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Functionalized Polyisobutylene and Polyisobutylene-Based Block Copolymers by Mechanistic Transformation from Cationic to Radical Process

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The strategy for the preparation of polyisobutylene-based block copolymers via mechanistic transformation from cationic to radical polymerization is reported. This strategy involves the synthesis of 2-bromo-2-methylpropanoyl-terminated difunctional polyisobutylene macroinitiator (BiBB-PIB-BiBB) via consecutive cationic polymerization, in situ preparation of hydroxyl-terminated polyisobutylene and its acylation by 2-bromo-2-methylpropanoyl bromide. The $Mn_2(CO)_{10}$—triggered photo-induced radical polymerization of styrene in bulk using this macroinitiator leads to the formation of multiblock copolymer, while predominantly triblock copolymer is generated during the polymerization of methyl methacrylate. The possibility to functionalize the polyisobutylene by pyrene via photo-induced radical addition of 1-bromomethyl pyrene in the presence of $Mn_2(CO)_{10}$ is also demonstrated in this work.

1. Introduction

Photo-induced polymerizations are considered interesting in academia and industry due to their clear advantages over traditional methods.[1] Benefits include low energy and solvent requirements with high reaction rates and spatiotemporal control, creating relatively safer reaction conditions to handle. Implementing photo-induced techniques to existing processes is of great importance today as we aim to embrace more environmentally friendly routes without compromising on the quality of materials.[2] These light-induced polymerization reactions, with their precise control enabled by light, unlock a toolbox for the targeted synthesis of various macromolecular architectures simply and efficiently, including telechelics, star shapes, crosslinks, blocks, and grafts.[3–7] Even though conventional photopolymerization techniques mainly feature a photosensitizer or a photoinitiator to trigger polymerization, more complex methodologies including the use of macroinitiators or transformation of polymerization mechanisms may be required to synthesize mentioned polymers with advanced architectures.[8]

Mechanistic transformation is a potent polymerization approach that combines various polymerization methods to create challenging copolymers that would be unachievable with a single mechanism.[9] All addition polymerizations, including radical, cationic, and anionic, can undergo mechanistic transformation by taking advantage of the reactive functional group at the chain ends of the prepolymer.[10,11] Several studies have demonstrated the synthesis of various block copolymers through mechanistic transformation, incorporating photo-induced polymerization to alleviate harsh reaction conditions of conventional methods that may require elevated temperatures and high costs.[12,13] Additionally, the approach of mechanistic transformation has also made it possible to prepare complex structured polymers of certain monomers such as isobutylene that can be only polymerized through a single polymerization mechanism.

Polyisobutylene (PIB) is a rubbery polymer that can be only synthesized through the cationic polymerization of isobutylene, which is widely used in the industry for example, for the preparation of precursors for ashless additives.[14] Since Kennedy et al. first reported on the quasiliving cationic polymerization of isobutylene, it has become possible to synthesize various block copolymers of isobutylene with complex architectures and other well-defined polymers.[15–18] Among them, triblock copolymer of isobutylene with styrene poly(styrene-*block*-isobutylene-*block*-styrene) represents significant interest due to its high biostability and biocompatibility.[19] Currently, such polyisobutylene-based block copolymers are used as a drug-eluting coating

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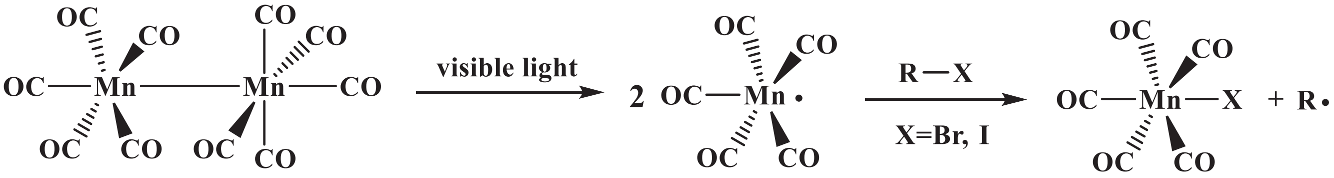


Scheme 1. Photoinduced halogen abstraction from alkyl halides using $Mn_2(CO)_{10}$ photochemistry.

on the TAXUS coronary stent and can be also considered as a promising material for the fabrication of ophthalmic implants, artificial vascular grafts, and synthetic heart valves.[19–22] While the living cationic polymerization limits to the triblock copolymers only with polystyrene and its derivatives as the side blocks, the combination of cationic and radical mechanisms opens up possibilities for a wide range of novel PIB-based block copolymers with unique properties. Since the pioneering work of Matyjaszewski et al.[23] in 1997 reporting the synthesis of poly(styrene-*block*-isobutylene-*block*-styrene) by a combination of living cationic polymerization and atom transfer radical polymerization (ATRP), other PIB-based triblock copolymers with poly(methyl methacrylate), poly[poly(ethylene glycol) methacrylate], poly(methacrylic acid) were prepared using polyisobutylene as a macroinitiator.[23–30] In a series of publications, Storey et al. reported the synthesis of dual initiators that allow combining the living cationic polymerization of isobutylene and ATRP to afford PIB-based diblock copolymers and miktoarm star-shaped polymers.[31,32] In addition, macro-chain transfer agents were synthesized from low molecular weight hydroxyl-terminated polyisobutylene and used then in reversible addition–fragmentation chain transfer (RAFT) polymerization of various radically polymerized monomers to prepare diblock copolymers,[33,34] which displayed unique self-assemble properties in both aqueous and organic media.[35,36] However, the synthesis of most of these block copolymers is rather challenging and requires high temperatures and a change of solvent system for cationic and radical polymerization. Therefore, the photoinitiated radical polymerization of methyl methacrylate or other monomers from PIB macroinitiator could be a good alternative to ATRP or RAFT to address the stated limitations. Among numerous reported photoinitiating systems, dimanganese decacarbonyl ($Mn_2(CO)_{10}$), in conjunction with alkyl halides, is a well-known photocatalytic platform to generate free radical species and induce radical polymerizations.[37,38] Notably, under visible light, the Mn—Mn bond of $Mn_2(CO)_{10}$ undergoes homolytic cleavage to form $Mn(CO)_5$, which readily triggers halogen atom abstraction reactions to generate mentioned free radicals (**Scheme 1**).[39,40] It should be also noted, that despite great progress in photocontrolled cationic polymerization of vinyl ethers achieved during the last years,[41,42,43] there is very little information available about the photoinduced polymerization of isobutylene or modification of polyisobutylene.[44]

