

Supporting Information

Polymerization of Isobutylene Catalyzed by EtAlCl₂/Bis(2-chloroethyl) Ether Complex in Steel Vessels

Sanjib Banerjee,[†] Jack Emert,[‡] Peter Wright,[‡] Thomas Skourlis,[‡] Rich Severt[‡] and Rudolf Faust^{*,†}

[†]Department of Chemistry, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854, United States

[‡]Infineum USA, 1900 E. Linden Avenue, Linden, New Jersey 07036, United States

Correspondence to: Rudolf Faust (E-mail: Rudolf_Faust@uml.edu)

Procedure for Preparation of Standard ZnSO₄ solution.

The amount of zinc sulfate heptahydrate (ZnSO₄·7H₂O) needed to prepare 250 mL of 0.02 M Standard ZnSO₄ solution was weighed out as accurately as possible and transferred to a 250 mL volumetric flask using a funnel. The funnel was rinsed with small amount of de-ionized water through it. The flask was then filled to the mark with deionized water and swirl until all of the powder has dissolved. Concentration of ZnSO₄ solution = 1.002×0.02 M.

Procedure for Preparation of 0.05 M EDTA solution.

EDTA solution was freshly prepared. The amount of ethylenediaminetetraacetic acid (EDTA) needed to prepare 250 mL of 0.05 M EDTA solution was weighed out and transferred to a 250 mL volumetric flask using a funnel. The funnel was rinsed with small amount of de-ionized water through it. Then the flask was filled to the 250 mL mark with deionized water and swirl until all of the EDTA has dissolved.

Titration Procedure for Standardization of EDTA Solution

The concentration of the EDTA solution was determined as secondary standard by titration with primary standard ZnSO₄ solution using dithizone as indicator. Typically, 15 mL of the EDTA solution was taken in a beaker. The solution was diluted with 50 mL of de-ionized water and the pH was adjusted to 5 with dilute NaOH. 10 mL of sodium acetate buffer was added to the solution. Then 10 mL of ammonium acetate, 75 mL of 2-propanol and 1 mL of dithizone indicator solution were added. The solutions were titrated against a standard 0.02 M ZnSO₄ solution to determine the concentration of EDTA.

Determination of Cr Content of the hexane solution after Aging EADC in SS Reactor.

Typically, 1.0 mL of 0.02 M EADC solution in dry hexanes was aged in a SS reactor for 5 min inside the glove box. After this, this aged EADC solution was transferred to a 20 mL sealed vial using a gas tight syringe. The vial was taken out of the glove box and the aged solution was dissolved in de-ionized water by adding dilute HNO₃. The solution was then diluted to 10 mL by adding de-ionized water. The Cr content in the solution was then determined by Agilent 200 series model 240 AA flame atomic absorption spectrometer (see Characterization section for the instrument detail and parameters). Three standard solutions of Cr (10 ppm, 20 ppm and 30 ppm) were prepared by diluting Cr standard (1000 ppm or 1000 mg L⁻¹, Atomic Absorption Standard, VWR International). These solutions were then used for preparing the calibration curve (Figure S3). The Cr content in the solution was determined from the calibration curve, as follows:

From the calibration curve shown as Figure S3:

$$\text{Slope} = 0.00169 \text{ and Intercept} = 0.00417$$

$$\text{So, Absorbance} = (0.00169 \times C) + 0.00417 \dots \dots \dots (1)$$

where, C = concentration of Cr in mg/L

Now, absorbance of the solution containing soluble Cr complex = 0.0372,

$$\text{So, from equation 1, } C = 19.5 \text{ mg/L}$$

This leads to 0.195 mg Cr in 10 mL stock solution of the aged EADC.

So, aging of 1 mL 0.02 M or 0.02 mmol EADC in SS reactor produces 0.195 mg or 0.00375 mmol Cr which is 19% of the amount of initial EADC.

Thus, we conclude that aging of EADC in SS reactor leads to 19% soluble Cr containing complex formation.

Table S1. Estimation of Al content.

Sample	Volume of aliquot (mL)	Vol. of ZnSO₄ reqd. (mL)	Strength of EADC (M)
0.1 M EADC in hexane (fresh)	1.0	29.6	0.0986
0.1 M EADC in hexane (aged in SS reactor)	1.0	29.7	0.0966

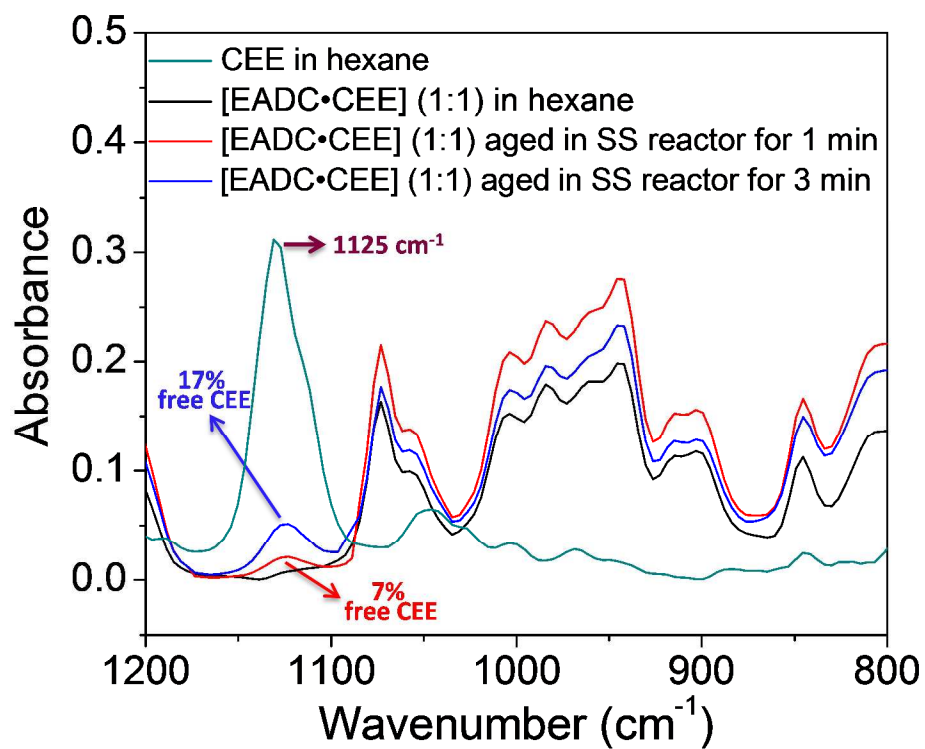


Figure S1. ATR FTIR spectroscopic analysis of the effect of aging EADC:CEE (1:1) complex in SS reactor at different times.

