# Multiblock Copolymers by Thiol Addition Across Norbornene

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S *Supporting Information*

ABSTRACT: Multiblock copolymers, composed of different combinations and number of blocks, offer appreciable opportunities for new advanced materials. However, exploring this parameter space using traditional block copolymer synthetic techniques, such as living polymerization of sequential blocks, is time-consuming and requires stringent conditions. Using thiol addition across norbornene chemistry, we demonstrate a simple synthetic approach to multiblock copolymers that produces either random or alternating architectures, depending on the choice of reactants. Past reports have highlighted the challenges associated with using thiol−ene chemistry for polymer−polymer conjugation; however, using norbornene as the "ene" yielded multiblock copolymers at least four or five blocks. Preparation of new multiblock copolymers containing two or three block chemistries highlights the versatility of this new approach. These materials were thermally stable and showed microphase separation according to characterization by DSC, SAXS, and AFM. This chemical platform offers a facile and efficient route to exploring the many possibilities of multiblock copolymers.
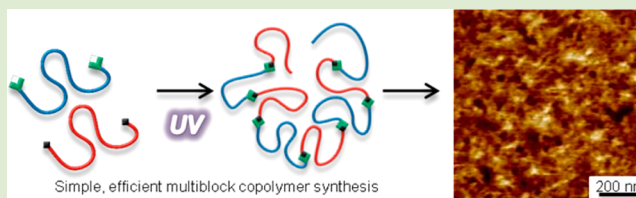
Utilizing different block chemistries, block lengths, and number of blocks, nearly endless combinations of multiblock copolymers (MBCs) can be generated. However, covering this vast territory of combinations cannot be efficiently accomplished with traditional block copolymerization techniques.[1] Few combinations of monomers can be alternatingly polymerized as their propagating centers need to have nearly equivalent reactivities to initiate subsequent blocks.[1] Furthermore, block copolymer synthesis often requires the stringent conditions of living polymerizations.[1−5] While living polymerizations have been used to generate sequence-controlled MBCs with up to 20 blocks, these techniques remain highly specialized.[2,3,6] The coupling of individual blocks through telechelic functional groups is an alternative MBC synthesis technique. This simplified synthetic approach allows for broader ranges of block chemistries, milder polymerization techniques, and the incorporation of commercially available starting blocks. One key requirement of this approach is that the coupling chemistry be high yielding.

Generally, linear MBCs fall into three categories: alternating (ABABAB); random (AABBAB); and sequence-specific (ABCDEF). Lee and Bates synthesized alternating and random MBCs from α,ω-dihydroxy functionalized polystyrene (PS), polybutadiene (PB), and polylactide (PLLA).[7,8] Random MBCs were formed by linking these macromonomers with a diisocyanate to form urethane bonds. Alternating MBCs were formed by first end-capping PS with the diisocyanate, purifying this macromonomer, then adding the alcohol-terminated PB.[7,8] While polyurethane chemistry is a reasonable approach, it has limitations, including sensitivity to moisture, and side reactions resulting in biurets and allophanates that lead to branching. Other examples of this general route to MBCs include disulfide linked poly(n-butyl acrylate)/poly(methyl methacrylate) sys-

tems in which ABA triblocks with α,ω-dithiols were synthesized by RAFT and subsequently reduced to form MBCs,[9] and poly(arylene ether sulfone)-based MBCs synthesized by step growth.[10,11] Expanding MBC chemistry will require the development of additional high-yielding conjugation reactions.

