The role of chain transfer processes in inifer/boron trichloride initiated polymerizations of isobutene

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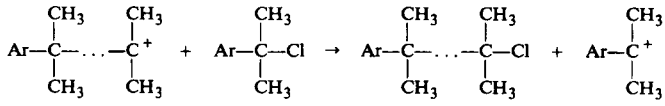
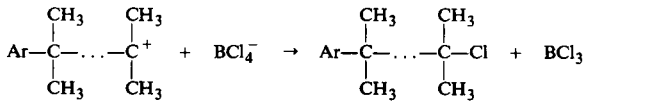
Introduction

Kennedy et al. have introduced mixtures of mono- or polyfunctional aralkyl chlorides with BCl_3 as initiating systems for the polymerization of isobutene[1]. This so-called inifer technique has been demonstrated to be a valuable method for the production of telechelic polymers[2]. The mechanism of initiation, which has been suggested for these polymerizations[1,2], is in full agreement with the results of our model studies[3]. The growth of the polyisobutene chain may be interrupted either by chain transfer to inifer [Eq. (1)] or by the termination step shown in Eq. (2)[1,2].



(1)



(2)

The decrease of $\overline{P}_n$ with increasing inifer concentration in polymerizations of isobutene initiated by 1,4-bis(1-chloro-1-methylethyl)benzene/BCl_3 in CH_3Cl has been used as an argument for the operation of both mechanisms. Process (1) has been suggested to be predominant at inifer concentrations >5 mmol $\cdot$ l^{-1} [1b]. This analysis, however, was based on the assumption that only paired ions are present in the reaction mixture. If ion-pair dissociation is taken into account, a similar $\overline{P}_n$ vs. [Inifer] relationship is also expected in the absence of the chain transfer process (1): Now the rate of termination (2) will depend on $[BCl_4^-]$, which increases with increasing inifer concentration. The model study presented in this paper suggests that the termination step (2) is more important than chain transfer to inifer.

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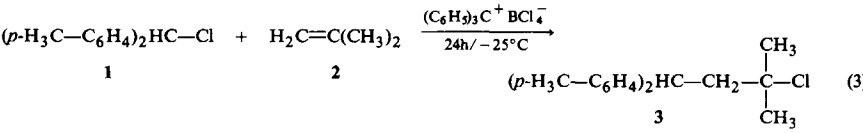
Results and discussion

In the preceding paper[4] we have demonstrated that trityl salts may act as co-initiators of carbocationic polymerizations. Trityl tetrachloroborate, for example, catalyzes the formation of adduct **3** from di-*p*-tolylmethyl chloride (**1**) and isobutene (**2**).

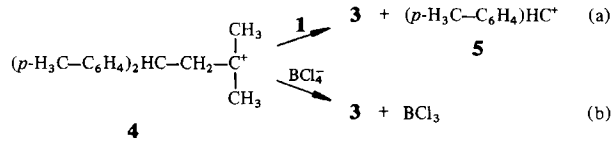


$$(p\text{-}H_3C\text{—}C_6H_4)_2HC\text{—}Cl \quad + \quad H_2C{=}C(CH_3)_2 \xrightarrow[24h/-25°C]{(C_6H_5)_3C^+\,BCl_4^-} (p\text{-}H_3C\text{—}C_6H_4)_2HC\text{—}CH_2\text{—}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{—}Cl \qquad (3)$$

1 **2** **3**

In analogy to Eqs. (1) and (2), adduct **3** might be formed via Cl^- transfer to cation **4** from either **1** [path(a)] or BCl_4^- [path(b)], (*Scheme 1*). If pathway (a) were responsible for the formation of compound **3**, replacement of the counter ion in the trityl salt should not affect the outcome of the reaction[3b].

Scheme 1:



