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ARTICLE

Metallopolymer-*block*-oligosaccharide for sub-10 nm microphase separation

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High- χ (where χ is the Flory–Huggins interaction parameter) block copolymers (BCPs) have great potential to achieve ultra-small microphase-separated structures with domain spacings (d) of <10 nm, which in turn are promising for nanofabrication applications. However, when considering their practical application in next generation lithographic processes, sufficient heat resistance and high etching selectivity are also required to attain high- χ BCPs for precise pattern transfer to the substrate. Herein, we report novel high- χ BCPs comprising poly(vinyl ferrocene) (PVFc) and an oligosaccharide (maltotriose and maltohexaose), which simultaneously accomplish small d values, sufficient thermal stability, and high etching selectivity. These novel BCPs, which displayed different architectures and saccharide volume fractions, were synthesized by combining living anionic polymerization and the “click” reaction. Small angle X-ray scattering measurement revealed that PVFc-*b*-maltohexaose and PVFc-*b*-(maltotriose)₂ formed hexagonal cylinder morphology with d values of ~8 nm. Furthermore, lamellar morphology with d values of 9.3 nm was realized by mixing PVFc-*b*-(maltotriose)₂ and glucose. The thermal properties and etching resistance of PVFc and the oligosaccharides were also investigated. As expected, PVFc displayed a high thermal stability (PVFc: T_g , ~140 °C and decomposition temperature, ~350 °C) and higher etching resistance than the oligosaccharides.

Introduction

Block copolymers (BCPs) comprising two chemically distinct polymer segments undergo self-assembly into periodic lamellar, gyroid, cylindrical, and spherical structures with nanometer-scale periodicity in the bulk or thin film form, known as microphase-separated structures. Such nanostructures have attracted considerable attention for their potential applications in nanotechnological fields such as next-generation lithographic templates,^{1–8} nanoporous material templates,⁹ optical materials,^{10–13} nanowire arrays,¹⁴ and others.¹⁵ Particularly, much research has focused on their application in lithography technology, where a microphase-separated BCP thin film on a semiconductor substrate is used as the resist material for fabricating electronic circuits. To improve the lithographic resolution, even down to the few-nanometer scale, the development of new BCPs that can achieve microphase-separated structures with extremely small domain spacings (d , <10 nm), has been an important subject in this research field. In

general, d can be decreased by reducing the degree of polymerization (N) of the BCP. However, to promote phase separation, the product of χ and N must be sufficiently higher than the critical value (10.5 for a symmetric BCP), where χ is the Flory-Huggins interaction parameter and indicates the incompatibility of the two segments in the BCP.^{16,17} Thus, much research has recently focused on the formation of high- χ BCPs that can microphase separately, even with low N values, to attain d values ≤ 10 nm.

The basic methodology to design high- χ BCPs is to combine the hydrophobic and hydrophilic polymer segments to increase incompatibility. Many reports of high- χ BCPs comprising vinyl polymer main chains, including poly(cyclohexylethylene)-*b*-poly(methyl methacrylate),¹⁸ poly(dihydroxystyrene)-*b*-poly(styrene),¹⁹ poly(*tert*-butylstyrene)-*b*-poly(2-vinylpyridine),²⁰ poly(3-hydroxystyrene)-*b*-poly(*tert*-butylstyrene),²¹ poly(glycerol monomethacrylate)-*b*-poly(styrene),²² poly(hydroxyisobutylene)-*b*-poly(styrene),²² and poly(hydroxypropylene)-*b*-poly(styrene),²³ have been published to date. In addition, Borsali and our research groups have created a series of high- χ BCPs by combining hydrophobic synthetic polymers [e.g., poly(styrene), poly(*n*-butyl acrylate), poly(methyl methacrylate), poly(ϵ -caprolactone), and poly(δ -decanolactone)] and oligosaccharides (maltotriose and maltoheptaose), some of which successfully achieved microphase separation with d values of <10 nm.^{24–29} Owing to the strong hydrophilicity and rigid chain nature of

