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# Relative Reactivity of C4 Olefins toward the Polyisobutylene Cation

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ABSTRACT: The capping reaction of living polyisobutylene cation ($PIB^+$) with 1-butene, *cis*-2-butene, *trans*-2-butene, or 1,3-butadiene in hexanes (Hex)/methyl chloride (MeCl) 60/40 (v/v) solvent mixtures at −80 °C was studied. The reaction products were characterized by elemental analysis, gel permeation chromatography, and NMR spectroscopy. Monoaddition (capping) was observed with 1-butene and *cis*-2-butene but not with *trans*-2-butene, which did not react with $PIB^+$. Monoaddition of 1,3-butadiene followed by instantaneous halide transfer from the counteranion and selective formation of the 1,4-adduct were observed in Hex/MeCl 60/40 (v/v) solvent mixtures at −80 °C at [1,3-butadiene] ≤ 0.05 mol $L^{-1}$. The polymerization of isobutylene (IB) was studied in the presence of 1-butene, *cis*-2-butene, *trans*-2-butene, or 1,3-butadiene as capping agent in Hex/MeCl 80/20 to 40/60 (v/v) in the temperature range of −40 to −80 °C. From the limiting conversion and limiting number-average degrees of polymerization the reactivity ratio, $k_p^{\pm}/k_c^{\pm}$ (where $k_p^{\pm}$ is the absolute rate constant of propagation for IB and $k_c^{\pm}$ is the cross-propagation (capping) rate constant from $PIB^+$ cation to the C4 olefins), was calculated. Since the propagation of IB (addition of IB to $PIB^+$) does not have an enthalpic barrier, the activation energy for cross-propagation was calculated to be 5.1−6.0 kJ $mol^{-1}$. By extrapolating the plot of $k_p^{\pm}/k_c^{\pm}$ vs hexanes (vol %), the reactivity ratios were calculated for 100% hexanes at −80 °C. From the cross-propagation activation energy and the calculated reactivity ratios at −80 °C in 100% hexanes, the reactivity ratios for 0 °C have also been calculated. According to these values at 0 °C, isobutylene is ∼17 times more reactive than 1,3-butadiene, ∼543 times more reactive than 1-butene, and ∼294 times more reactive than *cis*-2-butene.

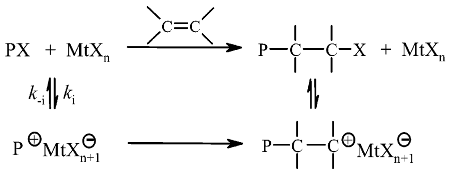
## Introduction

The C4 mixed feed is generally used for the production of polyisobutylene (PIB) dispersants, used as motor oil and fuel additives in the automobile industry.[1] In addition to isobutylene (IB), the presence of different amounts of 1-butene (1-Bu), *cis*-2-butene (*cis*-2-Bu), *trans*-2-butene (*trans*-2-Bu), and 1,3-butadiene (BD), which are transfer agents and/or terminators (poisons), affects the nature and distribution of olefin types in the product, which in turn influence the reaction with maleic anhydride and ultimately the product quality of polyisobutenylsuccinic anhydride.[2] The goal of the present research is to develop kinetic and mechanistic understanding of the polymerization of IB in the presence of other C4 olefins and to understand the effect of reaction conditions on the nature and distribution of double bonds in the polymer. The first step toward this goal is to determine the reactivity of 1-Bu, *cis*-2-Bu, *trans*-2-Bu, and BD relative to IB.

Carbocation and alkene reactivities have been extensively studied by Mayr, who first recognized the kinetic utility of the fact that under special conditions, when the formation of the [1:1] adduct is faster than its consumption, carbocations react with olefins to yield [1:1] adduct exclusively (Scheme 1).[3,4]

In case I, covalent products are formed from ionic reactants. This type of trapping employing diarylmethyl chlorides in conjunction with weak Lewis acids (which are, however, strong enough to rapidly and completely ionize PX) has been exploited by Mayr to characterize nucleophilic reactivity of alkenes,[5] characterized by the nucleophicity parameter, *N*. Careful selection of the of Lewis acid is necessary since the [1:1] product will be obtained only when fast halide transfer from the counteranion immediately traps the reaction product of stable carbocation salts with alkenes and ionization of the product halide can be neglected.

**Scheme 1**



In case II, ionic products are formed from covalent reactants. Our capping reactions of propagating carbocations with e.g. diarylethylenes fit this category.[6] In this case ionization of PX is negligible whereas the [1:1] product is fully ionized. The capping reaction, which can be conveniently monitored by UV−vis spectroscopy, has been most useful to determine the equilibrium constant of ionization ($K_i$), and thus the concentration of active chain ends, as well as the rate constant of ionization ($k_i$) and the absolute rate constant of deactivation ($k_{-i}$). With the knowledge of the cation concentration and the rate of polymerization, the absolute rate constant of propagation ($k_p$) can be calculated. This method has been employed by us to determine the rate constant of propagation for ion pairs ($k_p^{\pm}$) for the polymerization of IB,[7,8] styrene,[9] and styrene derivatives.[10]

In case III, both reactants and products are predominantly covalent. To avoid multiple additions after the crossover step, ion collapse must be faster than propagation and irreversible. The rate constant of ion collapse can be increased by lowering the Lewis acidity, decreasing the polarity of the solvent, or increasing the temperature.[8] On the basis of the above considerations cross-propagation and the selective formation of the [1:1] product can be accomplished only when the alkylating cation has higher stability than the cation formed in the addition. In case III the reaction cannot be easily followed, and the determination of the rate constant requires a different approach. This approach, based on competition experiments, however, is simple and highly effective. Competition experiments employing

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the diffusion clock method have often been used in studies of cationic reaction kinetics.[11] The reaction clock method references the unknown rate constant for reaction of the intermediate cation to that for a second reaction, which serves as a "clock". In the diffusion clock method the "clock" speed is the diffusion limit.

The reaction clock method could be easily utilized for the determination of cross-propagation rate constant. Under conditions where the reaction of $P_1^+$ cation with another monomer $M_2$ results in the exclusive formation of [1:1] adduct, the cross-propagation rate constant could be calculated from the reactivity ratio $r_1 = k_{11}/k_c$ using the known value of $k_{11}$. The value of $r_1$ could be easily determined from the limiting conversion or limiting number-average degree of polymerization from copolymerizations terminating after a single cross-propagation. This is feasible with most monomers when crossing over from the more reactive monomers to the less reactive one.

Very recently, in a preliminary publication the usefulness of the method was shown for the polymerization of α-methylstyrene (αMeSt) in the presence of IB as an example.[12] We have shown earlier that in conjunction with $BCl_3$ in methylcyclohexane/MeCl 60/40 (v/v) at −80 °C crossover from living poly(α-methylstyryl) cation to IB is immediately followed by termination and the selective and quantitative formation of the [1:1] adduct.[13] In this study, capping reactions of living polyisobutylene cation ($PIB^+$) with 1-Bu, *cis*-2-Bu, *trans*-2-Bu, and BD have been carried out to study the crossover reaction from living PIB chain end to these olefins in order to determine relative reactivities.

## Experimental Section

**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 glovebox prior to polymerization. Titanium tetrachloride ($TiCl_4$, Aldrich, 99.9%), 2,6-di-*tert*-butylpyridine (DTBP, Aldrich, 97+%), 1-butene (1-Bu, Aldrich, 99+%), *cis*-2-butene (*cis*-2-Bu, Aldrich, 99+%), *trans*-2-butene (*trans*-2-Bu, Aldrich, 99+%), 1,3-butadiene (BD, Aldrich, 99+%), and 2-methylpropene-$d_8$ (d-IB, CDN Isotopes, 99.8 atom % D) were used as received. The 2-chloro-2,4,4-trimethylpentane (TMPCl) was synthesized according to the literature.[14] Hexanes (Hex, Doe & Ingals, Technical grade), methanol (Doe & Ingals, Technical grade), etc., were purified as described previously[7] or used as received.

**Polymerization.** Polymerizations were carried out under a dry nitrogen atmosphere ($[H_2O] < 0.5$ ppm) in an MBraun 150-M glovebox (Innovative Technology Inc., Newburyport, MA). Large (75 mL) culture tubes equipped with Teflon-lined caps were used as polymerization reactors. The total volume of the reaction mixture was 25 mL. Throughout the study IB, 1-Bu, *cis*-2-Bu, *trans*-2-Bu, and BD were considered as nonpolar materials, and their volume was added to the volume of hexanes. After predetermined times, the polymerizations were terminated by the addition of 1.0 mL of prechilled methanol. The polymer was recovered and purified two times by reprecipitation from hexanes/methanol. Monomer conversions were determined by gravimetric analysis.

