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Halogen-free polyisobutylene by in situ methylation of living polyisobutylene using dimethylzinc

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Summary

Halogen-free polyisobutylene (PIB) was synthesized by in situ methylation of living PIB using dimethylzinc. Quantitative methylation of living PIB was achieved within 60 min using a ratio of $[(CH_3)_2Zn]/[TiCl_4]_0 = 1$ without any side reactions. Under similar conditions, living PIB capped with 1,1-diphenylethylene (PIB-DPE$^+$) yielded close to 1:1 mixture of methoxy- and methyl-functionality. By using the ratio of $[(CH_3)_2Zn]/[TiCl_4]_0 \geq 3$, however, quantitative methylation of PIB-DPE$^+$ could be achieved in 120 min without any side reactions as confirmed by spectroscopic and chromatographic analyses.

Introduction

The living cationic polymerization of isobutylene (IB) in the presence of Lewis acid involves cationic active species, which are in a dynamic equilibrium with dormant, inactive species. Most of the chain ends are in a dormant form, a polymeric *tert*-alkyl chloride, and the concentration of the active species, i.e., a *tert*-alkylcarbenium ion, is negligible. The quenching process of the living cationic polymerization of IB often involves deactivation of the Lewis acid with nucleophiles, such as methanol, to yield PIB with a terminal chlorine group. Since this terminal *tert*-chloro group is thermally and chemically labile, it is not compatible with processes using elevated temperature or alkaline conditions. The replacement of the *tert*-chloro group with a thermally stable and chemically inert end group is therefore desirable for these applications.

The reaction of a *tert*-alkyl chloride with selected organometallic reagents leads to the formation of a quaternary carbon atom by replacement of chlorine with an alkyl group (1-6). Kennedy et al. studied the methylation reaction of *tert*-alkyl chlorides using trimethyl aluminum as a model for initiation and termination in the cationic polymerization of IB (1-3). They reported that the reaction of *tert*-butyl chloride with trimethylaluminum leads to the quantitative formation of neopentane in methyl chloride at -78 °C (2). The proposed mechanism involves the ionization of *tert*-butyl chloride by trimethylaluminum followed by the rapid transfer of a methyl group to the *tert*-butylcarbenium ion.

During the investigation of the geminal dialkylation of ketones (4-7), Reetz et al. also reported the full scope of the methylation reaction of a variety of S_N1-active alkyl

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chlorides using methyltitanium chlorides in methylene chloride at low temperature (-78 to 0 °C). Although a question remains as to which is the best method, the methylation of S_N1-active alkyl chlorides was also reported to occur using trimethylaluminum in the presence of titanium chloride (6) or using dimethylzinc in the presence of catalytic amounts of zinc chloride (7). Similar to that proposed by Kennedy, the mechanism of the organotitanium-induced methylation of *tert*-alkyl chlorides was postulated to involve the formation of a *tert*-alkylcarbenium ion by the Lewis acidic methyltitanium trichloride or dimethyltitanium dichloride, followed by the rapid transfer of the methyl group.

We have described in situ methylation of living PIB using trimethylaluminum to prepare thermally stable and chemically inert PIB (8). Organoaluminum compounds are strong Lewis acids however, and may induce undesirable side reaction of some head- or in-chain functionalities (9). In this study, we report a detailed study of in situ methylation of living PIB using dimethylzinc, which yields much milder reaction conditions.

