Polyisobutylene Stars and Polyisobutylene-*block*-Poly(*tert*-Butyl Methacrylate) Block Copolymers by Site Transformation of Thiophene End-Capped Polyisobutylene Chain Ends

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ABSTRACT: A new synthetic route for the synthesis of polyisobutylene (PIB) stars and PIB-poly(methacrylate) block copolymers was developed by combining living carbocationic and anionic polymerizations. Rapid and quantitative monoaddition of thiophene to living PIB chains has been observed in conjunction with $TiCl_4$ as Lewis acid in *n*-hexane/CH_2Cl_2 60/40 v/v at −78 °C leading to the formation of 2-polyisobutylenyl-thiophene (PIB−T). PIB−T was quantitatively metalated with *n*-butyllithium in THF at −40 °C. ^1H NMR spectroscopic and GC studies of the corresponding model compound, 2-(1,1,3,3-tetramethylbutyl)thiophene, clearly verified quantitative metalation. The resulting stable macrocarbanion (PIB−T^-,Li^+) was used to initiate living anionic polymerization of *tert*-butyl methacrylate (*t*BMA) yielding PIB-*b*-P*t*BMA block copolymers with high blocking efficiency. PIB stars were prepared via the coupling reaction of the stable macrocarbanion with $SiCl_4$ as a coupling agent. Characterization of these block copolymers and PIB stars was carried out by size exclusion chromatography (SEC), liquid adsorption chromatography at critical conditions (LACCC), and NMR spectroscopy.

Introduction

Living polymerizations provide the most versatile synthetic routes for the preparation of a wide variety of well-defined polymer structures, such as end-functionalized polymers, star-shaped polymers, or block copolymers. Since specific living polymerization methods (e.g., anionic and carbocationic polymerizations) are applicable only to a limited number of monomers, the combination of different living polymerization techniques is expected to lead to new and unique combination of blocks in block copolymers. Recent success in the synthesis of functionalized polyisobutylene (PIB) with quantitative functionality and of block copolymers with high structural integrity is based on the applications of non-(homo)polymerizable monomers such as 1,1-diphenylethylene (DPE) in cationic polymerization.[1] These processes involve the intermediate capping reaction of living PIB with DPE or its derivatives. The resulting stable and fully ionized carbenium ions have been successfully employed for the quantitative end-functionalization of living PIB with soft nucleophiles such as silyl ketene acetals[2] and the controlled initiation of the second monomers such as *p*-methylstyrene[3] and isobutyl vinyl ether.[4]

Block copolymers of isobutylene (IB) and polar monomers, such as methacrylates, acrylamides, polyethers, or polyesters combine the high environmental stability of elastomeric, nonpolar PIB with the large variety of structures and properties of polar polymers. Since PIB can only be obtained by carbocationic polymerization, however, many attempts have been undertaken to transform living cationic PIB chain ends to radical[5] or anionic ones.[6]

Although many prior attempts were less successful, metalation of DPE end-capped PIB with Na/K alloy or cesium followed by anionic polymerization allowed to synthesize PIB-*b*-P*t*BMA diblock copolymers, PMMA-*b*-PIB-*b*-PMMA triblock copolymers, and (PMMA-*b*-PIB)$_3$ starblock copolymers with high blocking efficiency.[7,8] Metalation with alkali metals, however, is inconvenient and lithiation with butyllithium would be preferable. Unfortunately, lithiation of DPE end-capped PIB by alkyllithium does not proceed quantitatively. This led us to search for other capping agents which might be more easily lithiated. Recently, Faust et al. showed that furan (Fu) functional polyisobutylene (PIB−Fu) can be obtained by the quantitative reaction of living PIB and 2-tributylstannylfuran.[9] Using unsubstituted Fu, coupling of two living chain ends as a side reaction could not be avoided. PIB−Fu chain ends could be lithiated with *n*-BuLi, however, the polymerization of methacrylates using this macroinitiator was accompanied by side reactions.[10]

In place of PIB−Fu, thiophene (T) functional PIB (PIB−T) could also be used in the metalation reaction. An additional advantage is that unsubstituted T may be used to prepare PIB−T, since the reactivity of thiophene is about one tenth of that of Fu.[11] Iván et al. reported on attempts to use T as a coupling agent for living PIB, but under the conditions chosen (−80 °C, methylcyclohexane/dichloromethane 60/40 v/v, [$TiCl_4$]/[initiator]/[T] = 10/2/1) only 17% of the coupling product was formed after 2 h and 36% after approximately 24 h when stirred at room temperature.[12] Obviously, they did not aim at monofunctionalization of PIB with T.

In this report, we wish to present a new route to anionic PIB macroinitiators by end-capping of living PIB with one T molecule and subsequent lithiation with *n*-BuLi. These macroinitiators efficiently initiate the anionic polymerization of *tert*-butyl methacrylate (*t*BMA)

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to produce block copolymers in nearly quantitative yield. Moreover, we will show that they can also be used for the synthesis of PIB stars by coupling with chlorosilanes, a method well established for the coupling of anionic chain ends, e.g., living polybutadiene, to form star polymers.[13,14]

Experimental Section

Materials. 2,6-Di-*tert*-butylpyridine (D*t*BP, Aldrich, 97%) was purified by distillation from CaH_2. Isobutylene (IB, BASF) was passed through in-line gas purifier columns packed with $CaSO_4$ and no. 13 molecular sieves and condensed at −15 °C prior to polymerization. CH_3Cl was passed through in-line gas purifier columns packed with BaO/Drierite and condensed at −80 °C prior to polymerization. CH_2Cl_2 was purified by washing it with 10% aqueous NaOH and then with distilled water until neutral and dried over anhydrous $MgSO_4$ overnight. It was refluxed for 24 h and distilled from CaH_2, just before use. *n*-Hexane was rendered olefin free by refluxing it over concentrated sulfuric acid for 48 h. It was washed with 10% aqueous NaOH and then with deionized water until neutral and stored over $MgSO_4$ for 24 h. It was refluxed over CaH_2 overnight and distilled. Methylcyclohexane (MeCHX, Aldrich, 99%) and titanium(IV) chloride ($TiCl_4$, Aldrich, 99.9%) were used as received. Thiophene (T, Aldrich, 99%) was distilled the day before use and stored at 4 °C. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was prepared by hydrochlorination of 2,4,4-trimethyl-1-pentene (Fluka, 98%) with hydrogen chloride gas in dry dichloromethane at 0 °C.[15] The product was dried over $CaCl_2$ and distilled under reduced pressure before use. 5-*tert*-Butyl-1,3-bis(1-chloro-1-methylethyl)benzene (*t*BuDiCumCl) was synthesized following the procedure reported elsewhere.[16] Chlorotrimethylsilane (Me_3SiCl) and tetrachlorosilane ($SiCl_4$) (both Merck, 98%) were stirred over freshly ground CaH_2 for at least 24 h, followed by distillation prior to use. Triethylaluminum ($AlEt_3$, Aldrich, 1.0 M in hexane) was used as received. *tert*-Butyl methacrylate (*t*BMA, BASF) was predried with CaH_2, carefully degassed by freeze−thaw cycles in high vacuum, mixed with $AlEt_3$ solution until a yellow color persisted and then condensed into ampules. THF (Merck p.a) was purified first by distillation under nitrogen from CaH_2 and then by refluxing over potassium. *n*-Butyllithium (*n*-BuLi, 1.6 M in hexane) was purchased from Aldrich and its concentration was titrated by a standard method.[17]

