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ALKYL CHLORIDE-BORON TRICHLORIDE INITIATED POLYMERIZATIONS OF ISOBUTYLENE:
DETAILED ANALYSIS OF THE INITIAL PROPAGATION STEPS

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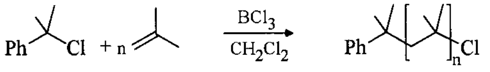
Dedicated to Professor P. H. Plesch on the occasion of his 80th birthday

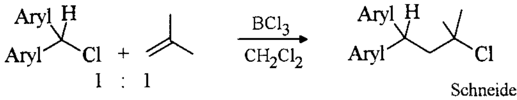
Abstract: Living oligomerizations of isobutylene initiated either by cumyl chloride, the [1:1]-adduct of cumyl chloride to isobutylene (**P1**), the [1:2]-adduct of cumyl chloride to isobutylene (**P2**), diisobutylene hydrochloride (**P1'**), or triisobutylene hydrochloride (**P2'**) have been studied in presence of BCl_3 and benzyltriethylammonium tetrachloroborate. In contrast to common opinion, the gross propagation rates of the various telechelics depended significantly on the degree of polymerization with k_{rel} = 0.07, 1.8, 2.3, 1.3, 1.1, 1.0, 1.0 for $Ph\text{-}C(CH_3)_2\text{-}[CH_2\text{-}C(CH_3)_2]_n\text{-}Cl$ with n = 1, 2, 3, 4, 5, 6, 7, respectively. These results are compared with the initiation efficiencies of $(CH_3)_3C\text{-}(CH_2\text{-}C(CH_3)_2]_n\text{-}Cl$ (k_{rel} = 0.3 and 0.8 for n = 1 and 2, respectively). The consequences for the synthesis of telechelics with very narrow molecular weight distribution are discussed.

In the early eighties Kennedy first reported about the cumyl chloride/boron trichloride initiated polymerizations of isobutylene (eq. 1, Ref. 1). At the same time we had obtained [1:1]-products selectively by BCl_3 induced reactions of benzhydryl chlorides with isobutylene (eq. 2, Ref. 2, 3), and we initially thought that the different outcome of the two experiments was only due to the different ratio of the reactants used by Kennedy and by us.



(1)

Kennedy et al.,1982-87



(2)

Schneider and Mayr, 1985

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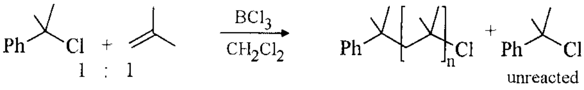
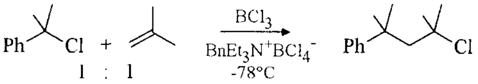
We were very surprised, therefore, that we also observed polymerization of isobutylene when a 1:1 mixture of cumyl chloride and isobutylene was treated with boron trichloride in dichloromethane (eq. 3). The expected [1:1]-product was not detectable under these reaction conditions (Ref. 4).



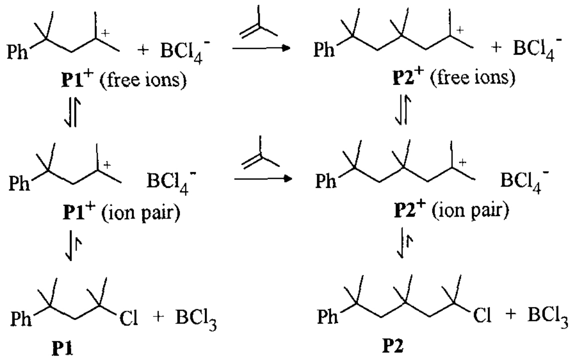
(3)

