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Study on cationic polymerization of isobutylene using electrochemical method

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Abstract

The cationic polymerization of isobutylene (IB) initiated by $H_2O/TiCl_4$ was carried out in a mixture of methylene dichloride and *n*-hexane at −60 °C in the presence of a variety of external electron pair donors (EDs), such as triethylamine (TEA), *N*,*N*-dimethyl acetamide (DMA) and pyridine (Py). The effects of ED concentration ([ED]), H_2O concentration ($[H_2O]$) on conductance and capacitance in $H_2O/TiCl_4/ED/CH_2Cl_2$ reaction system were investigated. The effects of [ED], $[H_2O]$, solven polarity and polymerization time on monomer conversion, molecular weight (MW), molecular weight distribution (MWD, M_w/M_n) of polyisobutylene (PIB) were also investigated. Conductance decreased while capacitance increased with increases in both [ED] and electron donicity of ED. Conductance and capacitance increased with $[H_2O]$ when $[H_2O]$ was more than [Py]. Both unpaired and paired ions existed as propagating species or chain carriers in the presence of relatively low [ED] and polymers with bimodal molecular weight distribution (*peak a* and *b*) were obtained. The *peak a* with high molecular weight was induced by propagation via unpaired ions while *peak b* with low molecular weight was induced by propagation via paired ions. The propagation via paired ions could be achieved and polymers with unimodal molecular weight distribution could be produced when sufficient amounts of external ED was introduced to polymerization system.

Keywords: Cationic polymerization; Isobutylene; Electron pairs donor; Conductance; Capacitance

1. Introduction

The conventional cationic polymerization of isobutylene (IB) by H_2O/Lewis acid (such as BF_3, $AlCl_3$ or $TiCl_4$) initiating system was extremely rapid and accompanied with serious side reactions, such as chain transfer reaction and chain termination. The quasiliving catioinic polymerization of IB had been achieved by using *tert*-alkyl ester or ether or chloride as initiator, $TiCl_4$ or BCl_3 as co-initiator in the presence of external electron donors (EDs) and proton traps in two decades [1–4]. Several theories have been advanced to describe the mechanistic roles of external EDs in quasiliving cationic polymerization. Kaszas et al. [3–5] have proposed "carbocation

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stabilization", which suggesting that electron donors and/or their complexes with Lewis acid interact with the growing chain end to reduced its "cationicity" and thus to decrease the polymerization rate, suppress chain transfer and termination reactions and narrow MWD. Faust et al. [6–8] have proposed that the function of external EDs is to react with protic impurities in the polymerization system and then to remove or trap protic impurities. Matyjaszewski et al. [9,10] and Szwarc [11] have ascribed the "apparent" stabilization of the growing chain ends to a reduction in the instantaneous carbocation concentration and living cationic polymerizations are the result of control of the reaction kinetics but not the change of mechanism. Storey et al. [12] theorized that basic additives suppress the concentration of unpaired chain carriers through in situ production of common ions via the scavenging of protic impurities. The investigations on quasiliving cationic polymerizations of IB coinitiated by $TiCl_4$ in the presence of EDs have been performed with results suggesting that only ion-paired species participate as chain carriers [12–14]. On the other hand, kinetics in quasiliving cationic polymerization of IB was successfully investigated by in situ attenuated total reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) [15–17]. Calibration with known IB concentrations demonstrated direct proportionality between both the area and height of the $1655\ cm^{-1}$ band (C=C stretch) in the range of 0.001–0.5 mol/L IB concentration and the $1780\ cm^{-1}$ band (second overtone of the $CH_2 = $ wag) in the range of 0.3–6 mol/L IB concentration.

The propagating species and mechanism in cationic polymerization were investigated by electrochemical method. The conductivity had been used to monitor the process in cationic polymerization of IB initiated by chlorine/aluminum organic compounds (Et_2AlCl) system [18–22]. The interaction of chlorine with Et_2AlCl gave mainly aluminum compounds ($EtAlCl_2$ and $AlCl_3$), leading to a small increase in conductivity. The conductivity-time curves had a lag compared to conversion–time curves during polymerization. A kinetic method to investigate the reactivity of carbenium ions toward alkenes had been described by determining absorbance with a fiber optics system (Scholly KGS 111) and conductance with a Tacussel CD 810 conductimeter and Platinum plate electrodes, respectively [23]. Diarylmethyl chlorides could be completely ionized by BCl_3 in CH_2Cl_2 to give color solutions of diarylcarbenium tetrachloroborates ($Ar_2CH^+BCl_4^-$), which presented absorbance and conductivity. Upon the addition of a model alkene, 2-methyl-1-pentene, conductance and absorbance disappeared due to the formation of the covalent and colorless adducts $Ar_2CHCH_2C(CH_3)C_3H_7$.

