

# Rapid Modular Synthesis and Processing of Thiol–Ene Functionalized Styrene–Butadiene Block Copolymers

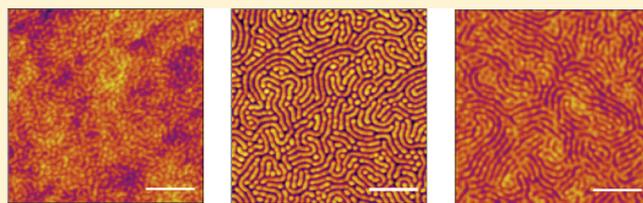
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## S Supporting Information

**ABSTRACT:** Diblock and triblock copolymers of poly(styrene)-*block*-poly(1,2-butadiene) (PS/PB) and PS/PB/PS were modified by photochemical thiol–ene chemistry to process selected functional nanopatterned polymers, with reaction completion in 1 h. PB molecular weight (MW) and thiol–ene ratios were systematically varied based on a model monomer, boc-cysteamine, to determine the efficiency of the reaction. The results demonstrate the polydispersity index (PDI) of modified block copolymers significantly increased when low thiol–ene ratios were employed and sometimes induced gelation of the reacted polymers. Using a 10-fold excess of thiol, functionalizations between 60% and 90% were obtained for amines, carboxylic acids, amides, and a pharmaceutical with a pendant thiol. Differential scanning calorimetry showed a 30–60 °C increase in the glass transition temperature of the daughter polymers. Subsequently, these polymers were spin-coated from solvents found suitable to form self-assembled block copolymer films. The microstructure domain spacing for each polymer was consistent with those originating from the parent polymer. This technique described allows for the formation of nanopatterned block copolymer films with controlled chemistries from a single source material.



## INTRODUCTION

The need for polymers with tailored properties has increased recently with applications ranging from optoelectronics to biomedical.<sup>1</sup> Anionic polymerization is the predominant synthetic scheme for producing monodisperse and well-defined polymer architectures.<sup>2</sup> However, the sensitivity of anionic polymerization to polar and acidic groups makes the synthesis of functional polymers difficult. Therefore, the development of facile and effective postpolymerization modification techniques which maintain monodispersity and architectural integrity of the parent polymer would be beneficial. Commodity polymers such as those containing poly(butadiene) or poly(isoprene) are ideal candidates for backbone modifications due to their widespread commercial availability.

Sulfur's reactivity with poly(isoprene) was discovered in the 19th century by Goodyear to enhance the mechanical integrity of natural rubber.<sup>3</sup> More recently, thiol–ene chemistry was explored by several groups to synthesize polymer networks, block copolymers, dendrimers, liquid crystals, end-functional, and backbone-modified polymers.<sup>4–8</sup> Thiol–ene reactions are directed by the attack of radically initiated  $\omega$ -functional thiols on unsaturated bonds.<sup>9</sup> Thiol–ene chemistry can be employed for interfacial modifications, including solvent dispersed nanoparticles or thin film surfaces.<sup>10–12</sup> Low-intensity ultraviolet sources are capable of generating radicals including renewable resources like sunlight.<sup>13</sup>

Photochemical and thermal initiation may be used to generate sulfonyl radicals, although photochemical strategies were

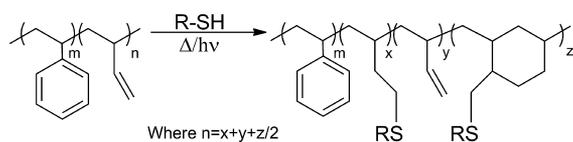
more effective.<sup>14</sup> Some limitations of thiol–ene chemistry were observed by several research groups, including reduced efficiency and higher side product formation when using low thiol–ene ratios.<sup>7</sup> Compared to low molecular weight compounds, polymeric starting materials exhibited large decreases in reactivity.

Previous research confirmed the pendant vinyl groups of poly(1,2-butadiene) (PB) were over 10-fold more reactive to thiols when compared to the backbone double bonds in poly(1,4-butadiene).<sup>15</sup> The modular capability of thiol–ene chemistry was demonstrated for the synthesis of low molecular weight (MW) ionomers without functional group limitations, including alcohols, amines, amino acids, carbohydrates, carboxylic acids, and fluorinated compounds.<sup>16–19</sup> The thiol–ene reaction on PB is limited by the formation of cyclic groups when intermediate radicals react with adjacent unreacted double bonds, schematically depicted in Figure 1. Possible reaction products are no reaction, thiol addition, and thiol addition followed by cyclic group formation. These studies confirmed that six-membered rings reduce the thiol addition yield despite full conversion of double bonds.<sup>16</sup> In spite of cyclic formation in the thiol–ene reaction of PB, high yields were reported in the range of 75% modification, with near-quantitative conversion of double bonds.

