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Solubilization of [60]Fullerene Owing to Inclusion Complex Formation between Syndiotactic Poly(methyl methacrylate) and the Fullerenes in Polar Solvents

Mariko Kawauchi, Takehiro Kawauchi,* and Tsutomu Takeichi

Department of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441-8580, Japan

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ABSTRACT: We found [60]fullerene (C_{60}) to be soluble in polar solvents such as acetonitrile and acetone in the presence of syndiotactic poly(methyl methacrylate) (st-PMMA). The solubility of C_{60} in acetonitrile drastically increased from 0.00 to 0.27 mg/mL upon the addition of st-PMMA at the polymer concentration of 4 mg/mL. Furthermore, the solubility increased with the concentration of st-PMMA. Transparent st-PMMA films containing C_{60} were prepared by casting an acetonitrile solution of C_{60} with st-PMMA. X-ray diffraction analysis of the films revealed the formation of st-PMMA/C_{60} inclusion complex in which the C_{60} molecules were encapsulated within a helical st-PMMA cavity. The st-PMMA films containing C_{60} showed high heat resistance, which resulted from the crystalline structure of the inclusion complex, and absorbed light in the UV−vis region because of the presence of chromophoric C_{60} molecules.

Introduction

[60]Fullerene (C_{60}) has attracted considerable interest in the fields of electrooptic and biological sciences because of its unique optical, electrical, magnetic, and biochemical properties.[1] However, the use of C_{60} is limited because it is insoluble in polar organic solvents, such as acetonitrile (CH_3CN) and acetone, as well as in water.[1,2] One of the methods to improve the solubility of C_{60} is chemical modification of C_{60}.[1,3,4] The solubility of C_{60} in polar solvents can be drastically increased by grafting the C_{60} molecules with functional groups[3] and polymer chains.[4] Another method is to use solubilizing agents.[5−7] For example, poly(vinylpyrrolidone)[6] and poly(phenylquinoline)-*block*-polystyrene[7] are known to effectively solubilize C_{60} molecules in water and in a trifluoroacetic acid/dichloromethane mixture, respectively.

It is known that syndiotactic poly(methyl methacrylate) (st-PMMA), which is a stereoregular commodity polymer, forms a thermoreversible physical gel in aromatic solvents such as toluene in which the st-PMMA chains assume the shape of a 74 unit per 4 turn helix with a large cavity of diameter ∼1 nm; hence, the solvent molecules are encapsulated in the cavity of the inner helix.[8] Recently, we found that in aromatic solvents such as toluene st-PMMA encapsulates C_{60} molecules in its helical cavity to form a supramolecular inclusion complex (st-PMMA/C_{60} inclusion complex); this complex formation is accompanied by gelation (Figure 1).[9,10] On the other hand, st-PMMA easily dissolves in polar solvents such as CH_3CN and does not form a gel in CH_3CN. Nevertheless, it has been reported that the st-PMMA chains tend to take helical conformation even in CH_3CN, and the helical conformation amount of st-PMMA chains is larger than that of isotactic (it-) PMMA chains in CH_3CN.[11]

In this study, we attempted to solubilize C_{60} in polar solvents by using st-PMMA as the solubilizing agent; we expect C_{60} to be encapsulated within the partial helical structure of st-PMMA formed in CH_3CN (Figure 1). We found that the st-PMMA/C_{60} inclusion complex formation occurred even in CH_3CN, thereby causing solubilization of C_{60}. We also report preparation of transparent st-PMMA films containing C_{60} by casting the CH_3CN solution and some optical and thermal properties of the films.

*To whom correspondence should be addressed. E-mail: kawauchi@tutms.tut.ac.jp.

Experimental Section

Materials. The st-PMMA was synthesized by the syndiotactic-specific polymerization of MMA in toluene at −95 °C using a typical Ziegler-type catalyst derived from $Al(C_2H_5)_3$ and $TiCl_4$.[12] The atactic (at-) PMMA was purchased from Aldrich. The it-PMMA was prepared by the isotactic-specific anionic polymerization of *tert*-butyl methacrylate in toluene at −78 °C with (1,1-diphenyl-3-methylpentyl)lithium,[13,14] followed by hydrolysis of the pendant esters[14,15] and methylation with diazomethane.[15,16] The number-average molecular weights (M_n), molecular weight distributions (M_w/M_n), and tacticities (*mm*:*mr*:*rr*) were as follows: st-PMMA: $M_n = 322\,000$, $M_w/M_n = 1.29$, and *mm*:*mr*:*rr* = 0:6:94; at-PMMA: $M_n = 97\,500$, $M_w/M_n = 2.61$, and *mm*:*mr*:*rr* = 3:37:60; it-PMMA: $M_n = 489\,000$, $M_w/M_n = 1.12$, and *mm*:*mr*:*rr* = 98:2:0. The M_n and M_w/M_n values were measured by size exclusion chromatography in tetrahydrofurn (THF) using PMMA standards (Shodex, Tokyo, Japan) for the calibration. The tacticities were determined from the ^{1}H NMR signals of the α-methyl protons. Extra-pure grade CH_3CN, acetone, THF, chloroform ($CHCl_3$), and toluene were purchased from Wako Chemicals (Osaka, Japan). C_{60} (99.5%) was obtained from Tokyo Kasei (Tokyo, Japan) and used without further purification.