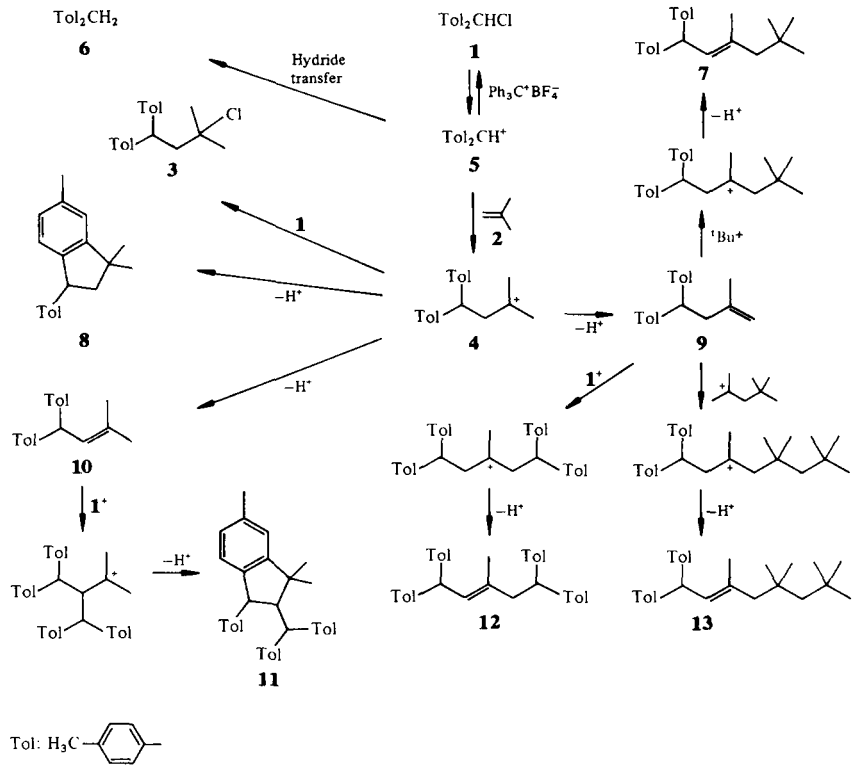
$$(p\text{-}H_3C\text{—}C_6H_4)_2HC\text{—}CH_2\text{—}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}} \quad \begin{matrix} \xrightarrow{\mathbf{1}} \; \mathbf{3} + (p\text{-}H_3C\text{—}C_6H_4)HC^+ \quad (a) \\ \qquad\qquad\quad \mathbf{5} \\ \xrightarrow{BCl_4^-} \; \mathbf{3} + BCl_3 \quad (b) \end{matrix}$$

4

A complex mixture of products was observed, however, when the reaction of **1** with **2** was catalyzed with trityl tetrafluoroborate (*Scheme 2*). In contrast to the trityl tetrachloroborate catalyzed reaction, only a small amount of compound **3** is formed under these conditions, probably via chloride transfer from **1** to **4**. Obviously, a rapid conversion of **4** into **3** is impossible in the absence of BCl_4^-, and the high yield of **3**, observed in the trityl tetrachloroborate catalyzed reaction must be due to Cl^- transfer from BCl_4^- [path(b) in Scheme 1]. Because of the lower nucleophilicity of BF_4^-, fluoride transfer does not take place, and cation **4** undergoes a variety of sequential reactions, if an efficient trapping agent is absent (*Scheme 2*).

How do the two chloride transfer processes (a), (b) in *Scheme 1* compare with the related reactions (1) and (2)? Reactions (2) and (b) (*Scheme 1*) involve Cl^- transfers from BCl_4^- to tertiary carbenium ions and can be assumed to be equally fast. The thermodynamic driving force of Eq. (1) will depend on the nature of Ar. From Arnett's calorimetric investigations in superacidic media one can derive that the ionization of di-*p*-tolylmethyl chloride (**1**) to give $\mathbf{1}^+$ is more exothermic by 6,7 kJ/mol than the corresponding formation of the cumyl cation ($Ph\text{—}C(CH_3)_2^+$) from cumyl chloride[5]. This result is in accord with the finding that **1** (k_1 (25 °C) =

Scheme 2:



$2{,}0 \cdot 10^{-2}\ s^{-1}$)[6] solvolyzes 50 times faster in ethanol than cumyl chloride [k_1 (25 °C) = $3{,}9 \cdot 10^{-4}\ s^{-1}$][7]. Since solvolysis rates have been shown to be linearily correlated with the thermodynamic stability of the resulting carbenium ions[8], both comparisons indicate that reaction (1) (Ar = Ph) has a smaller thermodynamic driving force than reaction (a) (*Scheme 1*) and should, therefore, be slower. The preference of (b) over (a) (*Scheme 1*), therefore, implies that chain transfer from cumyl chloride to a tertiary carbenium ion [Eq. (1), Ar = Ph] is negligible compared to the termination step [Eq. (2)].

Substituent constants close to zero have been reported for α-chloroalkyl groups[9], which implies that the thermodynamic driving force of Eq. (1) should be similar for inifer (cumyl chloride), binifer and trinifer systems. We, therefore, conclude that also in these systems the termination step (2) is more important than chain transfer to initiator [Eq. (1)].

Experimental part

General: See preceding paper[4].