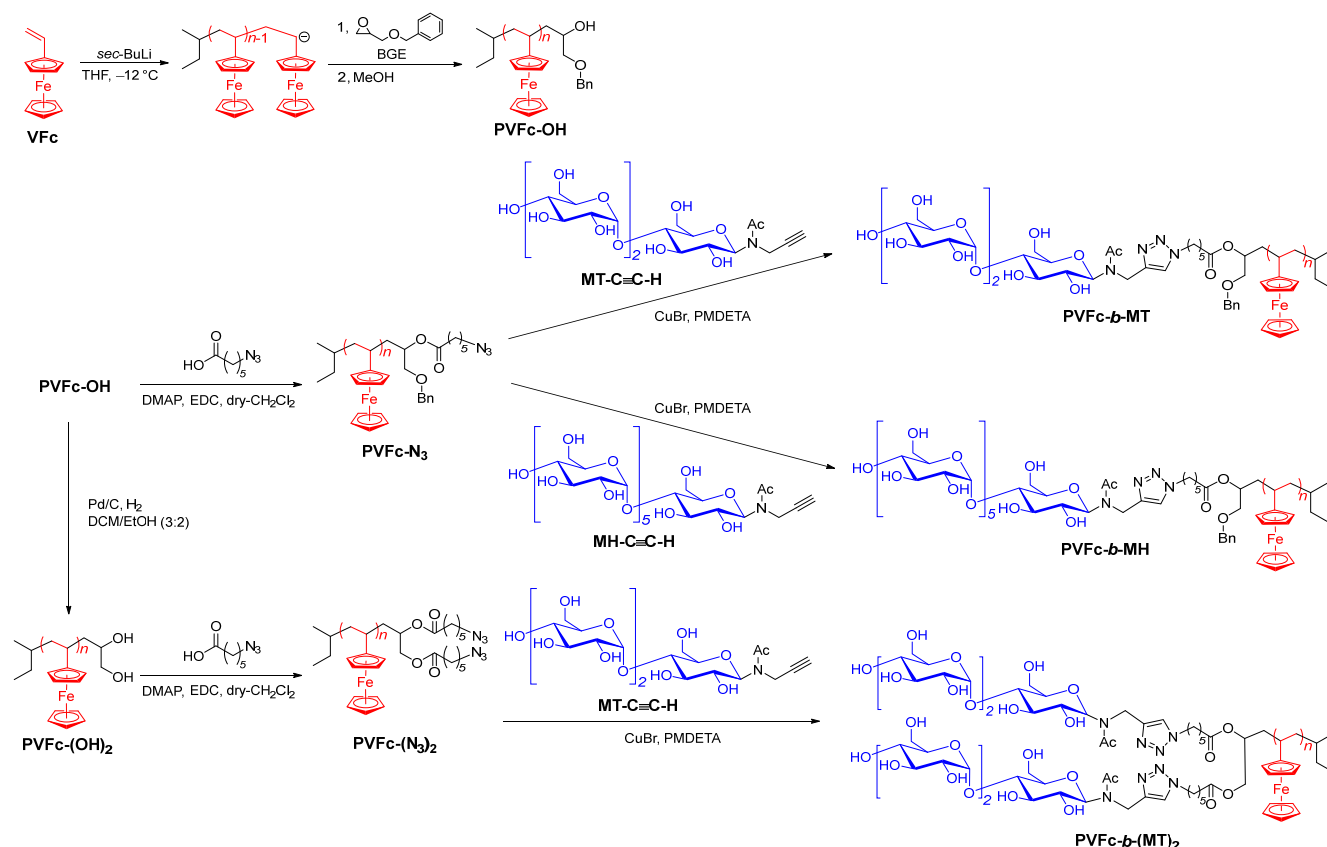
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Scheme 1. Synthesis of PVFc-*b*-MT, PVFc-*b*-MH, and PVFc-*b*-(MT)₂

oligosaccharides, the oligosaccharide-containing BCPs easily achieve strong segregation with the combination of any type of hydrophobic polymer.

Another important challenge in the development of novel BCPs is to improve their etching selectivity and thermal stability. For application in an actual lithographic process, the etching selectivity of two blocks must be high enough to achieve pattern transfer to the underlying semiconductor substrate. To enhance the etching selectivity, high- χ BCPs comprising an inorganic segment, such as poly(dimethylsiloxane) (PDMS), polyhedral oligomeric silsesquioxane (POSS), and poly(trimethylsilylstyrene), have been developed, where the inorganic segments show higher resistance toward the etching process.^{30–36} In addition, sufficient heat resistance is required for precise pattern transfer because the dry etching process is often implemented at high temperatures (~ 70 °C)³⁷. This is because a high glass transition temperature (T_g) is necessary to maintain the nanostructure of the resist material during the etching process. However, the molecular weights of high- χ BCPs for sub-10 nm microphase separation are in the range 2,200–7,000 g mol^{−1} and may lower the T_g . Thus, polymer pairs with sufficient etching selectivity and a high T_g should be employed to create new high- χ BCPs for high-resolution lithographic application.

To accommodate all these requirements in a high- χ BCP, we envisaged a BCP system comprising a metal-containing polymer segment. Metal-containing polymers, so-called metallopolymers, are a class of inorganic polymers. Among them, ferrocene-containing polymers, such as poly(ferrocenylsilane) and poly(vinyl ferrocene) (PVFc), are the most widely studied from a synthetic and application view point. For example, Manners and Nuyken reported novel strategies to precisely synthesize ferrocene-containing polymers,^{38,39} the properties of which have been revealed in detail.^{30,40} Importantly, Vansco *et al.* disclosed that poly(ferrocenylsilane) presented high etching resistance due to complex oxide formation when exposed to oxygen plasma.⁴¹ Furthermore, Nuyken, Higashihara, and Gallei reported high PVFc T_g values (~ 200 °C).^{38,42,43} However, despite the suitable and promising properties for lithographic applications, ferrocene-containing polymers have never been applied in the design of high- χ BCPs for sub-10 nm microphase separation.

