Polymerization of isobutylene initiated by *tert*-butyl chloride–boron trichloride. Synthesis of α-*tert*-butyl-ω-chloropoly(isobutylene) and α-*tert*-butyl-ω-isopropenylpoly(isobutylene)

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(*Received 3 September 1985; revised 10 February 1986*)

The initiation-transfer effect of t-BuCl on the polymerization of isobutylene in presence of BCl_3 in a CH_2Cl_2 solution at $-20°C$ was investigated. Kinetic measurement has revealed that the initiation rate r_0 is proportional to $[BCl_3][\text{t-BuCl}]^{0.58}$. The defined structure of the α-*tert*-butyl-ω-chloro-poly(isobutylene) (t-Bu-PIB-Cl) determined by ^1H n.m.r. indicated a minimal transfer to monomer, attributed to the complex [t-BuCl.BCl_3]. By dehydrochlorination of t-BuPIB-Cl samples, α-*tert*-butyl-ω-isopropenylpoly(isobutylene) was prepared.

(**Keywords: isobutylene; polymerization initiated by *tert*-butyl chloride–BCl_3**)

INTRODUCTION

Boron trichloride, along with BF_3, $TiCl_4$, $TiBr_4$ and $SnCl_4$, was included in the group of Lewis acids that require the presence of a protogenic compound to initiate the polymerization of isobutylene. The non-reactivity of boron trichloride for isobutylene in the absence of a protogenic compound was described by Plesch[1] as early as 1947, and later by other specialists in the field of cationic polymerization[2,3]. The study of the initiation of the polymerization of isobutylene by boron trichloride was neglected by comparison with study of other Lewis acids, probably due to its weak initiation activity, mentioned above. In the late nineteen-seventies, however, Kennedy and co-workers detected the ability of some aralkyl halides to initiate polymerization of isobutylene in the presence of BCl_3. The aralkyl halides used were, for example, 2-chloro-2-propylbenzene[4], 1,4-bis(2-chloro-2-propyl)benzene[5,6], 1,3-bis(2-chloro-2-propyl)-5-*tert*-butylbenzene[7], 1,3,5-tris(2-chloro-2-propyl)benzene[8], or 1,3,5-tris(2-bromo-2-propyl)benzene[9]. This initiation system was then used in the Inifer techniques for the preparation of telechelic polymers of isobutylene[5–9]. At this point it should be stressed, however, that unlike the aralkyl-halides–BCl_3 system, which strongly initiates the polymerization of isobutylene, it has been reported that the system RCl–BCl_3, where RCl is t-BuCl, is not capable[3,10–12] of initiating the polymerization of isobutylene. In 1983 Kennedy *et al.*[13] proved the initiation-transfer effect of 2,5-dichloro-2,5-dimethylhexane on the polymerization of isobutylene in the presence of BCl_3 in CH_2Cl_2. Later Nuyken[12] described the initiation of isobutylene by the systems 2-chloro-2,4,4-trimethylpentane/BCl_3 and α,ω-dichloropoly(isobutylene)–BCl_3. Although the unreactivity of the system t-BuCl–BCl_3–isobutylene has been described in the literature, this study reports a new detailed investigation of this system. The ability of t-BuCl to initiate the polymerization of isobutylene in the presence of BCl_3 is the basic finding, allowing us to explain the initiation reaction using other aliphatic halides that contain a chlorine atom bound to the tertiary carbon atom in their molecule.

EXPERIMENTAL

Chemicals

Isobutylene, 99.8% purity, was dried by standing it over sodium wire in a pressure glass ampoule for a week. Dichloromethane was dried by standing it for a week over CaH_2, refluxing for 48 h over CaH_2, and after that distilling off in a column under nitrogen while excluding all light. Tetrahydrofuran was dried by shaking with KOH, distillation and refluxing with $LiAlH_4$ under nitrogen. t-BuCl (Fluka) was dried by standing it for a week over CaH_2 and distillating in vacuum before use. BCl_3 (Merck) and *tert*-potassium butoxide (Janssen) were used as supplied. Nitrogen was freed from traces of oxygen on a deoxidation catalyst and dried by passage through columns with molecular sieves (Potasit 3) and columns packed with NaH. The moisture content in nitrogen and isobutylene measured with a Shaw hygrometer varied in the range 1–3 ppm. α-t-Butyl-ω-isopropenylpoly(isobutylene) was prepared by the dehydrochlorination of t-Bu-PIB-Cl samples in THF by t-BuOK using the method described in ref. 14.

Polymerization techniques

Initiation of the polymerization of isobutylene was brought about by employing two procedures: the reaction

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components t-BuCl–BCl_3 were instantaneously mixed with the monomer in CH_2Cl_2 at $-20°C$ (conventional mode), or the mixture t-BuCl–BCl_3–CH_2Cl_2 prepared in advance at $-20°C$ was heated to room temperature and stirred. After a certain time this mixture was cooled to $-20°C$ and added to a solution of isobutylene in CH_2Cl_2 thermostatically controlled to $-20°C$; this second procedure was denoted as the polymerization by complex. The polymerizations were investigated by the gravimetric and dilatometric methods at $-20 \pm 0.1°C$. For the former method, the polymerizations were made in an all-glass reactor, 100 ml in volume, provided with a stirrer and a three-way cock to ensure dosage of the components in a stream of nitrogen. For the latter, dilatometers 10 ml in volume were used. Interaction of the reaction components (t-BuCl with BCl_3 in CH_2Cl_2) took place in ampoules 5, 10 and 20 ml in volume. The dilatometers and ampoules were provided with a tight three-cock Teflon closure for closing and dosage of the reaction components in a stream of nitrogen. The reactors, dilatometers and ampoules were dried *in vacuo* with simultaneous heating by a direct luminous flame. The polymerizations were terminated by adding methanol; after evaporation of heavy volatile fractions, the polymer was dried in a vacuum drying box at room temperature for one week. All dosage, stirring and polymerizations proceeded under nitrogen with absolute exclusion of moisture.

