

Helical Arrays of Pendant Fullerenes on Optically Active Poly(phenylacetylene)s

Tatsuya Nishimura, Katsuhiro Maeda, Sousuke Ohsawa, and Eiji Yashima*^[a]

Abstract: Novel, optically active, stereoregular poly(phenylacetylene)s bearing the bulky fullerene as the pendant were synthesized by copolymerization of an achiral phenylacetylene bearing a [60]fullerene unit with optically active phenylacetylene components in the presence of a rhodium catalyst. The C₆₀-bound phenylacetylene was prepared by treatment of C₆₀ with *N*-(4-ethynylbenzyl)glycine in a Prato reaction. The obtained copolymers exhibit-

ed induced circular dichroism (ICD) in solution both in the main-chain region and in the achiral fullerene chromophoric region, although their ICD intensities were highly dependent on the structures of the optically active phenylacetylenes and the solution temper-

Keywords: chirality • circular dichroism • fullerenes • helical structures • polymers

ature. These results indicate that the optically active copolymers form one-handed helical structures and that the pendant achiral fullerene groups are arranged in helical arrays with a predominant screw sense along the polymer backbone. The structures and morphology of the copolymers on solid substrates were also investigated by atomic force microscopy.

Introduction

The design and synthesis of [60]fullerene-containing polymers has received considerable attention in the past decade^[1] because the incorporation of C₆₀ molecules into polymer backbones or pendant groups is the most convenient method of producing functionally useful C₆₀-based materials with high mechanical strength and good processability while maintaining the unique physical and chemical features of C₆₀ molecules.^[2] Such C₆₀-based polymers with well defined structures may be applied in wide fields of materials and biological sciences.^[1,3] However, previous studies of C₆₀-based polymers have mainly been carried out on their structures and properties in the solid state or as thin films. We have previously reported a series of studies on the synthesis

and unique properties of dynamic helical poly(phenylacetylene)s. The copolymerization of achiral phenylacetylenes with a small amount of optically active phenylacetylenes produced stereoregular poly(phenylacetylene)s with optical activity arising from predominantly one-handed helical conformations of the copolymers, thus showing induced circular dichroism (ICD) in the polymer backbone regions.^[4] The ICD intensities of the copolymers increased with increasing bulkiness of the substituents introduced on the phenyl groups of the achiral comonomers;^[4b,d] this is a typical example of the chiral amplification of covalent systems in a polymer and originates from the feature of dynamic macromolecular helicity unique to poly(phenylacetylene)s, polyisocyanates, and polysilanes.^[5] These helical polymers are believed to be equal mixtures of right- and left-handed helical conformations separated by helix reversal points that readily move along the polymer backbones. Therefore, a small chiral bias in the pendant chiral units covalently bonded to the main chain is significantly amplified to induce the same helix in the major achiral monomer units, resulting in a single-handed helical polymer.^[5] Similar chiral amplification is possible in dynamic helical poly(phenylacetylene)s through noncovalent chiral bimolecular interactions, when the polymers have a specific functional group capable of interacting with small chiral molecules.^[5e,6] These observations stimulated us to synthesize an optically active, C₆₀-based helical poly(phenylacetylene) by copolymerization of an achiral

[a] Dr. T. Nishimura, Dr. K. Maeda, S. Ohsawa, Prof. Dr. E. Yashima
Department of Molecular Design and Engineering
Graduate School of Engineering, Nagoya University
Chikusa-ku, Nagoya 464-8603 (Japan)
Fax: (+81) 52-789-3185
E-mail: yashima@apchem.nagoya-u.ac.jp

Supporting information for this article (¹H NMR, ¹³C NMR, and absorption spectra of **1**, Raman and IR spectra of the copolymers, CD and absorption spectra of poly(**1**_{0,1}-co-**2b**_{0,9}) in dichloromethane/DMSO (1:1, v/v), and AFM images of poly(**1**_{0,1}-co-**2a**_{0,9}) on mica and poly(**1**_{0,1}-co-**2b**_{0,9}) on HOPG) is available on the WWW under <http://www.chemeurj.org> or from the author.

C₆₀-bound phenylacetylene component with optically active phenylacetylene units, in which the achiral C₆₀ pendant groups might arrange in a helical array along the polymer backbone with a one-handed screw sense.

Recently, we have successfully prepared the first example of such C₆₀-based helical poly(phenylacetylene)s bearing achiral C₆₀ pendant groups, by copolymerization of an achiral C₆₀-bound phenylacetylene (**1**) with an optically active phenylacetylene (**2a**) (Scheme 1).^[7] The copolymers exhibit-

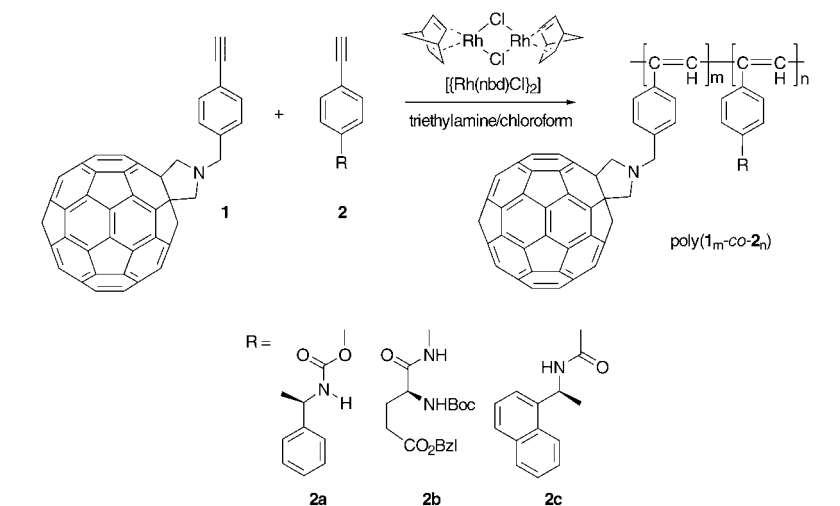
ized with the achiral C₆₀-bound phenylacetylene (**1**) in the presence of a rhodium catalyst (Scheme 1). We expected that helical poly(phenylacetylene)s with bulkier chiral pendant groups should yield more stable C₆₀-bound helical polymers. The chiroptical properties of the copolymers and their morphologies on substrates were characterized by UV/Vis and circular dichroism (CD) spectroscopy and by atomic force microscopy (AFM), respectively.

Results and Discussion

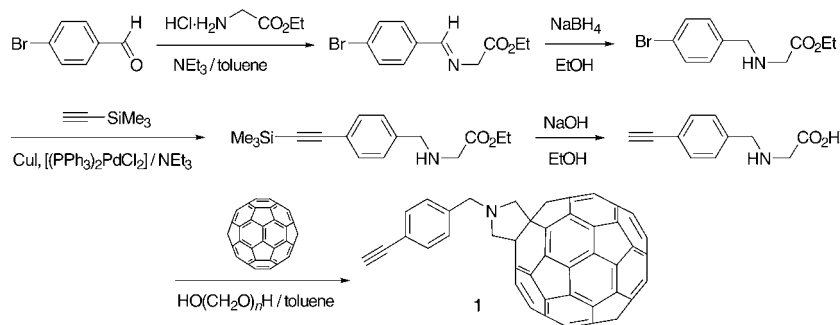
Synthesis and copolymerization of a phenylacetylene derivative bearing a C₆₀ pendant with optically active phenylacetylenes:

The achiral fullerene monomer **1** was prepared as shown in Scheme 2. A Prato reaction between C₆₀ and *N*-(4-ethynylbenzyl)glycine was employed to introduce a phenylacetylene residue on the C₆₀ surface.^[1a,8] The target monoadduct **1** was obtained in 30% yield, together with a small amount of the bis(adduct) as a by-product (25%), which could be easily separated by silica gel chromatography. The fullerene monomer **1** was characterized and identified by UV/Vis and ¹H and ¹³C NMR spectroscopy and by mass spectrometry (see Supporting Information). In the absorption spectrum, the characteristic absorptions due to the C₆₀ moiety were observed above 600 nm (ϵ_{702} 380, ϵ_{635} 400, and ϵ_{605} 560 M⁻¹ cm⁻¹).

Optically active phenylacetylenes bearing either an (*R*)-[(1-phenylethyl)carbamoyl]oxy group (**2a**) or an (*S*)-[1-(1-

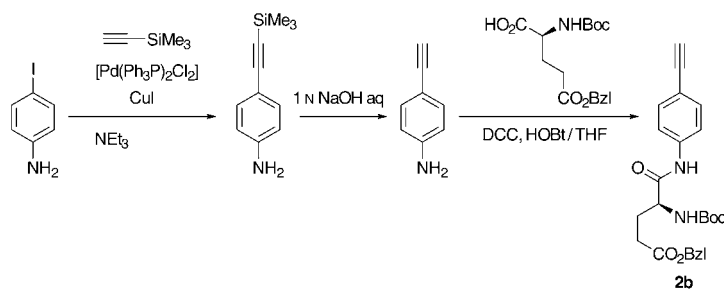


Scheme 1. Synthesis of C₆₀-containing helical poly(phenylacetylene)s (poly(**1**_m-co-**2**_n)).



