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Registry No. (MAN)(St) (copolymer), 33961-16-9; (AN)-(St) (copolymer), 9003-54-7; (DEF)(St) (copolymer), 29058-33-1; (FN)(St) (copolymer), 27882-58-2; (MAn)(St) (copolymer), 9011-13-6; (2-VN)(FN) (copolymer), 83094-11-5.

Electron Pair Donors in Carbocationic Polymerization. 2. Mechanism of Living Carbocationic Polymerizations and the Role of in Situ and External Electron Pair Donors†

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ABSTRACT: A new mechanism is proposed for the living carbocationic polymerization [LC$^+$Pzn) of isobutylene (IB) initiated by tertiary ester/MtCl$_n$ (MtCl$_n$ = BCl$_3$ or TiCl$_4$) complexes (Scheme I). According to this mechanism, the initiating systems, e.g., tertiary ester/MtCl$_n$ (I), first yield *tert*-C$^+$···OCORMtCl$_n^-$ ion pairs (II) which may initiate IB polymerization by monomer addition to the *tert*-C$^+$···OCORMtCl$_n^-$ species (III). Species III eventually will undergo collapse with the counteranion, yielding a tertiary chloride capped PIB chain (IV) plus MtCl$_{n-1}$OCOR, an in situ electron pair donor (ED). In line with previous observations, excess MtCl$_n$ will reionize IV, yielding the active propagating species PIB$^+$···MtCl$_{n+1}^-$ (V). Thus the temporarily dormant species IV are in dynamic equilibrium with the propagation-active species V. The function of the EDs, both in situ and external ones, is to stabilize the active carbocations, affecting beneficially the course of polymerization. The transitory formation of tertiary chlorides by collapse of the "mixed" counteranion OCORMtCl$_{n-1}^-$ (II → VI), however, may also occur prior to polymerization. The exact route leading to the final IV $\rightleftharpoons$ V equilibrium depends on reaction conditions, i.e., the nature of initiator and MtX$_n$, stability of the mixed counteranion, solvent polarity, temperature, etc. The latter equilibrium accounts for the presence of tertiary Cl end groups (PIB-Cl^t) upon quenching. This is a crucial deviation from the earlier mechanistic view according to which the dormant species are tertiary ester or tertiary ether terminated PIB. These propositions have been substantiated by a variety of means: (1) by demonstrating the existence of reversible termination in the PIB-Cl^t/excess BCl$_3$/IB system; (2) by analysis of literature sources dealing with the transformation of tertiary ester and tertiary ether/MtCl$_n$ complexes to the corresponding tertiary chlorides; (3) by observations that the equimolar 2-acetyl-2,4,4-trimethylpentane (TMPOAc)/TiCl$_4$ system is totally inactive; (4) by polymerizations induced by equimolar mixtures of cumyl acetate (CumOAc) + cumyl methyl ether (CumOMe)/excess TiCl$_4$ and CumCl + CumOMe/excess TiCl$_4$ systems, both of which give living polymerizations and narrow molecular weight distribution (MWD) PIBs; (5) by polymerizations of IB induced, on the one hand, by TMPOAc/excess TiCl$_4$ and, on the other hand, by TMPCl/excess TiCl$_4$/ethyl acetate (EtOAc) systems, where only the latter give narrow-MWD product; and (6) by comparing the MWDs of PIBs prepared by CumCl/excess TiCl$_4$ and CumCl/excess TiCl$_4$/EtOAc and demonstrating the MWD narrowing effect of the deliberately added external ED (EtOAc). The information generated in these studies has been analyzed, and a mechanistic interpretation of the observed facts is offered.

A. Introduction

In the course of our systematic investigations on LC$^+$Pzn, particularly those on the LC$^+$Pzn of IB,[1-3] evidence has increasingly been accumulating that the initial views concerning the mechanism of these polymerizations[4,5] are insufficient and must be revised. According to the original proposition, the LC$^+$Pzn of IB induced by tertiary ester/BCl$_3$[4] or tertiary ether/BCl$_3$[5] complexes involves initiation and propagation by monomer insertion into polarized non-

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† Paper 26 in the series "Living Carbocationic Polymerization". For paper 1, see: Kaszas, G.; et al. *Polym. Bull.* **1988**, *20*, 413.

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dissociated alkyl–oxygen bonds. Quenching (i.e., "forced termination") by heating or by the addition of nucleophilic quenching agents was visualized to occur by intramolecular rearrangement of the active sites,[4] and the recovered products were invariably PIB-Cl^t.[1-5] Extensive research involving many kinds of nucleophiles and quenching techniques (including the quenching of living charges into rapidly stirred bases, acetates, anhydrides, normal and cyclic ethers, alkyllithiums, etc.) aimed at the introduction of a terminal function of other than tertiary chloride has failed, and the only product recovered was always PIB-Cl^t.[6]

This paper mainly concerns a new mechanism of living IB polymerization and various means to substantiate it. Experiments have been designed to corroborate the new mechanism, and the findings are explained by a comprehensive view. Key to the new hypothesis is the assumption that in the course of events leading to initiation an ED arises in situ which very beneficially influences the further course of the polymerization, i.e., helps in producing narrow-MWD polymer and reduces or eliminates unwanted side reactions. The exact course of initiation and propagation depends on reaction conditions, i.e., solvent polarity, temperature, and the nature of the initiator and, most importantly, of the $MtCl_n$. For instance, substantial differences have been observed in the characteristics of IB polymerizations coinitiated by BCl_3 and $TiCl_4$: the CumCl/BCl_3 combination yields a transfer-dominated inifer system,[7] whereas the CumCl/$TiCl_4$ combination induces quasi-living polymerizations;[8] the stoichiometric TMPOAc/BCl_3 complex is an efficient initiating system,[9] whereas the stoichiometric CumOAc/$TiCl_4$ combination is totally inactive but polymerization occurs in the presence of excess $TiCl_4$.[1] In spite of these major and a series of more subtle differences,[1,4,10] both the BCl_3- and $TiCl_4$-based mechanisms can be combined to a comprehensive view of living carbocationic polymerizations.

