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One-Pot Synthesis of Natural Rubber-Based Telechelic *cis*-1,4-Polyisoprenes and Their Use To Prepare Block Copolymers by RAFT Polymerization

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ABSTRACT: We investigate the one-pot synthesis of a new α,ω-bistrithiocarbonyl-end functionalized telechelic *cis*-1,4-polyisoprene (Pip) via metathesis degradation from natural rubber (NR) in the presence of the Grubbs second generation catalyst (GII) and a bistrithiocarbonyl-end functionalized olefin as a chain transfer agent (CTA). When the metathesis degradation of the NR of 2×10^6 g mol^{-1} molecular weight is performed in toluene at 25 °C using the ratio of $[\mathrm{Ip}]_0/[\mathrm{GII}]_0/[\mathrm{CTA}]_0 = 100/1/1$ (Ip = isoprene units), a *cis*-1,4-polyisoprene of 14 000 g mol^{-1} after 4 h is obtained. The functionality estimated by ^{1}H NMR spectroscopy is equal to 1.5 ± 0.1. The structure of telechelic *cis*-1,4-polyisoprene was confirmed by combination of ^{1}H NMR, ^{13}C NMR spectroscopy and FTIR. The influence of the CTA concentration was investigated. It was found that using higher concentrations of CTA ($[\mathrm{Ip}]_0/[\mathrm{GII}]_0/[\mathrm{CTA}]_0$ of 100/1/2 and 100/1/5) lead to form a perfectly telechelic *cis*-1,4-polyisoprene with a functionality of 2 with no significant difference in $\overline{M}_n$ values (approximately 6400 g mol^{-1}) and in polydispersity indices (~1.70). The new well-defined α,ω-bistrithiocarbonyl-end functionalized telechelic *cis*-1,4-polyisoprenes were used successfully as macromolecular chain transfer agents (macroCTAs) to mediate the RAFT polymerization of *t*-BA using AIBN as the initiator ($[t\text{-BA}]_0/[\mathrm{macroCTA}]_0/[\mathrm{AIBN}]_0 = 500/1/0.4$) in toluene at 60 °C leading to well-defined P(*t*-BA)-*b*-PIp-*b*-P(*t*-BA) triblock copolymers.

Introduction

Telechelic unsaturated polymers are good candidates to obtain block copolymers with a wide range of applications. For instance, block copolymers containing polyisoprene (PIp) as a constituent have found applications as nanofibers,[1] thermoplastic elastomers,[2] pressure sensitive adhesives,[3,4] and biocompatible materials.[5,6] The PIp block is essentially synthesized by living anionic polymerization of isoprene (Ip),[7−16] by controlled/living radical polymerization (CRP) of isoprene,[17−27] or ring-opening metathesis polymerization of 1,5-dimethyl-1,5-cyclooctadiene.[28] The *cis*-1,4-polyisoprene block can be obtained from natural rubber (NR) which is a biomacromolecule and a renewable resource. It is well-known that strictly *cis*-1,4-microstructure of NR provides unique and special properties, including good elastomeric properties, very low glass transition temperature, excellent flexibility, good "green" strength, and building tack. Therefore, the synthesis of telechelic *cis*-1,4-polyisoprene from NR (TNR) opens new synthetic routes to develop materials based on a biopolymer from a renewable resource. The block copolymers obtained from NR can lead to new materials with properties suitable for a number of potential applications including microemulsion elastomers[29] for the paint industry, adhesives,[3,4] and nanoporous materials.[30] The transformation of NR into TNR can be obtained by combining chain cleavage reaction of NR with a postfunctionalization reaction. The most widely used methods to produce TNR derivatives are controlled oxidative degradation, photodegradation or metathesis degradation.[31] Our group has focused on selective degradation of synthetic *cis*-1,4-polyisoprene using well-controlled oxidative chain cleavage reaction leading to new carbonyl telechelic *cis*-1,4-polyisoprene[32] and the chemical modification of carbonyl end-groups has led to the development of new hydroxyl[6,33] and amino telechelic polyisoprenes.[34] The hydroxyl telechelic polyisoprene was engaged as a precursor in the synthesis of linear polyurethanes for biological materials[6] and foams applications.[35,36] However, this technique requires several steps to obtain the precursor of the desired products. Alternatively, we have also developed a method for the preparation of acetoxy-telechelic polyisoprene in a single-step process via the metathesis degradation of *cis*-1,4-polyisoprene.[37,38] To the best of our knowledge, no study has been reported on the single-step synthesis of telechelic *cis*-1,4-polyisoprene suitable to be employed as precursors for controlled/living radical polymerizations (CRPs) in order to obtain block copolymers. Among CRP techniques,[39] reversible addition/fragmentation chain transfer (RAFT) polymerization[40] is recognized as one of the most versatile method for the synthesis of block copolymers since it is compatible with a wide range of unprotected polar monomers[41] including acrylic acid.[42] The most common RAFT chain transfer agent (CTA) contains thiocarbonylthio groups that are easily removed or modified by a variety of methods.[43]

Herein, we have investigated the one-pot synthesis of original telechelic *cis*-1,4-polyisoprenes (PIp) through a metathesis degradation of NR using Grubbs second generation catalyst (GII) and a bistrithiocarbonyl-end functionalized olefin as a CTA (**2**, Scheme 1A). The resulting PIp were used as difunctional macroCTAs to mediate the polymerization of *tert*-butyl acrylate to form ABA triblock copolymers via the RAFT process. To the best of our knowledge, no previous studies have been reported on the one-pot synthesis of such α,ω-bistrithiocarbonyl-end functionalized telechelic *cis*-1,4-polyisoprene suitable to be used in RAFT polymerization.

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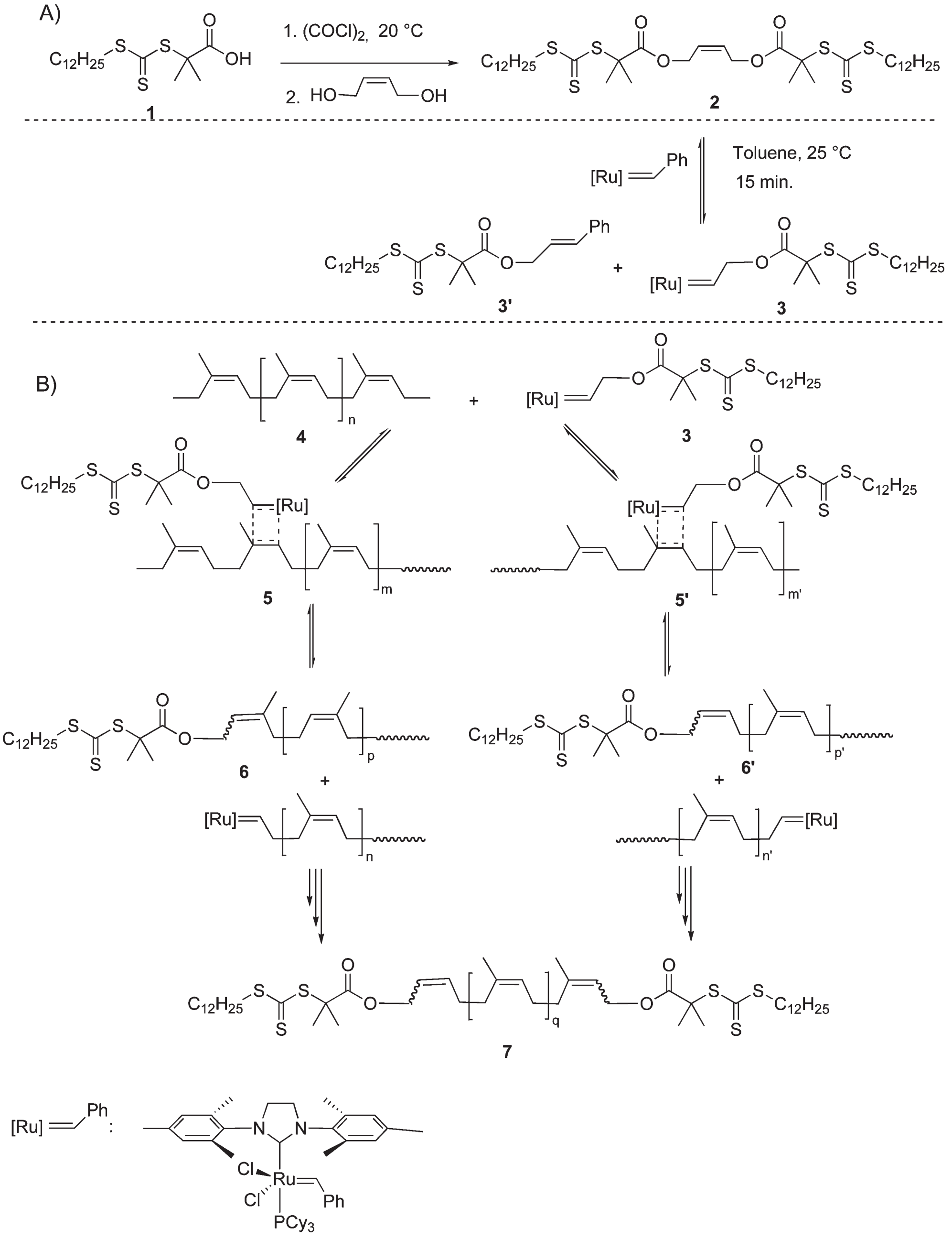
Scheme 1. Synthesis of the Bistrithiocarbonyl-End Functionalized CTA 2 (A) and Synthesis of α,ω-Bistrithiocarbonyl-*cis*-1,4-polyisoprene 7 from Natural Rubber (NR) *via* Metathesis Degradation (B)



