Scission of Diblock Copolymers into Their Constituent Blocks

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Phase segregation of amphiphilic block copolymers has been used to create nanoporous thin films by the removal of the minor component from self-assembled structures.[1−3] Potential applications of these materials include separation membranes, templates for the growth of oriented inorganic or metal nanostructures, and sensors. Currently, chemical etching and UV degradation are the methods that are commonly used for the removal of minor components to create the nanopores.[1−3] Chemical etching processes tend to require harsh conditions such as reactions with oxidizers, strong acids, or strong bases at elevated temperatures; these conditions may be incompatible with major component polymer or the underlying substrate or both. A key problem with UV degradation is that its application is limited to a few polymers such as poly(methyl methacrylate) (PMMA) and poly(α-methylstyrene) (PαMS). Our approach to address the limitations of the existing protocols is to introduce a linker between the amphiphilic blocks, which can be cleaved rapidly under mild reaction conditions. The linker should also be inert under polymer synthesis and processing conditions.

Triphenylmethyl (trityl) ethers, originally developed for carbohydrate chemistry, are now widely used as protecting groups in synthetic chemistry.[4] They are also used for the immobilization of molecules on resins in solid-phase organic synthesis.[5] Trityl ethers are stable to strong nucleophiles, bases, and radicals. Therefore, they will be stable to anionic and radical polymerization conditions—two commonly used methods for polymer synthesis. Nonetheless, the trityl ether linkage can be readily cleaved by Brønsted or Lewis acids at ambient conditions.[4] Moreover, the cleavage conditions can also be tuned by attaching functional groups to phenyl rings of the triphenylmethyl group.[4] These features make trityl ether a very versatile, acid-cleavable linker between the components of multiblock polymers. As a proof of concept, we report here the synthesis of a diblock copolymer, using nitroxide-mediated living radical polymerization, wherein a polystyrene (PS) block is linked to a methoxy-terminated poly(ethylene glycol) (MPEG) block by a trityl ether. We also show that the diblock copolymer can be rapidly cleaved into its constituent blocks under mild conditions.

To show the efficacy of our approach, we chose to focus on PS-*b*-MPEG diblock copolymers. Many PEG-based block amphiphilic polymers are widely studied in the context of nanostructure formation.[2a] Furthermore, the PS-*b*-PEG system is particularly interesting because it has been shown to form defect-free hexagonal columnar structures; the removal of PEG from this system will lead to defect-free nanoporous films.[1k,1l]

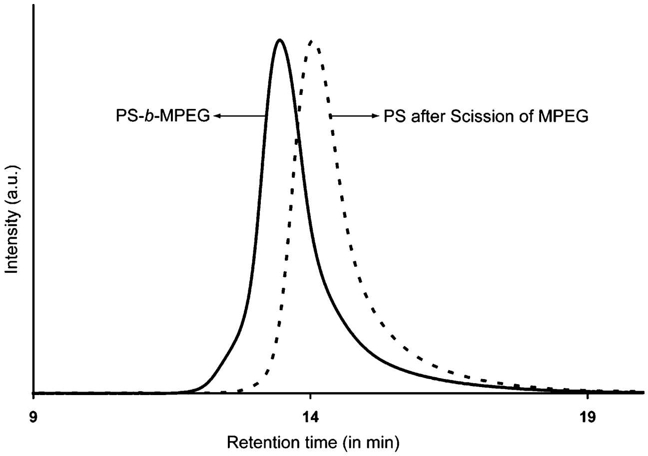

Figure 1. Gel permeation chromatographic traces for the diblock copolymer (solid line) and for the polymer after the scission and aqueous extraction of the MPEG block (dashed line).

