Transition of Self-assembled Structures in Poly(N-octadecyl acrylamide-co-hydroxylethyl acrylamide) Random Copolymer Films

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ABSTRACT: This paper shows that a simple random copolymer can form self-assembled lamellae, the structure of which depends upon the comonomer composition and annealing temperature. A random copolymer of octadecyl acrylamide and hydroxyethyl acrylamide [p(ODA/HEAm)] was prepared via free racial copolymerization. Thin films of p(ODA/HEAm) were prepared via a spin-coating method and their structures were studied using X-ray diffraction. It was found that copolymers with a HEAm content between 28% and 50% formed self-assembled lamellae upon annealing at 10 ˚C above the glass-transition temperature. The self-assembled form has a "side-chain-mixed" lamellar structure in which the ODA and HEAm side chains are oriented perpendicularly to the lamellar plane composed of the polymer main chain. Interestingly, a copolymer with HEAm content between 36% and 50% transforms from the side-chain-mixed lamellar structure to form a "side-chain-segregated" lamellar structure upon annealing at a much higher temperature (160 ˚C). In this structure, the ODA and HEAm side chains are oriented perpendicularly to the lamellar plane and in opposite directions to each other. We concluded that the lamellar structure that is formed is determined by the strain force generated during self-assembly and by the segregation force between the comonomers.

INTRODUCTION

Block copolymers consist of two homopolymers with different chemical properties tethered together. It is well known that microphase separation between each block of a block copolymer can facilitate the formation of unique self-assembled structures such as lamellae, cylinders, and spheres. It has been revealed experimentally and theoretically that the particular self-assembled structure that forms depends on the relationship $\chi \times N$ and the variable, ϕ_1. χ is the Flory–Huggins segmental interaction parameter, N is the degree of polymerization, and ϕ_1 is the volume fraction of one block.[1-4] The structures are determined primarily by ϕ_1 and change from a random sphere to a cylinder to lamellae as ϕ_1 increases from 0% to 50%.[4] The self-assembled structures can also convert from one structure to the another, such as from a cylinder to lamella by changing the annealing temperature, a process known as order-order transition.[5-7] Conversely, we have reported that simple homo and random copolymers of poly(alkyl acrylamide) and poly(alkyl acrylate) form highly oriented lamellar structures upon annealing above the glass-transition temperature (T_g) under humid conditions.[8-13] The driving force for the formation of this lamellar structure is segregation between water-adsorbed main chain and alkyl side chains (nanophase separation).[11-13] Furthermore, a random copolymer of dodecyl acrylamide and hydrophilic vinyl phosphoric acid forms a self-assembled lamellar structure upon conventional thermal annealing above the T_g due to phase separation between the hydrophilic dodecyl side chain and the hydrophilic phosphoric acid.[14] Terashima et al. have reported that a random copolymer of octadecyl acrylate and oligo(ethylene glycol) forms a lamellar structure driven by the phase separation between the crystalized octadecyl chains and the oligo(ethylene glycol) chains.[15-17] These studies indicate that, even in homo and random copolymers, self-assembled structures can be formed via the segregation of the main and side chains and/or comonomers. Recently, Ouchi et al. have reported that an alternate copolymer of *N*-octadecyl acrylamide (ODA) and hydroxyethyl acrylamide (HEAm) self-assembles to form a lamellar structure, whereas the same copolymer with a random sequence remains amorphous.[18] However, based on our reports on the formation of lamellae from alkyl acrylamide homo(co)polymers,[10-14] it is possible that thin films constructed from p(ODA/HEAm) random copolymers form lamellar structures based on the segregation between ODA and HEAm. Thus, in this study, random copolymers of ODA and HEAm with different compositions were synthesized and their thin-film structures were characterized. Analysis of the self-assembled lamellar films created from the random copolymers shows that the main chains form a lamellar plane and that the alkyl and hydrophilic side chains orient perpendicularly to the main chain. Thus, two types of lamellar structures can be created. One is a "side-chain-mixed" lamellar structure in which the alkyl side chains are oriented perpendicular to the main chain and on both sides of the main chain. In this structure each lamellar sheet is stacked by the association of their alkyl side chains (tail-to-tail) (Figure 1a).[19] The other is a "side-chain-segregated" lamellar structure in which the alkyl side chain orients in one direction with respect to the main chain and the hydrophilic side chain orients in the other direction (Figure 1b). The side-chain-segregated lamellar sheets are stacked so that the hydrophilic side chains (head-to-head) and the hydrophobic side chains (tail-to-tail) self-associate. This is similar to the lamellar structure formed from amphiphilic molecules. Although we and other groups have reported that random copolymers form lamellar structures via segregation, there are no reports of fabricating these two lamellar structures separately. Analogous to block copolymers, the structure formed depends on, among other factors, the content of the comonomers and temperature. Thus, in this paper, we report that the relative ratio of ODA to HEAm and the annealing temperature determine the lamellar structure formed, similar to the formation of lamellar structures in diblock copolymers. The structure of the comonomer films was determined using X-ray-diffraction analysis. We found that random copolymers with HEAm content in the range of 28% to 50% formed self-assembled side-chain-mixed lamellae upon annealing ~10 ˚C above T_g. Random copolymers with HEAm content in the range of 36% to 50% transformed into side-chain-segregated lamellae upon annealing above 140 ˚C. The effect of the HEAm content and annealing temperature on the lamellar structure is discussed based on the strain in the polymer chains and the miscibility of the comonomers.

