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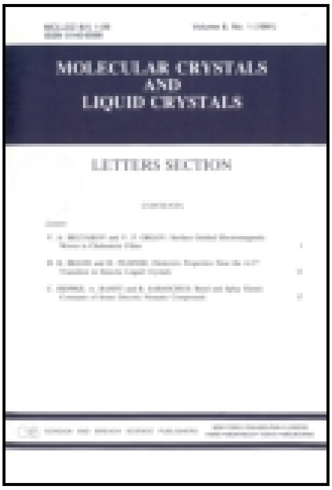

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# "Molecular Rope Curtain" Type of Liquid Crystals Based on a Sliding Graft Copolymer Having Mobile PEG Side Chains

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# “Molecular Rope Curtain” Type of Liquid Crystals Based on a Sliding Graft Copolymer Having Mobile PEG Side Chains

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*A sliding graft copolymer having a polyrotaxane main chain and side chains of polyethylene glycol with a molecular weight of 2000 (PEG2000) was found to be a novel “molecular rope curtain” type of liquid crystalline material, which displayed a smectic A mesophase between 51 °C and 250 °C without any rigid mesogenic moieties.*

**Keywords:** Polyrotaxanes; sliding graft copolymers; smectic A; Grandjean terrace textures; small angle X-ray diffraction

## Introduction

A series of supramolecules with topologically interlocked internal structures of their components, including polyrotaxanes, polycatenanes, calixarenes, and pillararenes, have been subjected to much more attention recently, not only for investigations of their fundamental properties [1] but also as applications of attractive functional materials with novel properties [2], arising from the degree of freedom of their components. Among the family of supramolecules, a polyrotaxane consisting of polyethylene glycol (PEG) axes and $\alpha$-cyclodextrin ($\alpha$-CD) wheels is one of the most enthusiastically investigated candidates [2] after the first successful synthesis by Harada et al. [3] A number of unique, intriguing, and fascinating properties of the PEG/CD polyrotaxane and polyrotaxane-derived materials arise from the distinctive free sliding and rotation of CD wheels in the polyrotaxane [2]. Changes in properties of the polyrotaxane such as its solubility, gelation behavior, and liquid crystallinity with introduction of various functional groups onto the CD rings have been reported [4,5]. As one of these polyrotaxane derivatives, “sliding graft copolymers (SGCs),” [6,7] i.e., novel types of copolymers possessing freely sliding/rotating side chains were also synthesized by polymerization or grafting of side chains onto the rings of the polyrotaxane. Previous studies on SGCs indicated the formation of a 3D supramolecular network by cross-linking of side chain terminals [6] or the construction of “molecular rope

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*Corresponding authors, J. Araki and K. Ohta. Fax: +81-268-21-5587. E-mail: jun@shinshu-u.ac.jp; Tel. & Fax: +81-268-21-5492. E-mail: ko52517@shinshu-u.ac.jp curtain" structure, in which each CD ring in a single polyrotaxane has one side chain grafted on to it [7].

Various modification strategies and resulting functionalization of polyrotaxanes are expected to provide new functional polymers having a high degree of freedom of molecular movements and therefore extend the usability of polyrotaxane derivatives in the field of materials chemistry. Among preceding investigations on such modifications, preparations of liquid crystalline polyrotaxane derivatives have been examined recently by several researchers; e.g., a thermotropic liquid crystalline polyrotaxane derivative with biphenyl mesogenic groups on CD rings was reported [8]. Another investigation indicated rigidification of a highly included moiety in a polyrotaxane [9], implying the formation of lyotropic liquid crystals; it was indeed indicated by formation of a lyotropic chiral nematic liquid crystal by a polyrotaxane consisting of $\alpha$-CDs and an axis of a $\pi$-conjugated polymer [10]. Formation of liquid crystalline phases by these polyrotaxane derivatives seems rather reasonable, since all of them possess a mesogenic moiety, which has a liquid crystalline phase on its own. On the other hand, we report in this study that the formation of a thermotropic liquid crystalline phase is induced by a flexible "rope-curtain like" SGC, i.e., a supramolecule with a relatively low degree of inclusion ($\sim$ 25%) and flexible PEG side chains, without any mesogenic moieties.