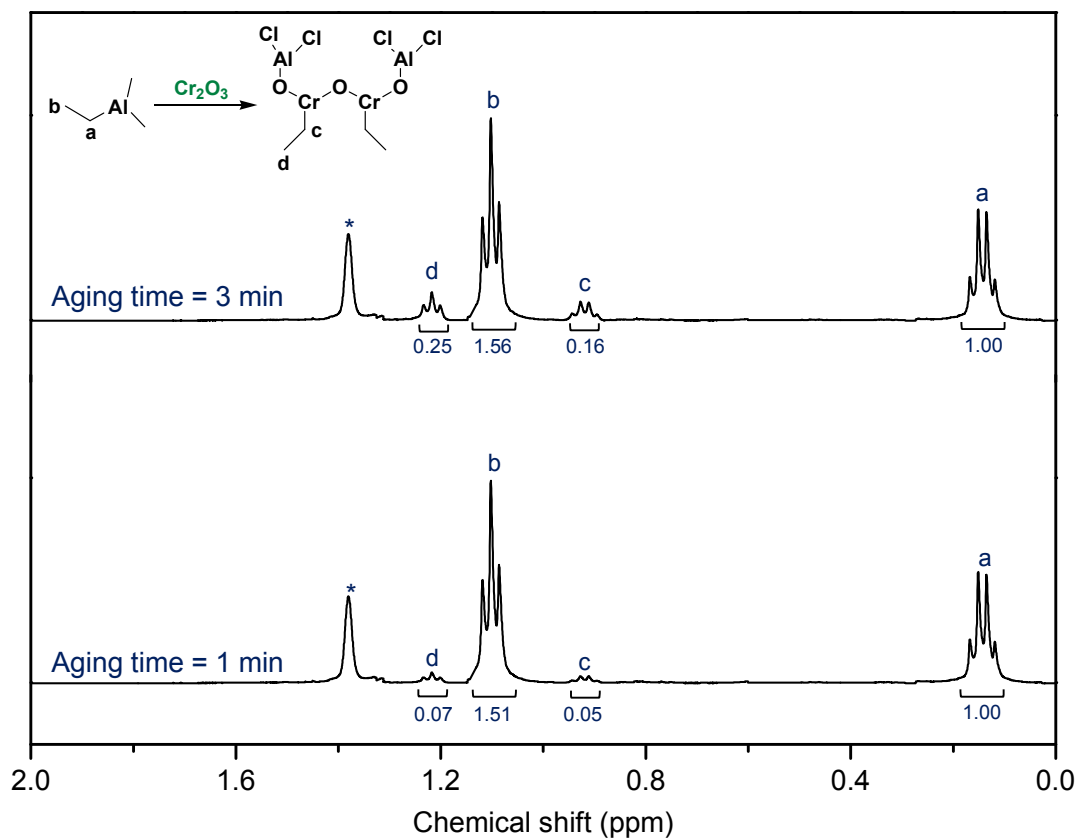


Figure S2. ^1H NMR spectra of the EADC after aging with Cr_2O_3 at different times. *: denote the cyclohexane- d_{11} H resonance.

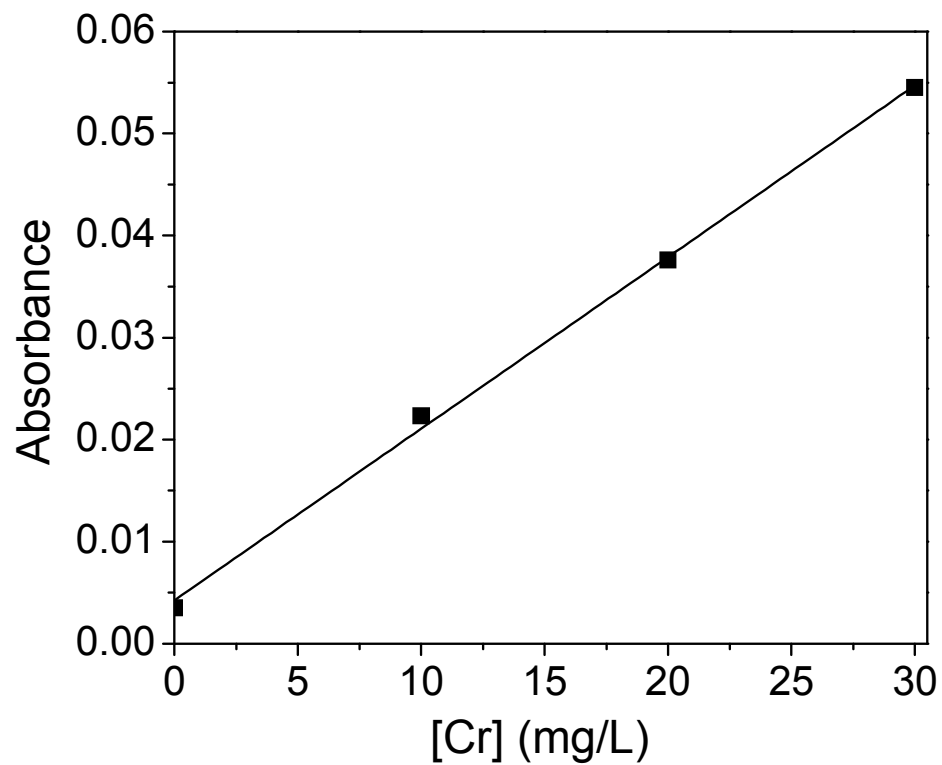


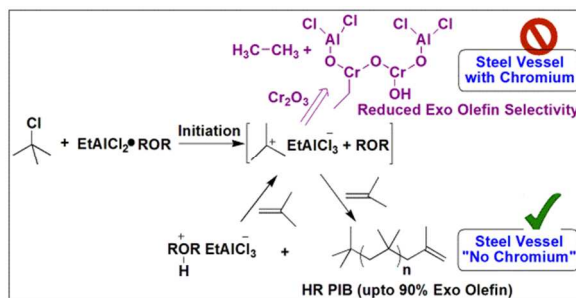
Figure S3. Calibration curve showing plot of absorbance vs Cr concentration obtained from the atomic absorption spectrometric estimation of Cr concentration of the standard Cr solution.

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Stainless steel reactors are unsuitable for polymerizations catalyzed by EtAlCl_2 due to a side reaction between Cr_2O_3 in stainless steel and EtAlCl_2 .



Polymerization of Isobutylene Catalyzed by EtAlCl₂/Bis(2-chloroethyl) Ether Complex in Steel Vessels

Sanjib Banerjee,[†] Jack Emert,[‡] Peter Wright,[‡] Thomas Skourlis,[‡] Rich Severt[‡] and Rudolf Faust^{*,†}

[†]Department of Chemistry, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854, United States

[‡]Infinium USA, 1900 E. Linden Avenue, Linden, New Jersey 07036, United States

Abstract: When synthesis of highly reactive polyisobutylene (HR PIB) via cationic polymerization of isobutylene (IB) using ethylaluminum dichloride•bis(2-chloroethyl) ether (EADC•CEE) complex were carried out in metal reactors made of 316 stainless steel (SS), PIB olefin with up to 20% lower exo-olefin content were obtained compared to that obtained in glass reactors (upto 90%). In an effort to investigate this reduction in exo-olefin selectivity in SS reactors, we have studied the polymerization of IB using EADC•CEE complex in SS (minimum of 10.5% chromium content by mass), carbon steel (CS) (0% chromium content by mass), monel alloy 400 (M400) (0% chromium content by mass) and glass reactors. The latter was examined in the presence and absence of SS balls. Mechanistic studies using ATR-FTIR and ¹H NMR spectroscopy suggest that this decrease in exo-olefin selectivity is due to a side reaction of EADC with Cr₂O₃ involving the loss of the ethyl group from EADC and decomplexation of the EADC•CEE complex which hinders the selective abstraction of the β-proton from the growing chain end. In the absence of chromium (CS and M400 reactors), the exo-olefin content is

virtually identical to that obtained in glass reactors. Therefore, CS and M400 reactors are suitable to produce HR PIB with high exo-olefin content.