Experimental Section

General Characterization. NMR spectra were recorded on a Bruker Avance 400 spectrometer for ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz). Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). Molecular weights and molecular weight distributions were measured using size exclusion chromatography (SEC) on a system equipped with a SpectraSYSTEM AS 1000 autosampler, with a Guard column (Polymer Laboratories, PL gel 5 μm Guard column, 50 × 7.5 mm) followed by two columns (Polymer Laboratories, 2 PL gel 5 μm MIXED-D columns, 2 × 300 × 7.5) and with a SpectraSYSTEM RI-150 detector. The eluent used was tetrahydrofuran (THF) at a flow rate of 1 mL min^{-1} at 25 or 35 °C. Narrow molecular weight linear polystyrene standards (ranging from 580 g mol^{-1} to 4.83 × 10^5 g mol^{-1}) were used to calibrate the SEC. Infrared spectra were recorded on a Nicolet Avatar 370 DTGS FT-IR spectrometer in the 4000−500 cm^{-1} range with KBr pellets and controlled by OMNIC software. Matrix-assisted laser desorption ionization time-of-flight (MALDI−TOF) mass spectra were recorded on a Bruker Biflex III equipped with a nitrogen laser (lZ337 nm). All mass spectra were obtained in the linear mode with an acceleration voltage of 19 kV. The delay time was 200 ns. Typically, 100 single-shot acquisitions were summed to give a composite mass spectrum. All data were reprocessed using the Bruker XTOF software. Thermal transition of samples was measured by DSC Q100 (TA Instrument) differential scanning calorimeter equipped with the cooling system that temperature can be decreased to −90 °C. Samples were put in the aluminum capsule and empty capsule was used as inert reference. All experiments were carried out under nitrogen atmosphere at flow rate 50 mL/min with weight of sample from 5 to 10 mg. Two scans from −80 to +60 °C were performed with a heating and cooling rate of 10 °C/min, and the glass transition temperature was recorded.

Materials. All chemicals were purchased from Aldrich unless otherwise noted. Oxalyl chloride (99%), *cis*-but-2-ene-1,4-diol

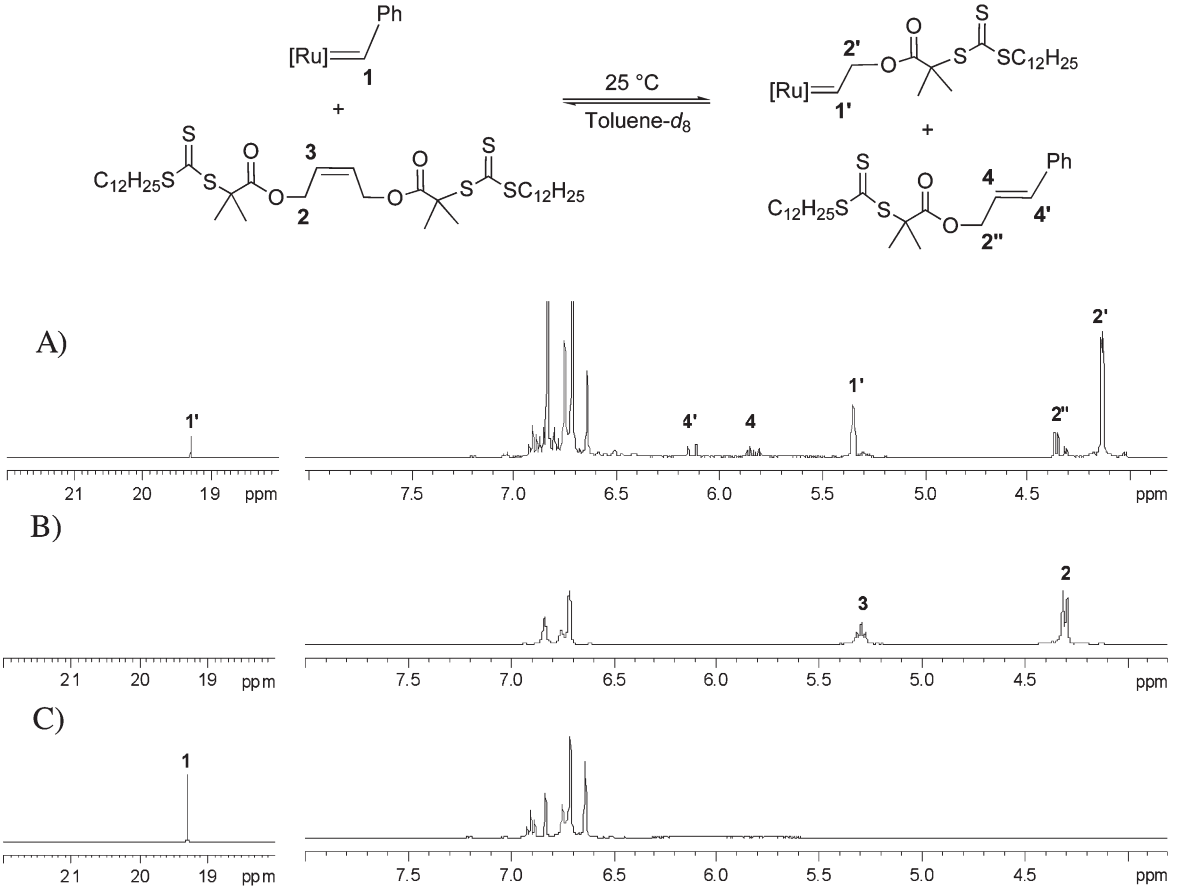


Figure 1. ^{1}H NMR spectra (toluene-d_8) of the resulting mixture solution between CTA and Grubbs II catalyst (A), CTA **2** (B), and Grubbs II catalyst (C).

(97%), toluene (99%), ethyl vinyl ether (99%), tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] benzylidineruthenium(IV) dichloride (99%+) (Grubbs second generation catalyst, GII), 2-propanol (99%) (Fisher Scientific), and anisole (99%) were used as received. Dichloromethane (99%+) and methanol (99%) were distilled over CaH_2 prior to use. *tert*-butyl acrylate (*t*-BA, 99%) was purified by passing through neutral alumina column to remove inhibitor. 2,2-Azobis(2-methylpropionitrile) (AIBN, 98%) was recrystallized into methanol prior to use. NR latex was preserved with ammonia solution 0.7% (w/w) (dry rubber content, DRC = 60%, $\overline{M}_w = 2 \times 10^6$ g mol^{-1}, Pattani Industrial, Thailand) and non rubber impurities were removed by urea treatment, nonionic surfactant washing and double centrifugation followed by coagulation with methanol and dried.[44] The RAFT agent, *S*-1-dodecyl-S′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate, (**1**, Scheme 1A) was prepared according to a procedure reported in the literature.[45] The bistrithiocarbonyl-end functionalized olefin used as CTA (**2**, Scheme 1A) was synthesized as described previously.[46]

Functional Metathesis Degradation Procedure. A general procedure for metathesis degradation of NR to obtain difunctional telechelic *cis*-1,4-polyisoprene (**7**, Scheme 1B) is described. A magnetic stirrer was charged to a dry Schlenk tube fitted with a rubber septum. A degassed solution of purified NR (0.7 g, 0.0103 mol) dissolved in toluene (20 mL) was added. Separately, a solution of the difunctional CTA (**2**, Scheme 1A) (0.1606 g, 0.2056 mmol) and Grubbs II catalyst (GII, 0.0873 g, 0.1028 mmol) in toluene (4 mL) was degassed by sparging with argon and stirred for 15 min. The resulting solution of difunctional CTA and Grubbs II catalyst was transferred into the solution of NR using a degassed syringe (defining t = 0) at 25 °C. Aliquots were withdrawn from the reaction solution after 2, 4, 6, and 8 h. When this time had elapsed the metathesis reaction was quenched by adding ethyl vinyl ether into the reaction solution under an argon atmosphere. The resulting solution was concentrated under vacuum at room temperature and was purified by a series of precipitations from dichloromethane (minimum volume) into 2-propanol (100 mL) at room temperature. The isolated polymer was dried under vacuum to remove any trace of solvent. It was then further analyzed by ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, FTIR spectroscopy and SEC. Yield: 76%. **^{1}H NMR** ($CDCl_3$): δ (ppm) 5.86−5.70 (br, chain-end, *cis* $-C\mathit{H}{=}C\mathit{H}$), 5.60−5.50 (br, chain-end, *trans* $-C\mathit{H}{=}C\mathit{H}$), 5.38−5.28 (br, chain-end; $-C(CH_3){=}C\mathit{H}-$), 5.14 (br, polyisoprene backbone, $-C(CH_3){=}C\mathit{H}$), 4.72−4.65 (d, chain-end, $-C(CH_3){=}CH-C\mathit{H_2}OC(O)-$), 4.65−4.56 (d, chain-end, $-C(CH_3){=}CH-C\mathit{H_2}OC(O)-$ and $-CH{=}CH-C\mathit{H_2}OC(O)-$), 4.56−4.50 (d, chain-end, $-CH{=}CH-C\mathit{H_2}OC(O)-$), 3.25 (t, $C(S)-SC\mathit{H_2}CH_2$-R), 2.12−1.95 (br, polyisoprene backbone, $-C\mathit{H_2}C(CH_3){=}CH-$ and $-C(CH_3){=}CHC\mathit{H_2}$), 1.70−1.60 (br, polyisoprene backbone, $-C(C\mathit{H_3}){=}CH$, and chain-end $-SC(C\mathit{H_3})_2C(O)O-$), 1.20−1.40 (br, chain-end, $-SCH_2(C\mathit{H_2})_{10}CH_3$), 0.86 (t, $-S(CH_2)_{11}C\mathit{H_3}$).

