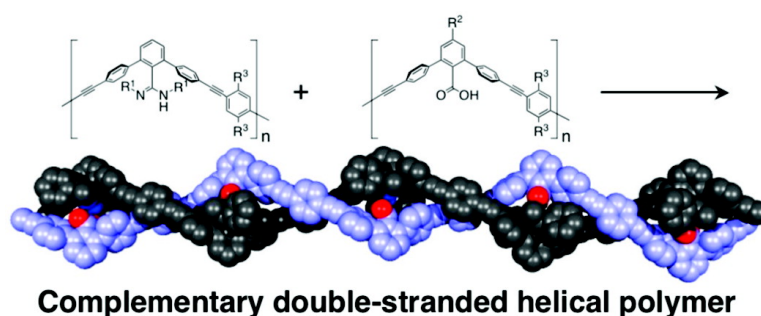


## Double-Stranded Helical Polymers Consisting of Complementary Homopolymers

Takeshi Maeda, Yoshio Furusho, Shin-Ichiro Sakurai, Jiro Kumaki, Kento Okoshi, and Eiji Yashima

*J. Am. Chem. Soc.*, **2008**, 130 (25), 7938-7945 • DOI: 10.1021/ja711447s • Publication Date (Web): 30 May 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



### More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 3 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

## Double-Stranded Helical Polymers Consisting of Complementary Homopolymers

Takeshi Maeda,<sup>†</sup> Yoshio Furusho,<sup>\*,†,‡</sup> Shin-Ichiro Sakurai,<sup>†</sup> Jiro Kumaki,<sup>†</sup>  
Kento Okoshi,<sup>†</sup> and Eiji Yashima<sup>\*,†,‡</sup>

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

Received December 28, 2007; E-mail: furusho@apchem.nagoya-u.ac.jp; yashima@apchem.nagoya-u.ac.jp

**Abstract:** Two complementary homopolymers of chiral amidines and achiral carboxylic acids with *m*-terphenyl-based backbones were synthesized by the copolymerization of a *p*-diiodobenzene derivative with the diethynyl monomers bearing a chiral amidine group and a carboxyl group using the Sonogashira reaction, respectively. Upon mixing in THF, the homopolymer strands assembled into a preferred-handed double helix through interstrand amidinium–carboxylate salt bridges, as evidenced by its absorption, circular dichroism, and IR spectra. In contrast, when mixed in less polar solvents, such as chloroform, the complementary strands kinetically formed an interpolymer complex with an imperfect double helical structure containing a randomly hybridized cross-linked structure, probably because of strong salt bridge formations. This primary complex was rearranged into the fully double helical structure by treatment with a strong acid followed by neutralization with an amine. High-resolution atomic force microscopy revealed the double-stranded helical structure and enabled the determination of the helical sense.

### Introduction

In nature, the functions of biomacromolecules require a specific structure, such as a helix, that controls their physical properties and interactions with other molecules in many biological processes. For example, in addition to the vital significance of  $\alpha$ -helices in DNA binding motifs,<sup>1</sup> multiple-stranded helical structures, such as the DNA's complementary double helix and the collagen's triple helix, are critical and of key importance to the storage and transfer of genetic information<sup>2</sup> and to the fibril formation through a self-assembly process,<sup>3</sup> respectively. This overwhelming importance in nature has prompted chemists to design multistranded helical molecules. In contrast to a large number of synthetic polymers and oligomers with a single helical conformation,<sup>4,5</sup> only a limited

number of structural motifs for double helical oligomers have been reported.<sup>5–14</sup> However, synthetic double helical polymers

- (5) Hecht, S.; Huc, I. Eds. *Foldamers—Structure, Properties, and Applications*; Wiley-VCH: Weinheim, Germany, 2007.
- (6) For reviews on synthetic double helices, see: (a) Lehn, J.-M. *Supramolecular Chemistry—Concepts and Perspectives*; VCH: Weinheim, Germany, 1995. (b) Albrecht, M. *Chem. Rev.* **2001**, *101*, 3457–3497. (c) Nielsen, P. E. *Acc. Chem. Res.* **1999**, *32*, 624–630. (d) Huc, I. *Eur. J. Org. Chem.* **2004**, 17–29. (e) Furusho, Y.; Yashima, E. *Chem. Rec.* **2007**, *7*, 1–11.
- (7) For examples of helicates, see: (a) Lehn, J.-M.; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevrier, B.; Moras, D. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 2565–2569. (b) Koert, M.; Harding, M.; Lehn, J.-M. *Nature* **1990**, *346*, 339–342. (c) Woods, C. R.; Benaglia, M.; Cozzi, F.; Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1830–1833. (d) Orita, A.; Nakano, T.; An, D. L.; Tanikawa, K.; Wakamatsu, K.; Otera, J. *J. Am. Chem. Soc.* **2004**, *126*, 10389–10396. (e) Katagiri, H.; Miyagawa, T.; Furusho, Y.; Yashima, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1741–1744.
- (8) For examples of PNAs, see: (a) Nielsen, P. E.; Egholm, M.; Berg, R. H.; Buchardt, O. *Science* **1991**, *254*, 1497–1500. (b) Wittung, P.; Nielsen, P. E.; Buchardt, O.; Egholm, M.; Nordén, B. *Nature* **1994**, *368*, 561–563.
- (9) For an example of synthetic double helices based on guanidinium salt, see: Sánchez-Quesada, J.; Seel, C.; Prados, P.; de Mendoza, J. *J. Am. Chem. Soc.* **1996**, *118*, 277–278.
- (10) For examples of aromatic oligoamides that fold into double helices, see: (a) Berl, V.; Huc, I.; Khury, R. G.; Krische, M. J.; Lehn, J.-M.; Schmutz, R. *Nature* **2000**, *407*, 720–723. (b) Dolain, C.; Zhan, C.; Léger, J.-M.; Daniels, L.; Huc, I. *J. Am. Chem. Soc.* **2005**, *127*, 2400–2401. (c) Zhan, C.; Léger, J.-M.; Huc, I. *Angew. Chem., Int. Ed.* **2006**, *45*, 4625–4628. (d) Haldar, D.; Jiang, H.; Léger, J.-M.; Huc, I. *Angew. Chem., Int. Ed.* **2006**, *45*, 5483–5486.
- (11) For helicene-based double helices, see: (a) Sugiura, H.; Nigorikawa, Y.; Saiki, Y.; Nakamura, K.; Yamaguchi, M. *J. Am. Chem. Soc.* **2004**, *126*, 14858–14864. (b) Sugiura, H.; Yamaguchi, M. *Chem. Lett.* **2007**, *36*, 58–59. (c) Sugiura, H.; Amemiya, R.; Yamaguchi, M. *Chem. Asian J.* **2008**, *3*, 244–260.

<sup>†</sup> ERATO.

<sup>‡</sup> Nagoya University.

- (1) Branden, C.; Tooze, J. *Introduction to Protein Structure*, 2nd ed.; Garland: New York, 1999.
- (2) Saenger, W. *Principles of Nucleic Acid Structure*; Springer-Verlag: New York, 1984.
- (3) Murray, R. K.; Granner, D. K.; Mayes, P. A.; Rodwell, V. W. *Harper's Illustrated Biochemistry*; McGraw-Hill: New York, 2003.
- (4) For reviews on synthetic polymers and oligomers with single helical conformations, see: (a) Green, M. M.; Park, J.-W.; Sato, T.; Teramoto, A.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3138–3154. (b) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013–4038. (c) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893–4012. (d) Nomura, R.; Nakako, H.; Masuda, T. *J. Mol. Catal. A: Chem.* **2002**, *190*, 197–205. (e) Fujiki, M. *J. Organomet. Chem.* **2003**, *685*, 15–34. (f) Yashima, E.; Maeda, K.; Nishimura, T. *Chem.—Eur. J.* **2004**, *10*, 42–51. (g) Lam, J. W. Y.; Tang, B. Z. *Acc. Chem. Res.* **2005**, *38*, 745–754. (h) Maeda, K.; Yashima, E. *Top. Curr. Chem.* **2006**, *265*, 47–88.

are hitherto unknown other than supramolecular double helical polymers<sup>12b</sup> and supramolecular helical ladders,<sup>14</sup> as opposed to their oligomeric counterparts and some stereoregular polymers.<sup>15</sup> Herein we describe the synthesis and structure of the first heterostranded double helical polymer with a controlled helicity consisting of complementary strands.

