Kinetic and Mechanistic Studies of the Carbocationic Precipitation Polymerization of Isobutylene in Polar Solvents

Ivaylo Dimitrov[†] **and Rudolf Faust***

Polymer Science Program, Department of Chemistry, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854

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ABSTRACT: The kinetic and thermodynamic parameters of the ionization−ion collapse of HCl, *tert*-butyl chloride (*t*-BuCl), and 2-chloro-2,4,4-trimethylpentane (TMPCl) in conjunction with ethylaluminum dichloride in CH_3Cl or CH_2Cl_2 in the temperature range of −60 to −90 °C were determined under high-purity conditions by following the kinetics of the capping reaction of the corresponding cations with 1,1-ditolylethylene. The apparent rate (k_i^{app}) and equilibrium constant of ionization (K_i^{app}) increased in the HCl < *t*-BuCl < TMPCl order. Both k_i^{app} and the rate of ion-collapse (k_{-i}) increased with increasing temperature; however, because of the higher increase in k_{-i}, the apparent equilibrium constant of ionization increased with decreasing temperature. On the basis of the kinetic results, a new mechanism was proposed for the precipitation polymerization of IB in polar solvents. This mechanism involves slow ionization followed by diffusion-limited propagation until ion collapse and polymer precipitation. The calculated molecular weight and composite activation energy for the degree of polymerization based on this mechanism were in excellent agreement with experimental findings.

Introduction

Homo- and copolymers of isobutylene (IB) are by far the most important industrial polymers produced by cationic polymerization. High molecular weight polyisobutylene (PIB) and butyl rubber are generally synthesized in a slurry process at −90 to −100 °C in methyl chloride (CH_3Cl) using water or HCl as initiator in conjunction with $AlCl_3$ as co-initiator.[1] Although worldwide production exceeds 10^6 metric tons, the kinetics and mechanism of the polymerization are not well established. This is partly due to the extremely rapid and heterogeneous nature of the polymerization where the polymer precipitates from the solution. Reliable rate constants, especially the rate constant of propagation (k_p), have not been available until recently even in the solution polymerization of IB. We have recently reported on the propagation rate constant for ion pairs ($k_p^{\pm}$) in the polymerization of IB in conjunction with $TiCl_4$ in hexanes (Hex)/CH_3Cl 60/40 (v/v) at −80 °C.[2] The $k_p^{\pm}$ was in the range $(3-10) \times 10^8$ L mol^{-1} s^{-1}, 4 orders of magnitude higher than previously accepted values. In a subsequent study,[3] we found that $k_p^{\pm}$ is independent of temperature and nature of Lewis acid and increases moderately with increasing solvent polarity to a practically diffusion-limited value ($\sim 2 \times 10^9$ L mol^{-1} s^{-1}) in CH_3Cl. In the present study we investigated the polymerization of IB in conjunction with ethylaluminum dichloride ($EtAlCl_2$), which is soluble and gives the highest molecular weights down to −100 °C,[4] in methyl chloride or dichloromethane at different temperatures. Since the value of $k_p^{\pm}$ is already known, emphasis was placed on the investigation of the kinetics of ionization (activation) and ion collapse (deactivation).

Experimental Section

Materials. Dichloromethane (CH_2Cl_2) was washed with 10% NaOH followed by water until neutral. After drying over Na_2SO_4 it was double distilled from CaH_2 and from P_2O_5 under high vacuum just prior to use. Methyl chloride (CH_3Cl) was purified by double distillation—first, the gas was passed through a column packed with BaO/Drierite, and then the liquid collected at −80 °C was distilled from triethylaluminum (Aldrich, 1.9 M in toluene). *tert*-Butyl chloride (*t*-BuCl, Aldrich) and 2-chloro-2,4,4-trimethylpentane (TMPCl, synthesized according to the literature[5]) were distilled from CaH_2. 1,1-Bis(4-methylphenyl)ethylene (DTE) was synthesized following a procedure reported elsewhere[6] and was dried in a vacuum prior to use. HCl solution was prepared by bubbling a high-purity HCl gas (99+%, Aldrich) through CH_2Cl_2 at −78 °C. The concentration of HCl solution was determined by titration in 2-propanol with 0.1 M NaOH. Ethylaluminum dichloride (Aldrich, 1 M in hexanes) was used as received.

General Reaction Procedure. All reactions were carried out under a dry nitrogen atmosphere in an MBraun 150-M glovebox (Innovative Technologies Inc., Newburyport, MA) using [initiator] = 5.0×10^{-4} mol L^{-1}, [$EtAlCl_2$] = 5.0×10^{-4} mol L^{-1}, and [DTE] = 5.0×10^{-4}−2.0×10^{-3} mol L^{-1}. The total volume of the reaction mixture was 150 mL. The DTE and initiator containing solutions in CH_2Cl_2 or CH_3Cl were prepared and kept at the capping temperature. Then, the reference spectrum was taken, and the program collecting the visible spectra was started. Finally, the Lewis acid solution was added under efficient stirring, and that was the reaction onset.

Visible Spectroscopy. The visible spectra were collected using an all-quartz immersion probe 661.300-UV (Hellma) with an optical path of 0.02 cm, connected to a fiber-optic visible tungsten light source (Ocean Optics) and a Zeiss MMS 256 photodiode array detector. The system was connected to a personal computer via a TEC5 interface, and the spectra were recorded using the “Aspect Plus” software (Zeiss).

Characterization. Molecular weights were measured using a Waters HPLC system equipped with a model 510 HPLC pump, a model 250 dual refractometer/viscometer detector (Viscotek), a model 486 UV/vis detector, a model 712 sample processor, and five ultra-Styragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. THF was used as eluent at a flow rate of 1.0 mL/min. The measurements were carried out at room temperature. The molecular weights and polydispersities were determined using the universal calibration curve and Viscotek TriSEC GPC software.

[†] Permanent address: Institute of Polymers, Bulgarian Academy of Sciences, 1113-Sofia, Bulgaria.

