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Living Oligomerization of Isobutylene Initiated by Cumyl Chloride/BCl_3 Mixtures: Kinetic Analysis of the Initiation and the Early Propagation Steps

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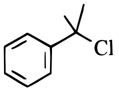
ABSTRACT: The living oligomerization of isobutylene initiated by cumyl chloride **1** or by the telechelics **P1** or **P2** in presence of BCl_3 and benzyltriethylammonium tetrachloroborate has been investigated. The tertiary chlorides **P2**−**P7** were separated by HPLC and analyzed as spectroscopically pure compounds. A kinetic model has been derived from which the gross propagation rate constants for the early propagation steps can be calculated. It has been found that the low reactivity of the adduct of cumyl chloride to one isobutylene unit (**P1**) is responsible for the broad MWD in the cumyl chloride/BCl_3/BCl_4^--initiated oligomerization of isobutylene. In contrast, a narrow MWD could be achieved by using the 2:1 product **P2** in combination with BCl_3/BCl_4^- as initiator.

Introduction

The formation of telechelic polymers by cumyl chloride **1** (1-chloro-1-methyl-ethyl)benzene/BCl_3-initiated



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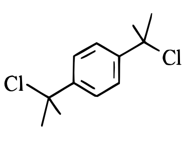

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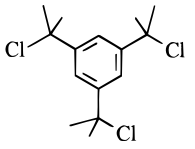

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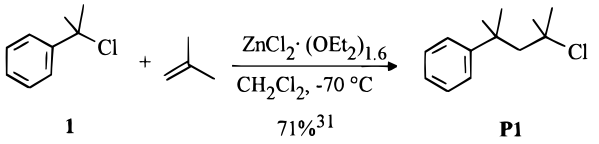
polymerizations of isobutylene has first been reported by Kennedy[1−5] and Nuyken[6] (Inifer mechanism). The analogous process using biscumyl chloride, **2**, and triscumyl chloride, **3**, led to the formation of bi- and trifunctional polymers.[5−19] While these polymerizations were not living under the original reaction conditions, slight modifications led to living systems.[5,20−30]

In contrast to these findings we had observed the exclusive formation of the 1:1 product **P1**,[31] when a mixture of isobutylene and cumyl chloride, **1**, was treated with the weaker Lewis acid $ZnCl_2{\cdot}OEt_2$[32] in dichloromethane.

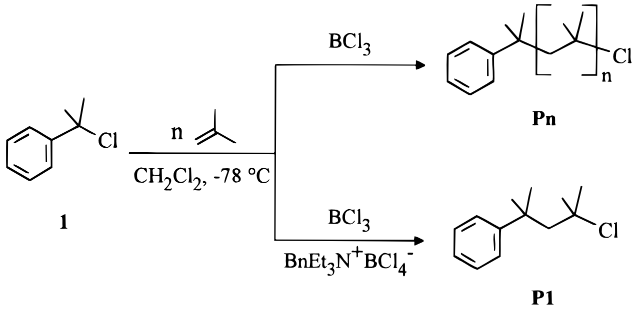


Since compound **P1** is considered to be an intermediate of the living **1**/BCl_3-initiated polymerization of isobutylene, we set out to investigate the mechanism of the initial steps of this reaction.

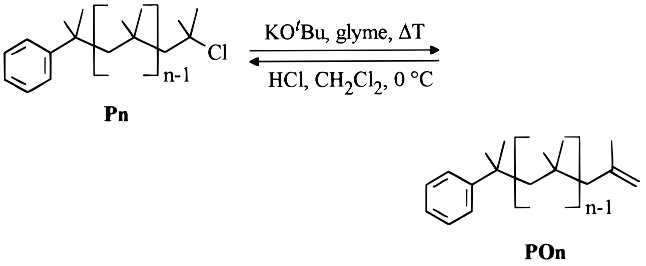
Results

In accordance with literature reports,[1−9] we have not been able to detect compound **P1** in the BCl_3-initiated reaction of cumyl chloride **1** with isobutylene, even when only 1 equiv of isobutylene was slowly added to a mixture of **1** and BCl_3 in CH_2Cl_2. The polymerization of isobutylene could be suppressed, however, when $BnEt_3N^+BCl_4^-$ was present in the reaction mixture, and under otherwise identical conditions, the selective formation of the 1:1-product **P1** was observed, even when an excess of isobutylene was present (Scheme 1).

