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A helical array of pendant fullerenes on a helical poly(phenylacetylene) induced by non-covalent chiral interactions†

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Novel [60]fullerene-based poly(phenylacetylene)s prepared by the copolymerization of achiral phenylacetylenes bearing a C_{60} or crown ether pendant form a one-handed helix upon complexation with L- and D-alanine, yielding a helical array of the pendant fullerenes with a predominant screw-sense along the polymer backbone.

Since the development of the large-scale production of [60]fullerene (C_{60}),[1] a number of C_{60} derivatives[2] and C_{60}-containing polymers[3] with a well-defined structure have been synthesized with great interest in recent years due to their unique physical and chemical properties and their possible applications in the fields of material and biological sciences.[4] We have recently reported the first example of optically active helical poly(phenylacetylene)s bearing C_{60} pendants by the copolymerization of an achiral C_{60}-bound phenylacetylene with an optically active phenylacetylene. The copolymers formed a predominantly one-handed helical structure and exhibited a characteristic induced circular dichroism (ICD) in the main chain region as well as in the fullerene chromophore region. The induction of chirality upon achiral fullerenes appears to be derived from their helical arrangements in the copolymers.[5] The macromolecular helicity with the pendant helical array of the fullerenes is completely controlled by the optically active comonomer introduced in the main chain through covalent bonding. On the other hand, the induction of macromolecular helicity in optically inactive poly(phenylacetylene)s can be possible through non-covalent bimolecular interactions when the polymers have functional groups such as carboxy,[6] amino,[7] boronate[8] and phosphonate[9] groups or macrocyclic host pendants such as a bulky 18-crown-6 ether.[10] Upon complexation with optically active compounds capable of interacting with the functional groups or the crown ether, the complexes exhibit a characteristic ICD in the polymer backbone regions due to one-handed helicity induction in the polymers. In particular, the crown ether-bound poly(phenylacetylene) is highly sensitive to the amino acid chirality and forms a one-handed helix with amino acids through a significant cooperative interaction.[10] On the basis of these observations, we have now designed and synthesized novel optically inactive, *cis–transoidal* C_{60}-bound poly(phenylacetylene)s bearing the crown ether pendant as the amino acid binding site. We anticipate that the amino acid-derived chiral information is transmitted to the polymer backbone through a non-covalent bonding interaction with the pendant crown ethers, leading to an excess of the one-handed helical sense in the polymer backbone, which further results in a helical array of the C_{60} pendants with a predominantly one handed screw-sense (Fig. 1).

Optically inactive, *cis–transoidal* C_{60}- and 18-crown-6-bound poly(phenylacetylene)s were prepared by the copolymerization of achiral phenylacetylenes bearing a C_{60} (**1**)[5] or an aza-18-crown-6 ether pendant (**2**)[10] using a rhodium catalyst $[Rh(nbd)Cl]_2$ (nbd = norbornadiene, Fig. 1). The results of the copolymerization at various feed monomer ratios are summarized in Table 1. The copolymers obtained at the feed ratio of [**1**]/([**1**] + [**2**]) ≤ 0.15 were soluble in chloroform and dichloromethane, while those obtained at [**1**]/([**1**] + [**2**]) ≥ 0.2 were insoluble in common organic solvents. The ^{1}H NMR spectra of the copolymers had a sharp singlet centered at 5.8 ppm due to the main chain protons, indicating that the copolymers possess a highly *cis-transoidal*, stereoregular structure.† The introduction of the C_{60} pendants into the polymer chain was clearly confirmed by the ^{1}H NMR, absorption, and IR spectra of the copolymers and the compositions determined by these measurements were in good agreement with those in feed.† Although the monomer reactivity ratio could not be determined due to the insolubility of the copolymers with a high C_{60} content, the monomer distribution in the copolymers of **1** and **2** seems to be random because the copolymer composition did not change regardless of the monomer conversion (see entries 1 and 2 in Table 1).

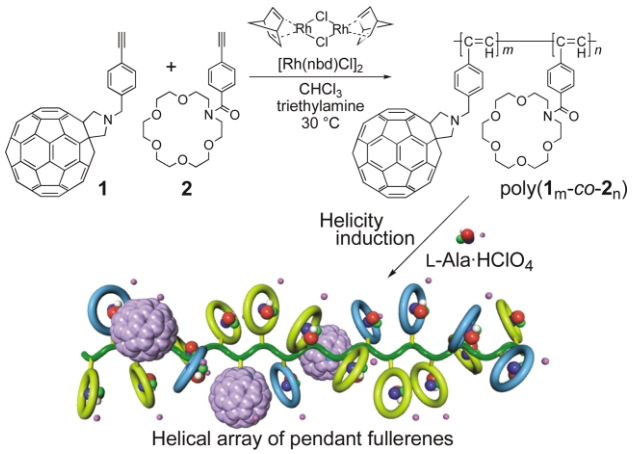

Fig. 1 Synthesis of poly($\mathbf{1}_m$-*co*-$\mathbf{2}_n$) and schematic representation of macromolecular helicity induction on poly($\mathbf{1}_m$-*co*-$\mathbf{2}_n$) upon complexation with L-alanine. The achiral fullerene and crown ether pendants represented by yellow and blue rings for clarity arrange in a helical array along the one-handed helical polymer backbone induced by non-covalent chiral interactions with L-alanine. The helix-sense is tentative.

