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Supramolecular Gel-Functionalized Polymer Film with Tunable Optical Activity

Hirokuni Jintoku[a], Momoko Dateki[a], Makoto Takafuji[a, b] and Hirotaka Ihara[a, b]*

We describe a new method for the fabrication of an optically active polymer film, involving the phase separation of self-assembled chiral nanofibres in a solid polymer matrix. The circular polarization properties of the films can be controlled by changing the morphology of the phase-separated nano domains.

Supramolecular chiral structures have attracted a large amount of attention in diverse fields, including optical materials,[1] molecular recognition systems,[2] catalysis,[3] and memory.[4] Interest in these supramolecular chiral structures which are generated from the self-assembly of small molecules[5] and polymers[6] is attributable to the reversible chirality control caused by external stimuli such as solvent,[7] temperature,[8] light,[9] and additives.[10] Their controllable circular polarization properties have become a current focus of research due to their potential applications as circular polarization filters and chiral memory devices, among others.[4a] As an objective toward these practical applications, the supramolecular chiral materials must be fabricated and evaluated in the solid state. Nevertheless, there are few reports concerning the control of chiroptical properties in the solid state.[11]

Herein, we present a new preparation method based on a controlled phase separation with the aim of regulating the circular polarization properties of the solid material. In our approach, we utilized a supramolecular gelation technique to achieve highly oriented nano-fibrillar aggregation in a polymer matrix.[12] In particular, we exploited the supramolecular gelator properties of glutamide lipids, which exhibit unique self-assembly behaviours. The glutamide lipids can form various nanostructures by slight adjustments to their surrounding environments, such as solvent, temperature, and additives.[13] This property comes from sterically arranged amide bonds around the chiral carbon atoms.

On this basis, an optically active polymer film exhibiting controlled circular polarization properties was fabricated. To the best of our knowledge, this is the first report of chiral-orientation control in the self-assembly of small molecules in a solid polymer matrix.

An N',N''-didodecyl L-glutamide parent, functionalized by a pyrene derivative (g_L-**Pyr**), was synthesized according to a previous report.[14] Pyrene is a good fluorophore candidate because of its high sensitivity toward external stimuli as well as its strong absorption and fluorescence emission properties. As the polymer matrix, poly(ethylene$_{60}$-co-vinyl acetate$_{40}$) (EVA) was selected. The g_L-**Pyr**-incorporated EVA films were prepared by the usual casting method onto a glass substrate from a mixture of g_L-**Pyr** and EVA (0.042 and 5 wt%, respectively) dissolved in a toluene/ethyl acetate (1:1) mixed solution, which forms an organogel through a nano-fibrous network (ESI†). The obtained EVA film, containing 0.84 wt% g_L-**Pyr** at a thickness of ca. 20 μm, shows a large positive Cotton effect (g_{abs} = 1.3 x 10^{-3} at 354 nm) around a red-shifted absorption band compared to the non-assembling pyrene butyric acid-incorporated EVA film (Figures 1 and ESI†). This circular dichroism (CD) signal, which is larger than that for g_L-**Pyr** in its molecular state, indicates its induction from the twisted structure of a g_L-**Pyr** assembly. Thus, the g_L-**Pyr** forms an ordered assembly with an R-chiral (right-handed) twist and J-type (slipped face-to-face) stacking of the pyrene moieties in the EVA film. As shown in Figure 1d, a broad fluorescence emission with moderate quantum yield (ϕ_{FL} = 0.36) is observed at 449 nm, indicating excimer formation in the pyrene moieties. We assigned this assembly as State I.

Interestingly, this film reveals two other assemblies (States II and III) upon heating. For example, thermal treatment for 10 min at 110 °C induces chiral inversion from positive to negative in the CD spectrum (g_{abs} = -2.3 x 10^{-3} at 356 nm), as shown in Figure 1a. This indicates that the chiral orientation of the pyrene moiety changed from a right-handed twist (R-chiral) to a left-handed twist (S-chiral) (State II). Thermal

