Efficient Surface Neutralization and Enhanced Substrate Adhesion through Ketene Mediated Crosslinking and Functionalization

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Balancing the interfacial interactions between a polymer and substrate is one of the most commonly employed methods to ensure the vertical orientation of nanodomains in block copolymer lithography. Although a number of technologies have been developed to meet this challenge, there remains a need for a universal solution for surface neutralization that combines simple synthesis, fast processing times, generality toward substrate, low density of film defects, and good surface adhesion. The chemistry of ketenes, which combines highly efficient polymer crosslinking through dimerization and surface adhesion through reaction with the substrate, is shown to be well suited to the challenge. The versatile chemistry of ketenes are accessed through the post-polymerization of Meldrum's acid, which can be easily incorporated into copolymers through controlled radical polymerization processes. Further, the Meldrum's acid monomer is synthesized on a large scale in one step without the need for chromatography. Processing times of seconds, low defect density, simple synthetic procedures, and good substrate adhesion make these materials attractive as robust block copolymer neutralization layers.

1. Introduction

Conventional "top-down" lithography processes present a number of fundamental limitations for next-generation microelectronics including prohibitive cost, highly-specialized equipment and processing, and material challenges as the feature size decreases. To overcome the inherent limitations of conventional lithography, "bottom up" approaches have garnered significant attention in both academic and industrial settings. Among these approaches, self-assembly of block copolymers has emerged as an attractive strategy for accessing feature sizes below 50 nm.[1,2] Termed block copolymer lithography, this approach has several advantages including the ability to cost-effectively produce uniform sphere, cylinder and lamella patterns on the nanometer scale.[3–17]

One of the grand challenges in the block copolymer lithography field has been controlling the orientation of the self-assembled nanodomains, which ideally should order perpendicular to the bottom substrate and maintain high uniformity over large length scales. In order to achieve this vertical orientation of polymer domains, it is imperative to balance the interfacial interactions between the polymer and substrate.[8,11,18–21] In the case of poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA), the PMMA blocks preferentially interact with silicon substrates and results in a disadvantageous parallel orientation of the microstructure.[22–24] To achieve vertical orientation, one of the most successful strategies for large-area applications has been to neutralize the substrate with a random copolymer of poly(styrene-methyl methacrylate) [P(S-*r*-MMA)].

The conventional and current commercial approach to surface neutralization is the anchoring of a hydroxyl end-functional random copolymer P(S-*r*-MMA) to a native silicon oxide substrate through condensation-type chemistry.[18] By adjusting the composition of PS and PMMA in the polymer backbone and covalently grafting the polymers to the substrate, the surface is effectively neutralized and one can achieve the desired perpendicularly oriented nanostructures over large areas. The disadvantages of this process include long processing times of hours to days and incompatibilities with substrates other than silicon. To overcome these issues, random copolymers containing cross-linkable units have been developed. The first polymer of this type contained a thermally reactive benzocyclobutene (BCB) comonomer, which provided crosslinked layers upon dimerization above 200 °C.[25,26] These BCB containing