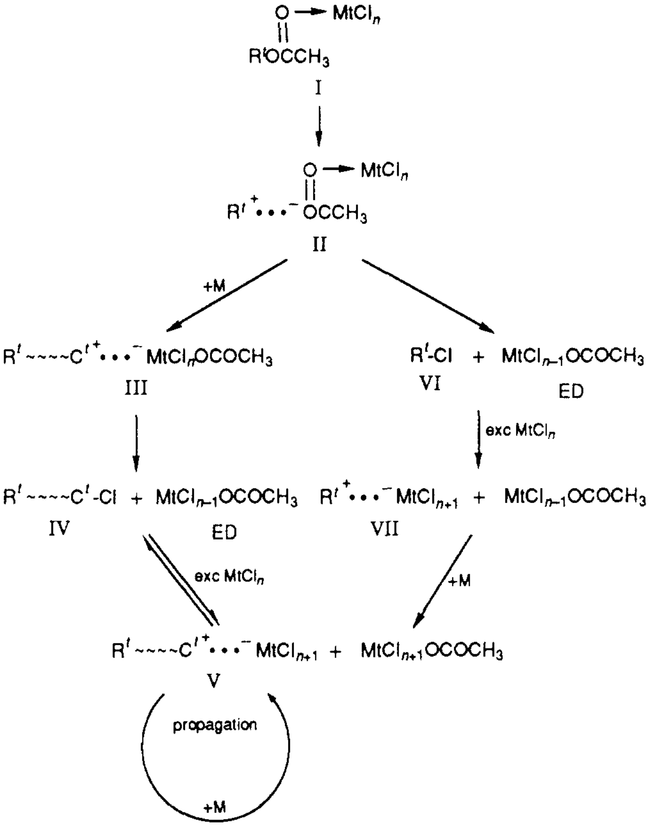
B. Experimental Section

B.1. Materials. The syntheses of 2-phenyl-2-acetylpropane (cumyl acetate, CumOAc), 2-phenyl-2-methoxypropane (cumyl methyl ether, CumOMe), 2-chloro-2-phenylpropane (cumyl chloride, CumCl), *p*-bis(2-chloro-2-propyl)benzene (dicumyl chloride, DiCumCl), 2-acetyl-2,4,4-trimethylpentane (TMPOAc), 2-chloro-2,4,4-trimethylpentane (TMPCl), and ditertiary chloride telechelic PIB (^tCl-PIB-Cl^t) with narrow MWD have been described.[1,3-5,11] The TMPOAc was freshly distilled over CaH_2 under vacuum on the day the experiment was performed. The source and purity of IB, CH_3Cl, *n*-hexane, $TiCl_4$, BCl_3 and ethyl acetate (EtOAc) have been described.[1,4] Methanol (Aldrich) was used as received.

B.2. Procedures. Polymerizations were carried out in a drybox under dry nitrogen in large test tubes by the incremental monomer addition (IMA) or conventional all monomer in (AMI) techniques[4] or round-bottom flasks as described.[1,4] Control experiments with BCl_3 (in the absence of initiator) gave insignificant conversion, indicating efficient drying. Detailed experimental conditions, concentrations, etc. are given in the text and table or figure captions. Initiator/$TiCl_4$ ratios were kept at 1/16 unless noted otherwise. PIB molecular weights were determined by a Waters high-pressure GPC instrument (Model 6000A pump) having a series of ultra-Styragel columns (100, 500, 10^3, 10^4, 10^5 Å), a differential refractometer (Model 21401), and a UV absorbance detector (Model 440). The flow rate of THF was 1 mL/min. The calibration curve was made with narrow-MWD ($\bar{M}_w/\bar{M}_n$ = 1.1) PIB samples. ^1H NMR spectra were recorded on a Varian T-60 spectrometer in carbon tetrachloride solutions using TMS standards.

C. Results and Discussion

Scheme I
Proposed Mechanism of Living IB Polymerizations



C.1. Outline of a Comprehensive Mechanism of Living IB Polymerization Initiated by Tertiary Ester/MtX_n and Tertiary Ether/MtX_n Complexes.

Scheme I outlines the proposed mechanism of living IB polymerizations induced by tertiary esters or tertiary ethers in conjunction with BCl_3 or $TiCl_4$ coinitiators. While the symbolism shows only the tertiary acetate/$MtCl_n$ combination, with substitution of OR for $OCOCH_3$, the mechanism can be extended to tertiary ether/$MtCl_n$ systems as well. R^t = cumyl, TMP; $MtCl_n$ = BCl_3, $TiCl_4$. The TMPOAc/BCl_3 and tertiary lactone/BCl_3 systems are exceptions and have been discussed elsewhere.[9]

According to this mechanism, the polymerizations start by the tertiary ester/$MtCl_n$ or tertiary ether/$MtCl_n$ complexes I yielding ionized complexes II; the degree of ionization of these species is obscure. These complexes, depending on the reaction conditions, may induce polymerization (II → III) or may be transformed to a tertiary chloride (VI) plus $CH_3OCOMtCl_{n-1}$ (in situ ED). The exact route will depend on the relative magnitude of the reaction rates R_{III} and R_{VI} (II → III and II → VI), respectively. If $R_{III} \gg R_{VI}$, polymerization will occur; however, if $R_{VI} \gg R_{III}$ the tertiary chloride VI will arise. For example, with CumOAc/$TiCl_4$, the polymerization most probably proceeds by the rapid formation of CumCl since excess $TiCl_4$ is needed to induce IB polymerization.[1] In contrast, the equimolar TMPOAc/BCl_3 complex readily initiates IB polymerization;[9] therefore in this case initiation most probably proceeds by II → III. Reactions II → III and II → VI may also proceed simultaneously. Whatever the exact mechanism during the early stages of the polymerization, the polymerization will be governed by the IV $\rightleftharpoons$ V equilibrium and the in situ EDs (e.g., $CH_3OCOTiCl_3$ or CH_3OTiCl_3) will have a profound influence on the process. Carbocation stabilization by in situ EDs is viewed to be of paramount importance in mediating LC^+Pzn yielding uniform PIBs. The observation that the product of living IB polymerizations

