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LIVING CARBOCATIONIC POLYMERIZATION. XXXVIII. ON THE NATURE OF THE ACTIVE SPECIES IN ISOBUTYLENE AND VINYL ETHER POLYMERIZATION†

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ABSTRACT

The nature of the species that gives rise to living carbocationic polymerization (LP$^+$Pzn) of isobutylene (IB) coinitiated by Friedel-Crafts acids (FCA) in the presence of electron pair donors (ED) has been investigated. It is proposed that the key species responsible for mediating LC$^+$Pzn of IB are FCA·ED complexes, formed by Lewis acid–Lewis base interaction, where FCA = BCl_3 and $TiCl_4$, and ED = ethyl acetate, tetrahydrofuran, etc. Free EDs are inhibitors of IB polymerization. These findings are in sharp contrast to those of LC$^+$Pzn of vinyl ethers coinitiated by $EtAlCl_2$ in which excess (i.e., free) EDs are *required* for the living polymerizations to occur. Comparison of IB polymerizations induced by the 2-chloro-2,4,4-trimethylpentane/BCl_3 and 2-acetyl-2,4,4-trimethylpentane/BCl_3 systems shows that these reactions do not proceed by the same intermediate (i.e., by *tert*-chlorides) and that the mech-

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anisms of BCl_3- and $TiCl_4$-coinitiated living polymerizations are different. Experiments with the proton trap 2,6-di-*tert*-butylpyridine indicate that proton scavenging by FCA·ED complexes may be responsible for the narrow molecular weight distribution (MWD) products obtained in BCl_3-coinitiated LC^+Pzn of isobutylene. These findings also prove that R_i (rate of initiation) $>$ R_p (rate of propagation), the relation required for narrow MWD in living polymerizations.

INTRODUCTION

Recent investigations [1-14] have shown that the addition of O-, N-, and S-containing electron pair donors (EDs) (also termed Lewis bases or nucleophiles) may beneficially influence the outcome of carbocationic polymerizations, e.g., may mediate LC^+Pzn and yield narrow molecular weight distribution (MWD) products. For example, in the LC^+Pzn of vinyl ethers, the addition of EtOAc [2-4, 6, 13], ethyl benzoate [3, 6], diethyl carbonate [3,6], tetrahydrofuran (THF) [4, 6], diethyl ether [4, 6], dioxane [4-6], and 2,6-dimethylpyridine [6] gives rise to polymers with narrow MWD. Similarly, the preparation of narrow MWD polyisobutylenes (PIBs) by LC^+Pzn in the presence of EDs, such as ethyl acetate (EtOAc) [1, 9, 10, 14], dimethylacetamide (DMA) [7, 9], and dimethylsulfoxide (DMSO) [1, 7-9], has also been reported.

Higashimura and coworkers [2-6] assumed that EDs stabilize propagating vinyl ether cations by direct nonspecific interaction. The effect of EDs on IB polymerization has been explained in a similar manner [9], i.e., by assuming that carbocation stabilization is due to a direct interaction between the propagating carbocation and the ED. According to this concept [9], the effect of EDs is governed by their electron donicity correlated with Gutmann's donor numbers [15]. It has also been postulated [9] that living IB polymerizations initiated by *tert*-ester or -ether/$TiCl_4$ systems involve the formation of *tert*-chlorides with the simultaneous appearance of so-called "*in-situ*" EDs.

The purpose of this paper is to investigate the validity of this assumption for BCl_3-based systems and, further, to gain insight into the nature of the species that arises upon the addition of EDs to BCl_3- or $TiCl_4$-coinitiated living IB polymerizations, i.e., the species that has been implicated to mediate LC^+Pzn of IB. The differences between the LC^+Pzns of IB and vinyl ethers will also be discussed.

EXPERIMENTAL

The syntheses, source, and purification of dicumyl chloride (DiCumCl), 2-chloro-2,4,4-trimethylpentane (TMPCl), 2-acetoxy-2,4,4-trimethylpentane (TMPOAc), IB, BCl_3, $TiCl_4$, CH_3Cl, and *n*-hexane, together with polymerization conditions and characterization methods, have been described [10, 14, 16, 17]. EtOAc, THF, diethyl ether (Et_2O), and ethylene oxide (EO) were distilled from CaH_2. 2,6-Di-*tert*-butylpyridine (D*t*BP, Aldrich Chemical Co., 97%) was used as received.

