

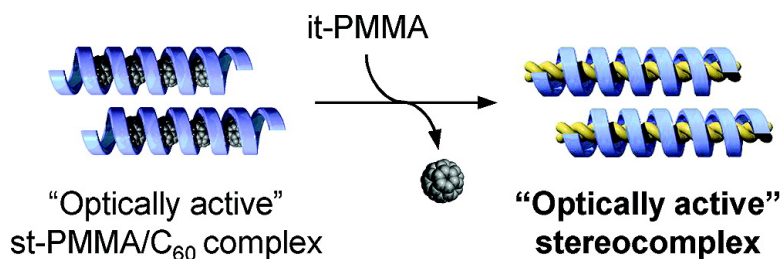
Communication

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## Helix-Sense-Controlled Synthesis of Optically Active Poly(methyl methacrylate) Stereocomplexes

Takehiro Kawauchi,<sup>\*,†,§</sup> Atsushi Kitaura,<sup>‡</sup> Jiro Kumaki,<sup>\*,†,⊥</sup> Hiroshi Kusanagi,<sup>†</sup> and Eiji Yashima<sup>\*,†,‡</sup>

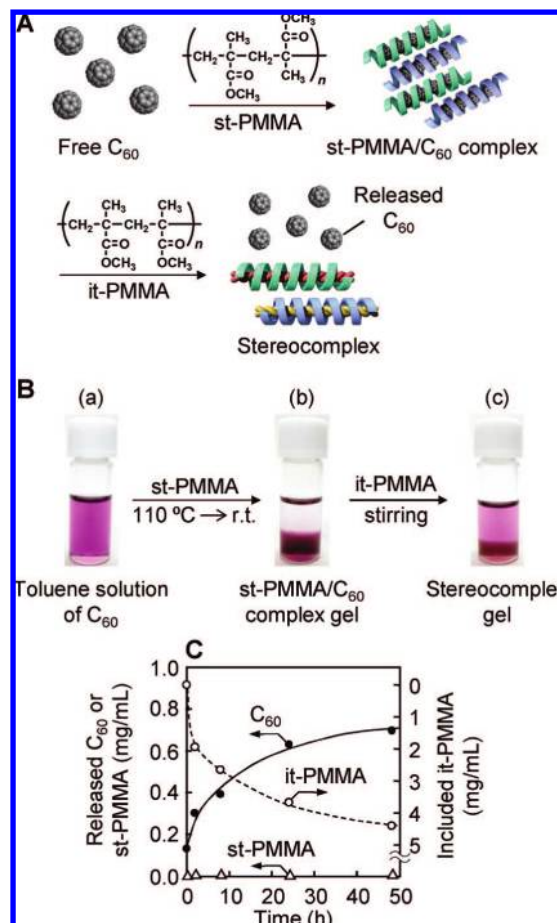
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The stereocomplex of poly(methyl methacrylate) (PMMA) is a unique polymer-based supramolecule composed of complementary isotactic (it)- and syndiotactic (st)-PMMAs with an it/st stoichiometry of 1:2 that exhibits a definite melting point in specific solvents or in solids.<sup>1</sup> Since the discovery of the PMMA stereocomplex,<sup>2</sup> the molecular basis of the structure and the mechanism of complex formation have been a long-standing question in polymer chemistry.<sup>1</sup> In 1989 Schomaker and Challa proposed a double-stranded helical structure composed of a  $9_1$  it-PMMA helix (nine repeating MMA units per turn) surrounded by an  $18_1$  st-PMMA helix with a monomer ratio of 1:2.<sup>3</sup> Recently, we proposed a triple-stranded helix model from the direct observation of a stereocomplex prepared using the Langmuir–Blodgett (LB) technique by high-resolution atomic force microscopy (AFM), which reveals that a double-stranded helix of it-PMMA is included in a single helix of st-PMMA, forming an inclusion complex with a triple-stranded helical structure.<sup>4</sup> “Molecular sorting” experiment results using uniform it- and st-PMMAs with different molecular weights support the triple-stranded helix model.<sup>5</sup>