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**Figure 1.** Reaction scheme of the thiol–ene reaction on PS/PB block copolymers. Possible reaction routes include thiol addition, no reaction, and cyclic group formation.

The low molecular weight polymer systems previously investigated for the thiol–ene reaction cannot be used for coating applications that require thin and bulk film processing. Styrene–butadiene block copolymers synthesized by numerous manufacturers have molecular weights in the range of 100–150 kDa, whose mechanical properties and solution viscosity are optimal for film applications. Few studies have examined thiol–ene addition on high molecular weight PB copolymers. Passaglia and Donati found significant issues with cross-linking and low functionalization using thermal initiation on styrene–butadiene random copolymers.<sup>20</sup> In order to decrease cross-linking, lower concentrations of initiator were used at the expense of reduced functionalization. More recently, David and Kornfield were able to graft thiol groups to high molecular weight PB using thermal initiation with a controlled range of yields within 2–6 h.<sup>21</sup> These polymers could be further reacted to create functionalities with potential optoelectronic or liquid crystalline properties.

In this study, modification of styrene–butadiene block copolymers of varying molecular weight by radical thiol addition is reported using a photochemical strategy that allows reaction completion within 1 h. While alkylation of PB was shown to control the orientation of self-assembled butadiene–ethylene oxide block copolymers,<sup>22</sup> this study seeks to synthesize and process a modular collection of highly functionalized BCP nanostructured films with similar morphologies. Low thiol–ene ratios increased the polydispersity index and in some cases induced gelation of the modified or “daughter” polymers. Increased thiol concentrations allowed for efficient grafting of various functional groups, including amines, acids, amides, and a pharmaceutical with a pendant thiol. Various characterization methods are shown and support the efficiency of the thiol–ene reaction. Additionally, microphase separation of the modified polymers into nanostructured domains from solution film casting is described. This work demonstrates the versatility of the thiol–ene reaction in creating a novel class of patterned block copolymers with tunable chemistry.

## EXPERIMENTAL SECTION

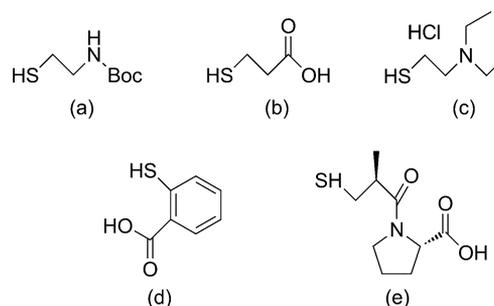
**Materials and Methods.** Captopril, thioglycolic acid, boc-cysteamine, thiosalicylic acid, 2-(diethylamino)ethanethiol hydrochloride (DAET), anhydrous tetrahydrofuran (THF), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO), propylene glycol monomethyl ether acetate, dimethylformamide, and chloroform were all purchased from Sigma-Aldrich (St. Louis, MO) and used as received. Deuterated chloroform and tetrahydrofuran were purchased from Cambridge Isotopes (Andover, MA). EasiVial poly(styrene) standards for gel permeation chromatography (GPC) calibration were purchased from Agilent Technologies (Santa Clara, CA). Various poly(styrene)-*block*-poly(1,2-butadiene) diblock and poly(styrene)-*block*-poly(1,2-butadiene)-*block*-poly(styrene) triblock copolymers (PS/PB) were purchased from Polymer Source (Montreal, Canada). The molecular weights and relative molar percentages, as determined by GPC and <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy, are summarized in Table 1.

**Table 1.** Summary of the Poly(styrene)-*block*-poly(1,2-butadiene) Diblock and Triblock Copolymers Used in This Study<sup>a</sup>

mol wt (kDa) <sup>b</sup>	PDI <sup>c</sup>	mol % PB <sup>d</sup>
8.5- <i>b</i> -8.0	1.08	65
19.3- <i>b</i> -18.9	1.06	65
63.5- <i>b</i> -33.0	1.13	53
14.1- <i>b</i> -67.0- <i>b</i> -24.0	1.13	71

<sup>a</sup>Mole percentages were used to determine the thiol–ene ratio for reactions. <sup>b</sup>As described by the manufacturer. <sup>c</sup>Determined by GPC. <sup>d</sup>Determined by NMR.