Analysis

Spectrophotometric measurements of the mixtures t-BuCl–BCl_3 and t-BuCl–BCl_3–CH_2Cl_2 were made at 25°C in Hellma quartz cells, 1 mm and 10 mm, adjusted for the dosage of the components in a stream of nitrogen by means of a Teflon three-way closure. Drying of the cells and dosage of the reaction components were achieved by employing the same techniques as for dilatometers and reactors. To check the u.v. and visible spectra of the samples in the cells provided with the Teflon closure, the same measurements of the samples were made in sealed cells. In both cases the same spectrum was obtained.

The measurements were made by using a Hewlett-Packard HP-8451 A apparatus. This diode array spectrophotometer allowed a fast (0.1 s) recording of complete spectra in the range 190–820 nm and presentation of the results in an arbitrary range of given wavelengths.

Gel permeation chromatography (g.p.c.)

The lower-molecular weight polymer was characterized by using the high-speed g.p.c. method. An HP-1084 B (Hewlett-Packard, USA) liquid chromatograph was provided with a separation system consisting of two stainless steel columns, $\phi = 4.6$ mm × 250 mm, packed with silica Li Chrospher Si 100 (Merck, FRG) of particle size 10 μm. Tetrahydrofuran was the mobile phase; flow rate 0.5 ml min^{-1}. A Knauer (FRG) 2025/50 differential refractometer, sensitivity 32×, was used for detection. Samples in the form of *ca.* 2% solutions in THF were injected into the columns in quantities of 15 μl by means of a pneumatic injecting device attached to the chromatograph.

The higher-molecular weight fraction in polyisobutylene samples was characterized by using an apparatus built in the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences and provided with a Waters (USA) R-403 differential refractometer as detector. Four stainless-steel separation columns, $\phi = 8$ mm × 1200 mm in size, were packed with Styragel styrene–divinylbenzene gel (Waters, USA) with variable porosity so as to obtain a wide separation range of the system. THF was the mobile phase and the flow rate was 0.35 ml min^{-1}. Samples in the form of *ca.* 0.5% solutions in THF were injected into the column separation system in quantities of 1.64 ml by means of a three-way valve and a loop. The output data from the detector and the siphon volume meter were recorded in the form of a chromatogram by means of a line recorder PR-2500 (Philips, The Netherlands). Both separation systems were calibrated by using commercial polystyrene standards (Waters, USA). The molecular-weight averages and the polydispersity index of polyisobutylene samples were calculated from the g.p.c. chromatograms by a known procedure based on the principle of universal calibration[15]. The Mark–Houwink equation was used in forms valid for polystyrene (PS) and polyisobutylene (PIB) in THF: PS[16], $[\eta] = 1.17 \times 10^{-2} M^{0.717}$; PIB[17] $[\eta] = 5 \times 10^{-2} M^{0.60}$ (the relations are expressed for $[\eta]$ in cubic centimetres per gram).

^1H n.m.r. spectroscopy

^1H n.m.r. high-resolution spectra were recorded with a JEOL PS-100 spectrometer at 100 MHz and 25°C. The n.m.r. tubes were filled with CCl_4 solutions of the samples at a concentration of 0.3 g of the sample per 1 ml of solvent. Hexamethyldisiloxane (HMDS), the signal from which lies at 0.05 ppm from TMS, was the internal standard. The integrated intensities of n.m.r. lines were determined both by means of an incorporated integrator and by using a multichannel data analyser, Tracor Northern TN-4000, after preceding digitizing of expanded n.m.r. spectra with a Summagraphic Intelligent Digitizer.

RESULTS AND DISCUSSION

Kinetic measurements by the conventional mode

The polymerization of isobutylene initiated with the system t-BuCl–BCl_3 in CH_2Cl_2 at $-20°C$ differs in the conversion curves from polymerizations initiated by known cationic initiation systems, especially if the system Lewis-acid–protogenic-compound is used. After the monomer has been mixed with t-BuCl and BCl_3 in CH_2Cl_2, the polymerization does not proceed immediately, but only after a certain inhibition period (4 to 15 min). The inhibition period depends on the concentration of both components (t-BuCl–BCl_3) and becomes shorter with increasing concentration of both BCl_3 and t-BuCl, as can be seen in dilatometric records of conversion curves given in *Figure 1*. The conversion curves show that the polymerizations are not stationary and that they are characterized by a slow initiation and a long induction period. Kinetic measurements provided evidence for an important finding that the polymerization rate linearly increases with the consumption of the monomer and becomes highest on reaching 80% conversion (then it decreases until all monomer is exhausted). As the polymerization rate increases as a function of the monomer consumed, it is obvious that in the system there is a continuous rise in the concentration of active propagation centres. An arising polymer (t-Bu-