More recently, we found that st-PMMA folded into a preferred-handed helical conformation assisted by chiral alcohols and encapsulated [60]fullerene ( $C_{60}$ ) within its helical cavity to form an optically active supramolecular peapod-like complex gel (st-PMMA/ $C_{60}$ ), whose helicity was retained after complete removal of the chiral alcohols.<sup>6</sup> On the basis of these results, we anticipated that the preferred-handed helical st-PMMA/ $C_{60}$  complex could serve as the template to further encapsulate the complementary it-PMMA through replacement of the encapsulated  $C_{60}$  molecules, resulting in a practically versatile stereocomplex with optical activity (Figure 1A). The PMMA stereocomplex has been applied to advanced materials in many fields, such as ultrathin films,<sup>7</sup> microcellular foams,<sup>8</sup> dialyzers,<sup>9</sup> thermoplastic elastomers,<sup>10</sup> and ion gels.<sup>11</sup> It is also a versatile structural motif for template polymerization<sup>12</sup> and self-assembled nanomaterials.<sup>13</sup> However, an optically active stereocomplex has not yet been synthesized.<sup>14</sup>

To this end, we first investigated if it-PMMA could replace the encapsulated  $C_{60}$  molecules within the st-PMMA cavity to form a stereocomplex. An optically inactive st-PMMA/ $C_{60}$  complex gel (0.91 mg of  $C_{60}$  (8.3 wt %)) was encapsulated in 10 mg st-PMMA<sup>15</sup> was prepared in toluene according to a previously reported method (photo b in Figure 1B and Figure S1A).<sup>6</sup> To this was added it-PMMA (10 mg),<sup>15</sup> and the changes in the concentrations of  $C_{60}$  and st-PMMA released from the st-PMMA/ $C_{60}$  complex gel and



**Figure 1.** (A) Schematic illustration of the encapsulation of  $C_{60}$  in the st-PMMA helical cavity upon gelation and the release of the  $C_{60}$  through stereocomplex formation with it-PMMA (orange and yellow). The right- (blue) and left-handed (green) helical st-PMMA complexes are equally produced. (B) Photographs of (a) a toluene solution of  $C_{60}$  (1 mg/mL, 1 mL), (b) st-PMMA/ $C_{60}$  gel (8.3 wt % of  $C_{60}$ ) after the addition of st-PMMA (10 mg) followed by heating to 110 °C and then cooling to room temperature, and (c) stereocomplex gel after the addition of it-PMMA (10 mg) followed by stirring at room temperature for 48 h. Samples b and c were centrifuged at 1700g for 10 min to precipitate the gels. (C) Changes in the concentrations (mg/mL) of released  $C_{60}$  and st-PMMA from the st-PMMA/ $C_{60}$  complex gel into the supernatant upon complexation with it-PMMA at room temperature. Changes in the concentration (mg/mL) of the included it-PMMA are also shown. The concentrations of  $C_{60}$  and it- and st-PMMA were determined by absorption and  $^1\text{H}$  NMR measurements of the supernatants, respectively.

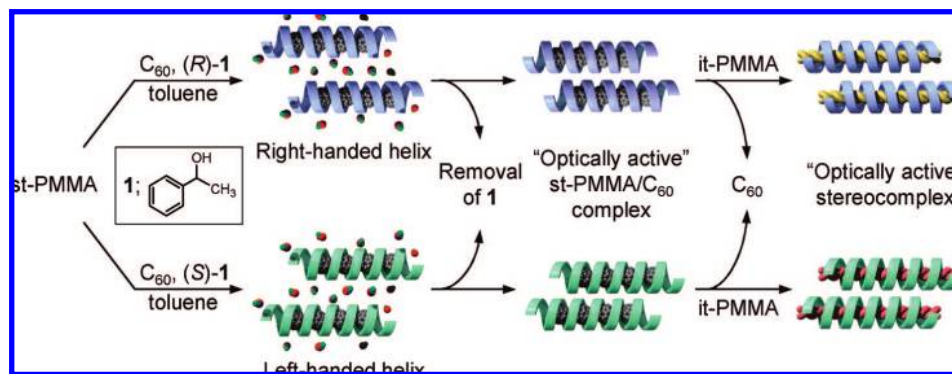
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that of it-PMMA included in the st-PMMA gel from the supernatant were followed by measuring the absorption and  $^1\text{H}$  NMR spectra