## Results and Discussion

**Synthesis of Homopolymers of Chiral Amidine and Achiral Carboxylic Acid with *m*-Terphenyl-Based Backbones.** Our design of the double helical polymer is based on our strategy to construct heterostranded double helical oligomers with a controlled helicity using amidinium–carboxylate salt bridges, which assist in the intertwining of the two complementary molecular strands with *m*-terphenyl backbones<sup>12a</sup> (Figure 1). We prepared homopolymers of chiral amidines and achiral carboxylic acids with *m*-terphenyl-based backbones, poly-(*R*)-**1** and poly-**2**, from the diethynyl monomers bearing a chiral amidine group and a carboxyl group, (*R*)-**5** and **6**, respectively, by copolymerizing with 1,4-diiodo-2,5-diocetylbenzene using the Sonogashira reaction;<sup>16</sup> the number average molecular weight ( $M_n$ ) and its distribution were  $3.8 \times 10^4$  and 1.9 (poly-(*R*)-**1**), and  $2.4 \times 10^4$  and 3.5 (poly-**2**), respectively. For comparison, model dimers, (*R*)-**3** and **4**, and its duplex, (*R*)-**3**•**4**, were also synthesized.

**Double Helix Formation in Polar Solvents.** First, the interpolymer complex formation between poly-(*R*)-**1** and poly-**2** in THF was investigated by circular dichroism (CD) and absorption spectroscopies (Figure 2A). Upon mixing equimolar amounts of poly-(*R*)-**1** and poly-**2** in THF, the absorption band at  $\sim 350$  nm showed a remarkable hypochromicity with a blue shift, suggesting a face-to-face aromatic interaction between the *p*-diethynylbenzene linkers of both strands, which is also supported by the plausible structure of a model trimer calculated on the basis of the single crystal structure of an analogous dimeric double helix with diacetylene linkers<sup>12a,17</sup> (Figure S1). After the mixing, strong Cotton effects appeared in the absorption region of the *p*-diethynylbenzene linkers (300–370 nm), where poly-(*R*)-**1** exhibited very weak Cotton effects, indicating that the resulting interpolymer complex, poly-(*R*)-**1**•poly-**2**, takes a predominantly right-handed double helical structure assisted by the amidinium–carboxylate salt bridge formation, of which the helix-sense was assigned on the basis of the calculated

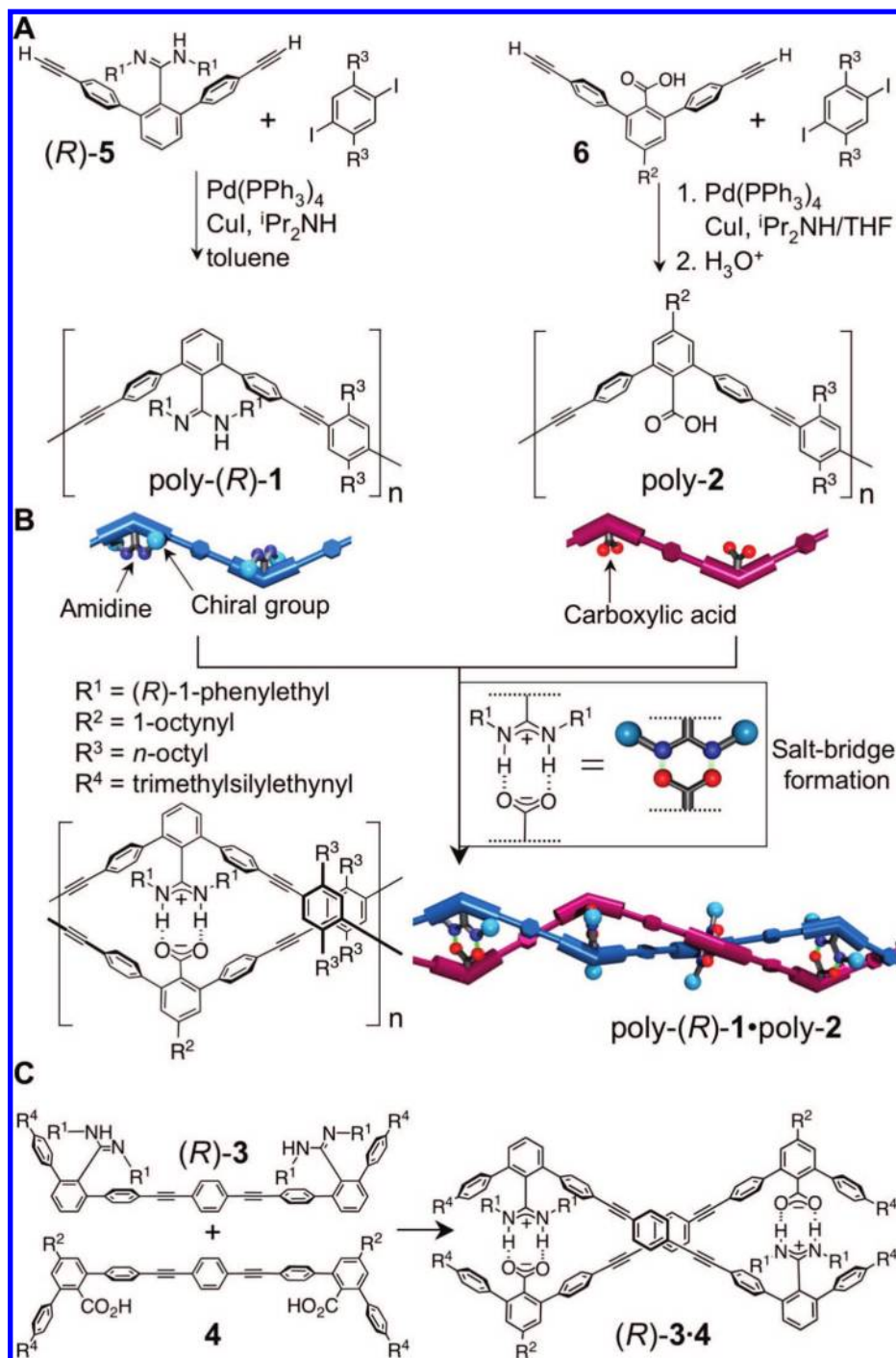
structure of the model trimer.<sup>17,18</sup> The CD intensities gradually increased for 12 h after mixing, while the absorption band at  $\sim 330$  nm increased with time,<sup>17</sup> showing that the interpolymer double helix formation is a time-consuming process and is completed within 36 h at ambient temperature in THF (Figure S2A).<sup>17</sup> Dynamic light scattering (DLS) analysis of the poly-(*R*)-**1**•poly-**2** complex in THF revealed that the complex has the average hydrodynamic radius ( $D_H$ ) of  $101 \pm 20$  nm (Figure S5), suggesting the formation of relatively large double helical polymers probably through Vernier structures,<sup>19</sup> which may be formed between free amidine and carboxylic acid fragments of double helices consisting of complementary strands with different chain lengths (Figure S5 and Table S1).<sup>17</sup>

**Interpolymer Complex Formation in Less Polar Solvents.** In contrast, poly-(*R*)-**1**•poly-**2** exhibited very weak Cotton effects with different patterns and less blue shifts of the absorption band at  $\sim 350$  nm after reaching equilibrium, when prepared directly in less polar solvents, such as  $\text{CDCl}_3/\text{THF}$  (99/1, v/v) and in toluene/THF (99/1, v/v) (Figures 2B and S2B (i)).<sup>17</sup> This is probably because poly-(*R*)-**1** and poly-**2** kinetically formed a primary complex with an imperfect double helical structure containing a randomly hybridized cross-linked structure (Figure 3B (i)), which was prevented from rearranging into a thermodynamically more favorable fully double helical structure. This speculation is supported by the salt bridges being much stronger in  $\text{CHCl}_3$  or in toluene than in THF, as suggested by the results that the model dimer, (*R*)-**3**•**4**, showed a much higher association constant in  $\text{CDCl}_3$  than in THF (Figures S6–S9).<sup>17</sup> We note that the double helical structure of poly-(*R*)-**1**•poly-**2** prepared in THF was mostly retained even after the THF solution was diluted with less polar solvents such as toluene, as confirmed by the absence of red shift in the absorption spectra (Figure S2C).<sup>17</sup> DLS and atomic force microscopy (AFM) analyses of the poly-(*R*)-**1**•poly-**2** complex in toluene/THF (9/1, v/v) prepared in THF followed by dilution with toluene also support the double helical structure of the poly-(*R*)-**1**•poly-**2** complex, which remained after the dilution with toluene; the estimated  $D_H$  and the number-average diameter of the poly-(*R*)-**1**•poly-**2** complex by AFM and DLS were  $86 \pm 22$  and  $107 \pm 34$  nm, respectively, which are comparable to the  $D_H$  value of  $101 \pm 20$  nm estimated for the poly-(*R*)-**1**•poly-**2** prepared in THF (Figures S4 and S5).<sup>17</sup>