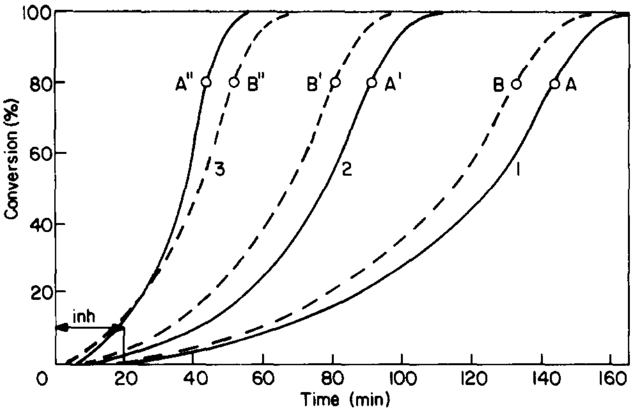

Figure 1 Conversion curves for polymerization of isobutylene ($[M] = 4.8\ mol\ l^{-1}$) in CH_2Cl_2 at $-20°C$. Effect of t-BuCl concentration (———): $[BCl_3] = constant = 0.520\ mol\ l^{-1}$, $[t\text{-}BuCl] = 0.0614\ mol\ l^{-1}$ (1), $0.245\ mol\ l^{-1}$ (2), $0.982\ mol\ l^{-1}$ (3); inh is inhibition period: 15 min (1), 14 min (2), 7 min (3). Effect of BCl_3 concentration (– – –): $[t\text{-}BuCl] = constant = 0.736\ mol\ l^{-1}$, $[BCl_3]$: $0.184\ mol\ l^{-1}$ (1), $0.460\ mol\ l^{-1}$ (2), $0.820\ mol\ l^{-1}$ (3); inhibition period 12 min (1), 11 min (2), 4 min (3). A, A′, A″ and B, B′, B″ are points of inflexion where polymerization proceeds at maximum rate

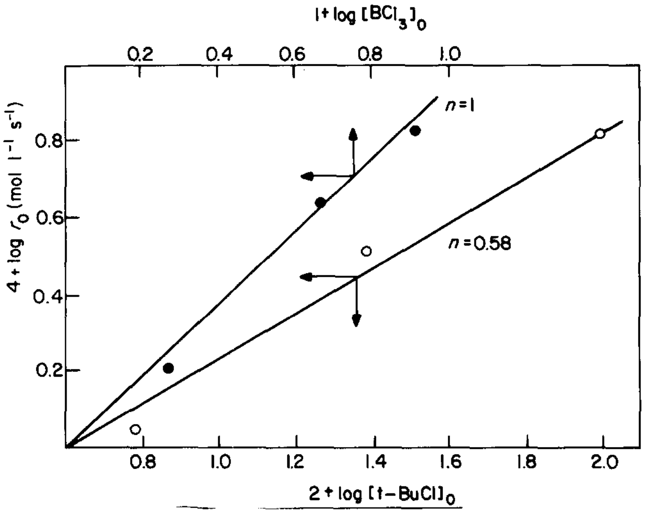

Figure 2 Polymerization of isobutylene in CH_2Cl_2 at $-20°C$; relation $\log r_0 = k \log[t\text{-}BuCl]_0^n$ (○) and relation $\log r_0 = k \log[BCl_3]_0^n$ (●) are solved; initial rates r_0 calculated from conversion curves in *Figure 1* in 5% conversion range

PIB-Cl) can initiate a new polymerization by the scheme:

$$\sim CH_2C(CH_3)_2Cl + BCl_3 \rightarrow \sim CH_2\overset{+}{C}(CH_3)_2BCl_4^-$$

Recently[12] it was proved, that an α,ω-dichloropoly(isobutylene) initiates the polymerization of isobutylene in the presence of BCl_3.

Obviously, polymerization is a living process and belongs to the group of polymerization systems in which the kinetic termination reaction is either absent or reversible, similar to the system isobutylene–t-BuOH–BF_3 described by Plesch[18]. The initial rate r_0 also increases with increasing concentration of t-BuCl and BCl_3, as documented by conversion curves given in *Figure 1*. The dependences $\log r_0 = k \log[t\text{-}BuCl]_0^n$ and $\log r_0 = k \log[BCl_3]_0^n$ are given in *Figure 2*. From these dependences it has been deduced that the initial rate r_0 at the initial monomer concentration $[M]_0 = 4.8\ mol\ l^{-1}$ is proportional to $[BCl_3][t\text{-}BuCl]^{0.58}$.

Molecular weights of the polymer

Analysis of g.p.c. chromatograms (*Figure 3*) has shown that two polymer fractions are formed during polymerization by the conventional mode: $\bar{M}_n = 800 \pm 200 (F_L)$ and $\bar{M}_n = 24\,000 \pm 100 (F_H)$. From chromatograms obtained with the high molecular-weight separation system (cf. Experimental section), *Figure 3a*, the molecular parameters ($\bar{M}_n$, $\bar{M}_w$, $\bar{M}_w/\bar{M}_n$) of the higher molecular-weight polymer fraction F_H were calculated. The lower molecular-weight polymer fraction F_L and the weight content of fraction F_L and F_H in the polymer were obtained from the results of measurements of the low molecular-weight separation system, *Figure 3b*.

The polymerization by conventional mode proved that the weight ratio of these fractions (F_L and F_H) depends on the conversion to which the polymerization is conducted, and on the initial content and $[BCl_3]/[t\text{-}BuCl]$ ratio at which the polymerization proceeds.

At the onset of polymerization, at a very low conversion, *ca.* 6%, the higher and lower molecular-weight polymer fractions are formed in the ratio 1:1. In the further course of the polymerization, however (conversion ⩾10%), formation of the lower molecular-weight polymer is already strongly prevalent, and the mutual weight ratio of the two fractions is $F_L : F_H = 4:1$ (at the molar ratio $[BCl_3]/[t\text{-}BuCl] = 1$). The results are summarized in *Table 1*. In the polymerization with BCl_3 in