Scheme 2. Synthesis of **1**.

ed characteristic ICD both in the polymer backbone region and in the achiral fullerene region. However, such a helical array of the C₆₀ pendant groups was achieved at low temperatures.^[7] Similar helicity induction and helical arrays of C₆₀ molecules have been reported for dynamically racemic helical poly(phenylacetylene)s bearing bulky [18]crown-6 ether and achiral C₆₀ pendant groups^[6b] or a phosphate group as the side group.^[6a] These polymers formed predominantly one-handed helices induced by noncovalent bonding chiral interactions with amino acids or optically active cationic C₆₀-bis(adducts), respectively. In the present study, we prepared two novel, optically active phenylacetylenes with bulkier side groups (**2b** and **2c**), and these were copolymer-



Scheme 3. Synthesis of **2b**. DCC = dicyclohexylcarbodiimide; HOBt = 1-hydroxybenzotriazole.

Table 1. Copolymerization results for the fullerene monomer **1** and optically active comonomers (**2**) in the presence of $[\text{Rh}(\text{nbd})\text{Cl}]_2$ in chloroform at 30 °C for 24 h.^[a]

Run	1 [mol %]	Comonomer	1 + comonomer [M]	Yield [%] ^[b]	Polymer			
					MeOH-insoluble part			
					Yield [%]	1 [mol %] ^[c]		$M_n \times 10^{-4}$ ^[d]
1	100	—	0.016	60.4	—	—	(—)	—
2	10	2a	0.043	—	52.0	12.3	(15)	8.4
3 ^[e]	10	2a	0.043	—	13.2 ^[f]	9.8	(—)	1.5
4	20	2a	0.033	15.2	72.0	22.1	(22)	1.8
5	30	2a	0.026	60.5	20.8	26.9	(30)	2.4
6	0	2b	0.50	—	91.0	—	(—)	62.3 ^[g]
7	10	2b	0.070	—	83.7	10.3	(13)	27.3 ^[g]
8	20	2b	0.040	—	75.0	17.4	(22)	21.8 ^[g]
9	30	2b	0.042	9.1	67.7 ^[h]	—	(—)	14.6 ^[g]
10	10	2c	0.099	—	100.0 ^[i]	—	(16)	4.6 ^[g]

[a] Polymerized under nitrogen; $[\mathbf{1} + \mathbf{2}]/[\text{Et}_3\text{N}] = 1$, $[\mathbf{1} + \mathbf{2}]/[\text{Rh}] = 100$. [b] Chloroform-insoluble part. [c] Estimated by ^1H NMR spectroscopy; those estimated by UV/Vis spectra on the basis of the molar absorptivity of **1** are shown in parentheses. [d] Determined by SEC (polystyrene standards) in THF. [e] Polymerized for 20 s. [f] Part insoluble in toluene/MeOH (1:1, v/v). [g] Determined by SEC (poly(ethylene glycol) and poly(ethylene oxide) standards) in DMF containing 10 mM lithium chloride. [h] The isolated copolymer was insoluble in common organic solvents. [i] The reaction proceeded homogeneously during the copolymerization, but the isolated copolymer was insoluble in common organic solvents.

naphthyl)ethyl]carbamoyl group (**2c**) were prepared by the previously reported methods.^[4b,9] A new optically active phenylacetylene with an (*S*)-2-*tert*-butoxycarbonylamino-1,5-dioxo-5-(phenylmethoxy)pentylamino pendant group (**2b**) was prepared as outlined in Scheme 3, and its formula and structure were confirmed by ^1H NMR and elemental analysis.

Optically active, *cis-transoidal* poly(phenylacetylene)s with C_{60} pendant groups were prepared by copolymerization of the achiral C_{60} -bound phenylacetylene (**1**) with optically active phenylacetylenes (**2a–2c**) in the presence of a rhodium catalyst $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (nbd = norbornadiene) (Scheme 1). The copolymerization results at various feed monomer ratios are summarized in Table 1. The homopolymerization of **1** proceeded rapidly, and a black polymer precipitated within a few minutes. The obtained homopolymer was insoluble in common organic solvents. In order to overcome this solubility problem with poly-**1**, we performed a copolymerization of **1** with optically active comonomers. The copolymerization of **1** with **2a** and **2b** at feed molar ratios of $[\mathbf{1}]/([\mathbf{1}] + [\mathbf{2a}]) = 0.1$ and $[\mathbf{1}]/([\mathbf{1}] + [\mathbf{2b}]) = 0.1$ and 0.2 proceeded homogeneously, and the obtained copolymers were soluble in THF and chloroform. However, the copolymerization of **1** with **2a** at $[\mathbf{1}]/([\mathbf{1}] + [\mathbf{2a}]) \geq 0.2$ and with **2b** at $[\mathbf{1}]/([\mathbf{1}] + [\mathbf{2b}]) \geq 0.3$ resulted in precipitation in chloroform during the copolymerization reaction. The chloroform-insoluble part was then separated by centrifugation, and the supernatant was poured into a large amount of methanol in order to collect the chloroform-soluble copolymers. After isolation, the isolated copolymers were partially soluble in—depending on the C_{60} unit content—THF, dichloromethane, and chloroform.

The copolymerization of **1** with **2c** at $[\mathbf{1}]/([\mathbf{1}] + [\mathbf{2c}]) = 0.1$ also proceeded homogeneously in chloroform to produce a methanol-insoluble copolymer quantitatively after 24 h. However, the copolymer became insoluble in common organic solvents once isolated. A part of the copolymerization

mixture (0.1 M) was therefore withdrawn after 24 h and diluted with chloroform to maintain the copolymer concentration at 0.01 M. The diluted solution was then subjected to CD measurements and size-exclusion chromatography (SEC).

The stereoregularity of the copolymers was investigated by ^1H NMR spectroscopy. The ^1H NMR spectra of poly(**1**_{0.1}-*co*-**2a**_{0.9}) (run 2 in Table 1) and poly(**1**_{0.1}-*co*-**2b**_{0.9}) (run 7 in Table 1) are shown in Figure 1 and Figure 2, respectively.

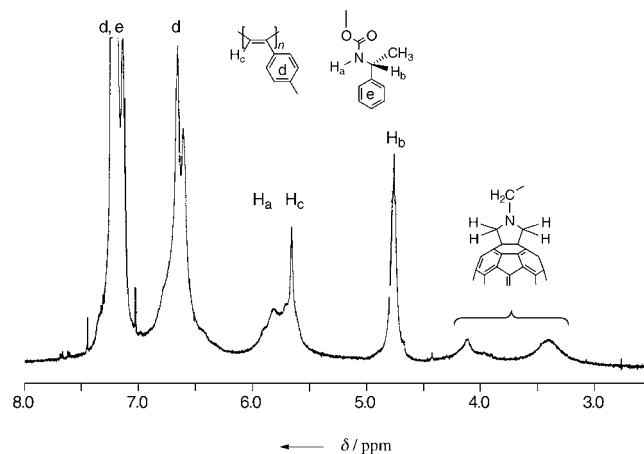


Figure 1. ^1H NMR spectrum of poly(**1**_{0.1}-*co*-**2a**_{0.9}) in $[\text{D}]\text{chloroform}$ at 60 °C.

The copolymers each showed a characteristic peak centered at around $\delta = 5.7$ ppm due to the main chain protons, attributable to their *cis-transoidal* main chains' olefinic protons,^[10] although the proton resonances of poly(**1**_{0.1}-*co*-**2b**_{0.9}) were rather broad in comparison with those of poly(**1**_{0.1}-*co*-**2a**_{0.9}). This difference in line broadening may be due to a difference in the rigidity of the copolymers; poly(**1**_{0.1}-*co*-**2b**_{0.9}) may have a more rigid helical structure than poly(**1**_{0.1}-*co*-**2a**_{0.9}). The stereoregularity of poly(**1**_{0.1}-*co*-**2c**_{0.9}) (run 10 in

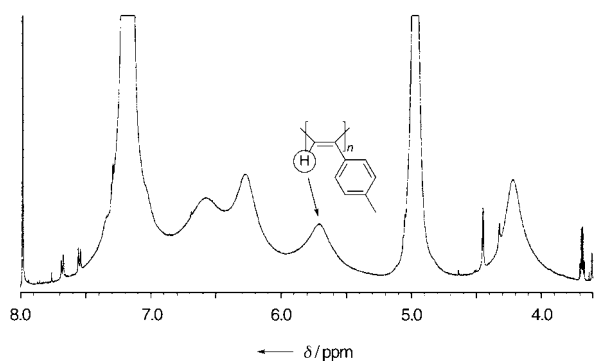


Figure 2. ^1H NMR spectrum of poly($\mathbf{1}_{0.1}\text{-co-2c}_{0.9}$) in $[\text{D}]\text{chloroform}/[\text{D}_6]\text{DMSO}$ (1:1, v/v) at 60°C .

Table 1) was investigated by laser Raman spectroscopy in the solid state, since poly($\mathbf{1}_{0.1}\text{-co-2c}_{0.9}$) was insoluble in common organic solvents after isolation. The Raman spectrum of poly($\mathbf{1}_{0.1}\text{-co-2c}_{0.9}$) showed intense peaks at 1577, 1377, and 891 cm^{-1} , assigned to the C=C, C–C, and C–H bond vibrations in the *cis* polyacetylenes, while those of the *trans* forms were not observed.^[11] Other copolymers, including poly($\mathbf{1}_{0.1}\text{-co-2a}_{0.9}$) and poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$), also showed similar Raman spectra, indicating that these copolymers possess highly *cis-transoidal* structures (see Supporting Information).

