

Chain End Group-Induced Surface Ordering in Poly(styrene-*b*-4-vinylpyridine) Symmetric Diblock Copolymer Films

Xiqun JIANG[†], Keiji TANAKA, Atsushi TAKAHARA, Seiichi NAKAHAMA*, Tisato KAJIYAMA^{††}

Department of Materials Physics & Chemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

**Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan*

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ABSTRACT: The proton-terminated and fluoroalkyl-terminated poly(styrene-*b*-4-vinylpyridine) [P(St-*b*-4VP)] symmetric diblock copolymers were synthesized by a sequential anionic polymerization. The surface chemical composition, surface morphology and surface mechanical properties of the diblock copolymer thin films were investigated on the basis of the angular-dependent X-ray photoelectron spectroscopic (ADXPS) measurement and transmission electron microscopic (TEM) observations. The XPS results revealed that in the case of the proton-terminated P(St-*b*-4VP) film, the surface weight fraction of poly(4-vinyl pyridine)(P4VP) decreased dramatically after annealing above the glass transition temperature, T_g of P(St-*b*-4VP), resulting in the formation of polystyrene (PS) surface layer in order to minimize the interfacial free energy at air-polymer interface. Whereas, in the cases of the fluoroalkyl-terminated P(St-*b*-4VP) films [P(St-*b*-4VP)- $C_2C^F_x$ where $-C_2C^F_x$ shows fluoroalkyl end group], the surface weight fraction of P4VP decreased slightly and still was more than 30% even after the annealing treatment. TEM observation revealed that the lamellar structure was formed in all P(St-*b*-4VP). The surface order and orientation of lamellar structure were strongly influenced by the chain end group species. That is, in the case of the proton-terminated P(St-*b*-4VP) film, the lamellar structure was oriented parallel to the film surface and the outermost layer was composed of PS. On the other hand, in the case of P(St-*b*-4VP)- $C_2C^F_x$, the well-developed lamellae was tilted ca. 45 deg to the film surface and the alternating PS and P4VP layers were exposed to the air interface. These results indicate that the surface order and orientation of microphase-separated lamellar structure strongly depend on the chemical structure of the chain end group.

KEY WORDS Diblock Copolymers / Chain End Group / Surface Structure / Lamellar Structure / Fluoroalkyl Group /

Numerous theoretical and experimental studies have been done in order to understand the interfacial aggregation structure of block copolymer film.¹⁻⁶ It is well known that the bulk phase behavior of diblock copolymers depends on the two parameters: (i) χN where χ is the Flory-Huggins interaction parameter between block components and N is the degree of polymerization of the diblock copolymer, and (ii) the relative volume fraction of block chains in the diblock copolymer. If the two components in the diblock copolymer have an equal volume fraction, the lamellar structure is generally formed below the order-disorder transition temperature. On the other hand, the molecular aggregation state of the diblock copolymer film at the interface is quite different from the bulk one, and it is strongly influenced by the characteristics of free surface and substrate. The surface-induced and substrate-induced microphase separation and orientation have been observed in diblock copolymers and polymer blends.⁷⁻¹⁴ The surface and interfacial phase behaviors of diblock copolymers are determined by surface free energy and the conformational entropy of two blocks, in addition to the two parameters mentioned above. Generally, the lamellar structure of symmetrical diblock copolymers oriented parallel to the free surface and substrate in order to minimize the interfacial free energy. In the case of poly(styrene-*b*-methyl methacrylate) [P(S-*b*-MMA)] diblock copolymers, lamellar structure which oriented perpendicular to the polymer-substrate interface have been reported when the thin film was

confined between two rigid, flat substrate or when the interfacial free energy between polymer-substrate was tuned by deposition of PS-*r*-PMMA random copolymer on the substrate surface.¹⁵

Recent studies have been revealed that the chain end groups play a key role on the surface segregation of multicomponent mixtures.¹⁶⁻¹⁸ A remarkable surface enrichment of fluoroalkyl chain end groups and a surface excess of the component capped with fluoroalkyl chain end groups were reported for the blend film of polystyrene (PS) and deuterated PS with fluoroalkyl end groups, whereas the blend of hydrogenous and deuterated low molecular weight PS without fluorinated end group did not exhibit appreciable segregation.¹⁹ In our previous study, it was found that the surface localization of fluoroalkylsilyl end group in poly(styrene-*b*-4-vinylpyridine) [P(St-*b*-4VP)] diblock copolymer made the surface fraction of the P4VP block increased.²⁰ This result indicates that the surface-active end group induces the segregation of the component linked with end group to the air/polymer interface, and the surface composition of multicomponent system can be controlled by the chemistry of chain end group. However, little work has been done on the end group-induced surface phase behavior of microphase-separated diblock copolymer.

