

Modification of the Surfaces of Silicon Wafers with Temperature-Responsive Cross-Linkable Poly[oligo(ethylene oxide) methacrylate]-Based Star Polymers

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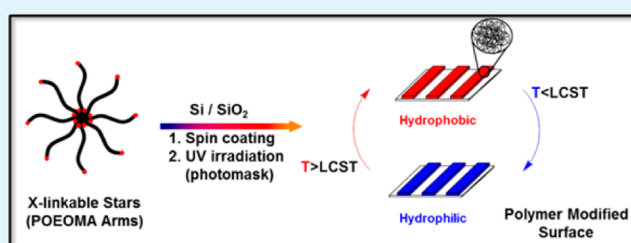
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Supporting Information

ABSTRACT: Temperature-responsive photo-cross-linkable poly[oligo(ethylene oxide) monomethyl ether methacrylate] (POEOMA)-based star polymers were synthesized by atom transfer radical polymerization (ATRP), for the modification of silicon (Si) wafer surfaces. The polymers showed a lower critical solution temperature (LCST) behavior in aqueous media. The polymers were modified with benzophenone (Bzp) functional groups that were utilized in UV-triggered ($\lambda = 365$ nm) cross-linking reactions for the preparation of polymer networks. The star polymers were deposited onto the surfaces of Si wafers by spin coating, and stable polymer films were formed by simple UV irradiation. The stability of thermoresponsive cross-linked polymer films deposited on the Si wafer was confirmed by changing their hydrophilicity by changing the temperature of the environment. In addition, the POEOMA-based star polymers could be utilized for the preparation of photolithography-patterned surfaces. The successful formation of uniform stable polymeric films indicates that Bzp-functionalized POEOMA star polymers can be used for a simple Si surface modification.

KEYWORDS: poly[oligo(ethylene oxide) methacrylate], star polymers, surface modification, cross-linkable polymers, UV-patternable polymers, temperature-responsive surface



INTRODUCTION

The modification of surfaces by the deposition of polymeric materials is an attractive procedure because of easy modification of the chemical/physical properties of the targeted surfaces. Examples include surfaces for cell cultivation or immobilization of bioactive compounds on surfaces for biomedical applications, preparation of high-efficiency antifouling/antibacterial surfaces, desalination filter membranes, etc.^{1–20} Typically, two polymer modification techniques have been exploited for the preparation of polymer-modified surfaces: grafting from and grafting onto. The grafting from technique can introduce dense grafting of well-defined polymer chains on the surfaces of substrates.^{21–27} However, the grafting from method requires several preparation steps: immobilization of the initiating groups on the target surface and inert conditions during polymerization. Nevertheless, in some cases, a high graft density and the formation of high-molecular-weight polymeric chains can be achieved. The grafting onto technique can modify the target surfaces by utilizing coupling reactions between reactive polymer chain ends and functional surfaces.^{28–32} However, it is difficult to accomplish a high grafting density when employing the grafting onto method. To overcome the limitations of both procedures, the development of a simple technique providing a uniform robust polymer film for surface modification is required. One of the feasible ways to overcome

the limitations should be to use star-shaped polymers with multiple-group binding to the surfaces. For instance, Sofia et al. used linear and star-shaped poly(ethylene oxide) (PEO) for silicon (Si) wafer surface modifications and compared their graft densities.³³ The results from star-shaped PEO-modified surfaces showed a higher grafting density than linear PEO because of effective overlap at the surfaces by spreading polymer chains (arms of star polymers). Kim et al. recently reported a high efficiency of antifouling membranes prepared by using star polymers.³⁴