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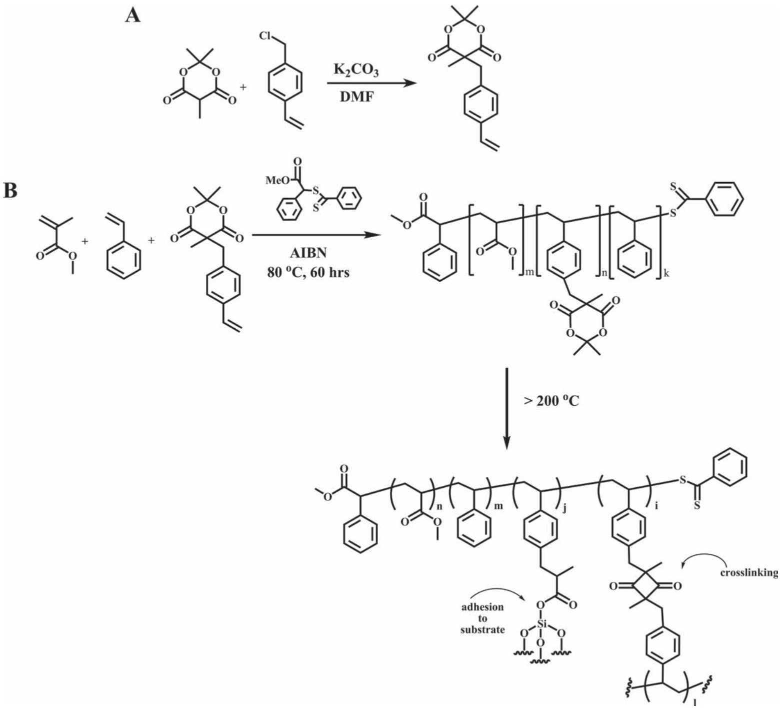
copolymers provided many advantages, including greatly reduced processing times and applicability to a variety of substrates, including Al, SiO_2, Si_3N_4, Au, etc. The BCB monomer, however, is not commercially available, difficult to synthesize and provides little, if any, covalent bonding to the underlying substrate. The other widely employed surface neutralization material relies on nitrene formation from photochemical or thermal treatment of an azide for crosslinking.[27] This method has been readily adopted as a result of the lack of availability of the BCB monomer, but the approach suffers from multiple processing steps to introduce the azide post-polymerization, a high surface defect density at moderate concentrations of azide and/or long irradiation times, undefined chemistry of the highly-reactive nitrene, and limited covalent attachment to the underlying substrate.

In response to the challenge of surface neutralization, we sought to develop a user-friendly methodology that combines the advantages of simple synthesis, fast processing times, highly-efficient crosslinking, low defect density, and covalent adhesion to the underlying substrate. Herein, we describe the synthesis and application of Meldrum's acid containing polymers for surface neutralization of block copolymer (BCP) lithography substrates. Recently, Meldrum's acid[28] has been employed as a monomer building block for thermal access to the valuable ketene functional group.[29–34] The versatile chemistry of ketenes provide for crosslinking via dimerization while also allowing for facile functionalization via nucleophilic addition. Significant potential for this chemistry therefore exists in the BCP lithography field, as ketenes provide an opportunity to both crosslink the polymer film and covalently attach it to the substrate in one thermal treatment step.[28–31,33,34]

2. Results and Discussion

A distinct advantage of these Meldrum's acid based materials is their simple and user-friendly synthesis. The functional comonomer (**1**) is synthesized by a one-step process from two commercially available starting materials in high yields. Specifically, 2,2,5-trimethyl-1,3-dioxane-4,6-dione (5-methyl Meldrum's acid) and 4-vinylbenzylchloride are reacted under mildly basic conditions and the crude product recrystallized to afford the desired monomer as an analytically pure crystalline solid (see **Scheme 1**a).

The ready availability of **1** provided the opportunity to thoroughly investigate the consequence of ketene crosslinking on surface neutralization properties. Specifically, by varying factors such as the concentration of **1** in a random copolymer and the crosslinking temperature and time, many of the processing parameters could be tuned to



Scheme 1. a) One-step synthesis of the Meldrum's acid containing comonomer, **1**. b) Synthesis of P(S-*r*-**1**-*r*-MMA) random copolymer and its corresponding chemistry, which provides crosslinking via ketene dimerization and adhesion via nucleophilic addition to surface-active silonols.