In our previous investigations [24,25], the desirable cationic polymerizations of IB initiated by $H_2O/TiCl_4$ could be achieved by introduction of a small amount of EDs with different chemical structure and polymers with narrow molecular weight distribution were obtained. This paper will further investigate the mechanistic role of EDs in IB polymerization initiated by $H_2O/TiCl_4$ in the presence of strong EDs, such as triethylamine (TEA), *N*,*N*-dimethyl acetamide (DMA) and pyridine (Py), respectively, by simultaneous determination of conductance and capacitance. The effects of $[H_2O]$ and [ED] on the corresponding polymerization and molecular weight distribution of polymers obtained will also be discussed.

2. Experimental section

2.1. Materials

Titanium tetrachloride ($TiCl_4$, 99.9%, packaged under nitrogen) and isobutylene (IB, 99.9%) were used as received. Methylene dichloride and *n*-hexane were dried prior to use by distillation from calcium hydride (CaH_2) under the atmosphere of dry nitrogen. Py, DMA and TEA were distilled from CaH_2 into dry glass ampules, respectively.

2.2. Procedures

Polymerizations were carried out in test tubes under dry nitrogen at −60 °C. Mixtures of the IB, ED and solvent (33 mL portions) were transferred to prechilled 20 mm × 140 mm test tubes via a 33 mL volumetric pipette. Then the reaction was started by the addition of the chilled solution of $TiCl_4$ in CH_2Cl_2 ($[TiCl_4] = 2$ mol/L) with syringes. The reactions were quenched by the injection of 2 mL methanol–water mixtures (1:1 v/v) at specified times from 2 to 20 min. The reaction mixtures were diluted with hexane, washed with 1 wt% NaOH aqueous solutions for the removal of Lewis acid residues, and repeatedly washed with H_2O until they were neutral. The polymers were dried in vacuo until constant weight was obtained.

2.3. Measurements

The conversion of IB was determined gravimetrically. The molecular weight and molecular weight distribution (MWD, M_w/M_n) of the polymers were determined using a gel permeation chromatography system (GPC-150C) at 25 °C. Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1.0 mL/min. Sample concentration of 2 mg/mL in THF with an injection volume of 100 μL. Molecular weight were calculated according to standard polystyrene calibration. The concentration of water in the polymerization system was measured electrochemically with a WA-1A water analyzer as previously reported [24]. The water concentration was kept constant by preparing a large quantity of monomer solution and $TiCl_4$ solution, which used for the series experiment runs under the same reaction conditions and under a pure N_2 atmosphere.

A JC-2 electrode and a rheostat were attached in series to the signal generator. Conductance (*G*) and capacitance (*C*) of electrode in the reaction system could be monitored in situ by inserting Platinum electrodes into the reaction system according to following equations:

$$R = U_0/I - R_0 = U_0R_0\cos\alpha/UR - R_0$$

$$G = 1/R$$

$$C = UR/2\Pi fR_0U\sin\alpha$$

where U_0 is voltage of the signal generator, U_R and R_0 are voltage and resistance of the rheostat respectively, U and R are voltage and resistance of the electrode respectively; α is the phase angle between U_0 and U_R; f is the signal frequency.

The electric current of the Platinum electrodes consists of Faraday current and double electrode layer current. Faraday current reflecting the value of conductance is affected more greatly by the amount of unpaired ions than by that of ion pairs. Double electrode layer current reflecting the value of capacitance was influenced mainly by property of the double electrode layer at the surface of Platinum electrodes. According to Bockris model [26], the first layer abut against platinum electrodes consist of solvent molecules and specific absorptive ions and the second layer consisted of polarized counterions in the double electrode layer. Conductance and capacitance mainly depend on the unpaired ions and paired ions in reaction system, respectively.

3. Results and discussion

The conductance and capacitance of the $H_2O/TiCl_4$ and $H_2O/TiCl_4/DMA$ reaction system at −60 °C were recorded at different ageing time to investigate the interaction of H_2O, $TiCl_4$ and DMA. The conductance and capacitance of $H_2O/TiCl_4/CH_2Cl_2$ system were 10.7×10^{-6} s and 67.6×10^{-12} F, respectively. As shown in Fig. 1, conductance decreased strikingly from 10.7×10^{-6} s to 9.8×10^{-6} s and capacitance increased from 67.6×10^{-12} F to 72.8×10^{-12} F when small amounts of DMA was introduced. It can be also observed from

