Direct synthesis of highly reactive polyisobutylenes via cationic polymerization of isobutylene co-initiated with TiCl$_4$ in nonpolar hydrocarbon media

Xiao-jian Yang, An-ru Guo, Hui-chao Xu, Yi-xian Wu

State Key Laboratory of Chemical Resource Engineering, Key Laboratory of Carbon Fiber and Functional Polymers (Ministry of Education), Beijing University of Chemical Technology, Beijing 100029, China
Correspondence to: Y. Wu (E-mail: yxwu@263.net)

ABSTRACT: Living cationic polymerization of isobutylene (IB) with 1-chlorine-2,4,4-trimethyl pentane (TMPCl)/TiCl$_4$/isopropanol (*i*PrOH) or isoamylol (*i*AmOH) has been achieved in the presence of 2,6-di-*tert*-butylpyridine (DtBP) at -80°C. Polyisobutylenes with nearly theoretical M_n based on TMPCl molecules and more than 90% of *tert*-chlorine-end groups could be obtained at high [TMPCl]. The β-proton elimination from —CH$_3$ in growing chain ends increased with increasing polymerization temperature and decreasing solvent polarity. A chain-transfer-dominated cationic polymerization process with H$_2$O/TiCl$_4$/*i*AmOH could be achieved in *n*-hexane at -30°C. The monomer conversion and content of *exo*-olefin end groups increased while molecular weight decreased with increasing [*i*AmOH]. To the best of our knowledge, this is the first example to achieve the direct synthesis of highly reactive polyisobutylene with low M_n of 1200~1600, carrying more than 80% of *exo*-olefin terminals by a single-step process *via* cationic polymerization co-initiated by TiCl$_4$ in nonpolar hydrocarbon. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42232.

INTRODUCTION

Polyisobutylene (PIB) has excellent properties in chemical stability, thermal stability, and resistance to oxidation, ozone, and UV.[1–8] As well known, the living cationic polymerizations of IB have been achieved to synthesize PIBs with theoretical molecular weight and *tert*-Cl end groups by using BCl$_3$, TiCl$_4$, FeCl$_3$, or organoaluminum chlorides, such as Et$_2$AlCl and Me$_2$AlCl as co-initiators in combination with an initiator selected from organic tertiary ester, ether, alcohol, halide, and substituted epoxide.[63–69] Strong electron donors, such as dimethylsulfoxide, *N,N*-dimethylacetyamide, amines, and pyridine, were normally introduced to these above polymerization systems co-initiated by BCl$_3$ or TiCl$_4$ to increase initiation efficiency, stabilize propagating species, and suppress chain transfer reaction and termination.[9–19] Highly reactive polyisobutylenes (HRPIBs) with low molecular weight and preferably more than 80 mol % have high reactivity for further functionalization and could be used as intermediates in the preparation of additives for fuels and lubricants.[4–8,20–33]

HRPIB can be mainly prepared by two major techniques: (A) single-step process and (B) two-step process. Commercial HRPIBs can be produced by process (A) *via* cationic polymer-

ization of isobutylene (IB) in hexane with the complexes of BF$_3$ with secondary aliphatic alcohol and/or tertiary ether initiating systems at temperature below 0°C.[20–38] Several research groups have also developed many other initiating systems for synthesis of HRPIBs, such as BF$_3$·cyclohexanol, solvent-ligated [M(NCMe)$_6$]$^{2+}$ (M^{II} = Mn, Cu, Mo, Fe, or Zn) complexes with bulky noncoordinating borate counteranions, *tert*-butyl chloride/EtZnCl, (NH$_4$$^+$)$_{2.5}H_{0.5}PW_{12}O_{40}$, AlCl$_3$/dialkyl ether, FeCl$_3$/dialkyl ether, GaCl$_3$/dialkyl ether, AlCl$_3$/*o*-cresol, FeCl$_3$/isopropanol, and EtAlCl$_2$/dialkyl ether.[39–62] However, HRPIBs with more than 80% of *exo*-olefin end groups has never been directly synthesized by a single-step process *via* cationic polymerization coinitiated by TiCl$_4$.

HRPIBs synthesis by process (B) could also be conducted *via* specific termination reaction after completion of living cationic polymerization coinitiated with TiCl$_4$ by addition of allyltrimethylsilane, strong hindered bases, such as 2,5-disubstituted pyrroles, hindered aliphatic tertiary amines, partially hindered pyridines or sulfides, or modification from *tert*-chloro-terminated functional PIB chains reaction.[63–75]

The TMPCl/FeCl$_3$/*i*PrOH initiating system has been recently developed in our research group to achieve living cationic

polymerization of IB in CH_2Cl_2/hexane mixture at $-80°C$.[19] Very interestingly, the chain-transfer-dominated cationic polymerization of IB with H_2O/$FeCl_3$/iPrOH initiating system in nonpolar hydrocarbons at -40 to $20°C$ has also been achieved in our research group, leading to direct synthesis of HRPIBs with more than 90 mol % of exo-olefin.[62] It indicates that living cationic polymerization of IB co-initiated by $FeCl_3$ could be transformed to chain-transfer-dominated process by changing reaction conditions. Moreover, a preliminary study on IB polymerization with H_2O/$TiCl_4$/CH_3OH initiating system in our research group indicated that the content of exo-olefin end groups increased with MeOH concentration in the polymerization system and PIBs with <71 mol % (normally ca 50 mol %) exo-olefin end groups could be prepared at $-30°C$.[76] Therefore, these previous research results encouraged us to further investigate the possibility of direct synthesis of HRPIB via cationic polymerization of IB with H_2O/$TiCl_4$/alcohol initiating system in nonpolar hydrocarbon media. In this article, we will present the characteristics of cationic polymerization of IB in hexane or in the mixed C_4 fraction feed with H_2O/ isoamylol/$TiCl_4$/isopropanol or isoamylol initiating systems under different polymerization conditions. The effect of polymerization temperature, solvent polarity, and alcohol concentration on number-average molecular weight, molecular weight distribution, and the content of end groups of the resulting PIBs has been investigated.

EXPERIMENTAL

Materials
Dichloromethane (CH_2Cl_2, A.R. Beijing Yili Fine Chemicals) and n-hexane (A.R. Beijing Yili Fine Chemicals) were dried by distillation from calcium hydride before use. The mixed C_4 fraction feed was dried with 4 Å molecular sieves for more than 30 days. The mixed C_4 fraction feed contains 1.9 wt % of n-butane, 49.1 wt % of isobutane, 21.9 wt % of n-butene, 24.9 wt % of IB, 2.0 wt % of 2-butene, and 0.15 wt % of 1,3-butadiene. The 2-chloro-2,4,4-trimethyl pentane (TMPCl) was prepared by passing dry HCl through a 30% solution of 2,4,4-trimethyl-1-pentene (purity: 99%, Aldrich) in dried CH_2Cl_2 at $0°C$ for 3 h.[17] Anhydrous titanium chloride ($TiCl_4$, purity: 99%, Acros, packaging under nitrogen), isobutylene (IB purity: 99.9%, Beijing Yanshan Petroleum Chemical Corp.), 2,6-di-tert- butylpyridine (DtBP, purity: 97%, Acros), isopropanol (iPrOH, A.R. Beijing Chemical Company), isoamylol (iAmOH, A.R. Beijing Chemical Company), and ethanol (A.R. Beijing Yili Fine Chemicals) were used as received.

Procedures
All the manipulation, reactions, and cationic polymerizations were carried out under a dry nitrogen atmosphere. General procedures of reagents were as described as our previous work.[19,58–62,76–80] Specific reaction conditions are listed in the captions of figures. The polymerizations were conducted under dry nitrogen atmosphere in a tube reactor (120 mL).

Living Cationic Polymerization of IB.
The monomer solution ([IB]$_0$ = 1.0 mol·L^{-1}) in the mixed solvents of hexane and CH_2Cl_2 with volume ratio of 60/40 was prepared in a chilled 1000 mL round-bottom flask at $-80°C$. Typically, 20 mL of the monomer solution was air-tightly transferred to every test tube (120 mL) via a 20 mL volumetric pipette followed by a specific amount of iPrOH or iAmOH, DtBP, and TMPCl and then the mixture was cooled at the desired reaction temperature for at least 30 min. The cationic polymerization was started by addition of the solutions of $TiCl_4$ in CH_2Cl_2 ([$TiCl_4$]$_0$ = 4.0 mol·L^{-1}) into the monomer solution with syringe at $-80°C$.

Cationic Polymerization of IB in Hydrocarbon Media for Synthesis of HRPIB.
The monomer solutions in hexane ([IB] = 2.9 mol·L^{-1}) or the mixed C_4 fraction feed ([IB]$_0$ = 2.9 mol·L^{-1}) were prepared in a chilled 1000 mL round-bottom flask at $-40°C$. The monomer solution was transferred to test tube as described above. The cationic polymerization was started by addition of iAmOH and $TiCl_4$ in CH_2Cl_2 with syringe at $-30°C$.

The above polymerization systems were quenched and neutralized at predetermined times by injection of 4 mL ethanol containing 1% NaOH. After evaporation of the volatiles, the polymer was rewashed with hexane and ethanol for three times. The polymer products were dried in a vacuum oven at $40°C$ to a constant weight. The monomer conversion was determined gravimetrically.

Instrumentation
The H_2O concentrations in the components and in the polymerization systems were monitored electrochemically with an SF-6 water determination apparatus (Shandong Zibo Water Analytical Company) in conjunction with a Karl–Fisher reagent for coulometric titration according to the method described.[19,58–62,76–80] The number-average molecular weights (M_n), weight-average molecular weight (M_w), and molecular weight distribution (MWD, M_w/M_n) of polyisobutylenes (PIBs) were measured by gel permeation chromatography (GPC) using a Waters 1515 isocratic HPLC pump connected to four Waters Styragel HT3, HT4, HT5, and HT6 columns and a Waters 2414 Refractive Index Detector at $30°C$. Tetrahydrofuran (THF) was served as a solvent of PIB with concentration of 20 mg of PIB/10 mL of THF and as a mobile phase at a flow rate of 1.0 mL·min^{-1}. The columns were calibrated against the standard polystyrene samples with molecular weights from 162 to 8,500,000 g·mol^{-1}. Nuclear magnetic resonance (NMR) spectra of PIB dissolved in deuterated chloroform ($CDCl_3$) in a 5 mm (o.d.) NMR tube with concentration of 15% were recorded by Bruker AV400 MHz NMR spectrometer operating at $25°C$. Chemical shifts (δ) were referenced to tetramethylsilane (TMS) as internal standard (δ_H = 0.00) or to the solvent signal (δ_C = 77.0) in the ^1H and ^{13}C NMR spectra. All NMR chemical shifts are reported in ppm. The distortionless enhancement by polarization transfer (DEPT) technique was further used for structural characterization of polymers.