In a typical experiment, the living carbocationic polymerization of isobutylene was carried out in Hex/MeCl 60/40 (v/v) at −80 °C using the following concentrations: $[TMPCl] = 0.004$ mol $L^{-1}$, $[DTBP] = 0.004$ mol $L^{-1}$, $[IB] = 0.13$ mol $L^{-1}$, and $[TiCl_4] = 0.036$ mol $L^{-1}$. Into a 75 mL culture tube at −80 °C 14.5 mL of Hex at room temperature, 9.8 mL of MeCl at −80 °C, 0.4 mL of DTBP stock solution in Hex (0.25 mol $L^{-1}$) at −80 °C, 0.4 mL of TMPCl stock solution in Hex (0.25 mol $L^{-1}$) at −80 °C, and 1.0 mL of IB stock solution in Hex (3.25 mol $L^{-1}$) at −80 °C were added and mixed thoroughly. The polymerization was started under stirring by the addition of 0.5 mL of $TiCl_4$ solution (1.8 mol $L^{-1}$, in Hex/MeCl 60/40 (v/v)) at −80 °C. After 60 min of IB polymerization, one of the tubes was quenched with 1.0 mL of prechilled methanol for the characterization of original PIB, and to the rest appropriate amounts of BD (1.0 mol $L^{-1}$, in Hex/MeCl 60/40 (v/v) at −80 °C) were added under stirring. After predetermined times, parallel runs were terminated by addition of 1.0 mL of prechilled methanol at −80 °C.

In a representative competition experiment, the polymerization was carried out in Hex/MeCl 60/40 (v/v) at −80 °C using the following concentrations: $[TMPCl] = 0.002$ mol $L^{-1}$, $[DTBP] = 0.004$ mol $L^{-1}$, $[BD] = 0.3$ mol $L^{-1}$, $[IB] = 0.4$ mol $L^{-1}$, and $[TiCl_4] = 0.036$ mol $L^{-1}$. Into a 75 mL culture tube at −80 °C 12.5 mL of Hex at room temperature, 9.8 mL of MeCl at −80 °C, 0.4 mL of DTBP stock solution in Hex (0.25 mol $L^{-1}$) at −80 °C, 0.4 mL of TMPCl stock solution in Hex (0.125 mol $L^{-1}$) at −80 °C, 2.0 mL of BD stock solution in Hex (3.75 mol $L^{-1}$) at −80 °C, and 0.78 mL of IB were added and mixed thoroughly. The polymerization was started under stirring by the addition of 0.5 mL of $TiCl_4$ solution (1.8 mol $L^{-1}$, in Hex/MeCl 60/40 (v/v)) at −80 °C. After a predetermined time, the polymerization was terminated by the addition of 1.0 mL of prechilled methanol at −80 °C.

**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 Ultrastyragel GPC columns connected in the following series: 500, $10^3$, $10^4$, $10^5$, and 100 Å. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1.0 mL/min. The measurements were carried out at room temperature. NMR spectroscopy was carried out on a Bruker 200 MHz spectrometer or 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 ($\delta_H$ 0.00) or to the solvent signal ($\delta_C$ 77.0), respectively.

## Results and Discussion

**Capping Reactions of Living Polyisobutylene ($PIB^+$) with 1,3-Butadiene.** To study the capping reaction of living $PIB^+$ cation with BD, first IB was polymerized for 60 min by the $TMPCl/TiCl_4$ initiating system in Hex/MeCl 60/40 (v/v) solvent mixture at −80 °C using $[IB] = 0.13$ mol $L^{-1}$, $[TMPCl] = 0.004$ mol $L^{-1}$, $[DTBP] = 0.004$ mol $L^{-1}$, and $[TiCl_4] = 0.036$ mol $L^{-1}$. Then BD ($[BD] = 1.0$ mol $L^{-1}$) was added to the reaction mixture, and after different polymerization time, the reaction was quenched with prechilled methanol. The original PIB exhibited $M_n = 2240$ and PDI = 1.12 ($M_{n,theoretical} = 2000$). After the addition of BD the polymer weight (conversion = 100 ± 2% based on IB), $M_n$ (2250 ± 150), and PDI (1.14 ± 0.08) remained approximately constant, indicating the absence of BD polymerization. The $^1H$ NMR spectra of the original PIB (PIB−Cl) and PIB obtained after the reaction of $PIB^+$ with BD at different times are shown in Figure 1.

Quenching living PIB with methanol invariably yields PIB with a terminal chlorine group (PIB−Cl, i.e., $PIB-C\boldsymbol{H}_2-C(C\boldsymbol{H}_3)_2-Cl$). The $^1H$ NMR spectrum of PIB−Cl exhibits characteristic resonance signals at $\delta = 1.94$ and 1.67 ppm, corresponding respectively to $-C\boldsymbol{H}_2-$ and $-C\boldsymbol{H}_3$ protons next to the terminal chloro group.[15] The $^1H$ NMR spectra in Figure 1 show that the characteristic resonance signals for PIB−Cl at $\delta = 1.94$ and 1.67 ppm diminished in less than 30 min at [BD] = 1.0 mol $L^{-1}$, indicating essentially quantitative conversion of PIB−Cl to PIB with a terminal BD. Based on the $^1H$ NMR spectrum, 92−94% 1,4-addition product and 8−6% 1,2-addition product were obtained at the present conditions. The $^1H$ NMR spectrum (additional peaks at 5−6 ppm) also shows a considerable amount of multiple additions of BD under the present reaction conditions.

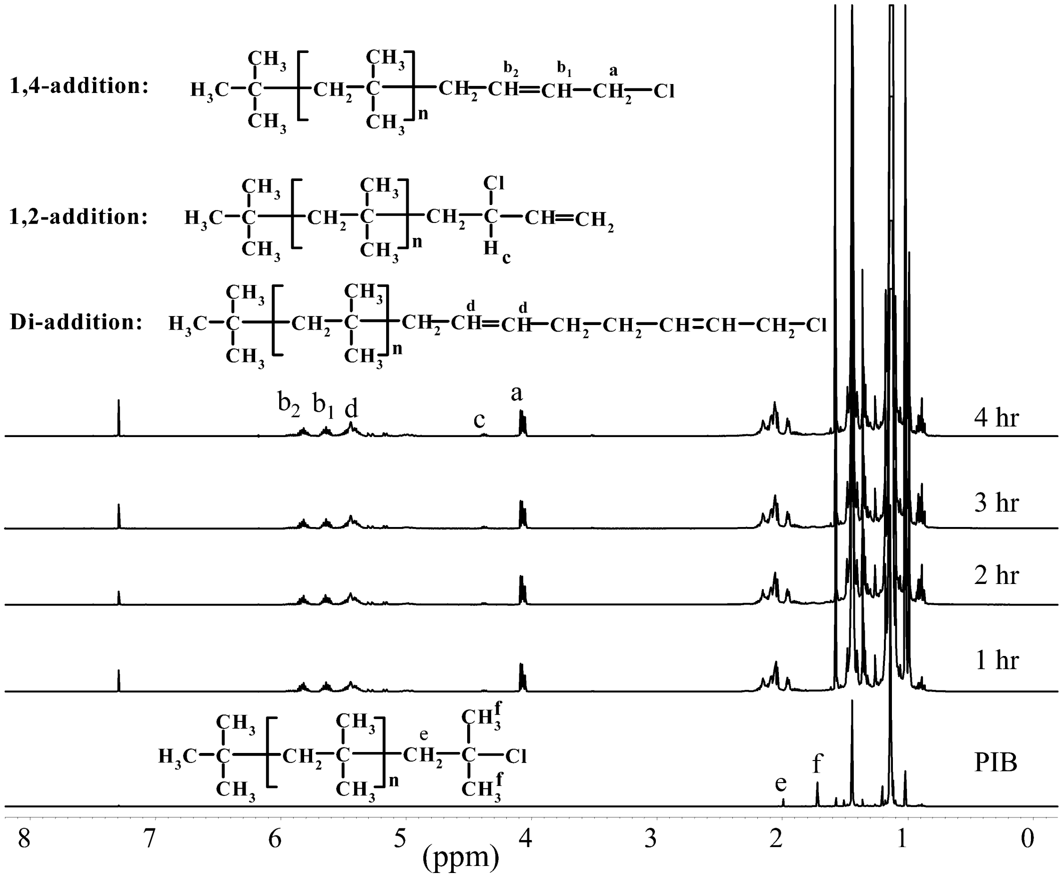


**Figure 1.** $^1$H NMR spectra of the original PIB (PIB−Cl) and PIB obtained after the capping reaction with BD at different times in Hex/MeCl 60/40 (v/v) at −80 °C using [IB] = 0.13 mol L$^{-1}$, [TMPCl] = 0.004 mol L$^{-1}$, [DTBP] = 0.004 mol L$^{-1}$, [TiCl$_4$] = 0.036 mol L$^{-1}$, and [BD] = 1.0 mol L$^{-1}$.

