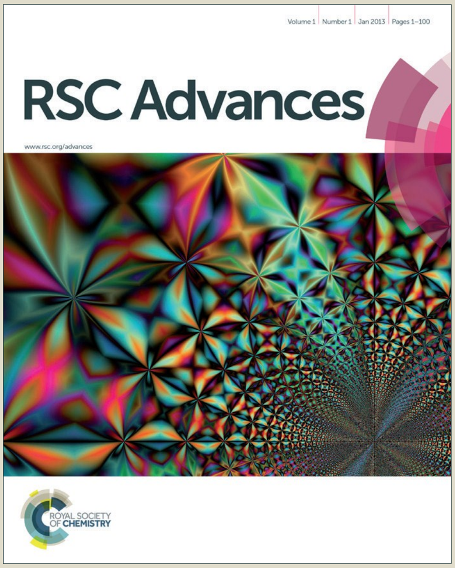
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

ARTICLE

Fast flow synthesis of highly reactive polyisobutylene coinitiated by $AlCl_3$/isopropyl ether complex

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

S. Zhu, Y. C. Lu,* K. Wang and G. S. Luo

In this work, with the $AlCl_3$ addition in the range from 4 to 10 mmol L^{-1} and enough isopropyl ether ($^iPr_2O$) addition, we successfully synthesized high reactivity polyisobutylene (HRPIB) using a micro-flow system within 12 s or less. The temperature window was extended from -20 ^oC to 50 ^oC, and the molecular weight (M_n) was adjustable between 500 to 15000. The evolutions of HRPIBs and the effects of reaction conditions were carefully investigated, revealing multiple effects of an excess of $^iPr_2O$ over $AlCl_3$ including: 1) decreasing the intensive isomerization coinitiated by free $AlCl_3$; 2) inhibiting the chain termination to present chain transfer dominated kinetics; 3) weakening the temperature sensitivity of M_n as a restriction on temperature elevation; 4) retarding the chain propagation to slow the reaction and increase the probability of isomerization. A key access to fast synthesis of high quality HRPIB is proposed to make a compromise of these effects by properly selecting $^iPr_2O:AlCl_3$.

Introduction

Polyisobutylenes (PIBs) have broad applications based on their merits in low gas permeability and chemical stability.[1-3] Because of strong isomerization tendency of protonated PIB before β-H abstraction, conventional PIBs, industrially produced using H_2O as initiator and $AlCl_3$ as coinitiator, have low content (<10 mol%) of *exo*-olefin end groups as well as low reactivity for further functionalization.[4-9] On the contrary, highly reactive polyisobutylenes (HRPIBs) are denoted as PIBs with high content of *exo*-olefin end groups ($\geq$60 mol%, preferably $\geq$75 mol%) and specific molecular weight distribution (M_n=500~5000)[10-12]. They draw many attentions from both industry and academia due to their usages as highly reactive intermediates for synthesizing additives to lubricants, fuels and rubbers, such as maleic anhydride modified PIBs[13,14].

Commercial HRPIBs can be produced by a single-step process *via* cationic polymerization of isobutylene (IB) in hexane using BF_3 complexes with either alcohols and/or ethers as initiating systems at temperatures far below 0 ^oC.[15-17] During last decades, several new methods have been reported to synthesize HRPIBs at elevated temperature to evade energy intensive process. For example, HRPIBs with M_n of 1400-7000 g mol^{-1} were prepared by using solvent-ligated complexes borate or aluminate $[M(NCMe)_6]^{2+}$ (M=Mn, Cu) at ambient temperatures, while long time required for high monomer conversion and high cost of initiating complex probably prevent their industrial acceptance.[18-20] Recently, Kostjuk and Wu independently reported HRPIB synthesis at moderate temperatures in CH_2Cl_2 or CH_2Cl_2-hexane mixture (80/20 v/v) *via* a cost-effective initiating system consisting of $AlCl_3$ with dialkyl ether, such as di-*n*-butyl ether (Bu_2O) and diisopropyl ether ($^iPr_2O$).[21-23] The adventitious water was regarded as initiator providing protons. In following, researchers investigated similar initiating systems consisting of various Lewis acids like $FeCl_3$, $TiCl_4$, $GaCl_3$ and alkylaluminum dichloride ($RAlCl_2$, R=Me, Et, ^iBu) and ethers like butyl methyl ether and ethyl ether, as to afford the adaptability of HRPIB synthesis to non-polar solvents like hexane and toluene or optimize ethers playing a key role in the selective β-H abstraction through electron donor effect. [24-36] As using non-polar solvents with low solubility of water, some initiators were also tested like cumyl alcohol, *tert*-butyl chloride and 1-chlorine-2,4,4-trimethyl pentane (TMPCl). Unfortunately, they usually show poor performance compared with chlorinated solvents in terms of the polydispersity index (PDI) of product.[37]

In most of reports with Lewis acids concentration in the range of 10 mmol L^{-1} to 40 mmol L^{-1}, considerable conversion could be reached within 2-3 minutes but 30 minutes or more were required for achieving a conversion platform or total conversion. Differently, we notice that $CumOH/AlCl_3OBu_2$ initiating system in CH_2Cl_2 could afford 60 % conversion at 3 min as high as that at 30 min and near 3 times of monomer conversion could be obtained with $H_2O/FeCl_3/^iPr_2O$ initiating system in CH_2Cl_2 under low concentration of $FeCl_3$ at 5 mmol L^{-1} compared with $H_2O/AlCl_3/Bu_2O$ initiating system. We envision fast synthesis of HRPIB within tens of seconds or less may be achievable under low concentration of $AlCl_3$ with acidity stronger than $FeCl_3$, as long the polymerization kinetics can benefit from the decrease of ether concentration accompanied with Lewis acid. The main challenge in decreasing the concentration of $AlCl_3$/ether complex and controlling an intensive HRPIB synthesis is how to realize effective mixing quickly