Introduction

Polyisobutylene (PIB)-based ashless dispersants are important motor oil and fuel additives with worldwide production in excess of 750, 000 tons per year. These dispersants are low molecular weight ($M_n \sim 500\text{--}5000 \text{ g mol}^{-1}$), oil-soluble surfactants with oligoamine end groups obtained from PIB or polybutenes (copolymers of IB with C4 olefins) with olefinic end groups.^{1,2} The precursor low molecular weight IB homo and/or copolymers with terminal olefin functionality are generally produced by two major industrial methods. The “conventional” method which uses a C4 olefin mixture and AlCl_3 or EtAlCl_2 based catalyst systems produces polybutenes with ~70% tri- and ~20% tetra-substituted olefin functionality.³⁻⁵ Due to the low reactivity of the tri- and tetra-substituted olefinic end groups, polybutenes have to be chlorinated and dehydrochlorinated before reacting with maleic anhydride (MA) to produce polybutenyl succinic anhydride (PIBSA). The PIBSA is subsequently reacted with oligoalkylenimines to yield polybutenyl succinimide (PIBSI) ashless dispersants that may contain up to 5000 ppm chlorine. The other method produces highly reactive PIB (HR PIB) with up to 75–85% exo-olefinic end-group content via cationic polymerization of pure IB using BF_3 complexes with either alcohols or ethers as catalysts.¹ PIB with terminal exo-olefin functionality readily reacts with MA in a thermal ene reaction to produce PIBSA and subsequently PIBSI ashless dispersants. HR PIB is more desirable compared to polybutenes because it does not contain chlorine.

Since, BF_3 is difficult to handle, detrimental for industrial equipment and the polymerization requires low temperature to produce HR PIB, several methods have been developed in the recent past to obtain HR PIB. Vierle et al. employed Mn(II) complexes as initiators to produce HR PIB.⁶ Bochmann and coworkers employed a new Zn(II)-based initiator system to synthesize HR PIB at room temperature.⁷ Krossing's group employed novel univalent gallium salts such as $[\text{Ga}-(\text{C}_6\text{H}_5\text{F})_2]^+[\text{Al}(\text{ORF})_4]^-$ and $[\text{Ga}(1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_2]^+[\text{Al}(\text{ORF})_4]^-$ (where $\text{RF} = \text{C}(\text{CF}_3)_3$) to produce HR-PIB in several solvents.⁸ Voit and associates reported production of HR PIB using different M(II) complexes ($\text{M} = \text{Mn}, \text{Cu}, \text{Zn}, \text{Mo}$) as catalysts.⁹⁻¹¹ Storey and coworkers achieved synthesis of HR PIB by quenching of living PIB with dialkyl ether/base, dialkyl (or) diaryl sulfide/base or with hindered base.¹²⁻¹⁴ Developments of these catalyst systems are discussed in some excellent recent reviews.¹⁵⁻¹⁷ The most promising ones have been first reported independently by Kostjuk and coworkers employing 2-phenyl-2-propanol (CumOH) as the initiator with $\text{AlCl}_3 \bullet$ dibutyl ether complex as the catalyst^{18, 19} and Wu and coworkers employing H_2O as the initiator with $\text{AlCl}_3 \bullet$ diisopropyl ether ($i\text{-Pr}_2\text{O}$) and $\text{FeCl}_3 \bullet i\text{-Pr}_2\text{O}$ complexes as catalysts^{20, 21} producing HR PIB with exo-olefinic end-groups up to 90%. However, the use of a chlorinated solvent (dichloromethane) for the synthesis of HR PIB is the major drawback for these systems, since rates and exo-olefin contents decrease drastically with decreasing solvent polarity. Furthermore, simple alkyl halides such as *tert*-butyl chloride (*t*-BuCl) do not initiate the polymerization in conjunction with $\text{AlCl}_3 \bullet$ ether complexes. Our recent studies²² clarified that only adventitious H_2O initiates the polymerization of IB in conjunction with $\text{AlCl}_3 \bullet$ ether complexes.^{18, 19}

We reported an improved initiating system comprising conventional cationic initiators such as *t*-BuCl and GaCl_3 or $\text{FeCl}_3 \bullet$ ether complexes in nonpolar solvents to produce PIB with up

to ~85% exo-olefinic end group content and close to complete monomer conversion.²³ We also described the steric and electronic effects of the ether structures on the polymerization rates and exo-olefin content using FeCl_3 •ether complexes.²⁴ More recently, we reported that with *t*-BuCl as the initiator, soluble ethylaluminum dichloride•bis(2-chloroethyl) ether (EADC•CEE) complex catalyzes an even faster polymerization of IB in hexanes at 0 °C producing HR PIB with up to 90% exo-olefin content.²⁵

While all polymerizations reported above were carried out in glass reactors, large glass reactors are seldom used in industry. Instead glass lined and metal reactors or metal reactors without lining are employed. Stainless steel, a steel alloy with a minimum 10.5% chromium content, is frequently used to prevent corrosion. Since in preliminary experiments the EADC•CEE catalyst system produced PIB olefin with significantly lower exo-olefin content in stainless steel tubes, we undertook a systematic investigation of HR PIB synthesis in metal alloy reactors to uncover the origin of this effect and to find the most suitable composition for industrial application.

Experimental section

Materials.

Isobutylene (IB, Matheson Tri Gas) was dried in the gaseous state by passing it through in-line gas-purifier columns packed with BaO/Drierite and then condensed in a receiver flask at -30 °C before use. *Tert*-butyl chloride (*t*-BuCl, 98%, TCI America) was used as received. Ethylaluminum dichloride (EADC, 25.7 wt% solution in toluene), EADC (1.0 M solution in hexane), bis(2-chloroethyl) ether (CEE, 99%), chromium oxide (Cr_2O_3 , 99.9%), potassium hydroxide (KOH, 90%), sodium hydroxide (NaOH, ≥98%), sodium sulfate (Na_2SO_4), 2-propanol

(IPA, $\geq 99.5\%$), sodium acetate (NaOAc, 99%), ethylenediaminetetraacetic acid (EDTA, $\geq 98.5\%$) and dithizone (85%) were purchased from Aldrich and used without any further purification. Ammonium acetate (NH_4OAc) and zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) were purchased from Fisher Scientific and used as received. The 316 stainless steel precision balls, 1/16" diameter (McMaster-Carr) were washed with hexanes and dried in a vacuum oven.

Hexanes, mixture of isomers (Hex, Sigma-Aldrich, $\geq 98.5\%$, ACS reagent), was purified by refluxing over concentrated sulfuric acid for 48 h. It was then washed with aqueous solution of KOH (10 wt%) three times followed by washing with distilled water until neutral to pH paper. Then it was kept over anhydrous Na_2SO_4 overnight at room temperature and finally distilled over CaH_2 under a dry nitrogen atmosphere twice before use in the polymerization.

Preparation of EADC•CEE Complexes.

Complexes of EADC and CEE were prepared just before the polymerization of IB. Inside a glove box, the required amount of CEE was added to EADC and vortexed to form a 1.0 M Lewis acid/ether complex. It was then diluted with an appropriate amount of hexane to form a 0.1 M Lewis acid/ether complex.

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 were co-initiated with *t*-BuCl and EADC•CEE complex at a monomer concentration of $[\text{IB}] = 1.0\text{ M}$ in hexanes at $0\text{ }^\circ\text{C}$ and terminated with either NH_4OH or MeOH. Monomer conversions were determined gravimetrically.

Determination of Al Content of EADC after interaction with SS.