In this paper, the effect of chain end group chemistry on the surface aggregation structure and phase behavior of diblock copolymers have been further investigated employing the various fluoroalkyl-terminated and proton-terminated poly(styrene-*b*-4-vinylpyridine) symmetrical diblock copolymers. Generally, the PS component in P(St-*b*-4VP) forms the outermost layer in order to minimize the interfacial free energy at the air/polymer interface.

[†]Present address: College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P.R. China

^{††}To whom correspondence should be addressed.

Table I. Characterization of Diblock Copolymers

| No | Sample | Mn _{PS} ^a | Mn _{co} ^b | Mw/Mn _{co} | P4VP/wt% ^c |
|----|---|-------------------------------|-------------------------------|---------------------|-----------------------|
| 1 | P(St- <i>b</i> -4VP)-H | 6.9k | 15.7k | 1.17 | 56 |
| 2 | P(St- <i>b</i> -4VP)-C ₂ C ₈ ^F | 6.9k | 14.0k | 1.13 | 51 |
| 3 | P(St- <i>b</i> -4VP)-C ₂ C ₄ ^F | 6.9k | 15.7k | 1.17 | 56 |
| 4 | P(St- <i>b</i> -4VP)-C ₂ C ₈ ^F | 6.8k | 12k | 1.17 | 44 |
| 5 | P(St- <i>b</i> -4VP)-C ₂ C ₈ ^F | 8.4k | 15k | 1.18 | 45 |
| 6 | P(St- <i>b</i> -4VP)-C ₂ C ₈ ^F | 13.8k | 32k | 1.14 | 57 |

^a Mn of PS was determined by GPC. ^b Mn of diblock copolymer was evaluated from the Mn of PS and ¹H-NMR of copolymer. ^c P4VP weight fraction was determined by ¹H-NMR

When the perfluoroalkyl groups are incorporated into the end of P4VP block with higher surface free energy, it is interesting to investigate whether the surface-active effect of the end group of P4VP makes the P4VP component dragged to the surface (buoy effect) and can compete with the formation of the PS layer at the surface to form the lamellar layers being parallel to the surface. P(St-*b*-4VP) system is chosen, because the P(St-*b*-4VP) system is suitable for this purpose of this study. Because of the large χ between two blocks, the microphase-separation can be observed even the diblock copolymer has a relatively low molecular weight in which the surface-active effect of end group is notable.

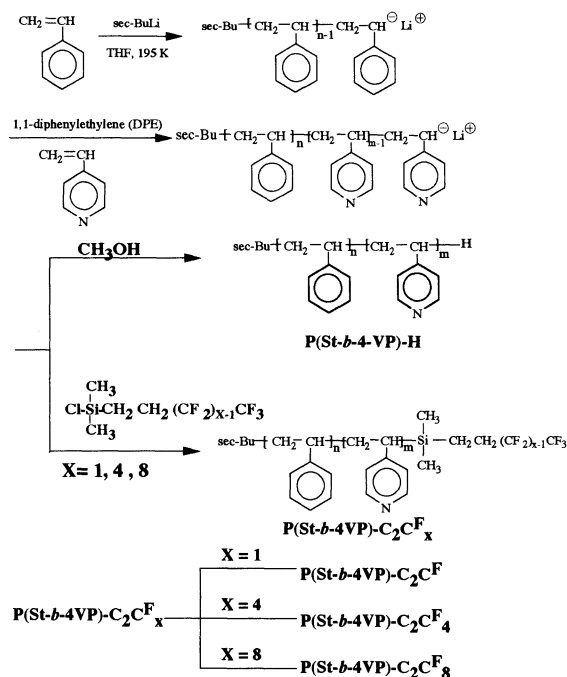
EXPERIMENTAL

Materials

Styrene (St) and 4-vinylpyridine (4VP) monomers were dried over CaH₂ for 24 hrs. and then, distilled under vacuum for two times. The purified monomers were stored in argon atmosphere. Just prior to use, the monomers were treated with triethylaluminum and then, vacuum-distilled again. 1,1-Diphenylethylene (DPE) was vacuum-distilled over CaH₂ and *n*-butyllithium. Tetrahydrofuran (THF) was distilled after refluxing 24 hrs. over sodium and benzophenone under nitrogen atmosphere. *sec*-Butyllithium (*sec*-BuLi), 1H, 1H, 2H, 2H-trifluoropropyl dimethylchlorosilane, 1H, 1H, 2H, 2H-perfluorohexyl dimethylchlorosilane and 1H, 1H, 2H, 2H-perfluorodecyl dimethylchlorosilane were used as received.

