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Synthesis of Tri- and Multiblock Polymers with Asymmetric Poly(ethylene oxide) End Blocks

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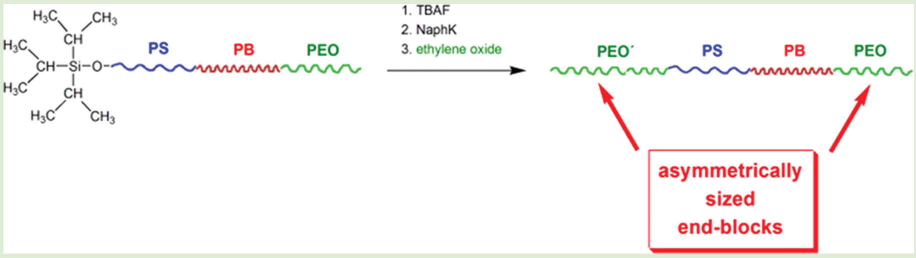
Supporting Information



ABSTRACT: We report the anionic synthesis of poly(ethylene oxide-*b*-isoprene-*b*-ethylene oxide) (OIO′) triblock copolymers and poly(ethylene oxide-*b*-styrene-*b*-butadiene-*b*-ethylene oxide) (OSBO′) tetrablock terpolymers with asymmetrically sized poly(ethylene oxide) (PEO) end blocks using triisopropylsilyloxy-1-propyllithium (TIPSOPrLi) as a protected initiator and diphenylmethyl potassium (DPMK) as the base activator for EO polymerization. All final products and precursors were characterized by size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR) techniques confirming monomodal and narrow molecular weight distributions and controlled molar masses. The growth of independently controlled PEO blocks was additionally demonstrated by the characterization of residual PEO blocks obtained from the ozonolysis of OIO′.

Block polymers are formed by joining polymer chains into hybrid macromolecules that are capable of self-assembling into microphase separated states.[1,2] These compounds are employed as principal ingredients in numerous commercial products,[3−5] for example, thermoplastic elastomers, adhesives, medical devices, surfactants, and as processing aids in lithography.[6,7] The scope of block polymer products will increase in the coming years, due in part to recent developments in controlled polymerization,[8] which afford access to nearly unlimited molecular design possibilities. However, targeting specific chemical and physical properties requires a judicious selection of block species and multiblock architectures with specific block sequences.[9]

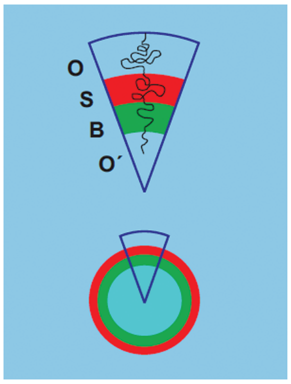


Figure 1. Structural model for vesicles with a controlled diameter based on asymmetric OSBO′ tetrablock terpolymers.

Two principal issues must be dealt with prior to attempting a new block polymer synthesis. The first consideration is the choice of monomers and the associated sequencing of the building blocks, as this determines nearly all properties of the resulting material. This in turn dictates synthetic strategies, which may include one or more controlled polymerizations, coupling reactions, and possibly postpolymerization functionalization chemistry.[10] Recent advances in controlled polymerization techniques permit the functionalization of chain ends for subsequent block growth during various stages of multiblock polymer preparation. Furthermore, protected initiators,[11] which contain inactivated functional sites, can permit the independent addition of certain monomers to either end of a core homopolymer or block polymer.

Sequencing limitations are particularly problematic when dealing with certain amphiphilic multiblock polymers that contain both hydrophobic and hydrophilic blocks. The internal structure, geometry, and overall size of micelles and polymersomes formed by such amphiphilic compounds is dictated by the molecular architecture (linear versus branched),[12] number and types of blocks,[13−15] and the overall composition.[16−21] Tetrablock terpolymers, such as poly(ethylene oxide-*b*-styrene-*b*-

