Syntheses and Chiroptical Properties of Optically Active Helical Poly(phenylacetylene)s Bearing [60]Fullerene Pendants

Sousuke Ohsawa, Katsuhiro Maeda, and Eiji Yashima*

Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan

Received October 6, 2007; Revised Manuscript Received October 22, 2007

ABSTRACT: Two novel C_{60}-bound chiral (**3**) and achiral (**2**) phenylacetylenes were synthesized by the treatment of C_{60} with (*R*)-*N*-[1-(4-ethynylphenyl)ethyl]glycine and *N*-(4-ethynylbenzyl)glycine by the Prato reaction in the presence of paraformaldehyde and dipentadecyl ketone, respectively. The homopolymerization of the achiral **2** bearing long alkyl chains and copolymerization with optically active phenylacetylenes including **3** using a rhodium catalyst in chloroform homogeneously occurred, giving the C_{60}-containing helical poly(phenylacetylene)s soluble in chloroform, while the homopolymers of the analogous achiral C_{60}-bound phenylacetylenes with no alkyl chain (**1**) and **3** were totally insoluble in common organic solvents. The obtained copolymers exhibited an induced circular dichroism (ICD) both in the main-chain region and in the fullerene chromophoric region, indicating that the optically active copolymers possess a preferred-handed helical conformation and that the pendant fullerene groups are arranged in helical arrays with a predominant screw-sense along the polymer backbones. The formation of a hierarchical supramolecular assembly of the homopolymers of **1** and **3** bearing fullerene pendants on each repeating unit was also studied by electron microscopy.

Introduction

Fullerene (C_{60})-containing polymers have recently attracted significant attention because the incorporation of C_{60} molecules into polymer backbones or pendants is the most versatile method of producing practically useful C_{60}-based materials with a high mechanical strength and good processability.[1,2] Such C_{60}-based polymers with a well-defined structure may be applied to many fields including the materials and biological sciences due to the unique physical and chemical features of C_{60} molecules.[1−3] In a series of studies, we reported the copolymerization of an achiral phenylacetylene bearing a C_{60} pendant (**1**) with optically active phenylacetylenes such as **4**, which produced preferred-handed helical copolymers in which the pendant C_{60} groups are arranged in a helical array with a predominant screw-sense along the polymer backbones.[4] The copolymers exhibited an induced circular dichroism (ICD) in the achiral fullerene chromophoric region as well as in the polymer backbone region. Similar preferred-handed helicity inductions accompanied by helical arrays of C_{60} molecules were possible for a dynamically racemic helical poly(phenylacetylene) bearing bulky 18-crown-6 ether and achiral C_{60} units as the pendants,[5] when complexed with L- or D-amino acids through noncovalent bonding interactions.[6]

These copolymerization approaches are certainly useful for producing optically active C_{60}-based helical polymers with a helical array of the pendant C_{60} molecules in the desired screw-sense. However, such a helical array of the C_{60} units showing optical activity in the achiral fullerene chromophore region was possible when the C_{60} units in the copolymers were less than 30 mol %. Because of the low solubility of fullerene, the incorporation of more than 30 mol % of the C_{60} units of **1** into the copolymers yielded copolymers insoluble in common organic solvents.[4,5] In order to overcome these solubility problem, we prepared a novel achiral C_{60}-bound phenylacetylene (**2**) by introducing two long pentadecyl chains on the pyrrolidine ring of the 3,4-fulleropyrrolidine residue, and this was copolymerized with an optically active phenylacetylene (**4**) to obtain optically active and highly soluble helical copolymers with a high C_{60} content (Scheme 1). A new optically active C_{60}-bound phenylacetylene (**3**) was also synthesized and copolymerized with **2** in order to produce soluble helical copolymers composed of fullerene moieties on each repeating monomer unit (Scheme 1). The chiroptical properties of the obtained copolymers were then investigated by circular dichroism (CD) and absorption spectroscopies. The morphologies of the insoluble homopolymers of **1** and **3** were also studied by electron microscopy.

Results and Discussion

Synthesis and Polymerization of Chiral and Achiral Phenylacetylenes Bearing Fullerene Pendants. In order to improve the solubility of the poly(phenylacetylene)s bearing C_{60} pendant groups, we designed a new achiral fullerene monomer **2**, which has two long pentadecyl chains on the pyrrolidine ring of the 3,4-fulleropyrrolidine residue. The Prato reaction of C_{60} with *N*-(4-ethynylbenzyl)glycine,[7] which had been prepared by a previously reported method,[4] in the presence of dipentadecyl ketone afforded the target monoadduct **2** in 12% yield (Scheme 2). The new optically active fullerene monomer **3** was prepared as outlined in Scheme 3 starting from the commercially available (*R*)-1-(4-bromophenyl)ethylamine hydrochloride followed by the Prato reaction of C_{60} with (*R*)-*N*-[1-(4-ethynylphenyl)ethyl]-glycine in the presence of paraformaldehyde[7] to give **3** in 14% yield.

The copolymerization of the achiral **2** with the optically active **3** or **4** was carried out with a rhodium catalyst, $[Rh(nbd)Cl]_2$ (nbd: norbornadiene), which is known to be effective for the polymerization of monosubstituted phenylacetylenes to give high-molecular weight, stereoregular (cis-transoidal) poly(phenylacetylene)s,[8] in chloroform containing a small amount of triethylamine according to Scheme 1. The copolymerization results are summarized in Table 1.

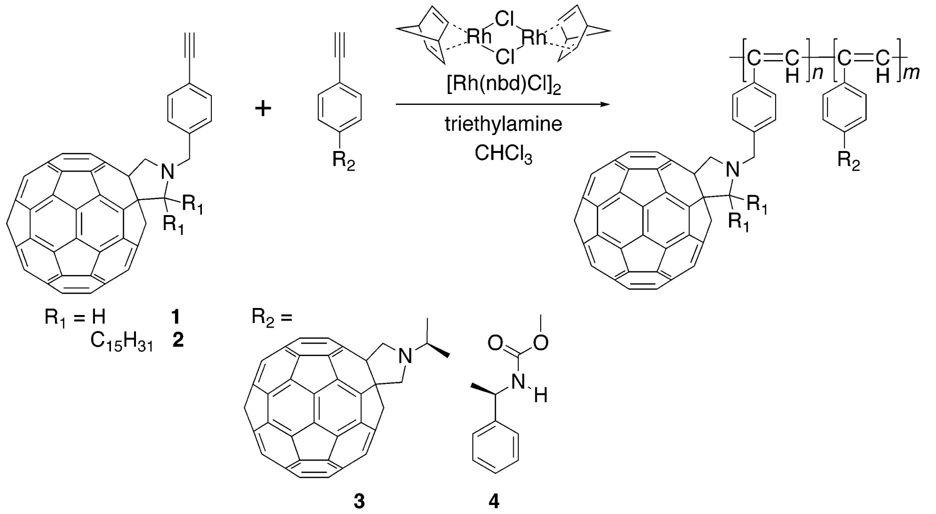
The homopolymerization of **2** (run 1 in Table 1) homogeneously proceeded and the obtained homopolymer (poly-**2**) was

---

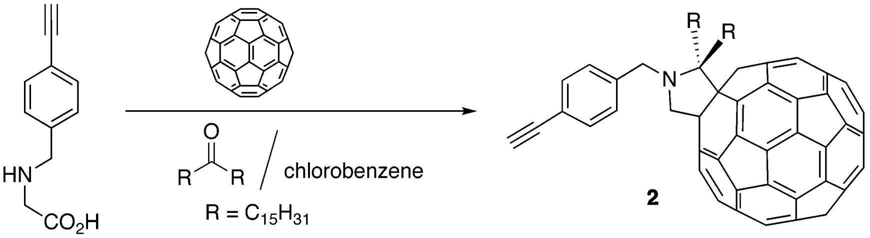
* To whom correspondence should be addressed. E-mail: yashima@apchem.nagoya-u.ac.jp.

