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Articles

Kinetic Investigation of the Carbocationic Polymerization of Isobutylene with the $H_2O/TiCl_4$/ED Initiating System

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ABSTRACT: The cationic polymerizations of isobutylene (IB) initiated by the $H_2O/TiCl_4$ in dichloromethane (CH_2Cl_2) at −30 °C were carried out in the absence and presence of various external electron pair donors (EDs). Controlled polymerization with a slow polymerization rate and a narrow molecular weight distribution (MWD, $M_w/M_n = 1.11-1.28$) of the polymer was achieved by using certain appropriate $H_2O/TiCl_4$/ED systems. The kinetics of the IB polymerization with the $H_2O/TiCl_4$/ED initiating system was investigated. It indicated that the polymerization rate was first-order with respect both to monomer and to initiator concentrations in the presence of strong or weak EDs. Polymerizations exhibited a second-order dependence on $TiCl_4$ concentration in those cases where weak EDs, such as methyl acetate (MAC), methyl acrylate (MA), sulfolane (HDF), or methyl benzoate (MB), were used. On the other hand, first order in $TiCl_4$ concentration was observed when strong EDs, such as dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), pyridine (Py), or triethylamine (TEA), were used.

Introduction

The living cationic polymerization of isobutylene (IB) was first reported by Kennedy et al. for polymerization using *tert*-alkyl ester or ether initiators in conjunction with Lewis acids BCl_3 co-initiator as initiating systems.[1,2] The livingness was attributed to the in-situ formation of electron pair donors derived from Lewis acid and the acetoxy or methoxy groups of initiator.[3] On the basis of these initiating systems, living cationic polymerization of IB has been developed to those by introducing some external EDs. The effectiveness of the external EDs has been recognized consistently, but their mechanistic roles in living carbocationic polymerizations still remains obscure. There are mainly two opinions on the mechanistic roles of EDs. Kaszas et al.[3] proposed the "carbocation stabilization" mechanism, in which the Lewis acid/ED complex interacts with the growing PIB chain ends, participating in the formation and stabilization of the propagating carbocation center, thereby suppressing chain transfer and termination reactions. The nature of this interaction is not clear; it may be that the EDs affect the ionization equilibrium and/or stabilize the carbocations. Faust et al.[4] challenged this "carbocation stabilization" mechanism and proposed the "proton scavenging" mechanism. They 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. Therefore, further investigation is needed to clarify the role of EDs.

There is also some disagreement regarding the kinetic order of the propagation rate with respect to the $TiCl_4$ in the cationic polymerization of IB initiated by dicumyl methyl ether,[4] 1,4-bis(2-chloro-2-propyl)benzene,[5] 2-chloro-2,4,4-trimethylpentane,[6−9] or 5-*tert*-butyl-1,3-bis-(2-chloro-2-propyl)benzene.[7,10] Under the most common reaction conditions, i.e., $[TiCl_4]_0 > [\text{initiator} + \text{EDs}]_0$, a second-order dependence on the $[TiCl_4]$ has been reported.[4−6,8,10] Faust et al.[4] got close to second-order behavior in $TiCl_4$ in the IB polymerization initiated by aromatic compounds, e.g., dicumyl chloride in the mixture solvent of hexane and CH_3Cl at −80 °C. Storey et al.[7] found reaction order in $[TiCl_4]_{eff}$ was approximately 2 in the similar IB polymerization initiated by 2-chloro-2,4,4-trimethylpentane (TMPCl) or 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene in the presence of substituted pyridine. However, there exists controversy over $TiCl_4$ reaction order for the polymerizations of IB. A first-order dependence on the $[TiCl_4]$ or $([TiCl_4] - [TEA])$ in the similar IB polymerization initiated TMPCl in the presence of triethylamine (TEA) was reported by Kennedy et al.[11] A first-order dependence on $[TiCl_4]$ for IB polymerization by TMPCl/$TiCl_4$ initiating system at −90 and −80 °C in which $[TiCl_4]_0 \leqslant [\text{initiator}]_0$ was also demonstrated by Kaszas and Puskas.[8,12] The reconciliation of the discrepancy between these observations must require further experimental data and a deeper understanding of the polymerization mechanism.