^{13}C NMR ($CDCl_3$). δ (ppm) 135.21(*cis*-1,4-polyisoprene backbone, $-\mathit{C}(CH_3){=}CH-$), 125.02 (*cis*-1,4-polyisoprene backbone, $-C(CH_3){=}\mathit{C}H-$), 36.8 (chain-end, $C(S)-S\mathit{C}H_2CH_2-$), 32.2 (*cis*-1,4-polyisoprene backbone, $-\mathit{C}H_2C(CH_3){=}CH-$), 31.92, 29.64, 29.63, 29.57, 29.46, 29.35, 29.12, 28.95, 27.86 (chain-end, $-SCH_2(\mathit{C}H_2)_9CH_2CH_3$, 26.39 (*cis*-1,4-polyisoprene backbone, $-C(CH_3){=}CH-\mathit{C}H_2-$), 25.36 (chain-end, $-SC(\mathit{C}H_3)_2$-$C(O)O-$), 23.44 (*cis*-1,4-polyisoprene backbone $-C(\mathit{C}H_3){=}CH-$), 22.70 (chain-end, $-SCH_2(CH_2)_8\mathit{C}H_2CH_3$), 14.14 (chain-end, $-\mathit{C}H_3$).

FTIR. ν (cm^{-1}) 3032 (H−C=C), 2962−2854 (CH_2, CH_3), 1735 (chain-end, −C=O), 1666 (polyisoprene backbone−C=C−), 1448 (polyisoprene backbone $-CH_2$), 1376 (polyisoprene backbone, $-CH_2$), 1259 (chain-end, C−O−), 1082 (chain-end, −C−S), 836 (polyisoprene backbone, −CH).

A Typical RAFT Polymerization. A typical procedure is given for the polymerization of *tert*-butyl acrylate (*t*-BA) mediated by

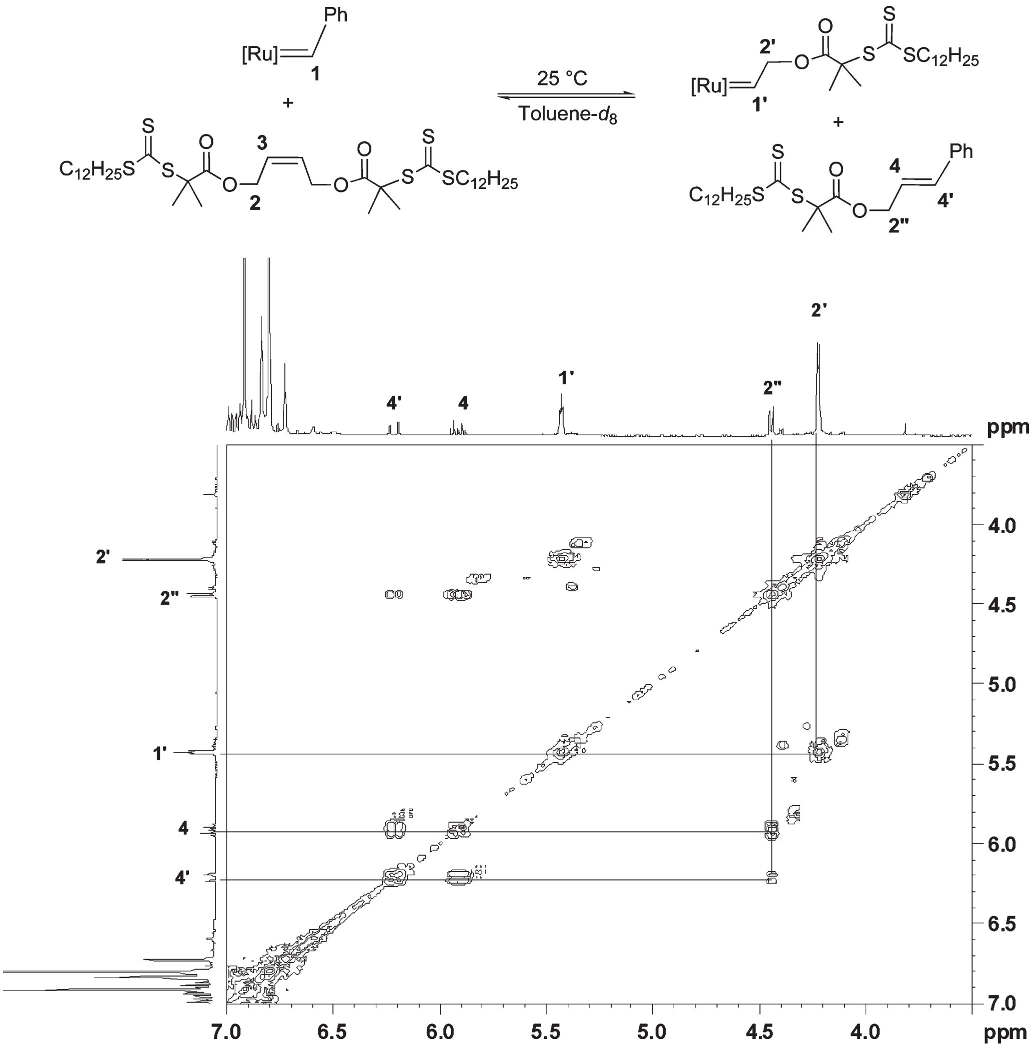


Figure 2. COSY spectrum (toluene-d_8) of the resulting mixture solution between CTA **2** and Grubbs II catalyst.

α,ω-bistrithiocarbonyl-end functionalized telechelic *cis*-1,4-polyisoprene (**7**, Scheme 1B) used as macroCTA and using AIBN as the initiator ([*t*-BA]$_0$/[macroCTA]$_0$/[AIBN]$_0$ = 500/1/0.4). A magnetic stir bar was charged to a Schlenk tube together with the CTA (0.3160 g, 0.051 mmol), *t*-BA (3.65 mL, 0.028 mol), AIBN (0.0033 g, 0.020 mmol), toluene (1 mL, 20% v/v), and anisole (0.17 mL, 5% v/v). Then, the reaction mixture was deoxygenated by bubbling with argon for 15 min. The polymerization was initiated by immersion in a thermostated oil bath at 60 °C. Samples were withdrawn from the reaction mixture via a degassed syringe for conversion monitoring (by ^{1}H NMR spectroscopy) and molecular weight analysis (by SEC). At the end of reaction, the polymer solution was concentrated under vacuum using rotary evaporation and was purified by a series of precipitations from dichloromethane (minimum volume) into an ice cold 1:1 mixture of water and methanol. The copolymer was separated by filtration and dried under vacuum until constant weight. It was then further analyzed by ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy and SEC. Yield: 80%. ^{1}H NMR (CDCl$_3$): δ (ppm) 5.86−5.70 (br, chain-end, *cis* $-\mathrm{C}\boldsymbol{H}{=}\mathrm{C}\boldsymbol{H}-$), 5.60−5.50 (br, chain-end, *trans*-$\mathrm{C}\boldsymbol{H}{=}\mathrm{C}\boldsymbol{H}-$), 5.16 (br, polyisoprene backbone, $-\mathrm{C(CH_3){=}C}\boldsymbol{H}$), 4.72−4.65 (d, chain-end, $-\mathrm{C(CH_3){=}CH{-}C}\boldsymbol{H_2}\mathrm{OC(O)}-$), 4.65−4.56 (d, chain-end, $-\mathrm{C(CH_3){=}CH{-}C}\boldsymbol{H_2}\mathrm{OC(O)}-$ and $-\mathrm{CH{=}CH{-}C}\boldsymbol{H_2}\mathrm{OC(O)}-$), 4.56−4.50 (d, chain-end, $-\mathrm{CH{=}CH{-}C}\boldsymbol{H_2}\mathrm{OC(O)}-$) 3.32 (t, $\mathrm{C(S){-}SC}\boldsymbol{H_2}\mathrm{CH_2R}$), 2.40−2.15 (br, P(*t*-BA) backbone, $-\mathrm{CH_2{-}C}\boldsymbol{H}\mathrm{C(O)}-$), 2.12−1.95 (br, polyisoprene backbone, $-\mathrm{C}\boldsymbol{H_2}\mathrm{C(CH_3){=}CH}-$ and $-\mathrm{C(CH_3){=}CH{-}C}\boldsymbol{H_2}-$), 1.90−1.70 (br, P(*t*-BA) backbone $-\mathrm{C}\boldsymbol{H_2}\mathrm{{-}CHC(O)}-$), 1.70−1.60 (br, polyisoprene backbone, $-\mathrm{C(C}\boldsymbol{H_3}\mathrm{){=}CH}-$, and chain-end $-\mathrm{SC(C}\boldsymbol{H_3}\mathrm{)_2{-}C(O)O}-$), 1.55−1.30 (br, P(*t*-BA) backbone $-\mathrm{OCH(C}\boldsymbol{H_3}\mathrm{)_3}$), 1.20−1.40 (br, chain-end $-\mathrm{SCH_2CH_2{-}(C}\boldsymbol{H_2}\mathrm{)_9CH_3}$), 0.86 (t, $\mathrm{S(CH_2)_{11}C}\boldsymbol{H_3}$).