Table I
Polymerization of IB by ^{t}Cl-PIB-Cl^t/BCl_3 and ^{t}Cl-PIB-Cl^t/BCl_3/DMA

sample	BCl_3, 10^{-2} mol	premixing, min	reaction time, min	IB conv, %	$\bar{M}_n$	MWD	N,[a] 10^{-4} mol
A. Conditions: ^{t}Cl-PIB-Cl^t ($\bar{M}_n$ = 2270, MWD = 1.22) = 2.20×10^{-4} mol; IB = 5.97×10^{-3} mol; CH_3Cl = 20 mL; −40 °C; AMI technique							
1	0.38	15	15	37.6	2780	1.43	2.25
2	1.01	15	15	58.2	3050	1.42	2.28
3	2.02	15	15	54.0	3090	1.36	2.20
B. Controls (Conditions as in (A) except with the Absence of ^{t}Cl-PIB-Cl^t)							
1a	0.38	15	15	29.6		multimodal	
3a	2.02	15	15	23.3		multimodal	
C. Conditions as in (A) in the Presence of DMA = 6.45×10^{-4} mol							
4	1.01	0	30	31.0	2840	1.16	2.13
5	1.01	0	60	44.8	3100	1.14	2.10
6	1.01	0	120	76.1	3560	1.12	2.12
D. Control (Conditions as in (C) except with the Absence of ^{t}Cl-PIB-Cl^t							
5a	1.01	0	60	1.1			

[a] N = g of PIB harvested/$\bar{M}_n$.

is invariably PIB-Cl^t is readily explained by the equilibrium IV $\rightleftharpoons$ V.

The proposed equilibrium IV $\rightleftharpoons$ V is conceptually identical with reversible termination introduced and discussed in detail in connection with quasi-living polymerizations (QLPzn), for example, with the CumCl/$TiCl_4$ system.[8] In both QLPzn and truly living polymerizations the concentration of polymer chains remains constant and the degree of polymerization increases linearly with the amount of monomer consumed.[12] While in living IB polymerizations initiated by tertiary ester/$TiCl_4$ and tertiary ether/$TiCl_4$ systems nearly uniform polymers are obtained,[1,2] quasi-living IB polymerizations initiated by CumCl/$TiCl_4$ yield polymers with broad MWDs.[8] The problem of MWD in these systems will be discussed elsewhere.[13] Resumption of growth in IB polymerizations by PIB-Cl^t in the presence of excess BCl_3 has recently been shown to occur by Nuyken et al.[14] and was confirmed by us under LC$^+$Pzn conditions (see section C.2). Thus in the presence of the reversible equilibrium V $\rightleftharpoons$ IV, termination is in fact absent (V is the true propagating species) and LC$^+$Pzn can arise.

While stoichiometric tertiary ester/BCl_3 complexes are able to induce IB polymerizations,[9] stoichiometric tertiary ester/$TiCl_4$ combinations are totally inactive.[1] In the presence of excess $TiCl_4$, however, IB polymerization occurs[1,2] and the rate increases linearly with the $TiCl_4$ concentration.[1] Prompted by these observations, we have scoured the literature to gain further insight into the nature of tertiary ester/$MtCl_n$ complexes and to relate this information to LC$^+$Pzn. The paragraph that follows concerns key references uncovered.

Mehrotra and Misra[15] reported that the reaction between *tert*-butyl acetate and $TiCl_4$ yielded *tert*-butyl chloride and $CH_3COOTiCl_3$ at room temperature. Lappert and Gerrard[16,17] studied the behavior of different ester/$MtCl_n$ complexes and reported that the dropwise addition of *tert*-butyl acetate to BCl_3 in pentane at −10 °C immediately leads to *tert*-butyl chloride and boron-containing compounds. Mach and Drahoradova[18] observed that the alkylation of benzene by the *tert*-butyl acetate·$TiCl_4$ complex at room temperature proceeds by *tert*-butyl chloride forming in situ, and they concluded that the complex itself is unable to induce alkylation. Faust and Kennedy[4] reported that the TMPOAc/BCl_3 complex rapidly yields TMPCl upon the addition of various nucleophiles in CH_3Cl at −30 °C. Matyjaszewski[19] demonstrated that the 2-phenylethyl acetate/BCl_3 complex yields 2-phenylethyl chloride in CH_2Cl_2 after 5 min at −30 °C and that the transformation of complexes containing the chlorinated ester moiety starts even at −78 °C. Similarly to esters, ethers also yield the corresponding chlorides under the influence of BCl_3; thus *n*-butyl *sec*-butyl ether is converted to *sec*-butyl chloride (plus *n*$BuOBCl_2$), and ethyl *n*-octyl ether gives *n*-octyl chloride (plus $EtOBCl_2$).[20] Evidently, ether cleavage occurs by $ROR' + BCl_3 \rightarrow RCl + R'OBCl_2$.

According to these references, both tertiary ester/BCl_3 and $TiCl_4$ complexes give rise to tertiary chlorides. In line with these findings tertiary chlorides may conceivably also arise in tertiary ester/$MtCl_n$ induced living polymerizations.

A final comment: according to the earlier view,[4] the dormant species in LC$^+$Pzn were tertiary esters, and the narrow MWDs (rapid counteranion exchange) observed in IB polymerizations initiated by mixed CumOAc + CumPr (cumyl propionate)/$TiCl_4$ systems were explained by ester exchange at the growing ionic site.[1] In line with the present proposition, the dormant species are tertiary chlorides and the ester moieties are incorporated into the in situ EDs.

C.2. Mechanistic Studies and MWD Control. This section concerns experiments to substantiate the propositions described in section C.1 and included in Scheme I.

