Polymer Bulletin 17, 157–162 (1987)

Polymer Bulletin

A possible "direct initiation" of cationic polymerization of isobutylene by boron trichloride in methylene chloride

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Summary.

Initiation of the cationic polymerization of isobutylene by BCl_3 requires a cocatalyst in most cases.However,we found conditions ($\Theta = -30°C$, CH_2Cl_2 as solvent, $BCl_3 \geqslant 0.01$ M) where a direct initiation by BCl_3 (i.e. with no cocatalyst) is possible.We showed that in such conditions HCl is not a cocatalyst and that H_2O content is too low to explain the results (high vacuum and highly purified reactants and solvent).The conversion increases linearly with the increasing concentration of BCl_3.A mechanism is proposed.

Introduction.

For a long time it has been accepted that isobutylene(IB) could be polymerized by Lewis acids,only in the presence of a cocatalyst(1).However,more recently,several authors claimed that,even in absence of a cocatalyst,IB polymerization can be initiated by various Lewis acids:$AlBr_3$ or $AlCl_3$(2), $TiCl_4$(3),$AlEtCl_2$(4).Depending on the mechanism they suggest,authors classified such polymerizations as "direct","spontaneous","ion radical" or"non protonic".In studies relative to the synthesis of telechelic oligoisobutylenes we carried out polymerizations at concentrations higher than those mentioned above;the results are reported in this article.

Experimental.

Two techniques have been used: vacuum line and high vacuum with completely sealed apparatus.

vacuum line: IB is dried through a column of molecular sieve and a column of BaO(both are heated under vacuum at 200°C for 24hr).CH_2Cl_2 is freshly distilled from P_2O_5 under nitrogen.BCl_3 is distilled just before use.

polymerization: A mixture of IB and CH_2Cl_2 is frozen in an all-glass recator which is connected to the vacuum line and degassed several times; when the solution is at the chosen temperature,BCl_3 is added;the polymerization is stopped by introducing methanol.

High vacuum: All reactants and solvent are dried using Sigwalt's technique(6).BCl_3 is distilled on two sodium films.

Molecular weight determination: GPC(Waters) µstyragel columns(500Å,

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500Å,100Å),solvent THF.Standard: diisobutylene,tetraisobutylene and polyisobutylene fractions(3 fractions M = 3500,7850 and 14740) whose molecular weights were determined by vapor pressure osmometry.Viscosity values were determined in diisobutylene;viscosimetric average molecular weights are calculated by Flory's relation for polyisobutylene(10).

Results and Discussions.

The results are reported in table 1.

Table 1.

Polymerization of isobutylene in various experimental conditions at t = -30°C.

Exp.	[IB] (M)	$[BCl_3]$ (M)	[Added cocatalyst] (M)	conversion Y% (e)	$\overline{M}$
1	1	0.13(a)	-	84	104500(c)
2	1	0.11(b)	-	60	190000(c)
3	0.9	0.11	-	>80	-
4	1	0.14	-	90	56000
5	1.2	0.13	-	95	-
6	0.9	0.05	-	21	-
7	0.9	0.02	-	12	-
8	1	0.01	HCl 0.0016	<2	-
9	1	0.19	H_2O 0.0017	65	4100(d)

(a) High vacuum,(b) High vacuum and reactants freshly distilled and dried over sodium films,(c) From viscosimetric determination,(d) From GPC (see experimental part),(e) After 30 mn. Y% =($[M]_o$ - $[M]_\infty$)/ $[M]_o$ x 100,where $[M]_\infty$ is the residual monomer when polymerization is stopped.

In experiments 3 and 4 the conversion is high (> 80%).In experiment 4, the conversion is 90% but the molecular weight of the resulting polymer is only 56000.According to Kennedy(5) such a polymerization is initiated by the BCl_3/H_2O system where H_2O is the residual water in the reaction medium (exp. 3 and 4 are carried out in vacuum line and not in high purity conditions).

Although experiments 1 and 2 were carried out in high vacuum conditions, their results are not incompatible with a cocatalytic initiation:if the reaction mixture contains a cocatalyst,its content is probably lower in experiment 2(high vacuum and freshly distilled reactants) than in experiment 1(high vacuum) which fits the fact that conversion decreases (84 and 60%)

and molecular weight increases (104500 and 190000) from experiment 1 to experiment 2.

If a cocatalytic initiation takes place,what could be the coinitiator?