RESULTS AND DISCUSSION

A. The Effect of Free EDs and FCA·ED Complexes on the LC^+Pzn of IB and Vinyl Ethers

In living vinyl ether polymerizations the concentration of added EDs (O-, N-, or S-bases) is generally, in most cases by several orders of magnitude, higher than that of the initiator or FCA (e.g., $EtAlCl_2$) used [1-6, 11-13]. This indicates that free (uncomplexed) EDs influence these processes and/or that nonspecific solvation effects, similar to those operating in the DiCumCl/BCl_3/IB system [16], affect these polymerizations. Recently stable dioxycarbenium formation between esters and vinyl ether cation has also been postulated [3]. Since esters, ethers, and substituted pyridines are known to form well-defined complexes with alkylaluminums [18], free $EtAlCl_2$ must be absent in these systems. According to Aoshima and Higashimura [3], complexation with bases decreases the Lewis acidity of the organoaluminum and thus side reactions due to the strongly acidic free $EtAlCl_2$ are suppressed. However, for some unknown reason, an *excess* of ED is *required* for the stabilization of vinyl ether cations.

In strong contrast to living vinyl ether polymerizations, in the LC^+Pzn of IB in the presence of added EDs, the molar concentration of BCl_3 or $TiCl_4$ is usually 2-20 times in excess to that of the sum of the initiator plus ED [1, 7-10]. Since BCl_3 or $TiCl_4$ rapidly form well-defined complexes with O-, S-, and N-containing EDs [19, 20], little if any free ED is expected to remain in the charge to influence the polymerization. For example, the LC^+Pzn of IB initiated by the DiCumCl/$TiCl_4$ initiating system rapidly produces 100% conversion in the presence of EtOAc as long as [EtOAc] < [$TiCl_4$]; however, the conversions precipitously

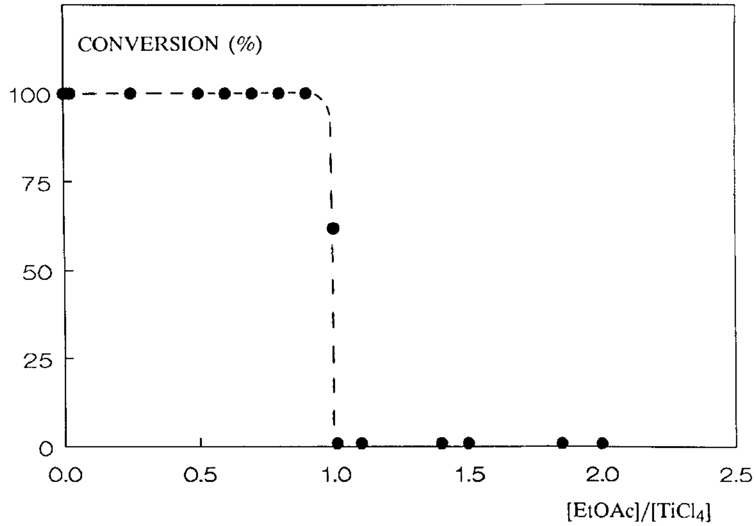


FIG. 1. The effect of the EtOAc/$TiCl_4$ ratio on IB conversion ([DiCumCl] = 7.0 × 10^{-3} mol/L, [$TiCl_4$] = 0.29 mol/L, [IB] = 0.51 mol/L, 40:60 v/v CH_3Cl/*n*-hexane, 25 mL, −75°C, 15 min polymerization time except 4 h at EtOAc/$TiCl_4$ = 1.88).

drop to negligible values as soon as [EtOAc] > [$TiCl_4$]. Figure 1 shows the results of an experiment that substantiate this statement. Evidently the $TiCl_4$·EtOAc complex mediates LC^+Pzn, and polymerization is inhibited in the presence of excess EtOAc (i.e., free ED).

