

“Helix-in-Helix” Superstructure Formation through Encapsulation of Fullerene-Bound Helical Peptides within a Helical Poly(methyl methacrylate) Cavity

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Abstract: A one-handed 3_{10} -helical hexapeptide is efficiently encapsulated within the helical cavity of *st*-PMMA when a fullerene (C_{60}) derivative is introduced at the C-terminal end of the peptide. The encapsulation is accompanied by induction of a preferred-handed helical conformation in the *st*-PMMA backbone with the same-handedness as that of the hexapeptide to form a crystalline *st*-PMMA/peptide- C_{60} inclusion complex with a unique optically active helix-in-helix structure. Although the *st*-PMMA is unable to encapsulate the 3_{10} -helical peptide without the terminal C_{60} unit, the helical hollow space of the *st*-PMMA is almost filled by the C_{60} -bound peptides. This result suggests that the C_{60} moiety can serve as a versatile molecular carrier of specific molecules and polymers in the helical cavity of the *st*-PMMA for the formation of an inclusion complex, thus producing unique supramolecular soft materials that cannot be prepared by other methods.

The development of host molecules, supramolecules, and polymers that possess a unique confined nano-space suitable for encapsulating specific guests has been attracting significant attention^[1] because of their broad applications ranging from molecular recognition, sensing, separation^[1c,g,j] and catalysis,^[1h,k,l,o,p] as well as electronic and optoelectronic materials.^[1d] Cyclic host molecules, such as modified cyclodextrins^[1a,g] and self-assembled metal-organic cages^[1f,h,i,l-n] and organic nanocapsules,^[1c] are among the most extensively investigated host molecules. However, owing to their rigid and distinct conformational scaffold, a limited number of guest molecules of complementary size and shape can be entrapped in their cavities. Biological helical polymers, such as amylose,^[2] schizophyllan,^[3] and assembled proteins,^[4] are also known to

form inclusion complexes with a variety of small molecules and polymers including carbon nanotubes.^[2a,b,3c] Although such biopolymer-based helical host systems have been well established, it remains challenging to develop synthetic helical polymers with an efficient encapsulation capability for a broad range of guest molecules and polymers.^[1p,5]

Previously, we found that syndiotactic poly(methyl methacrylate) (*st*-PMMA), a commodity plastic, folds into a preferred-handed helical conformation (18_1 -helix) with an inner cavity of approximately 1 nm in toluene in the presence of an optically active alcohol or amine, accompanied by gelation, in which a series of achiral (C_{60} and C_{70})^[6,7] and chiral fullerenes (e.g., C_{76} , C_{78} , C_{80} , C_{90} , and C_{96})^[8] are size- and enantioselectively encapsulated within its helical cavity through an induced-fit mechanism to form optically active peapod-like inclusion complexes which are retained after removal of the chiral additives^[6a-c,8] (helicity memory).^[1p,9] We also found that a preferred-handed helical *st*-PMMA can serve as an optically active polymeric host to encapsulate the complementary isotactic PMMA (*it*-PMMA) in a helix-sense-controlled manner to produce the first optically active PMMA stereocomplex.^[6b,10]

Based on these results, we envisaged that functionalization of various organic molecules and polymers with a C_{60} unit at their terminals would lead to inclusion complex formations with the *st*-PMMA thanks to the C_{60} moiety that could act as a molecular carrier of the C_{60} -bound molecules and polymers within the helical cavity of the *st*-PMMA, even if the molecules and polymers themselves do not form such an inclusion complex with the *st*-PMMA. Herein we report a novel strategy to construct a unique “helix-in-helix”^[3a,b,5,6b,12] supramolecular structure composed of C_{60} -bound one-handed 3_{10} -helical^[13] peptides (fulleropeptides)^[14] (**L-1** and **D-1**) wrapped by a helical *st*-PMMA (Figure 1 a), and at the same time, a preferred-handed helical structure is induced in the *st*-PMMA backbone during the inclusion complex formation.