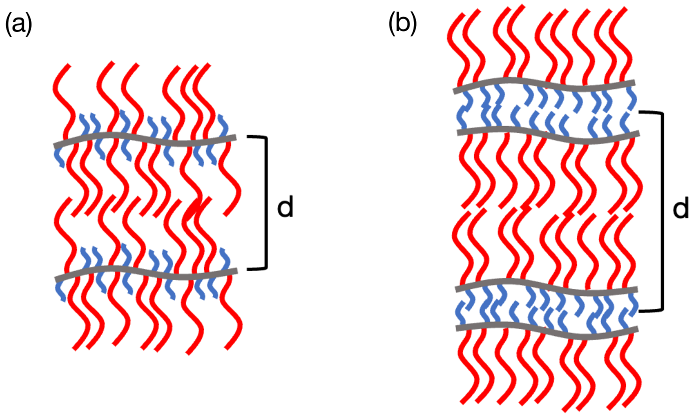


Figure 1 Schematic image of (a) the side-chain-mixed lamellae and (b) side-chain-segregated lamellae. Black, red, and blue lines represent the main chain, alkyl side chains, and hydrophilic side chains, respectively, while *d* is the lamellar periodicity.

Materials and Methods

Materials. Octadecyl amine (TCI), acryloyl chloride (TCI), 2-hydroxyethyl acrylamide (HEAm, TCI), triethylamine (TCI), trichloro(octyl)silane (Aldrich), acetone (nacalai), isopropyl alcohol (nacalai), chloroform (Kanto Chemical), and acetonitrile (nacalai) were used as received. 2,2′-Azobisisobutyronitrile (AIBN, FUJIFILM Wako) was recrystallized from ethanol.

Synthesis. Octadecyl acrylamide (ODA) was synthesized following a previously reported method.[18] Briefly, octadecyl amine (3.60 g) was dissolved in chloroform (60 mL). To this solution, triethylamine (2.00 mL) was added. The solution was stirred at 0 ˚C and then acryloyl chloride (1.17 mL) was added dropwise. After adding acryloyl chloride, the reaction mixture was stirred at room temperature for 4 h, before methanol (5 mL) was added.

Then, the majority of the solvent was evaporated under reduced pressure and methanol (300 mL) was added. The solution was kept in a refrigerator for one day to recrystallize the ODA (yield: 85%). The compound was characterized using ^{1}H NMR spectroscopy (Figure S1). Copolymers were synthesized via free radical polymerization using AIBN as the thermal initiator. The different feed ratios of ODA and HEAm that were used are shown in Table 1. ODA, HEAm, and 1 mol% of AIBN relative to the total monomer amount were added to a pressure-resistant glass tube (ACE GLASS). To this glass tube, toluene and DMF at a volume ratio of 4:1 were added in a glove box filled with N_2. The total concentration was kept constant at 0.2 M. The polymerization was carried out at 60 °C for 12 hours. After the reaction, the tube was exposed to air, and the majority of the solvent was evaporated under reduced pressure. The polymerization solution was added dropwise into a large quantity of stirred acetonitrile. The obtained polymer was dissolved in chloroform and reprecipitated twice from acetonitrile. Finally, the polymer was collected and dried at room temperature under reduced pressure. A Fineman-Ross plot was prepared following the termination of the polymerization at 60 ˚C after one hour. The copolymers were initially precipitated using methanol when the feed ratio of ODA: HEAm was 7:3 and 6:4. They were then precipitated twice from acetonitrile. The other copolymers used acetonitrile as a poor solvent and the reprecipitation process was carried out three times.

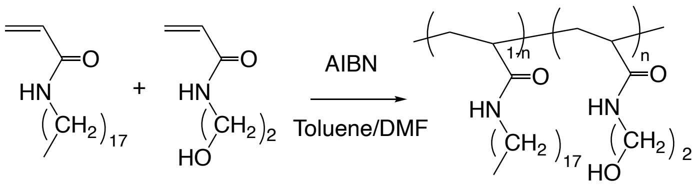
Equipment. The synthesized compounds were characterized using ^{1}H NMR spectroscopy on an ECA-500 JEOL spectrometer. All ^{1}H NMR spectra were recorded in $CDCl_3$. The monomer ratio in the copolymer was determined using the integration ratio of the methyl protons of ODA (~0.8 ppm) and the ethylene protons of HEAm (2.7-4.2 ppm) (Figure S2). The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the copolymers were measured using gel-permeation chromatography (GPC, Shodex GPC-101, Showa Denko K.K.) with THF as the eluent at 40 °C using polystyrene standards. The transition temperature of the copolymers was measured using a differential scanning calorimeter