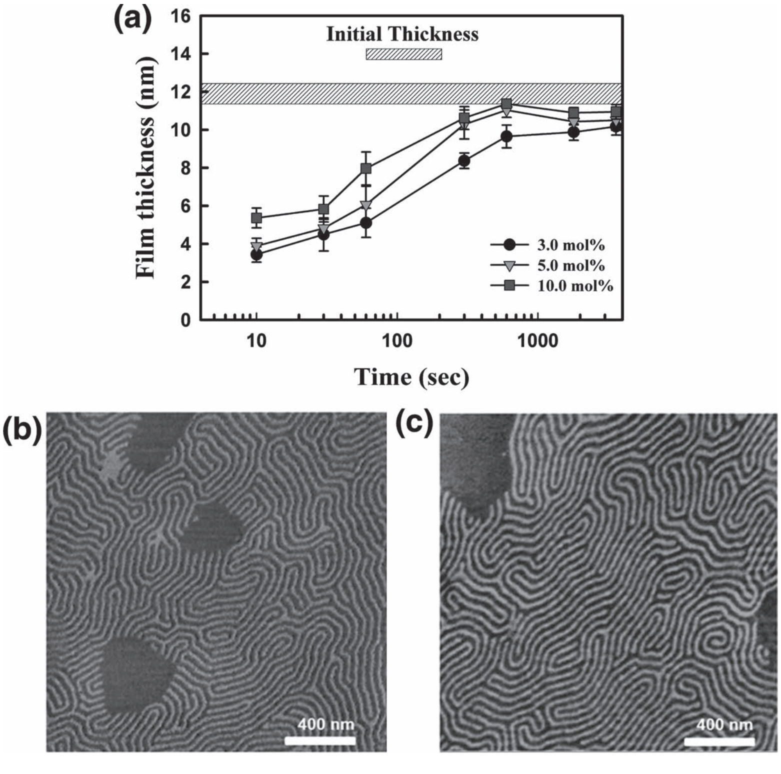


Figure 1. a) Crosslinked thickness of P(S-*r*-**1**-*r*-MMA) thin films as a function of crosslinking time at 200 °C. The representative SFM phase images of lamellar forming PS-*b*-PMMA diblock copolymer prepared on the crosslinked P(S-*r*-**1**-*r*-MMA) layers, in which b) 3.0 mol% of **1** in P(S-*r*-**1**-*r*-MMA) was crosslinked for 10 s, and c) 10.0 mol% of **1** in P(S-*r*-**1**-*r*-MMA) was crosslinked for 1 h.