Since the reactivity of the tertiary carbenium ions obtained from the reaction of isobutylene with benzhydryl or cumyl cations should be closely similar, we suspected another reason to be responsible for the different types of products obtained by reactions (2) and (3). The benzhydryl chlorides used in reaction (2) ionize to a greater extent than cumyl chloride (Ref. 3) and, as a consequence, the BCl_4^- concentration was higher in the experiments with the benzhydryl chlorides (eq. 2) than in those with cumyl chloride (eq. 3). Assuming that this was the reason for the selective trapping of the [1:1]-product in eq. 2, the BCl_3 initiated reaction of cumyl chloride with isobutylene was repeated in the presence of a quaternary ammonium salt: Now the [1:1]-product of cumyl chloride and isobutylene was isolated in quantitative yield (eq. 4). The selective formation of the [1:1]- product shown in eq. 4 was even observed, when an excess of isobutylene was employed.



(4)

It was thus demonstrated that the ion pair collapse of tertiary alkyl tetrachloroborates is faster than the reactions of these carbocations with isobutylene (cf. Scheme 1). At low BCl_4^- concentrations, however, when the ion-pairs are mostly dissociated (Ref. 5, 6), the propagation step is considerably faster than the trapping by the anions, and the [1:1]-product **P1** is not intercepted.



Scheme 1. Chain growth in the living polymerization of isobutylene

As indicated in Scheme 1, the tertiary alkyl chlorides **P1** can partially be reionized in presence of BCl_3, and in a slow consecutive reaction the growth of the carbon chain is observed. To our surprise, the incorporation of isobutylene did not occur steadily, however. Figure 1, for example, shows a situation during this polymerization process when cumyl chloride has yet completely reacted and most of the material is present as the [1:1]-product **P1**. While the concentration of **P2** and **P3** is very small, there is already a significant amount of the oligomers **P4** and **P5** with four or five isobutylene units, respectively.

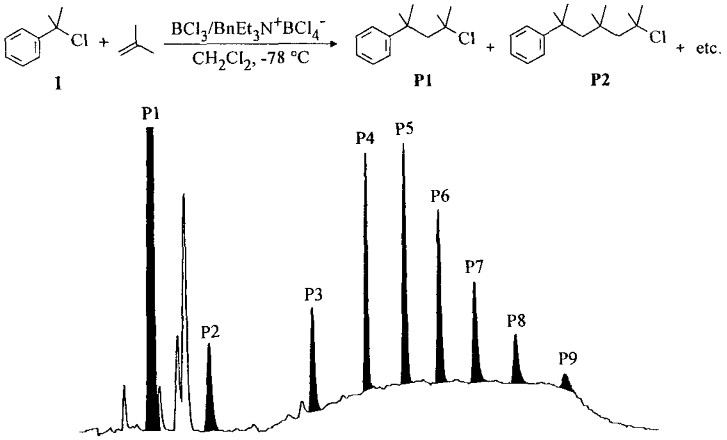


Fig. 1. Living oligomerizaton of isobutylene using cumyl chloride as initiator (HPLC)

While Figure 1 presents a snapshot during the oligomerization process, the product composition at various reaction times is summarized in Figure 2, which clearly shows that the reaction of the [1:1]-product **P1** is the bottle neck of this reaction cascade. Its reaction with isobutylene is considerably slower than the reactions of cumyl chloride and of the higher adducts **P2**, **P3** ... with isobutylene, and for that reason, we have not been able to produce telechelics with a narrow molecular weight distribution in this way. At a reaction time of 64 min (Figure 2) one calculates $M_w = 345$ and $M_n = 290$, yielding $M_w/M_n = 1.19$.