^{13}C NMR (CDCl$_3$): δ (ppm) 174.16 (P(*t*-BA) backbone, $-\boldsymbol{C}\mathrm{(O){-}O}-$), 135.21 (*cis*-1,4-polyisoprene backbone, $-\boldsymbol{C}\mathrm{(CH_3){=}CH}-$), 125.02 (*cis*-1,4-polyisoprene backbone, $-\mathrm{C(CH_3){=}}\boldsymbol{C}\mathrm{H}-$), 80.41 (P(*t*-BA) backbone, $-\mathrm{C(O){-}O{-}}\boldsymbol{C}\mathrm{(CH_3)_3}$), 42.42 (P(*t*-BA) backbone, $-\boldsymbol{C}\mathrm{HC(O){-}O{-}C(CH_3)_3}$), 37.41, (chain-end, $\mathrm{C(S){-}S}\boldsymbol{C}\mathrm{H_2CH_2}-$), 32.20 (*cis*-1,4-polyisoprene backbone, $-\boldsymbol{C}\mathrm{H_2C(CH_3){=}CH}-$), 31.92, 29.64, 29.63, 29.57, 29.46, 29.35, 29.12, 28.95, 27.86 (chain-end, $-\mathrm{SCH_2(}\boldsymbol{C}\mathrm{H_2)_9CH_2CH_3}$, 28.14 (P(*t*-BA) backbone, $-\mathrm{O{-}C(}\boldsymbol{C}\mathrm{H_3)_3}$), 26.39 (1,4-*cis*- polyisoprene backbone $-\mathrm{C(CH_3){=}CH{-}}\boldsymbol{C}\mathrm{H_2}-$), 23.44 (*cis*-1,4-polyisoprene backbone $-\mathrm{C(}\boldsymbol{C}\mathrm{H_3){=}CH}-$), 22.70 (chain-end, $-\mathrm{S(C}\boldsymbol{H_2}\mathrm{)_9{-}}\boldsymbol{C}\mathrm{H_2CH_3}$), 14.14 (chain-end, $-\boldsymbol{C}\mathrm{H_3}$).

Results and discussion

Functional Metathesis Degradation. Herein, we investigated the synthesis of α,ω-bistrithiocarbonyl-end functionalized telechelic *cis*-1,4-polyisoprene via metathesis degradation of NR using Grubbs second generation catalyst (GII) and a bistrithiocarbonyl-end functionalized olefin (**2**) as the CTA (Scheme 1). The difunctional CTA was reacted with Grubbs II catalyst in a stoichiometrical ratio in toluene-d_8 at 25 °C and the resulting product analyzed by ^{1}H NMR spectroscopy (Figure 1) and 2D-correlation spectroscopy (COSY) (Figure 2). New peaks were observed in ^{1}H NMR spectrum (Figure 1) at 5.35 and 4.14 ppm

Table 1. Metathesis Degradation of NR Using Grubbs II Catalyst and Difunctional Chain Transfer Agent 2 in Toluene at 25 °C after 4 h

entry	$[\mathrm{Ip}]_0/[\mathrm{GII}]_0/[\mathrm{CTA}]_0$	$\overline{M_{n,\mathrm{SEC}}}^{a}$ (g mol^{-1})	$\overline{M_{n,\mathrm{NMR}}}^{b}$ (g mol^{-1})	functionality^{c}	PDI^{d}	yield (%)
A-1	200/1/1	23 000	16 400	1.4 ± 0.1	1.83	78
A-2	100/1/1	10 200^{e}	7 200	1.5 ± 0.1	1.76	76
A-3	100/1/2	8 200^{e}	6 200	2.0 ± 0.1	1.70	76
A-4	100/1/5	8 200	6 400	2.0 ± 0.1	1.67	70

[a] Experimental number-average molecular weight measured by size exclusion chromatography (SEC) calibrated with polystyrene standards at 35 °C. [b] Determined by ^{1}H NMR spectroscopy according to $\overline{M_n} = [(I_4 \times 68)/(I_1/4)] + 848$. [c] Determined by ^{1}H NMR spectroscopy and using eq 1. [d] Polydispersity index measured by SEC. [e] Experimental number-average molecular weight measured by size exclusion chromatography (SEC) calibrated with polystyrene standards at 25 °C.

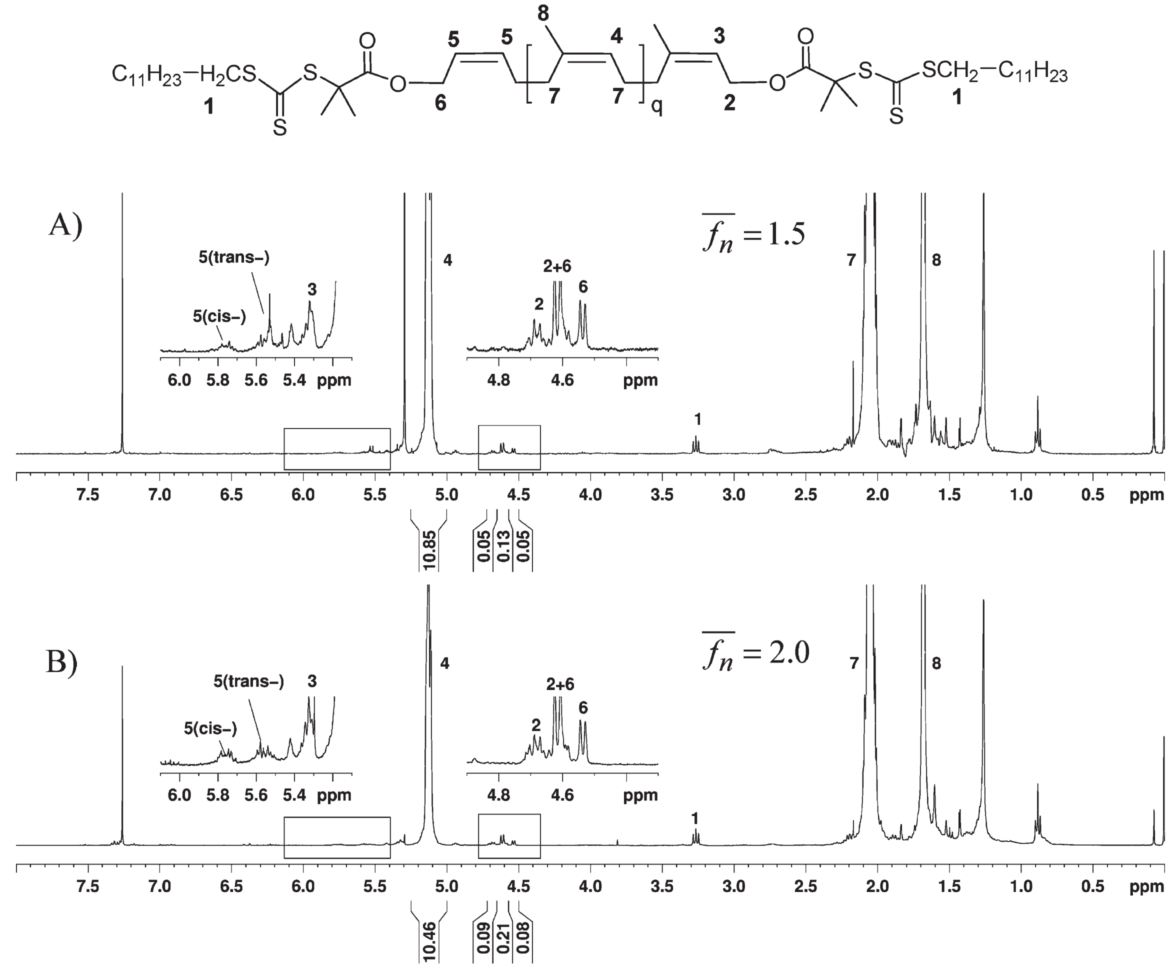


Figure 3. ^{1}H NMR spectra of difunctional telechelic *cis*-1,4-polyisoprenes: entry **A-2**, Table 1 (A) and entry **A-3**, Table 1 (B).

