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Carbocationic Copolymerization in the Presence of Electron Pair Donors. 1. Copolymerization of Isobutylene and Isoprene with the Cumyl Acetate/BCl_3 Initiating System

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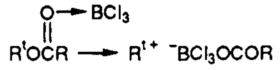
ABSTRACT: The copolymerization of the isobutylene (IB)–isoprene (IP) monomer pair by the cumyl acetate (CumOAc)/BCl_3 system has been reinvestigated, and the earlier proposition[1] in regard to the living nature of this system is questioned. In line with recent results on living carbocationic homopolymerizations initiated by *tert*-ester and -ether/MtX_n complexes, it is proposed that this copolymerization is initiated by the Cum^+ cation arising either directly by the ionization $CumOAc{\cdot}BCl_3 \rightarrow Cum^+\ {}^-OAcBCl_3$ or in two steps by the sequence $CumOAc + BCl_3 \rightarrow CumCl + BCl_2OAc$ + excess $BCl_3 \rightleftharpoons Cum^+\ {}^-BCl_4 + BCl_2OAc$. Propagation is ionic in character and termination leads to a chlorine-capped copolymer by collapse with the counteranion. Depending on the penultimate unit, reionization may occur and the chlorine-capped dormant polymers are in dynamic equilibrium with active propagating species: poly(IB–IP)–Cl + $BCl_3 \rightleftharpoons$ poly(IB–IP)$^+\ {}^-BCl_4$. The carbocation-stabilizing role of BCl_2OAc, an in situ electron pair donor, in isobutylene homopolymerizations was discussed in detail.[2] While BCl_2OAc mediates living IB homopolymerization under certain conditions, it is of insufficient nucleophilicity to yield living IB–IP copolymerization. IP invariably accumulates during copolymerization so that the earlier published reactivity ratio $r_{IP} = 4.5$[1] is in need of revision. Mechanistic considerations suggest that this complex copolymerization system cannot be described by a single pair of reactivity ratios, r_{IB} and r_{IP}.

A. Introduction

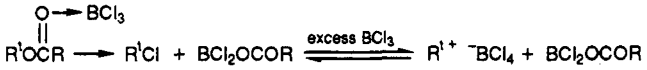
The copolymerization of isobutylene (IB) and isoprene (IP) by the cumyl acetate (CumOAc)/BCl_3 initiating system in CH_3Cl and CH_2Cl_2 diluents at −30 °C has recently been investigated[1] and was shown to exhibit living character over a limited composition (IP = 1.2–7.8 mol %) and molecular weight ($\bar{M}_n$ = 2400–12 100) range. However, the time dependence of the copolymerization was not addressed. Although the $\bar{M}_n$–weight of copolymer plot shown is linear, the individual points represent individual experiments and higher IP contents corresponded to lower molecular weights. Increasing the IP content from 11.4 to 22.1 mol % led to a molecular weight of one-fifth of the theoretical value ($\bar{M}_n$ = 1200 vs $\bar{M}_{n,theor}$ = 5500), indicating chain transfer. It was argued that the chain transfer present at 22.1 mol % IP diminishes at 11.4 mol % IP. It is more likely that chain transfer went undetected at or below 11.4 mol % IP, and the main reason seems to be the limited molecular weight range of the study. For example, at 2.1 mol % IP the measured molecular weight was 9100. With ±10% error in the molecular weight determination by GPC, chain transfer cannot be detected in the case of an apparent transfer constant of $C_{tr} = 6 \times 10^{-4}$ L/mol·s. With increasing IP content the extent of chain transfer is expected to increase. However, at the 11.4 mol % IP level the only datum given is $\bar{M}_n$ = 2400, at which $C_{tr} < 2 \times 10^{-3}$ L/mol·s cannot be detected. As was mentioned above, the higher the IP content, the lower the molecular weight in the work in question; thus chain transfer remained undetected. At higher IP contents (22.1 mol %), extensive chain transfer to monomer dominated the copolymerization and 1,4-polyisoprene (1,4-PIP) sequences underwent cyclization. While the reactivity ratio for IB, $r_{IB} = 2.4 \pm 0.35$, was found to be essentially identical to those of conventional cationic IB–IP copolymerizations,[3-6] the reactivity ratio for IP, $r_{ip} = 4.5 \pm 3.0$, was significantly larger than found in conventional systems.[6,7]

