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Living Cationic Homopolymerization of Isobutyl Vinyl Ether and Sequential Block Copolymerization of Isobutylene with Isobutyl Vinyl Ether. Synthesis and Mechanistic Studies

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ABSTRACT: The living polymerization of isobutyl vinyl ether (IBVE) and sequential block copolymerization of isobutylene (IB) with IBVE have been achieved using $TiCl_4$ coinitiator in methyl chloride/hexanes solvent mixtures in the −80 to −40 °C temperature range. Poly(IB-*b*-IBVE) with ~100% blocking efficiency has been synthesized for the first time. Close to 100% initiator efficiencies as well as 100% crossover efficiencies were obtained with 2,4,4-trimethyl-2-chloro-pentane (TMPCl) and PIBCl, respectively. The procedure involved capping with 1,1-diphenylethylene, followed by the addition of nBu_4NCl to reduce the concentration of free, uncomplexed $TiCl_4$ to $[TiCl_4]_{free} <$ [chain end] before the addition of IBVE. Mechanistic studies indicated that the presence of common ion salt is not necessary, and that living polymerization of IBVE and sequential block copolymerization of IB with IBVE can also be accomplished in its absence when $[TiCl_4] <$ [chain end]. It is proposed that under these conditions the gegenion is $TiCl_5^-$, a much stronger nucleophile compared to the $Ti_2Cl_9^-$ dimeric gegenion which dominates at $[TiCl_4]_{free}$/[chain end] ≥ 2.

Introduction

Living polymerization is a most valuable technique in polymer synthesis. In addition to the controlled and uniform size of the polymers, living polymerizations provide the simplest and most convenient method for the preparation of block copolymers by sequential monomer addition. The first example of living carbocationic polymerization, the polymerization of isobutyl vinyl ether (IBVE) with an equimolar mixture of hydrogen iodide and iodine (HI/I_2) in *n*-hexane at −15 °C was discovered in 1984.[1] Since then the scope has been rapidly expanded to different vinyl ethers, propenyl ethers and other cationically highly reactive monomers, such as *N*-vinylcarbazole and *p*-methoxystyrene, and to other initiating systems based on weak Lewis acids such as zinc halides.[2] The key to these living polymerizations is the high stability of the growing end where the nucleophilic counteranion strongly interacts with the cationic active site. Living polymerizations with stronger Lewis acids forming nonnucleophilic counteranions have also been reported, but only in the presence of added Lewis bases or in the presence of common ion salts.[3] Lewis bases are considered to nucleophilically stabilize the growing carbocations, while common ion salts are presumed to suppress the ionic dissociation to free ions that is believed to yield nonliving polymerization.[3]

The living polymerization of vinyl ethers has also been achieved by the combination HI/R_4NX where X is ClO_4^-, NO_3^-, BF_4^-,[4] or Cl^-.[5] The livingness was suggested to be the result of fast exchange of the chain end iodine with the anion of the salt. Similarly, the living polymerization of IBVE was reported by the MeCH(OiBu)Cl/$nBu_4N^+TiCl_5^-$ initiating system at −20 °C in CH_2Cl_2.[6] The mechanism of the polymerization was not investigated, although it was speculated that a salt effect or a possible Lewis acid activity of the salt is responsible for the polymerization.

While weak Lewis acids such as Zn halides may be necessary to effect living polymerization of the more reactive vinyl ethers, they are ineffective to induce polymerization of less reactive monomers such as isobutylene (IB) and styrene (St). Importantly, the living polymerization of IBVE was also reported by the MeCH(OiBu)Cl/$TiCl_4$ initiating system in the presence of electron donors at very low temperatures.[7] At higher temperatures, degradation by dealcoholation prevented living polymerization. Since $TiCl_4$ also induces the living polymerization of IB, attempts have been made to synthesize PIB-PIBVE diblock copolymers.[7] However, very low (<20%) blocking efficiencies were reported, due to the unfavorable crossover from a less reactive IB to a much more reactive IBVE. Efficient crossover may be obtained when the reactivities of the two monomers are similar or when crossing from the more reactive monomer to the less reactive one. It is difficult to attain, however, when the crossover is from the less reactive to the more reactive monomer. Thus, while the synthesis of poly(methyl vinyl ether-*b*-styrene) (PMeVE-*b*-PSt) block copolymer has been accomplished[8] that of PSt-*b*-PMeVE was unsuccessful due to unfavorable crossover rate relative to the homopolymerization rate of MeVE. However, using similar procedures, well-defined PIBVE-*b*-PSt block copolymers could not be obtained due to a very large difference in reactivity between IBVE and St (IBVE ≫ St).[8]

We recently developed a novel scheme for the synthesis of block copolymers by living carbocationic sequential block copolymerization when the second monomer is more reactive than the first one.[9,10] It involves capping with a highly reactive but nonpolymerizable monomer such as 1,1-diphenylethylene (DPE). This is followed by tailoring the Lewis acidity to the reactivity of the second monomer. The Lewis acidity modulation was accomplished by the addition of titanium alkoxides, or by replacing the Lewis acid with a weaker one in the synthesis of PIB-*b*-PpMeSt[9] and PIB-*b*-PαMeSt[11] diblock or PpMeSt-*b*-PIB-*b*-PpMeSt[12] and PαMeSt-*b*-PIB-*b*-PαMeSt triblock[13] copolymers. The success of the methods was demonstrated by ~100% crossover ef-

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ficiencies as well as by the excellent mechanical properties of the triblock copolymer thermoplastic elastomers.

In the present paper we report on results of block copolymerization of IB with IBVE by sequential monomer addition using our novel synthetic stragegy.

Experimental Section

Materials. 1,1-Diphenylethylene (DPE) and 2,6-di-*tert*-butylpyridine (DTBP) were used as received from Aldrich. Isobutyl vinyl ether (IBVE) (99%, Aldrich) was purified by washing it 5 times with 10% aqueous KOH solution. It was dried over KOH pellets overnight, filtered, and distilled twice over CaH_2. The purified IBVE was stored at −20 °C under nitrogen. Tetrabutylammonium chloride (nBu_4NCl) (99% Aldrich) was rendered anhydrous by storing its CH_2Cl_2 solution over CaH_2 for several days with occasional stirring. It was filtered under nitrogen, and the solvent was evaporated under vacuum. The dried nBu_4NCl was stored under nitrogen. CH_2Cl_2 was purified by washing it with distilled water until neutral and drying over $MgSO_4$ overnight. It was refluxed for 24 h and distilled twice over P_2O_5, the second time just before use.

