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### Carbocationic Polymerization in the Presence of Sterically Hindered Bases. IV. The Polymerization of Isobutylene by the “H<sub>2</sub>O”/AlCl<sub>3</sub> Initiating System

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## Carbocationic Polymerization in the Presence of Sterically Hindered Bases. IV. The Polymerization of Isobutylene by the "H<sub>2</sub>O"/AlCl<sub>3</sub> Initiating System

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### ABSTRACT

The effect of 2,6-di-tert-butyl-pyridine (DtBP) on isobutylene polymerization induced by AlCl<sub>3</sub> in n-hexane, CH<sub>2</sub>Cl<sub>2</sub>, and n-hexane/CH<sub>2</sub>Cl<sub>2</sub> mixtures has been investigated. Polymerization carried out in the presence of DtBP invariably yielded much reduced yields, much elevated molecular weights, and noticeably narrower molecular weight dispersities than those carried out under identical conditions except in the absence of this hindered pyridine. As expected, conversions increase while  $\bar{M}_n$ 's decrease and  $\bar{M}_w/\bar{M}_n$ 's broaden with increasing [AlCl<sub>3</sub>] in the absence of DtBP; however, in the presence of DtBP, increasing [AlCl<sub>3</sub>] leads to increased conversions, increasing  $\bar{M}_n$ 's, and narrowing  $\bar{M}_w/\bar{M}_n$ 's. At constant [AlCl<sub>3</sub>], increasing [DtBP] tends to decrease yields but at the same time increases  $\bar{M}_n$  and narrow  $\bar{M}_w/\bar{M}_n$ . Directionally these effects remain similar by changing the polarity of the medium. The proposition of proton scavenging during chain transfer to monomer by the hindered pyridine helps to explain these observations.

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## INTRODUCTION

This paper concerns the effect of 2,6-di-*tert*-butylpyridine (DtBP) on isobutylene polymerization induced by the "H<sub>2</sub>O"/AlCl<sub>3</sub> initiating system and particularly the effect of DtBP on MWD.

## EXPERIMENTAL

Experiments have been carried out in culture tubes under a nitrogen atmosphere (<100 ppm moisture level) in a stainless steel enclosure. Isobutylene (C.P., Matheson Co.) and methyl chloride (Matheson Co.) were dried by passing the gases through columns filled with a mixture of BaO and molecular sieves (4A). *n*-Hexane was refluxed with fuming sulfuric acid twice, then washed with dilute KOH solution, dried over CaSO<sub>4</sub>, and finally distilled over CaH<sub>2</sub>. Solvent, liquefied isobutylene and DtBP solution were pipetted into culture tubes, capped, and cooled to the desired temperature. Reactions were started by adding prechilled saturate of AlCl<sub>3</sub> in CH<sub>3</sub>Cl solution to the charges. This initiator solution was prepared by adding AlCl<sub>3</sub> (anhydrous, 99.5%) to liquid CH<sub>3</sub>Cl and refluxing for ~10 min. The liquid was cooled, decanted, and discarded. This procedure was repeated twice. Finally the remaining white salt was used for the preparation of a saturated solution by refluxing it in CH<sub>2</sub>Cl. Polymerizations were stopped by the addition of a few milliliters of prechilled methanol. Volatile products were evaporated and the polymer was dried to constant weight at 50°C in a vacuum oven.

Number-average molecular weight  $\bar{M}_n$ , weight-average molecular weight  $\bar{M}_w$ , and MWD were determined by gel permeation chromatography (GPC) using five  $\mu$ -Styragel columns (10<sup>6</sup>, 10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup>, 500 Å), and a Waters R401 differential refractometer at 25°C. Sample concentrations were from 0.1 to 0.2 wt% in tetrahydrofuran and the flow rate was 2.0 mL/min. Calibration curves of molecular weights against elution volumes were obtained with fractionated polyisobutylene samples.