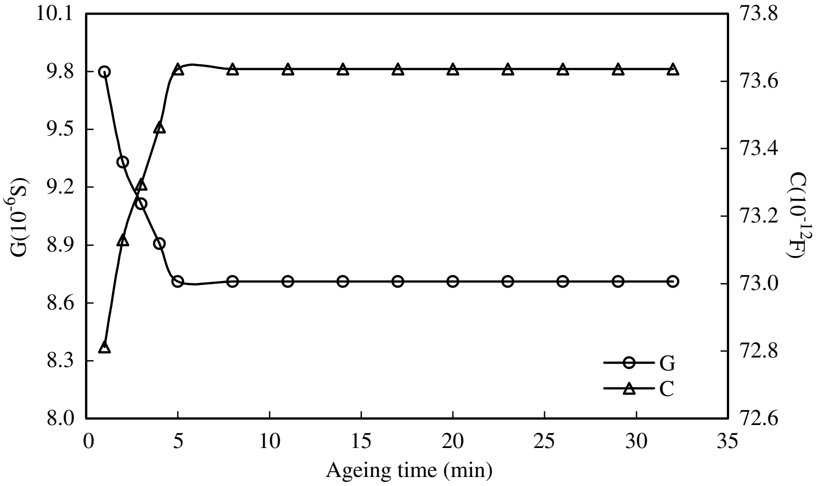


Fig. 1. The effects of ageing time on conductance and capacitance in $H_2O/TiCl_4/DMA$ system. Conditions: $[TiCl_4] = 4.6 \times 10^{-2}$ mol/L, $[DMA] = 1.82 \times 10^{-3}$ mol/L, $[H_2O] = 2.56 \times 10^{-3}$ mol/L, $CH_2Cl_2/n\text{-}C_6H_{14} = 60/40$ (v/v), T = −60 °C, $U_0 = 2$ V, $f = 2000$ Hz, $R_0 = 1.5 \times 10^4\ \Omega$.

Fig. 1 that conductance continuously decreased from 9.8×10^{-6} S to 8.7×10^{-6} S and capacitance increased from 72.8×10^{-12} F to 73.6×10^{-12} F within 5 min. After that, both conductance and capacitance kept almost constant in the range from 5 to 32 min. These experimental data suggest that unpaired active species gradually turned into paired ones within 5 min in the presence of DMA.

To gain further insight into the role of EDs on formation of active species in $H_2O/TiCl_4/CH_2Cl_2$ system, the control experiment in the absence of EDs was conducted and the effects of concentrations of DMA, Py and TEA on conductance and capacitance were investigated respectively. The experimental results are shown in Figs. 2 and 3. It can be seen that conductance decreased with increases both in ED concentration and in electron donicity of ED at their same concentrations. On the other hand, capacitance increased with ED concentration since ion paired species could be adsorbed to the surface of Platinum electrodes under electric field to make up of the first layer of double electrode layer. Both conductance and capacitance were influenced most greatly when TEA with strongest donicity was used as ED. Therefore, concentration of unpaired ions decreased while concentration of paired ion species

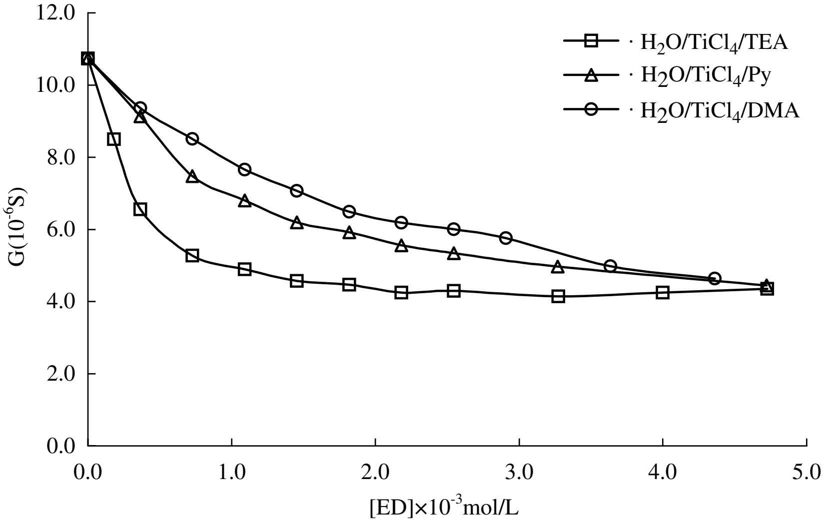


Fig. 2. The effects of ED concentration on the conductance of $H_2O/TiCl_4$ initiating system. Conditions: $[TiCl_4] = 4.6 \times 10^{-2}$ mol/L, $[H_2O] = 1.61 \times 10^{-3}$ mol/L, $CH_2Cl_2/n\text{-}C_6H_{14} = 60/40$ (v/v), $T = -60$ °C, $U_0 = 2$ V, $f = 2000$ Hz, $R_0 = 1.5 \times 10^4\ \Omega$.