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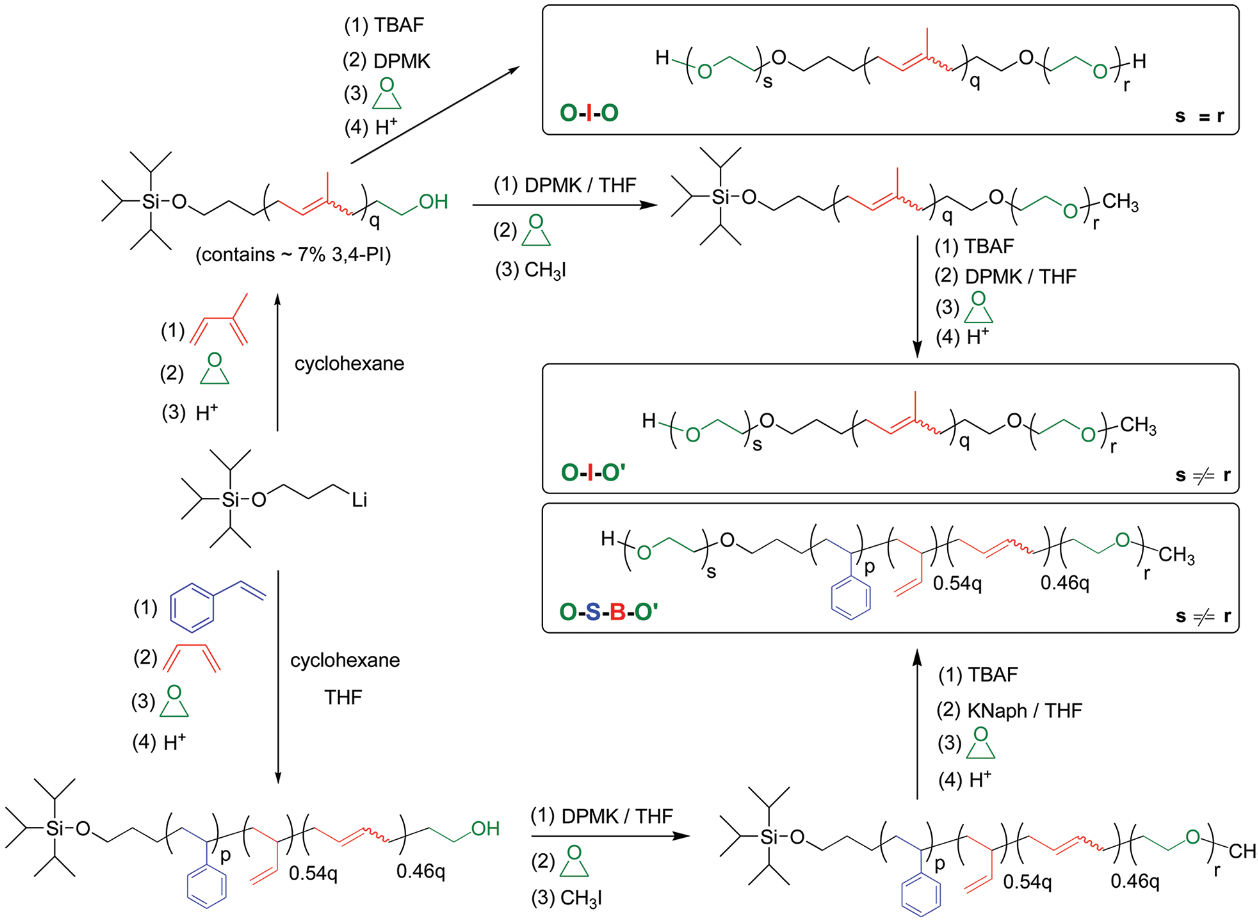
Scheme 1. Synthesis of OIO and OIO′ Triblock Copolymers and OSBO′ Tetrablock Terpolymer



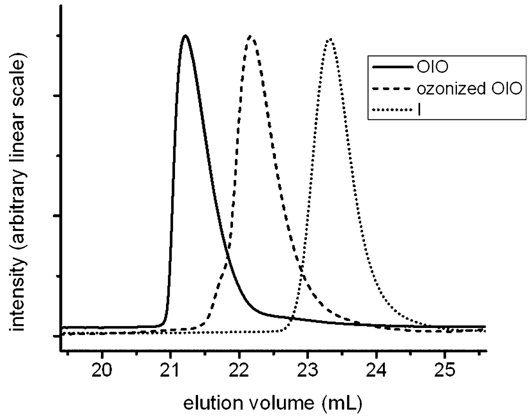


Figure 2. SEC chromatographs of centrosymmetric OIO and I precursors, as well as the trace of the triblock copolymer after ozonolysis (ozonized OIO).

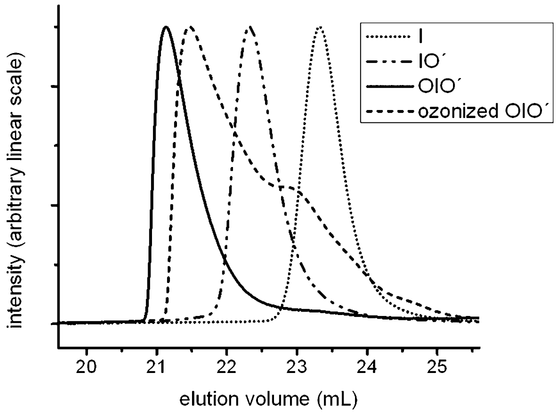


Figure 3. SEC chromatographs of OIO′-2, I, and IO′ precursors, as well as the trace of the triblock copolymer after ozonolysis.

butadiene-*b*-ethylene oxide) (OSBO) and poly(isoprene-*b*-styrene-*b*-2-vinylpyridine-*b*-isoprene) have been shown to yield interesting micelle and vesicle morphologies[22] as well as ordered microphase separated states.[23] However, independent tuning of the terminal PEO block lengths (i.e., O and O′ in OSBO′) is challenging. Methods for preparing multiblock polymers include the synthesis of chain-end functionalized copolymers, followed by appropriate polymer−polymer coupling reactions.[23−25] However, those routes are not always quantitative or require the addition of excess polymeric reagents to achieve high yields. As a consequence, complicated purification procedures are necessary to rid the final amphiphilic product of the uncoupled polymers.