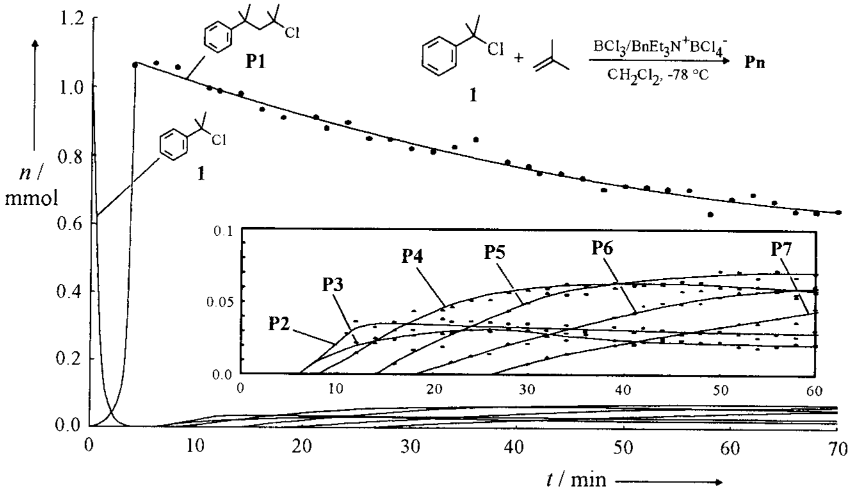
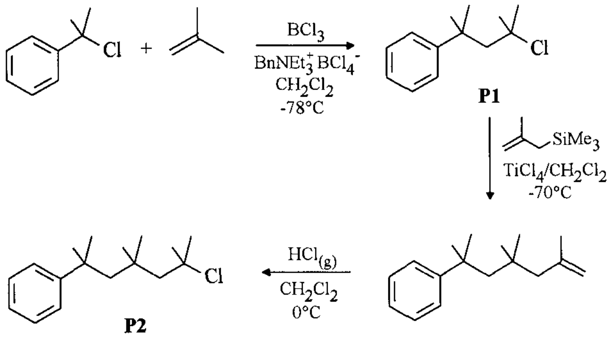


Fig. 2. Product distribution during the living oligomerization of isobutylene (Ref. 4)

One way to overcome this problem and to obtain oligomers with narrow MWD is to bypass the bottle neck by using the [2:1]-product **P2** as the initiator instead of cumyl chloride. However, as one can easily see from Figure 2, it is impossible to synthesize **P2** in fair yield from the Lewis acid catalyzed reaction of cumyl chloride with isobutylene since its stationary concentration remains low throughout the reaction.

We have therefore used the allylsilane method for its selective synthesis. While the [1:1]-product **P1** can selectively be obtained from cumyl chloride and isobutylene, as mentioned above, the reaction of **P1** with (2-methylallyl)trimethylsilane and subsequent hydrochlorination gave the [2:1]-product **P2** in excellent yield (Scheme 2, Ref. 4).



Scheme 2. Synthesis of the initiator **P2**

The chromatogram depicted in Figure 3 illustrates that our hypothesis proved to be correct: With **P2** as the initiator we observe a single maximum in the molecular weight distribution, which continuously moves to higher molecular weight as the reaction time increases. The ratio $M_w/M_n = 1.03$ corroborates that it is indeed possible to produce telechelics with a very narrow molecular weight distribution in this way. Furthermore, the continuous growth of the molecular weight proves that under these conditions dormant species are regenerated after each addition of a monomer unit.