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Table 1. Polymerization of Isobutylene in Hex/CH_3Cl 60/40 v/v at −85 °C[a]

[IB] (mol L^{-1})	$M_{n,theor}$[b]	$M_{n,exp}$	M_w/M_n
0.26	7 200	7 200	1.5
0.63	17 600	16 400	1.6
0.93	26 100	21 600	1.6
1.27	35 500	29 400	1.5
1.56	43 750	40 200	1.5

[a] [TMPCl] = 0.002 mol L^{-1}, [$EtAlCl_2$] = 0.01 mol L^{-1}, [DTBP] = 0.0035 mol L^{-1}. Polymerization time: 2 min; IB conversion: 100%. [b] Calculated by assuming that one initiator molecule initiates one polymer chain.

Table 2. Polymerization of Isobutylene in CH_3Cl at −90 °C[a]

[$EtAlCl_2$] × 10^4 (mol L^{-1})	conversion[b] (%)	$M_n \times 10^3$	M_w/M_n
2.0	3.2	310	1.6
2.0 (dropwise)	2.7	350	1.5
5.0[c] (dropwise)	7.6	350	1.5
15.0[c] (dropwise)	16.5	400	1.4

[a] [TMPCl] = 1.0 × 10^{-4} mol L^{-1}; [IB] = 1.0 mol L^{-1}; polymerization time: 30 min; total volume: 100 mL. [b] Determined gravimetrically. [c] $EtAlCl_2$ was added from a more diluted (0.05 M instead of 0.1 M) stock solution.

Results and Discussion

Polymerization of IB with $EtAlCl_2$. Most living cationic polymerizations feature a rapid exchange between dormant and active centers.[7] Although the propagation rate constant is independent of the nature of Lewis acid,[3] the position of the dormant/active equilibrium, i.e., the equilibrium constant of ionization, and therefore the overall polymerization rate very much depend on the strength of the Lewis acid.[3] $EtAlCl_2$ is a strong Lewis acid, and the solution polymerization of IB in conjunction with TMPCl/$EtAlCl_2$ initiating system in Hex/CH_3Cl 60/40 (v/v) at −85 °C is extremely rapid and complete in less than 2 min (Table 1). Although $EtAlCl_2$ is a strong Lewis acid, it is unlikely to ionize TMPCl or PIBCl completely (see later), and therefore several activation−deactivation cycles may take place before irreversible termination occurs. This irreversible termination (most likely by Et^- or H^- transfer), however, is relatively slow compared to propagation according to Table 1, since polymers with M_ns controlled by the monomer/initiator ratio can be obtained at least up to 40 000. A similar observation was reported with CH_3AlCl_2 as Lewis acid under similar conditions,[8] where PIBs with theoretical M_ns and molecular weight distributions M_w/M_n = 1.3−1.5 were obtained at least up to [IB]/[TMPCl] = 1000 with the all monomer in technique. Incremental monomer addition resulted in complete monomer conversion with M_ns that doubled or tripled after one and two increments, respectively, and the M_w/M_n remained unchanged. With $EtAlCl_2$, however, addition of a second IB increment after 2 min and subsequent polymerization for 8 min resulted in less than complete consumption of the second monomer increment, and the product exhibited a bimodal molecular weight distribution, confirming termination.

As the rate and extent of ionization in a more polar solvent such as CH_3Cl are higher, the overall polymerization rate is also higher compared to that in the mixed hexanes/CH_3Cl 60/40 (v/v) solvent system. Decreasing the initiator and/or co-initiator concentration may decrease the rate; however, there are limitations. The co-initiator concentration cannot be decreased below the concentration of protic impurities in the presence of a proton trap; polymerization at lower [$EtAlCl_2$] can only be accomplished in the absence of a proton trap. Even in the absence of a proton trap at low [$EtAlCl_2$] the polymerization is so fast that it is difficult to maintain isothermal conditions when $EtAlCl_2$ is added all at once. Table 2 lists results of IB polymerizations in CH_3Cl where $EtAlCl_2$ was introduced at a low enough rate that temperature increase was minimized.

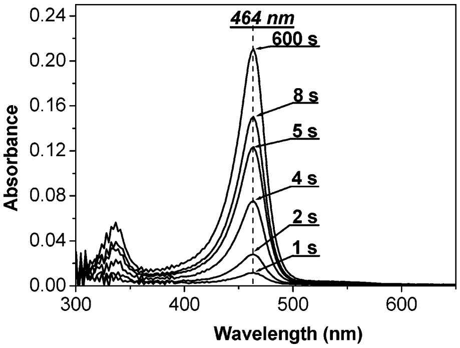


Figure 1. Selected visible spectra recorded during the capping reaction of *t*-BuCl (5.0 × 10^{-4} mol L^{-1}) with DTE (1.5 × 10^{-3} mol L^{-1}) in CH_2Cl_2 at −70 °C.

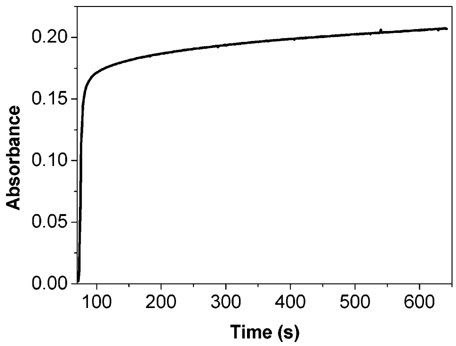


Figure 2. Plot of the absorbance at λ_{max} = 464 nm vs time for the capping of *t*-BuCl (5.0 × 10^{-4} mol L^{-1}) with DTE (1.5 × 10^{-3} mol L^{-1}) in CH_2Cl_2 at −70 °C.

The very rapid polymerization as well as preliminary ionization studies suggested that for the kinetic studies the $EtAlCl_2$ concentration must be below 0.001 M to follow these reactions with conventional instrumentation. Therefore, DTBP could not be used to trap adventitious protic impurities, and instead the experiments have been carried out under high-purity conditions.

