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Synthesis of Polyisobutylene-Based Miktoarm Star Polymers from a Dicationic Monoradical Dual Initiator

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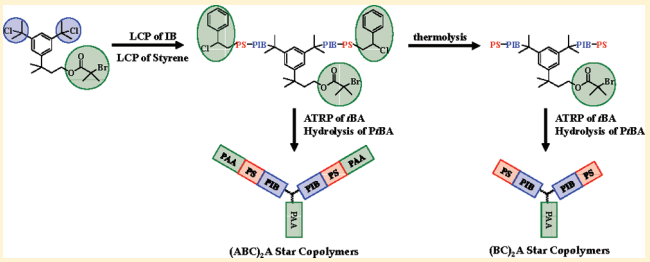
Supporting Information

ABSTRACT: A dicationic monoradical dual initiator 3-[3,5-bis(1-chloro-1-methylethyl)phenyl]-3-methylbutyl 2-bromo-2-methylpropionate (DCCBMP) was designed for the preparation of A_2B type miktoarm star copolymers, where A is a polyisobutylene (PIB)-based homo or block copolymer that is produced by living carbocationic polymerization (LCP), and B is a polyacrylate or other polymer block produced by atom transfer radical polymerization (ATRP). DCCBMP was obtained by chlorination of 3-[3,5-bis(1-hydroxy-1-methylethyl)phenyl]-3-methylbutyl 2-bromo-2-methylpropionate (DCOHBMP), which was synthesized in a pure form via aerobic oxidation of 3-(3,5-diisopropylphenyl)-3-methylbutyl 2-bromo-2-methylpropionate using *N*-hydroxyphthalimide (NHPI)/$Co(OAc)_2{\cdot}4H_2O$ catalyst system. Initiation efficiency of DCCBMP was 0.89−0.98 for LCP of isobutylene (IB) at −70 °C targeting molecular weights of 5K, 10K, and 20K g/mol, which was comparable to the standard dicationic initiator 5-*tert*-butyl-1,3-(1-chloro-1-methylethyl)benzene (*t*-Bu-*m*-DCC). Sequential monomer addition under LCP conditions produced narrow-polydispersity poly(styrene-*b*-isobutylene-*b*-styrene) (PS−PIB−PS) triblock copolymers. These polymers possessed a 2-bromo-2-methylpropionate (bromoester) ATRP initiating site in the approximate middle of PIB segment and two *sec*-benzylic chloride groups at the PS chain ends, which were also effective in initiating ATRP. With these PS−PIB−PS macroinitiators, poly(*tert*-butyl acrylate-*b*-styrene-*b*-isobutylene)$_2$-*s*-poly(*tert*-butyl acrylate) [(P*t*BA−PS−PIB)$_2$-*s*-P*t*BA] miktoarm star polymers were readily synthesized via ATRP of *tert*-butyl acrylate (*t*BA). The *sec*-benzylic chloride functionality was alternatively eliminated at high temperature (180−200 °C) under vacuum, yielding PS−PIB−PS macroinitiators containing only the bromoester site (thermolyzed PS−PIB−PS). Size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR) spectroscopy showed that thermolysis removed all *sec*-benzylic chlorides without destruction of bromoester moieties. Thermolyzed PS−PIB−PS allowed synthesis of poly(styrene-*b*-isobutylene)$_2$-*s*-poly(*tert*-butyl acrylate) [(PS−PIB)$_2$-*s*-P*t*BA] star polymers with the potential hydrophilic segment attached only to the core of PS−PIB−PS. For both star terpolymer configurations, the P*t*BA blocks were converted to PAA via thermolysis at 150 °C to produce amphiphilic PIB-based miktoarm star polymers with narrow polydispersity indices (<1.1).



INTRODUCTION

Block copolymers containing polyisobutylene (PIB) elastomeric segments are of great interest due to the outstanding environmental resistance, mechanical damping, impermeability, and biocompatibility of PIB. Poly(styrene-*b*-isobutylene-*b*-styrene) (PS−PIB−PS) triblock copolymers were first synthesized in the early 1990s by Kennedy and co-workers via living carbocationic polymerization (LCP) and the technique of sequential monomer addition, involving bidirectional polymerization of isobutylene (IB) followed by addition of styrene.[1,2] These copolymers exhibit strong phase separation in the bulk and display properties typical of thermoplastic elastomers (TPEs). They exhibit excellent low-temperature flexibility and elongation properties imparted by the rubbery PIB center block, and they possess elastic recovery and physical strength properties due to the glassy PS segments.[1−6] Because of its general inertness, PIB also possesses excellent biocompatibility, and in 2004, PS−PIB−PS was approved to sequester Paclitaxel on the highly successful Taxus drug-eluting coronary stent.[7,8]

Over the years, efforts have been made to combine PIB with other outer blocks to achieve different or improved properties. For example, the upper use temperature range has been extended by replacing the PS blocks with higher-T_g glassy segments produced from *p*-chlorostyrene,[9] *p*-methylstyrene,[10−12] *α*-methylstyrene,[13,14] indene,[10,15] or *p*-*tert*-butylstyrene,[16] or higher-T_g semicrystalline segments from *p*-chloro-*α*-methylstyrene,[17] and hydrophilic character has been imparted by replacing styrene with *p*-hydroxystyrene[18] or 4-(2-hydroxyethyl)styrene.[19] In all of these cases, sequential monomer addition was used to form the block structure; although in some cases a nonhomopolymerizable chain-capping

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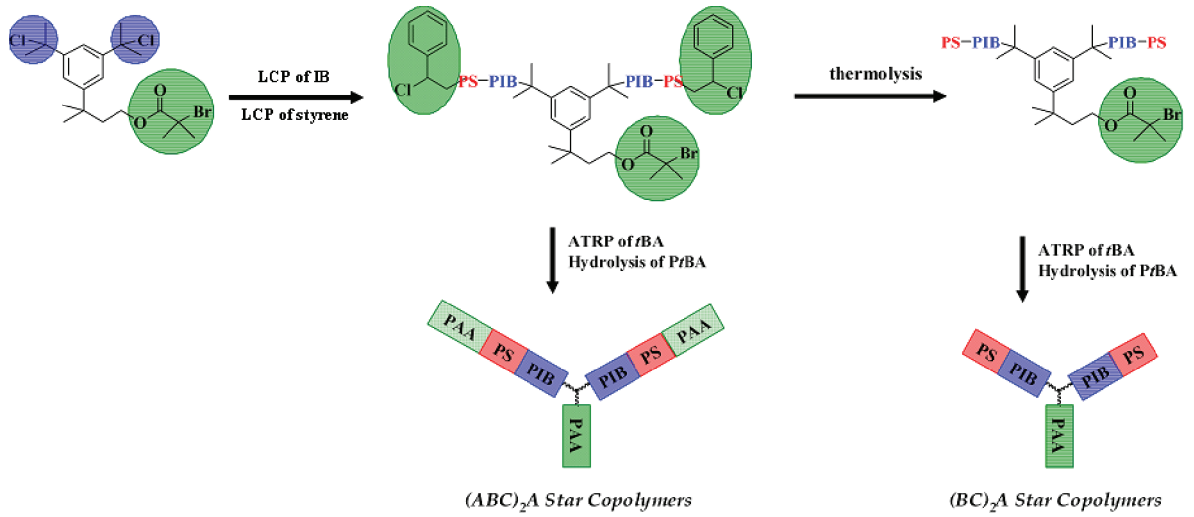
Scheme 1. Schematic Synthesis of Amphiphilic Poly(acrylic acid-*b*-styrene-*b*-isobutylene)$_2$-*s*-poly(acrylic acid) [(PAA−PS−PIB)$_2$-*s*-PAA] and Poly(styrene-*b*-isobutylene)$_2$-*s*-poly(acrylic acid) [(PS−PIB)$_2$-*s*-PAA] Miktoarm Star Terpolymers from DCCBMP, Combining Living Carbocationic Polymerization (LCP) and Atom Transfer Radical Polymerization (ATRP)



monomer such as diphenylethylene and/or a change in Lewis acid strength was used to facilitate the crossover reaction.[12,14,17,18]

Since PIB can only be produced via cationic polymerization, many monomer families, for example, methacrylates, acrylates, (meth)acrylamides, etc., that do not undergo cationic polymerization, cannot be combined with IB using sequential monomer addition. Therefore, new strategies combining LCP with different controlled/living polymerization mechanisms have been developed to expand the number of potential PIB-based block copolymers. Among the various controlled/living polymerization mechanisms, atom transfer radical polymerization (ATRP) is recognized to be versatile with regard to monomer type and tolerant to a wide variety of functional groups, such as allyl, amino, epoxy, hydroxyl, and vinyl; ATRP is also easy to implement due to the availability and/or relative ease of synthesis of ATRP initiators.[20] It is therefore not surprising that quite a number of reports have appeared involving synthesis of PIB-based block copolymers using a combination of LCP and ATRP. Site (mechanism) transformations involving addition of styrene to living PIB to produce *sec*-benzylic chloride functionality,[21−23] functionalizing hydroxyl-terminated PIB with bromoisobutyryl (or bromopropionyl) groups,[24,25] and addition of 1,3-butadiene to living PIB to produce allyl halide end groups,[26] have been used to transform the PIB growing chain end into an ATRP initiating site. Masar and co-workers also reported the synthesis of PIB−PS−PMMA−PS−PIB pentablock copolymers, where PMMA is poly(methyl methacrylate), by producing α,ω-dichloro−PS−PMMA−PS triblock copolymer via ATRP followed by LCP to add IB.[27] Dual initiators containing both cationic and ATRP initiating sites have also been successfully used to prepare PIB-based block copolymers.[28−30]