The introduction of the C_{60} units into the polymer chains was confirmed by the ^1H NMR, absorption, and IR spectra of the copolymers. The IR spectra of poly($\mathbf{1}_m\text{-co-2a}_n$) and poly($\mathbf{1}_m\text{-co-2b}_n$) showed characteristic absorptions for the C_{60} units at 527 cm^{-1} (see Supporting Information). The copolymer compositions were estimated by the ^1H NMR and absorption spectra, which were almost in accordance with those in the feed. The distribution of the two monomer units in the polymer chains varies depending on the polymerizability of the monomers. However, it was difficult to determine the monomer reactivity ratios of $\mathbf{2a-2c}$ to $\mathbf{1}$ because of the insolubility of the copolymers with high C_{60} contents. We then carried out the copolymerization of $\mathbf{1}$ and $\mathbf{2a}$ at a feed molar ratio of $[\mathbf{1}]/[\mathbf{2a}] = 10:90$ (mol/mol) (run 3 in Table 1), and the reaction was terminated at a low level of conversion (13%) in order to determine the copolymer composition. The value ($[\mathbf{1}]/[\mathbf{2a}] = 9.8/90.2$) was in fair agreement with that in the feed. This clearly indicates that the polymerizability of $\mathbf{1}$ is almost identical to that of $\mathbf{2a}$ and that the monomer distributions in the copolymers of $\mathbf{1}$ and $\mathbf{2a}$ may be random, independent of the level of monomer conversion.

Chiroptical properties of copolymers: Figure 3 shows the CD and absorption spectra of poly($\mathbf{1}_{0.1}\text{-co-2a}_{0.9}$) in THF (A) and of poly($\mathbf{1}_{0.1}\text{-co-2c}_{0.9}$) in chloroform (B). The copolymers exhibited intense, split-type ICDs in the π -conjugated main-chain regions (280–500 nm). The Cotton effect signs were opposite from each other because of the opposite configurations of the pendant stereogenic centers of $\mathbf{2a}$ (*R* enantiomer) and $\mathbf{2c}$ (*S* enantiomer), but their CD spectra were simi-

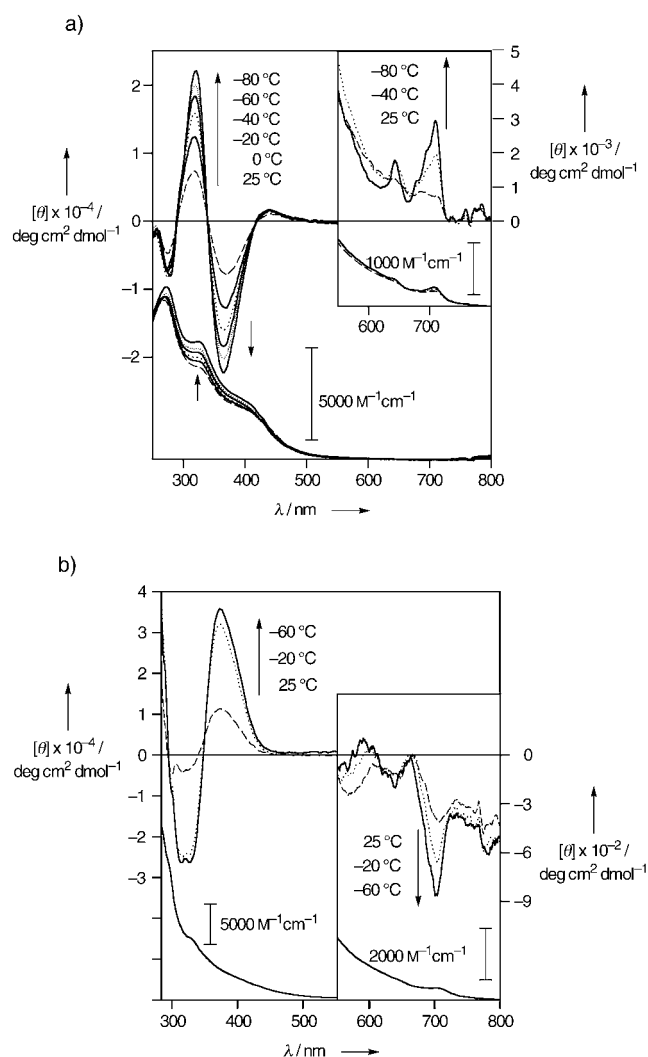


Figure 3. CD and absorption spectra of poly($\mathbf{1}_{0.1}\text{-co-2a}_{0.9}$) in THF (0.1 mg mL^{-1}) (a) and poly($\mathbf{1}_{0.1}\text{-co-2c}_{0.9}$) in chloroform (0.1 mg mL^{-1}) (b) at various temperatures. The insets show the corresponding CD and absorption spectra in the fullerene chromophore region at higher concentrations (4.6 (a) and 3.8 mg mL^{-1} (b)). The molar concentrations were calculated on the basis of the monomer units and C_{60} units (insets).

lar in pattern to those of the homopolymers (poly- $\mathbf{2a}^{[4b,d]}$ and poly- $\mathbf{2c}^{[9]}$) and of poly[(4-carboxyphenyl)acetylene] complexed with optically active amines or amino alcohols.^[6c] The magnitude of the ICDs (main-chain regions) of poly($\mathbf{1}_{0.1}\text{-co-2a}_{0.9}$) and poly($\mathbf{1}_{0.1}\text{-co-2c}_{0.9}$) monotonically increased with decreasing temperature. Similar temperature dependence of the Cotton effect intensities in the main-chain regions of optically active poly(phenylacetylene)s has also been observed for the homopolymers poly- $\mathbf{2a}^{[4d]}$ and poly- $\mathbf{2c}^{[9]}$. These results suggest that the induced helical conformations of the copolymers are dynamic in nature as a result of cooperative interactions among the pendant groups, and that the helical screw sense preference (right- and left-handed helices) of the copolymers, which is controlled by the pendant chirality, increased with decreasing temperature.

The copolymers of **1** both with **2a** and with **2c** showed almost no detectable absorption and CD at wavelengths over 600 nm in dilute solution (Figure 3 a and b), due to the low concentrations of the C₆₀ units. At higher concentrations, however, apparent and remarkable CDs were induced above 600 nm at temperatures lower than −40 °C (a) and −20 °C (b), characteristic of the fullerene chromophores in the copolymers (insets in Figure 3 a and b). The ICD intensities in this region increased further at lower temperatures. The sudden onsets and rapid increases in the optical activity of the achiral C₆₀ cores in the copolymers indicate helical arrays of the C₆₀ pendant groups with one-handed screw senses along the polymer backbones, because the C₆₀ units themselves are achiral (Figure 4).

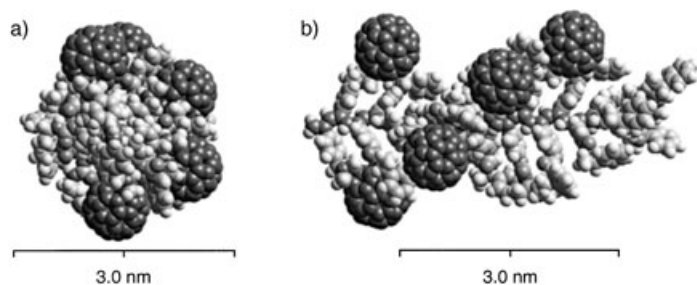


Figure 4. A possible helical structure of poly(**1**_{0.2}-co-**2a**_{0.8}) (20-mer). Space-filling models are shown: a) in top, and b) in side views. The fullerene units are assumed to arrange in a left-handed helical array along the right-handed polyacetylene main chain. The helix sense is tentative, but the copolymer should have either a right- or a left-handed helical conformation since it exhibits ICD both in the main-chain and in the fullerene chromophoric regions.

Recently, Xu and Tang reported that the polymerization of phenylacetylene with [Rh(nbd)Cl]₂ as a catalyst in the presence of C₆₀ produced a C₆₀-containing poly(phenylacetylene).^[12] We thus carried out the polymerization of **2a** with [Rh(nbd)Cl]₂ in the presence of C₆₀. However, the resulting THF-soluble polymer showed no ICD in the fullerene chromophore region even at −80 °C.^[13] Moreover, a solution of poly-**2a** in THF containing 10 mol% C₆₀ exhibited no ICD in the same fullerene region. These results support the structure of poly(**1**_{0.1}-co-**2a**_{0.9}) shown in Scheme 1 and the induction of chirality on the pendant C₆₀ units arranging in a helical array.

