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Self-Assembled Lamellar Nanostructures of Wholly Aromatic Rod–Rod-Type Block Molecules

**Teruaki Hayakawa,*,[†] Raita Goseki,[†] Masa-aki Kakimoto,[†] Masatoshi Tokita,[†]
Junji Watanabe,[†] Yonngui Liao,[‡] and Shin Horiuchi[‡]**

*Department of Organic and Polymeric Materials, Graduate School of Science and
Engineering, Tokyo Institute of Technology, 2-12-2-S8-26 O-okayama,
Meguro-ku, Tokyo 152-8552, Japan, and Nanotechnology Research Institute,
National Institute of Advanced Industrial Science and Technology, Central 5,
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

hayakawa.t.ac@m.titech.ac.jp

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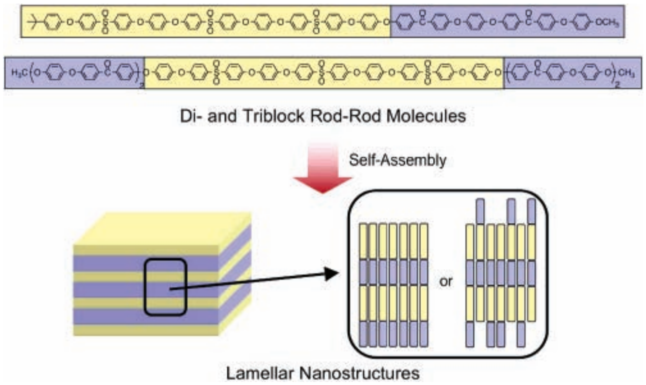
ABSTRACT



Wholly aromatic rod–rod type di- and triblock molecules, oligo(ether sulfone)-*b*-oligo(ether ketone)s (OES-OEK), were synthesized to study a solid-state self-assembled nanostructure. The OES and OEK segments in the block molecules form segregated crystalline domains. The energy-filtering transmission electron microscopy images revealed that the di- and triblock OES-OEK co-oligomers formed lamellar nanostructures with a periodicity of ∼9 and 13 nm, respectively.

The study of molecular self-assembly enables us to gain an understanding of the important factors leading to a variety of functional materials based on nano- or supramolecular structures.[1] Block molecules such as block co-oligomers or copolymers are well-known self-assembling materials that offer intriguing tunable built-in nanoscopic domains and tailored surface or bulk properties.[2] A variety of coil−coil-type[3] and rod−coil-type[4] block molecules have been widely studied and found to exhibit various microphase-separated nanostructures such as spheres, cylinders, lamellae, unique supramolecular structures such as mushroom-shaped nanostructures[4d] and nanoribbons,[4e] or hierarchical structures over multiple length scales.[4f,g] Coil segments are commonly based on polystyrene or poly(ethylene glycol), while rod segments are commonly based on liquid crystalline molecules or aromatic π-conjugated molecules. Very few attempts, how-

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[†] Tokyo Institute of Technology.
[‡] National Institute of Advanced Industrial Science and Technology.

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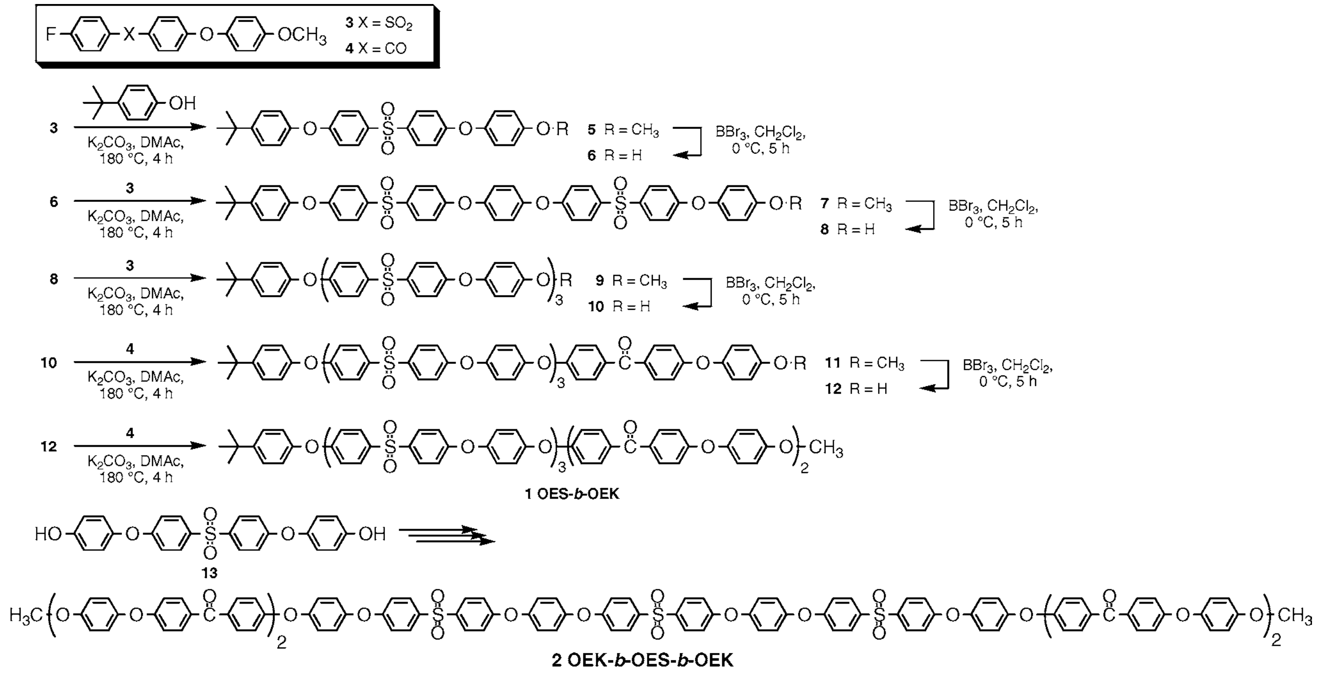
Scheme 1. Synthesis of OES-*b*-OEK **1** and Chemical Structure of OEK-*b*-OES-*b*-OEK **2**