RESULTS AND DISCUSSION

Living Cationic Polymerization of IB with TMPCl/$TiCl_4$/iPrOH or iAmOH Initiating Systems in the Presence of DtBP at $-80°C$
The cationic polymerizations of isobutylene (IB) with TMPCl/$TiCl_4$/iPrOH or iAmOH initiating systems were conducted in
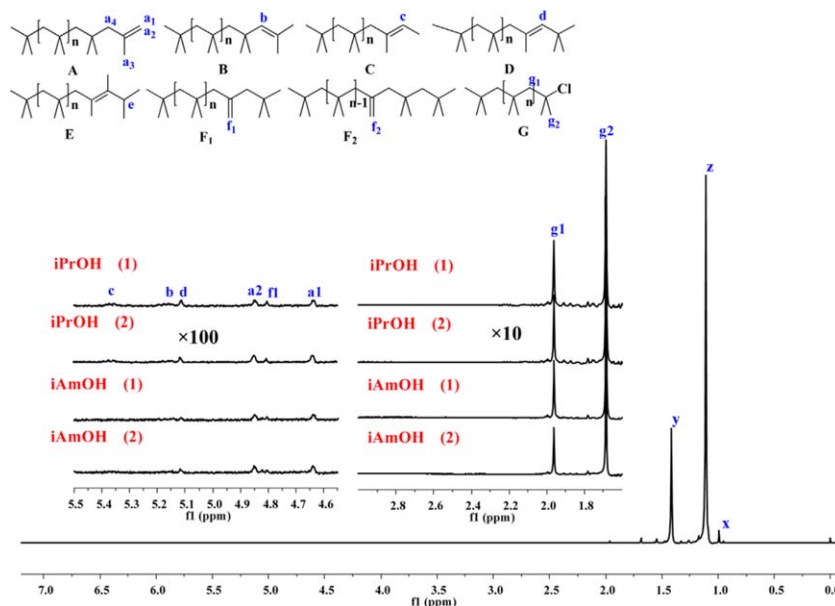
Figure 1. ^{1}H-NMR spectra of PIBs obtained with TMPCl/TiCl$_4$/iPrOH or iAmOH initiating systems in the presence of DtBP at $-80°$C. [IB] = 1.0 mol·L^{-1}, [H$_2$O] = 0.75 mmol·L^{-1}, [DtBP] = 2.1 mmol·L^{-1}, [TiCl$_4$] = 276 mmol·L^{-1}, Hex/CH$_2$Cl$_2$ = 60/40 (v/v), t_p = 10 min. iPrOH-1: [TMPCl] = 13.8 mmol·L^{-1}, [iPrOH] = 41.4 mmol·L^{-1}, G = 90.0 mol %, A = 3.6 mol %, internal double bonds = 5.4 mol %; iPrOH-2: [TMPCl] = 13.8 mmol·L^{-1}, [iPrOH] = 55.2 mmol·L^{-1}, G = 92.6 mol %, A% = 3.9 mol %, internal double bonds = 3.0 mol %; iAmOH-1: [TMPCl] = 2.7 mmol·L^{-1}, [iAmOH] = 13.8 mmol·L^{-1}, G = 96.7 mol %, A = 3.3 mol %. iAmOH-2: [TMPCl] = 2.7 mmol·L^{-1}, [iAmOH] = 55.2 mmol·L^{-1}, G = 94.6 mol %, A = 5.4 mol %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hexane/CH$_2$Cl$_2$ (60/40, v/v) solvent mixture in the presence of DtBP at low temperature of $-80°$C. The reaction conditions and representative experimental results are given in Figures 1
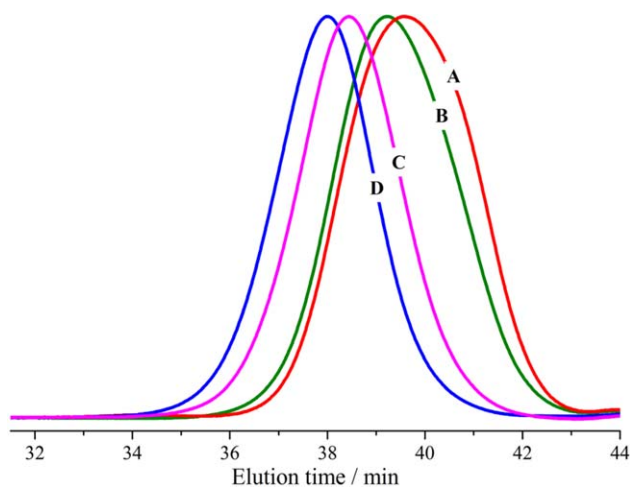

Figure 2. GPC profiles of PIBs obtained with TMPCl/TiCl$_4$/iPrOH or iAmOH initiating systems in the presence of DtBP at $-80°$C. Conditions are shown as in Figure 1. A: iPrOH-1, Conversion = 100%, M_n = 3930 g·mol^{-1}, $M_{n,theo}$ = 4050 g·mol^{-1}, M_w/M_n = 1.45; B: iPrOH-2, Conversion = 100%, M_n = 4900 g·mol^{-1}, $M_{n,theo}$ = 4050 g·mol^{-1}, M_w/M_n = 1.46; C: iAmOH-1, Conversion = 96.7%, M_n = 8700 g·mol^{-1}, $M_{n,theo}$ = 20100 g·mol^{-1}, M_w/M_n = 1.28; D: iAmOH-2, Conversion = 94.6%, M_n = 6700 g·mol^{-1}, $M_{n,theo}$ = 19600 g·mol^{-1}, M_w/M_n = 1.31. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and 2. The strong resonance signals at δ = 1.11 (z) and 1.41 (y) in Figure 1 are assigned to —CH_3 and —CH_2 protons of the structural units along the main chain of PIB respectively. The resonance appears at δ = 0.99 (x) for the protons in head group of —C(CH_3)$_3$ in PIB chains indicates TMPCl initiation and possible protic initiation from alcohol. Moreover, it can be clearly seen from Figure 1 that the two strong resonances at δ = 1.96 and 1.69 attributed to —CH_2–C(CH$_3$)$_2$–Cl and —CH$_2$–C(CH_3)$_2$–Cl (structure **G**) presented in all the four polymers. All the four polymers carried more than 90% of $tert$-Cl terminal groups (structure **G**), which is similar to our previous work for the synthesis of living PIBs with TMPCl/FeCl$_3$/iPrOH initiating system at $-80°$C.[19] There were still <10% of unsaturated terminal groups or isomers during polymerization at high DtBP concentration, which is attributed to elimination of β-proton from —CH$_3$ group in the growing PIB chain ends by DtBP and its derivate, leading to formation of small amount of —C(CH$_3$)=CH$_2$ terminal group (structure **A**) in the presence of high concentration of DtBP ([DtBP] = 2.1 mmol·L^{-1}).[81,82] As shown in Figure 2, all the resulting polymers exhibit monomodal molecular weight distribution and M_w/M_n keeps ranging from 1.28 to 1.46 under various polymerization conditions. Very interestingly, M_n of the resulting polymers was close to the theoretical one ($M_{n,theo}$) on the basis of initiation from TMPCl molecules at high TMPCl concentration of 13.8 mmol·L^{-1}, while it was much lower than $M_{n,theo}$ at low TMPCl concentration of 2.7 mmol·L^{-1}. It suggests that the dominant initiation from TMPCl molecules took place in the polymerization system at high TMPCl concentration ([TMPCl] = 13.8 mmol·L^{-1}), while both initiations from TPMCl and from alcohol (iPrOH or
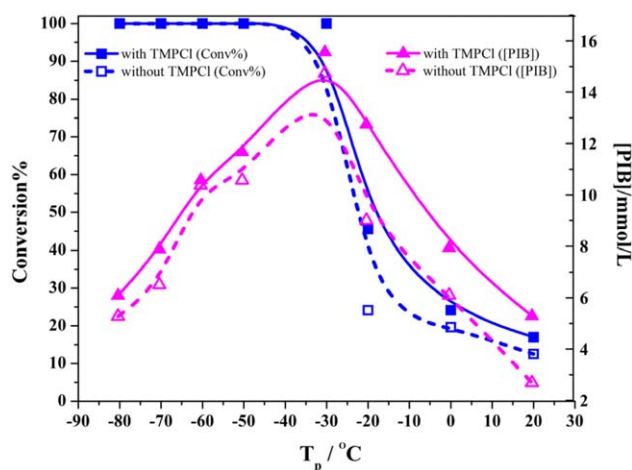
Figure 3. Effect of polymerization temperature on monomer conversion and PIB concentration ([PIB] in cationic polymerizations of IB with TMPCl/TiCl₄/iAmOH or TiCl₄/iAmOH initiating systems in the presence of DtBP. [TMPCl] = 2.8 mmol·L^{-1}, [iAmOH] = 28 mmol·L^{-1}; [TiCl₄] = 244 mmol·L^{-1}, [H₂O] = 0.81 mmol·L^{-1}; [DtBP] = 4.0 mmol·L^{-1}; $M_{n,theo}$= 19,000 for complete monomer conversion. Other conditions are shown as in Figure 1. [PIB]= [IB] × 56 × Conv./M_n. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

iAmOH) occurred in the polymerization system at low TMPCl concentration ([TMPCl] = 2.7 mmol·L^{-1}).