Experimental

Polymerization of Isobutylene and Methylation of Living Polyisobutylene

The living cationic polymerization of isobutylene (IB) was carried out using the 2,4,4-trimethyl-2-chloropentane (TMPCl)/$TiCl_4$/hexane:CH_3Cl (60:40, v:v)/-80 °C system in the presence of 2,6-di-*tert*-butylpyridine (DTBP) as reported previously (10). Typical concentrations of reactants are as follows: [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, and [DTBP] = 0.003 M. After 1 h of IB polymerization, aliquots of the living PIB solution were transferred to 75 mL test tubes equipped with teflon-lined caps. One of the tubes was quenched with prechilled methanol for the characterization of the original PIB, and to the rest were added appropriate amounts of a $(CH_3)_2Zn$ solution (2.0 M in toluene, Aldrich) to vary the ratio of [$(CH_3)_2Zn$]/[TiCl4]. After predetermined times, parallel runs were quenched with prechilled methanol at -80 °C. For the methylation of PIB capped with 1,1-diphenylethylene (DPE), 2 equiv of DPE was added to living PIB at ~100% conversion of the IB polymerization and the capping reaction was carried out for 120 min prior to the addition of dimethylzinc.

The quenched samples were poured over an equal volume of 10% ammoniacal methanol to neutralize the reaction mixture, and solvents were evaporated to yield a mixture of white inorganic materials and crude products. This was further dried in a vacuum oven for 24 h. The crude product was dissolved in hexane and inorganic materials were removed by a simple filtration. The polymer solution in hexane was then poured over an equal volume of methanol and the hexane layer was slowly evaporated to precipitate PIB on the methanol layer. The remaining methanol was decanted and the precipitated polymer was again dissolved in hexane to repeat this precipitation and decantation three times. Finally, PIB samples for chromatographic and spectroscopic analyses were prepared after 24 h drying in a vacuum oven.

Characterization

^1H and ^{13}C NMR spectra were recorded on a Bruker 250 MHz spectrometer. Molecular weights and their distributions were measured using a Waters GPC system equipped with a model 510 HPLC pump, a model 712 sample processor, a model 486 tunable UV/Vis detector, and a model 250 dual detector (refractometer/viscometer, Viscotek). Five ultrastyrygel columns (Waters) were connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å, and THF was used as a carrier solvent at a flow rate of 1 mL/min.

Results and Discussion

After ~100% conversion of the IB polymerization, the methylation of living PIB was started by adding a dimethylzinc solution to the reactor containing living PIB. Upon the addition of dimethylzinc, the color of the reaction mixture turned to bright yellow, indicating the formation of methyltitanium trichloride or dimethyltitanium dichloride (11). Before and during the methylation reaction, parallel runs were quenched with prechilled methanol for characterization. Figure 1 shows ^{1}H NMR spectra of PIBs before and after the methylation reaction. Quenching living PIB with methanol invariably yields PIB with a terminal-chlorine group (PIB-Cl), and PIB-Cl exhibits characteristic resonance signals at δ = 1.96 and 1.67 ppm, corresponding respectively to methylene and methyl protons next to the terminal-chloro group. After a 120 min methylation reaction using a ratio of $[(CH_3)_2Zn]/[TiCl_4] = 1$, these two signals were completely absent in the ^{1}H NMR spectrum of the product, indicating that the conversion of PIB-Cl to PIB with a terminal-methyl group (PIB-CH_3) is essentially quantitative. GPC results of PIBs quenched before and after the methylation reaction exhibited identical molecular weights (M_n ~ 2, 000) and molecular weight distributions ($M_w/M_n < 1.1$).

Kinetics of the methylation reaction was further studied using various ratios of $[(CH_3)_2Zn]/[TiCl_4]$, and a summary of results is given in Table 1. When the reaction mixture was quenched with prechilled methanol prior to completion, a mixture of PIBs with chloro- and methyl-groups was observed without any side reactions, such as β-proton elimination. Therefore, the conversion of PIB-Cl to PIB-CH_3 was calculated by comparing the characteristic resonance signals of PIB-Cl (peak *e* and *d* in Figure 1), and the resonance signals of the α, ω-*tert*-butyl group (peak *a* in Figure 1). As shown in Table 1, it was found that 50% conversion can be achieved in less than 5 min and the