We designed and synthesized an N-terminal-protected hexapeptide containing strongly helix-promoting α -aminoisobutyric acid (Aib)^[13,15] residues with the sequence Boc-L-Leu-Aib-L-Leu₂-Aib-Gly- (Boc = *tert*-butoxycarbonyl) and its enantiomer as a pendant of C_{60} (**L-1** or **D-1**, Figure 1 a and Scheme S1 in the Supporting Information), because of its predictable helical structure,^[13,15] such as 3_{10} - and α -helices, where the C-terminal Gly residue was incorporated as a flexible spacer to reduce the structural strain during the inclusion complex formation within the *st*-PMMA helical cavity. The theoretical studies of **L-1** and an **L-1**/*st*-PMMA (72mer) inclusion complex revealed that encapsulation of the

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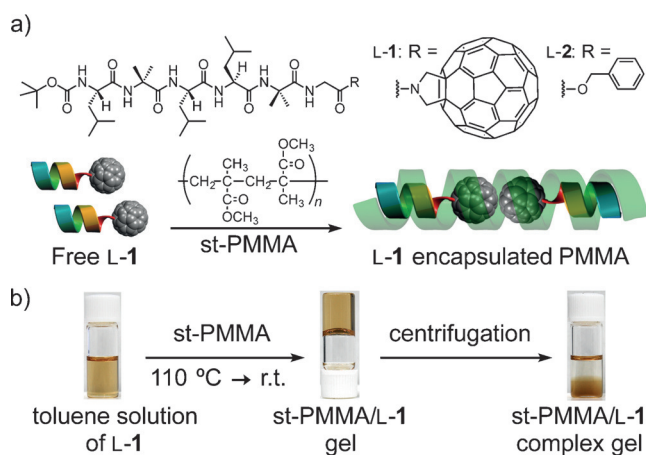


Figure 1. a) Chemical structures of the peptide-bound C_{60} (L-1), C_{60} -free peptide (L-2), and st-PMMA and a schematic illustration of the encapsulation of L-1 in the st-PMMA helical cavity upon gelation. b) Photographs of a toluene solution of L-1 (0.35 mg mL⁻¹, 1 mL; left), st-PMMA/L-1 gel after the addition of st-PMMA (10 mg) with subsequent heating to 110 °C and then cooling to room temperature (middle), and the st-PMMA/L-1 complex gel after centrifugation at 1700 g for 10 min (right).

right-handed 3_{10} -helical L-1 into the st-PMMA helix hardly disrupts both helical structures (Figures S1 and S2).

The enantiomeric L-1 and D-1 and a C_{60} -free hexapeptide model (L-2) bearing a C-terminal benzyl ester group instead of the fulleropyrrolidine^[16] (Figure 1a) were synthesized in a stepwise manner, and their structures were fully characterized by NMR spectroscopy and high-resolution mass spectroscopy measurements (see the Supporting Information). The 3_{10} -helical conformation of L-1 was confirmed by its ¹H NMR and two-dimensional NOESY spectra in CDCl₃ in combination with solvent-dependent chemical shift changes of the amide NH protons of L-1 upon the addition of the hydrogen-bond accepting [D₆]DMSO (Figures S3a and S4).^[17] Similar [D₆]DMSO-dependent chemical shift changes of the amide NH protons were also observed for L-2 (Figure S3b), indicating that L-2 possesses the identical 3_{10} -helical structure to that of L-1.

To confirm the st-PMMA/L-1 inclusion complex formation, st-PMMA (10 mg) was dissolved in a brown-colored toluene solution of L-1 (Figure 1b, left) by heating at 110 °C. The solution was then cooled to room temperature, resulting in gelation within 10 min (Figure 1b, middle). After centrifugation, a brown-colored condensed gel was obtained, whereas the supernatant solution was almost colorless (Figure 1b, right). Based on the difference in the absorption spectra between the feed L-1 solution and the supernatant, it was suggested that 0.3 mg of L-1 (2.9 wt %) was encapsulated within the st-PMMA cavities (Figure S5). The encapsulated L-1 content gradually increased by repeatedly adding the feed L-1 or D-1 toluene solution to the st-PMMA/L-1 gel followed by heating to 110 °C and cooling to room temperature, then centrifuging,^[18] and finally reaching a plateau value (ca. 25 wt %, Figure S6). We then roughly estimated the maximum amount of **1** (25.5 wt %) that fills the st-PMMA helical hollow space in a head-to-head close packing array