In this paper, we report a novel high- χ /low- N BCP system comprising PVFc and maltooligosaccharide [maltotriose (MT) or maltohexaose (MH)] segments, which simultaneously accomplishes a small d value, sufficient thermal stability, and high etching selectivity. We supposed that maltooligosaccharides would be the best counter block choice because of their strong hydrophilicity, high T_g , and weak etching

resistance.³⁷ Three types of BCPs comprising PVFc and an oligosaccharide, namely the linear-type PVFc-*b*-MT and PVFc-*b*-MH and the miktoarm-type PVFc-*b*-(MT)₂, were synthesized *via* living anionic polymerization followed by the click reaction (Scheme 1). PVFc-*b*-MH and PVFc-*b*-(MT)₂ formed hexagonally close-packed cylinder structures with single nano-order *d*-spacing in the bulk and thin film states. To the best of our knowledge, this paper is the first to report on metallopolymer-containing BCPs with *d* values in the sub-10 nm range. In addition, sub-10 nm lamellar structures could be obtained by mixing PVFc-*b*-(MT)₂ and glucose. Thus, we successfully obtained lithographically important morphologies from the novel BCP system.

Results and discussion

Synthesis of PVFc-*b*-MT, PVFc-*b*-MH, and PVFc-*b*-(MT)₂

The synthetic routes of PVFc-*b*-MT, PVFc-*b*-MH, and PVFc-*b*-(MT)₂ are illustrated in Scheme 1. First, PVFc possessing a hydroxyl group (PVFc-OH) at the ω -chain end was prepared by living anionic polymerization of vinylferrocene (VFc) followed by termination with benzyl glycidyl ether (BGE), according to previously reported methods.^{44,45} To obtain PVFc-OH with a target number-average molecular weight (M_n) of ~3,000 g mol⁻¹, the polymerization of VFc was conducted at the [VFc]₀/[*sec*-BuLi]₀ ratio of 18/1. BGE was added when the monomer conversion (conv.) reached 80%, so that the theoretical molecular weight ($M_{n,theo}$) was calculated as 3,280 g mol⁻¹. The ¹H NMR spectra of the obtained PVFc-OH exhibited a signal assigned to the benzene ring of the ω -chain end group [f in Figure 1(ai)]. End-group analysis by ¹H NMR revealed a molecular weight ($M_{n,NMR}$) of 3,190 g mol⁻¹, which agreed well with the $M_{n,theo}$ value. The size exclusion chromatography (SEC) trace of PVFc-OH presented a unimodal peak with the dispersity ($\mathcal{D}$) value 1.24 [Figure 1(c)]. The obtained PVFc-OH was then reacted with 6-azidohexanoic acid (N₃-COOH) to form PVFc possessing an azido group (PVFc-N₃) at the ω -chain end. The reaction was carried out with 4-dimethylaminopyridine (DMAP) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) as the catalyst and condensation reagent, respectively, at the [PVFc-OH]₀/[N₃-COOH]₀/[DMAP]₀/[EDC·HCl]₀ ratio 1/7/5/7, which afforded the desired PVFc-N₃ in high yield (97%). The ¹H NMR spectrum of PVFc-N₃ displayed a new signal in the range 3.12–3.29 ppm, assigned to the methylene proton adjacent to the azido group [A in Figure 1(aii)]. In addition, the FT-IR spectra presented a new absorption band at 2095 cm⁻¹, assigned to the azido group [Figure 1(bii)]. Finally, PVFc-*b*-MT was synthesized via the click reaction of PVFc-N₃ with *N*-maltotriosyl-3-acetamido-1-propyne (MT-C≡CH). The reaction was conducted using copper(I) bromide (CuBr) and *N,N,N',N',N'*-pentamethyldiethylenetriamine (PMDETA) as the catalyst and ligand, respectively, at the [PVFc-N₃]₀/[MT-C≡CH]₀/[CuBr]₀/[PMDETA]₀ ratio 1/1.3/1.4/1.3, which afforded PVFc-*b*-MT in 84% yield. The absence of the absorption band at 2095 cm⁻¹ [Figure 1(b) (bottom)]

