



Preparation of polymer brushes with well-controlled stereoregularity and evaluation of their functional properties

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Abstract

Polymer brushes in which one polymer chain end is tethered to a substrate show permanent properties related to the chemical structure of the polymer. However, they cannot accommodate functional molecules in the desired space because of the steric hindrance between neighboring polymer chains. To overcome this problem, the preparation of polymer brushes with ordered nanopores is strongly desired. High-density poly(methyl methacrylate) brushes with well-controlled stereoregularity were prepared using a surface-initiated living anionic polymerization method in the presence of a Lewis acid. A molecular weight range from 6 to 400 K with a narrow polydispersity index was obtained. Grazing incidence wide-angle X-ray diffraction measurements indicated that the polymer brushes formed a helical structure approximately 1 nm in diameter and consisting of encapsulated functional molecules or polymers, leading to the formation of inclusion complexes or stereocomplexes.

Introduction

Polymer brushes in which one polymer chain is tethered to the substrate show permanent and specific properties caused by the chemical structure [1]. They are roughly divided according to their synthetic approach into two types: “grafting to” and “grafting from” [2]. In the former approach, a polymer containing functional groups that can react or interact with the substrate is first prepared, and subsequently, the polymers are tethered to the substrate. Although this method is very simple, the preparation of high-density polymer brushes by this approach is extremely

difficult. On the other hand, in the “grafting from” method, polymerization is initiated from an initiator immobilized on the substrate. The size of monomers is much smaller than that of polymers, leading to a high-density polymer brush.

A polymer brush with a well-defined structure was first prepared in 1997 using a surface-initiated controlled radical polymerization method [3]. Accordingly, various kinds of high-density polymer brushes with well-controlled primary structures have been prepared using controlled radical polymerization [4–8], living anionic polymerization [8–12], living cationic polymerization [13–15], and chain-growth polycondensation [16, 17] methods. The advantages of these reactions are a high initiation efficiency and sustainable propagation without undesired side reactions, leading to the formation of polymer brushes with a high grafting density and well-controlled molecular weight (M_n), functional groups, and block sequences. The high-density polymer brushes obtained by this method have potential to be incorporated in sophisticated and smart functional surfaces, which is anticipated to be applicable in the fields of nanotechnology, biomaterials, and electronic devices.

High-density polymer brushes become swollen and orient perpendicular to the substrate in a good solvent because of the excluded volume effect, which applies to neighboring polymer chains under high osmotic pressure [18, 19]. The swollen state of polymer brushes leads to low friction [20, 21], specific adhesion [22, 23], and antifouling properties [24].

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Conventional high-density polymer brushes, however, cannot encapsulate functional molecules and polymers because of the steric hindrance between neighboring polymer chains. To overcome this problem, we have focused on the preparation of a polymer brush that forms a helical structure, which is anticipated to encapsulate functional molecules. A polymer brush with a helical structure was first prepared by surface-initiated ring-opening anionic polymerization of *N*-carboxy amino acid anhydrides [25, 26]. However, the cylindrical cavity in the helical structure of the polyamide brush was too small to encapsulate functional molecules and polymers. Moreover, the introduction of various kinds of functional groups in the polyamide brush remains synthetically difficult.

Poly(methyl methacrylate) (PMMA) with well-controlled stereoregularity shows a specific structure and properties. In particular, syndiotactic PMMA (*st*-PMMA) forms a helical structure and encapsulates fullerene molecules or isotactic PMMA (*it*-PMMA), leading to the formation of an inclusion complex or stereocomplex [27–33]. If PMMA with well-controlled stereoregularity can be grafted with a high density, this strategy offers an approach to introducing a high density of functional molecules and polymers on a desired substrate. This focus review describes recent work on the preparation of high-density PMMA brushes with well-controlled stereoregularity and the ability to encapsulate functional molecules and polymers.