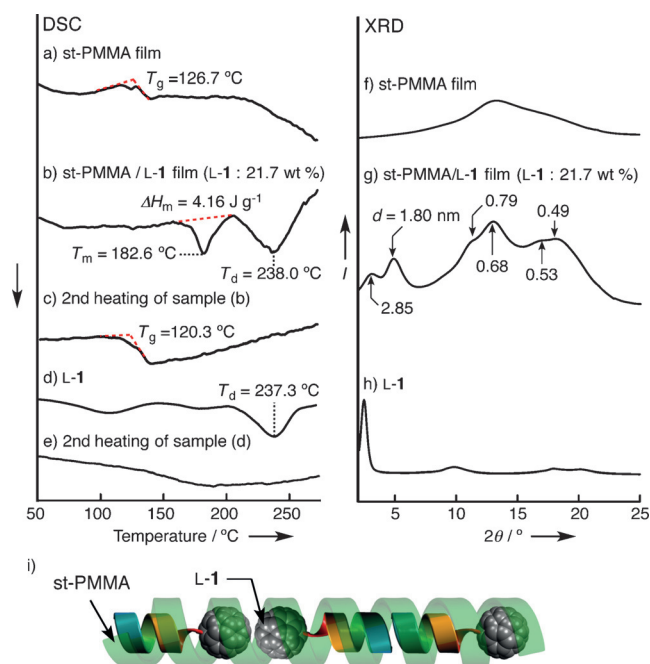


Figure 2. a)–e) DSC thermograms of: st-PMMA film (a), st-PMMA/L-1 complex film containing 21.7 wt % of L-1 (b), and L-1 (d). These films were prepared by evaporating the solvents from the st-PMMA and st-PMMA/L-1 complex gels in toluene. The DSC measurements were conducted after cooling the samples at $-30\text{ }^\circ\text{C}$, followed by heating to $280\text{ }^\circ\text{C}$ ($10\text{ }^\circ\text{C min}^{-1}$) under nitrogen. The samples (b) and (d) were then cooled to $-30\text{ }^\circ\text{C}$ ($40\text{ }^\circ\text{C min}^{-1}$), and then heated again ((c) and (e), respectively; $10\text{ }^\circ\text{C min}^{-1}$). The arrow to the left of the DSC data indicates the endothermic direction. f)–h) XRD profiles of: st-PMMA film (f), st-PMMA/L-1 complex film (21.7 wt % of L-1) (g), and L-1 powder (h). i) Schematic representation of a possible structure of the st-PMMA/L-1 complex with head-to-head arrangement of the included L-1 molecules.^[19]

(Figure 2i and see below)^[19] based on an 18_1 -helical st-PMMA structure^[6a] and a molecular length of the calculated 3_{10} -helical L-1 structure (2.2 nm; Figure S2), which is almost identical to the observed maximum amount of the encapsulated **1** (ca. 25 wt %)^[21] In sharp contrast, the C_{60} -free model peptide (L-2) did not form such an inclusion complex with st-PMMA at all, as revealed by the ¹H NMR experiments (Figure S9), indicating the indispensable role of the terminal C_{60} moiety of **1** for the inclusion complex formation with the st-PMMA.

Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) profiles of the st-PMMA/L-1 film obtained from the gel provided a detailed insight into the crystalline structure of the inclusion complex that is completely different from those of the st-PMMA film and L-1 powders (Figure 2). The DSC profile of the st-PMMA film, prepared by drying the st-PMMA gel in toluene, showed only a heat capacity change at the glass-transition temperature ($T_g = 126.7\text{ }^\circ\text{C}$) being typical for amorphous st-PMMA (Figure 2a), as supported by its featureless, and broad XRD pattern (Figure 2f).^[6a] In contrast, the DSC thermogram of the st-PMMA/L-1 film containing 21.7 wt % of L-1 displayed characteristic endothermic peaks at 182.6 and $238.0\text{ }^\circ\text{C}$ corresponding to the melting temperature (T_m) of the st-PMMA/L-1 complex and