(DSC, DSC8231, Rigaku Corp.) under a flow of N_2 (50 mL min^{-1}) at a heating rate of 10 °C min^{-1} over a temperature range of -40–200 °C. X-ray-diffraction (XRD) and X-ray-reflectivity (XRR) measurements were performed using a Rigaku Smartlab (Rigaku Corp.) with a Cu Kα (λ = 0.1542 nm) X-ray source and a scintillation counter. Two-dimensional grazing-incidence X ray-diffraction (2D GI-XRD) measurements were performed using a Rigaku Nanoviewer with a Cu Kα (λ = 0.1542 nm) X-ray source and a 2D detector (PILATTUS 2M). The incidence angle was ~0.15 ˚.

Thin-film preparation. Silicon and quartz substrates were ultrasonically cleaned in acetone and then continuously in isopropyl alcohol (20 minutes). This cleaning procedure was repeated twice before the substrate surfaces were treated with UV–O_3 (PL16-110, SEN Lights Corp.) to prepare the hydrophilic substrate. To prepare a hydrophobic substrate, the hydrophilic substrate was immersed in a solution of trichloro(octyl)silane/chloroform (~1×10^{-5} M) for 1 day at room temperature. Thin films were prepared via spin coating (MA-A100, Mikasa) where a chloroform solution of the polymer was dropped onto the hydrophobic substrate. The spin-coated film was prepared by spinning at 1,000 rpm for 5 seconds and then at 2,500 rpm for 60 seconds. Polymer concentrations of 5 wt% and 0.5 wt% were used to prepare the films for XRD and XRR measurements, respectively. The film was annealed at the target temperature for 90 min *in vacuo*. Then, the substrate was immediately taken out of the chamber and kept at room temperature (20-25˚).

RESULTS AND DISCUSSION

Copolymers of ODA and HEAm were synthesized via free-radical copolymerization using 2,2'-azobisisobutyronitrile as the thermal initiator (Scheme 1, Table 1). Using the Fineman-Ross method, the reactivity ratio of ODA and HEAm was determined to be r1 = 0.39 and r2 = 0.81, which suggests that the copolymers have a statistical sequence of monomers (Figure S3). The thermal properties of the copolymers were investigated using DSC (Figure S4). The DSC curve shows a strong exothermic peak at ~30 ˚C during the heating cycle of the copolymers. The peak was attributed to the melting of the crystalline octadecyl side chain (T_M). The baseline shift observed in the high-temperature region was attributed to the glass-transition temperature (T_g). All the copolymers have a T_g above 80 ˚C. The DSC results indicate that the random copolymers have no higher-ordered phase, such as a liquid-crystalline phase, which has previously been reported by Ouchi et al.[18]



Scheme 1 Synthesis of the p(ODA/HEAm) copolymers.

Table 1 Characterization of the p(ODA/HEAm) copolymers.

Copolymer	Molar feed ratio ODA : HEAm	Resulting molar ratio ODA : HEAm	$Mn^{b)}$	$M_w/M_n^{b)}$	T_g / °C$^{c)}$	T_M / °C$^{c)}$	d / nm
p(ODA10/HEAm90)$^{a)}$	10 : 90	-	-	-	-	-	-
p(ODA40/HEAm60)	30 : 70	36 : 64	7200	1.73	95.2	26.3	-
p(ODA50/HEAm50)	50 : 50	50 : 50	6600	2.15	104	22.7	3.7$^{d)}$, 4.6$^{e)}$
p(ODA60/HEAm40)	60 : 40	64 : 36	16700	1.71	96.2	25.1	3.6$^{d)}$, 4.4$^{e)}$
p(ODA70/HEAm30)	70 : 30	72 : 28	14200	1.79	92.1	29.5	3.3$^{d)}$
p(ODA90/HEAm10)	90 : 10	88 : 12	20700	1.72	82.4	30.8	-

a) A gel was formed and further characterization was not carried out. b) Determined based on GPC measurements using polystyrene standards. c) Determined based on DSC measurements (Figure S4). d) For side-chain-mixed lamellae. e) For side-chain-segregated lamellae.

The copolymer thin films were prepared on a silicon substrate via spin coating and their structures were characterized using XRD measurements. None of the spin-coated films exhibited clear diffraction suggesting that the initial films were amorphous (Figure 2, black lines). The broad scattering observed in the XRD patterns of the thermally annealed (T_g + ~10 ˚C) films of p(ODA40/HEAm60) (q_{nd} ~ 1.4 nm^{-1}; Figure 2a) and p(ODA90/HEAm10) (q_{nd} ~ 1.8 nm^{-1}; Figure 2e) is attributed to diffraction from the alkyl nanodomains.[11,20] The diffraction at q_{cr} = 3.8 nm^{-1} (d = 1.6 nm) in the XRD pattern of the p(ODA90/HEAm10) film originates from the crystalized domains of ODA.[11] The presence of alkyl nanodomains indicates that p(ODA40/HEAm60) and p(ODA90/HEAm10) are randomly oriented films,[20,21] which is consistent with the DSC results. The diffraction patterns for p(ODA40/HEAm60) and p(ODA90/HEAm10) exhibited negligible changes upon increasing the annealing time to 24 h. Thus, we concluded that p(ODA40/HEAm60) is too hydrophilic, and p(ODA90/HEAm10) is too hydrophobic to form a self-assembled structure via nanophase separation. Indeed, two-dimensional grazing-incident XRD (2G-GIXRD) patterns of p(ODA40/HEAm60) and p(ODA90/HEAm10) exhibited a weak Debye-Scherrer ring (Figures S5a and S5b) confirming the absence of unidirectional orientation in these copolymer films.[20,22]