Click reactions could be ideal for MBC synthesis due to their high yield, limited side reactions, and modularity. End-linking individual blocks proceeds similarly to step-growth polymerization, which requires high conversion to obtain reasonable degrees of polymerization. Click reactions have demonstrated utility in polymer chemistry for the synthesis of a variety of polymer networks and architectures and are often used for postpolymerization functionalization.[12−19] The most well-known click reaction involves the copper-catalyzed coupling of an alkyne and an azide to form a triazole.[20,21] Several di-, tri-, and multiblock copolymers have been reported using this method.[22−26] Thiol−ene Michael addition, commonly used for polymer−polymer conjugation,[27] has rarely been used to make MBCs, with the exception of an enzymatically degradable chain-extended PHPMA.[28]

Radical thiol−ene chemistry has many advantages as a small molecule click reaction, such as high tolerance to functional groups, water, and oxygen.[29] Additionally, it does not require a metal catalyst, and a variety of radical initiators offer spatial and temporal control of the reaction.[27,30] However, this technique has thus far proven to be unsuccessful for polymer−polymer conjugation reactions.[31] Koo et al., attempted the photo-initiated coupling of thiol-terminated PS and vinyl-terminated poly(vinyl acetate), a reaction that yielded only 25% of the

desired diblock, largely due to side reactions.[32] Further theoretical work showed that these side reactions have a large impact in photoinitiated polymer−polymer conjugation using thiol and vinyl ether functional groups.[33] Approaches to overcome this problem required a 10 mol excess of thiol-functionalized polymer, which precludes MBC synthesis.[34]

We describe a chemically simple, commercially accessible synthetic approach, capable of yielding both random and alternating MBCs, as depicted in Figure 1. To access the
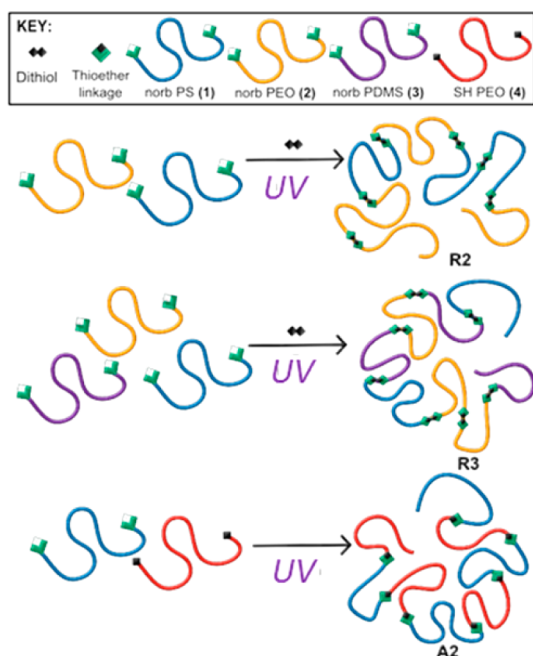

Figure 1. Illustration of synthetic approach to random and alternating MBCs. Black diamonds represent thiols, while the larger green and white diamonds represent unreacted norbornene. Polymers are color coded according to the legend.

random architecture, several polymers with varying backbone chemistries were end-functionalized with a highly reactive ene (norbornene), then coupled with a dithiol. Norbornene was specifically chosen because the ring strain caused by the bicyclic structure of norbornene enables it to undergo thiol−ene reactions much more rapidly than all other enes studied to date.[35,36] It was subsequently predicted that norbornene generates the highest possible thiol−ene conversion, which likely results in fewer side reactions.[35−37]

Commercially available α,ω-dihydroxyl- PEO, PS, and PDMS were end-functionalized via Mitsunobu coupling with norbornene carboxylic acid, as described in the Supporting Information (SI). Norbornene functionalized macromonomers (**1**−**3**) were reacted with a small molecule dithiol and photoinitiator (PI) to produce random MBCs, as shown in Figure 2. The MBCs in this paper are referred to by their block arrangements (R for random or A for alternating) and by their number of different block chemistries (2 or 3). Both a binary MBC (**R2**) containing PS and PEO, and a ternary MBC (**R3**) containing PS, PEO, and PDMS, were achieved using this method (Figure 2a and b, respectively). Synthesizing alternating MBCs involved a similar procedure; however, instead of using a small molecule dithiol to join the blocks, commercially available α,ω-dithiol PEO was reacted with dinorbornene PS (**1**) to give **A2** (Figure 2c).

