J|A|C|S COMMUNICATIONS

Published on Web 08/18/2010

Separation of C_{70} over C_{60} and Selective Extraction and Resolution of Higher Fullerenes by Syndiotactic Helical Poly(methyl methacrylate)

Takehiro Kawauchi,*,† Atsushi Kitaura,‡ Mariko Kawauchi,† Tsutomu Takeichi,† Jiro Kumaki,§ Hiroki Iida,‡ and Eiji Yashima*,‡

Department of Environmental and Life Sciences, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441-8580, Japan, Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan, and Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16, Jonan, Yonezawa 992-8510, Japan

Received June 7, 2010; E-mail: kawauchi@ens.tut.ac.jp; yashima@apchem.nagoya-u.ac.jp

Abstract: A one-handed helical polymer, syndiotactic poly(methyl methacrylate) (st-PMMA), recognizes the size and chirality of higher fullerenes through an induced-fit mechanism and can selectively extract enantiomers of the higher fullerenes, such as C_{76}, C_{80}, C_{84}, C_{86}, C_{88}, C_{90}, C_{92}, C_{94}, and C_{96}. This discovery will generate a practical and valuable method for selectively extracting the elusive higher fullerenes and their enantiomers and opens the way to developing novel carbon cage materials with optical activities.

The development of a practical and efficient method for the separation of higher fullerenes ($>C_{76}$) with a specific size, geometry, and, in particular, chirality is among the urgent and emerging challenges in advanced materials science due to their attractive applications, such as electronic and optoelectronic materials.[1,2] The iterative chromatographic separation provides a tiny amount of the higher fullerenes, and the supramolecular approach using designer host molecules with a rigid concave cavity or through self-assemblies has been a powerful method for selectively encapsulating C_{60} and/or C_{70} rather than higher fullerenes.[3−12] The cyclic dimers of zinc porphyrins possess an exceptionally high affinity toward the higher fullerenes due to flexible linkers between the metalloporphyrins.[13] We recently reported that syndiotactic poly(methyl methacrylate) (st-PMMA), a stereoregular commodity plastic, can encapsulate fullerenes, such as C_{60} and C_{70}, within its helical cavity to form a robust, processable, and crystalline complex with optical activity.[14] Here we show that the helical st-PMMA folds into a spring-like helical conformation in response to the size and chirality of the higher fullerenes through an induced-fit mechanism, thus generating a practical and valuable method for the size- and enantiomer-selective extraction of the elusive higher fullerenes.[15−17]

The inclusion or encapsulation of specific guests into helical cavities is an intriguing feature of biological helical polymers, such as amylose and assembled proteins. For example, amylose can form inclusion complexes with not only small organic molecules[18] but also synthetic polymers[19−21] and carbon nanotubes[22,23] via an induced fit. However, almost all synthetic helical polymers and oligomers encapsulate specific guest molecules of complementary size and shape into their helical cavities due to a lack of flexibility and adaptability.[24]

We first investigated the binding affinity of st-PMMA with C_{60} and C_{70} that have the same small diameter (Figure 1a). When 0.5 mg of st-PMMA was dissolved in 1 mL of toluene solution of C_{60} (0.1 mg/mL) upon heating at 110 °C, followed by cooling to room temperature, the resulting st-PMMA gel encapsulated 0.02 mg of C_{60} within its helical cavity as determined by an electronic absorption analysis (Figure 1b and the Supporting Information). The encapsulated C_{60} content increased with the increasing feed C_{60} concentration, whereas a larger amount of C_{70} was trapped in the st-PMMA hollow spaces under the same experimental conditions (Figure 1b), indicating a higher affinity of st-PMMA to C_{70} over C_{60}, although the difference is not significant. Surprisingly, when equally mixed amounts of C_{60} and C_{70} in toluene (0.1−0.5 mg/mL, 1 mL) were used, st-PMMA (0.5 mg) preferentially extracted C_{70} with almost perfect selectivity (99.8%) as demonstrated by the HPLC chromatograms of the fullerenes before and after a single extraction by st-PMMA (Figure 1c−g). Release of