Scheme 1



Scheme 2



When the reaction time was extended, the 1:1-product **P1** was observed to further react with isobutylene, and in a series of consecutive reactions the formation of higher adducts $Ph-CMe_2-[CH_2-CMe_2]_n-Cl$ took place. Treatment of these mixtures with KO^tBu in glyme[17,33] yielded the terminal olefins **POn** (Scheme 2), which were separated by HPLC to yield 0.2−0.5 g quantities of the oligomers **PO1**−**PO7**. The latter were hydrochlorinated in methylene chloride to give the tertiary chlorides **P1**−**P7** as analytically pure compounds (Table 1). The direct separation of the telechelics **P1**−**P7** was not possible since these compounds partially solvolyzed in the MeOH/H_2O mixtures used for the reversed phase HPLC.

In order to follow the course of the cumyl chloride/BCl_3/BCl_4^--initiated reactions, the oligomerizations were

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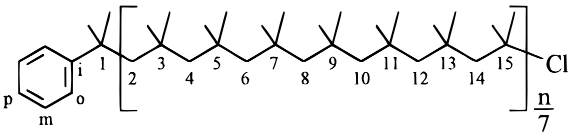
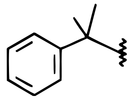
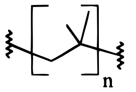
Table 1. ^{13}C NMR Data [δ (ppm)] of Cumyl Chloride 1 (n = 0), and the Isobutylene Oligomers P1 (n = 1), P2 (n = 2), P3 (n = 3), P4 (n = 4), P5 (n = 5), and P7 (n = 7) in CDCl$_3$



		
1, n = 0	127.5 (C_p), 125.5 (C_m), 128.2 (C_o), 146.2 (C_i), 34.2 (1-Me), 69.6 (C-1)	
P1, n = 1	125.7 (C_p), 126.0 (C_m), 128.1 (C_o), 148.8 (C_i), 30.9 (1-Me), 38.5 (C-1)	58.2 (C-2), 34.3 (3-Me), 71.8 (C-3)
P2, n = 2	125.3 (C_p), 126.1 (C_m), 127.8 (C_o), 149.9 (C_i), 31.8 (1-Me), 38.6 (C-1)	57.6, 58.4 (2 t), 29.8 (3-Me), 35.1 (5-Me), 37.3 (C-3), 71.7 (C-5)
P3, n = 3	125.1 (C_p), 126.1 (C_m), 127.8 (C_o), 150.2 (C_i), 31.9 (1-Me), 38.7 (C-1)	57.9, 58.5, 58.6 (3 t), 30.1, 30.5 (2 q), 35.1 (7-Me), 37.3, 37.7 (2 s), 72.0 (C-7)
P4, n = 4	125.1 (C_p), 126.1 (C_m), 127.7 (C_o), 150.3 (C_i), 32.0 (1-Me), 38.7 (C-1)	57.7, 58.6, 59.0, 59.3 (4 t), 30.2, 30.6, 30.9 (3 q), 35.2 (9-Me), 37.5, 37.7[a] (2 s), 72.0 (C-9)
P5, n = 5	125.1 (C_p), 126.1 (C_m), 127.7 (C_o), 150.3 (C_i), 32.0 (1-Me), 38.7 (C-1)	58.3, 58.5, 58.9, 59.0, 59.4 (4 t), 30.3, 30.6, 31.0[a] (3 q), 35.2 (11-Me), 37.6, 37.8, 37.86, 37.93 (4 s), 72.0 (C-11)
P7, n = 7	125.1 (C_p), 126.1 (C_m), 127.7 (C_o), 150.3 (C_i), 32.0 (1-Me), 38.7 (C-1)	58.3, 58.5, 59.0,[a] 59.45,[a] 59.48 (5 t), 30.3, 30.6, 31.0, 31.1,[a] 31.15 (5 q), 35.2 (15-Me), 37.6, 37.8, 37.87, 37.99, 38.02, 38.07 (6 s), 71.9 (C-15)

[a] Double intensity.