Cationic Polymerization of IB with TMPCl/TiCl₄/iAmOH or TiCl₄/iAmOH Initiating Systems at Various Temperatures in the Presence of DtBP

In order to further prove the possible initiation from alcohol, the cationic polymerizations of IB initiated by TMPCl/TiCl₄/iAmOH or TiCl₄/iAmOH systems were conducted at low [TMPCl] of 2.8 mmol·L^{-1}, high [iAmOH] of 28 mmol·L^{-1} in the presence of a large amount of DtBP at −80°C by keeping other reaction conditions constant. The experimental results of monomer conversion, M_n, M_w/M_n, and content of terminal groups of the resulting polymers are given in Figures 3–5. It can be seen from Figure 3 that the cationic polymerization of IB with TMPCl/TiCl₄/iAmOH initiating system at −80°C could result in near 100% of monomer conversion and the formation of PIB chains with relatively narrow molecular weight distribution (M_w/M_n = 1.35) carrying ca 96.7 mol % of tert-Cl terminals. The M_n of the resulting PIB was only 9200 g·mol^{-1}, which was much lower than the theoretical value of 19,000 g·mol^{-1} on the basis of single initiation from TMPCl molecules. Surprisingly, the cationic polymerization of IB with TiCl₄/iAmOH initiating system in the absence of TMPCl at −80°C could also result in 100% of monomer conversion and formation of PIB chains with M_n of 10,600 g·mol^{-1} and relatively narrow molecular weight distribution (M_w/M_n = 1.51), carrying ca 94.0 mol % of tert-Cl terminals. Therefore, it can be inferred that iAmOH could also be used as an effective initiator in combination with TiCl₄ to create protic initiation and start the living polymerization at −80°C, leading to PIB chains carrying a large amount of tert-Cl terminals. It is worth mentioning that 100% of polymer yield could be obtained by using iAmOH/TiCl₄ ini-
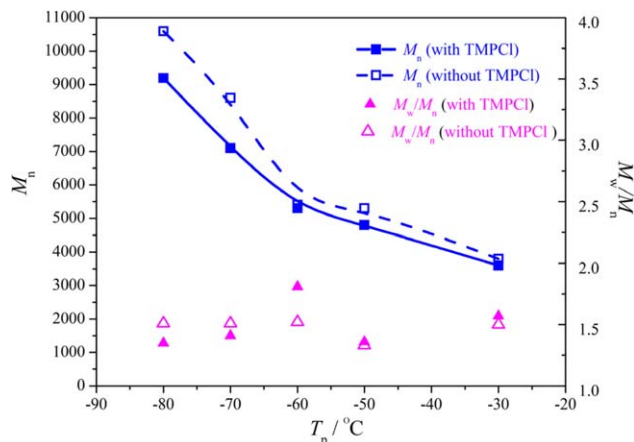

Figure 4. Effect of polymerization temperature on M_n and M_w/M_n of PIBs obtained with TMPCl/TiCl₄/iAmOH or TiCl₄/iAmOH initiating systems in the presence of DtBP in Hex/CH₂Cl₂ mixture (60/40, v/v). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tiating system in the absence of TMPCl at [iAmOH] = 28 mmol·L^{-1}, suggesting that the protic initiation from iAmOH did occur under these conditions. This experimental result is similar to the report of living cationic polymerization of vinyl ether with methanol/metal chloride initiating systems by Aoshima,[83,84] but quite different from that in the FeCl₃-coinitiated polymerizations in our previous works.[19,62]

Polymerization temperature is a critical factor for initiation, propagation, and termination in the cationic polymerization of IB. To examine the effect of polymerization temperature, the cationic polymerizations of IB with TMPCl/TiCl₄/iAmOH or TiCl₄/iAmOH initiating systems were further conducted at various temperatures ranging from −80 to 20°C. It can be seen from Figure 3 that monomer conversion kept 100% by varying reaction temperature from −80 to −30°C and then sharply decreased to ca 15% with further increasing reaction temperature to 20°C for both the polymerization systems in the presence of TMPCl and in the absence of TMPCl. The average concentration of the resulting PIB chains ([PIB]) in polymerization system gradually increased with polymerization temperature from −80 to −30°C due to the obvious chain transfer reaction while decreased with further increasing polymerization temperature from −30 to 20°C due to the serious termination of growing chains. The corresponding M_n and MWD (M_w/M_n) for the resulting polymers at various polymerization temperatures ranging from −80 to −30°C are given in Figure 4. It can be clearly observed from Figure 4 that M_n of PIB decreased from 9200 to 3600 g·mol^{-1} and from 10,600 to 3800 g·mol^{-1} with increasing polymerization temperature from −80 to −30°C in the presence of TMPCl and in the absence of TMPCl, respectively. The molecular weight distributions of the resulting polymers at temperatures from −80 to −30°C almost kept relatively narrow (M_w/M_n~1.5). The inverse effect of polymerization temperature (T_p) on molecular weights (M_n) has been quantitatively expressed by Arrhenius equation, i.e., ln M_n = ln $A − \Delta E/RT_p$.[85,86] Arrhenius plots of ln M_n versus 1/T_p for IB polymerizations with TMPCl/TiCl₄/iAmOH or TiCl₄/iAmOH
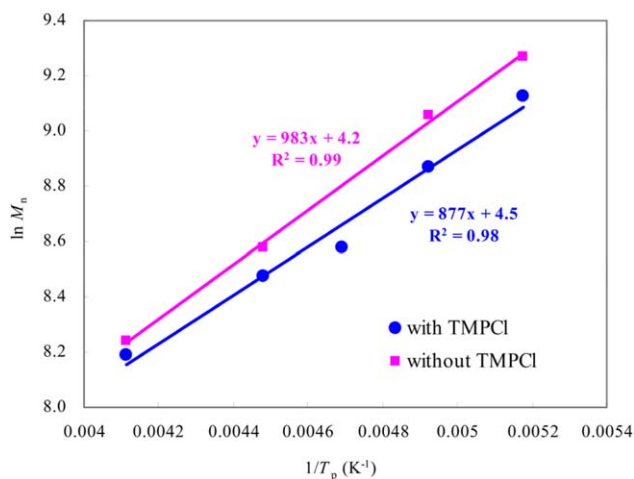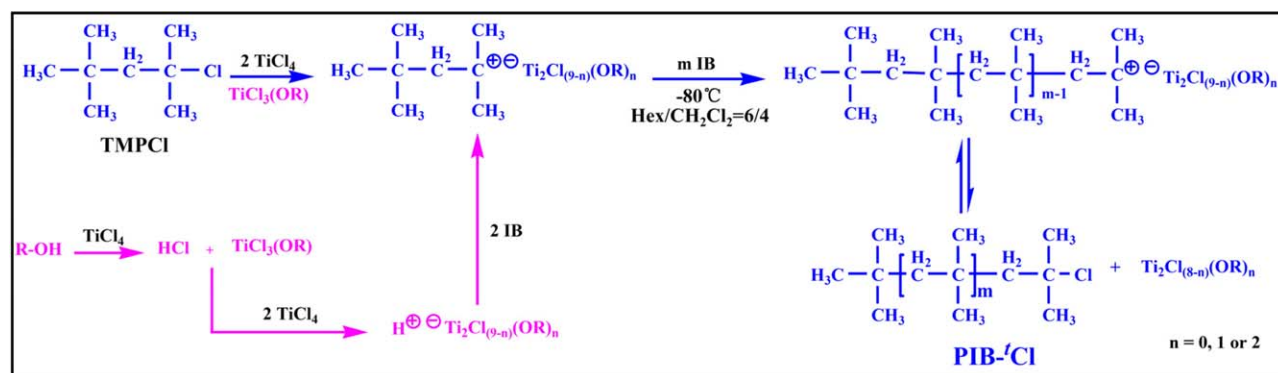
Figure 5. Arrhenius plots of ln M_n versus $1/T_p$ for IB polymerizations with TMPCl/TiCl$_4$/iAmOH or TiCl$_4$/iAmOH initiating systems in the presence of DtBP in Hex/CH$_2$Cl$_2$ mixture (60/40, v/v). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

initiating systems in the presence of DtBP are given in Figure 5. It can be seen from Figure 5 that the two linear Arrhenius plots of ln M_n versus $1/T_p$ for IB polymerizations with TMPCl/TiCl$_4$/iAmOH and TiCl$_4$/iAmOH initiating systems were nearly parallel to each other. The overall activation energy differences (ΔE or E_{DP}) were calculated to be −7.3 and −8.2 kJ·mol^{-1} from the slopes of the linear Arrhenius plots for the temperature interval from −80 to −30°C. The molecular weights of PIBs obtained with TMPCl/TiCl$_4$/iAmOH and TiCl$_4$/iAmOH initiating systems were less temperature dependent than that for the polymerizations of IB with H$_2$O/FeCl$_3$/iPr$_2$O (−20.5 kJ·mol^{-1}), H$_2$O/AlCl$_3$/iPr$_2$O (−13.9 kJ·mol^{-1}), and H$_2$O/FeCl$_3$/iPrOH (−10.7 kJ·mol^{-1}) initiating systems.[58–62]

The living cationic polymerization of IB with TPMCl/TiCl$_4$/ROH (iPrOH or iAmOH) initiating systems could be achieved at −80°C to produce PIBs with dominant tert-Cl terminal groups (~95 mol %) and the side reactions, such as β-proton elimination from normal growing cations, chain transfer reac-

tion, and irreversible termination, could be effectively suppressed. The possible mechanism for living cationic polymerization of IB with TPMCl/TiCl$_4$/ROH (iPrOH or iAmOH) initiating systems was proposed and is shown in Scheme 1.