---

State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China.
Email: luyc@tsinghua.edu.cn

enough matching with fast reaction process. From this point of view, the microflow system, with the merits of perfect mixing and heat transfer performances and narrow residence time distribution, may be an idea platform.[38,39] Many polymerizations have been successfully carried out in the microflow reactor with improved product or process.[40-42]

In this work, with the $AlCl_3$ concentration in the range from 4 mmol L^{-1} to 10 mmol L^{-1} and enough $^iPr_2O$ addition, we firstly successfully synthesized HRPIB (PDI<1.9) with over 60 % monomer conversion at 20 °C after a 12 s stay in a microflow system. The evolutions of HRPIBs were measured at various molar ratios of $^iPr_2O$ to $AlCl_3$ to reveal the effects of free $^iPr_2O$ on active species initiating or deactivating. And then, we extended the temperature range for HRPIBs synthesis from -20 °C to 50 °C and found the depression effect of free $^iPr_2O$ on the temperature-sensitivity of M_n. Through adjusting the molar ratio of $^iPr_2O$ to $AlCl_3$ to assure smooth and distinct reaction within tens of seconds, we tailored M_n proportionally by varying monomer concentration with guarantee of good mixing conditions. Finally, we proposed a mechanism with respect to the generation and transformation of complex of $AlCl_3$ with $^iPr_2O$ for understanding and designing an easily controllable and fast synthesis for HRPIB with M_n in a broad range from 500 to 10000+.

Experimental

Materials

Dichloromethane (CH_2Cl_2, 99.9+%, anhydrous), isopropyl ether ($^iPr_2O$, 99.0+%), and aluminum chloride (AlCl3, 99+%, anhydrous) were purchased from J&K Scientific (China). Isobutylene (IB, 99.9+%, anhydrous) and ethanol (analytical reagent) were obtained from Korea Noble Gas (Korea) and Sinopharm Chemical (China), respectively. CH_2Cl_2 was dried over Molecular Sieves 5A overnight to decrease the content of water to about 7 ppm (determined by Coulometric Karl fischer moisture meter (METTLER TOLEDO, Switzerland)), and then kept in a sealed bottle before use. Isopropyl ether was distilled to remove stabilizer butylated hydroxytoluene (BHT), and then dried over Molecular Sieves 5A overnight. Isopropyl ether and $AlCl_3$ were preserved in a glovebox (MIKROUNA, China).

Preparation of catalytic complex solution

The catalytic complex solution, composed of $AlCl_3$, isopropyl ether ($^iPr_2O$), and CH_2Cl_2 as solvent, was prepared in a glovebox, shortly before experiments. In details, $AlCl_3$ and $^iPr_2O$ were quantitatively added into a dry bottle in sequence. And then, CH_2Cl_2 was poured into the bottle to obtain transparent solution. The content of $AlCl_3$ in the solution was determined by UV-Vis Spectrophotometer (UV-2450, SHIMADZU). It should be noted that most of the adventitious water, as initiator in the system, comes from the catalytic complex solution.

Polymerization of IB

The polymerization of IB was carried out in a microflow system composed of three T-shaped micromixers (**M1** for the mixing of IB and diluent, CH_2Cl_2), **M2** for the mixing of IB solution and catalytic complex solution, and **M3** for the injection of terminator agent, ethanol), two precooling (or preheating) coiled tubes (**C1** and **C2**, inner diameter 900 μm), and a microtube reactor (**R**, inner diameter 900 μm), as shown in Figure 1. The polymerization of IB proceeds throughout **R1**, and the reaction time could be changed by the flow rate and the length of **R1**. Three syringe pumps were used to deliver IB, CH_2Cl_2, and catalytic complex solution, respectively. IB transferred as vapour from cylinder was liquefied at -30 °C into the syringe and perfused under a pressure of about 3 bars. The additional CH_2Cl_2 was introduced to adjust IB concentration in the reaction system.

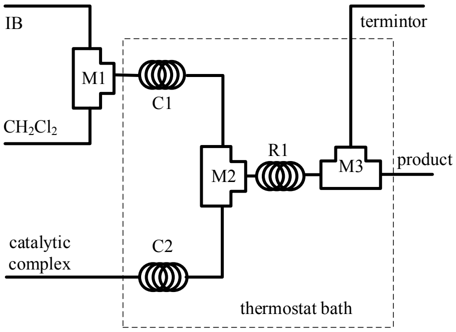


Fig 1. Schematic diagram of flow synthesis setup. M1, M2 and M3 are tees as micromixers; C1 and C2 are curved tubes for achieving the pre-set temperature; R1 is microtube as reactor.

Characterization

Molecular weight and dispersity of the polymers were measured by a Waters gel permeation chromatography (GPC) composed of a Waters 2707 auto sampler, a 1515 Isocratic HPLC pump, a 2414 refractive index detector and three GPC columns (the molecular weight could be detected from 500~4×10^6) placed in a 38 °C thermostat. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min. The instrument was calibrated with narrow molecular weight distribution polystyrene standards. The results were processed by the Breeze 2 software from Waters. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a JNM-ECA 600 MHz spectrometer using $CDCl_3$ as solvents.