10.1021/ma7022342 CCC: \$37.00

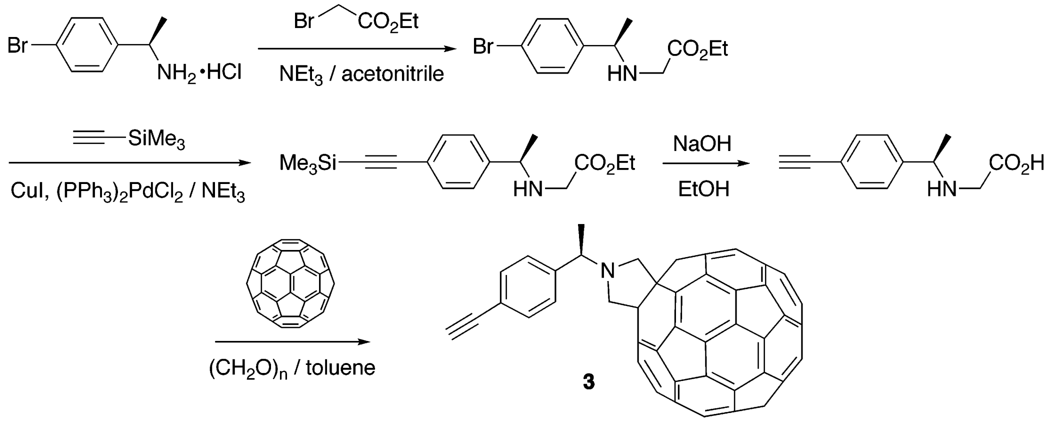
Scheme 1. Synthesis of C_{60}-Bound Helical Poly(phenylacetylene) Derivatives



Scheme 2. Synthesis of an Achiral C_{60}-Bound Phenylacetylene Derivative (2)



Scheme 3. Synthesis of an Optically Active C_{60}-Bound Phenylacetylene Derivative (3)



soluble in chloroform, while the homopolymer of **1** (poly-**1**) was insoluble in the common organic solvents, such as chloroform and tetrahydrofuran (THF), as previously reported (run 8 in Table 1).[4] The copolymerization of **2** with **3** (run 3 in Table 1) and **4** (runs 5−7 in Table 1) also homogeneously proceeded and the obtained copolymers were soluble in chloroform. On the other hand, the homopolymerization of **3** (run 2 in Table 1) and the copolymerization of **2** with **3** at the feed ratio of [**2**]/([**2**] + [**3**]) = 0.8 (run 4 in Table 1) rapidly proceeded, and the black polymers precipitated within a few minutes due to the poor solubility of the **3** units. The chloroform soluble fractions were confirmed to be unreacted monomers (**2** and **3**) by size exclusion chromatography (SEC) measurements and the obtained poly-**3** was hardly soluble in the common organic solvents, but the poly($\mathbf{2}_{0.8}$-*co*-$\mathbf{3}_{0.2}$) was partially soluble in carbon disulfide (CS_2).

The stereoregularity of the copolymers was investigated by ^{1}H NMR and Raman spectroscopies. The ^{1}H NMR spectrum of poly($\mathbf{2}_{0.1}$-*co*-$\mathbf{4}_{0.9}$) in $CDCl_3$ at 60 °C showed a relatively sharp singlet centered at 5.7 ppm due to the main-chain protons, which can be assigned to the cis-transoidal main-chain's olefinic protons (Figure S1).[8,9] However, the peaks due to the main-chain protons of poly($\mathbf{2}_{0.3}$-*co*-$\mathbf{4}_{0.7}$) and poly($\mathbf{2}_{0.5}$-*co*-$\mathbf{4}_{0.5}$) became considerably broadened with the increasing C_{60} contents (Figure S1), probably due to the rigidity of the copolymers which increased with the increasing bulky C_{60} contents. The ^{1}H NMR spectra of poly-**2** and poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{3}_{0.1}$) were also too broad to determine the stereoregularity. Therefore, the stereoregularities of poly-**2** and poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{3}_{0.1}$) as well as poly($\mathbf{2}_{0.3}$-*co*-$\mathbf{4}_{0.7}$) and poly($\mathbf{2}_{0.5}$-*co*-$\mathbf{4}_{0.5}$) were investigated by laser Raman spectroscopy. The Raman spectra of these copolymers showed intense peaks at 1535, 1330, and 966 cm^{-1}, which were assigned to the C=C, C−C, and C−H bond vibrations in the cis polyacetylenes,[10] while those in the trans polyacetylenes were not observed, indicating that these copolymers possess highly cis-transoidal structures (for example, see Figure S2).[11] The stereoregularity of the insoluble poly-**3** was also highly cis-transoidal based on its laser Raman spectrum.

Table 1. Copolymerization Results of Achiral Fullerene Monomers (1 and 2) and Optically Active Comonomers (3 and 4) with [Rh(nbd)Cl]$_2$ in Chloroform in the Presence of Triethylamine at 30 °C for 24 h[a]

					polymer				
							diethyl ether-insoluble part		
run	M$_1$	M$_2$	[M$_1$] in feed (mol %)	[M$_1$ + M$_2$] (M)	sample code	yield (%)[b]	yield (%)	[M$_1$] in polymer (mol %)[c]	$M_n \times 10^{-4}$ [d]
1	**2**		100	0.043	poly-**2**		42	100	3.0
2	**3**		100	0.016	poly-**3**	31[e]		100	
3	**2**	**3**	90	0.043	poly(**2**$_{0.9}$-*co*-**3**$_{0.1}$)		51		5.1
4	**2**	**3**	80	0.043	poly(**2**$_{0.8}$-*co*-**3**$_{0.2}$)	37			4.7[f]
5	**2**	**4**	50	0.043	poly(**2**$_{0.5}$-*co*-**4**$_{0.5}$)		86	46.5	5.0
6	**2**	**4**	30	0.043	poly(**2**$_{0.3}$-*co*-**4**$_{0.7}$)		88	30.5	4.2
7	**2**	**4**	10	0.043	poly(**2**$_{0.1}$-*co*-**4**$_{0.9}$)		81	12.2 (9.8[g])	5.5
8[h]	**1**		100	0.016	poly-**1**	60[e]		100	
9[h]	**1**	**4**	10	0.043	poly(**1**$_{0.1}$-*co*-**4**$_{0.9}$)		52	12.3[g]	8.4

[a] Polymerized under nitrogen; [M$_1$ + M$_2$]/[triethylamine] = 1. [M$_1$ + M$_2$]/[Rh] = 100. [b] Chloroform insoluble part. [c] Estimated by IR spectroscopy. [d] Determined by SEC with polystyrene standards using chloroform as the eluent. [e] Insoluble in common organic solvents. [f] CS$_2$ soluble part. [g] Estimated by ^{1}H NMR spectroscopy. [h] Cited from ref 4a.

The copolymer compositions of poly(**2**-*co*-**4**)s were estimated by their IR spectra on the basis of the ratio between the characteristic absorption for the carbonyl group of **4** at 1716 cm^{-1} and that of the fullerene unit of **2** at 527 cm^{-1} (Figure S3). The calibration curve was obtained by plotting the corresponding peak intensity ratios of monomers **2** and **4** vs the content of **4** in the various mixtures of **4** and **2**. The copolymer compositions estimated by their IR spectra were nearly in accordance with those in the feed.[12] This method, however, cannot be used for estimating the copolymer composition of poly(**2**$_{0.9}$-*co*-**3**$_{0.1}$) having C$_{60}$ units in each repeating monomer unit. Moreover, the ^{1}H NMR spectrum of poly(**2**$_{0.9}$-*co*-**3**$_{0.1}$) was too broad to determine the copolymer composition.

