

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/263990587>

Synthesis of Highly Reactive Polyisobutylene Catalyzed by EtAlCl₂/Bis(2-chloroethyl) Ether Soluble Complex in Hexanes

ARTICLE in MACROMOLECULES · MARCH 2014

Impact Factor: 5.8 · DOI: 10.1021/ma500042f

CITATIONS

8

READS

84

5 AUTHORS, INCLUDING:



Rajeev Kumar

University of Massachusetts Lowell

5 PUBLICATIONS 43 CITATIONS

SEE PROFILE



Bin Zheng

Xi'an University of Science and Technology

42 PUBLICATIONS 271 CITATIONS

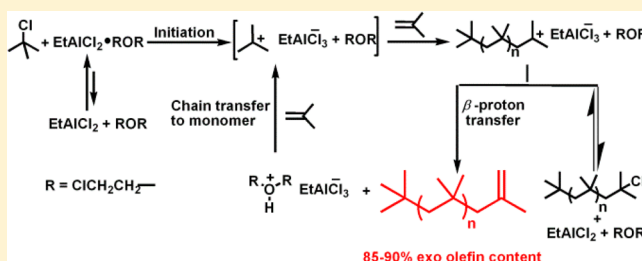
SEE PROFILE

Synthesis of Highly Reactive Polyisobutylene Catalyzed by EtAlCl₂/Bis(2-chloroethyl) Ether Soluble Complex in HexanesRajeev Kumar,[†] Bin Zheng,[‡] Kuo-Wei Huang,[‡] Jack Emert,[§] and Rudolf Faust^{*,†}[†]Polymer Science Program, Department of Chemistry, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854, United States[‡]KAUST Catalysis Center and Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 2355-6900, Saudi Arabia[§]Infineum USA, 1900 E. Linden Avenue, Linden, New Jersey 07036, United States

Supporting Information

ABSTRACT: The polymerization of isobutylene (IB) to yield highly reactive polyisobutylene (HR PIB) with high exo-olefin content using GaCl₃ or FeCl₃·diisopropyl ether complexes has been previously reported.¹ In an effort to further improve polymerization rates and exo-olefin content, we have studied ethylaluminum dichloride (EADC) complexes with diisopropyl ether, 2-chloroethyl ethyl ether (CEEE), and bis(2-chloroethyl) ether (CEE) as catalysts in conjunction with *tert*-butyl chloride as initiator in hexanes at different temperatures. All three complexes were readily soluble in hexanes.

Polymerization, however, was only observed with CEE. At 0 °C polymerization was complete in 5 min at [*t*-BuCl] = [EADC-CEE] = 10 mM and resulted in PIB with ~70% exo-olefin content. Studies on complexation using ATR FTIR and ¹H NMR spectroscopy revealed that at 1:1 stoichiometry a small amount of EADC remains uncomplexed. By employing an excess of CEE, exo-olefin contents increased up to 90%, while polymerization rates decreased only slightly. With decreasing temperature, polymerization rates decreased while molecular weights as well as exo-olefin contents increased, suggesting that isomerization has a higher activation energy than β-proton abstraction. Density functional theory (DFT) studies on the Lewis acid-ether binding energies indicated a trend consistent with the polymerization results. The polymerization mechanism proposed previously for Lewis acid-ether complexes¹ adequately explains all the findings.



INTRODUCTION

Low molecular weight ($M_n \sim 500\text{--}5000$ g/mol) olefin end-functional polyisobutylene (PIB) is a precursor to motor oil and fuel additives. Currently, two major industrial methods are utilized to produce low molecular weight IB homo- or copolymers with olefinic end groups. The “conventional” method uses a C₄ mixture and AlCl₃- or EtAlCl₂-based catalyst systems, which provides polybutenes with high tri- and tetrasubstituted olefinic content.^{2,3} BF₃ complexes with alcohols or ethers are employed as catalysts in the other method for the polymerization of IB, yielding highly reactive PIB (HR PIB) with high exo-olefinic end-group content.⁴ In contrast to the highly 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 polyisobutenyl succinimide ashless dispersants. Since chlorination is not necessary for maleation of HR PIB, the final product does not contain any chlorine, making HR PIB more desirable than conventional polybutenes. However, BF₃ is difficult to handle, and the polymer may contain fluorine especially when utilized with the commonly available mixed C₄ Raffinate I stream.

In recent decades, several new methods have been reported for the synthesis of HR PIB. This subject was recently reviewed,

and the advantages and disadvantages were discussed.⁵ Arguably the most promising method, first reported independently by Kostjuk and co-workers^{6,7} and Wu and co-workers,⁸ employed AlCl₃/dialkyl ether complexes as catalysts. However, high conversions and exo-olefin content were only obtained in dichloromethane (DCM) or DCM/hexane solvent mixtures. Furthermore, simple alkyl halide initiators such as *tert*-butyl chloride (*t*-BuCl) were inactive, and initiation was only observed from H₂O.