Reinvestigation of the above copolymerization system was warranted in light of the new mechanism proposed for the living polymerization of IB initiated by *tert*-ester or -ether/MtX_n (MtX_n = BCl_3 and $TiCl_4$) complexes.[2] According to this proposition the polymerization is ionic in character and initiation occurs by the ion pair arising from the complex (shown for a *tert*-ester/MtX_n complex)



$$\mathrm{R^tO\overset{\overset{O\rightarrow BCl_3}{\|}}{C}R \longrightarrow R^{t+}\ {}^{-}BCl_3OCOR}$$

or by the ion pair arising by the sequence



$$\mathrm{R^tO\overset{\overset{O\rightarrow BCl_3}{\|}}{C}R \longrightarrow R^tCl + BCl_2OCOR \xrightleftharpoons{excess\ BCl_3} R^{t+}\ {}^{-}BCl_4 + BCl_2OCOR}$$

Depending on the reaction conditions both reactions may proceed simultaneously: complexes with BCl_3 in a 1:1 molar ratio initiate polymerizations but quickly lose their initiating activity.[2] In contrast, complexes with $TiCl_4$ were shown to be inactive in a 1:1 molar ratio, indicating that in this latter case the second reaction sequence prevails.[2] The dormant *tert*-Cl-capped PIB chains (R^tCl) are in dynamic equilibrium with the active chains stabilized by the in situ formed electron pair donor BCl_2OCOR. These new insights into the mechanism of living IB polymerizations prompted a reinvestigation of the CumOAc/BCl_3/IB–IP copolymerization system.[1] This paper concerns such a reinvestigation and gives an evaluation of this system in line with the new mechanism.[2]

B. Experimental Section

B.1. Materials. The syntheses of *2-phenyl-2-acetoxypropane* (cumyl acetate, CumOAc) have been reported.[8] The purity of the product was checked by ^1H NMR spectroscopy. The purification of *CH_3Cl, IB,* and *IP* (Aldrich) has also been reported.[1,2,8]

B.2. Procedures. Copolymerization and characterization procedures were identical to those reported earlier.[1,2,8] Detailed

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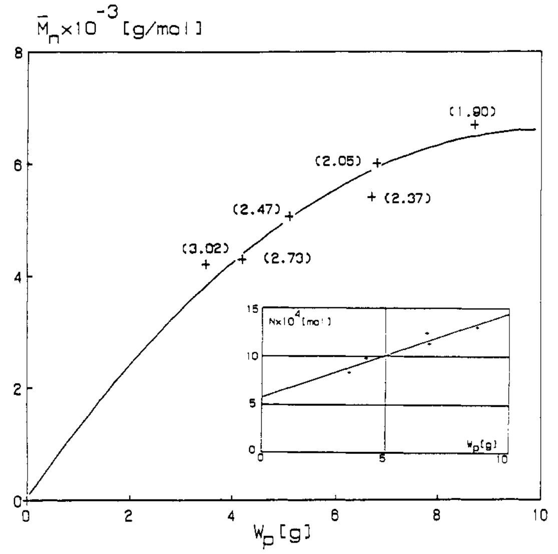


Figure 1. $\bar{M}_n$–W_p (g of copolymer formed) and N (number of polymer moles)–W_p plots for the copolymerization of IB and IB by the CumOAc/BCl_3/CH_3Cl/−40 °C system. Numbers in parentheses are $\bar{M}_w/\bar{M}_n$ values. $[CumOAc]_0 = 9.76 \times 10^{-4}$ mol (9.2×10^{-3} mol/L); $[BCl_3]_0 = 2.52 \times 10^{-2}$ mol (2.4×10^{-1} mol/L); IB = 16 mL (1.80 mol/L); IP = 5 mol % (9.4×10^{-2} mol/L); V_0 = 106 mL. IP in copolymer by ^{1}H NMR: 3 mol %.