**Synthesis.** PS/PB and PS/PB/PS were modified with various thiol compounds radically initiated using BAPO and UV irradiation. The thiol compounds investigated in this study are summarized in Figure 2.



**Figure 2.** Summary of thiols investigated in this study: (a) boc-cysteamine; (b) thioglycolic acid; (c) 2-(diethylamino)ethanethiol hydrochloride; (d) thiosalicylic acid; (e) captopril.

50 mg of each respective block copolymer (BCP), 25 mg of BAPO photoinitiator, and thiol were preweighed into vials with Teflon septa and purged with nitrogen for 10 min. During the purging process, a minimal amount of anhydrous THF was added via syringe, yielding an ~5 wt % solution with respect to polymer. Because of the low solubility of captopril and 2-(diethylamino)ethanethiol hydrochloride (DAET) in THF, a minimal amount of chloroform was used. After purging, the vials were placed into an UltraLum photo-cross-linking oven ( $\lambda = 365$  nm) and irradiated for 60 min to generate sulfenyl radicals. The distance between the UV lamps and the base of the vials was ~15 cm. After UV irradiation, the polymers were concentrated and precipitated three times in hexane or acetone, followed by redissolution in THF or chloroform each time. Finally, they were dried under vacuum at room temperature until reaching constant mass. It is vital to note that applying heat during vacuum drying often yielded an insoluble product.

For determination of the effects of PB molecular weight on the functionalization and/or gelation of styrene–butadiene BCPs, molar ratios of thiol to double bonds were systematically varied from 1:1 to 10:1. The results reported were calculated from <sup>1</sup>H NMR spectra. After recognizing that excess amounts of thiols were required, 10-fold excess of thiol monomers were used to synthesize modified PS/PB block copolymers for calorimetry and thin film analysis.

**Characterization.** Gel permeation chromatography (GPC) confirmed molecular weight distribution and polydispersity of the stock and modified polymers using a Waters 515 HPLC pump, in-line degasser, a Waters 2410 refractive index detector, and PolyPore columns in series. PS/PB block copolymers were dissolved at 2 mg/mL in THF. THF was used as the eluent at a flow rate of 1 mL/min, and the poly(styrene) equivalent molecular weights reported were determined by constructing a multipoint calibration curve using EasiVial standards (Agilent).

<sup>1</sup>H NMR spectra were recorded with a Bruker AV-400 high-resolution NMR operating at 400 MHz to assess reaction completion. The stock polymers as received and modified polymers were scanned

using deuterated chloroform (d-chloroform), with the exception of the thioglycolic acid and captopril modified polymers, which required the use of deuterated tetrahydrofuran (d-THF). Typically, polymers were dissolved at ~2 wt % and scanned 64 times.

Differential scanning calorimetry (DSC) was used to determine the glass transition temperature of the polymers with a TA Instruments Q100 system. The polymers were analyzed using a heat/cool/heat method to erase thermal history with heating rates of 10 °C/min followed by cooling at 5 °C/min. The glass transition temperatures reported are the midpoint of the slope change as determined by the Universal Analysis software package provided by TA Instruments. Prior to conducting DSC measurements, the calorimeter was calibrated with an indium standard.

Block copolymer solutions were prepared at 0.5 wt % and spin-coated at 2000 rpm onto silicon wafers with a native oxide layer. Prior to spin-coating, silicon wafers were cleaned with isopropyl alcohol, acetone, and dried with a nitrogen stream. Tapping mode atomic force microscopy (AFM) was used to image the surface topography of spin-coated block copolymer films using an Asylum MFP-3D system. VistaProbe AFM tips were purchased from Nanoscope Instruments with a nominal tip radius less than 10 nm, spring constant of 48 N/m, and resonant frequency of 190 kHz.  $2 \times 2 \mu\text{m}$  scans were completed at 1 Hz with a resolution of  $512 \times 512$  pixels. Image analysis was performed using ImageJ, which is freeware offered by the National Institutes of Health. Average domain sizes were determined in ImageJ with a minimum of 20 measurements on three different areas, and the error reported is the standard error of the mean.