The other copolymers (poly(**1**_{0.2}-co-**2a**_{0.8}) (run 4 in Table 1) and poly(**1**_{0.3}-co-**2a**_{0.7}) (run 5 in Table 1)) also exhibited similar ICDs in the same wavelength region (600–800 nm) as well as in the main-chain region. This is the first observation of chirality induction in achiral fullerenes originating from their helical arrangement in polymers.^[7] The observed CD intensities in the fullerene chromophore regions of the copolymers were calculated on the basis of the contents of C₆₀ units incorporated into the copolymer chains.^[14] These CD values were as large as those seen for chiral monosubstituted fullerenes^[15] and C₁-symmetric chiral bis-substituted fullerenes,^[16] but were smaller than those of their C₂-

symmetric counterparts by one or two orders of magnitude.^[17]

Poly(**1**_{0.1}-co-**2b**_{0.9}) with protected L-glutamate residues as the pendant groups also showed ICD in the main-chain region in dichloromethane, but the ICD pattern was quite different from those of poly(**1**_{0.1}-co-**2a**_{0.9}) in THF and poly(**1**_{0.1}-co-**2c**_{0.9}) in chloroform (Figure 3), and the absorption maximum due to the main chain chromophore was shifted to a longer wavelength (Figure 5 a) than seen in the

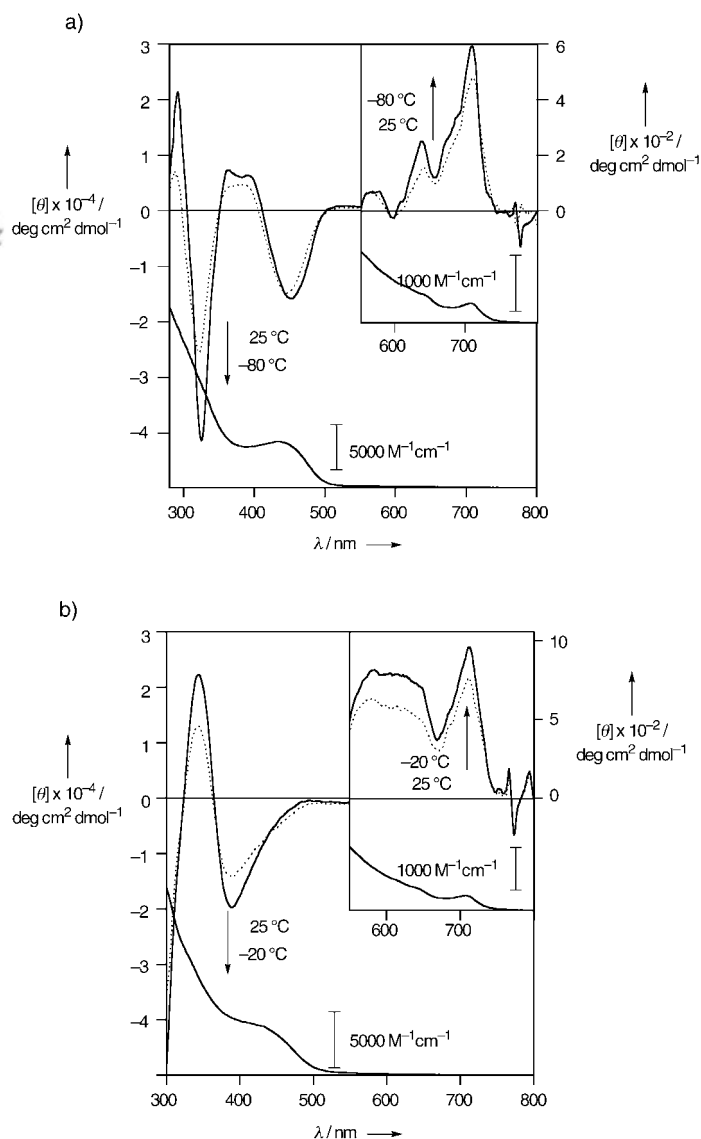


Figure 5. CD and absorption spectra of: a) poly(**1**_{0.1}-co-**2b**_{0.9}) in dichloromethane (0.1 mg mL^{−1}), and b) dichloromethane/DMF (1:1, v/v) (0.1 mg mL^{−1}) at various temperatures. The insets show the corresponding CD and absorption spectra in the fullerene region at a higher concentration—a) 4.3 mg mL^{−1} and b) 3.0 mg mL^{−1}. The molar concentrations were calculated on the basis of the monomer and C₆₀ units (inset).

homopolymers of **2a** and **2c** and their copolymers with **1**. In the presence of polar solvents such as DMF and DMSO, however, poly(**1**_{0.1}-co-**2b**_{0.9}) exhibited a dramatic change in

its CD spectrum (Figure 5b and Supporting Information), its ICD pattern changing to one similar to those of poly($\mathbf{1}_{0.1}\text{-co-2a}_{0.9}$) and poly($\mathbf{1}_{0.1}\text{-co-2c}_{0.9}$) (Figure 3). This unique CD spectral change in poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) may be attributable to a change in the helical structure; that is, a change in the twist angle of the conjugated double bonds, probably through intramolecular association and dissociation of hydrogen bonding at the pendant groups induced by the polar solvents. Similar stabilization of helical polyacetylenes by intramolecular hydrogen bonding has been reported for poly(*N*-propargylamide) derivatives bearing optically active substituents as the side groups and amino acid bound, optically active poly(phenylacetylene)s.^[18]

Another possible explanation for the change in the ICD of poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) depending on the solvent may be aggregation of the copolymer main chains in the nonpolar dichloromethane.^[19] It is well known that aggregations are highly sensitive to the concentrations of polymers. However, the ICD pattern of poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) in dichloromethane hardly changed over a poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) concentration range from 4.0 to 0.01 mg mL⁻¹, indicating that the formation of aggregates could be ruled out. Moreover, dynamic light scattering (DLS) experiments also support this speculation. The estimated hydrodynamic radius (R_h) value for the poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) in dichloromethane (22 nm) was very similar to that in DMF/dichloromethane (1:1, v/v) (31 nm), which excludes the possibility of the formation of aggregates of the polymer chains in dichloromethane.^[9] AFM analyses of poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) on mica, discussed in detail later on, also support this conclusion.

We then used IR spectroscopy to investigate whether poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) could enter into intramolecular hydrogen bonding in dichloromethane. As shown in Figure 6a, the monomer **2b** showed absorptions in dichloromethane at 1702 and 3415 cm⁻¹, which can be assigned to the free amide I and the free N–H stretching vibrations, respectively, while in the solid state (Figure 6b) these peaks were shifted to lower wavenumbers, at 1670 and 3310 cm⁻¹, respectively. This indicates that the pendant amide groups of **2b** are engaged in intermolecular hydrogen bonding in the solid state.^[20] Similar hydrogen-bonded amide I and N–H stretching bonds were observed at 1670 and 3310 cm⁻¹, respectively—identical to those of the monomer **2b** in the solid state—for poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) in dichloromethane (Figure 6c). Moreover, the IR spectra of poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) in dichloromethane hardly changed over the poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) concentration range from 1 to 50 mM. These results suggest that poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) engages in intramolecular hydrogen bonding between the adjacent side groups in dichloromethane. Such hydrogen bonding results in the formation of a helical structure with a different conjugation length and a helical pitch, which might be responsible for the difference in the ICD patterns of the copolymer in solvents. In fact, in dichloromethane/DMSO (1:1, v/v), the N–H stretching vibration of poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) was strongly shifted to 3251 cm⁻¹ (Figure 6e), which is identical to that of the monomer **2b** in the same solvent mixture (Figure 6d). These large shifts of

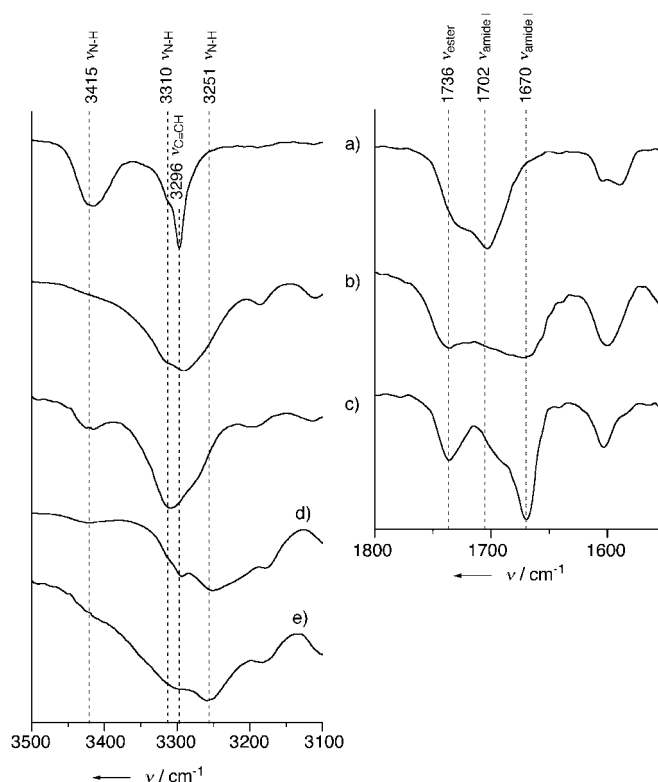


Figure 6. FT-IR spectra of monomer **2b**: a) in dichloromethane (10 mM), b) in the solid state, and d) in dichloromethane/DMSO (1:1, v/v), and of poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$): c) in dichloromethane (10 mM), and e) in dichloromethane/DMSO (1:1, v/v). The solution IR measurements were carried out in a 150 μm BaF₂ cell at room temperature.

the N–H vibration to lower wavenumbers can be assigned to strong hydrogen bonding with DMSO molecules.^[21] These IR spectral results demonstrate that the intramolecular hydrogen bonding is broken by the addition of DMSO. We note that poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) exhibited almost the same ICD in DMSO and in dichloromethane/DMF (1:1, v/v) (Figure 5b and Supporting Information).

Poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) exhibited rather intense ICD in the fullerene region even at 25 °C and the ICD intensity hardly changed at lower temperatures (Figure 5). The ICD pattern of poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) in the fullerene region was similar to those of poly($\mathbf{1}_{0.1}\text{-co-2a}_{0.9}$) and poly($\mathbf{1}_{0.1}\text{-co-2c}_{0.9}$), indicating that the pendant fullerenes also arrange in a helical array along the one-handed helix of the poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) main chain and that the bulky chiral pendant of **2b** may efficiently assist the helical arrangement of the C₆₀ molecules, which are stable at 25 °C.