In reference 23, we reported the synthesis and characterization of P*t*BA−PS−PIB−PS−P*t*BA pentablock terpolymers as potential permselective barrier elastomers with enhanced moisture transmission capabilities. The synthesis employed LCP to first produce PS−PIB−PS, followed by site transformation to ATRP to create the poly(*tert*-butyl acrylate) (P*t*BA) outer blocks. Acid-catalyzed[23,31] or thermal cleavage[32] of the *tert*-butyl ester side groups yielded PAA−PS−PIB−PS−PAA, with water transmitting poly(acrylic acid) (PAA) block segments. Transmission electron microscopy (TEM) revealed a PIB continuous phase, and concentric PS (outer) and PAA (inner) cylinders. At a composition of 50:25:25 PIB:PS:PAA (wt %), the membranes were elastomeric and water permeable (10^{-5}−10^{-4} g^{-1} h^{-1} mmHg^{-1}); below 25 wt % PAA, the PAA domains were discontinuous within the PS cylinders and water permeation decreased by an order of magnitude.[31] However, polymers prepared via site transformation from PS−PIB−PS are limited to structures in which the third block (e.g., PAA) is covalently attached to the PS block. This precludes morphologies possessing an interface between PIB and the third block, causing the PAA domains to be constrained within the rigid PS cylinders and potentially limiting water swelling and permeation. To address this issue, we have targeted a new miktoarm star-branched configuration whereby the third block is covalently attached to the PIB block (Scheme 1). This structure retains the PS−PIB−PS configuration, providing elastic recovery and strength by physically constraining the PIB segments at their ends. In addition, phase-separated morphologies possessing an interface between PIB and the third block are possible.

Miktoarm star polyisobutylene-based block copolymers have been previously reported. Faust et al.[33] reacted 2-(PIB)furan with living PIB, thereby creating coupled PIB with an active furanyl cation at the coupling junction. After adjustment of Lewis acidity and solvent medium polarity, sequential addition of methyl vinyl ether was carried out to produce the miktoarm star block copolymer. This method was shown to provide independent control over the degrees of polymerization of the two PIB segments. In more recent work, Faust and Hirao[34] used a postpolymerization, iterative divergent approach, using functionalized diphenylethylene, to place 2^n benzyl bromide functions at the termini of either mono or difunctional PIB (B). The bromide functions were then coupled with living anionic poly(methyl methacrylate) (A) to make A_2B, A_4B, and A_8B miktoarm star polymers, and A_2BA_2, A_4BA_4, and A_8BA_8 "pompom" polymers. However, these methods, which construct the PIB segments in a "toward the core" manner, do not easily lend themselves to the synthesis of the star polymers of Scheme 1, especially the $(ABC)_2A$ variety.

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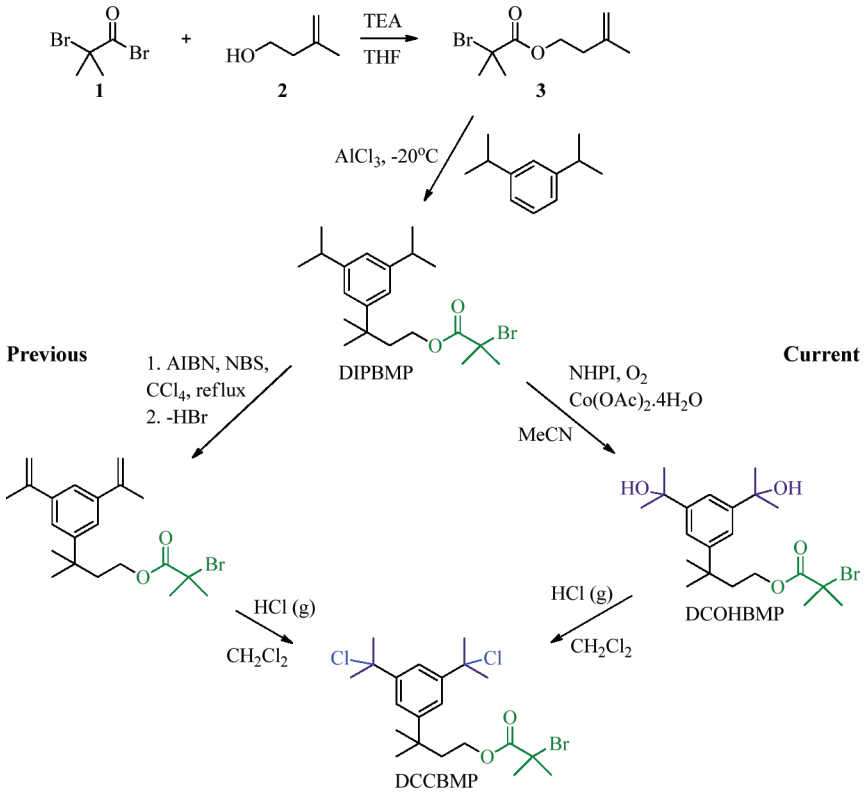
Scheme 2. Synthetic Routes to 3-[3,5-Bis(1-chloro-1-methylethyl)phenyl]-3-methylbutyl 2-Bromo-2-methylpropionate (DCCBMP) via 3-(3,5-Diisopropylphenyl)-3-methylbutyl 2-Bromo-2-methylpropionate (DIPBMP): Radical Bromination (Left, Previous[33]) and Aerobic Oxidation (Right, Current)



The architectures shown in Scheme 1 are readily prepared using a dicationic initiator with an initiation site for another polymerization process such as ATRP. We recently reported[35] the synthesis of such an initiator, 3-[3,5-bis(1-chloro-1-methylethyl)phenyl]-3-methylbutyl 2-bromo-2-methylpropionate (DCCBMP) (Scheme 2, left). The key intermediate, 3-(3,5-diisopropylphenyl)-3-methylbutyl 2-bromo-2-methylpropionate (DIPBMP), was produced by the Friedel−Crafts alkylation of diisopropylbenzene by 3-methyl-3-butenyl 2-bromo-2-methylpropionate, **3**. Selective radical bromination of DIPBMP proved problematic, however, and after chromatographic dehydrobromination, yielded a liquid diolefin intermediate that was difficult to purify by vacuum distillation. We therefore sought a different synthetic route, particularly one that yielded a crystalline intermediate that could be purified by recrystallization. It has been reported that benzylic CH of alkylbenzenes can be oxidized with *N*-hydroxyphthalimide (NHPI) and $Co(OAc)_2 \cdot 4H_2O$ catalyst system under oxygen atmosphere at ambient pressure.[36−38] Herein, we report a new synthetic route (Scheme 2, right), in which DIPBMP is oxidized using this procedure to yield the crystalline dihydroxy intermediate, (DCOHBMP). This compound is a stable solid and may be purified by recrystallization. It is convenient to store the initiator in the form of DCOHBMP, and then to carry out the final, high-yielding chlorination step immediately prior to use.

The proper use of DCCBMP requires that the carbocationic polymerization be done first, followed by ATRP. The LCP of styrene naturally creates *sec*-benzylic chloride PS chain ends, known ATRP initiators.[39] Therefore, PS−PIB−PS polymers synthesized from DCCBMP require a procedure that will remove these groups and leave only the desired bromoester function. Iván et al. found that poly(vinyl chloride) readily and quantitatively dehydrochlorinates upon heating to 180−200 °C.[40] Here the PS−PIB−PS macroinitiator is processed in the same way to deactivate the PS chain ends and produce the miktoarm star, poly(styrene-*b*-isobutylene)$_2$-*s*-poly(*tert*-butyl acrylate) [(PS−PIB)$_2$-*s*-P*t*BA] after ATRP of *tert*-butyl acrylate (*t*BA). The *tert*-butyl ester side groups are then cleaved using the simple thermal treatment described by Kopchick et al.[32] to convert P*t*BA to PAA and yield the desired amphiphilic poly(styrene-*b*-isobutylene)$_2$-*s*-poly(acrylate acid) [(PS−PIB)$_2$-*s*-PAA] miktoarm star terpolymers (Figure 1, right).

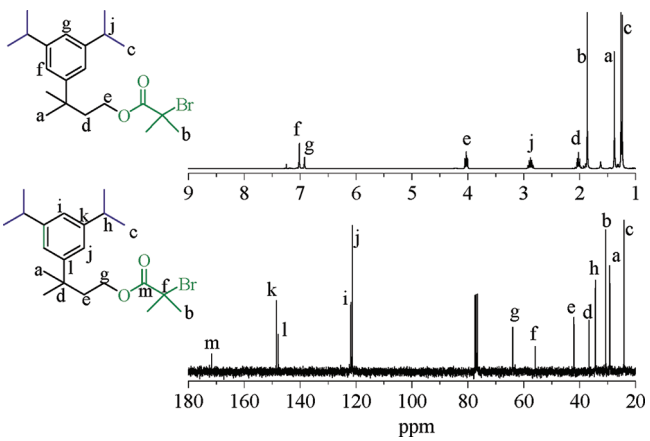


Figure 1. ^{1}H and ^{13}C NMR spectra of 3-(3,5-diisopropylphenyl)-3-methylbutyl 2-bromo-2-methylpropionate (DIPBMP).