## RESULTS AND DISCUSSION

**Influence of Molecular Weight on Polydispersity and Functionalization.** The molecular weight and polydispersity index (PDI) of the stock polymers, as purchased, are summarized in Table 1. NMR integrations were calibrated to the aromatic hydrogens of poly(styrene) to determine the relative block ratios. The mole percentage of the butadiene block was determined by  $^1\text{H}$  NMR spectroscopy (NMR) and was further applied to calculate thiol–ene ratios for all subsequently described reactions. The reaction of boc-cysteamine with various butadiene molecular weights was employed as a model reaction to determine the efficiency of the thiol–ene reaction. Radical addition of boc-cysteamine to the pendant vinyl groups of PS/PB block copolymers generally occurred in an efficient manner. Modifications between approximately 50% and 90% were possible with the lowest molecular weight block copolymer. However, the range of functionalization narrowed to between approximately 70% and 90% when starting from higher molecular weight parent polymers. Less than quantitative thiol addition derives from the cyclic reaction between active radicals and adjacent, unreacted double bonds. This reaction is confirmed by the lack of remaining double bonds in the modified polymers without quantitative thiol addition. The cyclic reaction is unique to the thiol–ene reaction of PB and is thoroughly discussed in the literature.<sup>18</sup>

After UV irradiation, several of the higher molecular weight polymer products showed visible viscosity increases. Despite the solubility of reaction stocks from equimolar concentrations of thiol and vinyl groups during purification, some of these polymers formed an insoluble gel with the exception of the lowest molecular weight PS/PB polymer. Thus, determinations of the PDI and functionalization degree were not possible for these polymers and are described in Table 2 as “gel”. GPC determination for the 8.5-*b*-8.0 and 19.3-*b*-18.9 kDa with equimolar thiol–ene concentrations show slight PDI increases on the order of 0.2–0.3 compared to their parent polymers. The PDI of polymer products generally decreases when higher

**Table 2. Effects of Boc-cysteamine Concentration on the Polydispersity Index and Functionalization Degree<sup>a</sup>**

mol wt (kDa)	thiol:ene	PDI $\pm$ SEM <sup>b</sup>	<i>f</i> $\pm$ SEM (%) <sup>c</sup>
8.5- <i>b</i> -8	stock	1.08	N/A
	1	1.45	51 $\pm$ 1
	5	1.19	70 $\pm$ 3
	10	1.12	87 $\pm$ 3
19.3- <i>b</i> -18.9	stock	1.06	N/A
	1	1.23	58 $\pm$ 2
	5	1.20	82 $\pm$ 2
	10	1.16	93 $\pm$ 3
63.3- <i>b</i> -33	stock	1.13	N/A
	1	gel	gel
	5	1.32	70 $\pm$ 2
	10	1.25	79 $\pm$ 1
14.1- <i>b</i> -67- <i>b</i> -24	stock	1.13	N/A
	1	gel	gel
	5	1.41	83 $\pm$ 2
	10	1.28	88 $\pm$ 2

<sup>a</sup>The errors presented are the standard error of the mean ( $n = 3$ ).

<sup>b</sup>Determined by GPC. <sup>c</sup>Determined by NMR.

excess of thiol are applied in the polymer modifications, regardless of molecular weight. Specifically, a 10-fold excess of boc-cysteamine increased the PDIs of daughter polymer by ~0.1, when compared to the high molecular weight parent polymer. In contrast, equimolar and 5-fold excess concentrations of thiol led to gelation or a 1.41 PDI, respectively. This indicated that the PDI of modified polymers increased due to low thiol–ene ratios; when using equimolar concentrations, this induced gelation of the daughter polymers.

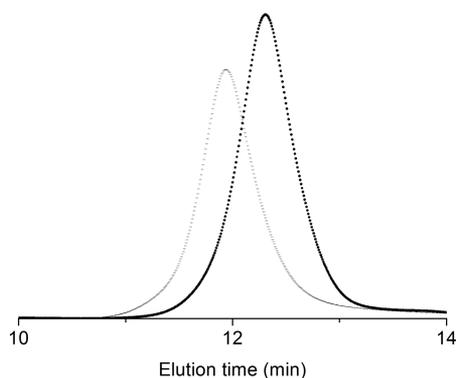
As shown in Table 2, the functionalization degree increased with higher thiol–ene ratios and saturated near 90% for the lowest molecular weight polymer. As the molecular weight of the polymers increased, the efficiency of the thiol–ene reaction slightly decreased and resulted in modifications around 80%. Despite the ability to control functionalization on low molecular weight PS/PB block copolymers, low thiol–ene ratios generally increased the PDI of high molecular weight polymers and in some cases induced gelation. Additionally, the potential range of functionalization was narrowed with high molecular weight BCPs. Assuming that all chains within a relatively monodisperse polymer solution have equal reactivity toward thiols, the PDI increase suggests a low density of cross-links.