Table 1 Copolymerization results of **1** and **2** with $[Rh(nbd)Cl]_2$ in chloroform in the presence of triethylamine at 30 °C[a]

					Polymer		
Entry	**1** (mol%)	**2** (mol%)	**1** + **2** (M)	Time	Yield (%)	**1** (mol%)[b]	$M_n \times 10^{-4}$[c]
1	10.0	90.0	0.071	22 h	78.9[d]	10.1 (10.7)	5.1
2	10.0	90.0	0.069	20 s	2.1[e]	10.6 (—)	0.8
3	14.9	85.1	0.050	22 h	93.9[d]	14.5 (16.7)	6.0
4	20.0	80.0	0.032	22 h	32.1[d]	22 ± 1[f]	—

[a] Polymerized under nitrogen; [**1** + **2**]/[triethylamine] = 1; [**1** + **2**]/[Rh] = 100. [b] Estimated by ^{1}H NMR spectroscopy. In the parentheses are shown those estimated by absorption spectra on the basis of molar absorptivity of **1**. [c] Determined by SEC (polystyrene standards, eluent: THF containing 0.1 wt% tetra-*n*-butylammonium bromide). [d] Diethyl ether insoluble part. [e] Diethyl ether–toluene (1/1, v/v) insoluble part. [f] Estimated by IR spectroscopy.

† Electronic Supplementary Information (ESI) available: Full synthetic and analytical details and UV-vis, CD, IR and NMR spectra of the copolymers. See http://www.rsc.org/suppdata/cc/b3/b312511d/

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Fig. 2 shows the CD and absorption spectra of poly(**1**$_{0.1}$-*co*-**2**$_{0.9}$) in the presence of L- and D-alanine (Ala) perchlorate in dichloromethane–acetonitrile (8/2, v/v) at [Ala·$HClO_4$]/[poly(**1**$_{0.1}$-*co*-**2**$_{0.9}$)] = 2. The copolymer exhibited mirror images of the split-type intense ICDs in the π-conjugated main chain region (300–500 nm) and the magnitude of the ICD increased with a decrease in temperature. The Cotton effects were similar in pattern to those of the homopolymer, poly-**2** complexed with L- or D-Ala perchlorate in acetonitrile.[10] These observations suggest that the copolymer forms a predominantly one-handed helix assisted by non-covalent complexation with the optically active alanine perchlorate.

Similarly to the previously prepared, optically active C_{60}-containing poly(phenylacetylene)s,[5] poly(**1**$_{0.1}$-*co*-**2**$_{0.9}$) showed almost no detectable absorption and ICD signals at wavelengths over 600 nm at −20 °C because of the low concentration of C_{60} units. At higher concentration, however, apparent CDs were induced in the fullerene chromophore region over 600 nm even at 25 °C and the ICD magnitude further increased with decreasing temperature. The L- and D-Ala·$HClO_4$ induced mirror images of the ICDs in the fullerene chromophore region where the ICD patterns were similar to those of the optically active, C_{60}-containing poly(phenylacetylene)s.[5] These results indicate that the achiral C_{60} pendants of the copolymer may arrange in a helical array with a predominant screw-sense along the polymer backbone. The other copolymer (poly(**1**$_{0.15}$-*co*-**2**$_{0.85}$)) also exhibited similar ICDs in the same wavelength region (600–800 nm).†

As previously reported, poly-**2** forms an almost one-handed helix with 0.5 equiv. L-Ala·$HClO_4$ at −10 °C, indicating strong chiral amplification with cooperative interaction in the crown ether pendants with L-Ala through non-covalent interactions.[10] CD titration using L-Ala·$HClO_4$ at a higher concentration of poly(**1**$_{0.15}$-*co*-**2**$_{0.85}$) was then carried out to investigate if such a chiral amplification process during the helix induction in the polymer backbone followed by a one-handed helical arrangement in the crown ether segments could lead to the helical array of the C_{60} units in the copolymer. The ICD intensities of the main chain region (300–500 nm) as well as the fullerene chromophore region (over 600 nm) increased with increasing concentration of L-Ala at rt and the changes in the ICD intensities in both regions correlated well