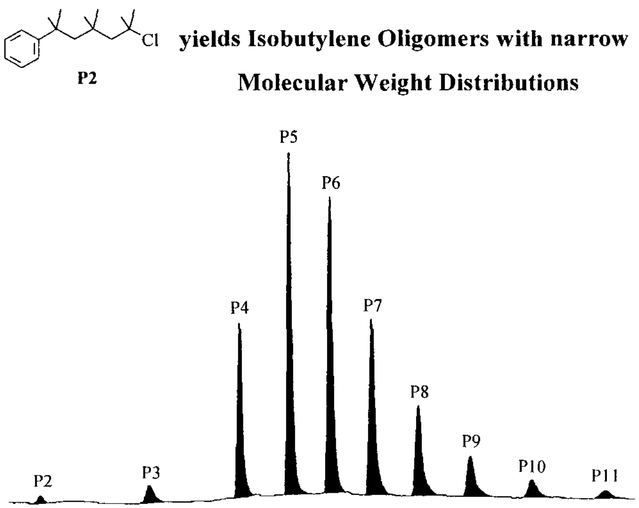
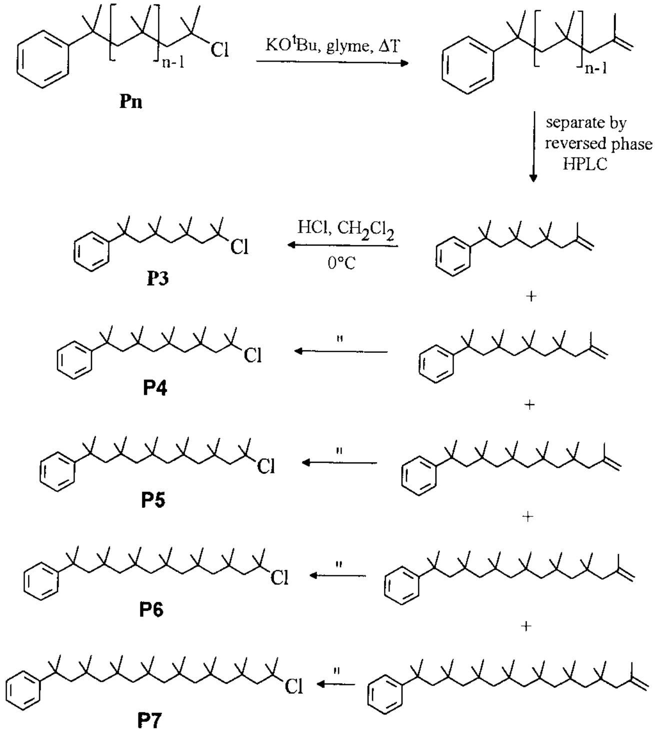


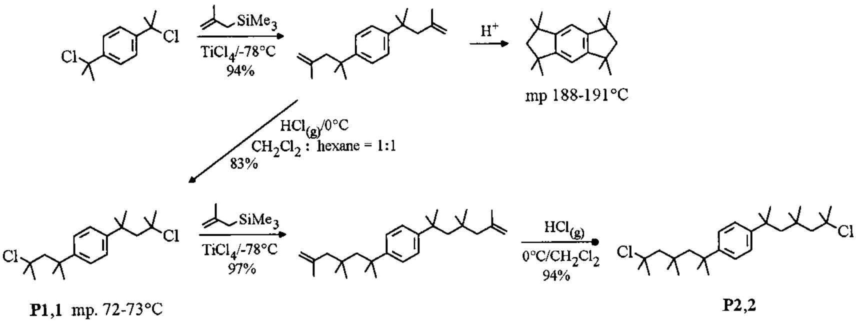
Fig. 3. Living oligomerization of isobutylene initiated by the [2:1]-product **P2** ($BCl_3/BnEt_3N^+BCl_4^-/CH_2Cl_2$/-78°C, analysis by HPLC)

Organic chemists like us traditionally want to have analytically pure compounds, and so we have tried to isolate the individual compounds from this mixture. Under the conditions used for the preparative HPLC separations partial elimination took place, however, and we were not able to isolate the individual oligomers. We, therefore, treated the mixture of tertiary alkyl chlorides prepared as shown in Figure 3 with potassium *tert*-butoxide and obtained a mixture of terminal alkenes (Scheme 3) which could be separated by HPLC. Subsequent treatment of the individual olefins with HCl yielded the analytically pure monodisperse telechelics **P3** - **P7**, each of which was completely characterized by its ^1H and ^{13}C NMR spectra (Ref. 4).