in the FT-IR spectrum of the product suggested sufficient conversion from the azido group to the corresponding triazole ring. Moreover, the new strong absorption band at ~3,400 cm⁻¹, assigned to the hydroxyl group, indicated the successful installation of the MT block. The SEC data provided good evidence of BCP formation; the elution peak maximum shifted to the higher molecular weight region following the click reaction [Figure 1(c)]. Although a small elution peak due to the PVFc homopolymer was observed, its fraction was calculated as ~18%. Nevertheless, the $\mathcal{D}$ value of PVFc-*b*-MT was estimated to be as narrow as 1.08. The ¹H NMR spectrum of PVFc-*b*-MT exhibited a characteristic signal in the range 7.92–8.34 ppm, ascribed to the triazole ring, along with a series of signals corresponding to both the PVFc and MT blocks [Figure 1(aiii)]. The $M_{n,NMR}$ of the obtained PVFc-*b*-MT was calculated as 3,910 based on the ¹H NMR data. Beginning with the same PVFc-OH sample, PVFc-*b*-MH was synthesized in the same manner, using *N*-maltotetraosyl-3-acetamido-1-propyne (MH-C≡CH) instead of MT-C≡CH. The FT-IR, NMR, and SEC data revealed the successful synthesis of the desired PVFc-*b*-MH (Figure S1).

The miktoarm-type BCP, PVFc-*b*-(MT)₂, was synthesized in a similar manner with PVFc-*b*-MT and PVFc-*b*-MH (Scheme 1). Prior to esterification with 6-azidohexanoic acid, the benzyl group on PVFc-OH was deprotected by treatment with Pd-C/H₂ to afford PVFc possessing two hydroxyl groups at the ω -chain end [PVFc-(OH)₂] in 72% yield.^{44,45} The deprotection reaction proceeded completely as evidenced by the disappearance of the signal, owing to the presence of the benzene ring without any side reactions [Figures S2 and S3]. Next, the obtained PVFc-(OH)₂ was reacted with N₃-COOH ([PVFc-(OH)₂]₀/[N₃-COOH]₀/[DMAP]₀/[EDC·HCl]₀ = 1/12/9/10) to afford PVFc possessing two azido groups (PVFc-(N₃)₂) in 87% yield. Finally, PVFc-*b*-(MT)₂ was afforded in 83% yield by the click reaction of PVFc-(N₃)₂ with MT-C≡CH ([PVFc-(N₃)₂]₀/[MT-C≡CH]₀/[CuBr]₀/[PMDETA]₀ = 1/2.5/2.4/2.3). The FT-IR, NMR, and SEC data revealed the successful formation of the desired PVFc-*b*-(MT)₂ (Figure S2). Although SEC analysis revealed the presence of the PVFc homopolymer (~16%), the $\mathcal{D}$ value for the PVFc-*b*-(MT)₂ fraction was estimated to be quite narrow (1.08).

The PVFc volume fractions (f_{PVFc}) were calculated as 0.86, 0.75, and 0.74 for PVFc-*b*-MT, PVFc-*b*-MH, and PVFc-*b*-(MT)₂, respectively, based on the $M_{n,NMR}$ and density values (Table 1). Here, the reported density value for PVFc (1.28 g cm⁻³) was used for the calculation, while the reported density value for amylose (1.36 g cm⁻³) was used instead of those of MT and MH. PVFc-*b*-MT, PVFc-*b*-MH, and PVFc-*b*-(MT)₂ were insoluble in protic solvents such as H₂O and MeOH, which are good solvents for MT. This occurred because the majority component (i.e., PVFc) dictated the overall solubility. Indeed, the PVFc homopolymer is insoluble in such solvents. Among the tested organic solvents, the BCPs were molecularly dissolved in DMF and dimethyl sulfoxide. The ¹H NMR spectra obtained in these D-solvents presented signals from both the PVFc and saccharidic blocks. On the other hand, the ¹H NMR spectra obtained in CDCl₃ only displayed signals corresponding to the PVFc block, probably due to micellar aggregate formation with the PVFc outer shell.