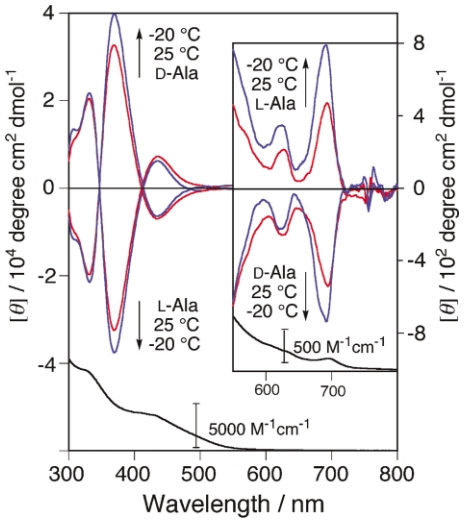

Fig. 2 CD spectra of poly(**1**$_{0.1}$-*co*-**2**$_{0.9}$) with L- and D-Ala·$HClO_4$ ([Ala·$HClO_4$]/[poly(**1**$_{0.1}$-*co*-**2**$_{0.9}$)] = 2) in dichloromethane–acetonitrile (8/2, v/v) at 25 and −20 °C at a dilute concentration ([poly(**1**$_{0.1}$-*co*-**2**$_{0.9}$)] = 0.1 mg mL^{-1}). Absorption spectrum of poly(**1**$_{0.1}$-*co*-**2**$_{0.9}$) with L-Ala·$HClO_4$ at 25 °C is also shown. The inset shows the corresponding CD and absorption spectra in the fullerene region at a higher concentration (2.9 mg mL^{-1}). The molar concentrations were calculated based on the monomer units and fullerene units (inset).

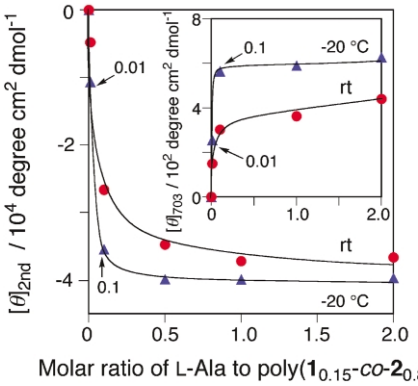

Fig. 3 Titration curves of poly(**1**$_{0.15}$-*co*-**2**$_{0.85}$) ([θ]$_{2nd}$) with L-Ala·$HClO_4$ in dichloromethane–acetonitrile (8/2, v/v) at rt (●, red) and −20 °C (▲, blue). Here [θ]$_{2nd}$ indicates the ICD intensity at the second Cotton (365 nm). The inset shows the titration curves ([θ]$_{703}$) of the fullerene chromophore region at rt (●, red) and −20 °C (▲, blue).

with each other (Fig. 3). However, interestingly, the ICD intensity of the fullerene region reached an almost constant value at 0.1 equiv. L-Ala at −20 °C. This indicates that at lower temperature, the small monomeric crown ether units of the copolymer complexed with L-Ala are significantly amplified to induce the same helix on the free monomeric crown ether units[10] together with the achiral fullerene units, resulting in a one-handed helical array of the pendant fullerenes, thus exhibiting an ICD.

In conclusion, we have found that the optically inactive, C_{60}-containing poly(phenylacetylene)s bearing crown ether pendants as the amino acid binding site can be transformed into a predominantly one-handed helical conformation upon complexation with optically active amino acids, and the achiral C_{60} pendants arrange in a helical array with the desired helix-sense along the polymer backbone *via* chiral, non-covalent bonding interactions. This method will be applicable to other induced helical polymers with the desired pendant in a one-handed helical array.

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Notes and references

1 W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature*, 1990, **347**, 354.
2 S. R. Wilson, D. I. Schuster, B. Nuber, M. S. Meier, M. Maggini, M. Prato and R. Taylor, in *Fullerenes: Chemistry, Physics, and Technology*, ed. K. M. Kadish and R. S. Ruoff, Wiley, New York, 2000.
3 (*a*) M. Prato, *J. Mater. Chem.*, 1997, **7**, 1097; (*b*) Y. Chen, Z. Huang, R. F. Cai and B. C. Yu, *Eur. Polym. J.*, 1998, **34**, 137.
4 (*a*) M. Prato and M. Maggini, *Acc. Chem. Res.*, 1998, **31**, 519; (*b*) A. W. Jensen, S. R. Wilson and D. I. Schuster, *Bioorg. Med. Chem.*, 1996, **4**, 767; (*c*) A. M. Cassell, W. A. Scrivens and J. M. Tour, *Angew. Chem., Int. Ed.*, 1998, **37**, 1528.
5 T. Nishimura, K. Takatani, S. Sakurai, K. Maeda and E. Yashima, *Angew. Chem., Int. Ed.*, 2002, **41**, 3602.
6 (*a*) E. Yashima, T. Matsushima and Y. Okamoto, *J. Am. Chem. Soc.*, 1997, **119**, 6345; (*b*) E. Yashima, K. Maeda and Y. Okamoto, *Nature*, 1999, **399**, 56.
7 K. Maeda, S. Okada and E. Yashima, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 3180.
8 (*a*) E. Yashima, T. Nimura, T. Matsushima and Y. Okamoto, *J. Am. Chem. Soc.*, 1996, **118**, 9800; (*b*) H. Kawamura, K. Maeda, Y. Okamoto and E. Yashima, *Chem. Lett.*, 2001, 58.
9 H. Onouchi, K. Maeda and E. Yashima, *J. Am. Chem. Soc.*, 2001, **123**, 7441.
10 R. Nonokawa and E. Yashima, *J. Am. Chem. Soc.*, 2003, **125**, 1278.