Visible Spectroscopic Measurements. The capping of TMPCl, *t*-BuCl, and HCl with the non(homo)-polymerizable DTE was studied in CH_2Cl_2 or CH_3Cl at temperatures from −90 to −60 °C. Since ditolylalkylcarbenium ions exhibit a maximum absorption in the visible light range (λ_{max} = 458−464 nm) with a high molar absorption coefficient (ϵ_{max} = 44 000 L mol^{-1} cm^{-1}, used in both solvents),[2] visible spectroscopy was applied for on-line monitoring of the reaction. Selected visible spectra obtained during the capping of *t*-BuCl at −70 °C in CH_2Cl_2 and the respective absorbance vs time plot are shown in Figures 1 and 2. Time-dependent evolution of the absorbance shows that this reaction is extremely fast and is complete within a few seconds.

Control experiments were also performed in the absence of initiator under otherwise identical conditions as for the capping reactions. After an initial period of time a colored species slowly started to generate (Figure

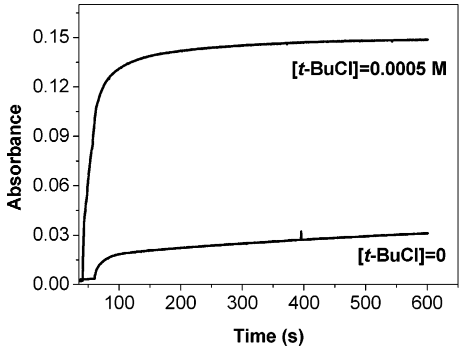


Figure 3. Absorbance vs time plots for the capping reaction of *t*-BuCl (5.0×10^{-4} mol L^{-1}) and for the control experiment in CH_3Cl at −80 °C; [DTE] = [$EtAlCl_2$] = 5.0×10^{-4} mol L^{-1}.

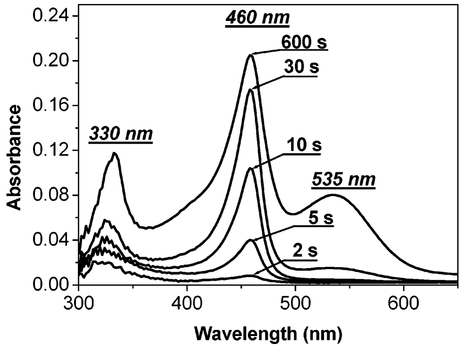


Figure 4. Selected visible spectra recorded during the capping reaction of HCl with DTE (1.5×10^{-3} mol L^{-1}) in CH_2Cl_2 at −70 °C; [HCl] = [$EtAlCl_2$] = 5.0×10^{-4} mol L^{-1}.

3). The visible spectra recorded during the control experiments are slightly shifted (λ_{max} = 460 nm in CH_2Cl_2) compared to those observed in the capping reactions of *t*-BuCl and TMPCl (464 nm in CH_2Cl_2) and exhibit the same λ_{max} observed in the capping reaction of HCl. Since the capping reactions and control experiments were carried out in the absence of a proton trap, formation of colored species in the latter can be attributed to the presence of adventitious protic impurities in the solvents. Apparently this does not affect the initial slopes for the capping reactions due to the inhibition period of time detected during control experiments and the much lower concentration of protic impurities compared to that of the initiator.

In the cases when HCl was used as an initiator the maximum absorbance was observed at λ_{max} = 460 nm (Figure 4). A new peak at 535 nm and a much larger 330 nm peak also appeared in the recorded spectra (Figure 4). The intensity of these peaks increases with increasing DTE concentration. At −80 and −90 °C we also observed that after reaching a maximum the peak intensity at λ_{max} = 460 nm decreased with time. The observed phenomenon is most likely due to the cationic dimerization of DTE initiated by HCl. Similar results have already been reported for 1,1-diphenylethylene (DPE), which dimerizes in CH_2Cl_2 at low temperatures.[9] The absorption at 520 nm has been attributed to the formation of DPE solvated monomeric and dimeric cations. Stopped-flow/rapid-scan spectroscopic measurements of DPE dimerization initiated by CF_3SO_3H showed that this reaction proceeds through a very fast protonation followed by much slower dimer formation.[10] Thus, dimer formation is a slow process and does not affect the initial stages of the capping reaction.

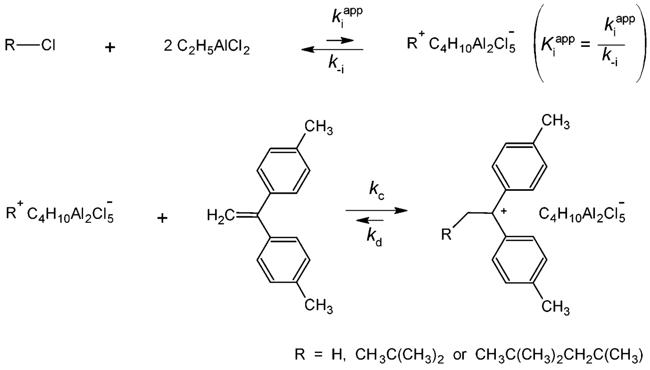
Table 3. Ratios of k_{tr}/k_p and Calculated k_{tr} Values in the Polymerization of IB Using Hex/CH_3Cl Solvent Mixtures

temp (°C)	solvent mixture (Hex/CH_3Cl, v/v)	k_{tr}/k_p (mol L^{-1})	k_{tr} (s^{-1})
−25	40/60	1.1×10^{-2}	9.4×10^{6}
−40	40/60	7.2×10^{-4}	6.1×10^{5}
−40	60/40	3.3×10^{-3}	1.1×10^{6}