Because of these ambiguities, we decided to simplify the polymerization system and then utilize only the protic impurity "H_2O" as initiator, without purposely added initiators, such as *tert*-alkyl ester, ether, to avoid the possible formation of the in-situ electron pair donor derived from these initiators. This paper will investigate the controlled cationic polymerization of IB by the $H_2O/$

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$TiCl_4$/ED system and the effect of several external electron pair donors with different chemical structure and donicity on the kinetics of polymerization.

Experimental Section

Materials. Dichloromethane (CH_2Cl_2), methyl acetate (MAC), dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), pyridine (Py), triethylamine (TEA), methyl acrylate (MA), methyl benzoate (MB), or sulfolane (HDF) was dried prior to use by distillation from calcium hydride. $TiCl_4$ (99.9%, packaged under nitrogen), IB, and methanol were used as received.

Instrumentation. Gel permeation chromatography (GPC) was performed on PIB samples to determine number-average molecular weight (M_n) and molecular weight distribution (MWD, M_w/M_n). Tetrahydrofuran (THF) served as solvent of PIB with the concentration of 20 mg of PIB/10 mL of THF and the mobile phase at a flow rate of 1.0 mL/min. The content of H_2O in the components of the polymerization system was determined electrochemically based on the following reaction and equation:

$$H_2O + I_2 + SO_2 + CH_3OH + 3RN \rightarrow 2RN{\cdot}HI + RN{\cdot}HSO_4CH_3$$

$$2I - 2e \rightarrow I_2$$

$$m = (c/96500)(M/n) = (it)/10722$$

where m is the weight of water in the sample (unit of measurement: mg), c the quantity of electric charge needed in the electrolysis (unit of measurement: mc), M the molecular weight of water, n the number of electron transfer, i the electric current in the electrolysis (unit of measurement: mA), t the time for the electrolysi (unit of measurement: s), 96500 the Farady constant, and 10722 the quantity of electric charge needed in the electrolysis of 1 mg of water (unit of measurement: mc). The water concentration was kept constant by preparing a large quantity of monomer solution and $TiCl_4$ solution, which used for the experiment runs under the same reaction conditions and under a pure N_2 atmosphere.

Procedures. Polymerizations were carried out under a dry nitrogen atmosphere at −30 °C. Specific reaction conditions are listed in the figure captions and tables. A representative polymerization procedure was as follows: 600 mL of CH_2Cl_2, 200 mL of IB, and corresponding ED were added sequentially to a chilled 1 L round-bottomed flask. The mixture was stirred, and then 20 mL portions were airtightly transferred to 25 mm × 160 mm culture tubes via a 20 mL volumetric pipet. Then ED was added to the monomer solution. In another 100 mL two-neck flask which had been flame-dried under vacumm and filled with N_2 gas, 31.0 mL of CH_2Cl_2 and 9.0 mL of pure $TiCl_4$ were introduced by syringe under a N_2 atomsphere to get $TiCl_4$ solution with 2.0 mol/L. Polymerization reaction was started by the rapid addition of the $TiCl_4$ solution at −30 °C and terminated by 2 mL methanol of 0.5% NaOH at the specified time. The polymers were washed with distilled water until neutral and dried in a vacuum at 40 °C until a constant weight was obtained. The conversion was determined gravimetrically.

Results and Discussion

1. Controlled Polymerizations of IB by "H_2O"/$TiCl_4$/ED Initiating Systems.

Carbocationic polymerizations of isobutylene (IB) co-initiated by $TiCl_4$ were carried out in CH_2Cl_2 in the absence of and in the presence of various electron pair donors (ED) at −30 °C. ED was chosen from the following compounds with different chemical structure and different electron donicity: dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), pyridine (Py), triethylamine (TEA), methyl acetate (MAC), methyl acrylate (MA), methyl benzoate (MB), and sulfolane (HDF). The polymer products were subjected to GPC analysis, and the GPC traces of polymers with more than 40% yields and narrow MWD of around 1.20 are given in Figure 1.