treatment above 110 °C reveals a gradual decrease in the CD intensity from negative to zero (State III) (Figure 1a and b). In comparison, the UV and fluorescence spectra do not show significant changes after the thermal treatments (Figure 1c and d). As shown in Figure 1c, the absorbance changes because the thermal treatment causes the planarization of the film surface. The wavelength of the maximum absorption shifts slightly to a shorter wavelength, from 352 to 350 nm (ESI†). However, the *J*-type stacking formation of the pyrenyl moieties is retained after thermal treatment with only slight change. After heating, the fluorescence spectra exhibit an excimeric emission with a slightly shifted wavelength, and no significant change in a fluorescence quantum yield was observed by fabrication in a film (φ = 0.38 in a film). This result indicates that the pyrene moieties closely maintain their orientations and distances after thermal treatment. Therefore we deduced that the g_L-**Pyr** assembly was not changed to a dispersed state, but rather, to non-chiral aggregates, upon thermal treatment. The inverted-chirality aggregate (State II) can be obtained not only by thermal treatment but also by slow evaporation. At the time of film preparation, a slow solvent evaporation rate promotes the assembly that exhibits a negative Cotton effect with a *J*-type orientation (ESI†).
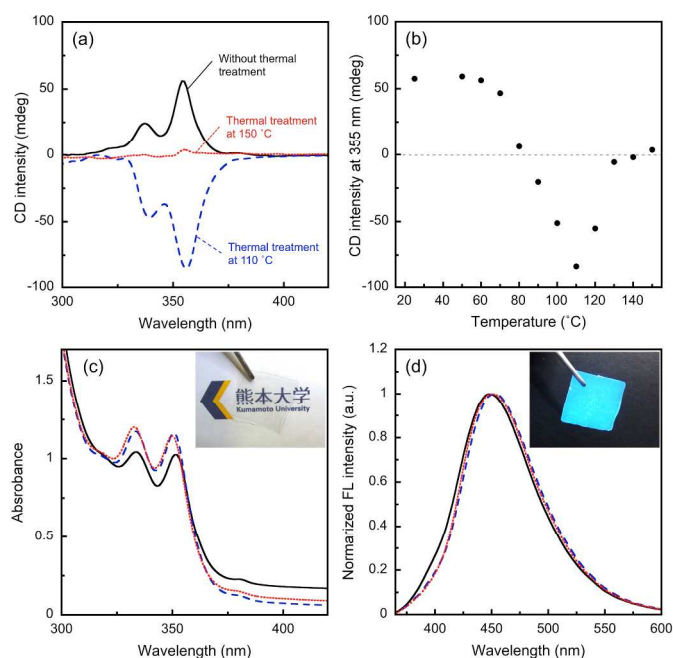

Figure 1. Thermal-treatment-temperature-dependent spectral changes of the g_L-**Pyr**-incorporated EVA film. (a) CD spectra, (b) plots of CD intensity change at 355 nm, (c) UV-vis spectra, and (d) fluorescence spectra. Black line: film without thermal treatment; blue dashed line: with thermal treatment at 110 °C; and red dotted line: with thermal treatment at 150 °C. Inset photos are g_L-**Pyr**-incorporated EVA film under room light and UV (365 nm) light. Measurement temperature is 25 °C. Excitation wavelength = 350 nm.

The EVA film incorporating the D-glutamic acid-derived pyrene (g_D-**Pyr**) demonstrates similar formation changes during assembly. Before thermal treatment, this film has a negative Cotton effect, mirroring that of the g_L-**Pyr**-incorporated EVA film (Figure 2). Upon thermal treatment below 110 °C, its CD signal changes from negative to positive. As with the g_L-**Pyr**-incorporated EVA film, the CD signal disappears upon thermal treatment at 150 °C.