that are attributed to the olefinic proton, **1′**($[\mathrm{Ru}]{=}\mathrm{C}\mathit{H}\mathrm{CH_2OC(O)}{-}\mathrm{R}$) and to aliphatic protons, **2′** ($[\mathrm{Ru}]{=}\mathrm{CHC}\mathit{H}_2\mathrm{OC(O)}$-R), respectively. In addition, new peaks were found at 4.36 ppm, at 5.87−5.80 ppm and at 6.15−6.10 ppm corresponding to **2″** ($\mathrm{Ph{-}CH{=}CHC}\mathit{H}_2\mathrm{OC(O){-}R}$), to **4** ($\mathrm{Ph{-}CH{=}C}\mathit{H}\mathrm{CH_2OC(O){-}R}$), and to **4′** ($\mathrm{Ph{-}C}\mathit{H}\mathrm{{=}CHCH_2OC(O){-}R}$), respectively. COSY two-dimensional NMR experiment was used to confirm these structures. In the COSY spectrum (Figure 2), the signal at 4.14 ppm corresponding to aliphatic protons **2′** is correlated with the signal centered at 5.35 ppm, corresponding to the olefinic proton, **1′**. We can also observe the correlation between the signals 6.15−6.10 ppm and 5.87−5.80 ppm, corresponding to alkenes proton **4′** and **4**, with the signal at 4.36 ppm, corresponding to aliphatic protons **2″**. Thus, it was confirmed that the Grubbs II catalyst reacts with difunctional CTA (**2**, Scheme 1A) to result in the new ruthenium carbene molecule (**3**, Scheme 1A). This new catalyst (**3**, Scheme 1A) undergoes the metathesis degradation at 25 °C with double bonds of NR (**4**, Scheme 1B) to form α,ω-bistrithiocarbonyl-end functionalized telechelic *cis*-1,4-polyisoprene (**7**, Scheme 1B). Therefore, the one-pot degradation and functionalization reactions can continuously take place in a catalytic fashion.

A first attempt for the preparation of telechelic NR (entry **A-2**, Table 1) was performed in toluene using Grubbs II catalyst and bistrithiocarbonyl-end functionalized olefin (**2**, Scheme 1A) as the CTA. The reaction was carried out at room temperature for 4 h with a ratio of $[\mathrm{Ip}]_0/[\mathrm{GII}]_0/[\mathrm{CTA}] = 100/1/1$. The resulting polymer was characterized by ^{1}H NMR spectroscopy (Figure 3) and 2D-correlation spectroscopy (COSY) (Figure 4). An intense signal corresponding to ethylenic protons at 5.16 ppm (**4**, $-(\mathrm{CH_3})\mathrm{C{=}C}\mathit{H}\mathrm{CH_2}-$) was observed in ^{1}H NMR spectroscopy (Figure 3). This result indicates that telechelic polyisoprenes with 1,4-microstructure are obtained. In addition, new peeks were also observed at 5.86−5.70 ppm, at 5.60−5.50 ppm, at 5.38−5.28 ppm and at 4.72−4.50 ppm corresponding to **5** (*cis* $-\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}$), **5** (*trans* $-\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}$), **3** ($-\mathrm{C(CH_3){=}C}\mathit{H}$) and **2** ($-\mathrm{C(CH_3){=}CH{-}C}\mathit{H}_2\mathrm{OC(O)}-$) or **6** ($-\mathrm{CH{=}CH{-}C}\mathit{H}_2\mathrm{OC(O)}-$), respectively. COSY two-dimensional NMR experiment

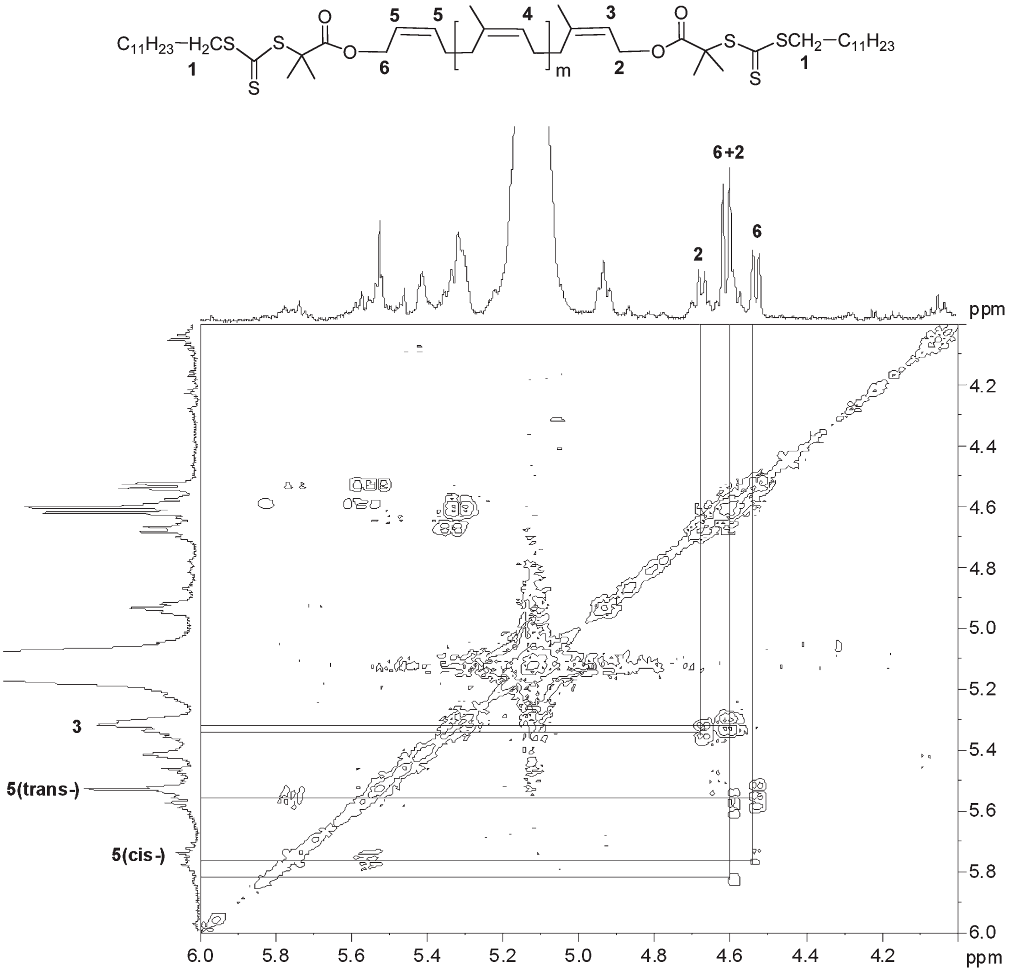


Figure 4. COSY spectrum of the difunctional telechelic *cis*-1,4-polyisoprene (entry **A-2,** Table 1).

was used to confirm these structures. In the COSY spectrum (Figure 4), the signals centered at 5.78 and at 5.55 ppm corresponding to *cis*- and *trans*-ethylenic protons, **5**, are correlated with the signal centered at 4.53 ppm corresponding to aliphatic proton **6**. We can also observe the correlation of the signal at 5.83 ppm, the signal centered at 5.55 ppm and the signal centered at 5.34 ppm corresponding respectively to *cis*-ethylenic proton, **5(cis-)**, *trans*-ethylenic proton, **5(trans-)**, and isoprenic proton, **3**, with the signal centered at 4.62 ppm corresponding to aliphatic protons, **6** and **2**. In addition, we can observe the correlation of the signal at 5.34 ppm corresponding to isoprenic proton, **3**, with the signal centered at 4.68 ppm corresponding to aliphatic protons, **2**.