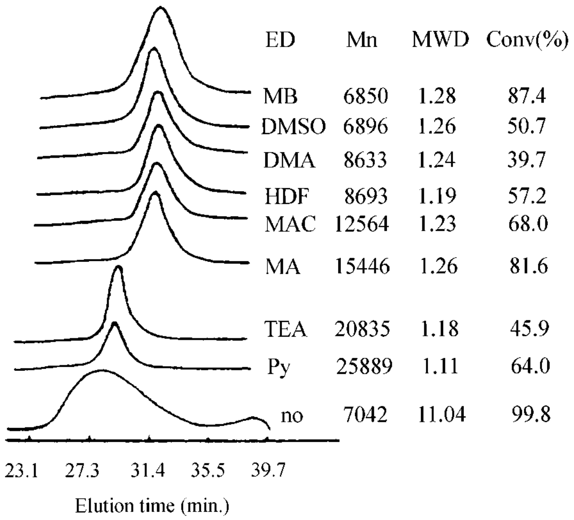


Figure 1. GPC traces demonstrating the obvious effects of EDs on MWDs of polymers $[IB]_0 = 2.90$ M, $[H_2O]_0 = 1.092 \times 10^{-3}$ M, $[TiCl_4]_0 = 5.83 \times 10^{-2}$ M, CH_2Cl_2 as solvent, −30 °C, 20 min, $[MB]_0 = [MAC]_0 = [MA]_0 = [HDF]_0 = 2.33 \times 10^{-2}$ M, $[DMSO]_0 = 1.17 \times 10^{-2}$ M, $[Py]_0 = [DMA]_0 = 5.83 \times 10^{-3}$ M, $[TEA]_0 = 2.91 \times 10^{-3}$ M.

From the GPC results and the experimental observations, we can find that (1) the conventional cationic polymerization of IB initiated by the combination of moisture with $TiCl_4$ without purposely added other initiator and external ED was an uncontrolled process with extremely rapid reaction rate and led to polymers with a quite broad MWD ($M_w/M_n = 11.04$). (2) Interestingly, the above undesired polymerization process could be effectively transferred to controlled polymerizations in the presence of adequate EDs. The polymerizations proceeded with slow polymerization rate, and the polymers with narrow MWD ($M_w/M_n = 1.11-1.28$) were obtained. This polymerization system is attractive for the controlled polymerization by protic impurity "H_2O" and for the prospective of practical application in the future.

The results indicate that these EDs with different chemical structure and donicity play very important roles in the controlled polymerization. The effectiveness of EDs on the polymerization processes and MWDs of the polymer products would seem to have a contradiction with the "proton scavenging" mechanism. Indeed, it is difficult to account for the experimental results that the polymerization proceeded with high conversion and the polymer produced had narrow MWD even when [ED] was higher than [H_2O].

The results also showed that the controlled polymerizations of IB with $H_2O/TiCl_4$/ED initiating system provided good conditions for further kinetic study.

The kinetics of the cationic polymerization of IB using the $H_2O/TiCl_4$ system in the presence of external EDs were determined by gravimetrically monitoring polymer yield as a function of reaction time. The data were interpreted in terms of the kinetic rate law for cationic polymerization:

$$r_p = -\frac{d[M]}{dt} = k_p[R^+][M] = k[H_2O]^a[TiCl_4]^b[M] = k_p^A[M]$$

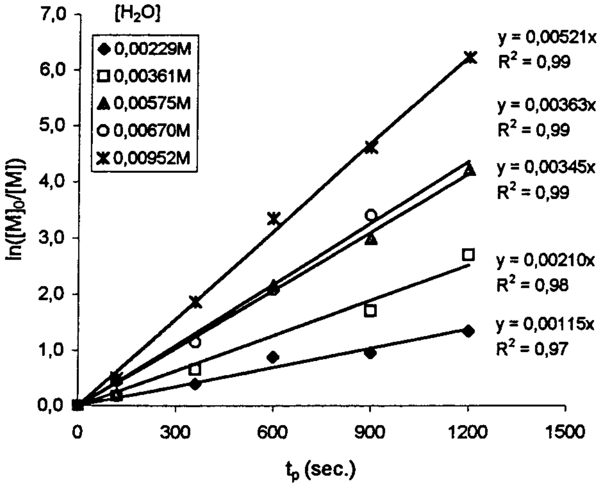


Figure 2. ln([M]$_0$/[M] vs time plots for IB polymerization at various [H_2O] in the presence of DMA [IB]$_0$ = 2.90 M, [$TiCl_4$]$_0$ = 3.92 × 10^{-2} M, [DMA]$_0$ = 3.92 × 10^{-3} M, −30 °C, CH_2Cl_2 as solvent.