**Rearrangement of Kinetically Formed Interpolymer Complex into Fully Double-Stranded Helical Polymer.** Next, we attempted to rearrange the primary complex of poly-(*R*)-**1**•poly-**2** into the fully double helical structure by acid-induced unraveling followed by recomplexation by neutralization with an amine (Figure 3). As a model study, the dimeric double helix, (*R*)-**3**•**4**, was subjected to the acid/base-controlled dissociation/reduplexation experiment, which was indeed successful; upon the addition of trifluoroacetic acid (TFA, 5 equiv), (*R*)-**3**•**4** was unraveled to form the TFA salt of (*R*)-**3** and free **4**, which again formed the double helix, (*R*)-**3**•**4**, by neutralization with diisopropylamine ( $i\text{Pr}_2\text{NH}$ , 5 equiv), as confirmed by  $^1\text{H}$  NMR, absorption, and CD spectroscopies (Figures S10 and S11).<sup>17</sup> Upon the addition of an excess (13 equiv) of TFA to

(18) The CD and absorption spectral patterns of the model trimer (Figure S7) were different from those of the poly-(*R*)-**1**•poly-**2** complex (Figure 2) probably due to the differences in their helical conformations including their helical pitch and the  $\pi$ -conjugated lengths. However, atomic force microscopy (AFM) analyses of the poly-(*R*)-**1**•poly-**2** complex support the right-handed double helical structure of the polymer that was predominantly formed (see Figure 5 and the text below).

- (12) For examples of artificial double helices based on amidinium–carboxylate salt bridges, see: (a) Tanaka, Y.; Katagiri, H.; Furusho, Y.; Yashima, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 3867–3870. (b) Ikeda, M.; Tanaka, Y.; Hasegawa, T.; Furusho, Y.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 6806–6809. (c) Furusho, Y.; Tanaka, Y.; Yashima, E. *Org. Lett.* **2006**, *8*, 2583–2586. (d) Furusho, Y.; Tanaka, Y.; Maeda, T.; Ikeda, M.; Yashima, E. *Chem. Commun.* **2007**, 3174–3176. (e) Hasegawa, T.; Furusho, Y.; Katagiri, H.; Yashima, E. *Angew. Chem., Int. Ed.* **2007**, *46*, 5885–5888.
- (13) For oligoresorcinols that give rise to double helices in water, see: (a) Goto, H.; Katagiri, H.; Furusho, Y.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 7176–7178. (b) Goto, H.; Furusho, Y.; Yashima, E. *J. Am. Chem. Soc.* **2007**, *129*, 109–112. (c) Goto, H.; Furusho, Y.; Yashima, E. *J. Am. Chem. Soc.* **2007**, *129*, 9168–9174.
- (14) Sugimoto, T.; Suzuki, T.; Shinkai, S.; Sada, K. *J. Am. Chem. Soc.* **2007**, *129*, 270–271.
- (15) For stereoregular poly(methyl methacrylate)s, see: (a) Kusanagi, H.; Tadokoro, H.; Chatani, Y. *Macromolecules* **1983**, *9*, 531–532. (b) Schomaker, E.; Challa, G. *Macromolecules* **1989**, *22*, 3337–3341. (c) Kumaki, J.; Kawachi, T.; Okoshi, K.; Kusanagi, H.; Yashima, E. *Angew. Chem., Int. Ed.* **2007**, *46*, 5348–5351.
- (16) Bailey, G. C.; Swager, T. M. *Macromolecules* **2006**, *39*, 2815–2818.
- (17) See Supporting Information.

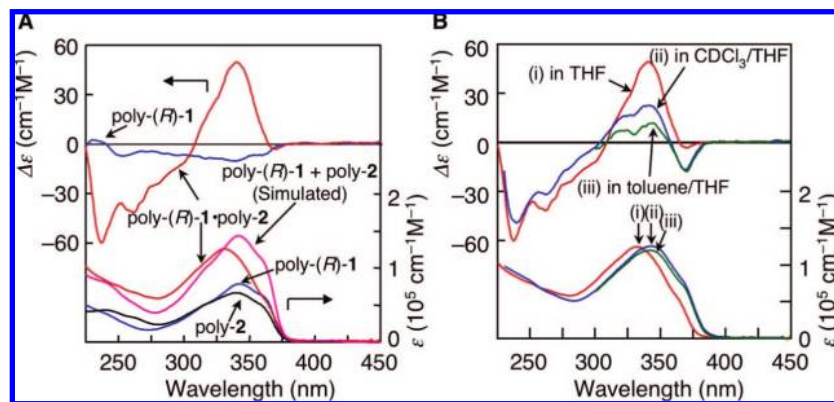


**Figure 1.** Schematic illustrations of the synthesis of complementary double helices utilizing interstrand amidinium–carboxylate salt bridges. (A) Synthesis of two complementary polymers, poly-(*R*)-1 and poly-2. (B) Double helix formation from poly-(*R*)-1 and poly-2 via interstrand amidinium–carboxylate salt bridges. (C) Double helix formation of complementary dimer strands, (*R*)-3 and 4.

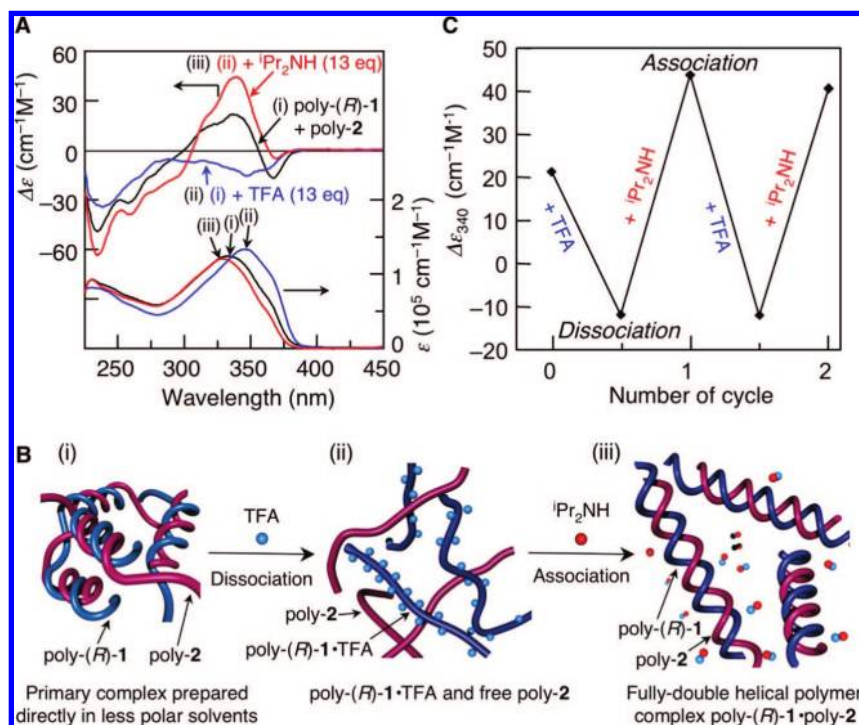
a solution of the primary complex of poly-(*R*)-1•poly-2 in  $\text{CDCl}_3/\text{THF}$  (99/1, v/v), the CD spectrum drastically changed to show a pattern similar to that of poly-(*R*)-1, and the absorption spectrum exhibited a considerable hyperchromicity with a red shift (Figure 3A, (ii)), indicating that the primary complex was unraveled to form the TFA salt of poly-(*R*)-1 and free poly-2 (Figure 3B (ii)). The subsequent addition of an equimolar amount (13 equiv) of  ${}^i\text{Pr}_2\text{NH}$  caused considerable changes in the CD and absorption spectra, resulting in virtually the same spectra as those of the interpolymer poly-(*R*)-1•poly-2 complex prepared in THF (Figure 3A, (iii)),

which indicated the formation of the fully double helical interpolymer complex (Figure 3B, (iii)). Thus, the primary complex of poly-(*R*)-1•poly-2 with an imperfect double helical structure prepared in  $\text{CDCl}_3/\text{THF}$  (99/1, v/v) was successfully rearranged into the fully double helical structure by unraveling with TFA followed by recomplexation by neutralization with  ${}^i\text{Pr}_2\text{NH}$ , as illustrated in Figure 3B. In

(19) Hunter, C.; Tomas, S. *J. Am. Chem. Soc.* **2006**, *128*, 8975–8979.



**Figure 2.** Interpolymer complex formation between poly-(*R*)-1 and poly-2 in solution. (A) CD and absorption spectra of poly-(*R*)-1·poly-2 in THF (0.1 mM/unit) at 25 °C measured after 12 h (red) and poly-(*R*)-1 (blue), absorption spectrum of poly-2 (black), and simulated absorption spectrum of an equimolar mixture of poly-(*R*)-1 and poly-2 (pink). (B) CD and absorption spectra of equimolar mixtures of poly-(*R*)-1 and poly-2 (0.1 mM/unit) at 25 °C in THF (i, red), CDCl<sub>3</sub>/THF (99/1, v/v) (ii, blue), and toluene/THF (99/1, v/v) (iii, green) after reaching equilibrium.