We reported that the polymerization of IB initiated with tertiary alkyl chlorides in conjunction with GaCl₃ or FeCl₃·ether complexes in hexanes in the −20 to +10 °C temperature range yield up to ~85% exo-olefinic end group content and close to complete monomer conversion.¹ More recently, we studied the steric and electronic effects of ethers on polymerization rates and exo-olefin content. Since FeCl₃·*i*-Pr₂O complexes exhibit limited solubility (0.012 M) in hexanes, we experimented with longer α-branched dialkyl ethers.⁹ To our surprise, however, these complexes had even lower solubility in

Received: January 7, 2014

Revised: February 25, 2014

Published: March 10, 2014

hexanes. Kinetic investigations showed that although the initial polymerization rate was high, rates decreased with conversion. Further research to be published elsewhere revealed that the $i\text{-Pr}_2\text{OH}^+\text{FeCl}_4^-$ protonated ether salt precipitates out due to its very low solubility in hexanes. Higher initial rates were observed with ethers containing electron-withdrawing substituents; however, these rates also decreased with conversion.

From these results we concluded that a Lewis acid complex soluble in hexanes is necessary. In this paper we report that with $t\text{-BuCl}$ as initiator, soluble ethylaluminum dichloride (EADC)·bis(2-chloroethyl) ether (CEE) complexes in hexanes catalyze a fast polymerization of IB to PIB olefin with up to 92% exo content.

2. EXPERIMENTAL SECTION

Materials. Technical grade hexanes (Doe & Ingalls) were refluxed over H_2SO_4 for 48 h, then washed with 10% KOH aqueous solution, and finally washed with distilled water until the aqueous layer was neutral. The hexanes were predried by vigorously mixing with anhydrous Na_2SO_4 for 30 min and then refluxed over CaH_2 for 48 h. Then the hexanes were distilled onto CaH_2 , refluxed again for 24 h, and freshly distilled. Isobutylene (IB, Matheson Tri Gas) was dried by passing it through in-line gas-purifier columns packed with BaO/Drierite and then condensed in a receiver flask at $-30\text{ }^\circ\text{C}$ before use. $t\text{-Butyl chloride}$ ($t\text{-BuCl}$, 98%, TCI America), and 2,6-di- $t\text{-butylpyridine}$ (DTBP, 97%, Aldrich) were used as received. Toluene (anhydrous 99.8%), diisopropyl ether (anhydrous 99%), aluminum chloride (AlCl_3 , 99%), ethylaluminum dichloride (EADC, 25.7 wt % solution in toluene), EADC (1 M solution in hexane), 2-chloroethyl ethyl ether (CEEE 1, 99%), and bis(2-chloroethyl) ether (CEE, 99%)

were purchased from Aldrich and used without any further purification.

Preparation of EADC·Ether Complexes. EADC·ether complexes were prepared just before the polymerization of IB. In a glove-box, an equimolar amount of ether was added to EADC, 25.7 wt % in toluene, while stirring to form a 1.0 M Lewis acid/ether complex solution. To determine the solubility of EADC·CEE, a stoichiometric amount of CEE was added to EADC (1 M) in hexanes. Immediately two liquid phases separated: the solution of the complex on top and the insoluble complex at the bottom. It was quite unexpected since separately both EADC and CEE are completely soluble in hexanes. The upper layer was removed, and the hexanes were evaporated under reduced pressure to determine the soluble complex concentration (0.115 M).

Polymerization of IB. Polymerizations were performed under a dry N_2 atmosphere in an MBraun glovebox (MBraun, Inc., Stratham, NH). IB was condensed and distributed to the polymerization reactors, screw-top culture tubes (75 mL), at $-30\text{ }^\circ\text{C}$. The polymerizations, which were co-initiated with EADC/ether complexes (typically 0.01 M) at monomer concentrations of $[\text{IB}] = 1.0\text{ M}$, were performed in hexanes at temperatures ranging from -20 to $10\text{ }^\circ\text{C}$ and terminated with either NH_4OH or MeOH. Monomer conversions were determined gravimetrically.