On the other hand, the copolymers with HEAm content in the range of 28% to 50% show strong integer order peaks (q_{lm}, Figures 2b-2d; green pattern) after thermal annealing, suggesting that the copolymer films form a lamellar structure. Annealing for a further 24 h results in an increase in the Bragg peak intensity and a decrease of the full width at half maximum (FWHM) of the peaks (Figures 2b-2d; red pattern). Thus, the lamellar uniformity increases with annealing time, which is consistent with previous result obtained from a copolymer of dodecyl acrylamide and hydrophilic vinyl phosphoric acid.[14] 2D-GIXRD images of the thermally annealed films of p(ODA50/HEAm50), p(ODA60/HEAm40), and p(ODA70/HEAm30) exhibit a diffraction spot in the out-of-plane direction where the q value is close to the that of the first-order Bragg peak in the 1D XRD pattern (Figure S6). The spot images demonstrate the formation of unidirectionally oriented lamellae in which the main chain forms the lamellar plane aligned parallel to the substrate plane with the side chains aligned perpendicularly to the main chains.[23] As revealed in the DSC measurements, the copolymers did not exhibit a liquid-crystalline phase (Figure S4). Furthermore, the lamellar periodicity of these films (d), calculated using the first Bragg peak ($d = 2\pi/q$), is close to that obtained in the lamellar domains of aligned pODA fibers (Table 1).[19] Therefore, we concluded that side-chain-mixed lamellae are formed in these copolymer films via segregation between the hydrophobic ODA side chains and hydrophilic main-chain region composed of amide and HEAm side chains (Figure 1a). The following study on the effect of the annealing temperature on the XRD patterns supports this conclusion.

