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A Complexed Initiating System $\text{AlCl}_3\cdot\text{Phenetole}/\text{TiCl}_4\cdot\text{H}_2\text{O}$ with Dominant Synergistic Effect for Efficient Synthesis of High Molecular Weight Polyisobutylene

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Abstract: A complexed initiating system $\text{AlCl}_3\cdot\text{phenetole}/\text{TiCl}_4\cdot\text{H}_2\text{O}$ was prepared by simply compounding $\text{AlCl}_3/\text{phenetole}$ and $\text{TiCl}_4/\text{H}_2\text{O}$ and used for cationic polymerization of isobutylene. It was found $\text{AlCl}_3\cdot\text{phenetole}/\text{TiCl}_4\cdot\text{H}_2\text{O}$ exhibited activities 1.2–3 times higher than those of $\text{AlCl}_3/\text{phenetole}$, and more than an order of magnitude higher than those of $\text{TiCl}_4/\text{H}_2\text{O}$, which indicated a notable synergistic effect produced in the complexed system. In addition, due to the higher activity of $\text{AlCl}_3\cdot\text{phenetole}/\text{TiCl}_4\cdot\text{H}_2\text{O}$, lower coinitiator concentration and polymerization temperature, as well as higher monomer concentration were more favored for this complexed initiating system to produce polyisobutylene (PIB) with reasonable molecular weight (M_w) and molecular weight distribution (MWD). Furthermore, high molecular weight polyisobutylene (HPIB) with $M_w = 1\text{--}3 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ could be successfully produced by the complexed catalyst system at $T_p = -60$ to -40 °C. As a whole, the high activity as well as the simple preparation procedures of the complexed initiating system offer us a unique approach for the production of HPIB with improved efficiency.

Keywords: cationic polymerization; isobutylene; complexed catalyst; high molecular weight; synergistic effect

1. Introduction

High molecular weight polyisobutylene (HPIB), which owns viscosity average molecular weight (M_v) higher than $10^5 \text{ g}\cdot\text{mol}^{-1}$, is one of the most unusual polymers and exhibits numerous excellent properties such as extremely low gas permeability, outstanding thermal stability and low fragility [1,2]. Thus it has been applied in the manufacture of sealant, automotive, medical equipment and so forth [3]. Commercially, HPIB is produced with Lewis acid based initiating systems through the cationic polymerization of isobutylene (IB), and polymerization temperature (T_p) as low as -100 °C is necessary to depress the chain transfer or termination reaction and achieve high molecular weight (M_w) polymers [4–6]. However, it is obvious that such a low T_p is critical to both energy and equipment costs. Therefore, developing novel initiating systems and manufacture processes for the synthesis of HPIB at elevated T_p is significant.

The novel organometallic catalysts were reported to have an advantage over the synthesis of HPIB [7]. For examples, in the presence of $B(C_6F_5)_3$ and zirconocenes, Bochmann et al. found polyisobutylene (PIB) with M_w higher than 10^6 g·mol⁻¹ could be obtained at T_p closed to -70 °C [8]. Jörg et al. reported a dicationic zirconocene for the synthesis of HPIB with M_w higher than 3×10^5 g·mol⁻¹ at T_p below -50 °C [9]. Baird et al. reported that HPIB with $M_w = 1-6 \times 10^5$ g·mol⁻¹ could be produced at $T_p = -50$ to -10 °C by a half-titanocene coordinated with $B(C_6F_5)_3$ [10]. It is generally recognized that the weakly coordinating anions (WCAs) such as $B(C_6F_5)_3$ is indispensable for the organometallic catalysts, as the WCAs act as stabilizer to the active sites and retard the chain transfer reaction [11]. However, much attention has still been paid on the conventional Lewis acid systems both in the academic and industrial fields, as the synthetic routes for these organometallic catalysts are much more complicated, and the cost is also relatively higher. [12]. On the other hand, HPIB could also be produced at elevated T_p with Lewis acid initiating systems, if proper reaction conditions are chosen. Particularly, the $AlCl_3$ -based initiating systems, which are widely investigated in both academy and industry for the production of PIB, butyl rubber and other cationic polymers, are among the most favored candidates for the synthesis of HPIB because of the low price, low dosage and high activity [3,13–20]. Lu and coworkers took advantage of the microflow reaction system in perfect mixing and heat transfer performances, as well as narrow residence time distribution, thus a reaction system with enhanced homogeneity and controllability could be created, and PIB with weight-average molecular weight (M_w) higher than 1×10^5 g·mol⁻¹ was produced by $AlCl_3/H_2O$ at $T_p = -30$ to -10 °C [21]. Csihony et al. reported a novel initiating system of Lewis acid anion $Al_2Cl_7^-$ trapped in micelles consisting of functionalized low molecular weight PIB. The activity of the system was high enough that HPIB with $M_w = 1.7-9 \times 10^5$ g·mol⁻¹ and molecular weight distribution (MWD) = 13–47 could be produced at $T_p = -76$ °C [2]. Wu et al. prepared a series of $AlCl_3/H_2O/ED$ (ED = electron donor = methyl benzoate, ethyl benzoate, and methyl acrylate) initiating systems. It was found that in the presence of EDs, the M_w of the PIB could reach to $6-8 \times 10^5$ g·mol⁻¹ at $T_p = -80$ to -70 °C, which was even higher than that produced by $AlCl_3/H_2O$ at $T_p = -100$ °C [3,22]. Later on, the same group reported another novel initiating system of $AlCl_3/H_2O/veratrole$, and HPIB with M_w higher than 1×10^6 g·mol⁻¹ could be synthesized at $T_p = -80$ °C. It was argued that the EDs were able to interact with the active centers and affect the nucleophilicity and polarity of the microsurrroundings around the active centers. As a consequence, the cationic polymerization proceeded in a more controllable way, and side reactions such as chain transfer and termination were depressed, but the propagation rate mostly declined with the increased concentration of EDs [23]. Kostjuk and coworkers found $H_2O/iBu_2AlCl/toluene$ was able to afford PIB with high M_w at $T_p = -20$ °C because of the weak basicity of toluene, which would help to stabilize the active species. While for $iBuAlCl_2$ with stronger Lewis acidity, additional ether was needed to suppress side reactions and obtain HPIBs [24]. The same group also disclosed that alkoxy aluminum chlorides-based systems $H_2O/(RO)_{0.8+n}AlCl_{2.2-n}/n$ -hexane (R = Bu, Hex or *i*Pr; $n = 0-0.4$) could produce PIBs with low to medium M_w and relatively narrower MWD. It was found the oxygen in the coinitiator played a key role as electron donor to stabilize the active species, which would retard the isomerization of the macrocation and chain scission and benefit the synthesis of high M_w polymers. Therefore, PIBs with M_w up to 1.2×10^5 g·mol⁻¹ could be produced at elevated $T_p = -20$ to 20 °C [25].