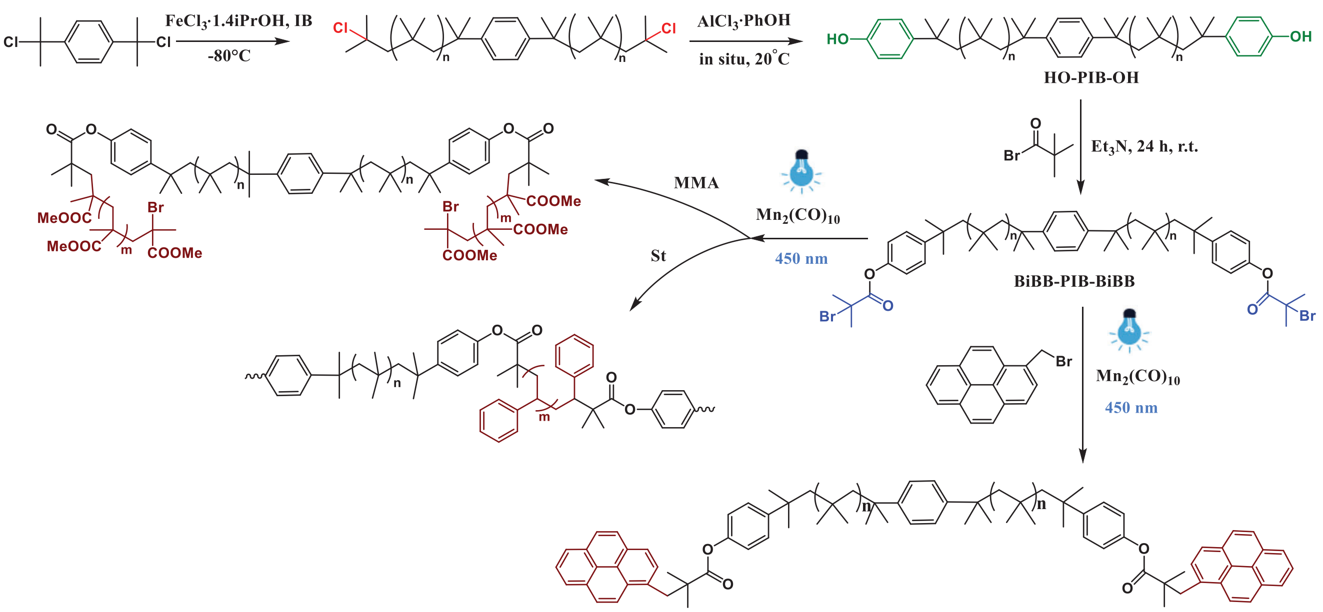
In this work, polyisobutylene-based macroinitiator was synthesized in two steps via cationic polymerization of isobutylene and in situ modification with phenol followed by acylation with 2-bromo-2-methylpropanoyl bromide. This macroinitiator was then employed for the initiation of photo-induced free radical polymerization to afford block copolymers via a mechanistic transformation approach, where the polymerization mechanism was converted from cationic to free radical (**Scheme 2**). Dimanganese decacarbonyl photochemistry allows the generation of radicals at the chain ends of the **BiBB-PIB-BiBB** macroinitiator to transform the overall synthesis from cationic to radical and obtain a series of polyisobutylene-based block copolymers, namely multiblock copolymer of isobutylene with styrene (PS-*b*-PIB)$_n$ and triblock copolymer of isobutylene with methyl methacrylate (PMMA-*b*-PIB-*b*-PMMA). Moreover, dimanganese decacarbonyl photochemistry opens a new way for the functionalization of polyisobutylene (Scheme 2).

2. Results and Discussion

2.1. Synthesis of PIB Macroinitiators

The synthesis of macroinitiators (**BiBB-PIB-BiBB**) was performed in two steps. In the first step, the hydroxyl-terminated difunctional polyisobutylene was prepared via one-pot two steps procedure consisting of living cationic polymerization of isobutylene with DiCumCl/$FeCl_3 \times {}^iPrOH$ initiating system in CH_2Cl_2/*n*-hexane mixture at −80 °C followed by the addition of the complex of $AlCl_3$ with phenol in conjunction with the increase of the temperature to 20 °C (see Scheme 2) according to procedure developed by our team.[45] The successful preparation of hydroxyl-terminated telechelic polyisobutylene (**HO-PIB-OH**) was confirmed by ^1H NMR (Figure S1, Supporting Information) and SEC (Figure S2, Supporting Information). Then, the desired macroinitiator (**BiBB-PIB-BiBB**) was synthesized via acylation of **HO-PIB-OH** with 2-bromo-2-methylpropanoyl bromide at room temperature (Scheme 2) in conditions similar to those reported by Storey et al. for acylation of trifunctional phenol-terminated PIB by methacryloyl chloride.[46] The quantitative acylation with the formation of **BiBB-PIB-BiBB** was confirmed by the complete disappearance of the signal of proton of hydroxyl group at 4.5 ppm and the appearance of the new signal of protons of methyl groups of initiator moiety at the chain end at 2.06 ppm (**Figure 1**; Figure S1, Supporting Information).