This finding also helps to understand why the polymerization of IB was found to be extremely slow with the cumyl acetate (CumOAc)/$TiCl_4$ = 1/1 system [14]. It was postulated that CumOAc + $TiCl_4$ yields CumCl + $TiCl_3OAc$, and that polymerization occurs only in the presence of excess $TiCl_4$ required for ion generation: CumCl + $TiCl_4$ → $Cum^+TiCl_5^-$ [9]. Whatever the products, CumCl + $TiCl_3OAc$ or a stable $TiCl_4$·CumOAc complex, $TiCl_4$-coinitiated systems are unsuitable for studying the effect of free EDs on IB polymerization since this system requires excess $TiCl_4$ for polymerization to occur. Similar considerations also hold for cumyl methyl ether/$TiCl_4$ combinations [10].

In contrast to $TiCl_4$-based systems, living polymerizations of IB induced by *tert*-ester/BCl_3 combinations [17] are suitable to study the effect of free EDs on polymerization details because even equimolar *tert*-

ester/BCl_3 systems efficiently induce polymerization of IB. Thus we have carried out a set of experiments in which the effect of the TMPOAc/BCl_3 ratio on the $\overline{M}_n$, MWD, and initiating efficiency (I_{eff}) was studied with the TMPOAc/BCl_3/IB/CH_3Cl/-30°C system. Table 1 shows the experimental conditions and results. Evidently excess BCl_3 relative to TMPOAc is not necessary for polymerization to occur, and theoretical $\overline{M}_n$ with ~100% conversion can be obtained even in the presence of a slight excess of TMPOAc, i.e., with TMPOAc/BCl_3 = 1.1. Interestingly, the narrowest MWDs have been obtained at about equimolar TMPOAc/BCl_3. By increasing the TMPOAc/BCl_3 above 1 higher than theoretical $\overline{M}_n$s, lower than 100% I_{eff}s and relatively slow polymerizations are obtained. (The 4100 $\overline{M}_n$ was obtained at 33% conversion; thus, at 100% I_{eff} the theoretical $\overline{M}_n$ would have been 1600.) Thus, free TMPOAc cannot be an initiator, and initiation by the TMPOAc/BCl_3 system in the presence of the free ester is prevented (cf. declining I_{eff}s in proportion to TMPOAc concentration). Evidently the carbonyl oxygen in TMPOAc is more nucleophilic than the double bond of IB, and thus the free ester (free ED) is a polymerization inhibitor.

Since the TMPOAc/BCl_3 = 1 system was found to be efficient for the polymerization of IB, we were able to study the effect of various EDs (i.e., EtOAc, Et_2O, EO, THF) on the living polymerization of this monomer with this initiating combination. Thus, experiments were carried out with TMPOAc/BCl_3/ED = 1:1:1 stoichiometry under the con-

TABLE 1. The Effect of the TMPOAc/BCl_3 Ratio on the Polymerization of IB ([TMPOAc] = 1.1×10^{-2} mol/L, [IB] = 0.94 mol/L, CH_3Cl, 25 mL, -30°C, 30 min)

TMPOAc/BCl_3	Conversion, %	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	I_{eff}, %[a]
0.1	100	4.6	3.6	104
0.2	100	4.8	3.0	100
0.5	100	4.8	2.7	100
1.0	100	5.3	2.3	90
1.1	100	5.9	2.0	81
1.5	33	4.1	2.6	39
2.0	0	—	—	—

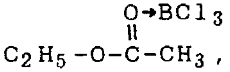
[a] $I_{eff} = (W_P/\overline{M}_n)/I$, where W_P and I are the weight of polymer formed and moles of initiator used, respectively.