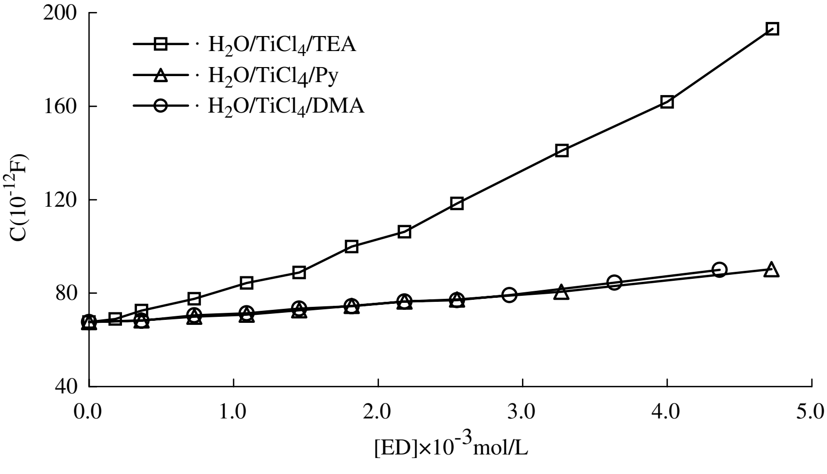


Fig. 3. The effects of ED concentration on the capacitance of $H_2O/TiCl_4$ initiating system conditions are shown as in Fig. 2.

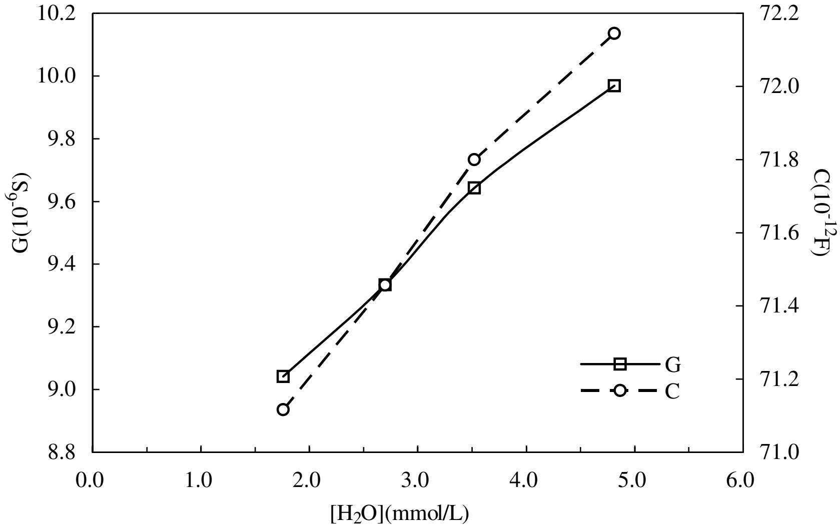
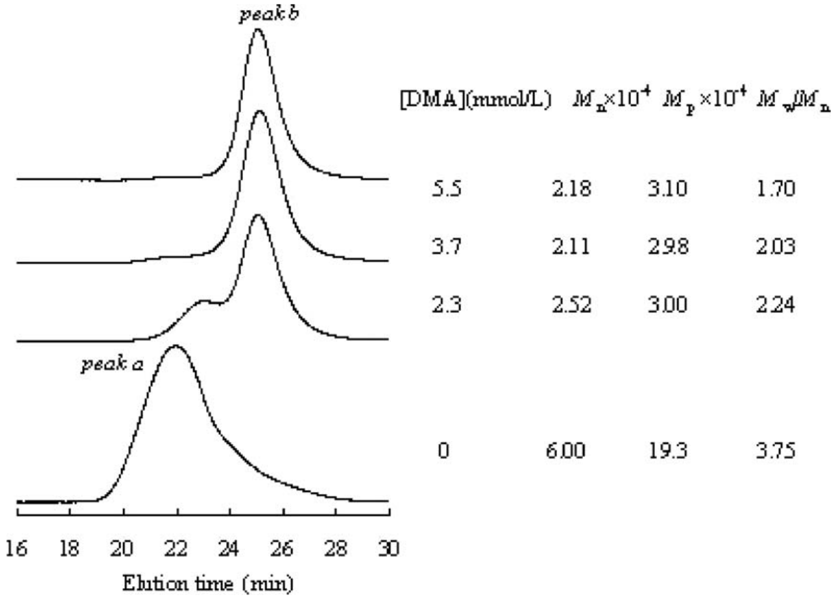


Fig. 4. The effects of H_2O concentration on conductance and capacitance in $H_2O/TiCl_4/Py$ system. Conditions: [Py] = 1.46×10^{-3} mol/L, others are shown as in Fig. 2.

increased with increasing [ED] and its electron donicity.

The effects of H_2O concentration on conductance and capacitance in $H_2O/TiCl_4/Py/CH_2Cl_2$ system were further investigated when $[H_2O] > [Py]$ and the experimental results are shown in Fig. 4. The amount of Py was insufficient to transform all the unpaired ions into the paired ions. The concentration of active species including unpaired ion and paired ions increased with H_2O concentration, leading to large increase in conductance and a slight increase in capacitance.