**Table 1. Experimental Results for the Polymerization of IB and the Capping Reaction of PIB$^+$ Cation with BD in Hex/MeCl 60/40 (v/v) Solvent Mixture at −80 °C$^a$**

| [BD] (mol L$^{-1}$) | time (min) | $M_n$ (GPC) | PDI | $M_n$ (NMR) |
|---|---|---|---|---|
| | 60 | 2360$^b$ | 1.08 | 2240 |
| 0.05 | 60 + 60 | 2500 | 1.07 | |
| 0.05 | 60 + 120 | 2400 | 1.13 | |
| 0.05 | 60 + 180 | 2350 | 1.13 | |
| 0.05 | 60 + 240 | 2430 | 1.11 | 2380 |

$^a$ [DTBP] = 0.004 mol L$^{-1}$, [TiCl$_4$] = 0.036 mol L$^{-1}$, [TMPCl] = 0.004 mol L$^{-1}$, and [IB] = 0.13 mol L$^{-1}$. $^b$ $M_{n,\text{theoretical}}$ = 2000. Based on IB, conversion = 100 ± 2%.

Multiple additions could be suppressed by lowering [BD]. This was verified by lowering [BD] (= 0.4, 0.3, 0.1, and 0.05 mol L$^{-1}$). For more accurate calculations, experiments were also carried out using cumyl chloride as initiator, which provides an internal reference for calculating functionality by $^1$H NMR spectroscopy. Analysis of these experiments showed that by decreasing the concentration of BD and increasing the time of the capping reaction mono-addition of BD could be possible. Detailed analysis indicated 28−36% chains having multiple addition of BD at [BD] = 0.4 mol L$^{-1}$, which decreased to 15−20% at [BD] = 0.2 mol L$^{-1}$ and 5−8% at [BD] = 0.1 mol L$^{-1}$. Multiple addition was virtually absent at [BD] = 0.05 mol L$^{-1}$. The results obtained at [BD] = 0.05 mol L$^{-1}$ are summarized in Table 1. The GPC RI traces of the original PIB and PIB obtained after the reaction of PIB$^+$ with BD at [BD] = 0.05 mol L$^{-1}$ at different times confirmed that the number-average molecular weight and molecular weight distribution remain unchanged. The $^1$H NMR spectra of the original PIB and PIB obtained after the reaction of PIB$^+$ with BD at [BD] = 0.05 mol L$^{-1}$ at different times are shown in Figure 2. The olefinic protons of the end group show two characteristic multiplets of the ABX$_2$ spin system at 5.63 and 5.83 ppm.[16] The PIB−C$H_2$−CH=CH−C$\boldsymbol{H}_2$−Cl group appears as doublet at 4.08 ppm, while the allylic C$H_2$ on the PIB side gives a doublet at 2.05 ppm. From the disappearance of the characteristic resonance signals for PIB−Cl at $\delta$ = 1.94 and 1.67 ppm 100% capping was obtained in 4 h. The $^{13}$C NMR shows that the PIB−CH$_2$−CH=CH−$\boldsymbol{C}$H$_2$−Cl carbon appears at 56.2 ppm, while the olefinic carbons gives resonance signals at 128.7 and 133.7 ppm. Another important indication of complete conversion is the disappearance of the signal at 72.4 ppm, which is due to PIB−CH$_2$−$\boldsymbol{C}$(CH$_3$)$_2$−Cl carbon. The NMR analysis shows exclusive formation of 1,4-addition product (shown in Figure 2) in the final PIB capped with BD.

For the capping reaction of PIB$^+$ cation with 1,3-butadiene selective formation of the 1,4-adduct was observed in Hex/MeCl 60/40 (v/v) solvent mixtures at −80 °C although theoretically 1,2-addition is also possible. For instance mixtures (1:1) of 1,2- and 1,4-addition products were obtained in the reaction of *p*-methoxydiphenylcarbenium tetrachloroborate with BD in CH$_2$Cl$_2$ at −70 °C.[17] It is to be noted that the 1,2-addition product gives a secondary cation and the 1,4-addition product gives a less stable primary cation. We hypothesized that 1,2-addition does take place, but the secondary chloroallyl product could be reionized by TiCl$_4$ and isomerized to the 1,4-addition product, which cannot be reionized by TiCl$_4$. To prove this hypothesis, isomerization of 3-chloro-1-butene (3C1B) was studied in conjunction with TiCl$_4$ and in the presence of proton trap, DTBP in pentane/MeCl 60/40 (v/v) solvent mixtures at −80 °C. The $^1$H NMR spectrum (Figure 1 in the Supporting Information) shows that 3-chloro-1-butene isomerizes exclusively to 1-chloro-

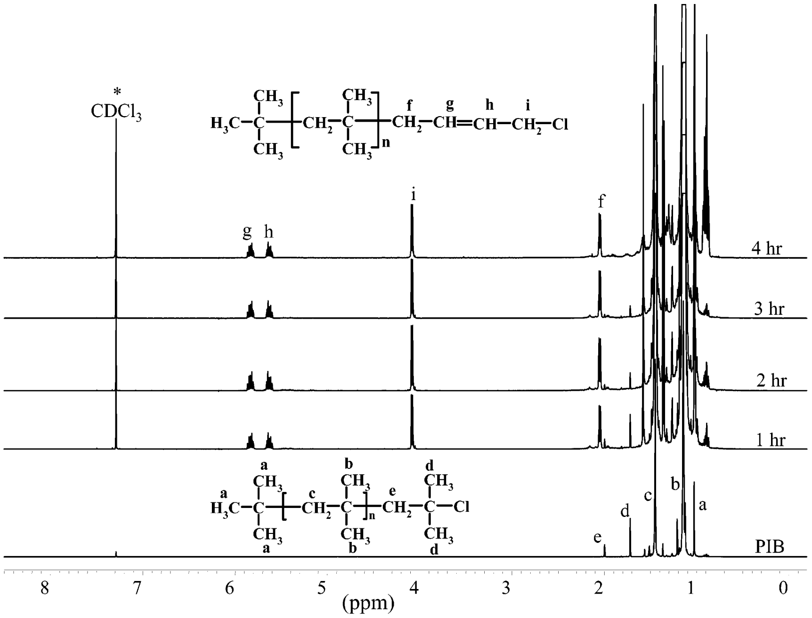
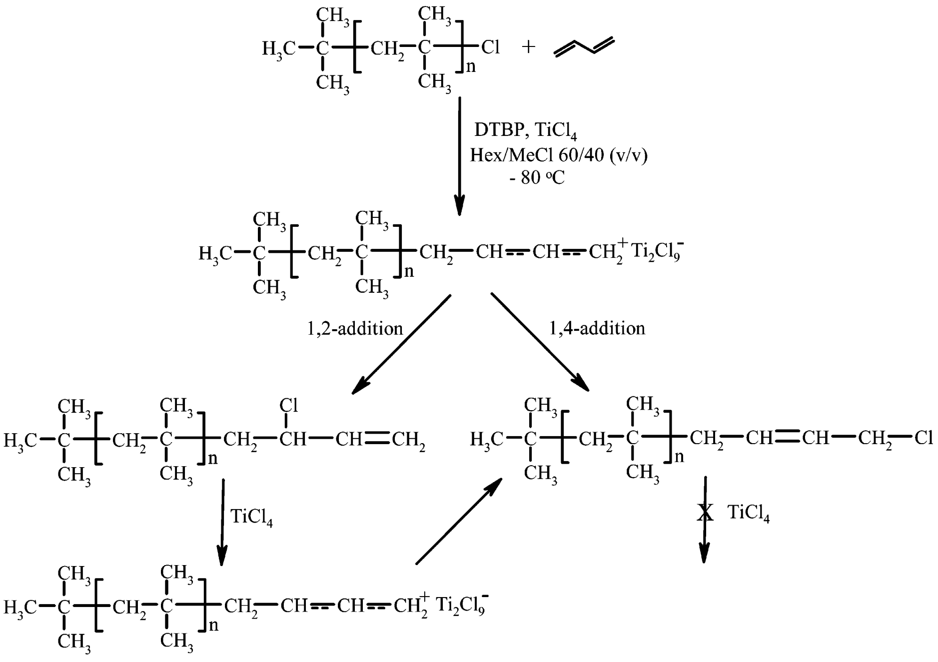


**Figure 2.** $^1$H NMR spectra of the original PIB (PIB−Cl) and PIB obtained after the capping reaction with BD at different times in Hex/MeCl 60/40 (v/v) at −80 °C using [IB] = 0.13 mol L$^{-1}$, [TMPCl] = 0.004 mol L$^{-1}$, [DTBP] = 0.004 mol L$^{-1}$, [TiCl$_4$] = 0.036 mol L$^{-1}$, and [BD] = 0.05 mol L$^{-1}$. BD was added under stirring after 60 min of IB polymerization.

**Scheme 2. Capping Reaction of PIB$^+$ Cation with BD in Hex/MeCl 60/40 (v/v) Solvent Mixture at −80 °C**



2-butene. Accordingly, the capping reaction of PIB$^+$ cation with BD can be presented as shown in Scheme 2.