Typically, 0.1 M EADC solution was prepared in dry hexanes inside the glove box. 1.1 mL of this solution was transferred to a sealed SS reactor and aged for 5 min. After this, 1 mL of this aged EADC solution was taken up in a 20 mL sealed vial using a gas tight syringe. For comparison, in another vial, 1 mL of the fresh 0.1 M EADC solution was placed. The vials were taken out of the glove box and EADC was dissolved in de-ionized water by adding dilute HCl and by refluxing. The solutions were allowed to cool to room temperature. 15 mL of the standardized 0.05 M of EDTA solution was added into the beaker containing the decomposed EADC solution. The solution was diluted with 50 mL of de-ionized water. The pH was adjusted to 5 with dilute NaOH. 10 mL of sodium acetate buffer was added to the solution, refluxed for 3 minutes and allowed to cool to room temperature. Then 10 mL of ammonium acetate, 75 mL of 2-propanol and 1 mL of dithizone indicator solution were added. The solutions were titrated against a standard 0.02 M ZnSO₄ solution to a pink end point to give the concentration of Al.

Characterization.

Size Exclusion Chromatography (SEC) Measurements. The absolute number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the purified polymers were measured by SEC using a Waters model 717 Plus autosampler, a model 515 HPLC pump, a model 2410 differential refractometer, a model 2487 UV-vis detector, an on-line multiangle laser light scattering (MALLS) detector (MiniDawn, Wyatt Technology Inc.) (measurement angles are 44.7°, 90.0°, and 135.4°), an online differential viscometer (ViscoStar, Wyatt Technology Inc.), and five Styragel HR SEC columns connected in the following order of pore diameters: 500, 10³, 10⁴, 10⁵, and 100 Å. RI was the concentration detector. THF was used as the

eluent at a flow rate of 1.0 mL min^{-1} at room temperature. The results were processed by the Astra 5.3.4 software (Wyatt Technology Inc.).

Nuclear Magnetic Resonance (NMR) Spectroscopy. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker 500 MHz spectrometer using CDCl_3 or cyclohexane- d_{12} as solvents (Cambridge Isotope Laboratory, Inc.). A typical ^1H NMR spectrum of a representative HR PIB sample obtained in this study is shown in Figure 1. The two protons

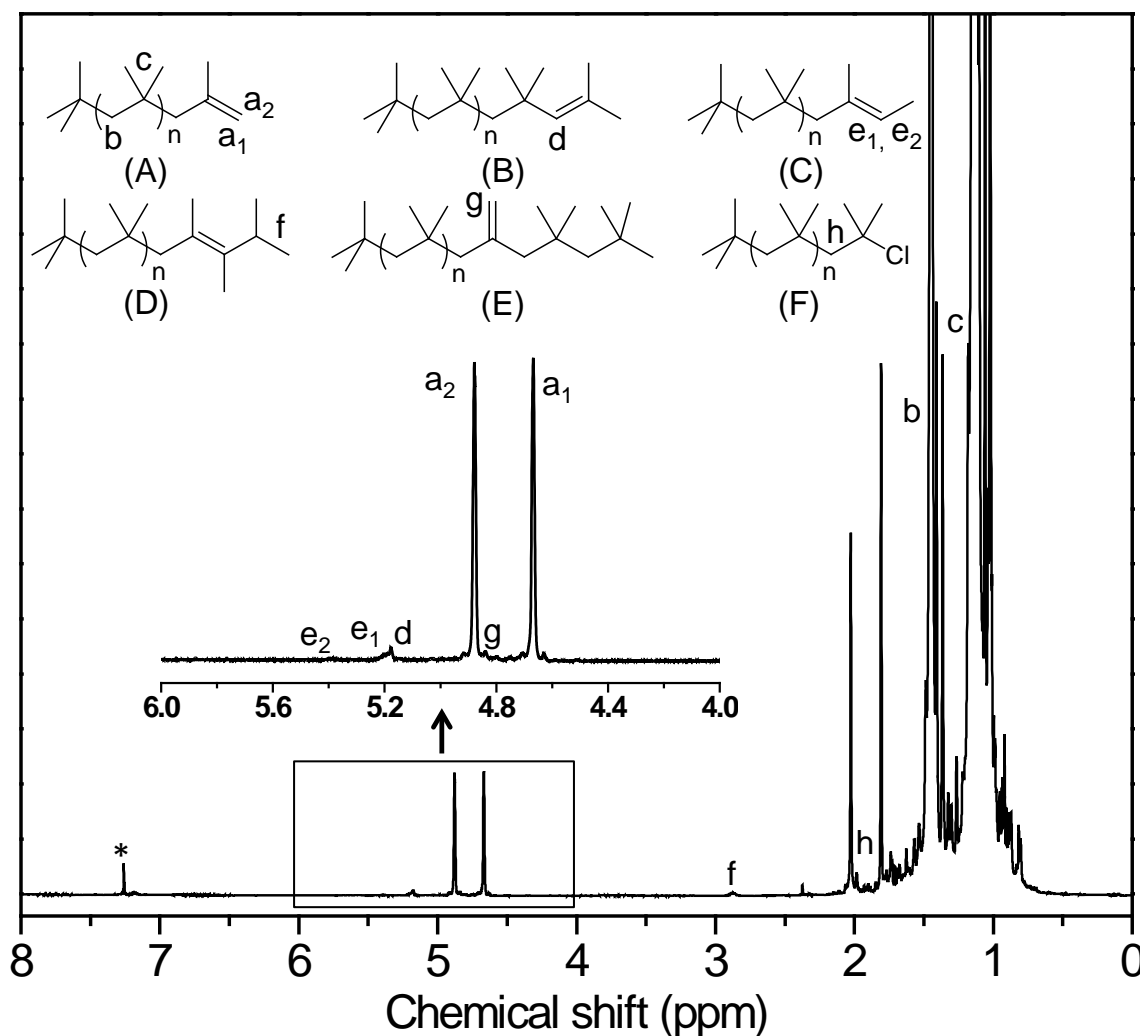


Figure 1. Typical ^1H NMR spectrum of HR PIB obtained in this study. *: denote the CHCl_3 resonance.

characteristic of the exo-olefin end group (Structure A, protons a_1 and a_2) appear as two well resolved peaks at 4.85 and 4.64 ppm, while the endo-olefin end group (Structure B, proton d) appears as a single peak at 5.15 ppm. Small amounts of the *E* and *Z* configurations of another tri-substituted olefin end group (Structure C, protons e_1 and e_2) could also be noticed in some samples at 5.37 and 5.17 ppm. The signal corresponding to the tetra-substituted olefin end group (Structure D, proton f) appears as a broad multiplet at 2.85 ppm. Resonances for coupled PIB chains (Structure E, protons g) normally appear at 4.82 ppm. The methylene protons in the PIBCl end group (Structure F, protons h) which appear at 1.96 ppm were used to calculate the content of PIBCl in the HR PIB. The methylene and methyl protons of the IB repeat unit (Structure A, protons b and c , respectively) appeared at 1.42 and 1.11 ppm, respectively. The number average molecular weights of the HR PIB were determined from ^1H NMR spectroscopic study ($M_{n,\text{NMR}}$) by using the following formula

$$M_{n,\text{NMR}} = 56.11 \times [(b/2)/\{(a_1 + a_2)/2 + d + e_1 + e_2 + f + (g/2) + (h/2)\}]$$

where 56.11 is the molecular weight of IB, and a_1 , a_2 , b , c , d , e_1 , e_2 , f , g , h represents the area corresponding to the respective protons as designated in Figure 1.