Atomic force microscopy studies: AFM analyses of the copolymers on solid substrates such as a freshly cleaved mica surface and highly oriented pyrolytic graphite (HOPG) were then conducted in order to observe the structures and morphologies of the helically arranged C₆₀-based copolymers. Figure 7 shows typical AFM images of poly($\mathbf{1}_{0.1}\text{-co-2a}_{0.9}$) and poly($\mathbf{1}_{0.1}\text{-co-2b}_{0.9}$) cast from dilute solutions in

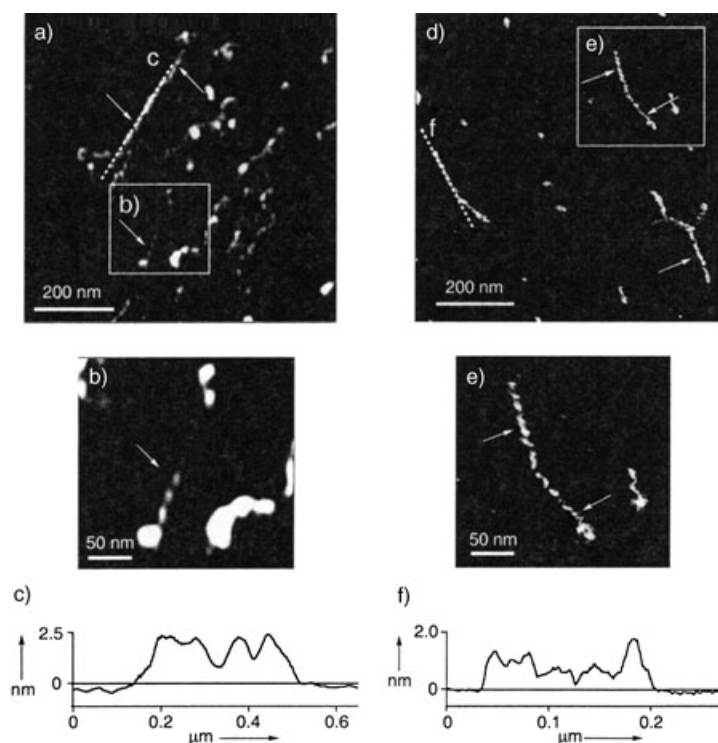


Figure 7. Tapping mode AFM images of poly(**1**_{0,1}-co-**2a**_{0,9}) (a, b) and poly(**1**_{0,1}-co-**2b**_{0,9}) (d, e) cast from dilute solutions of THF (a, b) and chloroform (d, e) on HOPG (a, b) and mica (d, e). The height profiles measured along the white lines in the images (a, d) are also shown in (c) and (f), respectively. The arrows in (a, b, c, d) indicate the typically observed left-handed helices.

THF and chloroform on HOPG (a) and mica (d), respectively. The morphology of the copolymers was significantly influenced by the substrates. Individual copolymer chains of poly(**1**_{0,1}-co-**2a**_{0,9}) (average height: 2.1 ± 0.8 nm) together with isolated particles can be seen on HOPG (Figure 7a), whereas isolated particles (average height: 2.6 ± 1.3 nm) were observed on mica after preparation by the same procedure as for HOPG (see Supporting Information) because the pendant C₆₀ groups of the copolymer aggregate on mica to form assemblies (clusters) through repulsive interactions between the hydrophobic C₆₀ units and the hydrophilic mica substrates.^[22] These results indicate that the attractive force between the pendant C₆₀ groups and the substrate plays a critical role in the morphologies of the C₆₀-based polymers. The average height of poly(**1**_{0,1}-co-**2a**_{0,9}) on HOPG was, however, shorter than the molecular diameter of a helical copolymer model (Figure 4). Tip-induced deformation of the samples may account for the reduced height of the copolymer.^[23]

In contrast to the morphology observed for poly(**1**_{0,1}-co-**2a**_{0,9}), poly(**1**_{0,1}-co-**2b**_{0,9}), with hydrophilic glutamate residues as the chiral pendant groups, showed a different morphology on the substrates. On the mica surface, with preparation from a dilute solution of poly(**1**_{0,1}-co-**2b**_{0,9}) in chloroform, individual copolymer chains can be observed together with bundle chains (Figure 7d), whereas the copolymer chains aggregate to form an assembly on HOPG (see Supporting Information).

The height profiles along the copolymer chains (Figure 7c, f) appear to be uneven; lower profiles for poly(**1**_{0,1}-co-**2a**_{0,9}) (0.72 ± 0.10 nm) and for poly(**1**_{0,1}-co-**2b**_{0,9}) (0.77 ± 0.15 nm) and higher profiles for poly(**1**_{0,1}-co-**2a**_{0,9}) (1.48 ± 0.21 nm) and for poly(**1**_{0,1}-co-**2b**_{0,9}) (1.37 ± 0.22 nm) segments were observed in the copolymers on HOPG (b) and mica (d). Because the average heights of the homopolymers of poly-**2a** and poly-**2b** on mica were 0.71 ± 0.15 and 0.75 ± 0.11 nm, respectively, the segments with higher height values may involve the C₆₀ pendant groups. This means that we may be able to predict the position of the C₆₀ pendant groups in the copolymer chains by AFM.

The images of the copolymers poly(**1**_{0,1}-co-**2a**_{0,9}) on HOPG and poly(**1**_{0,1}-co-**2b**_{0,9}) on mica feature a particularly interesting left-handed helical shape, as marked by arrows in Figure 7a, and 7d, respectively.^[24] Although we could not distinguish the C₆₀ and chiral pendant groups of the copolymers by AFM, these helical-shaped images may be closely correlated to the helical conformation of the poly(phenylacetylene)s, which are rather difficult to explore by spectroscopic means.

Conclusion

A series of optically active poly(phenylacetylene)s based on optically active phenylacetylene units and an achiral C₆₀-bound phenylacetylene component were prepared by co-

polymerization, and their chiroptical properties and structures were investigated by CD and AFM measurements. We found that the copolymers predominantly formed one-handed helical structures with the pendant fullerenes arranged in helical arrays with a predominant screw sense, thus exhibiting characteristic ICD both in the achiral fullerene chromophore region and in the main-chain region. The copolymers with bulky chiral pendant groups enhanced the one-handedness excess of the polymer main chain, which simultaneously produced helical arrays of the C₆₀ units, resulting in their adopting helical arrangements at high temperatures, because the copolymers with less bulky chiral pendant groups exhibited optical activity in the C₆₀ chromophore region at low temperatures. Moreover, these results demonstrate that the copolymerization of chiral and achiral monomers should be useful for further construction of a variety of helical polymers with the desired pendant groups in one-handed helical arrays.

Experimental Section

Instrumentation: 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. Elemental analyses were performed by the Nagoya University Analytical Laboratory in the School of Engineering. ¹H (500 or 300 MHz) and ¹³C (125 or 75 MHz) NMR spectra were measured on a Varian VXR-500S or a Varian Mercury-300 spectrometer with tetramethylsilane (TMS) as an internal standard. SEC was performed with a Jasco PU-980 liquid chromatograph fitted with a Jasco DG-980-50 degasser and a UV/Vis detector (254 nm; Jasco UV-970) on a Tosoh TSK-GEL Multipore H_{XL}-M column with THF as the eluent with polystyrene standards or on TSK-GEL α-3000 and α-5000 columns connected in series with DMF containing LiCl (10 mM) as the eluent with poly(ethylene oxide) and poly(ethylene glycol) standards. IR spectra were recorded with a Jasco Fourier Transform IR-620 spectrophotometer. A 150 μm BaF₂ cell was used for the measurements in solution. Laser Raman spectra were recorded on a Jasco RMP200 spectrometer. Absorption spectra were recorded on a Jasco V-570 spectrophotometer in a 0.5 cm quartz cell. CD spectra were measured on a Jasco J-725 spectropolarimeter in a liquid nitrogen-controlled quartz cell (0.5 cm) in a cryostat. AFM measurements were performed on a Nanoscope IIIa microscope (Digital Instruments, Santa Barbara, CA) in air with use of standard silicon tips (NCH-10 V) in the tapping mode. Height and phase images were simultaneously measured at the resonance frequency of the tips with 125 μm long cantilevers (235–240 kHz). All the images were collected with the maximum available number of pixels (512) in each direction (1 μm). Scanning speed was at a line frequency of 1.0 Hz.

Materials: THF and toluene were dried over sodium benzophenone ketyl, and were distilled under nitrogen. Chloroform and dichloromethane were dried over CaH₂ 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. 1-Hydroxybenzotriazole monohydrate (HOBt) and glycine ethyl ester hydrochloride were purchased from Wako (Osaka, Japan) and Aldrich, respectively. (Trimethylsilyl)acetylene was kindly supplied by Shinetsu Chemical (Tokyo, Japan). Paraformaldehyde, copper(I) iodide, sodium borohydride, and *N,N'*-dicyclohexylcarbodiimide (DCC) were obtained from Kishida (Osaka, Japan). Bis(triphenylphosphine)palladium dichloride, 4-bromobenzaldehyde, and γ-benzyl-*N*-tert-butoxycarbonyl-L-glutamate were obtained from Tokyo Kasei (TCL, Tokyo, Japan). C₆₀ was purchased from Materials Technologies Research (MTR Ltd., Ohio, USA). Norbornadienerhodium(I) chloride dimer

([Rh(nbd)Cl]₂) was obtained from Aldrich and used as received. (*R*)-(+)-4-[[[(1-Phenylethyl)carbamoyloxy]phenyl]acetylene] (**2a**) and (*S*)-[4-[(1-(1-naphthyl)ethyl)carbamoyl]phenyl]acetylene (**2c**) were prepared by the previously reported method.^[4b,d] The C₆₀-bound phenylacetylene (**1**) and the novel optically active phenylacetylene **2b** were prepared as shown in Schemes 2 and 3, respectively.