TABLE 2. Polymerization of IB with the TMPOAc/BCl_3 System in the Presence of Added EDs ([TMPOAc] = 1.1×10^{-2} mol/L, [BCl_3] = 0.051 mol/L when ED/TMPOAc = 1; [BCl_3] = 0.102 mol/L when ED/TMPOAc = 3; [BCl_3] = 0.153 mol/L when ED/TMPOAc = 10; [IB] = 0.94 mol/L, CH_3Cl, 25 mL, −30°C, 30 min)

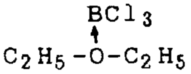
ED	ED/TMPOAc	Conversion, %	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	I_{eff}, %
EtOAc	1	100	5.0	1.57	96
	3	100	5.7	1.35	84
	10	47	3.2	1.60	70
Et_2O	1	100	5.0	2.2	96
	3	100	4.7	2.1	102
	10	100	5.3	1.9	90
EO	1	100	5.0	1.57	96
	3	100	5.0	1.30	96
	10	5	1.1	1.49	22
THF	1	100	4.8	1.88	100
	3	100	4.9	1.7	98
	10	100	7.4	1.3	65

ditions given in Table 1. The results of four series of experiments with four EDs are shown in Table 2. Polymerization did not occur when BCl_3 or when IB was added last to premixed charges. According to the results of these experiments, free EDs also prevent the polymerization of IB. Specifically, in line with the results of the latter experiment (that is, when IB was added last, and the TMPOAc and ED competed for the BCl_3), the absence of polymerization must be due to the presence of free ED and not to the absence of the TMPOAc/BCl_3 initiating system. The results of these experiments are in sharp contrast to those obtained with the living polymerization of vinyl ethers with $EtAlCl_2$ in the presence of large excess of EDs [2-6], and indicate that while free EDs beneficially influence vinyl ether systems, they are inhibitors of IB polymerization.

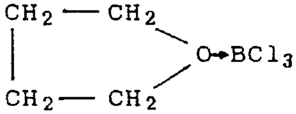
Polymerization occurred when the EDs were complexed by an excess of BCl_3. The addition sequence of the ingredients did not influence the results, i.e., the results were the same when BCl_3 and EtOAc were premixed and added last. This is further proof that it is not the free EDs but rather the FCA·ED complexes, i.e.,



$$C_2H_5-O-\overset{O\rightarrow BCl_3}{\overset{\|}{C}}-CH_3\ ,$$



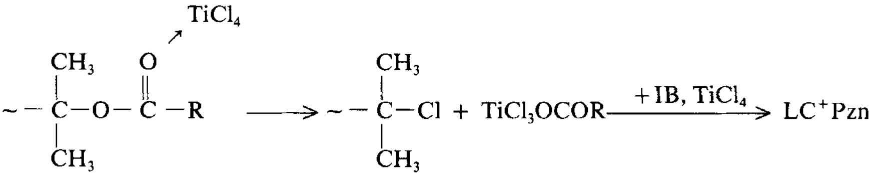
$$C_2H_5-\overset{BCl_3}{\overset{\uparrow}{O}}-C_2H_5$$



that are the species that beneficially influence the course of these living polymerizations by leading to slower rates and narrowing of MWDs. The MWDs (see the $\overline{M}_w/\overline{M}_n$ entries in Table 2) were narrower in the presence of EtOAc, EO, and THF than with Et_2O. With THF, $\overline{M}_w/\overline{M}_n$ decreased with increasing THF concentration. At relatively high EtOAc and EO concentrations, conversions were lower than 100%. In vinyl ether polymerizations, the efficiency of ethers decreased as THF > dioxane >Et_2O [3, 4]. According to the $\overline{M}_w/\overline{M}_n$ values in Table 2, THF is also more efficient than Et_2O in LC^+Pzn of IB. The efficiency is expected to depend on the nucleophilicity of the above complexes, and a higher concentration is needed of the weaker nucleophile than of the stronger one to achieve an equivalent effect. The lower reactivity of the $BCl_3\cdot Et_2O$ than of the $BCl_3\cdot THF$ may be due to the limited steric accessibility of the oxygen in Et_2O. An important difference between EO and THF is that EO readily interacts with BCl_3 to give 2-chloroethyl dichloroboronite ($Cl-CH_2-CH_2-OBCl_2$) whereas THF forms a well-defined 1:1 complex [20]. Thus, in the case of the $BCl_3\cdot EO$ the active species is most likely a neutral molecule in which the nucleophilicity of the oxygen is much reduced by the adjacent BCl_2 moiety.