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR). ATR-FTIR spectra were taken using a Mettler Toledo React IR 4000 instrument equipped with a DiComp probe connected to an MCT detector with a K6 conduit in the spectral range from 4000 to 650 cm^{-1} at a resolution of 2 cm^{-1} .

Atomic Absorption Spectroscopy (AAS). An Agilent 200 series model 240 AA flame atomic absorption spectrometer was used as a detector. A chromium hollow cathode lamp was used as light source operated at 7 mA. The wavelength was set at 357.9 nm resonance line and the slit at 0.2 nm. The flame type was air/acetylene with air flow rate of 3.50 L min^{-1} and acetylene flow

1.50 L min⁻¹. Signals were recorded for 10 s, and the results were processed by the Agilent's innovative AA worksheet software (version 5.2).

Results and discussion

Effect of Metal on the Polymerization of IB with EADC•CEE Complexes in Hexanes.

A series of experiments were carried out in 316 stainless steel (SS) (minimum of 10.5% chromium content by mass), carbon steel (CS) (0% chromium content by mass) and monel alloy 400 (M400) (0% chromium content by mass) reactors in hexanes at 0 °C at [CEE]/[EADC] = 1.5 and [CEE]/[EADC] = 1.0 and the results were compared with experiments performed in a glass reactor (G) with and without SS balls.

According to Table 1, the exo-olefin content of PIB obtained in a SS reactor at [CEE]/[EADC] = 1.5 is independent of the polymerization time but low (~60%) compared to that obtained in a G reactor (~83%) (please compare Entries 2-5 with Entry 1 in Table 1). In addition, the rate of the polymerization is somewhat lower in a SS reactor compared to a G reactor.

Table 1. Polymerization of [IB] = 1.0 M using [EADC•CEE] = 0.01 M and [*t*-BuCl] = 0.01 M in hexanes at 0 °C at [CEE]/[EADC] = 1.5.

#	Reactor	Time (min)	Conv. ^a (%)	<i>M</i> _{n,NMR} ^b (g/mol)	<i>M</i> _{n,SEC} ^c (g/mol)	PDI ^c	Exo ^d (%)	Tri+ Endo ^d (%)	Tetra ^d (%)	PIB Coupled ^d (%)
1	G	20	91	1200	1400	3.5	83.3	9.2	6.7	0.8
2	SS	5	18	2900	2600	3.2	57.5	30.5	10.5	1.5
3	SS	10	45	2100	2200	3.3	58.9	27.6	12.2	1.3
4	SS	20	75	1300	1200	3.5	60.0	22.8	15.6	1.6

5	SS	40	77	1100	1300	3.1	61.7	21.6	16.0	0.7
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^aDetermined gravimetrically based on monomer feed; ^bDetermined from NMR analysis;

^cObtained from SEC measurements; ^dCalculated from NMR spectroscopic study.

We also performed polymerizations in a G reactor in the presence of SS balls at [CEE]/[EADC] = 1.5 and the results are compiled in Table 2. With the increase in number of SS balls from 100 to 1000 (i.e. increase in SS surface area), the exo-olefin content decreased from 72% to 62%, compared to 83% in the absence of any SS balls (please compare Entries 1-3 in Table 2 with Entry 1 in Table 1). The exo-olefin content obtained in a G reactor in the presence of 1000 SS balls was similar to that obtained in a SS reactor (please compare Entry 3 in Table 2 with Entry 4 in Table 1). This is attributed to the similar surface area calculated for the 1000 SS balls and the SS reactor. To investigate whether the EADC•CEE complex interacts with the stainless steel surface, we aged the complex in G vials in the presence of SS balls and then performed the polymerization with the aged complex in a G reactor in the absence of SS balls. This polymerization gave identical conversion and exo-olefin content compared to polymerizations carried out in the presence of SS balls (please compare Entries 4 and 5 vs 2 and 3 in Table 2). Thus, we conclude that the EADC•CEE complex interacts with the surface of SS which results in a less effective catalyst.

Table 2. Polymerization of [IB] = 1.0 M using [EADC•CEE] = 0.01 M and [*t*-BuCl] = 0.01 M in hexanes at 0 °C at [CEE]/[EADC] = 1.5.

#	Reactor	Time (min)	Conv. ^a (%)	$M_{n,NMR}$ ^b (g/mol)	$M_{n,SEC}$ ^c (g/mol)	PDI ^c	Exo ^d (%)	Tri+ Endo ^d (%)	Tetra ^d (%)	PIB Coupled ^d (%)
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1	G + 100 SS balls	20	82	2800	3000	3.6	72.5	15.2	9.4	2.9
2	G + 500 SS balls	20	78	2900	2600	3.2	68.9	17.9	10.3	2.9
3	G + 1000 SS balls	20	74	1700	1800	3.4	61.9	21.1	13.6	3.4
4	G + complex aged with 500 SS balls ^e	20	80	2300	2100	3.2	70.7	18.4	8.5	2.4
5	G + complex aged with 1000 SS balls ^e	20	74	2000	2100	3.5	62.1	24.8	11.8	1.3
6	G + complex aged in SS ^e	20	73	2200	1900	3.6	64.1	20.5	11.5	3.9
7	G + EADC aged in SS ^e	20	71	1900	1800	3.4	64.9	22.7	11.0	1.4
8	G + complex aged in SS ^f	20	71	1700	1800	3.5	62.3	23.7	12.5	1.5
9	G + EADC aged in	20	70	1900	1700	3.6	64.1	23.7	10.9	1.3

SS ^f										
10	SS reactor	20	0	-	-	-	-	-	-	-
	after									
	decanting									
	the									
	complex									

^aDetermined gravimetrically based on monomer feed; ^bDetermined from NMR analysis;

^cObtained from SEC measurements; ^dCalculated from NMR spectroscopic study; ^eAging time = 5 min; ^fAging time = 20 min.

Similar conversions and exo-olefin contents were obtained when the polymerizations were carried out in a G reactor and the EADC•CEE complex or EADC solution (which was then used to prepare the EADC•CEE complex) were aged in a SS reactor prior to polymerization (please compare Entries 6-9 in Table 2). The results were also independent of aging time, as aging for 5 min and 20 min resulted in similar exo-olefin content 62-64%. To examine whether any active catalyst is adsorbed on the walls of the SS reactor, we aged the EADC•CEE complex in the SS reactor for 5 min, and then took the entire complex solution out of the sealed SS reactor using a gas tight syringe and added the required amount of hexanes, *t*-BuCl and IB to this SS reactor and carried out the polymerization for 20 min (please see Entry 10 in Table 2). Polymerization was absent indicating that no active catalyst was adsorbed on the walls of the SS reactor. The identical Al content of the solution before and after contact with stainless steel also confirmed this (please see the Experimental Section for the detailed procedure for the determination of Al content and Table S1 in the Electronic Supplementary Information for the result).

Stainless steels does not rust since chromium forms a continuous film of chromium (III) oxide strongly bound to the surface, which prevents further surface corrosion by blocking the diffusion of oxygen. Therefore it is rational to assume that the interaction between chromium oxide and EADC yields a less effective catalyst. For comparison, polymerizations were also performed at $[CEE]/[EADC] = 1.5$ in CS and M400 reactors. These alloys do not contain any chromium. Importantly, in these reactors the products exhibited similar exo-olefin content (~77-81%) to that obtained in a G reactor (~83%) (please compare Entries 1-2 and 5-8 in Table 3 with Entry 1 in Table 1). Similarly, aging of the complex EADC•CEE or EADC solution (which was used subsequently to prepare the EADC•CEE complex) in CS and M400 reactors did not affect the conversions or exo-olefin content (please compare Entries 3-4 and 9 in Table 3 with Entry 1 in Table 1).