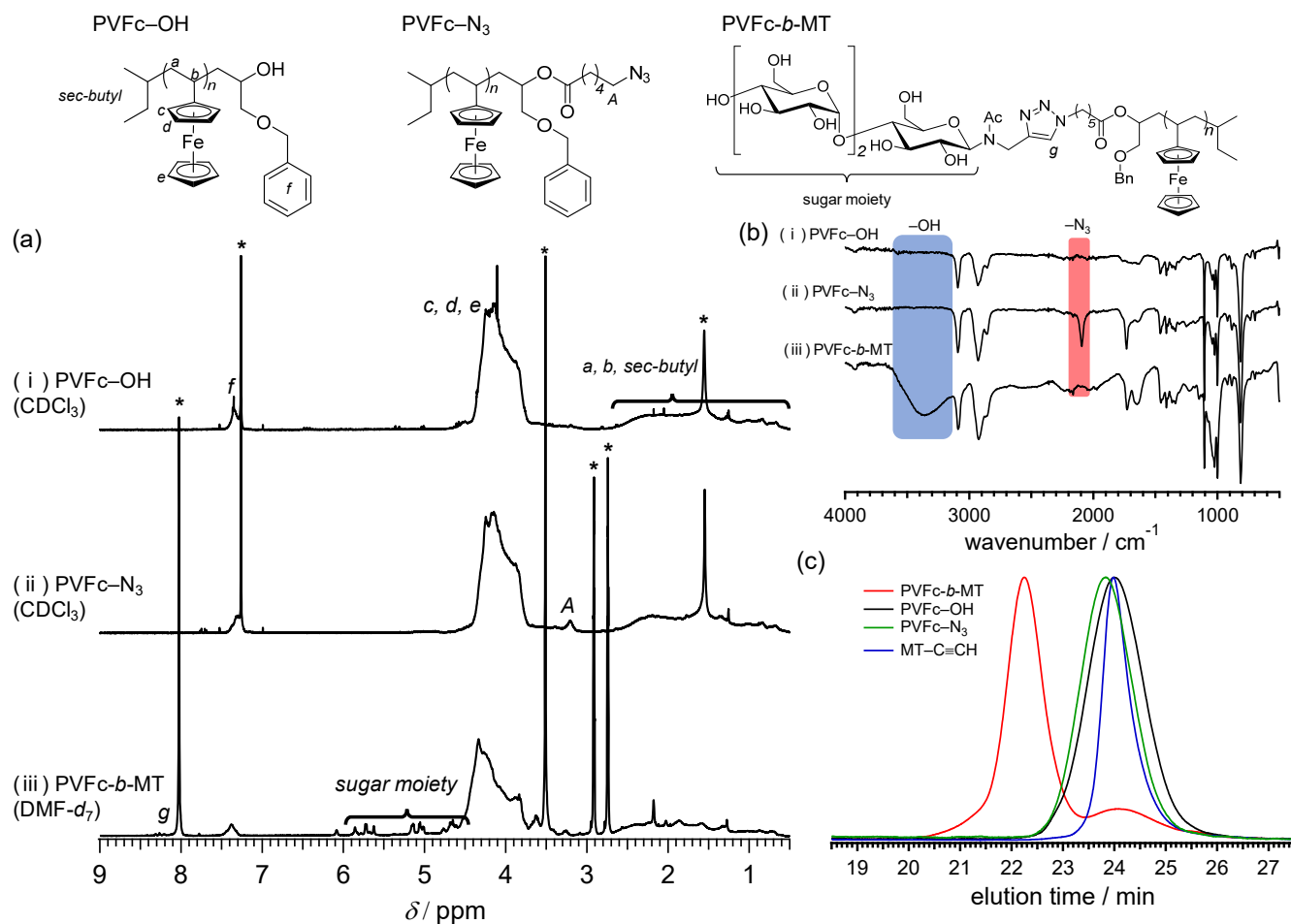


Figure 1. Characterization of PVFc-*b*-MT. (a) ¹H NMR spectra of PVFc-OH (i) and PVFc-N₃ (ii) in CDCl₃ and PVFc-*b*-MT (iii) in DMF-*d*₇ (400 MHz). (b) FT-IR spectra of PVFc-OH (i), PVFc-N₃ (ii), and PVFc-*b*-MT (iii). (c) SEC traces of PVFc-*b*-MT (red), PVFc-OH (black), PVFc-N₃ (green), and MT-C≡CH (blue) eluent, DMF containing 0.01 mol L⁻¹ LiCl; flow rate, 0.60 mL min⁻¹.

Table 1. Molecular characteristics of the block copolymers (BCPs) and their precursors

Polymer	<i>M</i> _{n,NMR} ^a	<i>M</i> _{n,SEC}	<i>Đ</i>	<i>f</i> _{PVFc} ^d	Yield / %
PVFc-OH	3,190	1,020 ^b	1.24 ^b	-	80
PVFc-N ₃	3,330	1,180 ^b	1.21 ^b	-	97
PVFc- <i>b</i> -MT	3,910	4,180 ^c	1.07 ^c	0.86	84
PVFc- <i>b</i> -MH	3,980	6,370 ^c	1.05 ^c	0.74	41
PVFc-(OH) ₂	3,100	1,020 ^b	1.23 ^b	-	72
PVFc-(N ₃) ₂	3,380	1,270 ^b	1.37 ^b	-	87
PVFc- <i>b</i> -(MT) ₂	4,330	6,680 ^c	1.08 ^c	0.75	83

^aDetermined by ¹H NMR. ^bDetermined by size exclusion chromatography (SEC) in THF using polystyrene standards. ^cDetermined by SEC in DMF using polystyrene standards. ^dPVFc volume fractions (*f*_{PVFc}) were calculated using the known density values *d*_{PVFc} = 1.28 g cm⁻³ and *d*_{amylose} = 1.36 g cm⁻³.