Preparation of *st*-PMMA brushes on the basis of surface-initiated living anionic polymerization

Pioneering research on the surface-initiated anionic polymerization of methyl methacrylate (MMA) monomer was reported by Schomaker and coworkers [9]. They immobilized 3-(methacryloxy)propyltrimethoxysilane on a silica substrate and subsequently added phenylmagnesium bromide to prepare the initiator. Then, MMA was added to the reaction mixture, resulting in the formation of *it*-PMMA. During this reaction, however, side reactions between neighboring initiators occur. Hence, high-density polymer brushes could not be obtained using this process. To remedy this problem, 2-bromo-2-methyl propionoyloxyhexyltriethoxy silane (BHE) was immobilized on flat and spherical silica substrates, and subsequently, an initiator was prepared using a lithium/halogen exchange reaction in the presence of excess tertiary butyl lithium (*tert*-BuLi) and triethyl aluminum (Et₃Al) [8, 34]. Then, MMA was added to the system to obtain the target PMMA brushes (Fig. 1a). Here, Et₃Al serves not only to increase the stereoregularity but also acts as a dehydrating agent in the reaction system. During this polymerization reaction, free polymer that is not tethered to the solid substrate is generated. The M_n , polydispersity index (PDI), and stereoregularity of the free polymers are summarized in Table 1.

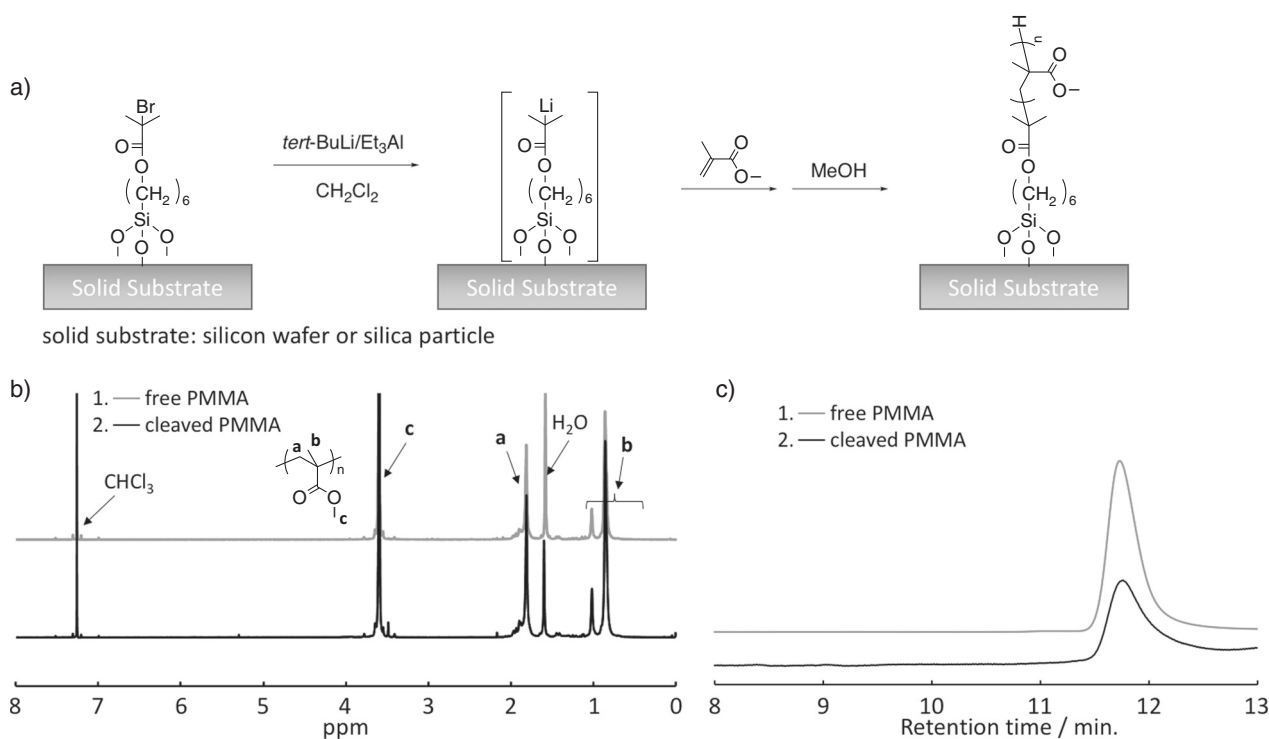


Fig. 1 a Synthetic strategy for preparing *st*-PMMA brushes using living anionic polymerization. b ¹H NMR spectra and c SEC curves of free and cleaved PMMA

Table 1 Summary of the primary structures of polymer brushes prepared on a silicon wafer