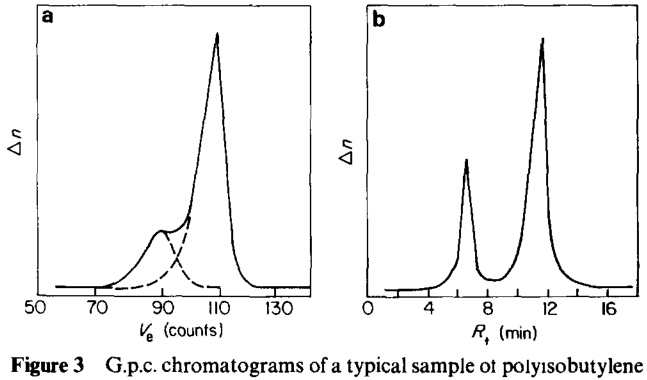

Figure 3 G.p.c. chromatograms of a typical sample of polyisobutylene obtained by the conventional mode using the system t-ButCl–BCl_3 in CH_2Cl_2 at $-20°C$. (a) Chromatogram obtained with a high-molecular weight separation system (cf. Experimental section); (b) chromatogram of the same PIB sample obtained with a low molecular-weight separation system

Table 1 Polymerization of isobutylene at $-20°C$ in CH_2Cl_2 by the conventional and complex mode: content of the lower molecular-weight fraction F_L in the polymer as a function of conversion[a]

Conversion (%)	$F_L/(F_L + F_H)$ (wt%)	F_L $\bar{M}_n$ (g mol^{-1})	 $\bar{M}_w/\bar{M}_n$
6.6	46	769	2.20
8.6	62	594	1.55
10.2	85	609	1.50
12.8[b]	100	1418	1.59
19.6	85	668	1.52
20.8[b]	100	1435	1.60
34.0	80	773	1.55
53.3[b]	100	1528	1.68
100	83	1014	1.52
100	82	1035	1.59
100[b]	100	1549	1.79

[a] F_H was in the range $\bar{M}_n \approx 23\,000$–$25\,000$ with the polydispersity index $(\bar{M}_w/\bar{M}_n) = 2.0$–$3.3$. Concentration in both modes: $[BCl_3] = [t\text{-}BuCl] = 7.7 \times 10^{-1}\ mol\ l^{-1}$, $[isobutylene] = 5.1\ mol\ l^{-1}$

[b] Polymerization by the complex mode

a molar excess over t-BuCl ($[BCl_3]/[t\text{-}BuCl] = 2.4$), a polymer that contains almost only the low molecular-weight fraction is already formed, $F_L/(F_L + F_H) = 0.95$, as shown in *Table 2*. The effect of t-BuCl on the molecular weight of the polymer was also followed during the polymerization. In particular, with increasing concentration of t-BuCl at a constant concentration of BCl_3, there is a decrease in the molecular weight of the low molecular-weight polymer fraction, the weight content of which in the polymer is $\geq 80\%$, as given in *Table 3*. When the polymerization was achieved via the complex mode, the polymers did not contain two polymer fractions any more. The polymer was only a low molecular-weight one, as can be seen in *Tables 1* and *2*.

Spectrophotometric measurements

To extend our knowledge of the initiation mechanism of polymerization, we investigated spectrophotometrically the mixtures t-BuCl–BCl_3 alone and the mixtures t-BuCl–BCl_3 in CH_2Cl_2. Immediately on mixing BCl_3 in excess, with t-BuCl in molar ratios $[BCl_3]/[t\text{-}BuCl] = 5, 4, 3, 2$, a weak, wide absorption band was formed in the range 290–300 nm, as shown in *Figure 4b*, spectrum A. The measurement was repeated after 48 h; no other absorption band was detected, and the mixture was colourless. At the molar ratio of the components $[BCl_3]/[t\text{-}BuCl] = 1$, however, an absorption band in the range 290–300 nm, having a shape similar to the preceding case, was formed first, but after 48 h this was followed by the formation of further absorption bands with $\lambda_{max} = 376$ nm and 468 nm having the spectrum B (*Figure 4b*). In CH_2Cl_2 the spectrophotometric measurement revealed the formation of the same absorption bands as in the preceding case for the mixture $[BCl_3]/[t\text{-}BuCl] = 1$, but also at a large excess of BCl_3 with respect to t-BuCl ($[BCl_3]/[t\text{-}BuCl] = 20$). First, an absorption band in the range 290–300 nm appeared (cf. *Figure 4a*, spectrum C), and after 48 h bands with $\lambda_{max} = 376$ and 468 nm were detected (*Figure 4a*, spectrum D). Measurement with the same mixture was repeated for several days and showed a rise in the extinction only in the maxima of the originally observed bands; no other absorption band was detected. The rise in extinction as a function of time dependence of the same mixture is shown in *Table 4*. It can be seen that after the seventh day there were no pronounced changes in the extinction of the bands obtained with the mixture; probably, in the reaction system equilibrium had already been established between the complexes formed and the starting components of the reaction mixture.

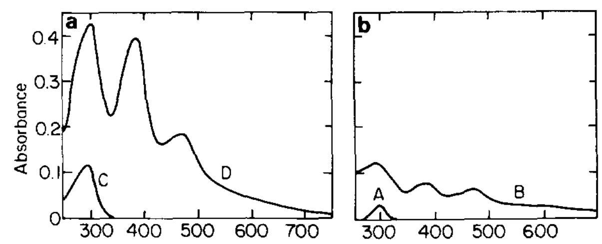

Figure 4 Spectrophotometric measurement of the mixture t-BuCl–BCl_3 at 25°C. (a) In a 10 mm cell in CH_2Cl_2, $[t\text{-}BuCl] = 2.1 \times 10^{-2}\,mol\,l^{-1}$, $[BCl_3] = 4.2 \times 10^{-1}\,mol\,l^{-1}$; C, recorded immediately after mixing BCl_3 with t-BuCl; D, spectrum of the mixture t-BuCl–BCl_3 recorded 48 h after mixing. (b) In a 1 mm cell, $[t\text{-}BuCl] = [BCl_3] = 5.08\,mol\,l^{-1}$; A, spectrum recorded immediately after mixing BCl_3 with t-BuCl; B, spectrum of the mixture t-BuCl–BCl_3 recorded 48 h after mixing