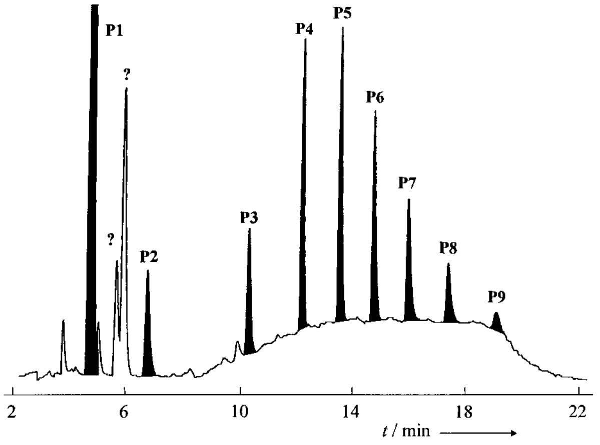


Figure 1. Living oligomerization of isobutylene initiated by cumyl chloride **1**/BCl$_3$/BnEt$_3$N$^+$BCl$_4^-$ in CH$_2$Cl$_2$ at −78 °C monitored by HPLC (RP-C$_{18}$/5 μm, gradient from MeOH:H$_2$O/95:5 to MeOH:H$_2$O:CH$_2$Cl$_2$/57:3:40).

discontinued after certain intervals by quenching with aqueous ammonium chloride solution.

As indicated by Figures 1 and 2, at no stage of the reaction the 2:1-product **P2** was the main component of the mixture. Obviously its reaction with additional isobutylene is faster than its formation. The fact that the 1:1-product **P1** is still present in considerable concentration while the higher oligomers **P3**−**P9** have already been formed (Figure 1) indicates that one criterion of ideally controlled polymerization is not fulfilled: Though the first initiation step (**1** + isobutylene) is fast compared to the propagation steps, the consecutive reaction of the 1:1-product **P1** with isobutylene is slow, and the complete initiation sequence (**1** → **P2**) is slower than the later chain growth steps. Thus, the reaction of the 1:1-product **P1** with isobutylene is the bottleneck of the reaction cascade, and as a consequence a broad molecular weight distribution is observed during all stages of the oligomerization (Figure 2). A further complication that may arise from using cumyl chloride **1** as initiator is indane formation from **P1**, a side reaction which becomes important at elevated temperatures. It should be noted, however, that the polydispersities observed in this experiment still lead to M_w/M_n ratios below 1.2 (Table 2).

The low concentration of **P2** during the whole oligomerization process (Figure 2) indicates its fast reaction with isobutylene. Therefore, the 2:1-product **P2** has been assumed to be a better initiator than cumyl chloride, **1**, for these oligomerizations.

Since only small quantities of **P2** can be isolated from the oligomerization experiments described above, a different synthesis for **P2** was needed. The two-step sequence,[34] TiCl$_4$-promoted reaction of **P1** with 2-methallyltrimethylsilane and successive hydrochlorination provided **P2** in good yield (Scheme 3).

The conclusion that the 2:1-product **P2** is a more suitable initiator than the 1:1-product **P1** (or cumyl chloride, **1**) is corroborated by Figure 3.

When the **P2**-initiated oligomerization of isobutylene is performed under the same conditions as those described for the analogous reactions above, the initiator **P2** is almost completely consumed when the oligomer **P5** constitutes the major component (Figure 3). The living character of this oligomerization is shown by the time concentration correlation in Figure 4 as well as by the M_w/M_n-ratios smaller than 1.04 (Table 3).

As discussed for the diisobutylene hydrochloride and the triisobutylene hydrochloride-initiated oligomerizations of isobutylene in presence of BnEt$_3$N$^+$BCl$_4^-$, the decay of the initiator can be described by eq 1 where K_2

$$-\frac{d[\mathbf{P2}]}{dt} = K_2 k_{p2}[\mathbf{P2}][\mathrm{BCl_3}][\mathrm{C_4H_8}] \qquad (1)$$