2,2,4,4-Tetramethyl-6,6-diphenyl-6-chlorohexane (TMDHCl) was synthesized according to the following representative procedure: 2,4,4-trimethyl-2-chloropentane (TMPCl) (1.3×10^{-3} mol in 20 mL of MeCl/Hex 40/60 v/v solvent mixture) was capped with DPE (1.8×10^{-3} mol in the presence of $TiCl_4$ (2.4×10^{-3} mol) at −80 °C. After capping, nBu_4NCl (1.45×10^{-3} mol) dissolved in 10 mL of CH_2Cl_2 was added under stirring and allowed to react for 40 min. A slightly higher than stoichiometric ($nBu_4NCl = 0.5TiCl_4$) amount of nBu_4NCl was used to ensure that all $TiCl_4$ and nBu_4NCl is complexed either as $nBu_4N^{+}Ti_2Cl_9^{-}$ or $nBu_4N^{+}TiCl_5^{-}$. Upon addition of nBu_4NCl the orange color of the diphenyl carbenium ion disappeared. The mixture was poured into 170 mL of hexanes (Hex) at −80 °C to ensure complete precipitation of the inorganic complex salt. After 1 h the precipitate was removed by vacuum filtration. The filtrate was clear and colorless indicating the absence of $TiCl_4$. Since TMDHCl is unstable at room temperature,[14] this solution was kept at −80 °C and used without isolating TMDHCl.

$nBu_4N^{+}Ti_2Cl_9^{-}$ was synthesized by reacting 2 equiv of $TiCl_4$ and 1 equiv of nBu_4NCl in methyl chloride (MeCl) for 40 min at the polymerization temperature before the required volume was delivered.

The synthesis and purification of MeCH(OiBu)Cl[6] and all other materials have been described.[15]

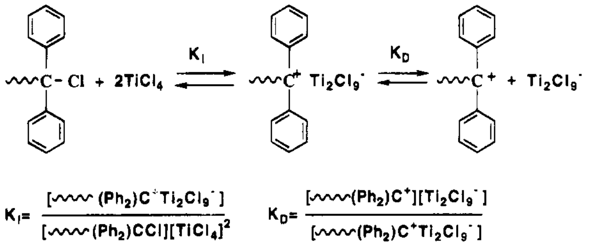
Procedures. Polymerizations were carried out in a stainless steel glove box[15] using MeCl/Hex solvent mixtures.

The homopolymerizations of IBVE was initiated by TMDHCl (see Materials) or by first capping TMPCl with DPE,[15] followed by the addition of nBu_4NCl dissolved in MeCl. After 40 min the monomer IBVE was added. In the diblock preparation, IB was first polymerized followed by capping with DPE. The polymerization and capping reaction was carried out in a MeCl/Hex (40/60 v/v solvent mixture (10 mL) at −80 °C. On the basis of a large body of published[16] and unpublished kinetic data the capping time was determined to yield ~100% capping. UV and ^1H NMR analysis of representative samples taken after capping indicated that capping is indeed ~100%. The capping was followed by the introduction of nBu_4NCl solution in MeCl and IBVE. The total volume of the polymerization system was 20 mL. When larger volumes were used, the reactions were carried out in a round bottom flask, and samples were withdrawn using a precooled pipet.

All reactions were quenched with prechilled methanol and the reaction mixtures were poured into excess 10% ammonical methanol. The polymers were purified by repeated precipitation into methanol.

The solubility of the common ion salt $nBu_4N^{+}Ti_2Cl_9^{-}$ ($[nBu_4N^{+}Ti_2Cl_9^{-}] = 6.21 \times 10^{-3}$ M) was tested in several mixtures of Hex/MeCl (60/40, 50/50, 40/60), v/v at −80 °C. Upon the introduction of nBu_4NCl to a $TiCl_4$ solution in Hex/MeCl 60/40 v/v immediate precipitation occurred. The characteristic yellow-green color of the common ion salt was absent. This indicated low solubility in the Hex/MeCl 60/40 v/v mixture. In Hex/MeCl 50/50 v/v, a green-yellow color developed immediately accompanied by a small amount of precipitate. Precipitation was not observed in the Hex/MeCl 40/60 v/v solvent mixture during 3 h of inspection.

Scheme 1



Conductivity measurements were carried out using a YSI Model 35 conductance meter equipped with a cell of 1 mho cm^{-1} cell constant and a BBC Goertz Metrawatt SE120 plotter.

Molecular weights were measured using a Waters HPLC system equipped with Model 510 HPLC pump, Model 410 differential refractometer, Model 486 tunable UV/vis detector, on-line MultiAngle Laser Light Scattering (MALLS) detector (MiniDawn, Wyatt Technology Inc.), Model 712 sample processor, and five ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. The flow rate of THF was 1.0 mL/min. For data acquisition (RI and UV) and computing, using a calibration curve obtained by PSt standards (Polysciences Inc.), a Waters Baseline chromatography workstation was used. The detector signals (RI, UV, and LS) were simultaneously recorded on a MacIntosh computer for absolute molecular weight and molecular weight distribution determination by the laser light scattering detector using the ASTRette software. Refractive index increments (d*n*/d*c*) were measured by a laser interferometer (Optilab, Wyatt Technology Inc.). Interestingly, the M_ns obtained by the MALLS detector were in good agreement with M_ns calculated based on a linear calibration curve obtained using polystyrene standards. The crossover efficiency was determined by mathematical resolution (Peakfit by Jandel Scientific) of the GPC RI traces using exponential Gaussian distribution. NMR spectroscopy was carried out on a Bruker 270 MHz instrument.

Results and Discussion

Experimentation started by using the conditions found successful for the living homopolymerization of IBVE using $TiCl_4$ as coinitiator.[7] Thus IB was polymerized by the TMPCl/$TiCl_4$ initiating system in Hex/MeCl 60/40 v/v at −90 °C. When the polymerization of IB was complete, the chain ends were converted to the diphenyl carbenium ions by capping with DPE. Finally, IBVE was introduced. The GPC traces of the product, however, were bimodal, and the presence of large amount of unreacted homoPIB indicated low crossover efficiency (~10%).

This result demonstrated that in the presence of large excess of $TiCl_4$, the propagation rate is much higher than the rate of initiation. According to earlier kinetical and mechanistic studies,[16] complete ionization of the DPE-capped chain ends is reached upon the addition of 2 equiv of $TiCl_4$ (Scheme 1).