^{13}C NMR spectroscopy (Figure 5) was used to identify the 1,4-microstructure of telechelic polyisoprenes. The signals observed at 135.21 (**1**, $-\boldsymbol{C}(CH_3)=CH-$), 125.02 (**2**, $-C(CH_3)=\boldsymbol{C}H-$), 32.2 ppm (**3**, $-\boldsymbol{C}H_2C(CH_3)=CH-$), 26.39 (**5**, $-C(CH_3)=CH\boldsymbol{C}H_2-$), and 23.44 ppm (**7**, $-C(\boldsymbol{C}H_3)=CH-$) correspond to the *cis*-1,4- polyisoprene unit. There are no signals at 131.2 ppm ($-\boldsymbol{C}(CH_3)=CH-$), 124.27 ($-C(CH_3)=\boldsymbol{C}H-$), 40.02 ppm ($-C(CH_3)=CH\boldsymbol{C}H_2-$), 16.00 ($-C(\boldsymbol{C}H_3)=CH-$) corresponding to the *trans*-1,4-polyisoprene unit.[47] This result confirmed that the telechelic polyisoprene is a strictly *cis*-1,4-polyisoprene. By contrast, the synthesis of telechelic polyisoprene through anionic polymerization,[48,49] NMP[21] or RAFT polymerization[24−26] gives a mixture of 1,4-addition, 1,2-addition, and 3,4-addition products. On the other hand, the synthesis of telechelic polyisoprene via the ring-opening metathesis polymerization of 1,5-dimethyl-1,5-cyclooctadiene gives a mixture of telechelic *cis*-1,4 and *trans*-1,4-polyisoprene.[28]

In order to determine the average functionality ($\overline{f_n}$) of telechelic *cis*-1,4-polyisoprene, the number-average polymerization degree ($\overline{DP_n}$) of the oligomers determined by ^{1}H NMR spectroscopy was compared with the $\overline{DP_n}$ determined by SEC. The $\overline{DP_n}$ of *cis*-1,4-polyisoprene from ^{1}H NMR spectroscopy was calculated by comparing the relatives integrations of the methylene protons (**2** and **6**, Figure 3) of the chain-ends at 4.72−4.50 ppm, with those of the isoprenic protons (**4**, Figure 3) of polyisoprene backbone at 5.16 ppm. The functionality was then calculated according to eq 1 which is an adaptation of the equation used by Pham et al.[50,51] for hydroxytelechelic polybutadiene obtained by radical or anionic polymerization.

$$\overline{f_n} = \frac{I_2 + (I_{6+2})/2 + I_6}{I_4} \times \frac{\overline{M_{\mathrm{n,\,sec}}}^* \times B}{M_{\mathrm{isoprene}}} \qquad (1)$$

with I_2 corresponding to the relative integration of aliphatic protons **2** of isoprene chain-end unit at 4.72−4.68 ppm (Figure 3); I_{6+2} corresponding to the relative integration of aliphatic protons **6** + **2** of isoprene and butadiene chain-ends unit at 4.68−4.56 ppm (Figure 3); I_6 corresponding to the relative integration of aliphatic protons **6** of butadiene chain-end unit at 4.56−4.50 ppm (Figure 3); I_4 corresponding to the relative integration of vinylic protons **4** of isoprene backbone unit at 5.16 ppm (Figure 3); $\overline{M_{\mathrm{n,SEC}}}^*$ is the number-average molecular weight of telechelic *cis*-1,4-polyisoprene determined

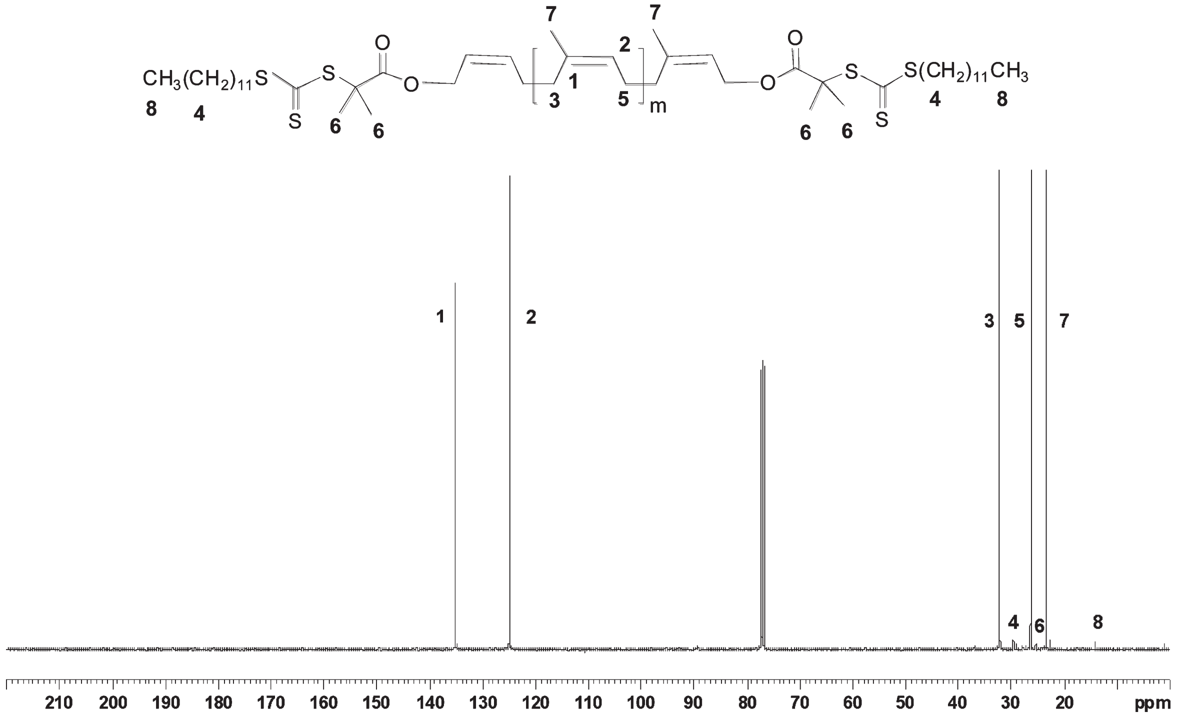
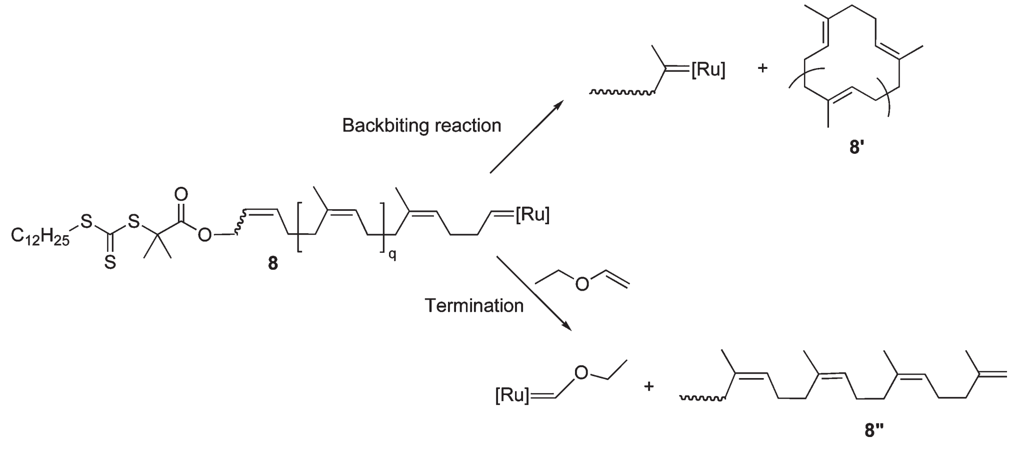


Figure 5. ^{13}C NMR spectrum of telechelic *cis*-1,4-polyisoprene (entry **A-2**, Table 1).

Scheme 2. Formation of Non-Functional Chain-Ends



by SEC at 25 °C; B is the Benoît factor value[52] of polyisoprene equal to 0.67; M_{isoprene} is the molar mass of isoprene unit equal to 68 g mol^{-1}.

The resulting functionality for the *cis*-1,4-polyisoprene telechelic (entry **A-2**, Table 1) was equal to 1.5 ± 0.1. We believe that under these conditions the low concentration of CTA gives rise to some active free ruthenium carbene (**8**, Scheme 2), which could be involved in backbiting reactions leading to the formation of nonfunctional cyclic products (**8′**, Scheme 2). Finally, ethyl vinyl ether used to stop the reaction leads to oligomer vinylic chain-ends (**8″**, Scheme 2). These reactions limit the functionality of the so-obtained polyisoprenes.

The evolution of number-average molecular weight of telechelic *cis*-1,4-polyisoprene with reaction time is presented in Figure 6. It illustrates that metathesis degradation proceeds in two relatively distinct steps. A very rapid decrease of the molecular weights of the *cis*-1,4-polyisoprene is observed over the first 2 h, corresponding to a drop from 2×10^6 g mol^{-1} to 14 000 g mol^{-1}. In the initial stage of the reaction, an active ruthenium carbene reacts rapidly with the double

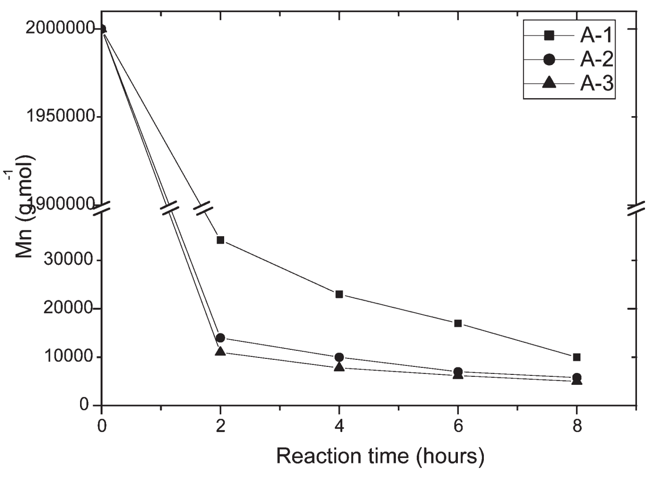


Figure 6. Evolution of the telechelic *cis*-1,4-polyisoprene number-average molecular weight as a function of reaction time (entries **A-1** to **A-3**, Table 1).

