A Helical Array of Pendant Fullerenes on an Optically Active Polyphenylacetylene**

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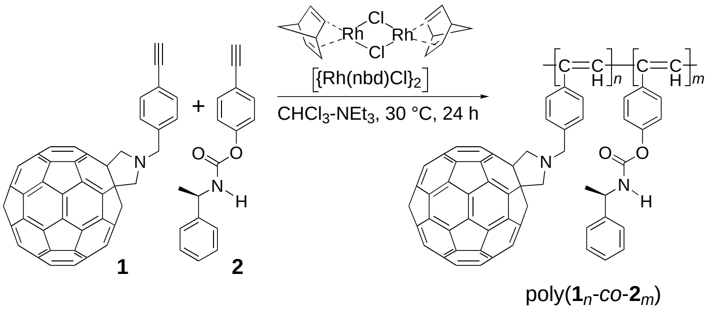
The synthesis of [60]fullerene-containing polymers with a well-defined structure has aroused considerable interest in recent years because of their possible applications in the wide fields of materials[1] and biological sciences.[2] However, previous studies of C_{60}-based polymers have mainly focused on their structures and properties, either in the bulk state or as thin films. We have previously reported that stereoregular polyphenylacetylenes bearing optically active side groups form a predominantly one-handed helical structure and exhibit a characteristic induced circular dichroism (CD) in the main chain region, both in solution as well as in the solid state.[3] We have also investigated the effect that the bulkiness of the phenyl-group substituents of the achiral comonomers had on the formation of the helical conformations derived from copolymers with optically active bulky phenylacetylenes in solution. We found that the optical activity (CD intensity and specific rotation) of the copolymers increased with increased bulkiness of the achiral comonomers.[3b] This unique cooperative property of helical polyphenylacetylenes stimulated us to synthesize an optically active, C_{60}-based helical polyphenylacetylene where the pendant achiral C_{60} moieties would possibly be arranged in a helical array, with a one-handed screw-sense, thus showing optical activity in the fullerene region. Tour and co-workers recently reported an elegant method to construct a helical array of C_{60} molecules through electrostatic interactions of a water-soluble, cationic C_{60} derivative, with the phosphate groups along the DNA backbone acting as a template. However, the chiroptical property of the complex has not yet been reported.[4]

Optically active, *cis-transoidal* polyphenylacetylenes with pendant C_{60} groups were prepared by the copolymerization of an achiral C_{60}-bound phenylacetylene (**1**) and an optically active phenylacetylene with an (*R*)-[(1-phenylethyl)carbamoyl]oxy substituent (**2**) on the phenyl group,[3b] using a rhodium catalyst [{Rh(nbd)Cl}$_2$] (nbd = norbornadiene, Scheme 1). The fullerene monomer was prepared by the reaction of C_{60} with *N*-(4-ethynylbenzyl)glycine by using the Prato reaction.[1a,5] The copolymerization results are summarized in Table 1. The fullerene homopolymer was insoluble in common organic solvents, but the copolymers were partially soluble in THF and chloroform, depending on the content of the C_{60} units. Figure 1 shows the CD and absorption spectra of poly($\mathbf{1}_{0.1}$-*co*-$\mathbf{2}_{0.9}$) in THF. The copolymer exhibited an intense induced CD (ICD) in the π-conjugated main-chain region (280–500 nm), the magnitude of which monotonically increased with decreasing temperature. A similar temperature-dependent relationship for the Cotton effect observed in the main-chain region of optically active polyphenylacetylenes was also observed for the homopolymer, poly-**2**.[6] These observations suggested that the induced helical conformation of the copolymer was dynamic in nature as a result of cooperative interactions among the pendant groups, and the helical screw-sense preference (right- and left-handed helices) of the copolymer increased with a decrease in temperature.



Scheme 1. Synthesis of poly($\mathbf{1}_n$-*co*-$\mathbf{2}_m$).

Table 1. Copolymerization results of achiral **1** and optically active **2** with [{Rh(nbd)Cl}$_2$] in chloroform in the presence of triethylamine at 30 °C for 24 h.[a]

Entry	**1** [mol %]	**2** [mol %]	**1** + **2** [M]	Yield [%][b]	Polymer MeOH-insoluble part Yield [%]	**1** [mol %][c]	$M_n \times 10^{-4}$[d]
1	100	0	0.016	60.4	–	100	–
2	10	90	0.043	–	52.0	12.3	8.4
3	20	80	0.033	15.2	72.0	22.1	1.8
4	30	70	0.026	60.5	20.8	26.9	2.4

[a] [**1** + **2**]/[triethylamine] = 1; [**1** + **2**]/[Rh] = 50. [b] Chloroform insoluble part. [c] Estimated by ^{1}H NMR spectroscopy. [d] Determined by SEC (polystyrene standards).

