Polystyrene-\textit{b}\text{-}\text{poly}(4-hydroxy styrene) (SH) with narrow molecular weight distribution $(M_w/M_n<1.1)$ has been successfully synthesized by living anionic polymerization technique. It was confirmed that the SH diblock copolymer with molecular weight of 27k and with volume fraction of S of 0.68 showed the definite alternative lamellar structure with domain spacing of 20.8 nm (the half pitch (HP) of 10.4 nm). Furthermore, monodisperse SHSH tetraliblock copolymers with molecular weight of 27k and 23k have been also synthesized, and from these copolymers formations of lamellar structure with the HP of 5.4nm and 4.9nm, respectively, were observed by TEM and SAXS measurements. Moreover, not only the synthesis of the block copolymers by anionic polymerization in experimental lab scale up to 25 g, but a preparation of well-defined block copolymers by large-scale anionic polymerization over 3 kg was also developed.

**Key words:** living anionic polymerization, block copolymer, high chi, multiblock copolymer, TEM, SAXS, large-scale polymerization

1. **Introduction**

It is well-known that block copolymer forms self-assembled structure, so-called microphase-separated structure in bulk [1-4]. The domain spacing of the microphase-separated structure corresponds to the molecular weight (degree of polymerization), which can be controlled by the living polymerization technique. Using the characteristics of block copolymers, they are considered to be utilized in various kinds of fields, e.g. material for bioscience, electric devices, chemical processing devices and lithography.

Nanolithography using block copolymer, also known as directed self-assembly (DSA), is an essential technology for next generation lithography to achieve nanoscale-, and cost-effective patterning technology [5-8]. A microphase-separated structure with the half pitch pattern formation around 10nm has been already accomplished to combine DSA with conventional lithography technique. The size and the resolution of the pattern are closely related to the chain dimension of the block copolymers. The next target for the nanoscale patterning using block copolymers is to form the microphase-separated structure with the half pitch less than 5 nm. For this purpose, precise synthesis such as living anionic polymerization has been utilized.

In previous three decades, fundamental and applied works concerning block copolymers by using living anionic polymerization have been remarkably progressed. Various kinds of multiblock copolymer such as ABC [9-11], ABCA [12], ABCD [13], ABC \textit{mikto}arm star copolymers [14-18], ABn \textit{mikto}arm graft copolymers [19] and etc. were synthesized for the morphological study for the academic viewpoints. Furthermore, the functional polymeric materials from the multiblock copolymers have been also prepared for the industrial viewpoint, that is, preparation of charge-mosaic membrane from BABCB pentablock copolymers by Fujimoto et al. [20-24] and fabrication of solid polymer electrolyte from block-graft copolymers by Hirahara et al. [25-31] was one of the outstanding examples of the frontier works using living anionic polymerization technique.

Recently, using highly-skilled living anionic polymerization techniques, we have successfully synthesized diblock copolymers with low molecular weight, and the obtained block copolymer has formed the definite microphase-separated structure
(alternative lamellar structure) with the half pitch of less than 10 nm [32]. However, the formation of the microphase-separated structure with the narrower half pitch (less than 5 nm) by the same diblock copolymer species should be difficult. Because the interaction parameter, $\chi$, of two polymers is relatively low, the block copolymers tend to become miscible. Therefore, molecular design of block copolymer consisting of strong segregated components (high $\chi$) such as polystyrene (S) and poly(4-hydroxystyrene) (H) are required and furthermore multiblock copolymers such as HSH-type and SHSH-type instead of the simple SH diblock copolymer are utilized to obtain narrower domain spacing.

Moreover, not only the synthesis of the multiblock copolymers by anionic polymerization in experimental lab scale around 10g, but a preparation of well-defined block copolymers by an advanced large-scale anionic polymerization apparatus over 3kg was also developed.

2. Experimental
2.1. Materials
Monomers such as styrene and 4-tert-butoxy styrene were purchased from Nakarai Tesque Inc. and Hokko Chemical Co., Ltd, respectively. They were purified with benzophenone sodium. The procedures for the purification of the monomers were the same manner reported previously [33]. An initiator, sec- butyl lithium (sec-BuLi) was purchased from Asia lithium Co. Solvent for polymerization, tetrahydrofuran (THF) were purified by distillation in vacuo in the presence of the 1,1-diphenyl hexyllithium after the usual purification [33].

2.2. Preparation of block copolymers
Block copolymers were synthesized by living anionic polymerization by multi-step sequential monomer addition in tetrahydrofuran with sec-BuLi as an initiator at -78 °C under vacuum or argon atmosphere. After being quenched with methanol, the obtained polymer was precipitated in excess amount of methanol, and freeze-dried. Poly(4-tert-butoxy styrene) (B) was transformed into poly(4-hydroxystyrene) by hydrolysis with hydrochloric acid in 1,4-dioxane. Example of the synthetic scheme for SH diblock and SHSH tetrablock copolymer are shown in Scheme 1.

2.3. Molecular characterization
Weight-average molecular weights, Mw, of the samples were measured by light scattering in THF at 35 °C with a multi-angle light scattering apparatus, MALD, Dawn-EOS (Wyatt Technology Co.), and molecular weight distribution, Mw/Mn, was determined by SEC. The SEC system was composed of pump, LC-20AD (Shimadzu Co.), UV detector, SP2-20A (Shimadzu Co.), RI detector, RID-10A (Shimadzu Co.), column oven, CTO-20A (Shimidzu Co.) and three SEC columns, KW-804 (Shodex Co.). The eluent was THF and the flow rate was 1.0 mL/min. All samples were dissolved in the eluent, THF, at a polymer concentration of 0.1-0.2 %. The column temperature was kept constant at 40 °C. The compositions of the block copolymers were estimated from $^1$H NMR experiments with a 500 MHz $^1$H NMR spectrometer.