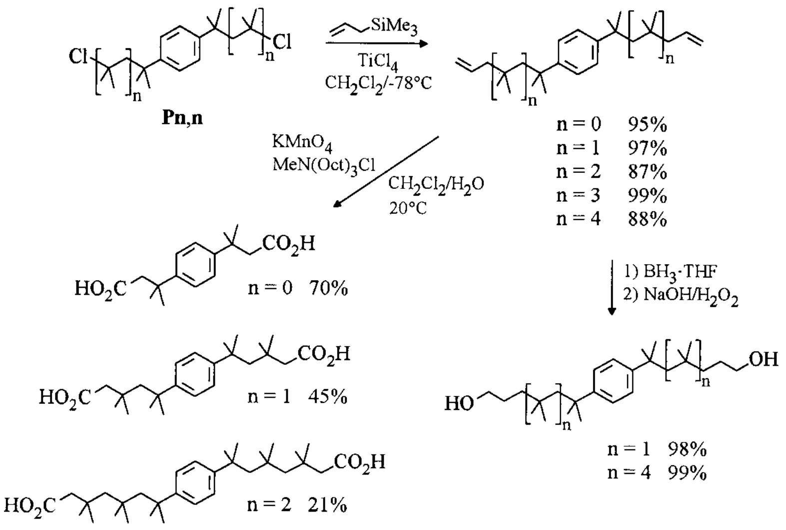
Scheme 3. Isolation of analytically pure monodisperse telechelics by consecutive elimination, separation, and hydrochlorination of the initial oligomer mixture

The possibility to produce telechelics with very narrow molecular weight distribution is of special interest for bifunctional compounds which may serve as building blocks in polycondensation reactions (Ref. 1). Since in the case of the biscumyl chloride initiated isobutylene oligomerizations, compound **P1,1** was expected to be the bottle neck of the reaction sequence (in analogy to **P1**, Figure 2), a similar procedure as before was used to synthesize **P2,2**, the counterpart of **P2** in the cumyl case (Scheme 4). In analogy to **P2**, the initiator **P2,2** can be expected to give rise to a narrow molecular weight distribution.



Scheme 4. Synthesis of the bifunctional initiator **P2,2**

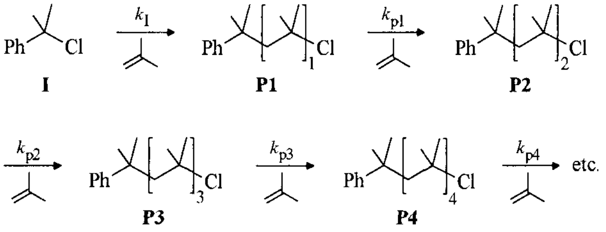
When the monodisperse telechelics **Pn,n** (n = 2-5) produced by repetition of the procedure described in Scheme 4 were treated with allyltrimethylsilane, terminal alkenes were obtained



Scheme 5. Functionalization of the telechelic dichlorides **Pn,n**

in almost quantitative yield (Scheme 5). The oxidation of the terminal double bonds under phase transfer conditions caused problems, however. While the diene with n = 0 was converted into the dicarboxylic acid with 70 % yield, the homologous dicarboxylic acid with n = 2 was obtained in only 21% yield. In contrast, hydroboration worked well even with the compound derived from **P4,4** (Scheme 5).

Let us now turn to a quantitative description of the dependence of the gross propagation rates on the length of the oligomer. For the time-dependent concentration of the oligomer **P3**, for example, we write the differential equation given in Scheme 6, which represents the difference between the rate of formation and the rate of consumption. At the maximum concentration of **P3** (d[**P3**]/dt = 0), the ratio of the gross constants for consumption and



$$\frac{d[\mathbf{Pn}]}{dt} = k_{p(n-1)}[\mathbf{P(n\text{-}1)}]\text{-}k_{p(n)}[\mathbf{Pn}]\ ;\quad \text{e.g.,}\ \frac{d[\mathbf{P3}]}{dt} = k_{p2}[\mathbf{P2}]\text{-}k_{p3}[\mathbf{P3}]$$

At concentration maximum:

$$\frac{d[\mathbf{Pn}]}{dt} = 0 \qquad \text{e.g.,}\ \frac{d[\mathbf{P3}]}{dt} = 0$$

$$\frac{k_{p(n)}}{k_{p(n-1)}} = \frac{[\mathbf{P(n\text{-}1)}]}{[\mathbf{Pn}]_{max}} \qquad \text{e.g.,}\ \frac{k_{p3}}{k_{p2}} = \frac{[\mathbf{P2}]}{[\mathbf{P3}]_{max}}$$