Recently, an endeavor was made in our group to make HPIB with $AlCl_3/ROH$ (R = H, Me, Et, Bu, ^tBu and Ph) or $AlCl_3/ether$ (ether = diethyl ether, butyl ether, anisole and phenetole) initiating systems as well, and HPIB with $M_w > 1 \times 10^5$ g·mol⁻¹ could be generally produced at relatively elevated $T_p = -60$ °C. Particularly, $AlCl_3/phenetole$ showed the highest efficiency for the synthesis of HPIB among these systems [26]. More recently, a novel complexed system consisting of $BF_3 \cdot EtOH/TiCl_4 \cdot H_2O$ was reported in our group, and remarkable synergistic effect in its catalytic efficiency could be observed due to this complexation [27]. However, it should be noted that BF_3 is highly toxic and environmental unfriendly. Therefore, in this contribution, we tried to make use of $AlCl_3$, which is relatively greener and more economical than BF_3 , to give another complexed initiating system $AlCl_3 \cdot phenetole/TiCl_4 \cdot H_2O$, aiming to produce HPIB with improved efficiency.

2. Materials and Methods

2.1. Raw Material

Isobutylene (Wetry Standard Gas (Shanghai) Co., Ltd., 99.80%, Shanghai, China), anhydrous AlCl_3 (Shanghai Aladdin Bio-Chem Technology Co., LTD, 99%, Shanghai, China), TiCl_4 (Lingfeng Chemical Co., Ltd., 99%, Shanghai, China) and Phenetole (Shanghai Aladdin Bio-Chem Technology Co., LTD, 99%, Shanghai, China) were used as received. CH_2Cl_2 (Lingfeng Chemical Co., Ltd., 99%, Shanghai, China) was distilled over CaH_2 under the atmosphere of N_2 for more than 6 h before use. N_2 (Wetry Standard Gas (Shanghai) Co., Ltd., 99.999%, Shanghai, China) was further purified by passing through two columns packed with 4A and silver molecular sieves, respectively.

2.2. Catalyst Preparation and Polymerization

All the polymerizations were implemented in three-necked flasks (ca. 250 mL) under the atmosphere of N_2 . Standard Schlenk technique was applied to avoid the introduction of air into the reaction system. The isobutylene (IB) gas was firstly liquefied by being introduced to a three-necked flask prechilled in a cooler at the target T_p , and a certain amount of CH_2Cl_2 was transferred to the flask by a syringe to get the monomer solution. Afterwards, in a glove box under N_2 atmosphere, a certain amount of AlCl_3 powder was weighted and sealed in a glass tube. To make the solution of the complexed catalyst, the powder was introduced to another three-necked flask and flushed by CH_2Cl_2 , then phenetole, TiCl_4 and H_2O were sequentially injected into the flask by syringes. Subsequently, both the monomer and catalyst solutions were kept at T_p for at least half an hour. To start polymerization, the catalyst solution was transferred to the monomer solution, and then the reaction system was magnetically stirred and kept for a scheduled time. Subsequently, about 2 mL NaOH /ethanol mixture was poured into the reactor to terminate the polymerization process. The quenched mixture was separated from the solvent by vacuum filtration and washed by deionized water and EtOH three times, respectively. Afterwards, it was dried in vacuum at 40°C overnight, and the product was attained and weighted. Activities = $m_{(\text{PIB})}/(n_{\text{cat}} \cdot t)$ were calculated to compare the efficiencies of these catalysts, where $m_{(\text{PIB})}$ was the weight of the obtained polymers in kilograms, n_{cat} was the amount of the added AlCl_3 and TiCl_4 in molar number, and t was the reaction time in hour.

2.3. Polymer Characterization

The weight average molecular weight (M_w) and MWD (M_w/M_n) of the obtained PIBs were characterized by gel permeation chromatography (GPC, Waters-1515) combined with two Mixed-C columns. Typically, 10 mg PIB was dissolved in 10 mL tetrahydrofuran (THF) to make polymer solutions with a concentration of $1\text{mg}\cdot\text{mL}^{-1}$, which was then measured at 35°C at a flow rate of $1.0\text{ mL}\cdot\text{min}^{-1}$. The columns were calibrated by polystyrene standards with narrow MWD.