Synthesis of Polymers

Scheme 1 describes the synthesis route of P(St-*b*-4VP) diblock copolymers. P(St-*b*-4VP) terminated with neutral hydrogen or a fluoroalkylsilyl end group were prepared by a sequential anionic polymerization in THF under an argon atmosphere at 195 K using *sec*-Butyllithium as an initiator. Firstly, THF was transferred into a glass reactor by a capillary technique, then the reactor was cooled to 195 K and the calculated amount of *sec*-butyllithium was added to a well-stirred THF solution by a syringe. Next, the desired amount of styrene monomer was added dropwise. After 60 minutes at 195 K, DPE was added to the reactor. Then, 10 minutes later, 4VP as the second monomer was added to the reactor. After waiting 3 h. at 195 K, the 3-5 fold excess amount of methanol or fluoroalkyl dimethyl chlorosilane was added to the reactor in order to prepare proton-terminated P(St-*b*-4VP) or fluoroalkylsilyl-terminated



Scheme 1. Synthesis route of diblock copolymers.

P(St-*b*-4VP) diblock copolymers. The diblock copolymers were precipitated in hexane and dried in vacuo. Polymers are designated according to their end groups and molecular weight. For example, P(St-*b*-4VP)-C₂C₈^F-12k represents the perfluorodecyl end group with Mn of 12,000.

The number-average molecular weight, Mn, and the molecular weight distribution, Mw/Mn, of the synthesized diblock copolymers, where Mw denotes the weight-average molecular weight, were determined with gel permeation chromatography (GPC) (L-6000, HITACHI Co., Ltd) with dimethyl formamide (DMF) as an eluent, employing the calibration with a polystyrene standard. The P4VP weight fraction of the copolymers was determined by proton nuclear magnetic resonance (¹H-NMR) measurement in DMF-*d*₇ solution with NMR spectrometer (JEOL GSX-400) and also, an elemental analysis.

Film Preparation

The diblock copolymer thin films were prepared by a spin-coating method from a DMF solution onto silicon wafer with native oxide layer at room temperature. The film thickness before annealing was measured by using spectroscopic ellipsometer (M-150, JASCO Co., Ltd.). The diblock copolymer films were dried for 48 h. at room temperature and then, vacuum-dried at 343 K for 24 h. An equilibration state with respect to surface molecular aggregation structure was obtained by annealing the thin films at 423 K for 90 h. under vacuum.

Bulk and Surface Characterization

In order to evaluate the bulk glass transition temperature, T_g of the diblock copolymers, the differential scanning calorimeter (DSC) (Rigaku Thermoflex 8230) measurement was performed. The specimen was heated up to 453 K at a heating rate of 5 K min⁻¹ under dried nitrogen purge.

The surface chemical composition of the diblock copolymer films was evaluated on the basis of X-ray

photoelectron spectroscopy (XPS) with ESCA-850 (Shimadzu Co., Ltd.). XPS measurement was carried out with MgK α radiation at 8 kV and 30 mA under reduced pressure of 10^{-6} Pa. The analytical depths ($d = 3\lambda\sin\theta$) were calculated by using the value of inelastic mean-free path (λ) evaluated from Ashley's equation²¹ and the emission angle of photoelectron, θ . The magnitudes of d were 4.8, 6.8 and 9.7 nm corresponding to the θ of 30°, 45° and 90°, respectively. The values of surface weight fraction of P4VP, ω of the diblock copolymer films were evaluated from the integrated intensity of nitrogen and carbon atoms in a core-electron photoemission spectrum.