Measurements. Absorption spectra were measured in a 0.1 or 0.2 mm thick quartz cell on a JASCO V-500 spectrophotometer (JASCO, Tokyo, Japan). X-ray measurements were performed with a Rigaku R-AXIS VII system (Rigaku, Tokyo, Japan) equipped with a Rigaku FR-E rotating-anode generator with confocal mirror monochromated Cu Kα radiation (0.154 18 nm) focused through a 0.5 mm pinhole collimator, which was

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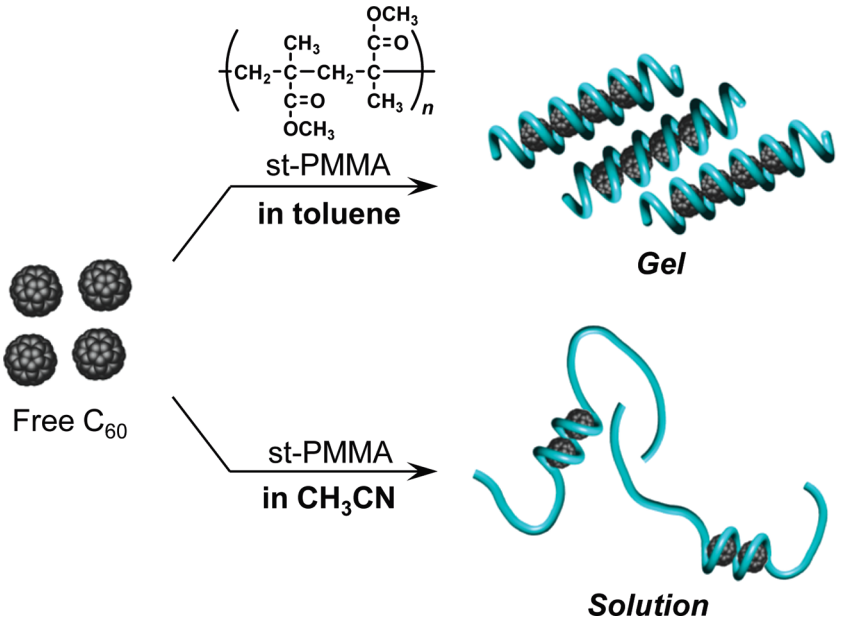

Figure 1. Schematic illustration of the st-PMMA/C_{60} inclusion complex in toluene (top) and solubilization of C_{60} in CH_3CN in the presence of st-PMMA through the partial formation of the inclusion complex (bottom).

supplied at 45 kV and 45 mA current, equipped with a flat imaging plate having a specimen-to-plate distance of 300 mm. Optical microscopic observations were carried out with a Nikon (Nikon, Tokyo, Japan) ECLIPSE-LV100POL optical microscope equipped with a DS-Fi1 CCD camera (Nikon) connected with a DS-L2 control unit (Nikon).

Solubilization of C_{60} in Polar Solvents with st-PMMA and Preparation of st-PMMA/C_{60} Film from the Solution. A typical experimental procedure is described below. 2 mg of st-PMMA was dissolved in CH_3CN (1 mL) at room temperature (ca. 25 °C). To the solution was added 10 mg of C_{60}. The mixture was then vigorously stirred by a magnetic stirrer at room temperature. After 24 h, the mixture was centrifuged at 1700*g* for 10 min to separate the undissolved C_{60} in the form of precipitates. The CH_3CN solution of C_{60} in the presence of st-PMMA was obtained by filtration of the supernatant using a membrane filter (pore size 0.2 μm). The st-PMMA film containing C_{60} was prepared by gradual solvent evaporation of the CH_3CN solution in a CH_3CN vapor atmosphere at room temperature.