***N*-(4-Bromobenzyl)glycine ethyl ester:** This compound was prepared by treatment of 4-bromobenzaldehyde with glycine ethyl ester hydrochloride in toluene in the presence of triethylamine, followed by hydrogenation with sodium borohydride (70% yield). The coupling of (trimethylsilyl)acetylene to *N*-(4-bromobenzyl)glycine ethyl ester in the presence of a palladium catalyst (bis(triphenylphosphine)palladium dichloride), followed by alkaline hydrolysis of the trimethylsilyl and ethyl groups, gave *N*-(4-ethynyl)benzylglycine. The crude product was chromatographed on silica gel with chloroform/methanol/acetic acid (100:10:5, v/v) as the eluent and purified by recrystallization from a mixture of ethanol and water (5:1, v/v) (53% yield).

Mp > 205 °C (decomp). ¹H NMR (D₂O, RT, 500 MHz): δ = 7.47 (d, ³J(H,H) = 8.0 Hz, 2H; aromatic), 7.44 (d, ³J(H,H) = 8.0 Hz, 2H; aromatic), 4.26 (s, 2H; ArCH₂NH), 3.62 (s, 2H; NHCH₂CO), 3.58 ppm (s, 1H; H-C≡); ¹³C NMR (D₂O, RT, 125 MHz): δ = 172.14, 133.80, 132.60, 130.98, 123.77, 84.11, 80.43, 51.37, 49.54 ppm; elemental analysis calcd (%) for C₁₁H₁₁NO₂·0.1 C₂H₅OH: C 69.41, H 6.03, N 7.23; found: C 69.38, H 5.90, N 7.32.

***N*-(4-Ethynylbenzyl)-3,4-fulleropyrrolidine (**1**):** *N*-(4-Ethynylbenzyl)glycine (0.79 g, 4.2 mmol), paraformaldehyde (0.31 g, 10 mmol), and C₆₀ (1.5 g, 2.1 mmol) were dissolved in toluene (600 mL), and the mixture was heated at reflux for 10 h with stirring. After the mixture had cooled, the solvent was evaporated under reduced pressure. The crude solid material was purified by chromatography on silica gel with toluene/hexane (5:1, v/v) as the eluent, yielding **1** as a black powder (0.59 g, 30%).

Compound 1: Mp > 300 °C. ¹H NMR ([D]chloroform, 500 MHz, 25 °C): δ = 7.69 (d, ³J(H,H) = 8.5 Hz, 2H; Ph), 7.63 (d, ³J(H,H) = 8.5 Hz, 2H; Ph), 4.43 (s, 4H; N(CH₂)₂), 4.31 (s, 2H; Ph-CH₂), 3.12 ppm (s, 1H; C≡C-H); ¹³C NMR ([D]chloroform, 125 MHz): δ = 154.88, 147.30, 146.23, 146.06, 146.04, 145.67, 145.40, 145.28, 144.55, 143.09, 142.62, 142.23, 142.05, 141.87, 140.13, 138.90, 136.23, 132.52, 128.76, 121.35, 83.49, 77.35, 70.66, 67.48, 58.46 ppm; IR (KBr): ν̄ = 3289, 2921, 2850, 2782, 1461, 1427, 1338, 821 cm⁻¹; UV/Vis (chloroform): λ_{max} (ε) 702 (380), 635 (440), 608 (560), 431 (4100), 323 (37000), 307 (39000), 254 (130000); MS (FAB+): *m/z* 878 [C₇₁H₁₁N+H]⁺.

(*N*-tert-Butoxycarbonyl-γ-benzylxyglutamoyl)aminophenylacetylene (2b**):** HOBt (23.0 g, 150 mmol) and DCC (41.2 g, 200 mmol) were added at 0 °C to a solution of 4-ethynylaniline (5.8 g, 50 mmol), prepared by the previously reported method,^[25] in dry THF (270 mL). After the reaction mixture had been stirred under nitrogen at 0 °C for 1 h and then at room temperature for 2 h, γ-benzyl *N*-tert-butoxycarbonyl-L-glutamate (17.0 g, 50.4 mmol) was added. The dispersion solution was stirred at room temperature for 17 h. After filtration, the solvent was removed under reduced pressure. The crude product was then dissolved in ethyl acetate (50 mL), and the solution was washed successively with aqueous NaHCO₃, citric acid, and NaCl solutions. The organic layer was dried over Na₂SO₄ before evaporation of the solvent. The residue was purified by silica gel chromatography with hexane/ethyl acetate (1:1, v/v) as the eluent. After evaporation of the solvent, the residue was freeze-dried to give **2b** as white crystals (10.0 g, 47% yield).

Compound 2b: Mp 40.7–41.9 °C. ¹H NMR ([D]chloroform, RT, 300 MHz): δ = 8.58 (b, 1H; NHCO), 7.50 (dd, 2H; aromatic), 7.45 (dd, 2H; aromatic), 7.36 (s, 5H; benzyl), 5.34 (d, 1H; NH-Boc), 5.15 (s, 2H; benzyl), 4.29 (m, 1H; CH), 3.04 (s, 1H; H-C≡C), 2.66 (m, 1H; CH₂), 2.48 (m, 1H; CH₂), 2.22 (m, 1H; CH₂), 2.00 (m, 1H; CH₂), 1.61 ppm (s, 9H; Boc); IR (KBr): ν̄ = 2107 (ν_{C≡C}), 1736 (ν_{ester}), 1671 (ν_{amide I}), 1529 (ν_{amide II}) cm⁻¹; elemental analysis calcd (%) for C₂₅H₂₈N₂O₅·1/3 H₂O: C 67.86, H 6.52, N 6.63; found: C 67.97, H 6.52, N 6.63.

Polymerization: Polymerization was carried out as shown in Scheme 1 in a dry glass ampoule under a dry nitrogen atmosphere in the presence of [[Rh(nbd)Cl]₂] as the catalyst. A typical polymerization procedure is described below.

Monomer **1** (26.1 mg, 29.7 μmol) and monomer **2a** (74.4 mg, 0.279 mmol) were placed in a dry ampoule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation–flush procedure had been repeated three times, a three-way stopcock was attached to the ampoule, and dry chloroform (6.7 mL) and triethylamine (40 μL) were added by syringe. A solution of $[\text{Rh}(\text{nbd})\text{Cl}]_2$ in chloroform (0.30 mL) was added to this at 30 °C. The concentrations of the monomer and the rhodium catalyst were 0.043 M and 0.86 mM, respectively. After 24 h, the resulting polymer $[\text{poly}(\mathbf{1}_{0.1}\text{-co-}\mathbf{2a}_{0.9})]$ was precipitated in a large amount of methanol, collected by centrifugation, and dried in vacuo at room temperature for 10 h (52 mg, 52 % yield). $\text{Poly}(\mathbf{1}_{0.1}\text{-co-}\mathbf{2a}_{0.9})$ was soluble in chloroform and THF. The molecular weight (M_n) was 8.4×10^4 as determined by SEC with polystyrene standards in THF. The ^1H NMR spectrum of $\text{poly}(\mathbf{1}_{0.1}\text{-co-}\mathbf{2a}_{0.9})$ in $[\text{D}]\text{chloroform}$ showed a singlet centered at 5.56 ppm, due to the main chain protons, indicating that the polymer possesses a highly *cis-transoidal*, stereoregular structure.^[10]

$\text{Poly}(\mathbf{1}_{0.1}\text{-co-}\mathbf{2a}_{0.9})$: ^1H NMR ($[\text{D}]\text{chloroform}$, 500 MHz, 60 °C): δ = 6.2–7.4 (m, 8.5H; aromatic), 5.80 (br, 0.9H; NH), 5.56 (s, 1H; C=C–H), 4.77 (m, 0.9H; CH), 4.13 (br, 0.2H; Ph–CH₂), 3.40 (br, 0.4H; N(CH₂)₂), 1.40 ppm (d, 2.7H; CH₃).

Other copolymers of **1** with **2a–2c** were also prepared in the same way.

Dynamic light scattering measurements: Dynamic light scattering measurements were performed on a DLS-7000HK (Otsuka Electronics–Co. Ltd., Osaka, Japan) instrument fitted with a 10 mW He–Ne Laser (632.8 nm) at 25 °C. A stock solution of $\text{poly}(\mathbf{1}_{0.1}\text{-co-}\mathbf{2b}_{0.9})$ (run 6 in Table 1) (4 mg mL^{−1}) in dichloromethane was prepared in a 10 mL flask fitted with a stopcock, and the solution was filtered through a 0.2 μm syringe filter (Toyo Roshi Co. Ltd., Tokyo, Japan). Aliquots of the stock solution (2.5 mL) were transferred by Hamilton microsyringe to two 10 mL flasks fitted with stopcocks. DMF or dichloromethane—previously filtered through a 0.2 μm syringe filter—was added to the flasks, so as to keep the total volume (10 mL) and the $\text{poly}(\mathbf{1}_{0.1}\text{-co-}\mathbf{2b}_{0.9})$ concentration at 1.0 mg mL^{−1}, and the DLS measurements were then performed on the samples at a fixed scattering angle of 90°. The obtained autocorrelation functions were analyzed by the method of cumulants to give the translational diffusion coefficients (D_s). The corresponding hydrodynamic radius (R_h) was calculated by use of the Stokes–Einstein equation: $R_h = k_B T / (6\pi\eta D)$, where k_B , η , and T are the Boltzmann constant, the solvent viscosity, and the absolute temperature, respectively. The η value for DMF/dichloromethane (1:1) at 25 °C was separately determined to be 0.6876 mPas.