Characterization. Size Exclusion Chromatography. Molecular weights and polydispersities were obtained from size exclusion chromatography (SEC) with universal calibration using a Waters 717 Plus autosampler, a 515 HPLC pump, a 2410 differential refractometer, a 2487 UV-vis detector, a MiniDawn multi angle laser light scattering (MALLS) detector (measurement angles are 44.7° , 90.0° , and 135.4°) from Wyatt Technology Inc., a ViscoStar viscosity detector from Wyatt, and five Ultrastaygel GPC columns connected in the following order: 500, 10^3 , 10^4 , 10^5 , and 10^6 Å . The RI was the concentration detector. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min at room temperature. The results were processed using the Astra 5.4 software from Wyatt Technology Inc.

Nuclear Magnetic Resonance. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker 500 MHz spectrometer using CDCl_3 or CD_2Cl_2 as solvents (Cambridge Isotope Lab., Inc.). The PIB end-group content was determined by ^1H NMR spectroscopy (Figure 1).

The two protons characteristic of the exo-olefin end group (structure A, protons a_1 and a_2) are well resolved and appear at 4.85 and 4.64 ppm, while the one proton characteristic of the endo-olefin end group (structure B, proton d) appears at 5.15 ppm. Small amounts of the *E* and *Z* configurations of another trisubstituted olefin end group (structure C, protons e_1 and e_2) could also be detected in some samples at 5.37 and 5.17 ppm. The tetrasubstituted olefin end group (structure D, proton f) appears as a broad multiplet at 2.85 ppm.

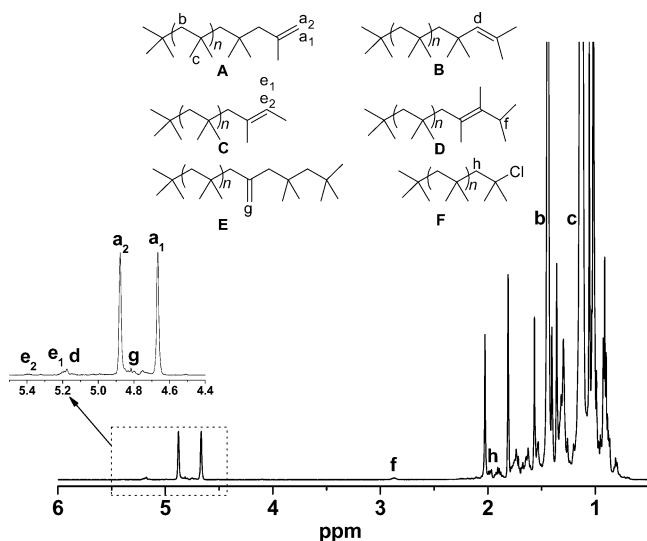


Figure 1. Typical ^1H NMR spectrum of HR PIB obtained in this study.

Table 2. Calculated Binding Energies of Ethers with EADC at B3LYP/6-31G* (kcal/mol)

ether	binding energy
$i\text{-Pr}_2\text{O}$	−7.5
CEEE	−7.1
CEE	−5.1

Table 1. Polymerization of IB (1 M) in Hexanes for 20 min at $0\text{ }^\circ\text{C}$ ($[\text{EADC}\cdot\text{Ether}] = 0.02\text{ M}$; $[\text{EADC}]:[\text{Ether}] = 1:1$)

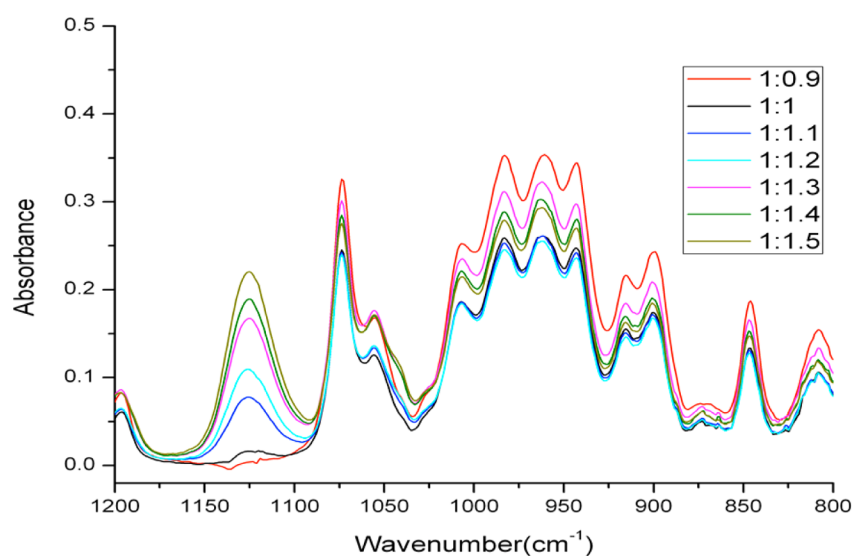
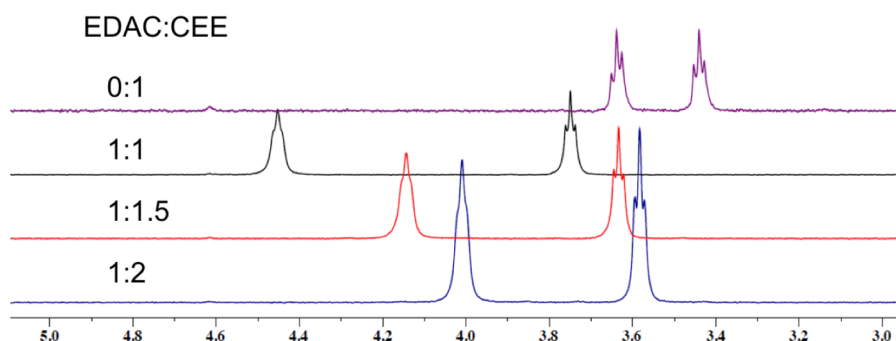
complex	$[t\text{-BuCl}]$	$[\text{DTBP}]$	conv (%)	M_n^a (NMR)	exo (%)	tri + endo (%)	tetra (%)	PIB-Cl (%)	PIB-coupled (%)
EADC·CEEE	0.02	0.005	0						
EADC·CEEE	0.02	0	0						
EADC·CEEE	0	0	5						
EADC·CEE	0.02	0	100	1000	72	18	10	0	0
EADC·CEE	0.02	0.005	14	1400	70	19	11	0	0
EADC·CEE	0	0.005	0						