In order to get insight into the mechanistic difference between conventional and controlled cationic polymerizations of IB, the control experiment was conducted in *n*-hex/CH_2Cl_2 (40/60 v/v) mixture at



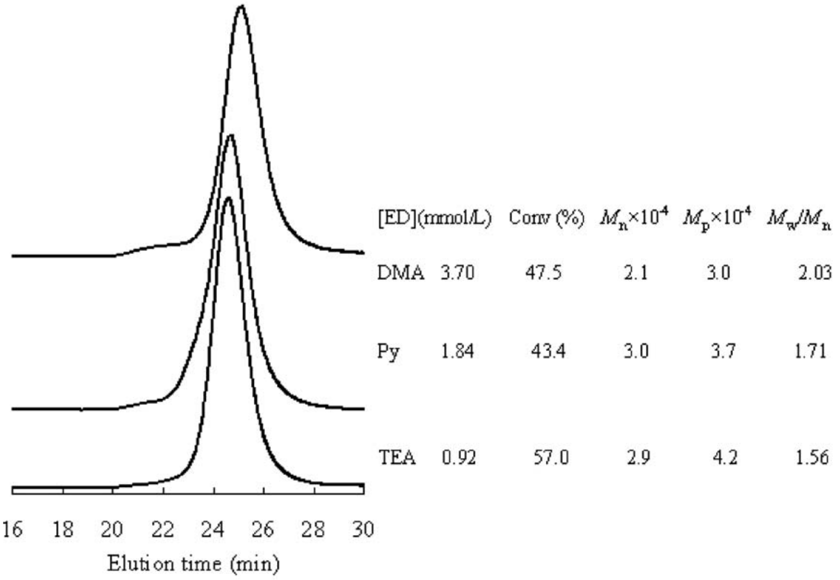
[DMA](mmol/L)	$M_n \times 10^4$	$M_p \times 10^4$	M_w/M_n
5.5	2.18	3.10	1.70
3.7	2.11	2.98	2.03
2.3	2.52	3.00	2.24
0	6.00	19.3	3.75

Fig. 5. GPC traces of PIB obtained in the absence and at different DMA concentrations. Conditions: $[IB]_0 = 1.0$ mol/L, $[H_2O] = 1.61 \times 10^{-3}$ mol/L, $[TiCl_4] = 4.6 \times 10^{-2}$ mol/L, $CH_2Cl_2/n\text{-}C_6H_{14} = 60/40$ (v/v), polymerization temperature = −60 °C, polymerization time = 15 min.

−60 °C initiated by $H_2O/TiCl_4$ in the absence of external EDs. It was observed that the conventional cationic polymerization of IB by $H_2O/TiCl_4$ proceeded extremely fast and reached near complete conversion in less than 5 s. The dramatically high polymerization rate in the absence of EDs is due to the highly reactive unpaired ion propagating species. GPC analysis of the polymer in Fig. 5 presents a broad molecular weight distribution (MWD, $M_w/M_n = 3.75$) and high molecular weight (M_n) of 6.0×10^4 g/mol at *peak a*.

The cationic polymerization of IB initiated by $H_2O/TiCl_4$ in the presence of different concentration of DMA was investigated under the same conditions as in the above control experiment. The GPC traces of polymers formed at different DMA concentrations and the corresponding data of conversion, M_n, molecular weight at peak (M_p) and polydispersity index (M_w/M_n) are presented in Fig. 5. The polymerization rate significantly decreased with an increase in DMA concentration. The GPC trace of polyisobutylene obtained at [DMA] of 2.3×10^{-3} mol/L exhibits a bimodal molecular weight distribution (*peak a* and *peak b*), suggesting that propagation proceeded via two distinctly different active species if the amount of DMA was insufficient. The *peak a* on the leading edge of GPC chromatogram with high molecular weight is ascribed to the fraction of unpaired propagating species and *peak b* with low molecular weight is ascribed to the fraction of ion pair propagating species. The *peak a* decreased while *peak b* increased with increasing DMA concentration. Then *peak a* diminished and almost melted into the base line and the GPC trace exhibits an unimodal molecular weight distribution (*peak b*) when DMA concentration was 5.5×10^{-3} mol/L. It suggests that the participation of free carbocation in propagation could be reduced or even eliminated and thus propagation proceeded via paired ion species by adding sufficient amounts of DMA.

To confirm the effectiveness of EDs in the cationic polymerization, IB polymerization was further investigated by $H_2O/TiCl_4$ initiating system in the presence of relatively high concentration of TEA, Py and DMA, respectively. All the GPC traces of the resultant polymers in Fig. 6 exhibit relatively narrow unimodal molecular weight distributions. As Kaszas et al. pointed out [27], the effectiveness of EDs in preventing side reactions and improving initiator efficiencies in living IB polymerization was classified according to their Gutmann donor number (DN) and the most effective EDs are those with high Gutmann DN. The DN was defined as the molar enthalpy value of the interaction of the donor with the reference acceptors $SbCl_5$ [28]. The higher the DN, the stronger the donicity of EDs. The DN is 61.0, 33.1 and 27.8 for TEA, Py and DMA, respectively. Comparatively, less amounts of TEA was required to mediate the IB polymerization



[ED](mmol/L)		Conv (%)	$M_n \times 10^4$	$M_p \times 10^4$	M_w/M_n
DMA	3.70	47.5	2.1	3.0	2.03
Py	1.84	43.4	3.0	3.7	1.71
TEA	0.92	57.0	2.9	4.2	1.56

Fig. 6. GPC traces of PIB obtained in the presence of EDs Conditions: polymerization time: 20 min, others are shown as in Fig. 5.