In order to observe the cross section of the diblock copolymers at the air/polymer interface, the film samples for TEM were prepared by a cast method from a DMF solution onto polyimide film at 323 K. After the solvent was evaporated, the samples were annealed at 423 K for 90 h. in vacuum oven in order to obtain an equilibrium state. Then, the film samples were embedded in epoxy and cured. The ultrathin sections of ca. 60 nm thick were cut using a ultramicrotome (MT 6000, Meiwa Co., Ltd.). Microtoming was performed at room temperature employing diamond knives. The ultrathin sections were picked up on copper-grids and then, stained in the vapor of OsO₄. This treatment selectively stains the P4VP phase.²² The TEM observation was performed with a transmission electron microscope (H-7000, HITACHI Co., Ltd) operated at 75 kV.

RESULTS AND DISCUSSION

Synthesis of Fluoroalkylsilane-terminated Diblock Copolymers

Five fluoroalkylsilane-terminated P(St-*b*-4-VP)-C₂C_x^F diblock copolymers were synthesized by living anionic polymerization. As a reference material, proton-terminated P(St-*b*-4VP)-H diblock copolymer was also synthesized by living anionic polymerization. In the case of fluoroalkylsilane-terminated P(St-*b*-4VP)-C₂C_x^F, the termination reaction was achieved by addition of CF₃(CF₂)_{x-1}CH₂CH₂Si(CH₃)₂Cl (X = 1, 4, 8) into a living P(St-*b*-4VP) anion solution with the deep yellow color in order to functionalize the chain end group of the P(St-*b*-4VP). Since the P(St-*b*-4VP) formed the micelles being composed of PS as the arms and P4VP as the cores in THF, the deep yellow color of anionic P(St-*b*-4VP) did not disappear instantaneously and remained even after 30 min. at 195 K. Finally, the deep yellow color of the solution disappeared after reaction for 1 hrs at room temperature. Because only the fluoroalkylsilane molecules diffusing into the micelle arms can react with P4VP anions, the termination reactions seem to proceed slowly. The resulting diblock copolymers were carefully precipitated from the THF solution into hexane and then, were further purified by soxhlet extraction with cyclohexane in order to remove any PS homopolymer. Finally, the fluoroalkylsilane-terminated diblock copolymers were dissolved in THF and reprecipitated in Daiflon (a mixture solvent of fluoroalkyl compounds, TM of Daikin Co., Ltd.) for two times in order to remove any unreacted fluoroalkylsilane terminating agents. Table I shows the characterization of the synthesized diblock copolymers. The magnitudes of Mn for P(St-*b*-4VP)-H and P(St-*b*-4VP)-C₂C_x^F were in the range between

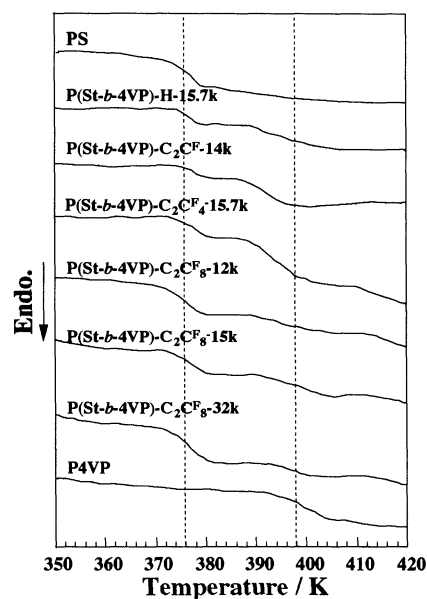


Figure 1. DSC curves of the PS homopolymer, the P4VP homopolymer and the P(St-*b*-4VP) diblock copolymers with different end group and Mn.

12k and 32k. The values of Mw/Mn determined by GPC for P(St-*b*-4VP)-H and P(St-*b*-4VP)-C₂C_x^F were in the range of 1.13 to 1.18. Since no amine compounds such as tetramethylethylenediamine were added to the eluent to avoid the adsorption of P4VP on polystyrene gels during GPC measurement, the real values of Mw/Mn may be smaller than those values listed in Table I. The bulk P4VP weight fractions of diblock copolymers were determined to be in the range between 44% and 57% based on ¹H-NMR and element analysis measurements. In addition, the functionality of the fluoroalkylsilane end group evaluated based on ¹H-NMR spectrum was more than 0.8 for P(St-*b*-4VP)-C₂C_x^F. Thus, the synthesized diblock copolymers have the well-defined chemical structure and narrow molecular weight distributions.