C.2.a. Reversible Termination in the Presence and Absence of EDs. As mentioned in section C.1, experiments have been carried out to demonstrate the existence of reversible termination, i.e., equilibrium IV $\rightleftharpoons$ V. In these experiments IB has been added to well-characterized narrow-MWD ^{t}Cl-PIB-Cl^t/excess BCl_3 charges in the presence and absence of an external ED (dimethylacetamide, DMA), and the $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the products have been determined. To facilitate analysis (GPC by UV detection), the starting ^{t}Cl-PIB-Cl^t was prepared by the aromatic DiCumCl/BCl_3 initiating system and thus contained a UV-active residue (internal marker).

Table I and Figure 1 show representative results. While the controls (i.e., polymerizations carried out in the absence of the ^{t}Cl-PIB-Cl^t diinitiator) gave ill-defined (multimodal MWD) products, experiments with ^{t}Cl-PIB-Cl^t, particularly in the presence of DMA, yielded rather narrow MWD PIB with close to theoretical $\bar{M}_n$s. The $\bar{M}_n$s exhibited growth proportional with IB consumption. The increase in $\bar{M}_n$ can be seen by the RI and UV traces shown in Figure 1, where I is the GPC trace of the starting material. The $\bar{M}_n$ growth is particularly clearly visible in the series of experiments carried out from 30 to 120 min in the presence of DMA (the effect of external EDs, e.g.,

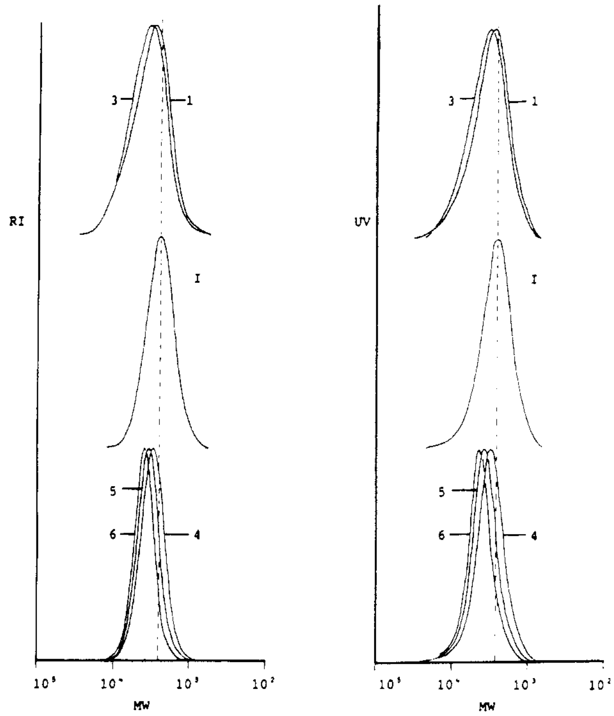


Figure 1. RI and UV GPC traces of ^{t}Cl-PIB-Cl^t initiator (I) and PIBs obtained by the ^{t}Cl-PIB-Cl^t/BCl_3 bifunctional initiating system in the absence (1, 3) and presence (4–6) of DMA.

ethyl acetate (EtOAc) or DMA, on polymerization characteristics will be introduced in section C.3 and discussed in detail in forthcoming publications of this series). The $\bar{M}_n$ growth is particularly convincing in the series of experiments 4–6, where the $\bar{M}_n$s increase essentially linearly with conversions (reaction time) at rather narrow MWDs ($\bar{M}_w/\bar{M}_n$ = 1.16–1.12). The $\bar{M}_n$ growth is further corroborated by the UV (GPC) traces sensitive exclusively to the internal marker in the PIB product. In the presence of ED the polymerization is slower than in the absence of this reagent; i.e., the ED reduces the reactivity of the growing species and gives rise to relatively narrow MWD products.

According to these experiments, similarly to $TiCl_4$-coinitiated polymerizations, BCl_3-coinitiated IB polymerizations also include reversible termination–reinitiation most likely by ion pairs of various reactivities typical of ionic polymerizations.

C.2.b. Initiation and Propagation by Tertiary Ester/$TiCl_4$ Complexes and MWD Control. According to the new mechanism, IB polymerization induced by the CumOAc/excess $TiCl_4$ system involves the formation of CumCl (VI) plus $TiCl_3OAc$, an "in situ" ED. To substantiate this proposition we have carried out a series of IB polymerizations with CumCl/excess $TiCl_4$ in the presence of EtOAc (a noninitiating primary ester) to simulate the in situ ED. The $TiCl_4$·EtOAc complex expected to form in this system is structurally similar to $TiCl_3OAc$. Table II shows the results and Figure 2 representative GPC traces. The sharp RI peak is due to the polymer fraction W formed by CumCl. Since conventional PIB is UV transparent, the UV trace is assigned to the incorporated UV-absorbing cumyl fragment. The small broad hump at higher molecular weights does not show UV absorption; consequently it is most likely due to the polymer fraction W_u formed by adventitious protic initiation (moisture). Since W_u remains essentially constant throughout the IMA series, initiation by moisture most likely occurs only during the first stage of the reaction.

Table II
Polymerization of IB by the CumCl/$TiCl_4$/EtOAc System[a]

W,[b] g	W_u*,[b] g	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$N \times 10^4$,[c] mol
0.236	0.092	2600	1.25	0.91
0.379	0.059	3600	1.34	1.05
0.726	0.113	7550	1.21	0.96
0.873	0.102	8640	1.19	1.01
1.213	0.088	12900	1.13	0.94

[a] [CumCl] = [EtOAc] = 1.05×10^{-4} mol; n-hexane/CH_3Cl (60/40 (v/v)); v_0 = 25 mL; −40 °C; IMA technique, 5 × 1 mL of IB/30 min). [b] W and W_u are the amounts of polymer formed by CumCl and moisture initiation, respectively; calculated from GPC traces (visual deconvolution). [c] $N = W/\bar{M}_n$.

