H. M.; Nolte, R. J. M.; Cornelissen, J. J. L. M.; Rowan, A. E. *Chem.—Eur. J.* **2007**, *13*, 950–960. (d) Metselaar, G. A.; Wezenberg, S. J.; Cornelissen, J. J. L. M.; Nolte, R. J. M.; Rowan, A. E. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 981–988.

(7) (a) Nomura, R.; Tabei, J.; Masuda, T. *J. Am. Chem. Soc.* **2001**, *123*, 8430–8431. (b) Nomura, R.; Tabei, J.; Nishiura, S.; Masuda, T. *Macromolecules* **2003**, *36*, 561–564. (c) Cheuk, K. L.; Lam, J. W. Y.; Tang, B. Z. *Macromolecules* **2003**, *36*, 9752–9762. (d) Lam, J. W. Y.; Tang, B. Z. *Acc. Chem. Res.* **2005**, *38*, 745–754.

(8) (a) Okoshi, K.; Sakajiri, K.; Kumaki, J.; Yashima, E. *Macromolecules* **2005**, *38*, 4061–4064. (b) Sakurai, S.-i.; Okoshi, K.; Kumaki, J.; Yashima, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1245–1248. (c) Sakurai, S.-i.; Okoshi, K.; Kumaki, J.; Yashima, E *J. Am. Chem. Soc.* **2006**, *128*, 5650–5651. (d) Okoshi, K.; Sakurai, S.-i.; Ohsawa, S.; Kumaki, J.; Yashima, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 8173–8176. (e) Okoshi, K.; Kajitani, T.; Nagai, K.; Yashima, E. *Macromolecules* **2008**, *41*, 258–261.

(9) *Foldamers: Structure, Properties, and Applications*; Hecht, S., Huc, I., Eds.; Wiley-VCH: Weinheim, 2007.

(10) Kajitani, T.; Okoshi, K.; Sakurai, S.-i.; Kumaki, J.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 708–709.

(11) Kajitani, T.; Okoshi, K.; Yashima, E. *Macromolecules* **2008**, *41*, 1601–1611.

(12) Although a number of rodlike helical polymers have been prepared, only a limited number of q values have been determined for helical polymers. The reported high q values for synthetic helical polymers are 13.5 nm (poly(*N*-propargylamide)),[7b] 20−40 nm (poly(*n*-hexyl isocyanate)),[13] 42 nm (poly(*N*-(1-phenylethyl)-*N*′-methylcarbodiimide)),[14] 76 nm (polyisocyanopeptides),[6b] 103 nm (poly(((*R*)-3,7-dimethyloctyl)-((*S*)-3-methylpentyl)-silylene)),[15] and 135 nm (poly(4-ethynylbenzoyl-L-alanine *n*-decyl ester).[8d]

(13) Gu, H.; Nakamura, Y.; Sato, T.; Teramoto, A.; Green, M. M.; Andreola, C. *Polymer* **1999**, *40*, 849–856.

(14) Nieh, M.-P.; Goodwin, A. A.; Stewart, J. R.; Novak, B. M.; Hoagland, D. A. *Macromolecules* **1998**, *31*, 3151–3154.

(15) Teramoto, A.; Terao, K.; Terao, Y.; Nakamura, N.; Sato, T.; Fujiki, M. *J. Am. Chem. Soc.* **2001**, *123*, 12303–12310.

(16) (a) Yamakawa, H.; Fujii, M. *Macromolecules* **1974**, *7*, 128–135. (b) Yamakawa, H.; Yoshizaki, T. *Macromolecules* **1980**, *13*, 633–643.

(17) Onouchi, H.; Okoshi, K.; Kajitani, T.; Sakurai, S.-i.; Nagai, K.; Kumaki, J.; Onitsuka, K.; Yashima, E *J. Am. Chem. Soc.* **2008**, *130*, 229–236.

(18) Sato, T.; Teramoto, A. *Adv. Polym. Sci.* **1996**, *126*, 85–161.

(19) Saito, T.; Iso, N.; Mizuno, H.; Onda, N.; Yamato, H.; Odashima, H. *Biopolymers* **1982**, *21*, 715–728.

(20) (a) Yanai, T.; Norisuye, T.; Fujita, H. *Macromolecules* **1980**, *13*, 1462–1466. (b) Kashiwagi, Y.; Norisuye, T.; Fujita, H. *Macromolecules* **1981**, *14*, 1220–1225.

(21) Godfrey, J. E.; Einsenberg, H. *Biophys. Chem.* **1976**, *5*, 301–318.

(22) Sato, T.; Norisuye, T.; Fujita, H. *Polym. J.* **1984**, *16*, 341–350.

(23) Polyisocyanides including poly-**1** adsorbed strongly on the SEC columns in THF and chloroform, and therefore, TBAB was used as an additive in the THF as the eluent.

(24) A poly-**1** with similar molecular weight ($M_n = 22.2 \times 10^4$) but lower optical activity ($\Delta\varepsilon_{1st} = -1.28$ and $[\alpha]^{25}_D = -59$) prepared in different polymerization conditions[11] also showed a large q value (175 nm), indicating that the excess of one-helical sense of poly-**1** may not influence its main-chain stiffness, although the reason for the apparent difference in their q values of the poly-**1**s is not clear at present.

MA8015954