## RESULTS AND DISCUSSION

Polymerizations of isobutylene in CH<sub>3</sub>Cl or CH<sub>2</sub>Cl<sub>2</sub> are heterogeneous because polyisobutylene (PIB) is insoluble in these diluents. In contrast, polymerizations of isobutylene in *n*-hexane are homogeneous and precipitation of PIB does not occur. The influence of temperature, monomer and AlCl<sub>3</sub> concentration on isobutylene polymerization in *n*-hexane has been investigated [1]. Due to the low solubility

TABLE 1. The Effect of  $[AlCl_3]$  on Isobutylene Polymerization in the Presence and Absence of DtBP ( $[isobutylene] = 1.44 M$ , n-hexane solvent,  $-50^\circ C$ , 5 min; polymerizations were triggered by adding 2 mL saturated  $AlCl_3$  in  $CH_3Cl$  solution to 25 mL charge)

$[AlCl_3]$ ( $\underline{M} \times 10^3$ )	$[DtBP]$ ( $\underline{M}$ )	Conversion (%)	$\overline{M}_n$ $\times 10^{-4}$	$\overline{M}_w$ $\times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
1.6	0	24	2.6	11.0	4.3
3.2	0	45	1.8	8.7	5.4
4.8	0	65	1.6	8.9	5.7
1.6	$1.6 \times 10^{-2}$	5	10.3	20.1	1.96
3.2	$1.6 \times 10^{-2}$	12	11.4	21.6	1.90
4.8	$1.6 \times 10^{-2}$	16	12.1	22.0	1.82

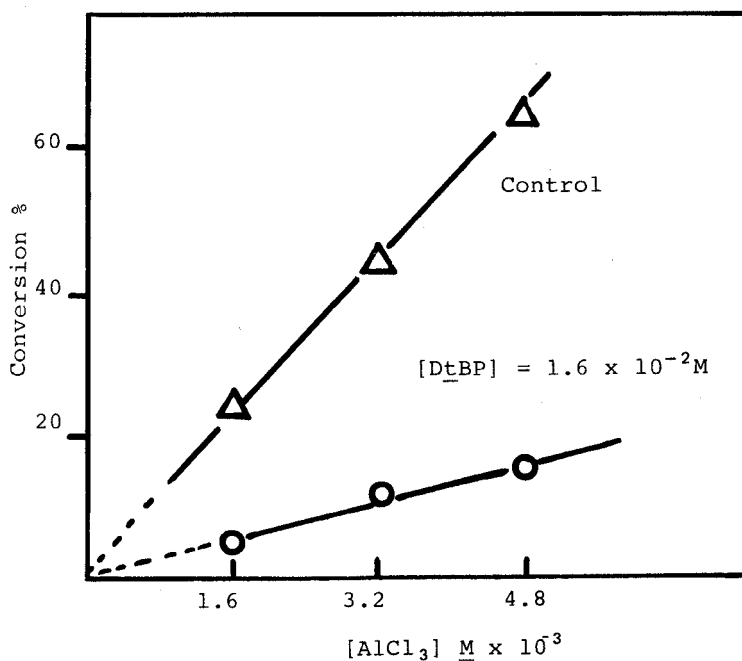


FIG. 1. Effect of  $[AlCl_3]$  on conversion of isobutylene polymerization in the presence and absence of DtBP.

TABLE 2. The Effect of DtBP Concentration on Isobutylene Polymerization Induced by the "H<sub>2</sub>O"/AlCl<sub>3</sub> Initiating System ([isobutylene] = 1.44 M, n-hexane solvent, [AlCl<sub>3</sub>] = 3.2 × 10<sup>-3</sup> M, -50°C, 5 min; polymerizations were induced by the introduction of 2 mL saturated AlCl<sub>3</sub> in CH<sub>3</sub>Cl to a charge of 25 mL)