Radicals remain active after thiol addition, and there are several possibilities for their fate. The active radical can undergo chain transfer and initiate another sulfenyl radical.<sup>7</sup> Radicals can also react with adjacent and unreacted double bonds to form cyclic groups.<sup>16</sup> Finally, two radicals can cause recombination termination by intrachain or interchain cross-linking.<sup>7</sup> A combination of these processes may occur; however, recombination termination is most likely the culprit in increased PDIs and gelation products since neither chain transfer nor cyclic group formation would result in gelation.

The observed results from PS/PB modification at low thiol–ene ratios with different molecular weights are supported by theory, where the critical cross-link density for gelation scales inversely with the degree of polymerization (DP).<sup>23</sup> Thus, higher molecular weight polymers are more susceptible to forming infinite networks. The DP of the butadiene block of the BCPs investigated range from approximately 150 to 1240 repeat units. The critical cross-link densities for these molecular

weights are approximately 0.6% and 0.08% of mer units, respectively. For the highest molecular weight polymer, this corresponds approximately to one cross-linked mer unit per 1000 inducing gelation. These theoretical numbers support the observed experimental in Table 2, which shows that higher molecular weight polymers have a higher propensity for gel formation.

When the thiol–ene ratio was systematically increased, a trend of decreased polydispersity was observed. The chromatogram for the 63 kDa-*block*-33 kDa parent polymer and the daughter polymer with a 10-fold excess of boc-cysteamine is shown in Figure 3. The chromatogram shows a modest shift in



**Figure 3.** Gel permeation chromatography of 14.1 kDa-*b*-67.0 kDa-*b*-24.0 kDa PS/PB/PS triblock copolymer and another modified with a 10:1 thiol–ene ratio of boc-cysteamine (stock: dark dots; modified: light dashes).

the peak elution volume toward a higher molecular weight range when comparing the modified polymer to that of the stock. Additionally, a similar narrow molecular weight distribution is conserved between the stock and modified polymers.

Various applications, including those for biomedical devices, require materials that can withstand cyclical loading. High molecular weight polymers are typically used for coatings due to their advantageous mechanical properties. The experimental observations indicate a large excess of thiol is required to maintain narrow PS/PB molecular weight distribution and inhibit gelation. While lower degrees of functionality were not presented in this study, perhaps the use of thiolated alkanes as comonomers may allow for modifications of PS/PB BCPs on the order of 20–70%. Despite these issues, the photoinitiated thiol–ene reaction presents an effective and facile route for rapid functionalization of butadiene BCPs.

**Synthesis of Functional Block Copolymers.** After investigating the molecular weight effects of thiol addition, block copolymers were synthesized with a wide set of functionalities. The monomers used in this study were boc-cysteamine, thioglycolic acid, thiosalicylic acid, captopril, and 2-(diethylamino)ethanethiol hydrochloride (DAET), whose structures are depicted in Figure 2. Modified polymers were easily produced and obtained in yields of ~70%, with the exception of thiosalicylic acid. The PS/PB BCPs reacted with thiosalicylic acid contained a similar amount of vinyl groups as the parent polymer. Thus, thiol addition did not occur and was confirmed by NMR. The steric constraints from the carboxylic acid group ortho to the thiol group may inhibit thiosalicylic acid's reactivity with the pendant vinyl groups on PB.<sup>24</sup>

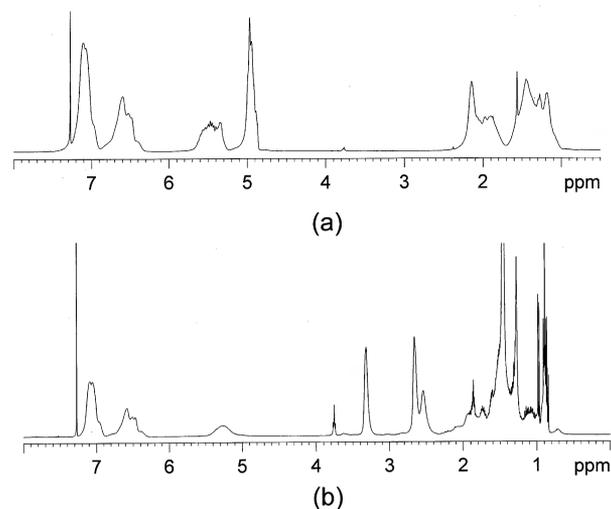
The results from the reaction of the 63.5-*block*-33.0 kDa stock BCP with various thiolated monomers are described in