Chiroptical Properties of Copolymers. The CD and absorption spectra of poly(**2**$_{0.1}$-*co*-**4**$_{0.9}$) and poly(**2**$_{0.5}$-*co*-**4**$_{0.5}$) in chloroform are shown in Figure 1, parts A and B, respectively. The copolymers exhibited an ICD in the π-conjugated main-chain region (300−500 nm), although their ICD patterns were slightly different from each other. The magnitude of the ICDs increased with the decreasing temperature, but their increase was not significant when compared with poly(**1**$_{0.1}$-*co*-**4**$_{0.9}$) (run 9 in Table 1).[4] These observations suggest that the helical screw-sense preference increased with the decreasing temperature. The ICD intensity of poly(**2**$_{0.1}$-*co*-**4**$_{0.9}$) was quite weak compared to that of the previously reported poly(**1**$_{0.1}$-*co*-**4**$_{0.9}$) (run 9 in Table 1), which consists of the same chiral unit (**4**) and an analogous achiral fullerene unit except for the long alkyl chains in **2** with almost the identical chiral/achiral molar ratio (12 mol %).[4] This weak ICD of the poly(**2**$_{0.1}$-*co*-**4**$_{0.9}$) may be attributed to the dissymmetric substitution of the alkyl chains on the pyrrolidine ring of the achiral 3,4-fulleropyrrolidine units. Similar weak ICDs were previously observed for poly(phenylacetylene)s having chiral pendants at the meta position[13] and the poly(phenylacetylene) bearing a carboxy group at the meta position complexed with optically active amines.[14] Such a dissymmetric substitution may afford various types of chiral interactions among the pendant groups, which may prevent an effective preferred-handed helicity induction.[13,14]

Poly(**2**$_{0.1}$-*co*-**4**$_{0.9}$) and poly(**2**$_{0.5}$-*co*-**4**$_{0.5}$) displayed almost no detectable absorption and CD at wavelengths over 600 nm in dilute solution due to the low concentrations of the C$_{60}$ units. At higher concentrations, however, weak, but apparent ICDs were observed above 600 nm (Figure 1, parts A and B). These results suggest that the copolymers form a preferred-handed helix and the achiral C$_{60}$ pendants of the copolymers may arrange in a helical array with a predominant screw-sense along the polymer backbones. Especially, poly(**2**$_{0.5}$-*co*-**4**$_{0.5}$) exhibited a split-type ICD in the fullerene chromophore region as shown in Figure 1B. Such a split-type ICD was not observed for the previously prepared C$_{60}$-bound poly(phenylacetylene)s, such as poly(**1**-*co*-**4**) with C$_{60}$ contents of less than 30 mol %.[4,5] This positive CD couplet in the fullerene region is likely indicative of a right-handed helical array of the pendant fullerenes.

Poly(**2**$_{0.9}$-*co*-**3**$_{0.1}$) also exhibited a similar ICD in the fullerene chromophore region above 600 nm as well as in the π-conjugated main-chain region (250−500 nm) and the ICD intensity hardly changed at lower temperatures (Figure 1C). The CD spectrum of the optically active monomer **3** (Figure 1C) showed a very weak ICD in the same fullerene chromophore region. These results indicated that the pendant fullerenes are arranged in a helical array along the preferred-handed helical poly(**2**$_{0.9}$-*co*-**3**$_{0.1}$) main-chain and that the bulky fullerene pendants appear to efficiently assist with the helical arrangement of the C$_{60}$ molecules, which are stable at 25 °C, although the helix-sense excess of the main-chain is small due to the above-mentioned dissymmetric substitution effect of the alkyl chains on the pyrrolidine ring and also due to the small chiral units of **3** incorporated in the copolymer. However, this is the first example of a soluble helical poly(phenylacetylene) bearing fullerene pendants on each monomer unit.[15]

Recently, we successfully determined the helical structure of a poly(phenylacetylene) bearing an L- or D-alanine residue with a long *n*-decyl chain as the pendants (poly-**5**L and poly-**5**D, respectively) including the helical pitch and handedness by direct atomic force microscopy (AFM) observations together with their X-ray structural analyses and CD measurements.[16] Poly-**5**L has a left-handed helical array with respect to the pendant arrangements, while the main-chain has the opposite, right-handed helical structure. The ICD pattern of poly(**2**$_{0.9}$-*co*-**3**$_{0.1}$) in the main-chain region is similar to that of poly-**5**L.[16] Therefore, the main-chain of the poly(**2**$_{0.9}$-*co*-**3**$_{0.1}$) is assigned to have a right-handed helical structure and the helical array of the pendant fullerenes may be assigned as left-handed. However, poly(**2**$_{0.9}$-*co*-**3**$_{0.1}$) seems to have an opposite right-handed helical array of the pendant fullerenes on the basis of the exciton chirality method because the poly(**2**$_{0.9}$-*co*-**3**$_{0.1}$) exhibited a positive exciton-coupled ICD in the fullerene chromophore region similar to that of poly(**2**$_{0.5}$-*co*-**4**$_{0.5}$) in their patterns (Figure 1, parts B and C). This contradiction can be explained by taking into consideration the direction of the 3,4-fulleropyrrolidine units.

Parts A and B of Figure 2 show two possible right-handed helical structures of poly(**2**$_{0.9}$-*co*-**3**$_{0.1}$) with right- and left-handed helical arrays of the pendant C$_{60}$ units, respectively. When the initial dihedral angle between the phenyl group and fulleropy-