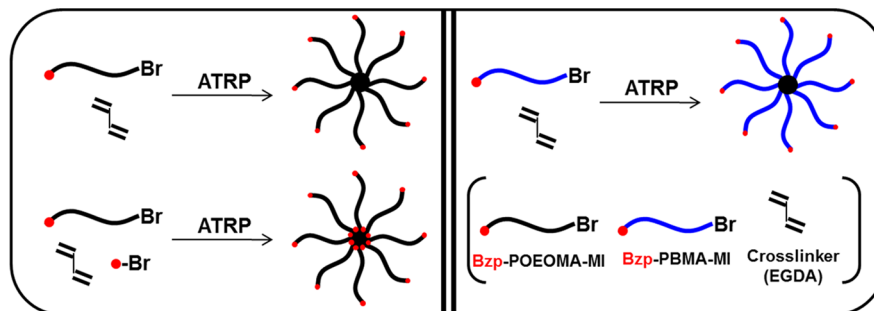
A recent development in the atom transfer radical polymerization (ATRP) technique provides a convenient procedure for the synthesis of functional polymers with complex architectures.^{35–42} Star-shaped polymers possess an architecture with multiple linear arms linked to a central core and combine interesting properties of a branched-architecture, globular-shaped, and chemically cross-linked structure.^{37,43–46} One approach to star macromolecules is the synthesis of α -functionalized linear macroinitiators (MIs) by ATRP and subsequent chain extension with divinyl or multivinyl compounds to form the cross-linked core of a star polymer.^{47,48}

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Scheme 1. Preparation of Bzp-Functionalized POEOMA and PBMA Linear and Star Polymers



This approach can provide star polymers with various chemical composition, stimuli responsiveness, and site-specific functionalities.^{37,44}

Recently, PEO-based polymeric materials have been successfully used because of their physical adhesion to metal–oxo surfaces. For example, Soler-Illia and Sanchez⁴⁹ reported the interaction between PEO-based surfactants and transition-metal alkoxides and discussed the mechanism for interactions between the PEO surfactants and transition-metal surface, while Voronin et al.⁵⁰ reported interactions between PEO and fumed silica. However, in most cases, the degree of coordination is too weak to sustain long-term adsorption between the PEO-based materials and metallic substrates. This paper reports the results of a systematic study that provides a simple and robust procedure for the preparation of thermally responsive, stable polymer films on the surfaces of Si wafers by star polymers. Linear and star polymers, with variable composition and functionalities based on oligo(ethylene oxide) methyl ether methacrylate (OEOMA), a derivative of PEO, and *n*-butyl methacrylate as comonomers, were prepared. The introduction of UV-reactive groups, benzophenone (Bzp), into the polymers, at the α chain end for linear polymers and within the core and/or at the periphery of the star polymers, provided the ability for cross-linking polymer films, deposited on the surfaces of a Si wafer, and a simple procedure for stable surface modification.

EXPERIMENTAL SECTION

Materials. 2-(2-Methoxyethoxy)ethyl methacrylate (MEO₂MA; 95%), oligo(ethylene oxide) methacrylate with four (to five) ethylene oxide units (OEOMA₃₀₀; $M_n = 300$), *n*-butyl methacrylate (BMA; 99%), and ethylene glycol diacrylate (EGDA; 90%) were purchased from Aldrich, purified by passing through a column filled with basic alumina to remove the inhibitor, and then stored at -5 °C. CuBr (99%, Aldrich) and CuCl (90%, Aldrich) were purified using literature procedures.⁵¹ All other reagents, 4-hydroxybenzophenone, 2-bromoisobutyl bromide, 4,4'-dinonyl-2,2'-bipyridine (dN bpy), 2,2'-bipyridine, copper(II) bromide (CuBr₂), *N,N,N',N'*-pentamethyldiethylenetriamine (PMDETA), and triethylamine (TEA), and solvents were purchased at the highest purity from Aldrich and used without further purification. A heavily doped *n*-type Si substrate, with a thermally grown 250 nm silicon dioxide layer, was purchased from MEMC Electronic Materials, Inc.