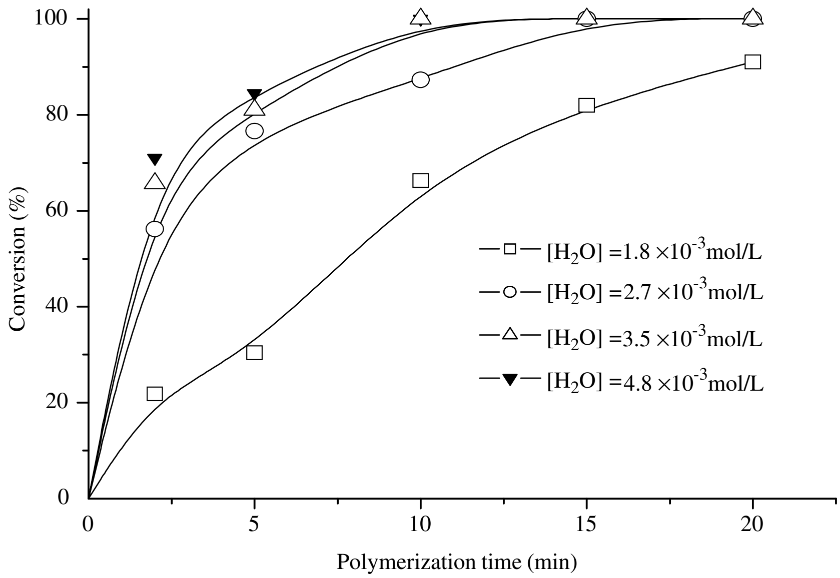
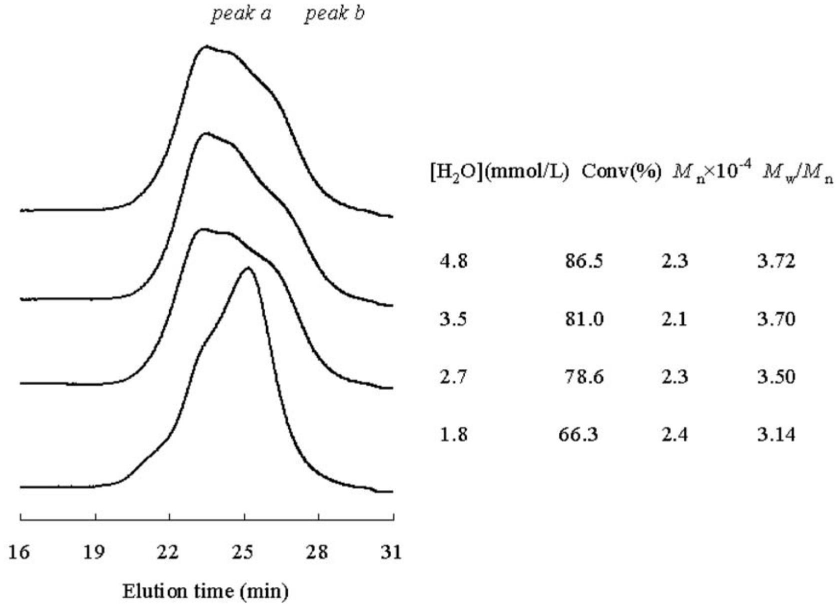


Fig. 7. The dependence of monomer conversions on polymerization time in the presence of Py Conditions: $[IB]_0 = 1.0$ mol/L, $[H_2O] = 1.61 \times 10^{-3}$ mol/L, $[Py] = 1.46 \times 10^{-3}$ mol/L, $[TiCl_4] = 4.6 \times 10^{-2}$ mol/L, $CH_2Cl_2/n\text{-}C_6H_{14} = 60/40$ (v/v), polymerization temperature = −60 °C.

and polymer formed with narrow molecular weight distribution ($M_w/M_n = 1.56$). Interestingly, it can be also observed from Fig. 6 that the GPC trace exhibited narrow unimodal molecular weight distribution in the presence of TEA even when its concentration (0.92×10^{-3} mol/L) was lower than H_2O concentration (1.6×10^{-3} mol/L), whereas the concentration of DMA or Py should be higher than that of H_2O. The experimental results show that ion-paired species participated as chain carrier in cationic polymerization of IB initiated by $H_2O/TiCl_4$ in the presence of sufficient amounts of ED. This result is in



$[H_2O]$(mmol/L)	Conv(%)	$M_n \times 10^{-4}$	M_w/M_n
4.8	86.5	2.3	3.72
3.5	81.0	2.1	3.70
2.7	78.6	2.3	3.50
1.8	66.3	2.4	3.14

Fig. 8. GPC traces of PIB obtained at different H_2O concentration. Conditions are shown as in Fig. 7.

accord with those in the investigations [12–14], in which revealed that unpaired ions do not participate as chain carriers within IB polymerization mediated by nucleophilic additives.