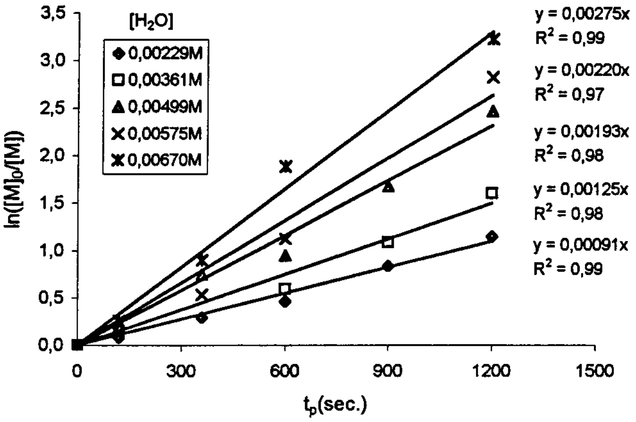


Figure 3. ln([M]$_0$/[M] vs time plots for IB polymerization at various [H_2O] in the presence of MB [IB]$_0$ = 2.90 M, [$TiCl_4$]$_0$ = 3.92 × 10^{-2} M, [MB]$_0$ = 1.57 × 10^{-2} M, −30 °C, CH_2Cl_2 as solvent.

where r_p is the rate of polymerization, [R^+] is the concentration of instantaneously active growing chains, k_p^A is the apparent first-order rate constant for propagation, [M] is the concentration of monomer, and [H_2O] is the concentration of moisture in the polymerization system.

2. Effect of H_2O Concentration on the Rate of Polymerization. The dependence of the rate of polymerization on the concentration of H_2O at −30 °C was investigated by using several H_2O concentrations while keeping the concentrations of all other components the same. The linear plots of ln([M]$_0$/[M]) vs polymerization time passing through the origin are shown in Figure 2 and Figure 3 in the presence of DMA and MB, respectively. These experiment results demonstrate that all the first-order dependences on monomer concentration were obtained when [H_2O]$_0$ was 2.29 × 10^{-3}, 3.61 × 10^{-3}, 4.99 × 10^{-3}, 5.75 × 10^{-3}, 6.70 × 10^{-3}, or 9.52 × 10^{-3} mol/L. The k_p^A values were obtained from the slopes of these linear plots. The dependence of the lines shows that the rate of polymerization increases with H_2O concentration. By plotting ln(k_p^A) vs ln[H_2O]$_0$, as shown in Figure 4, we can see that the rate of polymerization varied with the first power of H_2O concentration in the presence of either DMA or MB.

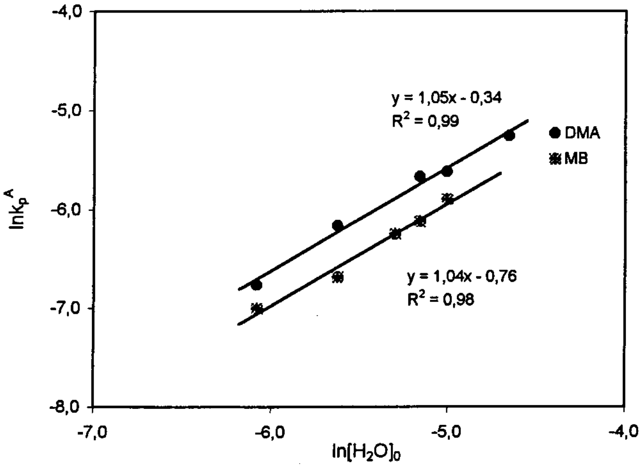


Figure 4. Reaction order of H_2O concentration for polymerization of IB in CH_2Cl_2. [IB]$_0$ = 2.90 M, [$TiCl_4$]$_0$ = 3.92 × 10^{-2} M, [DMA]$_0$ = 3.92 × 10^{-3} M, [MB]$_0$ = 1.57 × 10^{-2} M, −30 °C, CH_2Cl_2 as solvent.

