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Cyclic and Multiblock Polystyrene-*block*-polyisoprene Copolymers by Combining Anionic Polymerization and Azide/Alkyne "Click" Chemistry

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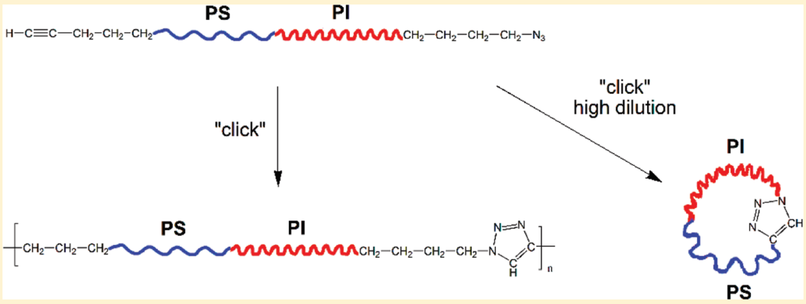
ABSTRACT:



An α,ω-heterotelechelic block copolymer of polystyrene (PS) and polyisoprene (PI), α-acetylene-ω-azido-PS-*b*-PI, with M_n = 18 900 and PDI = 1.05, was synthesized by (a) sequential anionic polymerization of styrene and isoprene with 5-triethylsilyl-4-pentynyllithium (TESPLi) as initiator to afford α-(TES-acetylene)-ω-lithium-PS-*b*-PI, (b) reaction of the living heterofunctionalized copolymer with 1,4-dibromobutane and sodium azide to give α-(TES-acetylene)-ω-azido-PS-*b*-PI, and (c) deprotection of the acetylene group to afford the final product α-acetylene-ω-azido-PS-*b*-PI. This α,ω-heterotelechelic block copolymer with "clickable" groups, in the presence of CuBr and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine, led to cyclic block copolymer in dilute solution (lower than the equilibrium concentration $<6 \times 10^{-5}$ g/mL), whereas in concentrated solutions (5.3×10^{-2} g/mL) gave multiblock copolymers.

INTRODUCTION

Block copolymers consisting of immiscible blocks can self-assemble either in bulk or in selective solvents. In bulk,[1−3] depending on the composition and architecture, block copolymers form highly ordered nanostructures, including spheres, cylinders, gyroid, lamellae, etc. In selective solvents[4,5] block copolymers self-assemble into a wide variety of micellar aggregates (spherical, cylindrical, vesicular, etc.) depending on temperature, solvent quality, concentration, pH, copolymer structure, molecular weight, and composition.

On the other hand, cyclic polymers, due to the absence of end groups, exhibit different physical characteristics than their linear counterparts, including smaller hydrodynamic volumes, a property that can be exploited during SEC analysis to differentiate cyclic polymers from their linear precursors. Therefore, cyclic block copolymers combine both unique topology and chemical incompatibility, rendering these materials very interesting in polymer science. Exploration of cyclic polymers in general and in particular of cyclic block copolymers has been limited, mostly because of the technical difficulties throughout the synthesis and purification. In the beginning, anionic polymerization was used exclusively for the synthesis of cyclic diblock copolymers[6−11] via coupling reactions between α,ω-dianionic-ABA chains and an appropriate coupling agent (e.g., dichlorodimethylsilane). However, the poor efficiency of the coupling reaction led in all cases to significant quantities of unreacted linear precursor and polycondensation products. The need to purify the cyclic product for physical studies thus required a very difficult fractionation procedure.[12] In another approach, the telechelic triblock terpolymer α-amino-ω-carboxyl-poly(styrene)-*b*-poly(isoprene)-*b*-poly(methyl methacrylate) was prepared by anionic polymerization, followed by an intramolecular coupling reaction to form an amide linkage. Again, the low efficiency of the coupling required extensive purification of the cyclic terpolymer.[13]

Recently, the combination of controlled radical, ring-opening and cationic polymerizations with "click" chemistry has provided synthetic chemists with a new methodology for preparing cyclic polymers. The Huisgen 1,3-dipolar cycloaddition "click" reaction is a very efficient route[14] and has been proved to be an invaluable intramolecular coupling reaction of linear α-acetylene-ω-azido-polymers for the preparation of poly(styrene),[15−18] poly(*N*-isopropylacrylamide),[19] poly(*tert*-butyl acrylate),[20] poly(ε-caprolactone),[21,22] poly(δ-valerolactone),[23] polyisobutylene,[24]

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polyazobenzenes,[25,26] poly(methyl acrylate)-*block*-poly(styrene),[27] and poly(2-(2-methoxyethoxy)ethyl methacrylate)-*block*-poly-(oligo(ethylene glycol) methyl ether methacrylate)[28] macrocyclics. However, although radical polymerization methods, which are mostly combined with alkyne/azide "click" cyclization reaction, are easy to set up, unwanted termination reactions take place during polymerization, yielding polymers with nonquantitative chain-end functionalization and consequently polymers that cannot be further processed by "click" chemistry. Moreover, radical polymerizations are restricted to styrenic and acrylic monomers, while they are incapable of initiating the polymerization of a very interesting and challenging class of monomers, the dienes.