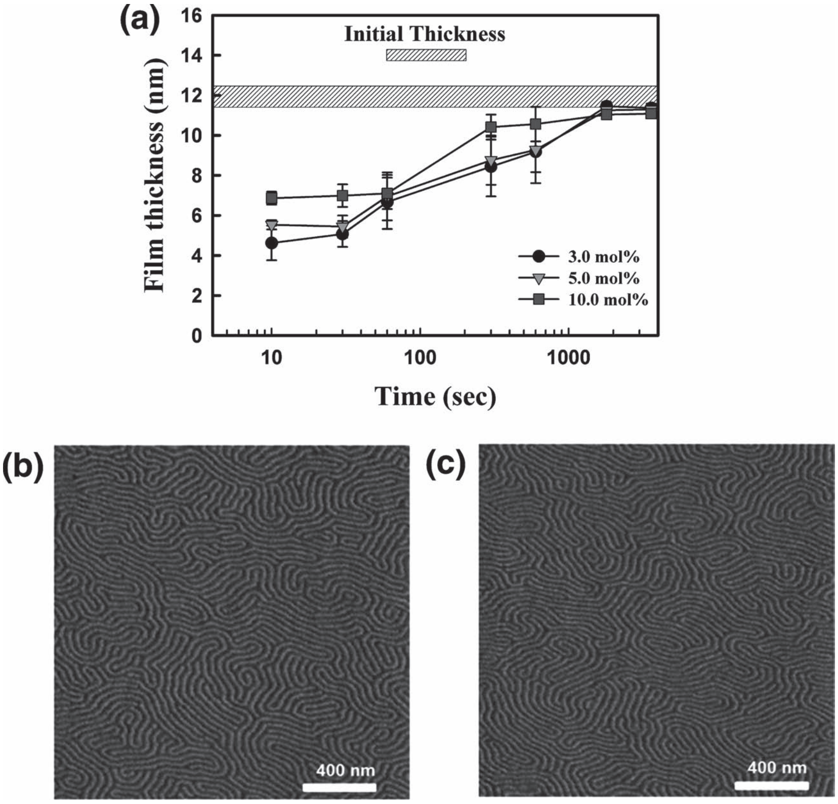


Figure 2. a) Crosslinked thickness of P(S-*r*-**1**-*r*-MMA) thin films as a function of crosslinking time at 230 °C. The representative SFM phase images of lamellar forming PS-*b*-PMMA diblock copolymer prepared on the crosslinked P(S-*r*-**1**-*r*-MMA) layers, in which b) 3.0 mol% of **1** in P(S-*r*-**1**-*r*-MMA) was crosslinked for 10 s, and c) 10.0 mol% of **1** in P(S-*r*-**1**-*r*-MMA) was crosslinked for 1 h.

optimize the performance of the polymer neutralization layer. The synthetic versatility of **1** allows the synthesis of random copolymers [P(S-*r*-**1**-*r*-MMA)] by reversible addition fragmentation chain transfer (RAFT) polymerization[35,36] from styrene, MMA, and **1** without any post-polymerization requirements (Scheme 1b). This is in contrast to the widely used azide containing crosslinkable copolymer, which requires a two-step, post-polymerization removal of the dithioester and azide displacement to obtain the desired copolymer. In order to determine the effect of crosslink density on material properties, P(S-*r*-**1**-*r*-MMA) copolymers containing 3, 5, and 10 mol% of **1** were synthesized by adjusting the stoichiometry of the polymerization. Specifically, as **1** is similar to styrene, the proportion of styrene and **1** was held constant at a combined 55 mol% of the final random copolymer and the methacrylate was held constant in all polymers at 45 mol% (Figure S1, Supporting Information). The total molecular weight of all polymers was controlled between 20 000 and 30 000 g/mol with polydispersities below 1.2.

Polymer neutralization layers were subsequently prepared by spin casting a toluene solution containing the P(S-*r*-**1**-*r*-MMA) random copolymer (0.4 wt%, 3000 rpm) on a silicon wafer, providing uniform films with thicknesses of 11.5 to 13 nm. Thin-films containing different concentrations of **1** were subsequently crosslinked at various temperatures over a period of one hour. Gel content, or the amount of remaining polymer after crosslinking and subsequent solvent extraction, was measured by the ratio between the initial film thickness and the film thickness after thermal treatment and extensive washing with toluene. These crosslinked and washed samples were then used as substrates for the self-assembly of a lamellar forming diblock copolymer of (PS-*b*-PMMA) and their ability to induce vertical orientation was investigated by scanning force microscopy (SFM).

To understand the influence of ketene crosslinking on film neutralization properties, thin films of the random copolymers were heated at 200 °C and the change in film thickness was monitored as a function of time. As previous work demonstrated, 200 °C is the lowest temperature at which ketene generation was observed in polystyrene systems.[29] As seen in **Figure 1**, final film thickness increased with the time of heat treatment, requiring approximately 15 min at 200 °C for the 5% and 10% Meldrum's acid containing polymers to reach approximately 100% gel content, i.e., full retention of film thickness. Each experiment was repeated numerous times to ensure consistent results, as denoted by the error bars in Figure 1a. As expected for partial neutralization layers such as those crosslinked for 10 s at 200 °C, the self-assembly of (PS-*b*-PMMA) showed a mix of parallel and perpendicular orientation of domains on the surface (Figure 1b). When the crosslinking time was increased, the neutralization was partially improved as seen in Figure 1c. Although the crosslinked film thickness reached over 80% gel content after 10 min heating time, a significantly high defect density was observed over large areas of the thin-film, proving that copolymer layers crosslinked at 200 °C do not act as effective neutral substrates.

