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Mechanism of Isomerization in the Cationic Polymerization of Isobutylene

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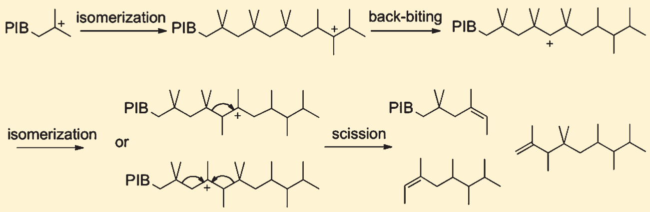
S *Supporting Information*



ABSTRACT: The complex mechanism of the carbocationic rearrangements leading to a variety of olefin (exo-, endo-, tri-, and tetra-substituted) end groups in the cationic polymerization of isobutylene (IB) catalyzed by ethylaluminum dichloride ($EtAlCl_2$) in nonpolar solvents in the temperature range of −40 to 25 °C was studied by model ionization experiments employing poly(isobutylene chloride) (PIB-Cl) of low molecular weight ($M_n \sim 1000-2000$) obtained by living cationic polymerization. Ionizations were performed with $EtAlCl_2$ in hydrocarbon media to mimic a conventional cationic polymerization of IB, but in the presence of a proton trap to suppress reprotonation of the first formed olefin and subsequent decomposition of the resulting PIB cation. In the absence of a proton trap, ionization of PIB-Cl resulted in about 70% of tri-substituted olefin end groups in the studied temperature range. The exo and endo olefin end-group content was negligible. MALDI and APPI TOF MS indicated that the tri-substituted PIB olefins contained irregular carbon numbers, suggesting chain scission. Ionizations carried out in the presence of the proton trap 2,6-di-*tert*-butylpyridine (DTBP) at 0 and −40 °C also gave mainly the tri-substituted olefin; however, at 25 °C only exo-, endo-, and tetra-substituted olefins were formed with regular carbon numbers. Ionization of $PIB_{d8}(IB)_n$-Cl with $n = 1-6$ showed that on average 4 IB units are cleaved at −40 °C, which suggests that the tri-substituted olefins are formed by backbiting via hydride transfer followed by chain scission. A mechanism is proposed to account for the olefin structures involving a sterically hindered cation arising via hydride and methyde shifts, which either eliminates a proton to yield the tetra-substituted olefin or undergoes a distant hydride shift by backbiting followed by a methyde shift and chain scission to yield the tri-substituted olefin of irregular carbon number.

INTRODUCTION

The carbocationic polymerization of isobutylene (IB) is a subject of great scientific and industrial interest.[1] The unique properties of polyisobutylene (PIB), a chemically stable fully saturated polymer of low T_g, make it a desirable material with applications ranging from medical devices[2] to ashless dispersant in motor oils and fuel additives.[3] These motor oil and fuel additives are low molecular weight ($M_n \sim 500-5000$) oil-soluble surfactants with oligoamine end groups obtained from PIB or polybutenes (copolymers of IB with C4 olefins) with olefinic end groups.

Two major industrial methods were developed to produce low molecular weight IB homo- or copolymers with olefinic end groups. The first one, which is also referred to as "conventional", uses a C4 mixture and $AlCl_3$- or $EtAlCl_2$-based catalyst systems and gives polybutenes with high tri-substituted olefinic content.[4,5] Because of the low reactivity of the tri-substituted olefinic end groups, polybutenes need to be chlorinated to react with maleic anhydride to give poly(butenylsuccinic anhydride), which is reacted with oligo-alkylenimines to yield poly(butenyl succinimide) ashless dispersants. The other method employs pure IB and BF_3 complexes with either alcohols or ethers and yields highly reactive PIBs (HR PIBs) with high exo-olefinic end-group content.[6] In contrast to the tri-substituted olefins of conventional polybutenes, PIB exo-olefins readily react with maleic anhydride in a thermal "ene" reaction to produce PIB succinic anhydride and subsequently poly(isobutenyl succinimide) ashless dispersants. Because the final product does not contain any chlorine, HR PIB is more desirable than polybutenes.

While the multiplicity of olefinic end groups in polybutenes has generally been ascribed to isomerizations, the mechanism of chain transfer is not clear. It is also unclear why the BF_3 system yields almost exclusively exo-olefin. In order to understand this difference and to control the end-functionality of PIB in conventional cationic polymerization, the chain transfer mechanism

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should be determined. While the living carbocationic polymerization of IB is fairly well studied,[1a] only a few contributions deal directly with the problems associated with the complex set of reactions occurring in the conventional polymerization of IB. More than 30 years ago, Puskas et al. reported that the cationic polymerization of IB leads to polymers of irregular, uneven carbon number as a result of chain scission, suggesting the release of C1 to C3 cations.[4,5] This was further extended by Harrison et al., who proposed a similar polymerization scheme.[3]

In the present investigation, ionization studies were performed on model PIB-Cl oligomers with $EtAlCl_2$ at conditions mimicking a conventional carbocationic polymerization of IB. A proton trap was used in order to abort the recurring protonation/deprotonation reactions in order to observe the olefins first formed. Varying the reaction temperature provided control of the structure and distribution of the olefins, which allowed us to isolate and address the formation of major olefins by employing partially deuterated PIB-Cl oligomers. With the results of characterization of the ionization products with NMR spectroscopy, ESI-TOF MS, and SEC and also with the help of some DFT calculations, we were able to construct a reaction scheme explaining the complex nature of the carbocationic rearrangements occurring during the conventional polymerization of IB.

EXPERIMENTAL SECTION

Materials. Hexanes and dichloromethane (DCM) were purified as described previously.[7] Cumyl chloride (CumCl) was synthesized by bubbling HCl through 10% solution of α-methylstyrene in dry DCM[8] at −78 °C for 6 h. Isobutylene (IB, Matheson Tri Gas) gas was dried by passing it through in-line gas-purifier columns packed with BaO/Drierite and then condensed in a receiver flask at −80 °C before use. $CDCl_3$ (Cambridge Isotope Laboratories Inc.), isobutylene-d_8 (IB-d_8, CDN Isotopes, 99.8 atom % D), methallytrimethylsilane MATMS (Gelest), ethylaluminum dichloride ($EtAlCl_2$, 1 M solution in hexane, Aldrich), methylaluminum dichloride ($MeAlCl_2$, 1 M solution in hexane, Aldrich), and di-*tert*-butylpyridine (DTBP, 97%, Aldrich) were used as received. HR PIB sample from BASF had $M_n = 2200$ and $M_w/M_n = 1.8$