SEC trace of acylated **HO-PIB-OH** is symmetrical and slightly shifts into a high molecular weight region thus confirming successful acylation of **HO-PIB-OH** (Figure 1b). In addition, M_n determined by SEC (M_n(SEC) = 11 600 g mol^{-1}) is in good agreement with molar mass calculated from ^1H NMR spectrum based on the integral intensity of signals of the head (M_n(NMR) = 11 300 g mol^{-1}) and end (M_n(NMR) = 11 800 g mol^{-1}) groups, respectively (Figure 1a) (see Experimental Section in Supporting Information for equations).



Scheme 2. Synthesis of polyisobutylene-based macroinitiator, functional polyisobutylenes as well as multiblock copolymer of isobutylene with styrene and triblock copolymer of isobutylene with methyl methacrylate.

2.2. Synthesis of Copolymers

2.2.1. Block Copolymers of Isobutylene with Styrene

Selecting the appropriate solvent is crucial for transformation from cationic to radical polymerization, as polyisobutylene dissolves in non-polar alkanes or in polar tetrahydrofuran, which are generally unsuitable solvents for conducting the radical polymerization. Therefore, toluene was typically used as a solvent to conduct ATRP of styrene (S) or methyl methacrylate (MMA) starting from polyisobutylene macroinitiator in previous works.[23,24,26,31,32] To simplify the preparation of block copolymers, we performed the photo-induced radical polymerization of styrene in the presence of dimanganese decacarbonyl ($Mn_2(CO)_{10}$) under bulk conditions. It should be noted that according to visual test **BiBB-PIB-BiBB** showed good solubility in styrene and much poorer solubility in methyl methacrylate (Figure S3, Supporting Information). The monomer conversion was determined from ^{1}H NMR spectrum of crude triblock copolymer sample taken before its precipitation into cold methanol (**Figure** 2a), and was of 36% after persistent irradiation for 6 h at room temperature indicating slow polymerization of styrene under investigated conditions. This observation is consistent with the much slower organocatalytic photoinitiated ATRP of styrene than (meth)acrylates reported in the literature.[47,48] According to Figure 2b, SEC trace shifts toward high molecular weight region during the polymerization of styrene from PIB-based macroinitiator thus confirming the successful formation of the block copolymer. However, the shoulder in low molecular weight region indicates that part of **BiBB-PIB-BiBB** remains unreacted. In addition, the obtained block copolymer is characterized by relatively high polydispersity and non-symmetrical shape of the molecular weight distribution curve pointing out that side reactions occurred to some extent in the course of photoinitiated radical polymerization of styrene.

Aiming at confirming the formation of block copolymer, ^{1}H NMR spectrum of synthesized copolymer was analyzed (Figure 2a). Apart from the signals of main chain protons of both isobutylene and styrene units in a block copolymer, the signal arising due to the cumyl group of PIB macroinitiator at 0.78 ppm is also visible (Figure 2a). Using these signals, the length of the styrene block and the molecular weight of block copolymer were calculated (see Supporting Information for equations). However, the results were significantly lower than those determined by SEC: $M_n(NMR) = 13\,600$ g mol^{-1} and $M_n(SEC) = 37\,300$ g mol^{-1}, respectively. Note that, the latter value was obtained through the resolution of the original chromatogram (Figure 2b, $M_n(SEC) = 29\,000$ g mol^{-1}) using the Gaussian method (Figure S4, Supporting Information) due to the overlapping of peaks of block copolymer and unreacted **BiBB-PIB-BiBB**. The rational explanation for the observed discrepancy between molecular weights determined by SEC and NMR could be the formation of multiblock copolymer (**Scheme** 3). An indirect proof of the formation of multiblock copolymer may be the absence of signal of bromine end group in ^{1}H NMR spectrum at 4.0–4.5 ppm. It should be also noted that although signals of protons of methyl groups in **BiBB-PIB-BiBB** macroinitiator at 2.06 ppm (Figure 1) overlapped with the signals of methine main chain protons of styrene units (Figure 2a), the signal **m** at 3.5 ppm can be assigned to methine proton of styrene unit connected to the 2-methylpropanoyl moiety of **BiBB-PIB-BiBB** (Figure 2a). To further confirm the formation of multiblock copolymer under investigated conditions, DSC analysis was performed (Figure 2c; Figure S5, Supporting Information). Along with intense transition at −56.9 °C corresponding to the glass transition temperature of PIB block, the very weak transition is observed at 57.3 °C due to the short polystyrene block ($M_n \leq 2000$ g mol^{-1}). This notably weak transition for polystyrene