Table 3. Additionally, NMR spectra from a typical thiol–ene reaction are shown in Figure 4. NMR spectra with raw

**Table 3. Functionalization Degree of 63.5 kDa-*b*-33.0 kDa PS/PB Polymers Modified Using 10:1 Thiol–Ene Ratios on the Monomers Studied<sup>a</sup>**

monomer	thiol:ene	$f \pm \text{SEM} (\%)^b$
boc-cysteamine	10	79 $\pm$ 1
thioglycolic acid	10	78 $\pm$ 3
2-(diethylamino)ethanethiol hydrochloride	10	93 $\pm$ 2
captopril	10	69 $\pm$ 3
thiosalicylic acid	10	0

<sup>a</sup>The errors presented are the standard error of the mean ( $n = 3$ ).  
<sup>b</sup>Determined by NMR.



**Figure 4.** <sup>1</sup>H NMR spectroscopy of stock and typical functionalized block copolymer obtained from radical thiol additions: (a) stock polymer; (b) boc-cysteamine.

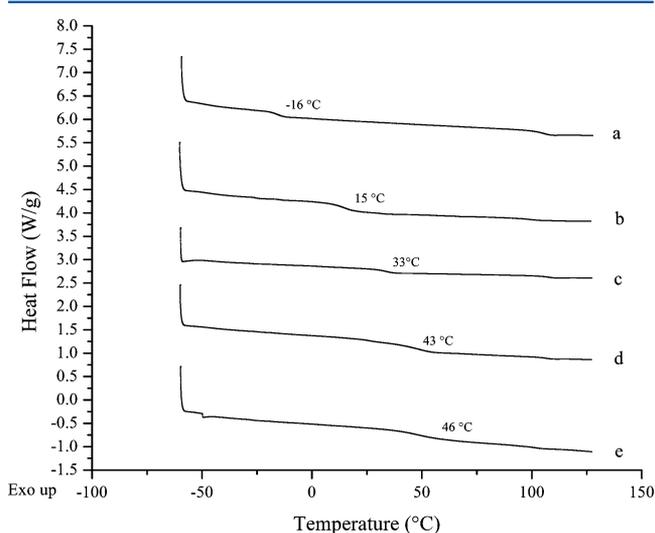
integrations, peak assignments, and sample calculations are included in the Supporting Information. Similar to previous studies, wide functional group tolerance was observed using a photochemical strategy for grafting various groups onto PS/PB block copolymers. With the exception of thiosalicylic acid, PS/PB BCPs thiol addition yields were obtained in the range of 70–90%. Despite variable functionalizations, all products show full conversion of vinyl groups between 4.9 and 5.7 ppm in NMR spectra.

The lowest yield was 69  $\pm$  3% from captopril. As the bulkiness of the group increased, such as with captopril, the functionalization degree decreased. The experimental conditions approach the solubility limit of captopril; thus, steric hindrance cannot be explicitly confirmed as the cause of reduced functionalization. However, experiments completed on low MW PB demonstrated that larger R groups resulted in lower modification degrees, despite full conversion of double bonds.<sup>13</sup> Because of the cyclic reaction between active radicals on the PB backbone and adjacent, unreacted double bonds, less than quantitative addition occurred. The appearance of a broad peak at 2.5–2.7 ppm, corresponding to the four protons at the thioether linkage, shows the successful addition of thiols to the polymer side chains.

**Thermal Characterization.** Maintenance of elastomeric behavior is a vital property of styrene–butadiene block

copolymers, which are used in a variety of applications, ranging from tires to biomedical devices. The glass transition temperature ( $T_g$ ) is a key material property to determine whether a polymer conforms to the requirements of a thermoplastic elastomer. Using a heat/cool/heat method to erase thermal history, the  $T_g$ 's reported are from the PB block only, since the poly(styrene)  $T_g$  remained unmodified during the thiol–ene reactions.