Preparation of Cum(IB-d_8)$_{13}$(IB)$_n$Cl (n = 1−6). The polymerization of IB-d_8 was carried out at −80 °C in hexanes:methyl chloride = 60:40 (v/v) mixture under a dry N_2 atmosphere in a MBraun 150-M glovebox (Innovative Technology Inc., Newburyport, MA). A polymerization reactor equipped with magnetic stir bar was immersed in the heptane bath at −80 °C and calculated amount of prechilled to −80 °C solvents and stock solutions of the reagents were added, and the polymerization was started by adding cold stock solution of $TiCl_4$ in hexanes:methyl chloride = 60:40 (v:v). The reagent concentrations were as follows: [CumCl] = 0.008 M, [$TiCl_4$] = 0.036 M, [IB-d_8] = 0.1 M, [DTBP] = 0.004 M. MATMS was added after 1 h in 3 times molar excess toward the CumCl initiator in order to form exo-olefinic polymer.[9] The capping reaction was allowed to continue for 2 h, after which the reaction mixture was quenched with aqueous NH_3 to terminate the polymerization and to trap the released HCl from the Lewis acid. Polymers were recovered by reprecipitation from hexane/methanol and then dried under vacuum. The product was dissolved in DCM and subjected to quantitative hydrochlorination.[9] In order to obtain Cum(IB-d_8)$_{13}$(IB)$_n$Cl, Cum(IB-d_8)(IB)$_{n-1}$Cl and 3-fold excess of MATMS were dissolved in DCM at −80 °C. $TiCl_4$ (0.01 M) was added to start the reaction. After 2 h aqueous NH_3 was poured into the reactor. The mixture was filtered, and then the organic layer was washed three times with distilled water. The reaction product was recovered after evaporation of the solvent. The hydrochlorination/end-capping with MATMS procedure was repeated up to five times to obtain Cum(IB-d_8)$_{13}$(IB)$_6$. Nondeuterated PIB-Cl was prepared, similarly to Cum(IB-d_8)$_{13}$Cl. Molecular weight characteristics of the synthesized model polymers are summarized in Table S1.

Ionization Experiments. In a MBraun M-150 glovebox, PIB-Cl was dissolved in hexane at 25, 0, or at −40 °C to form 0.015 M solution. Proton trap DTBP (0.015 M) was also added. Ionizations were performed for 30 min in culture tubes, or in NMR tubes, at $EtAlCl_2$ concentrations of 0.015 M. Then aqueous ammonia was poured into the culture tube, and the ionization product was isolated from the upper organic layer.

Characterization. *Size Exclusion Chromatography (SEC).* Molecular weights and polydispersities of the polymers were obtained from size exclusion chromatography with universal calibration using a Waters 717 Plus autosampler, a 515 HPLC pump, a 410 differential refractometer, a 2487 dual λ absorbance detector, a MiniDawn multiangle laser light scattering (MALLS) detector (measurement angles are 44.7°, 90.0°, and 135.4°) (Wyatt Technology Inc.), ViscoStar viscosity detector (Wyatt Technology Inc.), and five Styragel HR GPC columns connected in the following order: 500, 10^3, 10^4, 10^5, and 100 Å. The differential refractometer was used as a concentration detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min at room temperature. The results were processed by the Astra 5.3 software from Wyatt Technology Inc.

Nuclear Magnetic Resonance. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker 500 MHz spectrometer using $CDCl_3$, as solvent (Cambridge Isotope Lab., Inc.).

Matrix-Assisted Laser Desorption/Ionization Spectrometry (MALDI MS). The MALDI MS measurements were performed with a Bruker BIFLEX III mass spectrometer equipped with a time-of-flight (TOF) analyzer. In all cases 19 kV total acceleration voltage was used with pulsed ion extraction (PIE). The positive ions were detected in the reflectron mode. A nitrogen laser (337 nm) operating at 4 Hz was used to produce laser desorption, and 200−300 shots were summed. The samples were prepared with a dithranol matrix dissolved in THF (20 mg/mL). The solutions of the polymers in THF were made in a concentration of 10 mg/mL. To enhance the cationization of PIBs, silver trifluoroacetate (AgTFA) in THF (5 mg/mL) was added to the corresponding matrix/analyte solutions. The solutions were mixed in a 10:2:1 v/v ratio (matrix:analyte:cationization agent). A volume of 0.5−1.0 μL of these solutions was deposited onto the sample plate (stainless steel) and allowed to air-dry.

Atmospheric Pressure Photoionization Ionization Mass Spectrometry (APPI-MS). Atmospheric pressure photoionization ionization mass spectrometric measurements were performed in the negative ion modes with a MicroTOF-Q type quadrupole-time-of-flight (Qq-TOF MS) instrument (Bruker Daltonik, Bremen, Germany) equipped with an atmospheric pressure photoionization (APPI) source (PhotoMate, Kr discharge lamp) from Syagen Ltd. (Syagen Technology, Inc., Tustin, CA). The PIB samples were dissolved in toluene (dopant) at a concentration of 1 mg/mL. The PIB solutions were delivered directly into the APPI source with a syringe pump (Cole-Parmer Ins. Co., Vernon Hills, IL) at a flow rate of 25 μL/min together with a carrier flow of CCl_4 at a flow rate of 200 μL/min by means of a T-piece. The heater of the APPI source was kept at 450 °C. End-plate offset and capillary voltage were set to −500 and 2500 V, respectively.

Computer Simulations. Model molecules were initially geometrically optimized in Avogadro software[10] using the MMFF94 force field.[11] Then the optimized structures were subjected to energy optimization by DFT B3LYP 6-31G performed by GAMESS software,[12] which gave the Hartree−Fock (HF) energies, from which relative energies were calculated.

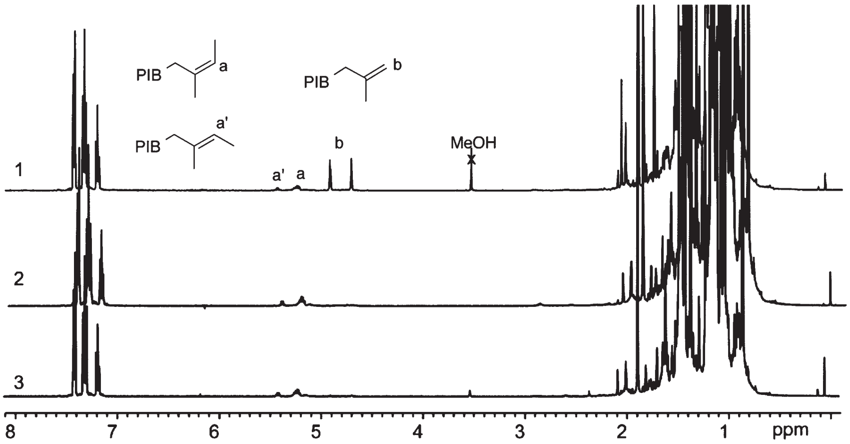


Figure 1. ^{1}H NMR spectra of products obtained via the ionization of PIB-Cl by $EtAlCl_2$: (1) in the presence of PIB exo-olefin and DTBP; (2) in the presence of PIB exo-olefin without DTBP; (3) in the absence of both PIB exo-olefin and DTBP.