Table 2 Polymerization of isobutylene[a] at −20°C in CH_2Cl_2 by the conventional and complex mode: content of the lower molecular-weight fraction F_L in the polymer as a function of the molar ratio $[BCl_3]/[t\text{-}BuCl]$

$[BCl_3] \times 10^1$ (mol l^{-1})	$\frac{[BCl_3]}{[t\text{-}BuCl]}$	$F_L/(F_L + F_H)$	$\bar{M}_n$ (g mol^{-1})
5.6	0.72	0.80	959
7.7	1.00	0.83	1014
7.7[b]	1.00	1.00	1549
10.5	1.36	0.83	957
15.4[b]	2.00	1.00	1389
18.5	2.40	0.95	1050

[a] In both modes: [isobutylene] = 5.1 mol l^{-1}, conversion 90–100%
[b] Polymerization by the complex mode

Table 3 Effect of t-BuCl on molecular weight of the polymer

	F_L		F_H
[t-BuCl] × 10^1 (mol l^{-1})	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$ (g mol^{-1})
2.57	1412	2.01	25100
6.42	1139	1.71	24518
12.85	917	1.66	23820
19.48	679	1.64	23430

Polymerization of isobutylene in CH_2Cl_2 at −20°C, $[BCl_3] = 6.1 \times 10^{-1}\,mol\,l^{-1}$, [isobutylene] = 5.1 mol l^{-1}, conversion 60–70%, content of the lower molecular-weight fraction F_L in the polymer ≥ 80 wt%

For many years the absorption range 290–300 nm has been attributed by various authors[19–25] to the formation of trialkylcarbonium ions. Later, however, the possibility of the absorption of $t\text{-}Bu^+$ in the range of wavelengths higher than 210 nm was rejected[26]. Bearing in mind refs. 26 and 27, it is assumed that only the interaction t-BuCl with BCl_3 take place, giving rise to a complex. A complex is probably formed in the molar ratio $[t\text{-}BuCl]/[BCl_3] = 1$ and in a polar medium it passes into a dissociated form according to the scheme:

$$t\text{-}BuCl + BCl_3 \rightleftharpoons t\text{-}BuCl\text{–}BCl_3 \rightleftharpoons t\text{-}Bu^+BCl_4^- \rightleftharpoons t\text{-}Bu^+/BCl_4^-$$

Polymerization by complex mode

Although the spectrophotometric measurement has proved the interaction between BCl_3 and t-BuCl accompanied by complex formation, first in the range 290–300 nm, and after 48 h, also with $\lambda_{max} = 376$ and 468 nm, it was necessary to find out whether formation of the complexes, especially of the complex formed later, contributes to the activation of the initiation system or leads to its total or partial deactivation, for example

$$t\text{-}BuCl + BCl_3 \rightarrow \text{isobutylene} + H^+BCl_4^- \rightarrow \text{PIB oligomers}$$

For this purpose, solutions of the t-BuCl and BCl_3 mixtures in CH_2Cl_2 were prepared ([t-BuCl] concentration was 3.0×10^{-1}–$7.7 \times 10^{-1}\,mol\,l^{-1}$, $[BCl_3]/[t\text{-}BuCl] = 1.0$–$2.0$). After ten days these solutions were used for the polymerization of isobutylene. The monomer concentration after mixing all reaction components was in the range $[M] = 1.0$–$5.1\,mol\,l^{-1}$.

Table 4 Spectrophotometric measurement of the mixture t-BuCl–BCl_3 in CH_2Cl_2 at 25°C

Measurement of the mixture Time after mixing (days)	Absorbance for λ_{max} (nm)		
	290–300	376	468
0	0.117	0.0	0.0
2	0.426	0.393	0.184
3	0.478	0.458	0.189
4	0.506	0.462	0.187
5	0.546	0.513	0.182
6	0.592	0.549	0.183
7	0.603	0.549	0.183

[t-BuCl] = 2.1×10^{-2} mol l^{-1}
[BCl_3] = 4.2×10^{-1} mol l^{-1}

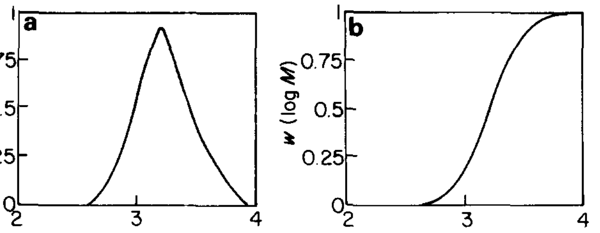

Figure 5 Molecular-weight distribution curves of a typical sample of polyisobutylene prepared by the polymerization of isobutylene in CH_2Cl_2 at −20°C by the complex [t-BuCl.BCl_3] prepared in advance; ($[M]_0 = 1.0$ mol l^{-1}, [t-BuCl] = 7.7×10^{-1} mol l^{-1}, [BCl_3]/[t-BuCl] = 2, conversion 92.0%, $\bar{M}_n = 1534$, $\bar{M}_w = 2051$, $\bar{M}_w/\bar{M}_n = 1.34$). (a) Differential molecular-weight distribution curve; (b) integral molecular-weight distribution curve

Solutions of the [t-BuCl]/[BCl_3] mixtures were already light brown and did not contain precipitates or PIB oligomers (verified by ^1H n.m.r. analysis). The polymerizations by complex resembled those proceeding after immediate mixing of the reaction components and monomer (conventional mode), i.e. the polymerizations also always proceeded up to 100% conversion. A distinct difference between both types of polymerization (i.e. by complex and conventional) existed in the polymerization rate and polydispersity index. For polymerizations by complex, r_{max} (i.e. in the range at a *ca.* 80% conversion) was found to be approximately twice as high as that of the conventional polymerizations. The polymers prepared by the polymerization by complex did not contain two polymer fractions any more (high and low molecular-weight): the polymer was only the latter, with a low polydispersity index ($\bar{M}_w/\bar{M}_n$) = 1.6–1.8 (when $[M]_0 = 5.1$ mol l^{-1}) and 1.34–1.50 (when $[M]_0 = 1.0$–2.0 mol l^{-1}), as can be seen in *Table 1* and *Figure 5*.