Kinetic Scheme of the Capping Reaction with DTE. We have recently reported that by UV−vis monitoring of the addition of nonhomopolymerizable π-nucleophiles (e.g., DTE or 2-phenylfuran) to hydrochlorinated isobutylene *n*-mers in the presence of Lewis acid the apparent rate constants of capping, k_cK_i, and the rate constant of ionization, k_i, can be determined.[11] We have also shown that the addition of DTE to PIB^+ cations is diffusion limited, which allows us to determine K_i, and from this value and k_i the rate constant of ion collapse k_{-i} can be calculated.[1] The kinetic equations derived for the capping reaction were based on the absence of side reactions, shown by the living nature of the polymerization of IB. Living polymerization cannot be verified by the usual methods in the precipitation polymerization of IB, and therefore we have to consider possible side reactions, more specifically the rate of these side reactions relative to the rate of capping. The most important side reaction in the polymerization of IB, especially at higher temperatures, is chain transfer to monomer. Therefore, we have to consider the possibility of direct (bimolecular) or indirect (unimolecular or counterion assisted) proton transfer from the *t*-Bu^+ or TMP^+ cation to DTE. Since addition of DTE to these cations is diffusion limited, direct proton transfer can be neglected unless the rate constant of proton transfer is also close to the diffusion limit. Direct proton transfer could not be detected in the addition reaction of DTE to PIB^+ cations in conjunction with $TiCl_4$ or $EtAlCl_2$ in hexanes(Hex)/CH_3Cl mixtures at −80 °C. Direct proton transfer to 2-phenylfuran in conjunction with $TiCl_4$ was absent even at −50 °C;[2] apparently this process is much slower than capping. Since the reactivity of PIB^+ cation is independent of the nature of Lewis acid, direct proton transfer should also be negligible with $EtAlCl_2$.

Chain transfer constants for indirect chain transfer to monomer have been reported in conjunction with $TiCl_4$ in the polymerization of IB in Hex/CH_3Cl mixtures; these are listed in Table 3. From the known values of k_p the values of k_{tr} were calculated, which are also shown in Table 3. The slower proton elimination in the more polar solvent is in line with the transition state being more polar than the ground state. On the basis of the k_{tr} values for −25 and −40 °C ($E_a \sim 19$ kcal/mol), $k_{tr} \sim 10^4$ and 10^2 s^{-1} are estimated for −60 and −80 °C, respectively. Furthermore, $EtAlCl_2$ yields a less nucleophilic counteranion compared to $TiCl_4$; this effect and the increase in the solvent polarity (100% CH_3Cl) should further reduce the k_{tr} value. Therefore, proton elimination appears to be slow compared to capping even at the lowest [DTE] employed. A comparison of the visible spectroscopic measurements carried out with HCl and *t*-BuCl or TMPCl also verifies that direct or indirect proton transfer to DTE is negligible, since the dimeric DTE cation is not observed in the capping reaction of *t*-BuCl or TMPCl. Therefore, visible absorption at 464 nm is due to the capped *t*-Bu-DTE^+ or TMP-DTE^+ cation, and side reactions can be ignored.

Scheme 1. Ionization of R−Cl with $EtAlCl_2$ Followed by the Capping Reaction with DTE



Capping of the initiator (R−Cl) with DTE is a two-step reaction—the ionization of the initiator is followed by the addition of 1 unit from the DTE monomer (Scheme 1).The equilibrium constant of ionization is expressed as

$$K_i^{app} = \frac{k_i^{app}}{k_{-i}} = \frac{[R^+C_4H_{10}Al_2Cl_5^-]}{[R-Cl][C_2H_5AlCl_2]^2} \tag{1}$$

where $K_i^{app} = K_iK_{D0}$ is the apparent equilibrium constant of ionization (K_i is the absolute equilibrium constant of ionization and K_{D0} is the equilibrium constant of $EtAlCl_2$ dimerization) and k_i^{app} is the apparent rate constant of ionization, consisting of the product of absolute rate constant of ionization (k_i) and K_{D0}.

We have already shown[1] that only ion pairs need to be considered even in the absence of proton trap when capping is fast. Capping with diarylethylenes also results in the formation of common anions since the capped species are fully ionized with an equilibrium constant of dissociation $K_d \sim 10^{-4}$ mol L^{-1}. Considering exclusively $R^+C_4H_{10}Al_2Cl_5^-$ ion pairs, the initial evolution of capped species with time therefore is given by eq 2.

$$\frac{d}{dt}([R-DTE^+C_4H_{10}Al_2Cl_5^-] + [R-DTE^+]) = k_c[R^+C_4H_{10}Al_2Cl_5^-][DTE] \tag{2}$$

The left side of eq 2 contains the sum of concentrations of the capped ion pairs and free ions which should exhibit the same λ_{max} and ϵ_{max}. Therefore, it is not necessary to determine the extent of dissociation.

Assuming steady state for $R^+ C_4H_{10}Al_2Cl_5^-$ ion pairs, i.e.

$$\frac{d}{dt}[R^+C_4H_{10}Al_2Cl_5^-] = k_i^{app}[R-Cl][C_2H_5AlCl_2]^2 - k_{-i}[R^+C_4H_{10}Al_2Cl_5^-] - k_c[R^+C_4H_{10}Al_2Cl_5^-][DTE] = 0 \tag{3}$$

their concentration is expressed according to eq 4.

$$[R^+C_4H_{10}Al_2Cl_5^-] = \frac{k_i^{app}[R-Cl][C_2H_5AlCl_2]^2}{k_{-i} + k_c[DTE]} \tag{4}$$

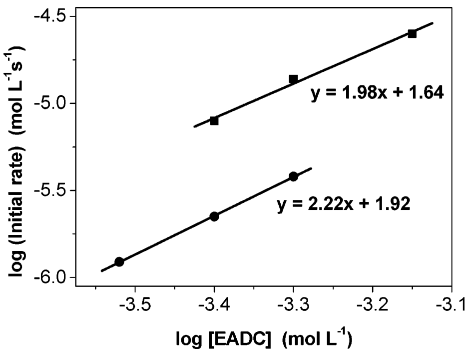


Figure 5. Bilogarithmic plot of the initial rate of capping vs the concentration of $EtAlCl_2$ for determining the order in $EtAlCl_2$ in the capping reaction of *t*-BuCl (■) and HCl (●) with DTE in CH_2Cl_2 at −80 °C; [*t*-BuCl] = [HCl] = [DTE] = 5.0×10^{-4} mol L^{-1}.