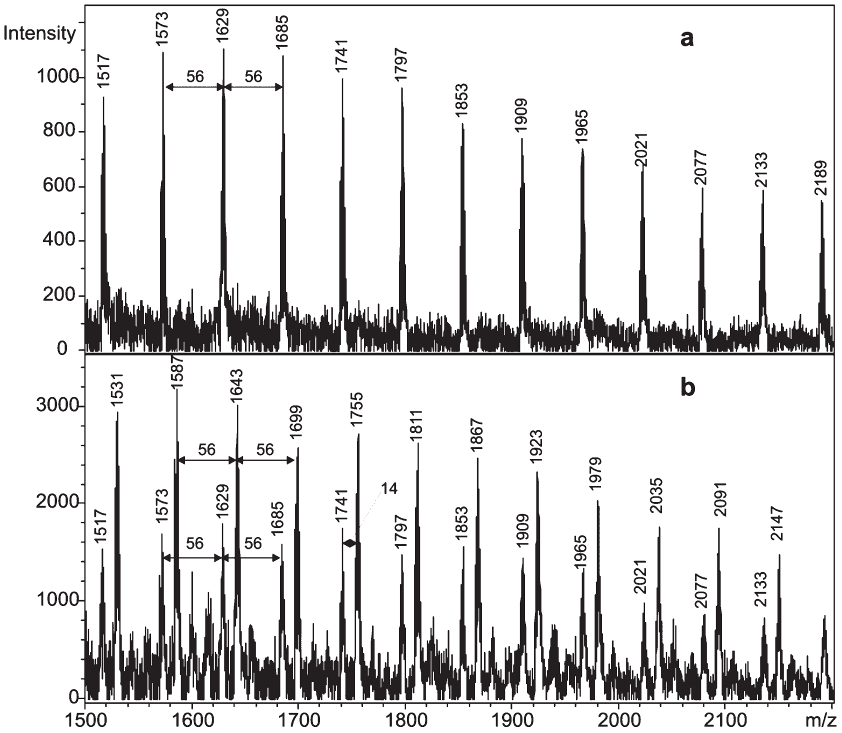


Figure 2. MALDI-TOF MS spectra of (a) PIB-Cl and (b) the product of ionization of PIBCl in the absence of DTBP cationized with silver ions.

RESULTS AND DISCUSSION

Ionization of PIB-Cl as a Model Reaction. Although the conventional polymerization employs a C4 monomer mixture, the double-bond analysis of the polybutenes hardly differs from PIB obtained when pure IB feed is used under identical condition.[4] Thus, the presence of 1-butene, butadiene, and 2-butenes in concentrations found in C4 mixtures does not substantially alter the mechanism, and a much simpler polymerization of pure IB can be used as a model. This can be attributed to the much lower reactivity of 1-butene, butadiene, and 2-butenes compared to that of IB determined recently.[13] Indeed, polymerization of IB in hexanes with various initiators (H_2O, MeOH, *t*BuCl, TMPCl, CumCl, etc.) in conjunction with EADC in the temperature range of −40 to 25 °C yielded PIB with ~70% tri-substituted and ~30% tetra-substituted olefins with negligible terminal exo-olefinic groups. As expected, comparison of the concentration of initiator and that of PIB indicated that the M_n is controlled by chain transfer to monomer. A proton trap, 2,6-di-*tert*-butylpyridine (DTBP), has been used frequently in carbocationic macromolecular engineering to abort chain transfer to monomer by trapping the eliminated protons. However, up to [DTBP] = 10 mM could not prevent complete conversion of IB initiated with TMPCl/EADC at −40 °C with the concentration of PIB about 4 times higher than that of TMPCl, indicating chain transfer to monomer by a process other than proton transfer. Direct initiation by protic impurities was ruled out since polymerizations in the absence of TMPCl and in the presence of DTBP resulted in negligible (~2%) conversion. To elucidate the mechanism of chain transfer, which is most likely intrinsically

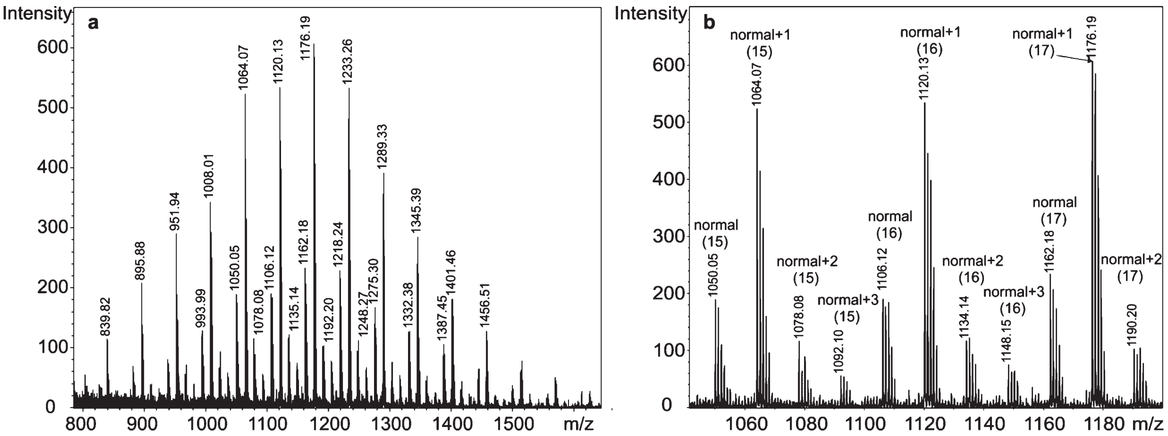


Figure 3. APPI-TOF mass spectrum (a) and zoomed APPI-TOF mass spectrum (b) of the product of ionization of PIBCl in the absence of DTBP recorded in the negative ion mode. The numbers in parentheses represent the number of isobutylene units.

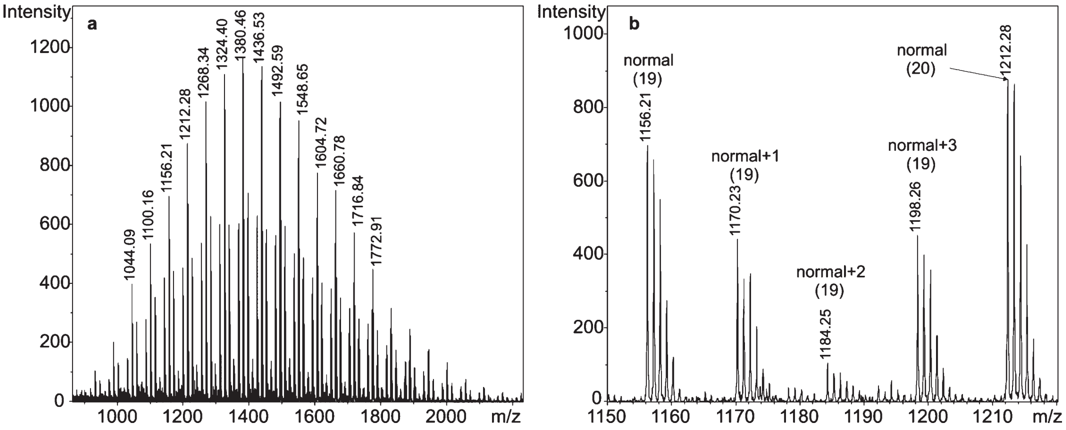


Figure 4. (a) Negative-ion APPI-TOF(−) mass spectrum of polybutene (Infineum). (b) Zoomed APPI-TOF(−) mass spectrum of polybutene (Infineum).

related to the formation of the tri-substituted olefins, we have decided to use ionization studies of model PIB-Cl synthesized by living polymerization in the presence of DTBP. The proton trap is necessary to abort secondary processes initiated by reprotonation of the olefin ends. The effectiveness of a proton trap is shown by Figure 1 which compares the ^{1}H NMR spectra of products obtained via the ionization of PIB-Cl in the presence of PIB exo-olefin, prepared by dehydrochlorination of PIB-Cl with tBuOK, in the presence and absence of DTBP.