As hydrogen chloride might be present when BCl_3 concentration is high, we carried out a polymerization (exp.8) in presence of this compound:BCl_3 is added to an IB solution maintained at -30°C;after 30 mn,gazeous dry HCl (0.0016 M) is introduced and reaction is stopped after one hour.Practically no polymer is obtained (conversion below 2%) showing that HCl/BCl_3 system does not initiate isobutylene polymerization,at least in these conditions.The fact that HCl is not a cocatalyst in isobutylene polymerization was already mentioned by Pham (8) when the initiator is $TiCl_4$ and by Plesh (9) who studied IB-Aluminium halide systems.It is interesting to mention that Mazure (11) showed that HCl is a cocatalyst of Diphenyl-1,1-ethylene dimerization when initiator is $AlCl_3$ but is not when initiator is $TiCl_4$.

As shown in experiment 3 and 4,water is a cocatalyst for the polymerization of isobutylene initiated by BCl_3;could residual water be responsible for the polymerization in experiments 1 and 2 ?This is hardly probable as water content of the reaction medium in experiments 1 and 2 is too low to obtain such conversions.It could be assumed that H_2O is introduced as a BCl_3 complex;however such a complex has never been mentioned and is probably very unstable.Experiments carried out in the presence of a proton trap (2,6-Ditertbutylpyridine) (15) did not change the conversion but decreased molecular weihgts of the polymers which does not favour the hypothesis of a cocatalytic process.

This analysis of the results obtained in experiments 1 to 4 shows that polymerizations 1 and 2 result very probably from a direct initiation by BCl_3.The variation of Ln Y against $[BCl_3]_\circ$ (Figure 1) is linear;it shows that conversion decreases with decreasing $[BCl_3]$ and that no polymerization takes place when $[BCl_3] < 0.01$ M which fits Kennedy's results which were obtained in somewhat different conditions (16).

Sauvet and al. (12) analyzed the different ways initiation can take place when no coinitiator is added.Longworth and Plesch (13) assumed that a self-initiation of the Lewis acid could take place;However,the kinetic analysis of such a system leads to conversion proportional to $C_\circ^2$ or $C_\circ^3$ ($C_\circ$ is the initial initiator concentration).

The hypothesis of a solvent coinitiation:

$$CH_2Cl_2 \; + \; BCl_3 \longrightarrow BCl_4^{\ominus} \;,\; {}^{\oplus}CH_2Cl$$

$${}^{\oplus}CH_2Cl,BCl_4^{\ominus} \; + \; H_2C{=}C\langle \longrightarrow ClCH_2{-}C\langle^{\oplus},\; BCl_4^{\ominus}$$

leads to conversion proportional to $C_\circ$ but is not supported by conductivity experiments (13).

On the other hand,the direct addition of Lewis acid on the double bond (12,14) can fit our results:

$$\underset{}{BCl_3} \; + \; \underset{(M)}{CH_2{=}C(CH_3)_2} \longrightarrow \underset{(C,M)}{Cl_3\overset{\delta-}{B} - CH_2\overset{\delta+}{C}(CH_3)_2}$$

However,there is a competitive formation of an inactive complex :

$$BCl_3 \; + \; M \xrightarrow{k_\circ} [BCl_3,M] \begin{cases} \xrightarrow[M]{k_1} TiCl_4,M_2 \\ \xrightarrow{k_2} Cl_3\overset{\delta-}{B}\;\overset{\delta+}{M} \end{cases}$$

Let C and $R^{\oplus}$ be respectively the concentration in BCl_3 and in active centers at time t: Assuming that initiation is very rapid and $[M]_\circ \gg C_\circ$

$$-\frac{dC}{dt} = k_\circ [M][C] \simeq k_\circ [M]_\circ [C] \qquad \underline{1}$$

$$-\frac{d[C,M]}{dt} = k_1 [M]_\circ [C,M] + k_2 [C,M] - k_\circ [M]_\circ [C] \qquad \underline{2}$$

$$-\frac{d[R^{\oplus}]}{dt} = k_2 [C,M] - k_t [R^{\oplus}] \qquad \underline{3}$$

where k_t is the rate constantof termination reaction.