Synthesis of Thiophene-Ended PIB (PIB−T). The synthesis of PIB−T was carried out under a dry nitrogen atmosphere in a glovebox. Living polymerizations of IB with TMPCl as initiator were carried out according to the following representative procedure. Into a 1 L three-necked flask equipped with a septum, a magnetic stirrer, and a nitrogen inlet were added of 240 mL of CH_3Cl, 404 mL of *n*-hexane, and 0.355 mL (0.302 g, 1.58 mmol) of D*t*BP and then the mixture was cooled to −78 °C. 15 mL (10.57 g, 0.188 mol) of IB was charged to the reactor by a syringe. After 10 min of stirring, 0.6 mL (0.525 g, 3.53 mmol) of TMPCl was transferred to the reactor by a transfer needle. After 5 min of stirring, 1.5 mL (2.68 g, 0.014 mol) of $TiCl_4$ was transferred to the reactor by a transfer needle. One hour later, 28.3 mL (29.74 g, 0.353 mol) of T was added to the polymerization system; the color of the solution changed from slightly yellow to red. T was allowed to react with the living chain ends for 60 min. Finally, the reaction was quenched by addition of 30 mL (23.55 g, 0.75 mol) of prechilled methanol. The crude product was dissolved in *n*-hexane and the mixture was filtered in order to remove inorganic precipitates. Then, the hexanes phase was isolated and washed once with NH_3(aq) and subsequently with water until neutral. The organic layer was separated and dried over $MgSO_4$ for about 2 h. Subsequently, the solution was filtered, and the solvent was removed on a rotary evaporator. Then, the polymer was dissolved in a small amount of *n*-hexane and precipitated two or three times into acetone in order to remove excess T.

Synthesis of α,ω-Dithiophene-Ended PIB (T−PIB−T). The polymerizations were initiated with the difunctional initiator 5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene (*t*BuDiCumCl). After the completion of IB polymerization, equal volumes of the polymer solution in the reactor were delivered into culture tubes. To each culture tube additional amount of $TiCl_4$ or D*t*BP was charged to vary the ratio of [$TiCl_4$] to [*t*BuDiCumCl] or [D*t*BP] to [*t*BuDiCumCl] in the polymer solution. The functionalization of PIB was conducted by two different methods: addition of T/CH_3Cl solution into the polymer solution (T to polymer) and addition of the polymer solution into T/CH_3Cl solution (polymer to T). A total of 200 equiv of T was used for the functionalization of PIB. After 1 h, the reaction mixture was quenched with prechilled methanol and poured into methanol. The polymer was purified by the precipitation of the polymer solution into methanol, followed by drying in a vacuum.

Synthesis of PIB-*b*-P*t*BMA. All copolymerizations were carried out in 1 L stirred glass reactor (Büchi) with a thermostated cooling jacket, steel capillary connections to introduce gases and solvents, and devices to measure temperature and pressure. Solvents were directly introduced from the distillation apparatus into the reactor. Monomer was introduced from glass ampules via a spherical joint or with dry syringe. Solutions of *n*-BuLi and macroinitiator (PIB−T) were handled with syringes. In a typical procedure 5 mL (8 mmol) *n*-BuLi solution were added to 400 mL purified THF and aged at room temperature overnight. On the next day macroinitiator, monomer, and *n*-BuLi were introduced and cooled to −40 °C.[18] A 1.21 g (0.355 mmol) of PIB−T ($M_n = 3.40 \times 10^3$ g/mol) were freeze-dried from benzene solution for 8 h and then vacuum-dried for more than 10 h. On a vacuum line, the dried PIB−T was dissolved in THF and then the mixture was added to the stirred glass reactor and cooled to −40 °C. 0.23 mL (0.368 mmol) *n*-BuLi solution was added with a dry syringe afterward. The reaction was held at −40 °C for 1 h and then 5.34 g (0.037 mol) *t*BMA was added in bulk to the macroinitiator solution. After 2.5 h the polymerization was quenched with methanol. Finally, the polymer was precipitated into 2-propanol and dried under vacuum at room temperature. In a second experiment a 4-fold excess of *n*-BuLi was used and the unreacted BuLi was destroyed by heating to +40 °C for 1 h.

Synthesis of 2-(1,1,3,3-Tetramethylbutyl)thiophene (TMP−T). Model reactions with TMPCl were carried out under identical conditions to living cationic polymerizations of IB at −78 °C. In a 500 mL three-necked flask equipped with a septum, a magnetic stirrer, and a nitrogen inlet were added 16 mL of CH_2Cl_2, 20 mL of *n*-hexane, and 0.07 mL (0.059 g, 0.312 mmol) of D*t*BP, and then the mixture was cooled to −78 C. After 10 min of stirring, 5.07 mL (4.43 g, 29 mmol) of TMPCl was transferred to the reactor by a transfer needle. After 5 min of stirring, 6.57 mL (11.38 g, 60 mmol) of $TiCl_4$ was transferred to the reactor by a transfer needle. One hour later 2.6 mL (2.73 g, 32 mmol) of T in a solution of 6 mL of *n*-hexane and 4 mL of CH_2Cl_2 was added to the system. T was allowed to react with the living chain ends for 60 min. Finally, the reaction was quenched by addition of 20 mL (15.7 g, 0.51 mol) of prechilled methanol. Finally, the solvent was removed on a rotary evaporator, and the product (TMP−T) was dried and distilled under reduced pressure before use.

Lithiation of TMP−T and Reaction with Me_3SiCl. Reaction of lithiated TMP−T with Me_3SiCl was carried out under identical conditions to living anionic polymerizations of *t*BMA. In a 1 L stirred glass reactor were added 400 mL of THF and 1.75 g (8.93 mmol) of TMP−T, and then the mixture was cooled to −40 °C. After 10 min of stirring, 7.25 mL (11.6 mmol) of *n*-BuLi was transferred to the reactor by a transfer needle. *n*-BuLi was allowed to react with TMP−T for 60 min to form the anion ($PIB-T^-,Li^+$). The system was warmed to +40 °C and stirred for 1 h in order to destroy the excess of *n*-BuLi, followed by addition of 1.46 mL (1.26 g, 11.6 mmol) of Me_3SiCl. Finally, the solvent was removed on a rotary evaporator and the product (TMP−T−$SiMe_3$) was dried and distilled under reduced pressure.

Synthesis of Star-Shaped PIB Using $SiCl_4$. The synthesis of star-shaped PIB using $SiCl_4$ was carried out in a glass

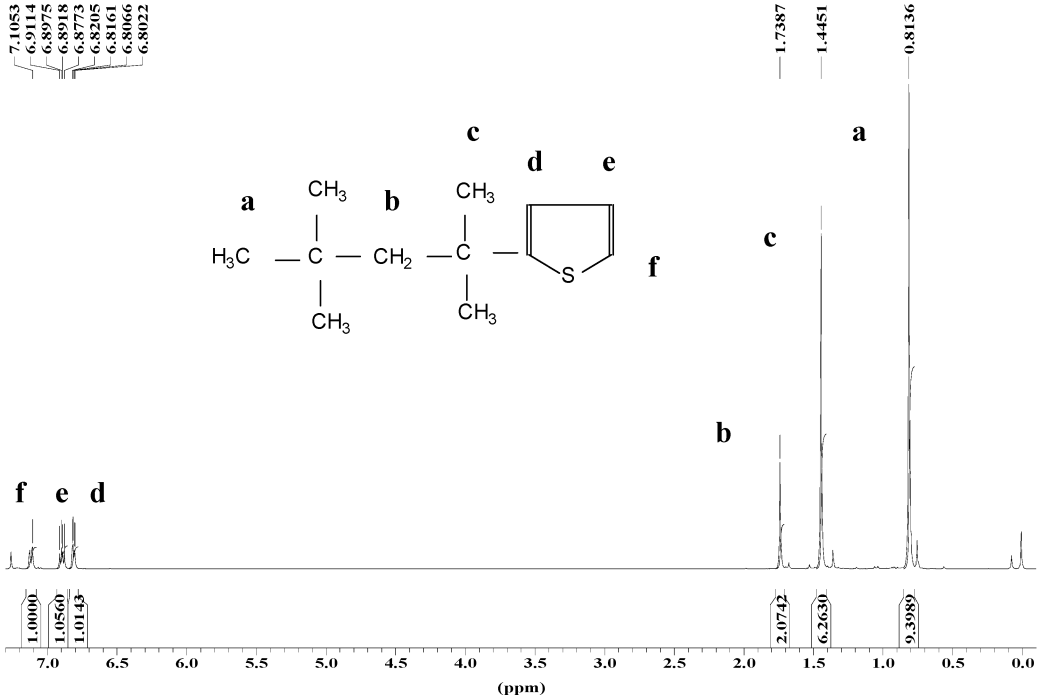


Figure 1. ^{1}H NMR spectrum of 2-(1,1,3,3-tetramethylbutyl)thiophene.