Results and discussion

Feasibility of fast HRPIB synthesis

Exploiting relatively low $^iPr_2O$ and $AlCl_3$ concentrations (10 mmol L^{-1} or less), we firstly conducted the polymerization of IB at 20 °C with the residence time of 12 s to test the feasibility of fast HRPIB synthesis. The results listed in Table 1 can be classified into two groups. The first group, including entries 1 to 3, is featured that the $^iPr_2O$ concentration is clearly lower than the $AlCl_3$ concentration. In this group, the conventional PIBs containing mainly *endo*-, *tri*- or *tetra*-substituted double bonds were obtained, the polydispersity index (PDI) is around 5.0 or higher, and the conversion of monomers is kept at a high level (>80 %). It should be noticed that the concentration of $AlCl_3$, much higher than the concentration of adventitious water, is always far lower than the concentration of PIB, indicating the occurrence of intensive chain transfer process. The second group, including entries 4 and 5, is featured that the $^{i}Pr_2O$ concentration is close to or higher than the $AlCl_3$ concentration. The PIBs with a high *exo*-olefin group content (>70 %) and low PDI (<2.0) were obtained in this group, indicating a success in HPRIBs synthesis. With the increase of the $^{i}Pr_2O$ concentration, the conversion of monomers is still considerable but decreases to some extent. By comparison, the second group shows high and stable number-average molecular weight (M_n), but much weak chain transfer processes. Obviously, besides of regulating the end group distribution, the addition of $^{i}Pr_2O$ could decrease the conversion of monomers by reducing the chain propagation rate (related to PDI value) and the chain transfer rate.

Table 1. Polymerization of IB co-initiated by $AlCl_3 \times {}^{i}Pr_2O$ at various $^{i}Pr_2O$ and $AlCl_3$ concentrations in CH_2Cl_2[a]

entry	$^{i}Pr_2O$ (mmol L^{-1})	$AlCl_3$ (mmol L^{-1})	convn[b] (%)	M_n (g mol^{-1})	PDI	[PIB][c] (mmol L^{-1})	end groups distribution (mol%)		
							exo	*tri+endo*	*tetra*
1	1.4	4.1	81	880	5.8	38.7	9	50	41
2	3.6	6.0	83	890	6.0	39.1	10	50	40
3	8.6	10.0	85	1240	4.6	28.8	12	43	45
4	7.1	7.5	60	2180	1.9	11.5	76	12	12
5	10.7	8.1	50	2040	1.8	10.3	72	17	11

[a] $T = 20\,^{o}C$; $t = 12$ s; [IB] = 0.75 mol L^{-1}. [b] Gravimetric conversion. [c] [PIB] = [IP]×56×convn/M_n.

Figure 2 presents the ^{1}H NMR spectra of entry 1 and entry 4. Main resonance signals observed are located at δ = 1.1 (**z**), 1.41(**y**), 0.99 (**x**), 4.85 (**a1**), 4.64 (**a2**), 5.17 (**c1**), 5.37 (**c2**), and 2.83 (**e**).[43] Therein, the single peaks, **z** and **y** are assigned to $–CH_3$ and $–CH_2$ protons of the structural units along the main chain of PIB, respectively; the single peak, **x** is assigned to the protons in head groups of $–C(CH_3)_3$ in PIB chains; the single peaks, **a1** and **a2** in the expansion of olefin region, are assigned to the protons of *exo*-olefin end groups, $–CH_2–C(CH_3)=CH_2$; the quartet peaks, **c1** and **c2** are attributed to $–C(CH_3)=CH(CH_3)$ end groups in PIB chains; the single peak, **e** is assigned to the protons in $–CH(CH_3)_2$ end groups in PIB chains. Accordingly, most PIB chains generated in the experiments have structures **A**, **C**, or **E**, as presented in Figure 2. Compared with entry 1, structure **A** takes the majority instead of structures **C** and **E** in entry 4. Besides, the absence of the signals at 1.68 and 1.96 ppm in both of entries indicates that the PIB chains were free of *tert*-Cl terminal groups and the termination via chlorine transfer from counter anion did not take place during polymerization.[44]

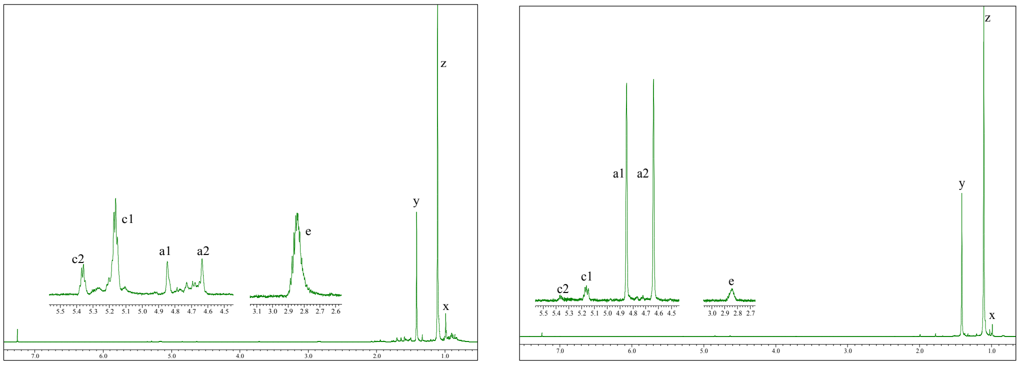


Fig 2. ^{1}H NMR spectra of selected PIBs from Table 1. (a) entry 1; (b) entry 4.