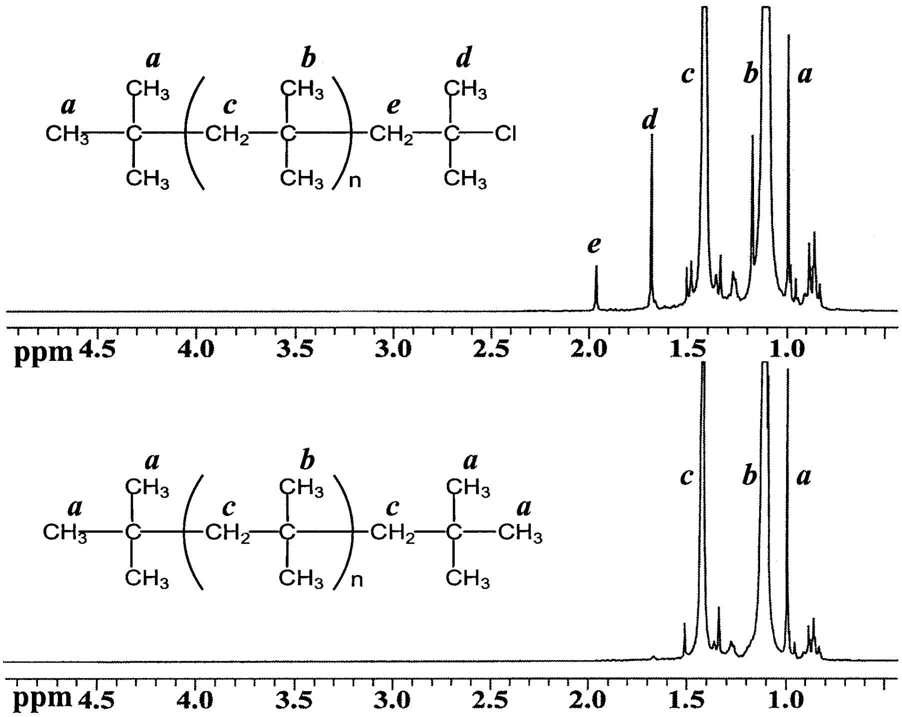


Figure 1. ^{1}H NMR spectra ($CDCl_3$) of the original PIB (top) and PIB obtained after 2 h methylation reaction (bottom) using the ratio of $[(CH_3)_2Zn]/[TiCl_4] = 1$.

Table 1. Methylation Reaction of living PIB using $(CH_3)_2Zn$

sample no.	$[(CH_3)_2Zn]$ /$[TiCl_4]$	reaction time, min	PIB-Me, %	PIB-Cl, %
1	1	5	56.5	43.5
2	1	15	91.2	8.8
3	1	30	97.8	2.2
4	1	60	~100	~0
5	2	5	77.4	22.6
6	2	15	95.5	4.5
7	2	30	~100	~0
8	3	5	80.3	19.7
9	4	5	91.6	8.4

Polymerization conditions: [TMPCl] = 0.002 M, $[TiCl_4]$ = 0.036 M, [DTBP] = 0.003 M and [IB] = 0.075 M in hexane/CH_3Cl (60/40 v/v) at –80 °C.

reaction goes to completion within 60 min using the ratio of $[(CH_3)_2Zn]/[TiCl_4] = 1$ (entry no. 1-4). Further increase in the methylation rate was also observed using a ratio of $[(CH_3)_2Zn]/[TiCl_4] > 1$, and using the ratio of $[(CH_3)_2Zn]/[TiCl_4] = 4$, 91.6 % methylation was obtained in 5 min.