reactor. To the reactor 40 mL of THF and 0.5081 g (0.149 mmol) of PIB−T ($M_n = 3.40 \times 10^3$ g/mol) were added, and then the mixture was cooled to −40 °C. After 10 min of stirring, 0.280 mL (0.448 mmol) of *n*-BuLi was transferred to the reactor by a transfer needle. *n*-BuLi was allowed to react with PIB−T for 60 min Afterward the system was warmed to 40 °C and stirred for 1 h in order to destroy the excess of *n*-BuLi. Then 4.34 μL (0.037 mmol) of $SiCl_4$ was added and allowed to react with the living chain ends for 2 h at 40 °C or for 22 h at 22 °C. Finally, the reaction was quenched by adding 5 mL (3.93 g, 0.12 mol) of prechilled methanol. The product was precipitated into 2-propanol and dried under vacuum at room temperature.

Characterizations. ^{1}H NMR spectroscopy was carried out on a Bruker AC-250 MHz spectrometer at 25 °C in $CDCl_3$ using TMS as an internal standard.

Gas chromatography (GC) was carried out on a Fisons GC 8000 model equipped with flame ionization detection (FID). A DB1 methylpolysiloxane column (30 m × 0.53 mm I. D.) was used with hydrogen as carrier gas.

Size exclusion chromatography (SEC) was performed using THF as eluent at a flow rate of 1 mL/min equipped with four 30 cm PSS SDVgel columns (particle size 5 μm, porosity $10^2 - 10^5$ Å) heated to 40 °C. Calibration was based on PIB and PtBMA standards (PSS, Mainz, Germany). Molecular weights of PIB stars were determined by universal calibration using three 30 cm PSS SDVgel columns of 5 μm with 10^3, 10^5, and 10^6 Å porosity; detectors: Shodex RI-71 refractive index detector; Jasco Uvidec-100-III UV detector (λ = 254 nm); Viscotek viscosity detector H 502B.

Liquid adsorption chromatography under critical conditions (LACCC) was conducted on a TSP HPLC system at a flow rate of 0.5 mL/min. An Evaporative Light Scattering detector (ELSD, PL-EMD 960) operating at 50 °C with a gas flow rate of 3.5 L/min was used for mass detection. Then 10 μL samples of ca. 0.5 wt % polymer solutions were injected. All measurements were carried out at a constant column temperature of 35 °C. Two reversed phase columns (YMC, 250 × 4 mm) with 5 μm average particle size and 100 and 300 Å pore diameters were used. The critical solvent composition for PIB is THF/methanol 80.5/19.5 (w/w). Premixing of the mobile phase by weight is necessary for a constant and exact composition.

Results and Discussion

1. End-Capping of PIB with Thiophene. Model Experiments with TMPCl. Orienting model experiments were carried out with TMPCl, which mimics the end group structure of *tert*-chloro-terminated PIB and the living chain ends upon addition of $TiCl_4$ as a Lewis acid. These reactions were carried out in order to investigate the end-capping with T. The ^{1}H NMR spectrum of 2-(1,1,3,3-tetramethylbutyl)thiophene is shown along with the assignments in Figure 1. The resonances identified in the aromatic range at 6.82 (1H on C_d), 6.89 (1H on C_e), 7.10 (1H on C_f) confirmed one thiophene ring substituted by the TMP residue). In the aliphatic region the ^{1}H NMR spectral assignments are as follows: 0.81 ppm (s, 9H, CH_3), 1.44 ppm (s, 6H, CH_3), 1.73 ppm (s, 2H, CH_2), 6.82 ppm (m, 1H, thiophene CH), 6.89 ppm (m, 1H, thiophene CH), 7.10 ppm (m, 1H, thiophene CH).

Synthesis of Thiophene-Ended PIB (PIB−T). It was of interest to determine whether the end-functionalization results obtained with the model compounds could be applied to the synthesis of thiophene-ended PIB. Thiophene end-quenching of living PIB chain ends initiated by the TMPCl/$TiCl_4$ system took place at −78 °C according to Scheme 1. Figure 2 shows the ^{1}H NMR spectrum of the resulting polymer. This spectrum indicates quantitative end-functionalization and formation of 2-polyisobutylenyl−thiophene (PIB−T) by this process. This confirms results obtained with the corresponding model compound. Quantitative addition was indicated by the disappearance of the peaks at 1.9 (PIB−$\mathbf{CH_2}$−$C(CH_3)_2$−Cl) and 1.69 ppm (PIB−CH_2−$C(\mathbf{CH_3})_2$−Cl). A new set of peaks at 1.82, 6.80, 6.88, and 7.09 ppm appeared due to the presence of the thiophene ring at the chain end. Undesirable coupling products (double addition of PIB at thiophene[12]) or other side reactions, e.g., as determined with furan,[9,19] were not detectable under the conditions used. The details of the capping experiments are given in Table 1.

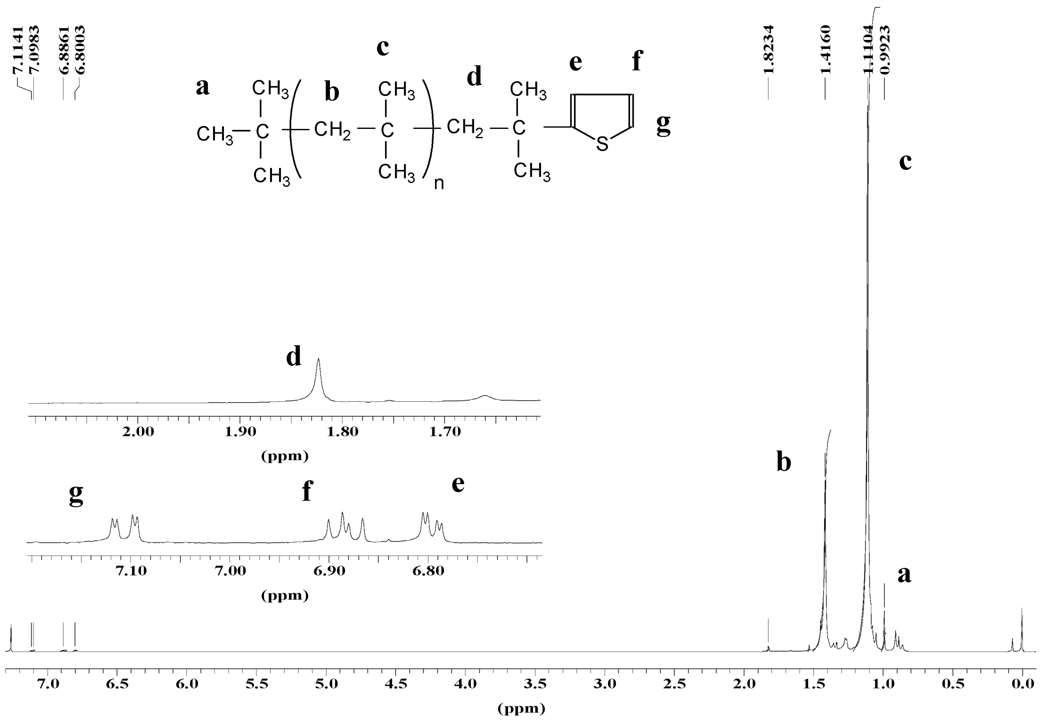


Figure 2. ^{1}H NMR spectrum of thiophene-functionalized PIB.