Thus a $[TiCl_4]/[\text{chain end}] > 2$ ratio is not preferred to achieve high crossover efficiency, since the excess $TiCl_4$ may only increase the rate of IBVE polymerization while the rate of initiation is not affected. The polymerization of IB and the subsequent capping reaction can be accomplished with $[TiCl_4]/[TMPCl] = 2$ for low molecular weight PIBs when the chain end concentration is high. Alternatively, the effective $TiCl_4$ concentration can be decreased prior to the addition of IBVE by the addition of nBu_4NCl.

Table 1. Polymerization of IBVE in Hex/MeCl at −80 °C[a]

Hex/MeCl, v/v	$nBu_4N^+Ti_2Cl_9^-$, M	$TiCl_{4\,free}$/TMPCl	conversion, %	M_w/M_n	I_{eff}, %
60/40	7×10^{-3}	2	100	5.0	60
40/60	2.6×10^{-3}	2	100	5.3	58
	5.2×10^{-3}	2	100	5.9	71
	2.6×10^{-3}	1	100	1.7	59
	5.2×10^{-3}	0	2[b]		
30/70	4.5×10^{-3}	1	100	1.3	86
	5.6×10^{-3}	0.3	6[c]		
	3×10^{-3}	0	75[c]	1.1	90

[a] [TMPCl] = 5.2×10^{-3} M; [DPE] = 6.5×10^{-3} M; [$TiCl_4$] = 1.04×10^{-2} M; [DTBP] = 5.0×10^{-3} M; [IBVE] = 0.52 M. [b] In 3 h. [c] In 4 h.

The latter approach was used in the next set of experiments carried out using DPE capped TMPCl. On the basis of our earlier reports, which indicated that $TiCl_4$ forms dimers and dimeric gegenions under the polymerization conditions,[16-18] a 1:2 stoichiometry was assumed (and subsequently proved; see in Mechanistic Studies) for the reaction of nBu_4NCl with $TiCl_4$. Since the structure of TMPCl mimics the chain end of PIB, the initiator efficiency (I_{eff} % = 100 × $M_{n\ \mathrm{theoretical}}/M_{n\ \mathrm{observed}}$), which can be easily measured, was used to predict crossover efficiency. The results are summarized in Table 1.

The polymerizations were very fast at $[TiCl_4]_{free}/[TMPCl] > 1$ ($[TiCl_4]_{free} = [TiCl_4]_{total} - 2[nBu_4NCl]$) and complete conversions were reached in less than 5 min in all three solvent mixtures. The products exhibited broad molecular weight distributions, and the I_{eff}s were lower than 100%. According to tests described in the Experimental Section, the solubility of the common ion salt is very low in Hex/MeCl 60/40 v/v solvent mixture at −80 °C. Interestingly, however, the beneficial effect of the common ion salt was not observed even when the experiments were carried out in Hex/MeCl 40/60 v/v, where precipitation was absent. The polymerizations were also fast with $[TiCl_4]_{free}/[TMPCl] = 1$ in Hex/MeCl 40/60 as well as in 30/70 v/v mixtures, and similarly low I_{eff}s were obtained. However, the molecular weight distributions were relatively narrow. Only traces of polymer were obtained even after 3 h with $[TiCl_4]_{free}/[TMPCl] = 0-0.3$ when the concentration of common ion salt was low. When high concentration of common ion salt was used at $[TiCl_4]_{free}/[TMPCl] = 0$, although the polymerization was very slow (75% conversion in 4 h), polymers with narrow molecular weight distribution ($M_w/M_n = 1.1$) and close to 100% I_{eff} were obtained.

Further kinetic experiments were carried out with the $[TiCl_4]_{free} = 0$ system at −40, −60, and −80 °C to determine the livingness of the polymerization. The M_n vs conversion plots, shown in Figure 1 for all three temperatures, are linear, indicating the absence of chain transfer to monomer. The observed M_ns are somewhat higher than the theoretical values (I_{eff} ~80%). The molecular weight distributions are narrow and decrease to $M_w/M_n = 1.05$ at 100% conversion. Furthermore the linear first-order plots (Figure 2) prove that the concentration of growing centers remains constant. Thus, termination is also absent, i.e., the polymerization is living. The identical polymerization rates at −40 °C and at −60 °C suggest that the decreased polymerization rate at −80 °C is due to the lower common ion concentration rather than the result of the lower temperature. The identical polymerization rates at different temperatures also suggest that the active center concentration ($[M_n^+]$) decreases with increasing temperature (a common phenomena in cationic polymerization) and cancels the increase in the propagating rate constant k_p.

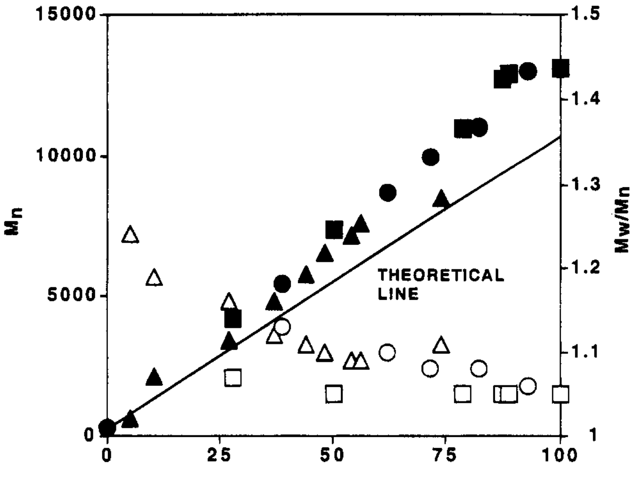


Figure 1. The M_n (filled symbols) and M_w/M_n (open symbols) versus conversion plot for the polymerization of IBVE in Hex/MeCl 30/70 v/v at $[TiCl_4]_{free} = 0$. [TMPCl] = 1.32×10^{-2} M. [DPE] = 1.6×10^{-2} M; [DTBP] = 5.0×10^{-3} M; [IBVE] = 1.30 M. (■, □) −40 °C; [$TiCl_4$] = 1.25×10^{-1} M; [nBu_4NCl] = 7.0×10^{-2} M. (●, ○) −60 °C; [$TiCl_4$] = 1.25×10^{-1} M; [nBu_4NCl] = 7.0×10^{-2} M. (▲, △) −80 °C; [$TiCl_4$] = 5.2×10^{-2} M; [nBu_4NCl] = 2.9×10^{-2} M.