The results from the second differential scanning calorimetry (DSC) heating cycle are shown in Figure 5. The glass transition temperature of the PS/PB parent polymer, 63 kDa-*block*-33.5 kDa, was determined to be  $-15$  °C. The daughter polymers'



**Figure 5.** Differential scanning calorimetry of monomer dependency of glass transition temperature of functionalized block copolymers using a thiol–ene ratio of 10:1 on PS/PB with a molecular weight of 63.5 kDa-*b*-33.0 kDa: (a) parent polymer, as received; (b) boc-cysteamine; (c) thioglycolic acid; (d) 2-(diethylamino)ethanethiol hydrochloride; (e) captopril.

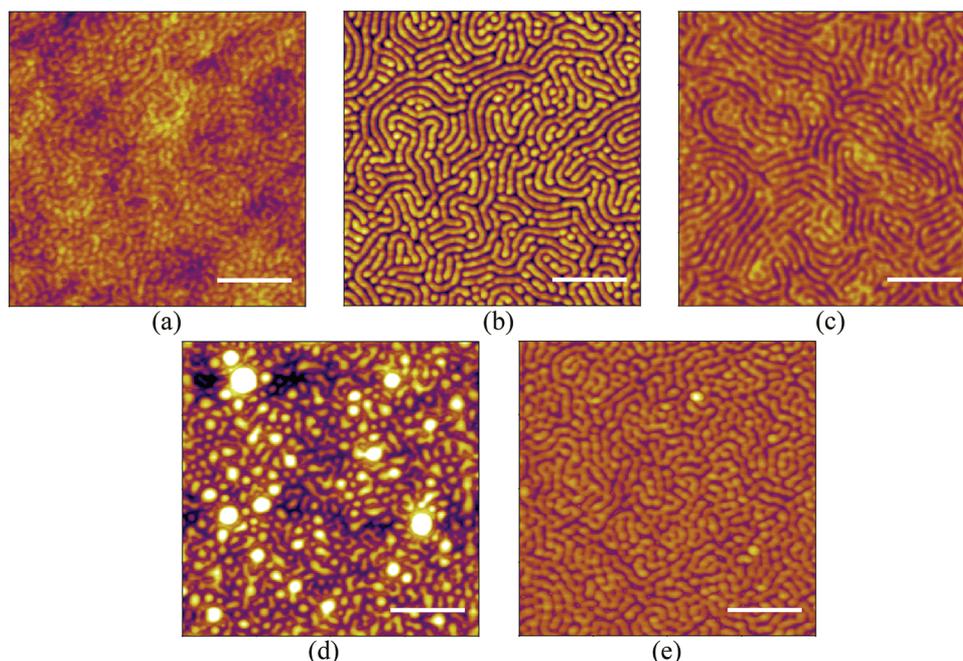
$T_g$ 's increased between 30 and 60 °C, depending on the specific monomer modification. The glass transition temperatures for the polymers modified with boc-cysteamine, thioglycolic acid, DAET, and captopril were determined to be 15, 33, 43, and 46 °C, respectively.

An increase in  $T_g$  is believed to result from the modification process, which leads to increased steric bulk on the side chains of the PB block. Additionally, the cyclic groups inherent in the thiol–ene reaction of PB led to an elevated  $T_g$ ; it was previously shown that lower configurational entropy in cyclic systems effectively increases the  $T_g$  when compared to linear analogues.<sup>25</sup> These two compounding factors account for the large increase in  $T_g$  after thiol–ene-based modification of the PS/PB block copolymers.

**Thin Film Processing.** After NMR, GPC, and DSC characterization, optimal conditions for processing the grafted block copolymers were determined. Common solvents used for PS/PB BCPs such as chlorinated solvents, tetrahydrofuran, and toluene yielded opaque solutions or dispersions which suggested micellar self-assembly. Dynamic light scattering analysis (DLS) indicated the formation of sub micrometer particles and was confirmed by film spin-coating and AFM analysis.

Various solvents were used to process nanopatterns from each daughter polymer. Generally, the daughter polymers exhibited solubility in dimethylformamide (DMF), propylene glycol monomethyl ether acetate (PGMEA), or dimethyl sulfoxide (DMSO) and were insoluble in water. Thin films were spin-coated from low humidity conditions (<40% RH) from a 0.5% solution at 2000 rpm. The stock 63-*block*-33 kDa PS/PB diblock copolymer was processed from dichloroethane and formed disordered cylindrical nanostructures after spin-coating. Both parallel and perpendicular cylindrical domains existed at the surface from AFM measurements.