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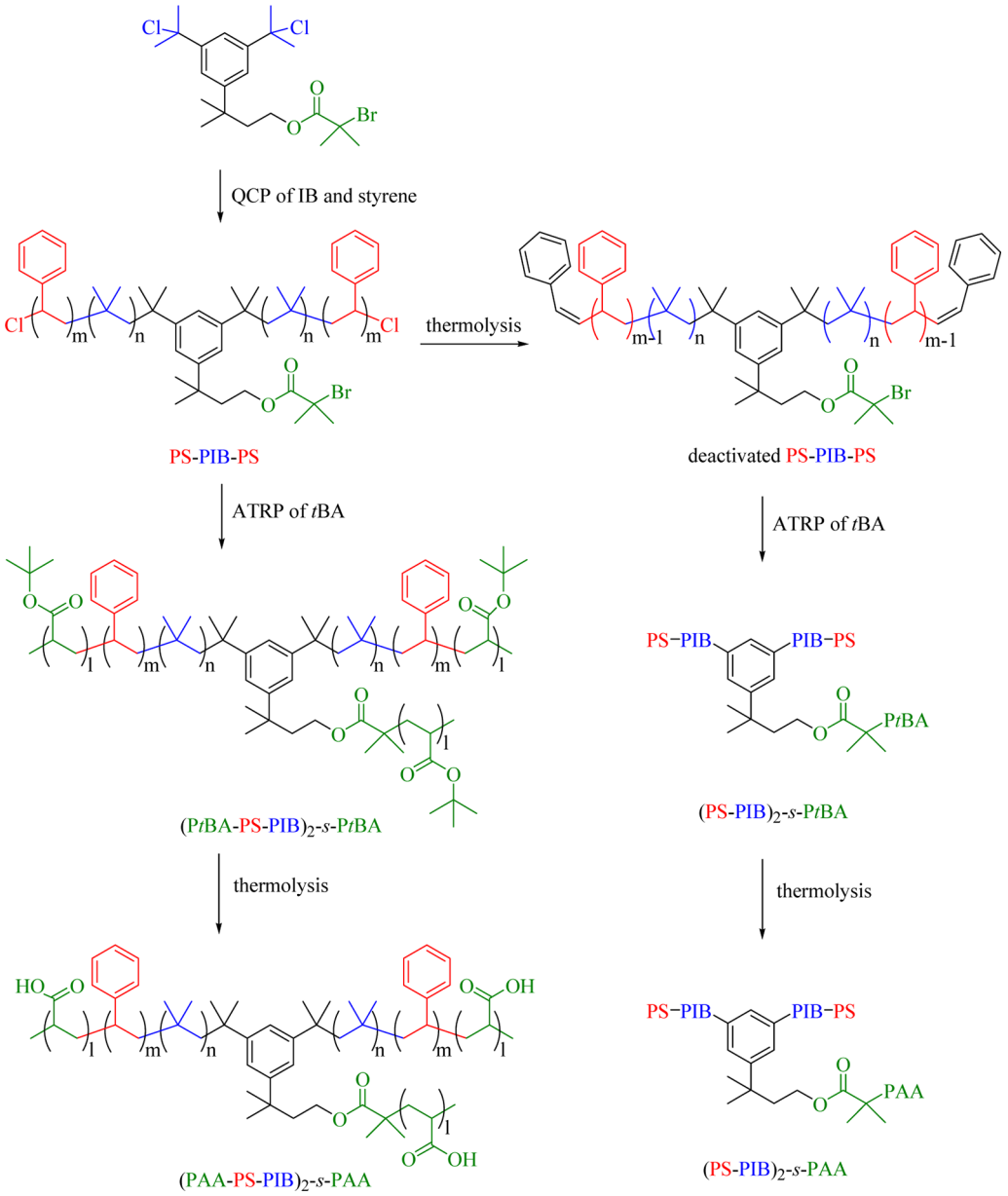
Scheme 3. Synthesis of (PAA−PS−PIB)$_2$-*s*-PAA and (PS−PIB)$_2$-*s*-PAA miktoarm star polymers



The original PS−PIB−PS macroinitiator can also be used to initiate *t*BA in three directions to produce poly(*tert*-butyl acrylate-*b*-styrene-*b*-isobutylene)$_2$-*s*-poly(*tert*-butyl acrylate) [(P*t*BA−PS−PIB)$_2$-*s*-P*t*BA] miktoarm star terpolymers, which could be further converted into poly(acrylate acid-*b*-styrene-*b*-isobutylene)$_2$-*s*-poly(acrylate acid) [(PAA−PS−PIB)$_2$-*s*-PAA] in the same manner described above. Bates et al. reported that architecturally asymmetric tetrablock terpolymer, poly-[(ethylene oxide)-*b*-styrene-*b*-butadiene-*b*-(ethylene oxide)], forms interesting bilayer vesicles at a high weight percentage of the hydrophilic block when placed in a solvent selective for the outer block.[41] In addition, Balsara and co-workers discovered platelet self-assembly of an amphiphilic tetrablock copolymer, poly(styrenesulfonate-*b*-methylbutylene-*b*-ethylethylene-*b*-styrenesulfonate).[42] We anticipate similar morphological behavior will be observed for our (ABC)$_2$A star polymers.

EXPERIMENTAL SECTION

Materials. 3-Methyl-3-buten-1-ol (≥97%), 2-bromo-2-methylpropionyl bromide (98%), 1,3-diisopropylbenzene (96%), *N*-hydroxyphthalimide (NHPI) (97%), Co(OAc)$_2$·4H$_2$O (≥98.0%), acetonitrile (anhydrous, 99.8%), methylcyclohexane (MCHex) (anhydrous, ≥ 99%), triethylamine (TEA) (99.5%), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) (99%), hexane (anhydrous, 99%), 2,6-lutidine (99+%), $TiCl_4$ (99.9%), Cu^IBr (99.999%), $AlCl_3$ (99.99%), toluene (anhydrous, 99.8%), $CDCl_3$, and balloons with wall thickness of 15 mil were used as received from Sigma-Aldrich, Inc. Compressed oxygen was used as received from Praxair, Inc. Petroleum ether, CH_2Cl_2, K_2CO_3, THF, $MgSO_4$, and $NaHCO_3$ were used as received from Fisher Chemical Co. Dowex HCR-W2 ion-exchange resin (strong cationic type) was used as received from Dow Chemical, Germany. Isobutylene (IB) (99.5%, BOC Gases) and MeCl (99.5%, Alexander Chemical Co.) were dried through columns packed with $CaSO_4$ and $CaSO_4$/4 Å molecular sieves, respectively. *tert*-Butyl acrylate (*t*BA) (99%) was passed through a K_2CO_3 and Al_2O_3 column to remove inhibitor.

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Instrumentation. Absolute molecular weights and polydispersity indices (PDIs) of polymers were determined using a size exclusion chromatography (SEC) system (35 °C, THF, 1 mL/min) consisting of a Waters Alliance 2695 Separations Module, online multiangle laser light scattering (MALLS) detector (MiniDAWN, Wyatt Technology, Inc.), interferometric refractometer (Optilab rEX, Wyatt Technology Inc.), and two mixed D (5 μm beadsize) PL gel (Polymer Laboratories Inc.) GPC columns connected in series. The dn/dc values used for PIB homopolymers were calculated from the following equation:[43] dn/dc = 0.116(1 − 108/$\bar{M}_n$) ($\bar{M}_n$ = number-average molecular weight); the dn/dc values for block and miktoarm star copolymers were calculated from the interferometric refractometer detector response and assuming 100% mass recovery from the columns. Solution ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained at 22 °C using $CDCl_3$ as the solvent and tetramethylsilane as the internal reference. Progress of the cationic polymerization of IB was monitored using real-time, remote-probe (light conduit type) attenuated total reflectance Fourier transform infrared spectroscopy (FTIR) (ReactIR 4000). Detailed descriptions of the SEC, NMR, and FTIR instrumentation and corresponding procedures have been previously published.[44]

The melting point of 3-[3,5-bis(1-hydroxy-1-methylethyl)phenyl]-3-methylbutyl 2-bromo-2-methylpropionate (DCOHBMP) was measured using a Q200 (TA Instruments) differential scanning calorimeter. The furnace atmosphere was purged with a 50 mL/min nitrogen stream. Standard capped aluminum crucibles were loaded with ∼5 mg of DCOHBMP solid, and the sample was subjected to a temperature ramp of 1 °C/min from 35 to 100 °C.

High resolution mass spectrometry of DCOHBMP was performed using a Waters LCT Premier XE benchtop orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer, and the sample was analyzed by solids probe by electron-impact (EI) mode at 70 eV. A crystal was placed into a borosilicate glass capillary, which was then placed into the probe. Once the probe was inserted into the instrument, the sample was heated quickly to 400 °C. The 218 mass of heptacosa was used for a lockmass.