In this paper, we report a new strategy for the synthesis of well-defined cyclic block and multiblock copolymers by combining anionic polymerization and "click" chemistry. Contrary to post-anionic polymerization reactions used to introduce "clickable" groups with subsequent loss of the lithium site,[29−38] this strategy, applied for the first time, features the use of a "protected" acetylene-functionalized lithium initiator, taking advantage of both the lithium site and the "clickable" acetylenic moiety. The unique characteristics of anionic polymerization, which include very narrow molecular weight distributions, high efficiency in reinitiating macroinitiators, and quantitative addition of chain-end functional groups onto the synthesized polymers, are combined with the high efficiency and tolerance of the "click" coupling reaction to prepare well-defined complex macromolecular architectures of styrene and isoprene.

■ EXPERIMENTAL SECTION

Materials. The purification of styrene (Aldrich, 99%), isoprene (Aldrich, 99%), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA; Aldrich, 99%), and the solvents (Aldrich; tetrahydrofuran, cyclohexane, methanol, and benzene) was performed using standard high-vacuum techniques reported elsewhere.[39,40] The preparation of 5-triethylsilyl-4-pentynyllithium (TESPLi) was reported elsewhere.[41] *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA; Aldrich, 99%) was dried by stirring with KOH pallets overnight and distilled out under vacuum. 1,4-Dibromobutane (Aldrich, 99%) was distilled under vacuum just before use. Copper(I) bromide (CuBr; Aldrich, 99.999%), sodium azide (NaN_3; Aldrich, 99.99%), tetrabutylammonium fluoride solution 1 M in THF (TBAF; Aldrich, 99%), *N,N*-dimethylformamide (DMF; Aldrich, 99.8%) and Merrifield resin (Aldrich; 100−200 mesh, 3.5−4.5 mmol/g Cl^- loading, 1% cross-linked) were used without further purification.

Synthesis of α-(TES-acetylene)-ω-bromo-PS-*b*-PI. The apparatus in Figure 1a was initially used for the synthesis of the living polystyrene block. High-vacuum techniques[39,40] for the construction, degassing, and the thorough washing of the reactor with *n*-BuLi benzene solution (∼100 mL) were used, followed by the removal of the purge section by heat-sealing at the constriction (A). By rupturing the corresponding break-seals, TMEDA (2.2 mmol), TESPLi (0.54 mmol), and styrene (37 mmol) were then added to the reactor, turning the color of the solution vivid red. During the polymerization of styrene, the reaction solution was collected in the cylinder (B), was heat-sealed at constriction (C), and was attached to a second apparatus (Figure 1b) through brake seal (D). The same steps were followed as above, i.e., degassing, washing the apparatus, and removing the purge section by heat-sealing at the constriction (E). Two hours after the initiation of the styrene polymerization, isoprene (100 mmol) was added to the reactor by rupturing the brake seal (F), turning the color of the solution to yellow (about 7 min time was necessary for the complete color shift). After 1 h, 20 mL (167.4 mmol) of 1,4-dibromobutane was added into the flask (G), rapid stirring was applied, and the flask contents were cooled down to 4 °C. Finally, 1.5 h after the addition of isoprene, the brake seal (H) was ruptured, and the living copolymer was added dropwise into the flask (G), causing the disappearance of the yellow color of the copolymer solution. The final product was recovered after precipitation in methanol, followed by filtration and drying overnight at the vacuum line. ^1H NMR ($CDCl_3$, δ, ppm): 0.4−0.7 ppm (15H, $-Si(CH_2CH_3)_3$), 1.0−2.2 ppm (aliphatic main chain), 3.3 ppm (2H, $-CH_2Br$), 4.5−5.6, 5.5−5.8 ppm (unsaturated nonaromatic), 6.2−7.2 ppm (aromatic). Characteristic IR peaks (KBr): 2170 cm^{-1} ($-C{\equiv}C-$).