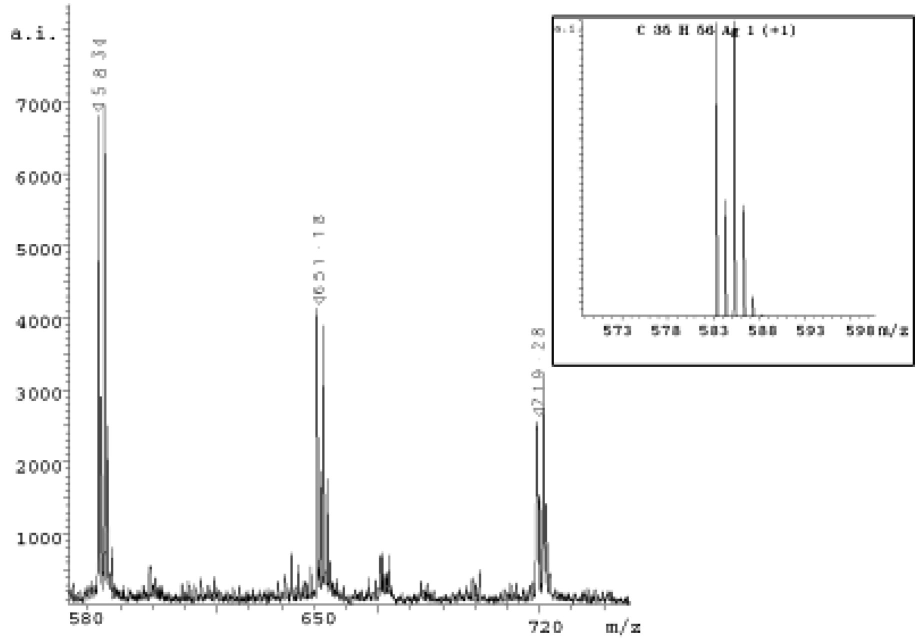
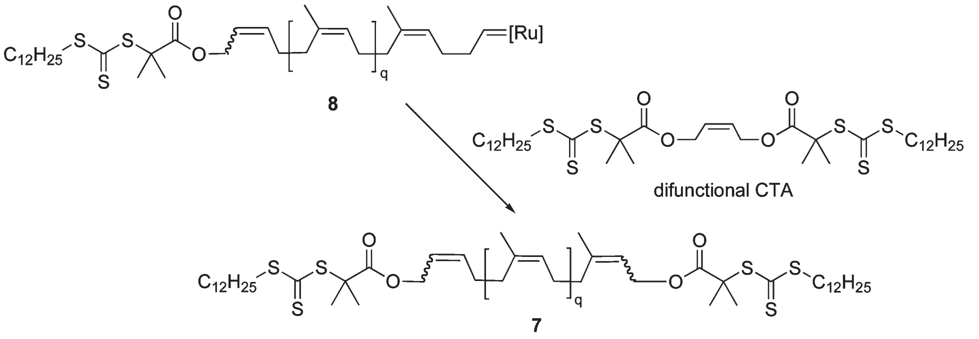
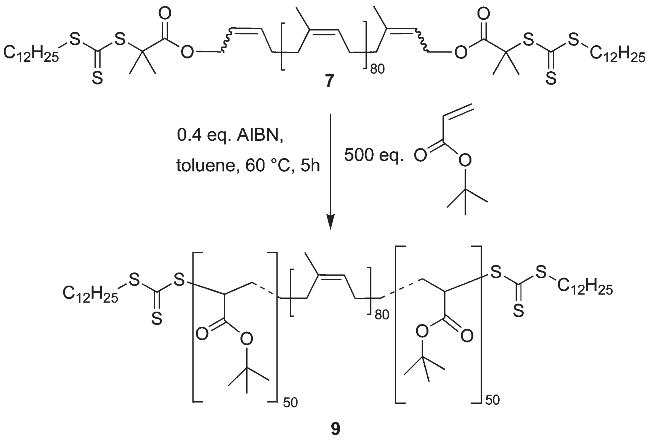


Figure 7. MALDI−TOF mass spectrum of the cyclic polyisoprene oligomers obtained via backbiting reaction. The inset shows the theoretical distribution at *m*/*z* 583.

Scheme 3. Formation of Difunctionalized Telechelic *cis*-1,4-Polyisoprene



Scheme 4. Synthesis of P(*t*-BA)-*b*-PIp-*b*-P(*t*-BA) by RAFT Polymerization Using α,ω-Bistrithiocarbonyl End-Functionalized Telechelic *cis*-1,4-Polyisoprene as MacroCTA



bonds of the *cis*-1,4-polyisoprene backbone leading to a decrease of molecular weight. In addition, the active ruthenium carbene at the chain-end can also react with the double bonds of *cis*-1,4-polyisoprene via intermolecular metathesis reactions. Then, in a second period from 2 to 8 h, the molecular weight of the polymer decreases slowly but continually to form telechelic *cis*-1,4-polyisoprene with a final average molecular weight of approximately 5800 g mol^{-1}. This is also proved[53−55] by the fact that at very long reaction times intramolecular metathesis reactions can occur to form cyclic oligomers. The resulting cyclic oligomers were confirmed by MALDI−TOF MS analysis (Figure 7). The Ag^+ ionized MALDI spectrum of oligomers isolated after precipitation of the higher molecular weight fraction using 2-propanol reveals cyclic polyisoprenic species. For example, the signal at m/z = 583 corresponds to a cyclic polyisoprene consisting of n = 7 isoprene units ionized by Ag^+ ($M_{cal} = 107 + 7 \times 68 = 583$ g mol^{-1}; where 107 g mol^{-1} is the mass of silver atom and 68 g mol^{-1} is the mass of isoprene unit). This experimental value is in good agreement with the theoretical mass calculated (583 g mol^{-1}, monoisotopic peak), confirming the formation of cyclic oligomers via backbiting reaction.

In order to obtain better control of the molecular weight and chain-end functionality of telechelic *cis*-1,4-polyisoprene, the effect of changing the ratio of $[Ip]_0/[GII]_0/[CTA]_0$ (entries **A-1** to **A-4**, Table 1) was studied. When the ratio of $[Ip]_0/[GII]_0/[CTA]_0$ is equal to 200/1/1(entry **A-1**, Table 1), it was found that the evolution of the number-average molecular weight of telechelic *cis*-1,4-polyisoprene with time followed a similar two-step profile to that observed for sample **A-2** (Table 1). During the first

Table 2. Synthesis of ABA Triblock Copolymers *via* RAFT Polymerization of *tert*-Butyl Acrylate (*t*-BA) Using the MacroCTA (A-3, Table 1) and AIBN as Initiator at 60°C in Toluene

copolymer	reaction time (h)	convn[a] (%)	$\overline{M_{n,cal}}$[b] (g mol^{-1})	$\overline{M_{n,SEC}}$[c] (g mol^{-1})	PDI[d]
S-1	2	2	9080	8200	1.75
S-2	4	15	17400	16000	1.50
S-3	4.5	21	21240	20000	1.50
S-4	5	26	24440	23300	1.50

[a] Monomer conversion determined using ^{1}H NMR spectroscopy. [b] Number-average molecular weight calculated using: $\overline{M_{n,calc}}$ = (conversion (%) × $[M]_0/[MacroCTA]_0 \times M_M) + M_{macroCTA}$ where $[M]_0$, $[MacroCTA]_0$, M_M and $M_{macroCTA}$ are the initial concentration of monomer, the initial concentration of difunctional telechelic *cis*-1,4-polyisoprene macroCTA, the molecular weight of monomer and the molecular weight of the difunctional telechelic *cis*-1,4-polyisoprene macroCTA respectively. [c] Number-average molecular weight measured by size exclusion chromatography (SEC) calibrated with polystyrene standards. [d] Polydispersity index measured by SEC.

