

Synthesis of Halogen-Free Polyisobutylene by in situ Hydride Transfer to Living Polyisobutylene from Tributylsilane

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Summary

Hydride transfer reaction between living polyisobutylene cation (PIB⁺) and tributylsilane in hexanes/methyl chloride 60/40 (v/v) solvent mixtures at –80, –70 and –60 °C was studied to synthesize halogen-free polyisobutylene (PIB). The hydride transfer reaction between tributylsilane and living PIB capped with 1,1-ditolylethylene (PIB-DTE⁺) have also been carried out under similar conditions at –80 °C. The rate of hydride transfer reaction increases with the increase of tributylsilane concentration for the reaction of both PIB⁺ and PIB-DTE⁺ with tributylsilane. Gel Permeation Chromatography and NMR Spectroscopy suggested practically complete capping of the polymeric cation and the absence of side reactions.

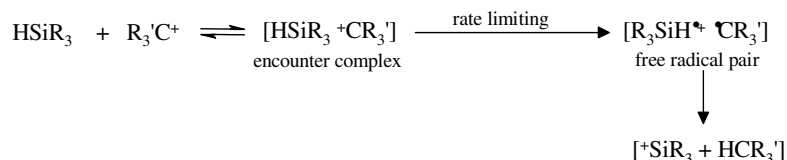
Introduction

Polyisobutylene (PIB), obtained by the cationic polymerization of isobutylene (IB), possesses excellent oxidative, chemical and thermal stability due to its saturated chain structure [1]. However, the living carbocationic polymerization of IB in the presence of Lewis acid yield PIB with thermally sensitive and chemically labile terminal chlorine group, a polymeric *tert*-alkyl chloride. In recent years, there has been a resurgence of interest in replacement of the *tert*-chloro end group with a thermally stable and chemically inert end group e.g., for the transformation from living cationic polymerization to living anionic polymerization [2].

Earlier reports show that organometallic reagents have been used extensively for the replacement of chlorine with an alkyl group from a *tert*-alkyl chloride [3-9]. In a previous publication [10], Takacs and Faust reported in situ methylation of living PIB using trimethylaluminum, a strong Lewis acid, which can induce undesirable side reactions such as head- or in-chain functionalities [11]. Recently, we have described in situ methylation of living PIB using dimethylzinc under much milder reaction conditions [12].

Hydrosilanes are often used as reducing agent for selective reduction of a variety of functional groups [13]. In the presence of a Brønsted or Lewis acid, hydride transfer from silicon to positively charged carbon with the formation of silicenium ions (a very short lived reaction intermediate) takes place [14]. The reaction of hydrosilanes with

carbenium ions involves rate-limiting single electron transfer, followed by a rapid hydrogen shift as shown below in Scheme 1.



Scheme 1. The reaction of hydrosilanes with carbenium ions.

It is also known that TiCl_4 does not react with ordinary silanes at low temperature [14]. In-situ reaction of the living PIB capped with 1,1-phenylethylene (DPE) with tributyltin hydride showed no side reactions and quantitative formation of PIB-DPE-H [15]. In this report, in situ hydride transfer reaction between living polyisobutylene (PIB) cation and living PIB capped with 1,1-ditolylethylene with tributylsilane in hexanes/methyl chloride (MeCl) 60/40 (v/v) solvent mixtures was studied.

Experimental

Materials

Methyl chloride (MeCl) and isobutylene (IB) were dried in the gaseous state by passing them through in-line gas-purifier columns packed with BaO/Drierite. They were condensed in the cold bath of a glove box prior to polymerization. Titanium tetrachloride (TiCl_4 , Aldrich, 99.9 %), 2,6-di-*tert*-butylpyridine (DTBP, Aldrich, 97+ %), and tributylsilane (Bu_3SiH , Aldrich, 97+ %) were used as received. The 2-chloro-2,4,4-trimethylpentane (TMPCl) was synthesized according to the literature [16]. The 1,1-di-*p*-tolylethylene (DTE) was synthesized according to the literature [17-18]. Hexanes (Hex, Doe & Ingals, Technical grade) was refluxed for 60 hours with concentrated sulfuric acid. It was washed three times with 10 % NaOH and then with distilled water repeatedly until neutral. After drying overnight over anhydrous Na_2SO_4 , it was refluxed under nitrogen overnight with calcium hydride (CaH_2) for 24 hours and distilled to a round bottom flask containing CaH_2 . It was again refluxed overnight with CaH_2 under nitrogen and distilled just before use. Methanol (MeOH, Doe & Ingals, Technical grade) was purified by simple distillation.