Upon ionization of PIB-Cl with EADC in hexanes at 0 °C, rapid isomerization (complete in 5 min) yields mainly the tri-substituted olefin (3 in Figure 1). When a mixed PIB-Cl and PIB exo-olefin ([PIB-Cl]/[PIB exo-olefin] = 1) is treated with EADC in the absence of DTBP, the PIB exo-olefin end group is also converted to a tri-substituted olefinic structure (2 in Figure 1). In contrast, in the presence of DTBP, the PIB exo-olefin remains unchanged (1 in Figure 1). The GPC traces remained monomodal, indicating the absence of coupling.

MALDI-TOF MS spectra of both PIB-Cl and the product of ionization in the absence of DTBP are shown in Figure 2. The upper spectrum (Figure 2a) is that of the starting PIB-Cl which shows a series of peaks spaced by 56 Da, which corresponds to the mass of isobutylene unit. The starting PIB-Cl loses HCl in situ under MALDI conditions, and the masses of this series match that of the composition corresponding to $[\mathrm{Cum(IB)}_n\mathrm{C_4H_7} + \mathrm{Ag}]^+$ adduct ions, where Cum and IB represent the initiator (cumyl) moiety and the isobutylene units, respectively, and n stands for the number of repeat units. The measured and the calculated masses for this series are in good agreement; e.g., the measured and the calculated masses for $[\mathrm{Cum(IB)}_n\mathrm{C_4H_7} + \mathrm{Ag}]^+$ (composition is $\mathrm{C_{101}H_{194}Ag}$) were found to be 1516.6 and 1516.4, respectively. On the other hand, the lower spectrum (Figure 2b) contains two main series of peaks. The lower intensity series is identical with that of the starting PIB, while the more intense series is 14 Da (mass of one $-\mathrm{CH_2}-$ group) higher corresponding to the mass of a series denoted by the formula $[\mathrm{Cum(IB)}_n\mathrm{C_4H_7} + \mathrm{Ag}]^+$ as supported by the good agreement between the measured and calculated masses. For example, for the $[\mathrm{Cum(IB)}_n\mathrm{C_4H_7} + \mathrm{Ag}]^+$ (composition is $\mathrm{C_{114}H_{220}Ag}$) the measured and calculated masses are 1698.5 and 1698.6, respectively. It is also evident from the MALDI-TOF MS investigations that this fraction contains irregular carbon numbers (1 higher than normal, normal + 1) and could only form by a loss of C_3, or C_7, or C_{11}, etc., fragment from the original chain end.

To extend further our MS investigations, we also applied atmospheric pressure photoionization[14,15] time-of-flight mass spectrometry (APPI-TOF MS). APPI-TOF MS gives better resolution and mass accuracy compared to MALDI TOF MS. As it has been shown, APPI-MS is suitable for the mass analysis of

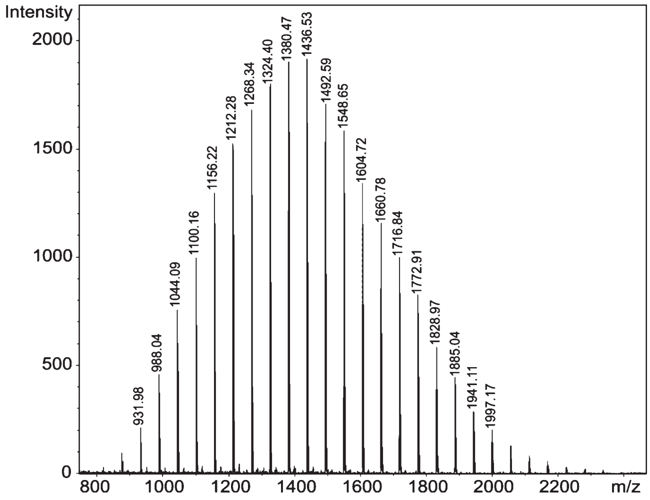


Figure 5. Negative-ion APPI-TOF mass spectrum of HR PIB sample from BASF.

Table 1. Ionization of [PIB-Cl] = 0.015 M with [EADC] = 0.015 M in Hydrocarbons for 30 min in the Presence or [DTBP] = 0.015 M

	olefin end-group distribution			
T (°C)	tri-substituted (%)	exo (%)	endo (%)	tetra-substituted (%)
−40	77	8	4	11
0	61	18	9	12
25	0	40	20	40

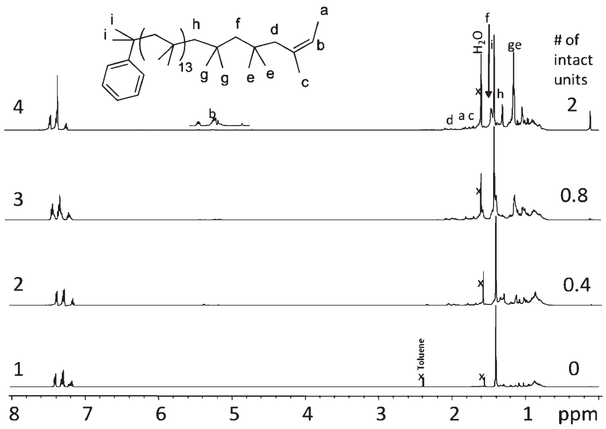


Figure 6. Products of ionization of (1) Cum(IB-d_8)$_{13}$(IB)$_{1-3}$Cl, (2) Cum(IB-d_8)$_{13}$(IB)$_4$Cl, (3) Cum(IB-d_8)$_{13}$(IB)$_5$Cl, and (4) Cum(IB-d_8)$_{13}$(IB)$_6$Cl after ionization in hexanes at −40 °C for 30 min at [Cum(IB-d_8)$_{13}$(IB)$_n$Cl] = 0.015 M, [$EtAlCl_2$] = 0.015 M, and [DTBP] = 0.015 M.

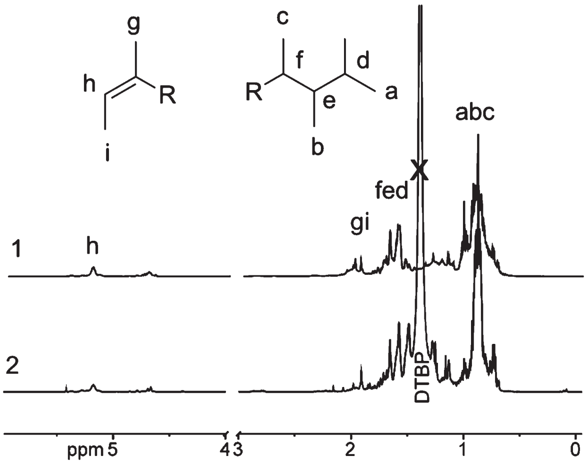


Figure 7. ^{1}H NMR overlay of (1) Infineum's "light polymer" and (2) the low molecular weight ionization products of $(IB)_{22}Cl$ in $CDCl_3$ at −40 °C for 30 min at [$(IB)_{22}Cl$] = 0.015 M, [$EtAlCl_2$] = 0.015 M, and [DTBP] = 0.015 M.

nonpolar polymers by using a chloride ion attachment technique.[16,17] The APPI-TOF MS spectrum of PIB recorded in the negative ion mode is shown in Figure 3a, while a zoomed part of this spectrum is presented in Figure 3b. Consistent with our previous findings by MALDI-TOF MS (Figure 2a), the APPI-TOF MS spectrum also reveals the dominant presence of PIB olefins with irregular carbon number, i.e., normal + 1 in the form of $[Cum(IB)_nC_5H_9 + Cl]^-$ adduct ions. The composition of this series was also supported by accurate mass measurements; e.g., the measured and the calculated masses for $[Cum(IB)_{16}C_5H_9 + Cl]^-$ (the composition is $C_{78}H_{148}Cl$) were found to be 1120.129 and 1120.128, respectively. From the corresponding peak intensities it can also be concluded that about 70% of PIB olefins have anomalous carbon number (normal + 1), which is largely independent of temperature in the −40 to 20 °C temperature range. However, two lower intensity series (normal + 2, normal + 3) are also observable as indicated in Figure 3b.