We decided to synthesize the diblock copolymer by first synthesizing a MPEG-trityl-macroinitiator (**3**), which is chain end functionalized with a trityl ether that bears TEMPO (Scheme 1).[6] We were able to successfully add TEMPO to 4-bromostyrene using the Hawker protocol (see Supporting Information).[7] The bromide in 4-bromostyrene−TEMPO adduct (**1**) was then converted to its lithium analogue by a lithium−halogen exchange with *n*-BuLi. Addition of the lithiated styrene−TEMPO adduct to benzophenone resulted in diphenyl[4-(2,2,6,6-tetramethyl-1-piperidinyloxy)phenyl]methanol (**2**). Reaction of **2** with MPEG$_{5000}$-mesylate resulted in the MPEG$_{5000}$-trityl-macroinitiator (**3**). Reaction of **3** with styrene at 130 °C provided diblock copolymers with narrow molecular weight distributions ($M_n = 31\,600$, $M_w = 37\,300$, PDI = 1.18).

To test the cleavage of trityl ether under acidic conditions, we dissolved the PS-*b*-MPEG diblock copolymer in d_8-toluene and added d_1-trifluoroacetic acid (TFA), which is miscible with toluene. The color of the solution changed to yellow-orange immediately upon addition of TFA. The absorptions in the UV/vis spectra were consistent with the formation of a trityl cation (see Supporting Information). The solution was stirred for ~20 min after which D_2O (containing a small amount of d_1-TFA) was added to this solution until the color disappeared. The biphasic mixture was then separated into aqueous and organic layers. The organic layer was washed with water and then with saturated $NaCl_{(aq)}$ solution. The solvent was removed under vacuo. Gel permeation chromatography (GPC) of the resultant residue of the organic layer showed that the molecular weight was lower than that of diblock copolymer (Figure 1); the weight loss was consistent with complete removal of MPEG. ^{1}H NMR of the organic phase in CD_2Cl_2 showed peaks that were attributable only to polystyrene (see Figure 2); the ^{1}H NMR of the D_2O phase contained peaks that were attributable to MPEG. The number-average molecular weights obtained for MPEG and PS obtained from GPC were consistent with the values obtained by end-group analysis from ^{1}H NMR. If MPEG was not extracted from the cleavage reaction solution, then the GPC of the resultant polymer was bimodal showing peaks corresponding to PS and MPEG. From these experiments, we concluded that both the polystyrene and MPEG blocks were intact (see Figure 3 and Supporting Information). The scission occurs only at the trityl ether bond.

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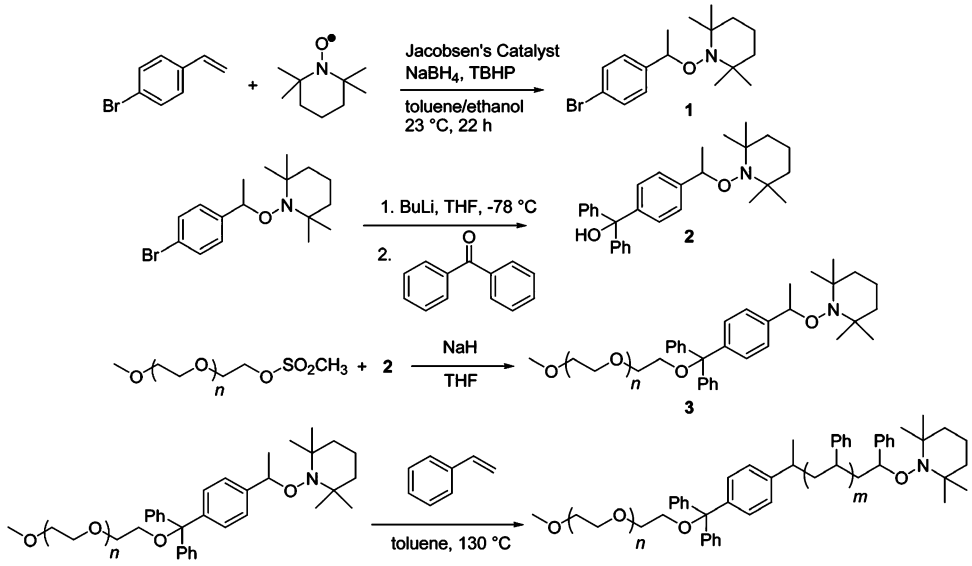
Scheme 1