Sample	M_n^a	PDI ^a	Tacticity ^b (%)			Thickness ^c (nm)	Grafting density (chains/nm ²)
			<i>rr</i>	<i>mr</i>	<i>mm</i>		
^d PMMA ₆₀	6,000	1.09	88	12	0	5.3	0.63
^e PMMA ₁₇₀	17,000	1.11	86	14	0	–	0.63
^d PMMA ₂₀₀	20,000	1.06	90	10	0	10.3	0.37
^e PMMA ₂₂₀	17,000	1.08	88	12	0	–	0.37
^e PMMA ₃₂₀	32,000	1.11	88	12	0	–	0.39
^d PMMA ₃₃₀	33,000	1.06	88	12	0	21.9	0.48
^d PMMA ₄₀₀	40,000	1.06	90	10	0	18.6	0.33
^d PMMA ₄₇₀	47,000	1.07	88	12	0	30.4	0.46
^d PMMA ₈₃₀	83,000	1.13	88	12	0	30.0	0.26
^d PMMA _{4,000}	400,000	1.31	89	11	0	68.0	0.12

^aThe molecular weight and polydispersity index were determined using SEC

^bThe stereoregularity of the PMMAs was evaluated by ¹H NMR spectroscopy

^cThe thickness was determined using ellipsometry.

^dPolymer brushes prepared on silicon wafer

^ePolymer brushes prepared on silica particles, respectively

It is clear that free polymers with a narrow PDI and well-controlled stereoregularity were obtained using surface-initiated living anionic polymerization.

The M_n , PDI, and stereoregularity of the polymer brush are not always the same as those of the free polymer. To reveal the relationship between the primary structure of the free polymer and the polymer brush, a PMMA₂₂₀ brush, which was prepared on silica particles with a diameter of 200 nm, was cleaved using a hydrogen fluoride aqueous solution, and the primary structure was evaluated. Figure 1b, c shows the proton nuclear magnetic resonance (¹H NMR) spectra and size exclusion chromatography (SEC) curves, respectively, of the free and cleaved polymers. The M_n , PDI, and stereoregularity of the free polymer and polymer brush were comparable. This indicates that the primary structure of the polymer brush prepared on the basis of surface-initiated living anionic polymerization in the presence of Et₃Al could be evaluated using the free polymer.

High-density polymer brushes are defined as having a graft density higher than 0.1 chains/nm². The graft density of the polymer brush was higher than 0.1 chains/nm², strongly supporting the conclusion that high-density polymer brushes with a well-controlled PDI and stereoregularity can be obtained on both flat and spherical substrates using the technique presented here (Table 1).

Formation of inclusion complex between a PMMA brush and fullerene molecules

st-PMMA has been previously reported to form a helical structure and encapsulate fullerene molecules in the helical

nanocavity [27, 28]. Moreover, the helical cavity in *st*-PMMA can recognize and adapt to the fullerene size, leading to the selective separation of C₇₀ from a mixture of C₆₀ and C₇₀ in solution [35]. If this principle can be applied in high-density PMMA brushes, a novel functional solid surface with a molecular recognition capability could be formed.

To investigate whether high-density PMMA brushes could form helical structures and encapsulate fullerene molecules in the helical nanocavity, a high-density PMMA brush was immersed in C₆₀/toluene and C₇₀/toluene solutions, and subsequently, grazing incidence wide-angle X-ray diffraction (GIWAXD) measurements were performed to characterize the structure of the polymer brush. The scattering vector is defined as $q = (4\pi/\lambda)\sin\theta$, where θ is the Bragg angle. Figure 2a–c shows the GIWAXD patterns and line profiles along the equatorial direction of the *st*-PMMA_{4,000}/C₆₀ and *st*-PMMA_{4,000}/C₇₀ brushes. *st*-PMMA_{4,000}/C₆₀ showed diffraction peaks at $q = 3.35 \text{ nm}^{-1}$ along the equatorial axis and $q = 7.79 \text{ nm}^{-1}$ along the meridional axis. The former peak can be assigned to the long-period structure of the PMMA/C₆₀ inclusion complex, while the latter peak is associated with the helical pitch of *st*-PMMA. This indicates that high-density *st*-PMMA forms a helical structure and encapsulates C₆₀ in the nanocavity, leading to the formation of an inclusion complex. Moreover, the *st*-PMMA brush/C₆₀ inclusion complex is oriented perpendicular to the substrate (Fig. 2d). The *st*-PMMA_{4,000} brush/C₇₀ also showed a diffraction peak at $q = 3.23 \text{ nm}^{-1}$ along the equatorial axis, which indicated that this system formed an inclusion complex that was oriented perpendicular to the substrate. The diffraction peak at $q = 7.79 \text{ nm}^{-1}$, which is assigned to the helical pitch of *st*-PMMA, could not be observed for the *st*-PMMA/C₇₀ brush. This is because the asymmetric nature of C₇₀ leads to a disordered alignment of C₇₀ in the *st*-PMMA helix, resulting in the formation of a poorly ordered inclusion complex compared with that of *st*-PMMA/C₆₀.