Scheme 1. Capping of Living PIB with Thiophene

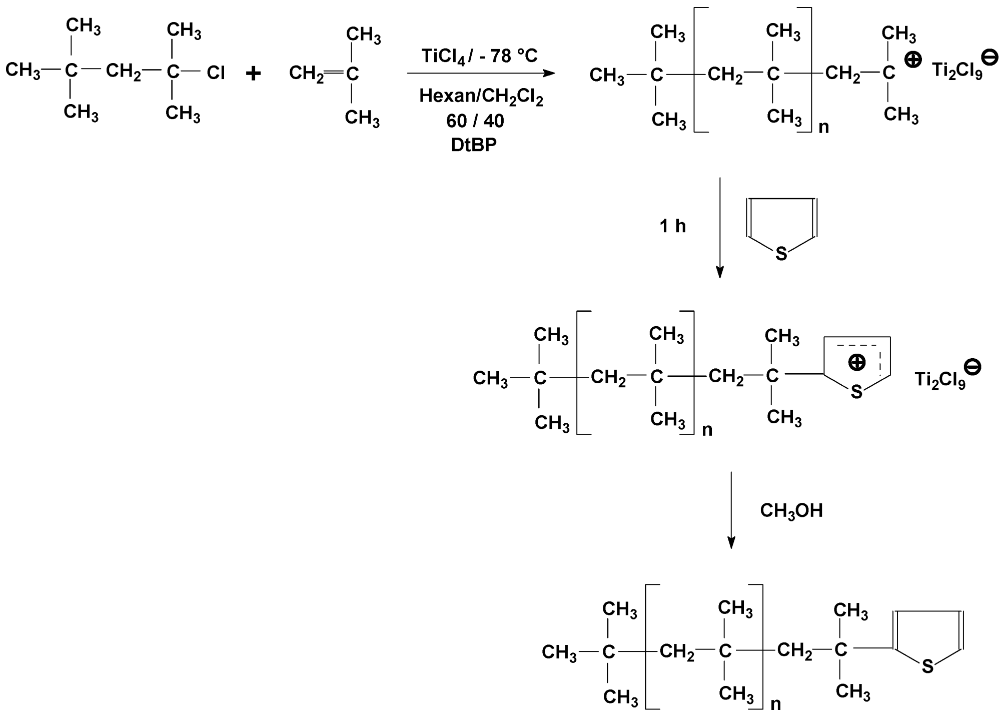


Table 1. Experimental Conditions and Results of IB Polymerization Using TMPCl as Initiator and Thiophene Endcapping

expt no.	$[IB]_o$ (M)	$[TMPCl]_o$ (mM)	$[DtBP]_o$ (mM)	$[TiCl_4]_o$ (mM)	$[T]_o$ (M)	$M_n \times 10^{-3}$ (g/mol)	M_w/M_n
1	0.28	5.35	2.39	21	0.53	3.41	1.25
2	0.44	8.33	3.7	34	0.71	3.23	1.26
3	0.47	8.33	3.7	34	0.71	3.46	1.28

Synthesis of α,ω-Dithiophene-Ended PIB (T−PIB−T). Living PIB was prepared by the polymerization of IB with the *t*BuDiCumCl (1.1×10^{-2} M)/$TiCl_4$ (1.1×10^{-2} M) initiator system in the presence of D*t*BP (3.0×10^{-3} M) as a proton trap in MeCHX/CH_3Cl at −80 °C. After polymerization of IB, the polymer solution was delivered to culture tubes to which additional amount of $TiCl_4$ were charged so that the ratios of [$TiCl_4$] to [*t*BuDiCumCl] in the polymer solution were varied from 1 to 8. T end-functionalization of PIB was conducted by using the methods as described in the Experimental Section. Figure 3 shows the ^{1}H NMR spectra of PIB and PIB−T. As the [$TiCl_4$]/[*t*BuDiCumCl] ratio increased, peaks at 2.0 and 1.7 ppm assigned to methylene and methyl protons at the chain ends of PIB decreased and peak at 1.85 ppm assigned to methylene

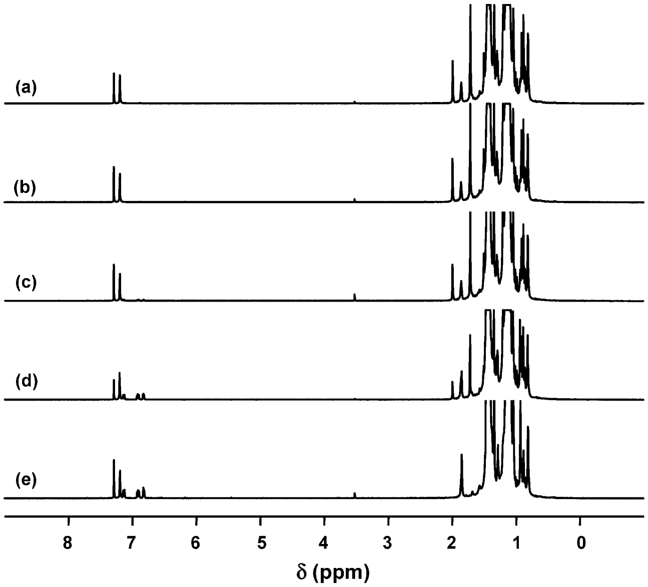


Figure 3. ^{1}H NMR spectra of PIB (a) and PIB−T prepared by the addition of T to polymer at the following ratios [TiCl$_4$]/[*t*BuDiCumCl]: (b) 1; (c) 2; (d) 4; (e) 8.

Table 2. Thiophene Functionalities of PIBs

PIB precursor		capping condition[c]	
M_n (g/mol)	M_w/M_n	[TiCl$_4$]/[*t*BuDiCumCl]	functionality (%)
6900[a]	1.34	1	0
		2	12
		4	50
		8	100
7300[b]	1.11	8	36
		16	85
		24	100
		32	100

[a] Polymerization condition: [*t*BuDiCumCl] = 1.1 × 10^{-2} M, [D*t*BP] = 3.0 × 10^{-3} M, [IB] = 1.1 M, [TiCl$_4$] = 1.1 × 10^{-2} M. [b] Polymerization condition: [*t*BuDiCumCl] = 2.7 × 10^{-3} M, [D*t*BP] = 3.0 × 10^{-3} M, [IB] = 0.27 M, [TiCl$_4$] = 2.2 × 10^{-2} M. [c] Addition method: *T* ([T]/[*t*BuDiCumCl] = 200/1) to polymer.

protons at the chain ends of PIB−T as well as methylene protons adjacent to initiator moiety increased. From the ^{1}H NMR spectra, the functionalities of PIBs were calculated as presented in Table 2. The functionality of PIB increased with [TiCl$_4$]/[*t*BuDiCumCl] and 100% T−PIB−T could be obtained in 1 h at [TiCl$_4$]/[*t*BuDiCumCl] = 8. It is noteworthy that the addition method of T did not affect the functionalization of PIB. The M_n and M_w/M_n of starting PIB and the product was independent of the ratio [TiCl$_4$]/[*t*BuDiCumCl], indicating the absence of coupling reactions.