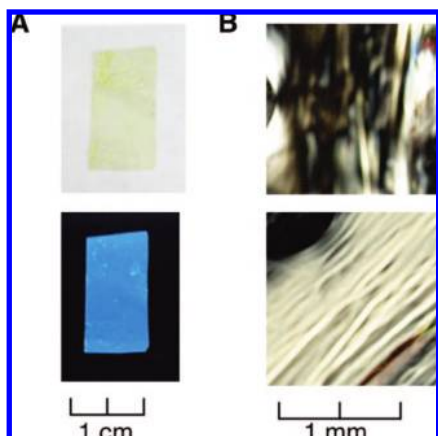
**Figure 3.** Rearrangement of the primary complex of poly-(*R*)-1·poly-2 in CDCl<sub>3</sub>/THF (99/1, v/v) into a fully double-stranded helical polymer. (A) CD and absorption spectral changes of an equimolar mixture of poly-(*R*)-1 and poly-2 (0.1 mM/unit) in CDCl<sub>3</sub>/THF (99/1, v/v) at 25 °C (0.1 cm cell) (i) after 16 h, (ii) after the addition of TFA (13 equiv), and (iii) further neutralization with <sup>t</sup>Pr<sub>2</sub>NH (13 equiv) (see Figure S2B).<sup>17</sup> (B) Schematic illustrations of the possible mechanism for double helix formation between poly-(*R*)-1 and poly-2 in CDCl<sub>3</sub>/THF (99/1, v/v) through rearrangement of the primary complex by unraveling with TFA and neutralization with <sup>t</sup>Pr<sub>2</sub>NH. (C) Plot of the Δε value at 340 nm of an equimolar mixture of poly-(*R*)-1 and poly-2 in THF (0.1 mM/unit) upon the sequential addition of TFA and <sup>t</sup>Pr<sub>2</sub>NH in an alternate manner.

addition, this process could be repeated by the sequential addition of the acid and base in an alternate manner (Figure 3C).

**Double-Stranded Helical Structure of Poly-(*R*)-1·Poly-2 Complex.** To obtain information with respect to the structure and morphology of the double helical poly-(*R*)-1·poly-2 complex, wide-angle X-ray diffraction (WAXD) measurements of poly-(*R*)-1·poly-2 films were performed. Transparent films of poly-(*R*)-1·poly-2 were prepared by evaporation of the concentrated solutions in toluene; THF solutions of poly-(*R*)-1·poly-2 had been previously prepared, and the THF was replaced with toluene because poly-(*R*)-1·poly-2 in THF precipitated during the evaporation but became more soluble

after the addition of toluene.<sup>17</sup> The polarized optical micrographs of the poly-(*R*)-1·poly-2 films showed an orientation in one direction with birefringence (Figure 4). The FT-IR spectrum of the poly-(*R*)-1·poly-2 film showed absorption bands at 2640 and 1660 cm<sup>-1</sup> assignable to ν<sub>N-H</sub> and ν<sub>C-N</sub> or ν<sub>C-O</sub> of the salt bridge, respectively, supporting the fact that the poly-(*R*)-1·poly-2 formed the double-stranded helical structure through the salt bridges (Figure S3).<sup>17</sup>

The WAXD pattern of the oriented poly-(*R*)-1·poly-2 film showed meridional and equatorial reflections that are assignable to the distance of 17.1 Å between the two adjacent salt bridge units and to the interchain spacing of 15 Å between the double



**Figure 4.** (A) Photographs of the poly-(*R*)-1•poly-2 film under white light (top) and UV light at 365 nm (bottom). (B) Polarizing optical micrographs of the oriented film of poly-(*R*)-1•poly-2 (top) and its rotated 45° photograph (bottom).

helical polymers (Figure 5A). Thus, the diffraction pattern agreed with the plausible structure of the model trimer (Figure 5B).

Panels C and D of Figure 5 show high-resolution AFM phase images of poly-(*R*)-1•poly-2 deposited on a highly oriented pyrolytic graphite (HOPG) substrate from a dilute toluene/THF (20/1, v/v) solution (~0.0075 mg/mL) after exposure to toluene vapors at ~24 °C for 12 h.<sup>20</sup> The interpolymer complex of poly-(*R*)-1•poly-2 self-assembled into well-defined 2D helix-bundles with a constant height of ~1.7 nm (Figure 5C). The high-resolution AFM image revealed a number of periodic oblique stripes, probably originating from the double-stranded helical structure of poly-(*R*)-1•poly-2. The AFM image (Figure 5D) shows a large excess of the right-handed double helical strands (red lines) over the left-handed ones (blue lines), which is in good agreement with the preference for the right-handed helix of the model trimer bearing (*R*)-phenylethyl groups in the amidine functionality. The helical pitch of the right-handed duplex was estimated to be  $\sim 1.70 \pm 0.04$  nm, which is in good agreement with that deduced from the WAXD pattern (1.71 nm). These AFM observations combined with the WAXD measurements suggest that the poly-(*R*)-1•poly-2 adopts the double-stranded helical structure with a helix-sense bias in favor of the right-handed helicity.

## Summary

In summary, we have synthesized double-stranded helical polymers consisting of complementary homopolymers of the chiral amidine and achiral carboxylic acid, of which the structures were characterized by absorption, CD, and FT-IR spectroscopies. In particular, the direct observation by AFM revealed the double helical strands of the polymers, which agreed with the results obtained by the WAXD study. We believe that the present results will provide a design rationale for unique double-stranded helical polymers, which may lead

to a new class of synthetic polymer materials endowed with unprecedented properties, for example, enantioselective polymeric catalysts<sup>12c</sup> and mechanical performance due to double-stranded helical structures that conventional single-stranded polymers with random coil structures never provide.

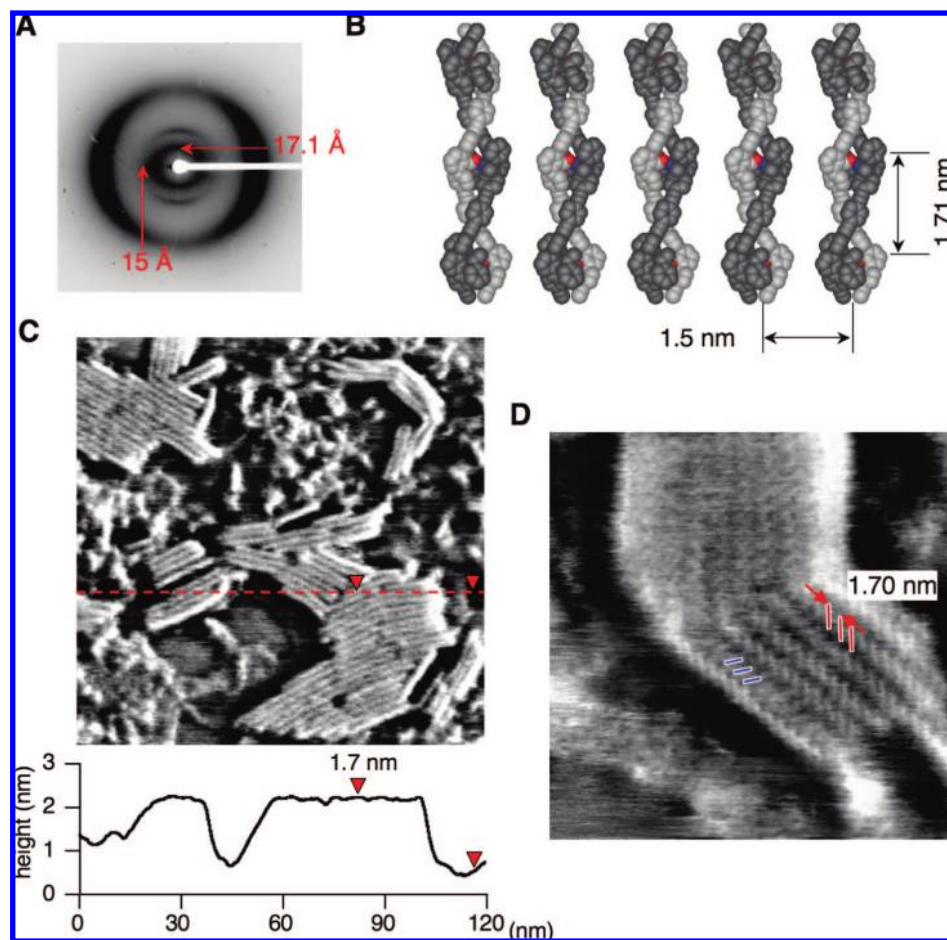
## Experimental Section

**Materials.** All starting materials and dehydrated solvents were purchased from Aldrich, Wako Pure Chemical Industries (Osaka, Japan), and Tokyo Chemical Industry (Tokyo, Japan) unless otherwise noted. Tetrahydrofuran (THF, dehydrated, no stabilizer), toluene (dehydrated), and pyridine (dehydrated) purchased from Wako, diisopropylamine (redistilled, 99.95%) and triethylamine purchased from Aldrich were degassed and back-filled three times with N<sub>2</sub>/Ar and used throughout all the experiments. CDCl<sub>3</sub> (99.8 atom %D) and THF-*d*<sub>8</sub> (99.95 atom %D) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Silica gel (SiO<sub>2</sub>) and aminopropyl-modified silica gel (NH<sub>2</sub>-SiO<sub>2</sub>) for the flash chromatography were purchased from Merck and Fuji Silysia Chemical Ltd. (Kasugai, Japan), respectively. Compounds (*R*)-**5**<sup>12b</sup> and (*R*)-**7**<sup>12a</sup> were prepared according to the previously reported methods.