To determine whether high-density *st*-PMMA brushes could achieve the selective separation of C₆₀ from a mixture of C₆₀ and C₇₀ in solution, a high-density *st*-PMMA₃₂₀ brush, which was prepared on silica particle with a diameter of 200 nm, was dispersed in a solution of C₆₀ and C₇₀ in toluene. Then, the particles were collected by centrifugation and washed with pure toluene. Subsequently, the fullerene that was encapsulated in the *st*-PMMA brush was extracted using *o*-dichlorobenzene. The fullerene molecules thus obtained were characterized by ultraviolet–visible (UV–vis) spectroscopy and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS). Figure 3a, b shows the UV–vis spectra of the mixed C₆₀/C₇₀ solution, the supernatant of the mixed solution following treatment by the *st*-PMMA₃₂₀ brush, and the extracted fullerene, respectively. The UV–vis spectra of the extracted fullerene showed good agreement with that of C₇₀, which

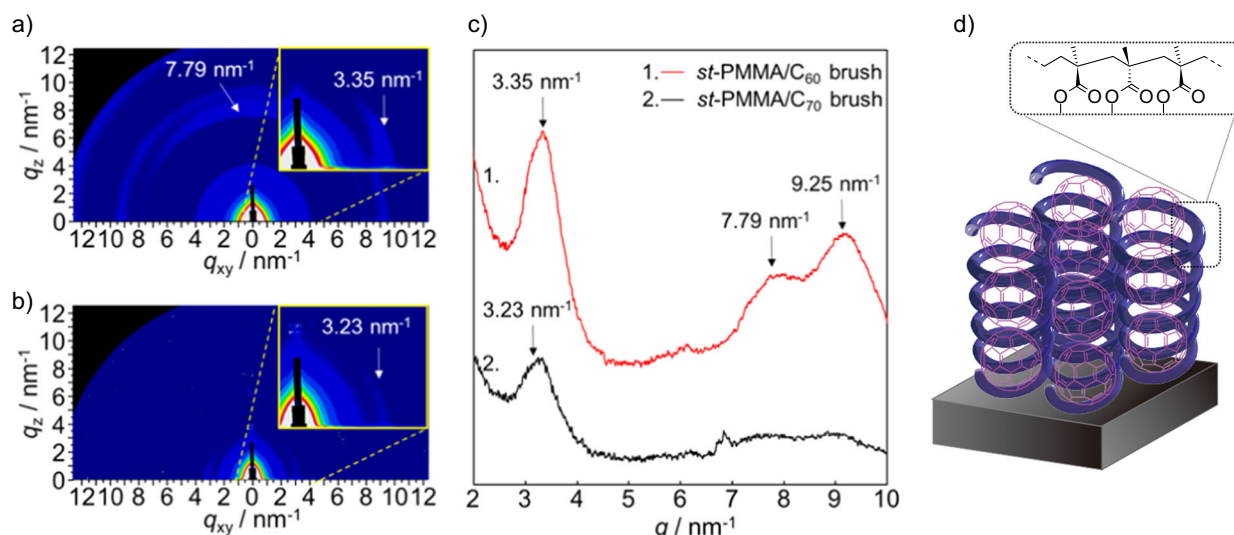


Fig. 2 a GIWAXD patterns of the *st*-PMMA_{4,000} brush/C₆₀ and (b) *st*-PMMA_{4,000} brush/C₇₀ inclusion complexes and (c) line profiles of the inclusion complexes along the equatorial axis