In order to improve the efficiency of crosslinking and, thus, the neutralization properties of the films, the thermal treatment temperature was increased to 230 °C. Notably, a heating time of one minute at this temperature produced crosslinked layers that had a gel content of greater than 50% regardless of incorporation of **1**, which is an appropriate thickness for a neutral surface (**Figure 2**a). To probe the neutralization effect of the crosslinked layers at this temperature, the same lamellar forming PS-*b*-PMMA diblock copolymer was prepared on the crosslinked and washed layers. In this case, we found excellent perpendicular orientation of the BCP nanodomains regardless of concentration or crosslinking time (Figure 2b,c, and Figure S2 in the Supporting Information). At crosslinking times of one minute, our results suggest that the surface defect density is comparable to neutralization layers fabricated using BCB or azide containing copolymers. Furthermore, it should be noted that long range perpendicular orientation was observed with neutralization layers crosslinked for less than one minute (Figure 2b), although the film thickness is less than 6 nm.

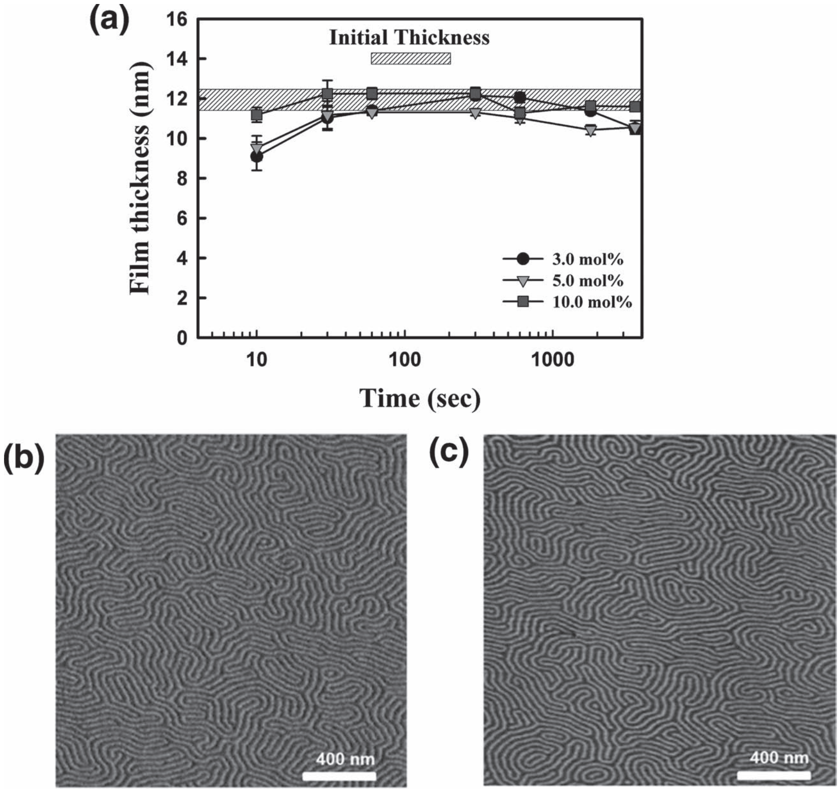


Figure 3. a) Crosslinked thickness of P(S-*r*-**1**-*r*-MMA) thin films as a function of crosslinking time at 250 °C. The representative SFM phase images of lamellar forming PS-*b*-PMMA diblock copolymer prepared on the crosslinked P(S-*r*-**1**-*r*-MMA) layers, in which b) 3.0 mol% of **1** in P(S-*r*-**1**-*r*-MMA) was crosslinked for 10 s, and c) 10.0 mol% of **1** in P(S-*r*-**1**-*r*-MMA) was crosslinked for 1 h.