In order to investigate the chain transfer reaction and termination with increasing polymerization temperature, the resulting PIBs with H$_2$O/TiCl$_4$/iAmOH initiating system at various polymerization temperatures from −80 to 20°C were performed on ^{1}H-NMR characterization. The effect of polymerization on the contents of tert-Cl end group (structure **G**, —CH$_2$—C(CH$_3$)$_2$—Cl), exo-olefin terminal group (structure **A**, —CH$_2$—C(CH$_3$)=CH$_2$) and endo-olefin terminal group (structure **B**, —CH$_2$—CH=C(CH$_3$)$_2$) on the basis of the integral calculation is presented in Figure 6. It can be clearly observed from Figure 6 that the termination via chlorine transfer from counteranion decreased with increasing polymerization temperature from −80 to 20°C, leading to a decrease in the content of tert-Cl end group (structure **G**) from around 95 to 6%. Simultaneously, the content of exo-olefin terminal group (structure **A**; δ = 4.64, 4.85) increased gradually from 6 to 66.8 mol % when reaction temperature increased from −80 to −30°C and then slightly decreased to 54.3 mol % when reaction temperature further increased due to the corresponding increase in the content of —CH$_2$—C**H**=C(CH$_3$)$_2$ terminal group (structure **B**, δ = 5.15). It can be inferred that the β-proton elimination could be increased while the selectivity of β-proton elimination from —CH$_3$ in the growing PIB chain end could be decreased with increasing reaction temperature. The transfer side reactions (isomerizations) could be effectively suppressed below the reaction temperature of −30°C. The chain transfer to monomer after the β-proton elimination did take place to form new polymer chains, leading to an increase in [PIB] in polymerization system and a decrease in molecular weight of the resulting PIBs with increasing polymerization temperature. Very importantly, PIB with 100% yield, relatively low molecular weight (M_n = 3800 g·mol^{-1}) and relatively narrow molecular weight distribution (M_w/M_n = 1.5), carrying 66.8 mol % of exo-olefin terminal group (structure **A**) could be directly prepared with TiCl$_4$/iAmOH initiating system in Hex/CH$_2$Cl$_2$ mixture (60/40, v/v)

Scheme 1. Possible mechanism for living cationic polymerization of isobutylene with TMPCl/TiCl$_4$/ROH (iPrOH or iAmOH) initiating system in Hex/CH$_2$Cl$_2$ mixture (60/40, v/v) in the presence of DtBP at −80°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

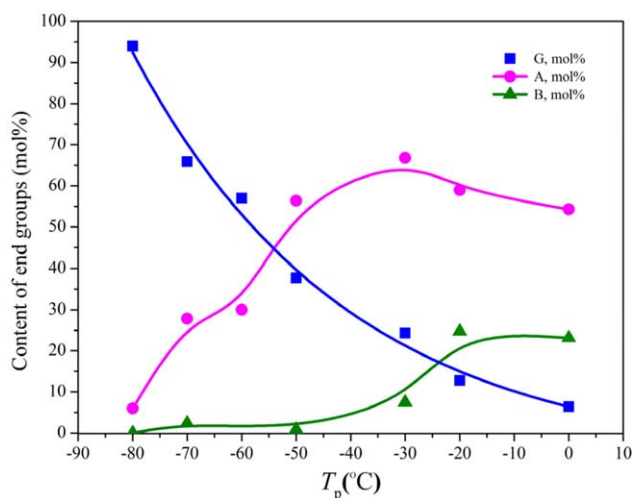**Figure 6.** Effect of polymerization temperature on the content of end-groups in PIB chains obtained with TiCl$_4$/iAmOH initiating systems without TMPCl and in the presence of DtBP in Hex/CH$_2$Cl$_2$ mixture (60/40, v/v). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at −30°C in the absence of TMPCl and in the presence of DtBP.

Effect of Solvent Polarity on Cationic Polymerization of IB with H$_2$O/TiCl$_4$/iAmOH Initiating System in the Absence of DtBP at −30°C

Solvent polarity is an important factor for solvation, character of active centers, and ion-pair species in cationic polymerization of IB. It is necessary to investigate the effect of solvent polarity on IB polymerization with H$_2$O/TiCl$_4$/iAmOH initiating system in the absence of both TMPCl and DtBP at high monomer concentration ([IB]$_0$ = 2.9 mol·L^{-1}) at −30°C by changing the fraction of hexane in hexane/CH$_2$Cl$_2$ mixtures from 60 to 100% while keeping other conditions constant. The effect of solvent polarity on monomer conversion, M_n, M_w/M_n, [PIB], and content of end-groups of PIB chains is given in Figures 7–9. It can be seen from Figure 7 that solvent polarity had little effect on the monomer conversion and more than 95% of polymer yield could be obtained in all the different solvents with the fraction of hexane in hexane/CH$_2$Cl$_2$ mixtures from 60 to 100%. As shown in Figure 8, molecular weight (M_n) of the resulting PIBs increased slightly from 2700 to 3400 g·mol^{-1} when the fraction of hexane in hexane/CH$_2$Cl$_2$ mixtures increased from 60 to 100% due to weaker salvation and more contact ion-pair propagating species in the solvents with lower polarity. Molecular weight distribution became broad and M_w/M_n increased gradually from 1.57 to 3.09 when the fraction of hexane in hexane/CH$_2$Cl$_2$ mixtures increased from 60 to 100%. The concentration of PIB chains in polymerization system slightly decreased from 51 to 42 mmol·L^{-1} with decreasing solvent polarity. The protic initiation from both H$_2$O ([H$_2$O] = 0.75 mmol·L^{-1}) and iAmOH ([iAmOH] = 133 mmol·L^{-1}) might occur during polymerization in the absence of DtBP. Interestingly, it can be clearly observed from Figure 9 that the content of $tert$-Cl end group (structure **G**) in PIB chains decreased from 76.7 to 7.5 mol % while the content of exo-olefin end group (structure
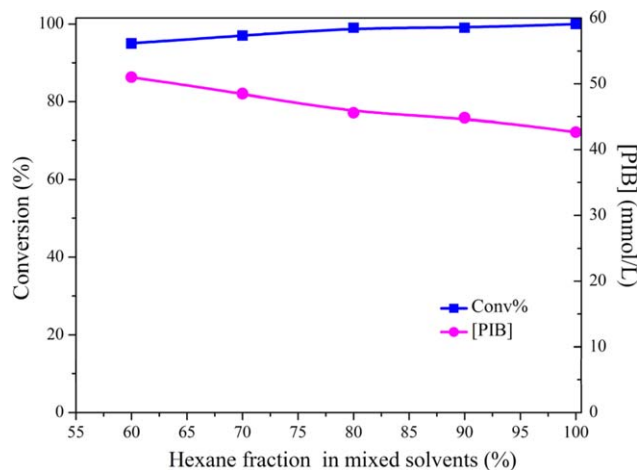

Figure 7. Effect of solvent polarity on monomer conversion and [PIB] for IB polymerization with H$_2$O/TiCl$_4$/iAmOH initiating system in the absence of DtBP at −30°C. [IB] = 2.9 mol·L^{-1}, [H$_2$O] = 0.75 mmol·L, [iAmOH] = 133 mmol·L^{-1}, [TiCl$_4$] = 429 mmol·L^{-1}, t_p = 60 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A) in PIB chains increased from 14.1 to 82.6 mol % with increasing the fraction of hexane in hexane/CH$_2$Cl$_2$ mixtures from 60 to 100%. The ^{1}H-NMR spectrum of the resulting PIB obtained with H$_2$O/TiCl$_4$/iAmOH initiating system at −30°C in hexane is presented in Figure 10. The expansion of the olefin region (inset in Figure 10) at δ = 4.64, 4.85 (a$_1$, a$_2$) and δ = 5.15 (b) indicates high content (82.6 mol %) of structure **A** and very low fraction (2.8 mol %) of structure **B** in the PIB chain ends. The content of $tert$-Cl end group was only 4.7 mol %. A weak singlet peak at δ = 5.12 was attributed to the proton in —C(CH$_3$)=CHC—(CH$_3$)$_2$ (structure **D**) and the content of structure **D** was calculated to be 6.0 mol %. The visible peaks at δ = 4.80 and 4.82 were assigned to internal vinylene isomers **F$_1$** and **F$_2$**, respectively, and their total content was 2.2 mol %. The internal double bond isomer at δ = 2.85 (structure **E**,
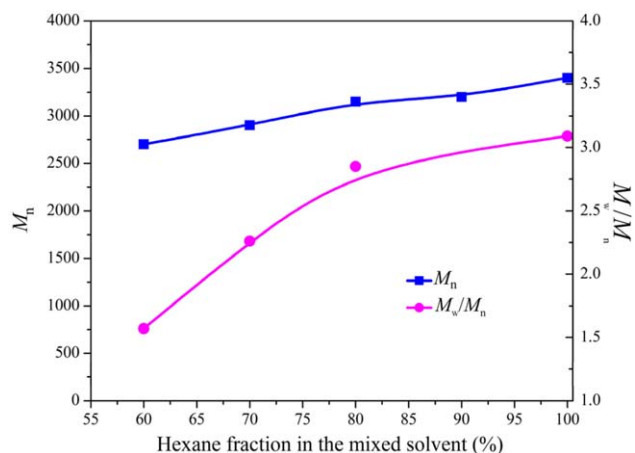

Figure 8. Effect of solvent polarity on M_n and M_w/M_n of PIBs obtained with H$_2$O/TiCl$_4$/iAmOH initiating system in the absence of DtBP at −30°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
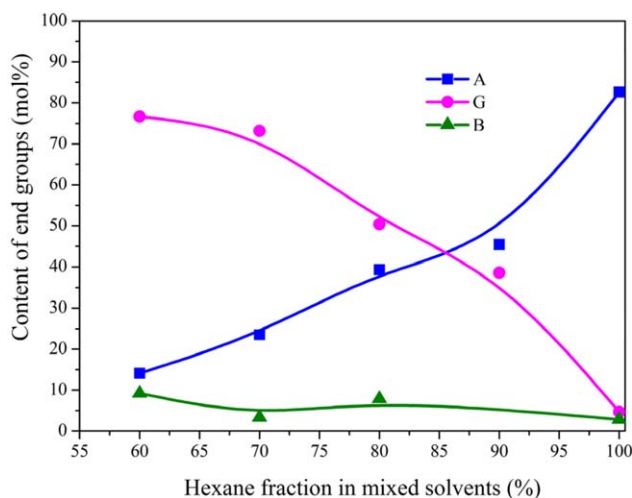
Figure 9. Effect of solvent polarity on the content of *end*-groups of PIB chains obtained with $H_2O/TiCl_4/i$AmOH initiating system in the absence of DtBP at $-30°C$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

—CH_2—$C(CH_3)$═$C(CH_3)$—$CH(CH_3)_2$) was almost undetectable. The isomerization *via* carbenium ion rearrangement to form isomers, such as structure C, D, E, or F, was little dependent on the solvent polarity. The direct synthesis of high-quality highly reactive polyisobutylene with more than 80% of *exo*-olefin terminals has been achieved by a single-step process *via* cationic polymerization of IB co-initiated by $TiCl_4$ in hexane. Therefore, this cationic polymerization of IB with $H_2O/TiCl_4/i$AmOH initiating system in hexane at $-30°C$ was a chain-transfer-dominated process *via* highly selective β-proton elimination from —CH_3 in the growing chain ends, leading to formation of HRPIB with large content of *exo*-olefin end groups (structure **A**). However, M_n of this resulting HRPIB was still rel-

atively high (3400 g mol^{-1}) and its molecular weight distribution was also still broad ($M_w/M_n = 3.09$).

