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The Effect of H_2O and HCl on Isobutylene Polymerization Coinitiated by BCl_3

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Abstract

The effect of H_2O and HCl initiators on the BCl_3 coinitiated polymerization of isobutylene was investigated by comparative experiments carried out in CH_2Cl_2 solvent in the range range from -50 to -100°C under high vacuum (superdry conditions) and in the dry box (conventional condition). H_2O is a much more efficient initiator than HCl and the reasons for this are discussed.

Introduction

In the course of our continuing systematic studies on the polymerization of olefins with BCl_3 coinitiator need arose to investigate the effect of small quantities of H_2O and HCl initiators on the polymerization details of isobutylene particularly in polar solvents, i.e., methylene chloride. Thus comparative polymerization experiments have been carried out under high vacuum conditions with super-dried chemicals and under conventional laboratory conditions under a nitrogen atmosphere in a stainless steel safety enclosure (dry box). While HCl was found to be an initiator it was far less efficient than H_2O.

Experimental

A. Chemicals

Boron trichloride (99.9% minimum purity, Linde specialty gas) was distilled into Dry Ice cooled closed tubes placed in the dry box and the liquefied BCl_3 was then pipetted into solvents for dry box experiments. For vacuum line experiments the purification procedure was as follows: BCl_3 was condensed, degassed several times and fractionally distilled in three stages, from -78 to -50°C, from -50° to -30° and from -30° to 0°C.

Isobutylene (99% c.p. grade, Linde Division, Union Carbide Co.) was dried by passing the gas through a 6 foot glass column packed with Molecular Sieves (3Å) and barium oxide and condensing in the dry box under a dry nitrogen atmosphere. For vacuum line experiments the gas was dried by passage through two stainless steel traps filled with molten Na/K alloy at 150° and 300°C respectively. Subsequently the gas was condensed and stored in liquid form over a shiny sodium mirror under vacuum at -36°C.

Methylene chloride (reagent grade, Matheson, Coleman and Bell Co.) was refluxed over and distilled from Me_3Al in blackened glass equipment under a blanket of nitrogen and stored in amber bottles to exclude light. For vacuum line experiments the liquid was refluxed over Me_3Al overnight under nitrogen and degassed. Then it was refluxed over and distilled from CaH_2 onto a sodium dispersion (50% Na and 50% paraffin, Matheson Coleman and Bell Co.), stirred for 3-4 days over the sodium dispersion and degassed a few times. Finally the pre-dried CH_2Cl_2 was distilled over a fresh sodium mirror and stored over a fresh shiny sodium mirror for at least 8 hrs before use.

Methyl chloride (minimum purity 99.5%, Linde Division, Union Carbide Co.) was dried by passing the gas through a 6 foot glass column packed with Molecular Sieves (3Å) and barium oxide.

HCl gas (99.0% purity) was fractionally distilled on the vacuum line. A forecut was collected from -130° (n-pentane slush) to -95° (toluene slush). Then the HCl was distilled at -95°C and used for the preparation of HCl in CH_2Cl_2 solutions. The amount of HCl was calculated by knowing the volume of the system and the pressure. The HCl in CH_2Cl_2 solutions were stored in vials equipped with breakseals at -78°C.

B. Apparatus and Polymerization Techniques

1. The Dry Box System

Polymerizations and manipulation of chemicals were carried out in a stainless steel enclosure (dry box) under a dry nitrogen atmosphere. The reaction vessels were maintained at a constant temperature by immersion in a heptane or hexane bath. The temperature of the bath was regulated by circulating liquid nitrogen or, occasionally, Dry-Ice cooled isopropanol through copper coils placed in the bath. The rate of circulation of the cooling liquid through the coils was controlled by a solenoid valve actuated by a Guardsman temperature controller connected to the thermocouple immersed in the bath. The cooling system was automatically regulated and provided an accuracy of bath temperature within 0.5°C.