3. Results and Discussion

3.1. Effect of Coinitiator Concentration

The effect of coinitiator concentration on the polymerization behaviors of reference and complexed catalysts was investigated, and the results were listed in Table 1. At coinitiator concentration lower than $2.5\text{ mmol}\cdot\text{L}^{-1}$, it was obviously for both catalysts that the monomer conversions were enhanced with the increasing catalyst concentration, but to achieve a parallel conversion, lower catalyst concentration was needed for the complexed one, which implied the higher efficiency of the complexed catalyst. It could also be directly reflected by the Δ value in Table 1, showing that the activities of $\text{AlCl}_3\cdot\text{phenetole}/\text{TiCl}_4\cdot\text{H}_2\text{O}$ were 2–3 times higher than those of $\text{AlCl}_3/\text{phenetole}$ at identical reaction conditions. When the concentration of coinitiator was lower than $1\text{ mmol}\cdot\text{L}^{-1}$, no polymer could be detected for the $\text{AlCl}_3/\text{phenetole}$ system, probably due to the comparable trace concentration of impurity to that of the active sites [28]. However, for the complexed catalyst, a monomer conversion

higher than 30% could still be obtained at this low coinitiator concentration. With respect to polymer products, monomodal HPIB with M_w higher than $2 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ and $MWD = 2\text{--}4$ could be produced with both catalysts at low concentration, but the complexed catalyst system was apt to produce PIB with lower M_w and broader MWD when compared with $\text{AlCl}_3/\text{phenetole}$, as the high polymerization activity made the process control more difficult. When the concentration of coinitiator further increased to higher than $2.5 \text{ mmol}\cdot\text{L}^{-1}$, the efficiencies between the two catalyst systems were indistinct.

Table 1. Effect of coinitiator concentration on the polymerization results ^a.

No	Catalysts	$[\text{AlCl}_3 + \text{TiCl}_4]$ ($\text{mmol}\cdot\text{L}^{-1}$)	Conv. (%)	Act. ^c	M_w ^d	M_n ^d	MWD	Δ ^e
1	1 AlCl_3 ·1phenetole	0.84	0	-	-	-	-	-
2	1 AlCl_3 ·1phenetole/1 TiCl_4 ·1 H_2O	0.84	34.9	186.14	20.89	5.50	3.8	-
3	1 AlCl_3 ·1phenetole	1.67	16.0	42.67	35.78	14.31	2.5	1
4	1 AlCl_3 ·1phenetole/1 TiCl_4 ·1 H_2O	1.67	53.0	141.34	20.88	5.09	4.1	3.31
5	1 AlCl_3 ·1phenetole	2.51	40.5	72.00	28.86	7.59	3.8	1
6	1 AlCl_3 ·1phenetole/1 TiCl_4 ·1 H_2O	2.51	95.0	168.90	20.03	0.96	20.9	2.35
7	1 AlCl_3 ·1phenetole	3.35	100	133.34	20.42	5.24	3.9	1
8	1 AlCl_3 ·1phenetole/1 TiCl_4 ·1 H_2O	3.35	98.7	131.61	14.37	0.98	14.7	0.99
9	1 AlCl_3 ·1phenetole	4.19	100	106.67	12.20	0.26	46.1	-
10	1 AlCl_3 ·1phenetole/1 TiCl_4 ·1 H_2O	5.02	97.1	86.32	12.87	0.67	19.2	-
11 ^b	1 TiCl_4 ·1 H_2O	50.00	71.5	4.86	6.41	1.78	3.6	-
12	1 AlCl_3 ·1 H_2O	3.35	59.8	79.76	21.21	3.98	5.3	-
13	1 TiCl_4 ·1phenetole	1.67	N.D ^f	N.D ^f	N.D ^f	N.D ^f	N.D ^f	-
14	1 AlCl_3 ·1phenetole·1 H_2O	1.67	0.6	1.47	-	-	-	-
15	1 TiCl_4 ·1phenetole·1 H_2O	1.67	0.4	0.90	-	-	-	-
16	1 AlCl_3 ·2phenetole/1 TiCl_4	1.67	0.1	0.21	-	-	-	-

^a For each catalyst, the molar ratio of the components is equal to that of the number in front of each component. 100 mL $\text{C}_2\text{H}_2\text{Cl}_2$, $T_p = -60^\circ\text{C}$, $t_p = 30 \text{ min}$, $[\text{IB}] = 4 \text{ mol}\cdot\text{L}^{-1}$; ^b high $[\text{TiCl}_4]$ was necessary to achieve reasonable polymerization rate (see Figure S3 in Supporting Information), $[\text{IB}] = 2.9 \text{ mol}\cdot\text{L}^{-1}$; ^c activity, $\text{kg PIB}\cdot\text{mol}^{-1}(\text{AlCl}_3+\text{TiCl}_4)\cdot\text{h}^{-1}$; ^d ($\times 10^4 \text{ g}\cdot\text{mol}^{-1}$); ^e $\Delta = \text{activity}_{(\text{complexed catalyst})}/\text{activity}_{(\text{reference catalyst})}$, where both catalysts contained the same coinitiator concentration. ^f Not detected.