[DtBP] (M)	Conversion (%)	$\bar{M}_n$ × 10 <sup>-4</sup>	$\bar{M}_w$ × 10 <sup>-4</sup>	$\bar{M}_w/\bar{M}_n$
0	45	1.8	9.7	5.4
8.0 × 10 <sup>-4</sup>	37	2.2	10.1	4.7
4.0 × 10 <sup>-3</sup>	19	6.4	15.5	2.4
8.0 × 10 <sup>-3</sup>	14	6.2	14.3	2.3
2.4 × 10 <sup>-2</sup>	9	9.9	19.7	2.2
4.0 × 10 <sup>-2</sup>	15	12.5	22.4	1.8

of AlCl<sub>3</sub> in n-hexane, a saturated AlCl<sub>3</sub> in CH<sub>3</sub>Cl<sub>3</sub> solution was used to initiate the polymerization of isobutylene.

The data collected in Table 1 reflect the effect of [AlCl<sub>3</sub>] on the polymerization of isobutylene in n-hexane solvent in the presence and absence of 1.6 × 10<sup>-2</sup> M DtBP. As emphasized by Fig. 1, the yields increase linearly with increasing [AlCl<sub>3</sub>] in both cases; however, they are much lower in the presence than in the absence of DtBP. The molecular weights obtained in the absence of DtBP are much lower than those prepared in the presence of DtBP. This big difference in molecular weights cannot be due simply to differences in conversion. Apparently the mechanism of molecular weight control has been altered by the hindered pyridine. The polydispersity ratio obtained in the absence of DtBP is quite broad ( $\bar{M}_w/\bar{M}_n = 4.3-5.7$ ) whereas it becomes considerably narrower ( $\bar{M}_w/\bar{M}_n = 1.8-2.0$ ) in the presence of DtBP.

Table 2 and Figs. 2 and 3 show the effect of [DtBP] on isobutylene polymerization induced by the "H<sub>2</sub>O"/AlCl<sub>3</sub> initiating system in n-hexane at -50°C. Conversions decrease with increasing [DtBP] and level off at 14-15%, while the molecular weights increase several-fold with increasing [DtBP] (see Fig. 2). Importantly, the MWD's decrease significantly with increasing [DtBP] (see Fig. 3).

Directionally similar effects have been obtained by the use of the "H<sub>2</sub>O"/AlCl<sub>3</sub> initiating system and CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub>/n-hexane (1:1) diluents, i.e., with systems in which PIB precipitated during polymerization. Thus in the presence of DtBP conversions decrease, molecular weights increase, and MWD's narrow. Representative data are shown in Table 3.