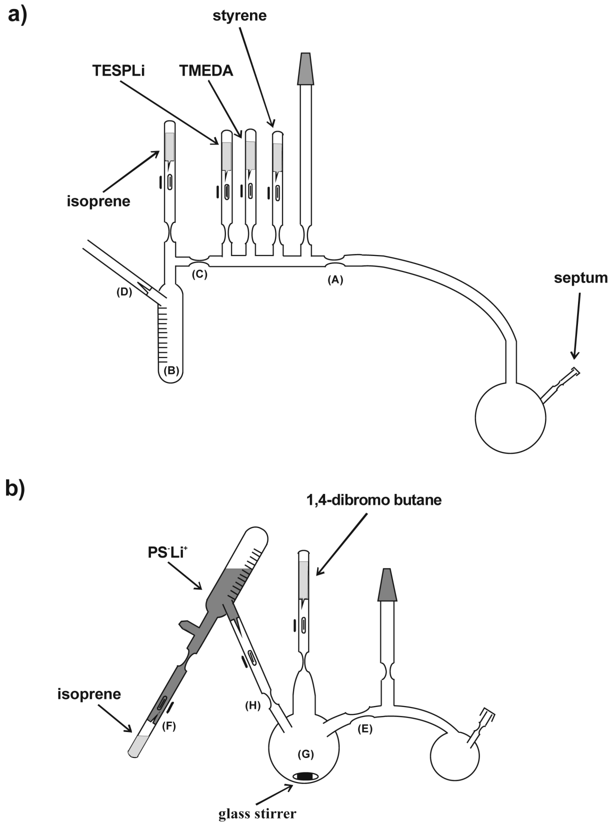
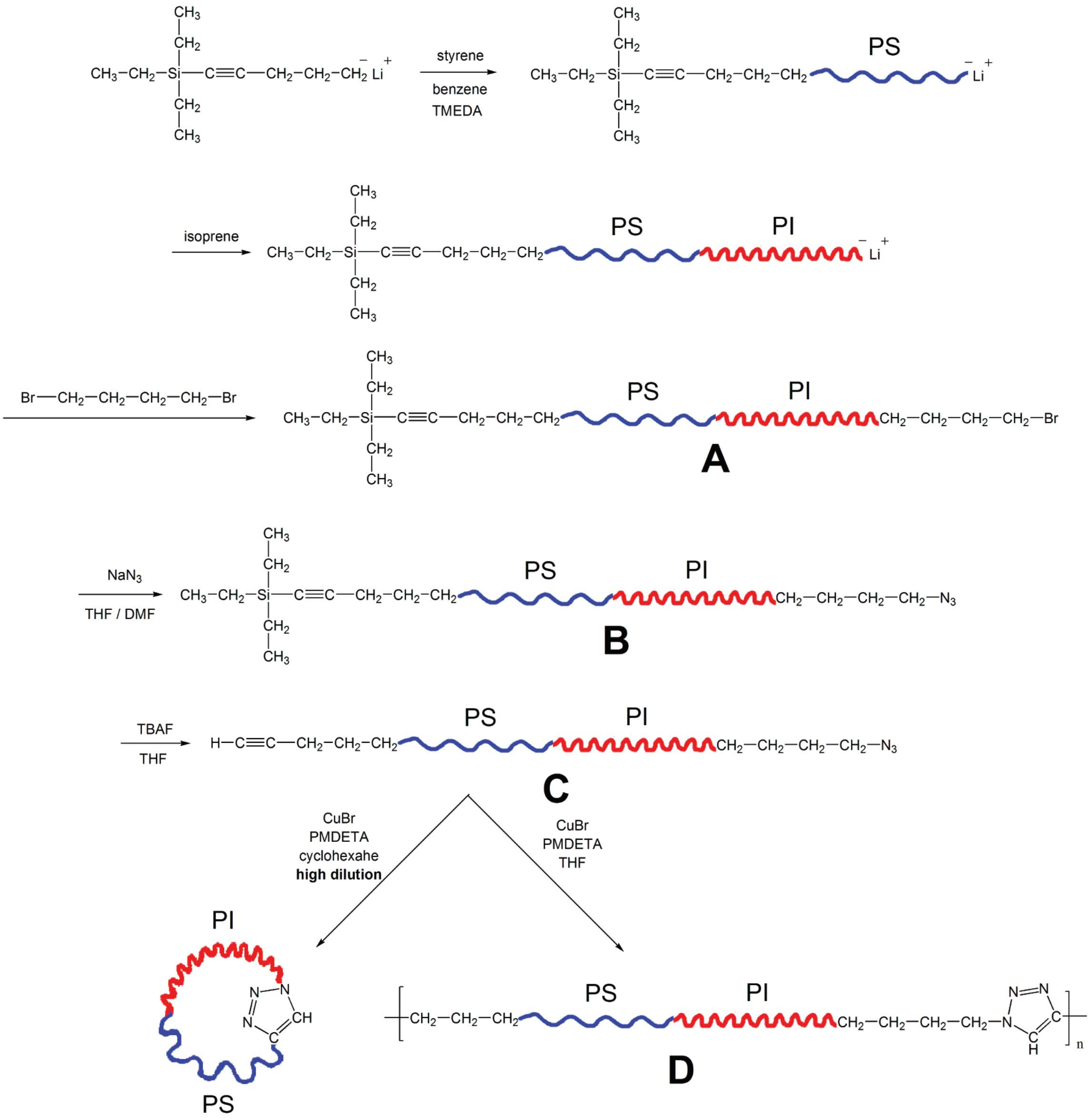


Figure 1. Apparatuses for the synthesis of α-(TES-acetylene)-ω-bromo-PS-*b*-PI.

Synthesis of α-(TES-acetylene)-ω-azido-PS-*b*-PI. To a three-neck round-bottom flask, 1.5 g (0.079 mmol) of α-(TES-acetylene)-ω-bromo-PS-*b*-PI was dissolved in 10 mL of THF under inert gas, followed by the addition of 10 mL of DMF and 1.3 mmol of NaN_3. The reaction was allowed under vigorous stirring for 2 days, and the product was precipitated in methanol, dissolved in 20 mL of toluene, and centrifuged for 15 min, before passed through a 0.2 μm diameter porous filter. The final product was collected after precipitation in methanol, filtered, and dried overnight at the vacuum line. Characteristic IR peaks (KBr): 2093 cm^{-1} ($-N_3$); 2170 cm^{-1} ($-C{\equiv}C-$).