Synthesis of a Benzophenone Initiator (Bzp-*ini*). Benzophenonyl 2-bromoisobutyrate (a Bzp-*ini*) was prepared according to a previously published procedure.⁵² Briefly, 10 g (50 mmol) of 4-hydroxybenzophenone was dissolved in methylene chloride (30 mL) with 7.6 mL of TEA (55 mmol), and the reaction flask was placed in an ice bath. Then 6.8 mL of 2-bromoisobutyl bromide (55 mmol) was slowly added to the reaction mixture and the solution stirred for 12 h. The desired product was separated by extraction with pure water three times, and the organic layer was collected and dried overnight.

Synthesis of Bzp-POEOMA and Bzp-PBMA Linear Polymers.

Similar procedures were used for the preparation of both macro-initiators (Bzp-POEOMA MI and Bzp-PBMA MI). Briefly, Bzp-*ini* (209 mg, 6.38×10^{-1} mmol), CuBr (37 mg, 2.55×10^{-1} mmol), CuBr₂ (13 mg, 6.38×10^{-2} mmol), and dN bpy (246 mg, 6.38×10^{-1} mmol) were added to a 25 mL Schlenk flask and vacuum-dried. The flask was backfilled with nitrogen. MEO₂MA (10 mL, 54.19 mmol), OEOMA₃₀₀ (2.7 mL, 9.56 mmol), and anisole (12.7 mL) were then added to the flask, and the mixture was stirred at 60 °C. The reaction was stopped after 2 h, and the solution was passed through neutral alumina to remove the copper complex. The product was precipitated by the addition of excess hexane and dried under vacuum overnight. Gel permeation chromatography (GPC) analysis showed $M_n = 9550$ and $M_w/M_n = 1.14$ [poly(methyl methacrylate) (PMMA) standards]. The Bzp-PBMA MI was prepared using the same molar ratio of reagents, and the M_n and M_w/M_n of the final products were measured by GPC [$M_n = 6410$ and $M_w/M_n = 1.08$ (PMMA standards)].

Synthesis of Bzp-POEOMA and Bzp-PBMA Star Polymers.

The Bzp-POEOMA and Bzp-PBMA star polymers were synthesized using the MI method (Scheme 1). In a typical experiment, a 15 mL Schlenk flask was charged with EGDA [98 μ L, 5% (w/w to MI), 6.28×10^{-1} mmol], Bzp-POEOMA MI (2 g, 2.09×10^{-1} mmol, $M_n = 9550$, $M_w/M_n = 1.14$), PMDETA (7 μ L, 4.19×10^{-2} mmol), and 5 mL of anisole. The flask was degassed and subjected to three freeze–pump–thaw cycles, and during the final cycle, the flask was filled with nitrogen and CuCl (10 mg, 4.19×10^{-2} mmol) was quickly added to the frozen mixture. The flask was sealed with a glass stopper and then evacuated and backfilled with nitrogen three times before it was immersed in an oil bath at 60 °C. Samples were taken at timed intervals to measure molecular weight evolution by GPC. The Bzp-PBMA star polymer was prepared with the same molar ratio of reagents.

Synthesis of Bzp-Dual-Functionalized POEOMA Star Polymers.

The Bzp-dual-functionalized POEOMA star polymers were synthesized using the MI method (Scheme 1). A 15 mL Schlenk flask was charged with EGDA [64 μ L, 5% (w/w to MI), 4.08×10^{-1} mmol], Bzp-POEOMA MI (1.3 g, 1.36×10^{-1} mmol, $M_n = 9550$, $M_w/M_n = 1.14$), Bzp-*ini* (47 mg, 1.36×10^{-1} mmol), PMDETA (6 μ L, 2.72×10^{-2} mmol), and 5 mL of anisole. The flask was degassed and subjected to three freeze–pump–thaw cycles, and during the final cycle, the flask was filled with nitrogen and CuCl (6 mg, 2.72×10^{-2} mmol) was quickly added to the frozen mixture. The flask was sealed with a glass stopper and then evacuated and backfilled with nitrogen three times before it was immersed in an oil bath at 60 °C. Samples were taken at timed intervals to measure molecular weight evolution by GPC. The final product was purified by fractional precipitation against an excess tetrahydrofuran (THF)/ethyl ether (10/90, v/v) mixture. T_g values of the purified star polymers were observed at -45 °C by differential scanning calorimetry (DSC; Figure S-5 in the Supporting Information).