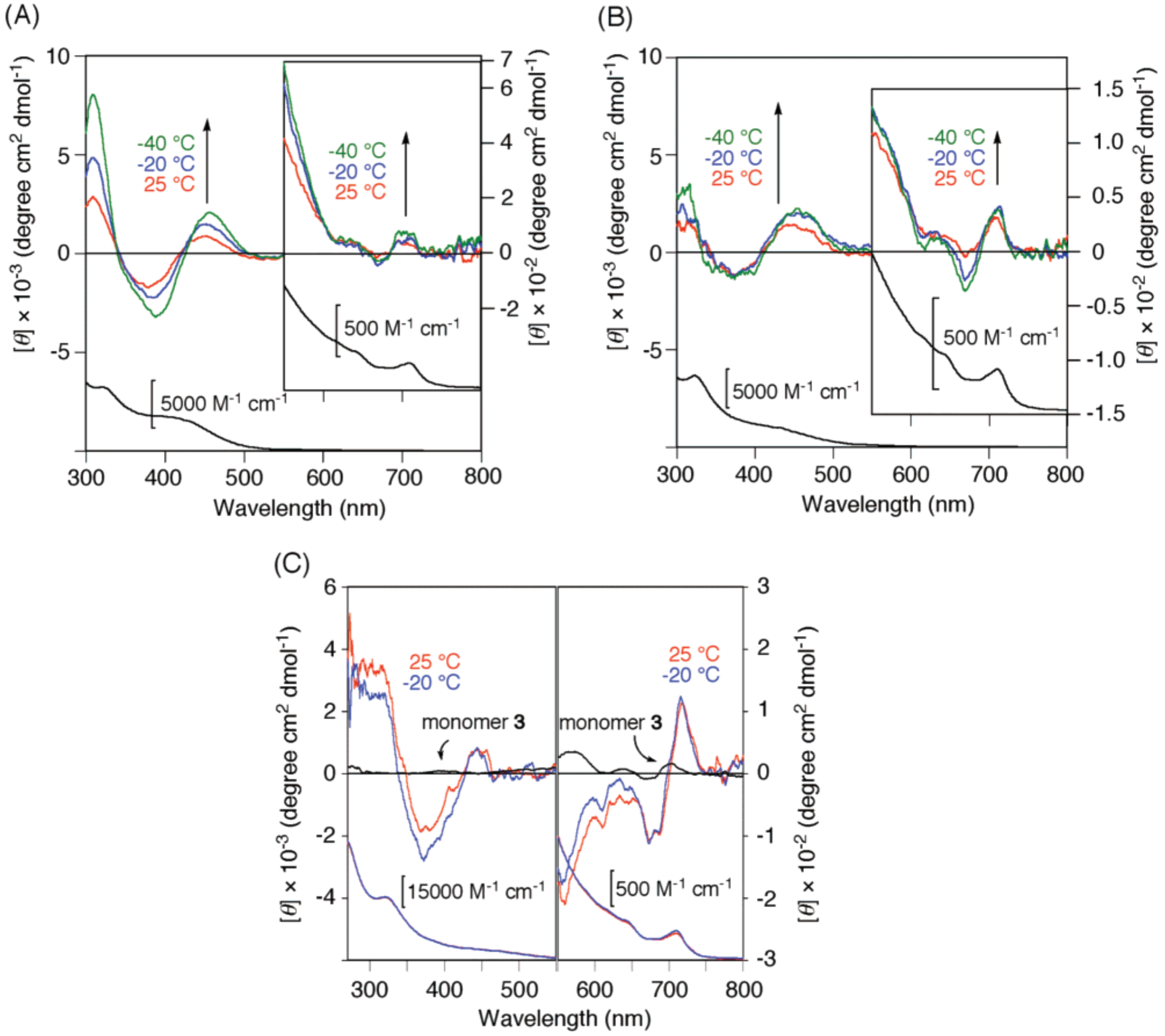


Figure 1. CD and absorption spectra of poly(**2**$_{0.1}$-*co*-**4**$_{0.9}$) (A), poly(**2**$_{0.5}$-*co*-**4**$_{0.5}$) (B), and poly(**2**$_{0.9}$-*co*-**3**$_{0.1}$) (C) in chloroform ([polymer] = 0.1 mg/mL) at +25 (red lines), −20 (blue lines), and −40 °C (green lines). The insets show the corresponding CD and absorption spectra in the fullerene region at a higher concentration (3.0 mg/mL). The molar concentrations were calculated on the basis of the monomer and C$_{60}$ units (inset). The CD spectrum of optically active monomer **3** is also shown in Figure 1C.

rrolidine moiety (ϕ) is set to $180° < \phi < 240°$ ($\phi = 180°$ for Figure 2B), the pendant fullerenes are arranged in a left-handed helical array along the polymer backbone. On the other hand, the helical array of the pendant fullerenes becomes opposite, right-handed when the dihedral angle is set to $0° < \phi < 120°$ ($\phi = 60°$ for Figure 2A). Therefore, these molecular modeling studies suggest that poly(**2**$_{0.9}$-*co*-**3**$_{0.1}$) may take a right-handed helical array of the pendant fullerenes along the same right-handed helical backbone, which is in accordance with the observed CD pattern.

SEM and TEM Studies. It is well-known that fullerene derivatives often self-assemble to form spherical particles through the $\pi-\pi^*$ stacking interaction of the carbon cage.[17] We anticipated that scanning electron microscopy (SEM) might provide an insight into the structure and morphology of the poly-**1** and poly-**3** aggregates being insoluble in common organic solvents. Samples were prepared by casting dilute dispersions of poly-**1** and poly-**3** in chloroform on freshly cleaved highly oriented pyrolytic graphite (HOPG) substrates.

Typical SEM images of the optically inactive poly-**1** and optically active poly-**3** are shown in Figures 3 (A and B) and 4 (A and B), respectively. Particles with an average diameter of about 100−200 nm were observed for poly-**1** (Figure 3B) and poly-**3** (Figure 4B).[18] Interestingly, the polymer particles could be visualized by SEM without sputter-coating with Au, suggesting that these polymers have an apparent conductivity. Transmission electron microscopy (TEM) was then used to investigate the structure and morphology of the polymers in greater detail. Figures 3 (C and D) and 4 (C and D) show the typical TEM images of poly-**1** and poly-**3**, respectively. Smaller particles with an average diameter of about 15 and 30 nm for poly-**1** and poly-**3**, respectively, can be directly visualized by TEM. Therefore, the large particles observed by SEM appeared to consist of smaller particles. We presume that poly-**1** and poly-**3** form nanometer-scale small particles, which further hierarchically aggregate to form larger particles during the polymerization.[18] The reason for the difference in their particle sizes between these aggregates on a nanometer-scale is not clear at present, but the difference in optical activity may be concerned. Poly-**1** composed of the achiral monomer **1** may possess a dynamically racemic helical conformation (an equal mixture of right- and left-handed helices), while poly-**3** might

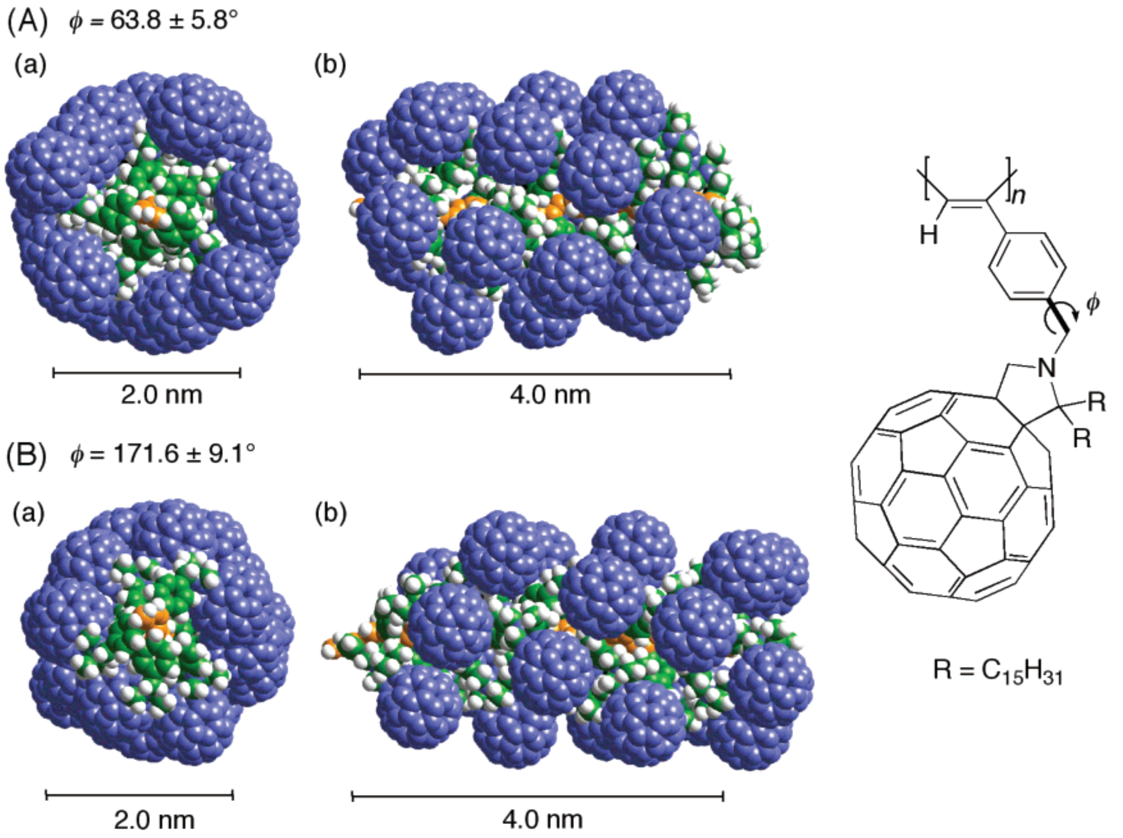


Figure 2. Possible helical structures of poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{3}_{0.1}$) (20-mer). Space filling models are shown in the top (a) and side views (b). The polymer backbones are shown in orange and the pentadecyl groups are omitted for clarity. The main chains have a right-handed helical structure. The fullerene units are arranged in right-handed (A) and left-handed helical arrays (B). The helix-sense of the main-chain is assigned from the Cotton effect sign of the ICD in the main-chain region (ca. 370 nm) according to the literature.[16] The initial dihedral angle between the phenyl group and the fulleropyrrolidine moiety (ϕ) was set to be 60 and 180° in parts A and B, respectively. The ϕ values after optimization are also shown in parts A and B.

have a predominantly one-handed helical conformation induced by the chiral pendants similar to other poly(phenylacetylene)s bearing optically active pendants.[19] Although we have no experimental evidence to support this assumption, such a one-handed helix formation in poly-**3** may contribute to the effective packing of the polymer chains with the same handedness during the aggregation process, resulting in formation of larger particles compared to those of poly-**1**.