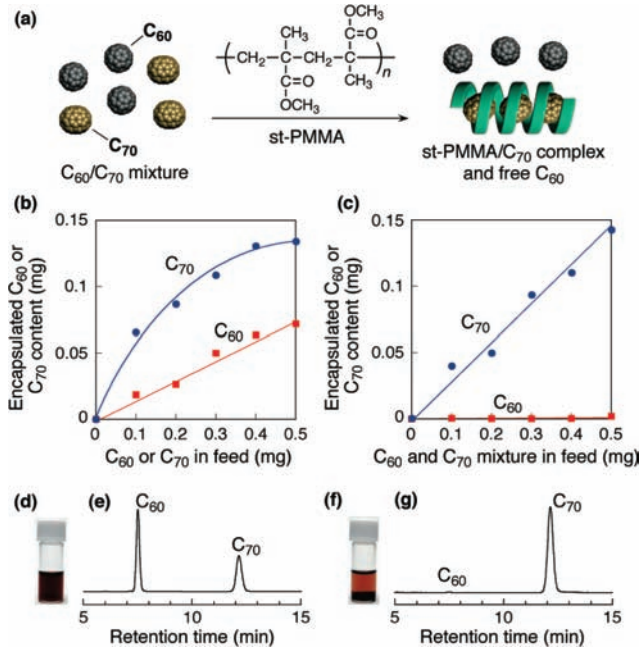

Figure 1. (a) Schematic illustration of the preferential encapsulation of C_{70} over C_{60} by the helical st-PMMA. Plots of encapsulated C_{60} (red squares) and C_{70} (blue circles) contents versus (b) the amount of C_{60} or C_{70} alone and (c) the amount of the C_{60}/C_{70} mixture (1/1, wt/wt) in the feed upon gelation of st-PMMA (0.5 mg) with toluene (1 mL). Photographs of a toluene solution of (d) C_{60}/C_{70} (1/1, wt/wt) mixture (0.3 mg/mL, 1 mL) and (f) st-PMMA/fullerene complex gel obtained after heating to 110 °C followed by cooling to room temperature and then centrifugation. UV (330 nm) detected HPLC chromatograms of C_{60} and C_{70} (e) before and (g) after extraction of C_{60}/C_{70} (1/1, wt/wt) mixture by st-PMMA.

† Toyohashi University of Technology.
‡ Nagoya University.
§ Yamagata University.

the fullerenes from the st-PMMA complex gel was performed by adding 1,2-dichlorobenzene (DCB), and after the solvent was evaporated, the residue was subjected to HPLC analysis to estimate the selectivity (Table S1).

Previously, we reported that X-ray diffraction (XRD) profiles of the st-PMMA films complexed with C_{60}, C_{70}, and C_{84} prepared by evaporating the solvents from the corresponding gels revealed that the *d* spacing values arising from the st-PMMA helical structures increased with an increase in the size of the encapsulated fullerenes from 1.67 (C_{60}) to 1.92 (C_{70}) and 2.04 nm (C_{84}),[14] indicating that the st-PMMA helical cavity most likely flexibly expands upon encapsulation of the larger fullerenes through an induced-fit mechanism and this change is most likely accompanied by a change in the helical pitch of the st-PMMA. If this is the case, once the larger fullerenes are encapsulated in the st-PMMA, smaller fullerenes can no longer be trapped.

To confirm this assumption, a toluene solution of C_{70} (0.5 mg/mL, 1 mL) was added to an st-PMMA/C_{60} complex gel (0.065 mg of C_{60} was encapsulated in 0.5 mg of st-PMMA). After the mixture stirred at room temperature for 12 h, the encapsulated C_{60} molecules were completely replaced by C_{70} as evidenced by the HPLC analysis (Figures 2a and S1a). In sharp contrast, entrapped C_{70} molecules in st-PMMA were scarcely released after the addition of a large excess of C_{60} (Figure S1b). More interestingly, titration experiments of the st-PMMA/C_{60} complex gel with C_{70} revealed that a very small amount of C_{70} (1 wt % to the encapsulated C_{60} in the st-PMMA) was sufficient to enlarge the entire st-PMMA helical cavity, resulting in the release of almost all of the C_{60} molecules (99.7%) entrapped in the st-PMMA helical cavity (Figure 2b). This extraordinary cooperative effect triggered by a larger fullerene is unprecedented and implies a spring-like motion of the stretchable st-PMMA helix in the gel state.

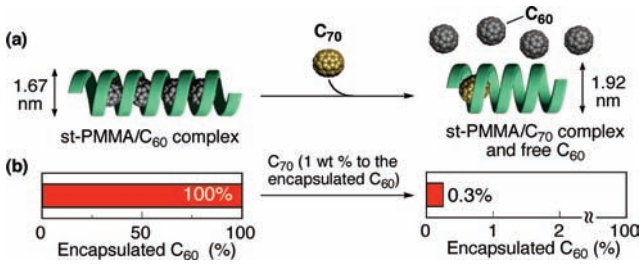

Figure 2. (a) Schematic illustration of the replacement of C_{60} accommodated in the helical st-PMMA cavity by C_{70}. (b) Changes in the encapsulated C_{60} in st-PMMA before (left) and after adding a small amount of C_{70} to the st-PMMA/C_{60} complex (right) (C_{60} 0.065 mg, st-PMMA 0.5 mg, toluene 1 mL).