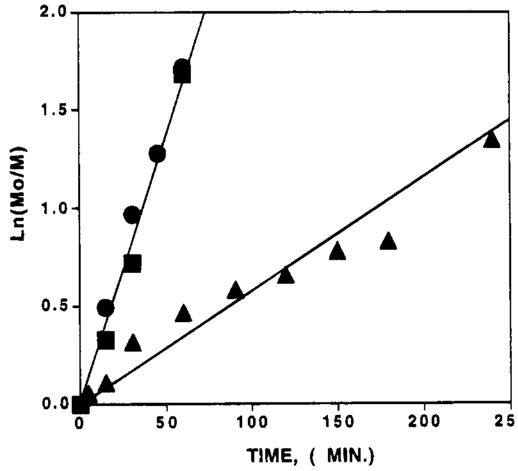


Figure 2. First-order plots, for the polymerization of IBVE in Hex/MeCl 30/70 v/v at $[TiCl_4]_{free} = 0$. [TMPCl] = 1.32×10^{-2} M; [DPE] = 1.6×10^{-2} M; [DTBP] = 5.0×10^{-3} M; [IBVE] = 1.30 M. (■) −40 °C; [$TiCl_4$] = 1.25×10^{-1} M; [nBu_4NCl] = 7.0×10^{-2} M. (●) −60 °C; [$TiCl_4$] = 1.25×10^{-1} M; [nBu_4NCl] = 7.0×10^{-2} M. (▲) −80 °C; [$TiCl_4$] = 5.2×10^{-2} M; [nBu_4NCl] = 2.9×10^{-2} M.

Although when low $[nBu_4N^+Ti_2Cl_9^-]$ was used the polymerization was extremely slow at −80 °C (see Table 1), by increasing the temperature to −40 °C the polymerization rate increased about 20 fold. The M_n vs conversion plot and the first order plot for polymerizations carried out at −40 °C, in Hex/MeCl 50/50 v/v are shown in Figures 3 and 4, respectively. The observed M_ns are close the theoretical values indicating close to 100% I_{eff}. It should be noted that this experiment was carried out using preformed TMDHCl and common ion salt $nBu_4N^+Ti_2Cl_9^-$. These form in situ when TMPCl is capped with DPE followed by the addition of nBu_4NCl at $[TiCl_4]_{total}/[nBu_4NCl] = 2$. This is corroborated by our visual observation that upon addition of nBu_4-

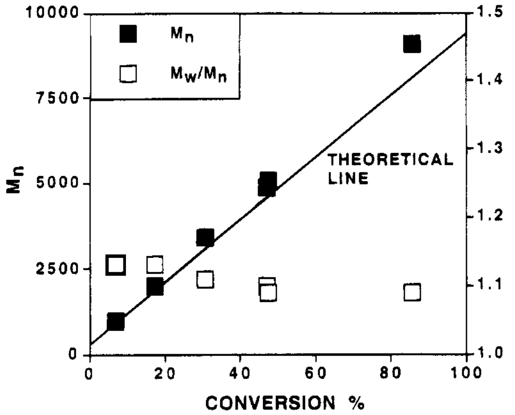


Figure 3. The M_n (■) and M_w/M_n (□) versus conversion plot for the polymerization of IBVE in Hex/MeCl 50/50 v/v at −40 °C. [TMDHCl] = 3.11 × 10^{-3} M; [DTBP] = 5.3 × 10^{-3} M; [$nBu_4N^+Ti_2Cl_9^-$] = 2.9 × 10^{-3} M; [IBVE] = 0.275 M.

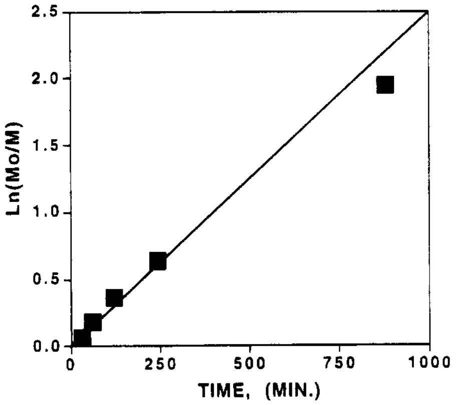


Figure 4. First-order plot for the polymerization of IBVE in Hex/MeCl 50/50 v/v at −40 °C. [TMDHCl] = 3.11 × 10^{-3} M; [DTBP] = 5.3 × 10^{-3} M; [$nBu_4N^+Ti_2Cl_9^-$] = 2.9 × 10^{-3} M; [IBVE] = 0.275 M.

NCl the orange color of the diphenyl carbenium ion disappeared and the characteristic yellow-green color of the common ion salt appeared. This indicates that the ionization equilibrium of Scheme 1 is shifted to the left to TMDHCl. Therefore we consider the two type of experiments equivalent.

Subsequently, a block copolymerization experiment was carried out by sequential monomer addition at −80 °C using [nBu_4NCl] = 6.3 × 10^{-2}M, in Hex/MeCl 30/70 v/v. PIB-*b*-PIBVE with 5000 PIB and 9000 PIBVE segment molecular weights was planned. Contrary to the results of homopolymerization however, the block copolymerization of IBVE was very slow, and negligible IBVE conversion was obtained in 3 h. Similar phenomenon, slow block copolymerizations when the corresponding homopolymerization suggested higher rates has been reported before[19] and also observed by us. It was suggested that a slow diffusion through the PIB coil lowers the propagation rate of the second monomer. Alternately, a decrease of chain end ionization and/or lower local monomer concentration due to specific solvation may also be responsible for the lower rates.

To increase the rates, we decided to study polymerizations at [$TiCl_4$]$_{free}$ > 0. TMPCl was capped with DPE followed by the addition of precalculated amount of nBu_4NCl to reach the desired [$TiCl_4$]$_{total}$/[nBu_4NCl] > 2 ratio. Kinetic experiments have been carried out at −80 °C with the [$TiCl_4$]$_{free}$/[TMPCl] = 1 and at −40 °C with the [$TiCl_4$]$_{free}$/[TMPCl] = 0.38 ratios. According to the linear M_n vs conversion (Figure 5) and ln([M]$_o$/[M]) vs. time plots (Figure 6), living polymerizations have been achieved. Close to theoretical M_ns were obtained at −80 °C, while they are somewhat higher at −40 °C. A comparison with results obtained at −80 °C with a similar [$TiCl_4$]$_{free}$/[TMPCl] = 0.3 ratio illustrates that the rate of the polymerization can be increased by increasing the temperature or the [$TiCl_4$]$_{free}$/[TMPCl] ratio.