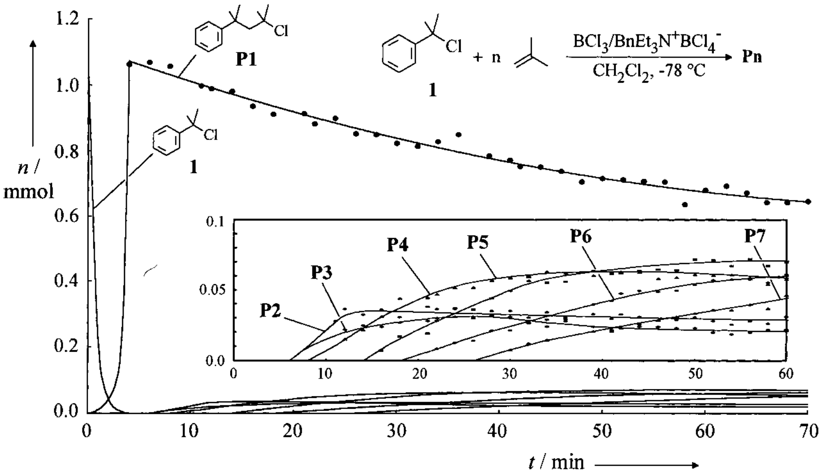


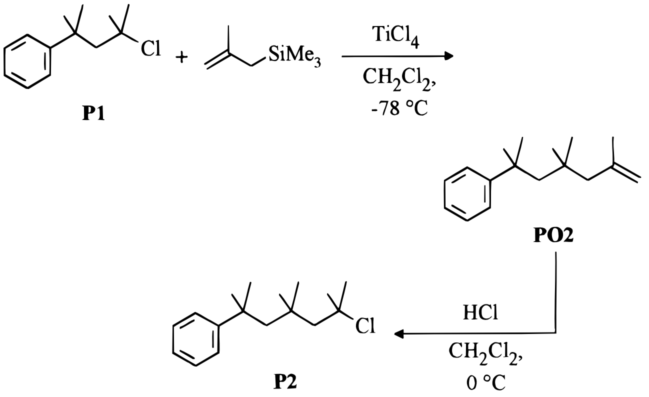
Figure 2. Time-dependent product distribution in the living oligomerization of isobutylene initiated by **1**/BCl_3/$BnEt_3N^+BCl_4^-$ in CH_2Cl_2 at −78 °C.

Table 2. Weight-Averaged and Number-Averaged Molecular Weights of the Products Obtained by Living Oligomerization of Isobutylene with Cumyl Chloride, 1, As Initiator ($BnEt_3N^+BCl_4^-$, BCl_3, CH_2Cl_2, −78 °C)

reaction time (min)	17	28	46	64
M_w (g mol^{-1})[a]	237.37	271.59	319.10	345.27
M_n (g mol^{-1})[a]	227.14	244.98	274.18	290.40
M_w/M_n	1.045	1.109	1.164	1.189

[a] Calculated from evaluation of the HPLC analysis.

Scheme 3



corresponds to the ionization constant of **P2**. The constant k_{p2} represents the second-order rate constant of the reaction of isobutylene with the tertiary carbocation derived from **P2**.[35]

Since [BCl_3] remains constant during the reaction and isobutylene is used in large excess (i.e., its concentration is almost constant during the consumption of **P2**), pseudo-first-order kinetics (eq 2) are expected in accordance with the experimental results depicted in Figure 5.

$$-\frac{d[\mathbf{P2}]}{dt} = k_{obs2}[\mathbf{P2}] \qquad (2)$$

As discussed previously,[35] the expected linear dependence on isobutylene concentration is not observed under these conditions since the increase of the reaction rate by increasing [C_4H_8] is compensated by a decrease of the ionization constant K resulting in a seemingly zeroth order in [C_4H_8]. The variation of [C_4H_8] and [BCl_3] in Table 4 was too small, however, to derive the reaction orders of [BCl_3] and [C_4H_8] in these experiments.

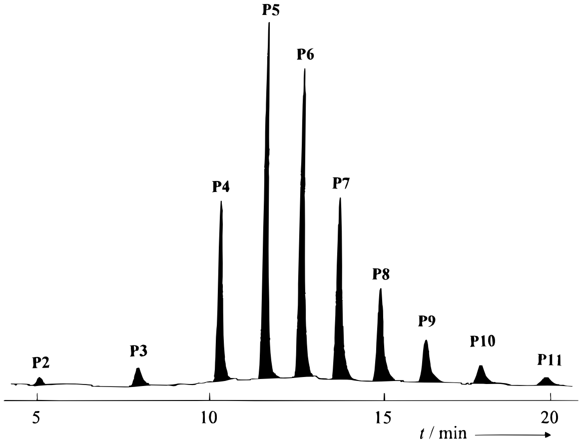


Figure 3. Living oligomerization of isobutylene initiated by the 2:1-product **P2**/BCl_3/$BnEt_3N^+BCl_4^-$ in CH_2Cl_2 at −78 °C monitored by HPLC (RP-C_{18}/5 μm, gradient from MeOH:H_2O/95:5 to MeOH:H_2O:CH_2Cl_2/57:3:40).