In addition, the M_w of the PIB decreased and multimodal MWD could be observed (see Figure 1). It was likely that active species with distinct kinetic characteristics existed at high complex concentration. When looking into the GPC curves about the polymers produced by the catalysts before and after complexation together (see Figure 2), it was found the curve of the PIB made by AlCl_3 ·phenetole/ TiCl_4 · H_2O was analogous to that by $\text{AlCl}_3/\text{phenetole}$ at low catalyst concentration. While it tended to be the combination of those by $\text{AlCl}_3/\text{phenetole}$ and $\text{TiCl}_4/\text{H}_2\text{O}$ at high catalyst concentration. However, it was not the result of separate working of the two reference catalysts. Since such a situation would bring about bimodal but not multimodal MWD, and the activities of the complexed catalyst were also difficult to get close to or even higher than those of $\text{AlCl}_3/\text{phenetole}$, if we consider the much lower efficiency of $\text{TiCl}_4/\text{H}_2\text{O}$ (see Figures S1–S4 in Supporting Information). Another possibility for the decreased M_w and broadened MWD was presumably owing to the monomer starvation, which would lead to intensified side reactions like chain transfer and termination [29]. Moreover, chain scission should be taken into account as well, because it got more importantly under monomer starvation and was reported to be frequent in the AlCl_3 -based system for cationic polymerization [15,30]. This could also be directly reflected by the severely decreased M_n when higher catalyst concentration was used. It indicated that low coinitiator concentration is more favored for both initiating systems, specifically for AlCl_3 ·phenetole/ TiCl_4 · H_2O because of its higher activity. It preliminarily indicated that an obvious synergistic effect was also produced in the complexed catalyst as that discovered in BF_3 · $\text{EtOH}/\text{TiCl}_4$ · H_2O [27]. To further ensure this synergy, several control experiments with initiating systems consisting of two or three components were also investigated (see Run 11–16 in Table 1). It could be seen that the three components catalysts, as well as 1 TiCl_4 ·1phenetole showed very low or even no activities, while 1 TiCl_4 ·1 H_2O and 1 AlCl_3 ·1 H_2O exhibited moderate activities of less than $5 \text{ kg PIB}\cdot\text{mol}^{-1}\text{TiCl}_4\cdot\text{h}^{-1}$ and $80 \text{ kg PIB}\cdot\text{mol}^{-1}\text{AlCl}_3\cdot\text{h}^{-1}$, respectively. However,

under the similar reaction conditions, $1\text{AlCl}_3 \cdot 1\text{phenetole}/1\text{TiCl}_4 \cdot 1\text{H}_2\text{O}$ gave activities of more than $130 \text{ kg PIB} \cdot \text{mol}^{-1}(\text{AlCl}_3 + \text{TiCl}_4) \cdot \text{h}^{-1}$ and presented an obvious synergistic effect. Such a synergistic effect is very interesting, but was difficult to be illustrated at present. Marek and coworkers also found a similar synergistic effect in mixture consisting of two types of Lewis acids for IB polymerization in the absence of initiators, and it was proposed to result from the formation of very active ion pair due to the inter-ionization between the two Lewis acids with different acidity. However, as a certain amount of H_2O and phenetole was added in our case, making the existence of a large amount of free Lewis acid unlikely, thus the inter-ionization mechanism was almost impossible. In addition, this synergistic effect could also originate from the modification of the counterion by TiCl_4 , improving the stability of the growing species for IB insertion [31–33]. Nevertheless, deeper investigation is still needed to uncover the mechanism behind.

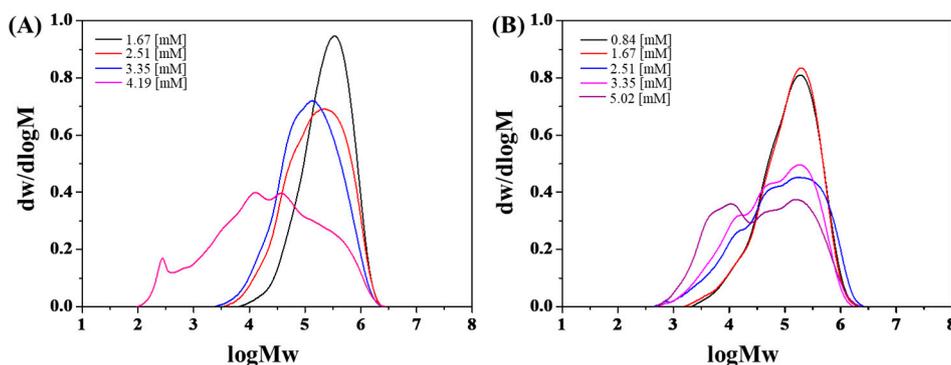


Figure 1. The gel permeation chromatography (GPC) curves of the PIB produced by (A) $\text{AlCl}_3/\text{phenetole}$ and (B) $\text{AlCl}_3 \cdot \text{phenetole}/\text{TiCl}_4 \cdot \text{H}_2\text{O}$ at various $[\text{AlCl}_3 + \text{TiCl}_4]$ concentrations. The other reaction conditions are listed in Table 1.