Results and Discussion

Solubilization of C_{60} in Polar Solvents by Using st-PMMA as the Solubilizing Agent. C_{60} is essentially insoluble in polar solvents such as CH_3CN and acetone.[1,2] Ruoff et al. reported the solubility of C_{60} in CH_3CN to be 0.000 mg/mL at 25 °C.[2] It was observed that C_{60} molecules (10 mg) did not dissolve in CH_3CN (1 mL) even upon stirring at room temperature (ca. 25 °C) for 24 h, as shown in Figure 2A(a). However, a suspension was obtained when 2 mg of st-PMMA (M_n = 322 000, *rr* = 94%) was added to the mixture and stirred at room temperature for 24 h by using a magnetic stirrer; this suspension was centrifuged in order to separate the undissolved C_{60} molecules in the form of precipitates. After filtrating the supernatant over a membrane filter (pore size: 0.2 μm), a yellow filtrate was obtained (Figure 2A(b)). The UV−vis spectrum of the filtrate showed a characteristic absorption band at 333 nm corresponding to the chromophoric C_{60} molecules (Figure 2B(c)), thereby indicating that the C_{60} molecules were dissolved in CH_3CN and that st-PMMA served as the solubilizing agent. The solubility of C_{60} in CH_3CN in the presence of st-PMMA (2 mg/mL) was calculated to be 0.114 mg/mL from the absorption

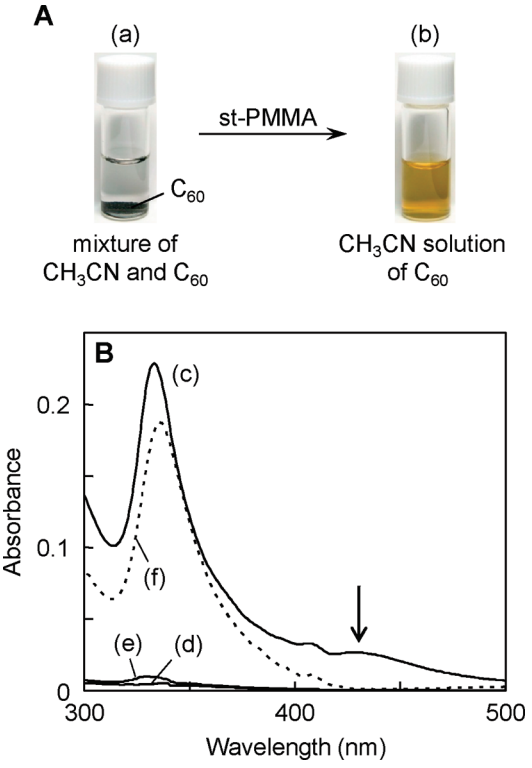

Figure 2. (A) Photographs of (a) a mixture of CH_3CN and C_{60} and (b) CH_3CN solution of C_{60} after the addition of st-PMMA, stirring at room temperature for 24 h, centrifugation, and subsequent filtration over a membrane filter (pore size: 0.2 μm) for removal of undissolved C_{60}. (B) UV−vis spectra of CH_3CN solutions of C_{60} with (c) st-, (d) it-, and (e) at-PMMAs prepared by stirring the mixtures at room temperature for 24 h and subsequent centrifugation and filtration. UV−vis spectrum of a toluene solution of C_{60} is also shown (f).

spectrum using the molar absorptivity measured in toluene (Figure 2B(f) and Table 1). This significant improvement in the solubility of C_{60} in the presence of st-PMMA may be attributed to the formation of the st-PMMA/C_{60} inclusion complex (Figure 1). The solubility of C_{60} increased with the

Table 1. Solubility of C_{60} in Polar Solvents in the Presence of PMMA

run	solvent	polymer[a]	polymer in feed (mg)	solubility of C_{60}[b] (mg/mL)
1	CH_3CN			0.000[c]
2		st-PMMA	2	0.114
3			4	0.267
4			5	0.291
5			6	0.288
6			10	0.353
7		at-PMMA	2	0.004
8		it-PMMA	2	0.002
9	acetone			0.001[c]
10		st-PMMA	2	0.218
11			10	0.264
12	THF			0.000[c]
13		st-PMMA	2	0.001
14	$CHCl_3$			0.16[c]
15		st-PMMA	2	0.165

[a] st-PMMA: M_n = 322 000, M_w/M_n = 1.29, and *mm*:*mr*:*rr* = 0:6:94; at-PMMA: M_n = 97 500, M_w/M_n = 2.61, and *mm*:*mr*:*rr* = 3:37:60; it-PMMA: M_n = 489 000, M_w/M_n = 1.12, and *mm*:*mr*:*rr* = 98:2:0. [b] Determined by UV−vis measurements on the basis of the molar absorptivity measured in toluene. [c] Reference 2.

concentration of st-PMMA (runs 2−6 in Table 1). In addition, the solutions remained stable for more than a year at room temperature.