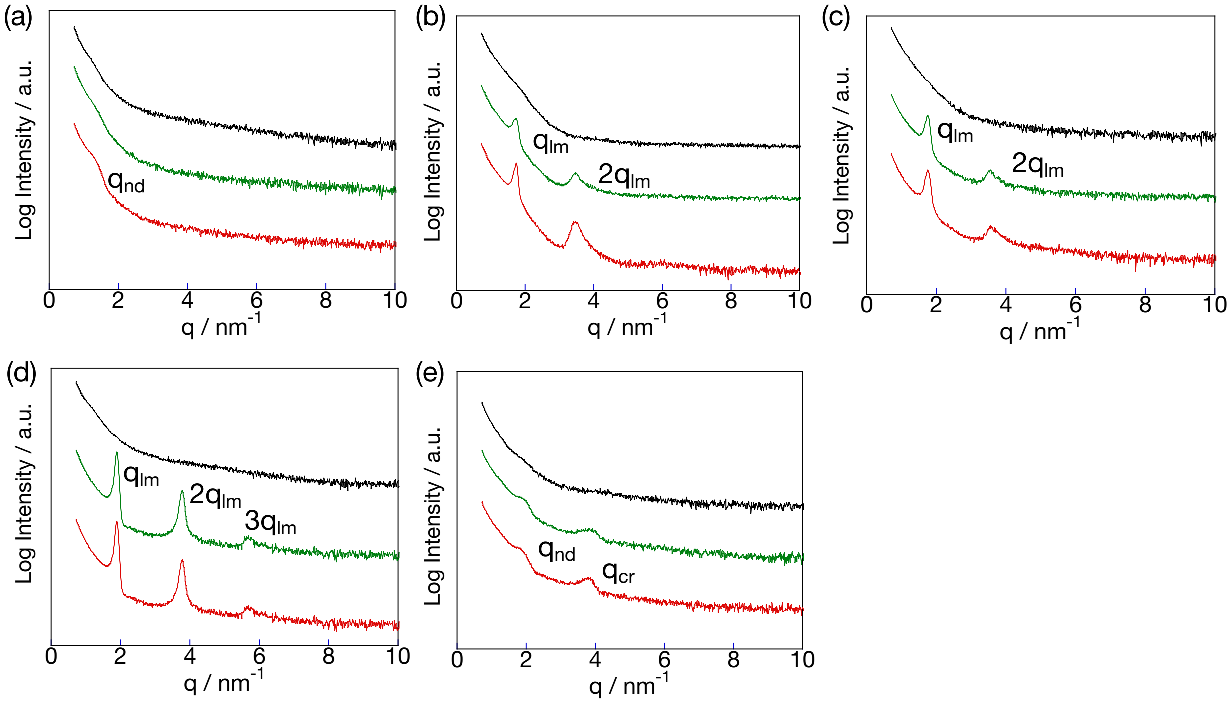


Figure 2 XRD patterns of the copolymers after different annealing times. (a) p(ODA40/HEAm60) (q_{nd} = 1.3 nm^{-1}), (b) p(ODA50/HEAm50) (q_{lm} = 1.7 and $2q_{lm}$ = 3.5 nm^{-1}), (c) p(ODA60/HEAm40) (q_{lm} = 1.8 and $2q_{lm}$ = 3.5 nm^{-1}), (d) p(ODA70/HEAm30) (q_{lm} = 1.9, $2q_{lm}$ = 3.8 nm^{-1}, and $3q_{lm}$ = 5.7), and (e) p(ODA90/HEAm10) (q_{nd} = 1.8 and q_{cr} = 3.9 nm^{-1}). For each sample a pattern was obtained for the spin-coated film (black), the film following 90 min of thermal annealing *in vacuo* (green), and following 24 h of thermal annealing in air (red).

Next, we studied the effect of the annealing temperature on the structure of the lamellar film. Figure 3 shows the XRD patterns of the copolymer films following different annealing temperatures. The Bragg peaks of the p(ODA50/HEAm50) film annealed at 120 ˚C broadened and slightly shifted to a lower q value. Further annealing resulted in both a significant shift of the peaks to a lower q value and in the sharpening of the peaks (Figures 3a and 4a). Indeed, the FWHM initially increases from 0.14 nm^{-1} to 0.28 nm^{-1} upon increasing the temperature from 115 ˚C to 120 ˚C, whilst it subsequently decreases to 0.20 nm^{-1} at 160 ˚C (Figure 4a). Moreover, second-order

Bragg diffraction peaks appear in the patterns of the films annealed at 180 ˚C for 1.5 h (Figure 3a; blue pattern) and 160 ˚C for 9 h (Figure S7). The first-to-second-order peak ratio (1:2) suggests that the copolymer transforms into another lamellar structure with a larger *d* value (4.6 nm). The large *d* value indicates that p(ODA50/HEAm50) forms side-chain-segregated lamellae upon annealing at 160 ˚C. Given that d for the side-chain-segregated lamellae is composed of two ODA and HEAm chains (Figure 1b), it is higher than that for the side-chain-mixed lamellae. On this basis, we concluded that the lamellae formed upon annealing at ~ 10 °C + *Tg* (Figures 2b-2d) are side-chain-mixed lamellae, in which d is composed of one polymer chain (two octadecyl side chain lengths; Figure 1a). The 2D-GIXRD image of the p(ODA50/HEAm50) film annealed at 160 ˚C for 1.5 h exhibited spot-like peaks at q = 1.2 nm^{-1} (side-chain-segregated lamellae) and at q = 1.6 nm^{-1} (side-chain-mixed lamellae) (Figure S8a). The simultaneous appearance of two peaks shows that by elevating the annealing temperature, the side-chain-mixed lamellae transform into side-chain-segregated lamellae. As seen in the p(ODA70/HEAm30) XRD patterns in Figure 3c, if increasing the temperature results in the disordering of the lamellar structure, then the peak intensity gradually decreases and broadens. On the other hand, if increasing the temperature increases the lamellar uniformity then the Bragg peak positions are almost unchanged and the peaks sharpen and increase in strength. In either case, no new peaks appear.

Increasing the annealing temperature of the p(ODA60/HEAm40) films resulted in trends in the XRD patterns similar to those seen in p(ODA50/HEAm50). A significant shift of the Bragg diffraction peaks to lower q values was observed as the annealing temperature increased (Figures 3b and 4b), whilst the 2D-GIXRD image for the film annealed at 160 ˚C for 1.5 h exhibited spot-like peaks at q = 1.2 nm^{-1} (side-chain-segregated lamellae) and at q =1.7 nm^{-1} (side-chain-mixed lamellae) (Figure S8b). Conversely, the FWHM gradually increases with increasing temperature

(Figure 4b). The broad diffraction peaks suggest that the uniformity of side-chain-segregated lamellae of p(ODA60/HEAm40) is low. A significant change in the q values of p(ODA50/HEAm50) and p(ODA60/HEAm40) is observed when the annealing temperature increases from 120 ˚C to 140 ˚C. Therefore, we concluded that an order-order transition from the side-chain-mixed lamellae to the side-chain-segregated lamellae begins in this temperature range. The Bragg diffraction peaks in the patterns of p(ODA70/HEAm30) broadened significantly upon increasing the annealing temperature from 100 ˚C (10 ˚C + *Tg*) to 120 ˚C and became shoulder-like diffractions upon annealing above 140 ˚C (Figures 3c and 4c). A shoulder-like diffraction indicates that the structure of the film becomes random and forms alkyl nanodomains. The broad peak that appeared at ~3.7 nm^{-1} was attributed to the crystalized domains of ODA. Thus, at higher annealing temperatures in p(ODA70/HEAm30), the formation of a randomly oriented film with crystalized ODA nanodomains, similar to that observed in p(ODA90/HEAm10), is observed. Indeed, the 2D-GIXRD pattern of the film annealed at 160 ˚C only exhibited a Debye-Scherrer ring at q = 1.8 nm^{-1}, which was attributed to diffraction from the alkyl nanodomains (Figure S8c). Thus, p(ODA70/HEAm30) transforms from an ordered side-chain-mixed lamellar structure to a disordered random structure at around 140 ˚C.