Substituting eq 4 into eq 2

$$\frac{d}{dt}([R-DTE^+C_4H_{10}Al_2Cl_5^-] + [R-DTE^+]) = \frac{k_ck_i^{app}[R-Cl][C_2H_5AlCl_2]^2[DTE]}{k_{-i} + k_c[DTE]} \tag{5}$$

The initial rate of capping is expressed as in eq 6, using the initial slope from the plots representing the absorbance at λ_{max} vs time for the capping reactions:

$$\frac{d}{dt}([R-DTE^+C_4H_{10}Al_2Cl_5^-] + [R-DTE^+]) = \frac{\text{initial slope (absorbance units s}^{-1})}{\epsilon_{max}d} \tag{6}$$

According to Scheme 1, the initiator ionization requires two molecules of Lewis acid. This is consistent with reports in the literature[12] that alkylaluminum halides (and even trialkylaluminum compounds) are dimeric in the vapor phase or in solutions especially at low temperatures. Our own experiments in the capping reactions of *t*-BuCl and HCl with DTE at different $EtAlCl_2$ concentrations also confirmed that two molecules of $EtAlCl_2$ are necessary for ionization. The corresponding bilogarithmic plots of the initial rates of capping vs $[EtAlCl_2]$ (Figure 5) give slopes close to 2, indicating that capping is second-order in $[EtAlCl_2]$.

For the determination of $k_cK_i^{app}$ and k_i^{app} eq 5 can be transformed to eq 7.

$$\frac{[R-Cl][C_2H_5AlCl_2]^2}{\frac{d}{dt}([R-DTE^+C_4H_{10}Al_2Cl_5^-] + [R-DTE^+])} = \frac{1}{k_cK_i^{app}[DTE]} + \frac{1}{k_i^{app}} \tag{7}$$

The plot of the left side of eq 7 vs 1/[DTE] should give a straight line with the slope of $1/k_cK_i^{app}$ and the intercept of $1/k_i^{app}$. An exemplary plot obtained for the capping of *t*-BuCl with DTE at −70 °C in CH_2Cl_2 is shown in Figure 6.

Although only the initial slopes are used in the calculations, it should be noted that the absorbance values at the plateau (Figure 2) are about half of what would correspond to complete capping of the initiator.

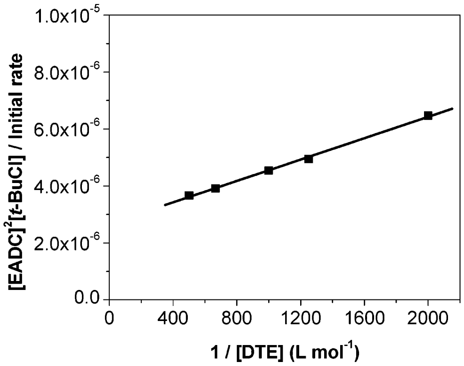


Figure 6. Plot of reciprocal initial rate of capping vs 1/[DTE] for the capping reaction of *t*-BuCl with DTE in CH_2Cl_2 at −70 °C; [$EtAlCl_2$] = [*t*-BuCl] = 5.0×10^{-4} mol L^{-1}.

Table 4. Rate Constant of Capping k_c as a Function of Temperature in CH_2Cl_2 and CH_3Cl

	$k_c \times 10^{-9}$ (L mol^{-1} s^{-1})			
solvent	−90 °C	−80 °C	−70 °C	−60 °C
CH_2Cl_2	1.2	1.6	2.0	2.5
CH_3Cl	4.6	5.4	6.1	7.0

Since capping requires two molecules of $EtAlCl_2$ (capping is second-order in [$EtAlCl_2$]), at [$EtAlCl_2$] = [initiator] the $EtAlCl_2$ concentration is only half of the stoichiometric amount. In other words, $EtAlCl_2$ is the limiting reagent.

From the composite rate constant of the capping reaction ($k_cK_i^{app}$) K_i^{app} can be derived. The value of the diffusion-limited second-order rate constant of capping k_c has been set to 3.0×10^9 L mol^{-1} s^{-1} in the solvent mixture Hex/CH_3Cl (60/40 v/v) at −80 °C.[1] However, k_c varies with temperature through the temperature dependence of the diffusion coefficient, which in turn is related to the solution viscosity. Therefore, the k_c values at different temperatures in CH_2Cl_2 and CH_3Cl were calculated relative to $k_c = 3.0 \times 10^9$ L mol^{-1} s^{-1} applying the Stokes−Einstein equation:

$$D = \frac{RT}{6\pi\eta rN} \tag{8}$$

where D is the diffusion coefficient, R is the universal gas constant, η is the dynamic viscosity of the solvent system, r is the radius of the molecule, and N is the Avogadro number.

The corrected k_c values in CH_2Cl_2 and CH_3Cl at different temperatures presented in Table 4 were used for the calculation of the K_i^{app} values.

Kinetic and Thermodynamic Parameters for HCl, *t*-BuCl, and TMPCl Ionization. All kinetic and thermodynamic parameters obtained from the capping reactions of the three investigated initiators evaluated from the visible spectroscopic measurements at different temperatures in CH_2Cl_2 and CH_3Cl are summarized in Table 5. The k_i^{app} and K_i^{app} values for HCl were calculated by assuming diffusion-limited addition of DTE. Since addition of DTE to *t*-Bu^+ or TMP^+ cations is diffusion limited, this assumption is reasonable.