ever, have been made to study wholly aromatic rigid-rod block molecules, namely, rod–rod-type block molecules.[5] Wang et al.[5b] developed rod–rod conjugated diblock copolymers of alkyl-substituted oligo(phenylenevinylene)-*b*-oligothiophene that self-assembled to lamellae. The study of wholly aromatic rod–rod type block molecules is essential not only for fundamental understanding but also to generate novel self-assembling nanomaterials with intriguing properties from a variety of conventional, but little studied, wholly aromatic condensation polymers. Herein, we report synthesis and self-assembly of wholly aromatic oligo(ether sulfone) (OES) and oligo(ether ketone) (OEK) di- and triblock co-oligomers (OES-*b*-OEK and OEK-*b*-OES-*b*-OEK). Amorphous aromatic poly(ether sulfone)s and crystalline poly(ether ketone)s are well-known super-engineering plastics. Crystallization of the block OEK oligomers is expected to induce nanostructure formation in the solid state. Characterization of crystalline nanostructures can be carried out by using wide and small-angle X-ray scattering (WAXS and SAXS) and energy-filtering transmission electron microscope (EFTEM).[6]

Well-defined block co-oligomers and copolymers have been prepared by a variety of facile and reliable synthetic methods such as living radical polymerization[7] and atom transfer radical polymerization.[8] However, it is difficult to synthesize block architechtures in condensation polymers as they are typically prepared by a step-growth mechanism. While Yokozawa et al. have developed a polymerization method of chain-growth polycondensation to yield condensation block copolymers based on aromatic polyamides with a narrow molecular distribution,[9] it is still too limited in scope to access polymers desired for this study. Thus, the well-defined di- and triblock molecules of OES-*b*-OEK and OEK-*b*-OES-*b*-OEK were synthesized by stepwise aromatic nucleophilic substitution and deprotection reactions (Scheme 1). For constructing OES and OEK segments, we first synthesized 4-fluoro-4′-(4″-methoxyphenyloxy)diphenyl sulfone (**3**) and 4-fluoro-4′-(4″-methoxyphenyloxy)diphenyl ketone (**4**) as building molecules from 4,4′-difluoro diphenyl sulfone or ketone and 4-methoxyphenol, respectively. For synthesis of diblock OES-*b*-OEK (**1**), **5** was prepared from **3** and *tert*-butyl phenol with subsequent deprotection of the methoxy group by boron tribromide to access the next nucleophile.

The aromatic nucleophilic substitution reaction of **6** with **3** was carried out in the presence of potassium carbonate in

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DMAc at 180 °C for 4 h in nitrogen atomosphere to yield **7**. The methoxy end group was then removed to access nucleophile **8**. The yield for each aromatic nucleophilic substitution and deprotection reaction pair was 94%. This procedure was repeated once more to afford nucleophile **10**. OEK was introduced to OES using identical substitution-deprotection chemistry, but using **4** rather than **3** to propagate the chain. After two cycles of adding **4**, the target OES-*b*-OEK was obtained. The triblock oligomer was prepared with identical methodology by using sulfone **13** as the starting molecule. After one cycle of **3** and two cycles of **4**, the target OEK-*b*-OES-*b*-OEK was obtained.