Synthesis of 3-(3,5-Diisopropylphenyl)-3-methylbutyl 2-Bromo-2-methylpropionate (DIPBMP). First, 3-Methyl-3-butenyl 2-bromo-2-methylpropionate, **3**, was produced by reacting 3-methyl-3-buten-1-ol (**2**) with 2-bromo-2-methylpropionyl bromide (**1**) using a variation of a previously reported procedure (Scheme 2).[28] DIPBMP was synthesized by the Friedel−Crafts alkylation of diisopropylbenzene by **3**, using a modification of the procedure described by Cheon and Yamamoto,[45] as follows: within an inert atmosphere glovebox equipped with a hexane/heptane cold bath, a 250 mL two-necked, round-bottom flask, equipped with mechanical stirrer, was charged with 1,3-diisopropylbenzene (85.7 g, 0.528 mol) and $AlCl_3$ (26.5 g, 0.200 mol). This mixture was chilled to −20 °C and stirred vigorously. Then, **3** (40.6 g, 0.173 mol) was slowly added, and the slurry was stirred vigorously for another 25 h. It was added to ice-cold water (500 mL), and this mixture stirred for 2 h. The organic phase was separated, and the water layer was extracted with CH_2Cl_2. The combined organic solutions were washed with brine and then DI water and dried over anhydrous $MgSO_4$. After filtration, CH_2Cl_2 was removed by vacuum stripping, and the desired compound, 3-(3,5-diisopropylphenyl)-3-methylbutyl 2-bromo-2-methylpropionate, was obtained as a light yellow oil (34.0 g, 49.5% yield) upon vacuum distillation. ^{1}H NMR ($CDCl_3$): δ = 1.25 (d, 12H, PhCH(CH_3)$_2$), 1.38 (s, 6H, 4-H), 1.86 (s, 6H, (CH_3)$_2$CBr), 2.02 (t, 2H, 2-H), 2.88 (m, 2H, PhCH(CH_3)$_2$), 4.03 (t, 2H, 1-H), 6.92 (m, 1H, 4-PhH), 7.02 (m, 2H, 2,6-PhH) ppm. ^{13}C NMR: δ = 24.1 (PhCH(CH_3)$_2$), 29.2 (C4), 30.7 ((CH_3)$_2$CBr), 34.3 (PhCH(CH_3)$_2$), 36.7 (C3), 42.1 (C2), 55.9 ((CH_3)$_2$CBr), 63.9 (C1), 121.3 (2,6-PhC), 121.8 (4-PhC), 147.8 (1-PhC), 148.5 (3,5-PhC), 171.5 (CO) ppm.

Synthesis of 3-[3,5-bis(1-hydroxy-1-methylethyl)phenyl]-3-methylbutyl 2-bromo-2-methylpropionate (DCOHBMP). The dihydroxy intermediate DCOHBMP was prepared via aerobic oxidation of DIPBMP (Scheme 2, right) using the *N*-hydroxyphthalimide (NHPI)/Co(OAc)$_2$·4H$_2$O catalyst system.[35] Into a 250 mL Erlenmeyer flask equipped with a magnetic stirrer were added DIPBMP (7.30 g, 18.4 mmol), NHPI (1.303 g, 8 mmol), Co(OAc)$_2$·4H$_2$O (0.101 g, 0.41 mmol), and 25 mL MeCN. Because Co(OAc)$_2$·4H$_2$O and NHPI are sparingly soluble in MeCN, an orange heterogeneous mixture was obtained. The flask was then capped with a balloon filled with pure oxygen. The reaction was stirred vigorously at 23 °C for 72 h. The solvent was vacuum stripped, and the solid was washed with CH_2Cl_2 (3 × 25 mL). A clear, light-yellow liquid was obtained after drying over $MgSO_4$. The oxidized diol product, DCOHBMP (2.61 g, 6.05 mmol, 33.1% yield) was obtained as a white solid after removing minor quantities of several byproducts, including dihydroperoxy, diolefin, and monohydroxy monohydroperoxy, as well as byproducts containing methyl ketone moieties, by column chromatography (SiO_2, hexane/THF (v/v) = 2:1 cosolvents as the eluent). The preliminarily purified product was dissolved to saturation in toluene at 60 °C. Upon cooling to −10 °C for several hours, pure DCOHBMP was formed as white crystals, which were collected by filtration. Melting point =91.3 °C by DSC. ^{1}H NMR ($CDCl_3$): δ = 1.40 (s, 6H, 4-H), 1.60 (s, 12H, PhCOH(CH_3)$_2$), 1.86 (s, 6H, (CH_3)$_2$CBr), 2.06 (t, 2H, 2-H), 2.31 (s, 2H, PhCOH(CH_3)$_2$), 4.01 (t, 2H, 1-H), 7.40 (m, 2H, 2,6-PhH), 7.43 (m, 1H, 4-PhH) ppm. ^{13}C NMR: δ = 29.4 (C4), 30.7 ((CH_3)$_2$CBr), 31.9 (PhCOH(CH_3)$_2$), 37.0 (C3), 41.9 (C2), 55.9 ((CH_3)$_2$CBr), 63.8 (C1), 72.8 (PhCOH-(CH_3)$_2$), 118.1 (4-PhC), 120.1 (2,6-PhC), 148.0 (1-PhC), 149.0 (3,5-PhC), 171.6 (CO) ppm. HRMS (EI): $C_{21}H_{33}O_4{}^{79}Br$ [M]$^+$, calcd 428.1562, found 428.1575; $C_{21}H_{33}O_4{}^{81}Br$ [M]$^+$, calcd 430.1542, found 430.1553.

Figures A, B, and C, Supporting Information, show ^{1}H and ^{13}C NMR spectra of diolefin, dihydroperoxy, and monohydroxy monohydroperoxy byproducts, respectively.

Synthesis of 3-[3,5-Bis(1-chloro-1-methylethyl)phenyl]-3-methylbutyl 2-Bromo-2-methylpropionate (DCCBMP). The final product, DCCBMP, was obtained as a pale yellow liquid (2.63 g, 93.2% yield) by chlorination of DCOHBMP using anhydrous, gaseous HCl, as previously reported.[42] ^{1}H NMR ($CDCl_3$): δ = 1.41 (s, 6H, 4-H), 1.86 (s, 6H, (CH_3)$_2$CBr), 2.01 (s, 12H, PhCCl(CH_3)$_2$), 2.06 (t, 2H, 2-H), 4.04 (t, 2H, 1-H), 7.50 (m, 2H, 2,6-PhH), 7.62 (m, 1H, 4-PhH) ppm. ^{13}C NMR: δ = 29.2 (C4), 30.6 ((CH_3)$_2$CBr), 34.4 (PhCCl(CH_3)$_2$), 37.0 (C3), 41.8 (C2), 55.8 ((CH_3)$_2$CBr), 63.5 (C1), 69.9 (PhCCl(CH_3)$_2$), 120.2 (4-PhC), 122.1 (2,6-PhC), 146.0 (1-PhC), 148.0 (3,5-PhC), 171.5 (CO) ppm.

Initiation Performance Test (Isobutylene Homopolymerization). LCPs of IB were carried out within an inert atmosphere glovebox equipped with a hexane/heptane cold bath, following the previously described procedure.[42] Polymerizations were performed at −70 °C, using DCCBMP or 5-*tert*-butyl-1,3-(1-chloro-1-methylethyl)-benzene (*t*-Bu-*m*-DCC) as the initiator. $TiCl_4$ served as the catalyst, and 2,6-lutidine as the Lewis base in 60/40 (v/v) MCHex/MeCl cosolvents.

PS−PIB−PS Synthesis. PS−PIB−PS triblock copolymers were produced via LCP and sequential monomer addition within a drybox at −70 °C, using DCCBMP as the initiator, $TiCl_4$ as the catalyst, and 2,6-lutidine as the Lewis base in 60/40 (v/v) MCHex/MeCl cosolvents. FTIR (ReactIR 4000) was used to monitor isobutylene and styrene conversions by observing the olefinic =CH$_2$ wag of IB (887 cm^{-1}) and syrene (907 cm^{-1}).[46] The DiComp probe was inserted into a 250 mL 4-necked round-bottom flask equipped with a temperature probe and a stirring shaft with a Teflon paddle. The reactor was placed into the cold bath and allowed to equilibrate to −70 °C. Into the flask were charged 57.9 mL of prechilled MCHex, 38.6 mL of prechilled MeCl, 2,6-lutidine (0.0489 mL, 4.23 × 10^{-4} mol), and DCCBMP (0.3005 g, 6.45 × 10^{-4} mol). The mixture was allowed to stir for 10 min to reach thermal equilibrium before a background spectrum was collected. Prechilled IB (8.50 mL, 0.106 mol) was added to the flask, and then about 15 spectra were acquired to establish the average intensity of the 887 cm^{-1} peak, A_0, corresponding to the initial monomer concentration. At this point, $TiCl_4$ (0.707 mL, 6.44 × 10^{-3} mol) was injected into the flask. The initial molar concentrations of reagents were [IB]$_0$ = 1.0 M, [DCCBMP]$_0$ = 6.1 mM, [2,6-lutidine]$_0$ = 4.0 mM, and [$TiCl_4$]$_0$ = 61.0 mM, and the total volume was 105.7 mL. Once the IB monomer was fully consumed (>99% conversion),

indicated by the 887 cm^{-1} absorbance approaching an asymptotic value (A_r), a mixture of prechilled 25.7 mL of MCHex, 17.1 mL of MeCl, and 7.1 g of styrene was added. These amounts were designed to achieve $[styrene]_0$ = 0.4 M, assuming no volume loss when IB monomer was converted into polymer, while maintaining a 60/40 (v/v) MCHex/MeCl cosolvents system. The FTIR instrument was reset to monitor the disappearance of the styrene band at 907 cm^{-1}. Once the styrene conversion reached ~50%, 20 mL of prechilled CH_3OH was added to quench the polymerization; styrene conversion was limited in order to prevent chain transfer to polymer (EAS side reaction). After warming to room temperature and loss of MeCl, MCHex solvent and remaining styrene monomer were vacuum stripped, and sufficient THF was added to completely dissolve the polymer. The PIB−PS−PIB sample was then precipitated into a 5−10× volume excess of MeOH and dried under vacuum to yield a white solid product.