Trityl tetrafluoroborate catalyzed reaction of p-tolylmethyl chloride (**1**) *with isobutene* (**2**). *Experiment 1:* Compound **1** (2,39 g; 10,4 mmol) and trityl tetrafluoroborate[10] (0,50 g; 1,51 mmol) were dissolved in 200 ml of CH_2Cl_2, cooled at −29 °C, and isobutene (**2**) (240 ml; 11 mmol) was added with a gastight syringe. The mixture was kept at −29 °C for 18 h, water was added, and the organic layer was dried over $CaCl_2$. The product, obtained after removal of CH_2Cl_2, was dissolved in pentane and filtered over a silica gel 60 column (diameter: 0,6 cm, length: 1 cm) to remove oligomeric material. After evaporation of the solvent i. vac., the residue was separated by medium pressure liquid chromatography (Merck Lichroprep Si 60 RP-18) (Tab. 1).

Experiment 2: In a second experiment 2,50 g (10,8 mmol) of **1** was reacted with **2** at −25 °C in the same way. Instead of silica gel 60, active charcoal was used for purification of the crude material (Tab. 1).

3-Chloro-3-methyl-1,1-di-p-tolylbutane (**3**) has been characterized previously[6].

3,5,5-Trimethyl-1,1-di-p-tolyl-2-hexene (**7**) *(probably (E)-isomer):* ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0,88 (s; 9H, $C(CH_3)_3$), 1,72 (br. s; 3H, 3-CH_3), 1,96 (s; 2H, 4-H), 2,28 (s; 6H, Ar-CH_3), 4,77 (d; J = 9,0 Hz, 1H, 1-H), 5,54 (br. d; J = 9,0 Hz, 1H, 2-H), 7,04 (s; 8H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 19,3 (q; 3-CH_3), 21,1 (q; Ar-CH_3), 30,3 (5-CH_3, C-6), 32,1 (s; C-5), 49,0 (d; C-1), 53,8 (t; C-4), 128,2, 129,1 (2d; Ar-H), 131,4 (d; C-2), 134,1 (s; C-3), 135,4 (s; para-C), 142,4 (s; ipso-C).

MS (70 eV): m/z = 307, 306 (8%, 31%, M^+), 236 (20), 235 (100), 195 (28), 157 (28), 143 (26), 105 (41), 57 (26).

3,3,5-Trimethyl-1-p-tolylindane (**8**): Colorless needles; m.p. 70 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1,24 (s; 3H, 3-CH_3), 1,39 (s; 3H, 3-CH_3), 1,93 (dd; J = 12,5 Hz and 10,0 Hz, 1H, 2-H), 2,36 (dd; J = 12,5 Hz and 7,5 Hz, 1H, 2-H), 2,34, 2,36 (2s; 6H, Ar-CH_3), 4,36 (br. dd; J = 10 Hz and 7,5 Hz, 1H, 1-H), 6,77, 6,95 (br. AB-system; J_{AB} = 7,8 Hz, 2H, 6-H, 7-H), 7,01 (br. s; 1H, 4-H), 7,12 (s; 4H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 21,0, 21,4, (2q; Ar-CH_3), 28,6, 29,0 (2q; 3-CH_3), 42,9 (s; C-3), 48,2 (d; C-1), 53,1 (t; C-2), 122,5 (d; C-7), 124,6 (d; C-4), 127,3 (d; C-6), 128,2 (d; ortho-C), 129,1 (d; meta-C), 135,7, 136,4 (2s; C-5, para-C), 142,2, 142,7 (2s; C-8, ipso-C), 152,8 (s; C-9).

Tab. 1. Reaction products isolated by means of MPLC, and retention times (t_R)

Compound	Experiment 1		Experiment 2	
	t_R /min[a]	yield in mg (in %)	t_R /min[b]	yield in mg (in %)
(p-CH_3—C_6H_4)$_2$CH—OCH_3	11,5	295 (12,5)	11,3	121 (5,0)
$(C_6H_5)_3C$-OCH_3	13,2	114	12,1	Not determ.
6	15,7	62 (3,0)	—	—
3	17,5	157 (5,3)	13,4	105 (3,4)
10	20,3	316 (12,1)	14,9	224 (8,3)
8	25,4	230 (8,8)	18,6	162 (6,0)
7	33,0	84 (2,6)	20,4	37 (1,1)
12	—	—	25,0	165 (6,9)
11	37	256 (11,1)	27,3	158 (6,6)
13	37	83 (2,2)	—	—

[a] CH_3OH/H_2O (vol. ratio: 95/5).
[b] CH_3OH.

MS (70 eV): m/z = 250 (47%, M^+), 236 (19), 235 (100), 206 (5), 143 (31), 128 (10), 105 (13), 91 (4).