Independent of the exact form of the kinetic equations, one can assume that analogous equations will hold for the production and consumption of the individual oligomers **P*n***. As a consequence, the differential eq 3 results, which corresponds to eq 4 in the case of the 3:1-product **P3** (Scheme 4).

$$\frac{d[\mathbf{P}\boldsymbol{n}]}{dt} = k_{obs(n-1)}[\mathbf{P}(\boldsymbol{n}-\mathbf{1})] - k_{obs(n)}[\mathbf{P}\boldsymbol{n}] \qquad (3)$$

$$\frac{d[\mathbf{P3}]}{dt} = k_{obs2}[\mathbf{P}2] - k_{obs3}[\mathbf{P3}] \qquad (4)$$

At the maximum concentration of **P*n***, d[Pn]/dt = 0, and from eqs 3 and 4 one derives eqs 5 and 6, respectively.

$$\frac{k_{obs(n)}}{k_{obs(n-1)}} = \frac{[\mathbf{P(n-1)}]}{[\mathbf{P}\boldsymbol{n}]_{max}} \qquad (5)$$

$$\frac{k_{obs3}}{k_{obs2}} = \frac{[\mathbf{P2}]}{[\mathbf{P3}]_{max}} \qquad (6)$$

We can now use Figure 4 to determine the concentration of **P(*n*−1)** at the maximum concentration of **P*n***.

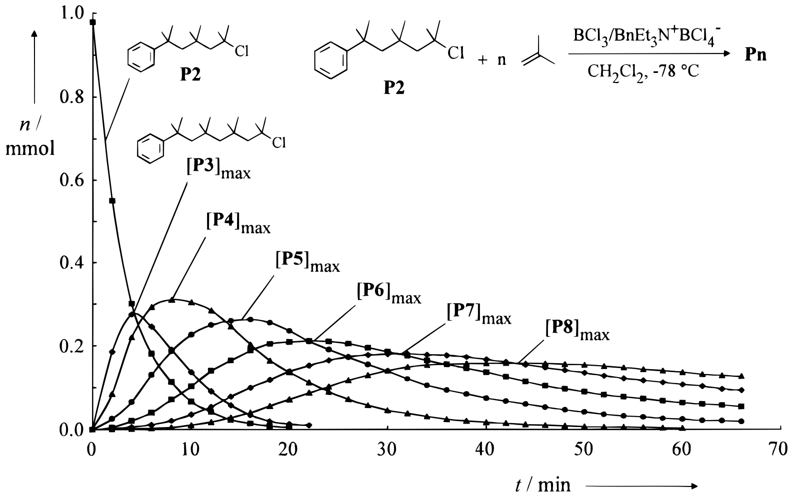


Figure 4. Time-dependent product distribution in the living oligomerization of isobutylene initiated by the 2:1-product **P2**/BCl_3/$BnEt_3N^+BCl_4^-$ in CH_2Cl_2 at −78 °C.

Table 3. Weight-Averaged and Number-Averaged Molecular Weights of the Products Obtained by Living Oligomerization of Isobutylene with the 2:1-Product P2 as Initiator ($BnEt_3N^+BCl_4^-$, BCl_3, CH_2Cl_2, −78 °C)

reaction time (min)	10	20	32	42	52	62
M_w (g mol^{-1})[a]	411.91	495.47	572.78	614.03	640.67	677.24
M_n (g mol^{-1})[a]	399.09	480.75	554.66	595.74	623.08	658.43
M_w/M_n	1.032	1.031	1.033	1.031	1.027	1.029

[a] Calculated from evaluation of the HPLC analysis.

Table 4. Rate Constants and Concentrations of the Living Oligomerization of Isobutylene Initiated by the 2:1-Product P2 (≈1 mmol P2, ≈0.1 mmol $BnEt_3N^+Cl^-$, ≈25 mL CH_2Cl_2, BCl_3, −78 °C)

[**P2**] (mmol, mol L^{-1})	$[C_4H_8]_0$ (mmol, mol L^{-1})[a]	$[BCl_3]_0$ (mL, mmol)	$[BCl_3]$ (mol L^{-1})[b]	$BnEt_3N^+Cl^-$ (mmol)	standard (mmol)	CH_2Cl_2 (mL)	k_{obs2} (s^{-1})	$k_{obs2}/[BCl_3]$ (L mol^{-1}s^{-1})
0.400, 3.79×10^{-2}	7.49, 7.07×10^{-1}	7.0, 0.31	2.56×10^{-2}	0.041	0.0208[c]	10.0	3.41×10^{-3}	1.33×10^{-1}
1.01, 3.10×10^{-2}	24.1, 7.38×10^{-1}	10, 0.45	1.06×10^{-2}	0.101	0.2555,[c] 0.0507[d]	30.7	1.11×10^{-3}	1.05×10^{-1}
1.01, 2.55×10^{-2}	16.9, 4.27×10^{-1}	12, 0.54	1.10×10^{-2}	0.100	0.2382,[c] 0.0508[d]	38.3	1.43×10^{-3}	1.30×10^{-1}
1.01, 3.80×10^{-2}	13.0, 4.90×10^{-1}	17, 0.76	2.48×10^{-2}	0.101	0.2555,[c] 0.0507[d]	25.5	3.08×10^{-3}	1.25×10^{-1}
0.978, 3.52×10^{-2}	29.8, 1.07	17, 0.76	2.38×10^{-2}	0.099	0.2298,[c] 0.0636[d]	25.4	4.23×10^{-3}	1.78×10^{-1}
								$(1.35 \pm 0.24) \times 10^{-1}$