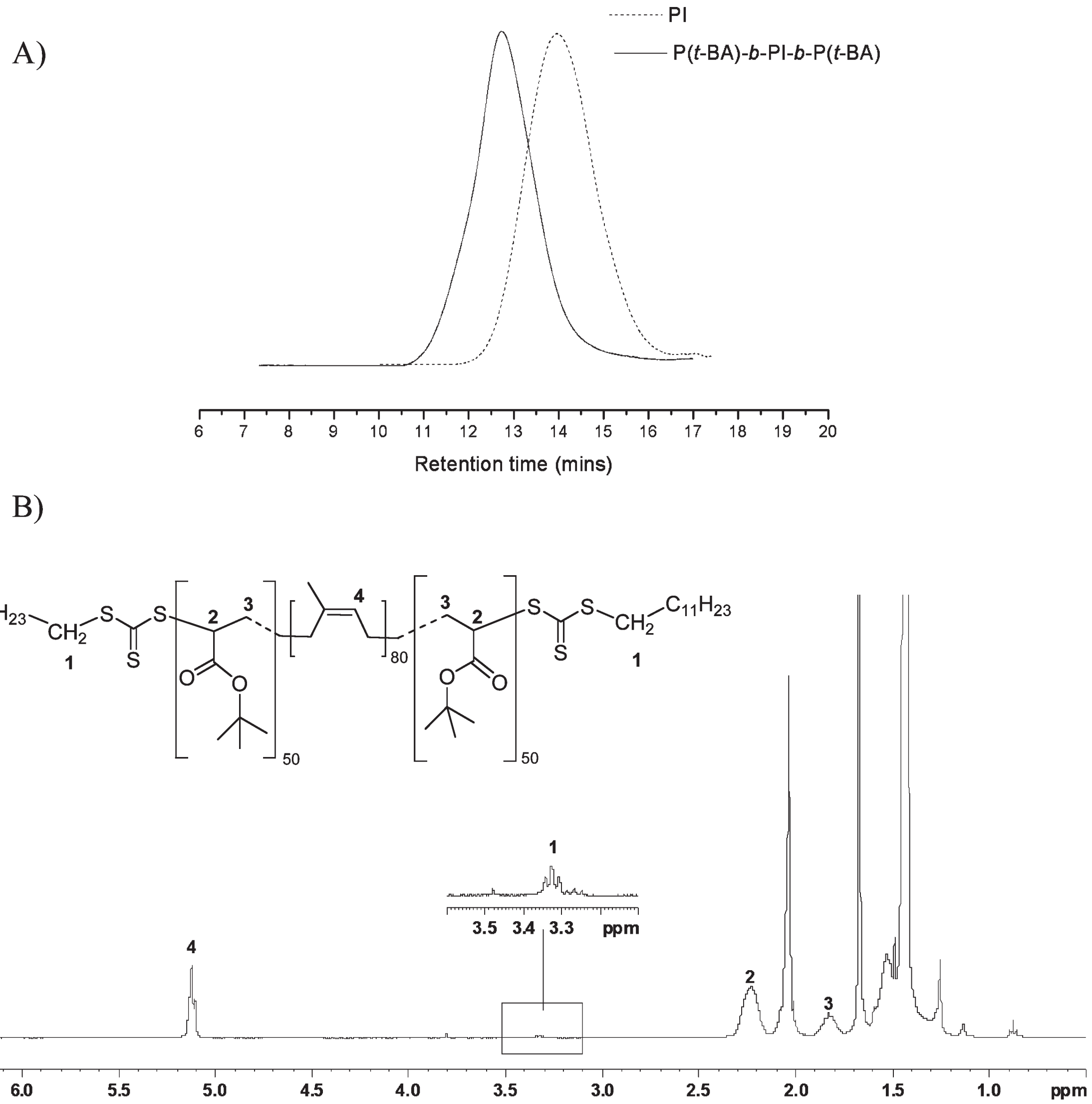


Figure 8. Overlaid SEC traces of telechelic *cis*-1,4-polyisoprene and of P(*t*-BA)-*b*-PIp-*b*-P(*t*-BA) triblock copolymers (A), and ^{1}H NMR spectrum of P(*t*-BA)-*b*-PIp-*b*-P(*t*-BA) triblock copolymers (B).

stage, a period of 2 h, the $\overline{M_n}$ decreased rapidly from 2 × 10^6 g mol^{-1} to 34 000 g mol^{-1}. After 2 h, the $\overline{M_n}$ decreased slowly to form telechelic *cis*-1,4-polyisoprene with a final molecular weight of about 10 000 g mol^{-1} after a period of 8 h (Figure 6). However, the final telechelic *cis*-1,4-polyisoprene has a higher molecular weight corresponding to a higher initial ratio of $[Ip]_0/[GII]_0/[CTA]_0$. Moreover, the functionality of telechelic *cis*-1,4-polyisoprene obtained was unaffected and remained less than 2. In order to form a perfectly difunctional telechelic *cis*-1,4-polyisoprene, the influence of the CTA concentration was investigated. The ratio of $[GII]_0/[CTA]_0$ was set to 1/2 and 1/5, and the ratio of $[Ip]_0/[GII]_0$ was fixed at 100/1 (entries **A-3** and **A-4**, Table 1). We observed that ratios of $[GII]_0/[CTA]_0$ of 1/2 and 1/5 formed polymers with a chain-end functionality of 2 as shown by ^{1}H NMR spectrum (Figure 3B) with no significant difference in $\overline{M_n}$values and in polydispersity indices of the final telechelic *cis*-1,4-polyisoprene. This is probably due to the fact that the CTA which have not reacted with the Grubbs II catalyst may react with the ruthenium carbene at the chain-end (**8**, Scheme 3) leading to difunctionalized *cis*-1,4-polyisoprene (**7**, Scheme 3).

Synthesis of P(*t*-BA)-*b*-PIp-*b*-P(*t*-BA) Triblock Copolymers. We investigated the synthesis of ABA triblock copolymers containing polyisoprene as the central block using a purified α,ω-bistrithiocarbonyl end-functionalized telechelic *cis*-1,4-polyisoprene as macroCTA (**7**, Scheme 4). The P(*t*-BA)-*b*-PIp-*b*-P(*t*-BA) (**9**, Scheme 4) was prepared from the RAFT polymerization of *tert*-butyl acrylate using the difunctional telechelic *cis*-1,4-polyisoprene (**A-3**, Table 1) as a macroCTA. The reaction was performed in toluene at 60 °C and AIBN was used as an initiator ($[t\text{-BA}]_0/[\text{macroCTA}]_0/[\text{AIBN}]_0 = 500/1/0.4$). Monomer conversion was determined by ^{1}H NMR spectroscopy by following the disappearance of the vinyl protons of *t*-BA at 6.40 to 5.60 ppm which were compared with methyl protons of anisole used as an internal standard at 3.75 ppm. The macromolecular characteristics of block copolymers were determined by SEC.

After a polymerization time of 5 h, the *t*-BA conversion reaches 26% (Table 2). The block copolymer had a number-average molecular weight of 23 300 g mol^{-1} and a polydispersity index of 1.50 by SEC. The SEC trace of the copolymer (Figure 8A) showed the absence of a peak corresponding to the PIp-macroCTA and a unimodal curve, illustrating that the polymerization of the second block underwent chain transfer quantitatively. The number-average degree of polymerization of the PIp block is equal to 80 and the one of P(*t*-BA) is equal to 100 as calculated by comparing the integral of the ethylenic protons **4** of the polyisoprene backbone resonance at 5.14 ppm to the methine protons **2** of P(*t*-BA) resonances at 2.4−2.1 ppm on the ^{1}H NMR spectrum of the copolymer (Figure 8B). The data obtained from SEC and ^{1}H NMR spectroscopy provide additional evidence for the formation of the ABA triblock copolymer based on the *cis*-1,4-polyisoprene from NR with the desired topology.

Glass transition temperature (T_g) of PIp-macroCTA and P(*t*-BA)-*b*-PIp-*b*-P(*t*-BA) triblock copolymer were investigated by thermal analysis by differential scanning calorimetry (DSC) under nitrogen at 10 °C/min heating rate. A single T_g of PIp-macroCTA was observed at −65 °C whereas the P(*t*-BA)-*b*-PIp-*b*-P(*t*-BA) triblock copolymers showed two values of T_g which the low temperature at −37 °C corresponds to the glass transition temperature of PIp and the higher temperature at 32 °C corresponds to the glass transition temperature of P(*t*-BA) as the T_g of P(*t*-BA) is equal to 48 °C.[56] This is a supplementary proof of the successful synthesis of P(*t*-BA)-*b*-PIp-*b*-P(*t*-BA) triblock copolymers.

Conclusion

A new α,ω-bistrithiocarbonyl-end functionalized telechelic *cis*-1,4-polyisoprene was successfully synthesized in one-pot reaction via metathesis degradation of NR using the Grubbs II catalyst and a bistrithiocarbonyl-end functionalized olefin as a CTA. The influence of the Grubbs II catalyst concentration and the CTA concentration were investigated. The functionality of telechelic *cis*-1,4-polyisoprene reaches 2 when the ratio of $[\text{GII}]_0/[\text{CTA}]_0$ is equal to 1/2 or/and 1/5 as demonstrated by ^{1}H NMR spectroscopy. The resulting α,ω-bistrithiocarbonyl-end functionalized telechlelic *cis*-1,4-polyisoprene was successfully used as macroCTA for the RAFT polymerization of *tert*-butyl acrylate to form P(*t*-BA)-*b*-PIp-*b*-P(*t*-BA) triblock copolymers. This polymer precursor could be of great interest in various block copolymers applications especially regarding adhesive properties which are still in studies currently in our laboratory. This interest is also reinforced by the fact that such functionalized oligomers are an alternative to few analogues coming from petroleum origin.

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