Based on these results, we conclude that the molecular g_L-**Pyr** can be converted into three kinds of nano-fibrillar chiral assemblies in a polymer film: an assembly with a positive Cotton effect that is kinetically stable (State I); an assembly with a negative Cotton effect that is thermodynamically metastable (State II); and an assembly with a small Cotton effect that is thermodynamically stable (State III) (Figure 3). These morphological change behaviours have been reported for the self-assembly of small molecular assemblies and polymers in the solution state.[15] However, there are few corollary reports with respect to solid polymer matrixes. The investigation of the thermal history of the g_L-**Pyr**-incorporated EVA film supports this conclusion. The g_L-**Pyr**-incorporated EVA film shows a small CD signal (State III) instead of a negative CD signal (State II) after thermal treatment for 10 min at 150 °C, which was maintained for 10 min at 110 °C (ESI†). On the other hand, the g_L-**Pyr** dissolved in toluene/ethylacetate (1:1), but the obtained gel showed no similar chiroptical change (ESI†).
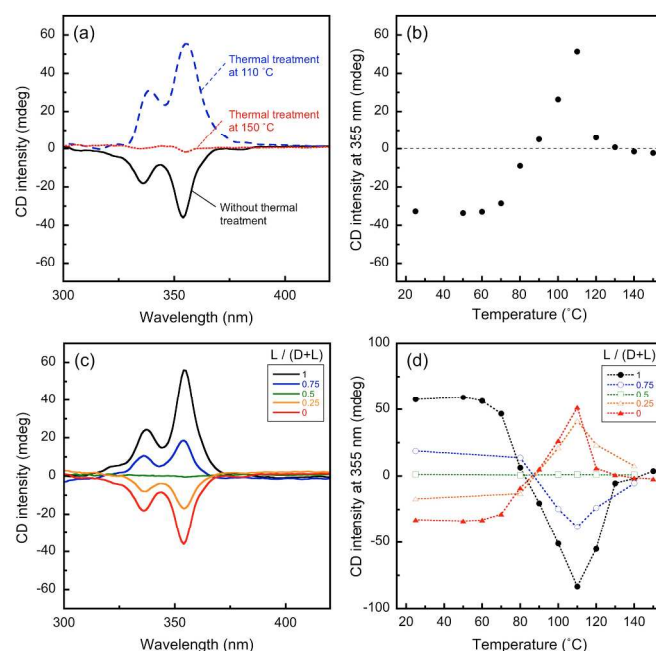

Figure 2. Thermal-treatment-temperature-dependent spectral changes of g_D-**Pyr**-incorporated EVA film. (a) CD spectra, (b) plots of CD intensity change at 355 nm. (c) CD spectra of a g_L-**Pyr**/g_D-**Pyr** mixture-incorporated EVA film. (d) Plots of the thermal-treatment-temperature-dependent CD intensity changes of a g_L-**Pyr**/g_D-**Pyr** mixture-incorporated EVA film at 355 nm. Measurement temperature is 25 °C.
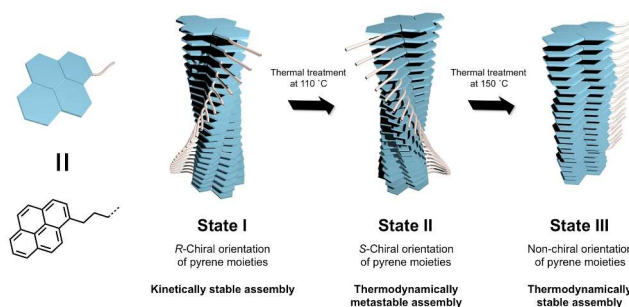

Figure 3. Schematic images of kinetically stable, thermodynamically metastable, and thermodynamically stable assemblies of g_L-**Pyr** in an EVA film.

To generate a large library of morphological change, thermomechanical analysis (TMA) and differential scanning calorimetry (DSC) were performed on the g_L-Pyr-incorporated EVA film (ESI†). As shown in the TMA curve, a phase-transition temperature is detectable at 46 °C. The DSC curve also shows a phase transition at 41 °C, which indicates the softening point of the EVA. When the temperature exceeds this softening point, the material becomes sufficiently flexible that the assembly of the incorporated g_L-Pyr changes. For this reason, the g_L-Pyr assembly can alter its morphology in the solid polymer matrix.

Transmission electron microscopy (TEM) observation strongly supports the concept of changes in the assembly of g_L-Pyr. As shown in Figure 4a, fibrous aggregates of g_L-Pyr can be detected in the EVA film. The length and diameter of the fibrillar aggregates are *ca.* 0.5–3 μm and 10 nm, respectively. Some areas exhibit a right-handed helical structure (Figure 4a, inset). Even after thermal treatments at 110 and 150 °C for 10 min, the fibrillar morphology is maintained. Interestingly, the thermal treatments at 110 and 150 °C promote fibre elongation in the g_L-Pyr aggregates to *ca.* 2–7 μm and *ca.* 5–10 μm, with bundling (Figure 4c, inset), respectively. On the other hand, in the solution state, it is well known that the supramolecular gel shows a gel-to-crystal transition as a metastable-to-stable state transition.[16] On this basis, we believe that the fibre growth and bundling indicate the transformation of the g_L-Pyr assembly from a metastable to a stable state upon thermal treatment. Unfortunately, we could not observe the left-handed helical structure in the g_L-Pyr aggregates in the thermally treated film, although the CD signal indicates the *S*-chiral aggregation of the pyrene moieties. This result suggests that the changes in the CD signal are effected by stacking formations between the pyrene moieties rather than a macroscopic helical structure of the g_L-Pyr assembly.
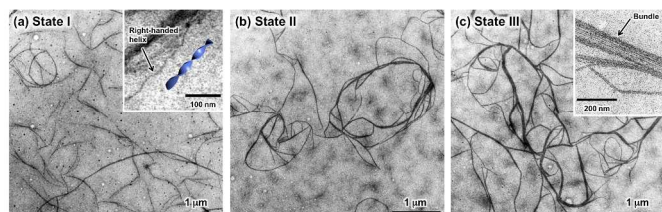