While T−PIB−T of relatively low M_n could be prepared, as described above, using initiator concentrations in the range of 10^{-2} M, the preparation of high M_n T−PIB−T requires initiator concentrations in the range of 10^{-3} M. To investigate the functionalization reaction of living PIB with T under these conditions, living PIB was prepared by using the following concentrations: [*t*BuDiCumCl] = 2.7 × 10^{-3} M; [TiCl$_4$] = 2.2 × 10^{-2} M; [D*t*BP] = 3.0 × 10^{-3} M. The [TiCl$_4$]/[*t*BuDiCumCl] ratios were varied from 8 to 32. Table 2 shows that when [TiCl$_4$]/[*t*BuDiCumCl] ≥ 24, the functionality of PIB was 100% independent of the addition method of T. While the M_n and M_w/M_n of functionalized PIB did not change with [TiCl$_4$]/[*t*BuDiCumCl], 4−5 mol % of disubstituted thiophene (PIB−T−PIB) was observed in the ^{1}H NMR spectra at [TiCl$_4$]/[*t*BuDiCumCl] ≥ 16.

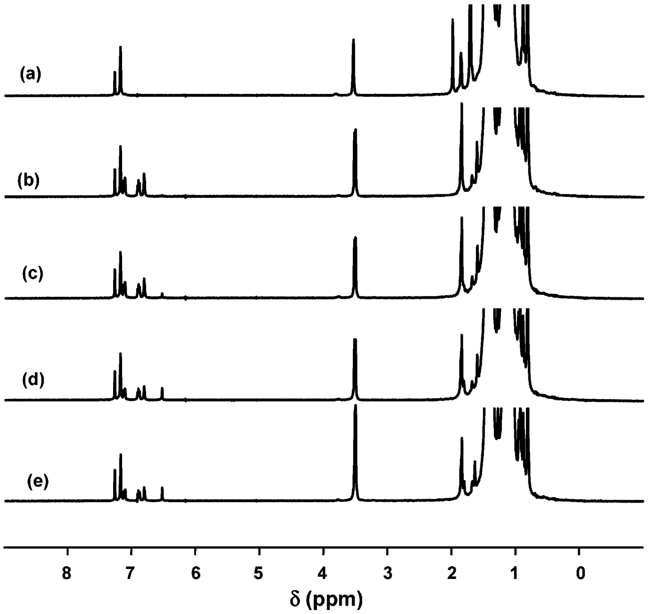


Figure 4. ^{1}H NMR spectra of PIB (a) and PIB−T prepared by the addition of T to polymer at the following ratios [D*t*BP]/[*t*BuDiCumCl]: (b) 0; (c) 1; (d) 2; (e) 3.

Table 3. Fraction of Disubstituted T in PIBs

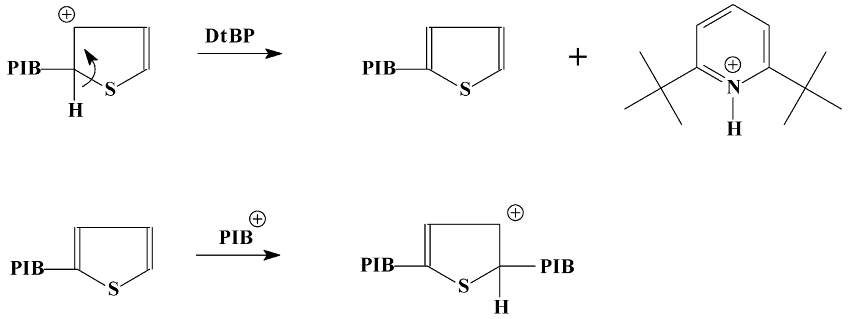
PIB precursor		capping condition[b]	
M_n (g/mol)	M_w/M_n	[D*t*BP]/[*t*BuDiCumCl]	disubstituted T (mol %)
9900[a]	1.67	0	2
		1	8
		2	21
		3	22

[a] Polymerization condition: [*t*BuDiCumCl] = 1.0 × 10^{-3} M, [D*t*BP] = 0 M, [IB] = 0.15 M, [TiCl$_4$] = 3.6 × 10^{-2} M. [b] Addition method: *T* ([T]/[*t*BuDiCumCl] = 200/1) to polymer.

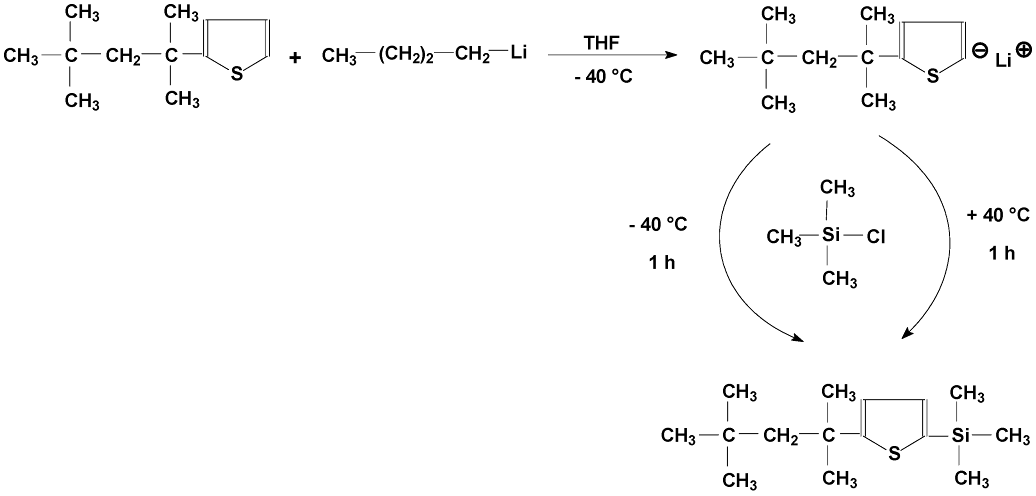
Effect of D*t*BP. Since coupling involves a reaction between living PIB and PIB−T, the first step must involve proton elimination from the PIB−T cation, formed upon addition of T to living PIB. To study the role of D*t*BP, living PIB was prepared without D*t*BP with [*t*BuDiCumCl] = 1.0 × 10^{-3} M and [TiCl$_4$] = 3.6 × 10^{-2} M. The obtained PIB precursor exhibited broad molecular weight distribution (M_w/M_n = 1.67). D*t*BP was then added to the polymer solution for the functionalization to vary the [D*t*BP]/[*t*BuDiCumCl] ratios from 0 to 3. Figure 4 shows the ^{1}H NMR spectra of PIB precursor and functionalized PIBs. As the [D*t*BP]/[*t*BuDiCumCl] ratio increased, the peak at 6.55 ppm assigned to protons at disubstituted T increased and peaks at 6.70−7.15 ppm assigned to protons at monosubstituted T decreased. The functionalities of all samples were calculated to be 100% irrespective of the ratio of [D*t*BP] to [*t*BuDiCumCl]. However, the mol % of disubstituted T moiety from the coupling reaction of PIB cation and T increased with [D*t*BP]/[*t*BuDiCumCl] (Table 3), resulting in the increase of M_n and M_w/M_n of functionalized PIB. From these results, it is evident that D*t*BP plays a major role in the coupling reaction.

Proposed Mechanism of Coupling. The results suggest that the PIB−T cation undergoes deprotonation generating PIB−T in situ (Scheme 2). Whether proton elimination is bimolecular, induced by D*t*BP, or unimolecular and the role of D*t*BP is only to capture the

Scheme 2. Mechanism for the Coupling Reaction of PIB Cation with PIB−T



Scheme 3. Lithiation of TMP−T and Reaction with Me₃SiCl



eliminated proton is not known at present. It is clear, however, that successful preparation of PIB−T is not directly related to the M_n. Low M_n PIB−T could only be prepared without coupled products because high initiator concentration (~10^{-2} M) relative to that of D*t*BP (~10^{-3} M) was used.