Star Polymer Synthesis. Miktoarm star terpolymers of the type (P*t*BA−PS−PIB)$_2$-*s*-P*t*BA were prepared by initiating *t*BA directly from unmodified PS−PIB−PS, which inherently carries *sec*-benzylic chloride PS chain ends as well as the bromoester functionality at the initiator moiety. However, to produce (PS−PIB)$_2$-*s*-P*t*BA, the *sec*-benzylic chloride chain ends had to be deactivated; this was achieved by heating PS−PIB−PS to 180−200 °C at 30 mmHg of vacuum overnight.

ATRP of *t*BA was performed using CuBr as the catalyst, PMDETA as the ligand, and PS−PIB−PS as the macroinitiator (MacroI) following the same procedure as previously reported for ATRP of methyl acrylate.[42] Polymerizations were performed using a molar ratio $[MacroI]_0$:$[CuBr]_0$:$[PMDETA]_0$ = 1:1:1 in toluene at 70 °C, with $[MacroI]_0$ = 0.01 M and with $[tBA]_0$ set at various levels to achieve different molecular weights. Conversion of *t*BA was limited to ~60% to avoid coupling. After polymerization, the solution was passed through a column packed with ion-change resin and neutral Al_2O_3 to remove copper salt. Then THF was added to completely dissolve the polymer, and the resulting solution was passed through a 0.2 μm filter to remove any remaining Al_2O_3. The solution was then precipitated into a 5−10× volume excess of MeOH, and white (PS−PIB)$_2$-*s*-P*t*BA was collected by filtration and dried under vacuum at room temperature.

To convert P*t*BA into PAA, the star polymers were exposed to 150 °C at 30 mmHg of vacuum overnight to obtain amphiphilic (PAA−PS−PIB)$_2$-*s*-PAA and (PS−PIB)$_2$-*s*-PAA miktoarm star polymers.

RESULTS AND DISCUSSION

Synthesis of DCCBMP. The key intermediate for DCCBMP, 3-(3,5-diisopropylphenyl)-3-methylbutyl 2-bromo-2-methylpropionate (DIPBMP), was produced by Friedel−Crafts alkylation of 1,3-diisopropylbenzene by 3-methyl-3-butenyl 2-bromo-2-methylpropionate, **3**, at −20 °C in a drybox. $AlCl_3$ was added at approximately an equal molar ratio to **3**, forming a thick, deep-red slurry. Low temperature was employed to prevent unwanted substitution reactions at other carbons on the 1,3-diisopropylbenzene.

^1H and ^{13}C NMR spectra of DIPBMP are shown in Figure 1. Upon alkylation, the olefinic protons in **3** disappeared, and the new methyl protons of the tether unit appeared at 1.38 ppm (peak a). The triplet at 4.03 ppm (peak e) was assigned to the methylene protons of the tether unit adjacent to the bromoester (1-H). The methylene protons further from the ester (2-H) were observed as a triplet at 2.02 ppm (peak d). The methyl groups of the 2-bromo-2-methylpropionate moiety (ATRP initiating site) exhibited a peak at 1.86 ppm (peak b). The splitting pattern of the aromatic proton peaks changed upon substitution at 1-Ph, yielding two main peaks at 6.92 ppm (peak g) and 7.02 ppm (peak f). Peak integration values were consistent with the proposed chemical structure. ^{13}C NMR data provided better resolved peaks for analysis. After **3** was attached to 1,3-diisopropylbenzene, the olefinic carbon peaks disappeared, and corresponding new peaks a and d appeared at 29.2 and 36.7 ppm, respectively. Peak l (1-PhC) shifted downfield to 147.8 ppm. Peaks i and j shifted upfield to 121.8 and 121.3 ppm, respectively. Only four peaks were observed in the aromatic carbon region, indicating that a symmetric structure was obtained and that substitution occurred only at the 1-Ph carbon.

In a previous report,[33] we used selective bromination of DIPBMP, followed by dehydrobromination, to produce the diolefin, 3-(3,5-diisopropenylphenyl)-3-methylbutyl 2-bromo-2-methylpropionate, an alternative intermediate for DCCBMP (Scheme 2, left). This route was less than satisfactory, however, because the purity of the liquid diolefin was only moderate, and it was difficult to purify by vacuum distillation. We therefore sought a different synthetic route, particularly one that yielded a solid intermediate that could be purified by recrystallization. We found that NHPI/$Co(OAc)_2$·$4H_2O$-catalyzed free radical aerobic oxidation (Scheme.2, right) works satisfactorily to convert DIPBMP into the di-*tert*-hydroxyl intermediate, DCOHBMP, which is a crystalline solid at room temperature.

Minisci et al. showed that aerobic oxidation of cumene using this catalyst system usually produces a methyl aryl ketone side product (i.e., acetophenone in the case of cumene);[35] however, selectivity toward the desired cumyl alcohol could be increased by using low reaction temperature and a nonpolar solvent medium. Solvents recommended by these authors, such as chlorobenzene and acetonitrile, as well as the nonpolar aliphatic solvent hexane, were tested as reaction solvents for the room temperature oxidation of DIPBMP. No reaction was observed for hexane, and only very low conversion was obtained with chlorobenzene. We next conducted a series of reactions in acetonitrile at various temperatures (40 °C, 23 and 0 °C). We found that the amount of methyl aryl ketone decreased from about 35% to 21% when the temperature was reduced from 40 to 23 °C, but the time to reach full conversion of the DIPBMP rose from <24 to about 72 h. At a reaction temperature of 0 °C, conversion was still very low (<10%) after 24 h; this was considered unreasonably slow, and the reaction was stopped. We concluded that the most convenient conditions for the reaction are the use of acetonitrile as the solvent at room temperature, despite the relatively long reaction time required.

Isolation and purification of DCOHBMP from the crude reaction mixture was carried out using a combination of column chromatography and recrystallization. The crude product was a sticky yellow liquid from which we were unable to obtain crystals from toluene without preliminary purification. Column chromatography (SiO_2) effectively removed both the methyl aryl ketone and hydroperoxy byproduct; however, it caused some loss of the desired product to olefin via dehydration. The product after column chromatography was a eutectic liquid that could be recrystallized from toluene to yield pure DCOHBMP as a stable, white solid. Since the olefin and hydroperoxy byproduct also yield the desired final product, DCCBMP, upon hydrochlorination, they could theoretically be further purified and hydrochlorinated to increase the overall yield; however, we did not attempt this optimization strategy in this initial study. High-resolution mass spectrometry (HRMS) analysis of the recrystallized product revealed two molecular ions, corresponding to the presence of either ^{79}Br and ^{81}Br, thus confirming the structure of DCOHBMP. Differential scanning calorimetry (DSC) revealed the mp to be 91.3 °C.

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Figure 2 shows the NMR characterization results for DCOHBMP. In the proton spectrum, the multiplet at 2.88

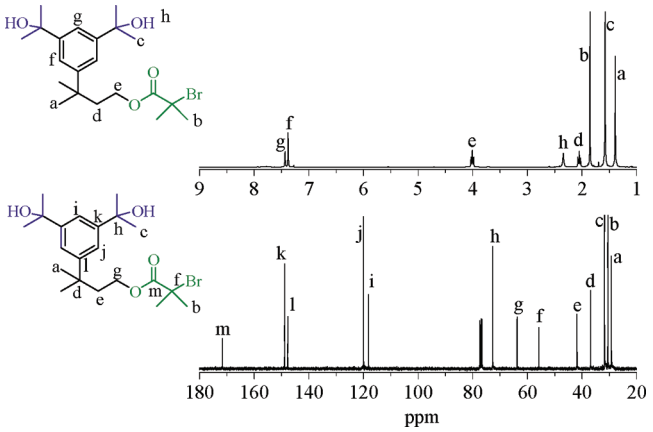

Figure 2. ^{1}H and ^{13}C NMR spectra of 3-[3,5-bis(1-hydroxy-1-methylethyl)phenyl]-3-methylbutyl 2-bromo-2-methylpropionate (DCOHBMP) obtained by the aerobic oxidation of DIPBMP.

ppm (peak j, Figure 1) associated with the benzylic protons of DIPBMP was absent. The doublet representing the methyl protons of the isopropyl groups, formerly at 1.25 ppm (peak c, Figure 1), was converted into a singlet at 1.60 ppm (peak c) upon aerobic oxidation. A new peak representing the hydroxyl proton appeared at 2.31 ppm (peak h). Peaks f and g shifted downfield to 7.40 and 7.43 ppm. Integrated areas of all peaks were within 98.7% of the theoretical value. In the carbon spectrum, the oxidized carbon and adjacent methyl carbons shifted downfield to 72.8 ppm (peak h) and 31.9 ppm (peak c), respectively, and peak i shifted upfield. The other three aromatic carbon peaks, as well as all carbon signals for the bromoester tail, were observed at essentially the same chemical shift in reactant and product.