On the basis of the preferential binding capability of st-PMMA to C_{70} over C_{60}, selective extraction of the higher fullerenes from carbon soot (a commercially available fullerene mixture) composed of C_{60}/C_{70}/higher fullerenes (64.0 : 27.2 : 8.8% determined by HPLC analysis) was performed as follows. An appropriate amount of st-PMMA was dissolved in a toluene solution of the fullerene mixture (fullerene mixture, 0.3 mg/mL) upon heating at 110 °C, followed by cooling to room temperature, resulting in the st-PMMA gel complexed with the fullerenes. The encapsulated fullerenes were recovered with DCB, and the content was determined by HPLC and matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF-MS) analyses. Because the encapsulated higher fullerenes may not be completely released from the st-PMMA with DCB, the content (selectivity) for higher fullerenes may be underestimated.

Remarkably, the higher fullerenes were selectively obtained from the carbon soot (ca. 0.3 mg/mL, 200 mL) and the higher fullerene content significantly increased to 95.4% from 8.8% in the feed by single extraction with st-PMMA (0.025 mg/mL (Table S1 and Figure S2g)). The higher fullerene extraction efficiency was highly dependent on the st-PMMA concentration, and an increase in the st-PMMA concentration tended to result in a decrease in efficiency (Table S1). The MALDI-TOF-MS profiles of the encapsulated fullerenes by st-PMMA (0.005 mg/mL) (Figure S2e) revealed that the extract obtained from a single extraction by st-PMMA was indeed enriched in the higher fullerenes up to C_{110}−C_{140} which are unprecedented to obtain by a conventional chromatographic separation and extraction with low molecular mass host molecules.

Finally, we demonstrated that an optically active st-PMMA with an excess single-handed helix can be used to enantiomer-selectively extract chiral fullerenes from carbon soot. However, judging from the tiny structural differences in the enantiomers and due to a lack of functionality, the direct separation of such carbon cage chiral molecules into enantiomers appears to be extremely difficult, and only D_2-symmetric C_{76} (C_{76}-D_2),[15,16a,17,25] C_{78}-D_3,[15b] and C_{84}-D_2[15b,16b] were successfully resolved into the enantiomers by recycling chiral HPLC, kinetic resolution, and enantioselective extraction with a chiral porphyrin dimer[25] and the covalent modification with chiral molecules followed by regeneration. The fact that the number of chiral isomers dramatically increases with increasing cage size (for example, 21 of 35 C_{88} isomers are possibly chiral) suggests that there are no feasible methods to resolve the higher fullerenes (>C_{84}) into optical antipodes.

The optically active st-PMMA gel was prepared according to a previously reported method[26] with a slight modification using (*R*)- or (*S*)-1-phenylethylamine (**1**) as the solvent to induce a preferred-handed helical conformation in st-PMMA followed by complete removal of **1** by repeatedly washing the gel with toluene and then isolated by centrifugation. A single extraction of a large amount of fullerene mixture in toluene (ca. 0.3 mg/mL, 800 mL) was then carried out using a low concentrated optically active st-PMMA gel (0.05 mg/mL), since using lower concentrated st-PMMA appears to encapsulate higher fullerenes more efficiently. We estimated that approximately 16% of the higher fullerenes, for example, 13% of feed C_{76} and 14% of feed C_{84} in toluene, were encapsulated by a single extraction as demonstrated by the HPLC chromatograms of the solution before and after extraction by the optically active st-PMMA (Table S2). The extraction provided a series of optically active fullerenes (C_{76}, C_{84}, C_{86}, C_{88}, C_{90}, C_{92}, C_{94}, and C_{96}) as supported by the circular dichroism (CD)-detected HPLC chromatograms of the extract, which showed the apparent CDs (Figure 3a and b). Among them, the optically active C_{86}, C_{88}, C_{90}, C_{92}, C_{94}, and C_{96} have never been isolated. A series of optically active fullerenes were then isolated by preparative HPLC using a COSMOSIL 5PBB column, and their CD and absorption spectra were measured in DCB at 25 °C, resulting in the characteristic CDs in the long absorption regions (Figure 3c−n). When an opposite enantiomer of 1-phenylethylamine (**1**) was used for the preparation of the preferred-handed helical st-PMMA, the opposite fullerene enantiomers could be extracted, as evidenced by the mirror image CDs. The enantiomeric excess (ee) of the isolated C_{76} was estimated to be approximately 4% by comparison with the reported CD intensity of the optically pure C_{76} in toluene (Figure S3).[16a] Two fractions assigned to the C_{84} isomers (C_{84}-major and C_{84}-minor in Figure 3a) were also fractionated from the extract, and the CD pattern of the major isomer (C_{84}-major) was in accordance with that reported for the optically pure C_{84}-D_2 (Figures 3g and S4a),[16b] suggesting that the minor fraction (C_{84}-minor) likely consists of