Thermal properties and etching resistance

The thermal properties of PVFc-*b*-MT, PVFc-*b*-MH, and PVFc-*b*-(MT)₂ were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The decomposition temperatures of PVFc-OH, MT-C≡CH, MH-C≡CH, and PVFc-*b*-MT were first investigated by TGA. The PVFc-OH, MT-C≡CH, and MH-

C≡CH TGA profiles displayed decomposition temperatures at 360, 210, and 260 °C, respectively (Figure S4), confirming the high heat resistance of PVFc. The TGA profile of PVFc-*b*-MT displayed two decomposition points at 230 and 380 °C corresponding to the decomposition temperatures of maltotriose and PVFc, respectively. The DSC curve of the PVFc homopolymer presented only one base-line shift (136.1 °C) corresponding to the glass transition. The DSC curves of PVFc-*b*-MT and PVFc-*b*-(MT)₂ displayed a base-line shift corresponding to the glass transition of the PVFc segment during the second heating run. On the other hand, the PVFc-*b*-MH DSC curve only displayed a base line shift during the first heating run (Figure 2). Notably, no transitions due to melting and crystallization were observed in the DSC traces of PVFc-*b*-MT, PVFc-*b*-MH, PVFc-*b*-(MT)₂, and the PVFc homopolymer, demonstrating the absence of crystalline structures in these polymers. The glass transition temperatures of the PVFc segments (*T*_{g,PVFc}) in PVFc-*b*-MT, PVFc-*b*-MH, and PVFc-*b*-(MT)₂ were determined as 153.6, 143.2, and 143.4 °C, respectively, values that are higher than that of the PVFc homopolymer (136.1 °C). This was attributed to the decrease in the chain mobility of the PVFc segment because of the presence of the

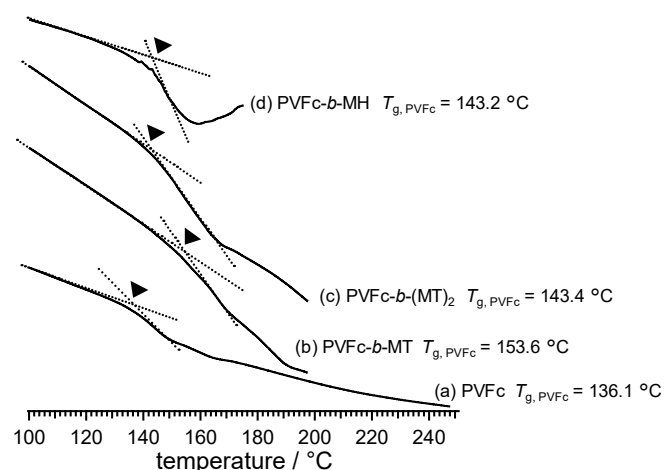


Figure 2. Differential scanning calorimetry (DSC) curves of (a) PVFc, (b) PVFc-*b*-MT, and (c) PVFc-*b*-(MT)₂ during the second heating run and (d) PVFc-*b*-MH during the first heating run.

large oligosaccharide segment that can form strong intra- and intermolecular hydrogen-bonding.

The etching resistances of the PVFc and oligosaccharide were also investigated. Thus, thin films of PVFc (film thickness, ~230 nm) and maltotriose (film thickness, ~180 nm) on a Si substrate were prepared by spin-coating. The etching depth of these thin films was determined after they were subjected to oxygen reactive ion etching (RIE). As expected, PVFc exhibited higher etching resistance towards oxygen RIE than maltotriose (Table S1 and Figures S5 and S6), and its etching selectivity (1.78) was superior to that of the well-known polystyrene-*b*-poly(methyl methacrylate).⁴⁶

Microphase-separated structures

The microphase-separated structures of PVFc-*b*-MT, PVFc-*b*-MH, and PVFc-*b*-(MT)₂ in the bulk state were investigated using small angle X-ray scattering (SAXS). Prior to the SAXS experiment, the samples were thermally annealed at 180 °C, a temperature that was higher than the *T_g* of the constitutional blocks.

The PVFc-*b*-MT SAXS profile only displayed a weak primary scattering peak, suggesting that no microphase separation occurred [Figure 3(a)]. This was attributed to the *N* value of PVFc-*b*-MT, which was too small to gain enough segregation strength. On the other hand, PVFc-*b*-MH successfully self-assembled into a microphase-separated structure as evidenced by the SAXS profile, even though *N* was ~20. Specifically, the SAXS profile of PVFc-*b*-MH displayed a primary scattering peak at $q^* = 0.767 \text{ nm}^{-1}$ and higher-ordered scattering peaks at $\sqrt{3}q^*$ and $2q^*$, which corresponded to hexagonally close-packed cylinder (HEX) morphology [Figure 3(b)]. Moreover, *d*, calculated based on the Bragg's equation ($d = 2\pi/q^*$), was extremely small (8.2 nm), while the center-to-center distance between the cylinders ($d_{\text{C-C,SAXS}} = 2d/\sqrt{3}$) was calculated as 9.5 nm. Thus, the addition of one more MT unit permitted the BCP to microphase-separate by overcoming the critical χN .