The dry box was flushed with dry nitrogen for several hours before use. Additional drying of the atmosphere was achieved by placing a two liter Dewar container filled with liquid nitrogen and an open Petri dish filled with anhydrous P_2O_5 powder inside the dry box.

The dry nitrogen was obtained from a nitrogen cylinder. The gas was passed through drying columns packed with barium oxide. The moisture content in the enclosure was maintained below 100 ppm during operations as determined by a moisture analyzer (MEECO Instrument Co.).

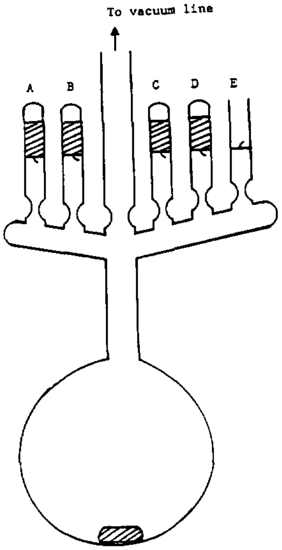
The glassware was dried overnight at 150°C before use, then transferred quickly into the dry box entry port and cooled under nitrogen. The equipment placed in the entry port was alternately flushed twice with dry nitrogen and evacuated to 25 mm Hg before the entry port was opened to the atmosphere of the dry box.

Polymerizations were carried out in test tubes (25 mm x 200 mm, fitted with Teflon caps) or in round bottom flasks. Monomer solutions were thermally equilibrated for about 30 minutes before the BCl_3 solution was added with constant stirring. Polymerizations began immediately and were noticeable by cloudiness and/or precipitation developing. About 1 ml of prechilled methanol was added dropwise to terminate polymerization. Solvent, unreacted monomer and volatile products were evaporated under vacuum, and the polymer was dried to constant weight in a vacuum oven.

2. The High Vacuum System

Polymerizations were conducted under isothermal conditions in an all glass reactor, shown in Figure 1. Vials containing various concentration of reagents were prepared on the vacuum line by a technique described by Morton and Fetters (1). First, the top part of the reactor was prepared by attaching ampoules A, B, C and D filled with isobutylene - CH_2Cl_2, BCl_3 - CH_2Cl_2, H_2O or HCl - CH_2Cl_2 and methanol, respectively. Then the inlet was attached to the vacuum line and the reactor was evacuated to below 10^{-5} mm Hg.

Figure 1. Polymerization Reactor for Experiments under High Vacuum



Subsequently a measured amount of CH_2Cl_2 was distilled into the reactor. The reactor was then removed from the vacuum line by sealing the constriction of the inlet.

After the solvent in the reactor was brought to the desired temperature, the seals of ampoules A and B containing the monomer and BCl_3 in CH_2Cl_2 were broken and their contents were drained into the reactor. Polymerization was started by crushing the breakseal of ampoule C containing the H_2O or HCl initiator dissolved in CH_2Cl_2. The reactants were allowed to react for 30 minutes. Termination was accomplished by adding a few milliliters of methanol from ampoule D. Breakseal E allowed access to the vacuum line, if needed. The reactor was opened, the polymer was recovered and dried in a vacuum oven at room temperature to constant weight.

3. Molecular Weight Determinations

Molecular weights were determined by gel permeation chromatography GPC using a Waters Associates high pressure instrument, Model 6000A pump, five micro-Styragel columns of 10^6, 10^5, 10^4, 10^3 and 500Å, dual detectors, at a flow rate of 2.0 ml/min, with 0.2-0.4 wt% solutions in THF. The calibration curve was constructed with well fractionated PIB samples whose $\overline{M}_w$ was determined by light-scattering. It is estimated that the error of the values obtained from the calibration curve was less than 0.5 ml elution volume, i.e., the reproducibility of $\overline{M}_n$ within 10%.