In summary, we have prepared and characterized optically active, soluble helical polymers and copolymers bearing fullerene groups on each repeating monomer unit, which arrange in a helical array with a predominant screw-sense along the polymer backbones, thus showing optical activities both in the main-chain and in the fullerene chromophore regions, although the helix-sense excesses may be small. The present study demonstrates that the introduction of long alkyl chains in the pendant fullerene monomer residue is quite effective for constructing soluble C_{60}-bound helical poly(phenylacetylene)s with high C_{60} contents. Moreover, we found that C_{60}-bound poly(phenylacetylene)s bearing no alkyl chains hierarchically aggregate during the polymerization to form regularly sized, spherical particles. We expect that optically active C_{60}-bound helical poly(phenylacetylene)s may show a unique chiral recognition ability as chiral adsorbents due to the preferred-handed helical array of the C_{60} molecules, and further studies along this line are now in progress.

Experimental Section

Instruments. Melting points were measured on a Büchi melting point apparatus and are uncorrected. Fast atom bombardment (FAB) mass spectra were obtained on a JEOL JMS-AX505HA spectrometer. ^{1}H (500 or 300 MHz) and ^{13}C (125 or 75 MHz) NMR spectra were measured on a Varian VXR-500S or Varian Mercury-300 spectrometer using tetramethylsilane (TMS) as an internal standard. SEC measurement was performed with a JASCO PU-980 liquid chromatograph equipped with a JASCO DG-980−50 degasser and a UV−visible detector (254 nm; JASCO UV-970). A Tosoh (Tokyo, Japan) TSKgel Multipore-H_{XL}-M SEC column (30 cm) was connected, and chloroform was used as the eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curve was obtained with polystyrene standards (Tosoh). IR spectra were recorded with a JASCO Fourier Transform IR-620 spectrophotometer. Laser Raman spectra were taken on a JASCO RMP200 spectrometer. Absorption spectra were taken on a JASCO V-570 spectrophotometer in a 0.5 cm quartz cell. CD spectra were measured on a JASCO J-725 spectropolarimeter with a liquid nitrogen-controlled 0.5 cm quartz cell in a cryostat. SEM measurements were performed on a JEOL JMS-5600 or a HITACHI S-5000 scanning electron microscope with the accelerating voltage of 10 kV and emission current of 10 μA. TEM measurements were performed on a HITACHI H-800 transmission electron microscope operating at 100 kV.

Materials. Toluene was dried over sodium benzophenone ketyl, and distilled under nitrogen. Chloroform was dried over CaH_2 and distilled under nitrogen. These solvents were stored under nitrogen over molecular sieves 4 Å (Nacalai Tesque, Kyoto, Japan). Triethylamine was distilled and dried over KOH pellets under nitrogen. (Trimethylsilyl)acetylene was kindly supplied from Shinetsu Chemical (Tokyo, Japan). Copper(I) iodide was obtained from Kishida (Osaka, Japan). (*R*)-1-(4-Bromophenyl)ethylamine hydrochloride, ethyl bromoacetoacetate, dipentadecyl ketone, and bis(triphenylphosphine)palladium dichloride ($[(Ph_3P)_2PdCl_2]$) were from Tokyo Kasei (Tokyo, Japan). C_{60} was purchased from Frontier Carbon (Tokyo, Japan). $[Rh(nbd)Cl]_2$ was obtained from Aldrich

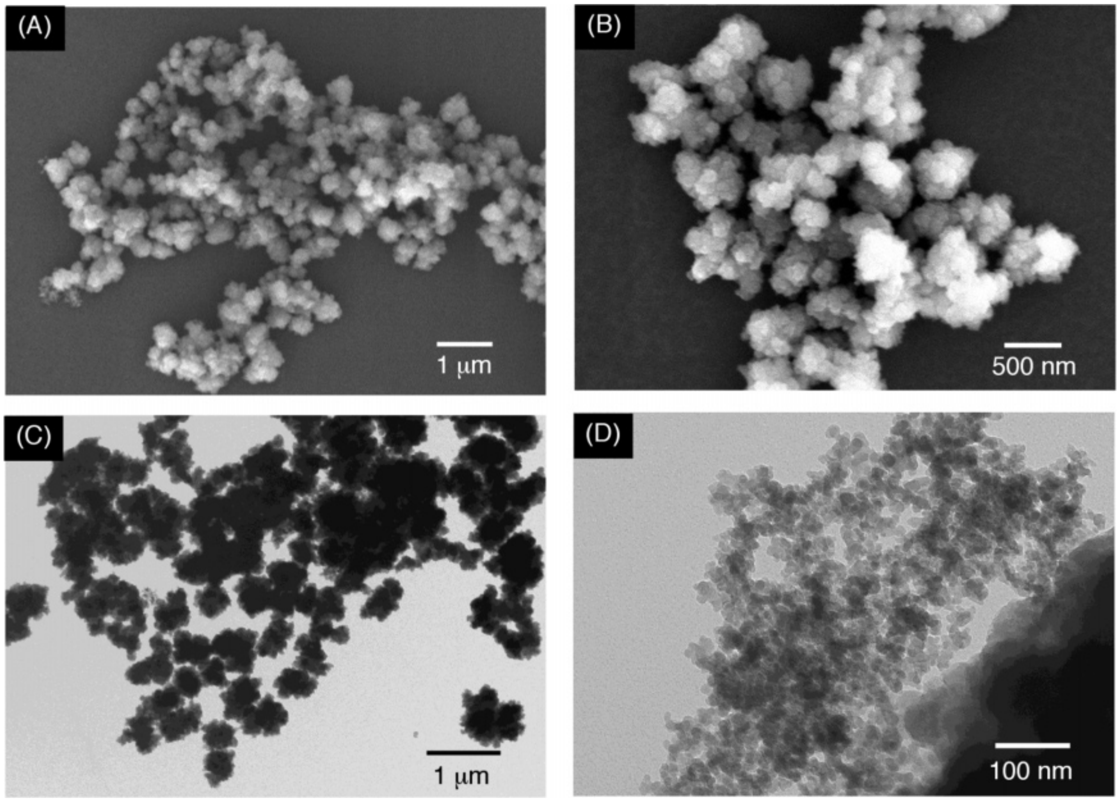


Figure 3. SEM (A, B) and TEM images (C, D) of poly-**1** on HOPG.

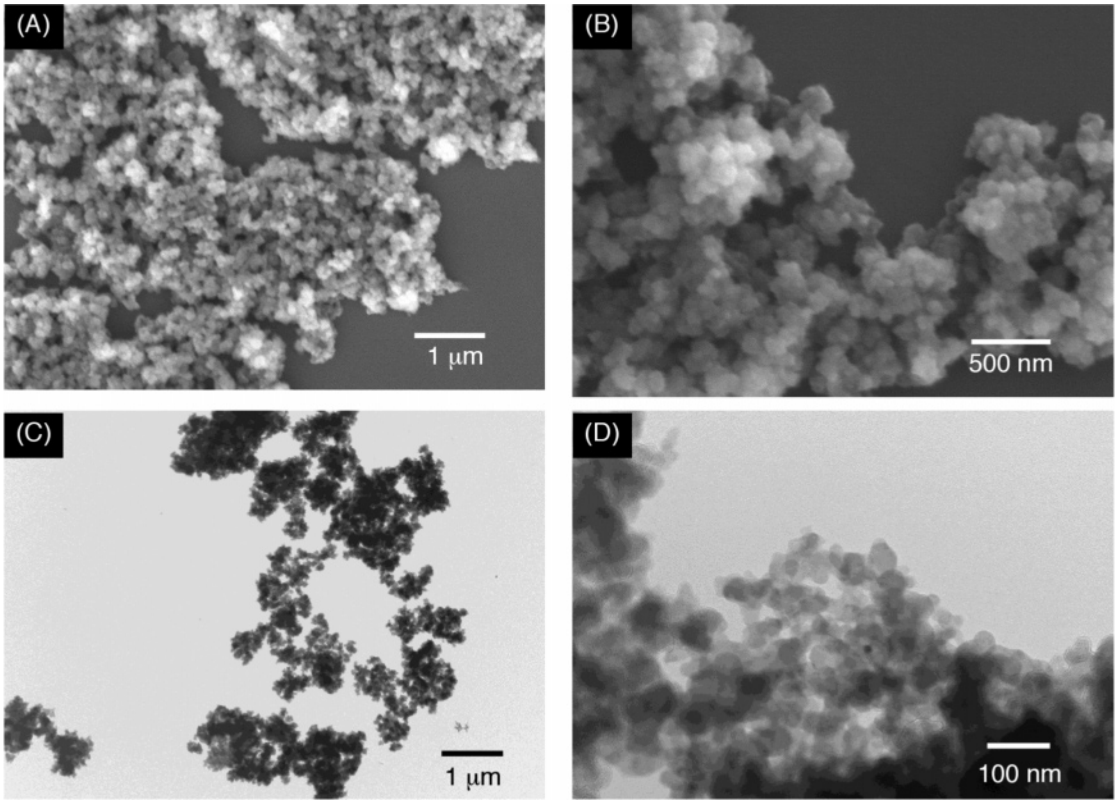


Figure 4. SEM (A, B) and TEM images (C, D) of poly-**3** on HOPG.