Note that the chloro analogues of **3** and **4** yielded significant scrambling of the starting material and side products such as 4,4′-(4″,4‴-di-*tert*-butylphenyloxy)diphenyl sulfone or ketone. Presumably, this is due to the nucleophilicity of the chloride ion to facilitate an ether exchange reaction. No reaction conditions were observed to eliminate the ether exchange reaction when the chloride analogues were used.

OES-*b*-OEK and OEK-*b*-OES-*b*-OEK chemical structures were characterized by FT-IR, ^{1}H NMR, and MALDI-ToF MS. The MALDI-ToF MS spectra (Figure 1) are consistent with calculated values for OES-*b*-OEK and deprotected OEK-*b*-OES-*b*-OEK at 1712.4 and 2236.4 *m*/*z*. The FT-IR and NMR spectra are also consistent with the formation of the desired block oligomers.

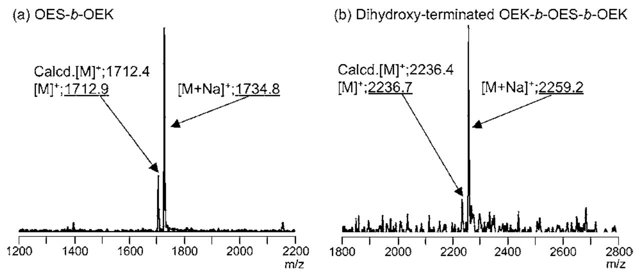

Figure 1. MALDI-ToF MS spectra of (a) OES-*b*-OEK and (b) dihydroxy-terminated OEK-*b*-OES-*b*-OEK.

The thermal behavior of OES-*b*-OEK and OEK-*b*-OES-*b*-OEK was examined by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and polarized optical microscopy (POM). The TGA 10% weight losses in nitrogen of OES-*b*-OEK and OEK-*b*-OES-*b*-OEK were observed at 500 and 483 °C, respectively. The DSC traces on the second heating showed two distinct thermal transitions for both OES-*b*-OEK and OEK-*b*-OES-*b*-OEK. Baseline shifts observed at 119 and 126 °C are consistent with the glass transition (T_g) of the OES block of OES-*b*-OEK and OEK-*b*-OES-*b*-OEK, respectively. Endothermic peaks were also observed at 202 and 223 °C. A phase transition to an isotropic phase was found to occur at these temperatures by means of POM observations. These transition temperatures showed good agreement with those of the homo-oligomer of OES and OEK. The T_g of the OES homo-trimer was 128 °C and the transition of the OEK homo-dimer from the crystalline to isotropic phase was observed at 213 °C by DSC.

Optical textures appeared under POM with crossed polarizers during annealing. The textures formed at 160 and 200 °C for OES-*b*-OEK and OEK-*b*-OES-*b*-OEK, respectively, after cooling at 10 °C min^{-1} from 250 °C. The texture growth was very slow, occurring over several hours. The WAXS pattern of the block molecules annealed under the same conditions includes several reflections (Figure 2a,b). These reflections are explained by the superposition of the respective diffraction patterns measured for the OES and OEK homo-oligomers (Figure 2c,d), suggesting that the OES and OEK segments in the block molecules segregate and crystallize, which is consistent with the optical textures observed in POM. The SAXS pattern of OES-*b*-OEK includes a scattering maximum with a spacing of 91 Å, which corresponds to the molecular length of 92 Å calculated for the most stretched configuration. These indicate that the more stretched molecules of OES-*b*-OEK must be in head-to-tail (OES-to-OEK) orientation, as if head-to-head or tail-to-tail configurations were present then the scattering maximum would indicate a spacing of approximately 184 Å and this is not seen. However, no such layered structure was not indicated for OEK-*b*-OES-*b*-OEK by the SAXS method.