Synthesis of α-Acetylene-ω-azido-PS-*b*-PI. To a three-neck round-bottom flask, 1.38 g (0.073 mmol) of α-(TES-acetylene)-ω-azido-PS-*b*-PI was dissolved in 12 mL of THF. The solution was thoroughly deoxygenated by bubbling with nitrogen and cooled at 0 °C prior to dropwise addition of the TBAF solution (1.3 mmol). The reaction was left at this temperature for 1 h and was terminated with the addition of 1 mL of methanol. The final product was purified after successive precipitations and dissolutions in methanol and THF correspondingly and dried overnight at the vacuum line. Characteristic IR peaks (KBr): 2093 cm^{-1} ($-N_3$); 3312 cm^{-1} ($-C{\equiv}C-H$).

Scheme 1. General Reactions for the Synthesis of α-Acetylene-ω-azido-PS-*b*-PI Cyclic Diblock and Multiblock Copolymers of Polystyrene (PS) and Polyisoprene (PI)



Cyclization "Click" Reaction of α-Acetylene-ω-azido-PS-*b*-PI. To a 5 L three-neck round-bottom flask, 2.8 L of cyclohexane, 200 mL of DMF, 300 mL of THF, and 0.4 mL (1.91 mmol) of PMDETA were added. The solution was thoroughly deoxygenated by bubbling with nitrogen for about 1.5 h. Then, 0.279 g (1.94 mmol) of CuBr was added, and nitrogen was bubbled through the solution for an extra 0.5 h, while in a second round-bottom flask 0.2 g (0.011 mmol) of α-acetylene-ω-azido-PS-*b*-PI was dissolved in 50 mL of cyclohexane. Upon deoxygenating by nitrogen bubbling, a syringe and syringe pump were used to transfer the polymer solution to the rapidly stirring and highly diluted CuBr/PMDETA solution at a rate of 2 mL/h at room temperature. After complete addition of the polymer solution, the reaction mixture was allowed to stir for an additional 24 h time period, and then it was concentrated and precipitated in an excess of methanol, followed by further purification after passing through a silica column to remove the copper catalysts. The obtained product was finally dried overnight in a vacuum oven for 24 h.

Synthesis of Azido-Loaded Merrifield Resin. Merrifield resin (1 g) (4 mmol Cl^-) and NaN_3 (0.75 g) (11.54 mmol) were added in 5 mL of DMF. The reaction was left under inert gas for 48 h, and then the resin was filtered, washed successively with DMF, $CHCl_3$, CH_2Cl_2, H_2O, and methanol, and was dried overnight at the vacuum line.

Purification of Cyclic PS-*b*-PI by "Click" Reaction with Azido-Loaded Merrifield Resin. To a three-neck round-bottom flask, 0.15 g (0.008 mmol) of cyclic PS-*b*-PI was dissolved in 15 mL of THF, followed by the addition of 31 μL (0.148 mmol) of PMDETA and 0.25 g (1 mmol of Cl^-) of Merrifield resin. The solution was deoxygenated by bubbling with nitrogen for about 1 h, and then 0.022 g (0.153 mmol) of CuBr was added. The reaction mixture was stirred for 48 h prior to filtration to remove the resin, precipitation in methanol, and copper removal after passing through a silica column. The crude product was dried overnight in a vacuum oven for 24 h.

Step-Growth "Click" Reaction of α-Acetylene-ω-azido-PS-*b*-PI. To a three-neck round-bottom flask, 0.8 g (0.042 mmol) of

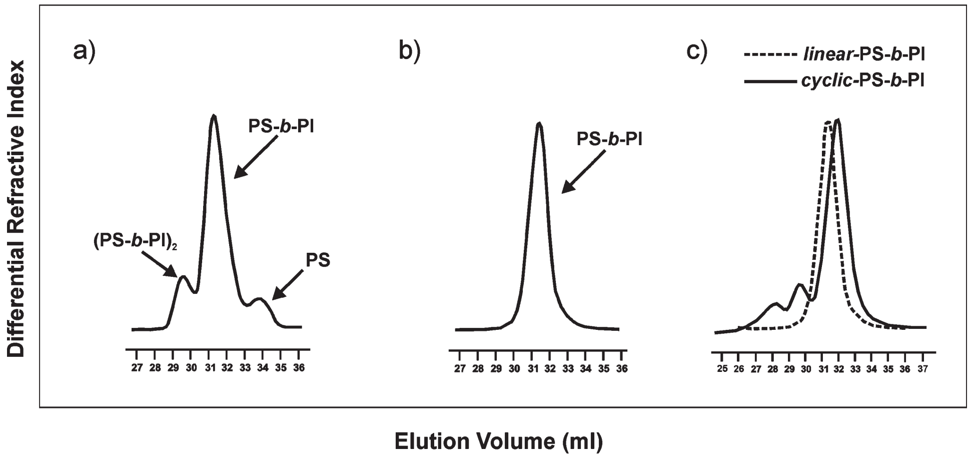


Figure 2. (a) SEC trace of α-(TES-acetylene)-ω-bromo-PS-*b*-PI, (b) the same polymer after fractionation, and (c) the cyclic product.