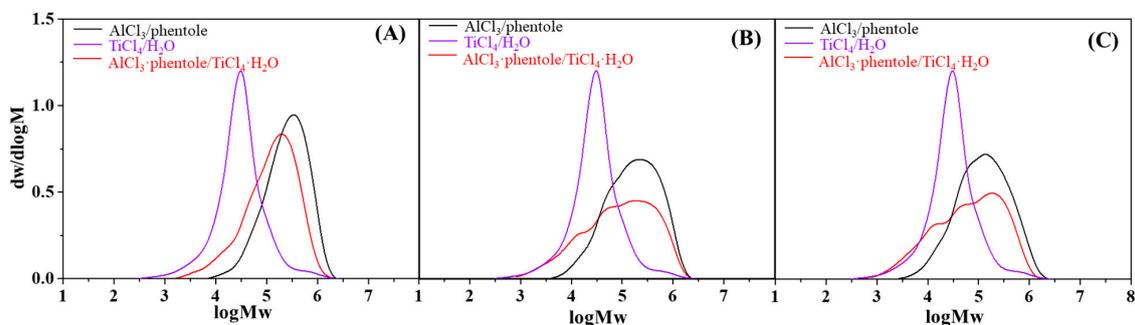


Figure 2. The GPC curves of PIB produced by $\text{AlCl}_3/\text{phenetole}$, $\text{TiCl}_4/\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot \text{phenetole}/\text{TiCl}_4 \cdot \text{H}_2\text{O}$, (A) the GPC curves of PIB produced from run 3, 4 and 11 in Table 1; (B) the GPC curves of PIB produced from run 5, 6 and 11 in Table 1 and (C) the GPC curves of PIB produced from run 7, 8 and 11 in Table 1.

3.2. Effect of Reaction Temperature

Reaction temperature (T_p) is one of the most important factors in the regulation of catalysis behaviors for cationic polymerization. Thus the effect of reaction temperature was also investigated at $T_p = -40$ to -60 °C commonly used for the synthesis of PIB (see Table 2). Primarily, it could be seen that the activities of the complexed catalyst were about 1.5–3 times higher than those of the uncomplexed ones under the investigated T_p . Additionally, it was conspicuous that both the monomer conversion and activities of the catalysts went up with increasing T_p , which were contrary to the results mostly reported for cationic polymerization that active sites collapsed more easily at higher T_p , and the conversion was kept almost the same or turned down consequently [5,13,34,35]. However, such a deviation was also disclosed elsewhere [9,28]. It was proposed the tightness of the initiator/coinitiator complex got strengthened at lower T_p . Consequently, the concentration of the free Lewis acids, which

play a role as coinitiator for cationic polymerization got lower as well [36]. It could also be partially attributed to the faster generation of active sites in comparison to their decay at higher T_p for both initiating systems. In addition, the viscosity of the reaction system got higher at lower T_p , and it could be more severe in the system for HPIB production, as gel-like PIB with relatively high M_w was generally produced and suspended in the solvent. This would inhibit the smooth going of heat and mass transfer processes, and also improve the possibility of the mechanical occlusion of catalysts by polymer and impair the efficiency of the catalysts [21]. While high T_p would help to create more homogeneous reaction conditions by improving the dissolubility of the polymer. Pertaining to the produced HPIB, the M_w decreased monotonously with increasing T_p , as the chain transfer reaction is more sensitive to temperature changes than chain propagation. The MWD of the HPIB also got slightly narrower at higher T_p . It is most likely that the initiation and chain transfer processes became more competent, while the apparent rate constant for chain propagation was kept almost the same at higher T_p [37,38]. In addition, the more homogeneous reaction conditions at increasing T_p should be taken into account as well. However, an exception was seen at run No 3 and 6 in Table 2, where an increase in MWD was observed. This could be possibly caused by chain scission during polymerization, which was exhibited by the additional low M_w tail in the GPC curves of the polymers (see Figure 3). In comparison to AlCl_3 /phenetole, the complexed catalyst still tended to produce HPIB with lower M_w and broader MWD, which indicated more dominant side reactions such as chain transfer, termination and scission in the latter initiating system. Moreover, with increasing T_p , a smaller difference in activities between the two systems could be observed, indicating the active sites in the complexed one were more sensitive to temperature and more frequently terminated at higher T_p . It implies the synergistic effect demonstrated in the complexed system not only improves the catalytic efficiency greatly but also poses a challenge to the process controllability of the polymerization reaction. Therefore, lower T_p seemed to be more crucial to AlCl_3 ·phenetole/ TiCl_4 · H_2O than AlCl_3 /phenetole. However, as a whole, HPIB with $M_w = 1\text{--}2.8 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ and MWD = 2.8–4.1 could be produced with both initiating systems.

Table 2. Effect of reaction temperature on the polymerization results ^a.

No	Coinitiator	T_p (°C)	Conv. (%)	Act. ^d	M_w ($\times 10^4 \text{ g}\cdot\text{mol}^{-1}$)	M_n ($\times 10^4 \text{ g}\cdot\text{mol}^{-1}$)	MWD	Δ ^e
1 ^b	AlCl_3	−60	40.5	72.07	28.86	7.59	3.8	1
2 ^c	$\text{AlCl}_3/\text{TiCl}_4$	−60	53.0	140.91	20.88	5.09	4.1	2.96
3 ^b	AlCl_3	−50	61.0	108.55	22.80	5.70	4.0	1
4 ^c	$\text{AlCl}_3/\text{TiCl}_4$	−50	88.8	236.10	13.72	4.04	3.4	2.17
5 ^b	AlCl_3	−40	98.0	174.40	12.70	4.54	2.8	1
6 ^c	$\text{AlCl}_3/\text{TiCl}_4$	−40	97.2	258.43	10.03	2.51	4.0	1.48