[a] $\rho_{isobutylene}$(−78 °C) = 0.707 g cm^{-3} from ref 36. [b] $[BCl_3] = [BCl_3]_0 - [BnEt_3N^+BCl_4^-]$. [c] Phenyloctane. [d] Phenylpentane.

Table 5. Relative Gross Propagation Rate Constants of the Successive Reaction Steps in the Living Isobutylene Oligomerization Initiated by the 2:1-Product P2 (BCl_3, $BnEt_3N^+BCl_4^-$, CH_2Cl_2, −78 °C, calculated from eq 5)

exptl	k_{obs3}/k_{obs2}	k_{obs4}/k_{obs3}	k_{obs5}/k_{obs4}	k_{obs6}/k_{obs5}	k_{obs7}/k_{obs6}	k_{obs8}/k_{obs7}	k_{obs9}/k_{obs8}
1	1.29	0.61	0.77	0.93			
2	1.31	0.53	0.82	0.94	1.04	1.00	
3	1.11	0.62	0.78	0.99	0.97	1.00	1.00
	∅ = 1.24	∅ = 0.59	∅ = 0.79	∅ = 0.95	∅ = 1.00	∅ = 1.00	∅ = 1.00

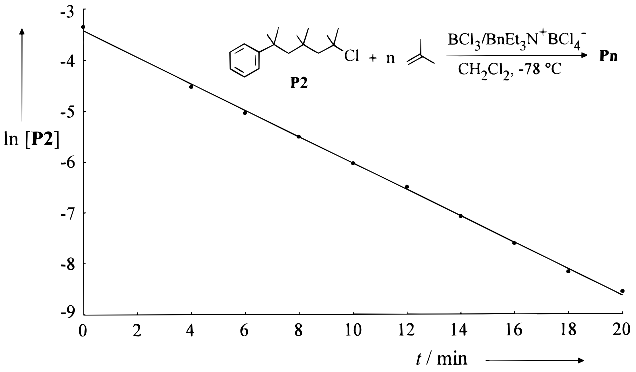
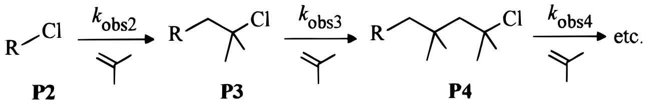


Figure 5. Pseudo-first-order consumption of the initiator **P2** in the living oligomerization of isobutylene (BCl_3, $BnEt_3N^+BCl_4^-$, CH_2Cl_2, −78 °C).

According to eq 5, this ratio yields the quotient of two successive gross propagation rate constants ($k_{obs(n)}/k_{obs(n-1)}$). As an example we derive $[\mathbf{P2}]/[\mathbf{P3}]_{max} = 1.11$ from Figure 4 corresponding to k_{obs3}/k_{obs2} (Table 5). The reactivity ratios for the further propagation steps have been determined analogously.

Scheme 4



It can be seen that the conversion of **P3** into **P4** is slightly faster than **P3**'s formation ($k_{obs3}/k_{obs2} = 1.24$), while the next two steps are somewhat slower ($k_{obs4}/k_{obs3} = 0.59$, $k_{obs5}/k_{obs4} = 0.79$). A further extension of the polyisobutylene chain does not have an influence on the gross propagation rates. The differences in the gross rate constants for the initial propagation steps are probably caused by different intramolecular solvation of the carbocationic center, as well as by the negative inductive effect of the phenyl ring, which fades as the polymer grows.

Since the maximum of [**P2**] cannot precisely be derived from Figure 2, only an approximate value of

$k_{obs2}/k_{obs1} \approx 20-35$ is obtained by this method.

The averaged reactivity ratios listed in the bottom line of Table 5 can be combined to derive $k_{obs9} = k_{obs8} = k_{obs7} = k_{obs6} = (1.24)(0.59)(0.79)(0.95)k_{obs2} = 0.55k_{obs2}$.