## Materials and Methods

### *Synthesis of SGC*

The SGC molecules having side chains of monomethoxy PEG with a molecular weight of 2000 (mPEG2000) were synthesized according to previously reported methods [7]. The synthesis is briefly summarized as follows: the terminal hydroxyl groups of mPEG2000 (20 g, 10 mmol hydroxyls) were converted to carboxyl groups *via* TEMPO-mediated oxidation (200 mg, $8.88 \times 10^{-4}$ mol), sodium bromide (200 mg, $1.94 \times 10^{-3}$ mol), and sodium hypochlorite (in a molar ratio of 2.2–2.5 times that of the hydroxyls in mPEG2000) in 200 mL of an aqueous solution at a pH ranging from 10 to 11, followed by extraction with dichloromethane and precipitation in diethyl ether. A polyrotaxane containing an axis of PEG with an average molecular weight of 35,000, 90–100 CDs, and end-cap moieties of adamantine was synthesized according to previous reports [11]. A solution of mPEG2000-COOH (2.6 g, 1.30 mmol of –COOH) and 1,1′-carbonylbis-1*H*-imidazole (0.213 g, 1.31 mmol) in dry DMAc (20 mL), which was stirred for 2 hr at room temperature, was added to a solution of the PR (100 mg, 1.31 mmol hydroxyls) in 10 mL of DMAc containing 6 wt% lithium chloride. The resulting mixture was further stirred at 60 °C overnight, followed by addition of 2 mL of methanol and further stirring at 60 °C for 2 hr. Finally, the sample was purified by thorough dialysis for 5 days against deionized water using a dialysis membrane (Spectra/Por®6, molecular weight cut off 50000) and subsequent fractionation using a size exclusion chromatography column (Cellufine GCL-2000, 2.6 cm i.d. × 90 cm) with water as the eluent at 4.32 mL/min, giving the SGC sample as a white solid (typical yield is 240–300 mg).

The obtained SGC can be briefly described as consisting of an axis of PEG with a molecular weight of 35,000, 90–100 of $\alpha$-CDs, adamantine end-cap moieties, and side chains of mPEG2000. The average number of the mPEG2000 side chains was estimated to be 75 per SGC from molecular weight determination [7], although this has not been precisely determined yet. The estimation suggests a schematic "rope-curtain like" structure for the SGC, i.e., one-by-one grafting of mPEG2000 onto a CD as stated above.

### *Measurements*

Phase transition behavior of the present polymer was observed using a polarizing optical microscope (Olympus BH2) equipped with a Mettler FP82HT hot stage and a Mettler FP-90 Central Processor, as well as using a Shimadzu DSC-50 differential scanning calorimeter. The mesophases were identified by using a small angle X-ray diffractometer (Bruker Mac SAXS System) using Cu-K$\alpha$ radiation ($\lambda = 0.1542$ nm) and equipped with a temperature-variable sample holder adopted from a Mettler FP82HT hot stage [12]. The measurable range of this SAXS system is from 0.30 nm to 10.00 nm and the temperature range is from room temperature to 375 °C [12].

## Results and Discussion

As can be seen from Fig. 1(a), the SGC virgin sample at room temperature displayed birefringent beads between cross polarizers, and it was rigid when pressed between the glass slide and the cover glass; hence, it is crystalline at room temperature. On heating up to 65 °C it turned into a viscous paste, which showed softness when the cover glass was pressed. As can be seen from Fig. 1(b), a Grandjean terrace texture appeared for this phase; it is a characteristic of layered structures in smectic mesophases [13]. Therefore, this mesophase is one of the smectic mesophases. As can be seen also from this photomicrograph, it showed partial homeotropic alignment without birefringence. The coexistence of birefringent and nonbirefringent domains is consistent with a smectic A phase. After cooling down to room temperature, the SGC virgin sample turned back into rigid crystals showing strong birefringence (Fig. 1(c)). The SGC sample has been already reported to show a large endothermic peak at 51 °C in DSC measurement [7]. Therefore, the endothermic peak corresponds to the melting point from a crystalline phase to a smectic phase.