Figure 3 shows the ^{1}H and ^{13}C NMR spectra of pure DCCBMP prepared by chlorination of DCOHBMP. The methyl protons adjacent to chlorine were observed at 2.01 ppm (peak c), which represents a downfield shift relative to their position in the precursor. Peaks associated with the aromatic protons shifted slightly downfield to 7.50 (peak f) and 7.62 (peak g) ppm. The carbon attached to chlorine and the

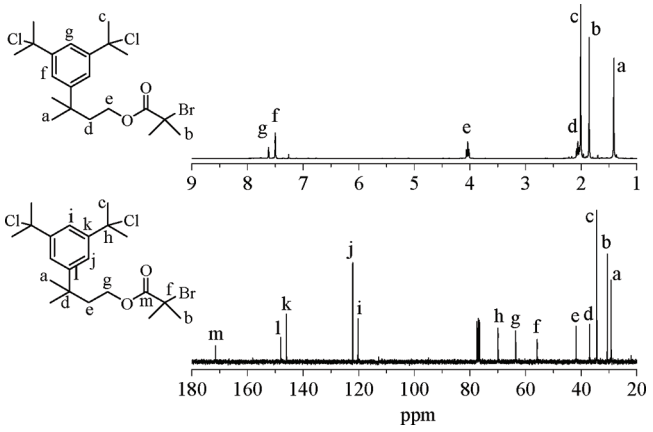

Figure 3. ^{1}H and ^{13}C NMR spectra of 3-[3,5-bis(1-chloro-1-methylethyl)phenyl]-3-methylbutyl 2-bromo-2-methylpropionate (DCCBMP).

adjacent methyl groups shifted to 69.9 and 34.4 ppm, respectively. Moreover, the ^{13}C NMR spectrum consisted of exactly 13 signals, which were unambiguously assigned to the 13 carbons in DCCBMP, providing further evidence that the targeted structure was obtained.

Initiation Performance Test. Three PIB samples, PIB-5K, PIB-10K, and PIB-20K, were prepared in order to study the cationic initiation performance of DCCBMP. Table 1 lists NMR and SEC characterization data for these samples. Figure 4 shows the proton NMR spectrum of a representative sample, PIB-5k. The PIB backbone methyl and methylene protons appear at about 1.1 ppm (peak o) and 1.4 ppm (peak p), respectively. Characteristic peaks for the DCCBMP initiator, b, e, f, and g, are present, indicating that the radical initiating site remains intact after cationic polymerization. Number-average functionality with respect to the ATRP initiating site, $\bar{F}_{n,Br}$, was quantified and found to be in the range 0.93−1 (Table 1). $\bar{F}_{n,Br}$ was calculated from ^{1}H NMR data using eq 1, where A_{CH_2O} is the integrated area of the methylene protons adjacent to the ester group (peak e) and A_{CE} is the sum of the integrated peak areas of characteristic resonances representing the various polymer chain ends, defined by eq 2.

$$\bar{F}_{n,Br} = \frac{A_{CH_2O}}{A_{CE}} \tag{1}$$

$$A_{CE} = A_{exo} + A_{endo} + A_{tert\text{-}Cl}/2 + 2A_{coupled} \tag{2}$$

In eq 2, A_{exo} is the area of the upfield *exo*-olefinic resonance at 4.64 ppm, A_{endo} is the area of the single *endo*-olefinic resonance at 5.15 ppm, and $A_{tert\text{-}Cl}$ is the area of the resonance at 1.96 ppm due to the methylene protons of the *tert*-chloride end group. $A_{coupled}$ was calculated as follows:

$$A_{coupled} = \frac{(A_{4.75-5.0} - A_{exo})}{2} \tag{3}$$

where $A_{4.75-5.0}$ is the integrated area of the convoluted peaks from 4.75 to 5.0 ppm associated with the downfield *exo*-olefinic proton and the two identical protons of the coupled product. Equation 2 represents our standard protocol for determination of PIB end group composition and accounts for the possible occurrence of all likely terminal chain end types, regardless of whether they are actually present in the sample. In the present case, the vast majority of the end groups are *tert*-Cl (>96% for all samples).

In Table 1, initiation efficiency of DCCBMP, I_{eff}, was calculated as $\bar{X}_{n,theo}/\bar{X}_{n,PIB}$ and $\bar{M}_{n,theo}/\bar{M}_{n,PIB}$ from NMR and SEC/MALLS data, respectively. $\bar{X}_{n,theo}$ was calculated as the molar ratio of monomer to initiator charged to the reactor; $\bar{M}_{n,theo} = (\bar{X}_{n,theo} \times M_{IB}) + M_I$, where M_{IB} and M_I are the molecular weights of isobutylene and the initiator, respectively. $\bar{X}_{n,PIB}$ was calculated from ^{1}H NMR data using eq 4,

$$\bar{X}_{n,PIB} = \frac{\frac{A_{Me}}{3}}{A_{CE}} + 2 \tag{4}$$

where, A_{Me} is the integrated peak area of the methyl protons in the PIB repeat unit. I_{eff} of DCCBMP characterized by NMR spectroscopy was 0.93−0.95. The SEC eulograms of all three PIBs were symmetrical, and PDIs were all less than 1.02. I_{eff} calculated from SEC data were in the range 0.89−0.98.

Control experiments were conducted under the same conditions using the standard difunctional cationic initiator,

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Table 1. Characterization of PIBs Prepared from Di-cationic Mono-radical Dual Initiator, DCCBMP, and Control Difunctional Cationic Initiator, *t*-Bu-*m*-DCC[a]

	NMR				SEC				
	$\bar{X}_{n,PIB}$	$\bar{X}_{n,theo}$	$\bar{F}_{n,Br}$	I_{eff}	$\bar{M}_{n,PIB}$ (g/mol)	$\bar{M}_{n,theo}$ (g/mol)	I_{eff}	PDI	$I_{eff,\ t\text{-Bu-}m\text{-DCC}}$
PIB-5K	89	82	0.97	0.92	5700	5070	0.89	1.02	0.97
PIB-10K	175	164	0.93	0.94	10 170	9670	0.95	1.01	1.00
PIB-20K	358	340	1.00	0.95	20 020	19 540	0.98	1.01	0.99

[a] −70 °C; 60/40 MCHex/MeCl cosolvents (v/v); $[IB]_0$ = 1.00 M; $[2,6\text{-lutidine}]_0$ = 4.00 mM. $[I]_0$ = 12.2 mM; $[TiCl_4]_0$ = 48.8 mM for 5K samples. $[I]_0$ = 6.10 mM; $[TiCl_4]_0$ = 48.8 mM for 10K samples. $[I]_0$ = 3.05 mM; $[TiCl_4]_0$ = 91.5 mM for 20K samples.

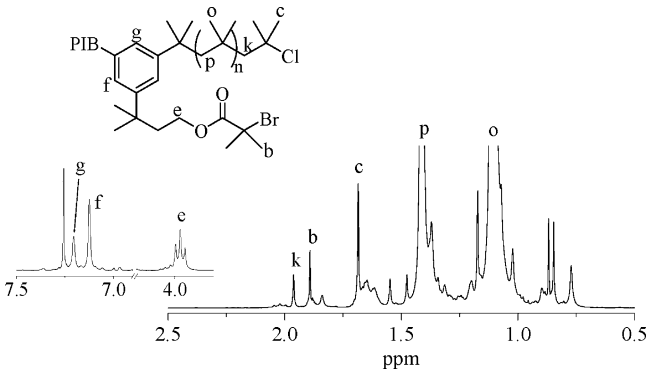

Figure 4. ^{1}H NMR spectrum of PIB-5K initiated by DCCBMP.

5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene (*t*-Bu-*m*-DCC). PDIs of the resulting PIBs were the same as those obtained from DCCBMP, i.e., less than 1.02. I_{eff}s calculated from SEC data were ∼1, comparable with those of DCCBMP. In addition, real-time ATR-FTIR monitoring of IB polymerizations initiated from DCCBMP yielded linear first order kinetic plots, similar to those obtained with *t*-Bu-*m*-DCC, as illustrated in Figure 5. These results show that the presence of

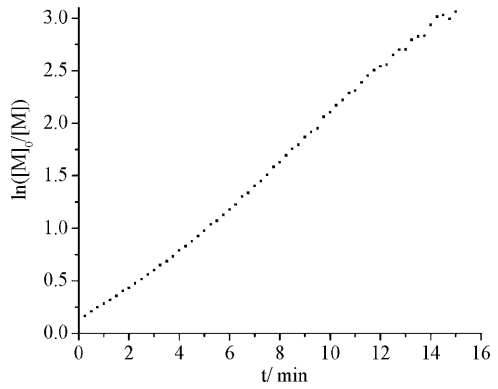

Figure 5. First-order kinetic plot for DCCBMP-initiated IB polymerization at −70 °C. Conditions were as follows: 60/40 Hex/MeCl cosolvents (v/v); $[IB]_0$ = 1.00 M; $[2,6\text{-lutidine}]_0$ = 4.00 mM; $[DCCBMP]_0$ = 12.2 mM; $[TiCl_4]_0$ = 48.8 mM targeting 5k.

the ATRP initiating site on DCCBMP does not interfere with or present any special problems in LCP and that pure DCCBMP prepared via the aerobic oxidation route enables precise control over molecular weight, polydispersity, and functionality of the resulting polymers.