Furthermore, in Figure 2B(c), we detected an absorption band at around 440 nm (indicated by the arrow), which was not detected in the spectrum of the toluene solution of C_{60} (f). The broad absorption band was indicative of stacking interactions between neighboring C_{60} molecules;[9,17] these interactions were possibly responsible for the yellow color of the CH_3CN solution of C_{60} and suggested the formation of the st-PMMA/C_{60} inclusion complex.

Influence of molecular weight of st-PMMA on the solubility was examined using a low-molecular-weight st-PMMA (M_n = 33 000, *rr* = 97%).[18] The solubility of C_{60} decreased to 0.052 mg/mL by using the st-PMMA at the polymer concentration of 2 mg/mL. This result indicates that the solubilization of C_{60} in CH_3CN requires a relatively long st-PMMA chain.

Next, we investigated the effect of the stereoregularity of PMMA on the solubility of C_{60} in CH_3CN. When it-PMMA (M_n = 489 000, *mm* = 98%) was used, the C_{60} molecules did not dissolve in CH_3CN (d in Figure 2B, and Table 1) because of the inability of the isotactic sequence in the it-PMMA chain to form a large helical cavity similar to that formed when using st-PMMA. The at-PMMA, which has low content of syndiotactic sequence in the chain (M_n = 97 500, *rr* = 60%), was not an effective solubilizing agent for C_{60} (e in Figure 2B, Table 1). These results clearly show that the stereoregularity of the polymer chain strongly affects the solubilization of C_{60} in CH_3CN and that the syndiotactic sequence in the polymer chain plays a crucial role in the solubilization via the formation of a helical cavity.

We further examined the solubilization of C_{60} in various polar solvents in the presence of st-PMMA (runs 8−13 in Table 1). In acetone, solubilization of C_{60} in the presence of st-PMMA was observed similarly as in CH_3CN. The solubility of C_{60} in acetone increased from 0.001 mg/mL (in the absence of st-PMMA)[2] to 0.218 mg/mL (in the presence of 2 mg/mL st-PMMA; runs 8 and 9).[19] However, the solubility of C_{60} did not increase in THF and $CHCl_3$ (runs 10−13).

It is known that in certain solvents st- and it-PMMA chains assemble to form a crystalline complex known as a "stereocomplex" with an apparent melting point.[20−22] CH_3CN and acetone are classified as "strong stereocomplexing solvents," which implies that st- and it-PMMA undergo

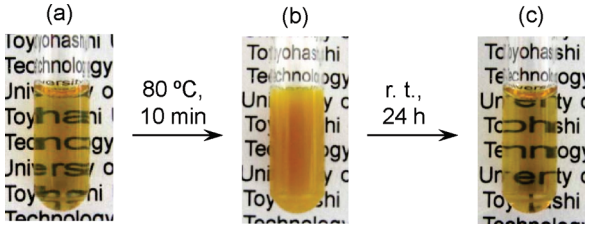

Figure 3. Photographs of a CH_3CN solution of C_{60} with st-PMMA (st-PMMA: 10 mg/mL) before (a) and after heating at 80 °C for 10 min (b) and then storing the sample at room temperature for 24 h (c).

efficient stereocomplex formation in these solvents[20,22] and that this stereocomplex formation is weaker in THF than in CH_3CN,[23] and the stereocomplex formation in $CHCl_3$ hardly occurs.[20,22] In this study, we found that solvents that are effective in solubilizing C_{60} are "strong stereocomplexing solvents"; this suggested that the st-PMMA chains adopt a helical conformation readily in strong stereocomplexing solvents in the presence of guest molecules such as C_{60} and it-PMMA.

Thermoresponsive Phase Transition of the CH_3CN Solution of C_{60} with st-PMMA. Thermal behavior of the CH_3CN solution of C_{60} with st-PMMA (st-PMMA: 10 mg/mL) was investigated. By heating at 80 °C for 10 min, the solution became opaque due to the C_{60} molecules separated out as shown in Figure 3b. Interestingly, the C_{60} molecules redissolved after the sample had been allowed to stand at room temperature for 24 h (Figure 3c), probably because of the solubilization through the formation of the st-PMMA/C_{60} inclusion complex. These changes are completely reversible.