and used as received. *N*-(4-Ethynylbenzyl)glycine[4,5] and (*R*)-4-[{-(1-phenylethyl)carbamoyloxy}phenylacetylene] (**4**)[13] were prepared according to the previously reported method.

***N*-(4-Ethynylbenzyl)-2,2-dipentadecyl-3,4-fulleropyrrolidine (2).** *N*-(4-Ethynylbenzyl)glycine (1.0 g, 7.0 mmol), dipentadecyl ketone (14.7 g, 41.7 mmol), and C_{60} (7.7 g, 14.0 mmol) were dissolved in chlorobenzene (500 mL) and the mixture was refluxed for 12 h under stirring. After cooling, the solvent was evaporated under reduced pressure. The residue was then dissolved in chloroform (50 mL) and the insoluble part was removed by filtration. The filtrate was evaporated under reduced pressure and the crude product was purified by chromatography on silica gel using hexane as the eluent, yielding a black powder **2** (0.87 g, 12%). Mp > 450 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 7.68

(d, $J = 8.5$ Hz, Ph, 2H), 7.59 (d, $J = 8.5$ Hz, Ph, 2H), 4.64 (s, NCH_2, Ph−CH_2, 4H), 3.09 (s, C≡C−H, 1H), 2.65 (m, CH_2, 2H), 2.54 (m, CH_2, 2H), 1.87 (m, CH_2, 4H), 1.24−1.55 (m, CH_2, 48H), 0.88 (t, CH_3, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 157.07, 155.07, 147.23, 147.19, 146.62, 146.31, 146.27, 146.08, 145.74, 145.40, 145.31, 145.25, 144.67, 144.58, 143.35, 142.80, 142.77, 142.39, 142.00, 141.76, 141.48, 140.36, 139.51, 136.25, 135.72, 132.65, 129.19, 128.37, 128.27, 121.02, 83.80, 82.23, 72.67, 63.11, 51.91, 35.92, 32.09, 31.74, 30.71, 29.90, 29.85, 29.80, 29.73, 29.68, 29.54, 25.10, 22.87, 22.81, 14.32. IR (KBr, cm^{-1}): 3299, 2920, 2850, 1460, 1182, 818, 527. MS (FAB+): calcd for $C_{101}H_{72}N$ $[M + H]^+$, $m/z = 1299.6$; found, $m/z = 1299.6$.

(*R*)-*N*-[1-(4-Ethynylphenyl)ethyl]-3,4-fulleropyrrolidine (3). (*R*)-*N*-[1-(4-Ethynylphenyl)ethyl]glycine ethyl ester was prepared from the reaction of (*R*)-1-(4-bromophenyl)ethylamine hydrochloride with ethyl bromoacetate in acetonitrile in the presence of triethylamine (34% yield). The coupling of (trimethylsilyl)acetylene to (*R*)-*N*-[1-(4-ethynylphenyl)ethyl]glycine ethyl ester with a palladium catalyst ($[(Ph_3P)_2PdCl_2]$), followed by alkaline hydrolysis of the trimethylsilyl and ethyl ester groups, gave (*R*)-*N*-[1-(4-ethynylphenyl)ethyl]glycine. The crude product was purified by chromatography on silica gel using chloroform−methanol (5:1, v/v) as the eluent (34% yield). (*R*)-*N*-[1-(4-Ethynylphenyl)ethyl]glycine (73.3 mg, 0.36 mmol), paraformaldehyde (65.0 mg, 1.65 mmol), and C_{60} (0.52 g, 0.72 mmol) were dissolved in toluene (50 mL) and the mixture was refluxed for 6 h under stirring. After cooling, the solvent was evaporated under reduced pressure. The residue was then dissolved in chloroform and the insoluble part was removed. The filtrate was evaporated under reduced pressure and the crude product was purified by chromatography on silica gel using hexane−toluene (3:1, v/v) as the eluent, yielding a black powder **3** (44.5 mg, 14%). Mp > 385 °C (decomposition). ^{1}H NMR (700 MHz, $CDCl_3$, 25 °C, TMS): δ 7.70 (d, $J = 7.7$ Hz, Ph, 2H), 7.62 (d, $J = 7.7$ Hz, Ph, 2H), 4.46 (d, $J = 8.4$ Hz, NCH_2, 2H), 4.31 (d, $J = 8.4$ Hz, NCH_2, 2H), 4.00 (q, Ph−CH, 1H), 3.10 (s, C≡C−H, 1H), 1.81 (d, $J = 7.0$ Hz, CH_3, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 155.18, 155.42, 147.48, 146.41, 146.27, 146.23, 146.20, 145.85, 145.58, 145.45, 144.74, 143.25, 142.78, 142.44, 142.39, 142.22, 142.04, 140.29, 136.44, 132.87, 127.38, 121.44, 70.49, 68.14, 66.42, 63.81. IR (KBr, cm^{-1}): 3294, 2964, 2850, 2780, 1427, 1260, 1096, 1026, 802, 527. MS (FAB+): calcd for $C_{72}H_{13}N$ $[M + H]^+$, $m/z = 892.1$; found, $m/z = 892.1$.

Polymerization. Polymerization was carried out in a dry glass ampule under a dry nitrogen atmosphere using $[Rh(nbd)Cl]_2$ as the catalyst. A typical polymerization procedure is described below.

Monomer **2** (15.0 mg, 11.6 μmol) and monomer **4** (27.5 mg, 0.10 mmol) were placed in a dry ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation-flush procedure was repeated three times, a three-way stopcock was attached to the ampule, and dry chloroform (2.5 mL) and triethylamine (16 μL) were added with a syringe. To this was added a solution of $[Rh(nbd)Cl]_2$ (3.8 mM) in chloroform (3.4 mL) at 30 °C. The concentrations of the monomer and the rhodium catalyst were 0.043 and 0.43 mM, respectively. After 24 h, the resulting polymer (poly($\mathbf{2}_{0.1}$-*co*-$\mathbf{4}_{0.9}$)) was precipitated into a large amount of diethyl ether, collected by centrifugation, and dried in vacuo at room temperature for 10 h (34.3 mg, 80.6% yield). Poly($\mathbf{2}_{0.1}$-*co*-$\mathbf{4}_{0.9}$) was soluble in chloroform and toluene. The number-averaged molecular weight (M_n) was determined to be 5.5×10^4 by SEC. The ^{1}H NMR spectrum of poly($\mathbf{2}_{0.1}$-*co*-$\mathbf{4}_{0.9}$) in $CDCl_3$ exhibited a singlet centered at 5.7 ppm due to the main-chain protons, indicating that the polymer processes a highly cis-transoidal, stereoregular structure.[8,9] Poly($\mathbf{2}_{0.1}$-*co*-$\mathbf{4}_{0.9}$): ^{1}H NMR (500 MHz, $CDCl_3$, 60 °C, TMS): δ 6.4 − 7.5 (m, aromatic, 8.5H), 5.82 (br, NH, 0.9H), 5.66 (s, C=C−H, 1H), 4.77 (m, CH, 0.9H), 4.41 (br, Ph−CH_2, 0.2H), 2.95 (br, $N(CH_2)_2$, 0.4H), 2.62 (br, CH_2, 2.7H), 2.43 (br, CH_2, 2.7H), 1.83 (br, CH_2, 2.7H), 1.1−1.6 (m, CH_2, 2.7H), 0.86 (br, CH_3, 2.7H).