Modification of Si Wafers with the Polymers. Polymers were deposited onto the surfaces of Si wafers by spin-casting solutions of the star macromolecules in chloroform at a velocity of 1000 rpm. UV irradiation ($\lambda = 365$ nm, for 10 min) was used to covalently cross-link star polymers and tether them to the Si wafer surface. The surface was

washed three times with methanol, three times with THF, and three times with water to remove any unstable and/or unreacted residue species.

Measurements. ^1H NMR (300 MHz) spectra were taken on a Bruker Avance 300 spectrometer using CDCl_3 as the solvent. The lower critical solution temperature (LCST) of the MI solutions in water was measured on a Varian Cary 5000 UV-vis spectroscope with a temperature-controlled circulator. Transmittance of polymer solutions in pure deionized (DI) water was monitored at 600 nm as a function of the temperature (cell path length = 10 mm; heating rate = $1\text{ }^\circ\text{C}/\text{min}$). Molecular weights were determined by GPC with Polymer Standards Services (PSS) columns (guard, 10^5 , 10^3 , and 10^2 Å), with THF as the eluent at $35\text{ }^\circ\text{C}$ and flow rate = $1.00\text{ mL}/\text{min}$, and a differential refractive index detector (Waters, 2410). The apparent molecular weights and dispersities (M_w/M_n) were determined with a calibration based on linear poly(methyl methacrylate) standards using *WinGPC 7.0* software from PSS. The contact-angle measurements of the polymer-modified surfaces were measured at two different temperatures (20 and $37\text{ }^\circ\text{C}$) with a contact-angle-measuring system VCA optima (AST Products, Inc.) including a microscopy heating plate TC 324 heating controller (Warner Instruments). DI water was gently placed on the sample surfaces using an autosyringe. Each sample was measured five times, and the results were averaged with standard deviations. Optical microscopic images were obtained by an Olympus STM6-F10-2 microscope machine with an Olympus LG-PS2 light source. Tapping-mode atomic force microscopy (AFM) experiments were carried out using a Dimension V scanning probe microscope with a NanoScope V controller (Veeco). The measurements were performed in air using commercial Si cantilevers with a nominal spring constant and a resonance frequency of $42\text{ N}/\text{m}$ and 330 kHz , respectively. Set-point values (A/A_0) were maintained 0.7 – 0.85 , where A and A_0 refer to the “tapping” and “free” cantilever amplitude, respectively. The thermal properties of polymers were analyzed using a Seiko Instruments Inc. DSC 220 calorimeter with a temperature range of -110 to $-50\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C}/\text{min}$ in both heating and cooling processes.

RESULTS AND DISCUSSION

Preparation of UV Cross-Linkable Polymers. The Bzp-*ini* was prepared by the reaction between 4-hydroxybenzophenone and 2-bromoisobutyryl bromide under basic conditions. The purity of the final product was measured by ^1H NMR (Figure S-1 in the Supporting Information). MIs containing α -Bzp, Bzp-POEOMA, and Bzp-PBMA (Figure S-2 in the Supporting Information) were synthesized by ATRP and successfully purified by fractional precipitation. Subsequently, each of the MIs was chain extended with a cross-linker (EGDA) to prepare Bzp-POEOMA and Bzp-PBMA star polymers, respectively. The Bzp-dual-functionalized POEOMA star polymers (core and periphery) were prepared by the addition of a fraction of low-molecular-weight Bzp-*ini* to the MI prior to the star-core-forming polymerization (Scheme 1).