Figure 3 shows possible shifts and β-proton abstraction processes causing the formation of various structures. The structures **C** and **E** are formed by isomerization from the normal growing tertiary carbocation *via* carbenium ion rearrangements by hydride and/or methide shifts and followed proton or isopropyl elimination. For the synthesis of conventional PIBs, extensive hydride and/or methide shifts take place before β-proton abstraction to create large amount of byproducts containing internal unsaturated bonds. On the contrary, the sufficient addition of $^{i}Pr_2O$ seems to inhibit these shifts or enhance the β-proton abstraction to obtain HRPIBs.[9]

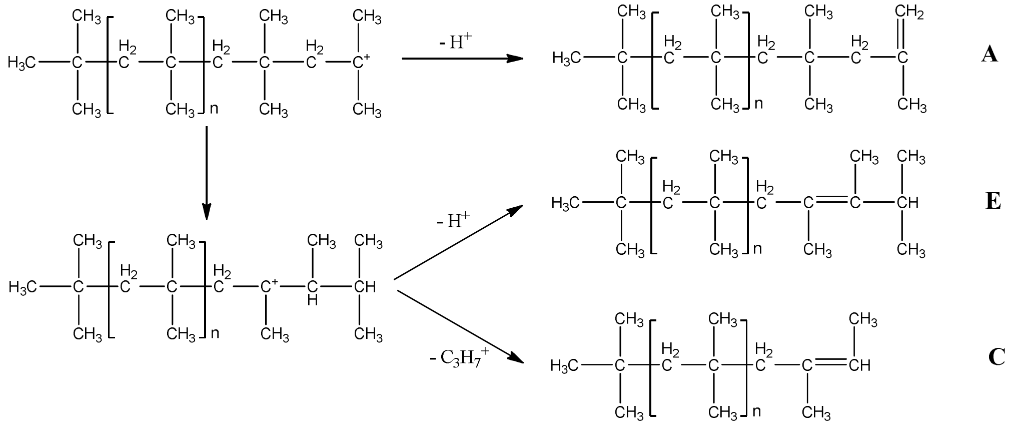


Fig 3. Possible shifts and β-proton abstraction processes in the synthesis of HRPIBs.

Evolution of IB polymerization in flow system

In the microflow system, the reaction time can be easily adjusted by changing the length of reaction tube individually. Monitoring the variance of monomer conversion and product's molecular weight distribution with time can help understand the proceeding of the polymerization. Considering that the molar ratio of iPr_2O to $AlCl_3$ (iPr_2O:$AlCl_3$) shows distinct influence on the monomer conversion after specific duration in Table 1, two groups of experiments with different values of iPr_2O:$AlCl_3$ were conducted for comparison. Table 2 lists the results. For the first group (entries 1 to 4, $^iPr_2O$:$AlCl_3$ = 1.1), we almost obtained consistent monomer conversion and HRPIB products, but the excess of PIB over $AlCl_3$ (much higher than water) indicates chain transfer evidently. A reasonable explanation is that most of PIB chains have been terminated within 1 s, but the characteristic time for chain transfer is far less than 1 s. For the second group (entries 5 to 11, iPr_2O:$AlCl_3$ = 1.4), the monomer conversion, as well as the PIB concentration, increased gradually with time ranging from 0.5 s to 18 s; M_n and PDI changed little. Compared with the first group, both the chain propagation and the chain termination were retarded much in the second group at high $^iPr_2O$:$AlCl_3$, and more times of chain transfer carried out before chain termination to achieve relatively high PIB concentration. A polymerization process dominated by fast but not instantaneous chain reactions is easy to control in a microflow system. Therefore, a proper excess of $^iPr_2O$ over $AlCl_3$ (such as $^iPr_2O$:$AlCl_3$ = 1.4) is preferred to making a compromise between the controllability and efficiency of IB polymerization. Besides, high $^iPr_2O$:$AlCl_3$ seems to afford high ratio of *exo*-olefin-terminated PIBs with low molecular weight, which can be interpreted by the ether-assisted chain transfer mechanism.[45,46]

Table 2. Time dependence of polymerization of IB co-initiated by $AlCl_3 \times {}^iPr_2O$ in CH_2Cl_2[a]

entry	t (s)	convn[d] (%)	M_n (g mol^{-1})	PDI	[PIB][e] (mmol L^{-1})	end groups distribution (mol%)		
						exo	tri+endo	tetra
1[b]	1	56	2250	1.9	10.4	75	14	11
2[b]	2	65	2230	2.0	12.2	75	13	12
3[b]	4	59	1960	1.8	12.6	80	11	9
4[b]	6	53	2110	1.9	10.5	83	10	7
5[c]	0.5	16	1290	1.6	5.19	90	5	5
6[c]	1	17	1240	1.6	5.74	90	8	2
7[c]	2	24	1320	1.7	7.61	88	7	5
8[c]	4	32	1270	1.6	10.6	90	6	4
9[c]	6	42	1380	1.7	12.7	88	7	5
10[c]	12	61	1290	1.7	19.8	89	6	5
11[c]	18	63	1280	1.7	20.6	89	6	5

[a] T = 20 °C; [IB] = 0.75 mol L^{-1}. [b] [$AlCl_3$] = 6.1 mmol L^{-1}; $^iPr_2O$:$AlCl_3$ =1.1. [c] [$AlCl_3$] = 7.5 mmol L^{-1}; $^iPr_2O$:$AlCl_3$ =1.4. [d] Gravimetric conversion. [e] [PIB] = [IP]×56×convn/M_n.