Release of C_{60} from the st-PMMA/C_{60} Inclusion Complex through Sterecomplex Formation. Stereocomplex formation of st- and it-PMMAs efficiently occurs in CH_3CN and in acetone.[20] When CH_3CN solutions of st- and it-PMMA are mixed, a precipitate immediately forms due to the stereocomplex formation.[23] Recently, by using atomic force microscopy (AFM), Kumaki et al. studied the stereocomplex between st- and it-PMMAs that were prepared by the Langmuir−Blodgett (LB) technique and proposed a triple-stranded helical model for the stereocomplex in which a double-stranded helix of it-PMMA was included in a single helix of st-PMMA. This stereocomplex could be considered as an inclusion complex in which st-PMMA is the host and it-PMMA is the guest.[21] Previously, we had reported that the C_{60} molecules encapsulated in an st-PMMA/C_{60} complex gel prepared in toluene were released by the addition of it-PMMA; this was because of the formation of a stereocomplex.[10] Thus, if the C_{60} molecules solubilized in CH_3CN are encapsulated in the st-PMMA helix, they may be released by stereocomplex formation even in the solution (Figure 4A). In order to confirm this probability, it-PMMA was added to the CH_3CN solution of C_{60} in the presence of st-PMMA at room temperature (a in Figure 4B). Immediately after the addition of it-PMMA, a precipitate was formed (b in Figure 4B) which was confirmed by X-ray diffraction analysis to be a stereocomplex between st- and it-PMMAs (see Figure S1 in Supporting Information). The UV−vis spectrum of the CH_3CN solution of C_{60} and st-PMMA shows the characteristic absorption band corresponding to C_{60} (c in Figure 4C). This absorption band disappeared upon the addition of it-PMMA to the aforementioned solution (d in Figure 4C); this indicated that the C_{60} molecules precipitated from the CH_3CN solution. From the above results, it was verified that the C_{60} molecules are solubilized in CH_3CN owing to the partial formation of the st-PMMA/C_{60} inclusion complex and are released by stereocomplex formation between st and it-PMMAs.

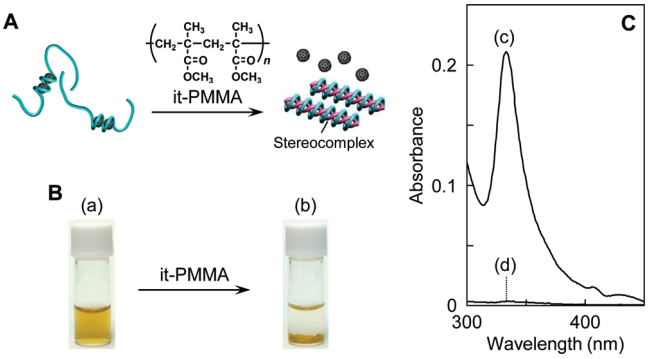

Figure 4. (A) Schematic illustration of the release of solubilized C_{60} molecules via the stereocomplex formation between st- and it-PMMAs. (B) Photographs of (a) a CH_3CN solution of C_{60} and st-PMMA and (b) the mixture after the addition of it-PMMA (st-PMMA: 2 mg/mL; it-PMMA: 1 mg/mL). (C) UV−vis spectra of (c) the CH_3CN solution of C_{60} and st-PMMA and (d) the supernatant after the addition of it-PMMA.

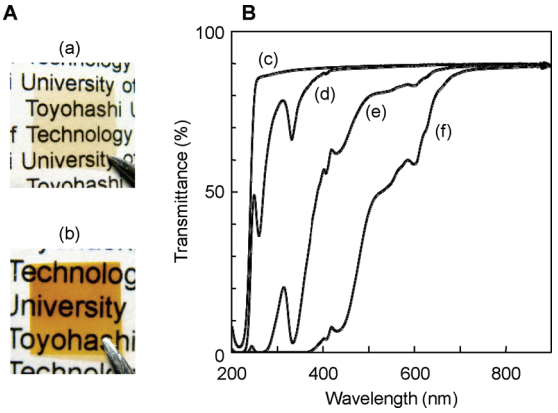

Figure 5. (A) Photographs of st-PMMA films containing C_{60} at (a) 0.58 wt % and (b) 5.8 wt %. Size: ca. 1 × 1 cm. (B) UV−vis spectra of (c) pristine st-PMMA film and st-PMMA films containing (d) 0.058, (e) 0.58, and (f) 5.8 wt % C_{60} prepared by casting the CH_3CN solutions on a glass substrate. The film thickness is ca. 30 μm.