Complete capping of PIB$^+$ cation with BD was also achieved when close to a stoichiometric amount of BD ([TMPCl] = 0.02 mol L$^{-1}$ and [BD] = 0.021 mol L$^{-1}$) was used, suggesting very high selectivity for the capping reaction. Detailed analysis of the NMR spectra showed that 100% capping was obtained in 20 h. Separate experiments with increased IB concentration (4.0, 2.0, and 0.3 mol L$^{-1}$) to prepare higher molecular weight PIBs at otherwise identical conditions also showed quantitative monoaddition of BD at [BD] = 0.05 mol L$^{-1}$. These results were confirmed by elemental analysis of a representative sample from which $M_n$ = 4220 was calculated for [IB] = 0.3 mol L$^{-1}$, in good agreement with molecular weights obtained from GPC ($M_{n,GPC}$ = 4800) and NMR ($M_n$ = 4500).

**Capping Reactions of Living PIB$^+$ Cation with 1-Butene.** The capping reactions of living PIB$^+$ cation with 1-Bu have been studied at reaction conditions similar to those employed in the capping reactions of living PIB$^+$ with BD. The polymerization of IB was carried out under identical conditions listed for Table 1. Then the capping agent [1-Bu] = 2.0 mol L$^{-1}$ was added to the reaction mixture, and after different time, the reaction was quenched with prechilled methanol. The original PIB has $M_n$ = 2300 and PDI = 1.11 ($M_{n,theoretical}$ = 2000). After the addition of 1-Bu the polymer weight (conversion = 100 ± 1% based on IB), $M_n$ (2300 ± 200), and PDI (1.11 ± 0.04) remained approximately constant, indicating the absence of 1-Bu polymerization. 100% capping was obtained after 3 h (Figure 3) indicated by the disappearance of the characteristic resonance signals (in the $^1$H NMR spectrum) at $\delta$ = 1.94 and 1.67 ppm

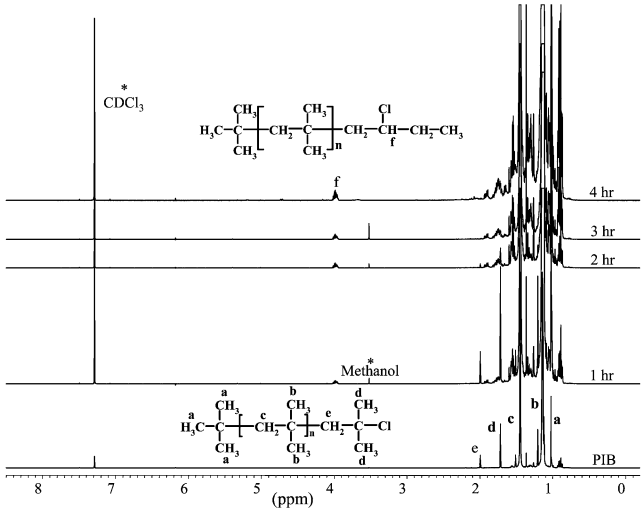


**Figure 3.** $^1$H NMR spectra of the original PIB (PIB−Cl) and PIB obtained after the capping reaction with 1-Bu at different times in Hex/MeCl 60/40 (v/v) at −80 °C using [IB] = 0.13 mol L$^{-1}$, [TMPCl] = 0.004 mol L$^{-1}$, [DTBP] = 0.004 mol L$^{-1}$, [TiCl$_4$] = 0.036 mol L$^{-1}$, and [1-Bu] = 2.0 mol L$^{-1}$. The 1-Bu was added under stirring after 60 min of IB polymerization.

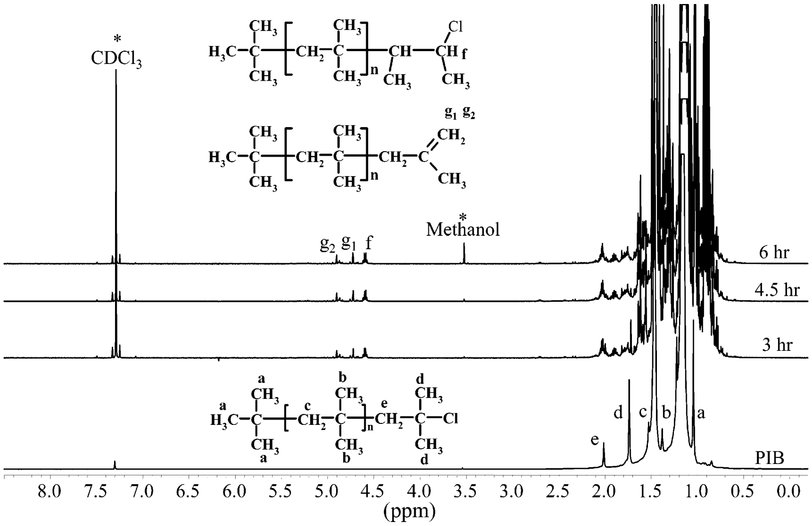


**Figure 4.** $^1$H NMR spectra of the original PIB (PIB−Cl) and PIB obtained after the capping reaction of living PIB$^+$ with *cis*-2-Bu in Hex/MeCl 60/40 (v/v) at −80 °C using [IB] = 0.4 mol L$^{-1}$, [TMPCl] = 0.01 mol L$^{-1}$, [DTBP] = 0.004 mol L$^{-1}$, [TiCl$_4$] = 0.036 mol L$^{-1}$, and [*cis*-2-Bu] = 2.0 mol L$^{-1}$.

for PIB−Cl corresponding to $-\mathrm{C}\boldsymbol{H}_2-$ and $-\mathrm{C}\boldsymbol{H}_3$ protons next to the terminal chloro group.

Since 1-Bu is a much weaker nucleophile than BD (according to the nucleophilicity data, see later), a high concentration of 1-Bu is needed to complete capping in a reasonable time. The $M_n$ of the polymers was determined from GPC and compared to the value calculated from the peak intensities of $-\mathrm{CH}_2-$ protons at the main chain and $-\mathrm{C}\boldsymbol{H}(\mathrm{Cl})-$ protons at the chain end. The $M_n$s obtained from GPC are somewhat lower than the $M_n$s determined from NMR spectroscopy. On the basis of the $^1$H NMR spectrum, capping of PIB$^+$ cation with 1-Bu gives 82−90% PIB−1-Bu−Cl addition product, as shown in Figure 3. The lower than complete capping might be due to multiple additions of 1-Bu units, which would invalidate the calculations, since protons from 1-Bu repeating units would be counted as PIB protons. However, similar results were found when the capping reaction of PIB$^+$ with 1-Bu was carried out at lower [1-Bu] = 0.4 mol L$^{-1}$ to suppress multiple addition. Finally, the “missing” chain ends were identified from capping reactions using cumyl chloride-initiated PIB$^+$ (where the aromatic residue serves as an internal reference) and TMP$^+$ with 1-Bu ([1-Bu] = 2.0 mol L$^{-1}$), which showed ~15% HCl eliminated product (PIB−CH=CH−CH$_2$−CH$_3$).

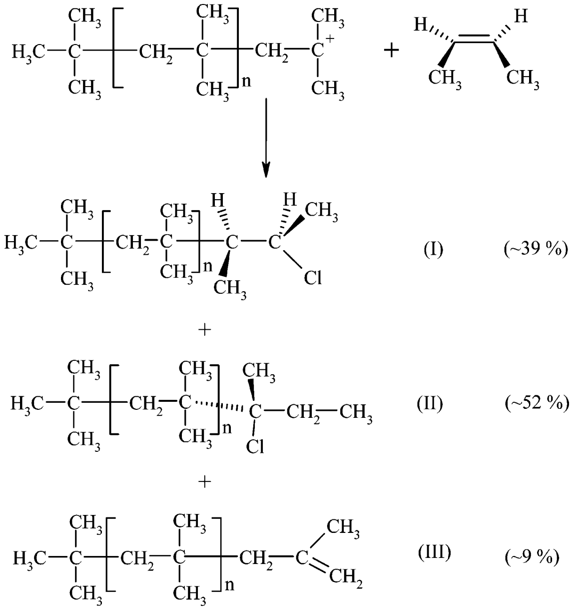
**Capping Reactions of Living PIB$^+$ Cation with *cis*-2-Butene or *trans*-2-Butene.** To study the capping reaction of living PIB$^+$ cation with *cis*-2-Bu and *trans*-2-Bu, first IB was polymerized in Hex/MeCl 60/40 (v/v) at −80 °C using [IB] = 0.4 mol L$^{-1}$, [TMPCl] = 0.01 mol L$^{-1}$, [DTBP] = 0.004 mol L$^{-1}$, and [TiCl$_4$] = 0.036 mol L$^{-1}$, and after 60 min [*cis*-2-Bu] = 2.0 mol L$^{-1}$ or [*trans*-2-Bu] = 2.0 mol L$^{-1}$ was added. The $^1$H NMR spectra in Figure 4 show that the characteristic resonance signals for PIB−Cl at $\delta = 1.94$ and 1.67 ppm slowly diminish with increasing reaction time with *cis*-2-Bu, and after 4.5 h the signal at $\delta = 1.94$ ppm is completely absent, indicating that the conversion of PIB−Cl to PIB with *cis*-2-Bu at the chain end is essentially quantitative. With *trans*-2-Bu, however, $^1$H NMR spectroscopy confirmed the absence of capping even after 6 h. The results are summarized in Table 2. The capping reaction was also studied at −40 °C at otherwise identical reaction conditions. At this temperature too, capping of PIB$^+$ cation with *cis*-2-Bu was obtained but not with *trans*-2-Bu.