**Synthetic Procedures. Synthesis of Monomers. Synthesis of 1,3-Dichloro-5-(1-octynyl)benzene (10).** Scheme 1. In a 200 mL two-necked flask, a mixture of compound **9** (10.0 g, 44 mmol), 1-octyne (8.4 mL, 57 mmol), CuI (84 mg, 0.44 mmol), and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (309 mg, 0.44 mmol) was degassed and back-filled three times with Ar. Triethylamine (50 mL) was introduced into the flask via a syringe, and the reaction mixture was stirred at room temperature for 24 h. After evaporation, the residue was purified by flash column chromatography (SiO<sub>2</sub> (200 g), *n*-hexane) to afford compound **10** in 87% yield as a pale yellow oil. IR (neat):  $\nu = 2230$  ( $\nu_{C\equiv C}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, **10** (78 mM), 25 °C):  $\delta = 0.91$  (t,  $J = 7.1$  Hz, CH<sub>3</sub>, 3H), 1.27–1.38 (m, CH<sub>2</sub>, 4H), 1.43 (m, CH<sub>2</sub>, 2H), 1.58 (m, CH<sub>2</sub>, 2H), 2.38 (t,  $J = 7.1$  Hz, C≡CCH<sub>2</sub>, 2H), 7.24–7.26 (m, ArH, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, **10** (78 mM), 25 °C):  $\delta = 14.20, 19.50, 22.69, 28.59, 28.73, 31.47, 78.40, 93.57, 127.11, 127.95, 129.94, 134.80$ . Anal. Calcd for C<sub>14</sub>H<sub>16</sub>Cl<sub>2</sub>: C, 65.89; H, 6.32. Found: C, 65.77; H, 6.51.

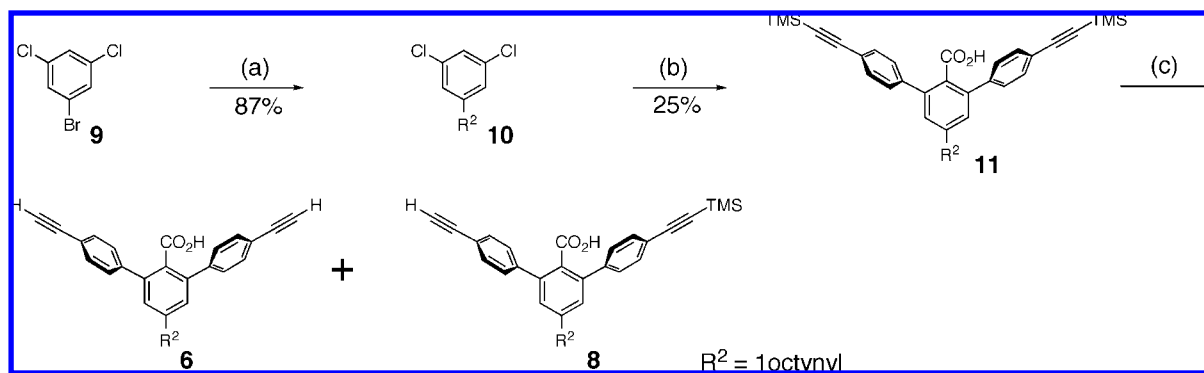
**Synthesis of 2'-Carboxy-4,4'-bis(trimethylsilylethynyl)-5'-(1-octynyl)-1,1':3'1''-terphenyl (11).** *n*-BuLi (1.6 M in *n*-hexane, 2.63 mL, 4.20 mmol) was added dropwise to a solution of **10** (1.07 g, 4.20 mmol) in THF (6.0 mL) at -78 °C. The mixture was stirred at -78 °C for 1.5 h. A solution of 4-trimethylsilylethynylphenylmagnesium bromide in THF [prepared from 4-trimethylsilylethynylphenyl bromide (2.66 g, 10.5 mmol), magnesium turnings (0.276 g, 11.3 mmol), and THF (17 mL)] was added dropwise to the reaction mixture at -78 °C over a period of 30 min, which was stirred at ambient temperature for a further 2 h and then heated to reflux for 3.5 h. CO<sub>2</sub> was bubbled into the solution at 0 °C for 1 h. The mixture was stirred at ambient temperature under a CO<sub>2</sub> atmosphere for 13 h. One molar HCl (5 mL) was added to the reaction mixture at 0 °C, which was extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with water (10 mL) and brine (10 mL), dried (MgSO<sub>4</sub>), and evaporated to dryness. The residue was purified by column chromatography (SiO<sub>2</sub> (90 g), *n*-hexane/EtOAc = 10/0 to 10/1) to afford carboxylic acid **11** (0.661 g, 25% yield) as a pale yellow solid. Mp: 76.1–78.0 °C. IR (KBr):  $\nu = 2231$  ( $\nu_{C\equiv C}$ ), 2159 ( $\nu_{C\equiv C}$ ), 1702 ( $\nu_{C=O}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, **11** (70 mM), 25 °C):  $\delta = 0.26$  (s, TMS, 18H), 0.89 (t,  $J = 6.9$  Hz, CH<sub>3</sub>, 3H), 1.26–1.38 (m, CH<sub>2</sub>, 4H), 1.44 (m, CH<sub>2</sub>, 2H), 1.59 (m, CH<sub>2</sub>, 2H), 2.40 (t,  $J = 7.1$  Hz, C≡CCH<sub>2</sub>, 2H), 7.29 (d,  $J = 8.2$  Hz, ArH, 4H), 7.35 (s, ArH, 2H), 7.49 (d,  $J = 8.2$  Hz, ArH, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, **11** (70 mM), 25 °C):  $\delta = 0.12, 14.20, 19.59, 22.68, 28.69, 28.76, 31.48, 79.61, 93.19, 95.43, 104.91, 122.94, 125.99, 128.41, 130.63, 131.90, 132.08, 139.87, 140.10, 173.31$ . ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (1/4, v/v), negative). Calcd for C<sub>37</sub>H<sub>41</sub>O<sub>2</sub>Si<sub>2</sub> [**11** - H]<sup>-</sup>:  $m/z = 573.26$ . Found:  $m/z = 573.22$ . Anal. Calcd for C<sub>37</sub>H<sub>41</sub>O<sub>2</sub>Si<sub>2</sub>: C, 77.30; H, 7.36. Found: C, 77.27; H, 7.41.

(20) This method is very useful for constructing highly ordered two-dimensional (2D) helix-bundles for helical polyacetylenes and polyisocyanides on HOPG, and their helical structures were visualized by AFM. See: (a) Sakurai, S.-i.; Okoshi, K.; Kumaki, J.; Yashima, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1245–1248. (b) Kajitani, T.; Okoshi, K.; Sakurai, S.-i.; Kumaki, J.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 708–709. (c) Sakurai, S.-i.; Ohsawa, S.; Nagai, K.; Okoshi, K.; Kumaki, J.; Yashima, E. *Angew. Chem., Int. Ed.* **2007**, *46*, 7605–7608.



**Figure 5.** WAXD pattern and AFM images of the complementary double helix of poly-(*R*)-1•poly-2. (A) WAXD pattern of an oriented film of the interpolymer complex of poly-(*R*)-1•poly-2 from a toluene/THF solution. (B) Space-filling drawing of a trimer model for poly-(*R*)-1•poly-2 complex constructed by molecular-mechanics calculations based on the results of X-ray single crystal structure of an analogous dimer double helix.<sup>12a,17</sup> (C) AFM phase image (scale 120 nm × 120 nm) of poly-(*R*)-1•poly-2 on HOPG with the height profile measured along the dashed line in the image (bottom). (D) Magnified AFM phase image (scale 40 nm × 40 nm) of poly-(*R*)-1•poly-2 on HOPG.