Preparation and Properties of st-PMMA/C_{60} Inclusion Complex Films. We reported the efficient formation of st-PMMA/C_{60} inclusion complex in toluene.[9] However, this inclusion complex formed a gel and was therefore difficult to process. In contrast, C_{60} dissolved in CH_3CN in the presence of st-PMMA, yielding a yellow solution that could be easily processed into films. St-PMMA films containing C_{60} could be easily prepared by casting the CH_3CN solutions on glass plates and then by evaporating the solvent at room temperature (ca. 25 °C) (Figure 5). A red-brown transparent st-PMMA film containing C_{60} was obtained without macroscopic phase separation even at a high C_{60} content (5.8 wt %) (b in Figure 5A). The obtained film absorbed light in the UV−vis region because of the presence of chromophoric C_{60} molecules, and the intensity of absorption could be controlled by controlling the C_{60} content (Figure 5B). The pristine st-PMMA film with a thickness of ca. 30 μm absorbed 10.8% of 400 nm light (c), while the st-PMMA film containing 5.8 wt % C_{60} absorbed 95.8% of 400 nm light (f).

X-ray measurements were then performed on the pristine st-PMMA film and the st-PMMA film containing 5.8 wt % C_{60} prepared by casting the CH_3CN solutions (Figure 6). The broad diffractogram patterns observed in the pristine st-PMMA film indicated that the film had an amorphous structure. In contrast, the X-ray diffractogram of the st-PMMA film containing C_{60} showed very weak but apparent reflection peaks, as indicated by the arrows in Figure 6b.

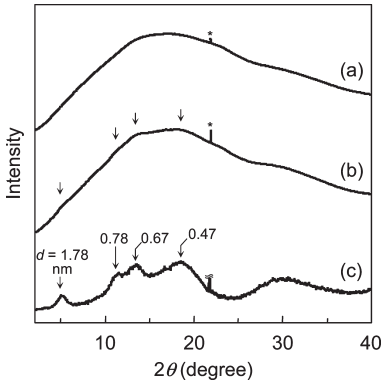

Figure 6. X-ray diffractograms of (a) pristine st-PMMA film and (b) the st-PMMA film containing 5.8 wt % C_{60} prepared by casting the CH_3CN solutions and (c) the differential diffractogram obtained by subtracting (a) from (b).

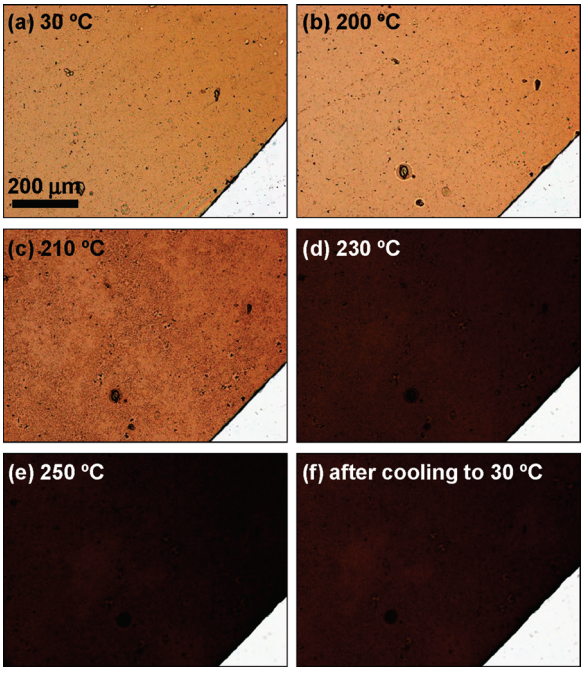

Figure 7. Optical micrographs of a st-PMMA film containing 5.8 wt % C_{60} after thermal treatment at various temperatures. The film was prepared by casting a CH_3CN solution of C_{60} with st-PMMA on a glass substrate and subsequent evaporation of the solvent. The observation was carried out at 30 °C (a) followed by heating to 250 °C (b−e) and then cooling to 30 °C (f) at the heating and cooling rates of 10 °C/min. The film thickness is ca. 30 μm.

Interestingly, the pattern of the differential diffractogram (c), which was obtained by subtracting (a) from (b), was similar to the previously reported X-ray diffractogram pattern of the st-PMMA/C_{60} inclusion complex prepared in toluene;[9] this confirmed the formation of the st-PMMA/C_{60} inclusion complex in the film. This confirmed our hypothesis that the st-PMMA/C_{60} inclusion complex is also formed in the CH_3CN solution.