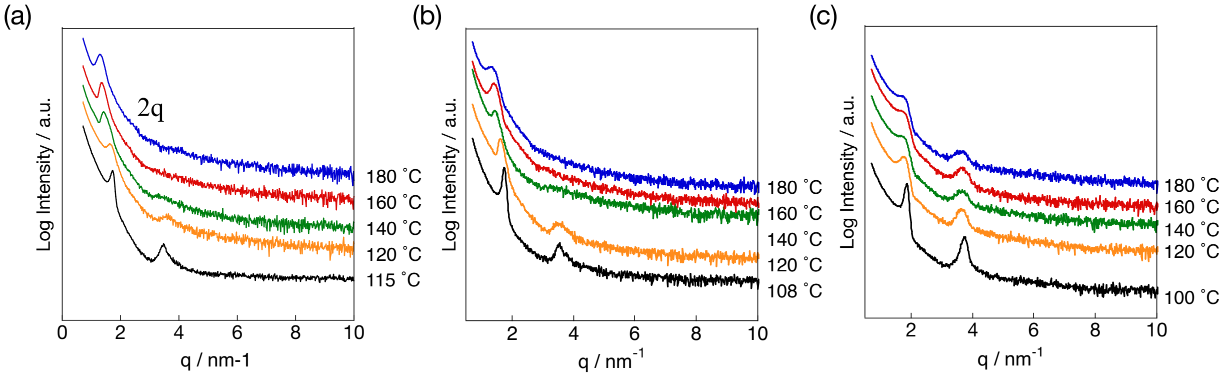


Figure 3. XRD patterns of the copolymer lamellar structures formed at different annealing temperatures. (a) p(ODA50/HEAm50), (b) p(ODA60/HEAm40), and (c) p(ODA70/HEAm30).

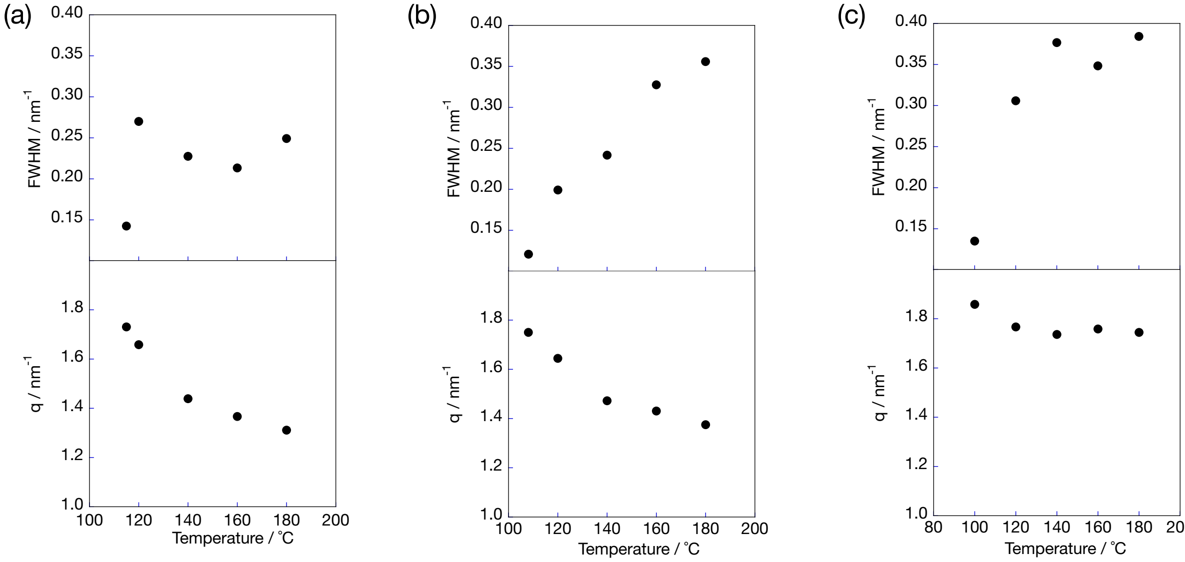


Figure 4 FWHM (top) and q values (bottoom) of the first-order peak at different annealing temperatures. (a) p(ODA50/HEAm50), (b) p(ODA60/HEAm40), and (c) p(ODA70/HEAm30). The values of FWHM and q were obtained by gaussian fitting the first-order peak using Multi-peak fitting in Igor Pro9.