Experiments showed that the interaction between BCl_3 and t-BuCl in CH_2Cl_2 does not bring about deactivation of the system even ten days after mixing; on the contrary, the complexes formed in the course of the polymer reaction lead to fast transfer reactions, especially from the onset of the reaction, and this is accompanied by the formation of a low molecular-weight polymer with narrow polydispersity ($\bar{M}_w/\bar{M}_n$).

The polymer chain end groups determined by ^1H n.m.r. spectroscopy

The ^1H n.m.r. spectra of typical samples of polyisobutylene were recorded. The samples were obtained by polymerizing isobutylene in a conventional mode and by polymerization with the [t-BuCl–BCl_3] complex prepared in advance. The t-Bu-PIB-Cl samples were then dehydrochlorinated, and the structure of the polymer chain was analysed. The results are given in *Figures 6* and *7*; characteristic resonances of various groups in the polymer chain are given in *Table 5*. The shape of the spectra of the t-Bu-PIB-Cl samples (before dehydrochlorination) prepared by the conventional procedure, and those prepared by the polymerization by complex, was the same. At high amplification, weak bands appeared, which indicated the presence of an external (resonance 4.58 and 4.78 ppm) and an internal (5.09 ppm) double bond in the polymer. From the integrated intensities of the n.m.r. bands, the concentrations of the individual end groups were determined; values related to one mole of the PIB constituent units are given in *Table 6*. This table also contains the $\bar{M}_n$ values determined from the concentrations of endgroups of the polymer chain.

The shape of the ^1H n.m.r. spectra and the values summarized in *Table 6* confirm the finding that the polymer samples before dehydrochlorination have a structure schematically shown in *Figure 6*, i.e. that the chain head is formed by the *tert*-butyl group, while at the other chain end there is a chlorine atom bound at the *tert*-

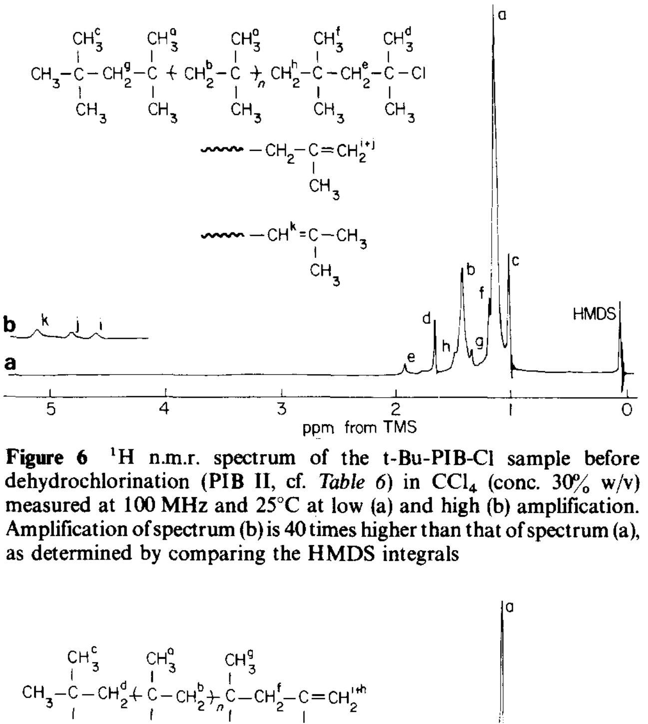

Figure 6 ^1H n.m.r. spectrum of the t-Bu-PIB-Cl sample before dehydrochlorination (PIB II, cf. *Table 6*) in CCl_4 (conc. 30% w/v) measured at 100 MHz and 25°C at low (a) and high (b) amplification. Amplification of spectrum (b) is 40 times higher than that of spectrum (a), as determined by comparing the HMDS integrals

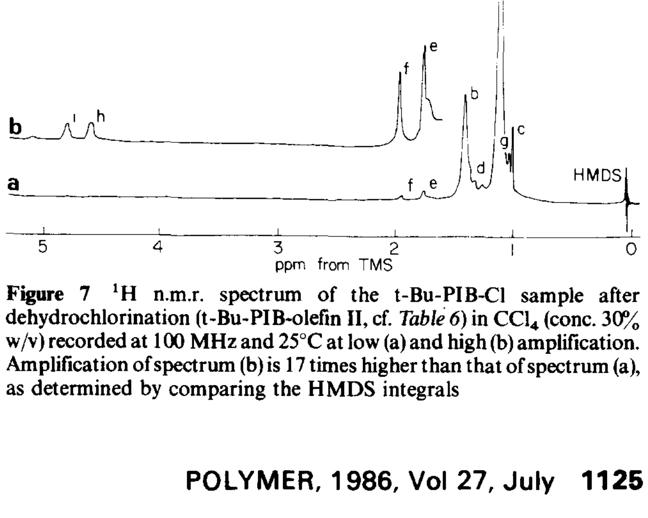

Figure 7 ^1H n.m.r. spectrum of the t-Bu-PIB-Cl sample after dehydrochlorination (t-Bu-PIB-olefin II, cf. *Table 6*) in CCl_4 (conc. 30% w/v) recorded at 100 MHz and 25°C at low (a) and high (b) amplification. Amplification of spectrum (b) is 17 times higher than that of spectrum (a), as determined by comparing the HMDS integrals

carbon atom, the concentration being about 2.2 mol%. The content of external and internal double bonds in t-Bu-PIB-Cl (before dehydrochlorination) is lower by one order of magnitude, lying in the range 0.15–0.3 mol%, as documented by *Table 6*. Dehydrochlorination of the t-Bu-PIB-Cl samples resulted in a 100% elimination of chlorine bound at the tertiary carbon atom; a polymer having the structure shown in *Figure 7* was thus prepared.