We examined the heat resistance of the st-PMMA film containing C_{60}. Figure 7 displays the optical micrographs of the st-PMMA film containing 5.8 wt % C_{60} prepared by casting the CH_3CN solution after thermal treatment at different temperatures. The as-prepared film was red-brown in color at 30 °C (a). The color did not change even after heating the film to 200 °C on a slide glass at a rate of 10 °C/min (b); however, the color began to change at around 210 °C (c), and

the film turned dark-brown at 230 °C (d). It was reported that the st-PMMA/C_{60} inclusion complex prepared by evaporating the solvent from the gel in toluene had a melting point of ca. 210 °C, as observed by using a differential scanning calorimeter.[9] Hence, the change in the film color upon heating corresponds to the melting of the st-PMMA/C_{60} inclusion complex. After the melting of the inclusion complex, the original color of the film was not restored upon cooling, indicating the irreversible release of the encapsulated C_{60} molecules in the film without solvent.[9]

Toluene is known to be a good solvent for C_{60}.[2] The it-PMMA (rr = 0%) and at-PMMA (rr = 60%) also dissolve easily in toluene. We attempted to prepare it- and at-PMMAs films containing C_{60} from their toluene solutions and compared the thermal property of the films with that of the st-PMMA/C_{60} film.

A homogeneous it-PMMA film containing C_{60} was not obtained upon evaporating the solvent because of the occurrence of macroscopic phase separation between C_{60} and it-PMMA.[9] In the case of at-PMMA, a transparent film containing 5.0 wt % C_{60} was obtained by casting the toluene solution. However, the heat resistance of the film was relatively low. The film color changed from red to black upon heating to 180 °C (Figure S2 in Supporting Information), indicating that the C_{60} molecules in the film precipitated at this temperature. In contrast, the st-PMMA (rr = 94%) film containing 5.8 wt % C_{60} maintained the structure even at 200 °C (Figure 7), which was considerably higher than the glass transition temperature of st-PMMA ($T_g \sim 120$ °C). The enhanced thermal stability of the film was considered to be due to the crystalline structure of the st-PMMA/C_{60} inclusion complex, whose melting point was 210 °C. The results clearly demonstrate the advantage of using st-PMMA in the formation of C_{60} composite films that have a high thermal stability.

In summary, we found C_{60} molecules to be solubilized in polar solvents such as CH_3CN and acetone at room temperature in the presence of st-PMMA (solubilizing agent); this was due to the encapsulation of C_{60} in the helical st-PMMA cavity. The formation of the st-PMMA/C_{60} inclusion complex in CH_3CN was confirmed by X-ray diffraction analysis of the film prepared by casting the CH_3CN solution. The C_{60} molecules solubilized in CH_3CN in the presence of st-PMMA were released upon the addition of it-PMMA; this occurred because of stereocomplex formation between st- and it-PMMAs. Furthermore, the transparent st-PMMA films containing C_{60} absorbed light in the UV−vis region owing to the presence of chromophoric C_{60} molecules and high heat resistance owing to the crystalline nature of the inclusion complex. The proposed solubilization method, which involves the use of st-PMMA, is expected to be a novel approach to the design and synthesis of C_{60} nanocomposites for nonlinear optic devices and photovoltaic cells.[4b,24]