Effects of temperature

It is well known that the stability of carbenium ions is highly sensitive to temperature, and temperature is usually a critical and complicated influence factor on the carbonic polymerization. Meanwhile, for the AlCl$_3$/^{i}Pr$_2$O coinitiating system, the strength of such influences may be related to the amount of ^{i}Pr$_2$O addition. We carried out the polymerization of IB at various temperatures ranging from -20 °C to 50 °C and listed the results in Table 3. At a glance, HRPIBs could be successfully synthesized throughout the wide range of temperature; high temperature corresponds to low M_n and low content of *exo*-olefin terminated chains; the adjustment of M_n from 500 to 5000 is available. In details, for the entries 1 to 5 with ^{i}Pr$_2$O:AlCl$_3$ = 1.6, even larger than 1.4, it can be speculated that there still exists considerable unterminated chains after a duration of 12 s. At -20 °C or -10 °C, nearly 100 % monomers could convert into HRPIBs with relatively high M_n, which implies the chain propagation is still a fast step. Further increasing the temperature, the conversion decreases, but the PIB concentration increases gradually. It indicates chain transfer may be accelerated with the temperature increasing. For the entries 6 to 7 with ^{i}Pr$_2$O:AlCl$_3$ = 1.1, a 12 s stay is enough for totally chain terminating. The PIB concentration is dependent on the chain transfer ability before chain termination. Obviously, the increasing of temperature could afford intensive chain transfer, which can compensate the effect of M_n decreasing to sustain the conversion. In general, the high temperature is favour for chain transfer, and the excessive ^{i}Pr$_2$O could weaken this temperature dependency. Besides, the inverse effect of polymerization temperature on molecular weights can be described by Arrhenius equation, i.e. $\ln M_n = \ln A - \Delta E/RT$. The overall activation energy (ΔE) could be calculated from the slope of the linear Arrhenius plot of $\ln M_n$ *vs* 1/T for specific coinitiating system and temperature intervals. Figure 4 shows that the ΔE is strongly dependent on the molar ratio of ^{i}Pr$_2$O to AlCl$_3$, corresponding to -9.1 kJ mol^{-1} at ^{i}Pr$_2$O:AlCl$_3$ = 1.6 and -34.6 kJ mol^{-1} at ^{i}Pr$_2$O:AlCl$_3$ = 1.1, respectively. The former is higher than what reported by Kostjuk[47] (-19.8 kJ mol^{-1}) and Wu (-13.9 kJ mol^{-1})[22] for similar initiating systems. Considering the large presence of free ether in our system, it indicates the free ether could remarkably affect the chain transfer (β-proton abstraction) by weak interaction. Moreover, low temperature sensitivity is preferred to assuring an expected range of molecular weight at elevated temperature, while high temperature sensitivity afford convenience for molecular weight regulation by changing temperature.

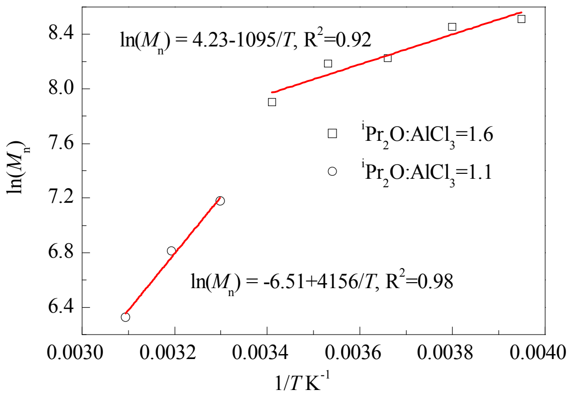


Fig 4. Arrhenius plots of ln(M_n) versus 1/*T* for polymerization of IB coinitiated by AlCl$_3$ × ^{i}Pr$_2$O.

Table 3. Polymerization of IB co-initiated by AlCl$_3$ × ^{i}Pr$_2$O in CH$_2$Cl$_2$ at various temperatures in CH$_2$Cl$_2$^{a}

entry	*T* (°C)	convn^d (%)	M_n (g mol^{-1})	PDI	[PIB]^e (mmol L^{-1})	end groups distribution (mol%)		
						exo	tri+endo	tetra
1^b	-20	100	4980	2.4	8.41	95	2	3
2^b	-10	100	4690	2.2	8.93	93	3	4
3^b	0	88	3740	2.1	9.85	88	6	6
4^b	10	86	3580	2.1	10.1	76	13	11
5^b	20	73	2710	1.9	11.3	71	14	15
6^c	30	52	1310	1.7	16.6	85	8	7
7^c	40	67	910	1.8	30.8	77	12	11
8^c	50	61	560	1.7	45.6	74	12	14

^{a} *t* = 12 s; [IB] = 0.75 mol L^{-1}. ^{b} [AlCl$_3$] = 4.2 mmol L^{-1}; ^{i}Pr$_2$O:AlCl$_3$ =1.6. ^{c} [AlCl$_3$] = 6.1 mmol L^{-1}; ^{i}Pr$_2$O:AlCl$_3$ =1.1. ^{d} Gravimetric conversion. ^{e} [PIB] = [IP]×56×convn/M_n.