AFM measurements: A typical procedure is described. A stock solution of $\text{poly}(\mathbf{1}_{0.1}\text{-co-}\mathbf{2a}_{0.9})$ (1.0 mg mL^{−1}) in THF was prepared and filtered with a 0.50 μm membrane filter, and 100 μL of this stock solution was injected into the SEC system. The higher molecular weight part was fractionated (7.5 $\mu\text{g mL}^{-1}$) and immediately dropped onto the freshly cleaved mica and HOPG substrates. For AFM measurements of $\text{poly}(\mathbf{1}_{0.1}\text{-co-}\mathbf{2b}_{0.9})$, such SEC fractionation was not done. For all samples, the solutions were blown off simultaneously with a stream of nitrogen, and the substrates were dried in vacuo overnight to measure the AFM images in the tapping mode. All the experiments were performed in air at ambient temperature.

Molecular modeling and calculations: Molecular modeling and molecular mechanics calculation were performed with the Dreiding force field (version 2.21)^[26] as implemented in the CERIUSt software package (version 3.8; Molecular Simulations Inc., Burlington, MA, USA) running on an Indigo2-Extreme graphics workstation (Silicon Graphics). The polymer model with a random sequence of **1** and **2a** (20 repeating monomer units with $[\mathbf{1}]/[\mathbf{2a}] = 2:8$) of $\text{poly}(\mathbf{1}_{0.2}\text{-co-}\mathbf{2a}_{0.8})$ was constructed by use of a Polymer Builder module in CERIUSt by a method similar to that reported previously.^[4b] Charges on the atoms of the copolymer were calculated by charge equilibration (QEq) in CERIUSt; 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 (φ) could be varied. As in the case of homopolymer, poly-**2a** with an (*R*)-[(1-phenylethyl)carbamoyl]oxy group, the chiral side groups could

control a helical state to one-handedness in excess since poly-**2a** showed an intense ICD in the UV/Vis region.^[4b] However, no preferable helical conformation of poly-**2a** (right- or left-handed helix) has yet been determined, so we assumed that poly-**2a** and its copolymer with **1** may have a right-handed helix and the initial dihedral angle (φ) was set to 150° (*transoid*) on the basis of the calculated structure of poly[4-(*tert*-butyldimethylsiloxy)phenylacetylene], in which the pendant group was similar in bulkiness to that of **2a**. The constructed model (20-mer) was optimized by the conjugate gradient method. The energy minimization was continued until the root-mean-square (rms) value became less than 0.1 kcal mol^{−1} Å^{−1}. The average divergence of the dihedral angles of the double and single bonds from planarity were $158.2 \pm 3.3^\circ$ and $-4.4 \pm 2.8^\circ$, respectively. The obtained right-handed helical structure of $\text{poly}(\mathbf{1}_{0.2}\text{-co-}\mathbf{2a}_{0.8})$ is shown in Figure 4. The helix sense of the copolymer is tentative and the opposite helix sense cannot be ruled out. To presume a more stable helical state, more detailed molecular mechanics and molecular dynamics calculations of model polymers of **2a** and $\text{poly}(\mathbf{1}_n\text{-co-}\mathbf{2a}_m)$ would be necessary.

Acknowledgement

This work was partially supported by a 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.

- For reviews, see: a) M. Prato, *J. Mater. Chem.* **1997**, 7, 1097–1109; b) V. V. Tsukruk, *Prog. Polym. Sci.* **1997**, 22, 247–311; c) Y. Chen, Z. Huang, R. F. Cai, B. C. Yu, *Eur. Polym. J.* **1998**, 34, 137–151; d) M. Prato, M. Maggini, *Acc. Chem. Res.* **1998**, 31, 519–526; e) L. Dai, A. W. H. Mau, *Adv. Mater.* **2001**, 13, 899–913; f) A. Cravino, N. S. Sariciftci, *J. Mater. Chem.* **2002**, 12, 1931–1943.
- S. R. Wilson, D. I. Schuster, B. Nuber, M. S. Meier, M. Maggini, M. Prato, R. Taylor, *Fullerenes: Chemistry, Physics, and Technology* (Eds.: K. M. Kadish, R. S. Ruoff), Wiley, New York, **2000**.
- a) A. W. Jensen, S. R. Wilson, D. I. Schuster, *Bioorg. Med. Chem.* **1996**, 4, 767–779; b) A. M. Cassell, W. A. Scrivens, J. M. Tour, *Angew. Chem.* **1998**, 110, 1670–1672; *Angew. Chem. Int. Ed.* **1998**, 37, 1528–1531; c) E. Nakamura, H. Isobe, N. Tomita, M. Sawamura, S. Jinno, H. Okayama, *Angew. Chem.* **2000**, 112, 4424–4427; *Angew. Chem. Int. Ed.* **2000**, 39, 4254–4258; d) T. D. Ros, M. Bergamin, E. Vázquez, G. Spalluto, B. Baiti, S. Moro, A. Boutorine, M. Prato, *Eur. J. Org. Chem.* **2002**, 405–413.
- a) E. Yashima, S. Huang, Y. Okamoto, *J. Chem. Soc. Chem. Commun.* **1994**, 1811–1812; b) E. Yashima, S. Huang, T. Matsushima, Y. Okamoto, *Macromolecules* **1995**, 28, 4184–4193; c) E. Yashima, K. Maeda, O. Sato, *J. Am. Chem. Soc.* **2001**, 123, 8159–8160; d) K. Morino, K. Maeda, Y. Okamoto, E. Yashima, T. Sato, *Chem. Eur. J.* **2002**, 8, 5112–5120; e) E. Yashima, *Anal. Sci.* **2002**, 18, 3–6. For other recent examples, see: e) V. Percec, M. Obata, J. G. Rudick, B. B. De, M. Glodde, T. K. Bera, S. N. Magonov, V. S. K. Balagurusamy, P. A. Heiney, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, 40, 3509–3533; f) A. P. H. J. Schenning, M. Fransen, E. W. Meijer, *Macromol. Rapid Commun.* **2002**, 23, 265–270; g) T. Aoki, T. Kaneko, N. Maruyama, A. Sumi, M. Takahashi, T. Sato, M. Teraguchi, *J. Am. Chem. Soc.* **2003**, 125, 6346–6347; h) B. S. Li, K. K. L. Cheuk, L. Ling, J. Chen, X. Xiao, C. Bai, B. Z. Tang, *Macromolecules* **2003**, 36, 77–85. For aliphatic polyacetylenes, see: i) R. Nomura, Y. Fukushima, H. Nakako, T. Masuda, *J. Am. Chem. Soc.* **2000**, 122, 8830–8836; j) R. Nomura, S. Nishiura, J. Tabei, F. Sanda, T. Masuda, *Macromolecules* **2003**, 36, 5076–5080.
- a) M. M. Green, N. C. Peterson, T. Sato, A. Teramoto, R. Cook, S. Lifson, *Science* **1995**, 268, 1860–1866; b) M. M. Green, J.-W. Park, T. Sato, A. Teramoto, S. Lifson, R. L. B. Selinger, J. V. Selinger, *Angew. Chem.* **1999**, 111, 3329–3345; *Angew. Chem. Int. Ed.* **1999**, 38, 3138–3154; c) T. Nakano, Y. Okamoto, *Chem. Rev.* **2001**, 101, 4013–4038; d) M. Fujiki, J. R. Koe, K. Terao, T. Sato, A. Teramoto,