To check for the presence or absence of PIBs with irregular carbon numbers in industrial PIB samples, two samples (one from Infineum and the other from BASF) were investigated by APPI(−)-TOF MS. The APPI(−)-TOF and the zoomed APPI(−)-TOF mass spectra of polybutenes obtained from Infineum are shown in Figure 4. By comparison, the APPI TOF MS spectra of HR PIB (BASF) are shown in Figure 5.

As can be seen in Figure 4, multiple series are present in the negative ion APPI-TOF mass spectra. The most intensive series is due to the presence of polyisobutylene with regular carbon numbers represented by the formula $H(IB)_nC_4H_7$. This is also supported by accurate mass measurements. For example, the measured and the calculated masses for $[H(IB)_{19}C_4H_7 + Cl]^-$ (composition is $C_{80}H_{160}Cl$) are 1156.214 and 1156.221, respectively. On the other hand, three additional series can also be observed. The mass differences between the series correspond to the mass of a methylene unit. Therefore, these additional series indicate the presence of PIB with irregular carbon numbers corresponding to normal + 1, normal + 2, and normal + 3 carbon numbers in the Infineum sample as indicated in Figure 4b.

In contrast, in the case of HR PIB sample from BASF only one series of peaks appears in the APPI-TOF mass spectrum (Figure 5), which can be assigned to the PIB olefin with regular carbon numbers with a formula of $H(IB)_nC_4H_7$.

Formation of Tri-substituted Olefins. In order to clarify the mechanism of formation of tri-substituted olefins, ionization studies of model PIB-Cl were carried out in the presence of DTBP to prevent reprotonation. Table 1 shows the distribution of the olefinic chain ends obtained at different temperatures.

In the presence of DTBP, exo- and endo-olefins are present, and their amount increases with increasing temperature. This suggests that the activation energy for proton elimination is

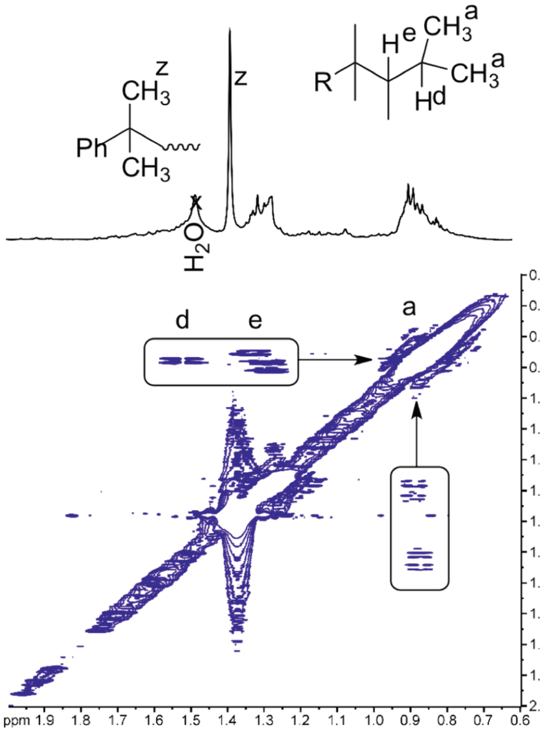


Figure 8. COSY correlation of products of ionization of [Cum(IB-d_8)$_{13}$IB-Cl] = 0.015 M with [$GaCl_3$] = 0.015 M in $CDCl_3$ at −40 °C for 1 min; [DTBP] = 0.015 M.

higher than that for isomerization/chain scission. We recall that exo- and endo-olefins were virtually absent at all temperatures in the absence of DTBP, which can be attributed to a preference for reprotonation, subsequent isomerization, and chain scission. Tri-substituted olefins were not obtained at 25 °C, which will become important in the identification of the mechanism leading to tetra-substituted olefins (see later).

To minimize depropagation and possible other side reactions in the presence of IB, further ionization studies were performed at −40 °C where the equilibrium monomer concentration ($[M]_c$) determined by the relationship[18]

$$\ln[M]_c = \frac{1}{R}\left(\frac{\Delta H}{T} - \Delta S\right) \qquad (1)$$

is negligible (3.6×10^{-5} M) and depropagation is essentially absent. The presence of irregular carbon numbers in the majority of the chains in the products of ionization at −40 °C suggests chain scission, as first proposed by Puskas et al. yielding C1 and C3 cations.[4,5] In order to determine where the chain scission takes place, partially deuterated model polymers having the composition Cum(IB-d_8)$_{13}$(IB)$_n$Cl, where n ranges from 1 to 6, were synthesized (Scheme S1, Figure S1, and Table S2). Thus, if chain scission reactions occur, they can be easily monitored by ^{1}H NMR spectroscopy where the deuterated PIB backbone would be invisible and only the cumyl headgroup and the remaining nondeuterated IB end units would give chemical shifts. These model polymers were subjected to ionization with $EtAlCl_2$ at −40 °C in the presence of DTBP, and the products were characterized by ^{1}H NMR spectroscopy (Figure 6) and SEC (Figure S5). As seen from the ^{1}H NMR spectra of the ionization products in Figure 6, all of the nondeuterated units up to n = 3 were cleaved. For n = 4 some protonated residues were visible at 1−1.1 ppm, typical for the methyl groups from the PIB chain. At n = 5, the sum of the integral at 1.1 ppm corresponded to around 1 IB unit, and at n = 6 the integrals gave area corresponding to two unaffected IB units. The peaks at 1−1.1 ppm were somewhat broad, indicating that chain scission reaction is not strictly confined to one C−C bond. Thus, on average, ∼4 IB units are cleaved during the formation of tri-substituted olefins. This is in very good agreement with the SEC data, collected in Table S3.