$^a M_{n,\text{NMR}} = 56.11 \times ((b/2)/((a_1 + a_2/2) + d + e_1 + e_2 + (g/2) + (h/2)))$. See Figure 1 for proton assignments.

Table 3. Polymerization of IB in Hexanes at 0 °C Initiated by *t*-BuCl and Co-initiated by EADC·CEE^a

no.	time (min)	conv (%)	M_n (NMR)	M_n (GPC)	PDI	exo (%)	tri + endo (%)	tetra (%)	PIB-Cl (%)	PIB-coupled (%)
1	1	19	4000			65	15	15	5	0
2	2	51	3000	3600	2.2	68	15	12	4	0
3	3	75	2400	2300	2.7	68	19	13	0	0
4	4	95	1900	1900	3.1	65	21	14	0	0
5	5	100	1800	1800	2.7	68	19	14	0	0
6	10	100	1600	1700	3.0	70	19	11	0	0

^a[EADC·CEE] = 0.01 M; [*t*-BuCl] = 0.01 M; [EADC]:[CEE] = 1:1; [IB] = 1 M.

**Figure 2.** ATR FTIR spectra at different EADC:CEE ratios.**Figure 3.** ¹H NMR spectra of free CEE and EADC:CEE mixtures at different ratios in cyclohexane-*d*₁₂.**Table 4.** Polymerization of IB in Hexanes at 0 °C Initiated by *t*-BuCl and Co-initiated by EADC·CEE at [EADC]:[CEE] = 1:1.1^a

no.	time (min)	conv (%)	M_n (NMR)	M_n (GPC)	PDI	exo (%)	tri + endo (%)	tetra (%)	PIB-Cl (%)	PIB-coupled (%)
1	1	10	3300			68	14	12	6	0
2	2	35	3100	3500	2.5	70	13	12	5	0
3	3	70	2400	3000	2.8	68	18	14	0	0
4	4	88	2100	1800	2.9	70	18	12	0	0
5	5	100	1800	1900	2.7	72	16	12	0	0
6	10	100	1600	1700	2.8	68	20	11	0	1
7	20	100	1500	1800	3.0	62	23	13	0	2

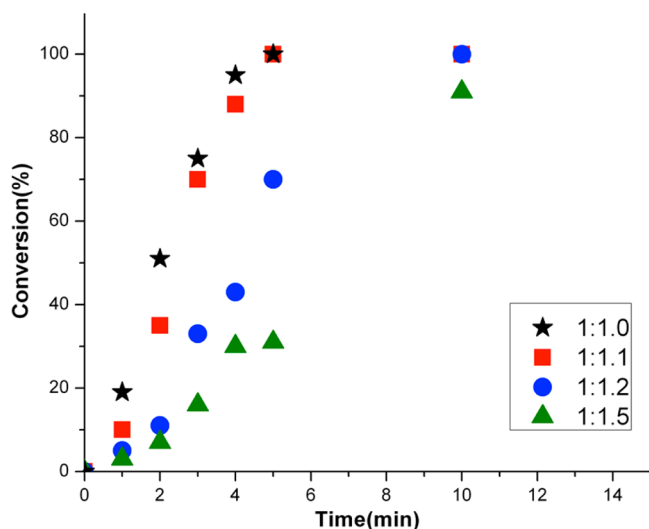
^a[EADC·CEE] = 0.01 M; [*t*-BuCl] = 0.01 M; [IB] = 1 M.