According to this finding, D*t*BP should be used in a concentration similar to the concentration of adventitious protic impurities (~1.0×10^{-3} M) and excess of D*t*BP should be avoided especially at low initiator concentrations. Accordingly, high M_n PIB−T was prepared under the following conditions: [IB] = 1.5 M; [*t*BuDiCumCl] = 1.5×10^{-3} M; [D*t*BP] = 1.0×10^{-3} M; [$TiCl_4$] = 3.6×10^{-2} M. M_n and M_w/M_n of PIB−T prepared from the reaction of living PIB with T (M_n = 52 000 g/mol) and those of PIB precursor (M_n = 50 100 g/mol) are virtually identical. ^{1}H NMR spectroscopy of the products confirmed the quantitative functionalization and disubstituted thiophene in PIB−T was undetectable.

2. Lithiation of PIB−T. Lithiation of the Model Compound 2-(1,1,3,3-tetramethylbutyl)thiophene (TMP—T). Orienting model experiments were carried out with TMP−T which mimics the end group structure of PIB−T. These reactions were carried out in order to optimize the lithiation of PIB−T and to test the stability of the anionic chain ends, PIB−T$^-$,Li$^+$, at elevated temperature. The major consequence of incomplete lithiation is the presence of unreacted precursor together with the desired block copolymer. Besides, unreacted *n*-BuLi can separately initiate the anionic polymerization of *t*BMA or it can attack the ester group by a nucleophilic substitution.[20] The easiest way to remove excess *n*-BuLi is to heat the THF solution, since *n*-BuLi reacts with THF at elevated temperature, forming ethylene and alkoxides.[21] Thus, an excess of *n*-BuLi can be used for the lithiation and then it can be destroyed by warming. This method can only be used if the formed anion (PIB−T$^-$,Li$^+$) is stable under these conditions. Some organolithium compounds are known to react with THF and other ethers[22] but no information exists on the thermal stability of the anion PIB−T$^-$,Li$^+$. Thus, a model reaction was carried out using TMP−T. This reaction is shown in Scheme 3.

The lithiation of TMP−T was performed at −40 °C, using an excess of *n*-BuLi. Prior to the lithiation, a sample was taken to determine the exact concentration of TMP−T from gas chromatography (GC) and NMR spectroscopy. After 1 h of reaction, Me_3SiCl was added to part of the reaction solution. Then the remaining reaction mixture was warmed to +40 °C for 1 h, to destroy the residual *n*-BuLi. After 1 h at +40 °C, Me_3SiCl was added. The reaction products were characterized by GC and NMR spectroscopy. Figure 5 shows the ^{1}H NMR spectrum of the resulting product. This spectrum indicates quantitative formation of 2-(trimethylsilyl)-5-(1,1,3,3-tetramethylbutyl)thiophene. Quantitative addition was indicated by the disappearance of the peak at 7.10 ppm. A new peak at 0.29 ppm appeared due to the presence of the trimethylsilyl group. The conversion of this reaction was determined by GC (Figure 6). The GC characterization was carried out using decane as an internal standard. Both samples taken at −40 and at +40 °C showed high yields (>98.9%) in the formation of 2-(trimethylsilyl)-5-(1,1,3,3-tetramethylbutyl)thiophene. This means that the anion formed during the lithiation (TMP−T$^-$,Li$^+$) is stable for an hour even after the warming of the reaction mixture to +40 °C. Thus, the results of the model experiments indicated that the lithiation of the precursor (PIB−T)

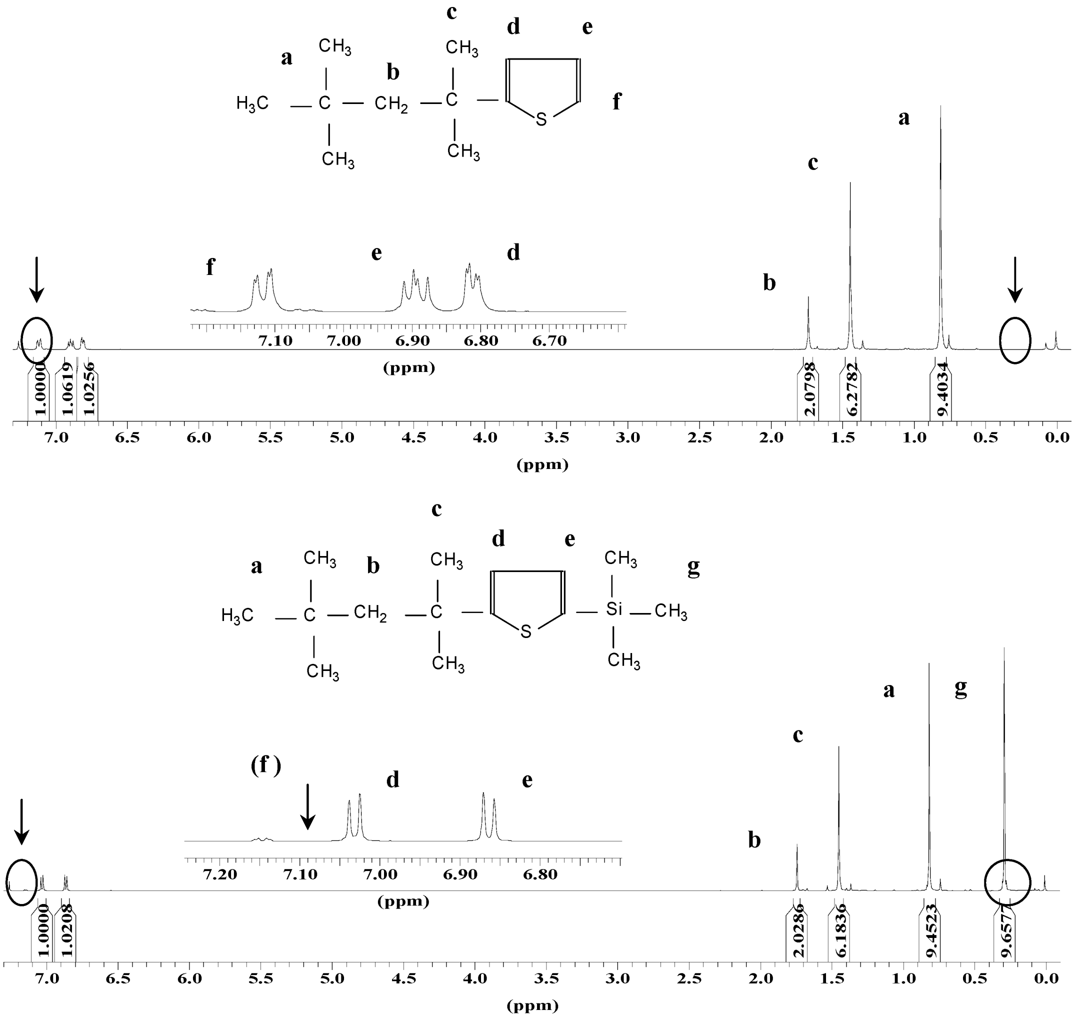


Figure 5. ^{1}H NMR spectrum of TMP−T before and after quenching with Me_3SiCl at +40 °C.