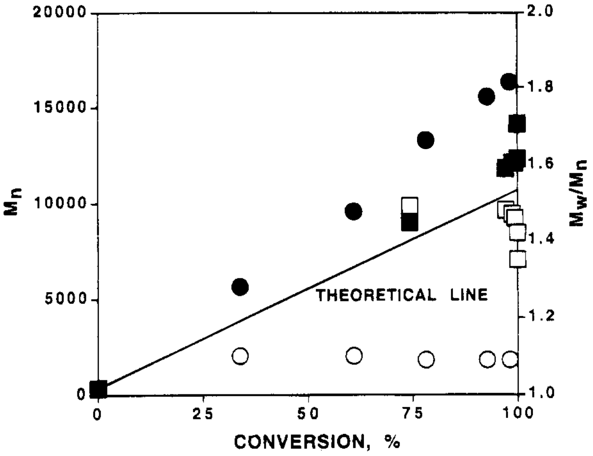


Figure 5. The M_n (filled symbols) and M_w/M_n (open symbols) versus conversion plot for the polymerization of IBVE in Hex/MeCl 30/70 v/v. [TMPCl] = 3.0 × 10^{-3} M; [DTBP] = 6.0 × 10^{-3} M; [IBVE] = 3.0 × 10^{-1} M. (■, □) [$TiCl_4$]$_{free}$/[TMPCl] = 1.0; [$nBu_4N^+Ti_2Cl_9^-$] = 4.5 × 10^{-3} M; T = −80 °C. (●, ○) [$TiCl_4$]$_{free}$/[TMPCl] = 0.38; [$nBu_4N^+Ti_2Cl_9^-$] = 5.4 × 10^{-3} M; T = −40 °C.

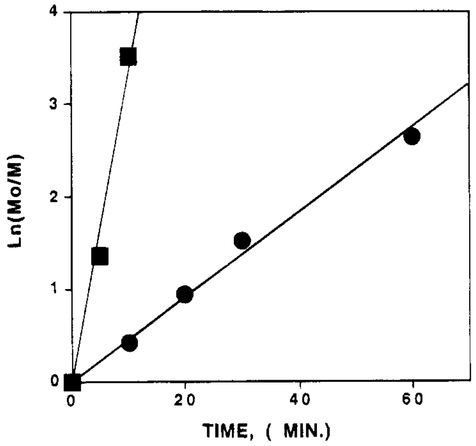


Figure 6. First-order plot for the polymerization of IBVE in Hex/MeCl 30/70 v/v. (■) [$TiCl_4$]$_{free}$/[TMPCl] = 1.0. (●) [$TiCl_4$]$_{free}$/[TMPCl] = 0.38. Other conditions described in the legend of Figure 5.

In Figure 7, the GPC chromatogram of a diblock prepared at −40 °C is shown. The ~66% crossover efficiency was similar to the I_{free}s obtained in the homopolymerizations. In Figure 8 the GPC chromatogram of a diblock prepared at −80 °C is shown. In agreement with the close to 100% I_{eff}s obtained in homopolymerizations >90% crossover efficiency was obtained. In Figure 9 the M_n of the diblock copolymer is plotted against the weight of the copolymer. In Figure 10 the ^1H NMR spectrum of the diblock is shown along with the assignments.

Mechanistic Studies

The activity of an initiating system and the livingness of the polymerization is greatly affected by the nature and strength of the Friedel−Crafts acid. Recent successes are based on efforts to match the reactivity of

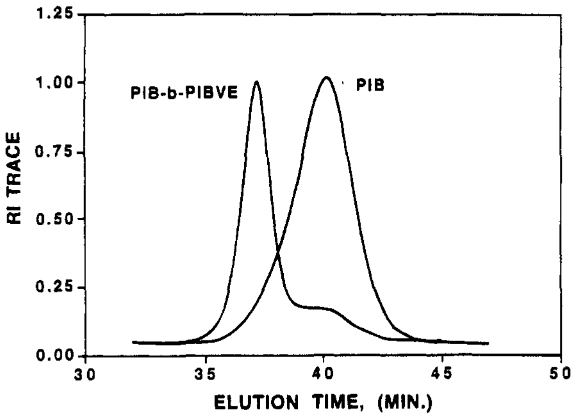


Figure 7. GPC chromatogram of the starting PIB and the PIB-*b*-PIBVE diblock copolymer obtained at −40 °C at $[TiCl_4]_{free}$/[TMPCl] = 0.38; 85.1% diblock; 14.9% PIB starting homopolymer. Blocking efficiency ~ 66%. Isobutylene polymerization and capping: [TMPCl] = 6.0 × 10^{-3} M; [DPE] = 8.6 × 10^{-3} M; [DTBP] = 1.2 × 10^{-2} M; $[TiCl_4]$ = 2.4 × 10^{-2} M; [IB] = 0.6 M; solvent mixture Hex/MeCl 60/40 v/v, T = −80 °C, volume = 10 mL. Isobutyl vinyl ether polymerization: $[TiCl_4]$ = 1.2 × 10^{-2} M; [DTBP] = 6.1 × 10^{-3} M; [IBVE] = 0.29 M, $[nBu_4NCl]$ = 5.4 × 10^{-3} M; [IBVE] = 0.29 M; solvent mixture Hex/MeCl 30/70 v/v; total volume = 20 mL; M_{nPIB} = 7300; M_w/M_n = 1.38.