3-Methyl-1,1-di-p-tolyl-2-butene (**10**): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1,71, 1,77 (2 br. s; 6H, CH_3), 2,31 (s; 6H, Ar-CH_3), 4,82 (d; J = 9,6 Hz, 1H, 1-H), 5,59 (br. d; J = 9,6 Hz, 1H, 2-H), 7,08 (s; 8H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 18,0, 25,9, (2q; C-4, 3-CH_3), 21,0 (q; Ar-$\underline{C}H_3$), 48,6 (d; C-1), 127,6 (d; C-2), 128,1, 129,0 (2d; ortho, meta-C), 132,0 (s; C-3), 135,4 (s; para-C), 142,4 (s; ipso-C).

IR (KBr): 3116, 3012, 2885 (CH), 1509 (C=C), 1444 (CH_3-def.), 1374, 1182, 1035, 887, 828, 802 (out of plane), 762 cm^{-1}.

MS (70 eV): m/z = 251, 250 (16%, 75%, M^+), 235 (100, $M^+ - CH_3$), 159 (12), 143 (70), 128 (17), 105 (33), 91 (17).

3,3,5-Trimethyl-2-di-p-tolylmethyl-1-p-tolylindane (**11**): Colorless needles; m.p. 178 – 179 °C (pentane).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1,11 (s; 3H, 3-CH_3), 1,18 (s; 3H, 3-CH_3), 2,12, 2,22, 2,26, 2,30 (4s; 12H, Ar-CH_3), 3,37 (dd; $J_{2,1}$ = 9,4 Hz, $J_{2,10}$ = 11,4 Hz, 1H, 2-H), 3,85 (d; J = 9,4 Hz, 1H, 1-H), 4,05 (d; J = 11,4 Hz, 1H, $C\underline{H}Ar_2$), 6,40 – 7,32 (m; 15H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 20,8, 21,0 (double int.), 21,4, (3q; Ar-$\underline{C}H_3$), 25,7, 29,7 (2q; 3-CH_3), 46,3 (s; C-3), 54,7, 54,8 (2d; C-1, $\underline{C}HAr_2$), 62,5 (d; C-2), 122,0 (d; C-7), 124,7 (d; C-4), 127,5 (d; C-6), 128,05, 128,14, 128,3, 128,9 (4d), 133,9, 134,9, 135,5, 136,2 (4s; para-C), 141,2 141,8, 142,8, 143,0 (4s; ipso-C), 152,6 (s; C-9).

MS (70 eV): m/z = 445, 444 (3%, 10%, M^+), 250 (9), 249 (44), 248 (11), 205 (17), 196 (53), 195 (100), 105 (10).

3-Methyl-1,1,5,5-tetra-p-tolyl-2-pentene (**12**) *(probably (E)-isomer):* Slightly contaminated oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1,68 (br. s; 3H, 3-CH_3), 2,28, 2,32 (2s; 12H, Ar-CH_3), 2,77 (d; J = 7,8 Hz, 4-H_2), 4,12 (t; J = 7,8 Hz, 5-H), 4,70 (d; J = 9,6 Hz, 1H, 1-H), 5,42 (d; J = 9,6 Hz, 1H, 2-H), 6,70 – 7,16 (m; 16H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 16,3 (q; 3-CH_3), 21,00, 21,03 (2q; Ar-CH_3), 46,2 (t; C-4), 48,3, 48,4 (2d; C-1, C-5), 127,8, 128,1, 128,8, 129,9 (4d; ortho-C, meta-C), 130,5 (d; C-2), 133,1 (s; C-3), 135,2, 135,4 (2s; para-C), 141,9, 142,0 (2s; ipso-C).

3,5,5,7,7-Pentamethyl-1,1-di-p-tolyl-2-octene (**13**) *(probably (E)-isomer):* Slightly contaminated oil.

^{1}H NMR (90 MHz, $CDCl_3$): δ = 0,95 (s; 9H, $C(CH_3)_3$), 0,96 (s; 6H, 5-CH_3), 1,38 (s; 2H, 6-H), 1,73 (s; 3H, 3-CH_3), 2,04 (s; 2H, 4-H), 2,28 (s; 6H, Ar-CH_3), 4,81 (d; J = 9Hz, 1H, 1-H), 5,59 (br. d; J = 9Hz, 1H, 2-H), 7,06 (s; 8H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 19,5 (q; 3-CH_3), 21,0 (q; Ar-CH_3), 29,1 (q; 5-CH_3), 32,2 (q; ^{t}Bu), 32,3 (s; C-5), 36,5 (s; C-7), 48,9 (d; C-1), 55,4, 55,7 (2t; C-6, C-4), 128,1, 129,0 (2d; ortho-C, meta-C), 132,0 (d; C-2), 133,8 (s; C-3), 135,3 (s; para-C), 142,3 (s; ipso-C).

MS (70 eV): m/z = 363, 362, (5%, 16%, M^+), 250 (23), 235 (40), 195 (24), 159 (17), 157 (26), 133 (61), 105 (34), 57 (100).

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