Polymerization

A typical experimental procedure is as follows: Polymerizations were carried out under a dry nitrogen atmosphere in an MBraun 150-M glove box (Innovative Technology Inc., Newburyport, Massachusetts). Large (75 mL) culture tubes were used as polymerization reactors. Throughout the study IB was considered as apolar solvent and its volume was added to the volume of hexanes. The total volume of the reaction mixture was 25 mL. After predetermined time the polymerization was terminated by the addition of excess prechilled methanol (1.0 mL). The polymer was recovered and purified two times by reprecipitation from Hex/methanol. Monomer conversions were determined by gravimetric analysis.

Characterization

Molecular weights were measured with a Waters HPLC system equipped with a model 510 HPLC pump, model 410 differential refractometer, model 441 absorbance detector, on-line multiangle laser light scattering (MALLS) detector (MiniDawn, Wyatt Technology Inc.), Model 712 sample processor, and five Ultrastyrigel GPC columns connected in the following series: 500, 10^3 , 10^4 , 10^5 , and 100 Å. Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL/min at room temperature. The measurements were carried out at room temperature. The ^1H and ^{13}C NMR spectroscopy was carried out on a Bruker 500 MHz spectrometer using CDCl_3 as a solvent (Cambridge Isotope Lab., Inc.). The ^1H and ^{13}C NMR spectra of solutions in CDCl_3 were calibrated to tetramethylsilane as internal standard (δ_{H} 0.00) or to the solvent signal (δ_{C} 77.0), respectively.

Results and Discussion

Reaction of Living PIB^+ Cation with Bu_3SiH

First, IB was polymerized for 75 minutes by the $\text{TMPCl}/\text{TiCl}_4$ initiating system in Hex/MeCl 60/40 (v/v) at $-80\text{ }^\circ\text{C}$ using $[\text{IB}] = 0.08\text{ mol L}^{-1}$, $[\text{TMPCl}] = 0.002\text{ mol L}^{-1}$, $[\text{DTBP}] = 0.004\text{ mol L}^{-1}$ and $[\text{TiCl}_4] = 0.036\text{ mol L}^{-1}$. Complete conversion of the IB polymerization was reached by this time. Then Bu_3SiH solution was added under stirring to the reaction mixture containing living PIB. Before and during the reaction between Bu_3SiH and living PIB, after predetermined time samples were quenched with prechilled methanol (1.0 mL) for characterization. The experimental results are given in Table 1. The GPC RI traces of the original PIB and PIB obtained after the reaction of PIB^+ with Bu_3SiH ($[\text{Bu}_3\text{SiH}] = 0.004\text{ mol L}^{-1}$) at different times are shown in Figure 1, which confirms that the number average molecular weight and molecular weight distributions remain unchanged. The ^1H NMR spectra of the original PIB and PIB obtained after the reaction of PIB^+ with Bu_3SiH at different times are shown in Figure 2.

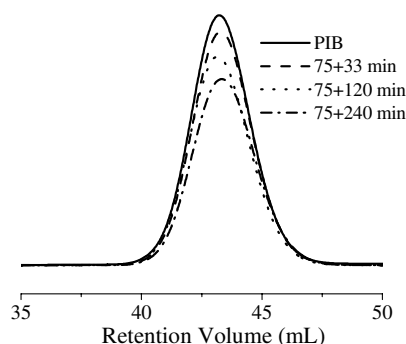


Figure 1. The GPC RI traces of the original PIB (PIB-Cl) and PIB obtained after the reaction of PIB^+ with Bu_3SiH at different times in Hex/MeCl 60/40 (v/v) at $-80\text{ }^\circ\text{C}$ using $[\text{IB}] = 0.08\text{ mol L}^{-1}$, $[\text{TMPCl}] = 0.002\text{ mol L}^{-1}$, $[\text{DTBP}] = 0.004\text{ mol L}^{-1}$, $[\text{TiCl}_4] = 0.036\text{ mol L}^{-1}$ and $[\text{Bu}_3\text{SiH}] = 0.004\text{ mol L}^{-1}$. Bu_3SiH was added under stirring after 75 minutes of IB polymerization.