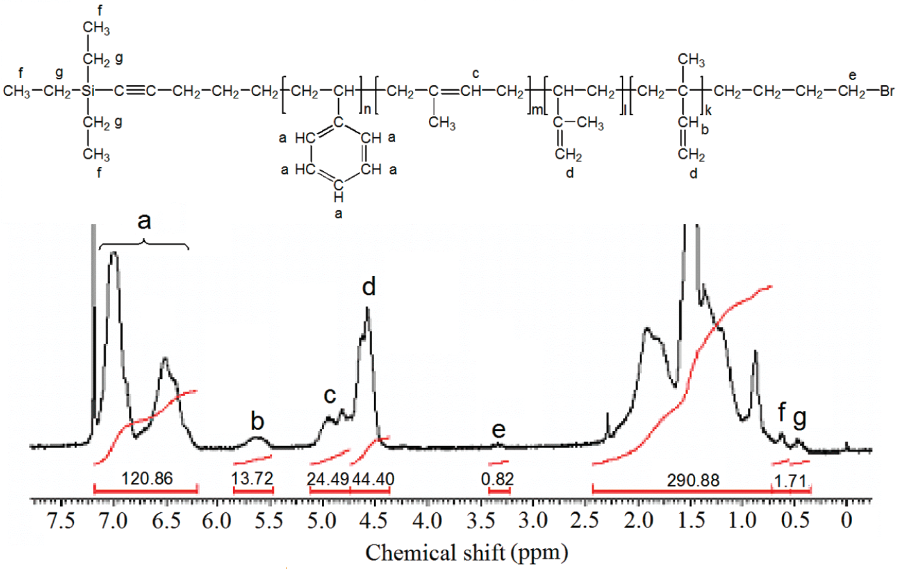


Figure 3. ^{1}H NMR spectrum of the α-(TES-acetylene)-ω-bromo-PS-*b*-PI diblock copolymer.

α-acetylene-ω-azido-PS-*b*-PI was dissolved in 15 mL of THF, followed by the addition of 33 μL (0.158 mmol) of PMDETA. The solution was deoxygenated by bubbling nitrogen for about 1 h, and then 0.023 g (0.160 mmol) of CuBr was added under vigorous stirring. The progress of the reaction was monitored by SEC, after extracting small aliquots from the reaction mixture. The final product was obtained after precipitation in methanol, purified by silica column chromatography and dried in a vacuum oven.

Characterization. Size exclusion chromatography (SEC) experiments were conducted at 40 °C with a modular instrument consisting of a Waters model 510 pump, a U6K sample injector, a 401 refractometer, a 486 UV spectrometer, and a set of four μ-Styragel columns with a continuous porosity range of 10^6-10^3 Å. The columns were housed in an oven thermostatted at 40 °C. THF was the carrier solvent at a flow rate of 1 mL/min. The system was calibrated with seven PS standards having molecular weights between 2000 and 1 000 000.

All nuclear magnetic resonance (NMR) spectra were recorded in chloroform-*d* at 25 °C with a Varian Unity Plus 300/54 NMR spectrometer.

Fourier transform infrared (FTIR) spectroscopy was used for the determination of the structure of the telechelic polymers. A Perkin-Elmer Spectrun One model was used.

■ RESULTS AND DISCUSSION

The general reactions used for the preparation of the linear precursor, the cyclic diblock copolymer, and the high molecular weight multiblock copolymer are presented in Scheme 1. All synthetic steps followed are summarized below.

Preparation of α-Acetylene-ω-azido-PS-*b*-PI Linear Precursor. Using a previously reported alkyne-functionalized anionic initiator (TESPLi),[41] styrene and isoprene were copolymerized by sequential addition. The resulting α-(TES-acetylene)-ω-bromo-PS-*b*-PI copolymer was characterized by SEC (Figure 2), ^{1}H NMR (Figure 3), and IR (Figure 4) spectroscopy. Styrene was left only for 2 h to polymerize due to the acceleration of the polymerization kinetics generated by the addition of TMEDA, while the short reaction time is of vital importance in order to avoid termination reactions[41,42] occurring after the completion of the polymerization process.

As seen in Figure 2a, only a small proportion of polystyryllithium underwent a termination reaction and did not initiate the polymerization of isoprene. The polymerization reaction of the isoprene was left only for 1.5 h for the same reasons aforementioned and was then added dropwise to a large excess of 1,4-dibromobutane at relatively low temperature. However, even under those conditions the formation of dimeric product was not fully avoided due to the highly reactive anionic center,[43] which results in the reaction of two living macromolecules with one 1,4-dibromobutane molecule. The pure diblock copolymer was obtained by fractionation using toluene as the solvent and methanol as the nonsolvent (Figure 2b). The ^{1}H NMR spectrum of the synthesized copolymer (Figure 3) reveals the characteristic peaks of the two blocks and the end groups (TES at 0.4 and 0.7 ppm and bromomethyl groups at 3.3 ppm). The molecular weight (and the composition) of the diblock copolymer was calculated from the same spectrum by integrating the aromatic protons (6.3−7.2 ppm) of the styrene repeat units with respect to the methylene (4.6 ppm) and methine (5.0 and 5.7 ppm) protons of the isoprene repeat units. The molecular characteristics of the synthesized copolymer are given in Table 1.