Results and Discussion

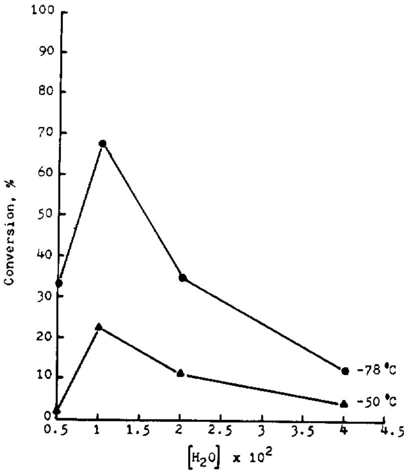
A. The Effect of Water Concentration on Isobutylene Conversion

The effect of H_2O on the BCl_3 coinitiated low temperature polymerization of isobutylene IB in CH_2Cl_2 diluent has been thoroughly investigated (2). It was found that H_2O is an efficient initiator at relatively low temperatures, e.g., -78°C, in the presence of large quantities of CH_2Cl_2. Polymerization is absent at -78° in neat systems (IB + BCl_3) or in nonpolar (hexane) solvent, and conversions are very low (<10%) even in 50/50 CH_2Cl_2/n-C_6H_{14} mixtures. However, when precooled CH_2Cl_2 was added to quiescent IB/BCl_3 mixtures at -78°C, immediate polymerization ensued ("polymerization by solvation")(3).

The percent IB conversion increased linearly from a low [H_2O] level (1×10^{-3} M) until stoichiometric equivalence with BCl_3 was reached, i.e., until H_2O:BCl_3 = 1:1 (3).

Recent experiments carried out by the use of H_2O concentrations below and above the BCl_3 concentration used, showed that the highest IB conversion was obtained at the stoichiometric equivalence point at -78° and -50°C. Figure 2 shows the findings. Evidently the most efficient initiating system is reached with $H_2O \cdot BCl_3$ and when the H_2O concentration exceeds that of BCl_3 rapid hydrolysis may occur which would limit conversions. It has been shown that BCl_3 rapidly hydrolyzes in the presence of H_2O (4,5) and gives rise to polymerization-inactive products:

Figure 2. The Effect of Water Concentration on Conversion [IB] = 1.15M, $[BCl_3] = 1.15 \times 10^{-2}M$, CH_2Cl_2, 30 min., dry box)



$$BCl_3 + H_2O \longrightarrow HCl + BCl_2(OH)$$

$$BCl_2(OH) + H_2O \longrightarrow HCl + BCl(OH)_2$$

$$BCl(OH)_2 + H_2O \longrightarrow HCl + B(OH)_3$$

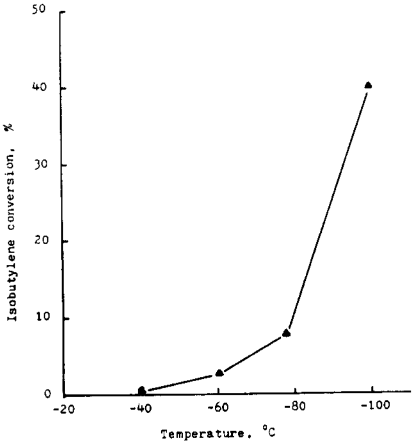
and perhaps

$$2BCl_3 + H_2O \longrightarrow HCl + Cl_2B\text{-}O\text{-}BCl_2 \text{, etc.}$$

These results also suggest that H_2O and BCl_3 should not be premixed in the absence of isobutylene, otherwise BCl_3 will be partially hydrolyzed resulting in reduced conversion.

Conversions were found to be increasing with decreasing temperatures as shown by the data in Figure 3 (cf. also Figure 2). These results are consistent with earlier findings (3) that showed that the rate of termination of isobutylene polymerization initiated by $H_2O{\cdot}BCl_3$ is strongly reduced by cooling and thus conversions increase with decreasing temperatures to -78°C.

Figure 3. Isobutylene Conversion at Various Temperatures ([IB] = 1.15M, [BCl_3] = 1.15 x 10^{-2}, CH_2Cl_2, 30 min., dry box)



2. The Effect of HCl Concentration on Isobutylene Conversion

Since HCl is formed during the hydrolysis of BCl_3 (even in the presence of traces of water), it was of interest to examine the effect of HCl on the polymerization of isobutylene coinitiated by BCl_3.