Typical results for AFM images are shown in Figure 6. The average center-to-center distance of the stock polymer microstructures was determined to be  $65.7 \pm 1.5$  nm. An iterative method was used to process similar nanopatterns from



**Figure 6.** Atomic force micrographs of 63 kDa-*block*-33.5 kDa stock and modified PS/PB block copolymers: (a) parent polymer, as received; (b) boc-cysteamine; (c) thioglycolic acid; (d) 2-(diethylamino)ethanethiol hydrochloride; (e) captopril. Scale bars: 500 nm.

each daughter polymer using the solvents resulting in optically clear solutions, which were typically DMF, PGMEA, or DMSO. The boiling point of DMSO was too high for evaporation to occur during spin-coating, even after longer times. The center-to-center domain sizes are tabulated in Table 4. Spin-coating

**Table 4. Domain Size Summary of 63 kDa-*block*-33.5 kDa Stock and Modified PS/PB Block Copolymers<sup>a</sup>**

monomer	center-to-center spacing $\pm$ SEM (nm)
stock	65.7 $\pm$ 1.5
boc-cysteamine	66.3 $\pm$ 1.5
thioglycolic acid	74.1 $\pm$ 1.9
2-(diethylamino)ethanethiol hydrochloride	80.7 $\pm$ 2.7
captopril	74.5 $\pm$ 2.1

<sup>a</sup>The results were calculated from AFM images, and the error presented is the standard error of the mean.

yielded cylindrical microstructures from the boc-cysteamine, thioglycolic acid, and captopril modified polymers with center-to-center domain sizes of 66.3  $\pm$  1.5, 74.1  $\pm$  1.9, and 74.5  $\pm$  2.13 nm, respectively. The captopril-modified polymer required the addition of  $\sim$ 25% (v/v) THF for solubility in PGMEA. The DAET-modified polymer was spin-coated from PGMEA/DMF (90/10 v/v %) due to insolubility in pure PGMEA. The center-to-center domain sizes of the DAET modified polymer were 80.72  $\pm$  2.72 nm.

DLS showed monodisperse micelles on the order of 20–40 nm for the polymers in PGMEA (not shown). It is postulated that during spin-coating the micelles shear open and reveal the core of the micelle, resulting in a microphase-separated film. This phenomena was observed in other amphiphilic block copolymer systems with aromatic blocks, such as poly-(2-vinylnaphthalene)-*block*-poly(acrylic acid).<sup>26</sup> Reasonably ordered nanostructures resulting from PGMEA spin-coating make it an exceptional solvent choice for amphiphilic block copolymers.

Despite the high modification degree of the daughter polymers, there was no visible shift into the lamellar region of the block copolymer phase diagram for symmetric block copolymers. This may be due to the micellar template from solution. Seemingly, as the functionalization degree increased, the level of parallel cylindrical domain formation also increased, most notably in the boc-cysteamine modified BCP films. The parallel orientation of quasi-cylindrical domain is in agreement with studies detailing alkylation of PB side chains.<sup>22</sup> An additional factor in parallel domain orientation may be due to the nature of thin films. When film thicknesses are less than the equilibrium domain size of the block copolymers, parallel domains can form, as validated by theory and experimental data in other systems.<sup>27</sup>

## CONCLUSION

We have described a photochemical thiol–ene strategy for creating a versatile set of functional styrene–butadiene block copolymers. The polymers synthesized and characterized confer the ability to control chemistry at the nanoscale and contain precursors that are readily available as commodity polymers. Amine, carboxylic acid, amide, and pharmaceutical compounds were successfully grafted onto the block copolymers in reasonable yields. Although the polydispersity index increased with higher

molecular weight polymers, high grafting yields were possible with excess thiol.

These novel functional block copolymers maintained glass transition temperatures near or below room temperature, allowing for their application as elastomeric materials. Despite the amphoteric nature of the daughter polymers, microphase separation of the individual polymer blocks was observed when the casting solvent used was polar with a high boiling point. The highly functional polymers described can be used to make modular nanopatterns.

## ASSOCIATED CONTENT

### Supporting Information

<sup>1</sup>H NMR spectra with peak assignments of modified polymers, integrations, and sample calculations for the functionalization degree. 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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