$\frac{k_{p1}}{k_I}$	$\frac{k_{p2}}{k_{p1}}$	$\frac{k_{p3}}{k_{p2}}$	$\frac{k_{p4}}{k_{p3}}$	$\frac{k_{p5}}{k_{p4}}$	$\frac{k_{p6}}{k_{p5}}$	$\frac{k_{p7}}{k_{p6}}$	$\frac{k_{p8}}{k_{p7}}$	$\frac{k_{p9}}{k_{p8}}$
small	20-35	1.24	0.59	0.79	0.95	1.0	1.0	1.0

Scheme 6. Determination of the relative rates of the propagation steps. - $k_{p(n)}$ are gross propagation constants for a given concentration of monomer and of Lewis acid; they include the ionization constants K_i as well as the rate constants k for the reactions of the carbocations with the monomers.

formation is given by the ratio of the concentration of the lower homologue **P2** and the concentration of **P3** (=$[\mathbf{P3}]_{max}$) at this moment. In this way, Figure 4 can be evaluated to give the reactivity ratios k_{p3}/k_{p2} to k_{p8}/k_{p7}, which are listed on the bottom of Scheme 6.

It can be seen that these rate constants are not at all identical. At the maximum of [**P4**] and [**P5**], for example, the concentration of these oligomers is considerably higher than the corresponding concentration of their precursors, indicating that the rate constants of their formations are greater than the rate constants of their consumptions. Only when we go to higher oligomers as **P7** or **P8**, we find the crossings with the graphs of their precursors at their maximum concentration, indicating identical rate constants for their formation and consumption. In other words, for **P7** and the higher oligomers, the gross propagation constant becomes independent of the chain length.

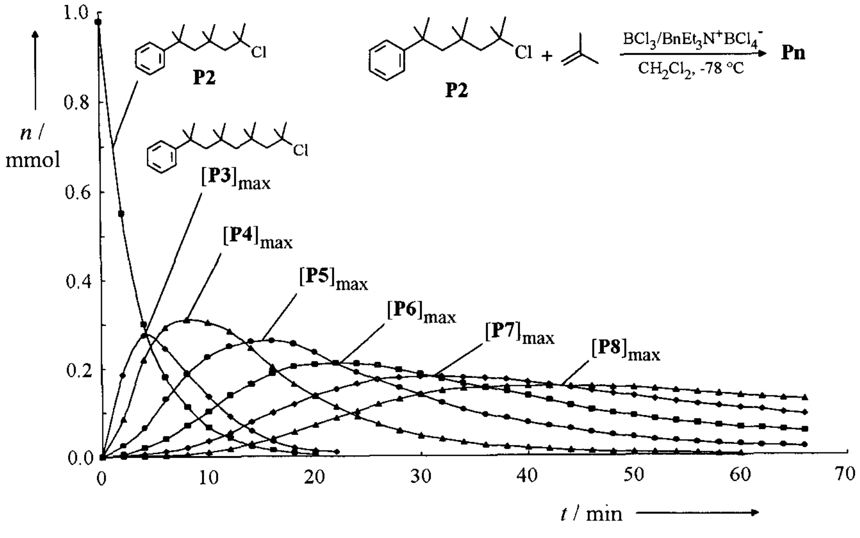
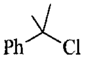
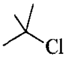
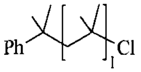
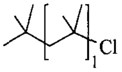
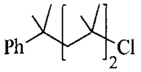
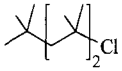
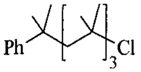
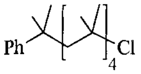
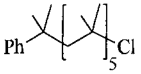
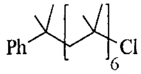
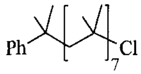
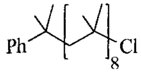