2.4. Morphological observation
Sample films for morphological observation were prepared by solvent casting from dilute solution of THF, the experimental procedures were described previously. As-cast films were dried in a vacuum oven for 6 hours, followed by annealing at 150 °C for 3 days. The glass transition temperature ($T_g$) was

Scheme 1. Synthetic scheme of SH and SHSH block copolymers.
measured with differential scanning calorimetry (DSC). The measurements were performed at a heating rate of 10 °C/min after heating for 1 h and quenching to -50 °C under a nitrogen atmosphere. \( T_g \) was estimated from the midpoint of the heat capacity jump. For transmission electron microscopy (TEM) observation, the ultrathin sections were cut from film specimens by an ultramicrotome, Leica Ultracut UCT, and a diamond knife. For the electron staining, the ultrathin sections of sample films were stained with aqueous cesium carbonate (Cs₂CO₃) solution. It is known that when the ultrathin sections are stained with Cs₂CO₃, while the contrast for H domain is enhanced. The TEM instrument used was JEM-1400, operated under the acceleration voltage of 120 kV. Small-angle X-ray scattering (SAXS) measurements were performed using Nanoviewer of Rigaku Co. Ltd. The camera length, \( L (\text{mm}) \), and the wavelength of the X-ray beam, \( \lambda (\text{nm}) \), were ca. 1.0 m and 0.150 nm. X-ray beam was irradiated from the edge direction, where incidents X-ray are parallel to the film surface.

3. Results and discussion

3.1. Preparation of block copolymers

Table 1 summarizes the molecular characteristics of three block copolymers, it was confirmed that all the block copolymers have narrow molecular weight distribution (\( M_w/M_n < 1.1 \)), and the volume fractions of two components are almost the same. And it was also confirmed that degree of hydrolysis in the transformation from poly(4-tert-butoxystyrene) into poly(4-hydroxystyrene) by acidolysis was almost quantitative (over 0.95).

3.2. Morphological observation and quantitative analysis of domain size

Table 2 lists glass transition temperatures determined by DSC for SH diblock and two SHSH tetrablock copolymers. Three block copolymer samples show two distinct \( T_g \)s originated in polystyrene and poly(4-hydroxystyrene). It was expected from the results that three block copolymers had phase-separated structures.

Figure 1 shows TEM images of microphase-separated structures of SH diblock and two SHSH tetrablock copolymers.

All the samples show definite alternating lamellar structures. From the TEM images, the domain spacing of the lamellar structures were roughly estimated as 20 nm, 12 nm and 10 nm, respectively.

Furthermore, the period of the lamellar structures of these block copolymers were quantitatively determined by SAXS measurements shown in Figure 2 as 20.8, 10.8 and 9.9 nm, respectively, that means the half pitch (HP) of the lamellar structures are 10.4, 5.4 and 4.9 nm, respectively.
To prepare the narrower domain spacing of microphase-separated structure by block copolymers, utilization of multiblock copolymer instead of simple diblock copolymer should be effective. In the case of AB diblock copolymer, the diblock copolymers have only end blocks that always take a tail conformation, while multiblock copolymers such as ABAB have a middle block that can take either a loop and bridge conformation. Comparing between the chain dimensions of a tail conformation and that of loop/bridge conformation with the same molecular weight, the latter should be smaller than the former. Accordingly, the domain spacing of multiblock copolymer with many block number should be shorter than that for simple diblock copolymer as shown in Figure 3.

Furthermore, we have recently attempted to synthesize the more strong-segregated XY block copolymer system with higher $\chi$ for narrower DSA patterning. Not only experimental lab scale synthesis of block copolymers by conventional anionic polymerization technique around 10g, but we have developed advanced large-scale anionic polymerization apparatus to prepare the well-defined block copolymers scaled over 3kg. Figure 4 shows the large-scale anionic polymerization apparatus. This apparatus consists of stainless steel reactor with high-speed rotating fin, electrical controller and turbo molecular vacuum pump. Degree of evacuation is measured by ULVAC Heliot 900. Attained evacuation of total system is $< 5 \times 10^{-5}$ Pa. Helium leak rate of total system is $< 5 \times 10^{-9}$ Pa·m$^3$/sec.

After setting of monomers, solvent, initiator and quencher to this apparatus, temperature and pressure can be controlled and multiblock copolymers with narrow molecular weight distribution are synthesized automatically. By using the apparatus, 3 kg of the block copolymer is synthesized in single batch.

Furthermore, development of larger-scale anionic polymerization apparatus to prepare the block copolymers scaled over 50 kg are on-going right now.

4. Conclusion

In this study, we have successfully synthesized a SH diblock copolymer with $M_w$ of 27k and two SHSH tetrablock copolymers with $M_w$ of 27k and 23k with narrow molecular weight distribution by
living anionic polymerization, and the obtained SH and SHSH copolymers have formed the alternative lamellar structure with the half pitch of 10.4 nm, 5.4 nm and 4.9 nm, respectively, observed by SAXS measurements.
Moreover, a large-scale living anionic polymerization apparatus for the preparation of well-defined block copolymers scaled over 3 kg per batch was developed.

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References