Effect of Alcohol Concentration on Cationic Polymerization of IB in the Mixed C_4 Fractions in the Absence of DtBP at $-30°C$

The mixed C_4 fraction feed come from cracking of crude oil contains saturated and unsaturated C_4 hydrocarbons including *n*-butane, isobutane, *n*-butene, IB, *cis*-2-butene, *trans*-2-butene, and 1,3-butadiene. The direct synthesis of HRPIB *via* highly selective cationic polymerization of IB from the nonpolar mixed C_4 fractions is attractive and challenged due to its simple process and low cost. On the basis of the above optimistic results of synthesis of HRPIBs with 82.6 mol % of *exo*-olefin end groups in hexane, we further try to extend the investigation on HRPIB synthesis *via* highly selective cationic polymerization from the mixed C_4 fraction feed. Then, in order to further decrease molecular weight and narrow molecular weight distribution of the resulting PIBs obtained by using $H_2O/TiCl_4/i$AmOH in nonpolar medium, the effect of iAmOH concentration (expressed by iAmOH/$TiCl_4$ molar ratio) on the selective cationic polymerization of IB in the mixed C_4 fractions ($[IB]_0 = 2.9$ mol·L^{-1}) was investigated in the absence of DtBP at $-30°C$. The cationic polymerizations of IB from the mixed C_4 fractions with $H_2O/TiCl_4/i$PrOH initiating system were also conducted at various iPrOH concentrations (expressed by iPrOH/$TiCl_4$ molar ratio) under the same other conditions for comparison. The experimental results of monomer conversion, [PIB], M_n, M_w/M_n, and content of end groups of PIBs obtained at different concentrations of alcohol are given in Figures 11–14. It can be seen from Figure 11 that the cationic polymerization of IB with $H_2O/TiCl_4$ initiating system in the mixed C_4 fractions in the absence of alcohol had low monomer conversion (6.2%), suggesting that the protic initiation from H_2O ($[H_2O] = 0.83$ mmol·L^{-1}) actually happened in the
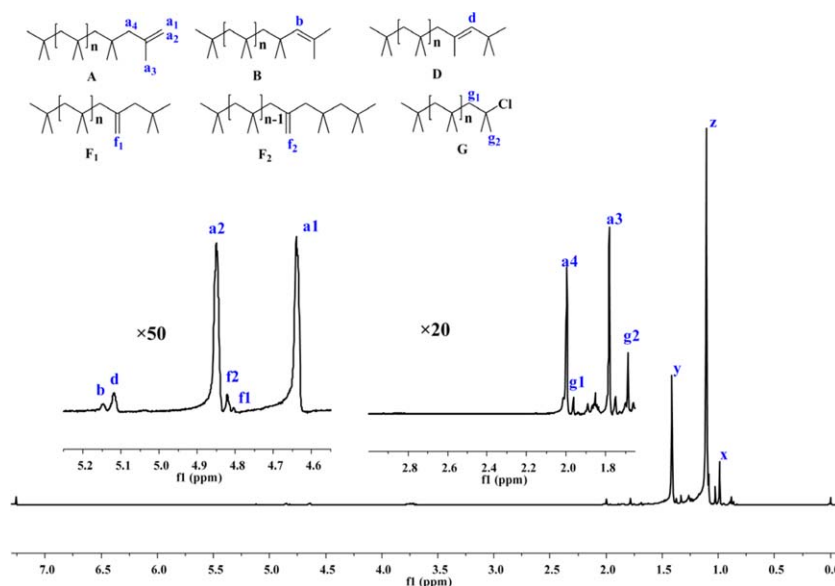

Figure 10. ^{1}H NMR spectrum of PIB obtained with $H_2O/TiCl_4/i$AmOH initiating system in hexane at $-30°C$. A = 82.6 mol %, B = 2.8 mol %, D = 6.6 mol %, E = 1.0 mol %, $F_1 + F_2 = 2.2$ mol %, G = 4.7 mol %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
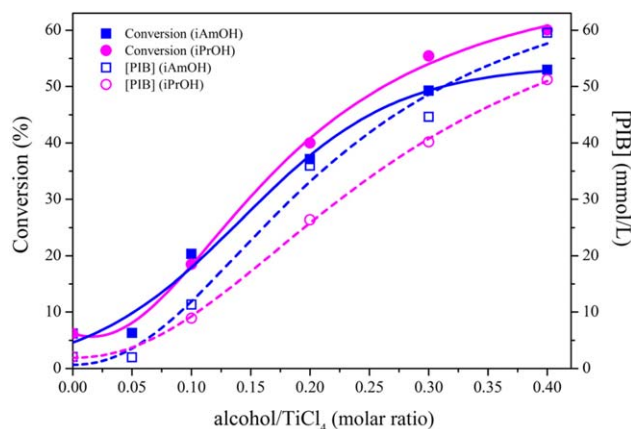
Figure 11. Effect of the molar ratio of alcohol/TiCl$_4$ on monomer conversion and [PIB] *via* IB polymerization from the mixed C$_4$ fractions with H$_2$O/TiCl$_4$/alcohol initiating systems at $-30°$C in the absence of DtBP. [IB] = 2.9 mol L^{-1}, t_p = 60 min, [H$_2$O] = 0.83 mmol L^{-1}, [TiCl$_4$] = 429 mmol L^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymerization system. Moreover, both the monomer conversion and [PIB] in polymerization system increased gradually from <6.2 to near 60% with increasing molar ratios of *i*AmOH/TiCl$_4$ or *i*PrOH/TiCl$_4$ from 0 to 0.4. These experimental results further prove the protic initiation from alcohol, i.e., *i*AmOH or *i*PrOH, which is similar to the report by Aoshima.[83,84] As shown in Figure 12, the desired PIBs with lower molecular weight and narrower molecular weight distribution could be prepared at higher concentration of alcohol, which is attributed to the increase in the initiation from alcohol and concentration of initiating species. The M_n of the resulting PIB was 1200 g·mol^{-1} and M_w/M_n was 1.54 when *i*AmOH/TiCl$_4$ = 0.4 (molar ratio). The M_n of the resulting PIB was 1800 g·mol^{-1} and M_w/M_n was 1.32 when *i*PrOH/TiCl$_4$ = 0.4 (molar ratio). The effect of the molar ratio of *i*AmOH/TiCl$_4$ on the cationic polymerization of IB in hexane was similar to that in C$_4$

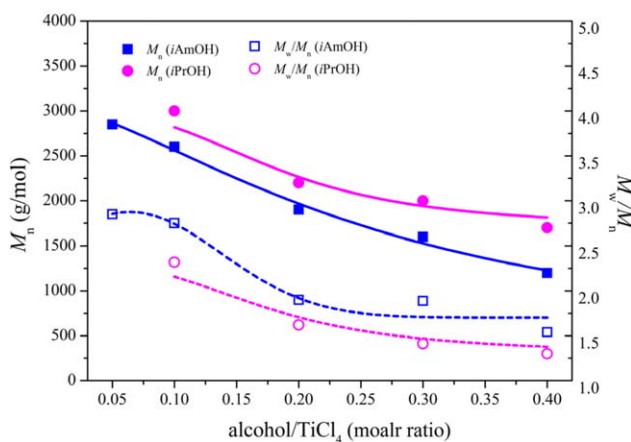**Figure 12.** Effect of the molar ratio of alcohol/TiCl$_4$ on M_n and M_w/M_n of PIBs obtained *via* IB polymerization from the mixed C$_4$ fractions with H$_2$O/TiCl$_4$/alcohol initiating systems at $-30°$C in the absence of DtBP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 13. Effect of the molar ratio of alcohol/TiCl$_4$ on the content of PIBs prepared *via* IB polymerization from the mixed C$_4$ fractions with H$_2$O/TiCl$_4$/alcohol initiating systems at $-30°$C in the absence of DtBP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
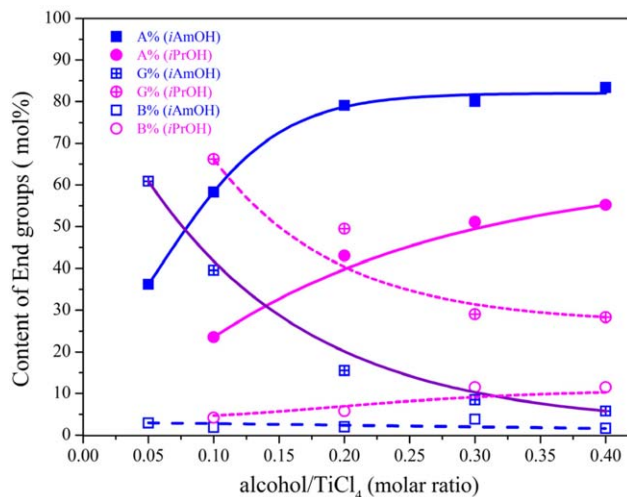
fraction mixtures. The monomer conversion and content of *exo*-olefin increased and molecular weight decreased with increasing the molar ratio of *i*AmOH/TiCl$_4$. The monomer conversion of pure IB in pure hexane was higher than that of selection of IB from C$_4$ fraction mixtures.