Table 1. Experimental results for the reaction of PIB⁺ with Bu₃SiH^a

Expt. No.	Temp. (°C)	[Bu ₃ SiH] (mol L ⁻¹)	Time (min)	<i>M_n</i> (GPC)	PDI	PIB-H (%)
PIB	-80	-	75	2480	1.08	0
1	-80	0.004	75+33	2520	1.12	38.1
2	-80	0.004	75+60	2530	1.12	67.2
3	-80	0.004	75+120	2640	1.11	97.9
4	-80	0.004	75+180	2540	1.14	~100
5	-80	0.004	75+240	2440	1.12	~100
6	-80	0.007	75+33	2500	1.12	64.3
7	-80	0.007	75+60	2630	1.16	88.8
8	-80	0.007	75+120	2550	1.15	~100
9	-80	0.01	75+33	2460	1.10	79.7
10	-80	0.01	75+60	2480	1.11	96.1
11	-80	0.01	75+120	2500	1.11	~100
12	-80	0.015	75+33	2540	1.19	86.3
13	-80	0.015	75+60	2570	1.18	~100
14	-80	0.02	75+33	2500	1.14	90.8
15	-80	0.025	75+33	2500	1.20	92.3
16	-80	0.03	75+33	2540	1.18	95.4
17	-80	0.03	75+60	2600	1.16	~100
18	-70	0.03	150+60	2650	1.13	88.4
19	-60	0.03	240+60	2590	1.10	77.6
20	-60	0.03	240+180	2640	1.13	85.3

^a [IB] = 0.08 mol L⁻¹, [TMPCl] = 0.002 mol L⁻¹, [DTBP] = 0.004 mol L⁻¹, [TiCl₄] = 0.036 mol L⁻¹ in Hex/MeCl 60/40 (v/v).

Quenching living PIB with methanol always yields PIB with a terminal-chlorine group (PIB-Cl, i.e., PIB-CH₂-C(CH₃)₂-Cl), and the ¹H NMR spectrum of PIB-Cl exhibits characteristic resonance signals at δ = 1.94 ppm and 1.67 ppm, corresponding respectively to -CH₂- and -CH₃ protons next to the terminal-chloro group. When the reaction mixture of living PIB⁺ and Bu₃SiH was quenched with methanol prior to completion, a mixture of PIB-Cl with PIB-CH₂-C(CH₃)₂-Cl and PIB-H with PIB-CH₂-C(CH₃)₂-H functionalities was observed from ¹H NMR spectra of the products (Figure 2). The ¹H NMR spectra in Figure 2 shows that the characteristic resonance signals for PIB-Cl at δ = 1.94 ppm and 1.67 ppm slowly diminishes with increasing reaction time with Bu₃SiH ([Bu₃SiH] = 0.004 mol L⁻¹) and after 3 hours the signal at δ = 1.94 ppm is completely absent, indicating that the conversion of PIB-Cl to PIB with a terminal-H (PIB-H) is essentially quantitative. The % PIB-H was calculated by comparing the characteristic resonance signal of PIB-CH₂-C(CH₃)₂-H at 1.65-1.75 ppm, and the resonance signals of PIB-CH₂-C(CH₃)₂-Cl at δ = 1.94 ppm and 1.67 ppm using the relation: % PIB-H = [(I_{δ=1.65-1.75} - 3xI_{1.94})/I_{δ=1.65-1.75}] x 100. The results are given in Table 1.