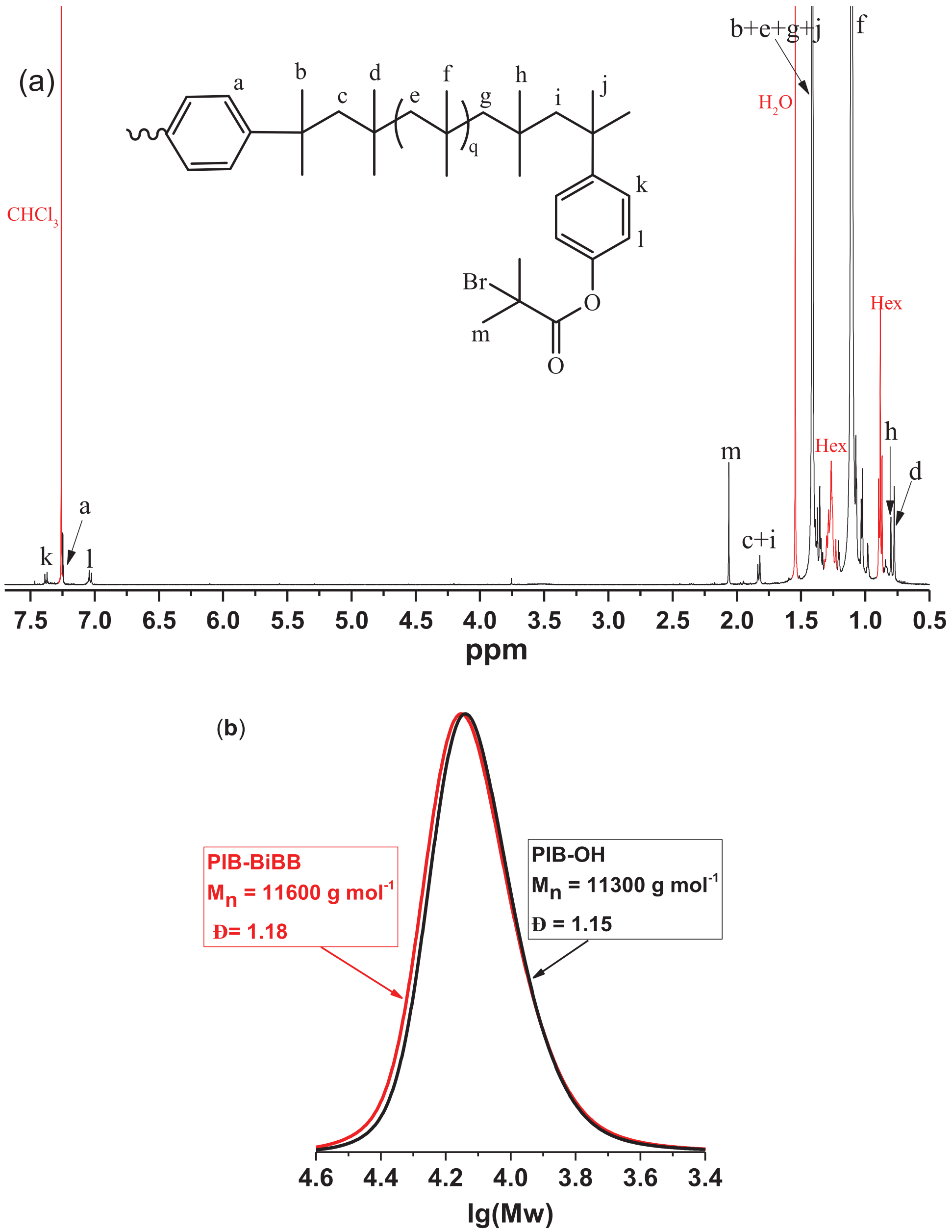


Figure 1. a) ^{1}H NMR spectrum and b) SEC trace of HO-PIB-OH and PIB-based difunctional macroinitiator **BiBB-PIB-BiBB** (see Scheme 2).

block is consistent with a rather low fraction of polystyrene (≈18 mol% according to ^{1}H NMR spectroscopy, see Supporting Information for equation) in multiblock copolymer.

According to the obtained results, the following mechanism of the formation of multiblock copolymer during photoinitiated radical polymerization of styrene from **BiBB-PIB-BiBB** was proposed (Scheme 3). The key step of this mechanism is the reaction of growing diblock copolymer macroradical BiBB-**PIB-*b*-S**· with newly generated **BiBB-PIB-BiBB·** radical that results in the formation of **BiBB-PIB-*b*-S-*b*-PIB-BiBB** with terminal 2-bromo-2-methylpropyl groups. The latter can generate the growing macroradical upon visible light-triggered bromine atom abstraction by $Mn(CO)_5$, which can add 10–20 styrene units until interaction with **BiBB-PIB-BiBB·** resulting in the formation of multiblock copolymer (Scheme 3). In addition, since the termination in radical polymerization of styrene occurs mainly by recombination, this process can also facilitate the formation of multiblock copolymer.

2.2.2. Poly(Methyl Methacrylate-Block-Isobutylene-Block-Methyl Methacrylate)

Photo-induced radical polymerization of methyl methacrylate from **BiBB-PIB-BiBB** macroinitiator in the presence of dimanganese decacarbonyl ($Mn_2(CO)_{10}$) proceeded at a much faster