B. Mechanistic Considerations Concerning the TMPOAc/BCl_3 System

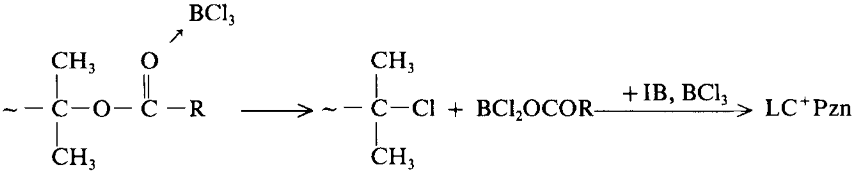
It has been postulated that LC^+Pzn of IB initiated by *tert*-ester or -ether/$TiCl_4$ systems involves the formation of *tert*-chlorides and subsequent initiation by excess $TiCl_4$ [9]. For example, with *tert*-ester/$TiCl_4$ systems the following reaction was proposed:



$$\sim\sim\overset{CH_3}{\underset{CH_3}{C}}-O-\overset{\overset{TiCl_4}{\nearrow}\,O}{\overset{\|}{C}}-R \longrightarrow \sim\sim\overset{CH_3}{\underset{CH_3}{C}}-Cl + TiCl_3OCOR \xrightarrow{+IB,\ TiCl_4} LC^+Pzn \qquad (1)$$

Polymerization was assumed to occur in a quasi-living manner, i.e., by reversible termination involving the formation of *tert*-chlorine chain ends followed by reinitiation by excess $TiCl_4$ [9]. The two key intermediates were thought to be the *tert*-chlorine terminus capable of reversible termination and the "*in-situ*" ED, $TiCl_3OCOR$.

While these views adequately explain the observations with $TiCl_4$-based systems, the question arises whether chlorination similar to that in Eq. (1) also occurs in IB polymerization initiated by TMPOAc/BCl_3:



$$\sim\sim C(CH_3)_2{-}O{-}\overset{\overset{BCl_3}{\nearrow}}{\underset{}{C}}(=O){-}R \longrightarrow \sim\sim C(CH_3)_2{-}Cl + BCl_2OCOR \xrightarrow{+IB,\ BCl_3} LC^+Pzn \qquad (2)$$

A similar chlorination of the growing site may also be visualized to proceed with the TMPOMe/BCl_3 system [21]. If these processes do occur, living polymerizations would also be expected to arise with the TMPCl/BCl_3 system in the presence of an external ED (e.g., EtOAc) whose nucleophilicity is similar to that of BCl_2OCOCH_3 or BCl_2OCH_3. Thus, experiments have been carried out with the TMPCl/BCl_3 system in the presence and absence of EtOAc together with control experiments, i.e., in the absence of TMPCl or EtOAc, or both. Table 3 shows the results. Conversions and molecular weights were similar in the presence

TABLE 3. Polymerization of IB with the TMPCl/BCl_3/CH_3Cl/−30°C System in the Presence of EtOAc ([TMPCl] = 5.6×10^{-3} mol/L, [BCl_3] = 5.1×10^{-2} mol/L, [IB] = 0.94 mol/L; BCl_3 was added last to premixed charges)

Initiator	[EtOAc] × 10^3 mol/L	Time, min	Conversion, %	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
—	—	30	6	36.0	2.0
TMPCl	—	30	9	34.0	2.3
—	—	360	100	32.0	2.8
TMPCl	—	360	100	34.0	2.7
—	5.6	60	Trace	—	—
TMPCl	5.6	30	14	23.2	3.1

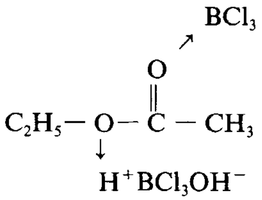
and absence of TMPCl, indicating that TMPCl is not or at best a very inefficient initiator (relative to protogenic impurities) under these conditions. The EtOAc/BCl_3/IB/CH_3Cl/−30°C system (that is, the control run in the absence of TMPCl) gave only traces of polymer, indicating that initiation by protogenic impurities (by "$H^+BCl_3OH^-$") was inhibited. That initiation from protogenic impurities is absent in the presence of (initiating or noninitiating) esters or other nucleophiles has already been described [10, 14, 17]. In the presence of TMPCl, the $BCl_3 \cdot$EtOAc complex gave low but significant conversions, and PIBs with molecular weights similar to those obtained in the absence of $BCl_3 \cdot$EtOAc.