Multiplication of $k_{obs2}/[BCl_3]$ from Table 4 with 0.55 thus yields $k_{obs9}/[BCl_3] = 7.41 \times 10^{-2}$ L mol^{-1}s^{-1} closely similar to the corresponding value of $k_{obs}/[BCl_3] = 6.06 \times 10^{-2}$ L mol^{-1}s^{-1} determined for the triisobutylene hydrochloride-initiated oligomerization of isobutylene.[35] The independence of the gross propagation rate constant of the nature of the remote head group is thus demonstrated.

Conclusion

Because of the low reactivity of the 1:1-product **P1**, the combination of cumyl chloride, **1**, with BCl_3 does not produce isobutylene oligomers with narrow molecular weight distributions. This problem can be avoided by using the 2:1-product **P2** as an initiator, which yields oligomers of very narrow MWD as previously reported for the analogous diisobutylene hydrochloride- and triisobutylene hydrochloride-initiated oligomerizations of isobutylene.[35]

Experimental Section

Dichloromethane (Merck, pa) was stirred with sulfuric acid for 3 d, washed with water, followed by aqueous $NaHCO_3$ solution, then again with water, and then dried with $CaCl_2$ and distilled from CaH_2 before use. Boron trichloride (Messer Griesheim, 99.9%) was taken from a steel cylinder using gas-tight syringes; isobutylene, phenyloctane, and phenylpentane (internal standards) and benzyltriethylammonium chloride were used without further purification.

The analyses of the oligomerization experiments were carried out on a HPLC system containing a Knauer HPLC Pumpe 64, a VICI-Valco Motorventil, and a Hitachi-Merck UV-Detektor 655A-22; peak integration was performed on a Hitachi-Merck Integrator D2000.

The ^{1}H and ^{13}C NMR spectra were obtained on Varian XL 200 and Bruker WM 300 spectrometers with $CDCl_3$ as solvent and tetramethylsilane ($\delta = 0.00$) as internal standard.

(3-Chloro-1,1,3-trimethylbutyl)benzene (P1). **P1** was synthesized as indicated in ref 31. In a two-necked flask (50 mL) benzyltriethylammonium chloride (0.228 g, 1.00 mmol) was dissolved in dry CH_2Cl_2 (25 mL) and cooled in a dry ice bath. After isobutylene was condensed (2.16 g, 38.5 mmol) into the precooled mixture, a $ZnCl_2{\cdot}(OEt_2)_{1.6}$ solution in CH_2Cl_2 (3.9 mmol $ZnCl_2$)[32] was added, and a solution of cumyl chloride, **1** (1.38 g, 8.92 mmol), in dry CH_2Cl_2 (5 mL) was dropped into the mixture during 1 h. The colorless solution was stirred for 2 h at −78 °C before aqueous NH_4Cl solution (20 mL) was added. The aqueous layer was extracted with CH_2Cl_2, and the combined organic fractions were dried with $MgSO_4$. After filtration and evaporation of the solvent, the residue was dissolved in a small amount of *n*-pentane and the benzyltriethylammonium salt was filtered off. The solvent was again removed and **P1** could be isolated as a colorless liquid (bp 95−100 °C/6 × 10^{-3} mbar, 1.30 g, 69%; ref 31, 71%): ^{1}H NMR $\delta = 1.31$ (s, 6 H, 1-Me), 1.45 (s, 6 H, 3-Me), 2.38 (s, 2 H, 2-H), 7.17−7.19, 7.26−7.31, 7.36−7.39 (3 m, 5 H, phenyl); ^{13}C NMR, see Table 1.

(1,1,3,3,5-Pentamethylhexenyl)benzene (PO2). In a two-necked flask (50 mL) dry CH_2Cl_2 (25 mL) was cooled in a dry ice bath. After distilled $TiCl_4$ (0.80 mL, ~7.3 mmol) was added, 2-methallyltrimethylsilane (1.03 g, 8.00 mmol) was added dropwise and the color of the reaction mixture turned to dark red. Afterward a solution of **P1** (0.840 g, 4.00 mmol) and 2-methallyltrimethylsilane (1.03 g, 8.00 mmol) in CH_2Cl_2 (5mL) was dropped into the mixture during 1 h. The solution was stirred for 2 h at −78 °C before adding aqueous ammonia (20 mL). The suspension was filtered over celite, the aqueous layer was extracted with CH_2Cl_2, and the combined organic fractions were dried with $MgSO_4$. After evaporation of the solvent, **PO2** was isolated as a colorless oil (bp 95−103 °C/6 × 10^{-3} mbar, 0.58 g, 63%): ^{1}H NMR $\delta = 0.54$ (s, 6 H, 3-Me), 1.23 (s, 6 H, 1-Me), 1.55 (br. s, 3 H, 5-Me), 1.64 and 1.66 (2 s, each 2 H, 2-H, 4-H), 4.42 and 4.66 (2 m, each 1 H, 6-H), 6.96−7.03, 7.07−7.14, 7.21−7.23 (3 m, 5 H, phenyl); ^{13}C NMR $\delta =$ 25.6 (q, 5-Me), 28.7 (q, 3-Me), 31.8 (q, 1-Me), 35.8 (s, C-3), 38.5 (s, C-1), 53.2, 56.0 (2 t, C-2, C-4), 114.3 (t, C-6), 125.2 (d, C_{para}, phenyl), 126.1, 127.8 (2 d, C_{ortho}, C_{meta}, phenyl), 143.7 (s, C-5), 150.1 (s, C_{ipso}, phenyl).