Compared to the H$_2$O/TiCl$_4$/*i*AmOH initiating system, the resulting PIBs *via* cationic polymerizations with H$_2$O/TiCl$_4$/*i*PrOH initiating system had higher M_n and narrower MWD when alcohol/TiCl$_4$ (molar ratio) was in the range of 0.05–0.4. The polymerization was started from proton initiation generated from alcohol and counteranion $[Ti_2Cl_{(9-n)}·(OR)_{(n)}]^-$ accompanied with the propagating species. The structure of counteranion could influence the propagation and thus the molecular weight of the resulting polymer. The basicity of secondary alcohol (*i*PrOH) was stronger than that of a primary alcohol (*i*AmOH), leading to more tightness and stabilization of propagation ion pair species and less side reactions, such as chain transfer reaction and termination. Therefore, PIBs obtained by H$_2$O/TiCl$_4$/*i*PrOH system had relatively high molecular weight, narrow molecular weight distribution.

Very interestingly, it can be seen from Figure 13 that the content of *exo*-olefin end groups (structure **A**) also gradually increased and reached upto around 80 mol % when *i*AmOH/TiCl$_4 \geq 0.2$ (molar ratio). HRPIBs with near content of *exo*-olefin end groups could be obtained in both hexane and C$_4$ fraction mixtures. And the resulting PIBs with H$_2$O/TiCl$_4$/*i*AmOH initiating system carried much larger amount of *exo*-olefin end groups (structure **A**) than those with H$_2$O/TiCl$_4$/*i*PrOH initiating system. The content of *tert*-Cl end group (structure **G**) in PIB chains decreased with increasing the concentration of alcohol and was higher in polymerization system in the presence of *i*PrOH than that in the presence of *i*AmOH. The representative ^{1}H-NMR spectra of HRPIB obtained at *i*AmOH/TiCl$_4$ (molar ratio) of 0.3 and 0.4 are given in Figure 14. The highly reactive

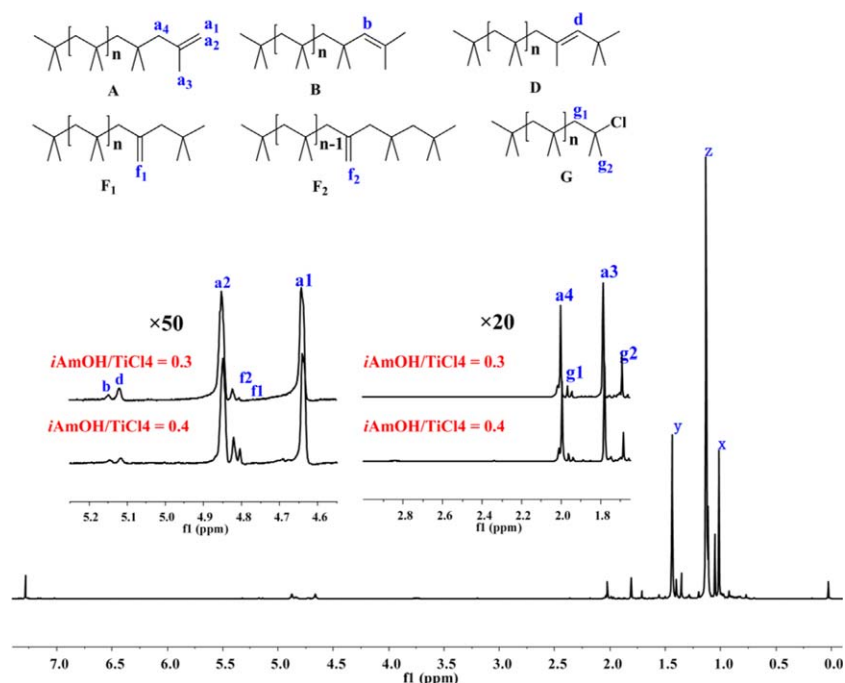**Figure 14.** ¹H NMR spectra of PIBs obtained with $H_2O/TiCl_4/i$AmOH initiating system at various iAmOH concentrations in C_4 fractions at $-30°C$. iAmOH/TiCl$_4$=0.3: M_n = 1600 g·mol⁻¹, M_w/M_n = 1.89, A = 80.0 mol %, B = 3.9 mol %, other internal double bonds = 8.7 mol %, G = 7.3 mol %; iAmOH/TiCl$_4$=0.4: M_n = 1200 g·mol⁻¹, M_w/M_n = 1.54, A = 81.8 mol %, B = 1.6 mol %, other internal double bonds = 10.8 mol %, G = 5.8 mol %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polyisobutylene with more than 80 mol % of *exo*-olefin end groups (structure **A**) could be directly achieved *via* the selective cationic polymerization of IB from the mixed C_4 fractions at $-30°C$ in the absence of D*t*BP for the first time. $H_2O/TiCl_4/$ iAmOH was recognized a preferred initiating system for direct synthesis of HRPIB. The multiplet resonances at $\delta = 2.85$ (e) attributed to —CH$_2$C(CH$_3$)=C(CH$_3$)—CH(CH$_3$)$_2$ (structure **E**) in PIB chain ends were almost undetectable. The little termination *via* chlorine transfer from counteranion at high concentration of iAmOH led to low content of *tert*-Cl terminal groups —CH_2—C(CH_3)$_2$—Cl (structure **G**) in the resulting PIB sample. The absence of the characteristic resonance signals for *n*-butene structural unit indicates that no copolymerization of IB and *n*-butene occurred and no *n*-butene incorporated into polyisobutylene chain even at high content of *n*-butene in the C_4 mixed feed. The cationic polymerization of IB in the C_4 mixed feed was also conducted at $-20°C$ and the resulting HRPIB with 81.1 mol % of *exo*-olefin end groups could be obtained.

It is necessary to further investigate the possibility of incorporation of other olefins (*n*-butane and 2-butene) or butadiene into PIB polymer chains during IB polymerization from the mixed C_4 fractions with $H_2O/TiCl_4/i$AmOH initiating system at $-30°C$ even though IB was more highly reactive than other C_4 isomers (butadiene, *n*-butene, and *cis*−2-butene) in the cationic polymerization co-initiated by TiCl$_4$.[87] In order to get further insight into the chemical structure of resulting polymer chains, ¹³C NMR characterization was performed on the representative polymer sample obtained from selective cationic polymerization of IB in the mixed C_4 fraction feed with $H_2O/TiCl_4/i$AmOH ini-

tiating system at iAmOH/TiCl$_4$ = 0.3 at $-30°C$, and the comparative commercial HRPIB (BASF, Glissopal 1000, *exo*-double bond = 90.1 mol %) obtained from IB polymerization in hexane. The DEPT-135 technique was also used to analyze the chemical structure of this resulting polymer since only the lines of carbons bonded to hydrogen are detected and lines of methine and methylene carbons exhibit a different phase in DEPT-135 spectra. The ¹³C NMR spectra and DEPT-135 spectra of the above two samples, and the lines were assigned to the labeled carbons are shown in Figures 15 and 16, respectively. It could be observed that very strong resonance signals at $\delta = 114.1$ and 143.5 for *exo*-olefin bond end groups (structure **A**) existed in PIB chains and any other —CH$_2$— (in opposite direction) groups in polymer chain resulted from butadiene, *n*-butene, or 2-butene were undetectable. Compared to the commercial HRPIB sample (Glissopal 1000), the resulting PIB sample from selective polymerization of IB in the mixed C_4 fraction feed with $H_2O/TiCl_4/i$AmOH initiating system is almost the same except for some differences in the relative strength of corresponding resonance signals. Therefore, the detailed NMR analysis shows that $H_2O/TiCl_4/i$AmOH initiating system shows extremely high selectivity toward IB polymerization rather than other 4C unsaturated fractions in the feed. The other C_4 fractions were just used as inert solvents during the cationic polymerization of IB with $H_2O/TiCl_4/i$AmOH initiating system, leading to an economical simple process for preparing the desired HRPIB products directly. Consequently, alcohol plays very important roles in improving monomer conversion, decreasing molecular weight, narrowing molecular weight distribution, and accelerating the selective β-H elimination from
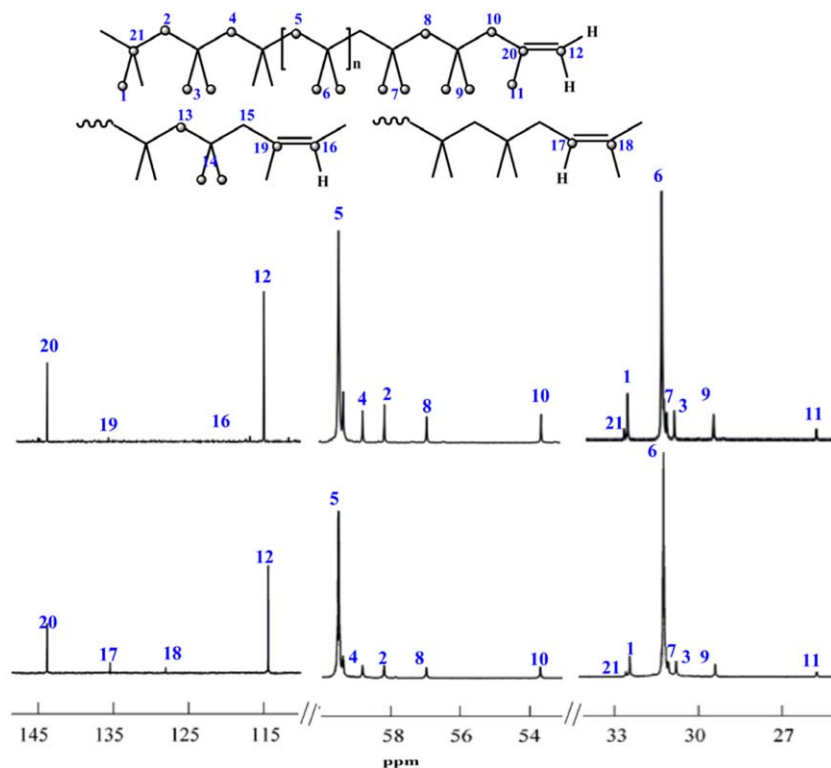
Figure 15. ^{13}C-NMR spectra of HRPIB prepared from the mixed C_4 fraction feed with $H_2O/TiCl_4/iAmOH$ initiating systems ($iAmOH/TiCl_4=0.3$, top) and commercial HRPIB (Glissopal 1000, bottom). PIB sample (top): A = 80.0 mol %, B = 3.9 mol %, D = 3.0 mol %, E= 4.8 mol %, G = 7.3 mol %, M_n = 1600 g·mol^{-1}; Glissopal 1000 (bottom): A = 90.1 mol %, B = 6.3 mol %, D= 3.6 mol %, M_n = 1000 g·mol^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