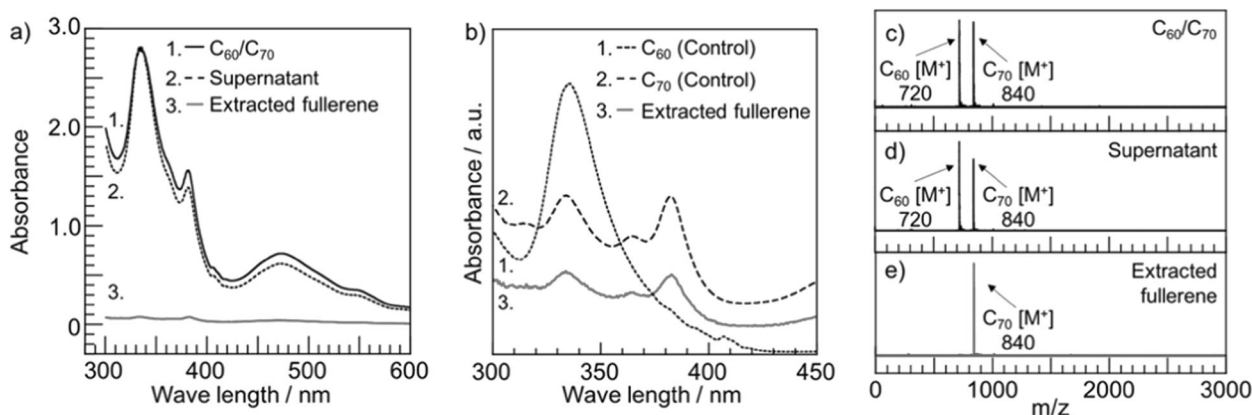


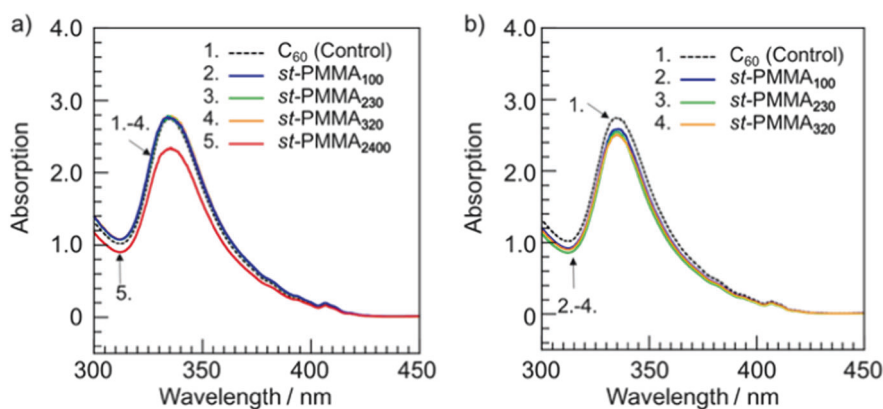
Fig. 3 a UV-vis spectra of the fullerene extracted from the mixture of C₆₀ and C₇₀ using the *st*-PMMA₃₂₀ brush and (b) the magnified spectra. c MALDI-TOF-MS spectra of the C₆₀/C₇₀ mixture, (d) supernatant, and (e) fullerene extracted from the *st*-PMMA brush

implied that C₇₀ was selectively separated from the mixture of C₆₀ and C₇₀ in solution using the high-density *st*-PMMA brush. Figure 3c–e shows the MALDI-TOF-MS spectra of the C₆₀/C₇₀ mixed solution, the supernatant, and the extracted fullerene. The MALDI-TOF-MS spectrum of the C₆₀/C₇₀ mixture showed two peaks for C₆₀ and C₇₀ ($m/z = 720$ (C₆₀-M⁺) and 840 (C₇₀-M⁺)), while the spectrum of the extracted fullerene showed only the C₇₀ peak.