This suggests that the ketene crosslinking reaction is much more efficient at 230 °C. Finally, by increasing the thermal crosslinking temperature to 250 °C, the kinetics of the Meldrum's acid to ketene reaction speeds up considerably and fully crosslinked neutralization layers could be obtained with only 10 s of thermal treatment (**Figure 3**a). This allows perpendicularly orientated BCP domains to be obtained regardless of heating time at 250 °C, providing evidence of a large processing window for these materials (Figure 3b,c, and Figure S2 in the Supporting Information). The orientation of BCP domains on these surfaces was also examined by grazing-incidence small-angle X-ray scattering (GISAXS), which was carried out at the 9A beamline at the Pohang Accelerator Laboratory (PAL), Korea. For the BCP patterns prepared on the neutralization layers crosslinked at 230 and 250 °C, sharp bragg peaks were clearly observed, indicating that the perpendicular orientation of PS-*b*-PMMA lamellae persist throughout the film thickness (Figure S3, Supporting Information).

As these results demonstrate, employing thermally generated ketenes as a crosslinking group allows the gel content and surface properties of BCP neutralization layers to be tuned by varying parameters such as crosslinker concentration, reaction temperature and processing time. The power of this approach, however, derives from the ability of ketenes to not only dimerize, but also provide covalent attachment to the substrate via nucleophilic addition of ketenes with silanol groups on the surface of silicon wafers.[37,38] To probe the strength of this binding on neutralization properties, ultrathin crosslinked films were prepared by thermal crosslinking at 230 °C for 60 min and then exposure to mechanical stress. The water contact angle, film thickness, and neutralization properties were subsequently examined to provide a qualitative measure of the mechanical integrity of the neutralization layers. The ketene crosslinked films were tested against the widely employed photo-crosslinked azide random copolymer neutralization layers, which should not undergo appreciable reaction with silicon substrates.

In order to model mechanical stress, the neutralization layers were sonicated in benzene for varying amounts of time and the film thickness and water contact angle was subsequently measured. The superior surface adhesion of the ketene films is immediately apparent, as the ketene based films remain adhered to the substrate and do not change thickness even after sonication for an hour in a good solvent. This is in direct contrast to the azide-based films, which lose thickness rapidly even after short sonication times (**Figure 4**a). This behavior is further supported by water contact angle measurements, which show that the ketene based films show no change in surface properties after sonication, whereas the azide based films undergo a marked decrease in contact angle (Figure 4b). Lastly, as a true test of the viability of these films to act as neutralization layers even after significant mechanical stress, a lamellar forming (PS-*b*-PMMA) diblock copolymer was assembled on the surfaces after 60 min of sonication. As shown in Figure 4c, the films assembled on the azide crosslinked neutralization layer show a mix of parallel and perpendicular domains, signifying a significant reduction in the ability to neutralize the surface. All films crosslinked by ketenes, however, show long-range perpendicular ordering of the block copolymers (Figure 4d) and clearly indicate the robust nature and increased performance of a ketene based crosslinking strategy for surface neutralization in block copolymer lithography. Furthermore, the same adhesion test was also performed on a different substrate, thermally deposited Al_2O_3 layer. As with the results on the silicon wafer in Figure 4, the ketene films on Al_2O_3 layer exhibited superior surface adhesion and gave rise to perpendicular ordering of PS-*b*-PMMA block copolymers (Figure S4, Supporting Information), demonstrating the excellent versatility and adaptability of this strategy.