Poly($\mathbf{1}_{0.1}$-*co*-$\mathbf{2}_{0.9}$) displayed almost no detectable absorption and CD at wavelengths over 600 nm in dilute solution (Figure 1) because of the low concentration of the C_{60} units. However, at higher concentrations, a remarkable CD induction was observed above 600 nm at temperatures lower than −40 °C, which is characteristic of the fullerene chromophore for the copolymer (inset in Figure 1); the ICD intensity further increased at −80 °C. The sudden onset and rapid increase in the optical activity of the achiral C_{60} cores in the copolymer are indicative of a helical array of the C_{60} units with

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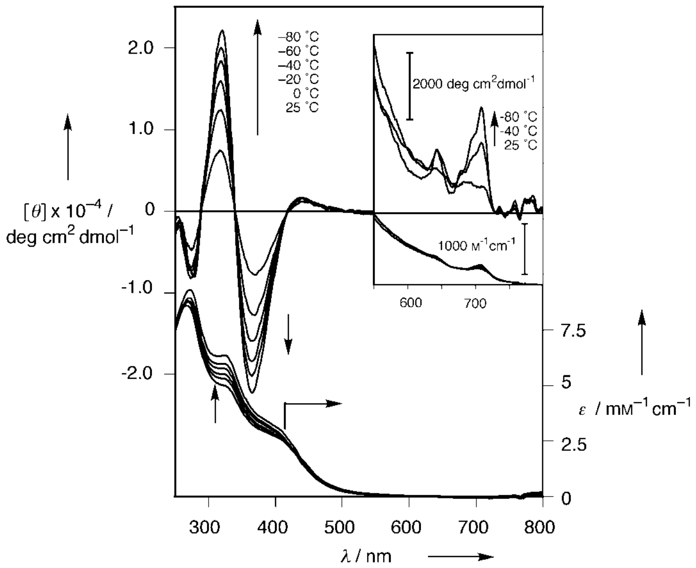

Figure 1. CD and absorption spectra of poly($\mathbf{1}_{0.1}$-*co*-$\mathbf{2}_{0.9}$) in THF solution (0.11 mg mL^{-1}) at various temperatures. The inset shows the corresponding CD and absorption spectra in the fullerene region in THF at a higher concentration (4.6 mg mL^{-1}). The molar concentrations were calculated based on the monomer units and C_{60} units (inset).

a one-handed screw-sense through the polyphenylacetylene (Figure 2) because the C_{60} units themselves are achiral.[7] The other copolymers (poly($\mathbf{1}_{0.2}$-*co*-$\mathbf{2}_{0.8}$) and poly($\mathbf{1}_{0.3}$-*co*-$\mathbf{2}_{0.7}$)) also exhibited similar ICDs in the same wavelength region (600–800 nm). This is, to the best of our knowledge, the first induction of chirality upon achiral fullerenes, derived from their helical arrangement in polymers. The estimated CD intensities for the fullerene chromophore region of the copolymers were based on the content of C_{60} incorporated into the copolymer chains.[8] These values were as large as those for chiral monosubstituted fullerenes[9] and C_1-symmetric chiral bis-substituted fullerenes,[10] but were smaller by one or two orders of magnitude than their C_2-symmetric counterparts.[11]

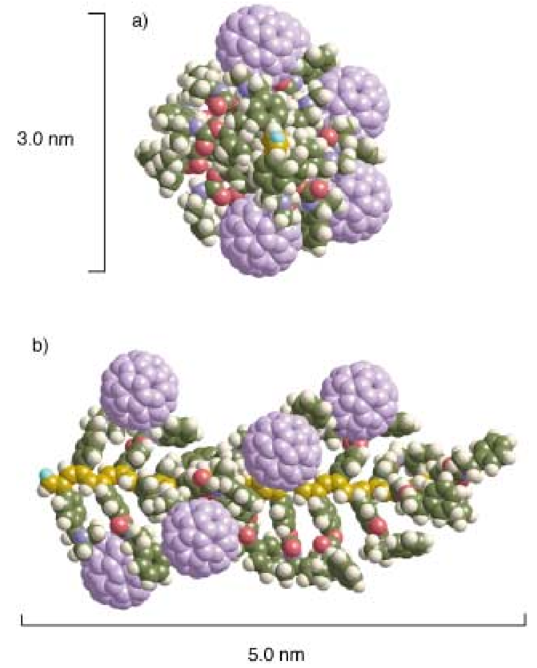

Figure 2. A possible helical structure of poly($\mathbf{1}_{0.2}$-*co*-$\mathbf{2}_{0.8}$) (20-mer). Space-filling models are shown in the top (a) and side views (b). The fullerene units are assumed to arrange in a left-handed helical array along the right-handed polyacetylene main chain. The helix-sense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