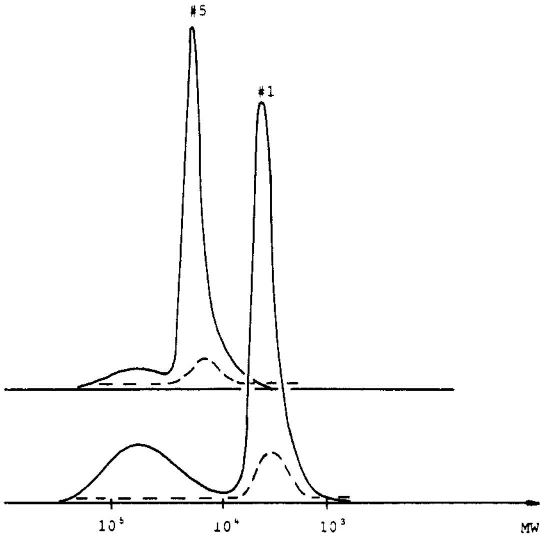


Figure 2. GPC traces of the first and last (nos. 1 and 5) polymer sample of Table II: (—) RI; (- - -) UV.

The polymerization is living; i.e., $\bar{M}_n$ grows linearly with W, MWDs are narrow (the MWDs have been estimated by visual deconvolution of two fairly well separated GPC traces as shown in Figure 2 and therefore may be somewhat inaccurate), the number of moles of polymer formed N remains constant, and initiating efficiencies (I_{eff}s) are ~100%. Interestingly, average conversions were ~40% in every step of the IMA series: While incremental monomer additions increased the IB concentration in the charges, the rate of polymerization remained constant. IB polymerizations induced by the CumOAc or CumOPr/excess $TiCl_4$ systems under similar conditions showed a very similar behavior.[1]

The similarity between the products obtained by the CumOAc/excess $TiCl_4$ and CumCl/excess $TiCl_4$/EtOAc systems substantiate the hypothesis that IB polymerizations initiated by these combinations proceed by essentially the same route; i.e., the first step with the former system is the formation of CumCl plus the in situ ED $TiCl_3OAc$. Due to the presence of EDs in both systems (in situ $TiCl_3OAc$ in the former and deliberately added EtOAc in the latter which complexes with the excess $TiCl_4$), polymers with narrow MWD arise in both systems. In contrast, the QLPzn of IB initiated by CumCl/excess $TiCl_4$ yields rather broad MWD polymer ($\bar{M}_w/\bar{M}_n$ = 4.5–2.6).[8]

To gain further insight into the reaction mechanism IB polymerizations were initiated by the aliphatic TMPOAc and TMPCl/excess $TiCl_4$/EtOAc systems. If living polymerizations proceed by monomer insertion into the C–O of the tertiary ester/$MtCl_n$ complex[4] and the dormant chain ends are ester groups, TMPOAc would be a model for the dormant species. If, however, the polymerizations proceed by V generated by the routes proposed in Scheme

Table III
Polymerization of IB by the TMPOAc/TiCl$_4$ and TMPCl/TiCl$_4$/EtOAc Systems[a]

W, g	W_c, g	W_u, g	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	I_{eff}, %
A. [TMPOAc] = 1.3 × 10^{-4} mol; [TiCl$_4$] = 1.82 × 10^{-3} mol					
0.052[b]			4220	6.21	<9[c]
0.201[b]			7200	4.29	<22[c]
0.494[b]			12200	2.37	<32[c]
1.216[b]			17850	2.24	<52[c]
B. [TMPCl] = 0.94 × 10^{-4} mol; [TiCl$_4$] = 1.82 × 10^{-3} mol; [EtOAc] = 1.0 × 10^{-4} mol					
	0.302	0.069	3370[d]	1.06[d]	95[d]
	0.465	0.058	7100[d]	1.06[d]	70[d]
	0.912	0.082	10900[d]	1.11[d]	90[d]
	1.159	0.093	14800[d]	1.14[d]	83[d]
	1.849	0.092	19800[d]	1.13[d]	99[d]
C. Control Experiment, No EtOAc Added: [TMPCl] = 0.94 × 10^{-4} mol; [TiCl$_4$] = 1.0 × 10^{-3} mol; 1 mL of IB; 30 min					
	0.381	0.312	4100	1.21[d]	99[d]

[a] V_0 = 25 mL; n-hexane/CH$_3$Cl (60/40 (v/v)); −40 °C; IMA technique, 5 × (1 mL of IB/30 min). [b] W_u could not be separated from W due to the broad MWD. [c] I_{eff} is calculated from $W + W_u$; therefore the real I_{eff} should be lower. [d] Values calculated from controlled initiation W_c data. W_c and W_u were calculated from the integral value of GPC traces; $W = W_c + W_u$.

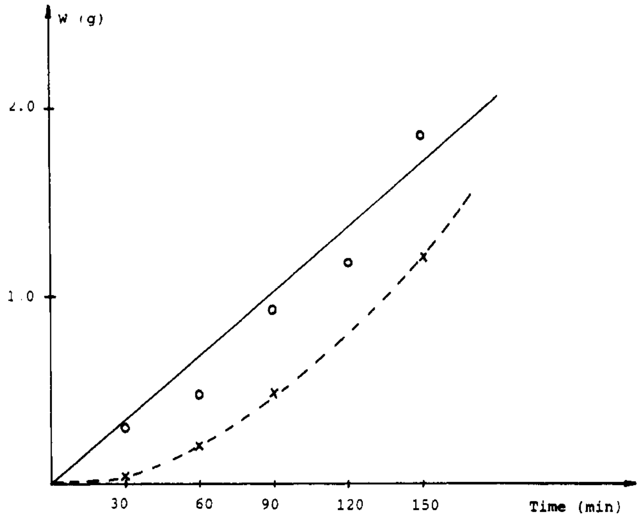


Figure 3. Rates of IB polymerizations initiated by the TMPOAc/TiCl$_4$ (×) and the TMPCl/TiCl$_4$/EtOAc (○) systems (see Table III).