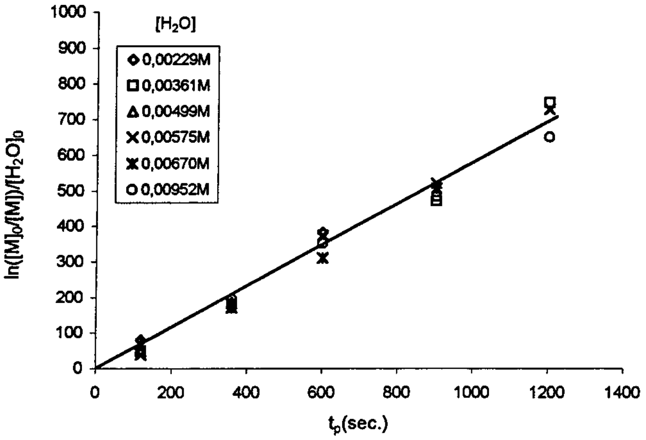


Figure 5. ln([M]$_0$/[M])/[H_2O]$_0$ vs time for IB polymerization at various H_2O concentrations [IB]$_0$ = 2.90 M, [$TiCl_4$]$_0$ = 3.92 × 10^{-2} M, [DMA]$_0$ = 3.92 × 10^{-3} M, −30 °C, CH_2Cl_2 as solvent.

Plots of ln([M]$_0$/[M])/[H_2O]$_0$ vs polymerization time for different H_2O concentrations from 2.29 × 10^{-3} to 9.52 × 10^{-3} mol/L are shown in Figure 5. The experimental results that all lines coincide show that the concentration of active centers is proportional to [H_2O]$_0$ and that only ion-paired species are present. If a polymerization in which propagations occur through both ion pairs and free ions with large different reactivity, there should be an increase in k_p^A/[I]$_0$ with increasing [I]$_0$ and a bimodal or broad MWD. The conclusion that the active centers were paired ions almost certainly in living IB polymerization in the presence of certain electron-pair donors was reached by Puskas et al.[15] The similar result that only ion-paired species participate as chain carriers was reported for IB polymerization by the dicumyl chloride/$TiCl_4$/pyridine initiating system by Storey et al.[5]

Therefore, the kinetic orders with respect both to monomer and to initiator are unity. The propagation reaction in this system can be regarded approximately as a bimolecular one by monomer insertion into the active ionic species.

3. Effect of $TiCl_4$ Concentration on the Rate of Polymerization. The reaction order with respect to $TiCl_4$ in the IB polymerizations at −30 °C was investigated in the presence of the above 8 EDs (DMSO, Py, DMA, TEA, MAC, MA, MB, and HDF).

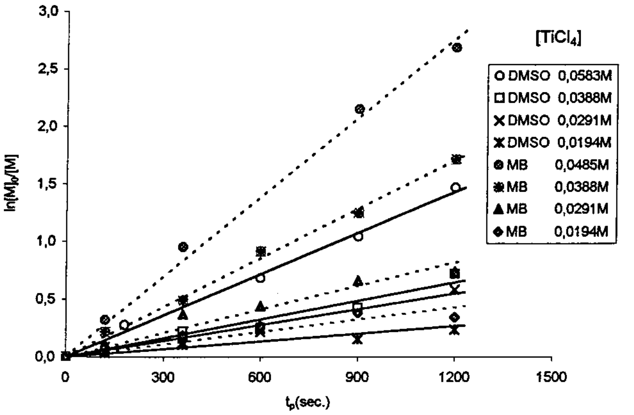


Figure 6. ln([M]$_0$/[M] vs time plots at various [$TiCl_4$] in the presence of DMSO or MB [IB]$_0$ = 2.90 M, [H_2O]$_0$ = 2.29 × 10^{-3} M, [MB] = 0.4 × [$TiCl_4$], [DMSO] = 0.2[$TiCl_4$], −30 °C, CH_2Cl_2 as solvent. Solid lines: in the presence of DMSO. Dotted lines: in the presence of MB.