For further confirmation of these phase identifications, we carried out temperature-dependent small-angle X-ray diffraction measurements of the SGC polymer at room temperature and at 65 °C. As shown in Fig. 2(a), the XRD pattern of the SGC at room temperature indicated sharp reflection peaks at $2\theta$ values of 14.84°, 18.92°, 23.01°, and 26.15°, which corresponded to the d-spacing values ($d_{\mathrm{obs}}$) of 0.597, 0.469, 0.387, and 0.341 nm. All these peaks coincided with those of crystalline PEG [14,15], and the first three peaks were those from (021), (120), and (112) planes [15]. None of the reflection peaks appeared at $2\theta$ regions lower than 5°, indicating an absence of long-ranging structures in the SGC at room temperature. On heating to 65 °C, all of the abovementioned reflection peaks disappeared to leave a broad shoulder over 5°–30°, whereas another reflection peak appeared at $2\theta = 1.25°$ ($d_{\mathrm{obs}} = 7.05$ nm), as shown in Fig. 2(b). The observed spacing $d_{\mathrm{obs}} = 7.05$ nm could be assigned to a (002) reflection, although it was impossible to detect the (001) reflection at 14.1 nm due to our instrumental limitations (see the experimental section). Our present study is consistent with the contour length of mPEG2000 of 13.18 nm, which can be estimated from calculations based on a PEG segment length of 0.29 nm [16]. The value of 14.1 nm agreed with the calculated contour length of mPEG2000. In addition, our previous DSC measurements of the SGC indicated a large endothermic peak at 51 °C, i.e., the melting point of mPEG2000, which was used as side chains, and the behavior was explained as a free sliding of the melted mPEG2000 side chains while the rest of the SGC molecule remained stationary [7]. By considering the present X-ray data and polarized optical microscopic observations, we concluded that the SGC shows a thermotropic smectic A phase having layers 14.1 nm in thickness.

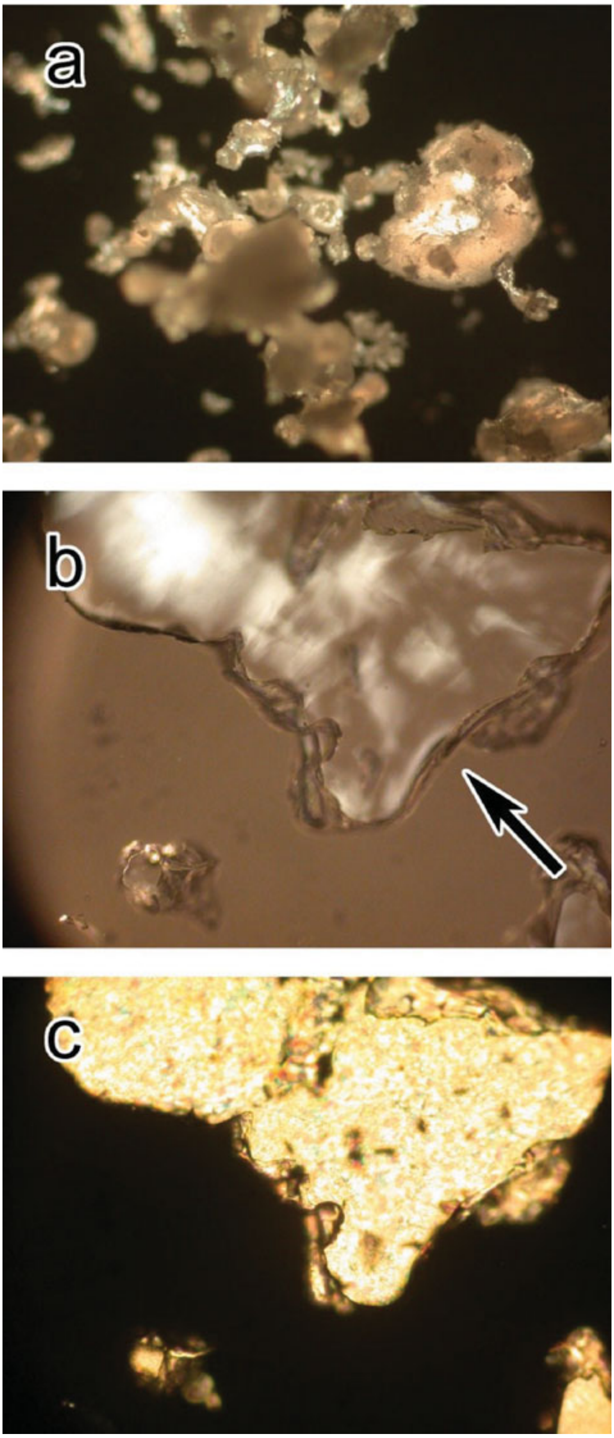

**Figure 1.** Polarized optical micrographs of mPEG2000-SGC: (a) crystalline phase at room temperature, (b) smectic A phase at 65 °C, and (c) crystalline phase after cooling down again to room temperature. The arrow in (b) indicates typical Grandjean terraces.