Effects of monomer concentration

The productivity of polymerization process is limited by the monomer concentration, and the latter affects the supply of monomers for chain propagation as well. We attempted to increase the monomer concentration to improve the productivity under controlled molecular weight distribution. Table 4 shows some results. As seen, with the increasing of the monomer concentration, the M_n almost increases proportionally, regardless of temperature and the ratio of ^{i}Pr$_2$O to AlCl$_3$. Correspondingly, other parameters, including conversion, the PIB concentration, and end groups distribution, change little. It seems that the monomer concentration has little effect on the rate of chain transfer, but determines the rate of chain propagation. Therefore, the molecular weight of HRPIBs may be quantitatively regulated by changing the monomer concentration individually. Meanwhile, considering the temperature difference between entries 1 to 3 and entries 4 to 6, the effects of temperature are mainly reflected on the variance of end group distribution as exploiting relatively high ratio of ^{i}Pr$_2$O to AlCl$_3$ (such as 1.4 or more). As for achieving high content of *exo*-olefin terminated chains, low temperature is preferred. However, a proper selection of the ratio of $^{i}Pr_2O$ to $AlCl_3$ (such as 1.4 for the second group in Table 2) seems available to synthesize PIBs with around 90 mol% of *exo*-olefin end groups and controllable molecular weight distribution at room temperature.

Table 4. Polymerization of IB co-initiated by $AlCl_3 \times {}^{i}Pr_2O$ at various IB concentration in CH_2Cl_2[a]

entry	[IB] (mol L^{-1})	convn[d] (%)	M_n (g mol^{-1})	PDI	[PIB][e] (mmol L^{-1})	end groups distribution (mol%)		
						exo	*tri+endo*	*tetra*
1[b]	0.75	73	2710	1.9	11.3	71	15	14
2[b]	1.50	52	4650	1.8	9.4	72	11	17
3[b]	2.24	60	7550	1.9	10.0	66	16	18
4[c]	0.75	56	3480	2.1	6.8	94	3	3
5[c]	1.50	54	6790	1.9	6.7	95	2	3
6[c]	2.24	52	10640	1.9	6.1	96	3	1

[a] *t*= 12 s; [b] *T* = 20 °C; $[AlCl_3]$ = 4.2 mmol L^{-1}; $^{i}Pr_2O:AlCl_3$ = 1.6. [c] *T* = -20 °C; $[AlCl_3]$ = 4.5 mmol L^{-1}; $^{i}Pr_2O:AlCl_3$ = 1.4. $[AlCl_3]$ = 6.1 mmol L^{-1}; [d] Gravimetric conversion. [e] [PIB] = [IP]×56×convn/M_n.

Roles of $^{i}Pr_2O$ in IB polymerization process control

As mentioned above, the addition of $^{i}Pr_2O$ has multiple effects on the polymerization process of IB due to its complex reaction mechanism, as schematically illustrated in Figure 5. In the catalytic complex solution, the $^{i}Pr_2O$ can combine with $AlCl_3$ to generate the catalytic complex, $^{i}Pr_2OAlCl_3$ (Equation 1). Both $^{i}Pr_2OAlCl_3$ and $AlCl_3$ can combine with adventitious water to generate active species initiating chain propagations (Equations 2 and 3). The molecular weight of chains is dependent on the ratio of chain propagation probability to chain transfer probability, and increasing the monomer concentration is favour for chain propagation (forward reaction in Equation 2) and molecular weight increment. Compared with the polymer chains initiated by $H^{+}AlCl_3(OH)^{-}$, the polymer chains initiated by $H^{+i}Pr_2OAlCl_3(OH)^{-}$ have low propagation rate and high chain transfer proneness due to the insertion of $^{i}Pr_2O$ in active species. The fast ether-assisted chain transfer reduces the probability of isomerization resulted from hydride or methide shifts in propagating chains. Intensive isomerization corresponding to a little deficiency of $^{i}Pr_2O$ implies that most of chains are initiated by $H^{+}AlCl_3(OH)^{-}$ with initiation efficiency higher than $H^{+i}Pr_2OAlCl_3(OH)^{-}$. So an excess of $^{i}Pr_2O$ to guarantee full conversion from $AlCl_3$ to the catalytic complex is necessary to synthesize HRPIBs. The collapse of active species according to Equations 4 and 5 may take place and result in chain termination, which can be inhibited by the existence of free $^{i}Pr_2O$ around counterions. However, abundant free $^{i}Pr_2O$ may retard propagation seriously, decreasing the conversion and allowing more isomerization. A selection of the mole ratio of $^{i}Pr_2O$ to $AlCl_3$ should be based on the overall consideration of decreasing free $AlCl_3$ as well as avoiding abundant free $^{i}Pr_2O$. In general, controlling the $^{i}Pr_2O$ addition at low amount is prerequisite for achieving fast HRPIBs synthesis.