It is well-known that *t*-BuCl is a slow initiator for the cationic polymerization of isobutylene compared to TMPCl.[7,13] This is due to the increased degree of back-strain (i.e., the release of steric strain during the rehybridization from sp^3 to sp^2 taking place in the course of ionization) for TMPCl.[14] The capping reaction of *t*-BuCl is 4.5 times slower than that of TMPCl (Table 5: CH_2Cl_2, −90 °C). Since the diffusion-limited k_c is the same in both cases ($k_c = 1.2 \times 10^9$ L mol^{-1} s^{-1}), the difference in $k_cK_i^{app}$ values should be due to a difference in K_i^{app}. This in turn can be attributed to a large difference in the values of the apparent rate constant of ionization. For example, k_i^{app} (as well as k_i) of *t*-BuCl in CH_2Cl_2 at −90 °C is about 20 times lower than that of TMPCl. The results are qualitatively similar to those obtained for the capping reactions of *t*-BuCl and TMPCl with DPE in the presence of $TiCl_4$ in Hex/CH_3Cl 60/40 (v/v), where an even larger difference in $k_cK_i^{app}$ values between the two initiators has been found.[7] According to the kinetic and thermodynamic parameters obtained (Table 5: CH_2Cl_2, −90 °C), HCl is the slowest initiator from all three. The values of $k_cK_i^{app}$ and k_i^{app} for the capping of HCl are 18 and 33 times lower than those of TMPCl and 4 and 2 times lower than those of *t*-BuCl.

Effect of Solvent Polarity on Kinetic and Thermodynamic Parameters. Visible spectroscopic kinetic experiments were carried out in two different solvents—CH_2Cl_2 and CH_3Cl. At constant temperature the concentration of active centers increases with increasing solvent polarity (Table 5). This is due to the higher values of the apparent equilibrium constant of ioniza-

Table 5. Kinetic and Thermodynamic Parameters for the Capping Reactions of *t*-BuCl, TMPCl, and HCl with DTE in CH_2Cl_2 and CH_3Cl in the Temperature Interval −70 to −90 °C

initiator	solvent	$k_cK_i^{app}$ (L^3 mol^{-3} s^{-1})	k_i^{app} (L^2 mol^{-2} s^{-1})	K_i^{app} (L^2 mol^{-2})	k_{-i} (s^{-1})
			−70 °C		
HCl	CH_2Cl_2	8.7×10^7	1.6×10^5	0.044	3.6×10^6
	CH_3Cl	1.7×10^8	7.4×10^4	0.028	2.6×10^6
t-BuCl	CH_2Cl_2	5.3×10^8	3.7×10^5	0.27	1.4×10^6
	CH_3Cl	1.3×10^9	2.0×10^5	0.21	9.5×10^5
			−80 °C		
HCl	CH_2Cl_2	1.3×10^8	5.7×10^4	0.081	7.0×10^5
	CH_3Cl	2.3×10^8	3.9×10^4	0.043	9.1×10^5
t-BuCl	CH_2Cl_2	6.8×10^8	1.7×10^5	0.43	3.9×10^5
	CH_3Cl	1.6×10^9	1.0×10^5	0.30	3.3×10^5
TMPCl	CH_2Cl_2	2.7×10^9	2.5×10^6	1.7	1.5×10^6
	CH_3Cl	5.0×10^9	1.4×10^6	0.93	1.5×10^6
			−90 °C		
HCl	CH_2Cl_2	2.1×10^8	2.7×10^4	0.17	1.6×10^5
	CH_3Cl	3.7×10^8	2.2×10^4	0.08	2.7×10^5
t-BuCl	CH_2Cl_2	8.2×10^8	4.9×10^4	0.68	7.2×10^4
	CH_3Cl	1.9×10^9	3.3×10^4	0.41	8.0×10^4
TMPCl	CH_2Cl_2	3.7×10^9	8.8×10^5	3.1	2.8×10^5
	CH_3Cl	6.3×10^9	5.2×10^5	1.4	3.7×10^5

Table 6. Kinetic and Thermodynamic Parameters for the Capping Reaction of *t*-BuCl with DTE in CH_2Cl_2

temp (°C)	k_c (L mol^{-1} s^{-1})	$k_cK_i^{app}$ (L^3 mol^{-3} s^{-1})	k_i^{app} (L^2 mol^{-2} s^{-1})	K_i^{app} (L^2 mol^{-2})	k_{-i} (s^{-1})
−90	1.2×10^9	8.2×10^8	4.9×10^4	0.68	7.2×10^4
−80	1.6×10^9	6.8×10^8	1.7×10^5	0.43	3.9×10^5
−70	2.0×10^9	5.3×10^8	3.7×10^5	0.27	1.4×10^6
−60	2.5×10^9	4.6×10^8	1.3×10^6	0.18	7.2×10^6

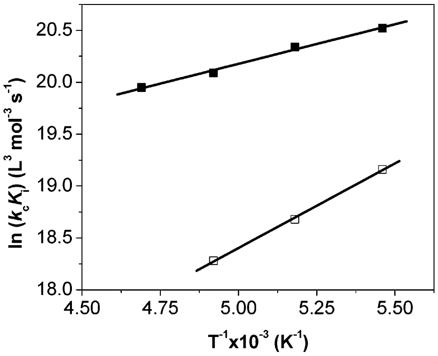


Figure 7. Arrhenius plot of the apparent rate constant of capping, $k_cK_i^{app}$, for *t*-BuCl (■) and HCl (□) in CH_2Cl_2.

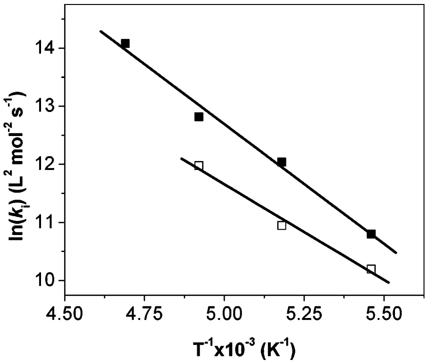


Figure 8. Arrhenius plot of the apparent rate constant of ionization, k_i^{app}, for *t*-BuCl (■) and for HCl (□) in CH_2Cl_2.

tion, K_i^{app}, in CH_2Cl_2. For all three initiators the increase of K_i^{app} values in CH_2Cl_2 is mainly due to increasing k_i^{app} values. There is only a slight change in k_{-i} values with increasing solvent polarity.