- J. Watanabe, *Polym. J.* **2003**, 35, 297–344; e) E. Yashima, K. Maeda, T. Nishimura, *Chem. Eur. J.* **2004**, 10, 42–51.
- [6] a) E. Yashima, T. Matsushima, Y. Okamoto, *J. Am. Chem. Soc.* **1995**, 117, 11596–11597; b) E. Yashima, T. Nimura, T. Matsushima, Y. Okamoto, *J. Am. Chem. Soc.* **1996**, 118, 9800–9801; c) E. Yashima, T. Matsushima, Y. Okamoto, *J. Am. Chem. Soc.* **1997**, 119, 6345–6359; d) E. Yashima, K. Maeda, Y. Okamoto, *Nature* **1999**, 399, 449–451; e) H. Onouchi, K. Maeda, E. Yashima, *J. Am. Chem. Soc.* **2001**, 123, 7441–7442; f) R. Nonokawa, E. Yashima, *J. Am. Chem. Soc.* **2003**, 125, 1278–1283; g) K. Maeda, K. Morino, Y. Okamoto, T. Sato, E. Yashima, *J. Am. Chem. Soc.* **2004**, 126, 4329–4342; h) T. Nishimura, S. Ohsawa, K. Maeda, E. Yashima, *Chem. Commun.* **2004**, 646–647; i) T. Nishimura, K. Tsuchiya, S. Ohsawa, K. Maeda, E. Yashima, Y. Nakamura, J. Nishimura, *J. Am. Chem. Soc.* **2004**, 126, 11711–11717. For other induced helical polymers, see: j) D. S. Schlitzer, B. M. Novak, *J. Am. Chem. Soc.* **1998**, 120, 2196–2197; k) E. Yashima, K. Maeda, T. Yamanaka, *J. Am. Chem. Soc.* **2000**, 122, 7813–7814; l) M. Ishikawa, K. Maeda, E. Yashima, *J. Am. Chem. Soc.* **2002**, 124, 7448–7458; m) M. Ishikawa, K. Maeda, Y. Mitsutsuji, E. Yashima, *J. Am. Chem. Soc.* **2004**, 126, 732–733; n) R. Sakai, T. Satoh, R. Kakuchi, H. Kaga, T. Kakuchi, *Macromolecules* **2004**, 37, 3996–4003.
- [7] T. Nishimura, K. Takatani, S. Sakurai, K. Maeda, E. Yashima, *Angew. Chem.* **2002**, 114, 3754–3756; *Angew. Chem. Int. Ed.* **2002**, 41, 3602–3604.
- [8] M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc.* **1993**, 115, 9798–9799.
- [9] K. Morino, K. Maeda, E. Yashima, *Macromolecules* **2003**, 36, 1480–1486.
- [10] a) C. I. Simionescu, V. Percec, S. Dumitrescu, *J. Polym. Sci. Polym. Chem. Ed.* **1977**, 15, 2497–2509; b) C. I. Simionescu, V. Percec, *Prog. Polym. Sci.* **1982**, 18, 133–214; c) A. Furlani, C. Napoletano, M. V. Russo, W. Feast, *J. Polym. Bull.* **1986**, 16, 311–317; d) Y. Kishimoto, P. Eckerle, T. Miyatake, M. Kainosho, A. Ono, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1999**, 121, 12035–12044.
- [11] a) H. Shirakawa, T. Ito, S. Ikeda, *Polym. J.* **1973**, 4, 460–462; b) M. Tabata, Y. Tanaka, Y. Sadahiro, T. Sone, K. Yokota, I. Miura, *Macromolecules* **1997**, 30, 5200–5204.
- [12] H. Xu, B. Z. Tang, *J. Macromol. Sci. Pure Appl. Chem.* **1999**, A36, 1197–1207.
- [13] The SEC analysis of the recovered polymer indicates that a small amount of C₆₀ (less than 10 mol%) was adsorbed on the polymer, although the amount of C₆₀ incorporated in the polymer main chain could not be determined.
- [14] For recent reviews of chiral fullerenes, see: a) C. Thilgen, F. Diederich in *Topics in Current Chemistry*, Vol. 199 (Ed.: A. Hirsch), Springer, Berlin, **1999**, pp. 136–166; b) F. Diederich, M. G. López, *Chem. Soc. Rev.* **1999**, 28, 263–277; c) A. Bianco, T. D. Ros, M. Prato, C. Toniolo, *J. Pept. Sci.* **2001**, 7, 208–219; d) Y. Nakamura, K. O-kawa, J. Nishimura, *Bull. Chem. Soc. Jpn.* **2003**, 76, 865–882.
- [15] a) M. Maggini, G. Scorrano, A. Bianco, C. Toniolo, M. Prato, *Tetrahedron Lett.* **1995**, 36, 2845–2846; b) C. K. F. Shen, K. M. Chien, C. G. Juo, G. R. Her, T. Y. Luh, *J. Org. Chem.* **1996**, 61, 9242–9244; c) D. I. Schuster, J. Cao, N. Kaprinidis, Y. Wu, A. W. Jensen, Q. Lu, H. Wang, S. R. Wilson, *J. Am. Chem. Soc.* **1996**, 118, 5639–5647; d) A. Bianco, M. Maggini, G. Scorrano, C. Toniolo, G. Marconi, C. Villani, M. Prato, *J. Am. Chem. Soc.* **1996**, 118, 4072–4080.
- [16] T. Ishi-i, K. Nakashima, S. Shinkai, A. Ikeda, *J. Org. Chem.* **1999**, 64, 984–990.
- [17] a) J. Crassous, J. Rivera, N. S. Fender, L. Shu, L. Echegoyen, C. Thilgen, A. Herrmann, F. Diederich, *Angew. Chem.* **1999**, 111, 1716–1721; *Angew. Chem. Int. Ed.* **1999**, 38, 1613–1617; b) F. Djojo, A. Hirsch, S. Grimme, *Eur. J. Org. Chem.* **1999**, 3027–3039; c) Y. Nakamura, K. O-kawa, M. Matsumoto, J. Nishimura, *Tetrahedron* **2000**, 56, 5429–5434; d) Y. Nakamura, K. O-kawa, T. Nishimura, E. Yashima, J. Nishimura, *J. Org. Chem.* **2003**, 68, 3251–3257; e) S. Sergeyev, F. Diederich, *Angew. Chem.* **2004**, 116, 1770–1773; *Angew. Chem. Int. Ed.* **2004**, 43, 1738–1740.
- [18] a) R. Nomura, J. Tabei, T. Masuda, *J. Am. Chem. Soc.* **2001**, 123, 8430–8431; b) R. Nomura, J. Tabei, S. Nishiura, T. Masuda, *Macromolecules* **2003**, 36, 561–564; c) K. K. L. Cheuk, J. W. Y. Lam, L. M. Lai, Y. Dong, B. Z. Tang, *Macromolecules* **2003**, 36, 9752–9762.
- [19] a) M. M. Bouman, E. E. Havinga, R. A. J. Janssen, E. W. Meijer, *Mol. Cryst. Liq. Cryst.* **1994**, 256, 439–448; b) L. Pu, *Acta Polym.* **1997**, 48, 116–141; c) E. Yashima, H. Goto, Y. Okamoto, *Macromolecules* **1999**, 32, 7942–7945; d) Z.-B. Zhang, M. Fujiki, M. Motonaga, H. Nakashima, K. Torimitsu, H.-Z. Tang, *Macromolecules* **2002**, 35, 941–944; e) H. Goto, E. Yashima, *J. Am. Chem. Soc.* **2002**, 124, 7943–7949; f) H. Goto, Y. Okamoto, E. Yashima, *Chem. Eur. J.* **2002**, 8, 4027–4036.
- [20] R. M. Silverstein, F. X. Webster, *Spectrometric Identification of Organic Compounds*, Wiley, New York, **1996**, Chapter 3.
- [21] R. C. Paul, P. Singh, S. L. Chadha, *Indian J. Chem.* **1968**, 6, 673–674.
- [22] a) L. Giovannelli, G. L. Lay, *Appl. Surf. Sci.* **2000**, 162–163, 513–518; b) D. M. Guldi, M. Maggini, S. Mondini, F. Guérin, J. H. Fendler, *Langmuir* **2000**, 16, 1311–1318; c) S. Barazzouk, S. Hotchandani, P. V. Kamat, *Adv. Mater.* **2001**, 13, 1614–1617; d) J. Li, D. Qin, J. R. Baker Jr, D. A. Tomalia, *Macromol. Symp.* **2001**, 166, 257–269; e) G. Das, L. Ouali, M. Adrian, B. Baumeister, K. J. Wilkinson, S. Matile, *Angew. Chem.* **2001**, 113, 4793–4797; *Angew. Chem. Int. Ed.* **2001**, 40, 4657–4661.
- [23] S. Gao, L. Chi, S. Lenhert, B. Anczykowski, C. M. Niemeyer, M. Adler, H. Fuchs, *ChemPhysChem* **2001**, 2, 384–388.
- [24] a) H. Tanaka, C. Hamai, T. Kanno, T. Kawai, *Surf. Sci.* **1999**, 432, L611–L616; b) P. Samori, V. Francke, K. Müllen, J. P. Rabe, *Chem. Eur. J.* **1999**, 5, 2312–2317; c) C. I. Zanetti, R. Khurana, J. R. Gillespie, J. S. Petrick, L. C. Trabachino, L. J. Minert, S. A. Carter, A. L. Fink, *Proc. Natl. Acad. Sci. USA* **1999**, 96, 13175–13179; d) Y. Maeda, T. Matsumoto, T. Kawai, *Surf. Interface Anal.* **1999**, 27, 450–455; e) T. Uchihashi, N. Choi, M. Tanigawa, M. Ashino, Y. Sugawara, H. Nishijima, S. Akita, Y. Nakayama, H. Tokumoto, K. Yokoyama, S. Morita, M. Ishikawa, *Jpn. J. Appl. Phys. Part 2* **2000**, 39, L887–L889; f) P. G. Khalatur, A. R. Khokhlov, S. A. Prokhorova, S. S. Sheiko, M. Möller, P. Reineker, D. G. Shirvanyanz, N. Starovoi-tova, *Eur. Phys. J.* **2000**, E1, 99–103; g) B. S. Li, K. K. L. Cheuk, F. Salhi, J. W. Y. Lam, J. A. K. Cha, X. Xiao, C. Bai, B. Z. Tang, *Nano Lett.* **2001**, 1, 323–328; h) K. Shinohara, S. Yasuda, G. Kato, M. Fujita, H. Shigekawa, *J. Am. Chem. Soc.* **2001**, 123, 3619–3620; i) S. S. Sheiko, M. Möller, *Chem. Rev.* **2001**, 101, 4099–4123; j) A. P. H. J. Schenning, A. F. M. Kilbinger, F. Biscarini, M. Cavallini, H. J. Cooper, P. J. Derrick, W. J. Feast, R. Lazzaroni, P. Leclère, L. A. McDonell, E. W. Meijer, S. C. J. Meskers, *J. Am. Chem. Soc.* **2002**, 124, 1269–1275.
- [25] P. R. Serwinski, P. M. Lahti, *Org. Lett.* **2003**, 5, 2099–2102.
- [26] a) S. L. Mayo, B. D. Olafson, W. A. Goddard III, *J. Phys. Chem.* **1990**, 94, 8897–8909; b) A. K. Rappé, W. A. Goddard III, *J. Phys. Chem.* **1991**, 95, 3358–3363.

Received: August 7, 2004

Published online: December 27, 2004