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Helicity Induction and Memory of Syndiotactic Poly(methyl methacrylate) Assisted by Optically Active Additives and Solvents and Chiral Amplification of Helicity

Atsushi Kitaura,[1] Hiroki Iida,[1] Takehiro Kawauchi,[2] and Eiji Yashima*[1]
[1]*Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya, Aichi 464-8603*
[2]*Department of Environmental and Life Sciences, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441-8580*

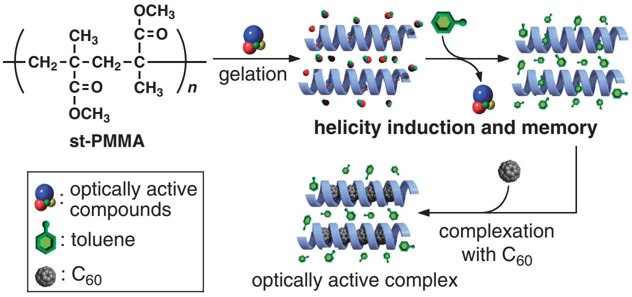
(Received October 21, 2010; CL-100897; E-mail: yashima@apchem.nagoya-u.ac.jp)

Syndiotactic poly(methyl methacrylate) (st-PMMA) was found to fold into a preferred-handed helix with amplification of helicity assisted by chiral additives and solvents and further encapsulated fullerenes within its helical cavity whose helicity was memorized after removal of the chiral molecules.

Syndiotactic poly(methyl methacrylate) (st-PMMA), a stereoregular commodity polymer, forms a thermoreversible gel in aromatic solvents, such as toluene and chlorobenzene, in which the st-PMMA possesses a 74/4 helical conformation with a large cavity of about 1 nm and the solvent molecules are encapsulated in the cavity of the st-PMMA interior.[1,2] Taking advantage of this unique helix formation of the st-PMMA with a specific cavity in the gel state, we recently succeeded in encapsulation of fullerenes in the cavity of st-PMMA, resulting in a robust, processable, and peapod-like complex.[3] In addition, preferred-handed helical structures in st-PMMA and its complex with fullerenes could be induced in the presence of an optically active alcohol **1**[3] and amine **6**[4,5] as an additive and solvent, respectively, as evidenced by electronic circular dichroism (ECD) induced in the encapsulated-C_{60}-chromophore regions and vibrational CD (VCD) in the PMMA IR regions. Furthermore, the induced st-PMMA helix was retained ("memorized")[6–8] after complete removal of the chiral molecules (Scheme 1)[3] and could recognize the size and chirality of higher fullerenes through an induced-fit mechanism to selectively extract enantiomers of the higher fullerenes.[5]

In this study, we investigated the effects of diverse optically active compounds **1**–**12** (Chart 1) as chiral additives in toluene or solvents on the gelation abilities and further efficiency of the helicity induction and memory in st-PMMA. During the course of our studies, we found that the chiral information of a nonracemic aromatic amine transfers with amplification in the st-PMMA as an excess of a single-handed helix through noncovalent bonding interactions, thus generating a unique "majority rule" effect (nonlinear effect)[8–10] on a helical system.

First, the helicity induction abilities of aromatic and aliphatic optically active alcohols **1**–**3** and amines **6**–**12**, and aliphatic (**5**) and carbonyl (**4**) compounds toward st-PMMA were systematically investigated in toluene (Tables 1 and S1).[11] The st-PMMA gel and its inclusion complex with C_{60} were prepared according to previously reported methods with a slight modification.[3,5,12] St-PMMA (4 mg) was dissolved in toluene (0.1 mL) containing **1**–**12** (2 equiv with respect to the monomer units of st-PMMA) upon heating at 110 °C. Cooling to room temperature, the gelation rapidly took place within 4 min except for the solutions with **1** (3 h) and **3** (10 min) (Table S1).[11] We note that a toluene solution of st-PMMA gelled within 3 min without any additives (Table 1). After complete removal of the chiral additives from the st-PMMA gels and further encapsulation of C_{60} molecules within its helical cavity in toluene, the ECD spectra of the st-PMMA/C_{60} complex gels were measured (for more detailed experimental procedures, see the Supporting Information).[11]



Scheme 1. Schematic illustration for the helicity induction and memory in st-PMMA and further encapsulation of C_{60} after complete removal of optically active compounds.

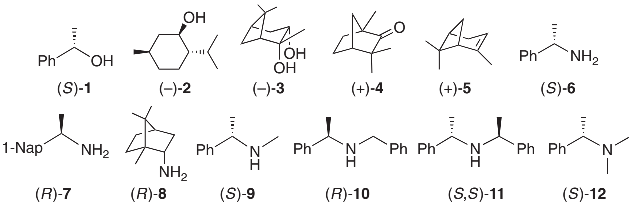


Chart 1.