PS−PIB−PS Synthesis. PS−PIB−PS triblock copolymers with bromoester functionality at the approximate center of PIB block were prepared via sequential LCP of IB and then styrene, using DCCBMP as the initiator. Results of SEC analysis of these copolymers are given in Table 2 and Figure 6. As listed in Table 2, PS−PIB−PS macroinitiators were prepared with very

Table 2. Molecular Weight Data for PS−PIB−PS Macroinitiators Prepared from DCCBMP via LCP and Sequential Monomer Addition[a]

	$M_{n,PIB}$ (g/mol)	$M_{n,PS-PIB-PS}$ (g/mol)	PDI
PS−PIB−PS-1[b]	11 380	20 150	1.06
PS−PIB−PS-2[c]	20 020	32 060	1.02

[a] −70 °C; 60/40 MCHex/MeCl cosolvents (v/v); $[IB]_0$ = 1.00 M; $[2,6\text{-lutidine}]_0$ = 4.00 mM; $[St]_0$ = 0.4 M. [b] $[DCCBMP]_0$ = 6.1 mM; $[TiCl_4]_0$ = 61.0 mM; $[St]_0/[DCCBMP]_0$ = 96; conv.(styrene) = 0.88 calculated based on SEC result. [c] $[DCCBMP]_0$ = 2.94 mM; $[TiCl_4]_0$ = 88.2 mM; $[St]_0/[DCCBMP]_0$ = 160; conv.(styrene) = 0.72 calculated based on SEC result.

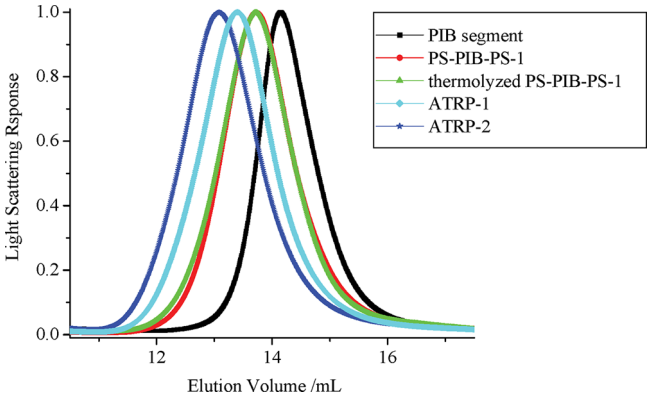

Figure 6. SEC elution curves of PIB segment in PS−PIB−PS-1 (black), PS−PIB−PS-1 (red), PS−PIB−PS-1 after thermolysis (green), which overlaps with PS−PIB−PS-1, and $(PS-PIB)_2$-*s*-P*t*BA star polymers, ATRP-1 (cyan) and ATRP-2 (blue).

narrow PDIs (1.06 for PS−PIB−PS-1, 1.02 for PS−PIB−PS-2). The targeted molecular weight of the PIB block in PS−PIB−PS-1 was 9670 g/mol; the experimental molecular weight was 11 380 g/mol, yielding I_{eff} = 0.85. For PS−PIB−PS-2, the experimental $\bar{M}_{n,PIB}$ (20 020 g/mol) was almost the same as $\bar{M}_{n,theo}$ (19 540 g/mol), yielding I_{eff} = 0.98. Conversion of styrene (0.88 for PS−PIB−PS-1, 0.72 for PS−PIB−PS-2) was higher than targeted (0.50), because of the difficulty of estimating the initial absorbance at 907 cm^{-1}, when styrene is added to the system already containing $TiCl_4$. Thus, the PS−PIB−PS polymers were composed of more PS volume than the designed value.

Figure 6 shows the progression of SEC elution curves during the synthesis of PS−PIB−PS-1, which is representative. PIB initiated by DCCBMP (black) was characterized by a narrow and symmetrical peak. Elution profile of the triblock copolymer

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(red) was still symmetrical but shifted to lower elution volumes, indicating that LCP of the second monomer, styrene, occurred to form the targeted triblock copolymer.

Figure 7 (upper) shows the ^{1}H NMR spectrum of a representative sample, PS−PIB−PS-2. The styrene backbone

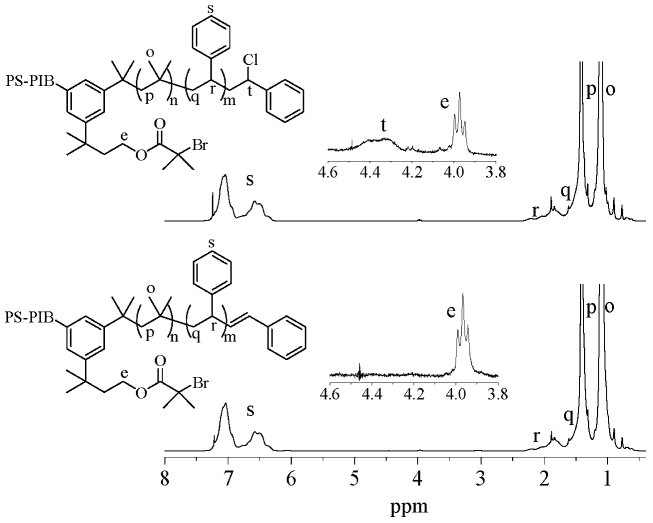

Figure 7. ^{1}H NMR spectra of PS−PIB−PS-2 before (upper) and after thermolysis (lower).

methylene and methine protons were observed at 1.4 ppm (peak q) and 1.8 ppm (peak r). The broad peaks at 6.4−7.2 ppm (collectively denoted s) were assigned to the aromatic protons both of the PS block and DCCBMP initiator. The methylene protons next to the bromoester group were observed as a well-defined triplet at 4.0 ppm (peak e). The characteristic broad absorbance due to the ultimate CH of the PS block (*sec*-benzyl chloride proton, peak t) was observed at 4.3−4.4 ppm.

Star Polymers Synthesis. As illustrated in Scheme 2, quenching LCP of styrene with MeOH produces *sec*-benzylic chloride end groups, which are known to be active ATRP initiation centers.[21−23] To selectively grow *t*BA only from the designated bromoesters, PS−PIB−PS macroinitiators were thermolyzed to eliminate HCl and thus deactivate the PS chain ends. After thermolysis, the broad peak associated with the *sec*-benzyl chloride CH at 4.3−4.4 ppm disappeared, as shown in the lower spectrum in Figure 7. Small peaks appeared at 3.1 and 6.1 ppm, which were attributed to the newly formed olefinic chain ends. PS−PIB−PS macroinitiators were reanalyzed by SEC after thermolysis, and as expected, the molecular weights of the treated and untreated PS−PIB−PS were about the same. As shown in Figure 7, the elution curve of the thermolyzed PS−PIB−PS-1 (green) overlaps with PS−PIB−PS-1 (red), indicating that the treated and untreated macroinitiators differ only at the PS chain ends.

ATRP of *t*BA was next used to produce (P*t*BA−PS−PIB)$_2$-*s*-P*t*BA and (PS−PIB)$_2$-*s*-P*t*BA miktoarm terpolymers from PS−PIB−PS and thermolyzed PS−PIB−PS macroinitiators, respectively. SEC characterization results for these star polymers are given in Table 3. PS−PIB−PS macroinitiators, either in their original state or after thermal deactivation of the PS chain ends, worked well in ATRP. The P*t*BA segments of the resulting miktoarm stars possessed molecular weights very close to the targeted values, and the overall PDIs were narrow (<1.1).

Table 3. Molecular Weight Data for (PS−PIB)$_2$-*s*-P*t*BA and (P*t*BA−PS−PIB)$_2$-*s*-P*t*BA Star Polymers Prepared via ATRP[a]

	$[t\text{BA}]_0/[\text{MacroI}]_0$	$M_{n,star}$ (g/mol)	$M_{n,PtBA}$ (g/mol)	$\bar{M}_{n,theo}$	PDI
ATRP-1[b]	100	26 120	5970	7690	1.08
ATRP-2[b]	200	36 350	16 200	15 380	1.07
ATRP-3[c]	100	40 250	8190	7690	1.02
ATRP-4[c]	580	77 450	45 390	45 140	1.03

[a]70 °C; toluene; $[\text{MacroI}]_0$ = 0.01 M; $[\text{MacroI}]_0$:$[\text{CuBr}]_0$:$[\text{PMDETA}]_0$ = 1:1:1; quenched at 60% *t*BA conversion. [b]using thermolyzed PS−PIB−PS-1 as macroinitiator, producing (PS−PIB)$_2$-*s*-P*t*BA star polymers. [c]using PS−PIB−PS-2 as macroinitiator, producing (P*t*BA−PS−PIB)$_2$-*s*-P*t*BA star polymers.

Figure 6 illustrates the SEC elution curves of (PS−PIB)$_2$-*s*-P*t*BA star polymers, ATRP-1 (cyan) and ATRP-2 (blue), initiated by thermolyzed PS−PIB−PS-1. Both star polymers possessed narrow PDIs (<1.1), and the elution profiles were symmetrical with no apparent shoulders, indicating very high blocking efficiency from the macroinitiator and negligible radical−radical coupling during ATRP. High blocking efficiency confirms that the ATRP initiating site of the DCCBMP initiator survives LCP and thermolysis at 180−200 °C.