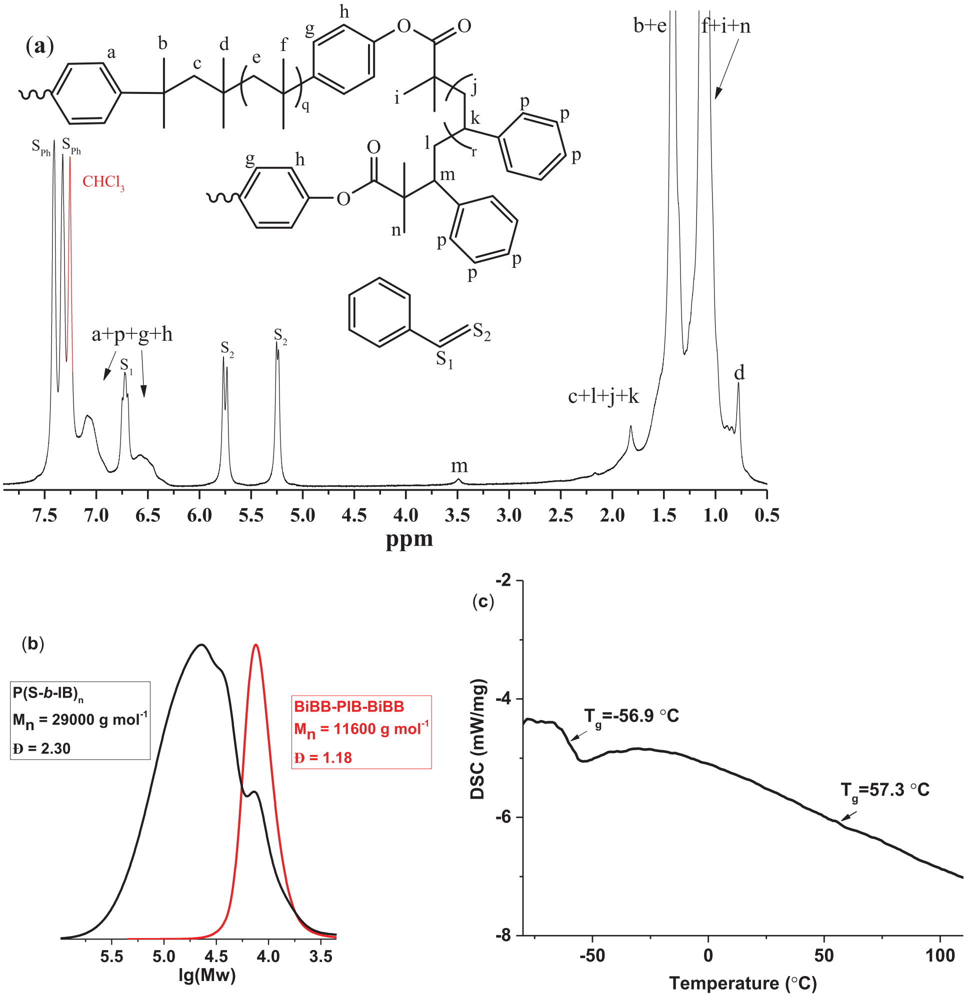
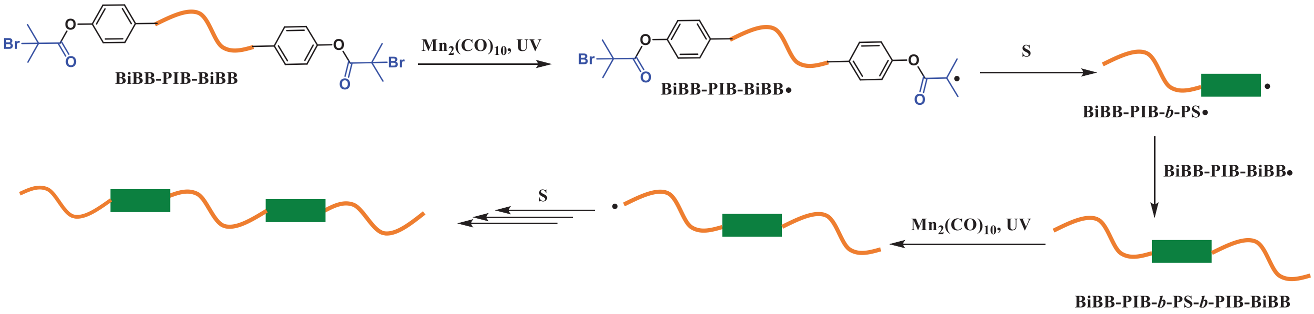


Figure 2. a) ^{1}H NMR spectrum and b) SEC trace of multiblock copolymer of styrene with isobutylene synthesized in bulk. Conversion of styrene was calculated as follows: conv. = $I(p)/[I(p)+I(S_1)\times 5]$, see Figure 2a for details. c) DSC curve of multiblock copolymer of styrene with isobutylene.

rate than styrene despite of poorer solubility of macroinitiator in MMA than in styrene (Figure S3, Supporting Information) reaching ≈94% of monomer conversion in 6 h under bulk conditions (**Figure 3a**). The absence of signal of two methyl groups of initiator moiety at the chain end at 2.06 ppm (Figure 1a) in the spectrum of triblock copolymer (Figure 3a) confirms the successful formation of poly(methyl methacrylate-*block*-isobutylene-*block*-methyl methacrylate). The complete shift of SEC trace of macroinitiator to high molecular weight region upon addition of MMA also proves the formation of poly(methyl methacrylate-*block*-isobutylene-*block*- methyl methacrylate) (Figure 3b). The resolution of original chromatogram using Gaussian method (Figure S6, Supporting Information) confirms the absence of unreacted **BiBB-PIB-BiBB**, while the molecular weight of



Scheme 3. Schematic representation of formation of multiblock copolymer.