Bulk Tg Measurement

Figure 1 shows the DSC curves for the P(St-*b*-4VP)-H and the P(St-*b*-4VP)-C₂C_x^F. The temperature at the midpoint of a base line shift was defined as bulk glass transition temperature, Tg. Surprisingly, two Tgs were observed for all samples even though the molecular weight for diblock copolymer is 12k. The lower Tgs at ca. 378 K were assigned to the PS component, whereas, the higher Tgs at about 395 K were assigned to the P4VP component. These results indicate that the bulk P(St-*b*-4VP)-H and P(St-*b*-4VP)-C₂C_x^F were in a microphase-separated state even though the molecular weight was not high, and also, suggest the relatively large magnitude of χ (> 1.0)²³ between PS and P4VP segments for P(St-*b*-4VP) system.

Surface Chemical Composition

To evaluate the surface chemical composition of end functionalized diblock copolymer films, the XPS measurement was carried out. Figure 2 shows the typical XPS C_{1s}, N_{1s} and F_{1s} spectra for the P(St-*b*-4VP)-H, P(St-*b*-4VP)-C₂C_x^F and P4VP homopolymer thin films after annealing at 423K for 90hrs. The characteristic peaks of C_{1s}, N_{1s} and F_{1s} were observed at ca. 285, 399 and 689 eV,

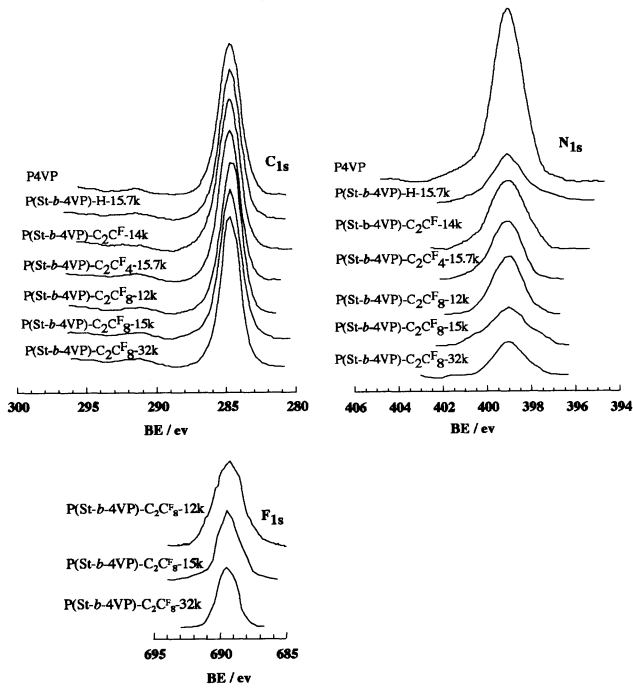


Figure 2. The XPS C_{1s} , N_{1s} and F_{1s} core-level spectra of the P4VP homopolymer, the P(St-*b*-4VP)-H and P(St-*b*-4VP)- $C_2C^F_x$ copolymers after annealing at 423 K for 90 h.

respectively. It is apparent from the spectra that the intensity ratios of N_{1s}/C_{1s} and F_{1s}/C_{1s} depend on the chain end group or molecular weight of diblock copolymers. These differences enable the analysis of the surface chemical composition of the P(St-*b*-4VP)-H and P(St-*b*-4VP)- $C_2C^F_x$ films. The low intensity of N_{1s} for P(St-*b*-4VP)-H suggests that the overlayer of PS is present. The surface P4VP fraction was calculated using the equation mentioned above on the basis of XPS measurement.

Figure 3 shows the surface depth profile of F/C ratios for the P(St-*b*-4VP)- $C_2C^F_8$ -12k, P(St-*b*-4VP)- $C_2C^F_8$ -15k and P(St-*b*-4VP)- $C_2C^F_8$ -32k thin films with the film thickness of 160, 140 and 190 nm, respectively, after annealing at 423 K for 90 h. The magnitudes of $\sin \theta$ of 0.50, 0.70 and 1.0 correspond to the analytical depth range of 0–4.8 nm, 0–6.8 and 0–9.7 nm, respectively. The F/C ratios show significant increases with decreasing the analytical depth of samples and the concentration gradient of fluoroalkyl chain end group in the depth region of ca 0–10 nm is observed. Also, the surface F/C ratios are higher than the bulk F/C ratios of samples. This result indicates that an appreciable surface excess of fluoroalkyl chain ends in an analytical depth studied here and this surface excess gradually increases with approaching the air/polymer interface. The effect of molecular weight on the preferential surface localization of fluoroalkyl end group is evident as shown in Figure 3. The surface F/C ratio increased with a decrease in the molecular weight of the diblock copolymers because the fraction of chain end group is inversely proportional to the molecular weight. Therefore, it seems reasonable to conclude that the fluoroalkyl chain end group of which surface free energy is lower than that of the main chain part, is enriched at the film surface of the microphase-separated P(St-*b*-4VP)- $C_2C^F_8$ diblock copolymers even though the fluoroalkyl end directly attached to the P4VP block with higher surface free energy.