The use of the polymer brush as a separation material has two advantages. One advantage is the molecular weight. Bulk *st*-PMMA could form a helical structure and encapsulate fullerene; however, this specific phenomenon is limited to *st*-PMMA with a high molecular weight. To separate fullerene from solution, gel formation is necessary. *st*-PMMA forms a helical structure and aggregates to form a network structure, leading to the formation of a gel. However, the formation of a gel by *st*-PMMA is strongly related to the molecular weight. Although *st*-PMMA with a low

molecular weight in the bulk state might form a helical structure and encapsulate fullerene molecules within the helical nanocavity in toluene, the *st*-PMMA/fullerene inclusion complex cannot form a gel, leading to regulation of the selective separation of fullerene molecules from solution. The *st*-PMMA brush prepared on silica particles can be easily separated from the fullerene solution even with the use of *st*-PMMA with a low molecular weight. To emphasize this advantage, bulk *st*-PMMA was added to a C₆₀ toluene solution and annealed at 383 K for 30 min. Subsequently, centrifugation was performed to separate the inclusion complex. Figure 4a shows the UV-vis spectra of the C₆₀ toluene solution before and after treatment using bulk *st*-PMMA with M_n values of 240,000, 32,000, 23,000, and 10,000, which are designated *st*-PMMA₂₄₀₀, *st*-PMMA₃₂₀, *st*-PMMA₂₃₀, and *st*-PMMA₁₀₀, respectively. Although *st*-PMMA₂₄₀₀ induced a significant change in the spectrum, the others did not produce any changes in the

Fig. 4 UV–vis spectra of a C_{60} toluene solution before and after the addition of (a) bulk *st*-PMMA with different molecular weights and (b) *st*-PMMA brushes with different molecular weights



spectrum before and after the addition of bulk *st*-PMMA to the solution. Figure 4b shows the UV–vis spectra of a C_{60} toluene solution before and after the above treatment using *st*-PMMA brushes with different M_n values. In the case of the polymer brushes, clear changes were observed before and after this treatment, indicating that even the *st*-PMMA brush with a low M_n could form a helical structure and encapsulate C_{60} in the helical nanocavity, leading to the selective separation of C_{60} from solution. The other advantage is the reusability of the polymer brush. The *st*-PMMA brush was tethered to a substrate, and thus, the polymer brush could be collected and reused after the separation of fullerene molecules from solution. Even after five cycles, the selectivity for the fullerene molecules remained at 99% [36].

Preparation of a high-density polymer brush consisting of a stereocomplex

High-density polymer brushes show excellent antifouling properties against various kinds of natural polymers, including peptides, at the surface in good solvents. Generally, free polymer cannot penetrate the high-density polymer brush owing to the enormous steric hindrance between neighboring polymer chains in the polymer brush. Mixtures of *it*-PMMA and *st*-PMMA are well known to form a stereocomplex consisting of a multihelical structure [29–33]. If this principle can be applied to a high-density polymer brush system, free polymer can penetrate the polymer brush, resulting in the formation of a stereocomplex. *st*-PMMA brushes prepared on silica particles and a silicon wafer were immersed in an *it*-PMMA acetonitrile/water solution to form the stereocomplex. Figure 5a shows the differential scanning calorimetry (DSC) measurements for the 1st and 2nd heating scans of the *st*-PMMA₃₂₀ brush prepared on silica particles following immersion in the *it*-PMMA solution. Two endothermic peaks, which are assigned to the crystalline structure formed from fringed

micellar growth and lamellar growth, could be observed during the 1st heating run [37]. This implies the formation of a stereocomplex in the high-density *st*-PMMA brush. The molecular aggregate structure of the *st*-PMMA brush₃₃₀ prepared on a silicon wafer was evaluated using GIWAXD measurements. Figure 5b, c, d shows the two-dimensional GIWAXD patterns and line profiles along the equatorial axis and a schematic illustration of the stereocomplex prepared in bulk, which was previously reported [32]. Although the diffraction contrast was weak, diffraction peaks were observed at $q = 2.79 \text{ nm}^{-1}$, 7.92 nm^{-1} , 9.84 nm^{-1} , and 10.8 nm^{-1} . These diffraction peaks could also be seen in the bulk stereocomplex, and each peak was characterized as follows: the domain spacing of the cylindrical structure forming the stereocomplex ($q = 2.79 \text{ nm}^{-1}$, $d = 2.25 \text{ nm}$), the pitch of the outermost helical structure in the stereocomplex induced by *st*-PMMA ($q = 7.92 \text{ nm}^{-1}$, $d = 0.79 \text{ nm}$), the pitch of the inside of the double-helical structure formed by *it*-PMMA ($q = 9.84 \text{ nm}^{-1}$, $d = 0.63 \text{ nm}$), and the distance between the *st*- and *it*-PMMA chains in the helical structure ($q = 10.8 \text{ nm}^{-1}$, $d = 0.58 \text{ nm}$), respectively (Fig. 5d). These results indicate the formation of a stereocomplex in the high-density *st*-PMMA brush. To evaluate the molecular aggregate structure of the *st*-PMMA brush in more detail, it is necessary to improve the contrast in the GIWAXD measurements. To overcome this problem, 2,2,2-trifluoroethyl methacrylate (FEMA), which consists of fluoroalkyl groups with a high electron density, was introduced into the *st*-PMMA brush (Fig. 6a). The resulting *st*-PMMA-*r*-PFEMA brush, which consisted of 80% PMMA and 20% PFEMA, was immersed in an *it*-PMMA acetonitrile/water mixture (M_n : 36,000, PDI: 1.42, $rr:mr:mm = 86:14:0$). Figure 6b, c, d depicts the 2D GIWAXD patterns with improved contrast, the line profile along the equatorial axis, and a schematic illustration of the stereocomplex formed in the polymer brush. The peaks could be assigned to the domain spacing of the cylindrical structure forming the stereocomplex ($q = 2.74 \text{ nm}^{-1}$, $d = 2.29 \text{ nm}$), the pitch of the outermost helical structure formed in the *st*-PMMA-*r*-PFEMA