Fig. 4. Time-dependent product distribution in the living oligomerization of isobutylene initiated by **P2**/BCl_3 in presence of $BnEt_3N^+BCl_4^-$ in CH_2Cl_2 at -78°C (Ref. 4)

Because of the very broad maximum of **P2** in Figure 2, the ratio k_{p2}/k_{p1} can only be derived roughly as 20-35, and from the fact that cumyl chloride has disappeared when **P1** reaches maximum concentration, we derive $k_{p1}/k_I \approx 0$.

Let us now consider the propagation rates of the long chain oligomers (≥ **P7**) as reference (k_{rel} = 1.00) and use the reactivity ratios listed on the bottom of Scheme 6 to calculate the relative reactivities of the lower oligomers. The k_{rel} values thus obtained (Table 1) show that the oligomers **P2** and **P3** are about two-fold as reactive as the long chain oligomers, and that the [1:1]-product **P1** is considerably less reactive.

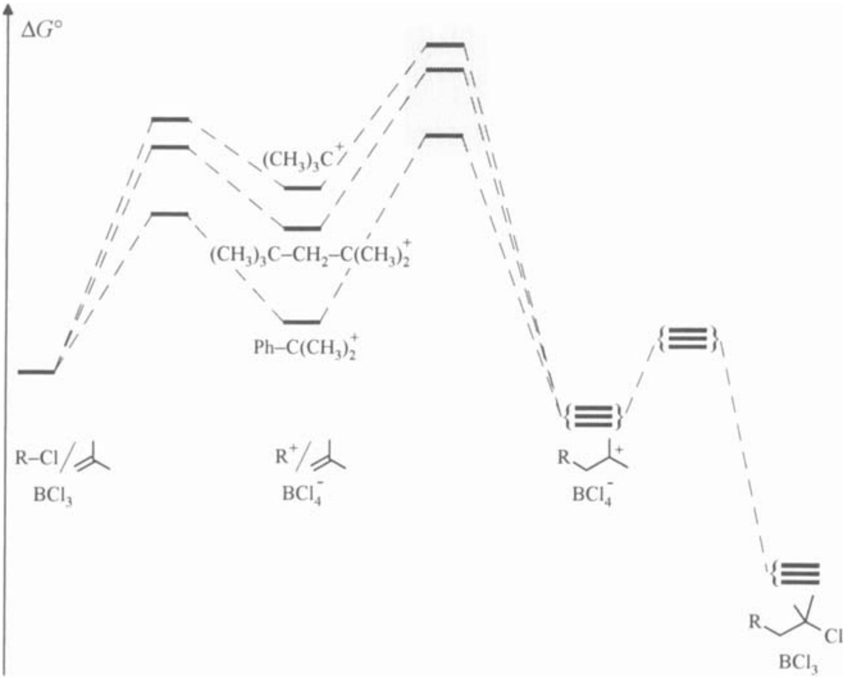
Table 1. Relative reactivities of tertiary alkyl chlorides towards isobutylene (-78°C, CH_2Cl_2, BCl_3, $BnEt_3N^+BCl_4^-$) and relative solvolysis rate constants (EtOH/H_2O = 80/20, 50°C)

		k_{rel}	k_{solv}			k_{rel}	k_{solv}
	**I**	very high	120		**I'**	very low	0.07
	**P1**	0.05-0.09	= 1.0		**(P1')**	0.31	1.2
	**P2**	1.82	2.0		**(P2')**	0.82	
	**P3**	2.26	2.1				
	**P4**	1.33	1.8				
	**P5**	1.05	1.5				
	**P6**	1.00					
	**P7**	1.00					
	**P8**	= 1.00					