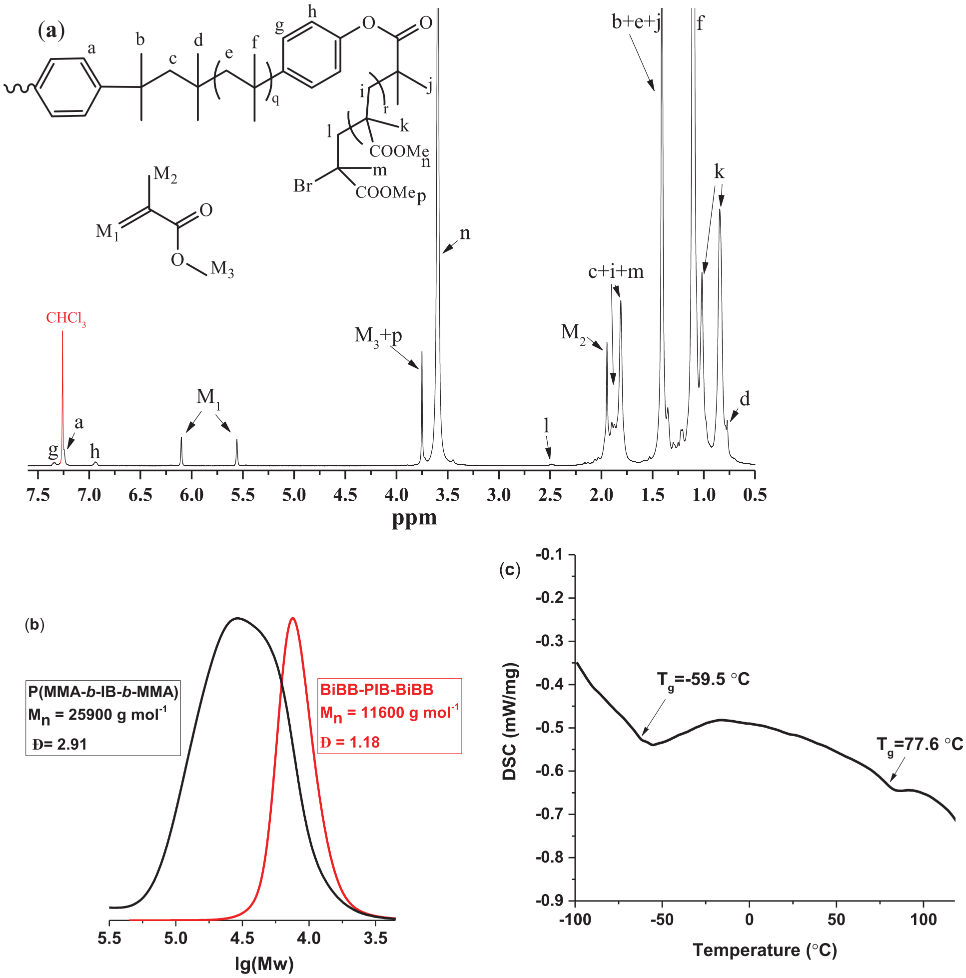


Figure 3. a) ^{1}H NMR spectrum and b) SEC trace of block copolymer of isobutylene with methyl methacrylate synthesized in bulk. Conversion of methyl methacrylate was calculated as follows: conv. = I(p)/[I(p)+I(5.5-6.2 ppm)×1.5], see Figure 3a for details. c) DSC curve for multiblock copolymer of isobutylene with methyl methacrylate.

block copolymer (M_n = 24 800 g mol^{-1}, Figure S5, Supporting Information) is close to one determined by SEC (M_n = 25 900 g mol^{-1}, Figure 3b). The molecular weight of block copolymer calculated from ^{1}H NMR spectrum (see Supporting Information for equations) is 20 100 g mol^{-1} that is slightly lower than one obtained by SEC (M_n = 25 900 g mol^{-1}). This observation in conjunction with non-symmetrical SEC curve and relatively high polydispersity (Figure 3b) may indicate that chains coupling leading to the formation of multiblock copolymers could also occur in this case similarly to the preparation of block copolymer of isobutylene with styrene (Scheme 3). However, considering much better correlation between M_n(NMR) and M_n(SEC) for block copolymer of isobutylene with MMA in comparison with block copolymer of IB with St, one can conclude that this side reaction is much less pronounced in the synthesis of PMMA-based copolymer and poly(methyl methacrylate-*block*-isobutylene-*block*-methyl methacrylate) is predominantly formed.

Additionally, DSC showed two distinct glass transition temperatures at −59.5 and 77.6 °C for polyisobutylene and poly(methyl methacrylate) blocks, respectively (Figure 3c), in strong contrast to multiblock copolymer of isobutylene with styrene, where the polystyrene block demonstrated very weak transition (Figure 2c). This difference can be explained by much higher content of MMA units in block copolymer (54% mol) as compared to styrene (18% mol). The relatively low glass transition for poly(methyl methacrylate) block is consistent with its low molecular weight ($M_n \leq$ 4200 g mol^{-1} for each PMMA block in triblock copolymer according to ^{1}H NMR spectroscopy).

2.3. Synthesis of Functional Polyisobutylene

Aiming at extending the scope of application of dimanganese decacarbonyl photochemistry, the possibility of synthesis of functional polyisobutylenes starting from **BiBB-PIB-BiBB** macroinitiator was briefly estimated. Particularly, the visible light-induced reaction of **BiBB-PIB-BiBB** with three equivalents of 1-(bromomethyl)pyrene in toluene in the presence of $Mn_2(CO)_{10}$ results in almost quantitative formation in 4 h of pyrene-terminated PIB (see Scheme 2). Indeed, according to the ^{1}H NMR spectrum (**Figure** 4a), the signal of protons of methyl groups of initiator moiety at the chain end at 2.06 ppm almost