Among the diverse optically active additives **1**–**12**, the chiral aromatic alcohol **1** and amines **6** and **7** successfully induced and memorized a preferred-handed helicity in st-PMMA, thus producing the optically active st-PMMA/C_{60} complex gels, which exhibited weak but apparent ECDs in the encapsulated-C_{60}-chromophore regions at around 346 nm (Entries 2–4 in Table 1 and Table S1).[11,13]

With these results in mind, we next investigated if optically active liquids **1**, **4**–**7**, and **9**–**12** could be used as a solvent to dissolve and then gelate the st-PMMA with a greater helical sense excess (Entries 5–14 in Table 1). St-PMMA was not soluble in **5**, and a solution of st-PMMA in **1** did not gel, but other chiral liquids (**4** and aromatic amines **6**, **7**, and **9**–**12**) dissolved the st-PMMA and then gelled. Interestingly, solutions of st-PMMA in **4** and **10**–**12** rapidly gelled within 1–4 min like that in toluene. The st-PMMA gels were then repeatedly washed

Table 1. Gelation and helicity induction of st-PMMA in various solvents with or without chiral additives[a]

Entry	Solvent	Additive[b]	Gelation time[c]	$\Delta\varepsilon_{346}$ /M^{-1} cm^{-1} [d]
1[e]	toluene	—	3 min	—
2	toluene	(*S*)-**1**	3 h	−0.3
3	toluene	(*S*)-**6**	4 min	0.2
4	toluene	(*R*)-**7**	4 min	−0.4
5	(*S*)-**1**	—	—[f]	—
6	(+)-**4**	—	1 min	—[g]
7	(+)-**5**	—	—[h]	—
8	(*S*)-**6**	—	15 h	1.3
9	(*R*)-**6**	—	15 h	−1.5
10	(*R*)-**7**	—	1 h	−1.4
11	(*S*)-**9**	—	1.5 h	1.0
12	(*R*)-**10**	—	2 min	−0.8
13	(*S*,*S*)-**11**	—	4 min	1.3
14	(*S*)-**12**	—	1 min	—[g]

[a]The concentration of st-PMMA was 40 mg mL^{-1}. [b]The molar ratio of additives to the monomer units of st-PMMA was 2. [c]The gelation time was estimated by the inverse flow method. [d]Measured after removal of chiral compounds followed by encapsulation of C_{60}. [e]Cited from ref. 3. [f]No gelation after 24 h. [g]Apparent CD (>0.2 M^{-1} cm^{-1}) was not observed. [h]St-PMMA was insoluble.

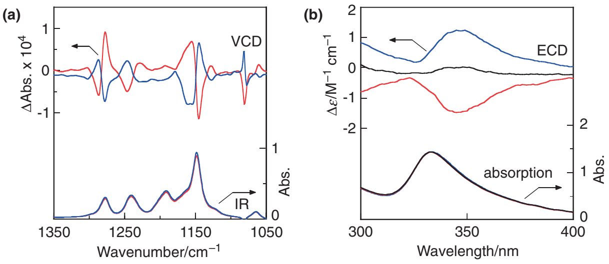


Figure 1. (a) VCD (top) and IR (bottom) spectra of isolated st-PMMA/C_{60} complex gels in toluene prepared by the complexation with C_{60} after the gelation of st-PMMA with (*R*)-**6** (red lines) and (*S*)-**6** (blue lines). (b) ECD (top) and absorption (bottom) spectra of isolated st-PMMA/C_{60} complex gels in toluene prepared by the complexation with C_{60} after the gelation of st-PMMA with racemic **6** (black lines), (*R*)-**6** (red lines), and (*S*)-**6** (blue lines). The racemic and (*R*)- and (*S*)-**6** were completely removed before the complexation with C_{60}.

with toluene to remove the chiral solvents, and subsequently, C_{60} molecules were encapsulated in the st-PMMA cavity to make the st-PMMA/C_{60} complex gels and their ECD and VCD spectra were measured.