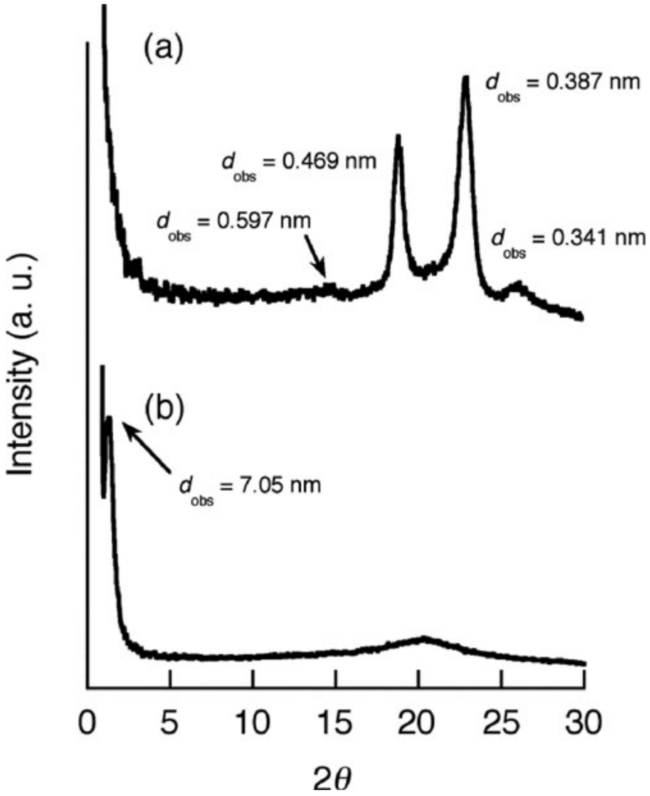

**Figure 2.** Small-angle X-ray diffraction patterns of mPEG2000-SGC: (a) at room temperature and (b) at 65 °C.

One of the unique features of the abovementioned smectic A phase shown by the SGC, is its origin of liquid crystallinity; the molecular structure of the SGC obviously lacks any mesogenic moieties like cyanobiphenyl groups, which could be responsible for liquid crystal formation. Although the high degree of coverage of the PEG axis by CDs might make the polyrotaxane molecules rigid as described above [9], the inclusion ratio

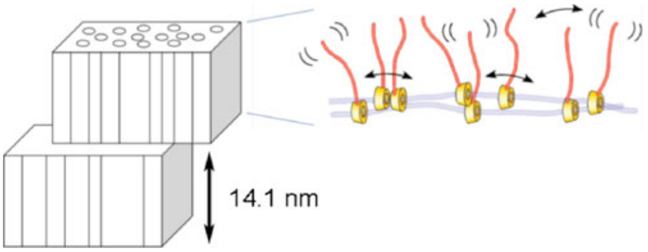

**Figure 3.** Proposed mechanism of liquid crystalline formation by the present SGC: one-directional free sliding of cyclodextrins together with PEG2000 side chains through the polyethylene glycol main chain. Accordingly, this smectic A mesophase has a 1D layer due to PEG2000 side chains with 2D disorder of the side chains due to the free sliding in the layer.

of the SGC molecules used in the present study was limited to 25% [7], and random distribution of CDs along the PEG axis should give diverse lengths of tubular moieties, leading to a decrease in the possibility of liquid crystal formation. Similar instances of liquid crystalline phases formed by flexible, non-mesogenic molecules has been quite limited to, e.g., those by an amphiphilic graft copolymer of a polystyrene main chain grafted with stearyl–polyethylene oxide side chains [17], although none of the details on the formed mesophase were given. The CD molecules grafted with mPEG2000 are "entrapped" on an axis of PEG35000, but they can freely slide along the PEG35000 axis as they are not covalently bound at fixed points. Therefore, they can demonstrate a melting behavior as if they are free molecules above 51 °C, i.e., a melting point of mPEG2000. Our proposed mechanism of liquid crystalline formation by the present SGC is illustrated in Fig. 3. As can be seen from this figure, this mesomorphism originates from one-directional free sliding of cyclodextrins together with PEG2000 side chains through the PEG main chain; i.e., this smectic A mesophase has a 1D layer due to PEG2000 side chains with 2D disorder of the side chains due to the free sliding in the layer. This "molecular rope curtain" type of liquid crystal is the first example in liquid crystals, to the best of our knowledge.