I, TMPCl would be a model for the dormant PIB-Cl^t chains (IV) and TiCl$_4$·EtOAc is regarded structurally similar to TiCl$_3$OAc.

The experimental results are presented in Table III and Figure 3. The TMPOAc/excess TiCl$_4$ complex is a very slow initiating system: After 30 min conversion is <9% and the MWD is very broad. As shown by the data in Figure 3 conversions increase in a manner characteristic of slow initiation, implying a slow increase of the number of active chains. Slow initiation is most likely due to slow ionization: TMPOAc·TiCl$_4$ → $\text{TMP}^+\cdots{}^-\text{OAcTiCl}_4$ (I → II). In contrast, initiation with TMPCl/excess TiCl$_4$/EtOAc is instantaneous and of high efficiency ($I_{eff} \cong 100\%$) and yields polymers with narrow MWDs (Table III). In line with these experiments slowly activatable dormant esters proposed earlier[4] would not give rise to narrow-MWD product: however, tertiary chloride termini just as TMPCl can rapidly be ionized and lead to narrow-MWD polymer.

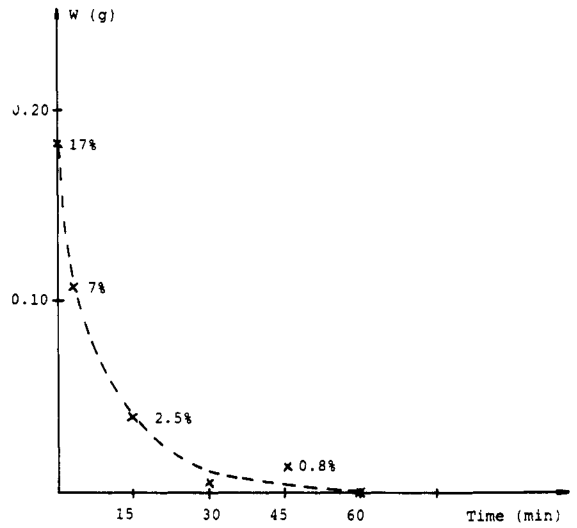


Figure 4. Weight of PIB (W) as a function of premixing (aging) time in IB polymerizations initiated by TMPOAc/BCl$_3$ (1:1 molar ratio). The percent values indicate initiator efficiencies. [TMPOAc] = [BCl$_3$] = 2 × 10^{-4} mol; V_0 = 25 mL; CH$_3$Cl; IB = 2 mL; −40 °C; polymerization time, 30 min.

The RI GPC traces of PIBs obtained by TMPCl/excess TiCl$_4$/EtOAc are similar to that shown in Figure 2. A small broad hump at higher molecular weights suggests some adventitious protic initiation similarly to IB polymerizations by moisture plus TiCl$_4$ at −40 °C[1] and by the CumCl/excess TiCl$_4$/EtOAc combination (see Table II). Reminiscent of the latter system W_u is constant throughout the IMA series; i.e., initiation by moisture occurs only during the initial phase. Initiation by moisture also occurs with the TMPCl/excess TiCl$_4$ system in the absence of EtOAc (see control in Table III), and the MWD of the polymer is broader than that obtained in the presence of EtOAc. (The MWDs have been estimated by visual deconvolution of two well-separated GPC traces, similarly to that shown in Figure 2.)

According to the above results, IB polymerizations initiated by both aromatic and aliphatic tertiary ester/excess TiCl$_4$ systems most likely proceed by V and not by esters as suggested earlier.[4] Efficient initiation by the TMPCl/excess TiCl$_4$ system suggests tertiary Cl dormant chain ends and polymerization by IV ⇌ V.

The MWD-narrowing effect of EDs may be due to a "reactivity-leveling" effect: the EDs are expected to interact with and thus to reduce the reactivity of carbocations; the extent of this reaction (i.e., the enthalpy of the C$^+$ ED interaction) will be proportional to the degree of dissociation of the active ion pair. Thus the reactivity of relatively more dissociated ion pairs will be reduced to a larger extent than those of less dissociated ion pairs. While the overall reactivity of the carbocations will be reduced, the individual reactivities will tend to become similar. In other words, the EDs shift the ionic equilibria toward less reactive species so that in the presence of suitable EDs (the manner of choosing EDs is addressed in the third paper of this series) the overall polymerization rates will be reduced (more accurately, the overall rate of propagation will be reduced relative to that of ion generation) and the MWDs will become narrower.

C.2.c. Effect of Aging Time on the Reactivity of the TMPOAc/BCl$_3$ System. In regard to Scheme I, the question arises as to the rate of formation of the tertiary chloride VI in the case of a tertiary ester/BCl$_3$ system. Thus a series of experiments have been carried out in which TMPOAc was mixed with an equimolar quantity of BCl$_3$, aged for various times at −40 °C, and then used to induce IB polymerization. Figure 4 shows the amount of PIB formed as a function of aging (premixing) time. Evidently,

Table IV
Polymerization of IB by the CumOMe + CumOAc/Excess $TiCl_4$ Initiating System[a]

IB, mL	W, g	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	I_{eff},[b] %
3 mL/15 min	2.376	18400	1.15	93
3 × (2 mL/15 min)[c]	4.511	31600	1.14	100

[a] [CumOMe] = [CumOAc] = 6.9×10^{-5} mol; [$TiCl_4$] = 2.2×10^{-3} mol; n-hexane/CH_3Cl (60/40 (v/v)); v_0 = 25 mL; -80 °C. [b] $I_{eff} = N \times 100/([\text{CumOMe}] + [\text{CumOAc}])$. [c] IMA technique.

contact between TMPOAc and BCl_3 drastically reduces the yield (I_{eff} is low even without aging); these effects are most likely due to the formation of TMPCl + BCl_2OCOCH_3 and that TMPCl is polymerization inactive in the absence of excess BCl_3. The addition of IB to 60-min-aged TMPOAc/BCl_3 has failed to give polymer. Significantly, ^1H NMR spectroscopy indicated tertiary chloride end groups in the PIB formed.