In conclusion, we have shown that a trityl ether can be readily introduced as a linker between a polystyrene block and a methoxy-terminated poly(ethylene glycol) block by using a MPEG-trityl-macroinitiator and nitroxide-mediated radical polymerization. We were able to rapidly cleave the diblock copolymer into its constituent blocks under mild conditions, using trifluoroacetic acid; the cleaved constituent blocks are chemically intact. Therefore, after scission, either of the constituent blocks can be removed from self-organized structures. This is in contrast to the current methods that rely on the degradation of one of the components. The use of a trityl ether linkage now provides a general strategy for site-specific scission of block copolymers. We are currently working on obtaining defect-free self-assembled structures using PS-*b*-MPEG and the cleavage of the MPEG block to obtain defect-free nanoporous films. Preliminary results indicate that the MPEG can indeed be cleaved in the solid state using TFA vapors.[8] The results of these investigations will be reported in detail in due course.

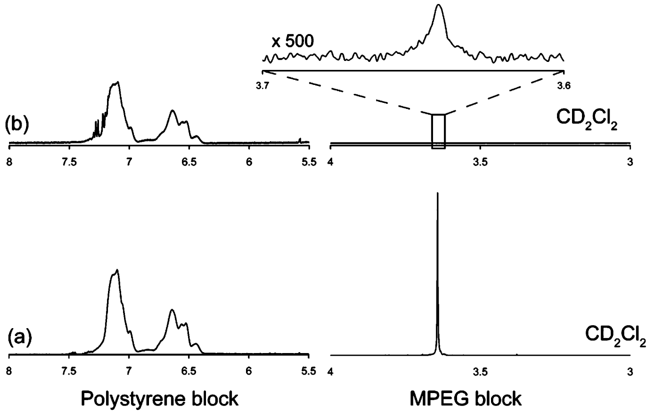


Figure 2. (a) ^{1}H NMR of the PS-*b*-MPEG copolymer in CD_2Cl_2 showing the PS and MPEG regions and (b) ^{1}H NMR (in CD_2Cl_2) of the organic phase after the scission and extraction of the MPEG block.

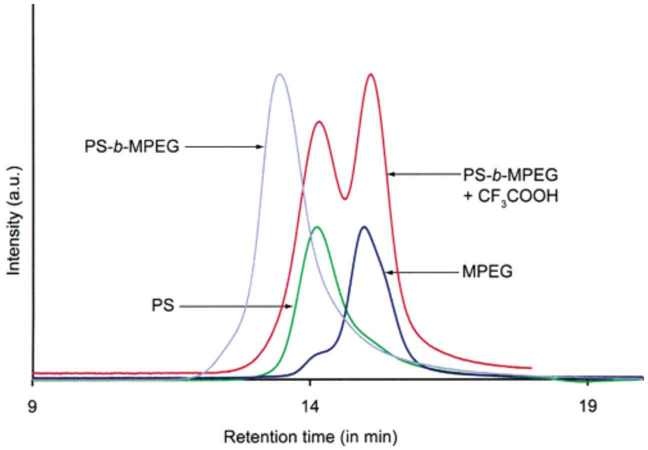


Figure 3. Gel permeation chromatographic traces showing the presence of PS and MPEG blocks after the treatment of the diblock copolymer with trifluoroacetic acid (red). For comparison, the GPC traces of the diblock copolymer (gray), polystyrene (green), and MPEG (blue) are also shown.

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Supporting Information Available: Detailed synthetic procedures and characterization data for **1**, **2**, **3**, and diblock polymer, experimental procedures for the cleavage of diblock polymers, and the characterization of the resultant polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) See Supporting Information for preliminary data.

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