Is the dependence of the propagation rates on the chain length only observed if there is a phenyl group at the head of the chain? It is generally known that *tert*-butyl chloride is a very inefficient initiator for the BCl_3 catalyzed polymerization of isobutylene while diisobutylene hydrochloride (**P1'**) and triisobutylene hydrochloride (**P2'**) work well (Ref. 1, 7, 8). Direct rate measurements have shown that triisobutylene hydrochloride (**P2'**) is almost as reactive as the long chain oligomers on the left of Table 1 (Ref. 9). In the same way, k_{rel} of diisobutylene hydrochloride (**P1'**) was found to be 0.31, indicating that **P2'** and **P1'** differ much less in reactivity than **P2** and **P1**. As a result, the **P1'** initiated living oligomerization of isobutylene can be expected to give a narrower molecular weight distribution than the processes initiated by cumyl chloride or **P1**. Yet, in order to get very narrow molecular weight distribution, it is preferable to use triisobutylene hydrochloride (**P2'**) instead of diisobutylene hydrochloride (**P1'**) as the initiator.

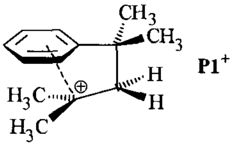
What is the origin of the different reactivities? For the BCl_3-initiated reactions of alkyl chlorides with alkenes, energy profiles as depicted schematically in Scheme 7 have been elaborated (Ref. 2, 3). Since the ionization step is reversible in presence of a high concentration of BCl_4^-, the rate determining step corresponds to the attack of R^+ at the olefin. According to the Curtin-Hammett principle (Ref. 10, 11), it is the relative height of these transition states (shaded area) with respect to the reactants (RX, BCl_3, isobutylene) which controls the relative reactivities. Since the carbocationic character of R^+ has not completely disappeared in these transition states, their ordering will be the same as that of the carbocations R^+ (Ref. 12).

It can thus be explained that cumyl chloride is more reactive than the two *tert*-alkyl chlorides in Scheme 7, because phenyl stabilization of the positive charge in the cumyl cation is more efficient than alkyl stabilization in the tertiary alkyl cations. The greater release of steric strain during ionization of $(CH_3)_3C\text{-}CH_2\text{-}C(CH_3)_2Cl$ compared to $(CH_3)_3CCl$ has been shown to be responsible for the faster ionization rate of the former in solvolysis reactions (Ref. 13-15). Though more steric strain will be regenerated during the reaction of isobutylene with $(CH_3)_3C\text{-}CH_2\text{-}C(CH_2)_2^+$ than with $(CH_3)_3C^+$, the higher overall reactivity of diisobutylene hydrochloride indicates that this effect plays a minor role and that the relative rates of the alkylations of the alkenes are still controlled by the relative stabilities of R^+ with respect to their precursors.



Scheme 7. Schematic free enthalpy profiles for the BCl_3 initiated reactions of alkyl chlorides with isobutylene

S_N1 solvolysis rates can, therefore, be used to generally predict the order of reactivities in alkylation reactions (Ref. 16). While we do not know the reason for the extraordinarily low reactivity of **P1** and the relatively high reactivities of **P2** and **P3** in alkylation reactions, it should be noted that the same order of reactivities, though attenuated, is observed in the solvolysis reactions of the corresponding alkyl chlorides (k_{solv}, Table 1). If the intramolecular stabilization of the carbocation **P1**$^+$ as shown in Scheme 8 (Ref. 17) were responsible for the low reactivity of **P1**, one had to postulate that this interaction which stabilizes **P1**$^+$ at the same time destabilizes the flanking transition states, contrary to the situation in all other systems. Alternatively one might assume that the inductive effect of the phenyl group in **P1**$^+$ causes a destabilization of **P1**$^+$ and of both flanking transition states (Scheme 8). Though this model qualitatively accounts for the observed low solvolysis and alkylation rates, it cannot explain



Scheme 8. Intramolecular stabilization of the cation **P1**$^+$?

the widely different magnitude of the effect in the two reactions. We, therefore, leave the rationalization for the unexpectedly low reactivity of **P1** open for further discussion.

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