Each of the polymerizations was monitored by THF GPC (Figure 1). The Bzp-POEOMA and Bzp-dual-functionalized POEOMA star polymers were successfully purified by fractional precipitation against an excess THF/ethyl ether ($10/90$, v/v) mixture (Figure 1A,B), while the Bzp-PBMA star polymers were precipitated against a THF/methanol ($10/90$, v/v) mixture to remove any unreacted MIs. The final products were dried overnight under vacuum. THF GPC curves show that purified products were successfully isolated. The absolute molecular weights were determined by GPC-MALLS. Table 1 lists the molecular weights of the linear and star polymers and the number of arms in the stars. The chemical structure of each star polymer was determined by ^1H NMR (Figure 2), and Bzp

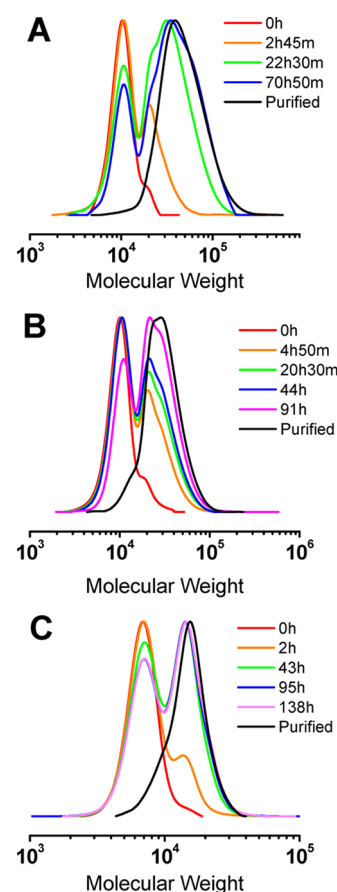


Figure 1. GPC traces of (A) Bzp-POEOMA, (B) Bzp-dual-functionalized POEOMA, and (C) Bzp-PBMA star polymers.

Table 1. Summary of the Bzp-Functionalized Polymers

entry	polymer	MW (M_w , g/mol)	MWD (M_w/M_n)	dn/dc^c	no. of arms ^d
1	Bzp-POEOMA MI	9550 ^a	1.14		
2	Bzp-PBMA MI	6410 ^a	1.08		
3	Bzp-POEOMA star	109500 ^b	1.50	0.077	11
4	Bzp-dual POEOMA star	109800 ^b	1.53	0.102	11
5	Bzp-PBMA star	51780 ^b	1.21	0.074	8

^aMWs were determined by THF GPC with a PMMA standard. ^bMWs of star polymers were determined by GPC-MALLS. ^c dn/dc values were obtained from 100% mass recovery by using the ASTRA program. ^dThe number of arms was calculated by MW_{star} (entries 3–5) divided by MW_{MI} (entries 1 and 2).

functionalities in the star polymers were confirmed by the presence of signals at 8–7 ppm.

Modification of the Surfaces of Si Wafers with Linear and Star Polymers. Table 2 provides a summary of polymer film thicknesses and stabilities before/after the multiple-washing procedures with THF, MeOH, water, and acetone. Polymer solutions (0.3% by w/v) were prepared, and the solutions were spin-coated onto Si wafers and then dried for 10 min. Ellipsometric analysis revealed the successful formation of polymer films after spin coating of the polymers onto the Si wafer. The polymers deposited on the silica surfaces were exposed to UV light ($\lambda = 365\text{ nm}$) to trigger Bzp cross-linking reactions, and then the surfaces were washed several times with

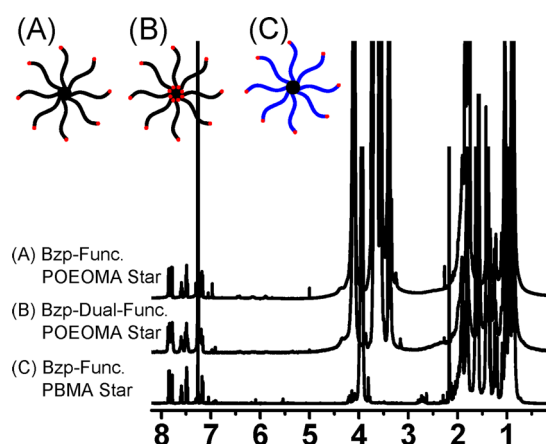


Figure 2. 300 MHz ^1H NMR spectra of (A) Bzp-POEOMA, (B) Bzp-dual-functionalized POEOMA, and (C) Bzp-PBMA star polymers.