The next step of the synthesis included the nucleophilic displacement of the bromomethyl end group of α-(TES-acetylene)-ω-bromo-PS-*b*-PI by an azido group. The low steric hindrance of the primary bromomethyl group ensures the quantitative yield of the S_N2 nucleophilic substitution reaction, using sodium azide as a nucleophile. However, for the successful accomplishment of this reaction the use of a polar aprotic solvent is required. DMF and DMSO are appropriate solvents and most commonly used for this reaction type, but in the present situation the PS-*b*-PI copolymer would form micelles with the insoluble block of polyisoprene lying in the core of the structure, thus rendering them unable to react with sodium azide. On the other hand, THF is an aprotic and good solvent for both blocks, but it is not polar enough to adequately solvate the intermediate anions for the nucleophilic substitution reaction. For this reason, a mixture of THF and DMF at a ratio of 1:1 was used to prepare the polymer solution, which would meet the above criteria. The successful reaction was evidenced by FTIR spectroscopy (Figure 4B). In comparison with the IR spectra of the starting material in Figure 4A, a new absorption band of azide at 2093 cm^{-1} appears in Figure 4B, which confirmed the introduction of azido group.

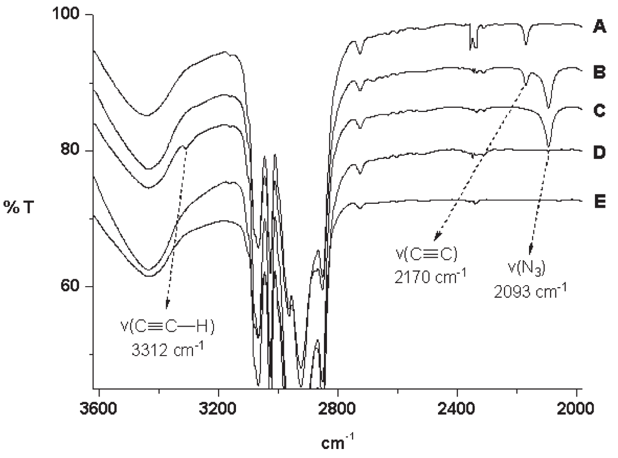


Figure 4. FTIR spectra of (A) α-(TES-acetylene)-ω-bromo-PS-*b*-PI, (B) α-(TES-acetylene)-ω-azido-PS-*b*-PI, (C) α-acetylene-ω-azido-PS-*b*-PI, (D) cyclic PS-*b*-PI, and (E) the cyclic copolymer after purification.

To provide the polymer with the desired "clickable" end groups, the chain-end TES protecting group was removed after treatment with tetrabutylammonium fluoride (TBAF). The conditions (temperature and reaction time) of this reaction were carefully selected in order to provide quantitative cleavage of the TES group and to avoid possible loss of the acetylene functionality in the final product. Treatment of the polymer with TBAF over an extended period of time was found to lead to a terminal alkyne content lower than expected. The successful cleavage is evidenced in the FTIR spectrum of α-acetylene-ω-azido-PS-*b*-PI (Figure 4C), where the absorption band of C≡C at 2170 cm^{-1} has disappeared and an absorption band at 3312 cm^{-1} has appeared, which corresponds to the alkyne C−H stretching. The quantitative deprotection was also monitored by ^{1}H NMR spectroscopy and was evidenced by the complete disappearance of the signals at 0.5 and 1 ppm attributed to the 15 protons of the TES group.

Intramolecular "Click" Cyclization of Linear α-Acetylene-ω-azido-PS-*b*-PI. A highly dilute solution was used for this synthesis in order to favor the cyclization reaction of the α-acetylene-ω-azido-PS-*b*-PI copolymer. An automated slow and continuous addition of the polymer to the reaction solution was set, ensuring the highly dilute conditions of the reaction (the linear polymer concentration was throughout the course of the reaction always $<6 \times 10^{-5}$ g/mL, which is the equilibrium concentration). Furthermore, cyclohexane was used and is a rather poor solvent for the copolymer (cyclohexane is a theta solvent for polystyrene at 35 °C), since the possibility for intramolecular reaction is increased for a compact coil.[44] However, because CuBr—the catalyst used—is insoluble in cyclohexane, a small quantity of DMF was used in order to dissolve CuBr, while a small volume of THF was necessary to achieve a single phase solution.

The SEC chromatograph of the final product is given in Figure 2c, and the cyclization of the block copolymer is verified by a shift in the SEC to slightly longer retention times relative to the linear precursor due to the more compact conformation of the copolymer upon cyclization. Apart from the desired peak in the chromatograph in Figure 2c, there are also two other minor peaks of double and triple molecular weight with respect to the main peak. This means that although high dilution conditions were used, the intermolecular "click" reaction was not fully avoided. Strong evidence that the reaction product is the desired cyclic copolymer arises from FTIR analysis in combination with SEC results. Comparing the IR spectra of the copolymer before (Figure 4C) and after (Figure 4D) the cyclization reaction, it is clear that the characteristic peaks of the acetylene and azido end groups have disappeared, which in combination with the shift in the SEC to lower molecular weights leads to the conclusion that the final product is the desired one. Moreover, by examining more thoroughly the IR spectra in Figure 4D, it can be seen that