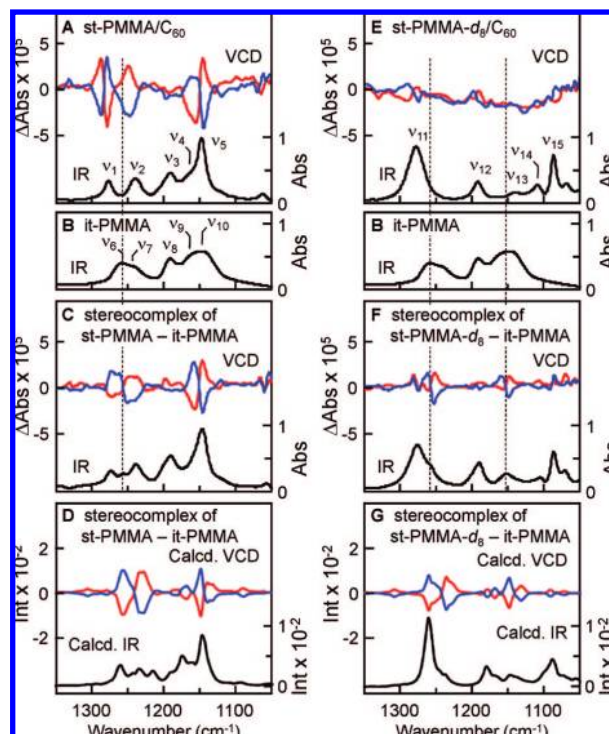
**Figure 2.** Schematic illustration of right- (top) and left- (bottom) handed stereocomplex formation with a triple-stranded helical structure. Right- and left-handed single helices are induced in the st-PMMA/ $C_{60}$  complex in the presence of (*R*)- or (*S*)-**1** (left). The induced helicity is memorized after **1** is completely removed (middle). The encapsulated  $C_{60}$  molecules are further replaced by it-PMMA along with the formation of an optically active stereocomplex (right).

of the supernatant at appropriate time intervals after centrifugation (Figures 1B, 1C, and S1B).

The encapsulated  $C_{60}$  molecules were gradually replaced by it-PMMA and the supernatant changed to a purple color (c in Figure 1B). After 48 h, ca. 80% of the  $C_{60}$  molecules were released to form the stereocomplex gel (Figure 1C). The film derived from the gel showed a characteristic differential scanning calorimetry (DSC) profile that is virtually the same as that of the bulk stereocomplex prepared from the it- and st-PMMA in acetonitrile (Figure S1C). These results clearly indicate that a stereocomplex certainly forms upon the addition of it-PMMA to the st-PMMA/ $C_{60}$  complex gel. This finding provides the first direct experimental evidence for the molecular basis of the PMMA stereocomplex formation mechanism; that is, a double-stranded helix of it-PMMA is included in a preformed single helix of st-PMMA, thus producing a supramolecular inclusion complex with a triple-stranded helical structure.<sup>4,5,16</sup>

Next, we used an optically active st-PMMA/ $C_{60}$  complex gel induced by (*R*)- or (*S*)-1-phenylethanol (**1**),<sup>6</sup> which will produce an optically active stereocomplex after replacement of the encapsulated  $C_{60}$  by it-PMMA (Figure 2). The optically active st-PMMA/ $C_{60}$  complex gel was prepared in the same manner as previously reported in toluene- $d_8$  in the presence of (*R*)- or (*S*)-**1** (20 vol %) followed by complete removal of the (*R*)- or (*S*)-**1**, and then isolated by centrifugation.<sup>6</sup> The it-PMMA was added to the optically active st-PMMA/ $C_{60}$  gel under vigorous stirring at room temperature. After 48 h, the resulting stereocomplex was isolated by centrifugation and its vibrational circular dichroism (VCD) and IR spectra (Figure 3C) were measured. For comparison, the VCD and IR spectra of the optically active st-PMMA/ $C_{60}$  gel prepared with (*R*)- or (*S*)-**1** and the IR spectrum of it-PMMA are shown in Figures 3A and 3B, respectively. The stereocomplex gels exhibited mirror-image VCDs in the PMMA IR regions, whose VCD patterns significantly changed from those of the optically active st-PMMA/ $C_{60}$  gels, in particular, at around the  $1260\text{ cm}^{-1}$  ( $\nu_6$ ) regions corresponding to the characteristic absorption band for it-PMMA (Table S1). These results suggest that the it-PMMA forms a helical conformation with an excess of one-handedness once encapsulated into the helical st-PMMA with a macromolecular helicity memory, which remains intact after the encapsulated fullerenes are replaced by the complementary it-PMMA with the formation of an optically active stereocomplex.