Table 2. Thicknesses and Stabilities of the Polymer-Modified Surfaces

entry	polymer	thickness (nm) ^a		stability
		before washing	after washing	
1	Bzp-POEOMA MI	28.8 ± 1.3	ND	ND
2	Bzp-PBMA MI	27.7 ± 1.2	ND	ND
3	Bzp-POEOMA star	32.3 ± 0.8	33.5 ± 2.8	partially stable
4	Bzp-dual-functionalized POEOMA star	30.5 ± 1.1	31.2 ± 1.5	stable
5	Bzp-PBMA star	28.8 ± 0.9	ND	ND

^aThe average thicknesses of polymer films were determined by ellipsometry with five measurements with standard deviations. ND: not detected.

solvents to remove residual/unreacted components. After washing, the surfaces were dried for 5 h under vacuum, and ellipsometric analysis was carried out to measure the thicknesses of the polymer films. The ellipsometric results showed that the polymer films prepared by the deposition of linear polymers and the BMA star polymer (Table 2, entries 1, 2, and 5) were vulnerable to solvent exposure and indeed were unstable; as a result, the polymers were easily removed from the surface. In contrast, different results were observed from Bzp-containing POEOMA-based star polymers. Both of the surfaces

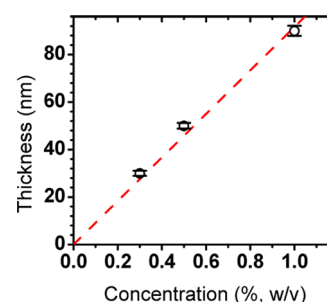


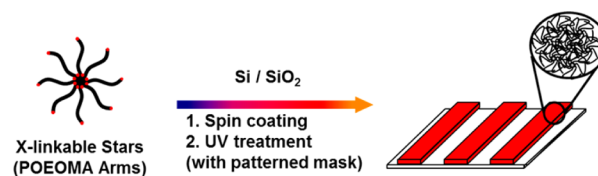
Figure 4. Variation in the polymer film thicknesses when using different concentrations of polymer solution. The average values were determined by averaging five ellipsometry measurements with standard deviations.

Table 3. Summary of Contact-Angle Measurements and Film Thicknesses

entry	solution concn ^a (%)	contact angle ^b (deg)		thickness ^c (nm)
		20 °C	37 °C	
1	0.3	50.0 ± 1.2	71.5 ± 1.4	31 ± 1.1
2	0.5	49.5 ± 0.7	72.1 ± 0.6	52 ± 1.2
3	1.0	56.3 ± 5.1	73.9 ± 1.2	89 ± 2.1

^aBzp-dual-functionalized POEOMA star polymers were dissolved in CHCl_3 (% w/v). ^bContact angles were determined by the sessile-drop method with five measurements. ^cThicknesses were determined by ellipsometry with five measurements.

Scheme 2. Surface Patterning by Bzp-Dual-Functionalized POEOMA Star Polymers



modified with Bzp-functionalized POEOMA (Table 2, entries 3 and 4) showed that the polymer films adhered to the Si wafer surfaces and were resistant to solvent washing. Figure 3 shows images of the two surfaces modified with POEOMA-based star polymers after washing. The surface modified with the Bzp-dual-functionalized POEOMA star (Table 2, entry 4) showed