Random and alternating MBCs were characterized initially by ^{1}H NMR and GPC to confirm the extent of reaction, followed by DSC and TGA to assess thermal properties and microphase separation. AFM and SAXS were performed to further characterize their microphase separation. For experimental details, see the Supporting Information (SI). The expected stoichiometric block ratios for all three MBCs were observed by ^{1}H NMR (see SI), demonstrating approximately equivalent conversion of each starting block. Additionally, the characteristic norbornene peak at 5.98 ppm was absent, indicating the consumption of the double bonds, within the detection limit of the instrument. Molecular weight characterization was performed by GPC.

GPC chromatograms (Figure 3) confirmed the presence of a higher molecular weight species and a sharp decline in the amount of lower molecular weight macromonomers for each MBC. MALLS GPC of R2 and R3 (SI, Figure S5) also confirm the presence of high molecular weight species. All three systems had M_n values close to 30 kg/mol, compared to the 5−9 kg/mol of the macromonomers, shown in the lower panels. (Molecular weights are described in detail in the SI.) Both random systems (**R2** and **R3** shown in Figure 3a) had an average of four blocks (based on multiblock M_n), while the alternating copolymer (**A2** in Figure 3b) had five. The apparent upper limit of average block numbers and molecular weights could be a result of incomplete norbornene macromonomer functionalization. For example, comparing the norbornene ene protons in ^{1}H NMR with the protons α to the ester/unfunctionalized alcohol in the PS macromoner, 91% conversion was obtained. Additionally, according to vendor specifications, only 1.9 chain ends were functionalized per polymer. This led to a final end group functionalization of only 86%, which, in accordance with the Carother's equation, would limit molecular weight.[38] Assuming quantitative coupling of norbornenes with thiols, the resulting number of blocks per MBC would be seven. We observed MBCs containing five macromonomers by GPC, which, using the Carother's equation, corresponds to an extent of reaction of 80%. If only 86% of chain ends are functionalized, this would give an adjusted efficiency of 93%. This calculated 93% yield would lead to MBCs of 14 blocks, provided quantitative end functionalization of the starting macromonomers. Therefore, it appears that thiol−ene is a highly efficient coupling reaction for MBC synthesis but requires macromonomers with more complete functionalization of end groups. Further optimization of the reaction conditions should lead to even larger numbers of blocks.