Experiments have been carried out under high vacuum and dry box conditions. Table I shows the results.

TABLE I. The Effect of HCl on Isobutylene Conversion Using the HCl/BCl_3 Initiating System*

IB mole/l	BCl_3 mole/l	HCl mole/l	Temp. °C	Conv. %	Remark
Dry box experiments					
1.16	0.012	-----	-50	2.7	Control
1.16	0.012	0.010	-50	0.4	
1.16	0.012	0.010	-50	2.1	
1.16	0.009	0.013	-50	2.5	
1.16	0.009	0.026	-50	2.6	
1.16	0.012	-----	-78	25.8	Control
1.16	0.012	0.010	-78	30.1	
1.16	0.012	0.010	-100	33.9	
Vacuum line experiments					
0.50	0.019	0.019	-78	43.9	482**
0.54	0.021	0.021	-78	40.8	614**
0.54	0.021	-----	-78	10.9	Control

* Solvent: CH_2Cl_2, Time: 30 mins.
** Initiation efficiency: g PIB/mole HCl

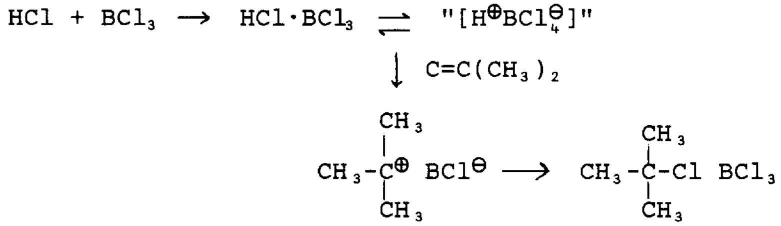
According to the results obtained under high vacuum conditions HCl is an initiator in conjunction with BCl_3 at -78°C. The conversions quadrupled upon the addition of $\sim 2 \times 10^{-2}$ M HCl. Under dry box conditions monomer conversion in the control run (i.e., without purposefully introducing any protogenic initiator) was 25.8%, most likely due to the presence of unscavenged moisture, and under the same conditions except with the addition of 1.0×10^{-2} M HCl a slight increase of the conversion to 30.1% occurred.

According to dry box experiments carried out at different temperatures HCl is not an efficient initiator in the presence of BCl_3 coinitiator for isobutylene polymerization: At -50°C there is no difference in conversions between the control and HCl-added experiments, and at -78° and -100°C HCl addition resulted only in a small increment above the control at -78°C.

Similarly to the observations made with the $H_2O \cdot BCl_3$ system, the $HCl \cdot BCl_3$ combination also gives higher conversions at lower temperatures (compare the conversions obtained at -50°, -78° and -100°C but otherwise under identical conditions in Table I). The explanation is most likely also similar, i.e., the rate of termination is reduced at lower temperatures (see above).

In contrast to the BCl_3 system, HCl is a very efficient initiator in conjunction with Al-containing Friedel-Crafts acids, e.g., Et_2AlCl, Me_3Al (6). This difference may be due to the higher chlorine affinity of Al than B and to the fact that Al-containing Friedel-Crafts acids are excellent coinitiators in conjunction with tert-chlorides (6) whereas BCl_3 does not coinitiate polymerizations with such halides (6), most likely because the $BCl_4^{\ominus}$ counter anion is quite unstable.

Thus it is postulated that the low polymerization efficiency of HCl in the presence of BCl_3 coinitiator is due to rapid chain termination by the unstable $BCl_4^{\ominus}$ and not because of slow ion generation or protonation:



$$HCl + BCl_3 \longrightarrow HCl \cdot BCl_3 \rightleftharpoons \text{"}[H^{\oplus}BCl_4^{\ominus}]\text{"} \xrightarrow{C=C(CH_3)_2} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^{\oplus}}}\ BCl^{\ominus} \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Cl\ \ BCl_3$$

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