Scheme 1

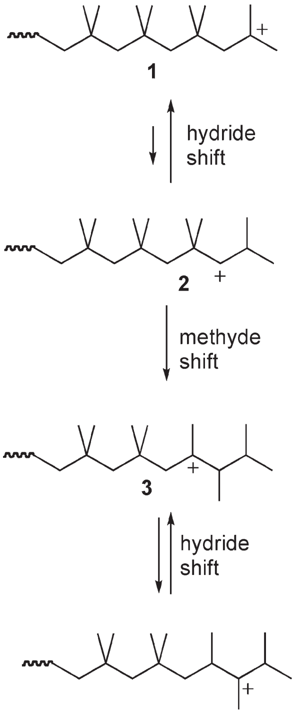
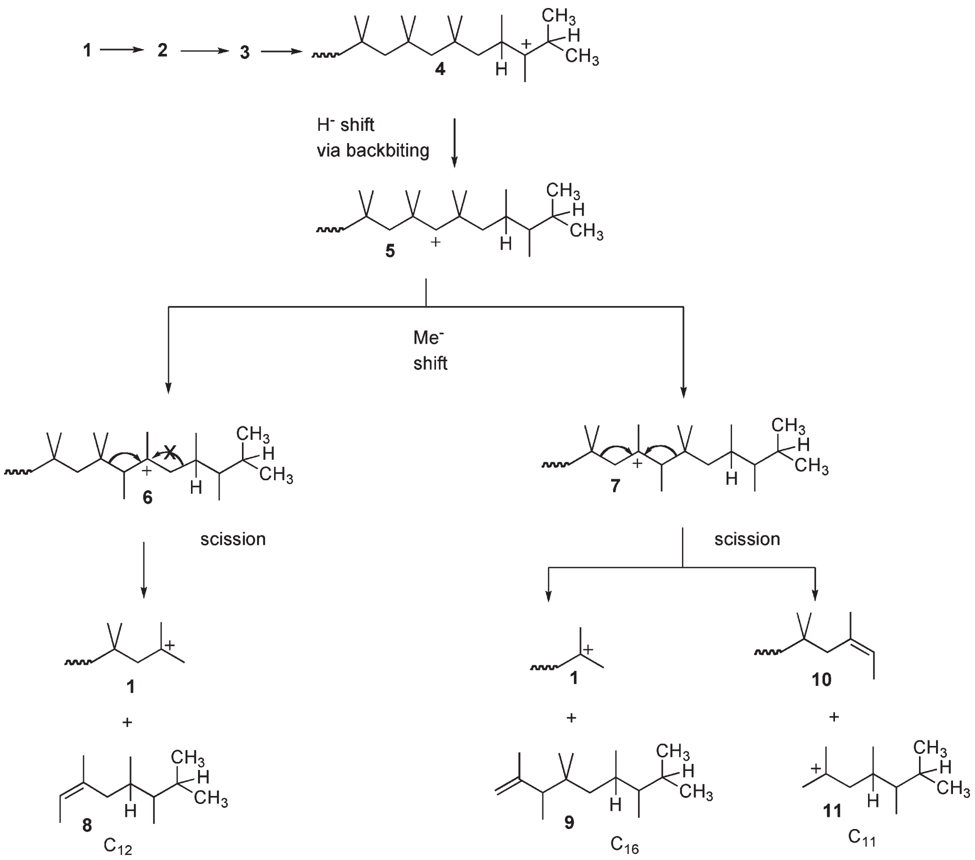


Table 2. Energy Minimization for IB Trimer (IB_3) Cations by DFT B3LYP, 6-31G

compd	E(HF)	relative E (kJ/mol)	relative E (kcal/mol)
4	−471.6060	0.00	0.00
3	−471.6036	6.30	1.51
1	−471.5995	17.07	4.08
2	−471.5910	39.38	9.41

The ^{1}H NMR spectrum of low molecular weight products from the cleaved IB units to a great extent resemble the spectrum of "light polymer" obtained from Infineum (Figure 7). The "light polymer" is a low molecular weight distillate removed from the crude product of conventional polymerization of IB initiated by $AlCl_3$ or $EtAlCl_2$. The M_n of the light polymer (∼250 Da) is equivalent to ∼4.5 IB units, in good agreement with our observation that around 4 IB units are cleaved during the formation of tri-substituted olefins. Previously published FI-MS data for a "light polymer" also obtained by conventional IB polymerization[3] correlate well with our results. Therefore, we conclude that the low molecular weight products formed in the ionization of a model PIB-Cl have similar chemical structures to that of "light polymer", and in both cases these products directly result from chain scission leading to the formation of a tri-substituted olefins.

Scheme 2



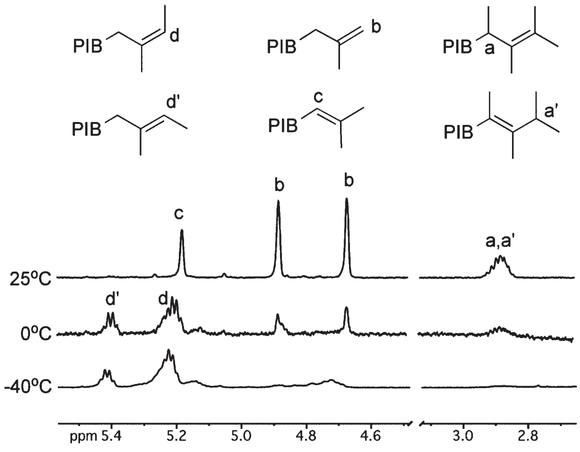


Figure 9. Effect of temperature on olefin end-group distribution during ionization with $EtAlCl_2$ in hexanes. [PIB-Cl] = 0.015M, [$EtAlCl_2$] = 0.015 M, and [DTBP] = 0.015 M.

The ^1H NMR spectra in Figure 7 are rather complex, indicating that carbocationic rearrangement has initially occurred at the end of the PIB chain before chain scission, and several groups of signals can be distinguished. The low MW products of ionization have a complex pattern at 0.8−2 ppm (protons *a*, *b*, *c*, *f*, and *e* in Figure 7) and olefinic end groups, represented by protons *g*, *h*, and *i*. The doublet at 4.7 ppm corresponds to a small fraction of exo-olefin (**9**, Scheme 2). In order to simplify the assignments of the ^1H NMR peaks for the low molecular weight cleavage products in Figure 7 and also to trace the eventual movement of protons by NMR, a partially deuterated model polymer, Cum(IB-d_8)$_{13}$(IB)$_1$Cl, was used for ionization experiments (Figure 8). Only the protonated starting cumyl group was intact. The single protonated isobutylene unit at the end of the PIB chain was cleaved and ended up in an isomerized form in the low molecular weight ionization products. The characteristic peaks for the products of isomerization could be more easily differentiated by the ^1H ^1H COSY correlation represented in Figure 8. The characteristic peak for the isobutyl group at 1.1 ppm (CH_3) is absent, which means that isomerization is not a simple hydride transfer (i.e., tertiary cation **1** to secondary cation **2** as in Scheme 1) which then backbites. Most likely several additional carbocationic rearrangements occur before backbiting (i.e., forming species **3** and **4** in Scheme 1). The characteristic protons for **4** and **5** after taking a H^- (*a*, *d*, and *e* in Figure 8) support that **4** or **5** formed before the backbiting reaction, and after chain cleavage, the structure remained in the low molecular weight products.