The low molecular weight polymer remaining in the two random MBCs is lower than that of any macromonomers used in those reactions (Figure 3) suggesting it is likely the cyclization product of a single macromonomer.[38] Such cyclizations would decrease both the hydrodynamic radius and, thus, the observed molecular weight by GPC.[39,40] Whether or not cyclization is present in the larger MBCs is still unknown and requires further characterization. Thermal stability and microphase separation often determine the properties of MBCs and their processability. Thermal gravimetric analysis of R2 and A2 demonstrated thermal stability at temperatures up to 340 °C, similar to that of both PS and PEO macromonomers (SI, Figure S6). Analysis by DSC of R2 and R3 yielded two and three different T_g values, respectively, one for each block chemistry, as summarized in Table 1. This demonstrated these MBCs are phase separated (see SI, Figure S7, for DSC
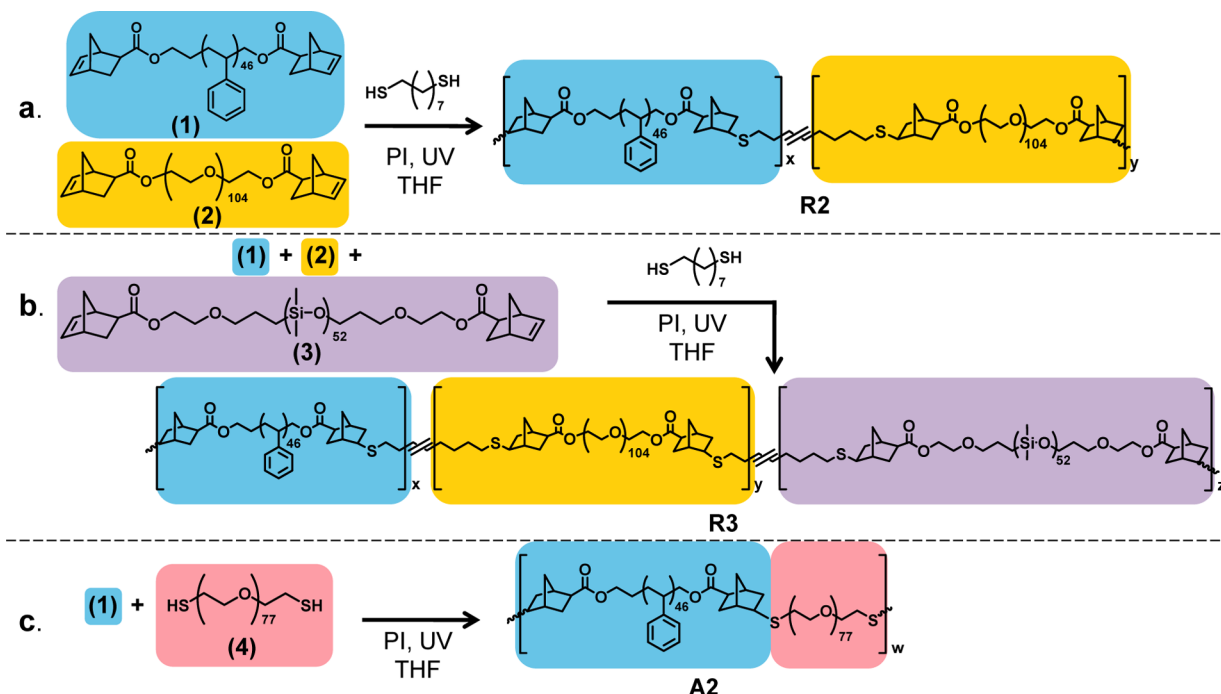
Figure 2. Synthetic scheme for the synthesis of (a) **R2**, (b) **R3**, and (c) **A2**. The random binary MBC (**R2**) was synthesized from norbornene(norb)-terminated PS, and -PEO, and a dithiol linker. The random ternary MBC (**R3**) was synthesized using norb-PS, -PEO, and -PDMS and a dithiol linker. The alternating MBC was synthesized using norb-PS and thiol-terminated PEO and did not require a linker.
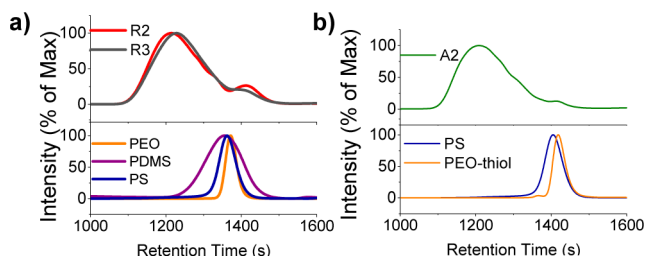

Figure 3. GPC traces of the precipitated (a) random MBCs (top) and corresponding precursor macromonomers (bottom), and (b) alternating MBCs (top) and corresponding precursor macromonomers (bottom). Plots represent normalized RI intensities vs elution time, where THF was used as the eluent and polystyrene standards were used for calibration.

Table 1. Values from DSC Traces of MBCs and Their Macromonomers (M)

sample	PDMS T_g	PEO T_g	PEO T_m	PS T_g
R2		−54 °C	41 °C	73 °C
R3	−141 °C	−64 °C	39 °C	86 °C
A2		−54 °C	26 °C	49 °C
M	−121 °C	−48 °C	58 °C	98 °C