concentration, etc., data are given in the text and table or figure captions. Copolymer compositions were determined by ^{1}H NMR spectroscopy by comparing the intensity of signals of the aromatic (cumyl) initiator fragment (7.2 ppm, 5 H) incorporated into the copolymer with that of the methine proton (5.12 ppm, 1 H) of IP units.

C. Results and Discussion

C.1. Copolymerization of IB and IP by the CumOAc/BCl_3 Initiating System in CH_3Cl at −40 °C.

C.1.1. Copolymerizations with 5 mol % IP in the Charge. A series of experiments were carried out with the CumOAc/BCl_3/IB–IP/CH_3Cl system at −40 °C with 5 mol % IP in the monomer charge in stirred round-bottom flasks. Previously,[1] polymerizations were carried out at −30 °C, which we thought was too close to the boiling point of CH_3Cl (−27 °C). The reactions were very slow compared to IB homopolymerizations, which go to completion within seconds under the same conditions.[8] The charges remained homogeneous throughout the reactions. The nonlinear $\bar{M}_n$–W_p (g of copolymer formed) plot and the slope of the N (number of copolymer moles)–W_p plot, presented in Figure 1, indicate chain transfer; IP was shown to be a powerful chain-transfer agent for IB polymerization.[9] $\bar{M}_w/\bar{M}_n$ values gradually decreased with increasing reaction time. Figure 2 shows W_p values plotted against time, indicating deceleration of the already slow copolymerization.

^{1}H NMR spectroscopy indicated 3.0 mol % IP in the copolymer. Since 5 mol % IP was charged and 3 mol % IP was incorporated into the copolymer samples taken at incomplete conversions (see Figure 2), IP accumulated in the charge during copolymerization, which appears to be in contradiction with the reported $r_{IP} = 4.5$ value.[1] The ^{1}H NMR spectrum of a representative copolymer sample shown in Figure 3 reveals that, besides the resonance at 5.12 ppm characteristic of the −CH= protons in *trans*-1,4-PIP, two other weak and broad resonances appear at 4.6 and 4.8 ppm; these resonances may be due to 1,2-PIP or 3,4-PIP enchainment[1] and/or olefinic chain-end structures such as $\sim CH_2C(CH_3){=}CH_2$ which may arise from propagating IB^+ cations by proton loss. Because the unsaturation measured by ^{1}H NMR spectroscopy is due to IP units *plus* other unsaturated structures, the IP content of the copolymers was probably overestimated in the earlier report.[1]

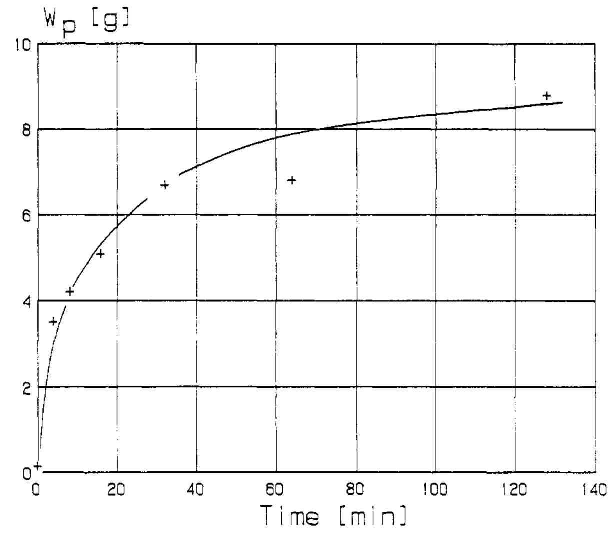


Figure 2. W_p–time plot for the copolymerization of IB with IP by the CumOAc/BCl_3/CH_3Cl/−40 °C system. Conditions as in Figure 1.