Other copolymers of **2** with **3** and **4** were also prepared in the same way.

Homopolymerization of **2** and **3** was also performed in the same way. The homopolymerization of **2** proceeded homogeneously and the resulting polymer (poly-**2**) was precipitated into a large amount of diethyl ether/toluene = 1/1 (v/v), collected by centrifugation, and dried in vacuo at room temperature overnight. On the other hand, the homopolymer of **3** was precipitated in chloroform during the polymerization. The precipitated poly-**3** was collected by centrifugation, washed with chloroform, and dried in vacuo at room temperature overnight.

Molecular Modeling and Calculations. Molecular modeling and molecular mechanics calculation of poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{3}_{0.1}$) were performed with the Dreiding force field (version 2.21)[20] as implemented in CERIUS^2 software (version 3.8; Molecular Simulations Inc., Burlington, MA) running on an Indigo^2-Extreme graphics workstation (Silicon Graphics). For the calculations, the homopolymer poly-**2** was used for clarity. The polymer model (20 repeating monomer units) of poly-**2** was constructed using a Polymer Builder module in CERIUS^2 in a similar method reported previously.[21] Charges on atoms of the polymer were calculated using charge equilibration (QEq) in CERIUS;^{2} the total charge of the molecule was zero. The starting main-chain conformation of a polymer model was defined as the double bond geometry (cis or trans) and a conformation of a rotational single bond. The double bond geometry was fixed to cis and the initial dihedral angle of a single bond from planarity could be varied. The initial dihedral angles of single and double bonds from planarity were set to 156.5 (transoid) and 15.6° (cis), respectively, so as to possess a right-handed helical structure and the phenyl rings were twisted out of the backbone by 57.8° on the basis of the calculated structure of poly(4-carboxyphenylacetylene).[21] The initial dihedral angle between the phenyl group and fulleropyrrolidine residue (ϕ) was allowed to rotate from 0° to 300° at 60° intervals. Each constructed model (20 mer) was then optimized by the conjugate gradient method. The energy minimization was continued until the root-mean-square (rms) values became less than 0.1 kcal mol^{-1}Å^{-1}. Parts A and B of Figure 2 show two possible right-handed helical structures of poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{3}_{0.1}$) in which the pendant C_{60} units arrange in right- (A) and left-handed (B) helical arrays when the average ϕ value was 63.8 ± 5.8° (A) and 171.6 ± 9.1° (B), respectively (see Figure 2).

SEM Observation. A typical procedure is described below. Poly-**1** or poly-**3** (1.0 mg) was placed in a 2 mL flask equipped with a stopcock. To this was added 1.0 mL of *o*-dichlorobenzene. The suspension was then sonicated for 2 h and then dropped on freshly cleaved HOPG substrates under heating on a hot stage at 80 °C. The substrates were further dried in vacuo overnight to measure the SEM images. Poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{3}_{0.1}$) (1.0 mg) was placed in a 2 mL flask equipped with a stopcock. To this was added 1.0 mL of chloroform and then 1.0 mL of isopropyl alcohol. After the solution was left at ambient temperature for 1 day, the precipitates were formed. The suspension was then dropped on freshly cleaved HOPG substrates. The substrates were then dried in vacuo overnight to measure the SEM images. All the experiments were performed in air at ambient temperature.

TEM Observation. A suspension solution of poly-**1**, poly-**3**, or poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{3}_{0.1}$) was prepared in the same method for the SEM observations. The suspension was dropped on carbon-coated cupper grids and the grids were dried in vacuo to measure TEM images.

Acknowledgment. We are deeply grateful to Dr. S. Arai (EcoTopia Science Research Center, Nagoya University) for TEM observations. This work was partially supported by Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science and the Ministry of Education, Culture, Sports, Science, and Technology, Japan (K.M.).

Supporting Information Available: Figures showing ^{1}H NMR spectra of poly($\mathbf{2}_n$-*co*-$\mathbf{4}_m$), laser Raman spectrum of poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{3}_{0.1}$), IR spectra of poly($\mathbf{2}_n$-*co*-$\mathbf{4}_m$) and poly-**2**, and SEM, and TEM images of poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{3}_{0.1}$). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For reviews, see: (a) Prato, M. *J. Mater. Chem.* **1997**, *7*, 1097−1109. (b) Tsukruk, V. V. *Prog. Polym. Sci.* **1997**, *22*, 247−311. (c) Chen, Y.; Huang, Z.; Cai, R. F.; Yu, B. C. *Eur. Polym. J.* **1998**, *34*, 137−151. (d) Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519−526. (e) Dai, L.; Mau, A. W. H. *Adv. Mater.* **2001**, *13*, 899−913. (f) Cravino, A.; Sariciftci, N. S. *J. Mater. Chem.* **2002**, *12*, 1931−1943. (g) Wang, C.; Guo, Z.-X.; Fu, S.; Wu, W.; Zhu, D. *Prog. Polym. Sci.* **2004**, *29*, 1079−1141. (h) Giacalone, F.; Martin, N. *Chem. Rev.* **2006**, *106*, 5136−5190. For examples of C$_{60}$-containing polymers, see: (i) Hawker, C. J. *Macromolecules* **1994**, *27*, 4836−4837. (j) Taki, M.; Takigami, S.; Watanabe, Y.; Nakamura, Y.; Nishimura, J. *Polym. J.* **1997**, *29*, 1020−1022. (k) Ozawa, M.; Li, J.; Nakahara, K.; Xiao, L.; Sugawara, H.; Kitazawa, K.; Kinbara, K.; Saigo, K. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 3139−3146. (l) Zhang, F.; Svensson, M.; Andersson, M. R.; Maggini, M.; Bucella, S.; Menna, E.; Inganäs, O. *Adv. Mater.* **2001**, *13*, 1871−1874. (m) Nava, M. G.; Setayesh, S.; Rameau, A.; Masson, P.; Nierengarten, J.-F. *New J. Chem.* **2002**, *26*, 1584−1589. (n) Xiao, L.; Shimotani, H.; Dragoe, N.; Sugita, A.; Saigo, K.; Iwasa, Y.; Kobayashi, T.; Kitazawa, K. *Chem. Phys. Lett.* **2003**, *368*, 738−744. (o) Nierengarten, J. F.; Guttierez-Nava, M.; Zhang, S.; Masson, P.; Oswald, L.; Bourgogne, C.; Rio, Y.; Accorsi, G.; Armaroli, N.; Setayesh, S. *Carbon* **2004**, *42*, 1077−1083. (p) Ball, Z. T.; Sivula, K.; Fréchet, J. M. J. *Macromolecules* **2006**, *39*, 70−72.

(2) Chiang, L. Y.; Wang, L. Y. In *Fullerenes: Chemistry, Physics, and Technology*; Kadish, K. M., Ruoff, R. S., Eds.; Wiley: New York, 2000; Chapter 7.

(3) (a) Jensen, A. W.; Wilson, S. R.; Schuster, D. I. *Bioorg. Med. Chem.* **1996**, *4*, 767−779. (b) Cassell, A. M.; Scrivens, W. A.; Tour, J. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1528−1531. (c) Nakamura, E.; Isobe, H.; Tomita, N.; Sawamura, M.; Jinno, S.; Okayama, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 4254−4258. (d) Wilson, S. R. In *Fullerenes: Chemistry, Physics, and Technology*; Kadish, K. M., Ruoff, R. S., Eds.; Wiley: New York, 2000; Chapter 10. (e) Ros, T. D.; Bergamin, M.; Vázquez, E.; Spalluto, G.; Baiti, B.; Moro, S.; Boutorine, A.; Prato, M. *Eur. J. Org. Chem.* **2002**, 405−413.