The reaction of living PIB⁺ with Bu₃SiH was also studied at higher [Bu₃SiH] and temperature (-70 and -60 °C), and the summary of results are given in Table 1. The apparent activation energy of polymerization, *E_a* = -8.5 kcal mol⁻¹ was reported for the cationic polymerization of IB in Hex/MeCl 60/40 (v/v) solvent mixture [19-20]. So, a longer polymerization time of IB was used to get 100 % conversion: 150 minutes at -70 °C and 240 minutes at -60 °C. Table 1 shows that the rate of hydrogen transfer

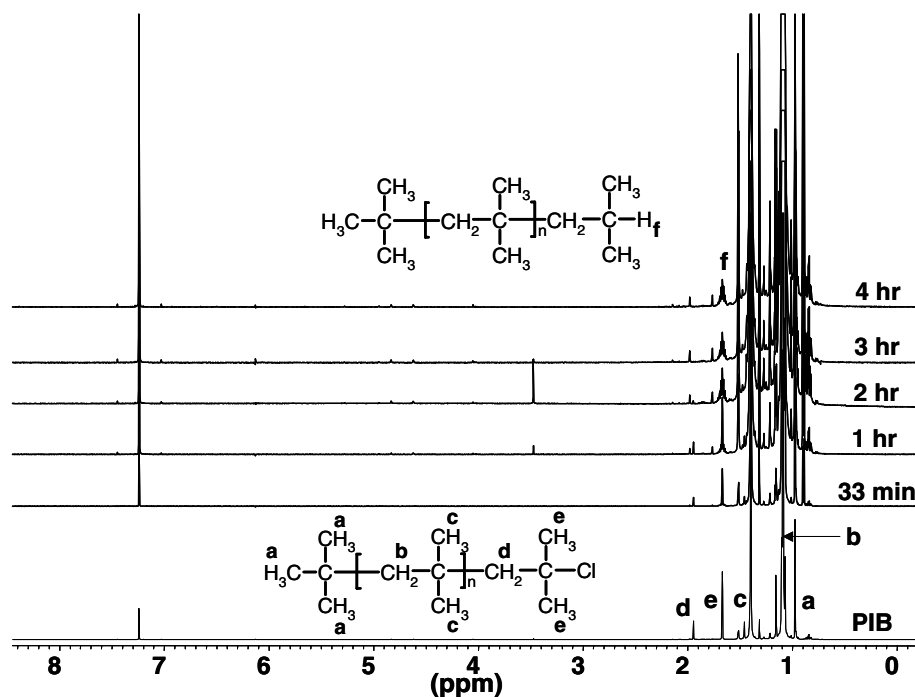
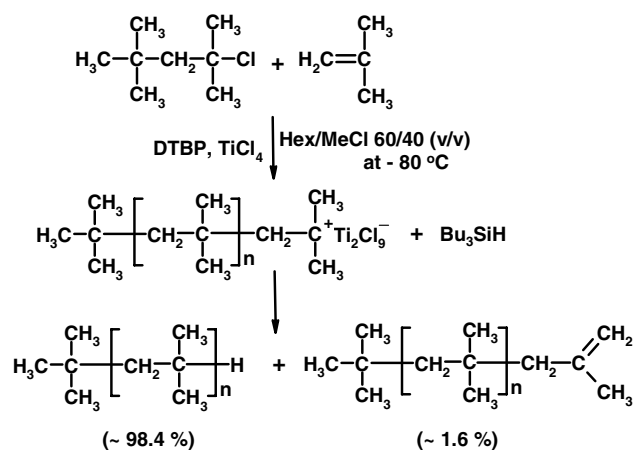


Figure 2. The ^1H NMR spectra of the original PIB (PIB-Cl) and PIB obtained after the reaction of PIB^+ with Bu_3SiH at different times in Hex/MeCl 60/40 (v/v) at -80°C . Reaction conditions are the same as in Figure 1.

reaction increases with increasing concentration of Bu_3SiH and decreasing temperature. The decreasing rate of hydrogen transfer reaction with increasing temperature can be attributed mainly to the changes in the active center concentration, which decreases with increasing temperature [21].



Scheme 2. The capping of PIB^+ cation with Bu_3SiH .