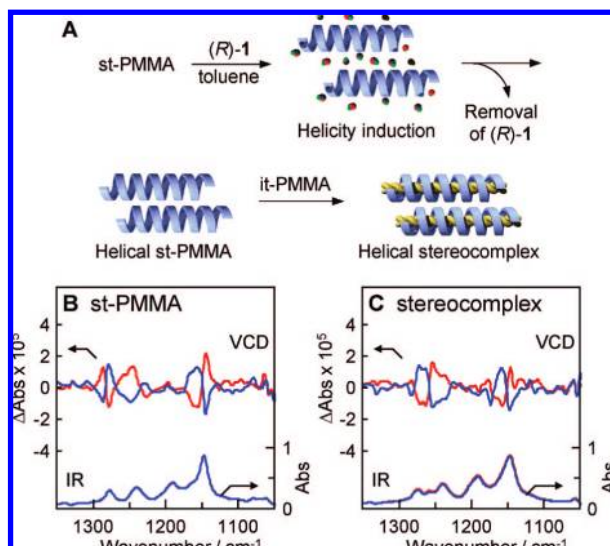
Inclusion of an it-PMMA helix into an outer st-PMMA helix may produce a pair of diastereomeric helical assemblies composed of the same or opposite handed it- and st-PMMA helices. We then



**Figure 3.** (A and E) Observed VCD (top) and IR (bottom) spectra of isolated st-PMMA/ $C_{60}$  complex (A) and st-PMMA- $d_8$ / $C_{60}$  complex (E) gels in toluene- $d_8$  prepared by (*R*)-**1** (red and black lines) and (*S*)-**1** (blue lines), measured after the complete removal of **1**. For the assignments of the experimental and calculated IR and VCD bands ( $\nu_1$ – $\nu_{15}$ ), see Table S1 in the Supporting Information. (B) IR spectrum of it-PMMA in toluene- $d_8$ . (C and F) Observed VCD (top) and IR (bottom) spectra of stereocomplex gels obtained from the optically active st-PMMA/ $C_{60}$  complex (C) and st-PMMA- $d_8$ / $C_{60}$  complex (F) gels induced by (*R*)-**1** (red and black lines) and (*S*)-**1** (blue lines) upon complexation with it-PMMA (it/st = 1/2, wt/wt). (D and G) Calculated VCD (top) and IR (bottom) spectra of stereocomplexes (it/st = 1/2, wt/wt) composed of the right- (red and black lines) and left- (blue lines) handed it- and st-PMMA (D), and it-PMMA and st-PMMA- $d_8$  (G). The contribution of the linear dichroism caused by the macroscopic anisotropy was negligible.

calculated the IR and VCD spectra for all the possible combinations of the triple-stranded helical stereocomplexes<sup>4,5</sup> on the basis of the right- and left-handed single helical 18<sub>1</sub> st-PMMA and double helical 9<sub>1</sub> it-PMMA at the B3LYP/6-31G(d) level (Figures 3D and S4C) (For more detailed calculations, see the Supporting Information). The experimental VCD spectral patterns of the stereocomplexes fit well to the calculated ones composed of helical it- and





**Figure 4.** (A) Schematic illustration of right-handed helicity induction in st-PMMA (blue) in the presence of (*R*)-1. The induced helicity is memorized after (*R*)-1 is completely removed and further encapsulation of it-PMMA (yellow). (B) Observed VCD and IR spectra of isolated st-PMMA gels in toluene-*d*<sub>8</sub> prepared by (*R*)-1 (red lines) and (*S*)-1 (blue lines). (C) Observed VCD and IR spectra of stereocomplex gels in toluene-*d*<sub>8</sub> obtained after the addition of it-PMMA to the isolated st-PMMA gels prepared by (*R*)-1 (red lines) and (*S*)-1 (blue lines).

st-PMMA with the same handedness (see Figures S4A–C). Thus, it-PMMA recognizes and interacts with the outer st-PMMA helix and folds into a double-stranded helix with the same handedness as that of the st-PMMA helix through the formation of a topological triple-stranded helix.<sup>4,5</sup>

Additional evidence of a preferred-handed helical structure induced in an it-PMMA encapsulated in the helical st-PMMA cavity with a macromolecular helicity memory was obtained from the experimental and calculated VCD spectra of an optically active stereocomplex prepared from the fully deuterated helical st-PMMA (st-PMMA-*d*<sub>8</sub>).<sup>15</sup> Figure 3E shows the IR and VCD spectra of the optically active st-PMMA-*d*<sub>8</sub>/C<sub>60</sub> complex.<sup>17</sup> Noticeable changes were observed in its IR and VCD spectral patterns caused by deuteration together with a significant decrease in its VCD intensities as compared to those of the st-PMMA/C<sub>60</sub> complex (Figure 3A). The calculated IR and VCD spectra for the right- and left-handed helical st-PMMA-*d*<sub>8</sub>s support the observed changes in their spectral patterns and intensities by deuteration of the st-PMMA (Figure S3D).