According to this evidence, in the absence of aging BCl_3-coinitiated polymerizations proceed simultaneously by I → II → III → IV $\rightleftharpoons$ V and I → II → VI → VII → V $\rightleftharpoons$ IV; aging in the absence of IB leads I → II → VI, i.e., to tertiary chloride. In this case initiation would require excess BCl_3 and polymerization would proceed by VII → V $\rightleftharpoons$ IV.

The [BCl_3]/[TMPOAc] ratio profoundly affects polymerization results. While the present experiments carried out with equimolar BCl_3 and TMPOAc gave much less than ~100% conversions, those carried out earlier[4] with [BCl_3]/[TMPOAc] ratios higher than unity (i.e., 4.6–46) but otherwise under identical conditions consistently gave 100% conversions. Also, systems with [BCl_3]/[TMPOAc] = 8–16 which contained all the ingredients for 15–30 min prior to the next monomer addition yielded very high, often 100%, conversions.

C.2.d. Evidence for the Formation of a Common Intermediate in Tertiary Ester/, Tertiary Ether/, or Tertiary Chloride/$TiCl_4$ Initiated Polymerizations. As outlined in section C.1, living IB polymerizations initiated by tertiary ether/excess $TiCl_4$ systems[3] may also proceed by the mechanism suggested in Scheme I. According to earlier propositions, living IB polymerizations initiated by tertiary ester/excess BCl_3,[4] tertiary ether/excess BCl_3,[5] and tertiary ester and tertiary ether/excess $TiCl_4$[1,2] systems proceed by monomer incorporation into $PIB^{+}\cdots BCl_3OCOCH_3^{-}$, $PIB^{+}\cdots BCl_3OR^{-}$, $PIB^{+}\cdots TiCl_4OCOCH_3^{-}$, and $PIB^{+}\cdots TiCl_4OR^{-}$ bonds, and the ester or ether groups are connected to the growing PIB chains[4,5] or are part of the counteranions.[1] Two series of experimental facts demonstrate that these earlier views must be revised: (1) If the earlier views were correct, living polymerizations initiated by a tertiary ester/excess $TiCl_4$ and a tertiary ether/excess $TiCl_4$ system would exhibit different rates and a mixed (tertiary ester + tertiary ether)/excess $TiCl_4$ system would give bimodal or at least broad MWDs due to the presence of the different active species in the systems. If, however, the polymerizations would proceed by Scheme I, either component of the mixed initiating systems would first yield tertiary chloride VI plus an in situ ED which then would mediate the formation of monomodal narrow-MWD product.

Thus a series of experiments have been carried out in which polymerizations were initiated by premixed 1:1 CumOAc + CumOMe mixtures plus excess $TiCl_4$. (To facilitate analysis the experiments were carried out at -80 °C to suppress initiation by moisture.) Table IV shows the results. Conversions were complete in every reactor, I_{eff}s were ~100%, and polymerizations were living, yielding polymers with very narrow MWDs ($\bar{M}_w/\bar{M}_n$ = 1.14–1.15). These results demonstrate that living IB polymerizations initiated by both the tertiary ester/$TiCl_4$ and tertiary ether/$TiCl_4$ systems most likely proceed by the same propagating entity stabilized by in situ EDs. The narrow MWDs obtained indicate rapid exchange of the two in situ EDs, i.e., $TiCl_3OAc$ and $TiCl_3OMe$.

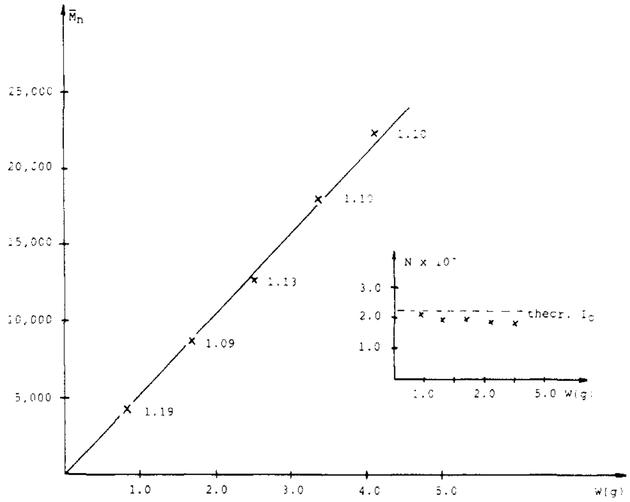


Figure 5. Diagnosis of living polymerization of IB by the mixed CumCl + CumOMe/$TiCl_4$ system. The numbers indicate $\bar{M}_w/\bar{M}_n$ values. Inset: Number of PIB moles (N) versus weight of PIB (W). [CumCl] = 1.2×10^{-4} mol; [CumOMe] = 1.09×10^{-4} mol; [$TiCl_4$] = 3.6×10^{-3} mol; V_0 = 25 mL; CH_3Cl/n-C_6H_{14} (40/60 (v/v)); -80 °C; IMA technique, 5 × (1 mL of IB/15 min).

We wish to interject that narrow MWDs obtained earlier by the mixed tertiary esters CumOAc + CumOPr/$TiCl_4$[1] are also due to the rapid exchange of $TiCl_3OAc$ and $TiCl_3OPr$ during the dormant period IV. Rapid exchange between $TiCl_4OAc^{-}$ and $TiCl_4OPr^{-}$ suggested earlier[1] would not give narrow MWDs due to the necessarily slow activation of hypothetical PIB-tertiary ester chain ends by $TiCl_4$ (see section C.2.b).

(2) If the earlier view were correct, living IB polymerization initiated by an equimolar mixture of a tertiary ether and a tertiary chloride plus excess $TiCl_4$ would give bimodal or at least broad-MWD product due to the two propagating species $PIB^{+}\cdots TiCl_4OR^{-}$ and $PIB^{+}\cdots TiCl_5^{-}$ involved and because this latter species, which also arises from CumCl/excess $TiCl_4$ in the absence of ED, leads to relatively broad MWDs.[8] If, however, the mixed system would follow the reaction path shown in Scheme I and discussed in section C.1, the tertiary chloride VI would be a common intermediate and, due to the formation of the in situ ED from the tertiary ether, the system would give narrow-MWD product. The observed facts bear out the latter scenario.