Table 5. Polymerization of IB in Hexanes at 0 °C Initiated by *t*-BuCl and Co-initiated by EADC·CEE at [EADC]:[CEE] = 1:1.2^a

no.	time (min)	conv (%)	M _n (NMR)	M _n (GPC)	PDI	exo (%)	tri + endo (%)	tetra (%)	PIB-Cl (%)	PIB-coupled (%)
1	1	5	3200			72	13	10	5	0
2	2	11	2500			71	14	11	4	0
3	3	33	2300	2500	2.7	74	14	9	3	0
4	4	43	2400	2600	2.7	78	11	8	2	0
5	5	70	1900	2000	3.1	75	15	9	0	0
6	10	100	1200	1300	2.8	74	16	10	0	0
7	20	100	1100	1300	2.5	77	15	8	0	1

^a[EADC·CEE] = 0.01 M; [*t*-BuCl] = 0.01 M; [IB] = 1 M.**Table 6.** Polymerization of IB in Hexanes at 0 °C Initiated by *t*-BuCl and Co-initiated by EADC·CEE at [EADC]:[CEE] = 1:1.5^a

no.	time (min)	conv (%)	M _n (NMR)	M _n (GPC)	PDI	exo (%)	tri + endo (%)	tetra (%)	PIB-Cl (%)	PIB-coupled (%)
1	1	3	1400			79	10	10	0	0
2	2	7	1500			84	8	8	0	0
3	3	16	1400			84	8	6	3	0
4	4	30	1300			90	5	5	0	0
5	5	31	1200	1100	3.2	90	5	5	0	0
6	10	91	1000	1200	3.0	86	7	5	2	0
7	20	100	900	1000	2.9	85	7	4	3	1

^a[EADC·CEE] = 0.01 M; [*t*-BuCl] = 0.01 M; [IB] = 1 M.**Figure 4.** Variation of conversion with time for the polymerization of IB in hexanes at 0 °C initiated by *t*-BuCl/EADC·CEE at different [EADC]:[CEE] ratios. [EADC·CEE] = 0.01 M; [*t*-BuCl] = 0.01 M; [IB] = 1 M.

Resonances for coupled PIB chains (structure E, protons g) are normally found at 4.82 ppm. The methylene protons of the PIBCl end

group (structure F, protons h) at 1.96 ppm were used to determine the content of PIBCl. Finally, the methylene and methyl protons of the IB repeat unit (structure A, protons b and c, respectively) could be observed at 1.42 and 1.11 ppm, respectively.

Fourier Transform Attenuated Total Reflectance Infrared Spectroscopy (FTIR-ATR). FTIR-ATR was performed using a Mettler Toledo React IR 4000 instrument equipped with a DiComp probe connected to an MCT detector with a K6 conduit. Sampling wave-numbers were from 4000 to 650 cm⁻¹ at a resolution of 2 cm⁻¹.

Density Functional Calculations. DFT calculations were conducted by employing the Gaussian 09 package,¹⁰ utilizing the B3LYP level of theory with the Pople basis set 6-31G* for all atoms in the gas phase.^{11,12} Difference rotamers were modeled, and the corresponding vibrational frequencies were computed to characterize and to obtain these structures as global minima for the binding energy calculation.

RESULTS AND DISCUSSION

The cationic polymerization of isobutylene with *t*-BuCl/EADC complexes was compared using *i*-Pr₂O, CEEE, and CEE in the presence or absence of the proton trap 2,6-di-*tert*-butylpyridine (DTBP). Polymerization was absent under all conditions with EADC·*i*-Pr₂O. Results with CEE and CEEE are summarized in Table 1. With EADC·CEE, *t*-BuCl did not initiate polymerization in the presence or absence of DTBP, and only 5% conversion was obtained in the absence of both *t*-BuCl and DTBP.

Table 7. Polymerization of IB in Hexanes at −20 °C Initiated by *t*-BuCl and Co-initiated by EADC·CEE^a

no.	time (min)	conv (%)	M _n (NMR)	M _n (GPC)	PDI	exo (%)	tri + endo (%)	tetra (%)	PIB-Cl (%)	PIB-coupled (%)
1	1	2								
2	2	4								
3	3	5								
4	4	6								
5	5	8	5000	4500	3.0	74	16	7	3	0
6	10	10	4000	3000	4.3	72	15	10	3	0
7	30	28	3800	3600	3.3	76	14	8	2	0
8	60	68	4000	4500	2.7	85	7	8	0	0

^a[EADC·CEE] = 0.01 M; [*t*-BuCl] = 0.01 M; [EADC]:[CEE] = 1:1.1; [IB] = 1 M.