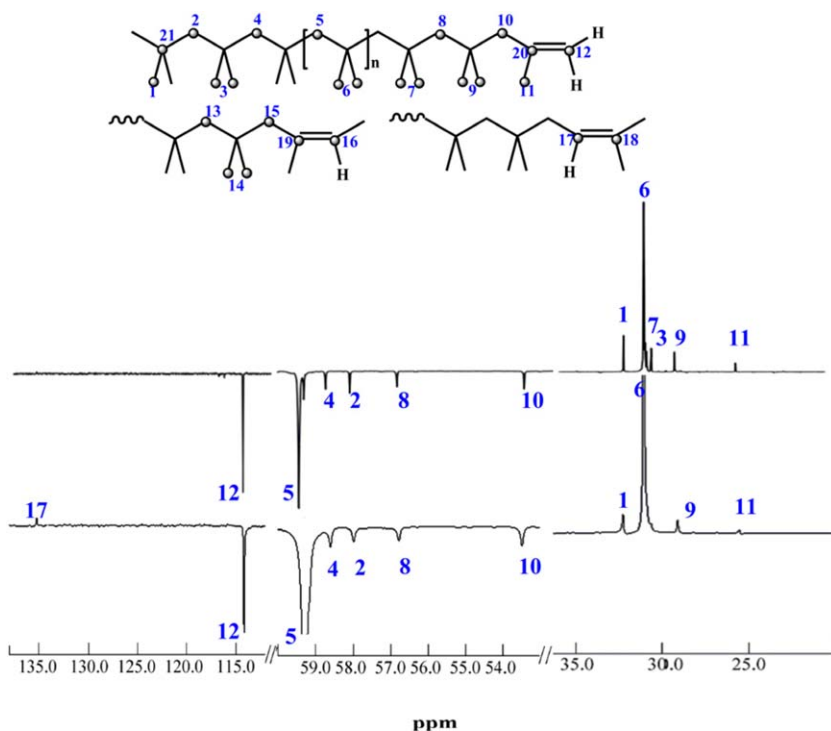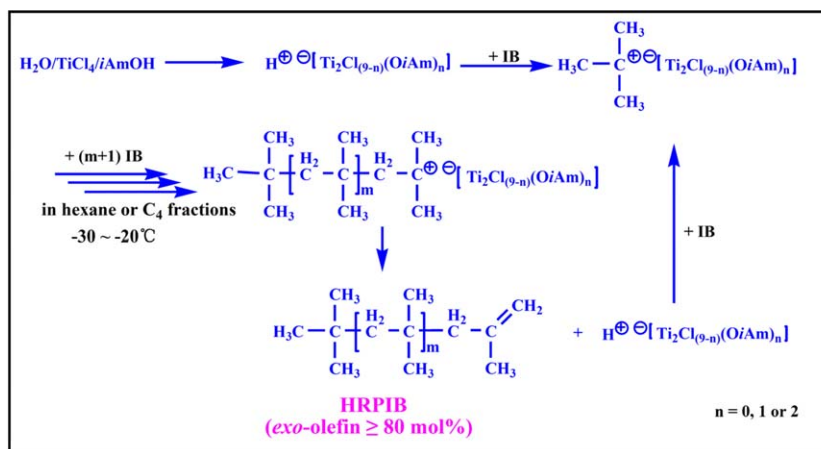**Figure 16.** DEPT spectra of HRPIB prepared from the mixed C_4 fraction feed with $H_2O/TiCl_4/iAmOH$ initiating systems ($iAmOH/TiCl_4=0.3$, top) and commercial HRPIB (Glissopal 1000, bottom). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 2. Possible mechanism for synthesis of HRPIB *via* cationic polymerization of isobutylene with $H_2O/TiCl_4/ROH$ (*i*PrOH or *i*AmOH) initiating system in nonpolar hydrocarbon media at $-30°C$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

—CH_3 group in the growing chain ends. This $H_2O/TiCl_4/$ *i*AmOH initiating system exhibits extremely high selectivity toward the cationic polymerization of IB from the mixed C_4 fractions and a good property for selective β-proton elimination from —CH_3 in the growing PIB chain ends, leading to direct synthesis of HRPIB with low molecular weight and relatively narrow molecular weight distribution, carrying more than 80 mol % of the desired *exo*-olefin end groups (structure **A**).

According to the above experimental results, a possible mechanism for direct synthesis of HRPIB *via* cationic polymerization of isobutylene with $H_2O/TiCl_4/i$AmOH initiating system was proposed, as shown in Scheme 2. The reaction between *i*AmOH and $TiCl_4$ led to formation of $TiCl_3(OiAm)$ and HCl. And $TiCl_3(OiAm)$ then used partially as co-initiator in the presence of high concentration of $TiCl_4$, in conjunction with initiators (H_2O an HCl; [HCl]$>>$[H_2O]) to create protic initiations with counteranion $[TiCl_{9-n}(OiAm)_n]^-$ ($n = 0$, 1, or 2), leading to formation of *tert*-butyl head group $(CH_3)_3C$— in polymer chain. Largely quick initiation from HCl resulted in higher monomer conversion, lower molecular weight, and narrower molecular weight distribution of PIBs at higher concentration of ROH in the polymerization system. The counteranion $[TiCl_{9-n}(OiAm)_n]^-$ ($n = 0$, 1, or 2) did affect the cationicity of the growing chain ends and selective β-proton elimination from —CH_3 groups in the growing PIB chain ends. The $H^+[TiCl_{9-n}(OiAm)_n]^-$ ($n = 0$, 1, or 2) resulted from β-proton scavenging from —CH_3 in the growing PIB chain ends could reinitiate IB polymerization and create new polymer chains, leading to an increase in [PIB] in polymerization system during polymerization.

and start the cationic polymerization in the polymerization systems, leading to an increase in monomer conversion and a decrease in molecular weight of the resulting polymers. Molecular weight of the resulting polymers could be mediated by polymerization temperature, alcohol concentration, and solvent polarity. On the other hand, β-proton elimination from —CH_3 or —CH_2— in the growing chain ends increased with increasing polymerization temperature and alcohol concentration, or decreasing solvent polarity. The character of polymerization could be turned from living polymerization without chain transfer reaction to β-proton elimination dominated polymerization with chain transfer reaction and termination by increasing polymerization temperature, increasing *i*AmOH concentration and decreasing solvent polarity. Moreover, $H_2O/$ $TiCl_4/i$AmOH initiating system possessed extremely high selectivity toward the cationic polymerization of IB from the mixed C_4 fractions, resulting in formation of HRPIBs with low molecular weight ($M_n = 1200\sim1600$ g·mol^{-1}) and relatively narrow molecular weight distribution ($M_w/M_n = 1.5\sim1.9$), carrying more than 80 mol % of *exo*-olefin end groups. To the best of our knowledge, this is the first example to achieve the direct synthesis of high-quality HRPIB with more than 80% of *exo*-olefin terminals by a single-step process *via* cationic polymerization of IB co-initiated by $TiCl_4$ in nonpolar hydrocarbon media (*n*-hexane or mixed C_4 fractions).

CONCLUSIONS

Living cationic polymerization of isobutylene initiated with TMPCl/TiCl$_4$/*i*PrOH or *i*AmOH systems could be achieved in the presence of 2,6-di-*tert*-butylpyridine (D*t*BP) at $-80°$ and polyisobutylenes (PIBs) carrying more than 90% of *tert*-chlorine end groups could be obtained. Alcohol could join the initiation

REFERENCES

1. Kresge, E. N.; Schatz, R. H.; Wang, H. C. Encyclopedia of Polymer Science and Engineering; Wiley: New York, **1985**; Vol. 8, pp 423.

2. Kennedy, J. P.; Ivan, B. Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice; Hanser: Munich, Germany, 1991; p 173.

3. De, P.; Faust, R. In Macromolecular Engineering. Precise Synthesis, Materials Properties, Applications; Matyjaszewski, K.; Gnanou, Y.; Leibler, L.; Eds., Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2007; p 1.

4. Puskas, I.; Banas, E. M.; Nerheim, G. J. Polym. Sci. Polym. Symp. 1976, 56, 191.

5. Kresge, E. N.; Schatz, R. H.; Wang, H. C. Encyclopedia of Polymer Science and Engineering; Wiley: New York, 1985; Vol. 8, p 423.