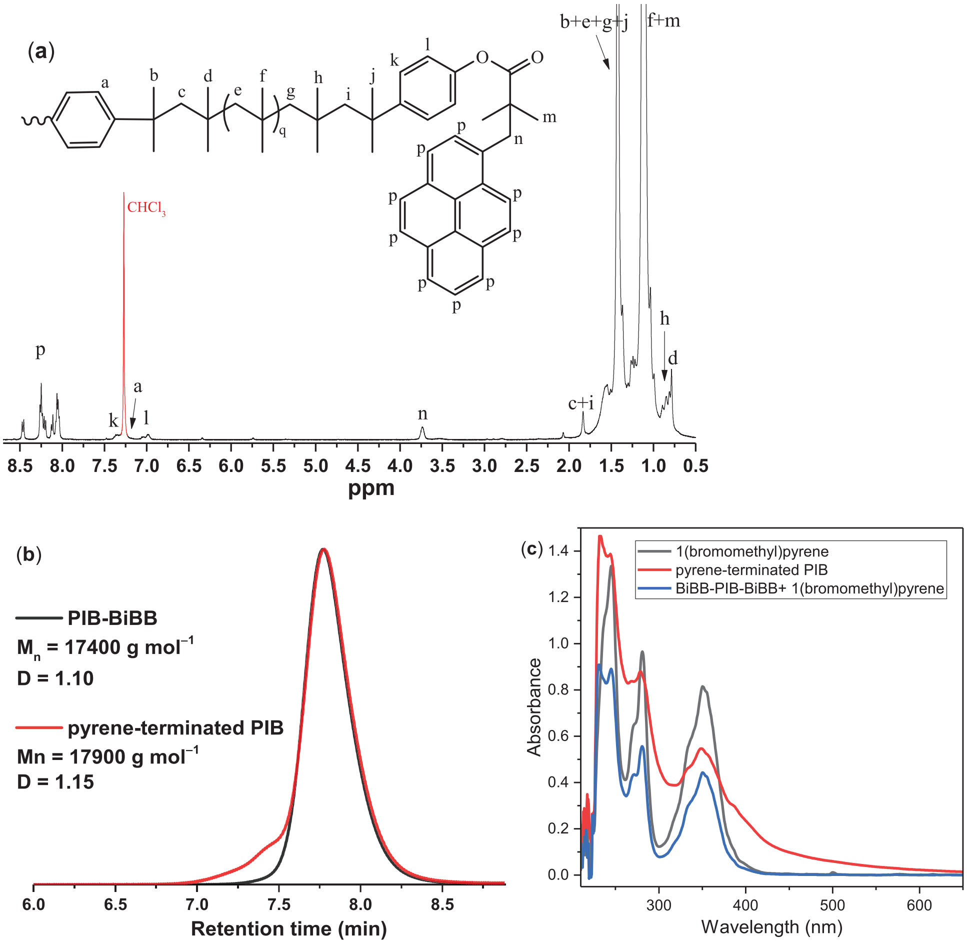


Figure 4. a) ^{1}H NMR spectrum and b) SEC traces of **BiBB-PIB-BiBB** (black line) and pyrene-terminated (red line) difunctional polyisobutylene and c) UV–vis spectra of pyrene-terminated PIB (red line), 1-(bromomethyl)pyrene (grey line) and physical mixture of **BiBB-PIB-BiBB** with 1-(bromomethyl)pyrene (blue line).

completely disappeared, while new signal due to methylene protons of pyrene moiety appeared at 3.75 ppm (signal **n**). The degree of functionalization calculated from ^{1}H NMR spectra based on integral intensities of above-mentioned signals was 91% (see Supporting Information for equations).

SEC trace almost did not change after the functionalization of **BiBB-PIB-BiBB** by pyrene keeping symmetrical shape, while functionalized PIB was characterized by low dispersity (Figure 4b). However, the appearance of a small shoulder in high molecular weight region indicates that the coupling of polyisobutylene chains could proceed to some extent similarly to the formation of multiblock copolymer (Scheme 3). In addition, the broadening of the signal and bathochromic shift of pyrene moiety in pyrene-terminated PIB as compared to 1-(bromomethyl)pyrene or its physical mixture with **BiBB-PIB-BiBB** in UV–vis spectrum confirmed the successful functionalization of polyisobutylene (Figure 4c).

Taking into account that synthesis of di- and multifunctional polyisobutylenes, especially those with primary amino, hydroxyl or bromine end groups, typically required cumbersome multistep procedures,[31,32,49,50] the proposed here new approach toward functionalization of PIB may open the simple and cost-efficient way for preparation of functionalized PIB. In addition, in view of recently reported visible-light induced cationic polymerization of IB catalyzed by $Mn_2(CO)_{10}$,[44] the combination of cationic polymerization and functionalization in one reactor could further simplify the functionalization of PIB.

3. Conclusion

In this work, we reported the synthesis of block copolymers of isobutylene with styrene and methyl methacrylate via $Mn_2(CO)_{10}$–triggered photoinduced radical polymerization in bulk. The proposed synthetic strategy consists of the preparation of difunctional PIB-based macroinitiator via consecutive cationic polymerization, in situ functionalization followed by acylation of phenol-terminated PIB by 2-bromo-2-methylpropanoyl bromide. In the second step, the photoinduced radical polymerization of styrene from PIB-based macroinitiator results in the formation of miltiblock copolymer due to the slow styrene polymerization and the coupling of growing diblock copolymer macroradical with newly generated radical from macroinitiator. In the case of photoinduced radical polymerization of methyl methacrylate, the reaction proceeded at a faster rate affording predominantly poly(methyl methacrylate-*block*-isobutylene-*block*-methyl methacrylate) triblock copolymer with some amount of multiblock copolymer. These preliminary results showed the great potential of the synthesis of block copolymers via mechanistic transformation from cationic to radical polymerization via such a cost-efficient approach as bulk polymerization. The most exciting achievement of this work is the demonstration of the possibility of polyisobutylene functionalization via photoinduced radical addition that potentially opens a simple approach toward the functionalization of PIB.