**Table 2. Experimental Results for the Polymerization of IB and the Capping Reaction of PIB$^+$ Cation with *cis*-2-Bu or *trans*-2-Bu in Hex/MeCl 60/40 (v/v) Solvent Mixture at −80 °C**[a]

| [CA] (mol L$^{-1}$) | time (min) | $M_n$ (GPC) | PDI |
|---|---|---|---|
| | 60 | 2600[b] | 1.18 |
| [*cis*-2-Bu] = 2.0 | 60 + 180 | 2700 | 1.08 |
| [*cis*-2-Bu] = 2.0 | 60 + 270 | 2700 | 1.16 |
| [*cis*-2-Bu] = 2.0 | 60 + 360 | 2700 | 1.11 |
| [*trans*-2-Bu] = 2.0 | 60 + 270 | 2600 | 1.17 |
| [*trans*-2-Bu] = 2.0 | 60 + 360 | 2800 | 1.08 |

[a] [IB] = 0.4 mol L$^{-1}$, [TMPCl] = 0.01 mol L$^{-1}$, [DTBP] = 0.004 mol L$^{-1}$, and [TiCl$_4$] = 0.036 mol L$^{-1}$. [b] $M_{n,\text{theoretical}}$ = 2400. Based on IB, conversion = 100 ± 2%.

**Scheme 3**



The mechanism of the Lewis acid-catalyzed reactions of benzhydryl chloride with *cis*-2-Bu and *trans*-2-Bu is reported in the literature.[18] On the basis of the reported mechanism and NMR analysis, the capping of PIB$^+$ cation with *cis*-2-Bu can be presented as shown in Scheme 3.

To confirm product III, the addition reaction was carried out between *cis*-2-Bu and living deuterated PIB cation (D-PIB$^+$) at the same conditions mentioned for the capping reaction of PIB$^+$ with *cis*-2-Bu. The $^1$H NMR spectra are shown in Figure 5. Here too, product III was observed from $^1$H NMR spectra, but the I/III product ratio was reduced by half. So, the product III in Scheme 3 is the proton elimination product from isomerized D-PIB-*cis*-2-Bu unit.

**Competition Experiments of IB with 1-Bu, BD, *cis*-2-Bu, or *trans*-2-Bu.** In the competition experiments,[7,19] polymerization of IB was carried out in the presence of 1-Bu, BD, *cis*-2-Bu, or *trans*-2-Bu as a capping/trapping agent ($\pi$-nucleophile, $\pi$-Nu) to study the cross-propagation rate constant from PIB$^+$ cation to these olefins. In the competition experiments the polymerization stops when all polymer chain ends are capped with the capping agent.

In the competition experiment, the conversion as well as number-average molecular weight reaches a liming value. From the limiting conversion ($x_\infty^{IB}$) or from the limiting number-average degree of polymerization ($DP_{n\infty}$) the rate constant ratio ($k_p^{\pm}/k_c^{\pm}$) ($k_p^{\pm}$ is the absolute rate constant of propagation for IB and $k_c^{\pm}$ is the rate constant of capping) can be calculated using eqs 1 and 2.[7] More details regarding the kinetic basis of eqs 1 and 2 are available in refs 7 and 19.

In eqs 1 and 2, $[PIBCl]_0$, $[\pi Nu]_0$, and $[IB]_0$ are the initial chain end, capping agent, and IB concentration, respectively.

$$\frac{k_p^{\pm}}{k_c^{\pm}} = \frac{\ln(1 - x_\infty^{IB})}{\ln(1 - [PIBCl]_0/[\pi Nu]_0)} \tag{1}$$

$$\frac{k_p^{\pm}}{k_c^{\pm}} = \frac{\ln(1 - DP_{n\infty}[PIBCl]_0/[IB]_0)}{\ln(1 - [PIBCl]_0/[\pi Nu]_0)} \tag{2}$$

First, the competition experiments of IB with BD were carried out in Hex/MeCl 60/40 (v/v) solvent mixtures at −80 °C at different BD concentrations, 0.3, 0.5, and 0.6 mol L$^{-1}$, respectively. Limiting conversion and limiting number-average degree of polymerization were reached at all [BD]. The limiting conversion $x_\infty^{IB}$ = 48.8%, 33.3%, and 29.4% at [BD] = 0.3, 0.5, and 0.6 mol L$^{-1}$, respectively, were obtained. On the basis of these experiments, to obtain reasonable conversion at different solvent polarity and temperature the following standard conditions were applied to the competition experiments of IB with BD: [IB] = 0.4 mol L$^{-1}$, [TMPCl] = 0.002 mol L$^{-1}$, [DTBP] = 0.004 mol L$^{-1}$, [BD] = 0.3 mol L$^{-1}$, and [TiCl$_4$] = 0.036 mol L$^{-1}$ in different Hex/MeCl solvent mixtures (Hex/MeCl 80/20 (v/v) to Hex/MeCl 40/60 (v/v)) and at different temperatures (−80 to −40 °C). Similarly, suitable experimental conditions were found for 1-Bu and *cis*-2-Bu capping agents from preliminary studies.

**Effect of Solvent Polarity on the Competition Experiment of IB with BD as Capping Agent.** The experimental results for polymerizations carried out in different Hex/MeCl (v/v) solvent mixtures are shown in Table 3. The GPC RI traces of polymers obtained at −80 °C in Hex/MeCl 40/60 (v/v) after 1, 2, and 3 h confirmed that the number-average molecular weight reaches a liming value in less than 1 h. Limiting conversion was reached in 5, 4, 3, 2, and 1 h respectively in 80/20, 70/30, 60/40, 50/50, and 40/60 Hex/MeCl (v/v) solvent mixtures at −80 °C. Since the overall polymerization rate decreases with decreasing solvent polarity, the time needed to reach the limiting conversion is much higher in Hex/MeCl 80/20 (v/v) than with Hex/MeCl 40/60 (v/v). The $M_n$s of the polymers calculated by $^1$H NMR spectroscopy, assuming one −BD−Cl moiety per chain, agreed well with those determined by GPC, suggesting complete capping and the absence of side reactions. The reactivity ratios were calculated from $x_\infty^{IB}$ using eq 1 and from the $DP_{n\infty}$ using eq 2. These two methods yielded similar $k_p^{\pm}/k_c^{\pm}$ values (Table 3).

It has already been reported in the literature that $k_p^{\pm}$ of IB increases moderately ($1.8 \times 10^8$ L mol$^{-1}$ s$^{-1}$ in Hex/MeCl 80/20 (v/v) to $8.5 \times 10^8$ L mol$^{-1}$ s$^{-1}$ in 40/60 (v/v)) with the increase of solvent polarity.[8] Table 3 shows that the $k_p^{\pm}/k_c^{\pm}$ ratio increases with the increase of solvent polarity; thus, $k_p^{\pm}$ increases more rapidly than $k_c^{\pm}$. By extrapolating the plot of $k_p^{\pm}/k_c^{\pm}$ vs hexanes (vol %) for the competition experiments of IB with BD at −80 °C, the reactivity ratio of 44.4 was calculated for 100% hexanes (Figure 6). This indicates that IB is ∼44 times more reactive than BD in 100% hexanes at −80 °C.

**Effect of Temperature on the Competition Experiment of IB with BD as Capping Agent.** The experimental results for the competition experiments of IB with BD in two different Hex/MeCl (v/v) solvent mixtures (Hex/MeCl 50/50 (v/v) and Hex/MeCl 60/40 (v/v)) at −80, −70, −60, −50, and −40 °C are shown in Tables 4 and 5. The $^1$H NMR spectra show that at −40 °C in addition to ∼95% addition products ∼5% exo-olefinic structure at the end of the polymer is obtained, which

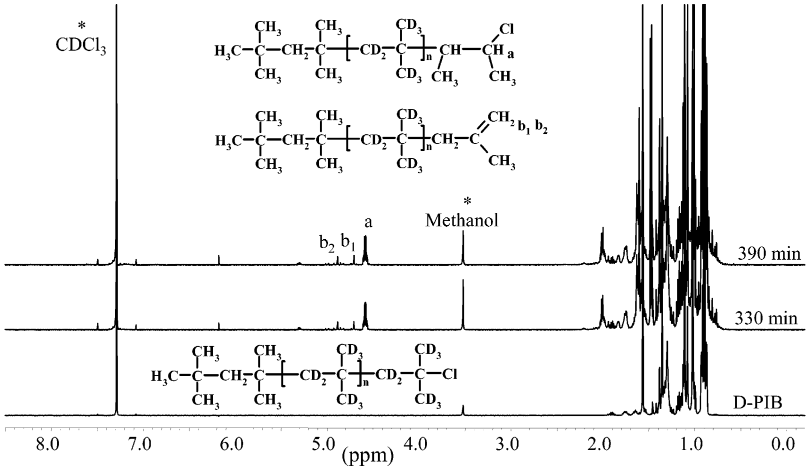


**Figure 5.** $^1$H NMR spectra of D-PIB and D-PIB obtained from the capping reaction of D-PIB$^+$ with *cis*-2-Bu as a capping agent.