the decomposition temperature (T_d) of L-1 (Figure 2b,d),^[23] respectively, but then showed only the T_g during its second heating (Figure 2c). Importantly, this st-PMMA/L-1 complex film had almost no T_g around 120–130 °C during the first heating (Figure 2b), suggesting that the st-PMMA hollow spaces may be mostly filled with the L-1 molecules. A similar DSC profile with the T_m of 212.4 °C was also observed for the st-PMMA/ C_{60} complex film (23.5 wt % of C_{60}),^[6a] which also supports the inclusion complex formation between the st-PMMA and L-1. The XRD profile of the crystalline st-PMMA/L-1 film (21.7 wt %) revealed a characteristic reflection at the d -spacing of 1.80 nm arising from the st-PMMA helix bundle structures (Figure 2g,i), which is larger than that of the st-PMMA complexed with C_{60} (1.67 nm),^[6a] but smaller than that with larger fullerenes, such as C_{70} (1.92 nm) and C_{84} (2.04 nm).^[6a,24]

To obtain further convincing evidence for the inclusion complex formation between the st-PMMA and L-1, the ^{13}C cross-polarization magic-angle spinning (CP-MAS) solid-state NMR measurements were carried out (Figure S10). The ^{13}C signals of the terminal C_{60} moieties in the st-PMMA/L-1 complex (21.7 wt %) were slightly shifted downfield relative to those of the free L-1, as observed for the st-PMMA/ C_{60} inclusion complex.^[25] In addition, the ^1H - ^{13}C heteronuclear correlation (HETCOR) spectrum of the st-PMMA/L-1 complex exhibited apparent intermolecular correlation peaks between the ^{13}C signals of the terminal C_{60} moieties and the ^1H signals of the methylene and methoxy groups of the st-PMMA (Figure S11d).^[26] Although the L-1 powders, which may be randomly packed close to each other, showed non-specific intermolecular correlation peaks between the ^{13}C signals of the terminal C_{60} moieties and ^1H of the neighboring L-1 molecules in addition to some intramolecular correlation peaks (Figure S11a,c), such non-specific intermolecular correlation peaks between L-1s could not be observed for the st-PMMA/L-1 complex because most of the L-1 molecules were encapsulated within the helical st-PMMA cavities. In addition, intermolecular correlation peaks between the ^{13}C signals of the C-terminal C_{60} moieties and the proton signals of the N-terminal Boc group of L-1 would be observed if the L-1 molecules exist in a head-to-tail close packing array in the st-PMMA helix. However, such intermolecular correlation peaks were not observed probably because the present method exceeds the detection limit (Figure S11c,d). Based on the solid-state NMR data together with the IR, DSC, and XRD results, we propose a unique “helix-in-helix” supramolecular structure for the st-PMMA/L-1 inclusion complex composed of the one-handed 3_{10} -helical L-1 chains entrapped in the hollow space of the helical st-PMMA (Figure 2i).^[19]

As expected, the electronic CD (ECD) spectral patterns corresponding to the fulleropyrrolidine absorption regions of L-1 and D-1 in toluene were drastically changed once encapsulated into the st-PMMA helical cavities in a gel formed in toluene (Figure 3), probably resulting from an exciton coupling interaction between the nearest neighbor fulleropyrrolidine residues in the st-PMMA helical cavity and/or an encapsulation-induced conformational change around the C-terminal region.

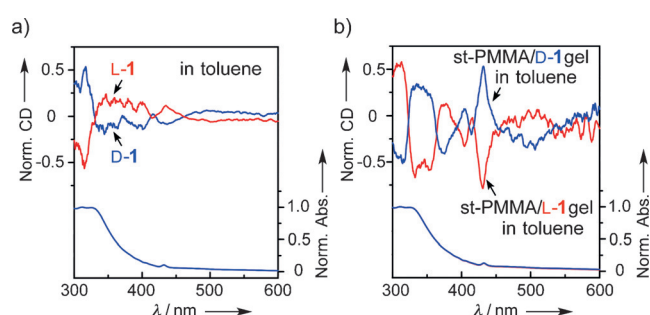


Figure 3. a) ECD (top) and absorption (bottom) spectra of L-1 (red) and D-1 (blue) in toluene at 25 °C: $[1] = 3.6 \times 10^{-4}$ M. b) ECD (top) and absorption (bottom) spectra of st-PMMA/L-1 gel (10.1 wt % of L-1) (red) and st-PMMA/D-1 gel (9.9 wt % of D-1) (blue) in toluene at 25 °C. The ECD and absorption spectra were normalized based on the corresponding absorption spectra at 25 °C. The contribution of the linear dichroism caused by the macroscopic anisotropy was negligible.