Table 8. Polymerization of IB in Hexanes at $-10\text{ }^{\circ}\text{C}$ Initiated by $t\text{-BuCl}$ and Co-initiated by EADC·CEE^a

no.	time (min)	conv (%)	M_n (NMR)	M_n (GPC)	PDI	exo (%)	tri + endo (%)	tetra (%)	PIB-Cl (%)	PIB-coupled (%)
1	1	4								
2	2	7								
3	3	9								
4	4	16								
5	5	19	3900	3900	2.5	71	15	14	0	0
6	10	50	4500	4100	2.6	80	9	11	0	0
7	30	95	2500	2700	2.8	84	8	8	0	0
8	60	100	2200	2300	2.8	80	12	9	0	0

^a[EADC·CEE] = 0.01 M; [$t\text{-BuCl}$] = 0.01 M; [EADC]:[CEE] = 1:1.1; [IB] = 1 M.**Table 9.** Polymerization of IB in Hexanes at $+10\text{ }^{\circ}\text{C}$ Initiated by $t\text{-BuCl}$ and Co-initiated by EADC·CEE^a

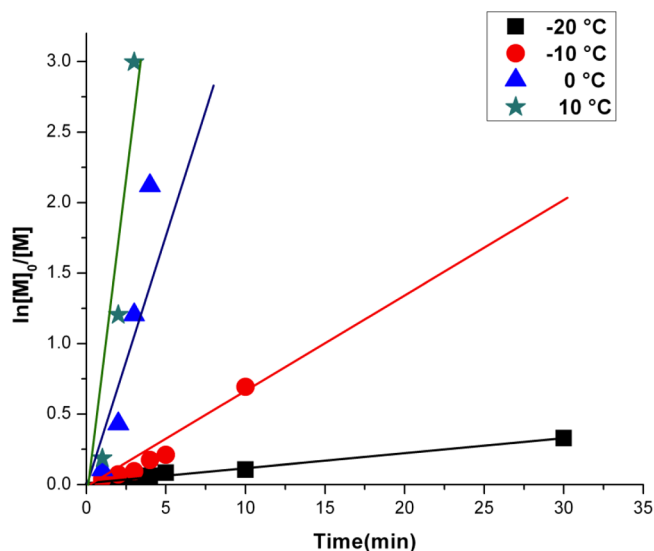
no.	time (min)	conv (%)	M_n (NMR)	M_n (GPC)	PDI	exo (%)	tri + endo (%)	tetra (%)	PIB-Cl (%)	PIB-coupled (%)
1	1	17	2700	2000	2.6	72	15	13	0	0
2	2	70	1700	1800	2.5	66	19	15	0	0
3	3	95	1200	1400	2.8	66	21	13	0	0
4	4	100	1200	1300	2.8	64	22	14	0	0
5	5	100	1200	1200	2.5	67	19	13	0	0
6	10	100	1100	1000	4.2	65	20	13	0	2
7	30	100	1000	1000	3.6	60	20	16	0	4

^a[EADC·CEE] = 0.01 M; [$t\text{-BuCl}$] = 0.01 M; [EADC]:[CEE] = 1:1.1; [IB] = 1 M.

However, $t\text{-BuCl}$ readily initiated polymerization with CEE in the presence or absence of DTBP. Complete monomer conversion with 72% of exo-olefin content was observed in the absence of DTBP (Table 1, entry 4). We previously reported that $\text{AlCl}_3\cdot i\text{-Pr}_2\text{O}$ could not ionize $t\text{-BuCl}$, and polymerization of IB was absent due to the high oxophilicity of AlCl_3 relative to its chlorophilicity. The lack of initiation from $t\text{-BuCl}$ with EADC· $i\text{-Pr}_2\text{O}$ or EADC·CEE is similarly attributed to strong interaction between EADC and the ether oxygen relative to the chlorine of the initiator. With CEE, the electron density on the oxygen is sufficiently decreased by the electron-withdrawing Cl substituents so that displacement of CEE and ionization of $t\text{-BuCl}$ are possible. These observations are in good agreement with the trend in the calculated binding energies of these ethers to EADC (Table 2). The weak coordination of EADC with the least nucleophilic CEE allows CEE to be displaced by $t\text{-BuCl}$ under the polymerization conditions. For the more nucleophilic CEEE and $i\text{-Pr}_2\text{O}$, displacement of the ether becomes much less favorable, and the ionization of $t\text{-BuCl}$ is absent.