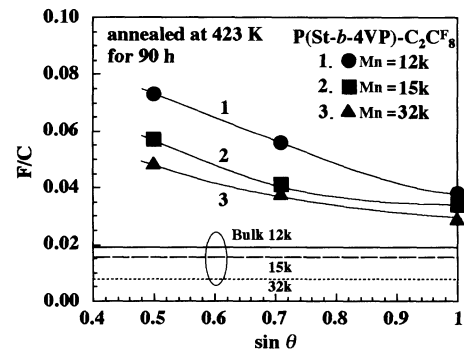


Figure 3. Angle dependence of surface F/C ratios for P(St-*b*-4VP)- $C_2C^F_8$ with different Mn. Continuous, broken and dotted lines denote the bulk composition with Mn of 12k, 15k and 32k, respectively.

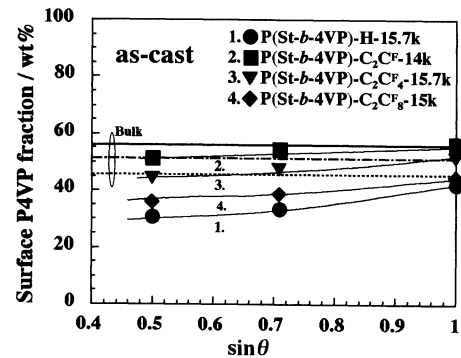


Figure 4. Composition depth profiles for P(St-*b*-4VP)-H and P(St-*b*-4VP)- $C_2C^F_x$ films with similar Mn before annealing. Continuous, broken and dotted lines correspond to the bulk composition of P(St-*b*-4VP)- $C_2C^F_4$ -15.7k, P(St-*b*-4VP)- $C_2C^F_4$ -14k, and P(St-*b*-4VP)- $C_2C^F_8$ -15k samples. Continuous line also represents bulk composition of P(St-*b*-4VP)-H-15.7k.

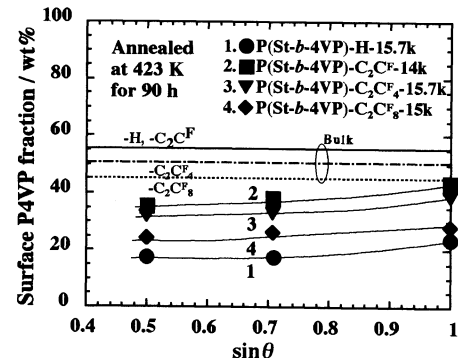


Figure 5. Composition depth profiles for P(St-*b*-4VP)-H and P(St-*b*-4VP)- $C_2C^F_x$ films with similar Mn after annealing. Continuous, broken and dotted lines correspond to the bulk composition of P(St-*b*-4VP)- $C_2C^F_4$ -15.7k, P(St-*b*-4VP)- $C_2C^F_4$ -14k, and P(St-*b*-4VP)- $C_2C^F_8$ -15k samples. Continuous line also represents bulk composition of P(St-*b*-4VP)-H-15.7k sample.

Figures 4 and 5 show the surface depth profile of P4VP weight fraction for P(St-*b*-4VP)-H-15.7k, P(St-*b*-4VP)- $C_2C^F_4$ -14k, P(St-*b*-4VP)- $C_2C^F_4$ -15.7k and P(St-*b*-4VP)- $C_2C^F_8$ -15k with the approximately same molecular weight before and after annealing. The thickness of the as-cast films is ca. 140 nm. In the case of the as-cast films, the all samples showed the relatively high P4VP fraction (more than 30%) in the analytic depth of XPS, and also, the surface P4VP fraction of P(St-*b*-4VP)- $C_2C^F_x$ was higher than that of P(St-

b-4VP)-H. It is apparent that the surface chemical composition of the diblock copolymer is influenced by the chain end group species even in the case of the as-cast films. After annealing treatment at 423 K for 90 h., the P4VP fractions of P(St-*b*-4VP)-H and P(St-*b*-4VP)-C₂C₈F_x decreased in comparison with those of as-cast films and bulk P4VP fraction. This result indicates that the annealing treatment induces preferential surface segregation of PS component with lower surface free energy relative to the P4VP. The decrease in P4VP fraction for the P(St-*b*-4VP)-C₂C₈F_x thin film after annealing was smaller than that for the P(St-*b*-4VP)-H. These results indicate that terminating P(St-*b*-4VP) with fluoroalkyl group increases the surface P4VP fraction over the P(St-*b*-4VP)-H in the both cases of as-cast film and annealed film due to the surface localization of fluoroalkyl end group linked with P4VP block.