Figure 8 (upper) shows the ^{1}H NMR spectrum of (P*t*BA−PS−PIB)$_2$-*s*-P*t*BA star polymer (ATRP-3). Addition of the

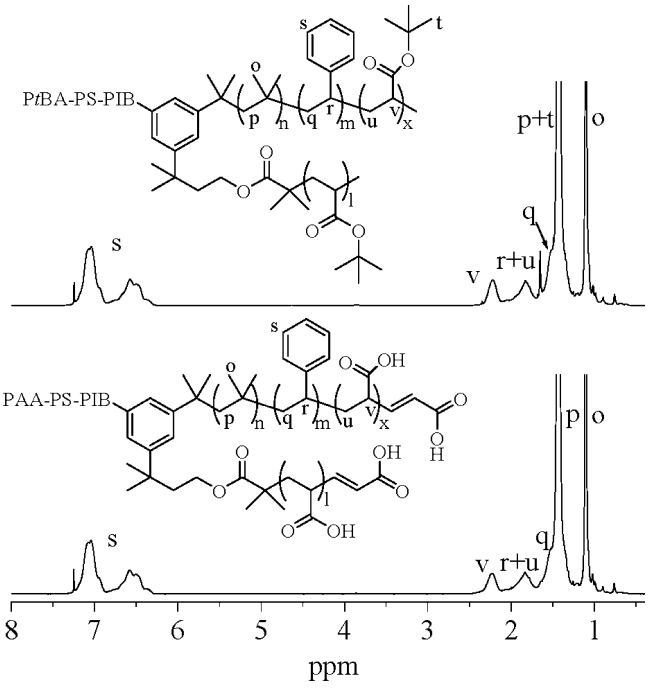

Figure 8. ^{1}H NMR spectra of (P*t*BA−PS−PIB)$_2$-*s*-P*t*BA (ATRP-3) star polymer (upper), and the corresponding (PAA−PS−PIB)$_2$-*s*-PAA obtained by thermolysis (lower).

P*t*BA blocks introduced new peaks at 1.5 (peak u) and 2.2 ppm (peak (v), corresponding to the methylene and methine backbone protons, respectively, of P*t*BA. As expected, (PS−PIB)$_2$-*s*-P*t*BA prepared from thermolyzed PS−PIB−PS showed the same characteristic proton signals.

Thermolysis has been reported to eliminate isobutylene molecules from P*t*BA via β-type scission and thus produce PAA hydrophilic blocks.[32] This technique proved to also work very

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well for the present systems. Figure 8 (lower) shows the ^{1}H NMR spectrum of (PAA−PS−PIB)$_2$-*s*-PAA polymer obtained after thermolysis. The integrated area for the combined PIB backbone methylene and P*t*BA *tert*-butyl protons (peak p and t) decreased. ^{13}C NMR gave better evidence for removal of the *tert*-butyl groups. Figure 9 shows ^{13}C NMR spectra of ATRP-3

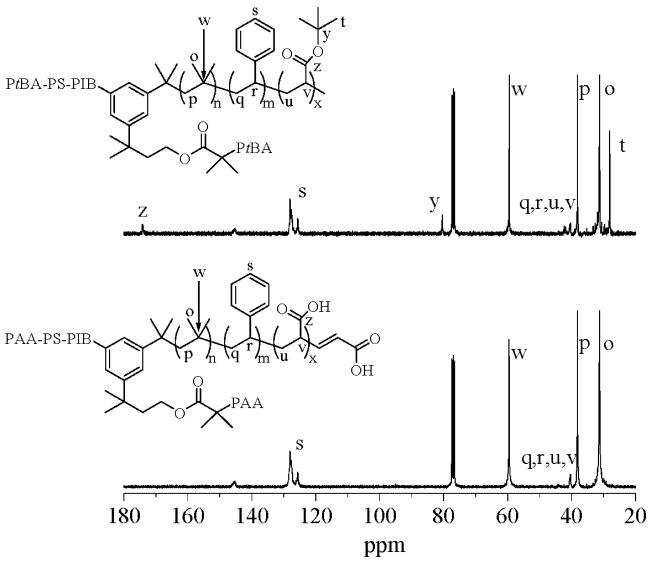

Figure 9. ^{13}C NMR spectra of (P*t*BA−PS−PIB)$_2$-*s*-P*t*BA (ATRP-3) star polymer (upper) and the corresponding (PAA−PS−PIB)$_2$-*s*-PAA obtained by thermolysis (lower).

before (upper) and after thermolysis (lower). The methyl and quaternary carbons of the *tert*-butyl groups of P*t*BA, which appear at 81 ppm (peak y) and 29 ppm (peak t) in the upper spectrum, as reported,[32,47] completely disappear after thermolysis.

CONCLUSIONS

The dual initiator DCCBMP containing two *tert*-benzylic chloride groups for LCP initiation and one α-bromoester for ATRP initiation was synthesized in four steps. Instead of free radical bromination of the DIPBMP intermediate,[33] a new aerobic oxidation using NHPI and Co(OAc)$_2$·4H$_2$O catalyst system was employed to convert DIPBMP into DCOHBMP, a new compound that may be purified by recrystallization. The chemical structure of this crystalline solid was confirmed by proton NMR spectroscopy and HRMS, and its melting point was determined by DSC to be 91.3 °C. Chlorination of DCOHBMP yielded the final product, DCCBMP, as a light yellow liquid. The chemical structure of DCCBMP was confirmed by NMR spectroscopy. Compared with free radical bromination, this mild aerobic oxidation reaction can easily convert benzylic CH(CH$_3$)$_2$ into COH(CH$_3$)$_2$ without destroying other functional groups. Although side products were observed, which reduced the yield, the technique provides a better synthetic route and can be potentially applied to the syntheses of other cumyl-type cationic polymerization initiators.

The initiation performance of DCCBMP was investigated by conducting TiCl$_4$-catalyzed IB polymerizations at −70 °C. FTIR spectroscopy demonstrated a linear first-order kinetic plot that passes through the origin, indicating fast initiation and a constant concentration of active chain ends during polymerization. SEC results showed that high initiation efficiency (I_{eff} = 0.89−0.98) and near-monodisperse polymers (PDI ≤ 1.02) were obtained when DCCBMP was used to polymerize IB, targeting molecular weights of 5k, 10k and 20K g/mol. The cationic initiation performance of DCCBMP was essentially identical to the standard aromatic difunctional cationic initiator, *t*-Bu-*m*-DCC, which was utilized as a control (Table 1). The bromoester functionality, which was designed for the subsequent ATRP, was observed in the proton NMR spectrum of the resulting PIB. The number-average functionality, $\bar{M}_{n,Br}$ was calculated to be 0.93−1.00, indicating that radical initiating group was intact during IB polymerization.

DCCBMP was utilized to prepare a series of amphiphilic (PAA−PS−PIB)$_2$-*s*-PAA and (PS−PIB)$_2$-*s*-PAA miktoarm star polymers using a combination of LCP, sequential monomer addition, and ATRP techniques. PS−PIB−PS triblock copolymers were produced by living carbocationic polymerization of IB followed by sequential addition of styrene. After quenching with MeOH, the polymers thus obtained carried *sec*-benzylic chloride groups at the PS chain ends, which are able to initiate radical polymerization. Thus, as obtained, these polymers possessed three ATRP initiating sites and were used to produce (P*t*BA−PS−PIB)$_2$-*s*-P*t*BA miktoarm star polymers.

The PS terminal functionality could alternatively be selectively deactivated by heating the polymers to 180−200 °C in a vacuum oven. Proton NMR spectra showed that only *sec*-benzylic chloride groups were removed, with no change observed for the bromoester group. SEC characterization of PS−PIB−PS macroinitiators before and after thermolysis generated identical polymer elution profiles, indicating that there were no backbone structural changes. Thermolyzed PS−PIB−PS macroinitiators enabled P*t*BA growth only from the bromoester group, yielding (PS−PIB)$_2$-*s*-P*t*BA star polymers under the same ATRP conditions.

Both types of miktoarm stars were prepared with designed composition and narrow PDIs (<1.1) as confirmed by NMR and SEC analysis. Upon thermolyzing these star polymers, P*t*BA was completely converted to PAA, yielding amphiphilic PIB-based star polymers (PAA−PS−PIB)$_2$-*s*-PAA and (PS−PIB)$_2$-*s*-PAA, in which the third block can share an interface with the PIB block. Their intriguing self-assembly behavior in aqueous solution as well as phase-separated morphology in the solid state are currently being investigated.

ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra (CDCl$_3$, 23 °C) of diolefin byproduct, 3-(3,5-diisopropenylphenyl)-3-methylbutyl 2-bromo-2-methylpropionate, dihydroperoxy byproduct, 3-[3,5-bis(1-hydroperoxy-1-methylethyl)phenyl]-3-methylbutyl 2-bromo-2-methylpropionate, and monohydroxy, monohydroperoxy byproduct, 3-[3-(1-hydroperoxy-1-methylethyl)-5-(1-hydroxy-1-methylethyl)phenyl]-3-methylbutyl 2-bromo-2-methylpropionate, of the NHPI/Co(OAc)$_2$·4H$_2$O catalyzed aerobic oxidation of DIPBMP. 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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