Figure 4. TEM images of g_L-Pyr-incorporated EVA films (a, b) without thermal treatment, and after thermal treatment (c) at 110 °C and (d) at 150 °C. These samples were stained with ruthenium tetroxide.

We succeeded in controlling the CD intensity of the film by changing not only the thermal treatment temperature but also the concentration of the *g*-Pyr component, the preparation solvent, and the optical purity of the *g*-Pyr. (1) When increasing the g_L-Pyr concentration from 0.17 to 1.68 wt% in the EVA film, the CD intensity rises concomitantly (ESI†). (2) By using toluene as a solvent instead of a 1:1 toluene/ethyl acetate mixture, the CD intensity increases three-fold (ESI†). Changing the ratio of toluene to ethyl acetate effects a gradual change in the CD intensity. In our previous report, we discussed the relationship between the local environment and the chiral orientation of the L-glutamide assembly.[12a] This phenomenon is based on the driving force for self-assembly. In a toluene-rich environment, the π-π stacking of the pyrenyl moieties is weakened due to π-π interactions between the toluene and pyrenyl substituents. Therefore, the intermolecular hydrogen bonding through the amide bonds that are located around the

chiral carbon promotes the twisted orientation. On the other hand, in an ethyl acetate-rich environment, the hydrogen bonds are weakened by the carbonyl groups of ethyl acetate molecules. Thus, the effect of the π-π stacking of the pyrenyl moiety is stronger, and the assembly of the pyrenyl groups is changed to a less twisted orientation. (3) An EVA film containing a racemic g_L-Pyr/g_D-Pyr (1:1) mixture shows no CD signal (Figure 2c). By changing the optical purity of the g_L-Pyr/g_D-Pyr mixture, the CD signal changes between positive and negative (Figure 2d).

This chiral film provides the possibility of chiral patterning and may have applicability for chiral memory. We succeeded in fabricating a film with a simple chiral pattern by partial thermal treatment at 110 °C. As shown in ESI†, this film exhibits a positive CD signal in the right part, and a negative CD signal to the left. This chiral film demonstrates high stability despite the facile change of the CD signal upon thermal treatment (ESI†). The CD signal of this chiral film did not change after 300+ days at 25 °C. Moreover, a film that was treated for 10 min at 110 °C did not show any spectral change after additional thermal treatment for 24 h at 100 °C. These results indicate that the chiral stability of these films would be sufficient for various uses such as display, filter, and memory applications.

Conclusions

In conclusion, we established a new method for fabricating chiral polymer films through a supramolecular-gelation self-assembly technique. These films exhibit interesting circular polarization properties that can be easily alternated between positive and negative values by thermal treatment. This phenomenon is based on the self-assembly behaviour of glutamic acid derivatives. The generated films have sufficient stability for use in chiral patterning. We believe that this method has the potential for producing novel and interesting chiroptical materials.

Notes and references

[a] Department of Applied Chemistry and Biochemistry, Kumamoto University, 2-39-1 Kurokami, Kumamoto, 860-8555 (Japan), Tel/Fax: (+81)96-342-3662, E-mail: ihara@kumamoto-u.ac.jp

[b] Kumamoto Institute for Photo-Electro Organics (PHOENICS), 3-11-38 Higashimachi, Kumamoto, 862-0901 (Japan)

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1 (a) K. Egami, T. Nakayama, Y. Kosaka, S. Tomita, A. Ishizumi, H. Yanagi, K.-i. Yamashita and K. Oe, *physica status solidi (c)*, 2012, **9**, 2485; (b) K. Watanabe, T. Sakamoto, M. Taguchi, M. Fujiki and T. Nakano, *Chem. Commun.*, 2011, **47**, 10996.