Combining and solving differential equations 1 to 3 leads to:

$$[C,M] = A\ (e^{Bt} - e^{Dt}) \qquad \underline{4}$$

where

$$A = \frac{k_\circ k_2 [M]_\circ [C]_\circ}{k_1 [M]_\circ + k_2 - k_\circ [M]_\circ}$$

$$B = -k_\circ [M]_\circ$$

$$D = -(k_1 [M]_\circ + k_2)$$

combination of 3 and 4 gives :

$$\frac{d[R^{\oplus}]}{dt} + k_t\ R^{\oplus} = A\ (e^{Bt} - e^{Dt}) \qquad \underline{5}$$

solving 5 gives :

$$[R^{\oplus}] = \frac{A}{B + k_t} e^{Bt} - \frac{A}{D + k_t} e^{Dt} + \left(\frac{A}{D + k_t} - \frac{A}{B + k_t}\right) e^{-k_t t} \qquad \underline{6}$$

Let k_p be the propagation rate constant :

$$-\frac{d[M]}{dt} = k_p [R^{\oplus}][M] \qquad \underline{7}$$

combining 6 and 7 and integrating the differential relation gives :

$$\mathrm{Ln}\frac{[M]_\circ}{[M]} = k_p A \left(\frac{e^{Bt}}{B(B + k_t)} - \frac{e^{Dt}}{D(D + k_t)} + \frac{e^{-k_t t}}{k_t(B + k_t)} - \frac{e^{-k_t t}}{k_t(D + k_t)}\right)$$

$$+ A\left(\frac{-1}{B(B + k_t)} + \frac{1}{D(D + k_t)} - \frac{1}{k_t(B + k_t)} + \frac{1}{k_t(D + k_t)}\right) \qquad \underline{8}$$

Let $[M]_\infty$ be the monomer concentration at the end of the polymerization :

$$\text{Ln}\frac{[M]_o}{[M]_\infty} = A\,\frac{k_p}{k_t}\left[\frac{D + k_t}{D(D + k_t)} - \frac{B + k_t}{B(B + k_t)}\right] \qquad \underline{9}$$

As A is proportional to $[C]_o = [BCl_3]_o$, relation 9 fits the plot in Figure 1.

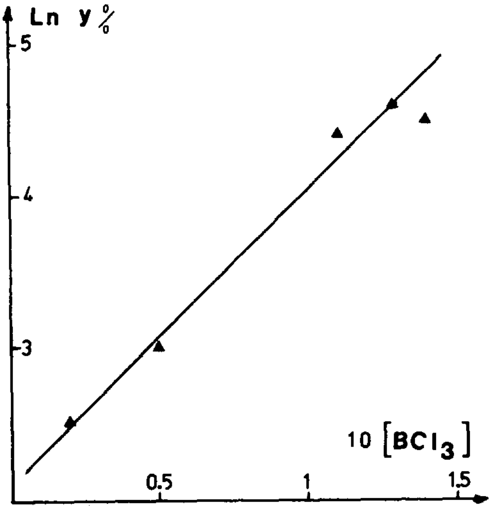

Figure 1 : Variation of Ln (conversion) against $[BCl_3]_o$

In experiment 9 where the water concentration is much higher than in experiments 3 and 4 the conversion is 65% but the molecular weight of the polymer is only 4100. This can be due to the high number of reactive sites and to termination involving water.

References.

1- P.H. Plesch. The Chem. of Cat. Polym. Pergamon Press (1963)
2- D.W. Grattan and P.H. Plesch., Makrom. Chem. 181,751,(1980)
3- M. Marek, J. Pecka and M. Maleska. 6è Intern. Symp. of Cat. Pol. Ghent p. 21 (1983)
4- F.R. Kalafov, F.M. Nasirov, N.E. Melnikova, B.A. Krentsel and T.N. Schakltakltinsky. Makrom. Chem. Rap. Commun. 6,29,(1985)
5- J.P. Kennedy, S.Y. Huang, S.C. Feinberg. J. Pol.Sci. Pol. Chem. 15, 2801,(1977)
6- G. Champetier, M. Fontanille, A.C. Korn and P. Sigwalt. J. Pol. Sci. 58,911,(1962)
7- P. Sigwalt. Polym. J. 17,1,57,(1985)
8-X.Y. Pham. Thesis, Paris,(1973)

9- P.H. Plesch,M. Polanyi and H.A. Skinner. J. Chem. Soc. 257,(1947)
10- P.J. Flory. J. Am. Chem. Soc. 65,372,(1943)
11- M. Mazure,These de Doctorat d'Etat,Paris,(1979)
12- G. Sauvet,J.P. Vairon and P. Sigwalt. J. Pol. Sci. Polym. Chem. Ed. 16,3047,(1978)
13- W.R. Longworthand P.H. Plesch. J. Chem. Soc.1887,(1959)
14- W.H. Hunter and R.V. Yohe. J. Am. Chem. Soc.55,1248,(1933)
15- L. Bui, H.A. Nguyen and E. Marechal. to be published.
16- J.P. Kennedy,S.Y. Huang and S.C. Feinberg. J. Pol. Sci.,Pol. Chem. Ed.,15,2869,(1977)

Accepted January 15, 1987 C