Since polymerization was very rapid, both initiator and complex concentrations were decreased to 0.01 M. Table 3 shows the evolution of the polymerization with time. Even at these reduced concentrations, polymerization was very rapid and complete monomer conversion was observed in 5 min. The M_n s decreased with increasing conversion from 4000 at 19% conversion to 1800 at complete monomer conversion while exo-olefin content remained essentially unchanged. The decrease of M_n with increasing conversion is expected since the propagation rate decreases with monomer concentration; however, the proton elimination rate is unaffected by conversion. This also explains why the polydispersity indices (PDIs) are higher than 2.0.

We have reported that complexation of FeCl_3 with CEE is incomplete at ratios up to 1:1.3. Since free FeCl_3 is insoluble in hexanes, polymerization rates and olefin exo contents remained similar when excess FeCl_3 was used.⁸ However, EADC is soluble in hexanes, so a broader range of EADC:CEE complex stoichiometries was examined by FT-IR spectroscopy.

**Figure 5.** Plot of $\ln [M]_0/[M]$ vs time plot for polymerization of IB initiated by $t\text{-BuCl}$ /EADC·CEE at different temperatures. [EADC·CEE] = 0.01 M; [$t\text{-BuCl}$] = 0.01 M; [IB] = 1 M.

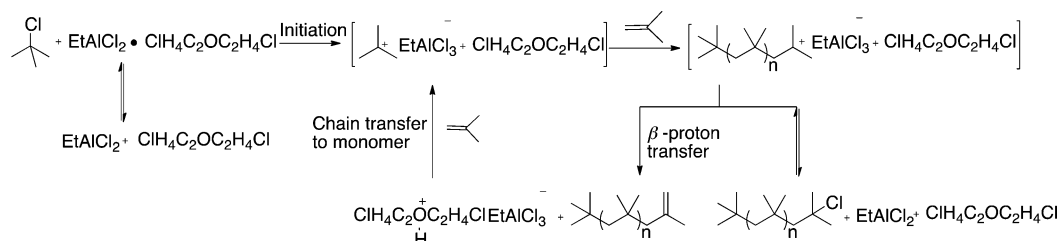
The spectra at different [EADC]:[CEE] ratios are shown in Figure 2. Uncomplexed ether is absent at [EADC]:[CEE] = 1:0.9. However, at a 1:1 ratio, a small peak attributed to free ether is visible. Based on the peak height, the extent of complexation is about 98%. Increasing the amount of ether results in a proportional increase of free ether peak height at 1125 cm^{-1} .

Further complexation studies were performed by ^1H NMR spectroscopy in cyclohexane- d_{12} . Addition of CEE to EADC in stoichiometric amount results in a downfield chemical shift of the CH_2 protons relative to those of free CEE clearly confirming the formation of a complex (Figure 3). Free ether resonances are not observed in the spectrum of EADC·CEE. However, free ether is not observed even in the presence of a

Table 10. Polymerization of IB in Hexanes Initiated by *t*-BuCl and Co-initiated by EADC·CEE at Different Temperatures^a

no.	time (min)	temp (°C)	conv (%)	<i>M_n</i> (NMR)	<i>M_n</i> (GPC)	PDI	exo (%)	tri + endo (%)	tetra (%)	PIB-Cl (%)	PIB-coupled (%)
1	20	−10	16	1900			88	7	5	0	0
2	40	−10	39	1400	1200	3.3	87	8	5	0	0
3	60	−10	65	1100	1000	3.2	91	5	4	0	0
4*	60*	−10	100	2100	2000	2.8	92	5	3	0	0
5	20	0	100	900	1000	2.8	85	7	4	3	1
6*	20*	0	100	1700	1600	3.5	85	9	6	0	0
7	5	+10	44	800	1000	2.9	87	7	6	0	0
8	10	+10	86	500	700	3.6	85	9	6	0	0
9	20	+10	100	500	600	3.6	79	11	8	0	2
10*	15*	+10	100	700	1000	4.4	70	16	13	0	1

^a[EADC·CEE] = 0.01 M; [*t*-BuCl] = 0.01 M; [EADC]:[CEE] = 1:1.5; [IB] = 1 M. *[IB] = 4 M.

Scheme 1. Suggested Mechanism for the Polymerization of IB by *t*-BuCl and EADC·CEE

large excess of CEE, suggesting a fast exchange between free and complexed CEE (Figure 3).