3. Conclusions

This study demonstrates that a ketene-based crosslinking strategy for the fabrication of neutralization layers in BCP lithography offers enhanced performance and substrate adhesion

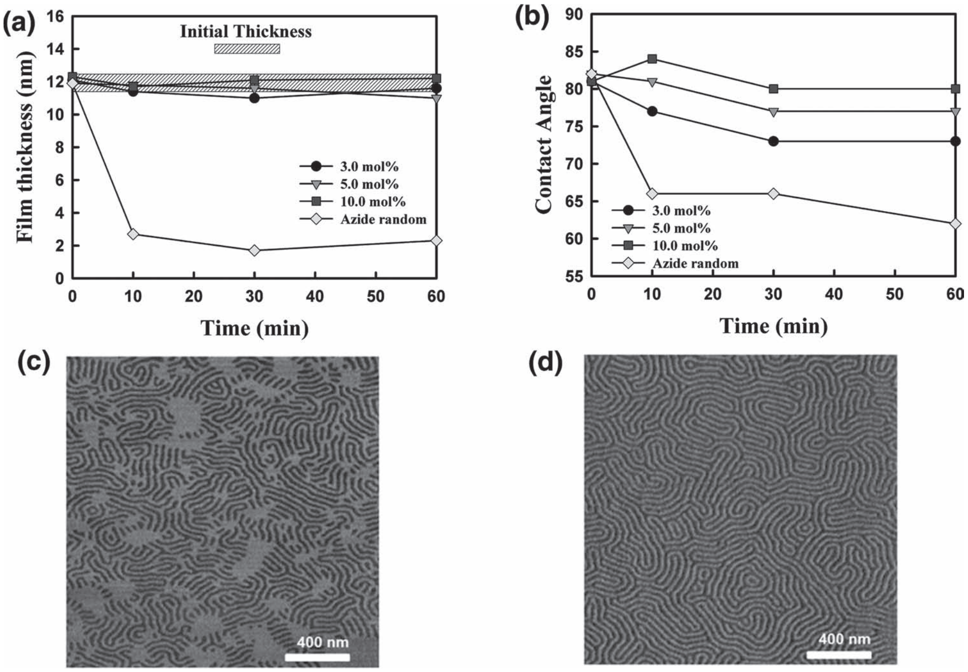


Figure 4. a) Crosslinked thickness of P(S-*r*-**1**-*r*-MMA) thin films compared to azide containing materials as a function of sonication time after crosslinking at 230 °C for 1 h. b) The water contact angle of P(S-*r*-**1**-*r*-MMA) surface compared to azide containing materials as a function of sonication time after crosslinking at 230 °C for 1 h. c) The representative SFM phase image of lamellar forming PS-*b*-PMMA diblock copolymer prepared on the crosslinked azide random copolymer after 1 h of sonication. d) The representative SFM phase image of lamellar forming PS-*b*-PMMA diblock copolymer prepared on the crosslinked P(S-*r*-**1**-*r*-MMA) layers, in which 10.0 mol% of **1** in P(S-*r*-**1**-*r*-MMA) was crosslinked for 1 h at 230 °C followed by 1 h of sonication.

compared to previous methods. These materials provide efficient surface neutralization for (PS-*b*-PMMA) self-assembly via thermal crosslinking of P(S-*r*-**1**-*r*-MMA) with short processing times and tunable surface properties. This is in contrast to previous methods, which either provide surface adhesion at the expense of long processing times and harsh conditions (>2 days at 140 °C) or provide short processing times at the expense of surface adhesion. Additional benefits of this strategy include synthetic utility, as the Meldrum's acid monomer is simple to prepare, and tunable surface properties through varying crosslinking temperature and time. Significantly, conditions were found that provided large area substrate neutralization and perpendicular orientation of the (PS-*b*-PMMA) domains with excellent substrate adhesion. The robust nature of these materials offer significant promise as a platform for the further development of block copolymer lithography.