In order to clarify the nature of these rearrangements, *ab initio* relative energies of the different possible carbocations in Scheme 1 were calculated (Table 2). Upon ionization of PIB-Cl, cation **1** (Scheme 1) is formed. According to Table 2, cation **1** is the least stable tertiary cation. A 2−1 hydride shift to form **2** (Scheme 1), which could explain the isopropyl headgroup, is energetically unfavorable; however, the energetic penalty is fairly low, about 5 kcal/mol, and it is not prohibitive.[19] When the

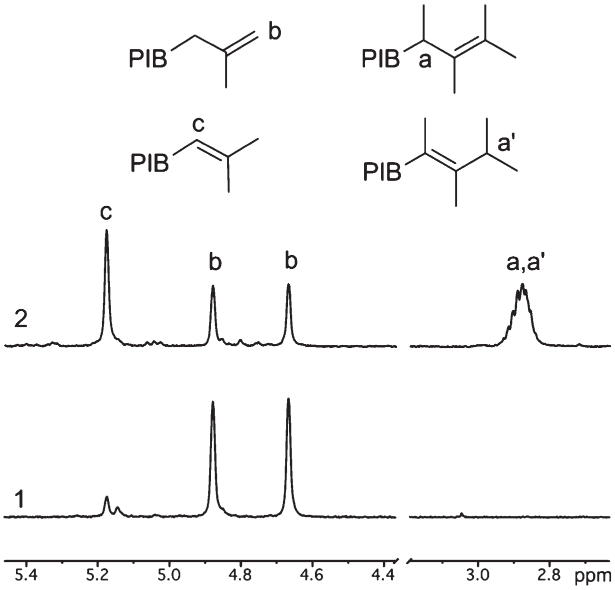


Figure 10. Overlay of ^{1}H NMR spectra of (1) olefinic products from Cum(IB)$_{22}$Cl in CDCl$_3$ after 1 week and (2) olefinic products from Cum(IB)$_{22}$Cl in CDCl$_3$ after 3 weeks. Olefinic distribution: exo, 16%; endo, 32%; tetra, 52%.

Scheme 3

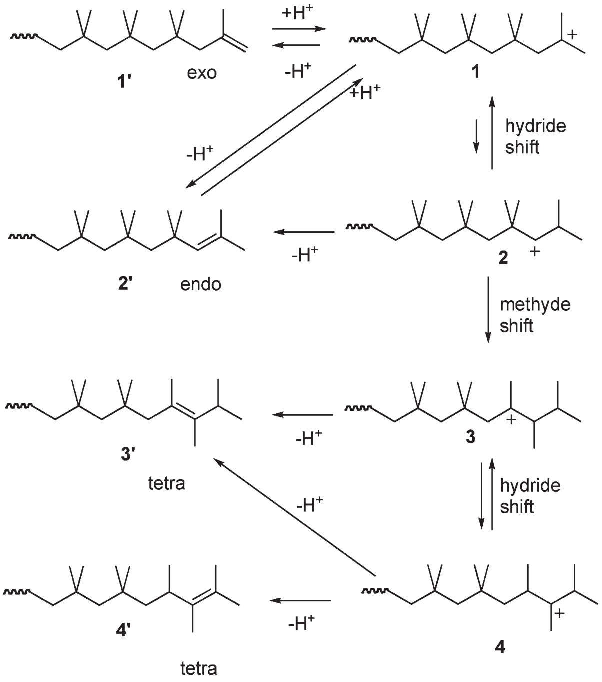


Table 3. Energy Minimization for IB$_3$ Olefins by DFT B3LYP, 6-31G

compd	E(HF)	relative E (kJ/mol)	relative E (kcal/mol)
3′	−471.2683	0.00	0.00
4′	−471.2673	2.63	0.63
1′	−471.2567	30.46	7.28
2′	−471.2554	33.87	8.09

secondary carbocation **2** is formed, the system compensates the loss of energy by further rearrangement via a methyde shift leading to **3**, which is the second most stable tertiary cation. For carbocations having the structure of **3** and **4**, it has been previously reported that hydride transfer between them requires very little activation energy and they also can be degenerative.[20]

Cation **3** or **4** could then backbite on the sixth and eighth position via a 5- or 6-membered ring transition state, respectively. The formation of a six-member transition state is preferred when backbiting takes place in both radical and anionic polymerizations.[15] A six-member ring is not possible from **3**, but in the case of **4**, a six-membered ring transition state is possible, leading to **5**. Although five-, seven-, and higher-member transition states are possible, their probabilities are lower.

Hydride shifts between distant carbons are not uncommon and require no activation energy if the newly formed cation is of equivalent stability compared to the original.[21] In the case of PIB$^+$ such a hydride shift would result in an energetically less favorable secondary cation **5** (Scheme 2). The penalty for that transition would not be much different than for the 2−1 hydride shift leading to **2** (Scheme 1). As with **2**, the secondary cation **5** is presumably short-lived as a methyde shift to **6** or **7** (Scheme 2) occurs rapidly to minimize the energy. However, a hydride shift resulting in a primary cation is highly unlikely because of the much higher energetic penalty of around 35 kcal/mol.[16]

The cleavage of several IB units resulting in products of molecular weight around 250 Da and the structure of the end groups in the light polymer support that a 2−1 hydride transfer and subsequent methyde transfer precede hydride transfer by backbiting and chain scission (Scheme 2). The complex pattern of NMR signals in Figure 8 at 0.8−1.5 ppm suggests that backbiting occurs via species **3** or **4** and not by **1** or **2**, most likely via five- or six-membered ring transition states, respectively.

Scheme 2 shows our proposed mechanism leading to PIB (**10**) and light polymer (**8**) with tri-substituted olefinic end groups. When **5** is formed, as in the case for the transition from **2** to **3**, a methyde shifts occurs in order to minimize the energy, resulting in cations **6** or **7**. Both cations **6** and **7** are sterically hindered, which promotes β-scission to release steric strain that results in **1** and **8** to **11**. Cation **11** can initiate IB polymerization, and now the "unexpected" occurrence of isopropyl at the beginning of the polymer chain of PIB observed by Harrison et al.[22] can be addressed. Tri-substituted olefin **10** has anomalous carbon number in accord with the APPI-TOF MS results for the polymer. The low molecular weight exo-olefin **9** is seen in Figure 7, but its fraction is rather low. This may be due to the lower stability of the less substituted exo-olefin compared to the tri-substituted olefin. The cations resulting from chain scission may undergo further rearrangements and proton elimination, or in the presence of monomer in conventional polymerization, they may add monomer.

Formation of Other Types of Olefins. In the simplest case, the ionization of PIB-Cl results in PIB$^+$, which then eliminates a proton and forms an olefinic end group. The elementary act of proton elimination requires an activation energy of at least 20 kcal/mol[23] and is, therefore, favored at elevated temperatures. As a result, in the case of PIB$^+$, temperature plays a crucial role for the type and molar content of the olefinic end groups obtained after elimination (Figure 9, Table 1). As Table 1 shows at −40 °C primarily tri-substituted olefins were formed (~80%). When the temperature was increased to 0 °C, the tri-substituted olefin content decreased to about 60% in favor of exo-, endo-, and tetra-substituted olefins. At 25 °C tri-substituted olefins were completely