The ability to independently specify both terminal PEO block molar masses in O[R]O′, where R represents a polymer containing one, two, or more hydrophobic blocks, could enable the preparation of nanoscale structures with unparalleled control over morphology, such as water-based polymersomes with a controlled diameter and size distribution.[20,21] For example, Figure 1 illustrates how the overall shape of an OBSO′ tetrablock could induce a specific interfacial curvature, hence the specified

Table 1. Molecular Characteristics of the Multiblock Polymers

sample	M_n[a] (kg/mol)	M_w/M_n[b]	M_n[a] PEO (kg/mol)	M_n[a] PS (kg/mol)	M_n[a] PB (kg/mol)	M_n[a] PI (kg/mol)	M_n[a] PEO′ (kg/mol)	% PEO[c]
OIO	42.5	1.06	18.6			5.3	18.6	87.5
OIO′-1	18.1	1.07	6.7			5.3	6.1	70.7
OIO′-2	51.3	1.09	39.9			5.3	6.1	89.7
OSBO′-1	85.8	1.20	56.1	6.0	5.8		17.9	86.2
OSBO′-2	101	1.17	68.4	6.0	5.8		21.0	88.5
OSBO′-3	116	1.18	83.2	6.0	5.8		21.0	89.8
OSBO′-4	182	1.21	149	6.0	5.8		21.0	93.4

[a] Calculated from the relative integrations of the TIPS end group and the corresponding characteristic peaks of the blocks in the ^{1}H NMR spectrum. [b] Determined by SEC using PS standards in THF at 25 °C. [c] Mass percent of PEO blocks calculated from ^{1}H NMR spectroscopy.

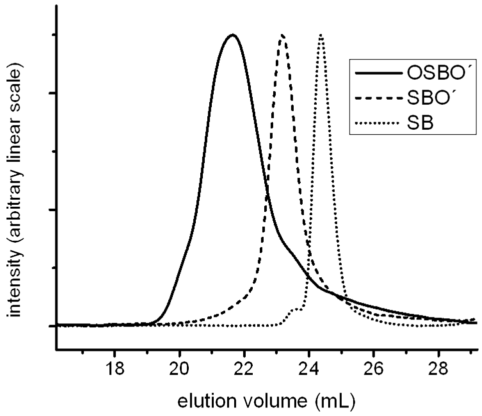


Figure 4. Representative SEC traces of the OSBO′-1 tetrablock terpolymer and the corresponding SBO triblock and SB diblock precursors.

size, in a polymer vesicle. The segregation of the hydrophobic S and B core blocks in combination with specifically sized O and O′ blocks should provide exquisite control over the sequence and geometric shape of the individual molecules, where we expect the larger O block would be preferentially located on the exterior corona of the vesicle and the smaller O′ block on the interior. (Note that the placement of S and B in the core is also influenced by the respective interfacial tension with water; i.e., the B block best accommodates the smaller inner-core interface due to its large interfacial tension with water).[22] In addition, asymmetric tetrablock terpolymers present opportunities to explore new structures, such as ferroelectric ordering,[9,26] in undiluted melt materials.

In this report, we describe a versatile procedure for preparing noncentrosymmetric poly(ethylene oxide-*b*-isoprene-*b*-ethylene oxide) (OIO′) triblock copolymers and poly(ethylene oxide-*b*-styrene-*b*-butadiene-*b*-ethylene oxide) (OSBO′) tetrablock terpolymers based on the use of a protected initiator and a mild base for the selective activation of the macromolecular initiators for EO polymerization. Only symmetric versions of the latter compound have been reported by the addition of equal molecular weight PEO blocks to HO−PS−PB−OH.[22] Previous attempts[27] at an asymmetric addition in our group (unreported) have failed due to cleavage of the protecting group during activation of the terminal hydroxyl functionality.