curves).[41] If the blocks were significantly mixed, one intermediate T_g between the T_g values of the macromonomers would have been observed. The absence of such an intermediate T_g indicates that microphase separation is present within these samples. Additionally, prominent endotherms were observed corresponding to the crystalline domain of PEO melting. Such a large peak (60.21 J/g for R2, 44.82 J/g for R3) demonstrated that the crystalline PEO domains were hardly perturbed by the multiblock architecture.[42] While **A2** behaved similarly to the random MBCs in that it maintained two T_g values, the T_g of the PS was lowered 20−30 °C further than

that of the other two MBCs. Moreover, PEO crystallinity was strongly disturbed, with an endotherm of 3.41 J/g in the **A2** sample and the T_m was lowered by 14 °C from the commonly observed 40 to 26 °C. These combined factors suggest that, while microphase separation was still present, more mixing occurred in **A2** than in **R2**. The random MBC architecture would allow for multiple PEO macromonomers to be chained together, potentially increasing the PEO domain size and, consequently, the degree of crystallinity and phase separation. Further corroborating microphase separation, a broad peak was observed in the SAXS pattern of **R2**, with a q value corresponding to a domain spacing of 24 nm (see SI, Figure S8). The breadth of the peak and lack of higher order reflections support the presence of disordered microphase separation in this MBC.[43] Due to the large χ parameter (∼0.1) for PS/PEO, weak to moderate segregation ($\chi N = 10.5$) was still easily achieved at the molecular weights reported here.[44,45]

Disordered phase separation is also observed in phase AFM images of **A2** (Figure 4). Sample preparation, annealing times, and temperatures had strong effects on the observed domain sizes, as expected.[41,46] After annealing for 1 day at 150 °C, domain sizes of 20−25 nm were observed, in contrast to the sample annealed for 3 days at 130 °C, which formed larger
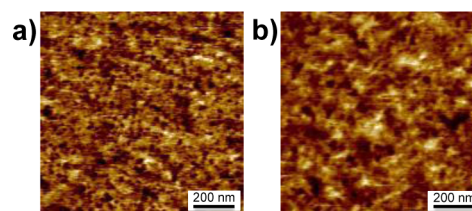

Figure 4. AFM phase images of **A2** annealed for (a) 1 day at 150 °C and (b) 3 days at 130 °C.

domains (>70 nm). The 130 °C annealing temperature was chosen because that temperature was more than 50 °C above the highest measured T_g. The longer annealing time was likely the main contributing factor to the increase in domain size,[41,46] as it gave the multiblocks more time to rearrange and form longer range, potentially "lamellar-like" sheets.[47] From a top-down view, these sheets, if lying flat, could look much larger than the maximum domain size dictated by the end-to-end distance of the individual blocks.

The disordered morphology observed by the SAXS and AFM has been observed previously and is expected because reorganization of MBCs is more difficult than traditional di- or triblock copolymers. Theory predicts MBCs face higher kinetic and thermodynamic barriers to reorganization than their shorter analogues because MBCs bridge several domains.[48] This barrier increases with the number of blocks in the MBC. These preliminary studies have not included optimization of annealing conditions. However, there is growing interest in this disordered, bicontinuous-like morphology for applications such as fuel cells, batteries, bulk heterojunction solar cells, oxygen transport materials, and selective removal of one phase to yield highly interconnected porous membranes.[49]

A set of alternating and random MBCs containing PEO, PS, and PDMS was synthesized using thiol–ene click chemistry. While other attempts at radical click chemistry involving polymers have been plagued by side reactions, the multiblocks synthesized here utilized highly reactive norbornene end groups to obtain better yields. These MBCs were shown to microphase separate in a disordered manner and demonstrated high thermal stability. The M_n of the MBCs reported here is around 30 kg/mol, equating to 4–5 blocks per chain. We plan to optimize reaction conditions to obtain higher molecular weights. More detailed studies are necessary to investigate the relationship between the composition of the multiblocks, phase separation behavior, and mechanical properties. Multiblock copolymers represent a rich and underdeveloped field that has, in the past, been difficult to study. The synthesis described here offers a simple, effective route to these fascinating materials.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Experimental detail, NMRs, GPC-MALLS, TGA, DSC and SAXS. 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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