2 (a) S. M. So, K. Moozeh, A. J. Lough and J. Chin, *Angew. Chem. Int. Ed.*, 2014, **53**, 829; (b) T. Ohzono, T. Yamamoto and J. Fukuda, *Nature communications*, 2014, **5**, 1; (c) A. Shundo, K. Hori, T. Ikeda,

N. Kimizuka and K. Tanaka, *J. Am. Chem. Soc.*, 2013, **135**, 10282; (d) E. Yashima, K. Maeda, H. Iida, Y. Furusho and K. Nagai, *Chem. Rev.*, 2009, **109**, 6102.

3 (a) C. Jahier, M.-F. Coustou, M. Cantuel, N. D. McClenaghan, T. Buffeteau, D. Cavagnat, M. Carraro and S. Nlate, *Eur. J. Inorg. Chem.*, 2011, **2011**, 727; (b) T. Hasegawa, Y. Furusho, H. Katagiri and E. Yashima, *Angew. Chem. Int. Ed.*, 2007, **46**, 5885; (c) L. Marinescu, M. Mølbach, C. Rousseau and M. Bols, *J. Am. Chem. Soc.*, 2005, **127**, 17578; (d) A. Schlatter, M. K. Kundu and W. D. Woggon, *Angew. Chem. Int. Ed.*, 2004, **43**, 6731.

4 (a) A. Ohira, K. Okoshi, M. Fujiki, M. Kunitake, M. Naito and T. Hagihara, *Adv. Mater.*, 2004, **16**, 1645; (b) A. Ohira, M. Kunitake, M. Fujiki, M. Naito and A. Saxena, *Chem. Mater.*, 2004, **16**, 3919.

5 (a) S. S. Babu, V. K. Praveen and A. Ajayaghosh, *Chem. Rev.*, 2014, **114**, 1973; (b) K. Sakajiri, T. Hirama, K. Yasuda, S. Kutsumizu and J. Watanabe, *Bull. Chem. Soc. Jpn.*, 2013, 940; (c) Y. Rong, P. Chen, D. Wang and M. Liu, *Langmuir*, 2012, **28**, 6356; (d) G. Zou, Y. Wang, Q. Zhang, H. Kohn, T. Manaka and M. Iwamoto, *Polymer*, 2010, **51**, 2229; (e) L. Zhang and M. Liu, *J. Phys. Chem. B*, 2009, **113**, 14015; (f) P. Xue, R. Lu, X. Yang, L. Zhao, D. Xu, Y. Liu, H. Zhang, H. Nomoto, M. Takafuji and H. Ihara, *Chem. Eur. J.*, 2009, **15**, 9824.

6 (a) J. Barbera, L. Giorgini, F. Paris, E. Salatelli, R. M. Tejedor and L. Angiolini, *Chem. Eur. J.*, 2008, **14**, 11209; (b) S. Sakurai, K. Okoshi, J. Kumaki and E. Yashima, *J. Am. Chem. Soc.*, 2006, **128**, 5650; (c) W. Peng, M. Motonaga and J. R. Koe, *J. Am. Chem. Soc.*, 2004, **126**, 13822; (d) L. Angiolini, R. Bozio, L. Giorgini, D. Pedron, G. Turco and A. Dauru¡, *Chem. Eur. J.*, 2002, **8**, 4241.

7 (a) Y. Li, B. Li, Y. Fu, S. Lin and Y. Yang, *Langmuir*, 2013, **29**, 9721; (b) K. Sakajiri, T. Sugisaki, K. Moriya and S. Kutsumizu, *Org. Biomol. Chem.*, 2009, **7**, 3757; (c) R. S. Johnson, T. Yamazaki, A. Kovalenko and H. Fenniri, *J. Am. Chem. Soc.*, 2007, **129**, 5735.

8 (a) B. M. W. Langeveld-Voss, M. P. T. Christiaans, R. A. J. Janssen and E. W. Meijer, *Macromolecules*, 1998, **31**, 6702; (b) A. P. H. J. Schenning, M. Fransen and E. W. Meijer, *Macromol. Rapid Commun.*, 2002, **23**, 265; (c) M. Fujiki, *J. Am. Chem. Soc.*, 2000, **122**, 3336.

9 (a) Y. Wang, T. Sakamoto and T. Nakano, *Chem. Commun.*, 2012, **48**, 1871; (b) S. Mayer, G. Maxein and R. Zentel, *Macromolecules*, 1998, **31**, 8522.