Table 3. Polymerization of $[IB] = 1.0$ M using $[EADC\bullet CEE] = 0.01$ M and $[t\text{-BuCl}] = 0.01$ M in hexanes at 0°C at $[CEE]/[EADC] = 1.5$.

#	Reactor	Time (min)	Conv. ^a (%)	$M_{n,NMR}$ ^b (g/mol)	$M_{n,SEC}$ ^c (g/mol)	PDI ^c	Exo ^d (%)	Tri+ Endo ^d (%)	Tetra ^d (%)	PIB Coupled ^d (%)
1	CS	10	54	1800	1500	3.7	77.2	10.8	10.8	1.2
2	CS	20	85	1600	1300	3.8	77.5	10.9	7.8	3.8
3	G + complex aged in CS ^e	20	84	1400	1600	3.7	78.7	11.0	7.9	2.4
4	G + EADC aged in CS ^e	20	82	1500	1400	3.6	75.2	11.3	9.8	3.7

5	M400	2	8	2300	2500	3.6	76.9	14.6	5.4	3.1
6	M400	5	23	2200	2300	3.7	78.4	11.0	9.4	1.2
7	M400	10	51	1500	1600	3.5	76.0	15.2	7.6	1.2
8	M400	20	82	1400	1500	3.4	80.9	9.7	6.5	2.9
9	G + complex aged in M400 ^e	20	80	1450	1600	3.6	80.3	9.6	7.2	2.9

^aDetermined gravimetrically based on monomer feed; ^bDetermined from NMR analysis;

^cObtained from SEC measurements; ^dCalculated from NMR spectroscopic study; ^eAging time = 5 min.

Limited experiments were also performed using $[CEE]/[EADC] = 1.0$ to confirm the effect of SS on the exo-olefin selectivity. Results were similar to those observed using $[CEE]/[EADC] = 1.5$. The exo-olefin content of the PIB obtained in a SS reactor was lower (~55%) compared to that obtained in a G reactor (~70%) and it was independent of the polymerization time (please compare Entries 2-4 with Entry 1 in Table 4). Aging the complex EADC•CEE or EADC solution (which was used subsequently to prepare the EADC•CEE complex) also resulted in low exo-olefin content ~50% (please compare Entries 5-8 with Entry 1 in Table 4).

Table 4. Polymerization of $[IB] = 1.0$ M using $[EADC\bullet CEE] = 0.01$ M and $[t\text{-BuCl}] = 0.01$ M in hexanes at 0 °C at $[CEE]/[EADC] = 1.0$.

#	Reactor	Time (min)	Conv. ^a (%)	$M_{n,NMR}$ ^b (g/mol)	$M_{n,SEC}$ ^c (g/mol)	PDI ^c	Exo ^d (%)	Tri+ Endo ^d (%)	Tetra ^d (%)	PIB Coupled ^d (%)
1	G	20	100	2800	2500	3.4	69.9	16.1	13.3	0.7

2	SS	10	62	3600	3800	3.5	53.7	23.7	21.0	1.6
3	SS	20	83	3500	3300	3.1	53.2	28.7	17.6	0.5
4	SS	40	88	3500	3600	3.2	55.4	18.8	23.8	2.0
5	G + complex aged in SS ^e	20	82	2850	3000	3.6	50.1	29.6	19.0	1.3
6	G + EADC aged in SS ^e	20	80	3100	3200	3.7	51.4	27.2	20.1	1.3
7	G + complex aged in SS ^f	20	81	2700	3000	3.7	49.0	27.9	22.1	1.0
8	G + EADC aged in SS ^f	20	80	2600	2800	3.8	48.3	28.5	22.2	1.0

^aDetermined gravimetrically based on monomer feed; ^bDetermined from NMR analysis;

^cObtained from SEC measurements; ^dCalculated from NMR spectroscopic study; ^eAging time = 5 min; ^fAging time = 20 min.

In contrast polymerizations performed in CS and M400 reactors at [CEE]/[EADC] = 1.0 (Table 5) gave similar exo-olefin content (~70%) to that obtained in a G reactor (~70%) (please compare Entries 1-2 and 5 in Table 5 with Entry 1 in Table 4). Aging the complex EADC•CEE or EADC solutions (which was used subsequently to prepare the EADC•CEE complex) had no effect (Entries 3-4 and 6 in Table 5).

Table 5. Polymerization of [IB] = 1.0 M using [EADC•CEE] = 0.01 M and [*t*-BuCl] = 0.01 M in hexanes at 0 °C at [CEE]/[EADC] = 1.0.

#	Reactor	Time (min)	Conv. ^a (%)	$M_{n,NMR}$ ^b (g/mol)	$M_{n,SEC}$ ^c (g/mol)	PDI ^c	Exo ^d (%)	Tri+ Endo ^d (%)	Tetra ^d (%)	PIB Coupled ^d (%)
1	CS	10	71	2900	2700	3.3	68.9	16.6	12.4	2.1
2	CS	20	92	2400	2500	3.5	69.6	18.1	10.5	1.8
3	G + complex aged in CS ^e	20	90	2400	2500	3.6	67.3	17.5	12.8	2.4
4	G + EADC aged in CS ^e	20	88	2700	2600	3.5	66.2	20.5	11.9	1.4
5	M400	20	92	3100	2900	3.5	71.2	14.9	12.1	1.8
6	G + complex aged in M400 ^e	20	91	3000	3100	3.6	70.4	16.9	11.3	1.4

^aDetermined gravimetrically based on monomer feed; ^bDetermined from NMR analysis;

^cObtained from SEC measurements; ^dCalculated from NMR spectroscopic study; ^eAging time = 5 min.

ATR-FTIR Spectroscopy.

The polymerization results discussed in Table 1-5 suggested that some side reaction is taking place with chromium (III) oxide (present as a passive layer in stainless steel to prevent corrosion), which decreases the exo-olefin selectivity of the produced PIB olefin. Thus, to

understand the interaction, the ATR-FTIR spectrum of the $[CEE]/[EADC] = 1$ complex in a G reactor, was compared to those of the complexes aged for 5 min in a SS reactor or in a G reactor in the presence of 1000 SS balls (Figure 2).