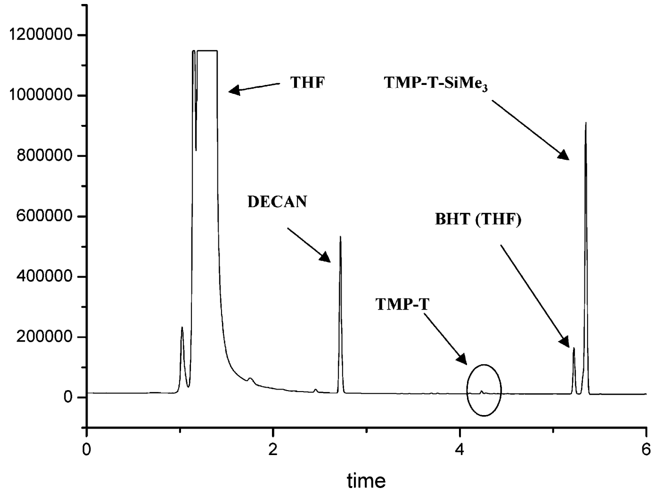


Figure 6. Gas chromatography analysis of TMP−T after quenching with Me_3SiCl at +40 °C, indicating complete conversion of TMP−T to TMP−T−$SiMe_3$.

should be carried out using an excess of *n*-BuLi, and then the excess can be destroyed by warming without affecting the stability of the formed anion (PIB−T^-,Li^+).

3. Synthesis of PIB-*b*-P*t*BMA. The synthesis of PIB-*b*-P*t*BMA was accomplished by using lithiated PIB−T as an anionic macroinitiator of *t*BMA polymerization in THF (Scheme 4). In the first experiment an equimolar amount of *n*-BuLi was used for the metalation, in the second one a 4-fold excess. Subsequent heating in THF to +40 °C was used to destroy the residual *n*-BuLi. The lithiated precursor PIB−T^-,Li^+ was used to initiate the polymerization of *t*BMA.

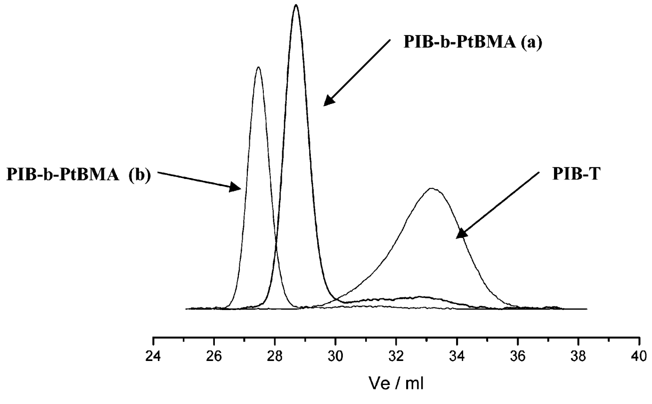
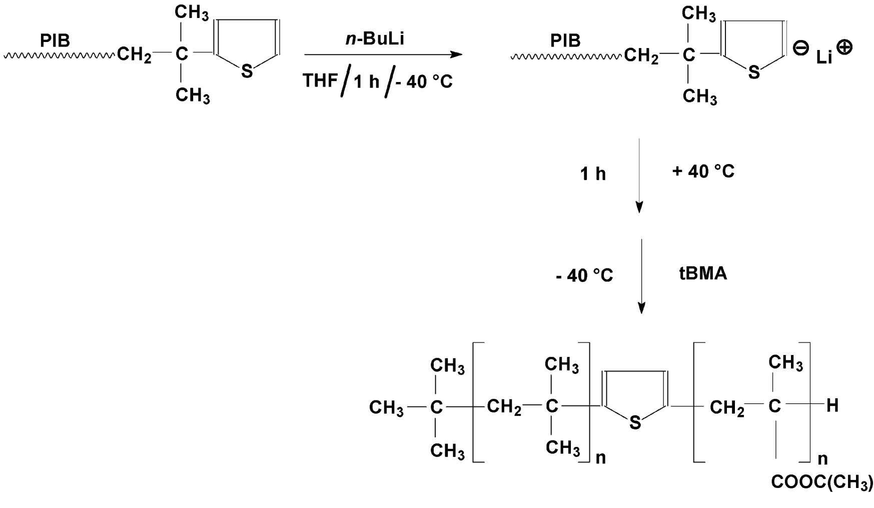


Figure 7. SEC traces (RI detector) of PIB-*b*-P*t*BMA (a) [*n*-BuLi]:[PIB−T] = 1:1 and (b) [*n*-BuLi]:[PIB−T] = 4:1.

The complete characterization of block copolymers, i.e., the measurement of molar mass distribution in combination with the chemical distribution of the components of the desired architecture (diblock, triblock, multiblock), is necessary for optimization of synthesis methods. Thus, the resulting polymers were first investigated by SEC. Figure 7 shows the SEC eluograms (RI signal) for these block copolymers. The molecular weights determined by GPC using P*t*BMA standards are appar-

Scheme 4. Synthesis of PIB-*b*-P*t*BMA Block Copolymer



PIB-b-PtBMA

Table 4. SEC and LACCC Characterization of PIB-*b*-P*t*BMA[a]

expt no.	[BuLi]/ [PIB−T]	[PIB−T] (mM)	[tBMA] (M)	$10^{-3}M_{n,th}$[b]	$10^{-3}M_{n,GPC}$ (block copolymer)	M_w/M_n (block)	$10^{-3}M_{n,GPC}$ (PtBMA block)	f_{block}(GPC) (M_n[c])	f_{block}(GPC) (area[d])	f_{block}(LACCC) (area[e])
2	1	1.18	0.125	15.0	27.3	1.02	24.1	0.62	0.67	0.77
3	4	0.93	0.196	30.0	47.3	1.02	43.8	0.63	0.82	0.87

[a] SEC molecular weights of block copolymers were determined with P*t*BMA standards and represent apparent values only, [b] expected molecular weight of P*t*BMA block, [c] blocking efficiency, $f_{block} = M_{n,GPC;PTBMA}/M_{n,th}$, [d] blocking efficience determined by GPC from the area of PIB precursor (UV at 254 nm), [e] as determined by LACCC with UV detector (245 nm).

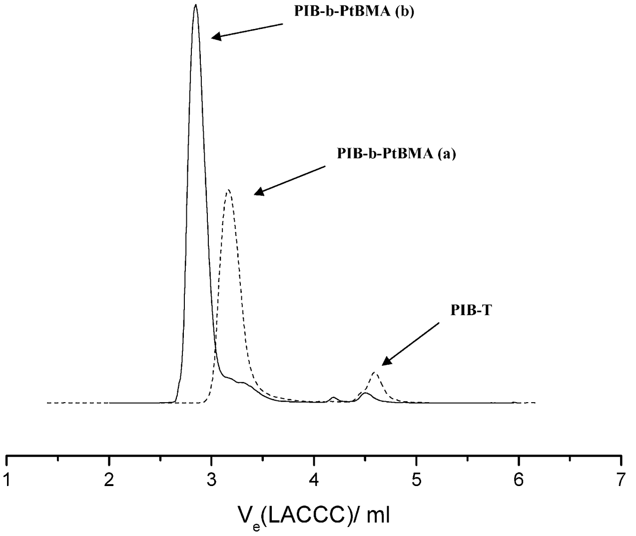


Figure 8. LACCC chromatograms of PIB-*b*-P*t*BMA at critical conditions of PIB (ELSD detector (a) [*n*-BuLi]:[PIB−T] = 1:1 and (b) [*n*-BuLi]:[PIB−T] = 4:1.