Effect of Temperature on the Kinetic and Thermodynamic Parameters. The apparent rate constant of capping, $k_cK_i^{app}$, decreases with increasing temperature (Table 6). This is due to a decrease in the K_i^{app} value with increasing temperature. The lower value of K_i^{app} at higher temperature is a result of a smaller increase of k_i^{app} and larger increase of k_{-i} with increasing temperature. Both ionization and deactivation (reversible termination) thus have a positive activation energy, but the latter is higher.

From the temperature dependence of ionization and capping the values of apparent activation energy (E_a^{app}) for the two processes can be obtained. The corresponding Arrhenius plots of $k_cK_i^{app}$ and k_i^{app} for *t*-BuCl and HCl in CH_2Cl_2 are presented in Figures 7 and 8. The values of the apparent activation energy, E_a^{app}, were determined from the slopes of respective plots. Negative values of E_a^{app} were calculated for the capping reactions and positive for the ionization (Table 7). Since fast reactions do not have an enthalpic barrier (i.e., the activation energy for capping is zero), E_a^{app} for capping equals the sum of the enthalpy of ionization and $EtAlCl_2$ dimerization.

Table 7. Apparent Activation Energies, E_a^{app}, for $k_cK_i^{app}$, k_i^{app}, and k_{-i} for *t*-BuCl and HCl in CH_2Cl_2 and CH_3Cl

		E_a^{app}/kJ mol^{-1} (E_a^{app}/kcal mol^{-1})	
	solvent	HCl	*t*-BuCl
$k_cK_i^{app}$	CH_3Cl	−12.06 (−2.88)	−5.74 (−1.37)
k_i^{app}		18.62 (4.45)	27.94 (6.67)
k_{-i}		34.84 (8.32)	38.08 (9.1)
$k_cK_i^{app}$	CH_2Cl_2	−13.55 (−3.24)	−6.32 (−1.51)
k_i^{app}		27.35 (6.54)	34.25 (8.19)
k_{-i}		47.97 (11.46)	48.80 (11.66)

Proposed Polymerization Mechanism. On the basis of the above results, the polymerization of IB in CH_3Cl can be envisioned as follows. Upon ionization of the initiator, e.g. HCl or *t*-BuCl, essentially diffusion-limited propagation takes place. In the absence of a common ion source the low concentration of active centers would suggest that propagation would mainly take place on free ions; however, this is not the case. Since the rate constant of dissociation ($k_d \sim 10^2-10^4$ s^{-1}) is much lower than that of propagation or ion collapse, and due to the heterogeneous nature of the polymerization the binary ionization equilibrium cannot be established, propagation will mainly involve ion pairs. Since PIB is not soluble in CH_3Cl, propagation may continue until the propagating chain (a) is terminated by chain breaking (chain transfer or termination) and then the polymer chain precipitates or (b) is deactivated by ion collapse (transfer of Cl^-), the polymer precipitates, and further chain growth is slow or absent. We also could consider another alternative that the polymer precipitates, and while the chain end is still active further propagation is very slow or absent. This consideration, however, was discounted since this process would yield molecular weights independent of the nature of the co-initiator, which is not supported by experimental evidence. It is generally believed that down to about −100 °C chain transfer to monomer is the most important chain-breaking event that determines the molecular weight. Thus, to "freeze out" chain transfer to monomer and obtain PIBs with high molecular weight very low temperatures (−90 to −100 °C) are used.

Here we propose an alternative explanation that involves deactivation of the propagating chains by transfer of Cl^-, and then the polymer precipitates. Since the reactivities of the propagating polymer and dimer ends are similar (although not identical),[1,7] we can use the k_i^{app} and k_{-i} values, determined with TMPCl, to calculate the sequence of events for a growing polymer chain. Using [IB] = 1.0 mol L^{-1}, the following time intervals (τ) between two consecutive events have been calculated for −90 °C in CH_3Cl.

$$\tau_{-i} = 1/k_{-i} = 2.7 \times 10^{-6}\ \text{s} = 2.7\ \mu\text{s}$$

$$\tau_p = 1/k_p[\text{IB}] = 5 \times 10^{-10}\ \text{s} = 0.5\ \text{ns}$$

The lifetime of active cationic ends is very short, only 2.7 μs before deactivation takes place. Propagation is 5500 times faster than deactivation, however (monomer incorporates on average every 0.5 ns), and 5500 monomer units are added during the active cycle. The deactivated chain's hypothetical lifetime before reionization (if it remained in solution) would be $\tau_i = 1/k_i^{app}[EtAlCl_2]^2 = 48$ s, more than enough for polymer precipitation. This mechanism of chain breaking would yield PIB with $M_n = 310\,000$ g/mol, in excellent agreement with experimental findings. It is also obvious from Table 2 that molecular weight control is lost although TMPCl has been found to be an efficient initiator in Hex/CH_3Cl solvent mixture (Table 1). It is important to recognize, however, that molecular weight control below that determined by the $k_p[M]/k_{-i}$ ratio, i.e., monomer incorporated in one activation/deactivation cycle, is not possible even in living solution polymerization. Initiation efficiencies are close to 100% in Table 1 because an average chain undergoes many activation/deactivation cycles.

It is interesting to compare our results with those reported by Kennedy and Milliman[15] for the polymerization of IB initiated by adventitious moisture/$EtAlCl_2$ in CH_3Cl in the temperature range of −30 to −100 °C. The viscosity-average molecular weights were strongly affected by temperature. The Arrhenius-type log(viscosity average molecular weight) vs $1/T$ plot was linear down to about −90 °C and gave a composite activation energy of ~6.6 kcal mol^{-1} for the degree of polymerization.[15] If, as we suggest, deactivation determines the molecular weights, the log(molecular weight) vs $1/T$ plot should give the activation energy difference between propagation and ion collapse. Although diffusion-limited reactions do not have an enthalpic barrier, their observed activation energy will not be zero but will be determined by the temperature dependence of the diffusion coefficients, which is related to the viscosity. The "activation energy" for the flow to occur is usually small, typically about 2 kcal/mol. The activation energy for ion collapse with *t*-BuCl is 9.1 kcal mol^{-1} (Table 7). This value is similar to the value of 11.2 kcal mol^{-1} that we obtained for the activation energy for ion collapse in the living polymerization of IB with $TiCl_4$ in CH_3Cl by extrapolation of the values determined for hexanes/CH_3Cl mixtures[2] to 100% CH_3Cl. We have not calculated a value for TMPCl since k_{-i} could be determined only at two temperatures; however, these two points are parallel to the Arrhenius plot with *t*-BuCl suggesting similar ~9 kcal mol^{-1} activation energy for ion collapse. Thus, the overall activation energy is ~7 kcal mol^{-1}, in good agreement with that found experimentally by Kennedy and Milliman.