The increasing methylation rate with an increasing $[(CH_3)_2Zn]/[TiCl_4]$ ratio beyond 2 suggests that the chloro to methyl exchange between $TiCl_4$ and $(CH_3)_2Zn$ is not complete, and probably involves an equilibrium. The modest increase in the rate by the increase of the ratio from 2 to 4, however, indicates that the equilibrium constant is most likely high. A possible mechanism of the methylation reaction of living PIB is shown in Scheme 1, which is similar to that proposed by Reetz et al. (6). Upon the addition of dimethylzinc to a living PIB solution, methyltitanium trichloride or dimethyltitanium dichloride is formed by the reaction of dimethylzinc with titanium chloride. When this newly formed Lewis acid, e.g., $(CH_3)_2TiCl_2$, ionizes a dormant polymeric *tert*-chloride (PIB-Cl), a more nucleophilic counterion $(CH_3)_2TiCl_3^-$ (or the dimeric equivalent) is generated and the irreversible transfer of a carbon nucleophile, i.e., a methyl anion, to a polymeric *tert*-carbenium ion takes place. This is due to the weaker Ti-C bond as compared to the Ti-Cl bond (6), rendering the ionization a rate-determining step.

Scheme 1

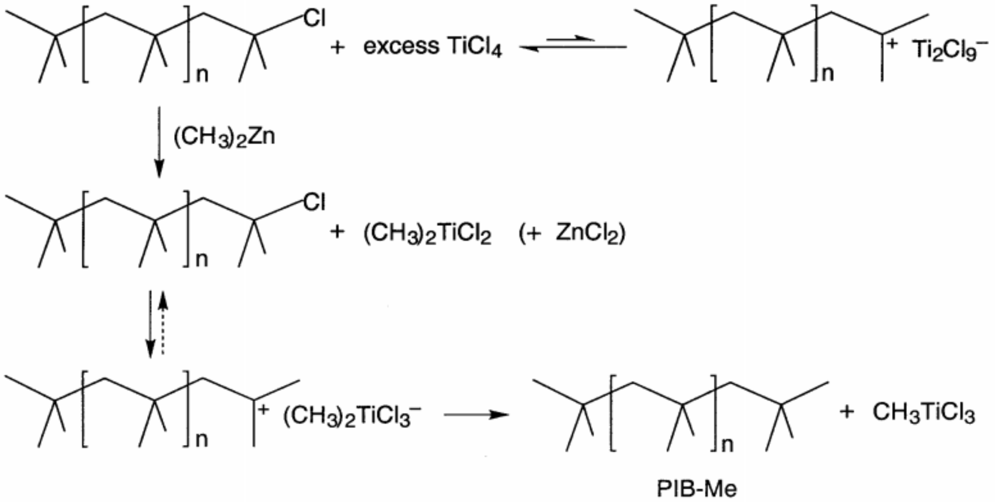


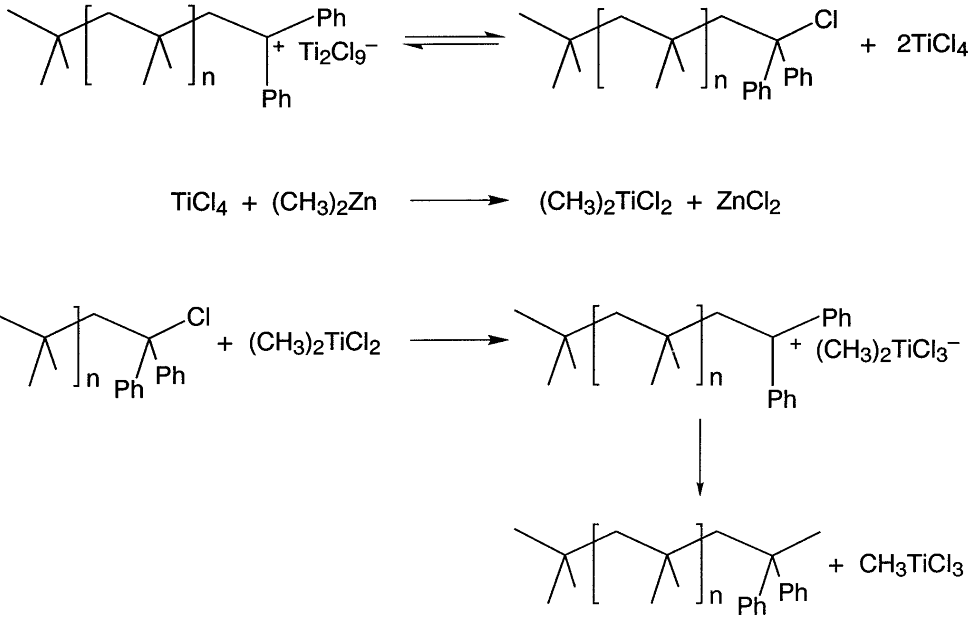
Table 2. Methylation of PIB-DPE$^+$ using $(CH_3)_2Zn$.