^a $[\text{IB}] = 4 \text{ mol}\cdot\text{L}^{-1}$; 100 mL $\text{C}_2\text{H}_2\text{Cl}_2$; $t_p = 30 \text{ min}$; ^b $[\text{AlCl}_3] = 2.51 \text{ mmol}\cdot\text{L}^{-1}$, $[\text{AlCl}_3]/[\text{phenetole}] = 1/1$;

^c $[\text{AlCl}_3] = 0.84 \text{ mmol}\cdot\text{L}^{-1}$, $[\text{AlCl}_3]/[\text{TiCl}_4]/[\text{phenetole}]/[\text{H}_2\text{O}] = 1/1/1/1$; ^d activity, $\text{kg PIB}\cdot\text{mol}^{-1}(\text{AlCl}_3 + \text{TiCl}_4)\cdot\text{h}^{-1}$;

^e $\Delta = \text{activity}(\text{complexed catalyst})/\text{activity}(\text{reference catalyst})$, where both the catalysts reacted at the same T_p .

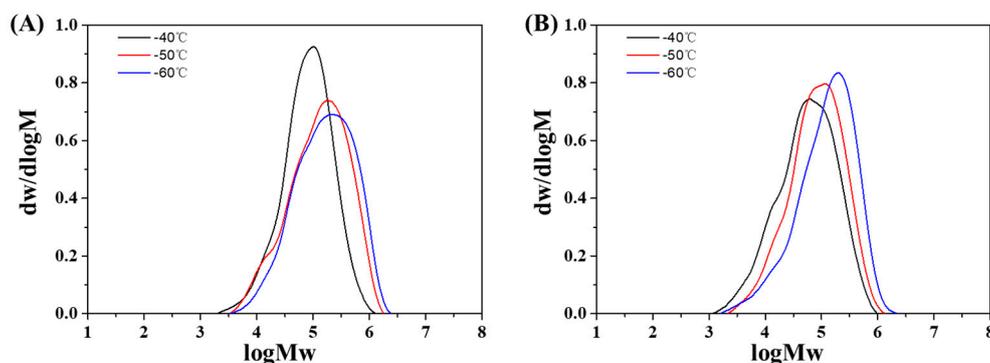


Figure 3. The GPC curves of the PIB produced by (A) AlCl_3 /phenetole and (B) AlCl_3 ·phenetole/ TiCl_4 · H_2O at different T_p . The other reaction conditions are listed in Table 2.

3.3. Effect of Monomer Concentration

High monomer concentration ([IB]) is always desired in industry to save the cost, if high conversion could be achieved at the same time. The effect of [IB] on the polymerization behaviors of both initiating systems is shown in Table 3. With regarding to AlCl_3 /phenetole, the monomer conversion decreased from 70% to 15% when [IB] increased from 2.4 to 5.1 $\text{mol}\cdot\text{L}^{-1}$, and the activity also followed the same trend. This decline was possibly derived from the decreasing concentration of the polar solvent CH_2Cl_2 caused by the increasing [IB], as an active ion pair in AlCl_3 /phenetole were more likely generated in more polar conditions (see Figure S5). For the complexed catalyst, the monomer conversion was kept at about 90% when [IB] increased from 2.4 to 4 $\text{mol}\cdot\text{L}^{-1}$, but obvious drop could also be observed when [IB] increased further. It implies a wider range of applicable [IB] for AlCl_3 /phenetole/ $\text{TiCl}_4\cdot\text{H}_2\text{O}$. In addition, the activities of the complexed one were still kept 1.2–2.3 times higher than those of the uncomplexed one. With respect to the produced polymers, the M_w increased with the increasing [IB], as chain propagation was more favored than transfer at higher [IB], and HPIB with $M_w = 1.5\text{--}3 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ could be generally produced. However, when compared with AlCl_3 /phenetole, the complexed catalyst was more likely to produce polymer with lower M_w and much broader MWD at the same reaction conditions, and this trend was more distinct at lower [IB]. Again, it is possibly due to the monomer starved condition met in the complexed system, as the high monomer conversion at low [IB] would result in more serious chain scission, which could bring about lowered M_w and broadened MWD [15]. Meanwhile, the polarity of the reaction environment was enhanced at lower [IB], which would facilitate the generation of active sites with stronger cationicity and result in more intensified side reactions [35].

Table 3. Effect of monomer concentration on the polymerization results ^a.

No	Coinitiator	[IB] ($\text{mol}\cdot\text{L}^{-1}$)	Conv. (%)	Act. ^d	M_w ($\times 10^4 \text{ g}\cdot\text{mol}^{-1}$)	M_n ($\times 10^4 \text{ g}\cdot\text{mol}^{-1}$)	MWD	Δ ^e
1 ^b	AlCl_3	2.4	73.8	131.27	17.90	4.97	3.6	1
2 ^c	$\text{AlCl}_3/\text{TiCl}_4$		91.7	163.10	17.90	1.24	14.4	1.24
3 ^b	AlCl_3	3.3	52.5	93.38	25.47	6.70	3.8	1
4 ^c	$\text{AlCl}_3/\text{TiCl}_4$		91.1	162.03	18.47	1.00	18.6	1.74
5 ^b	AlCl_3	4.0	40.5	72.04	28.86	7.59	3.8	1
6 ^c	$\text{AlCl}_3/\text{TiCl}_4$		95.0	168.97	20.03	0.96	20.9	2.35
7 ^b	AlCl_3	4.6	36.4	64.74	27.23	5.79	4.7	1
8 ^c	$\text{AlCl}_3/\text{TiCl}_4$		57.6	102.45	21.22	5.18	4.1	1.58
9 ^b	AlCl_3	5.1	15.4	27.39	30.30	11.22	2.7	1
10 ^c	$\text{AlCl}_3/\text{TiCl}_4$		24.1	42.87	31.58	13.73	2.3	1.56