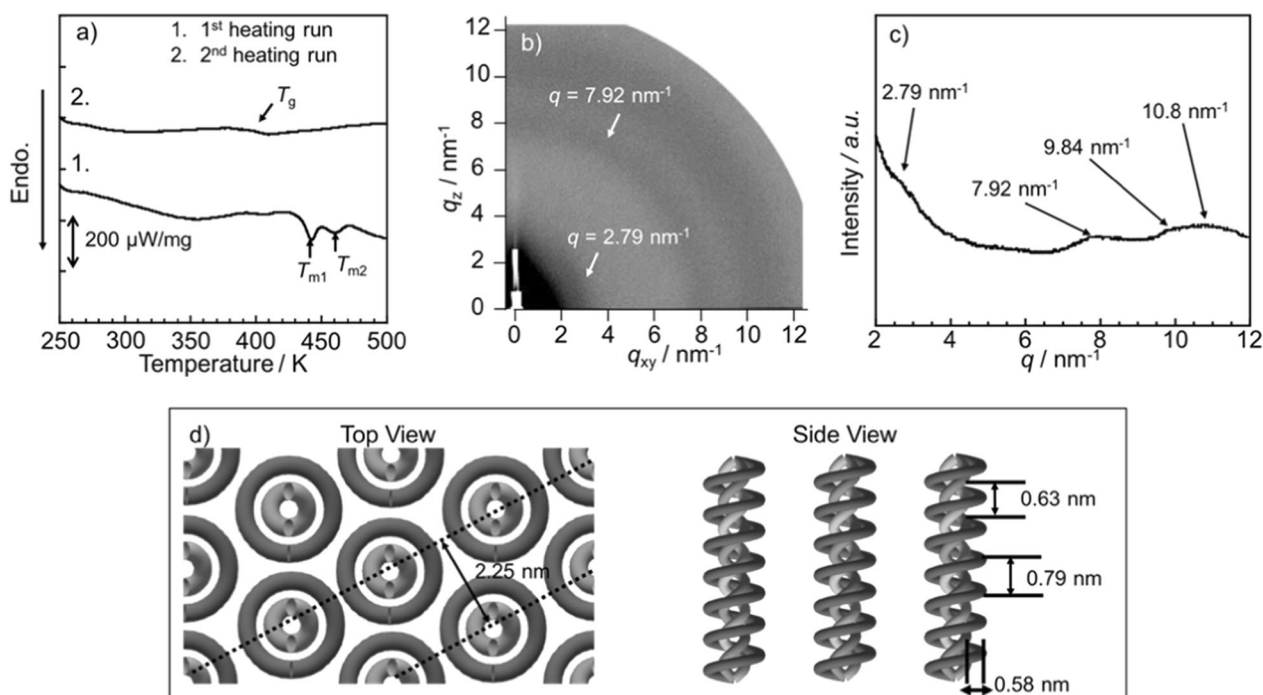
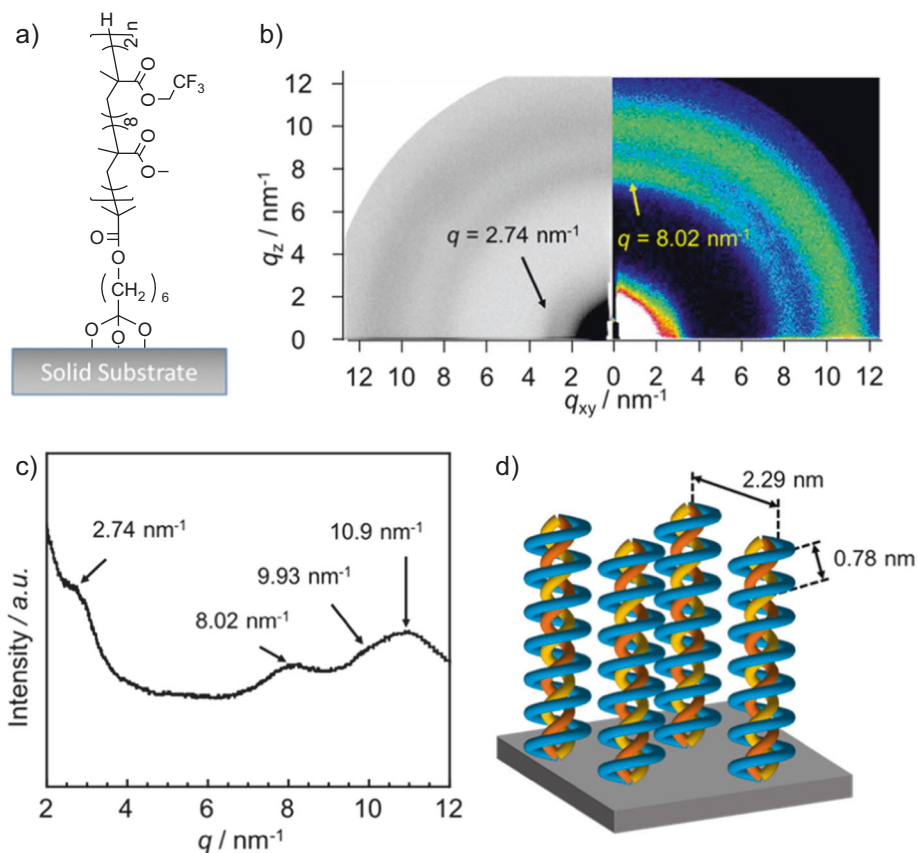