sample no.	$[(CH_3)_2Zn]/[TiCl_4]_0$	reaction time, min	PIB-DPE-CH_3, %	PIB-DPE-OCH_3, %
1	1	15	19.0	81.0
2	1	120	43.2	56.8
3	2	120	76.2	23.8
4	3	120	~100	~0
5	4	120	~100	~0
6	5	120	~100	~0

Polymerization conditions: same as in Table 1.
Capping reaction conditions: [DPE]/[living PIB] = 2 for 2h at –80 °C..

Quenching of stable cations, such as diaryl carbenium ions, with methanol results in the development of a methoxy end-functionality. 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 methylation reaction of the diphenyl carbenium ion was further studied. This was carried out by the capping reaction of living PIB with 1,1-diphenylethylene (DPE), which yields a stable and fully ionized PIB-DPE cation (PIB-DPE$^+$), followed by the addition of dimethylzinc. A summary of results is given in Table 2. When the reaction mixture was quenched with methanol prior to completion (entry no. 1-3), a mixture of PIB-DPE with methyl and methoxy functionalities (PIB-DPE-CH_3 and PIB-DPE-OCH_3, respectively) was observed from ^{1}H NMR spectra of the products. Interestingly, the methylation rate was much lower than that of PIBCl. Since the methoxy functionality results from the direct interaction of methanol with PIB-DPE$^+$ (12), a decrease in the methylation rate may indicate that either the transformation of PIB-DPE$^+$ $Ti_2Cl_9^-$ to PIB-DPE-Cl or the transfer of a methyl anion from $(CH_3)_2TiCl_3^-$ to PIB-DPE$^+$ is the rate-determining step, as shown in Scheme 2.

Scheme 2



With ratios of $[(CH_3)_2Zn]/[TiCl_4] \leq 2$, the formation of various Lewis acids, such as $(CH_3)_nTiCl_{4-n}$ ($n < 4$), CH_3ZnCl, and $ZnCl_2$, is possible. The relative amounts depend on their Lewis acidity since the driving force in the interchange of methyl and chlorine groups between Ti and Zn compounds lies in the partial abatement of the overall Lewis acidity of the system. The involvement of CH_3ZnCl in the methylation process cannot be excluded, since it was also reported to induce the methylation of *tert*-alkyl chloride in the presence of $ZnCl_2$ (7). Although less stable than $(CH_3)TiCl_3$ or $(CH_3)_2TiCl_2$ (11), the formation of $(CH_3)_3TiCl$ is also possible and its participation in the methylation process of PIB-DPE$^+$ cannot be neglected when the ratio of $[(CH_3)_2Zn]/[TiCl_4] \geq 3$ (entry no. 4-6). Although the exact identity of a methylation-responsible Lewis acid is unknown, with ratios of $[(CH_3)_2Zn]/[TiCl_4]_0 \geq 3$, a quantitative methylation of PIB-DPE$^+$ was achieved within 120 min. Figure 2 shows ^{1}H and ^{13}C NMR spectra of PIB-DPE-CH_3 along with peak assignments. No side reaction was detected based on spectroscopic (^{1}H and ^{13}C NMR) as well as chromatographic analyses. For example, the original PIB, quenched before the DPE capping reaction, exhibited $M_n = 1900$ and $M_w/M_n = 1.09$, and the methylation product (PIB-DPE-CH_3) exhibited $M_n = 2100$ and $M_w/M_n = 1.07$ with an increase in M_n corresponding to the DPE addition.