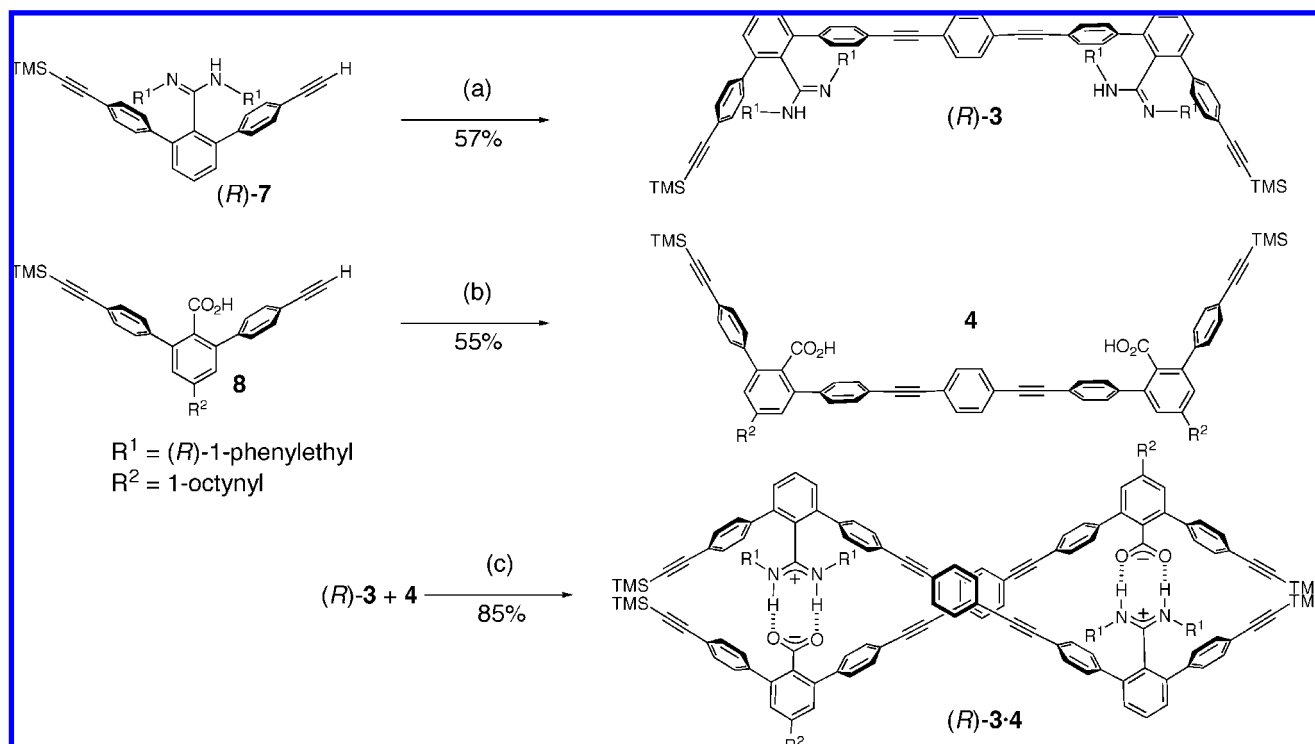
### Scheme 1<sup>a</sup>



<sup>a</sup> Reagents and conditions: (a) 1-octyne, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, Et<sub>3</sub>N, rt, 24 h; (b) (i) *n*-BuLi, THF, −78 °C, (ii) 4-TMS-ethynylphenylmagnesium bromide, −78 °C to reflux, (iii) CO<sub>2</sub>, rt; (c) (i) *n*-Bu<sub>4</sub>NF, THF, rt, 1 h, (ii) H<sub>3</sub>O<sup>+</sup>.

**Synthesis of 2'-Carboxy-4,4''-bis(ethynyl)-5'-(1-octynyl)-1,1':3'1''-terphenyl (6) and 2'-Carboxy-4-ethynyl-4''-trimethylsilyl-ethynyl-5'-(1-octynyl)-1,1':3'1''-terphenyl (8).** The title compounds were obtained from **11** by treatment with tetrabutylammonium fluoride (TBAF) in THF at ambient temperature, followed by column chromatography (SiO<sub>2</sub>, *n*-hexane/EtOAc = 1/0 to 7/3). **6**: Mp: 153–155 °C. IR (KBr):  $\nu = 3290$  ( $\nu_{\text{C}=\text{H}}$ ), 2230 ( $\nu_{\text{C}=\text{C}}$ ), 2108 ( $\nu_{\text{C}=\text{C}}$ ), 1697 ( $\nu_{\text{C}=\text{O}}$ ) cm<sup>−1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, **6** (20 mM), 25 °C):  $\delta = 0.89$  (t, CH<sub>3</sub>,  $J = 6.9$  Hz, 3H), 1.26–1.36 (m, CH<sub>2</sub>, 4H), 1.44 (m, CH<sub>2</sub>, 2H), 1.59 (m, CH<sub>2</sub>, 2H), 2.41 (t, C≡CCH<sub>2</sub>,  $J = 7.1$  Hz,

2H), 3.16 (s, C≡CH, 2H), 7.32 (d, ArH,  $J = 8.2$  Hz, 4H), 7.37 (s, ArH, 2H), 7.52 (d, ArH,  $J = 8.2$  Hz, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, **6** (20 mM), 25 °C):  $\delta = 14.21, 19.58, 22.68, 28.67, 28.75, 31.48, 78.42, 79.51, 83.42, 93.39, 121.99, 126.20, 128.48, 130.23, 132.08, 132.31, 140.01, 140.14, 173.35$ . ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (1/4, v/v), negative). Calcd for C<sub>31</sub>H<sub>25</sub>O<sub>2</sub> [**6** − H]<sup>−</sup>:  $m/z = 429.19$ . Found:  $m/z = 429.17$ . Anal. Calcd for C<sub>31</sub>H<sub>26</sub>O<sub>2</sub>: C, 86.48; H, 6.09. Found: C, 86.68; H, 5.87. **8**: Mp: 55.1–59.2 °C. IR (KBr):  $\nu = 3437$  ( $\nu_{\text{O}=\text{H}}$ ), 2230 ( $\nu_{\text{C}=\text{C}}$ ), 2159 ( $\nu_{\text{C}=\text{C}}$ ), 1703 ( $\nu_{\text{C}=\text{O}}$ ) cm<sup>−1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, **8** (29 mM), 25 °C):  $\delta = 0.26$  (s, TMS, 9H), 0.89 (t,  $J =$

Scheme 2<sup>a</sup>

<sup>a</sup> Reagents and conditions: (a) 1,4-diiodobenzene, Pd(PPh<sub>3</sub>)<sub>4</sub>, CuI, Et<sub>3</sub>N, toluene, 60 °C, overnight; (b) (i) 1,4-diiodobenzene, Pd(PPh<sub>3</sub>)<sub>4</sub>, CuI, <sup>t</sup>Pr<sub>2</sub>NH, THF, 30 °C, 5 h, (ii) H<sub>3</sub>O<sup>+</sup>; (c) CHCl<sub>3</sub>, ambient temperature.

6.9 Hz, CH<sub>3</sub>, 3H), 1.26–1.37 (m, CH<sub>2</sub>, 4H), 1.44 (m, CH<sub>2</sub>, 2H), 1.60 (m, CH<sub>2</sub>, 2H), 2.41 (t, *J* = 7.1 Hz, C≡CCH<sub>2</sub>, 2H), 3.15 (s, C≡CH, 1H), 7.29–7.34 (m, ArH, 4H), 7.35–7.37 (m, ArH, 2H), 7.49–7.54 (m, ArH, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, **8** (29 mM), 25 °C): δ = 0.14, 14.20, 19.59, 22.68, 28.69, 28.76, 31.49, 78.34, 79.56, 83.44, 93.29, 95.50, 104.86, 121.96, 122.98, 126.10, 128.42, 128.52, 130.40, 131.99, 132.02, 132.12, 132.31, 139.82, 139.97, 140.15, 140.22, 172.60. ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (1/4, v/v), negative). Calcd for C<sub>34</sub>H<sub>33</sub>O<sub>2</sub>Si<sub>1</sub> [**8** – H]<sup>–</sup>: *m/z* = 501.22. Found: *m/z* = 501.22. Anal. Calcd for C<sub>34</sub>H<sub>34</sub>O<sub>2</sub>Si<sub>1</sub>: C, 81.23; H, 6.82. Found: C, 81.13; H, 6.85.