^a 100 mL $\text{C}_2\text{H}_2\text{Cl}_2$; $T_p = -60$ °C; $t_p = 30$ min; ^b $[\text{AlCl}_3] = 2.51 \text{ mmol}\cdot\text{L}^{-1}$, $[\text{AlCl}_3]/[\text{phenetole}] = 1/1$; ^c $[\text{AlCl}_3] = 1.26 \text{ mmol}\cdot\text{L}^{-1}$, $[\text{AlCl}_3]/[\text{TiCl}_4]/[\text{phenetole}]/[\text{H}_2\text{O}] = 1/1/1/1$; ^d activity, $\text{kg PIB}\cdot\text{mol}^{-1}(\text{AlCl}_3 + \text{TiCl}_4)\cdot\text{h}^{-1}$; ^e $\Delta = \text{activity}_{(\text{complexed catalyst})}/\text{activity}_{(\text{reference catalyst})}$, where both the catalysts reacted at the same [IB].

3.4. Effect of Polymerization Time

The polymerization behaviors of the catalysts are likely to change with polymerization time (t_p), as the composition of the reaction system is very complex and would vary with time as well. Thus t_p in the range of 1–30 min was investigated, and the results are given in Table 4. It is evident that the monomer conversion got higher with longer t_p . However, the initial activity was so high that reasonable conversion higher than 50% could be achieved within 1 min, and 90% monomer could be consumed in 5 min. The activities of both catalysts dropped off monotonously over t_p , as the concentration of the active sites was higher and the reaction conditions were more homogeneous at the early stage. While the complexed catalyst was still more active than the uncomplexed one and showed activities about 1.2–1.7 times higher under the investigated conditions. In addition, the M_w of the obtained PIB decreased and the MWD got broader, as the t_p lasted longer. This could be ascribed to chain scission as the reaction went on, and this reaction became more serious after 5 min, as the monomer conversion went up to a level higher than 90% and gave rise to monomer

starvation, which would result in much broader MWD and a stronger reduction of M_n . However, within the first 3–5 min, the M_w was kept high, and HPIB with $M_w = 2\text{--}3 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ could be produced employing both catalysts, while the MWD was also kept relatively narrow. It indicates that t_p equals to 3–5 min is quite adequate to get a satisfactory monomer conversion for the synthesis of HPIB. This also implied that $\text{AlCl}_3\cdot\text{phenetole}/\text{TiCl}_4\cdot\text{H}_2\text{O}$ exhibited superior efficiency to the recently discovered $\text{BF}_3\cdot\text{EtOH}/\text{TiCl}_4\cdot\text{H}_2\text{O}$, as the former one generally showed much higher activities than the latter one, and a much shorter t_p was needed for $\text{AlCl}_3\cdot\text{phenetole}/\text{TiCl}_4\cdot\text{H}_2\text{O}$ to achieve a sufficient monomer conversion under similar reaction conditions [27].

Table 4. Effect of polymerization time on the polymerization results ^a.

No	Coinitiator	t_p (min)	Conv. (%)	Act. ^d	M_w ($\times 10^4 \text{ g}\cdot\text{mol}^{-1}$)	M_n ($\times 10^4 \text{ g}\cdot\text{mol}^{-1}$)	MWD	Δ ^e
1	AlCl_3 ^b	1.0	68.8	2200.29	27.21	6.80	4.0	1.00
2	$\text{AlCl}_3/\text{TiCl}_4$ ^c		51.4	2744.06	33.52	7.62	4.4	1.25
3	AlCl_3 ^b	3.0	77.7	1242.46	21.21	4.42	4.8	1.00
4	$\text{AlCl}_3/\text{TiCl}_4$ ^c		63.7	1700.36	34.43	13.24	2.6	1.37
5	AlCl_3 ^b	5.0	92.3	590.37	11.97	0.44	27.2	1.00
6	$\text{AlCl}_3/\text{TiCl}_4$ ^c		93.2	995.12	22.79	3.17	7.2	1.69
7	AlCl_3 ^b	10.0	95.8	306.38	11.03	0.53	20.8	1.00
8	$\text{AlCl}_3/\text{TiCl}_4$ ^c		90.1	481.02	23.60	4.37	5.4	1.57
9	AlCl_3 ^b	30.0	100.0	106.67	12.20	0.26	46.1	1.00
10	$\text{AlCl}_3/\text{TiCl}_4$ ^c		95.0	168.90	20.03	0.96	20.9	1.58

^a $[\text{IB}] = 4 \text{ mol}\cdot\text{L}^{-1}$; 100 mL $\text{C}_2\text{H}_2\text{Cl}_2$; $T_p = -60 \text{ }^\circ\text{C}$; ^b $[\text{AlCl}_3] = 4.19 \text{ mmol}\cdot\text{L}^{-1}$, $[\text{AlCl}_3]/[\text{phenetole}] = 1/1$;

^c $[\text{AlCl}_3] = 1.26 \text{ mmol}\cdot\text{L}^{-1}$, $[\text{AlCl}_3]/[\text{TiCl}_4]/[\text{phenetole}]/[\text{H}_2\text{O}] = 1/1/1/1$; ^d activity, $\text{kg PIB}\cdot\text{mol}^{-1}(\text{AlCl}_3 + \text{TiCl}_4)\cdot\text{h}^{-1}$;

^e $\Delta = \text{activity}_{(\text{complexed catalyst})}/\text{activity}_{(\text{reference catalyst})}$, where the same t_p lasted for the both initiating systems.