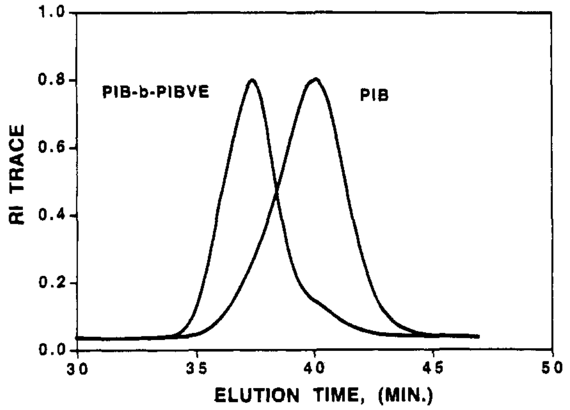


Figure 8. GPC chromatogram of the starting PIB and the PIB-*b*-PIBVE diblock copolymer obtained at −80 °C. $[TiCl_4]_{free}$/[TMPCl] = 1.0; 94.8 wt % block copolymer; 5.2 wt % PIB starting polymer. Blocking efficiency ~ 90%. Isobutylene polymerization and capping: [TMPCl] = 6.0 × 10^{-3} M, [DPE] = 8.8 × 10^{-3} M; [DTBP] = 1.2 × 10^{-2} M; $[TiCl_4]$ = 2.4 × 10^{-2} M; [IB] = 0.6 M; solvent mixture Hex/MeCl 60/40 v/v; T = −80 °C; volume = 10 mL. Isobutyl vinyl ether polymerization: $[TiCl_4]$ = 1.2 × 10^{-2} M; [DTBP] = 6.1 × 10^{-3} M; [IBVE] = 0.29 M; $[nBu_4NCl]$ = 4.5 × 10^{-3} M; [IBVE] = 0.31 M; solvent mixture Hex/MeCl 30/70 v/v; total volume = 20 mL; M_{nPIB} = 7300; M_w/M_n = 1.49; M_n(block) = 18 400; M_w/M_n = 1.42.

the monomer (i.e., the stability of the polymer cation) and the Lewis acidity of the coinitiator (i.e., the nucleophilicity of the counteranion) to obtain nondissociated growing centers. When the Lewis acid is stronger than desired, the use of a common ion salt is assumed to suppress the ionic dissociation of ion pairs to free ions and lead to living polymerization. However, when free ions are not involved in propagation, as in the polymerization of IB involving the BCl_4^- [20] or $Ti_2Cl_9^-$ [21] gegenions, rates, molecular weights, and distributions are not affected. Regrettably, the nature, activities, and concentration of the active species are unknown for most polymerizations. In our polymerization system rates, molecular weights and molecular weight distributions do not appear to be directly related to the concentration of common ion salt, and apparently are governed by the $[TiCl_4]_{free}$/[chain end] ratio. Controlled polymerization was only observed when this ratio was less than 1.

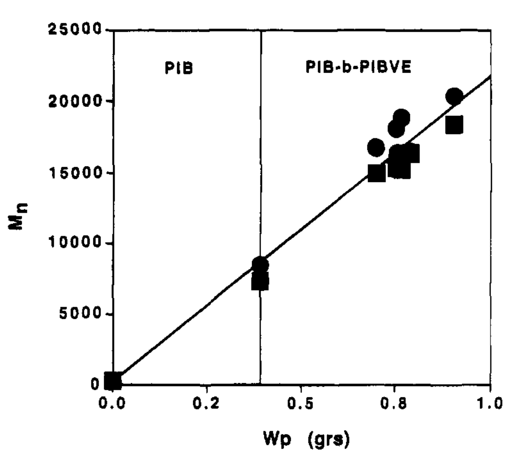


Figure 9. The linear plot of the molecular weight (M_n) versus the weight (W_p) of the obtained diblock: (●) MALLS; (■) PSt calibration. Reaction conditions provided in the legend of Figure 8.

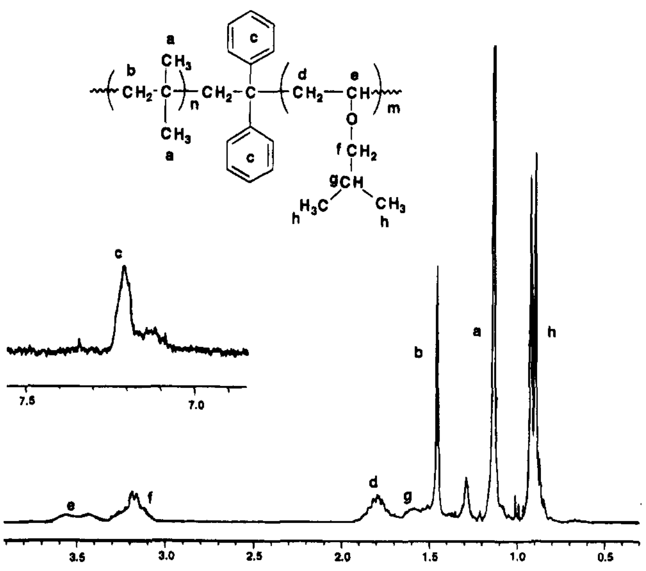


Figure 10. ^1H NMR spectrum of PIB-*b*-PIBVE copolymer, solvent 100% CD_2Cl_2.

In recent reports we suggested that $TiCl_4$ forms dimers and/or dimeric gegenions under the polymerization conditions. Raman spectroscopy of $nBu_4NCl/TiCl_4$ solutions in CH_2Cl_2 also demonstrated the exclusive formation of $Ti_2Cl_9^-$ dimeric gegenions with $[TiCl_4]/[nBu_4NCl]$ ≥ 2.[22] Importantly, with $[TiCl_4]/[nBu_4NCl]$ ≤ 1 only $TiCl_5^-$ monomeric gegenions were observed.

The same conclusion can be reached based on conductometric titration of a nBu_4NCl solution in Hex/MeCl 30/70 v/v with $TiCl_4$ at −80 °C (Figure 11). The equilibria shown in Scheme 2 were established. Since the negative charge is dispersed more effectively in the dimeric $Ti_2Cl_9^-$ gegenions, the dimeric gegenions are less nucleophilic than the monomeric $TiCl_5^-$. Therefore the ionic dissociation equilibrium with $Ti_2Cl_9^-$ is shifted to the right in comparison with the corresponding equilibrium with $TiCl_5^-$. Accordingly, further addition of $TiCl_4$, after the $[TiCl_4]/[nBu_4NCl]$ = 1 ratio has been reached, increases the conductivity further and limiting conductance is reached upon the addition of 2 equiv of $TiCl_4$. At this stage, ionization is complete and the gegenions are mostly $Ti_2Cl_9^-$, therefore further addition of $TiCl_4$ does not result in an increase in conductivity.