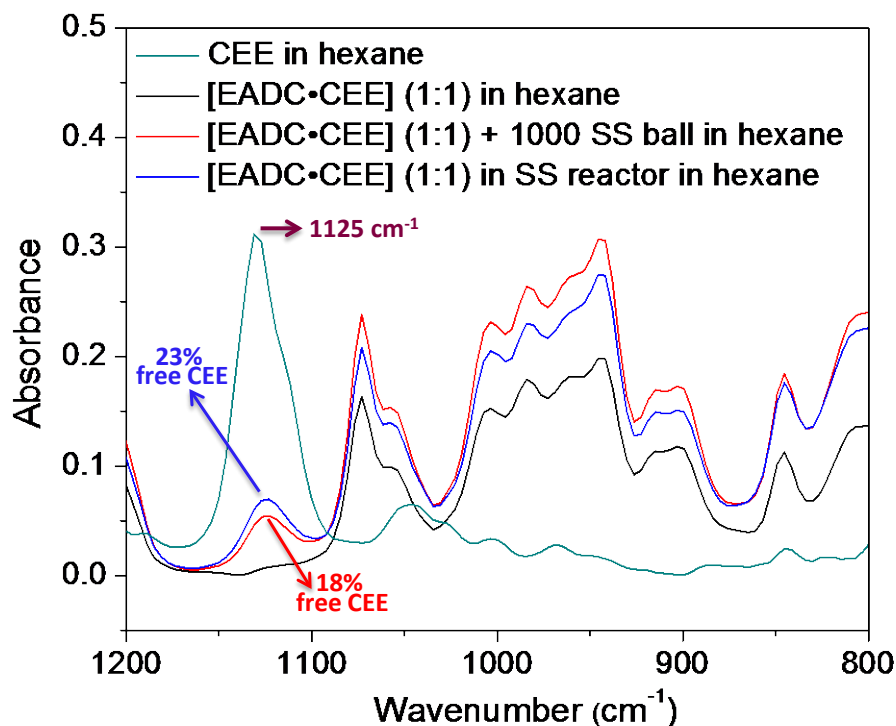


Figure 2. ATR FTIR spectroscopic analysis of the effect of SS on EADC:CEE (1:1) complex.

We reported earlier that EADC and CEE forms a 1:1 complex and free ether is absent.²⁵ This is shown in Figure 2 by the absence of a peak at 1125 cm^{-1} . After aging the complex with SS, the free ether peak is clearly visible. Comparing it to the peak height of CEE alone at 1125 cm^{-1} , the amount of free ether is 23% and 18% after aging for 5 min in a SS reactor and in a G reactor in the presence of 1000 SS balls, respectively. In order to determine how fast this decomplexation is, we aged the complex in SS reactor for lower time. The amount of free ether after aging the complex for 1 min and 3 min in the SS reactor were 7 and 17%, respectively (Figure S1).

^1H NMR Spectroscopy.

The ^1H NMR spectra of the $[\text{CEE}]/[\text{EADC}] = 1.0$ complex and the complex aged for 5 min in SS reactor are shown on Figure 3. Comparing the integrations of the peaks corresponding to EADC at 0.15 ppm ($-\text{CH}_2$) and 1.1 ppm ($-\text{CH}_3$) with that of CEE at 3.8 ppm, the extent of decomposition of EADC was determined to be $\sim 22\%$. This result is in agreement with the ATR-FTIR analysis (Figure 2) which suggests $\sim 23\%$ free ether after aging for 5 min in a SS reactor.

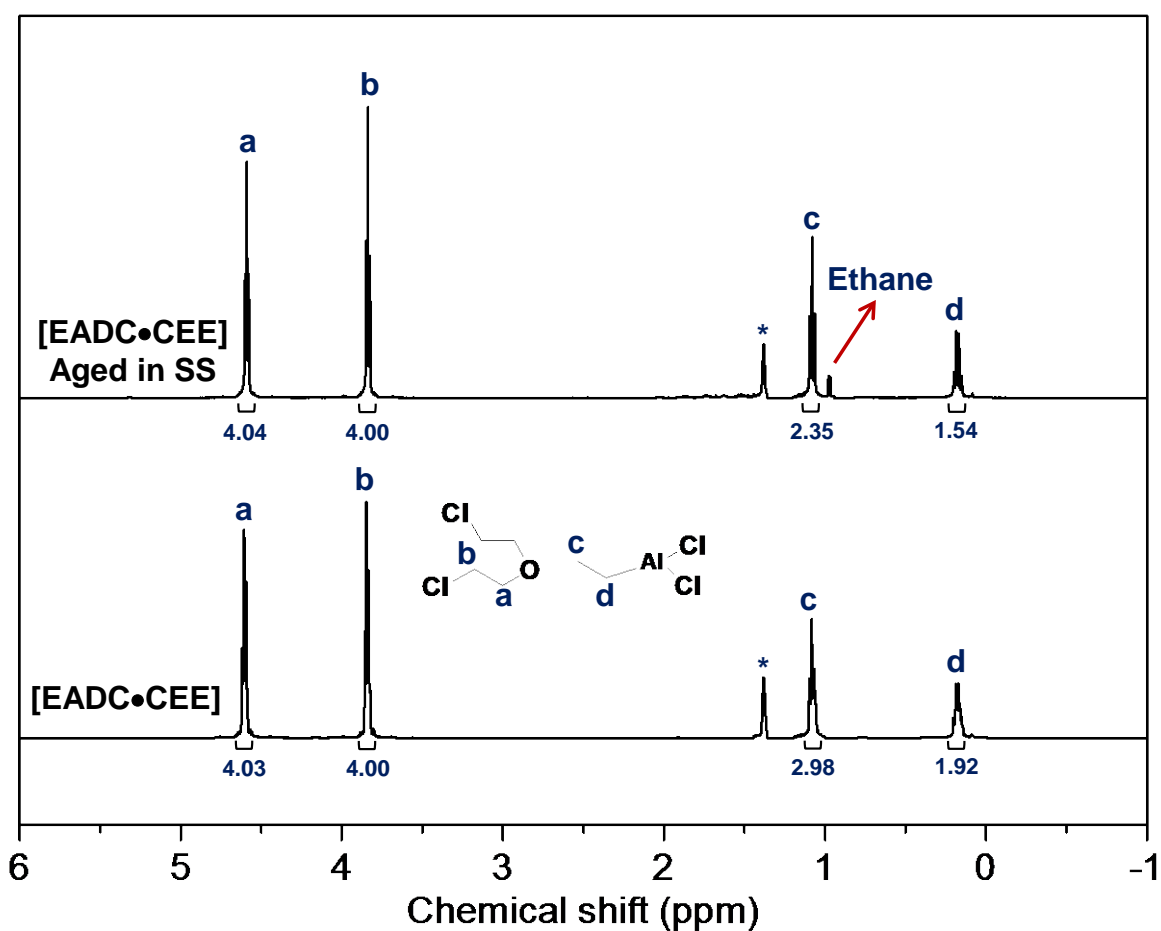


Figure 3. ^1H NMR spectra of the EADC:CEE (1:1) complex before and after aging in SS reactor. *: denote the cyclohexane- d_{11} H resonance.