Atomic force microscopy (AFM) provided an insight into the structure and morphology of the helically arranged C_{60}-based copolymers. Figure 3 shows typical AFM images of the high-molecular-weight fraction of poly($\mathbf{1}_{0.1}$-*co*-$\mathbf{2}_{0.9}$) deposited on a freshly cleaved mica surface and on highly oriented pyrolytic graphite (HOPG). The high-molecular-weight fraction of poly($\mathbf{1}_{0.1}$-*co*-$\mathbf{2}_{0.9}$) was obtained by size exclusion chromatography (SEC) fractionation using THF as the eluent. The AFM images on mica cast from the fractionated dilute THF solution reveal isolated particles (average height: 2.6 ± 1.3 nm), which are formed because the pendant C_{60} groups of the copolymer aggregate on mica to form an assembly (cluster) through repulsive interactions between the hydrophobic C_{60} units and hydrophilic mica substrates.[12] On the other hand, rather extended and individual copolymer chains (average height: 2.1 ± 0.8 nm) can be seen together with isolated particles on HOPG prepared by the same procedure. These results indicate that the attractive force between the pendant C_{60} groups and the substrate plays a critical role in the morphology of the C_{60}-based polymers.[13]

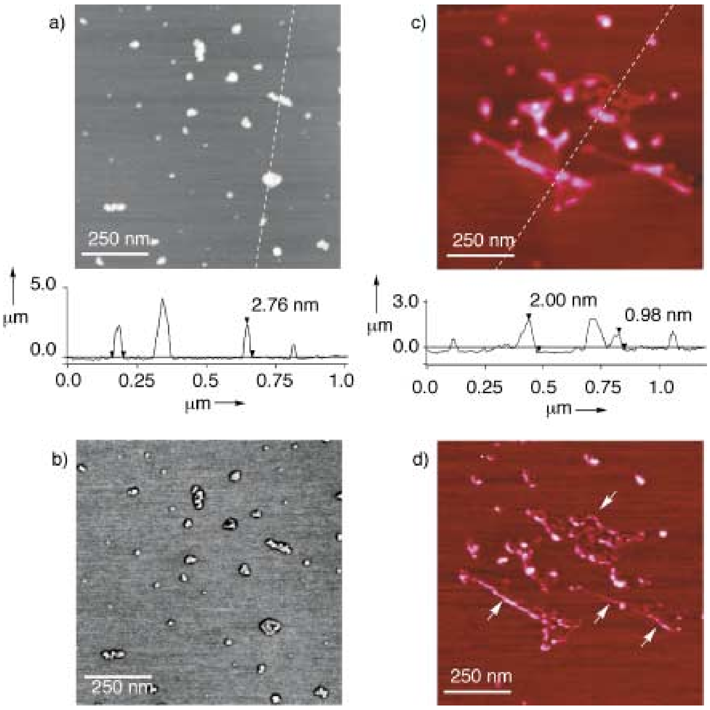

Figure 3. Tapping-mode AFM height (a, c) and phase (b, d) images of poly($\mathbf{1}_{0.1}$-*co*-$\mathbf{2}_{0.9}$) cast from a dilute solution in THF on mica (a, b) and HOPG (c, d). The higher-molecular-weight part of the copolymer obtained by SEC fractionation was used. The height profiles measured along the white lines in the images are also shown. The arrows in (d) indicate the typically observed left-handed helices.

The phase images of the copolymer on HOPG feature a particularly interesting left-handed helical shape (marked by arrows in Figure 3 d).[14] Although we could not distinguish the C_{60} and chiral pendant groups of the copolymer by using AFM, these helical-shaped images may be closely correlated to the macromolecular helical chirality of the polyphenylacetylenes. Scanning tunneling microscopy (STM) may be useful to obtain higher resolution images on HOPG and the results will give us direct information concerning the helicity of the copolymers.[15] The work is now in progress.

In summary, we have prepared and characterized the first example of an optically active helical polymer bearing pendant achiral C_{60} groups which arrange in a helical array with a predominant screw-sense along the polymer backbone. Although such a helical array of the C_{60} units, which exhibits optical activity in the fullerene chromophore region, is presently possible at low temperatures, we believe that the rational design and synthesis of helical polyacetylenes using more bulky chiral pendant groups will afford more stable C_{60}-based helical polymers. This methodology is also useful for constructing a novel helical polymer with the desired pendant in a one-handed helical array.

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Changeable Pore Sizes Allowing Effective and Specific Recognition by a Molybdenum-Oxide Based “Nanosponge”: En Route to Sphere-Surface and Nanoporous-Cluster Chemistry[**]

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Dedicated to Professor Jean-Marie Lehn

A current challenge in nanotechnology is to mimic material constructions and molecular-recognition-type responsive sensing of biological systems. This challenge becomes especially attractive when nanometer-sized objects can be constructed with tailor-made building blocks, this is possible with our unique giant sphere or ring-shaped molybdenum oxide based objects which are made up of $\{(Mo)Mo_5\}$ building blocks and show a huge variety of functionalities, and hence reactivities, comparable to the much smaller fullerenes.[1]

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