4. Conclusion

By simply compounding the high efficient $\text{AlCl}_3/\text{phenetole}$ for HPIB and the low efficient $\text{TiCl}_4/\text{H}_2\text{O}$ for HPIB or MPIB, a novel complexed initiating system consisting of $\text{AlCl}_3\cdot\text{phenetole}/\text{TiCl}_4\cdot\text{H}_2\text{O}$ was successfully prepared. The contrast studies that were carried out between $\text{AlCl}_3\cdot\text{phenetole}/\text{TiCl}_4\cdot\text{H}_2\text{O}$ and $\text{AlCl}_3/\text{phenetole}$ clearly showed that a notable synergistic effect was produced in the complexed catalyst, as the activities of the complexed system were generally 1.2–3 times higher than those of the $\text{AlCl}_3/\text{phenetole}$ under various reaction conditions. Hence, for the complexed catalyst system, even with very low coinitiator concentration ($2\text{--}5 \text{ mmol}\cdot\text{L}^{-1}$) and relatively high monomer concentration (ca. $4 \text{ mol}\cdot\text{L}^{-1}$), a satisfactory monomer conversion higher than 90% could be generally reached within 5 min. In addition, the very high activity of $\text{AlCl}_3\cdot\text{phenetole}/\text{TiCl}_4\cdot\text{H}_2\text{O}$ due to the synergistic effect made lower coinitiator concentration and polymerization temperature, as well as higher monomer concentration to be more favored for this complexed initiating system to produce PIBs with reasonable M_w and MWD. Moreover, the complexed catalyst also took advantage of $\text{AlCl}_3/\text{phenetole}$ in the production of HPIB, and HPIB with $M_w = 1\text{--}3 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ could be synthesized under the investigated conditions. It also indicated that $\text{AlCl}_3\cdot\text{phenetole}/\text{TiCl}_4\cdot\text{H}_2\text{O}$ showed an enhanced competence in producing HPIB when compared with $\text{BF}_3\cdot\text{EtOH}/\text{TiCl}_4\cdot\text{H}_2\text{O}$, as PIB with $M_w = 0.8\text{--}2.2 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ could be produced by the latter system as a whole. Generally, the high activity as well as the simple preparation procedures of the complexed catalyst offer us a unique method for the production of HPIB with improved efficiency.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4360/11/12/2121/s1>, Figure S1: The effect of solvent polarity on $\text{TiCl}_4/\text{H}_2\text{O}$ for IB polymerization ($[\text{IB}] = 2.9 \text{ mol}\cdot\text{L}^{-1}$; $[\text{H}_2\text{O}] = 20 \text{ mmol}\cdot\text{L}^{-1}$; $[\text{TiCl}_4] = 30 \text{ mmol}\cdot\text{L}^{-1}$; $t_p = 30 \text{ min}$; $T_p = -60 \text{ }^\circ\text{C}$); Figure S2: The effect of T_p on $\text{TiCl}_4/\text{H}_2\text{O}$ for IB polymerization ($[\text{IB}] = 2.9 \text{ mol}\cdot\text{L}^{-1}$; $[\text{H}_2\text{O}] = 20 \text{ mmol}\cdot\text{L}^{-1}$; $[\text{TiCl}_4] = 30 \text{ mmol}\cdot\text{L}^{-1}$; 60 mL $\text{C}_2\text{H}_2\text{Cl}_2$; 40 mL n-hexane; $t_p = 30 \text{ min}$); Figure S3: The effect of $[\text{H}_2\text{O}]$ and $[\text{TiCl}_4]$ on IB polymerization ((a) $[\text{TiCl}_4] = 50 \text{ mmol}\cdot\text{L}^{-1}$; (b) $[\text{H}_2\text{O}] = 40 \text{ mmol}\cdot\text{L}^{-1}$; (c) $[\text{TiCl}_4] = 4.56 \text{ mmol}\cdot\text{L}^{-1}$; Other conditions: $[\text{IB}] = 2.9 \text{ mol}\cdot\text{L}^{-1}$; 60 mL $\text{C}_2\text{H}_2\text{Cl}_2$; 40 mL n-hexane; $t_p = 30 \text{ min}$; $T_p = -60 \text{ }^\circ\text{C}$); Figure S4: The effect of monomer concentration on $\text{TiCl}_4/\text{H}_2\text{O}$ for IB polymerization ($[\text{H}_2\text{O}] = 30 \text{ mmol}\cdot\text{L}^{-1}$; $[\text{TiCl}_4] = 20 \text{ mmol}\cdot\text{L}^{-1}$; 60 mL $\text{C}_2\text{H}_2\text{Cl}_2$; 40 mL n-hexane; $t_p = 30 \text{ min}$; $T_p = -60 \text{ }^\circ\text{C}$); Figure S5: The effect of

solvent polarity on monomer conversion with AlCl_3 /phenetole initiating system ($[\text{IB}] = 4 \text{ mol}\cdot\text{L}^{-1}$; $V_{\text{dichloromethane}} + V_{\text{n-hexane}} = 100 \text{ mL}$; $T_p = -60 \text{ }^\circ\text{C}$; $t_p = 30 \text{ min}$; $[\text{AlCl}_3]/[\text{phenetole}] = 1/1$).

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