6. Günther, W.; Maenz, K.; Stadermann, D. Angew. Makromol. Chem. 1996, 234, 71.

7. Harrison, J. J.; Young, D. C.; Mayne, C. L. J. Org. Chem. 1997, 62, 693.

8. Burrington, J. D.; Johnson, J. R.; Pudelski, J. K. Top. Cat. 2003, 23, 175.

9. Faust, R.; Kennedy, J. P. Polym. Bull. 1986, 15, 317.

10. Faust, R.; Kennedy, J. P. J. Polym. Sci. Part A: Polym. Chem. 1987, 25, 1847.

11. Balogh, L.; Wang, L.; Faust, R. Macromolecules 1994, 27, 3453.

12. Storey, R. F.; Chisholm, B. J.; Brister, L. B. Macromolecules 1995, 28, 4055.

13. Roth, M.; Patz, M.; Freter, H.; Mayr, H. Macromolecules 1997, 30, 722.

14. Storey, R. F.; Choate, K. R., Jr. Macromolecules 1997, 30, 4799.

15. Puskas, J. E.; Brister, L. B.; Michel, A. J. J. Polym. Sci. Part A Polym. Chem. 2000, 38, 444.

16. Bahadur, M.; Shaffer, T. D.; Ashbaugh, J. R. Macromolecules 2000, 33, 9548.

17. Hadjikyriacou, S.; Acar, M.; Faust, R. Macromolecules 2004, 37, 7543.

18. Tawada, M.; Faust, R. Macromolecules 2005, 38, 4989.

19. Yan, P. F.; Guo, A. R.; Liu, Q.; Wu, Y. X. J. Polym. Sci. Part A: Polym. Chem. 2012, 50, 3383.

20. Boerzel, P.; Bronstert, K.; Hovemann, F. DE Patent 2,702,604, 1978.

21. Rath, H. P. US Patent 5,286,823, 1994.

22. Rath, H. P. US Patent 5,408,018, 1994.

23. Rath, H. P. US Patent 5,408,018, 1994.

24. Maxwell, K. J.; McMahon, J.; Mann, S. J. European Patent 0,671,419, 1995.

25. Rath, H. P. WO Patent 96/40808, 1996.

26. Rath, H. P. US Patent 5,910,550, 1997.

27. Rath, H. P.; Ulrich, K.; Deyck, V. F. US Patent 6,407,186, 1998.

28. Rath, H. P. WO Patent 99/64482, 1999.

29. Rath, H. P. US Patent 5,286,823, 1999.

30. Tokumoto, Y.; Ohashi, K.; Okada, T.; Takashima, T. EP Patent 1,026,175, 1999.

31. Rath, H. P.; Kanne, U.; Deyck, F. US Patent 6,407,186, 2002.

32. Edward, B. J.; Gilbert, V.; Christopher, L.; Timothy, L. US Patent 6,683,138, 2004.

33. Rath, H. P.; Lange, A.; Mach, H. US Patent 7,071,275, 2006.

34. Rath, H. P. US Patent 5,408,018, 1994.

35. Maxwell, K. J.; McMahon, J.; Mann, S. J. EP Patent 0,671,419, 1995.

36. Tokumoto, Y.; Ohashi, K.; Okada, T.; Takashima, T. EP Patent 1,026,175, 1999.

37. Rath, H. P.; Kanne, U.; Deyck, F. US Patent 6,407,186, 2002.

38. Edward, B.; Jr, Gilbert, V.; Christopher, L.; Timothy, L. US Patent, 6,683,138, 2004.

39. Vierle, M.; Zhang, Y.; Herdtweck, E.; Bohnenpoll, M.; Nuyken, O.; Kuhn, F. E. Angew. Chem. Int. Ed. 2003, 42, 1307.

40. Radhakrishnan,N.; Hijazi, A. K.; Komber, H.; Voit, B.; Zschoche, S.; Kuhn, F. E.; Nuyken, O.; Walter, M.; Hanefeld, P. J. Polym. Sci. Part A: Polym Chem. 2007, 45, 5636.

41. Hijazi, A. K.; Yeong, H. Y.; Zhang, Y.; Herdtweck, E.; Nuyken, O.; Kuhn, F. E. Macromol. Rapid Commun. 2007, 28, 670.

42. Hijazi, A. K.; Radhakrishnan, N.; Jain, K. R.; Herdtweck, E.; Nuyken, O.; Walter, H. M.; Hanefeld, P.; Voit, B.; Kuhn, F. E. Angew. Chem. Int. Ed. 2007, 46, 7290.

43. Hijazi, A. K.; Hmaideen, A. A.; Syukri, S.; Radhakrishnan, N.; Herdtweck, E.; Voit, B.; Kuhn, F. E. Eur. J. Inorg. Chem. 2008, 18, 2892.

44. Diebl, B. E.; Li, Y.; Cokoja, M.; Kuhn, F. E.; Radhakrishnan, N.; Komber, H.; Yeong, H. Y.; Voit, B.; Nuyken, O.; Hanefeld, P.; Walter, H. M. J. Polym. Sci. Part A: Polym. Chem. 2010, 48, 3775.

45. Li, Y.; Cokoja, M.; Kuhn, F. E. Coord. Chem. Rev. 2011, 255, 154.

46. Yeong, H. Y.; Li, Y.; Kuhn, F. E.; Voit, B. J. Polym. Sci. Part A: Polym. Chem. 2013, 51, 158.

47. Guerrero, A.; Kulbaba, K.; Bochmann, F. Macromolecules 2007, 40, 4124.

48. Burrington, J. D.; Johnson, J. R.; Pudelski, J. K. Top. Catal. 2003, 23, 175.

49. Dimitrov, P.; Emert, J.; and Faust, R. Macromolecules 2012, 45, 3318.

50. Kumar, R.; Dimitrov, P.; Bartelson, K. J.; Emert, J.; Faust, R. Macromolecules 2012, 45, 8598.

51. Bartelson, K. J.; De, P.; Kumar, R.; Emert, J.; Faust, R. Polymer 2013, 54, 4858.

52. Kumar, R.; Zheng, B.; Huang, K. W.; Emert, J.; Faust, R. Macromolecules 2014, 47, 1959.

53. Vasilenko, I. V.; Frolov, A. N.; Kostjuk, S. V. Macromolecules 2010, 43, 5503.

54. Vasilenko, I. V.; Shiman, D. I.; Kostjuk, S. V. J. Polym. Sci., Part A: Polym. Chem. 2012, 50, 750.

55. Kostjuk, S. V.; Yeong, H. Y.; Voit, B. J. Polym. Sci., Part A: Polym. Chem. 2013, 51, 471.

56. Shiman, D. I.; Vasilenko, I. V.; Kostjuk, S. V. Polymer 2013, 54, 2235.

57. Vasilenko, I. V.; Shiman, D. I.; Kostjuk, S. V. *Polym. Chem.* **2014**, *5*, 3855.

58. Liu, Q.; Wu, Y. X.; Zhang, Y.; Yan, P. F.; Xu, R. W. *Polymer* **2010**, *51*, 5960.

59. Liu, Q.; Wu, Y. X.; Yan, P. F.; Zhang, Y.; Xu, R. W. *Macromolecules* **2011**, *44*, 1866.

60. Zhang, L. B.; Wu, Y. X.; Zhou, P.; Wu, G. Y.; Yang, W. T.; Yu, D. S. *Chin. J. Polym. Sci.* **2011**, *29*, 360.

61. Zhang, L. B.; Wu, Y. X.; Zhou, P.; Xu, R. W. *Polym. Adv. Technol.* **2012**, *23*, 522.

62. Guo, A. R.; Yang, X. J.; Yan, P. F.; Wu, Y. X. *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *50*, 3383.

63. Kennedy, J. P.; Chang, V. S. C.; Simth, R. A.; Iván, B. *Polym. Bull.* **1979**, *1*, 575.

64. Iván, B.; Kennedy, J. P.; Chang, V. S. C. *J. Polym. Sci. Polym. Chem. Ed.* **1980**, *18*, 3177.

65. Iván, B.; Kennedy, J. P. *J. Polym. Sci. Part A: Polym. Chem.* **1990**, *28*, 89.

66. Feldthusen, J.; Iván, B.; Müller, A. H. E.; Kops, J. *Macromol. Reports* **1995**, *A32*, 639.

67. Feldthusen, J.; Iván, B.; Müller, A. H. E.; Kops, J. *Macromol. Rapid Commun.* **1997**, *18*, 417.

68. Nielsen, L. V.; Nielsen, R. R.; Gao, B.; Kops, J.; Iván, B. *Polymer* **1997**, *38*, 2529.

69. Feldthusen, J.; Ivan, B.; Muller, A. H. E. *Macromol. Rapid. Commun.* **1998**, *19*, 661.

70. Simison, K. L.; Stokes, C. D.; Harrison, J. J.; Storey, R. F. *Macromolecules* **2006**, *39*, 2481.

71. Morgan, D. L.; Stokes, C. D.; Meierhoefer, M. A.; Storey, R. F. *Macromolecules* **2009**, *42*, 2344.

72. Morgan, D. L.; Harrison, J. J.; Stokes, C. D.; Storey, R. F. *Macromolecules* **2011**, *44*, 2438.

73. Ummadisetty, S.; Morgan, D. L.; Stokes, C. D.; Storey, R. F. *Macromolecules* **2011**, *44*, 7901.

74. Ummadisetty, S.; Morgan, D. L.; Stokes, C. D.; Harrison, J. J.; Campbell, C. G.; Storey, R. F. *Macromol. Symp.* **2013**, *323*, 6.

75. Ummadisetty, S.; Storey, R. F. *Macromolecules* **2013**, *46*, 2049.

76. Lin, T.; Wu, Y. X.; Ye, X. L.; Zhang, L. B.; Huang, Q. G.; Wu, G. Y. *Acta Polym. Sinica* **2008**, 129.

77. Wu, Y. X.; Wu, G. Y. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 2209.

78. Wu, Y. X.; Tan, Y. X.; Wu, G. Y. *Macromolecules* **2002**, *35*, 3801.

79. Li, Y.; Wu, Y. X.; Xu, X.; Liang, L. H.; Wu, G. Y. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 3053.

80. Zhang, C. L.; Wu, Y. X.; Xu, X.; Li, Y.; Feng, L.; Wu, G. Y. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 936.

81. Guhaniyogi, S. C.; Kennedy, J. P.; Ferry, W. M. *J. Macromol. Sci., Part A, Pure Appl. Chem.* **1982**, *18*, 25.

82. Bae, Y. C.; Faust, R. *Macromolecules* **1997**, *30*, 7341.

83. Kanazawa, A.; Kanaoka, S.; Aoshima, S. *Macromolecules* **2010**, *43*, 2739.

84. Kanazawa, A.; Kanaoka, S.; Aoshima, S. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 2509.

85. Kennedy, J. P. Cationic Polymerization of Olefins: A Critical Inventory. Wiley Interscience: New York, **1975**.

86. Kennedy, J. P.; Marechal, E. Carbocationic Polymerization; Wiley Interscience: New York, **1982**.

87. De, P.; Faust, R. *Macromolecules* **2006**, *39*, 6861.