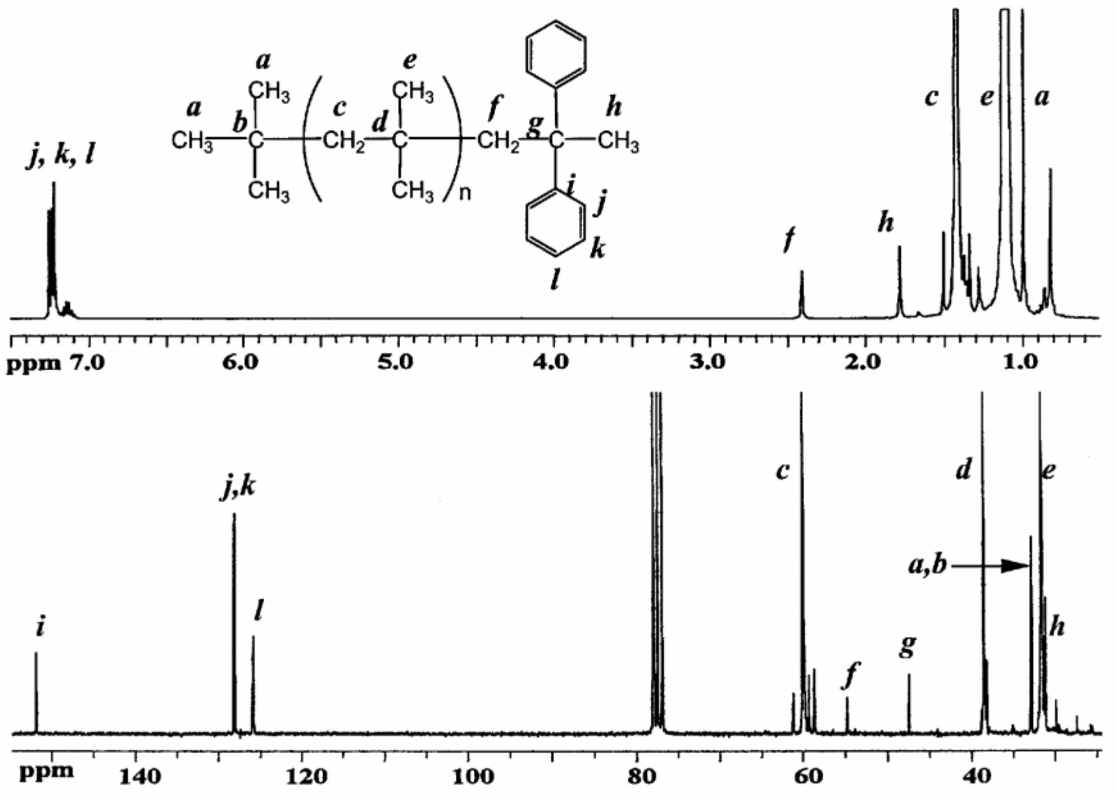


Figure 2. ^{1}H and ^{13}C NMR spectra ($CDCl_3$) of PIB-DPE-CH_3 obtained using the ratio of $[(CH_3)_2Zn]/[TiCl_4] = 3$ (entry no. 4 in Table 2).

Conclusion

The synthesis of thermally stable and chemically inert PIB can be easily carried out by in situ methylation of living PIB using dimethylzinc. Since this method can be used for the methylation of fully ionized living chain ends, such as PIB-DPE$^+$, the same principle may be also applicable to the methylation of relatively stable living cationic polymers such as poly(vinyl ethers). Using appropriate amino-containing organometal reagents, the synthesis of amino-functional PIBs may also be possible without the capping reaction of living PIB with DPE, since the bond strength for Ti decreases in the sequence Ti-O > Ti-Cl > Ti-N > Ti-C (6).

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