From the NMR analysis, it was found that 100 % capping was reached at $[\text{Bu}_3\text{SiH}] = 0.004 \text{ mol L}^{-1}$ in 3 hours at $-80 \text{ }^\circ\text{C}$. Based on the ^1H NMR analysis; the capping of PIB^+ cation with Bu_3SiH can be presented as shown in Scheme 2. In addition to $\sim 98.4 \%$ hydride transfer product, $\sim 1.6 \%$ exo-olefinic structure at the end of the polymer is obtained, which shows a multiplet at 4.67 and 4.87 ppm. Under the same condition at $-70 \text{ }^\circ\text{C}$ and $-60 \text{ }^\circ\text{C}$, $\sim 2.8 \%$ and $\sim 4.2 \%$ exo-olefinic structure at the end of the polymer were obtained, respectively.

Reaction of Living PIB-DTE⁺ Cation with Bu₃SiH

It was already reported in the literature that quenching stable carbocations, such as diaryl carbenium ions, with methanol produces methoxy end-functionality [22]. This functionality, however, is also labile and therefore undesirable when alkaline conditions are used in further reactions, e.g., addition reaction of double diphenylethylene functionalized PIB macromonomer to living polymeric anions. Therefore the hydride transfer reaction of living PIB with DTE was studied, which yields a stable and fully ionized PIB-DTE cation (PIB-DTE^+), followed by the addition of Bu_3SiH . First, IB was polymerized for 75 minutes by TMPCl/TiCl_4 initiating system in Hex/MeCl 60/40 (v/v) solvent mixture at $-80 \text{ }^\circ\text{C}$ using $[\text{IB}] = 0.08 \text{ mol L}^{-1}$, $[\text{TMPCl}] = 0.002 \text{ mol L}^{-1}$, $[\text{DTBP}] = 0.004 \text{ mol L}^{-1}$ and $[\text{TiCl}_4] = 0.036 \text{ mol L}^{-1}$. After 75 minutes, $[\text{DTE}] = 0.004 \text{ mol L}^{-1}$ was added to living PIB and the capping reaction was carried out for 60 minutes. Then Bu_3SiH solution was added to the reaction mixture. The results are given in Table 2.

Table 2. Experimental results for the reaction of PIB-DTE^+ with Bu_3SiH in Hex/MeCl 60/40 (v/v) at $-80 \text{ }^\circ\text{C}$ ^a

Expt. No.	$[\text{Bu}_3\text{SiH}]$ (mol L^{-1})	Time (min)	M_n (GPC)	PDI	PIB-DTE-H (%)
PIB	-	75	2500	1.10	-
PIB-DTE	-	75+60	2740	1.08	-
1	0.01	75+60+60	2850	1.11	95.1
2	0.01	75+60+120	2800	1.07	~ 100
3	0.01	75+60+180	2760	1.10	~ 100
4	0.01	75+60+240	2690	1.11	~ 100
5	0.02	75+60+60	2780	1.10	~ 100
6	0.03	75+60+60	2670	1.13	~ 100
7	0.045	75+60+60	2790	1.11	~ 100
8	0.06	75+60+60	2750	1.09	~ 100

^a $[\text{IB}] = 0.08 \text{ mol L}^{-1}$, $[\text{TMPCl}] = 0.002 \text{ mol L}^{-1}$, $[\text{DTBP}] = 0.004 \text{ mol L}^{-1}$, $[\text{TiCl}_4] = 0.036 \text{ mol L}^{-1}$. Capping reaction conditions: $[\text{DTE}]/[\text{living PIB}] = 2$ for 1 h at $-80 \text{ }^\circ\text{C}$.

The GPC RI traces of the original PIB-Cl, PIB from the reaction of PIB^+ with DTE and PIB from the reaction of PIB-DTE^+ with Bu_3SiH show that that number average molecular weight and molecular weight distributions remain unchanged (Figure 3). When the reaction mixture was quenched with methanol prior to completion, a mixture of PIB-DTE with PIB- $\text{CH}_2\text{-C}(\text{Tol})_2\text{-H}$ (PIB-DTE-H) and PIB- $\text{CH}=\text{C}(\text{Tol})_2$ functionalities was observed from ^1H NMR spectra of the products (Figure 4). The % PIB-DTE-H was calculated by comparing the characteristic resonance signal of PIB- $\text{CH}=\text{C}(\text{Tol})_2$ at $\delta = 6.12 \text{ ppm}$, and the resonance signal of PIB- $\text{CH}_2\text{-C}(\text{Tol})_2\text{-H}$ at