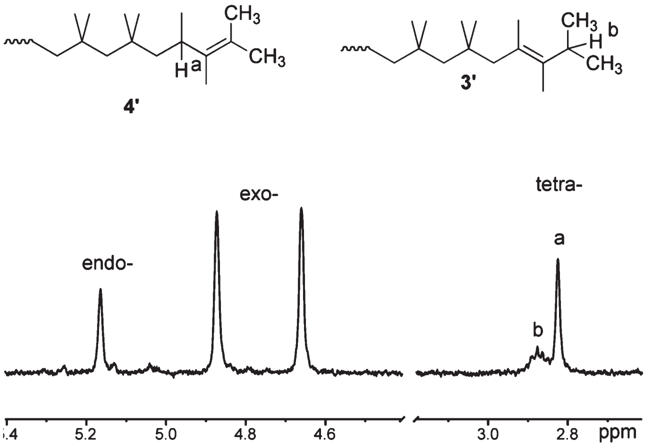
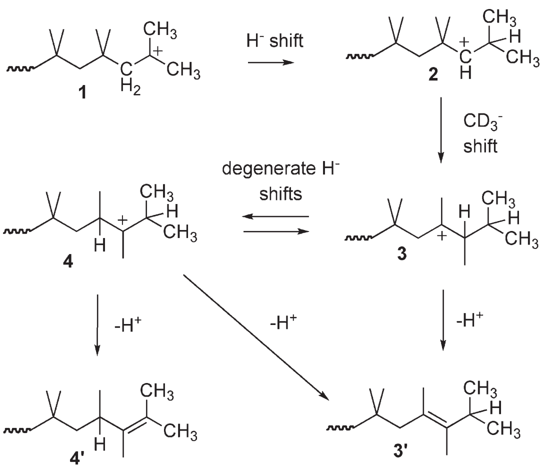


Figure 11. ^{1}H NMR spectrum of ionization product from Cum(IB-d_8)$_{13}$(IB)$_1$Cl. [Cum(IB-d_8)$_{13}$(IB)$_1$Cl] = 0.015 M, [MeAlCl$_2$] = 0.015 M, [DTBP] = 0.015 M, hexanes, 0 °C, 30 min. Protons are explicitly represented; the rest are deuterated carbons.

Scheme 4



absent, and only exo- (40%), endo- (20%), and tetra-substituted (40%) olefins formed (Figure 9). Therefore, the formation of tri-substituted olefins can be separated from the formation of exo-, endo-, and tetra-substituted olefins, and thus after careful characterization of the products of ionization the overall mechanism can be studied in detail.

The same exo-, endo-, and tetra-substituted olefins can form under much milder conditions, as has accidentally been found. The aging of PIB-Cl in CDCl$_3$ at room temperature in the absence of a proton trap results in the formation of these three olefins due to the presence of protic impurities. It should be pointed out that no low molecular weight byproduct could be isolated. As seen in Figure 10, after 1 week predominantly exo-olefins are formed, and at the same time some endo-olefins are distinguishable. If the aging is continued for 3 weeks, the product contains mostly tetra- and endo-olefins. The formation of these three types of olefins is represented in Scheme 3, and also the calculated energies are collected in Table 3. The deprotonation of **1** leads to the least stable olefins **1**′ or **2**″. Accordingly, cations **3** and **4** are more stable than **1** and **2** but have very similar relative energies (Table 2), and proton elimination leads to olefins **3**′ and **4**′. In Scheme 3, proton elimination is depicted as a reversible reaction for the exo- and endo-olefins but not for the tetra-substituted olefin. When the ionization product was subjected to hydrochlorination by HCl at 0 °C for 1 h, hydrochlorination of **3**′ and **4**′ did not take place while the hydrochlorination of exo- and endo-olefins was complete (Figure S4). Therefore, we suggest that reprotonation of **3**′ and **4**′ is unlikely.

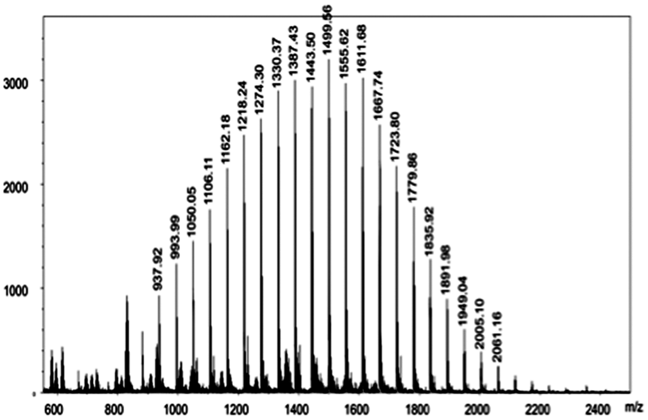


Figure 12. Negative-ion APPI-TOF mass spectrum of products of ionization of PIB-Cl. Ionization conditions: [PIB-Cl] = 0.015 M, [MADC] = 0.015 M, [DTBP] = 0.015M, 25 °C, 30 min in hexanes. Olefin composition: exo, 50%; endo, 20%; tetra, 30%.

In order to elucidate how **3** and **4** are formed, experimentally, one can follow the formation of tetra-substituted olefins by ionization of the partially deuterated Cum(IB-d_8)$_{13}$(IB)$_1$Cl at 25 °C. The rearrangements can be followed by proton signals in the ^{1}H NMR spectrum. The formation of exo- and endo-olefins involves only the protonated IB unit at the end of the chain (Figure 11). The formation of **3**′ and **4**′ is a result of initial hydride and methyde shifts (**2** and **3**), then a cascade of degenerate hydride shifts between structures **3** and **4** (Scheme 4), and finally a deprotonation step. From Figure 11 it is visible that the formation of structure **4**′ is preferred. The integrals of the protons from the last unit sum up to 7 (Figure S3), which indicates that no chain scission occurred during the formation of exo-, endo-, and tetra-olefins. In support of this, the negative-ion APPI-TOF mass spectrum of PIB containing exo-, endo-, and tetra-substituted olefins in Figure 12 showed only one set of peaks at intervals of 56.06 Da, which corresponds to PIB of a regular carbon number.

Thus, we have correlated all products to cations **3** or **4**. At ≤ 0 °C backbiting and chain scission are favored while at room temperature proton elimination is faster.

■ CONCLUSIONS

The mechanism of exo-, endo-, tri-, and tetra-substituted olefin end-group formation in the polymerization of IB in hydrocarbon media was studied by ionization of PIB-Cl with EtAlCl$_2$ in the presence of a proton trap. The distribution of olefins was effectively controlled with temperature, which allowed us to separate the formation of different olefins. A simple β-proton elimination from the tertiary PIB cation results in exo- and endo-olefins. Tetra-substituted olefins form after initial cationic rearrangements leading to tertiary cations at the second and third positions, followed by deprotonation. All three olefins possess regular carbon numbers. The formation of tri-substituted olefins follows a different mechanism. First, a hydride shift between distant carbons (backbiting) leads to a secondary cation, which undergoes a methyde shift to minimize the energy. The resulting hindered tertiary cation undergoes chain scission, yielding the tri-substituted PIB olefin with irregular carbon number. This also results in an oligomeric byproduct, which is known as "light polymer". This simplified mechanism accounts for the major products in the commercial production of polybutenes. However, many different minor products may also form by energetically less likely pathways. The commercial products are also complicated by the fact that a cationic fragment of irregular carbon number (**11**) in Scheme 2 may initiate the polymerization of IB and yield a tri-substituted olefin end with normal carbon numbers.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Synthesis and characterization of model PIB-Cl polymers, ^{1}H NMR spectra, and COSY correlation of products of ionization of model polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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