Effect of Increasing Lewis Base/Lewis Acid Ratio. In order to increase the exo-olefin content, the CEE:EADC ratio was increased to 1.1, 1.2, and 1.5 to drive complexation of EADC to completion. The results at these ratios are shown in Tables 4, 5, and 6. With increasing CEE:EADC ratios, exo-olefin content increased up to 90% while polymerization rates (see Figure 4) decreased only slightly. In contrast, excess CEE did not affect the polymerization rates or exo-olefin content when the FeCl₃·CEE complex was used.⁸

Effect of Temperature. The effect of temperature on the polymerization of IB with [EADC]:[CEE] = 1:1.1 from −20 to +10 °C are tabulated in Tables 4 and 7–9, and the first-order kinetic plots are shown in Figure 5. The rate of polymerization decreases with decreasing temperature. Since propagation does not have an enthalpic barrier, the rate decrease must be due to a decrease in the concentration of propagating PIB⁺ centers. The initial rate is controlled by the rate of initiation, while after all the *t*-BuCl has been depleted, the rate is influenced by the rate of proton transfer from the protonated ether to IB. Both of these are expected to have positive activation energies. Interestingly, the first-order plots are slightly curved upward, suggesting that chain transfer is faster than ionization. The *M_n*s are higher at lower temperature, indicating that proton elimination is slower at lower temperature. However, the finding that exo-olefin content increases with decreasing temperature suggests that temperature has a larger effect on the rate of isomerization relative to that of proton elimination.

Limited experiments were also carried out at a ratio of EADC:CEE = 1:1.5 at different temperatures. The results shown in Table 10 are consistent with the conclusions above; i.e., with decreasing temperature, polymerization rate decreases while the *M_n*s and exo-olefin contents increase.

Polymerization Mechanism. The polymerization mechanism (shown for EADC·CEE in Scheme 1) proposed previously for Lewis acid-ether complexes adequately explains all

the findings. Perhaps the only major difference is that ion collapse to yield PIB-Cl is virtually absent with the EADC·CEE catalyst system as a small amount of PIB-Cl was observed only at low conversions and/or low temperatures.

CONCLUSION

In conjunction with *t*-BuCl as initiator, the EADC·CEE complex readily catalyzed the fast polymerization of IB in hexanes at 0 °C and provided PIB with ~70% exo-olefin content. The exo-olefin content could be increased up to 90% by employing a stoichiometric excess of CEE, which brought about a slight decrease in the rate of polymerization. The increase of molecular weights as well as the exo-olefin content with decreasing temperature suggests that isomerization has a higher activation energy than β -proton abstraction. The previously proposed mechanism for the polymerization of IB with other Lewis acid-ether complexes satisfactorily explains all the findings. Major advantages of the current system are that the complex is soluble in hexanes and that PIB-Cl is virtually absent due to a much slower ion collapse compared to β -proton abstraction. Thus, this new method of HR PIB synthesis shows great promise for industrial adoption.

ASSOCIATED CONTENT

Supporting Information

Calculated energies and Cartesian coordinates of EADC, ether, and EADC·ether complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail rudolf_faust@uml.edu (R.F.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from Infineum USA is greatly appreciated.

■ REFERENCES

- (1) Kumar, R.; Dimitrov, P.; Bartelson, K. J.; Emert, J.; Faust, R. *Macromolecules* **2012**, *45* (21), 8598–8603.
- (2) Puskas, I.; Banas, E. M.; Nerheim, A. G. *J. Polym. Sci. Symp.* **1976**, *56*, 191–202.
- (3) Puskas, I.; Meyerson, S. *J. Org. Chem.* **1984**, *49*, 258–262.
- (4) Mach, H.; Rath, P. *Lubr. Sci.* **1999**, *11* (2), 175–185.
- (5) Kostjuk, S. V.; Yeong, H. Y.; Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 471–486.
- (6) Vasilenko, I. V.; Frolov, A. N.; Kostjuk, S. V. *Macromolecules* **2010**, *43* (13), 5503–5507.
- (7) Vasilenko, I. V.; Shiman, D. I.; Kostjuk, S. V. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50* (4), 750–758.
- (8) Liu, Q.; Wu, Y.-X.; Zhang, Y.; Yan, P.-F.; Xu, R.-W. *Polymer* **2010**, *51*, 5960–5969.
- (9) Bartelson, K. J.; De, P.; Kumar, R.; Emert, J.; Faust, R. *Polymer* **2013**, *54* (18), 4858–4863.
- (10) *Gaussian 09; Revision A.2*: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian, Inc.*: Wallingford, CT, 2009.
- (11) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785–789.
- (12) (a) Ditchfie, R. W.; Hehre, J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724–728. (b) Hehre, W. J.; Ditchfie, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261. (c) Harihara, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222.