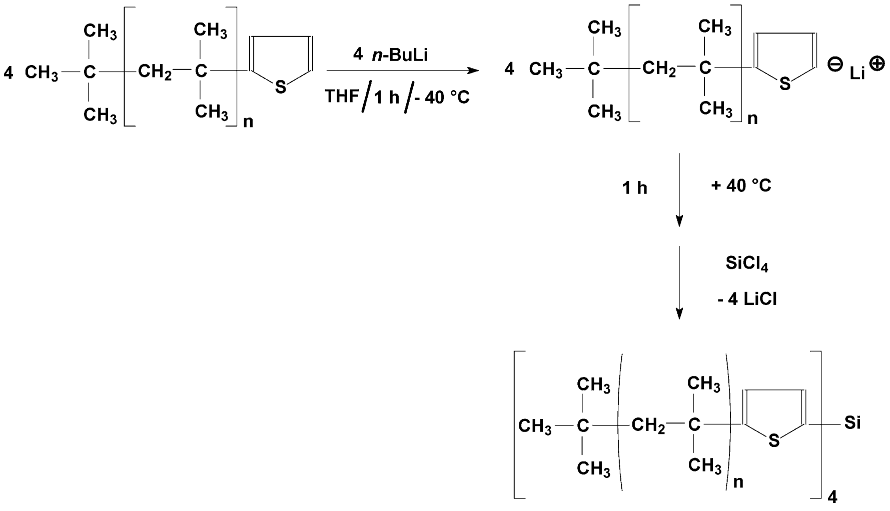
ent values, which can be higher than the real ones. Accordingly, the blocking efficiencies given in Table 4 should be taken as apparent ones, too. In addition, the blocking efficiencies were calculated from the area of the PIB precursor in the GPC eluogram. Since only thiophene is UV-active at 254 nm, the relative area under UV signal of the PIB−T precursor is directly related to the molar fraction of unreacted precursor. It can be seen that a peak appears for the unreacted PIB in the polymer lithiated by an equimolar amount of *n*-BuLi, however, much less precursor is detected when an excess of *n*-BuLi is used.

Liquid chromatography at critical conditions of adsorption (LACCC) is a recent and most powerful method for the characterization of block copolymers according to the chemical heterogeneity.[23−25] Separation of polymers at critical conditions of adsorption allows for the elution of homopolymers independent of their molar mass on porous separation phases using mixed mobile phases. Under these conditions, homopolymers can be separated according to the number and nature of functional groups, e.g., end groups or comonomers. Because of a better separation, LACCC is more sensitive for a quantitative determination of the precursor content than SEC. Figure 8 shows the LACCC chromatograms of the two PIB-*b*-P*t*BMA's at critical conditions of PIB. In line with the results of the lithiation of TMP−T, it is verified that the excess of *n*-BuLi is deactivated and that PIB−T$^-$,Li$^+$ is stable at +40 °C and it can initiate the polymerization of *t*BMA. These results clearly show high blocking efficiency and the formation of the desired PIB-*b*-P*t*BMA block copolymer (Table 4). For the quantitative evaluation of the data the UV signal was used (similar to GPC).

To prove the absence of homo-poly(*tert*-butyl methacrylate), we conducted a chromatography (LACCC) measurements of PIB-*b*-P*t*BMA at critical conditions of P*t*BMA (THF/acetonitrile 49.5/50.5), which should confirm the absence of homopolymer. Although the block copolymer completely adsorbs to the stationary phase under these conditions, no traces of P*t*BMA homopolymer were found.

Initiation of tBMA Polymerization by Thienyllithium. To obtain more information on the initiation process, we conducted a polymerization of *t*BMA, which was initiated by the model compound thienyllithium (2-lithiothiophene) in THF at −40 °C. Then 30.8 mmol of *t*BMA were added to 1.37 mmol of thienyllithium. After 2 h, 96% conversion was found by GC. ($M_{n,th}$ = 3152 g/mol.) GPC resulted in M_n = 4100 g/mol and M_w/M_n = 1.17, leading to an initiator efficiency f = 0.77. NMR

Scheme 5. Synthesis of PIB Stars



resulted $M_n = 3740$ g/mol and $f = 0.84$. NMR also showed the expected peaks of the thiophene moiety. Details are given as Supporting Information. Thus, we can conclude that lithiated thiophene has a high but not quantitative initiator efficiency.

4. Synthesis of Star-Shaped PIB Using $SiCl_4$. In the synthesis of star polymers the linking reaction is usually the slowest step and star polymers made by cationic polymerization usually require cryogenic cooling.[26] Up to now, no star coupling agent is known for living carbocationic PIB chain ends. Usually, coupling is brought about by the use of bifunctional monomers, e.g., divinylbenzene,[26] yielding a mixture of stars with different arm numbers. Thus, it was one of our incentives to develop a room-temperature linking method. We hypothesized that this objective may be reached by reacting lithiated PIB−T with chlorosilanes, e.g. $SiCl_4$. Chlorosilanes have been frequently used to couple anionic chain ends, e.g. living polybutadiene. Scheme 5 shows the synthetic strategy for the preparation of star PIB using lithiated PIB−T and $SiCl_4$.

An experiment was conducted at room temperature with a PIB-T precursor of SEC peak molecular weight $M_p = 4000$ g/mol. After 12 h, star formation was well underway; however, a large fraction of unreacted PIB chains remained (see Figure 9). The final star polymer was obtained after 22 h reaction time. The polymer at this stage shows the formation of a polymer with $M_p = 14\,600$ g/mol (as determined by a SEC−viscosity measurement using universal calibration), corresponding to a star with 3.7 arms on average. A certain amount of three-armed stars cannot be excluded, which may be due to insufficient reaction times or to steric hindrance caused by the thiophene ring. However, it was shown earlier that the addition of four molecules of thienyllithium to tetrachlorosilane or tetramethoxysilane is possible.[27,28]

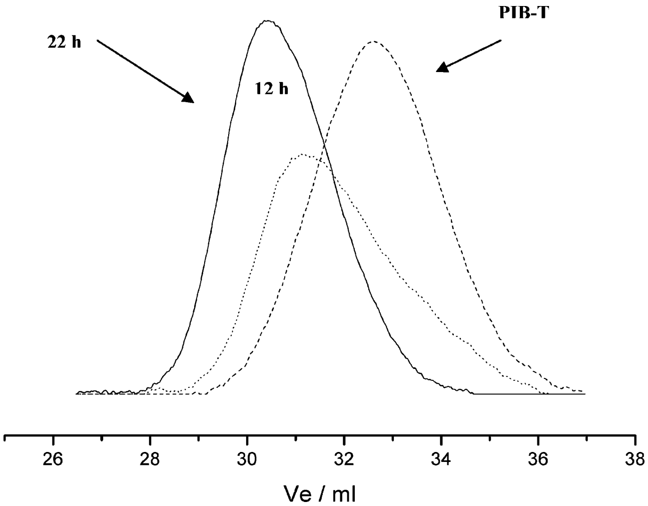


Figure 9. SEC traces (RI detector) of the arm precursor and samples taken during the linking reaction of PIB−T with $SiCl_4$.

Conclusions

Quantitative functionalization of living PIB with thiophene has been achieved. The process is complicated by coupling between living PIB and PIB−T formed by in situ deprotonation, in which D*t*BP plays an important role. Deprotonation can be avoided by using D*t*BP at a lowest concentration necessary to avoid protic initiation from adventitious protic impurities. By lithiation of PIB−T a new, convenient method has been demonstrated for the synthesis of PIB-based block copolymers, involving anionic initiation of methacrylic monomers. A major improvement is that for an industrial process, lithiation by *n*-BuLi is much more convenient than metalation by Na/K alloy. Linear block copolymers with narrow and unimodal MWD were synthesized under well-controlled conditions. The lithiated thiophene-capped PIB was used to prepare four-armed stars via chlorosilane coupling. Polymerization studies with further polar monomers, e.g., *N*,*N*-dimethylacrylamide, ethylene oxide, ϵ-caprolactone, and L-lactide are in progress. The resulting products are potential new thermoplastic elastomers, dispersing agents, compatibilizers, emulsifiers, nonionic surfactants, or biomaterials.

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Supporting Information Available: Text and figures giving the details of the polymerization of *t*BMA with thienyllithium. This material is available free of charge via the Internet at http://pubs.acs.org.

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