Figure 1 shows the typical absorption, VCD, and ECD spectra of the st-PMMA/C_{60} complex gels in toluene assisted by (*S*)- and (*R*)-**6** or racemic **6**. The st-PMMA/C_{60} complex gels, which contained no trace amount of **6**, showed mirror-imaged VCDs in the PMMA IR regions due to the preferred-handed helicity (a) and also ECDs in the encapsulated C_{60} chromophore regions (b). The VCD intensities of the st-PMMA/C_{60} complex gels at around 1150 and 1280 cm^{-1} were approximately three times larger than those prepared with (*S*)- and (*R*)-**1** (20 vol %),[3] indicating the remarkable increase in the helical sense excess of the st-PMMA induced by (*S*)- and (*R*)-**6**.[14]

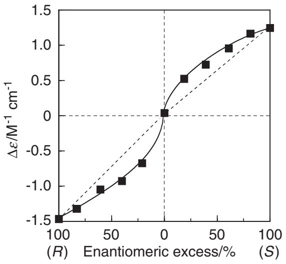


Figure 2. Changes in the ECD intensity at around 350 nm of st-PMMA/C_{60} complex gels versus the % ee of **6** during the gelation of st-PMMA. ECD spectra were measured after removal of **6** followed by encapsulation of C_{60}.

The ECD measurement results of the st-PMMA/C_{60} complexes assisted by optically active liquids are summarized in Table 1, which revealed that the use of optically active solvents (Entries 8–13), in particular, the aromatic optically active primary (**6** and **7**) and secondary (**9**–**11**) amines more efficiently induced an excess one-handedness in the st-PMMA backbone, thus showing intense ECDs in the C_{60}-chromophore regions as compared with those induced by chiral additives (Entries 2–4). On the other hand, the tertiary amine (*S*)-**12** as well as the aliphatic (+)-**4** showed no preference in the helical sense bias in st-PMMA, thus no ECD (Entries 6 and 14). These results suggest that the NH protons as well as the aromatic groups may play an important role in the helicity induction in st-PMMA, probably through intermolecular hydrogen-bonding interactions between the pendant ester groups of st-PMMA and the NH residues of the amines. Therefore, the aromatic primary and secondary chiral amines **6**, **7**, and **9**–**11** exhibited the same chiral bias for the helicity induction in st-PMMA, thus showing the ECDs with the same Cotton effect sign when their absolute configurations are the same. In contrast, the Cotton effect sign of the st-PMMA/C_{60} complex induced by (*S*)-**6** was opposite to that induced by (*S*)-**1** (Entries 2 and 3 or 8), indicating an opposite chiral bias for the helicity induction in st-PMMA. As for the helicity induction and gelation abilities assisted by chiral compounds, there is almost no clear relationship between them.

The helix formation of st-PMMA in the chiral amine **6** gel showed a unique positive nonlinear relationship between the enantiomeric excess (ee) of **6** and the observed ECD intensities of the corresponding st-PMMA/C_{60} complexes; the ECD intensities of the gels in the encapsulated-C_{60}-chromophore regions were out of proportion to the ee values of **6** (Figure 2). This is a typical example of chiral amplification ("majority rule" effect[8–10]) often observed in dynamic helical polymers[8,15] and self-assembled helical systems.[16–18] Although the convex deviation from linearity was not so impressive, this positive nonlinear relationship is of particular interest for understanding the mechanism of helix formation of st-PMMA followed by gelation in specific solvents. The st-PMMA backbone may possess dynamic nature in its helical conformation during gelation in the optically active **6**. Because the st-PMMA backbone may become static in the gel state, an excess of one-handed helical conformation with chiral amplification may be induced in st-PMMA before the noncovalent network formation generated by helix bundles as a crosslinker, resulting in the gelation. Therefore, once gelation takes place, the induced st-PMMA helix with a helicity memory is stabilized by helix-bundles and maintains before melting of the gel.

In summary, we have found that preferred-handed helicity was efficiently induced in st-PMMA with various optically active primary and secondary amines bearing aromatic groups as the gelling solvents and further memorized after removal of the chiral amines while maintaining its gel state. An excess of one-handed helix was also induced with nonracemic amines during the gelation, resulting in the amplification of helical chirality, suggesting that the helical st-PMMA chain may have dynamic characteristics during gelation. These findings will contribute to the development of readily available, unique chiral, and optoelectronic materials with a controlled helical sense and specific chiral cavity, in which a variety of functional molecules will be encapsulated.

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4 The chiral amine **6** was recently found to be an effective helix inducer in st-PMMA, but the detailed chiroptical property has not yet been reported.[5]

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13 We presume that a helical sense excess of st-PMMA induced and memorized by the chiral additives and the ECD intensity at the C_{60} chromophore regions encapsulated in the helical cavity of st-PMMA may be correlated, and hence, the ECD intensity most likely reflects the helical sense excess of st-PMMA, thereby, the helix-inducing ability of the chiral additives.

14 Based on the calculated IR and VCD spectra for the right- and left-handed helical 18/1 st-PMMAs at the B3LYP/6-31G(d) level, the st-PMMA induced by (*R*)-**6** likely possesses a left-handed helix.[3]

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