**Table 3. Limiting Conversion ($x_\infty^{IB}$), Molecular Weight ($M_n$), Molecular Weight Distribution (PDI), and Reactivity Ratios ($k_p^\pm/k_c^\pm$) from the Competition Experiments of IB with BD in Solvent Mixtures of Different Apolar/Polar Ratio**[a]

| (Hex + IB + BD)/MeCl (v/v) | $x_\infty^{IB}$ (%) | $M_{n,GPC}$ | PDI | $k_p^\pm/k_c^\pm$ ($x_\infty^{IB}$) | $k_p^\pm/k_c^\pm$ ($DP_{n\infty}$) | $k_p^\pm/k_c^\pm$ (average) |
|---|---|---|---|---|---|---|
| 80/20 | 36.9 | 4020 | 1.5 | 68.8 | 72.7 | 70.8 |
| 70/30 | 43.4 | 5000 | 1.7 | 85.1 | 88.2 | 86.6 |
| 60/40 | 46.8 | 5350 | 1.6 | 94.4 | 96.8 | 95.6 |
| 50/50 | 51.9 | 5890 | 1.7 | 109.4 | 111.2 | 110.3 |
| 40/60 | 55.6 | 6510 | 1.7 | 121.4 | 129.7 | 125.6 |

[a] [IB] = 0.4 mol L$^{-1}$, [TMPCl] = 0.002 mol L$^{-1}$, [DTBP] = 0.004 mol L$^{-1}$, [TiCl$_4$] = 0.036 mol L$^{-1}$, and [BD] = 0.3 mol L$^{-1}$ at −80 °C.

**Table 4. Limiting Conversion ($x_\infty^{IB}$), Molecular Weight ($M_n$), Molecular Weight Distribution (PDI), and Reactivity Ratios ($k_p^\pm/k_c^\pm$) from the Competition Experiments of IB with BD in Hex/MeCl 50/50 (v/v) at Different Temperatures**[a]

| temp (°C) | $x_\infty^{IB}$ (%) | $M_{n,GPC}$ | PDI | $k_p^\pm/k_c^\pm$ ($x_\infty^{IB}$) | $k_p^\pm/k_c^\pm$ ($DP_{n\infty}$) | $k_p^\pm/k_c^\pm$ (average) |
|---|---|---|---|---|---|---|
| −80 | 51.9 | 5890 | 1.7 | 109.4 | 111.2 | 110.3 |
| −70 | 47.2 | 5520 | 1.6 | 95.5 | 101.2 | 98.4 |
| −60 | 42.6 | 4950 | 1.6 | 83.0 | 87.0 | 85.0 |
| −50 | 37.8 | 4600 | 1.5 | 71.0 | 78.9 | 74.9 |
| −40 | 33.9 | 4020 | 1.7 | 61.9 | 66.3 | 64.1 |

[a] [IB] = 0.4 mol L$^{-1}$, [TMPCl] = 0.002 mol L$^{-1}$, [DTBP] = 0.004 mol L$^{-1}$, [TiCl$_4$] = 0.036 mol L$^{-1}$, and [BD] = 0.3 mol L$^{-1}$.

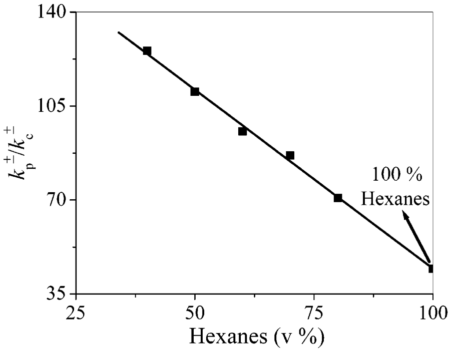


**Figure 6.** Correlation between the hexanes content and the reactivity ratio for the competition experiments of IB with BD at −80 °C.

shows resonance signals at 4.67 and 4.87 ppm. Proton elimination from PIB$^+$ has already been reported for the polymerization of IB at −40 °C.[20] The reactivity ratios were calculated from $x_\infty^{IB}$ using eq 1 and from the $DP_{n\infty}$ using eq 2. These two methods yielded similar $k_p^\pm/k_c^\pm$ values (Tables 4 and 5). Since propagation of IB does not have an enthalpic barrier,[8] the $k_p^\pm/k_c^\pm$ should decrease with increasing temperature. In accord with this expectation, Tables 4 and 5 show that $k_p^\pm/k_c^\pm$ decreases with increasing temperature. From the slope of the Arrhenius plot of $\ln(k_p^\pm/k_c^\pm)$ vs $1/T$ (Figure 2 in the Supporting Information), the apparent activation energy, $E_a$, was calculated to be −5.1 and −5.5 kJ mol$^{-1}$ respectively in Hex/MeCl 50/50 (v/v) and Hex/MeCl 60/40 (v/v) solvent mixtures. Since the $k_p^\pm$ is independent of temperature, the cross-propagation rate constant from PIB$^+$ cation to the BD has an activation energy of 5.1 and 5.5 kJ mol$^{-1}$ respectively in Hex/MeCl 50/50 (v/v) and Hex/MeCl 60/40 (v/v) solvent mixtures. The $k_p^\pm/k_c^\pm$ for the competition experiments of IB with BD at 0 °C in 100% hexanes was calculated by using the Arrhenius equation. The average $E_a/R$ ($R$ is the universal gas constant and $E_a$ is the apparent activation energy for the polymerization of IB in the presence of BD) from the plot of $\ln(k_p^\pm/k_c^\pm)$ vs $1/T$ in Hex/MeCl 50/50 (v/v) and Hex/MeCl 60/40 (v/v) is used for the calculation of $k_p^\pm/k_c^\pm = 17.0$, indicating IB is only 17 times more reactive than BD in 100% nonpolar solvent (hexanes) at 0 °C.

For the copolymerization of isobutylene with BD, $k_{IB-IB}/k_{IB-BD} = 43$[21,22] and 115 ± 15[23] have been reported using AlEtCl$_2$/MeCl/−100 °C and AlCl$_3$/MeCl/−103 °C systems, respectively. Our extrapolated results suggest a much higher reactivity difference ($k_{IB-IB}/k_{IB-BD} \sim 260$) for MeCl/−100 °C. This discrepancy may be attributed to the heterogeneous nature of the copolymerization where specific solvent effects may affect the copolymer composition. Similarly to our conclusions, Kennedy and Canter[22] found that in homogeneous copolymerization the BD incorporation strongly increases; i.e., $k_{IB-IB}/k_{IB-BD}$ decreases with increasing temperature.

**Effect of Solvent Polarity on the Competition Experiment of IB with 1-Bu as Capping Agent.** Since 1-Bu is a much weaker capping agent than BD, a high concentration of 1-Bu is needed to reach limiting conversion in the competition experiments of IB with 1-Bu. Hence, the competition experiments of

**Table 5. Limiting Conversion ($x_\infty^{IB}$), Molecular Weight ($M_n$), Molecular Weight Distribution (PDI), and Reactivity Ratios ($k_p^\pm/k_c^\pm$) from the Competition Experiments of IB with BD in Hex/MeCl 60/40 (v/v) at Different Temperatures**[a]

| temp (°C) | $x_\infty^{IB}$ (%) | $M_{n,GPC}$ | PDI | $k_p^\pm/k_c^\pm$ ($x_\infty^{IB}$) | $k_p^\pm/k_c^\pm$ ($DP_{n\infty}$) | $k_p^\pm/k_c^\pm$ (average) |
|---|---|---|---|---|---|---|
| −80 | 46.8 | 5350 | 1.6 | 94.4 | 96.8 | 95.6 |
| −70 | 42.4 | 5020 | 1.7 | 82.5 | 88.7 | 85.6 |
| −60 | 38.2 | 4350 | 1.6 | 71.9 | 73.3 | 72.6 |
| −50 | 34.0 | 4110 | 1.5 | 62.1 | 68.8 | 65.2 |
| −40 | 27.8 | 3460 | 1.7 | 48.7 | 55.1 | 51.9 |

[a] [IB] = 0.4 mol $L^{-1}$, [TMPCl] = 0.002 mol $L^{-1}$, [DTBP] = 0.004 mol $L^{-1}$, [$TiCl_4$] = 0.036 mol $L^{-1}$, and [BD] = 0.3 mol $L^{-1}$.