Fig. 5 a DSC chart of the *st*-PMMA brush. GIWAXD (b) patterns and (c) line profiles of the *st*-PMMA brush consisting of a stereocomplex. d Schematic illustration of the stereocomplex formed from the *st*-PMMA brush

Fig. 6 a Chemical structure of the *st*-PMMA-*r*-PFEMA brush. GIWAXD (b) patterns of the *st*-PMMA-*r*-PFEMA brush and (c) the line profile along the equatorial axis. d Schematic illustration of the stereocomplex formed from the *st*-PMMA-*r*-PFEMA brush



brush

($q = 8.02 \text{ nm}^{-1}$, $d = 0.78 \text{ nm}$), the pitch of the inside of the double-helical structure formed by *it*-PMMA ($q = 9.93 \text{ nm}^{-1}$, $d = 0.63 \text{ nm}$), and the distance between the *st*-PMMA-*r*-PFEMA brush and the *it*-PMMA chains ($q = 10.9 \text{ nm}^{-1}$, $d = 0.58 \text{ nm}$). Although the orientation is not high, the diffraction at $q = 2.74 \text{ nm}^{-1}$ is clearly concentrated along the equator, and that at $q = 8.02 \text{ nm}^{-1}$ is concentrated along the meridional axis, which indicates that the stereocomplex of the polymer brush is oriented perpendicular to the substrate [38].

Conclusion

The preparation of high-density *st*-PMMA brushes with well-controlled stereoregularity could be achieved using a novel surface-initiated living anionic polymerization method in the presence of a Lewis acid. The polymer brushes consisted of a narrow PDI and an M_n of up to 400,000, and they encapsulated functional materials and free polymers to form inclusion complexes and stereocomplexes. The polymer brushes can recognize the size of the functional molecules, leading to selective separation. We hope that this principle will be utilized in next-generation surface modification.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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