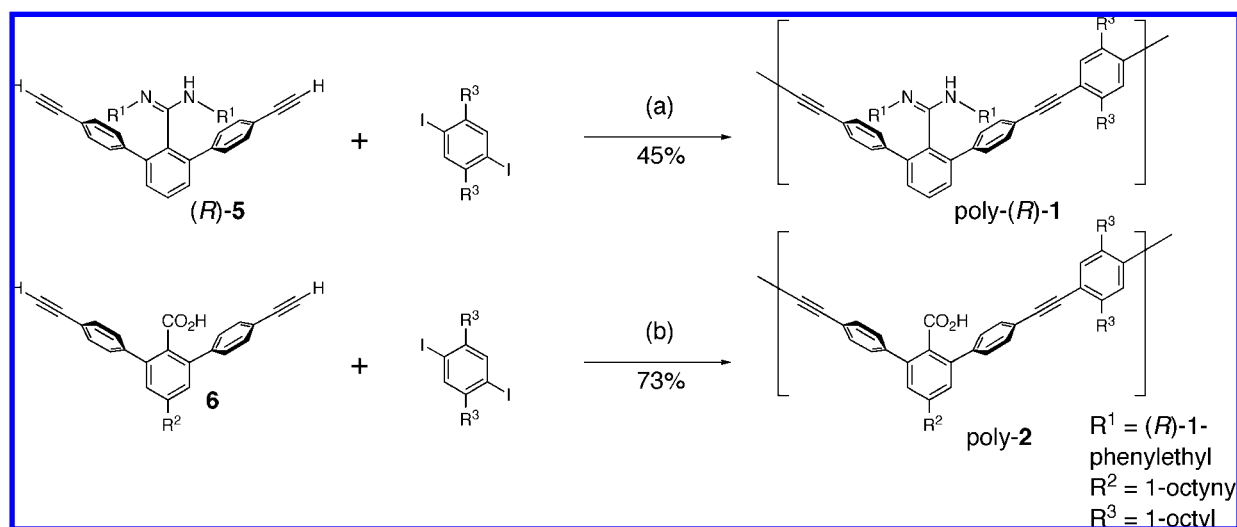
#### Synthesis of Model Dimers. Synthesis of Diamidine (*R*)-3. Scheme 2.

In a Schlenk flask, a mixture of (*R*)-**7**<sup>12a</sup> (150 mg, 0.25 mmol), 1,4-diiodobenzene (42 mg, 0.13 mmol), CuI (2.4 mg, 0.013 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (9.1 mg, 0.013 mmol) was degassed and back-filled three times with Ar. Triethylamine (2.0 mL) and toluene (8.0 mL) were introduced into the flask via a syringe, and the reaction mixture was stirred at 60 °C for 24 h. After evaporation, the residue was purified by column chromatography (NH<sub>2</sub>/SiO<sub>2</sub>, *n*-hexane/THF = 10/0 to 10/1) to afford amidine (*R*)-**3** (0.091 g, 57% yield) as a white solid. Mp: 157–158 °C. [α]<sub>D</sub><sup>20</sup> –193° (*c* = 0.1 in CHCl<sub>3</sub>). IR (KBr): ν = 3428 (ν<sub>N–H</sub>), 2157 (ν<sub>C≡C</sub>), 1638 (ν<sub>C=N</sub>) cm<sup>–1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, (*R*)-**3** (7.8 mM), CH<sub>3</sub>CO<sub>2</sub>H (20 mM), 25 °C): δ = 0.26 (s, TMS, 18H), 0.72 (m, CH<sub>3</sub>CHN, 12H), 2.10 (s, CH<sub>3</sub>CO<sub>2</sub>, 3H), 3.93 (m, CHN, 4H), 6.67 (d, ArH, *J* = 8.4 Hz, 4H), 6.72 (d, ArH, *J* = 8.4 Hz, 4H), 7.05 (m, ArH, 8H), 7.20–7.33 (m, ArH, 20H), 7.50–7.55 (m, ArH, 8H), 7.76 (t, ArH, *J* = 7.8 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, (*R*)-**3** (7.8 mM), CH<sub>3</sub>CO<sub>2</sub>H (20 mM), 25 °C): δ = 0.14, 22.34, 23.19, 55.62, 90.75, 90.85, 96.21, 104.32, 122.66, 123.14, 123.38, 123.49, 126.71, 126.74, 128.12, 128.58, 128.77, 129.18, 129.20, 130.67, 130.73, 131.75, 132.01, 132.23, 132.30, 132.39, 138.16, 141.70, 141.77, 142.81, 142.88, 162.72, 177.84. ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (1/4, v/v), positive). Calcd for C<sub>90</sub>H<sub>83</sub>N<sub>4</sub>Si<sub>2</sub> [(*R*)-**3** + H]<sup>+</sup>: *m/z* = 1276.81. Found: *m/z* = 1276.61. Anal. Calcd for C<sub>90</sub>H<sub>82</sub>N<sub>4</sub>Si<sub>2</sub>: C, 84.73; H, 6.48; N, 4.39. Found: C, 84.70; H, 6.38; N, 4.30.

**Synthesis of Carboxylic Acid Dimer 4.** The title compound was prepared from **8** and 1,4-diiodobenzene in a way similar to that for the (*R*)-**3**. The residual crude product was purified by column chromatography (SiO<sub>2</sub>, CHCl<sub>3</sub>/CH<sub>3</sub>OH = 10/0 to 10/1) to afford carboxylic acid **4** (55% yield) as a white solid. Mp: 227–229 °C. IR (KBr): ν = 2227 (ν<sub>C=C</sub>), 2157 (ν<sub>C=C</sub>), 1742 (ν<sub>C=O</sub>), 1703 (ν<sub>C=O</sub>) cm<sup>–1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, **4** (7.7 mM), 25 °C): δ = 0.27 (s, TMS, 18H), 0.89 (t, CH<sub>3</sub>, *J* = 7.0 Hz, 6H), 1.28–1.35 (m, CH<sub>2</sub>, 8H), 1.44 (m, CH<sub>2</sub>, 4H), 1.60 (m, CH<sub>2</sub>, 4H), 2.41 (t, C≡CCH<sub>2</sub>, *J* = 7.2 Hz, 4H), 7.30 (d, ArH, *J* = 8.2 Hz, 4H), 7.37–7.39 (m, ArH, 8H), 7.44 (s, ArH, 4H), 7.53 (d, ArH, *J* = 8.2 Hz, 4H), 7.59 (d, ArH, *J* = 8.2 Hz, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, **4** (7.7 mM), 25 °C): δ = 0.31, 14.21, 19.60, 22.67, 28.70, 28.77, 31.49, 79.60, 90.32, 91.01, 93.22, 95.58, 104.95, 122.95, 123.00, 123.18, 123.29, 126.06, 128.45, 128.60, 130.55, 131.68, 131.85, 131.92, 132.03, 132.13, 139.81, 139.83, 140.12, 173.35. ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (1/4, v/v), negative). Calcd for C<sub>74</sub>H<sub>69</sub>O<sub>4</sub>Si<sub>2</sub> [**4** – H]<sup>–</sup>: *m/z* = 1078.48. Found: *m/z* = 1078.40. Anal. Calcd for C<sub>74</sub>H<sub>70</sub>O<sub>4</sub>Si<sub>2</sub>: C, 82.33; H, 6.54. Found: C, 82.36; H, 6.35.

**Dimer Double Helix (*R*)-3·4.** The diamidine, (*R*)-**3** (3.78 mg, 0.00296 mmol), and the dicarboxylic acid, **4** (3.20 mg, 0.00296 mmol), were dissolved in CDCl<sub>3</sub> (0.7 mL), and the solution was stirred at ambient temperature. The solution was evaporated to dryness to afford (*R*)-**3**·**4** (6.98 mg, 100% yield) as a white solid. Mp: 237–241 °C. [α]<sub>D</sub><sup>20</sup> –359° (*c* = 0.1 in CHCl<sub>3</sub>). IR (KBr): ν = 2224, 2156 (ν<sub>C=C</sub>), 1637 cm<sup>–1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, (*R*)-**3**·**4** (4.0 mM), 25 °C): δ = 0.27 (s, TMS, 18H), 0.31 (s, TMS, 18H), 0.67 (m, NCHCH<sub>3</sub>, 12H), 0.91 (t, CH<sub>3</sub>, *J* = 6.9 Hz, 6H), 1.30–1.37 (m, CH<sub>2</sub>, 8H), 1.45 (m, CH<sub>2</sub>, 4H), 1.61 (m, CH<sub>2</sub>, 4H), 2.41 (t, C≡CCH<sub>2</sub>, *J* = 7.2 Hz, 4H), 3.80 (m, CHN, 2H), 3.87 (m, CHN, 2H), 6.58 (d, ArH, *J* = 8.1 Hz, 4H), 6.70 (d, ArH, *J* = 8.2 Hz, 8H), 6.78 (d, ArH, *J* = 7.5 Hz, 4H), 7.11 (t, ArH, *J* = 7.6 Hz, 4H), 7.16–7.23 (m, ArH, 12H), 7.27 (s, ArH, 4H), 7.34 (d, ArH, *J* = 8.3 Hz, 4H), 7.39–7.44 (m, ArH, 8H), 7.48 (t, ArH, *J* = 7.8 Hz, 4H), 7.61–7.70 (m, ArH, 12H), 7.72 (t, ArH, *J* = 7.8 Hz, 2H), 7.81 (m, ArH, 4H), 13.33 (br d, 2H, NH), 13.44 (br d, 2H, NH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, (*R*)-**3**·**4** (4.0 mM), 25 °C): δ = 0.15, 0.38, 14.23, 19.66, 22.67,