(4) (a) Nishimura, T.; Takatani, K.; Sakurai, S.; Maeda, K.; Yashima, E. *Angew. Chem., Int. Ed.* **2002**, *41*, 3602−3606. (b) Nishimura, T.; Maeda, K.; Ohsawa, S.; Yashima, E. *Chem.*−*Eur. J.* **2005**, *11*, 1181−1190.

(5) Nishimura, T.; Ohsawa, S.; Maeda, K.; Yashima, E. *Chem. Commun.* **2004**, 646−647.

(6) In a complementary approach, an enantiomerically pure cationic C$_{60}$-bisadduct was utilized to induce a predominantly one-handed helix in a dynamically racemic poly(phenylacetylene) with the opposite negative charges in DMSO−water mixtures through noncovalent bonding interactions, which further resulted in a helical array of the C$_{60}$-bisadducts with a predominant screw-sense along the polymer chain. See: Nishimura, T.; Tsuchiya, K.; Ohsawa, S.; Maeda, K.; Yashima, E.; Nakamura, Y.; Nishimura, J. *J. Am. Chem. Soc.* **2004**, *126*, 11711−11717.

(7) Prato, M.; Scorrano, G.; Maggini, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798−9799.

(8) (a) Furlani, A.; Napoletano, C. V.; Russo, M. V.; Feast, W. J. *Polym. Bull. (Berlin)* **1986**, *16*, 311−317. (b) Tabata, M.; Yang, W.; Yokota, K. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1113−1120.

(9) (a) Simionescu, C. I.; Percec, V.; Dumitrescu, S. *J. Polym. Sci.: Polym. Chem. Ed.* **1977**, *15*, 2497−2509. (b) Simionescu, C. I.; Percec, V. *Prog. Polym. Sci.* **1982**, *8*, 133−214. (c) Matsunami, S.; Kakuchi, T.; Ishii, F. *Macromolecules* **1997**, *30*, 1074−1078. (d) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Kainosho, M.; Ono, A.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1999**, *121*, 12035−12044. (e) Percec, V.; Rudick, J. G.; Peterca, M.; Wagner, M.; Obata, M.; Mitchell, C. M.; Cho, W.-D.; Balagurusamy, V. S. K.; Heiney, P. A. *J. Am. Chem. Soc.* **2005**, *127*, 15257−15264. (f) Nagai, K.; Sakajiri, K.; Maeda, K.; Okoshi, K.; Sato, T.; Yashima, E. *Macromolecules* **2006**, *39*, 5371−5380.

(10) (a) Shirakawa, H.; Ito, T.; Ikeda, S. *Polym. J.* **1973**, *4*, 460−462. (b) Tabata, M.; Tanaka, Y.; Sadahiro, Y.; Sone, T.; Yokota, K.; Miura, I. *Macromolecules* **1997**, *30*, 5200−5204. (c) Tabata, M.; Sone, T.; Sadahiro, Y. *Macromol. Chem. Phys.* **1999**, *200*, 265−282.

(11) Maeda, K.; Goto, H.; Yashima, E. *Macromolecules* **2001**, *34*, 1160−1164.

(12) The copolymerization of **2** and **4** at a feed molar ratio of [**2**]/[**4**] = 10/90 (mol/mol) was also performed for 20 s to obtain the copolymer at a low conversion (16.4%) in a similar way as previously reported for the copolymerization of **1** and **4**.[4b,5] The copolymer composition ([**2**]/[**4**] = 10.8/89.2 (mol/mol)) was in fair agreement with that in the feed. This clearly indicates that the polymerizability of **2** is almost identical to that of **4** and that the monomer distributions in the copolymers of **2** and **4** may be random, independent of the monomer conversion (see run 7 in Table 1).

(13) (a) Yashima, E.; Huang, S.; Matsushima, T.; Okamoto, Y. *Macromolecules* **1995**, *28*, 4184−4193. (b) Morino, K.; Maeda, K.; Okamoto, Y.; Yashima, E.; Sato, T. *Chem.*−*Eur. J.* **2002**, *8*, 5112−5120.

(14) Goto, H.; Morino, K.; Morishita, T.; Maeda, K.; Yashima, E. *Kobunshi Ronbunshu* **2006**, *63*, 325−330.

(15) An achiral homopolyacetylene bearing C$_{60}$ moieties with long *N*-dodecyl chains as the pendants was reported to be soluble in CS$_2$. Lu, F. S.; Xiao, S. Q.; Li, Y. L.; Liu, H. B.; Li, H. M.; Zhuang, J. P.; Liu, Y.; Wang, N.; He, X. R.; Li, X. F.; Gan, L. B.; Zhu, D. B. *Macromolecules* **2004**, *37*, 7444−7450.

(16) (a) Sakurai, S.-i.; Okoshi, K.; Kumaki, J.; Yashima, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1245−1248. (b) Sakurai, S.-i.; Okoshi, K.; Kumaki, J.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 5650−5651.

(17) For reviews, see: (a) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, 807−815. (b) Guldi, D. M.; Zerbetto, F.; Georgakilas, V.; Prato, M. *Acc. Chem. Res.* **2005**, *38*, 38−43. For recent examples, see: (c) Nath, S.; Pal, H.; Palit, D. K.; Sapre, A. V.; Mittal, J. P. *J. Phys. Chem. B* **1998**, *102*, 10158−10164. (d) Georgakilas, V.; Pellarini, F.; Prato, M.; Guldi, D. M.; Melle-Franco, M.; Zerbetto, F. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5075−5080. (e) Charvet, R.; Jiang, D.-L.; Aida, T. *Chem. Commun.* **2004**, 2664−2665. (f) Liu, Y.; Wang, N.; Li, Y. J.; Liu, H. B.; Li, Y. L.; Xiao, J. H.; Xu, X. H.; Huang, C. S.; Cui, S.; Zhu, D. B. *Macromolecules* **2005**, *38*, 4880−4887. (g) Nakanishi, T.; Schmitt, W.; Michinobu, T.; Kurth, D. G.; Ariga, K. *Chem. Commun.* **2005**, 5982−5984. (h) Murakami, H.; Nakanishi, T. T.; Morita, M.; Taniguchi, N.; Nakashima, N. *Chem. Asian, J.* **2006**, *1*, 860−867.

(18) Similar spherical particles with an average diameter of about 500 nm were also produced from a chloroform-soluble poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{3}_{0.1}$) by adding a poor solvent, such as isopropyl alcohol, into a chloroform solution of poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{3}_{0.1}$) (chloroform/isopropyl alcohol = 1/1 (v/v)) (see SEM images in Figure S4). However, smaller particles could not be observed in the TEM images (Figure S4).

(19) For reviews, see: (a) Nomura, R.; Nakako, H.; Masuda, T. *J. Mol. Catal. A: Chem.* **2002**, *190*, 197−205. (b) Yashima, E.; Maeda, K.; Nishimura, T. *Chem.*−*Eur. J.* **2004**, *10*, 43−51. (c) Lam, J. W. Y.; Tang, B. Z. *Acc. Chem. Res.* **2005**, *38*, 745−754. (d) Maeda, K.; Yashima, E. *Top. Curr. Chem.* **2006**, *265*, 47−88. (e) Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 165−180. (f) Yashima, E.; Maeda, K. In *Foldamers: Structure, Properties, and Applications*; Hecht, S., Huc, I., Eds.; WILEY-VCH: Weinheim, Germany, 2007, pp 331−366. (g) Rudick, J. G.; Percec, V. *New J. Chem.* **2007**, *31*, 1083−1096.

(20) (a) Mayo, S. L.; Olafson, B. D.; Goddard, W. A., III. *J. Phys. Chem.* **1990**, *94*, 8897−8909. (b) Rappé, A. K.; Goddard, W. A., III. *J. Phys. Chem.* **1991**, *95*, 3358−3363.

(21) Yashima, E.; Matsushima, T.; Okamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6345−6359.

MA7022342