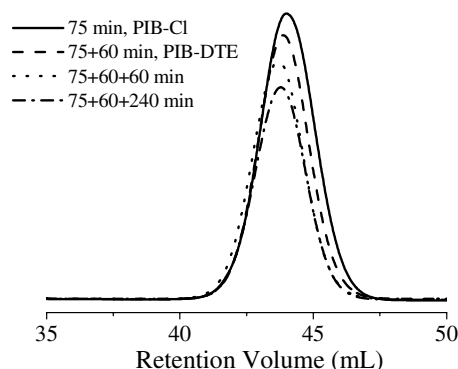


Figure 3. The GPC RI traces of the original PIB-Cl, PIB from the reaction of PIB⁺ with DTE and PIB from the reaction of PIB-DTE⁺ with Bu₃SiH (at two different times).

$\delta = 4.05$ ppm. The results are given in Table 2. By using [Bu₃SiH] = 0.01 mol L⁻¹ and 0.02 mol L⁻¹ 95.1% and ~100% PIB-CH₂-C(Tol)₂-H were obtained respectively in 1 hour indicates that the rate of hydrogen transfer reaction increases with the increase of [Bu₃SiH]. The reaction of living PIB-DTE⁺ with Bu₃SiH was also studied at higher [Bu₃SiH] and a summary of results is given in Table 2. Interestingly, the rate of hydrogen transfer reaction of PIB⁺ and PIB-DTE⁺ with Bu₃SiH are comparable.

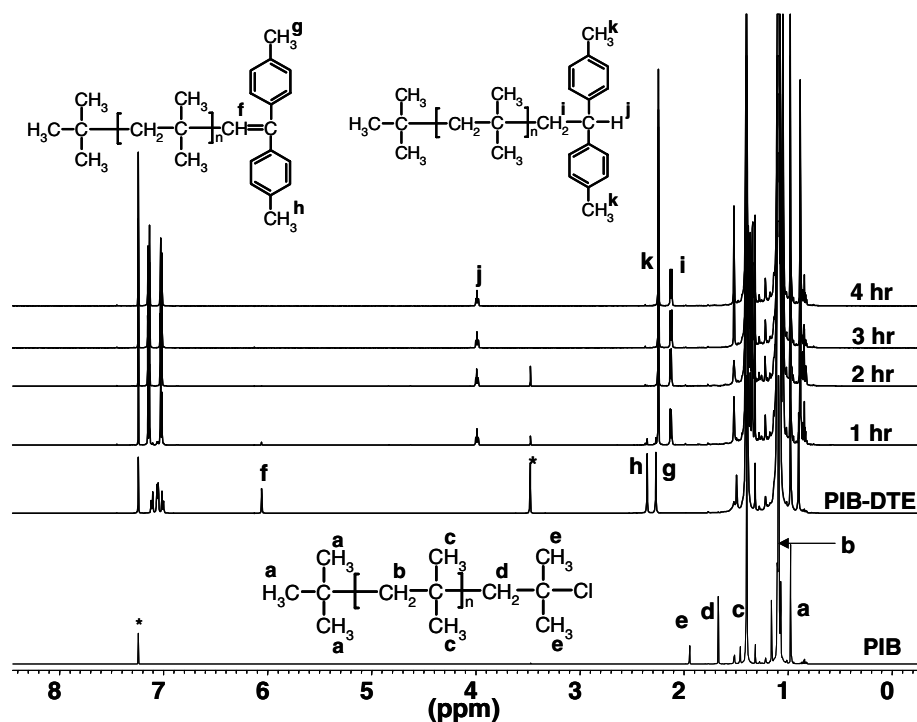
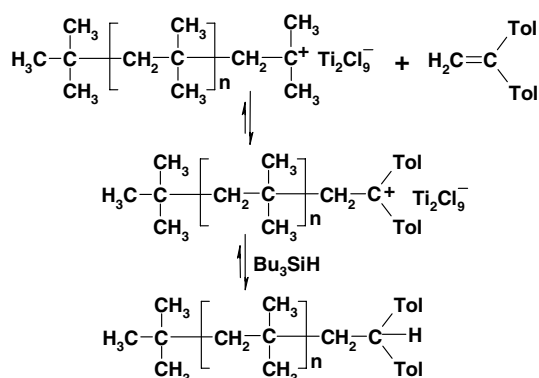


Figure 4. The ¹H NMR spectra of the original PIB-Cl, PIB from the reaction of PIB⁺ with DTE and PIB from the reaction of PIB-DTE⁺ with Bu₃SiH at 1, 2, 3, and 4 hours.