Scheme 3<sup>a</sup>

<sup>a</sup> Reagents and conditions: (a) Pd(PPh<sub>3</sub>)<sub>4</sub>, CuI, <sup>i</sup>Pr<sub>2</sub>NH, toluene, 60 °C, 12 h; (b) (i) Pd(PPh<sub>3</sub>)<sub>4</sub>, CuI, <sup>i</sup>Pr<sub>2</sub>NH, THF, 60 °C, 9 h, (ii) H<sub>3</sub>O<sup>+</sup>, CHCl<sub>3</sub>/methanol.

22.71, 22.79, 28.81, 28.90, 31.53, 55.71, 55.79, 80.65, 89.50, 90.30, 90.37, 90.87, 91.21, 94.82, 96.55, 104.29, 105.96, 121.82, 121.99, 122.70, 122.80, 122.87, 123.24, 123.55, 123.64, 126.39, 126.59, 127.81, 127.90, 128.69, 128.86, 129.12, 129.22, 130.38, 130.47, 131.24, 131.49, 131.50, 131.59, 131.84, 131.92, 132.16, 132.28, 136.96, 137.62, 138.11, 138.26, 140.30, 141.22, 141.70, 142.04, 142.48, 142.77, 162.43, 176.81. ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (9/1, v/v), positive). Calcd for C<sub>164</sub>H<sub>153</sub>N<sub>4</sub>O<sub>4</sub>Si<sub>4</sub> [(R)-3•4 + H<sup>+</sup>]; *m/z* = 2354.10. Found: *m/z* = 2354.20. Anal. Calcd for C<sub>164</sub>H<sub>152</sub>N<sub>4</sub>O<sub>4</sub>Si<sub>4</sub>: C, 83.63; H, 6.50; N, 2.38. Found: C, 83.43; H, 6.68; N, 2.27.

#### Polymerization. Synthesis of Poly-(R)-1. Scheme 3.

In a 10 mL Schlenk flask, a mixture of (R)-5<sup>12b</sup> (100 mg, 0.189 mmol), 1,4-diiodo-2,5-dioctylbenzene (105 mg, 0.189 mmol), CuI (3.6 mg, 0.0189 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (22.0 mg, 0.0189 mmol) was degassed and back-filled three times with Ar. Diisopropylamine (1.1 mL) and toluene (2.7 mL) were introduced into the flask via a syringe, and the reaction mixture was stirred at 60 °C for 12 h. After evaporation, the residue was dissolved in a minimum amount of CHCl<sub>3</sub>, and then the mixture was poured into a large amount of CH<sub>3</sub>OH. The precipitate was collected by centrifugation and dried under vacuum to give poly-(R)-1 as a pale yellow solid (70 mg, 0.0846 mmol, 45% yield). The number average molecular weight (*M<sub>n</sub>*) and molecular weight distribution were estimated to be 3.8 × 10<sup>4</sup> and 1.9, respectively, by SEC using polystyrene standards and THF containing 0.1 wt% tetrabutylammonium bromide as the eluent. [α]<sub>D</sub><sup>20</sup> -177° (*c* = 0.1 in CHCl<sub>3</sub>). IR (neat): *ν* = 3429 (*ν*<sub>N-H</sub>), 2204 (*ν*<sub>C=C</sub>), 1637 (*ν*<sub>C=N</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, poly-(R)-1 (20 mM), CH<sub>3</sub>CO<sub>2</sub>H (190 mM), 50 °C): δ = 0.78 (m, CH<sub>3</sub>CHN, 6H), 0.87 (m, CH<sub>2</sub>CH<sub>3</sub>, 6H), 1.22–1.48 (m, CH<sub>2</sub>, 20H), 1.72 (m, ArCH<sub>2</sub>CH<sub>2</sub>, 4H), 2.08 (s, CH<sub>3</sub>CO<sub>2</sub>, 3H), 2.82 (m, ArCH<sub>2</sub>, 4H), 3.99 (m, CHN, 2H), 6.74 (m, ArH, 4H), 7.06 (m, ArH, 4H), 7.20–7.34 (m, ArH, 10H), 7.38 (s, ArH, 2H), 7.55 (m, ArH, 2H), 7.78 (m, ArH, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, poly-(R)-1 (20 mM), CH<sub>3</sub>CO<sub>2</sub>H (190 mM), 50 °C): δ = 14.10, 20.87, 22.14, 22.71, 29.33, 29.57, 29.63, 30.44, 30.65, 31.97, 34.18, 55.78, 90.35, 93.31, 122.65, 124.02, 125.54, 126.73, 128.74, 129.15, 130.63, 131.85, 132.01, 132.55, 137.83, 141.85, 142.42, 142.62, 162.92, 176.79.

Anal. Calcd for C<sub>61</sub>H<sub>66</sub>N<sub>2</sub>: C, 88.57; H, 8.04; N, 3.39. Found: C, 88.60; H, 7.81; N, 3.31.

**Synthesis of Poly-2.** In a 10 mL Schlenk flask, a mixture of 6 (30.0 mg, 0.0697 mmol), 1,4-diiodo-2,5-dioctylbenzene (38.6 mg, 0.0697 mmol), CuI (0.65 mg, 0.0035 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (2.01 mg, 0.00174 mmol) was degassed and back-filled three times with Ar. Diisopropylamine (0.85 mL) and THF (1.95 mL) were introduced into the flask via a syringe, and the reaction mixture was stirred at 60 °C for 9 h. The reaction mixture was poured into acetonitrile to precipitate out the polymer in two portions. After centrifugation, the collected precipitate was dissolved in a mixed solvent of CHCl<sub>3</sub> and methanol. The solution was then acidified with aqueous HCl (1 M), and the precipitate was collected by centrifugation; the residue was dissolved in benzene and freeze-dried to obtain poly-2 as a pale yellow solid (37.0 mg, 0.0508 mmol, 73% yield). IR (neat): *ν* = 2230 (*ν*<sub>C=C</sub>), 1731 (*ν*<sub>C=O</sub>), 1701 (*ν*<sub>C=O</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, poly-2 (15 mM), 50 °C): δ = 0.81–0.92 (m, CH<sub>3</sub>, 9H), 1.20–1.56 (m, CH<sub>2</sub>, 26H), 1.62 (m, C=CCH<sub>2</sub>CH<sub>2</sub>, 2H), 1.76 (m, ArCH<sub>2</sub>CH<sub>2</sub>, 4H), 2.44 (m, C=CCH<sub>2</sub>, 2H), 2.66–2.90 (m, ArCH<sub>2</sub>, 4H), 7.35–7.44 (m, ArH, 4H), 7.45–7.62 (m, ArH, 8H). <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, poly-2 (15 mM), 50 °C): δ = 17.07, 17.13, 22.71, 26.15, 26.26, 32.27, 32.41, 32.98, 33.11, 33.25, 34.40, 35.08, 35.61, 37.74, 83.34, 92.57, 95.40, 97.57, 126.50, 126.56, 128.79, 132.57, 134.75, 135.30, 136.03, 136.98, 143.20, 144.22, 145.93, 172.66. Anal. Calcd for C<sub>53</sub>H<sub>60</sub>O<sub>2</sub>: C, 87.32; H, 8.30. Found: C, 87.11; H, 8.01. A part of poly-2 was converted to the corresponding methyl ester polymer by treatment with (trimethylsilyl)diazomethane to obtain a sample for SEC analysis. The *M<sub>n</sub>* and molecular weight distribution were estimated to be 2.4 × 10<sup>4</sup> and 3.5, respectively, by SEC using polystyrene standards and THF containing 0.1 wt % tetrabutylammonium bromide as the eluent.

**Supporting Information Available:** Full experimental details in the characterization of poly-(R)-1•poly-2 and (R)-3•4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA711447S