4. Experimental Section

General Methods: All commercially obtained solvents and reagents were used without further purification. ^{1}H and ^{13}C solution-state NMR were recorded on 600 MHz NMR and 500 MHz NMR spectrometers. Chemical shifts are reported relative to residual solvent peaks (δ 7.26 for $CDCl_3$ in ^{1}H NMR and δ 77.2 for $CDCl_3$ in ^{13}C NMR). IR spectra were obtained using a Thermo-Nicholet Avatar-330 IR spectrometer with single-bounce attenuated total reflection (ATR) (Ge crystal) accessory (Smart MIRacle). Gel permeation chromatography (GPC) was performed in THF on a Waters equipped with a refractive index detector. Molecular weights of polymers were calculated relative to linear polystyrene standards. Mass spectral data were collected on a Micromass QTOF2 Quadrupole/Time-of Flight Tandem mass spectrometer (ESI-MS). SFM images were obtained on a Digital Instruments Multimode scanning force microscope in tapping mode. GISAXS experiments were carried out at the Pohang Accelerator Laboratory (PAL) 4C2 beamlines, Korea. A CCD detector was used to record 2D GISAXS patterns, which was positioned at the end of a vacuum guide tube where the X-ray (wavelength: 1.38 Å) passed through the sample.

Synthesis of P(S-r-1-r-MMA) Random Copolymers: Thermally crosslinkable P(S-*r*-**1**-*r*-MMA) random copolymer was synthesized via RAFT polymerization. The initial stoichiometry of **1** compared to styrene was varied to provide polymers with 3, 5, and 10% of repeat units based on **1**. A representative procedure for the 5% random copolymer follows: Styrene (1.39 g, 13.3 mmol), methylmethacrylate (1.2 g, 12.0 mmol), **1** (0.365 g, 1.33 mmol), 2,2′-azobis(2-methylpropionitrile) (AIBN) (0.7 mg, 0.0042 mmol), and RAFT agent (12.7 mg, 0.042 mmol) were added to a Schlenk flask and degassed through three freeze-pump-thaw cycles. The reaction mixture was allowed to stir at 80 °C for 60 h. The reaction was quenched by exposing to air and precipitated into 150 mL methanol. The final product was collected by filtration as a pink powder. Physical properties were as follows: 3 mol% P(S-*r*-**1**-*r*-MMA): M_n = 24 000 g/mol, PDI = 1.13; 5 mol% P(S-*r*-**1**-*r*-MMA): M_n = 21 000 g/mol, PDI = 1.15; 10 mol% P(S-*r*-**1**-*r*-MMA): M_n = 27 000 g/mol, PDI = 1.22. 3 mol% of azide containing copolymer: M_n = 21 000 g/mol, PDI = 1.12.

Preparation of Random Copolymer and Crosslinking Test: A 0.4 wt% solution of P(S-*r*-**1**-*r*-MMA) in toluene was spin coated on a silicon substrate (3000 rpm, 40 s). The initial thickness of the random layer, which was measured by ellipsometry, was 12 nm (±1 nm). Thin films were crosslinked at 200, 230, 250 °C for 10 s to 1 h under nitrogen on a hot plate. To test the reproducibility of this process, at least 10 samples were prepared under each of the conditions. After thermal crosslinking, all samples were rinsed in a toluene solution, dried in a vacuum oven, and the residual thickness was measured. To confirm the neutral properties of the surface, 40 nm of lamella forming PS-*b*-PMMA (74 kg/mol total, PS 38 kg/mol, PMMA 36 kg/mol, purchased from polymer source) was spin coated on the residual random layer (1.2 wt% of toluene solution, 3000 rpm spin rate, 60 s). After 72 h at 190 °C of thermal annealing under vacuum, the lamella morphology was confirmed by SFM.

Adhesion Test: 0.4 wt% of P(S-*r*-**1**-*r*-MMA) solution in toluene was spin coated onto a silicon substrate (3000 rpm, 40 s). The initial thickness of the random layer, which was measured by ellipsometry, was 12 nm (±1 nm). Thin films were crosslinked at 230 °C for 10 s to 1 h under nitrogen on a hot plate. After crosslinking, the silicon wafer was immersed in benzene and sonicated for 10 to 60 min. The physical properties of residue polymer layer were then measured by ellipsometry and the water contact angle was also measured.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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