The SAXS profile of PVFc-*b*-(MT)₂ also displayed a scattering pattern corresponding to HEX morphology [Figure 3(c)]. Notably, the *d* and $d_{\text{C-C,SAXS}}$ values were calculated as 7.8 and 9.0 nm, respectively, both <10 nm. This result strongly supported the above discussions

that the χN exceeded the critical value to microphase-separate with the addition of one more MT unit. Notably, the scattering peaks for the PVFc-*b*-(MT)₂ sample were apparently sharper than those of PVFc-*b*-MH, suggesting the better long-range ordering in PVFc-*b*-(MT)₂. The lower *T_g* of maltotriose (110 °C) compared to that of maltohexaose (145 °C) suggested the superior chain mobility of PVFc-*b*-(MT)₂ during thermal annealing, which could facilitate grain coarsening in PVFc-*b*-(MT)₂.⁴⁷

The microphase-separated structure in the thin film state was visualized by atomic force microscopy (AFM). The PVFc-*b*-(MT)₂ thin film was prepared by spin coating its 5 wt% DMF solution onto a silicon substrate followed by thermal annealing at 180 °C for 5 h under vacuum. The AFM phase image exhibited a finger-print-like pattern corresponding to the HEX structure parallel to the substrate (Figure S7). The center-to-center distance between the cylinders ($d_{\text{C-C,AFM}}$) was 8.3 nm, as estimated by the Fast Fourier transform (FFT) analysis of the phase image; this value roughly matched the $d_{\text{C-C,SAXS}}$ value. Such a parallel cylindrical structure could be applied to the fabrication of line-and-space patterns with the aid of directed self-assembly.

It is quite important to obtain a variety of morphologies, such as spheres, cylinders, gyroids, and lamellars, to expand the possible nanofabrication applications. To diversify the available morphology from the present BCP system, we investigated the microphase-separated structures of a series of blend samples of PVFc-*b*-MT and PVFc-*b*-(MT)₂ with glucose and PVFc homopolymers. The addition of an A homopolymer into an AB diblock copolymer has been reported to alter the microphase-separated structures by the selective swelling of the A block microdomain.^{48,49} Thus, we first attempted to induce and control microphase separation in PVFc-*b*-MT by adding glucose. However, no ordered microphase-separated structure was found in the PVFc-*b*-MT/glucose blend, regardless of the total volume fraction of the saccharide portion (f_{sac}). Next, we prepared a PVFc-*b*-(MT)₂/Glc blend with an f_{sac} of 0.49, aiming at obtaining lamellar morphology (LAM). The SAXS profile of the thermally annealed PVFc-*b*-(MT)₂/Glc blend sample presented a primary peak at $q^* = 0.676 \text{ nm}^{-1}$ and an additional higher-ordered peak at the $2q^*$ position [Figure 3(d)], which corresponded to LAM morphology. The *d* value was calculated as 9.3 nm, based on the Bragg's equation, which was significantly larger than that of pristine PVFc-*b*-(MT)₂. As expected, this result demonstrates the shift in the microphase-separated structure, from HEX to LAM, owing to the selective swelling of the saccharide domain as a result of the added glucose. On the other hand, the PVFc-*b*-(MT)₂/PVFc blend ($f_{\text{sac}} = 0.21$), which was prepared aiming at achieving spherical morphology, only presented a broad primary peak. This suggested the absence of an ordered microphase-separated structure. Nevertheless, we successfully constructed lithographically important lamellar and cylindrical morphologies from PVFc-*b*-(MT)₂.