The Surface and Bulk Morphology

In order to investigate the effect of the chain end group on the surface and bulk morphology of P(St-*b*-4VP) as well as the orientation of microdomains near the surface, the TEM observation was carried out by using the ultrathin sections of P(St-*b*-4VP). Since the bulk compositions of synthesized P(St-*b*-4VP) diblock copolymers are not too far from the symmetric composition(50/50), the formation of lamellar structure is principally expected. Figure 6 shows the typical TEM micrograph of ultrathin cross section of the bulk phase of P(St-*b*-4VP)-C₂C₈F_x-12k film after annealing at 423 K for 90 h. The bright and dark areas correspond to PS block and the osmium tetroxide-stained P4VP block, respectively. The alternating PS (the bright part) and P4VP (the dark part) lamellae with sharp interfaces were observed. The long period was ca.11nm. Figure 6 indicates that the microphase separated structure is present even if the Mn is only 12k and the lamellar structure was formed in the bulk region of P(St-*b*-4VP)-C₂C₈F_x-12k. The formation of lamellar structure in the bulk specimen was also observed in the P(St-*b*-4VP)-H and P(St-*b*-4VP)-C₂C₈F_x films.

It would be interesting to investigate the influence of chain end group on surface morphology of the thin films. Figure 7 shows the TEM micrograph of ultrathin section of the P(St-*b*-4VP)-H-15.7k near the air-polymer interface after annealing at 423 K for 90 h. The alternating lamellar structure of PS (the bright part) and P4VP (the dark part) was formed being parallel to the film surface. Also, it was observed that the free surface was completely covered with the bright PS layer of which the thickness is approximately a half as large as that of the inner PS layer.²⁵ It is apparent that this surface structure is favorable to minimize the surface free energy of the system when the outermost of the film is covered by the component with the lower surface free energy. Thus, it is reasonable to conclude that in order to minimize the interfacial free energy, the PS component with lower surface free energy segregated preferentially to air-polymer interface, resulting in the formation of lamellar structure parallel to the free surface for the P(St-*b*-4VP)-H film after annealing treatment.

On the other hand, the surface molecular aggregation structure is quite different in the case of the fluoroalkyl-terminated P(St-*b*-4VP)-C₂C₈F_x films. Figure 8(a) shows the TEM micrograph of ultrathin section of the P(St-*b*-4VP)-C₂C₈F_x-14k film near the air-polymer interface after annealing at 423 K for 90 h. The bright layers correspond to the

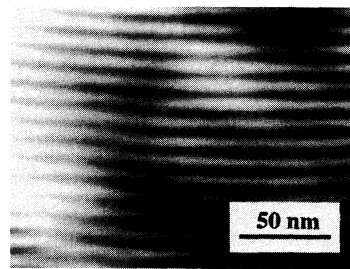


Figure 6. TEM micrograph of ultrathin section of P(St-*b*-4VP)-C₂C₈F₈-12k sample in the bulk after annealing at 423 K for 90 h.

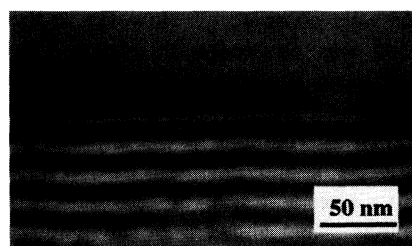
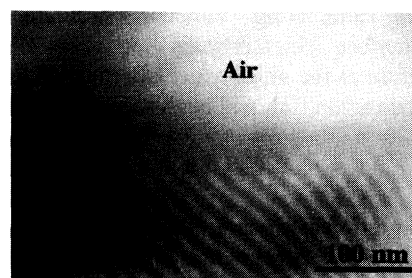
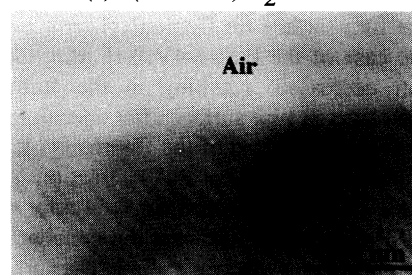