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Supporting Information Available: X-ray diffractogram of a stereocomplex prepared by the addition of it-PMMA into the CH_3CN solution of C_{60} and st-PMMA; optical micrographs of an at-PMMA film containing 5.0 wt % C_{60} at various temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Kadish, K. M., Ruoff, R. S., Eds. In *Fullerenes: Chemistry, Physics, and Technology*; Wiley: New York, 2000.
(2) Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. *J. Phys. Chem.* **1993**, *97*, 3379–3383.
(3) (a) Prato, M. *J. Mater. Chem.* **1997**, *7*, 1097–1109. (b) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, 807–815. (c) Nierengarten, J.-F. *New J. Chem.* **2004**, *28*, 1177–1191.
(4) (a) Chen, Y.; Huang, Z.-E.; Cai, R.-F.; Yu, B.-C. *Eur. Polym. J.* **1998**, *34*, 137–151. (b) Wang, C.; Guo, Z.-X.; Fu, S.; Wu, W.; Zhu, D. *Prog. Polym. Sci.* **2004**, *29*, 1079–1141. (c) Giacalone, F.; Martķn, N. *Chem. Rev.* **2006**, *106*, 5136–5190.
(5) (a) Andersson, T.; Nilsson, K.; Sundahl, M.; Westman, G.; Wennerström, O. *J. Chem. Soc., Chem. Commun.* **1992**, 604–606. (b) Hungerbuehler, H.; Guldi, D. M.; Asmus, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 3386–3387. (c) Liu, Y.; Wang, H.; Liang, P.; Zhang, H.-Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 2690–2694.
(6) Yamakoshi, Y. N.; Yagami, T.; Fukuhara, K.; Sueyoshi, S.; Miyata, N. *J. Chem. Soc., Chem. Commun.* **1994**, 517–518.
(7) Jenekhe, S. A.; Chen, X. L. *Science* **1998**, *279*, 1903–1907.
(8) (a) Kusuyama, H.; Takase, M.; Higashihara, Y.; Tseng, H.-T.; Chatani, Y.; Tadokoro, H. *Polymer* **1982**, *23*, 1256–1258. (b) Kusuyama, H.; Miyamoto, N.; Chatani, Y.; Tadokoro, H. *Polymer* **1983**, *24*, 119–122.
(9) Kawauchi, T.; Kumaki, J.; Kitaura, A.; Okoshi, K.; Kusanagi, H.; Kobayashi, K.; Sugai, T.; Shinohara, H.; Yashima, E. *Angew. Chem., Int. Ed.* **2008**, *47*, 515–519.
(10) Kawauchi, T.; Kitaura, A.; Kumaki, J.; Kusanagi, H.; Yashima, E. *J. Am. Chem. Soc.* **2008**, *130*, 11889–11891.
(11) Kamijo, M.; Saeatari, N.; Konishi, T.; Yoshizaki, T.; Yamakawa, H. *Macromolecules* **1994**, *27*, 5697–5703.
(12) Abe, H.; Imai, K.; Matsumoto, M. *J. Polym. Sci., Part C* **1968**, *23*, 469–485.
(13) Varshney, S. K.; Gao, Z.; Zhong, X.-F.; Eisenberg, A. *Macromolecules* **1994**, *27*, 1076–1082.
(14) Kawauchi, T.; Kumaki, J.; Yashima, E. *J. Am. Chem. Soc.* **2005**, *127*, 9950–9951.
(15) Kitayama, T.; He, S.; Hironaka, Y.; Iijima, T.; Hatada, K. *Polym. J.* **1995**, *27*, 314–318.
(16) Katchalsky, A.; Eisenberg, H. *J. Polym. Sci.* **1951**, *6*, 145–154.
(17) (a) Pantoş, G. D.; Wietor, J.-L.; Sanders, J. K. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 2238–2240. (b) Diederich, F.; Effing, J.; Jonas, U.; Jullien, L.; Plesnivy, T.; Ringsdoef, H.; Thilgen, C.; Weinstein, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1599–1602.
(18) The low-molecular-weight st-PMMA was prepared by the syndiotactic-specific polymerization of trimethylsilyl methacrylate in toluene at −78 °C with *tert*-butyllithium in the presence of bis(2,6-di-*tert*-butylphenoxy)methylaluminum, followed by hydrolysis of the pendant esters, and methylation with diazomethane: M_n = 33 000, M_w/M_n = 1.15, and *mm*:*mr*:*rr* = 0:3:97. See: Kitayama, T.; He, S.; Hironaka, Y.; Iijima, T.; Hatada, K. *Polym. J.* **1995**, *27*, 314−318.
(19) The solubility of C_{60} in acetone also depended on the concentration of st-PMMA (runs 10 and 11 in Table 1).
(20) (a) Spěváček, J.; Schneider, B. *Adv. Colloid Interface Sci.* **1987**, *27*, 81–150. (b) te Nijenhuis, K. *Adv. Polym. Sci.* **1997**, *130*, 67–81. (c) Hatada, K.; Kitayama, T. *Polym. Int.* **2000**, *49*, 11–47. (d) Serizawa, T.; Akashi, M. *Polym. J.* **2006**, *38*, 311–328.
(21) (a) Kumaki, J.; Kawauchi, T.; Okoshi, K.; Kusanagi, H.; Yashima, E. *Angew. Chem., Int. Ed.* **2007**, *46*, 5348–5351. (b) Kumaki, J.; Kawauchi, T.; Ute, K.; Kitayama, T.; Yashima, E. *J. Am. Chem. Soc.* **2008**, *130*, 6373–6380.
(22) Vorenkamp, E. J.; Bosscher, F.; Challa, G. *Polymer* **1979**, *20*, 59–64.
(23) Precipitation occurred in the mixture of st- and it-PMMAs (st/it = 2/1) in CH_3CN and acetone (total polymer concentration: 4 mg/mL) because of stereocomplex formation; however, precipitation of the stereocomplex did not occur in THF under the same conditions. These results indicated that the stereocomplexation in THF is weaker than that in CH_3CN and acetone.
(24) (a) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 15–26. (b) Brusatin, G.; Signorini, R. *J. Mater. Chem.* **2002**, *12*, 1964–1977.