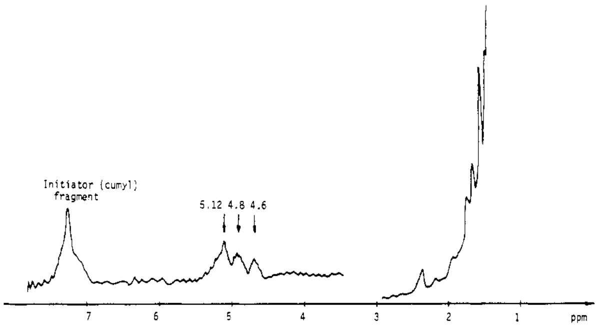


Figure 3. ^{1}H NMR spectrum of a representative IB–IP copolymer made by the CumOAc/BCl_3/CH_3Cl/−40 °C system. IP in the copolymer: 3 mol %. Conditions as in Figure 1.

At low IP concentrations the copolymer composition equation can be simplified as follows:

$$\frac{dm_{IB}}{dm_{IP}} = \frac{M_{IB}}{M_{IP}} \frac{r_{IB} + M_{IP}/M_{IB}}{r_{IP}M_{IP}/M_{IB} + 1}$$

With $M_{IP} \ll M_{IB}$ and $r_{IP}M_{IP}/M_{IB} \ll 1$

$$\frac{dm_{IB}}{dm_{IP}} \cong \frac{M_{IB}}{M_{IP}} r_{IB} \qquad (1)$$

where M_{IB}, M_{IP} and m_{IB}, m_{IP} are the molar concentrations in the charge and in the copolymer, respectively, and r_{IB} and r_{IP} are the corresponding reactivity ratios. Thus, using $r_{IB} = 2.4$, the copolymer was estimated to contain only 2.1 mol % IP.

This value is probably closer to the actual IP content than the 3 mol % obtained by ^{1}H NMR spectroscopy which overestimates unsaturation.

C.1.2. Copolymerizations with 3 mol % IP in the Charge. As discussed in section C.1.1, IP is a retarder in IB polymerization initiated by the CumOAc/BCl_3 system so that we assumed that the observed deceleration (Figure 2) might be due to IP accumulation in the charge. Thus, a series of test-tube experiments were carried out by the IMA technique[8] with 3 mol % IP in the charge. The double-bond content of the copolymers, estimated to be 1.2 mol % by eq 1, was found to be 1.5 mol % by ^{1}H NMR.