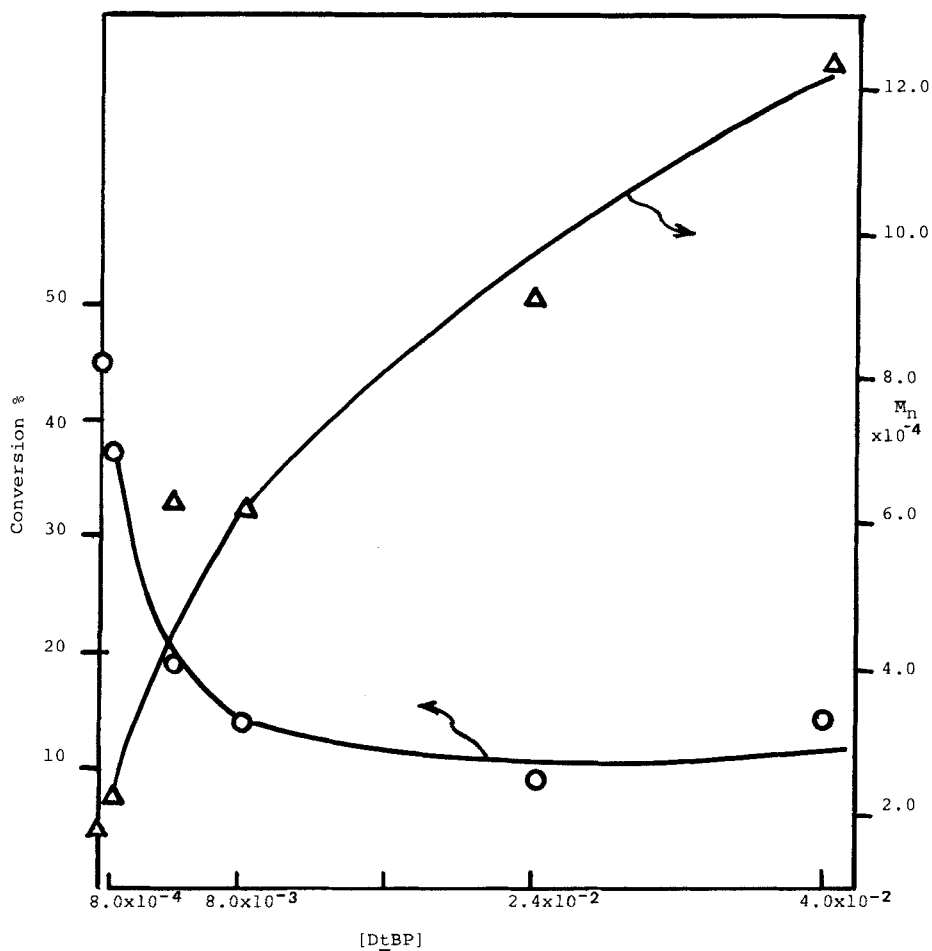


FIG. 2. Effect of [DtBP] on conversion and  $\bar{M}_n$  of isobutylene polymerization.

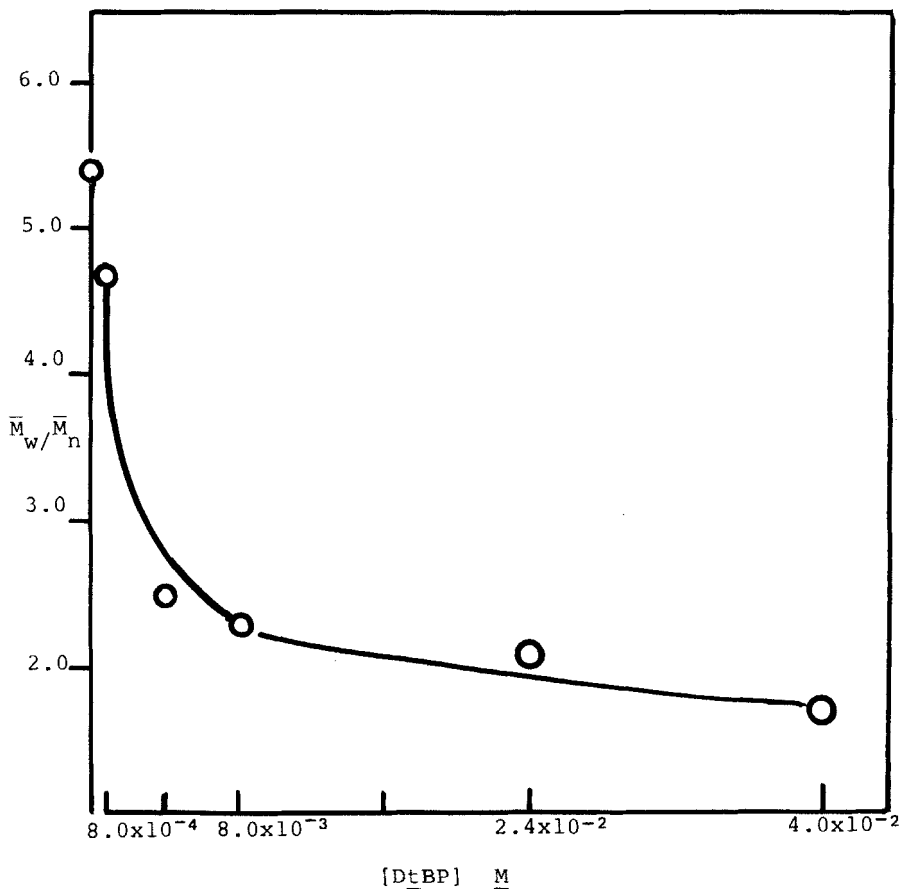
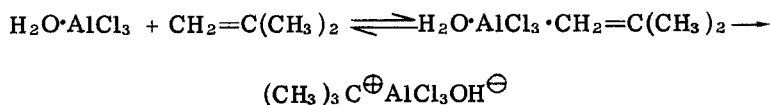