**Table 6. Limiting Conversion ($x_\infty^{IB}$), Molecular Weight ($M_n$), Molecular Weight distribution (PDI), and Reactivity Ratios ($k_p^\pm/k_c^\pm$) from the Competition Experiments of IB with 1-Bu in Solvent Mixtures of Different Apolar/Polar Ratio**[a]

| (Hex + IB + 1-Bu)/MeCl (v/v) | $x_\infty^{IB}$ (%) | $M_{n,GPC}$ | PDI | $k_p^\pm/k_c^\pm$ ($x_\infty^{IB}$) | $k_p^\pm/k_c^\pm$ ($DP_{n\infty}$) | $k_p^\pm/k_c^\pm$ (average) |
|---|---|---|---|---|---|---|
| 80/20 | 48.2 | 11 000 | 1.6 | 2631 | 2694 | 2663 |
| 70/30 | 53.5 | 12 300 | 1.7 | 3063 | 3176 | 3120 |
| 60/40 | 58.1 | 13 800 | 1.6 | 3479 | 3816 | 3648 |
| 50/50 | 64.5 | 14 700 | 1.7 | 4142 | 4256 | 4199 |

[a] [IB] = 0.4 mol $L^{-1}$, [TMPCl] = 0.001 mol $L^{-1}$, [DTBP] = 0.004 mol $L^{-1}$, [$TiCl_4$] = 0.036 mol $L^{-1}$ and [1-Bu] = 4.0 mol $L^{-1}$ at −80 °C.

**Table 7. Limiting Conversion ($x_\infty^{IB}$), Molecular Weight ($M_n$), Molecular Weight Distribution (PDI), and Reactivity Ratios ($k_p^\pm/k_c^\pm$) from the Competition Experiments of IB with 1-Bu in Hex/MeCl 50/50 (v/v) at Different Temperatures**[a]

| temp (°C) | $x_\infty^{IB}$ (%) | $M_{n,GPC}$ | PDI | $k_p^\pm/k_c^\pm$ ($x_\infty^{IB}$) | $k_p^\pm/k_c^\pm$ ($DP_{n\infty}$) | $k_p^\pm/k_c^\pm$ (average) |
|---|---|---|---|---|---|---|
| −80 | 64.5 | 14 700 | 1.7 | 4142 | 4256 | 4199 |
| −70 | 58.6 | 13 400 | 1.7 | 3527 | 3635 | 3581 |
| −60 | 54.9 | 12 400 | 1.6 | 3185 | 3216 | 3200 |
| −50 | 49.2 | 11 500 | 1.5 | 2709 | 2873 | 2791 |
| −40 | 39.8 | 9 800 | 1.6 | 2030 | 2295 | 2162 |

[a] [IB] = 0.4 mol $L^{-1}$, [TMPCl] = 0.001 mol $L^{-1}$, [DTBP] = 0.004 mol $L^{-1}$, [$TiCl_4$] = 0.036 mol $L^{-1}$ and [1-Bu] = 4.0 mol $L^{-1}$.

**Table 8. Limiting Conversion ($x_\infty^{IB}$), Molecular Weight ($M_n$), Molecular Weight Distribution (PDI), and Reactivity Ratios ($k_p^\pm/k_c^\pm$) from the Competition Experiments of IB with 1-Bu in Hex/MeCl 60/40 (v/v) at Different Temperatures**[a]

| temp (°C) | $x_\infty^{IB}$ (%) | $M_{n,GPC}$ | PDI | $k_p^\pm/k_c^\pm$ ($x_\infty^{IB}$) | $k_p^\pm/k_c^\pm$ ($DP_{n\infty}$) | $k_p^\pm/k_c^\pm$ (average) |
|---|---|---|---|---|---|---|
| −80 | 58.1 | 13 800 | 1.6 | 3479 | 3816 | 3648 |
| −70 | 52.6 | 12 300 | 1.6 | 2986 | 3176 | 3081 |
| −60 | 47.7 | 11 300 | 1.7 | 2592 | 2800 | 2696 |
| −50 | 41.4 | 10 300 | 1.5 | 2138 | 2456 | 2297 |
| −40 | 35.2 | 8 900 | 1.7 | 1735 | 2020 | 1878 |

[a] [IB] = 0.4 mol $L^{-1}$, [TMPCl] = 0.001 mol $L^{-1}$, [DTBP] = 0.004 mol $L^{-1}$, [$TiCl_4$] = 0.036 mol $L^{-1}$, and [1-Bu] = 4.0 mol $L^{-1}$.

**Table 9. Limiting Conversion ($x_\infty^{IB}$), Molecular Weight ($M_n$), Molecular Weight Distribution (PDI), and Reactivity Ratios ($k_p^\pm/k_c^\pm$) from the Competition Experiments of IB with *cis*-2-Bu in Solvent Mixture of Different Apolar/Polar Ratio**[a]

| (Hex + IB + *cis*-2-Bu)/MeCl (v/v) | $x_\infty^{IB}$ (%) | $M_{n,GPC}$ | PDI | $k_p^\pm/k_c^\pm$ ($x_\infty^{IB}$) | $k_p^\pm/k_c^\pm$ ($DP_{n\infty}$) | $k_p^\pm/k_c^\pm$ (average) |
|---|---|---|---|---|---|---|
| 80/20 | 32 | 8 000 | 1.7 | 1543 | 1763 | 1653 |
| 70/30 | 44 | 10 300 | 1.5 | 2319 | 2456 | 2388 |
| 60/40 | 50 | 12 100 | 1.6 | 2772 | 3098 | 2935 |
| 50/50 | 58 | 13 400 | 1.7 | 3470 | 3635 | 3552 |

[a] [IB] = 0.4 mol $L^{-1}$, [TMPCl] = 0.001 mol $L^{-1}$, [DTBP] = 0.004 mol $L^{-1}$, [$TiCl_4$] = 0.036 mol $L^{-1}$, and [*cis*-2-Bu] = 4.0 mol $L^{-1}$ at −80 °C.

IB with 1-Bu were carried out using the following conditions: [IB] = 0.4 mol $L^{-1}$, [TMPCl] = 0.001 mol $L^{-1}$, [DTBP] = 0.004 mol $L^{-1}$, [1-Bu] = 4.0 mol $L^{-1}$, and [$TiCl_4$] = 0.036 mol $L^{-1}$ in different Hex/MeCl solvent mixtures (Hex/MeCl 80/20 (v/v) to Hex/MeCl 50/50 (v/v)) and at different temperatures (−80 to −40 °C).

Polymerizations were carried out in different Hex/MeCl (v/v) solvent mixtures. The reactivity ratios for the competition experiments of IB with 1-Bu were calculated from $x_\infty^{IB}$ using eq 1 and from the $DP_{n\infty}$ using eq 2. These two methods yielded similar $k_p^\pm/k_c^\pm$ values. The experimental results in Table 6 show that $k_p^\pm/k_c^\pm$ for the competition experiments of IB with 1-Bu at −80 °C increases with the increase of solvent polarity. From the plot of $k_p^\pm/k_c^\pm$ vs solvent composition (Figure 3 in the Supporting Information) the reactivity ratio of 1608 was calculated for 100% hexanes at −80 °C by extrapolation. Thus, IB is ~1600 times more reactive than 1-Bu in 100% hexanes at −80 °C.

**Effect of Temperature on the Competition Experiment of IB with 1-Bu as Capping Agent.** Polymerizations were carried out at −80, −70, −60, −50, and −40 °C in Hex/MeCl 50/50 (v/v) and Hex/MeCl 60/40 (v/v) solvent mixtures. The reactivity ratios (calculated from $x_\infty^{IB}$ using eq 1 and from the $DP_{n\infty}$ using eq 2) and the experimental results are shown in Tables 7 and 8 for the competition experiments of IB with 1-Bu in Hex/MeCl 50/50 (v/v) and Hex/MeCl 60/40 (v/v), respectively. The $k_p^\pm/k_c^\pm$ values decrease with increasing temperature in both Hex/MeCl 50/50 (v/v) (Table 7) and Hex/MeCl 60/40 (v/v) (Table 8) solvent mixture. From the slope of the Arrhenius plot of $\ln(k_p^\pm/k_c^\pm)$ vs $1/T$ (Figure 4 in the Supporting Information) the $E_a = -5.9$ kJ $mol^{-1}$ and $-6.0$ kJ $mol^{-1}$ were obtained respectively in Hex/MeCl 50/50 (v/v) and Hex/MeCl 60/40 (v/v) solvent mixtures. By using average $E_a/R$ (from the plot of $\ln(k_p^\pm/k_c^\pm)$ vs $1/T$ in Hex/MeCl 50/50 (v/v) and Hex/MeCl 60/40 (v/v)) the reactivity ratio $k_p^\pm/k_c^\pm = 543$ was obtained at 0 °C in 100% hexanes, indicating that 1-Bu is about 540 times

**Table 10. Rate Constants for the Reactions of C4 Olefins with $PIB^+$ (Hex/MeCl 50/50 v/v) and $An(Ph)CH^+$ ($CH_2Cl_2$) at −70 °C**

| capping agent | $k_{PIB^+}$ (L $mol^{-1}$ $s^{-1}$) | $k_{rel}$ | $k_{An(Ph)CH^+}$ (L $mol^{-1}$ $s^{-1}$) | $k_{rel}$ |
|---|---|---|---|---|
| IB | $7.2 \times 10^8$ | $3.6 \times 10^3$ | 23.3 | $2.5 \times 10^4$ |
| BD | $7.3 \times 10^6$ | 37 | $1.93 \times 10^{-2}$ | 21 |
| 1-Bu | $2.0 \times 10^5$ | 1 | $9.39 \times 10^{-4a}$ | 1 |
| *cis*-2-Bu | $2.3 \times 10^5$ | 1.2 | $1.01 \times 10^{-3}$ | 1.1 |
| *trans*-2-Bu | 0 | 0 | $1.26 \times 10^{-3}$ | 1.3 |

[a] Rate constant for propene.

less reactive than IB toward $PIB^+$ cation in 100% hexanes at 0 °C.