Table 1. Apparent Rate Constants for IB Polymerization by the $H_2O/TiCl_4$/ED System[a]

ED	[$TiCl_4$]$_0$ × 10^2 (mol/L)	$k_p^A \times 10^3$ (s^{-1})	ED	[$TiCl_4$]$_0$ × 10^2 (mol/L)	$k_p^A \times 10^3$ (s^{-1})
DMA	1.94	0.51	MAC	0.97	0.21
	3.88	1.06		1.94	0.63
	4.85	1.39		3.88	3.71
	5.83	1.84		5.83	9.61
TEA	2.91	0.50	MA	0.97	0.11
	3.88	0.50		2.91	0.71
	4.85	0.65		3.88	1.66
	5.83	1.10		4.85	3.82
	6.80	1.10			
Py	2.91	0.50	MB	1.94	0.30
	3.88	0.63		2.91	0.62
	4.85	0.97		3.88	1.40
	6.80	1.25		4.85	2.20
DMSO	1.94	0.22	HDF	1.94	0.32
	2.91	0.45		2.91	0.67
	3.88	0.56		4.85	1.84
	4.85	0.72		5.83	2.50

[a] Conditions: [IB]$_0$ = 2.90 M, [H_2O] = 2.29 × 10^{-3} M, [TEA] = 0.05[$TiCl_4$], [DMA] = [Py] = 0.1[$TiCl_4$], [DMSO] = 0.2[$TiCl_4$], [MAC] = [MA] = [MB] = [HDF] = 0.4[$TiCl_4$], CH_2Cl_2 as solvent, −30 °C.

Plots of ln([M]$_0$/[M]) vs polymerization time were used to determined the value of k_p^A for each particular set of polymerization conditions. Figure 6 shows the representative plots of ln([M]$_0$/[M]) vs time in the presence of DMSO and MB, respectively. Linearity of these plots demonstrates first-order dependence on monomer concentration. The k_p^A values obtained from these linear plots are listed in Table 1. It may be seen that [$TiCl_4$] exerts a strong effect on the rate of polymerization. The rates increased with [$TiCl_4$] in the presence of all eight EDs used, without exception. Since the rate of propagation is proportional to the concentration of active species $H^{+\,-}(EDTi_nCl_{4n}OH)$, the value of n will dictate the observed kinetic order of the propagation reaction with respect to $TiCl_4$.

To classify EDs and elucidate the experiment results clearly, the plots of ln(k_p^A) vs ln[$TiCl_4$]$_0$ in the presence of MAC, MA, MB, or HDF with low donicity are shown in Figure 7 and in the presence of DMA, TEA, Py, or DMSO with high donicity are shown in Figure 8. From the plots of ln(k_p^A) vs ln[$TiCl_4$]$_0$, it was found that second-order dependence with respect to $TiCl_4$ occurred under the conditions of using an external ED with low donicity and first-order dependence with respect to $TiCl_4$ under the conditions of using an external ED with high donicity. Evidently, the donicity of the ED used strongly influenced the reaction order of $TiCl_4$ and thus the contribution form of $TiCl_4$ to active centers.

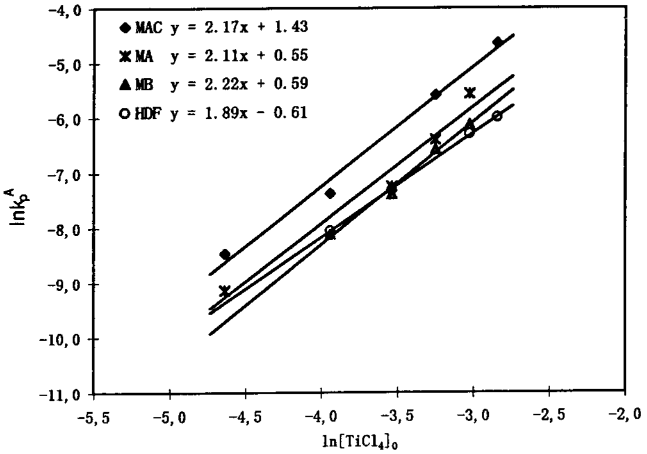


Figure 7. Reaction order of $TiCl_4$ in IB polymerization in the presence of MAC, MA, MB, or HDF.