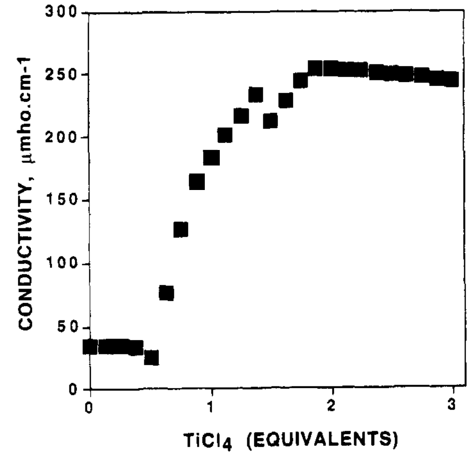
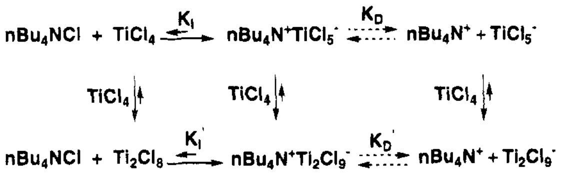


Figure 11. Conductometric titration of nBu_4NCl (4.0 mmol) with $TiCl_4$ in Hex/MeCl 30/70 v/v at −80 °C. Total volume 900 mL.

Scheme 2



Consequently, dimeric Friedel–Crafts acids are stronger acids than the monomeric counterpart. Thus, we hypothesized that the controlled polymerization is due to the presence of nucleophilic monomeric gegenions when $[TiCl_4] \leq$ [chain ends].

This is based on the assumption that the equilibrium constant of ionization of the PIBVE chain ends is high, i.e., the amount of uncomplexed $TiCl_4$ is negligible when $[TiCl_4] <$ [chain ends]. (Otherwise dimeric gegenions would still arise.) This was verified by conductometric titration of MeCH(OiBu)Cl as a model compound with $TiCl_4$ at −40 °C. According to the conductance vs the added $TiCl_4$ equivalents plot (Figure 12) the conductivity levels off after the addition of 2 equiv of $TiCl_4$. Complete ionization is reached at approximately 3 equiv of $TiCl_4$.

To test our hypothesis, three different polymerization schemes (Scheme 3) were designed to be compared. In Scheme 3A TMPCl is capped with DPE followed by the addition of nBu_4NCl to reach the $[TiCl_4]_{total}/[nBu_4NCl] = 2$ ratio, and by the addition of IBVE. Scheme 3C is similar except that preformed initiator and common ion salt are used. We have used both polymerization schemes. However, according to our hypothesis, living IBVE polymerization could also be achieved according to Scheme 3B without the use of common ion salt. Thus IBVE was polymerized by the TMDHCl/$TiCl_4$/DTBP/IBVE/Hex:MeCl, 50:50v/v/−40 °C system at $[TiCl_4] <$ [TMDHCl], without the use of nBu_4NCl. With $[TiCl_4]$/[TMDHCl] = 0.25 the polymerization was very slow and only traces of polymer were obtained in 3 h. Importantly, when the $[TiCl_4]$/[TMDHCl] ratio was increased to 0.5 the polymerization rate increased (60% conversion in 3 h) and polymers with close to theoretical M_ns and narrow molecular weight distributions ($M_w/M_n \sim 1.1$) were obtained. The M_n vs conversion (Figure 13) and $\ln([M]_0/[M])$ vs time (Figure 14) plots confirm that the polymerization is living. For comparison the $\ln([M]_0/[M])$ vs time plot obtained when the common ion salt $nBu_4N^+Ti_2Cl_9^-$ was used alone (Scheme 3C) but otherwise under identical conditions is also shown on Figure 14. Interestingly the slope of the plot is similar to that obtained with $TiCl_4$ alone indicating similar, $\sim 1.43 \times 10^{-3}$ M active center concentration.

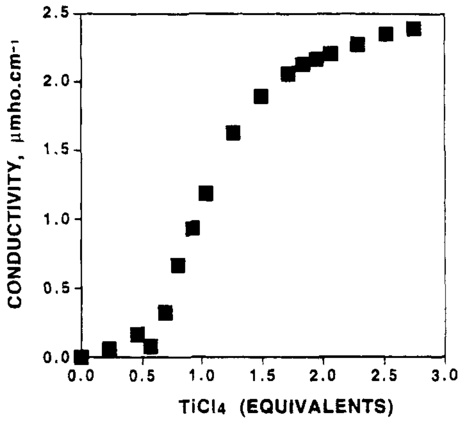
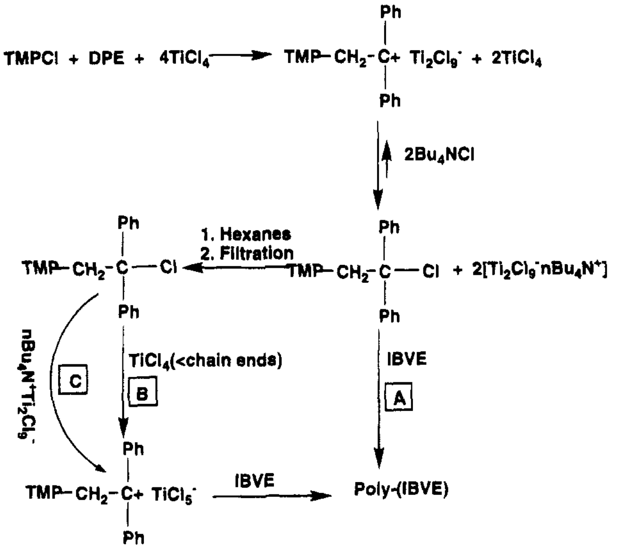


Figure 12. Conductometric titration of MeCH(OiBu)Cl (1.014 mmol) with $TiCl_4$ in Hex/MeCl 50/50 v/v at −40 °C. Total volume 900 mL.

Scheme 3



The polymerization was also carried out modifying Scheme 3B by adding $nBu_4N^+Ti_2Cl_9^-$ in equimolar amount to the initiator, after the addition of 0.5 equiv of $TiCl_4$, but otherwise under identical conditions. The linear M_n vs conversion and $\ln([M]_0/[M])$ vs time plots shown in Figures 14 and 15 verify that the polymerization remains living although the M_ns are somewhat higher than the theoretical values. Since the polymerization rates with $TiCl_4$ alone and with $nBu_4N^+Ti_2Cl_9^-$ alone were similar, a 2-fold increase in the rate would be expected based on the 2-fold increase of the active center concentration. Most importantly, the rate of the polymerization in the presence of $TiCl_4$ and common ion salt is about 9 times higher, which may indicate the presence of $Ti_2Cl_9^-$ counteranions and could account for some loss in the M_n control.