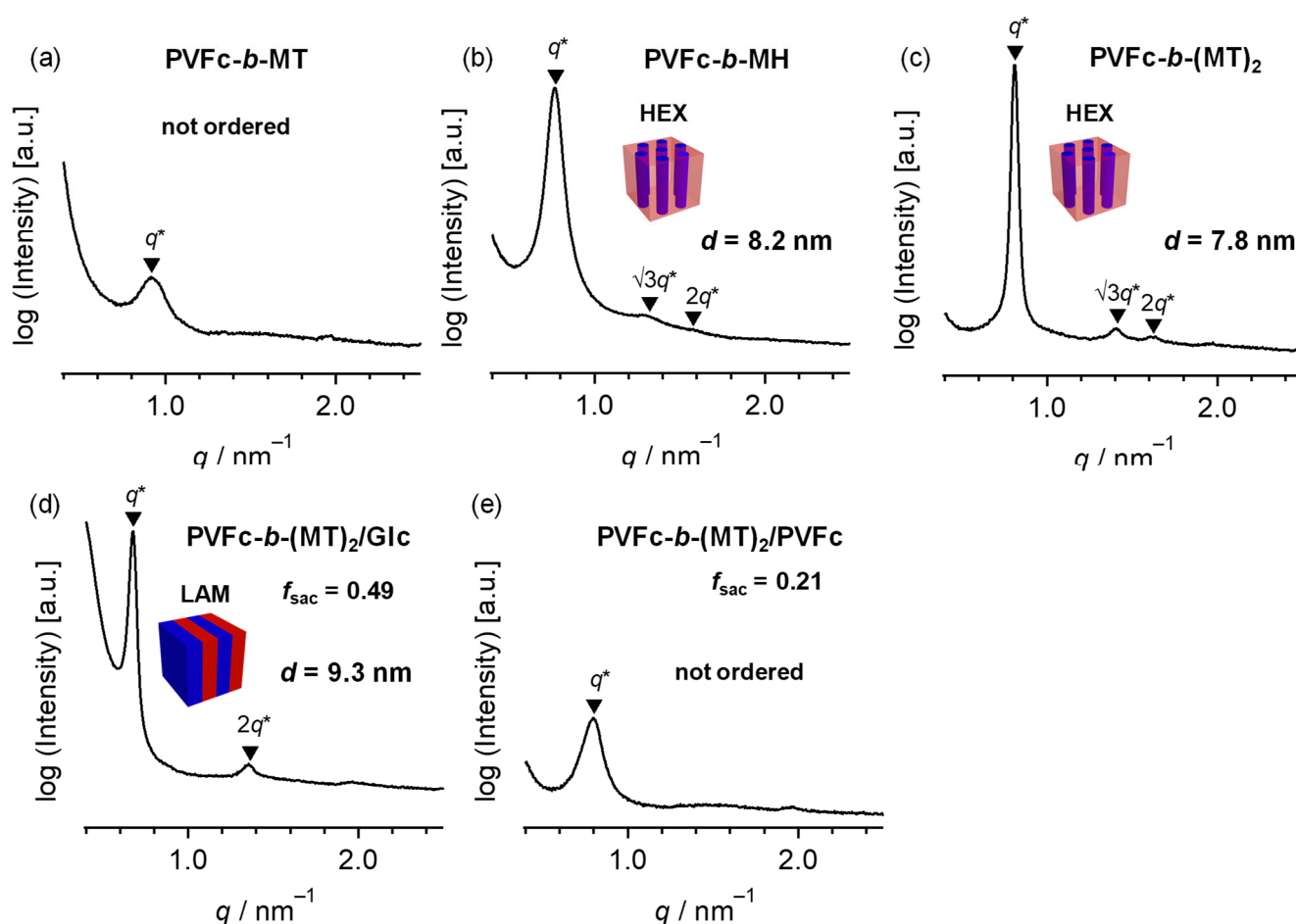


Figure 3. Small angle X-ray scattering (SAXS) profiles for the bulk samples of (a) PVFc-*b*-MT, (b) PVFc-*b*-MH, (c) PVFc-*b*-(MT)₂, (d) PVFc-*b*-(MT)₂/Glc, and (e) PVFc-*b*-(MT)₂/PVFc. All the samples were annealed at 180 °C for 1 h. The small peak at $q = 1.95 \text{ nm}^{-1}$ is artifact in the scattering data.

Conclusions

We successfully synthesized three types of novel oligosaccharide-based BCPs (PVFc-*b*-MT, PVFc-*b*-MH, and PVFc-*b*-(MT)₂) using living anionic polymerization followed by the click reaction. PVFc-*b*-MH and PVFc-*b*-(MT)₂ formed HEX microphase-separated structures with sub-10 nm d values, which were affected by the polymer architecture. These results are the first experimental demonstration of metal-containing BCPs that formed microphase-separated structures with a domain spacing of <10 nm. Interestingly, the microphase-separated structure of the PVFc-*b*-(MT)₂/glucose mixtures was different from that of PVFc-*b*-(MT)₂. Thus, the morphology was shifted from HEX to LAM. Importantly, we successfully obtained both LAM and HEX morphology, which are useful for the lithographic process. We are currently optimizing the etching conditions to realize higher etching selectivity for directed self-assembly applications.¹⁴ PVFc-*b*-oligosaccharide BCPs, featured by their small d value, sufficient thermal stability, and high etching selectivity, are highly promising lithographic materials and show great potential for use in other nanotechnological

applications such as functional membranes^{50,51} and polymer-based memory devices.^{52,53}

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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