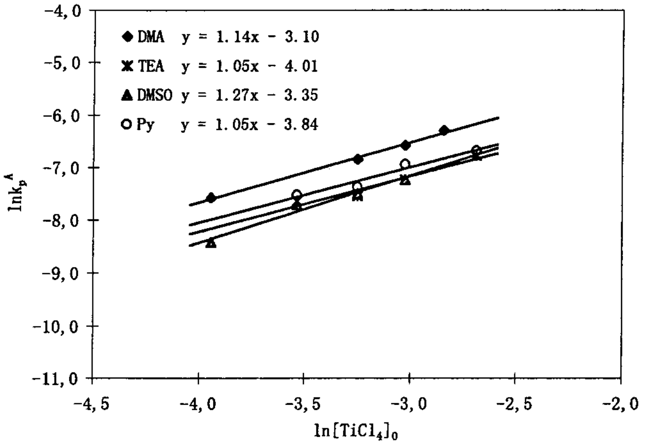
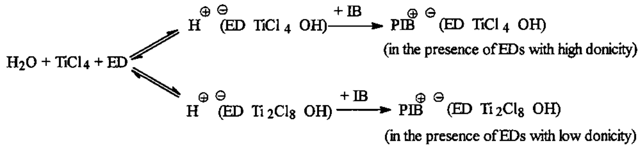


Figure 8. Reaction order of $TiCl_4$ in IB polymerization in the presence of DMA, Py, TEA, and DMSO.

Scheme 1. Mechanism for IB Polymerization by the $H_2O/TiCl_4$/ED Initiating System



A possible mechanism (Scheme 1) involving dimeric gegenions and monomeric gegenions was proposed to account for the above experimental results of second-order dependence and first-order dependence on [$TiCl_4$], respectively. The donicity of the external ED mainly affects the nature of the gegenions in the active species.

As Kaszas et al.[13] pointed out, the effectiveness of EDs in preventing side reactions and improving initiator efficiencies in IB polymerization was classified according to their Gutmann donor number (DN). It was indicated that the most effective EDs are those which have high Gutmann DN, such as DMA and DMSO.[13] The DN was defined as the molar enthalpy value of the interaction of the donor with the reference acceptors $SbCl_5$.[14] The higher the Gutmann DN, the stronger the donicity of ED. Here, MAC, MA, MB, and HDF are weak EDs with low donicity: $DN_{(MAC)} = 16.5$, $DN_{(HDF)} = 14.8$, and the DN values of MA and MB should be around that of MAC since they have similar structures. On the other hand, DMA, DMSO, Py, and TEA are strong EDs with high donicity; $DN_{(DMA)} = 27.8$, $DN_{(DMSO)} = 29.8$, $DN_{(Py)} = 33.1$, and $DN_{(TEA)} = 61.0$.[16]

It is possible that these external EDs play a dual role of interacting with the active centers and affecting the nucleophilicity of microsurroundings around the active centers. The strong EDs might exhibit strong interactions with the active centers and so obviously increase the nucleophilicity of microsurroundings around the active centers, leading to inhibition of the dimer formation of $TiCl_4$ as well as inhibition of the addition of monomer to the cations and thus decrease of the propagation rate. It was proposed that an external ED with strong donicity forces propagation to proceed through a mechanism that involves gegenions of the form $[(ED)TiCl_4(OH)]^-$ rather than $[(ED)Ti_2Cl_8(OH)]^-$. The experimental observation of a first-order dependency on $[TiCl_4]$ in IB polymerization by the $H_2O/TiCl_4/ED$ system suggested that propagation via monomeric gegenions $[(ED)TiCl_4(OH)]^-$ is significant. On the other hand, second-order dependence on $[TiCl_4]$ suggested that the propagation proceeded predominantly by chains activated with dimeric gegenions $[(ED)Ti_2Cl_8(OH)]^-$.

Conclusions

It is attractive that controlled cationic polymerizations of IB initiated by H_2O in the polymerization systems in conjunction with $TiCl_4$ could be achieved by introducing various electron pair donors with different chemical structure and donicity. The rate of polymerization was first-order in both monomer and initiator concentrations in the precence of all eight EDs used. The propagation reaction in this system can be regarded approximately as a bimolecular one by monomer insertion into the active ionic species. With regards to the nature of the active species, it was shown that ion-pair species participated in chain propagation. The donicity of the external EDs strongly influenced the nature of the gegenions in the active species. Polymerizations exhibited second-order dependence on $TiCl_4$ concentration in the presence of weak external electron pair donors MAC, MA, HDF, or MB. On the other hand, polymerizations exhibited first-order dependence on $TiCl_4$ concentration in the presence of strong external electron pair donors DMA, DMSO, Py, or TEA. Second order with respect to $TiCl_4$ concentration is assumed to the predominant participation of dimeric gegenions in propagation. First order with respect to $TiCl_4$ concentration suggests that propagation proceeds significantly via monomeric gegenions.

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