Table 1. Molecular Characteristics of α-(TES-acetylene)-ω-bromo-PS-*b*-PI Diblock Copolymer

sample	$M_n \times 10^{-3\,a}$ (PS-*b*-PI)	M_w/M_n ^{a}	$M_n \times 10^{-3\,a}$ (PS)	$M_n \times 10^{-3\,b}$ (PS-*b*-PI)	% (w/w)^c St/Is	% 1,2/1,4/3,4^c (PI)
PS-*b*-PI	14.9	1.05	8.1	18.9	44.5/55.5	29.4/52.4/18.2

[a] SEC analysis using polystyrene standards in THF at 40 °C. [b] ^{1}H NMR spectroscopy at 25 °C in $CDCl_3$, based on the M_n of the PS block. [c] ^{1}H NMR spectroscopy at 25 °C in $CDCl_3$.

there is a small residue of the azido band, probably due to the unreacted end groups of the dimers and trimers.

To easily purify the cyclic product, an azido-functionalized Merrifield resin was prepared. The azido loading was adjusted to be high enough in order to ensure the high "click" reactivity of the resin. The IR spectra of the Merrifield resin before and after functionalization are given in Figure 5, where the strong absorption band of azido groups appears at 2087 cm^{-1}. A "click" reaction between the cyclic copolymer and the azido-loaded Merrifield resin followed. A schematic representation of the procedure is given in Scheme 2. Surprisingly, after the removal of the resin by simple filtration, the SEC chromatograph of the copolymer was identical with the trace in Figure 2C, while the azido band has completely disappeared from the IR spectra (Figure 4E). The above implies that, apart from the cyclic diblock copolymer, dimers and trimers were produced, which due to the high dilution of the solution underwent cyclization reaction yielding the corresponding cyclic dimer and trimer copolymers. Consequently, by combining anionic polymerization and "click" chemistry, the synthesis of a cyclic diblock copolymer with a low impurity content has been made possible. It should be noted that the impurities consist of cyclic dimers and trimers copolymers, structures which seem to exhibit very interesting properties and could be easily separated by fractionation.

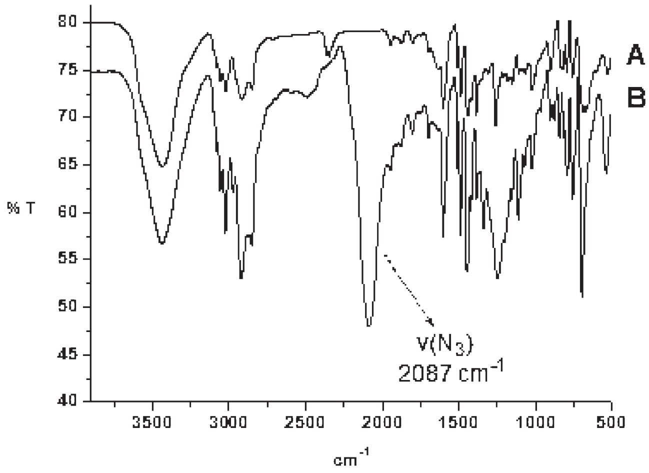
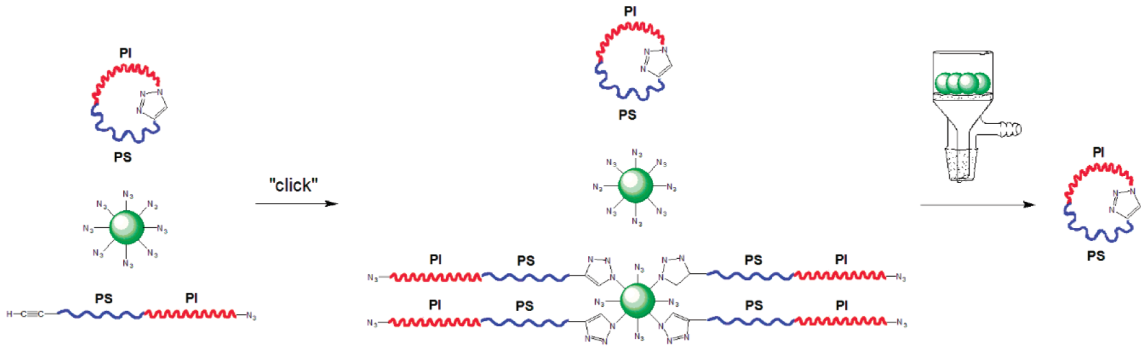


Figure 5. FTIR spectra of Merrifield resin (A) before and (B) after reaction with NaN$_3$.