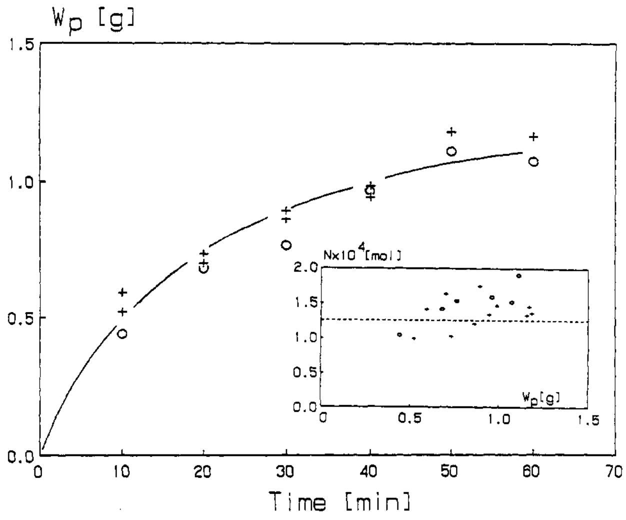


Figure 4. W_p–time and N–W_p plots for the copolymerization of IB and IP by the CumOAc/BCl_3/CH_3Cl/−40 °C system. $[CumOAc]_0 = 1.25 \times 10^{-4}$ mol (5×10^{-3} mol/L); $[BCl_3]_0 = 6.3 \times 10^{-3}$ mol (2.4×10^{-1} mol/L); $[IB]_0 = 4.3 \times 10^{-1}$ mol/L; $[IP]_0 = 1.3 \times 10^{-3}$ mol/L; $V_0 = 26.5$ mL. IMA technique, 6 × (1 mL of IB–IP/60 min): (○) 3 mol % IP in the charges; (+) constant 3% IP concentration in the IMA reactors by replenishing the consumed IP only (3 mol % IP in the charge added first to the IMA reactors, followed by the addition of monomer charges with 0.9 mol % IP as calculated from eq 1 using $r_{IB} = 2.4$).

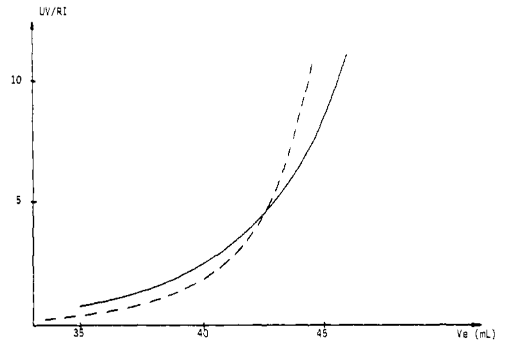


Figure 5. UV/RI ratio (GPC)–V_e plots of IB–IP copolymers prepared by the CumOAc/BCl_3/CH_3Cl/−40 °C system. Conditions as in Figure 4. (—) First and (- - -) last sample in the same IMA series.

The W_p–reaction time plot shown in Figure 4 demonstrates that the copolymerization decelerated in these experiments also. Maintaining the IP content constant, that is, replenishing only the IP consumed (see the additional two sets of IMA experiments in Figure 4), did not change the observations; therefore, it was concluded that the rate deceleration is not due to IP accumulation. According to UV/RI–V_e plots (Figure 5) constructed from GPC-RI and GPC-UV traces of the IMA series shown in Figure 4, chain termination may be responsible for rate deceleration. The intensities of the UV and RI traces at any elution volume are directly proportional to the number of chromophores (one cumyl initiator fragment per chain plus IP units) and to the molecular weight of the sample, respectively, so this ratio reflects the distribution of IP units as a function of the molecular weight. The UV/RI plot of the first sample indicates heterodisperse IP incorporation: initially more IP units are in the short chains since IP incorporation decelerates the reaction. This would be expected to occur[10] with $r_{IB} = 2.5$ and $r_{IP} = 0.4$ and considering the very slow IB–IP copolymerization relative to IB homopolymerization by the same initiating system.[8] As the copolymerization progresses, however, living propagation should result in random distribution of IP in the copolymer; i.e., the UV/RI ratios should decrease at low molecular weights. (The contribution of one cumyl initiator fragment per polymer chain remains constant throughout the reaction.) Contrary to this expectation, however, the UV/RI plot of the last sample indicates even more heterodispersity than that of the first sample. This demonstrates termination, and the increase of the UV/RI ratio at low molecular weights indicates that the incorporation of one or more IP units enhances the tendency of termination.