We further characterized the two lamellar structures via XRR analysis. The XRR patterns showed low-angle fringes for both the films annealed at 115˚C and 160˚C (Figure 5a, and 5c), with Bragg diffraction at q = 1.6 nm^{-1} for the films annealed at 115˚C and q = 1.3 nm^{-1} for the films annealed at 160˚C. These q values are comparable to the 1_{st} order Bragg diffraction in XRD patterns (Figure 2d and 3a). The XRR patterns were fitted with a two-box model with alternating hydrophobic and hydrophilic layers(ref) (Figure 6a and 6b). Results shows that XRR patterns are well-explained by periodic scattering length density (SLD) profiles, supporting the formation of a lamellar structure (Figure 5b and 5d). The thicknesses of the hydrophilic regions obtained by the fitting for the side-chain-segregated and mixed lamellar were similar; 5.9 Å for side-chain-segregated and 5.4 Å for the side-chain-mixed lamella. On the other hand, the hydrophobic layer formed by the alkyl chains was found to be 8 Å longer in the segregated (42 Å) than that in the mixed (34 Å) structure. This is because in the side-chain-segregated lamellar structure, the hydrophobic layer is formed entirely by the alkyl chains, whereas in the side-chain-mixed lamellar structure, some of the alkyl chains overlap with the hydrophilic layer, resulting in a thinner hydrophobic layer (Figure 6a and 6b). Thus, XRR measurements support that annealing at 115°C results in a mixed lamellar structure, while annealing at 160°C results in the formation of segregated lamellar structure.

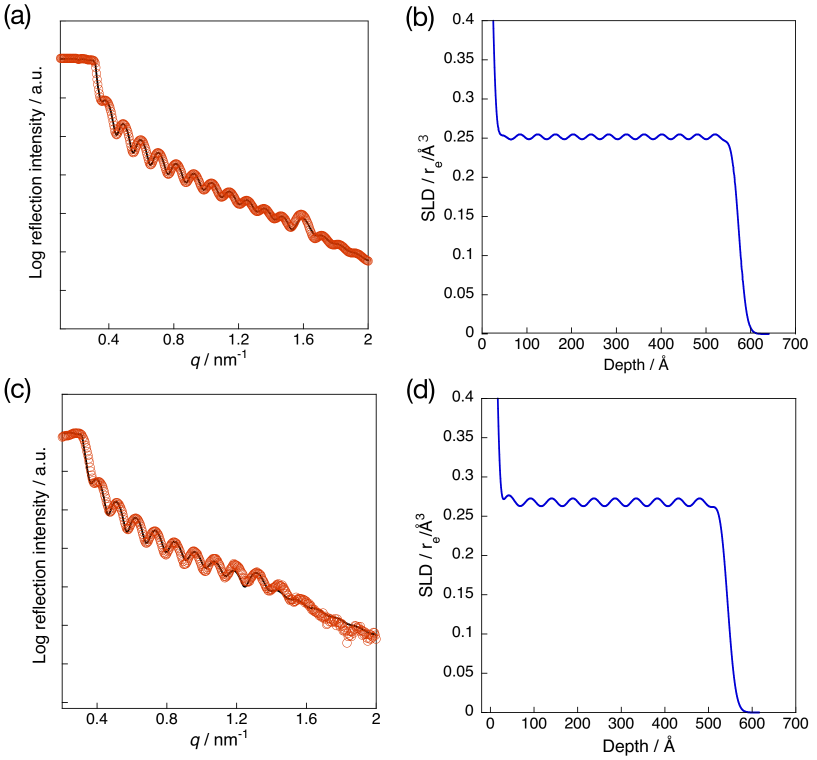


Figure 5. XRR patterns (a,c) and SLD profiles (b,d) of p(ODA50/HEAm50) films annealed at 115 °C for 1.5 h (a, b) or at 160 °C for 1.5 h (c, d). XRR curves and fitting results are shown as red circles and brack lines, respectively.

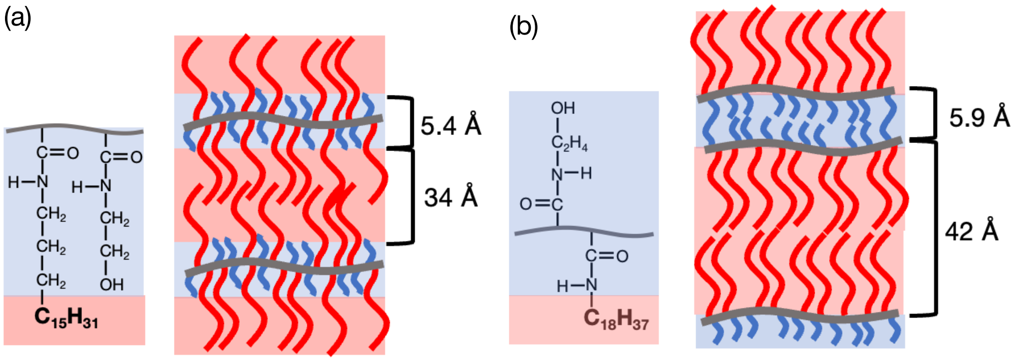


Figure 6. Two box model used in fitting p(ODA50/HEAm50) film annealed at 115°C for 1.5 h (a) and at 160°C for 1.5 h (b). The hydrophobic and hydrophilic layers in the 2-box model are indicated by red and blue boxes, respectively.