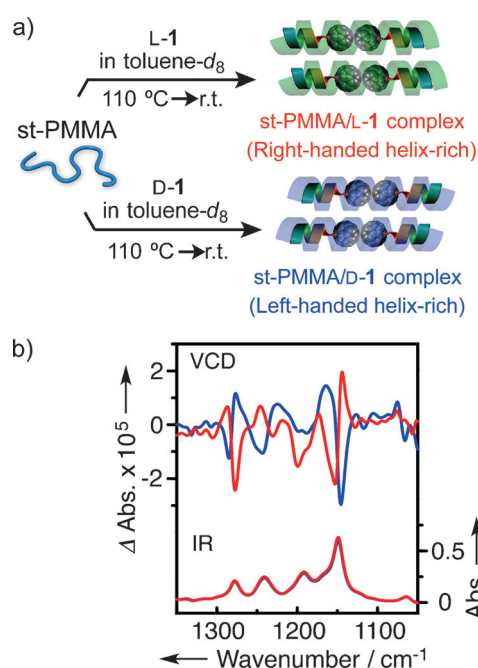


Figure 4. a) Schematic illustration of right-handed (top) and left-handed (bottom) helicity induction in st-PMMA upon encapsulation of L-1 and D-1, respectively. b) VCD (top) and IR (bottom) spectra of st-PMMA/L-1 (11.3 wt % of L-1) (red) and st-PMMA/D-1 (11.3 wt % of D-1) (blue) complex gels in $[D_8]$ toluene at room temperature.

Interestingly, a preferred-handed helical conformation could be induced in the st-PMMA backbone once the one-handed helical L-1 or D-1 was encapsulated within the st-PMMA helical cavity (Figure 4a). In fact, the st-PMMA/L-1 and st-PMMA/D-1 complex gels (11.3 wt % of 1) exhibited mirror-image vibrational CD (VCD) spectra in the PMMA IR regions (Figure 4b),^[27] whose spectral patterns are in good agreement with the calculated VCD spectra of the right- and left-handed 18_1 -helical st-PMMA.^[6a] Therefore, it is concluded that the right- and left-handed 3_{10} -helical L-1 and D-1 are able to induce predominantly right- and left-handed helical conformations in the st-PMMA chains, respectively,

thus producing optically active supramolecular helix-in-helix structures with the same-handedness to each other.

In summary, we have demonstrated an unprecedented approach to construct a unique supramolecular helix-in-helix structure through encapsulation of optically active helical peptides bearing a C₆₀ moiety at one end within the helical st-PMMA cavity as a result of a molecular carrier (or anchor) effect driven by a strong interaction between the terminal C₆₀ moiety and the hydrophobic st-PMMA helical cavity. This encapsulation process is accompanied by the preferred-handed helix formation of the st-PMMA backbone induced by the helical chirality of the encapsulated peptides. These findings will provide a rational design strategy not only for a novel helical st-PMMA-based separation system for various chiral fullerene derivatives, but also for developing a unique supramolecular nano-reactor, in which encapsulated C₆₀-based catalysts may catalyze organic and polymerization reactions in a confined helical nanospace of the st-PMMA, thus producing products with specific regio- and enantioselectivities.

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Conflict of interest

The authors declare no conflict of interest.

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- [24] The exact helical packing arrangements (hexagonal or orthogonal, for example) of the st-PMMA/**L-1** complex helices as well as those of the st-PMMA/fullerenes (C₆₀, C₇₀, or C₈₄) complex helices^[6a] have not yet been determined because all the reflections could not be reasonably indexed owing to rather broad reflections probably resulting from the samples that were not uniaxially oriented.^[6a]
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- [26] This observation is consistent with the energy-minimized structure of the st-PMMA/**L-1** inclusion complex (Figure S2).
- [27] The contribution of the encapsulated **1** within the st-PMMA (11.3 wt % of **1**) to the IR and VCD spectra (Figure 4b) was almost negligible under the present conditions.

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