(5-Chloro-1,1,3,3,5-pentamethylhexyl)benzene (P2). In a two-necked flask (100 mL) a solution of **PO2** (2.28 g, 9.90 mmol) in CH_2Cl_2 (60 mL) was cooled in an ice bath. After gaseous HCl was passed through the solution for 1 h, the organic layer was washed with water and aqueous $NaHCO_3$ solution. The organic fraction was dried with $MgSO_4$, the solvent was removed, and the residue was dried in vacuo to yield **P2** as colorless oil (2.40 g, 91%): ^{1}H NMR $\delta = 0.88$ (s, 6H, 3-Me), 1.39 (s, 6H, 1-Me), 1.56 (s, 6H, 5-Me), 1.66 (s, 2H, 2-H), 1.90 (s, 2H, 4-H), 7.15−7.40 (m, 5H, phenyl); ^{13}C NMR, see Table 1.

Oligomerization Experiments and Dehydrochlorination with KO^{t}Bu. *General Procedure.* In a two-necked flask (100 mL) cumyl chloride, **1** (3.02 g, 19.5 mmol), and benzyltriethylammonium chloride (0.47 g, 2.06 mmol) were dissolved in dry CH_2Cl_2 (50 mL) and cooled in a dry ice bath. Isobutylene (3.22 g, 57.4 mmol) was condensed into the precooled solution before adding boron trichloride (100 mL, 4.46 mmol). After 5 min, the yellow reaction solution was hydrolyzed with aqueous NH_4Cl solution, the organic layer was dried with $MgSO_4$, and the solvent was evaporated. The residue was dissolved in a small amount of *n*-pentane, and the benzyltriethylammonium salt was filtered off. The solvent was again removed, and the solution of the crude product (4.15 g) in glyme (20 mL) was added dropwise to a suspension of KO^{t}Bu (4.27 g, 38.1 mmol) in glyme (40 mL) and refluxed for 2 h. The suspension was hydrolyzed with aqueous Na_2CO_3 solution, the organic layer was dried with $MgSO_4$, and evaporation of the solvent yielded a mixture of the terminal olefins **PO*n*** (3.26 g). Separation of the residue by HPLC (RP-C_{18}/5 μm, MeOH: CH_2Cl_2/80:20, 258 nm, 12.5 mL min^{-1}) yielded 0.2−0.5 g quantities of the oligomers **PO1**−**PO7** as analytically pure compounds, which were successively converted into the tertiary chlorides **P1**−**P7** as described for **P2** (see above).

Kinetic Experiments. *General Procedure.* The tertiary chloride (**1**, **P1**, or **P2**), benzyltriethylammonium chloride and the phenylalkane (internal standard) were dissolved in dry CH_2Cl_2 and cooled in a dry ice bath. Isobutylene was condensed into the precooled solution before adding boron trichloride. After definite time intervals, 0.5-mL samples were taken from the solution and hydrolyzed with aqueous ammonium chloride solution (2 mL). The samples were analyzed by HPLC (RP-C_{18}/5 μm, gradient from MeOH:H_2O/95:5 to MeOH:H_2O:CH_2Cl_2/57:3:40, 258 nm, 1.4 mL min^{-1}) without prior purification. The calibration constants for the evaluation of the chromatograms were obtained from artificial mixtures of the pure compounds **P*n*** and the phenylalkanes (internal standard).

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Supporting Information Available: Data tables containing details of the oligomerization experiments, e.g., concentrations of the oligomers, weight averaged- and number-averaged molecular weight values, and M_w/M_n ratios (2 pages). Ordering information is given on any current masthead page.

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