The general reaction scheme used to generate the symmetric[22] and asymmetric multiblock polymers is presented in Scheme 1. In the case of OIO′ a poly(isoprene) homopolymer with a ~92% 1,4-microstructure was prepared in cyclohexane using a hydroxyl-functionalized 3-triisopropylsilyloxy-1-propyllithium (TIPSOPrLi) initiator.[28] The poly(isoprene) chains were end-capped with ethylene oxide (EO) yielding a α-(TIPS-hydroxyl)-ω-hydroxyl-PI (TIPS−O−PI−OH) homopolymer. Size exclusion chromatography (SEC) performed on the TIPS−O−PI−OH product (Figure 2) showed a monomodal and symmetric peak (Đ = 1.05). ^{1}H NMR analysis provided clear evidence of methylene units adjacent to the TIPS-protected α- (3.50 ppm) and unprotected ω-hydroxyl (3.65 ppm) groups; nearly identical integrations of these resonances indicated that all PI polymers were effectively functionalized at the α- and ω-sites.

In the case of the symmetric synthesis the TIPS−O−PI−OH homopolymer was treated with tetrabutylammonium fluoride (TBAF) to unmask the chain-end hydroxyl groups, followed by the EO growth from both ends to yield the symmetric OIO.[22,29] SEC analysis of the final product is presented in Figure 2. In the case of the asymmetric synthesis, the TIPS−O−PI−OH homopolymer was converted into a macroinitiator by stoichiometric titration with a mild nucleophilic agent,[30] diphenylmethyl potassium (DPMK), followed by addition of a predetermined amount of EO. This polymerization was terminated with iodomethane to cap the ω-hydroxyl group.[31] The resulting α-(TIPS-hydroxyl)-ω-methoxy-PI-*b*-PEO′ (TIPS−O−PI-*b*-PEO′) triblock terpolymer showed a monomodal peak with a low dispersity (Figure 3), and the intact terminal TIPS group was evidenced by the consistent integration ratio between the TIPS group and block copolymer components in ^{1}H NMR spectra before and after EO polymerization.[32−34] Also, the ω-methoxy group was clearly observed at 3.37 ppm, demonstrating quantitative capping of ω-hydroxyl groups as evidenced by the comparison of the integration of the methoxl peak to the TIPS peak in the ^{1}H NMR spectrum of the polymer.

Deprotection of TIPS−O−PI-*b*-PEO′ was effected by treatment with TBAF. The quantitative removal of the TIPS groups was confirmed by extinction of the associated resonances in the ^{1}H NMR spectrum. The resulting α-hydroxyl-ω-methoxy-PI-*b*-PEO (HO-PI-*b*-PEO′) was converted into a macroinitiator by titration using NaphK or DPMK, followed by polymerization of a second aliquot of EO. The final PEO-*b*-PI-*b*-PEO′ (OIO′) tetrablock terpolymer was characterized by SEC (Figure 3) and NMR spectroscopy and showed a monomodal molecular weight distribution with low dispersity. Table 1 summarizes the characterization data of the OIO and OIO′ triblock copolymers prepared in this way.

To ensure that we achieved asymmetric PEO growth in OIO′ (as opposed to simultaneous addition of ethylene oxide at both chain ends), the poly(isoprene) blocks of both the OIO and OIO′-2 specimens (Table 1) were selectively degraded by ozonolysis, leading in both cases to complete removal of PI (4.8 and 5.3 ppm), but leaving intact PEO blocks (3.6 ppm) as confirmed by ^{1}H NMR spectroscopy (Figure S1 of the Supporting Information).[35] Those PEO specimens were characterized by SEC. The resulting bimodal distribution of

PEO polymers in the case of OIO′ (Figure 3) confirmed the asymmetric growth of PEO end blocks, contrary to the ozonized OIO (Figure 2), where a single monomodal peak confirmed symmetric addition of EO at both terminal positions, verifying the absence of spurious reactions during PI degradation.

The same synthetic procedure, as in the case of OIO′, was followed for the preparation of asymmetric OSBO′ tetrablock terpolymers. A poly(styrene-*b*-butadiene) diblock copolymer was initially synthesized using TIPSOPrLi as an initiator and by sequentially adding styrene and butadiene, followed by the same steps, as described above. The experimental details as well as representative ^{1}H NMR spectra of all intermediate and final products are described in the Supporting Information. Table 1 summarizes the characterization data of the asymmetric OSBO′ tetrablock terpolymers prepared in this way. Large, highly asymmetric, PEO blocks were added to relatively low molecular weight PS-*b*-PB to ensure discrimination of the intermediate and final products by SEC (see Figure 4) and reveal the successful synthesis of asymmetric tetrablocks. The extension of this synthetic procedure to include more complex core block architectures, including three or more core block types, in linear or branched configurations, is possible, and this strategy offers valuable opportunities for preparing amphiphilic block polymers for directed self-assembly in aqueous solution with unprecedented control over the curvature of the associated hydrophobic−hydrophilic and other internal core interfaces.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures for all intermediate and final products as well as detailed ^{1}H NMR analyses. 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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