On the other hand, it is necessary to investigate IB polymerization and GPC traces of polymer resultants when $[H_2O] > [Py]$. The effect of H_2O concentration from 1.8×10^{-3} mol/L to 4.8×10^{-3} mol/L on IB polymerization initiated by $H_2O/TiCl_4$ at −60 °C in the presence of Py ($[Py] = 1.46 \times 10^{-3}$ mol/L) was further investigated while holding the concentrations of all other components constant. It is demonstrated in Fig. 7 that monomer conversion increased with H_2O concentration. The GPC traces of PIB obtained at different H_2O concentration are given in Fig. 8. The GPC trace mainly presented at *peak b* but a broad shoulder at *peak a* was observed on leading edge of GPC chromatogram of polymer, suggesting that the propagation proceeded mainly via paired ion species while the propagation via

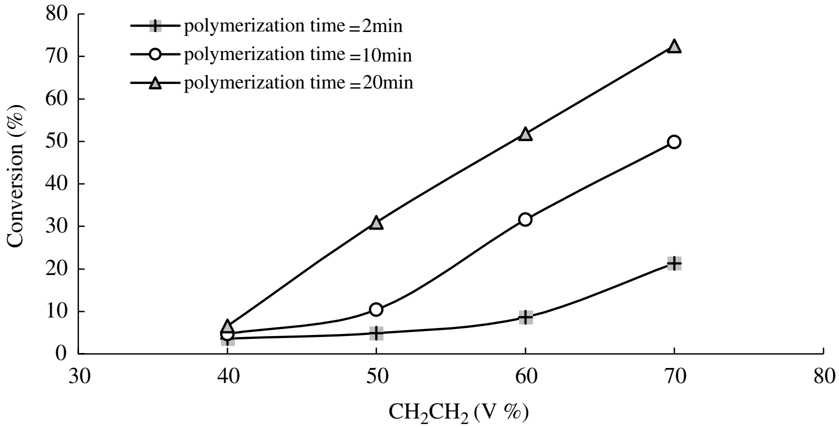
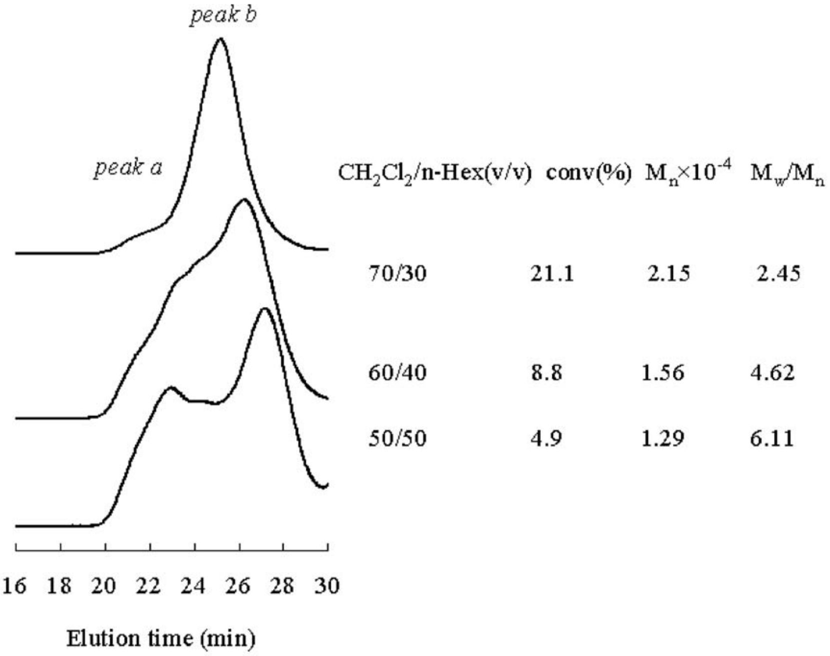


Fig. 9. The dependence of monomer conversion on solvent polarity. Conditions: $[Py] = 1.45 \times 10^{-3}$ mol/L, others are shown as in Fig. 5.