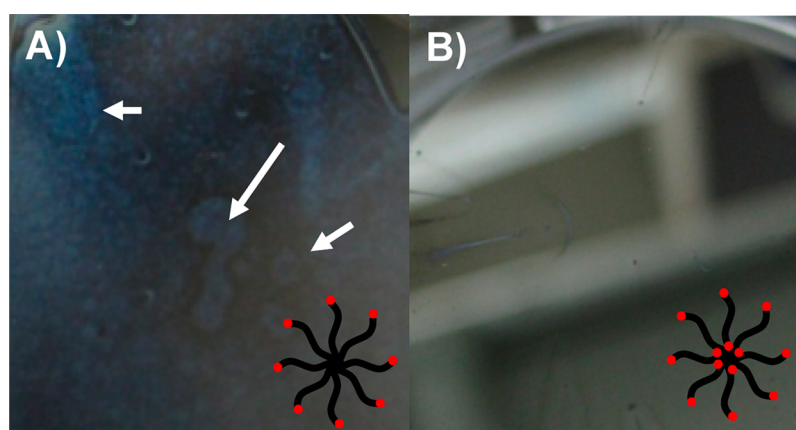


Figure 3. Photographs of star polymer-modified surfaces: (A) Bzp-POEOMA star polymers (arrows indicate bumpy surface regions); (B) Bzp-dual-functionalized POEOMA star polymers.

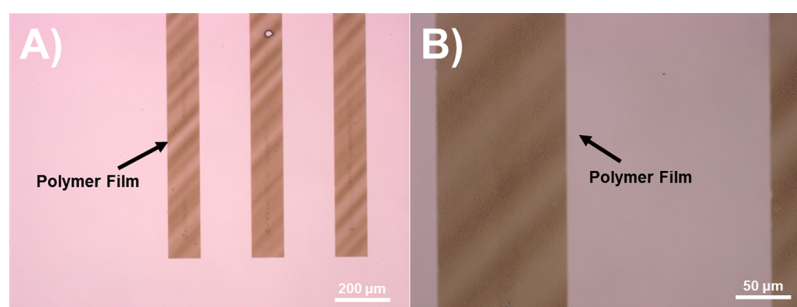


Figure 5. Optical microscopic images of polymer patterned surfaces: (A) scale bars correspond to 200 μm (magnification 5 \times); (B) 50 μm (magnification 20 \times).

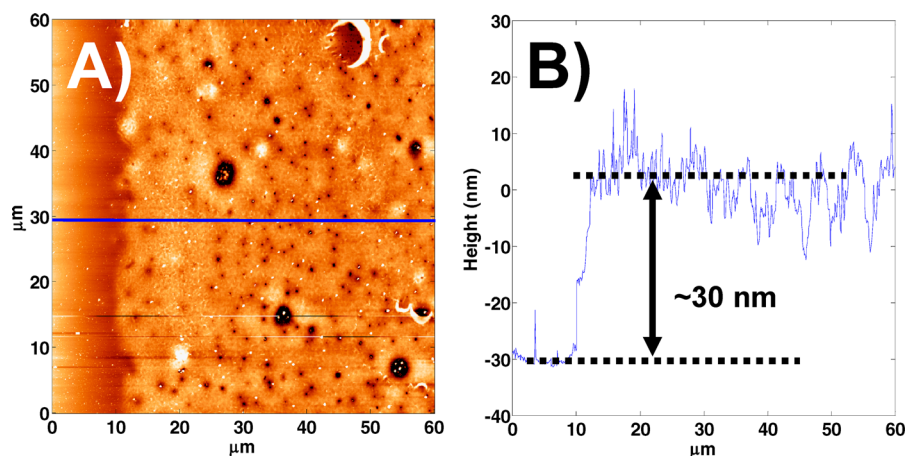


Figure 6. AFM analysis of a stripe-patterned surface (100 μm width): (A) height image; (B) height profile (blue line).

higher stability compared to the partially stable surface modified with the Bzp-periphery-functionalized POEOMA star (Table 2, entry 3). The polymer film from entry 3 showed a bumpy surface (Figure 3A, arrow), while that from entry 4 showed formation of a smooth surface (Figure 3B). The results could be attributed to better chelating effects and/or the effect of multiple hydrogen bonds between the densely cross-linked multiple-arm structure of the Bzp-dual-functionalized POEOMA and the surface Si/SiO₂ layers. Interaction of PEO with the Si/SiO₂ wafer surfaces was previously reported.^{49,50,53,54} The PEO moieties of the star polymers can interact with Si/SiO₂ in a similar way, also via hydrogen bonding with surface silanol groups. Because the POEOMA star polymers contain multiple PEO moieties (from the star arms), a large number of the ether oxygen atoms could effectively cover the Si/SiO₂ wafer surface. Among two POEOMA star polymers, Bzp-dual-functionalized star polymers can introduce additional cross-linking points to the polymer films and, therefore, a denser POEOMA network should enhance adhesion.