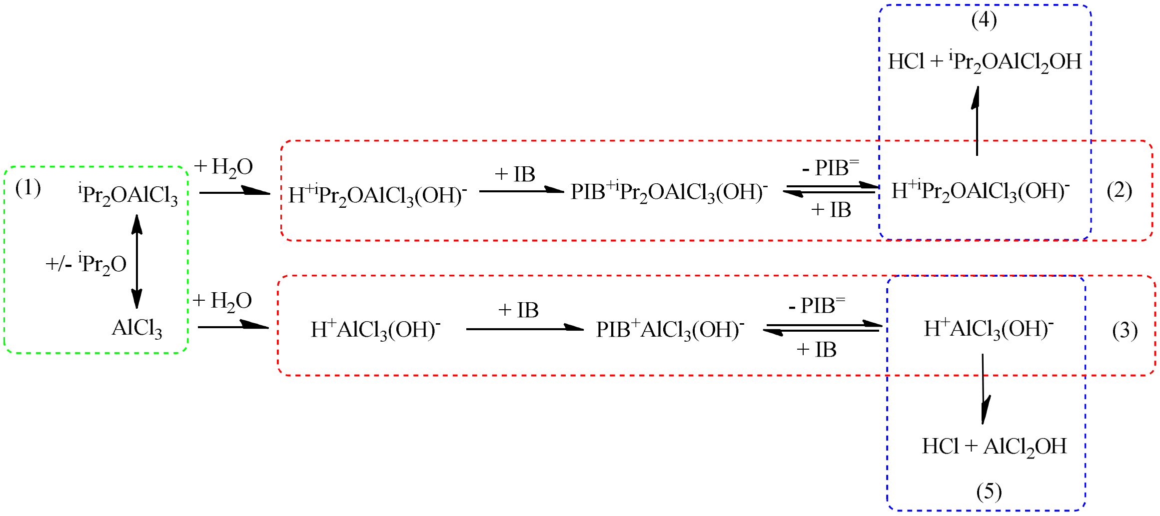


Fig 5. Suggested mechanism of polymerization of IB coinitiated by $AlCl_3 \times {}^{i}Pr_2O$.

Considering the monomer conversion follows the supply of monomers towards the propagating chain and the chain termination is independent of monomer supply, enhancing the mixing between monomer solution and catalytic complex solution can help increase the molecular weight or conversion. The comparisons of experiments conducted under various mixing conditions (Table 5) present the importance of high efficiency mixing for fast HRPIBs synthesis. A microflow system is easy to control the mixing performance, which usually approaches a platform when the flow capacity is over a threshold.

Table 5. Effects of mixing conditions on polymerization of IB co-initiated by $AlCl_3 \times {}^iPr_2O$ in CH_2Cl_2[a]

entry	$F(IB+CH_2Cl_2+\text{catalytic complex})^b$ mL/min	convn[c] (%)	M_n ($g\ mol^{-1}$)	PDI	$[PIB]^d$ ($mmol\ L^{-1}$)	end groups distribution (mol%) exo	tri+endo	tetra
1	3.2	30	2120	1.8	5.9	95	2	3
2	8	52	3580	2.4	6.1	93	4	3
3	16	56	3480	2.1	6.8	94	3	3

[a] t= 12 s; T = -20 °C; $[AlCl_3]$ = 4.5 mmol L^{-1}; ${}^iPr_2O:AlCl_3$ = 1.4. [b] $F(IB):F(CH_2Cl_2):F(\text{initiator})$ = 1:7:8. [c] Gravimetric conversion. [d] $[PIB] = [IP]\times 56\times \text{convn}/M_n$.

Conclusions

Through IB polymerization coinitiated by $AlCl_3/{}^iPr_2O$ at low concentrations (4 mmol L^{-1} to 10 mmol L^{-1}) in a microflow system, we achieved 50 % to 100 % conversion towards HRPIBs with 65 % to 96 % *exo*-olefin terminated chains after 12 s or less duration within a wide temperature window from -20 °C to 50 °C. The molecular weight distribution was narrow with a PDI around 1.9, and the average molecular weight was adjustable from 500 to 15000 by changing temperature or monomer concentration. The excess of ${}^iPr_2O$ over $AlCl_3$ is necessary to decrease the existence of free $AlCl_3$ and intensive isomerization coinitiated by free $AlCl_3$. The considerable existence of free ${}^iPr_2O$ can inhibit the chain termination and allow the polymerization to present chain transfer dominated kinetics. The increasing of free ${}^iPr_2O$ can weaken the temperature sensitivity of molecular weight and avoid the failure in molecular weight control at elevated temperature. The retarding effects of free ${}^iPr_2O$ on the chain propagation will decrease the apparent reaction rate and increase the probability of isomerization. A key access to fast synthesis of HRPIBs with 90% *exo*-olefin terminated chains is to make a compromise between multiple effects of the excessive ${}^iPr_2O$ by selecting a proper ratio of ${}^iPr_2O$ to $AlCl_3$, such as 1.4. This work provides useful information in aspect of fundamentals and methodology to produce high quality HRPIBs expeditiously and cost-effectively.

Acknowledgements

The authors are gratefully thankful for the support of the National Natural Science Foundation of China (21176136, 21422603) and National Science and Technology Support Program of China (2011BAC06B01) on this work.

References

1 J. P. Kennedy and B. Ivan, *Designed Polymers by Carbocationic Macromolecular Engineering*: Theory and Practice; Hanser: Munich, Germany, 1991, 173–177.
2 J. P. Kennedy and E. Marechal, *Carbocationic Polymerization*; John Wiley & Sons: New York, 1982, 475-488.
3 S. F. Rach and F. E. Kühn, *Sustainability*, 2009, **1**, 35-42.
4 J. D. Burrington, J. R. Johnson and J. K. Pudelski, *Top. Cat.* 2003, **23**, 175–181.
5 I. Puskas, E. M. Banas and G. Nerheim, *J. Polym. Sci: Polym. Symp*, 1976, **56**, 191–201.
6 J. J. Harrison, D. C. Young and C. L. Mayne, *J. Org. Chem.* 1997, **62**, 693–699.
7 W. Günther, K. Maenz and D. Stadermann, *Angew. Makromol. Chem.*, 1996, **234**, 71–90.
8 E. N. Kresge, R. H. Schatz and H. C. Wang, *Encyclopedia of Polymer Science and Engineering*: Wiley: New York, 1985, 423-450.
9 P. Dimitrov, J. Emert, J. Hua, S. Keki and R. Faust, *Macromolecules*, 2011, **44**, 1831-1840.
10 P. Boerzel, K. Bronstert and F. Hovemann, BASF AG, DE 2702604, 1978.
11 H. P. Rath, US 5,910,550, BASF AG, 1997, *Chem. Abstr.* 1997, 128, 23292.
12 J. M. Kerr, J. Mcmahon and J. M. Scotland, EP 0671419, BP Chemicals Ltd., 1995; *Chem. Abstr.* 1995, 123, 314902.
13 H. Mach and P. Rath, *Lubrication Science*, 1999, **11**, 175-185.
14 J. J. Harrison, C. M. Mijares and J. Hudson, *Macromolecules*, 2002, **35**, 2494-2500.
15 H. P. Rath, BASF AG, US 5,286,823, 1994.