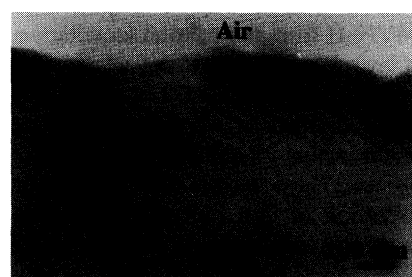
Figure 7. TEM image of ultrathin section of P(St-*b*-4VP)-H-15.7k film near surface region.



(a) P(St-*b*-4VP)-C₂C₈F₈-14k



(b) P(St-*b*-4VP)-C₂C₈F₈-15k



(c) P(St-*b*-4VP)-C₂C₈F₈-32k

Figure 8. TEM images of (a) P(St-*b*-4VP)-C₂C₈F₈-14k, (b) P(St-*b*-4VP)-C₂C₈F₈-15k and (c) P(St-*b*-4VP)-C₂C₈F₈-32k films near surface region after annealing at 423K for 90h.

unstained PS microdomains and the dark layers to the P4VP phases stained with OsO₄. A regular alternating lamellar morphology composed of PS and P4VP layers was observed for the P(St-*b*-4VP)-C₂C₈^F-14k film. It is apparent from Figure 8 that the lamellar structure at the air/polymer interface was tilted ca.45 deg. to the free surface. This surface aggregation structure is quite different from that of P(St-*b*-4VP)-H which indicated the parallel orientation of lamellar structure at the air/polymer interface as shown in Figure 7. Figure 8 shows that edges of both PS and P4VP layers were exposed to the free surface and the outermost layer of the film surface was not completely covered with low surface energy PS layer. In the cases of poly(styrene-*b*-isoprene)[P(St-*b*-Ip)] and poly(styrene-*b*-butadiene) [P(St-*b*-Bd)] diblock copolymers, the lamellar structure normal to the free surface were observed.^{25,26} However, in these cases, the free surface was covered with PIp or PB and the exposure of the edges of PIp or PBd and PS alternating lamellae at free surface was not observed. Figures 8(b) and (c) show the TEM micrographs of the ultrathin sections of P(St-*b*-4VP)-C₂C₈^F-15k and P(St-*b*-4VP)-C₂C₈^F-32k at air-polymer interface after annealing at 423 K for 90 h. These TEM micrographs also showed the alternating lamellar structure of PS and P4VP with tilted orientation with respect to the normal direction to the free surface. These results suggested that the surface free energy of the fluoroalkyl end group is low enough to change the orientation of alternating lamellar structure at the air/polymer interface. The formation mechanism of the tilted lamellar structure at the air/polymer interface of the P(St-*b*-4VP)-C₂C₈^F ultrathin film will be discussed elsewhere.

CONCLUSION

The proton-terminated and the various fluoroalkyl-terminated P(St-*b*-4VP) symmetric diblock copolymers were synthesized by a sequential anionic polymerization. XPS measurement revealed the fluoroalkyl-chain end group was enriched at the film surface for fluoroalkyl-terminated P(St-*b*-4VP). In the case of the P(St-*b*-4VP)-H film, the surface P4VP fraction decreased, resulting in the formation of polystyrene(PS) layer at film surface after annealing at 423K for 90 h. However, in the case of the fluoroalkyl-terminated P(St-*b*-4VP) films, the surface P4VP fraction decreased slightly and still maintained more than 30% after annealing treatment. TEM observations indicate the lamellar structure was formed in all samples after annealing. The surface order and orientation of lamellar structure near surface region are strongly influenced by chain end group species. In the case of the P(St-*b*-4VP)-H film, the parallel lamellar was formed and outermost layer was covered with PS layer. On the other hand, in the case of P(St-*b*-4VP)-C₂C₈^F, the well-developed lamellae of tilted orientation were formed at the surface region and the alternating PS and P4VP layers were exposed to the free surface. These results indicate that the surface order and orientation of thin film strongly depend on the chain end group. By varying chain end group species and

molecular weight of diblock copolymer, the surface aggregation structure can be controlled. This method is useful to control the surface phase structure in the block copolymer system.

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