10 (a) E. Yashima, K. Maeda and O. Sato, *J. Am. Chem. Soc.*, 2001, **123**, 8159; (b) K. Maeda, K. Morino and E. Yashima, *Macromolecular Symposia*, 2003, **201**, 135; (c) A. Sorrenti, Z. El-Hachemi, O. Arteaga, A. Canillas, J. Crusats and J. M. Ribo, *Chem. Eur. J.*, 2012, **18**, 8820.

11 (a) T. Fukushima, K. Takachi and K. Tsuchihara, *Macromolecules*, 2008, **41**, 6599; (b) T. Ikai and Y. Okamoto, *Chem. Rev.*, 2009, **109**, 6077.

12 (a) H. Jintoku, Y. Okazaki, M. Takafuji and H. Ihara, *Chem. Lett.*, 2013, **42**, 1297; (b) H. Jintoku, M. Yamaguchi, M. Takafuji and H. Ihara, *Adv. Funct. Mater.*, 2014, **24**, 4105.

13 (a) H. Jintoku, T. Sagawa, M. Takafuji and H. Ihara, *Org. Biomol. Chem.*, 2009, **7**, 2430; (b) H. Jintoku, T. Sagawa, M. Takafuji and H. Ihara, *Chem. Eur. J.*, 2011, **17**, 11628; (c) K. Miyamoto, H. Jintoku, T. Sawada, M. Takafuji, T. Sagawa and H. Ihara, *Tetrahedron Lett.*, 2011, **52**, 4030.

14 T. Sagawa, S. Fukuzumi, T. Yamada and H. Ihara, *Langmuir*, 2002, **18**, 7223.

15 (a) A. Lohr, M. Lysetska and F. Wurthner, *Angew. Chem. Int. Ed.*, 2005, **44**, 5071; (b) K. Jyothish, M. Hariharan and D. Ramaiah, *Chem. Eur. J.*, 2007, **13**, 5944.

16 Y. Xu, C. Kang, Y. Chen, Z. Bian, X. Qiu, L. Gao and Q. Meng, *Chem. Eur. J.*, 2012, **18**, 16955.

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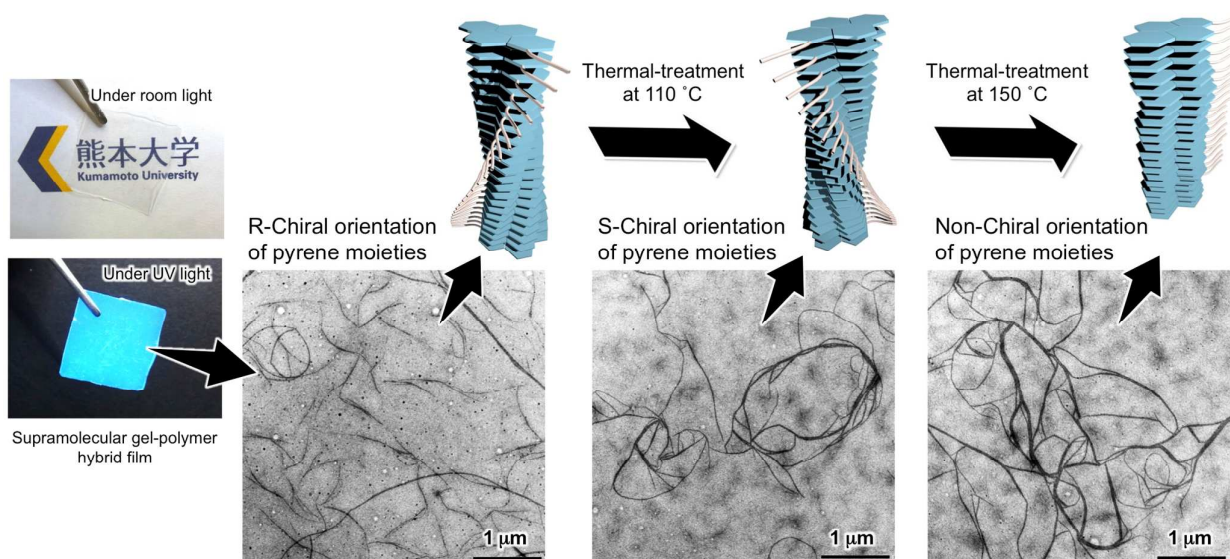
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