Since the SGC molecules used in the present study indicate no other endothermic peaks from 65 °C to 250 °C [7], transitions to any other liquid crystalline phases are unlikely to exist. However, variations of types, numbers, lengths (molecular weight values) of the side chains, and inclusion ratios of the parent polyrotaxane should drastically and diversely alter the liquid crystalline behavior of the obtained SGC molecules.

## References

[1] (a) Harada, A. (1996). *Coord. Chem. Rev.*, *148*, 115. (b) Takata, T. (2006). *Polym. J.*, *38*, 1.

[2] (a) Araki, J., & Ito, K. (2007). *Soft Matter*, *3*, 1456. (b) Ito, K. (2010). *Curr. Opin. Solid State Mater. Sci.*, *14*, 28. (c) Ito, K. (2007). *Polym. J.*, *39*, 489. (d) Loethen, S., Kim, J.-M., & Thompson, D. H. (2007). *Polym. Rev.*, *47*, 383.

[3] (a) Harada, A., Li, J., & Kamachi, M. (1992). *Nature*, *356*, 325. (b) Harada, A., Li, J., Nakamitsu, T., & Kamachi, M. (1993). *J. Org. Chem.*, *58*, 7524. (c) Harada, A., Li, J., & Kamachi, M. (1994). *J. Am. Chem. Soc.*, *116*, 3192.

[4] (a) Araki, J., & Ito, K. (2006). *J. Polym. Sci. A Polym. Chem.*, *44*, 532. (b) Araki, J., & Ito, K. (2006). *J. Polym. Sci. A Polym. Chem.*, *44*, 6312.

[5] (a) Kidowaki, M., Zhao, C.-M., Kataoka, T., & Ito, K. (2006). *Chem. Commun.*, *39*, 4102. (b) Kataoka, T., Kidowaki, M., Zhao, C.-M., Minamikawa, H., Shimizu, T., & Ito, K. (2006). *J. Phys. Chem. B*, *110*, 24377.

[6] Araki, J., Kataoka, T., & Ito, K. (2008). *Soft Matter*, *4*, 245.

[7] Araki, J., Ohkawa, K., Uchida, Y., & Murakami, Y. (2012). *J. Polym. Sci. A Polym. Chem.*, *50*, 488.

[8] (a) Kidowaki, M., Nakajima, T., Araki, J., Inomata, A., Ishibashi, H., & Ito, K. (2007). *Macromolecules*, *40*, 6859. (b) Inomata, A., Kidowaki, M., Sakai, Y., Yokoyama, H., & Ito, K. (2011). *Soft Matter*, *7*, 922. (c) Hu, T., Xie, H., Chen, L., Chen, S., & Zhang, H. (2011). *Polym. Bull.*, *67*, 937.

[9] (a) Araki, J., & Ito, K. (2007). *Polymer*, *48*, 7139. (b) Fleury, G., Brochon, C., Schlatter, G., Bonnet, G., Lapp, A., & Hadziioannou, G. (2005). *Soft Matter*, *1*, 378.

[10] Terao, J., Tsuda, S., Tanaka, Y., Okoshi, K., Fujihara, T., Tsuji, Y., & Kambe, N. (2009). *J. Am. Chem. Soc.*, *131*, 16004.

[11] (a) Araki, J., Zhao, C.-M., & Ito, K. (2006). *Macromolecules*, *38*, 7524. (b) Araki, J. (2010). *J. Polym. Sci: Part A: Polym. Chem.*, *48*, 5258 (Erratum: Araki, J. (2010). *J. Polym. Sci: Part A: Polym. Chem.*, *49*, 1298).

[12] (a) Hachisuga, A., Yoshioka, M., Ohta, K., & Itaya, T. (2013). *J. Mater. Chem. C*, *1*, 5315. (b) Tauchi, L., Nakagaki, T., Shimizu, M., Itoh, E., Yasutake, M., & Ohta, K. (2013). *J. Porphyrins Phthalocyanines*, *17*, 1080.
[13] Grandjean, M. F. (1918). *Compt. Rend.*, *166*, 165.
[14] Barnes, W. H., & Ross, S. (1936). *J. Am. Chem. Soc.*, *58*, 1129.
[15] Bortel, E., Hodorowicz, S., & Lamot, R. (1979). *Makromol. Chem.*, *180*, 2491.
[16] Zdyrko, B., Varshney, S. K., & Luzinov, I. (2004). *Langmuir*, *20*, 6727.
[17] Ji, J., Feng, L., Qiu, Y., Yu, X., & Barbosa, M. A. (2000). *J. Colloid Interface Sci.*, *224*, 255.