A stereocomplex was then prepared from the optically active st-PMMA-*d*<sub>8</sub>/C<sub>60</sub> complex gel upon the addition of it-PMMA. The resulting it-PMMA-st-PMMA-*d*<sub>8</sub> stereocomplex exhibited weak, but apparent VCD spectra (Figure 3F), whose spectral patterns roughly agree with the calculated VCD spectra of the stereocomplex composed of the helical it-PMMA and st-PMMA-*d*<sub>8</sub> with the same handedness (Figure 3G and Figures S4D–F).<sup>18</sup>

As previously reported, a similar optically active st-PMMA gel can be prepared with (*R*)- or (*S*)-1 in toluene-*d*<sub>8</sub> in the absence of C<sub>60</sub>.<sup>6</sup> The induced st-PMMA helix also remains after complete removal of the optically active 1, and this helical st-PMMA can serve as the template for the further inclusion of it-PMMA, resulting in a stereocomplex gel, thus showing virtually the same VCD spectrum (Figure 4). An optically active stereocomplex formation, however, requires the preformed helical st-PMMA with a controlled helical sense since a mixture of toluene-*d*<sub>8</sub> solutions of it- and st-

PMMA in the presence of (*R*)-1 (20 vol %) produced a stereocomplex gel with no net optical activity.

In summary, we have, for the first time, synthesized an optically active PMMA stereocomplex through the helix-sense-controlled supramolecular inclusion of an it-PMMA within the helical cavity of the st-PMMA with a macromolecular helicity memory. We believe that these unique helical st-PMMA and stereocomplexes with a controlled helical sense offer potentially useful chiral materials.

**Supporting Information Available:** Full experimental details, IR and VCD band assignments of it- and st-PMMA, DSC profiles of the stereocomplex films, molecular modeling of helical structures of it- and st-PMMA, calculated IR and/or VCD spectra of st-PMMA, st-PMMA-*d*<sub>8</sub>, it-PMMA, and stereocomplexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (15) The st-PMMA, fully-deuterated st-PMMA (st-PMMA-*d*<sub>8</sub>), and it-PMMA were synthesized using stereospecific polymerization technique (see the Supporting Information). The number-average molecular weights (*M*<sub>n</sub>) and stereoregularities (*mm*:*mr*:*rr*) were as follows: st-PMMA, *M*<sub>n</sub> = 544 kDa and *mm*:*mr*:*rr* = 0:6:94; st-PMMA-*d*<sub>8</sub>, *M*<sub>n</sub> = 710 kDa and *mm*:*mr*:*rr* = 0:5:95; it-PMMA, *M*<sub>n</sub> = 21.8 kDa and *mm*:*mr*:*rr* = 97:3:0, in which *m* and *r* represent the it- and st-tyads of the meso and racemo sequences, respectively, and *mm*, *mr* and *rr* are the corresponding triad sequences.
- (16) A low molecular weight and highly syndiotactic PMMA (*M*<sub>n</sub> = 16 kDa and *mm*:*mr*:*rr* = 0:4:96) immediately gelled in toluene upon heating at 110 °C followed by cooling to room temperature, whereas a low molecular weight and slightly lower syndiotactic PMMA (*M*<sub>n</sub> = 38 kDa and *mm*:*mr*:*rr* = 1:10:89) did not gel at all under the same experimental conditions. These results indicate that the molecular weight is not a critical factor for the gelation of st-PMMA, but high syndiotacticity of PMMA appears to be essential for its gelation in toluene. Low molecular weight and highly tactic it-PMMA (*M*<sub>n</sub> = 12 kDa and *mm*:*mr*:*rr* = 97:3:0) and st-PMMA (*M*<sub>n</sub> = 13 kDa and *mm*:*mr*:*rr* = 0:4:96) also form stereocomplexes as reported previously.<sup>5</sup>
- (17) The optically active st-PMMA-*d*<sub>8</sub>/C<sub>60</sub> complex gel was prepared in a similar way for the synthesis of the optically active st-PMMA/C<sub>60</sub> complex gel in toluene-*d*<sub>8</sub> in the presence of (*R*)- or (*S*)-1 followed by complete removal of the (*R*)- or (*S*)-1, and then isolated by centrifugation. See the Supporting Information.
- (18) Because of such an extremely weak VCD of the preferred-handed helical st-PMMA-*d*<sub>8</sub> as supported by its calculated one, the observed VCD of the it-PMMA-st-PMMA-*d*<sub>8</sub> stereocomplex likely reflects the VCD derived from the it-PMMA helix induced through encapsulation in the helical st-PMMA-*d*<sub>8</sub> cavity.

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