The dependence of the lamellar structure on temperature and the copolymer composition can be in terms of a competition between the strain generated by the orientation of the side chains and the miscibility of the comonomers. To form the side-chain-segregated lamellae, identical side chains (ODA or HEAm) must be aligned in the same direction relative to the main chain (Figure 1b). This orientation creates significant strain in these random copolymers. For example, in the continuous ODA-ODA sequence, to align the long octadecyl side chains in the same direction sizeable steric hindrance between the octadecyl side chains must be overcome and this generates considerable strain on the main chain. The segmental mobility of the polymer chains at a temperature slightly above T_g is not enough to exceed the strain energy. Thus, annealing at 10 ˚C + T_g results in the formation of the side-chain-mixed lamellae. In the side-chain-mixed lamellae, the HEAm comonomers “mix” with the ODA comonomers and form a hydrophilic “main chain” with amide groups (Figure 1a). The hydrophilic HEAm side chains increase the hydrophilicity around the main chain, which induces the segregation of the octadecyl side chains from the main chain.

However, considering the miscibility of the comonomers, phase separation between the hydrophobic octadecyl and hydrophilic hydroxyethyl side chains is preferred. Therefore, when the thermal energy is high enough to overcome the steric hindrance and the strain, segregation between the hydrophilic and hydrophobic comonomers dominates the self-assembly process to form side-chain-segregated lamellae. As a result, p(ODA50/HEAm50) and p(ODA60/HEAm40) transform from side-chain-mixed lamellae to side-chain-segregated lamellae at ~140 ˚C. The XRD pattern of p(ODA60/HRAm40) broadens upon annealing at 180 ˚C suggesting that the lamellar structure starts to become disordered due to the violent motion of the polymer chains. The segregation force between the comonomers in p(ODA70/HEAm30) is weak due to the low concentration of the hydrophilic HEAm groups. Therefore, the polymer directly changes from a side-chain-mixed lamellar structure to a disordered state.

We studied the effect of thermal annealing on the structure of p(ODA50/HEAm50) bulk powder. The powder XRD pattern of p(ODA50/HEAm50) following annealing at 115 ˚C for 24 h exhibited a broad diffraction arising from the alkyl nanodomains and the crystalized ODA side chains. In contrast, diffractions from the highly oriented lamellar structure were not observed (Figure S9). The result is similar to those reported by Ouchi et al., i.e., that the bulk powder of the random copolymer p(OD50/HEAm50) does not form an ordered structure.[18] Our results and those reported elsewhere indicate that the formation of lamellar structures in p(ODA/HEAm) is specific to thin films. At present, we think that a hydrophobic air/polymer interface with a large free volume is key to the formation of lamellae.

CONCLUSIONS

We have reported the formation of uniform lamellar structures in random copolymers via the segregation between the main chain and side chains or comonomers. The lamellar morphologies formed depend on the ratio of the comonomers (*N*-octadecyl acrylamide (ODA) and hydroxyethyl acrylamide (HEAm)) and the annealing temperature. Copolymers with HEAm content between 28% and 50% form side-chain-mixed lamellae upon thermal annealing at 10 ˚C + T_g. Moreover, p(ODA50/HEAm50) and p(ODA60/HEAm40) undergo an order-order transition from a side-chain-mixed lamellar structure to a side-chain-segregated lamellar structure at ~140 ˚C. Due to weak segregation forces between the comonomers, other copolymer compositions do not form self-assembled structures. We propose that the form of the self-assembled structure depends on the segregation force and the strain induced during self-assembly. The influence that the hydrophilic group and side-chain structure of the comonomers have on the formation process of the lamellae is currently investigated in our laboratories. We are convinced that the present results will give rise to a new phase diagram for self-assembled structures in random copolymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge

Experimental details, 1H NMR spectra of ODA and copolymers, Fineman-Ross plot, DSC spectra, 2D-XRD images of the copolymers.

AUTHOR INFORMATION

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Conflict of interest

There are no potential conflicts of interest to declare

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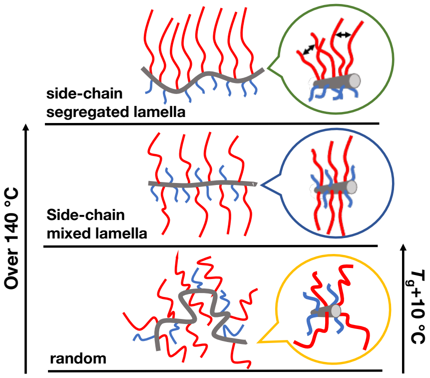
side-chain
segregated lamella
Side-chain
mixed lamella
random
Over 140 °C
T_g+10 °C