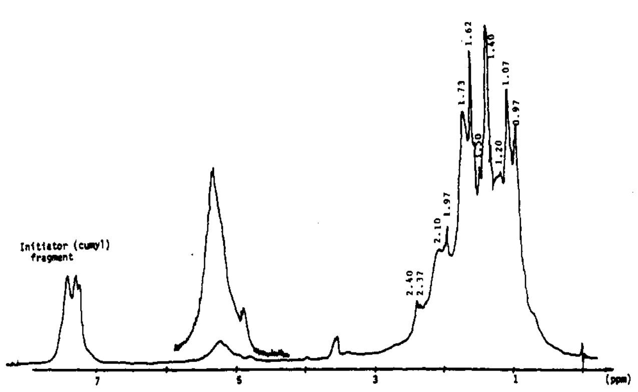
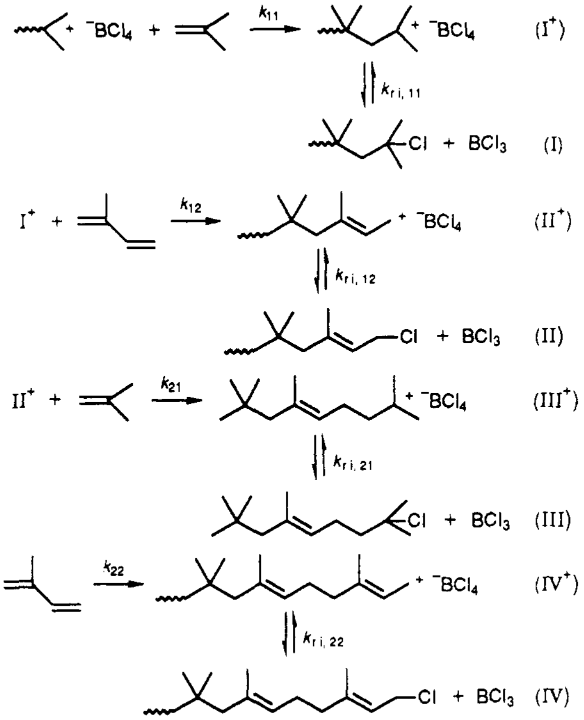


Figure 6. ^1H NMR spectrum of an IB–IP copolymer obtained in the CumOAc/BCl_3/CH_3Cl/−40 °C system. $[CumOAc]_0 = 6.7 \times 10^{-3}$ mol (6×10^{-2} mol/L); $[BCl_3]_0 = 3.15 \times 10^{-2}$ mol (2.8×10^{-1} mol/L); $[IB]_0 = 5.5 \times 10^{-2}$ mol (4.9×10^{-1} mol/L); $[IP]_0 = 50$ mol % (4.9×10^{-1} mol/L; $V_0 = 113$ mL; time = 5 min; conversion = 21%; $\bar{M}_n = 450$ (by ^1H NMR, assuming 1 cumyl group/chain).

C.2. Mechanistic Considerations. C.2.1. End-Group Analysis. According to earlier propositions[1,8] both IB homo- and copolymerizations initiated by *tert*-ester/BCl_3 complexes proceed by ester-capped growing chain ends, and the fact that homopolymerizations invariably yieled chloride-capped PIBs was explained by "forced" termination upon quenching.[8] According to the revised mechanism,[2] however, the transformation *tert*-ester/BCl_3 → *tert*-Cl + BCl_2OCOR occurs before/during polymerization (with the CumOAc/BCl_3 1:1 complex only 17% initiator efficiency was found, and no polymerization occurred when the complex was premixed for 30 min[2]) and the chlorine end group in the polymer is due to the rapid quasiliving equilibrium $PIB–Cl + BCl_3 \rightleftharpoons PIB^+ \,^-BCl_4$. IB–IP copolymerizations (see section C.1) were found to be much slower than IB homopolymerizations,[8] which suggests that the above transformation precedes initiation or occurs early during the copolymerization.

Figure 6 shows the ^1H NMR spectrum of a low molecular weight IB–IP copolymer ($\bar{M}_n = 450$ by ^1H NMR) obtained by the CumOAc/BCl_3/CH_3Cl/−40 °C system. IR spectroscopy failed to detect carbonyl resonances in the copolymer. The ^1H NMR spectrum shows the presence of the aromatic initiator (cumyl) fragment (7.2–7.6 ppm) in the copolymer. The aliphatic region displays several resonances: the two sharp peaks at 0.97 and 1.07 ppm are assigned to the *gem*-dimethyl groups of the IB units in BBB and BBP or PBB triads[11] (where B = IB and P = IP). The resonance at 1.40 ppm corresponds to the methylene protons of IB units. The sharp resonance at 1.62 ppm is assigned to the methyls of a chlorine-capped IB unit $\sim CH_2C(CH_3)_2Cl$[12] and seems to overlap with the $CH_2C(CH_3){=}CHCH_2$ resonance of an IP unit at 1.73 ppm.[11] The resonance at 1.97 ppm is characteristic of the methylene protons of the above IB end group[12] and overlaps with the methylene proton signals of PP diads (2.10 ppm).[11] The resonances in the 2.37–2.40 ppm range are due to the methylene protons of a 2-chloro-4-phenyl-2,4-dimethylpentane unit $C_6H_5C(CH_3)_2CH_2C(CH_3)_2Cl$.[12]