Temperature-Responsive Polymer Surfaces. The Bzp-dual-functionalized POEOMA star polymers (Table 2, entry 4) were evaluated as materials for the preparation of temperature-responsive polymer surfaces and then utilized to prepare UV-triggered patternable surfaces. Because the star polymers contained photo-cross-linkable moieties (Bzp), surface modification was simply conducted by exposing the deposited film to UV light ($\lambda = 365 \text{ nm}$). The thicknesses of the cross-linked polymer films were measured, and because the solutions were of relatively low concentrations (0.3–1.0%, w/v), they increased linearly with increasing polymer solution concentration (Figure 4).

The POEOMA-based star polymers have LCST behavior, and the critical temperature (T_c) was approximately 27 $^{\circ}\text{C}$ (Figure S-3 in the Supporting Information). The star polymers were deposited onto the Si wafer surfaces and cross-linked, and then the temperature responsiveness of the modified surfaces was measured. Contact-angle measurements were carried out to determine the thermal response behavior. Table 3 lists film thicknesses and contact angle results for the POEOMA-based star-modified surfaces. Two different temperatures were chosen to measure the surface contact angle, 20 and 37 $^{\circ}\text{C}$, one below and one above T_c of the star polymers, respectively. Below T_c (20 $^{\circ}\text{C}$), the contact angle of the modified surfaces was around 50 $^{\circ}$, and above T_c (37 $^{\circ}\text{C}$), it was approximately 72 $^{\circ}$, clearly showing that the hydrophilicity of the modified surfaces can be controlled by changing the temperature of the environment.

Surface Patterning Using the Bzp-Dual-Functionalized POEOMA Star Polymers. The Bzp-dual-functionalized star polymers were utilized to prepare patterned surfaces (Scheme 2). A solution of the star polymer (0.3%, w/v in CHCl₃) was deposited on the surface of a Si wafer by spin coating, and then the film was exposed to UV light ($\lambda = 365 \text{ nm}$) for 10 min using a stripe-patterned mask, 100 μm width with 4 mm length, for optical microscopic analysis and AFM measurements. After UV irradiation, the surface was gently washed several times with acetone, methanol, and THF and dried. Figure 5 shows the optical microscopic images of the patterned surfaces. Well-defined film patterns were successfully formed, and the shape and size of each pattern was well-matched to the photomask. AFM measurements were used for determination of the polymer film height profiles (Figure 6). The results showed that the polymer film thickness was $\sim 30 \text{ nm}$ with $\pm 10 \text{ nm}$

roughness. The film thickness was well-matched by non-patterned star polymer-modified surfaces.

CONCLUSIONS

The well-defined POEOMA and PBMA polymers, both linear and star-shaped, containing photo-cross-linkable Bzp groups were successfully prepared by ATRP. POEOMA star polymers with Bzp functional groups on the periphery and within the core (dual functionalization) formed films with good stability after deposition of a polymer solution onto the surface of Si wafers and UV-triggered cross-linking. The POEOMA star polymers have LCST at ~ 27 °C, and the temperature-responsive behavior of the deposited films could be observed for the modified surfaces by changing the temperature of the environment. Furthermore, patterned polymer surfaces were easily prepared by simple UV irradiation with a photomask.

ASSOCIATED CONTENT

Supporting Information

¹H NMR spectra of the Bzp ATRP initiator and MIs, GPC results of the linear polymers, transmittance of polymer solutions, AFM images for patterned surfaces, and DSC results of Bzp-dual-functionalized POEOMA (Figures S-1–S-5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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