The mechanism of isobutylene polymerization by the t-BuCl–BCl$_3$ initiation system

In view of the findings presented in the previous sections, the following mechanism is proposed for the polymerization of isobutylene in the presence of t-BuCl initiator.

Ion generation

$$\text{t-BuCl} + BCl_3 \rightleftharpoons [\text{t-BuCl}.BCl_3] \rightleftharpoons \text{t-Bu}^+ + BCl_4^-$$

Cationation

$$\text{t-Bu}^+ + CH_2{=}C(CH_3)_2 \rightarrow \text{t-Bu}{-}CH_2C^+(CH_3)_2$$

Propagation

$$\sim CH_2C^+(CH_3)_2 + CH_2{=}C(CH_3)_2 \rightarrow \sim CH_2C(CH_3)_2{-}CH_2C^+(CH_3)_2$$

Termination is absent or is reversible

$$\sim CH_2C^+(CH_3)_2BCl_4^- \rightleftharpoons \sim CH_2C(CH_3)_2Cl + BCl_3$$

Chain transfer to the complex [t-BuCl.BCl$_3$]

$$\sim CH_2C^+(CH_3)_2 + [\text{t-BuCl}.BCl_3] \rightarrow \sim CH_2C(CH_3)_2Cl + BCl_3 + \text{t-Bu}^+$$

Chain transfer to the monomer is absent or is negligible.

Kinetics of transfer reaction

The long inhibition period and the spectrophotometric measurement of t-BuCl–BCl$_3$ mixtures suggest an interaction between t-BuCl and BCl$_3$. Let it be assumed that t-BuCl alone is not the transfer compound, but the complex [t-BuCl.BCl$_3$] is responsible for the transfer. For conventional polymerizations the concentration of the complex [t-BuCl.BCl$_3$] is small in the reaction system, especially at the beginning, and hence its participation in transfer reactions is smaller by comparison with polymerizations in which solutions of t-BuCl–BCl$_3$ in CH$_2$Cl$_2$ prepared in advance are used. If, on the other hand, polymerization by complex mode is used, the concentration of the latter is much higher; hence, transfer reactions are operative to a greater extent in the reaction system during the polymerization, starting from the beginning. The polymerization by complex mode does not give rise to a higher molecular-weight polymer fraction: a lower molecular-weight PIB is synthesized by this procedure, with a narrow polydispersity $\bar{M}_w/\bar{M}_n = 1.34–1.80$. The complex [t-BuCl.BCl$_3$] is also responsible for the initiation reaction, and we may call this compound an 'initiation-transfer' one, or Inifer (I) if we accept Kennedy's[5] nomenclature.

The transfer to Inifer is distinctly operative only for the low molecular-weight fraction F_L (*Table 3*), in polymerizations made in the conventional way, and we do not commit too great a mistake if the transfer constant to Inifer, C_I, is calculated only from this polymer fraction, which is predominantly contained in the polymer ($F_L \geq 80$ wt%). Values from *Table 3* ($\bar{M}_{n,F_L}$ as a function of the t-BuCl concentration) are used in calculating C_I. The structure of the polymer chain of t-Bu-PIB-Cl determined by ^{1}H n.m.r. analysis (*Figure 6*) showed that the transfer to monomer was suppressed by Inifer, as can be seen in *Table 6*; hence, the transfer constant to Inifer, C_I, is much higher than that to monomer, C_M. Since the polymerizations were made to a 60–70% conversion (*Table 3*), an integral form[6] of the relation for the kinetic number-average degree of polymerization, DP_n, is used in calculating C_I, as demonstrated in *Figure 8*

$$\overline{DP}_n^{-1} = \frac{1}{[M]_0 - [M]} \ln\frac{[M]_0}{[M]} (C_I[\bar{I}] + k_t/k_p)$$

Table 5 ^{1}H n.m.r. analysis of t-Bu-PIB-Cl samples and of the same samples after dehydrochlorination (t-Bu-PIB-olefin)

Shift[a] (ppm)	Sample	Resonance of characteristic groups
1.00	t-Bu-PIB-Cl, t-Bu-PIB-olefin	$(CH_3)_3C-$
1.03	t-Bu-PIB-olefin	$-C(CH_3)_2-CH_2-C(CH_3){=}CH_2$
1.12	t-Bu-PIB-Cl, t-Bu-PIB-olefin	$-(CH_2(CH_3)_2C)-_n$
1.42	t-Bu-PIB-Cl, t-Bu-PIB-olefin	$-(CH_2(CH_3)_2C)-_n$
1.66	t-Bu-PIB-Cl	$-C(CH_3)_2Cl$
1.75	t-Bu-PIB-olefin	$-CH_2C(CH_3){=}CH_2$
1.92	t-Bu-PIB-Cl	$-CH_2C(CH_3)_2Cl$
1.95	t-Bu-PIB-olefin	$-CH_2C(CH_3){=}CH_2$
4.58 4.78	t-Bu-PIB-olefin	$-CH_2C(CH_3){=}CH_2$
5.09	t-Bu-PIB-olefin	$-CH{=}C(CH_3)_2$