Scheme I
Cross-Propagation in IB–IP Copolymerization Initiated by the CumOAc/BCl_3 System[a]



[a] 1 = IB, 2 = IP, k_{ri} = rate constant of reionization.

In the olefinic region, the broad resonance at 5.30 ppm is assigned to the methine proton of the 1,4-IP unit.[13] The 0.20 ppm upfield shift is probably due to the presence of a terminal chloride, i.e., $\sim CH_2C(CH_3){=}CHCH_2C(CH_3)_2$-Cl or $\sim CH_2C(CH_3){=}CHCH_2Cl$. Because the $-CH_2-$ resonance in the latter structure at 3.98 ppm can hardly be detected, the former structure is probably more likely. This indicates that termination preferably occurs after the incorporation of an IB unit following an IP unit.

C.2.2. Copolymerization Mechanism. Termination and rate deceleration found in the CumOAc/BCl_3/IB–IP/CH_3Cl/−40 °C copolymerization system are readily explained in terms of the new mechanism proposed for living IB polymerizations.[2] The equations in Scheme I summarize homo- and cross-propagation and reversible termination.

In the PIB–IP crossover step ($I^+ \rightarrow II^+$) an allylic cation (for simplicity's sake we show only the primary allylic chloride) (II$^+$) is formed from the growing tertiary PIB cation (I$^+$). Collapse with counteranion yields a primary allylic chloride (II), the reionization of which by BCl_3 is much slower than that of the *tert*-chloride (I) ($k_{ri,21} < k_{ri,11}$). *tert*-BuCl is not an initiator of IB polymerization in conjunction with BCl_3,[14,15] and internal strain facilitates the reionization of *tert*-Cl termini in PIB–Cl^t by Lewis acids.[7,16] ^{1}H NMR spectroscopy also suggests termination after incorporation of an IB unit following one or two IP units (see section C.2.1).

Rate deceleration is most likely due to chain termination by collapse with counteranion, that is, to the lack of reionization by BCl_3 III or to slower reionization of II–IV than of I. As a consequence of rate deceleration by IP incorporation, the *tert*-acetate/$BCl_3 \rightarrow$ *tert*-Cl + BCl_2OAc transformation occurs very early or may precede initiation.

Inspection of Scheme I also reveals that this complex copolymerization system cannot be described by a single pair of r_{IB}–r_{IP} values. Evaluation of the system is further complicated by massive cyclization of PIP sequences at higher IP contents.[1] The $r_{IP} = 4.5 \pm 3$ value calculated for the above system[1] is erroneous since (1) IP always accumulates in the system, (2) IP contents were determined by ^{1}H NMR and therefore were overestimated, and (3) data were collected only in the 0–12 mol % IP content range which is insufficient for r_1–r_2 calculations.

In summary, BCl_2OAc, the in situ electron pair donor forming in the CumOAc/BCl_3/IB–IP/CH_3Cl/−40 °C system, does not mediate living copolymerization, and chain transfer and termination occur. The next part of this series will concern IB–IP copolymerization by *tert*-ester or -ether/$TiCl_4$ initiating systems because they were shown to mediate living IB homopolymerization leading to narrow MWD polymers over a wide molecular weight range.[2,17]

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Registry No. IB, 115-11-7; IP, 78-79-5; CumOAc, 3425-72-7; BCl_3, 10294-34-5.