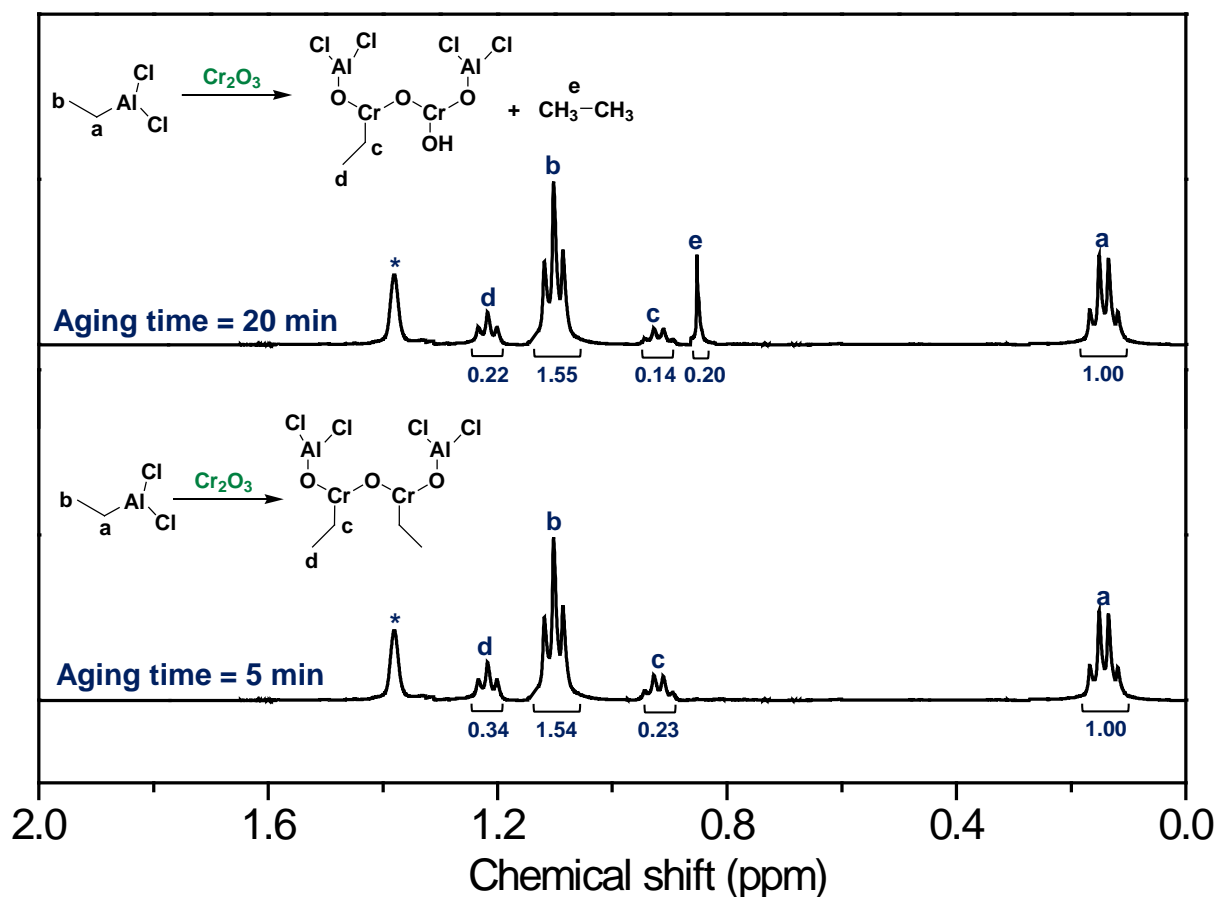


Figure 4. ^1H NMR spectra of the EADC after aging with Cr_2O_3 . *: denote the cyclohexane- $d_{11}\text{H}$ resonance.

To confirm the reaction between EADC and Cr_2O_3 , EADC was mixed with Cr_2O_3 and the ^1H NMR spectra were recorded after 5 min and 20 min of aging (Figure 4). After 5 min, new peaks appear at 0.91 and 1.21 ppm with an integration ratio of 2/3. We postulate that these two peaks are due to the formation of an ethyl group bonded to Cr. After 20 min of aging, an additional peak at 0.85 ppm appeared. This new peak is attributed to ethane formed by the reaction of ethyl-Cr with traces of moisture. Comparing the integrations of the peaks corresponding to EADC at 0.15 ppm ($-\text{CH}_2$) and 1.15 ppm ($-\text{CH}_3$) with that of the ethyl group at 0.91 and 1.21 ppm and ethane at 0.85 ppm, the extent of decomposition of EADC was

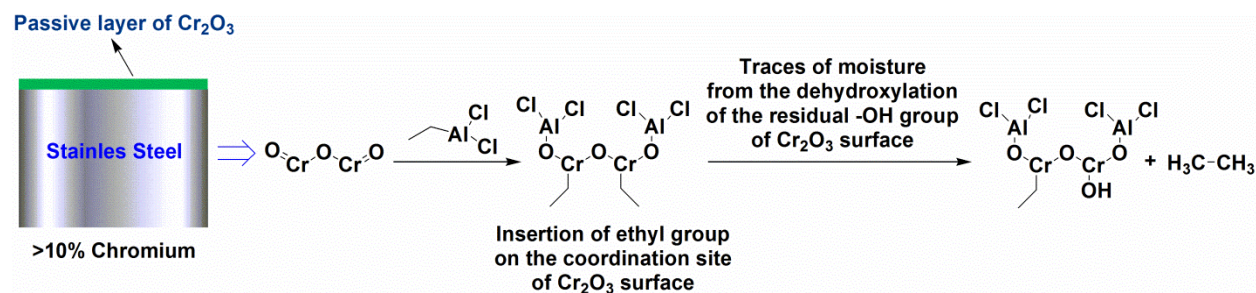
determined to be ~22%. In order to understand how fast this decomposition is, we aged EADC with Cr_2O_3 for lower time than 5 min. We found that the extent of decomposition of EADC after aging for 1 min and 3 min with Cr_2O_3 are 5 and 16%, respectively (Figure S2).

Determination of Cr content in solution after aging EADC in SS Reactor by Atomic Absorption Spectroscopy.

To confirm the presence of Cr in the soluble complex metallic compounds with alkyl-chromium bonds formed by the reaction between EADC and Cr_2O_3 in the SS reactor, EADC was aged in the SS reactor. Then, the Cr content in the solution was determined by atomic absorption spectroscopy (see Figure S3 for the calibration curve and Page S3 in the Electronic Supplementary Information for the detailed procedure and calculation). Result suggests 19% soluble Cr complex formation in the solution after aging EADC in SS reactor, which is consistent with ATR-FTIR (Figure 2) and ^1H NMR (Figure 3-4) spectroscopic results.

Proposed Mechanism.

Based on these results, we propose the mechanism presented in Scheme 1. Interaction of Cr_2O_3 with EADC•CEE results in decomplexation followed by alkylation and Cr-carbon bond formation, similar to that observed in the activation of Philips $\text{CrO}_x/\text{SiO}_2$ catalyst by alkyl aluminum compounds.²⁶



Scheme 1. Schematic representation of the decomposition of EADC in presence of Cr_2O_3 .

Conclusion

EADC or EADC•CEE complex catalysts should not be used in stainless steel reactors having large surface area. The Cr_2O_3 layer, which prevents the corrosion of the steel, readily reacts with EADC to yield soluble complex metallic compounds with alkyl-chromium bonds. These are strong Lewis acids themselves that could catalyze conventional polymerization and the reacted EADC is no longer complexed with CEE. Therefore, the polymerization of IB in stainless steel reactors with large surface area yields PIB olefin with much lower exo-olefin content compared to that obtained in a glass reactor. Reaction vessels not containing chromium (carbon steel, monel) can be used to produce HR PIB with high exo-olefin content.

Corresponding Author

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

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Electronic Supplementary Information (ESI): Procedure for standardization of EDTA and estimation of Cr content; Table containing the estimated value of Al content of EADC before and after aging in SS reactor; ATR-FTIR spectra showing effect of aging EADC•CEE complex in SS reactor; ^1H NMR spectra showing effect of aging EADC in SS reactor; calibration curve

for Cr estimation using AAS. This material is available free of charge via the Internet at <http://pubs.rsc.org>.

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Table of contents entry

Polymerization of Isobutylene Catalyzed by EtAlCl₂/Bis(2-chloroethyl) Ether Complex in Steel Vessels

Sanjib Banerjee, Jack Emert, Peter Wright, Thomas Skourlis, Rich Severt and Rudolf Faust*

Stainless steel reactors are unsuitable for polymerizations catalyzed by EtAlCl₂ due to a side reaction between Cr₂O₃ in stainless steel and EtAlCl₂.