Step-Growth "Click" Coupling of Linear α-Acetylene-ω-azido-PS-*b*-PI. One way to verify the degree of chain-end functionality of the linear α-acetylene-ω-azido-PS-*b*-PI precursor is to check the possibility of the intermolecular condensation reaction by step-growth "click" coupling of the linear α-acetylene-ω-azido-PS-*b*-PI. The "click" reaction was conducted at high polymer concentration (5.3 × 10^{-2} g/mL) using a good solvent (THF), a condition that favors the intermolecular coupling.[34] The evolution of the SEC traces with time is shown in Figure 6. From the first SEC trace of the reaction corresponding to 2 h, it is clear that the "click" coupling reaction evolved very quickly, yielding the predictable polycondensates, a sign of high degree chain-end functionality. Surprisingly, focusing on the trace corresponding to 216 h, it can be seen that even in this highly concentrated polymer solution in good solvent, the cyclic product is also produced, verified by the appearance of a peak in the SEC to longer retention times relative to the linear precursor, a result which was also observed in previous studies.[45,46] Moreover, the pattern of the chromatograph slightly changed after the 2 h, exhibiting a saturation of the "click" reaction. The latter is probably either due to the existence of a small quantity of the linear precursor, which somehow lost one of the end groups acting as a terminating agent, or is due to the increased viscosity of the solution and the very high molecular weight of the prepared polycondensates, which hinders the approach of the already vastly decreased concentration of chain end groups and the reaction between them. The second hypothesis is strengthened upon observation of the SEC traces corresponding to 2, 3.5, and 21 h (Figure 6) at the elution volume, where the linear precursor appears (SEC trace corresponding to 0 h). In this area on the chromatograph of 2 h, the peak appears at the same time with the starting material, but a shoulder appears at a slightly longer retention time. In the next chromatographs the intensity of this shoulder has increased, while after 52 h of reaction, one single peak appears with a clear shift to longer retention times relative to the initial peak at 0 h. From the above it can be concluded that the step-growth reaction evolved very quickly. However, due to the extensive coupling of the macromonomers, the concentration of the chain-end groups was drastically reduced, probably resulting in the increased possibility of intramolecular coupling of the remaining unreacted macromonomers, since the probability of intermolecular coupling had become very low, due to the very low mobility of the terminal azido and alkynyl groups, "buried" in the largely extended polycondensate coils. The above possibly explains why the step-growth coupling

Scheme 2. Schematic Representation of the Purification of the Cyclic PS-*b*-PI from the Unreacted Linear Precursor with Azido-Loaded Merrifield Resin



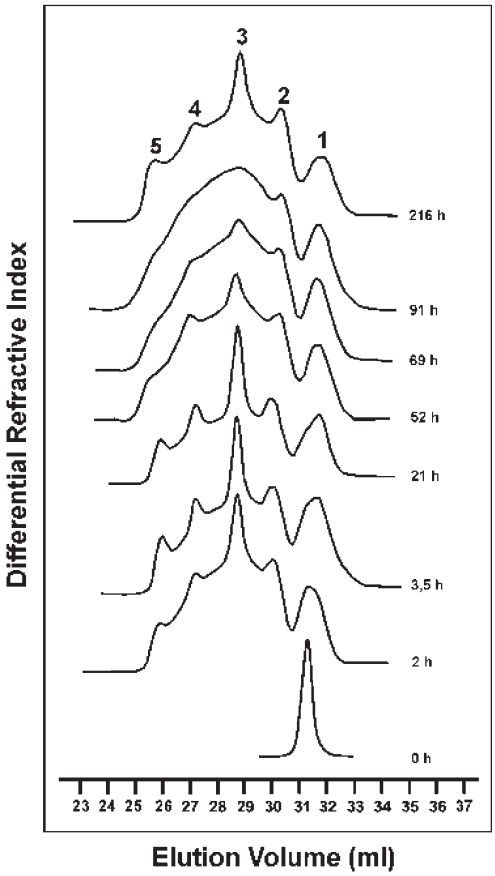


Figure 6. Monitoring by SEC the progress of the step-growth "click" coupling of α-acetylene-ω-azido-PS-*b*-PI.

Table 2. Composition of the Multiblock Copolymer of Styrene and Isoprene

peak[a]	$M_n \times 10^{-3}$ [b]	ratio[b] (%)	number of PS-*b*-PI macromonomers[b]
1	14.2	12	1
2	33.6	19	2
3	87.6	42	6
4	267	18	18
5	849	9.0	57

[a] Final SEC chromatograph (216 h) of Figure 6. [b] SEC analysis using polystyrene standards in THF at 40 °C.

reaction is practically completed after 2 h as well as why the cyclic product is produced even in this highly concentrated solution.

From the final SEC chromatograph corresponding to 216 h (Figure 6) it is also clear that the final intermolecular reaction product consists of a mixture of polycondensates with various degrees of condensation. This result was expected due to the random nature of the step-growth reaction. However, contrary to similar attempts,[19,45,46] where the final SEC trace appeared as one peak of very broad molecular weight distribution, in the current study five main peaks (Figure 6) with different coupling degrees are present (Table 2).

In conclusion, the multiblock copolymer of styrene and isoprene was prepared by combination of anionic polymerization and "click" chemistry. The final product consists of a few discrete multiblock copolymers of the same composition but different molecular weights and can be easily be fractionated.

■ CONCLUSIONS

An α,ω-heterotelechelic block copolymer of polystyrene (PS) and polyisoprene (PI), α-acetylene-ω-azido-PS-*b*-PI, with $M_n = 18\,900$ and PDI = 1.05, was synthesized, by using a novel acetylene functionalized initiator, 5-triethylsilyl-4-pentynyllithium, and appropriate postpolymerization reactions. In the presence of CuBr and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine, this heterotelechelic block copolymer led to well-defined cyclic block and multiblock copolymers. These are only a very few examples of the immense capability of anionic polymerization and "click" chemistry in preparing well-defined macromolecular architectures.

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