The fact that these conversions and molecular weights are quite different from those obtained with the TMPOAc/BCl_3 (Table 1) or the TMPOMe/BCl_3 initiating systems [21] indicates that these polymerizations do not proceed by the same intermediate (i.e., by *tert*-chlorides). The fact that the equimolar TMPOAc/BCl_3 system is an efficient initiating system points toward the same conclusion. In other words, in the presence of monomer, TMPCl is not formed as indicated in Eq. (2) and the LC^+Pzn's of IB initiated by the TMPOAc/BCl_3 or TMPOMe/BCl_3 systems do not proceed by reversible termination: $\sim CH_2C(CH_3)_2Cl + BCl_3 \rightleftharpoons \sim CH_2C^+(CH_3)_2BCl_4^-$. Evidently the mechanistic scheme based on results obtained with and valid for $TiCl_4$-coinitiated systems with or without strong nucleophiles cannot be applied to IB polymerizations initiated by TMPOAc/BCl_3 and TMPOMe/BCl_3 combinations.

C. Proton Scavenging by DtBP and FCA·ED Complexes in BCl_3-Coinitiated Polymerizations

As shown in this paper and earlier publications [7, 8], the addition of various EDs to *tert*-ester or -ether/BCl_3 initiating systems leads to reduced IB polymerization rates and narrow MWD products. In some cases these effects are proportional to the ED concentration, as shown in Section A. In the presence of free ED, termination is much faster than propagation. Interestingly, a narrowing of the MWD is observable *before* the polymerization rates decrease substantially, and a further increase in the ED concentration does not cause a corresponding narrowing of the MWD in most cases (cf. Table 2). Reduced rates and narrow MWD products obtained in the presence of FCA·ED complexes may be due to two kinds of propagating species. The following hypothesis, substantiated by experiments, may account for these observations.

Initiation by adventitious protogenic impurities is suppressed in the presence of FCA·ED complexes (cf. Tables 1–3). It has been shown that with the TMPOAc/BCl_3 system, parasitic protic initiation is absent, while with $TiCl_4$ an externally added ED is needed to achieve the same effect [9, 10, 14, 17]. Proton scavenging by the BCl_3·EtOAc complex may be due to the interaction between the protic impurity "$H^+BCl_3OH^-$" (arising from BCl_3 + "H_2O") and the unshared electron pair of the alkyl oxygen:



$$\begin{array}{c} BCl_3 \\ \nearrow \\ O \\ \| \\ C_2H_5-O-C-CH_3 \\ \downarrow \\ H^+BCl_3OH^- \end{array}$$

Proton scavenging can be studied by the use of the proton trap D*t*BP, which, due to steric hindrance, does not react with FCAs or carbocations [22–24]. This has recently been reaffirmed by showing that D*t*BP is essentially inert in the polymerization of vinyl ethers [2, 3]. Table 4 and Fig. 2 show the results of polymerizations obtained with the TMPOAc/BCl_3/IB/CH_3Cl/−30°C system in the presence of different D*t*BP concentrations. To our surprise, theoretical molecular weights, complete monomer conversions, and narrow MWDs have been obtained in every experiment, except in the control run. The $\overline{M}_w/\overline{M}_n$ versus [D*t*BP] plot (Fig. 2) dramatically emphasizes that proton scavenging must be responsible for MWD narrowing since by increasing the concentration of D*t*BP

TABLE 4. Polymerization of IB with the TMPOAc/BCl_3 System in the Presence of D*t*BP ([TMPOAc] = 1.1×10^{-2} mol/L, [IB] = 0.94 mol/L, [BCl_3] = 5.1×10^{-2} mol/L, CH_3Cl, 25 mL, −30°C, 30 min)

D*t*BP/ TMPOAc	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	Conversion, %	I_{eff}, %
0	4.8	2.60	100	100
0.01	4.6	1.40	100	104
0.05	4.6	1.20	100	104
0.1	4.65	1.18	100	103