Figure 5 shows the ^{13}C NMR spectra of the original PIB-Cl, PIB from the reaction of PIB^+ with Bu_3SiH (PIB-H) and PIB from the reaction of PIB-DTE^+ with Bu_3SiH (PIB-DTE-H) along with the peak assignments. No side reaction was detected based on spectroscopic (^1H and ^{13}C NMR) as well as chromatographic analysis. Based on the ^1H and ^{13}C NMR analysis; the reaction of PIB-DTE^+ cation with Bu_3SiH can be presented as shown in Scheme 3.



Scheme 3. The reaction of PIB-DTE^+ cation with Bu_3SiH .

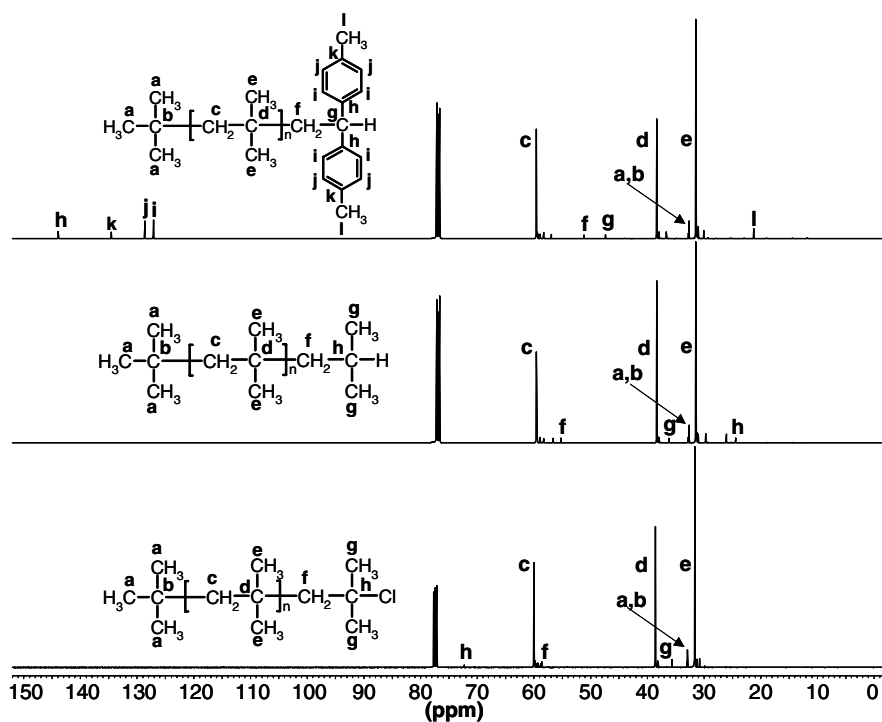


Figure 5. The ^{13}C NMR spectra of the original PIB-Cl, PIB from the reaction of PIB^+ with Bu_3SiH and PIB from the reaction of PIB-DTE^+ with Bu_3SiH .

Conclusions

Thermally stable and chemically inert polyisobutylene can easily be synthesized by one step hydride transfer reaction between tributylsilane and living polyisobutylene cation in hexanes/methyl chloride 60/40 (v/v) solvent mixtures at $-80\text{ }^{\circ}\text{C}$. Since this method can also be used for the reaction of fully ionized living chain ends, such as PIB-DTE⁺, the same principle may be also applicable to the hydride transfer reaction of relatively stable living cationic polymers such as poly(vinyl ethers). The living polymeric cation does not undergo any side reactions as suggested by GPC and NMR Spectroscopy. It was found that the rate of hydrogen transfer reaction increases with increasing concentration of Bu₃SiH, and decreases with increasing temperature due to decreasing active center concentration with temperature.

Acknowledgements

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