4. Experimental Section

Materials: 1,4-Bis(2-hydroxyisopropyl)benzene, (dicumyl alcohol, 97%, Sigma–Aldrich), $FeCl_3$ (97%, Fisher), ethanol (99.5%, Sigma–Aldrich), phenol (≥99%, Sigma–Aldrich), tetrahydrofuran (THF, Sigma–Aldrich, >99.9 for HPLC), CaH_2 (93%, Acros Organics), $SnCl_2 \times H_2O$ (98%, Sigma–Aldrich), 2-bromo-2-methylpropanoyl bromide (BiBB, 98%, Sigma–Aldrich), 1-(bromomethyl)pyrene (96%; Aldrich), methanol (Merck, 99.8%), and toluene (Aldrich, 99.7%) were used as received. ^{i}PrOH (99.5%, Sigma–Aldrich) was refluxed and then distilled over $SnCl_2 \times H_2O$ under argon atmosphere (98%, Sigma–Aldrich) and stored under 4 Å molecular sieves. Isobutylene (99%, Sigma–Aldrich) was dried in the gaseous state by passing through Laboratory Gas Drying Unit (Stock #26 800), condensed at −40 °C, and stored under molecular sieves. Dichloromethane (>99.5%, Sigma–Aldrich), n-hexane (>95%, Sigma–Aldrich) were treated with sulfuric acid, washed with aqueous sodium bicarbonate, dried over $CaCl_2$, and distilled twice over CaH_2 under an inert atmosphere and stored under 4 Å molecular sieves. Tetrahydrofuran (>99.9%, Sigma–Aldrich) was distilled over sodium under an inert atmosphere. Triethylamine (>99.5%, Sigma–Aldrich) was distilled over CaH_2 under an inert atmosphere. Methyl methacrylate (MMA, 99%; Aldrich) and styrene (St, 99%; Aldrich) were passed through a basic alumina column to remove the inhibitor. Dimanganese decacarbonyl ($Mn_2(CO)_{10}$, 99%, Aldrich) was purified by sublimation and stored in the fridge.

Characterization: ^{1}H NMR spectra were collected using 500 MHz Agilent VNMRS 500 or Bruker AC-500 spectrometers with $CDCl_3$ as a solvent with $Si(CH_3)_4$ as an internal standard. Size exclusion chromatography (SEC) was performed on an Ultimate 3000 Thermo Scientific apparatus with Agilent PLgel 5 μm MIXED-C (300 × 7.5 mm) and one precolumn (PL gel 5 μm guard 50 × 7.5 mm) thermostated at 30 °C and on a TOSOH EcoSEC GPC system equipped with an autosampler system, a temperature-controlled pump, a column oven, a refractive index (RI) detector, a purge, and degasser unit, and a TSK gel super hZ2000 4.6 mm ID × 15 cm × 2.0 cm column thermostated at 30 °C. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1.0 mL min^{-1}. The detection was achieved by differential refractometer (RI) as well as diode array detector (UV). The calculation of molecular weight and polydispersity was carried out using polystyrene standards (Polymer Labs, Germany). UV−vis spectra were recorded with a Shimadzu UV-1601 double-beam spectrometer equipped with a 50 W halogen lamp and a deuterium lamp which operate between 190 and 1100 nm. Glass transition (T_g) temperatures were determined by differential scanning calorimetry (DSC) (cooling/heating rate of 20 °C min^{-1}) recorded in helium as inert carrier gas on a NETZSCH STA 449 F3 instrument calibrated by adamantane and indium standards (NETZSCH). The data of second scan were used for the calculation of T_g.

Synthesis of Macroinitiator (BiBB-PIB-BiBB): Polyisobutylene was modified with 2-bromo-2-methylpropanoyl bromide in a glass tube under argon atmosphere at 20 °C. Hydroxyl-terminated polyisobutylene (3.9 g, $M_n = 10\,000$ Da, $M_w/M_n = 1.2$) was dissolved in THF (20 mL). Then Et_3N (0.58 mL, 4.2 mmol) and finally BiBB (0.48 mL, 3.9 mmol) was added. After 24 h the reaction mixture was diluted with 20 mL of *n*-hexane, filtrated, washed with 0.1 м HCl, then 2 times with 5% $NaHCO_3$ and 2 times with brine. The organic phase was dried under $MgSO_4$ then the polymer was precipitated in EtOH and dried under vacuum.

Synthesis of (PS-b-PIB)$_n$: Macroinitiator (200 mg, 0.01 mmol), styrene (1 mL, 8.64 mmol), and $Mn_2(CO)_{10}$ (16 mg, 0.04 mmol) were put into a Schlenk tube with a magnetic stirrer. The solution was then exposed to light from six fluorescent lamps of 25-Watt power each emitting light nominally at 450 nm in a photoreactor. After 6 h of irradiation, the mixture was subsequently precipitated in cold methanol. The obtained block copolymer was filtered and dried under a vacuum.

Synthesis of PMMA-b-PIB-b-PMMA: Macroinitiator (200 mg, 0.01 mmol), MMA (1 mL, 9.38 mmol), and $Mn_2(CO)_{10}$ (12 mg, 0.03 mmol) were added into a 25 mL Schlenk tube with a magnetic stirrer. The solution was then exposed to light from six fluorescent lamps of 25-Watt power each emitting light nominally at 450 nm in a photoreactor. After 6 h of irradiation in the photoreactor, the solution was precipitated into hexane, and obtained polymers were collected by filtration.

Synthesis of Pyrene-Functionalized Polyisobutylene: To a Schlenk tube, macroinitiator (100 mg, 0.005 mmol), 1-bromo methyl pyrene (10 mg, 0.03 mmol), and $Mn_2(CO)_{10}$ (19 mg, 0.04 mmol) were added and dissolved in toluene. The tube was degassed by three freeze–pump–thaw cycles. After that, the reaction mixture was placed in a photoreactor and irradiated at 450 nm. The mixture was stirred with a magnetic mixer during irradiation. At the end of 4 h, the mixture was precipitated in cold methanol and dried at room temperature under a vacuum.

Details of the preparation of initiator, complexes of $FeCl_3$ with isopropyl alcohol, complex of $AlCl_3$ with phenol and the phenol-terminated PIB were described in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

cationic polymerization, functional polyisobutylene, mechanistic transformation, photo-induced radical polymerization, polyisobutylene-based block copolymers

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