16 H. P. Rath, A. Lange and H. Mach, BASF AG, US 7,071,275, 2006.
17 H. P. Rath, BASF AG, WO 99/64482, 1999.
18 M. Vierle, Y. Zhang, E. Herdtweck, M. bohnenpoll, O. Nuyken and F. E. Kuhn. *Angew. Chem. -Inter. Edit.*, 2003, **42**, 1307-1310.
19 Y. Li, M. Cokoja, F. E. Kuehn, *Coord. Chem. Rev.*, 2011, **13-14**, 1541-1557.
20 S. V. Kostjuk, *RSC Adv.*, 2015, **5**, 13125-13144.
21 I. V. Vasilenko, A. N. Frolov and S. V. Kostjuk, *Macromolecules*, 2010, **43**, 5503-5507.
22 Q. Liu, Y. X. Wu, Y. Zhang, P. f. Yang and R. W. Xu, *Polymer*, 2010, **51**, 5960-5969.
23 S. V. Kostjuk, H. Y. Yeong, V. Brigitte, *J. Polym. Sci. Part A: Polym. Chem.*, 2013, **51**, 471-486.
24 R. F. Storey, B. J. Chisholm and L. B. Brister, *Macromolecules*, 1995, **28**, 4055-4061.
25 R. Kumar, P. Dimitrov, K. J. Bartelson, J. Emert and R. Faust. *Macromolecules*, 2012, **45**, 8598-8603.
26 J. P. Russum, C. W. Jones and F. J. Schork, *Macromol. Rapid Commun.*, 2004, **25**, 1064–1068.
27 R. Kumar, B. Zheng, K. W. Huang, J. Emert and R. Faust, *Macromolecules*, 2014, **47**, 1959-1965.
28 B. Yang and R. F. Storey, *Polym. Chem.*, 2015, **6**, 3764-3774.
29 X. Yang, A. Guo, H. Xu and Y. X. Wu, *J. Appl. Polym. Sci.*, 2015, **132**, 42232.
30 N. Hand, R. T. Mathers, K. Damodaran and S. P. Lewis, *Ind. Eng. Chem. Res.*, 2014, **53**, 2718-2725.
31 I. V. Vasilenko, D. I. Shiman and S. V. Kostjuk, *Polym. Chem.*, 2014, **5**, 3855-3866.
32 R. Kumar, J. Emert, and R. Faust, *Polym. Bull.*, 2015, **72**, 49-60.
33 R. Kumar, P. De, B. Zheng, K. W. Huang, J. Emert, R. Faust, *Polym. Chem.*, 2014, **6**, 322-329.
34 K. Bartelson, R. Kumar, P. De, J. Emert, R. Faust, *Polymer*, 2013, **54**, 4858-4863.
35 S. Banerjee, J. Emert, P. Wright, T. Skourlis, R. Severt and R. Faust, *Polym. Chem.*, 2015, **6**, 4902-4910.
36 S. Banerjee, B. H. Jha, P. De, J. Emert and R. Faust, *Macromolecules*, 2015, **48**, 5474-5480.
37 P. Dimitrov, J. Emert and R. Faust, *Macromolecules*, 2012, **45**, 3318-3325.
38 N. K. Madhvanand and K. M. Lioubov, *Ind. Eng. Chem. Res.*, 2009, **48**,6465-6485.
39 J. L. Steinbacher and D. T. McQuade, *J. Polym. Sci. Part A: Polym. Chem.*, 2006, **44**, 6505-6533.
40 A. Miyazawa, T. Kase and T. J. Shibuya, *J. Polym. Sci. Part A: Polym. Chem.*, 2004, **42**, 1841–1844.
41 A. Nagaki, K. Kawamura and J. Yoshida, *J. Am. Chem. Soc.*, 2004, **126**, 14702–14703.
42 T. Iwasaki, A. Nagaki and J. Yoshida, *Chem. Commun.*, 2007, 1263–1265.
43 I. Puskas, E. M. BanasX, G. J. Nerheim, and G. J. Ray, *Polym. Sci: Polym. Symp.*, 1976, **56**, 191–201.
44 K. L. Simison, C. D. Stokes, J. J. Harrison and R. F. Storey, *Macromolecules*, 2006, **39**, 2481-2487.
45 D. I. Shiman, V. V. Irina and S. V. Kostjuk, *Polymer*, 2013, **54**, 2235-2242.
46 S. V. Kostjuk, I. V. Vasilenko, D. I. Shiman, A. N. Frolov and L. V. Gaponik, *Macromol. Symp.*, 2015, **349**, 94-103.
47 I. V. Vasilenko, D. I. Shiman, S. V. Kostjuk, *J. Polym. Sci. Part A: Polym. Chem.*, 2012, **50**, 750–758.