Thus polymerizations have been carried out by 1:1 molar mixtures of (CumOMe + CumCl)/excess $TiCl_4$, and Figure 5 shows the results obtained. Evidently, the system is living (see the linear $\bar{M}_n$ and N versus W (inset) plots) and yields very narrow MWD PIB ($\bar{M}_w/\bar{M}_n$ = 1.09–1.19). Thus the polymerizations most likely proceed by one common intermediate VI and the in situ ED $TiCl_3OCH_3$ leads to narrow MWD.

According to the latter experiment, a less than equimolar amount of $TiCl_3OMe$ relative to the total amount of initiator added is sufficient for effective carbocation stabilization. This conclusion also supports the existence of the equilibrium IV $\rightleftharpoons$ V. Evidently, a sizable amount of the chain ends (a minimum of 50%) must be in the dormant tertiary Cl form IV.

C.3. Demonstration of the Effect of External ED on IB Polymerization Initiated by CumCl/$TiCl_4$. As

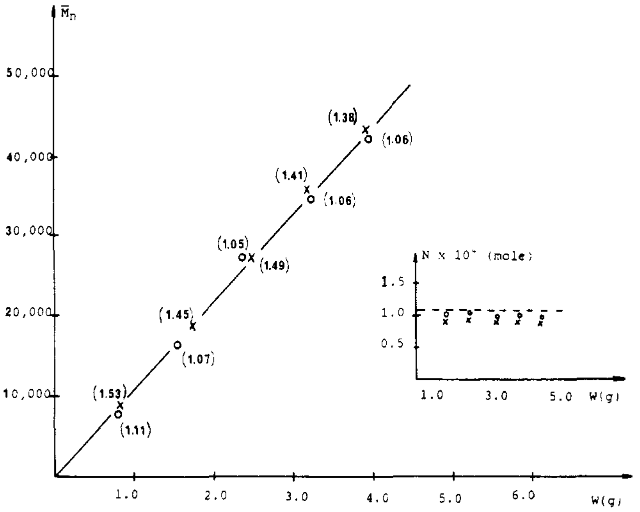


Figure 6. Diagnosis of living polymerization of IB initiated by the CumCl/TiCl$_4$ system in the absence (×) and in the presence (O) of EtOAc. Numbers indicate $\bar{M}_w/\bar{M}_n$ values. Inset: Number of PIB moles (N) versus weight of PIB (W). [CumCl] = 1.1 × 10^{-4} mol; [TiCl$_4$] = 1.8 × 10^{-3} mol; V_0 = 25 mL; CH$_3$Cl/n-C$_6$H$_{14}$ (40/60 (v/v)); -80 °C; IMA technique, 5 × (1 mL of IB/15 min).

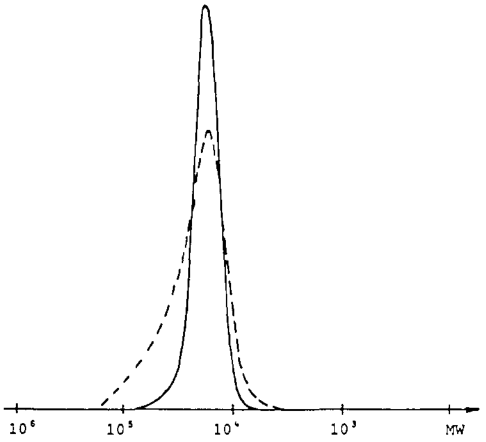


Figure 7. Comparison of normalized GPC traces of PIBs obtained in the absence (- - -) and in the presence (—) of EtOAc. Conditions as in Figure 6.

shown in sections C.2.b and C.2.d, living IB polymerizations induced by tertiary ester/excess TiCl$_4$ or tertiary ether/excess TiCl$_4$ systems readily yield narrow-MWD products under the influence of in situ EDs. In line with these findings we theorized that deliberately added ("external") EDs will also produce a MWD narrowing of PIBs which otherwise would have been relatively broad. This prediction was tested experimentally by initiating IB polymerizations by the CumCl/excess TiCl$_4$ combination in the presence and absence of EtOAc, a noninitiating external ED. The experiments were carried out at -80 °C because at this very low temperature adventitious initiation by moisture is largely absent.

According to the data shown in Figure 6, living polymerization occurred in both systems (i.e., PIB molecular weights increased linearly with yield); however, very narrow MWD product ($\bar{M}_w/\bar{M}_n$ = 1.05-1.1) was obtained only in the presence of EtOAc. Figure 7 further illustrates the MWD-narrowing effect by contrasting GPC traces of representative PIB samples obtained in the absence and presence of EtOAc and having approximately the same $\bar{M}_n$s.

The MWD-narrowing effect of in situ and deliberately added EDs is attributed to "reactivity leveling" (see section C.2.b). The added EtOAc is thought to modulate the reactivity of ion pairs and unpaired ions.

The mechanism of interaction between the charged species and EDs is the subject of ongoing systematic research. Whatever the mechanism, in the presence of EDs polymerization rates are slow by cationic standards (in conventional systems reactions are complete within seconds), indicating the presence of relatively less reactive carbocations. Highashimura and co-workers[21] have discussed carbocation stabilization by added bases in the living polymerization of vinyl ethers in a similar vein. The results obtained with EtOAc prompted us to extend these studies to other deliberately added EDs; further publications will concern research directed toward these areas.

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Registry No. IB, 115-11-7; CumCl, 934-53-2; TMPOAc, 27540-75-6; TMPCl, 6111-88-2; BCl, 10294-34-5; TiCl$_4$, 7550-45-0; EtOAc, 141-78-6; CumOMe, 27476-56-8; CumOAc, 3425-72-7.