[a] Chemical shift values in ppm are related to the TMS standard. Measured resonances of characteristic groups are in agreement with refs. 5 and 14

Table 6 Molar ratios of various end groups related to one mole of constitutional PIB units[a] and molecular weights of polymer samples, all determined from ^{1}H n.m.r. spectra

Sample	$\frac{[-C(CH_3)_3]}{[IB]}$ *a*	$\frac{[-C(CH_3)_2Cl]}{[IB]}$ *b*	$\frac{[-CH_2C(CH_3){=}CH_2]}{[IB]}$ *c*	$\frac{[-CH{=}C(CH_3)_2]}{[IB]}$ *d*	$\bar{M}_n$ (g mol^{-1})
t-Bu-PIB-Cl (I)	0.0226	0.022	0.0010	0.002	2478[b]
t-Bu-PIB-Cl (II)	0.0226	0.020	0.0005	0.001	2478[b]
t-Bu-PIB-olefin (I)	0.02	0	0.020	0.002	2545[c]
t-Bu-PIB-olefin (II)	0.02	0	0.022	0.003	2240[c]

[a] t-Bu-PIB-Cl (I) and (II) are typical polyisobutylene samples prepared by the conventional mode (I) and by polymerization complex (II); t-Bu-PIB-olefins (I) and (II) are samples (I) and (II) after dehydrochlorination

[b] $\bar{M}_n = 56/a$

[c] $\bar{M}_n = 56/(c + d)$

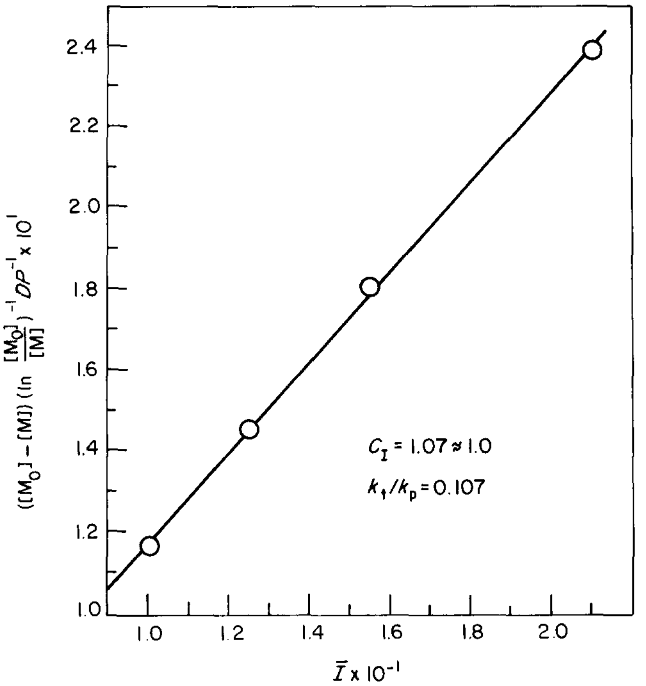

Figure 8 Determination of the transfer constant C_I from the lower molecular-weight fraction present in the polymer in an amount ≥ 80 wt%. Data for calculation taken from *Table 3*

Here, $[M]_0$ and $[M]$ are the initial and final monomer concentrations, respectively, $[\bar{I}]$ is the arithmetic average concentration of the Inifer consumed by the polymer reaction $([I]_0-[I])/2$, where $[I]_0$ and $[I]$ are the initial and final concentrations of the Inifer, respectively. The concentration $[I]$ was calculated from the Inifer efficiency[6] and the relation $[I]=[I]_0(1-I_{\text{eff}})$

$$I_{\text{eff}}=\frac{([M]_0-[M])}{\overline{DP}_n[I]_0} \qquad C_I=\frac{k_{trI}}{k_p}$$

where k_p, k_{trI} and k_t are, respectively, the rate constants of propagation, transfer to Inifer, and termination. It was found by calculation that $C_I=1.07$, and $k_t/k_p=0.107$. The C_I value for the complex [t-BuCl.BCl$_3$] is lower than C_I values for Kennedy's Binifers[9] 1,3-di(2-bromo-2-propyl)5-*tert*-butylbenzene and 1,3-di(2-chloro-2-propyl)5-*tert*-butylbenzene ($C_I=2.39$ and $C_I=2.54$ respectively; isobutylene/$CH_3Cl+n\text{-}C_6H_{14}$ at -50°C).

The experiments showed (cf. *Table 3*) that the formation [t-BuCl.BCl$_3$] is conditioned by the molar excess of BCl_3 with respect to t-BuCl, as can be seen from the value of Inifer efficiency. With decreasing [BCl_3]/[t-BuCl] ratio the Inifer efficiency also decreases. Thus, at [BCl_3]/[t-BuCl] $\simeq 2.4$, 1, 0.5 and 0.3, the Inifer efficiency I_{eff} is, respectively, 0.80, 0.40, 0.25 and 0.20 (the data are taken from *Table 3*, from the dependence of $\bar{M}_n$ of the low molecular-weight polymer fraction on the t-BuCl concentration).

CONCLUSION

The study has demonstrated a new initiation-transfer system t-BuCl–BCl_3, operative in the polymerization of isobutylene effected in the absence of a protogenic compound in CH_2Cl_2 at -20°C. The initial rate r_0 is proportional to $[BCl_3][\text{t-BuCl}]^{0.58}$ and the polymerization proceeds without kinetic termination always to a 100% conversion after the inhibition period. The defined structure of the polymer t-Bu-PIB-Cl determined by ^1H n.m.r. indicated a minimal transfer to monomer. The transfer has been attributed to the complex [t-BuCl.BCl$_3$].

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