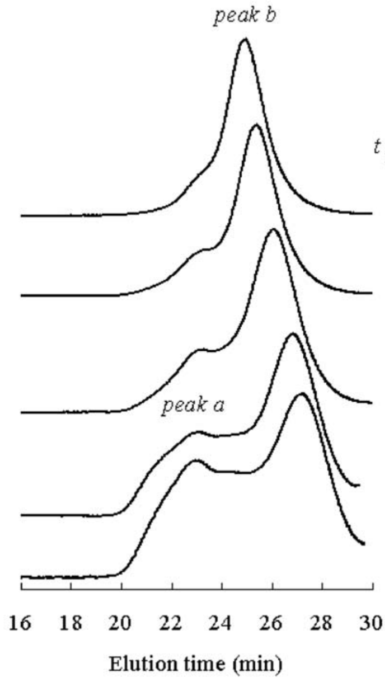


CH_2Cl_2/n-Hex(v/v)	conv(%)	$M_n \times 10^{-4}$	M_w/M_n
70/30	21.1	2.15	2.45
60/40	8.8	1.56	4.62
50/50	4.9	1.29	6.11

Fig. 10. GPC traces of PIB obtained in cosolvent with different polarity in the presence of Py Conditions: polymerization time = 2 min, others are shown as in Fig. 9.

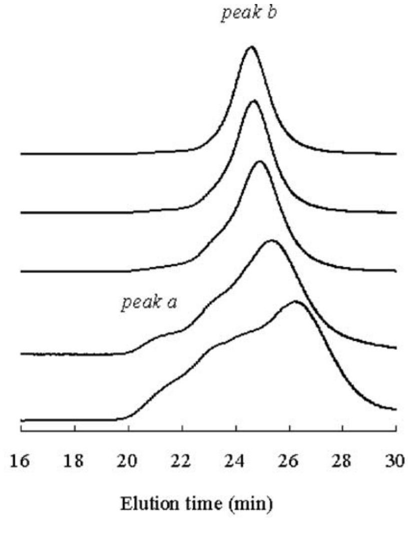
unpaired ion species could not be neglected when $[H_2O]$ (1.8×10^{-3} mol/L) was slightly higher than [Py] (1.46×10^{-3} mol/L). It can be also seen that *peak a* became stronger with increasing H_2O concentration and thus GPC traces exhibit obviously bimodal molecular weight distributions. Therefore, propagation proceeded via a combination of both paired and unpaired ions in the polymerization system and led to bimodal molecular weight distribution when $[H_2O]$ was higher than [Py]. The propagation via unpaired ion active species might become important with regard to the uncontrolled polymerization.

The IB polymerization by $H_2O/TiCl_4$ at −60 °C in the presence of Py ($[Py] = 1.45 \times 10^{-3}$ mol/L) in mixed solvents with various volume ratio of $CH_2Cl_2/n\text{-}C_6H_{14}$ was also investigated while



t_p(min)	Conv(%)	$M_n \times 10^{-4}$	$M_p \times 10^{-4}$	M_w/M_n
20	31.2	2.39	3.24	2.02
15	17.4	2.16	2.44	2.35
10	10.4	1.59	1.63	3.24
5	5.8	1.40	1.01	5.39
2	4.9	1.29	0.82	6.11

Fig. 11. GPC traces of PIB obtained at various polymerization time in CH_1Cl_2/*n*-hex (50/50 v/v).



t_p(min)	conv(%)	$M_n \times 10^{-4}$	$M_p \times 10^{-4}$	M_w/M_n
20	52.1	3.09	3.95	1.58
15	43.4	3.00	3.72	1.71
10	31.8	2.60	3.25	2.07
5	22.6	1.82	2.46	3.69
2	8.8	1.56	1.51	4.62

Fig. 12. GPC traces of PIB obtained at various polymerization time in CH_2Cl_2/*n*-hex (60/40 v/v).

holding other conditions constant. As shown in Fig. 9, IB polymerization gave low monomer conversion in CH_2Cl_2/n-C_6H_{14} (40/60 v/v) and monomer conversion increased with solvent polarity. Some representative GPC traces of PIB obtained in solvent mixtures with different polarity are given in Figs. 10–12. The GPC traces exhibit bimodal molecular weight distributions during the early stages of polymer growth. A broad shoulder (*peak a*) was clearly observed on the left of GPC chromatograms of polymers less than 10% conversion. Interestingly, this shoulder with high molecular weight gradually decreased and *peak b* gradually increased with monomer conversion. The GPC traces of polymers exhibit unimodal distribution at *peak b* in the polymerization system at high monomer conversion.

4. Conclusions

The propagation via unpaired and/or paired ion species were greatly affected by the concentrations of EDs and H_2O in cationic polymerization of isobutylene. The character of cationic polymerization was related to the propagation via unpaired or paired ion species. Conventional polymerization initiated by $H_2O/TiCl_4$ in the absence of external EDs produced a poor synthetic control due to the propagation via the highly active unpaired ions. The cationic polymerization of IB with $H_2O/TiCl_4$ in the presence of EDs was propagated via a combination of unpaired and paired ion active species leading to bimodal molecular weight distribution when [H_2O] was higher than [Py] or [DMA] or during the early stages of polymer growth. The sufficient amounts of ED were needed to suppress the propagation via unpaired ion species. A desirable polymerization in which propagation proceeded only via paired ion species could be achieved and polymers with unimodal molecular weight distribution could be obtained by adding sufficient amounts of EDs.

Acknowledgement

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