Subsequently the sequential diblock copolymerization of IB and IBVE was carried out similarly to Scheme 3B, using the $[TiCl_4]$/[chain end] = 0.5 ratio without the use of nBu_4NCl. PIB-*n*-PIBVE diblock copolymers with theoretical M_ns and narrow molecular weight distributions have been obtained. On Figure 15 the GPC traces of a PIB first segment and the final PIB-*b*-PIBVE are shown, indicating ~100% crossover efficiency.

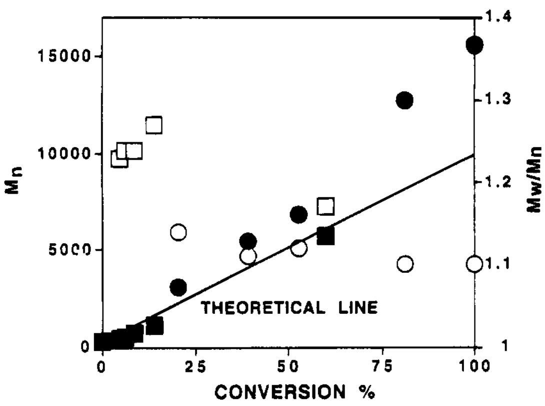


Figure 13. The M_n (filled symbols) and M_w/M_n (open symbols) versus conversion plot for the polymerization of IBVE in Hex/MeCl 50/50 v/v at −40 °C: (■, □) without common ion salt; (●, ○) with common ion salt. [$nBu_4N^+Ti_2Cl_9^-$] = 2.9×10^{-3} M; [TMDHCl] = 3.11×10^{-3} M; [DTBP] = 5.3×10^{-3} M; [$TiCl_4$] = 1.43×10^{-3} M; [IBVE] = 0.275 M.

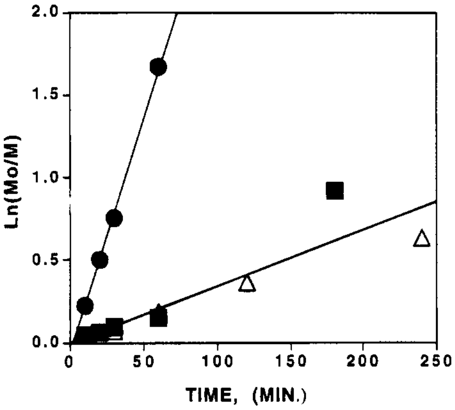


Figure 14. First-order plot for the polymerization of IBVE in Hex/MeCl 50/50 v/v at −40 °C: (●) $TiCl_4$ + $nBu_4N^+Ti_2Cl_9^-$; (■) $TiCl_4$ alone; (△) $nBu_4N^+Ti_2Cl_9^-$ alone. Reaction conditions described in the legend of Figure 13.

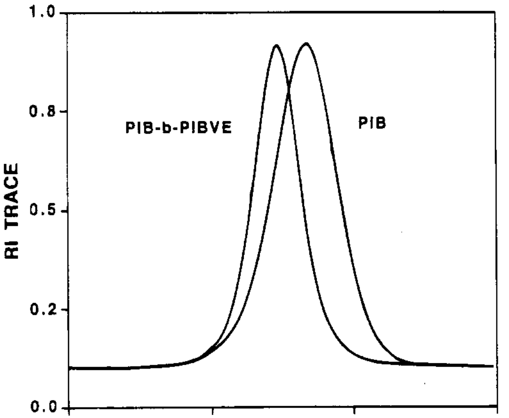
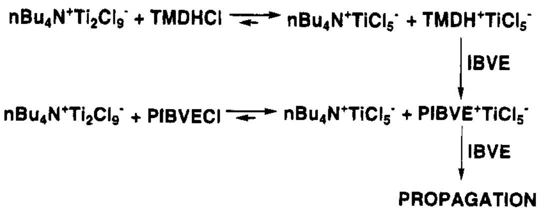


Figure 15. The synthesis of PIB-*b*-PIBVE copolymer in the absence of common ion salt. Reaction conditions: [PIB-DPE-Cl] = 2.0×10^{-3} M; [DTBP] = 5.5×10^{-3} M; [$TiCl_4$] = 1.0×10^{-3} M; [IBVE] = 0.29 M; solvent system Hex/MeCl 50/50 v/v; T = −40 °C; M_{nPIB} = 5400; M_w/M_n = 1.31; $M_{nPIB\text{-}b\text{-}PIBVE}$ = 8600; M_w/M_n = 1.19.

Conclusions

The living polymerization of IBVE and sequential block copolymerization of IB with IBVE has been accomplished using $TiCl_4$ coinitiator by capping TMPCl or PIBCl with DPE, followed by the addition of nBu_4NCl before the addition of IBVE. The amount of added nBu_4NCl relative to that of $TiCl_4$ is critical, controlled polymerization was observed only when [$TiCl_4$]$_{free}$ < [chain end]. Living polymerization was also achieved in the absence of nBu_4NCl when [$TiCl_4$] < [chain end]. Thus, we deduce that the purpose of nBu_4NCl is to reduce the effective concentration of $TiCl_4$ to [$TiCl_4$]$_{free}$ < [chain end].

Scheme 4



Conductometric titrations of nBu_4NCl and a MeCH(OiBu)Cl modeling the PIBVE chain end suggest that under these conditions the gegenion is $TiCl_5^-$. Compared to the $Ti_2Cl_9^-$ dimeric gegenion which dominates at [$TiCl_4$]$_{free}$/[chain end] ≥ 2, $TiCl_5^-$ is much more nucleophilic and the ionization and dissociation equilibrium is shifted toward the covalent chlorides and ion pairs, respectively. It is proposed that when a separately prepared common ion salt $nBu_4N^+Ti_2Cl_9^-$ is used or when nBu_4NCl is added to reach the $TiCl_4/nBu_4NCl$ = 2 ratio the polymerization of IBVE is coinitiated by monomeric $TiCl_4$ released from the common ion salt reservoir according to Scheme 4. A similar mechanism can be proposed when the $nBu_4N^+TiCl_5^-$ common ion salt is used.

The most important conclusion of the present research is that a Friedel−Crafts acid may be a weak Lewis acid when the monomeric counteranions arise, but a strong acid when it forms dimers and/or dimeric gegenions. This may explain why up until now a clear relation between Lewis acidity (determined for the monomeric Friedel−Crafts acid) and polymerization behavior could not be established with Friedel−Crafts acids forming dimers and dimeric gegenions under the polymerization conditions.

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