Conclusions

Kinetic and thermodynamic parameters of the ionization−ion collapse of HCl, *t*-BuCl, and TMPCl in conjunction with $EtAlCl_2$ in CH_3Cl and CH_2Cl_2 at −60 to −90 °C could be determined by following the kinetics of the capping reaction of the formed cations with DTE. As expected, the rate and equilibrium constant of ionization increased in the HCl < *t*-BuCl < TMPCl order. Both the rate of ionization and the rate of ion collapse increased with increasing temperature; however, because of the higher increase in k_{-i}, the apparent equilibrium constant of ionization increased with decreasing temperature. On the basis of the kinetic results, we proposed a new mechanism for the precipitation polymerization of IB (in CH_3Cl or CH_2Cl_2). This mechanism involves slow ionization followed by diffusion-limited propagation until ion collapse and polymer precipitation. Thus, the well-recognized fact that low temperature is necessary to obtain high molecular weights is attributed to a decrease in the rate of ion collapse (and not chain transfer to monomer) with decreasing temperature. Whether this proposal is valid for many co-initiators remains to be seen. It is almost certain, however, that the same mechanism operates with $(CH_3)_2AlCl$, CH_3AlCl_2, BCl_3, and $TiCl_4$, since chain transfer to monomer is negligible with these Lewis acids. The macromolecular engineer thus may be able to design new initiator/co-initiator systems, which could yield high molecular weights at elevated temperatures when ion collapse is slow. Some new initiating systems based on weakly coordinating anions have already been developed[16−19] that produce high molecular weight PIBs, similar to that obtained by γ-rays, at moderately low temperatures mostly in solution polymerizations. However, the explanation as to why the molecular weights are higher than those obtained with conventional Lewis acid invokes a reduced rate of chain transfer to monomer. Indeed, at the elevated temperatures investigated chain transfer may be the molecular weight controlling event. Other simpler and more efficient initiating systems should hold great promise for commercial development.

We must emphasize that the results of the present work cannot be extended for the synthesis of butyl rubber. Determining the rate constants of the copolymerization of IB and isoprene and the effect of temperature still remains a challenging task that we plan to undertake in the future.

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References and Notes

(1) Vairon, J.-P.; Spassky, N. In *Cationic Polymerizations: Mechanisms, Synthesis, and Applications*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996; pp 690−698.

(2) Schlaad, H.; Kwon, Y.; Sipos, L.; Faust, R.; Charleux, B. *Macromolecules* **2000**, *33*, 8225−8232.

(3) Sipos, L.; De, P.; Faust, R. *Macromolecules* **2003**, *36*, 8282−8290.

(4) Kennedy, J. P.; Squires, R. G. *Polymer* **1965**, *6*, 579.

(5) Fodor, Zs.; Faust, R. *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 305−324.

(6) Hadjikyriacou, S.; Faust, R. *Macromolecules* **1996**, *29*, 5261−5267.

(7) Matyjaszewski, K.; Sawamoto, M. In *Cationic Polymerizations: Mechanisms, Synthesis, and Applications*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996; pp 265−380.

(8) Faust, R. Presented at the International Symposium on Ionic Polymerization, Boston, 2003. Hadjikyriacou, S.; Acar, M.; Faust, R. *Macromolecules* **2004**, *37*, 7543−7547.

(9) Sauvet, G.; Vairon, J.-P.; Sigwalt, P. *J. Polym. Sci., Polym. Symp.* **1975**, *52*, 173−187.

(10) Takarabe, K.; Kunitake, T. *Polym. J.* **1980**, *12*, 239−244.

(11) Schlaad, H.; Kwon, Y.; Faust, R.; Mayr, H. *Macromolecules* **2000**, *33*, 743−747.

(12) Haraguchi, H.; Fujiwara, S. *J. Phys. Chem.* **1969**, *73*, 3467−3473. (b) Trazona, A.; Koglin, E.; Buda, F.; Coussens, B.; Renkema, J.; Van Heel, S.; Meier, R. *J. Phys. Chem. B* **1997**, *101*, 4370−4378. (c) Bahadur, M.; Shaffer, T.; Ashbaugh, J. *Macromolecules* **2000**, *33*, 9548−9552.

(13) Storey, R.; Donnalley, A. *Macromolecules* **1999**, *32*, 7003−7011.

(14) Brown, H.; Berneis, H. *J. Am. Chem. Soc.* **1953**, *75*, 10−14.
(15) Kennedy, J.; Milliman, G. *Adv. Chem. Ser.* **1969**, *91*, 287−305.
(16) Shaffer, T. D.; Ashbaugh, J. R. *J. Polym. Sci., Polym. Chem.* **1997**, *35*, 329−344.
(17) Pi, Z.; Jacob, S.; Kennedy, J. P. In *Ionic Polymerizations and Related Processes*; Puskas, J. E., Ed.; Kluwer: Dordrecht, 1999; pp 1−12.
(18) Kumar, K. R.; Hall, C.; Penciu, A.; Drewitt, M. J.; Mcinenly, P. J.; Baird, M. C. *J. Polym. Sci., Polym. Chem.* **2002**, *40*, 3302−3311.
(19) Carr, A. G.; Dawson, D. M.; Bochmann, M. *Macromolecules* **1998**, *31*, 2035−2040.

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