FIG. 3. Effect of  $[DtBP]$  on MWD of isobutylene polymerization initiated by  $AlCl_3$ .

TABLE 3. The Effect of DtBP Concentration on Isobutylene Polymerization Induced by "H<sub>2</sub>O"/AlCl<sub>3</sub> Using CH<sub>2</sub>Cl<sub>2</sub> and n-C<sub>6</sub>H<sub>14</sub>/CH<sub>2</sub>Cl<sub>2</sub> Diluents ([isobutylene] = 1.44 M, [AlCl<sub>3</sub>] = 1.0 × 10<sup>-2</sup> M, -50°C, 5 min, total volume 25 mL)

DtBP (M)	Conversion (%)	$\bar{M}_n$ × 10 <sup>-4</sup>	$\bar{M}_w$ × 10 <sup>-4</sup>	$\bar{M}_w/\bar{M}_n$
<u>In CH<sub>2</sub>Cl<sub>2</sub> Diluent</u>				
0	100	1.8	9.8	5.5
4.0 × 10 <sup>-3</sup>	94	2.4	11.0	3.8
1.6 × 10 <sup>-2</sup>	36	8.1	18.9	2.3
<u>In n-C<sub>6</sub>H<sub>14</sub>/CH<sub>2</sub>Cl<sub>2</sub> (1:1) Diluent</u>				
0	78	1.0	5.6	5.5
1.6 × 10 <sup>-2</sup>	29	5.8	15.1	2.5

These data hold important clues as to the mechanism of isobutylene polymerization with the "H<sub>2</sub>O"/AlCl<sub>3</sub> initiating system. The fact that polymerization occurs at all in the presence of the proton trap indicates "protonless" initiation, i.e., a process in which free or DtBP-trappable protons cannot participate. Initiation in the presence of DtBP may be visualized to occur by the proton migrating from the H<sub>2</sub>O·AlCl<sub>3</sub> complex directly to the monomer without the involvement of the often-postulated hypothetical acid H<sup>+</sup>AlCl<sub>3</sub>OH<sup>-</sup> (the source of H<sub>2</sub>O is impurities; quotation marks omitted for sake of clarity):



In the presence of proton trap, conversions decrease, and this is due to terminative proton entrapment, i.e., trapping the proton during chain transfer to monomer. The significant increase in molecular weights and narrowing of MWD's may suggest an interaction between the propagating chain end and the DtBP. These matters are discussed in a later publication of this series [2].

The MWD data are particularly revealing. The very broad MWD's obtained in the absence of DtBP (see Tables 1, 2 and 3) indicate, in addition to chain transfer to monomer, the operational presence of other MWD broadening factors, i.e., slow initiation, multiple initiating or propagating species, and partial solvation/dissociation of active



chain ends. The reduction or elimination of the most important MWD broadening event, that of chain transfer to monomer, goes a long way to explain the strong MWD narrowing effect of DtBP.

#### ACKNOWLEDGMENTS

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#### REFERENCES

- [1] J. P. Kennedy and R. M. Thomas, *J. Polym. Sci.*, **46**, 233 (1960).
- [2] J. P. Kennedy and R. T. Chou, *J. Macromol. Sci.-Chem.*, **A18**(1), 47 (1982).