**Competition Experiment of IB with *cis*-2-Bu or *trans*-2-Bu as Capping Agent.** The competition experiments of IB with *cis*-2-Bu or *trans*-2-Bu were carried out in Hex/MeCl 60/40 (v/v) solvent mixtures at −80 °C. With *trans*-2-Bu 100% conversion was obtained in less than 2 h in Hex/MeCl 60/40 (v/v) at −80 °C using [IB] = 0.6 mol $L^{-1}$, [TMPCl] = 0.001 mol $L^{-1}$, [DTBP] = 0.004 mol $L^{-1}$, [$TiCl_4$] = 0.036 mol $L^{-1}$, and [*trans*-2-Bu] = 4.0 mol $L^{-1}$. This result is in line with the previous capping studies where we have shown that $PIB^+$ does not react with *trans*-2-Bu in Hex/MeCl 60/40 (v/v) at −80 °C. However, the limiting conversion (47.5%) and limiting number-average degrees of polymerization ($M_n = 16\,400$, PDI = 1.7) were reached in 8 h with *cis*-2-Bu in Hex/MeCl 60/40 (v/v) solvent mixture at −80 °C using [IB] = 0.6 mol $L^{-1}$, [TMPCl] = 0.001 mol $L^{-1}$, [DTBP] = 0.004 mol $L^{-1}$, [$TiCl_4$] = 0.036 mol $L^{-1}$, and [*cis*-2-Bu] = 4.0 mol $L^{-1}$. Competition experiments were also carried out in different Hex/MeCl (v/v) solvent mixtures. The reactivity ratio, $k_p^{\pm}/k_c^{\pm}$, was calculated from $x_{\infty}^{IB}$ using eq 1 and from the $DP_{n\infty}$ using eq 2. The experimental results presented in Table 9 indicate that $k_p^{\pm}/k_c^{\pm}$ for the competition experiments of IB with *cis*-2-Bu at −80 °C increases with the increase of solvent polarity. By extrapolating the plot of $k_p^{\pm}/k_c^{\pm}$ vs hexanes (vol %) for the competition experiments of IB with *cis*-2-Bu at −80 °C, the reactivity ratio of 850 was calculated for 100% hexanes, suggesting IB is 850 times more reactive than *cis*-2-Bu (Figure 5 in the Supporting Information, 80/20 data point was neglected). By using an average $E_a/R = 700$ K, the reactivity ratio $k_p^{\pm}/k_c^{\pm} = 294$ was obtained at 0 °C in 100% hexanes. So, IB is ∼290 times more reactive than *cis*-2-Bu in 100% nonpolar solvent (hexanes) at 0 °C.

**Calculation of the Cross-Propagation Rate Constants and Relative Reactivities.** The calculated rate constants for the addition reaction of C4 olefins to $PIB^+$ for Hex/MeCl 50/50 (v/v) at −70 °C are shown in Table 10. These values, calculated from the reactivity ratios determined in this paper and the $k_p^{\pm}$ reported[24] earlier for the same solvent mixture and temperature, show that IB reacts 3600 times faster than 1-Bu and BD is 37 times more reactive than 1-Bu while the reactivity of *cis*-2-Bu is only slightly higher than that of 1-Bu. These relative reactivities may be compared to relative reactivities observed in the reaction of C4 olefins with the *p*-methoxy-substituted diphenylmethyl cation ($An(Ph)CH^+$) reported by Mayr in $CH_2Cl_2$ at −70 °C.[4] Although the solvent is different, generally solvent effects are small. There is good agreement between the two reactivity scales for BD, 1-Bu, and *cis*-2-Bu. The finding that *trans*-2-Bu reacts with benzhydryl cations but not with $PIB^+$ cations may be related to steric effects. The difference for IB is large; IB reacts with $An(Ph)CH^+$ $2.5 \times 10^4$ times faster than 1-Bu, while IB is only 3600 times more reactive than 1-Bu against $PIB^+$. This decrease of selectivity is clearly due to the fact that the propagation of IB is close to diffusion limited, and the constant selectivity relationship no longer applies.

**Conclusions.** Under certain conditions in Hex/MeCl solvent mixtures at −80 in conjunction with $TiCl_4$ as Lewis acid the $PIB^+$ cation combines with BD, 1-Bu, or *cis*-2-Bu to selectively give the 1:1 adduct. *trans*-2-Bu is unreactive toward the $PIB^+$ cation. Thus, when the polymerization of IB is carried out in the presence of BD, 1-Bu or *cis*-2-Bu in conjunction with $TiCl_4$ in Hex/MeCl (v/v) solvent mixture at −40 to −80 °C the polymerization stops short of completion, and limiting conversions and molecular weights are reached. These competition experiments could be used successfully to determine the cross-propagation rate constant from $PIB^+$ cation to 1-Bu, *cis*-2-Bu, and BD in Hex/MeCl 80/20 to 40/60 (v/v) in the temperature range of −40 to −80 °C. The reactivity ratio, $k_p^{\pm}/k_c^{\pm}$, increases with the increase of solvent polarity, suggesting that $k_p^{\pm}$ increases more rapidly than $k_c^{\pm}$. While the propagation of IB does not have an enthalpic barrier, the $k_c^{\pm}$ values increase with increasing temperature ($E_a$ = 5.1−6.0 kJ $mol^{-1}$). In 100% hexanes at 0 °C, IB is ∼17 times more reactive than BD, ∼543 times more reactive than 1-Bu, and ∼294 times more reactive than *cis*-2-Bu. These results may help understand the polymerization of IB using a C4 olefin feed.

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**Supporting Information Available:** $^1$H NMR spectrum of the original 3C1B and the product obtained after the isomerization study, 1-chloro-2-butene (Figure S1); Arrhenius plot of $\ln(k_p^{\pm}/k_c^{\pm})$ vs $1/T$ to determine apparent energy of activation, $E_a$, for the competition experiments of IB with BD in (a) Hex/MeCl 50/50 (v/v) and (b) Hex/MeCl 60/40 (v/v); [IB] = 0.4 mol $L^{-1}$, [TMPCl] = 0.002 mol $L^{-1}$, [DTBP] = 0.004 mol $L^{-1}$, [$TiCl_4$] = 0.036 mol $L^{-1}$, and [BD] = 0.3 mol $L^{-1}$ (Figure S2); correlation between the hexanes content and the reactivity ratio for the competition experiments of IB with 1-Bu at −80 °C (Figure S3); Arrhenius plot of $\ln(k_p^{\pm}/k_c^{\pm})$ vs $1/T$ to determine the apparent energy of activation, $E_a$, for the competition experiments of IB with 1-Bu in (a) hexanes/MeCl 50/50 (v/v) and (b) hexanes/MeCl 60/40 (v/v); [IB] = 0.4 mol $L^{-1}$, [TMPCl] = 0.001 mol $L^{-1}$, [DTBP] = 0.004 mol $L^{-1}$, [$TiCl_4$] = 0.036 mol $L^{-1}$, and [1-Bu] = 4.0 mol $L^{-1}$ (Figure S4); correlation between the hexanes content and the reactivity ratio for the competition experiments of IB with *cis*-2-Bu at −80 °C (Figure S5). This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

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(24) Based on the $k_p^{\pm} = (4.7 \pm 2) \times 10^8$ L mol$^{-1}$ s$^{-1}$ for IB homopolymerization in Hex/MeCl 60/40 (v/v) solvent mixture at −80 °C, the uncertainty limit in $k_p^{\pm}$ in Hex/MeCl 50/50 (v/v) solvent mixture at −70 °C is estimated to be $(7.2 \pm 2) \times 10^8$ L mol$^{-1}$ s$^{-1}$.

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