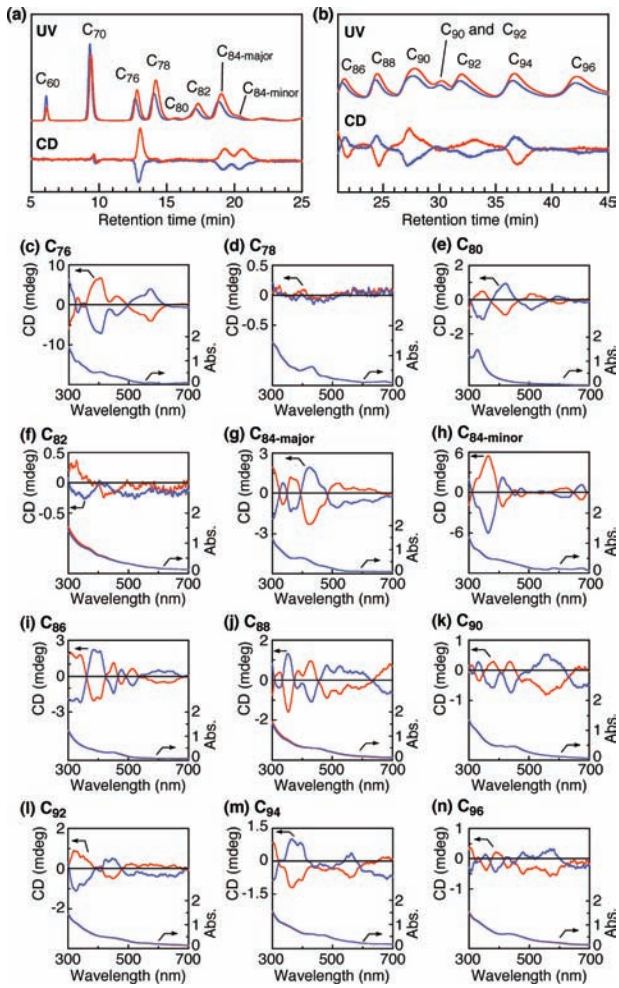

Figure 3. (a, b) UV (356 nm, top) and CD (375 nm, bottom) detected HPLC chromatograms of the extracted fullerenes from carbon soot using optically active helical st-PMMAs prepared with (*R*)-**1** (red lines) and (*S*)-**1** (blue lines). The HPLC measurements were carried out using a COSMOSIL 5PBB column with chlorobenzene as the eluent at a flow rate of 1.0 mL/min. CD (top) and absorption (bottom) spectra of fractionated (c) C_{76}, (d) C_{78}, (e) C_{80}, (f) C_{82}, (g) $C_{84\text{-major}}$, (h) $C_{84\text{-minor}}$, (i) C_{86}, (j) C_{88}, (k) C_{90}, (l) C_{92}, (m) C_{94}, and (n) C_{96} measured in DCB at 25 °C.

novel chiral isomers of C_{84} which have never been isolated (Figures 3h and S4b). Although the ee values of the isolated chiral fullerenes were low, this finding may lead to the development of unique and facile methods to resolve the higher fullerenes.

In conclusion, this strategy which relies on the inexpensive and readily available helical st-PMMA with a unique induced-fit feature has great potential in the isolation of not only higher fullerene isomers but also their enantiomers and, thus, opens the way to developing novel carbon cage materials with optical activities.

Acknowledgment. This work was supported in part by the Ogasawara Foundation, the Tatematsu Foundation, Research Foundation for Materials Science, the Sumitomo Foundation, a Grant-in-Aid for Scientific Research (S) from the Japan Society for the Promotion of Science (JSPS), and the Global COE Program "Elucidation and Design of Materials and Molecular Functions" of the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Supporting Information Available: Full experimental details, HPLC chromatograms and MALDI-TOF-MS spectra on selective extraction of fullerenes, and CD and absorption spectra of fractionated C_{76} in toluene and $C_{84\text{-major}}$ and $C_{84\text{-minor}}$ in dichloromethane. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA104969A