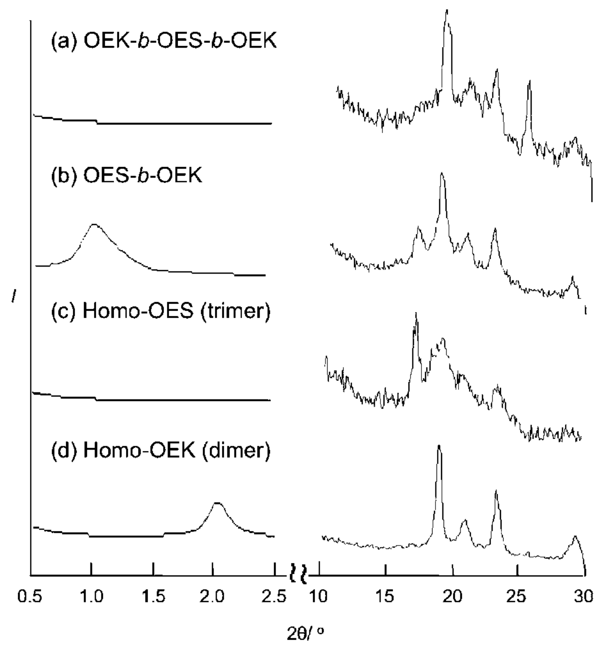

Figure 2. WAXS and SAXS profiles of (a) OEK-*b*-OES-*b*-OEK, (b) OES-*b*-OEK, (c) homo-OES (trimer), and (d) homo-OEK (dimer).

Further confirmation for the formation of self-assembled structures of OES-*b*-OEK and OEK-*b*-OES-*b*-OEK was provided by energy-filtering transmission electron microscopy (EFTEM). The annealed films were embedded in epoxy resin and microtomed to give specimens of 50 nm thickness. Micrographs of the energy-filtered images at 200 ± 10 eV

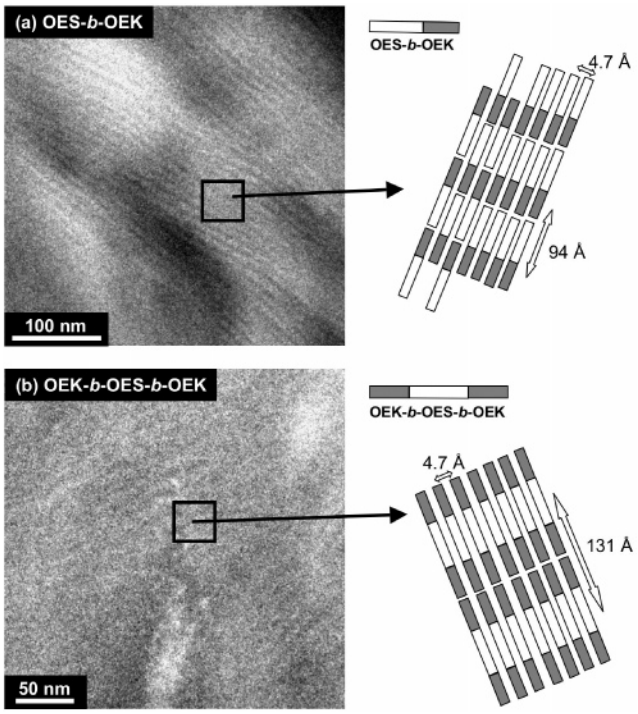

Figure 3. EFTEM images of (a) OES-*b*-OEK and (b) OEK-*b*-OES-*b*-OEK. Schematic illustrations of the lamellar nanostructures are oriented with respect to the EFTEM image.

energy losses are shown in Figure 3. These nanostructures were unobservable in the corresponding conventional TEM images with conventional staining techniques. Sulfur distribution images could be created by the "two-window jump ratio" method[6d] using the sulfur $L_{2,3}$-ionization edge at 160 eV, in which two energy-loss images at 130 and 200 eV with the energy windows of 20 eV were used for the pre- and postedge images, respectively.[6c] Those maps allows us to assign the brighter lamellae to the OES blocks. The images for both OES-*b*-OEK and OEK-*b*-OES-*b*-OEK films clearly show a layered nanosacle structure. However, the orientation along the long axis of OEK-*b*-OES-*b*-OEK is lower than that of OES-*b*-OEK. This is agreement with the absence of the scattering maximum in the SAXS of OEK-*b*-OES-*b*-OEK. The layer spacings in the nanostructures of OES-*b*-OEK and OEK-*b*-OES-*b*-OEK films were approximately 94 and 131 Å, respectively. The layer spacing of OES-*b*-OEK is in good agreement with that of the SAXS characterization. The EFTEM images confirmed the formation of lamellar nanostructures in OES-*b*-OEK and OEK-*b*-OES-*b*-OEK films.

In summary, we have studied syntheses and self-assembled structures for new block molecules of wholly aromatic rod−rod-type block molecules, OES-*b*-OEK and OEK-*b*-OES-*b*-OEK. The well-defined block molecules were successfully synthesized in high yields. The OES-*b*-OEK and OEK-*b*-OES-*b*-OEK formed self-assembled lamellar nanostructures with a periodicity of approximately 9 and 13 nm, respectively. These architectures are very promising to applications such as nano- or microelectronics, membranes, and templating through manipulation of the block length and composition.

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Supporting Information Available: Synthetic details and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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