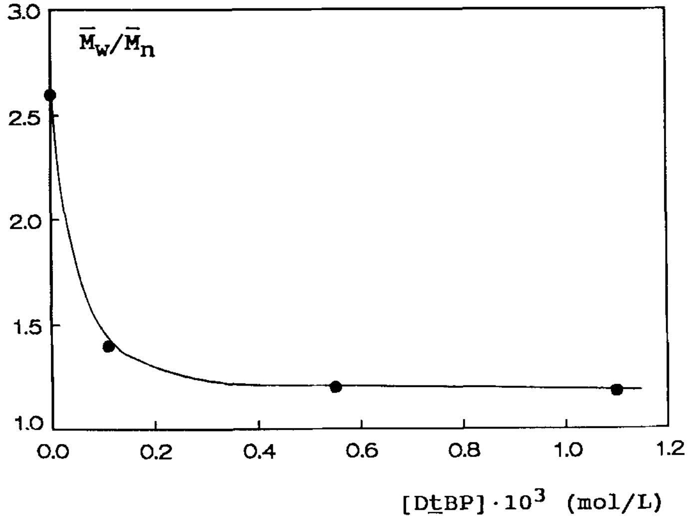
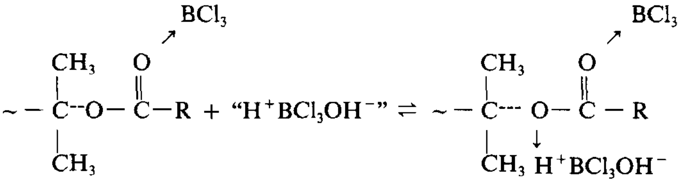


FIG. 2. The effect of D*t*BP concentration on $\overline{M}_w/\overline{M}_n$ of PIBs (experimental conditions as in Table 4).

beyond $\sim 5 \times 10^{-4}$ mol/L; that is, the concentration range of protogenic impurities in CH_3Cl [25–27] does not further affect the MWD.

These experiments may also help to explain the relatively broad MWDs ($\overline{M}_w/\overline{M}_n = 1.3$–$2.4$) obtained in the living polymerization of IB initiated by *tert*-ester or -ether/BCl_3 systems [17, 21]. We speculate that the broad MWDs are due to proton scavenging by the living initiator and/or growing centers, coupled with a relatively slow "$H^+BCl_3OH^-$" exchange between more reactive protonated species and less reactive unprotonated ones:



$$\sim-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{--}O-\overset{\overset{\overset{BCl_3}{\nearrow}}{O}}{\overset{\|}{C}}-R + \text{“}H^+BCl_3OH^-\text{”} \rightleftarrows \sim-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{---}\underset{\underset{H^+BCl_3OH^-}{\downarrow}}{O}-\overset{\overset{\overset{BCl_3}{\nearrow}}{O}}{\overset{\|}{C}}-R$$

where the relatively weaker C---O bond in the protonated form is denoted by --- while the stronger interaction in the nonprotonated species is given by --. Thus, two kinds of slowly equilibrating species sustain propagation which, as a consequence, gives rise to relatively broad MWDs. In the presence of D*t*BP, since the proton is scavenged by the proton trap, the protonated form is absent and only one kind of propagating species is present, which then yields narrow MWD PIBs. The narrow MWDs also prove that at least in the system under investigation, $R_i > R_p$.

In conclusion, these findings suggest that $BCl_3 \cdot ED$ complexes may behave as proton traps and thus yield narrow MWD products. In the absence of initiator but the presence of $BCl_3 \cdot ED$ complexes, such as $BCl_3 \cdot EtOAc$ (cf. Table 3), $BCl_3 \cdot DMA$, and $BCl_3 \cdot DMSO$ [9, 28], the impurity "H_2O"/BCl_3 does not yield polymer (or only traces of it). In contrast, high yields of polymers may be obtained in the presence of certain $TiCl_4 \cdot ED$ complexes, e.g., $TiCl_4 \cdot EtOAc$, which for some reason do not function as proton traps [28]. Further research is in progress in this direction in our laboratories.

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