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## Carbocationic Polymerization in the Presence of Sterically Hindered Bases. III. The Polymerization of Isobutylene by the Cumyl Chloride/ $\text{BCl}_3$ System

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### ABSTRACT

The mechanism of cationic olefin polymerization has been investigated by studying the effect of 2,6-di-tertbutylpyridine (DtBP) on the polymerization of isobutylene by the  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{Cl}/\text{BCl}_3$  initiating system. In the absence of DtBP, initiation is by cumylation, chain transfer to monomer is absent, and termination is by chlorination. In the presence of DtBP, conversions and molecular weights decrease as a function of DtBP concentration, indicating that while DtBP does not interfere with non-protic initiation by the  $\text{C}_6\text{H}_5\text{C}^+(\text{CH}_3)_2$  carbocation, it functions as a terminating agent. According to Mayo plots, chain transfer to monomer is absent with or without DtBP in the system; however, the ratio  $k_t/k_p$  (the slope of the plot) obtained in the presence of DtBP is  $\sim 25$  times larger than that obtained in the absence of this hindered base which also indicates termination by DtBP. The exclusive presence of  $\text{CH}_2=\text{C}(\text{CH}_3)\sim$  endgroups in polyisobutylene prepared in the presence of DtBP suggests that this base is able to abstract a proton from the propagating  $\sim\text{C}^+(\text{CH}_3)_2$  center. In contrast, according to initiator efficiency data, DtBP does not abstract a proton from the initiating  $\text{C}_6\text{H}_5\text{C}^+(\text{CH}_3)_2$  cation.

## INTRODUCTION

This article concerns a systematic examination of isobutylene (IB) polymerization induced by the  $C_6H_5C(CH_3)_2Cl$  (cumyl chloride, CC)/ $BCl_3$  initiating system in the presence and absence of DtBP. The following series of considerations led us to select specifically the  $C_6H_5C(CH_3)_2Cl/BCl_3$ /isobutylene system for kinetic-mechanistic investigations: 1) First and foremost, earlier investigations have demonstrated that chain transfer to monomer is absent in isobutylene polymerizations cointiated by  $BCl_3$  [1-6]. Thus, if the role of DtBP is only to scavenge protons emerging in the course of chain transfer to monomer, then DtBP should not affect the polymerization in this system. 2) The mechanism of initiation of isobutylene polymerization with  $BCl_3$ -based initiating systems is fairly well understood and it is known that certain substituted benzyl chlorides, e.g., cumyl chloride, are efficient initiators of isobutylene polymerization in conjunction with  $BCl_3$  [4]. 3) Since we did not want DtBP to interfere with initiation, a nonprotic initiating system had to be used. Initiation of isobutylene polymerization by the  $C_6H_5C(CH_3)_2Cl/BCl_3$  system would involve cationation by  $C_6H_5C^+(CH_3)_2$  and not protonation. 4) Termination in  $BCl_3$ -cointiated isobutylene polymerization has been shown to occur by chlorination [4], a process DtBP was expected not to affect.

Investigations described in this paper show that initiation is by cumylation, a process DtBP most likely does not affect. According to  $^1H$  NMR evidence, DtBP is not inert toward the propagating isobutylene cation  $\sim CH_2C^+(CH_3)_2$  and it is able to terminate the polymerization by proton abstraction. The absence of chain transfer in  $BCl_3$ -cointiated isobutylene polymerization has been reconfirmed.

## EXPERIMENTAL

**Materials:** The source and purification of isobutylene and  $BCl_3$  have been described [1]. Cumyl chloride was prepared by hydrochlorination of  $\alpha$ -methylstyrene by bubbling gaseous HCl through a solution of  $\alpha$ MeSt in  $CH_2Cl_2$  at  $0^\circ C$  for several hours. It was purified by distillation under high vacuum and freeze drying. Cyclohexane (SpectraAR, Mallinckrodt) was refluxed with  $CaH_2$  overnight under dry nitrogen atmosphere and distilled before use. Methylene chloride (Eastman Kodak, Reagent Grade) was refluxed successively with  $CaH_2$  and triethylaluminum under dry nitrogen atmosphere and distilled on the day of experiment. 2,6-Di-tert-butylpyridine (Chemical Samples Co., 99%) was used without any further purification.

Polymerizations were carried out under a nitrogen atmosphere ( $< 100$  ppm moisture level) in a stainless steel enclosure [7] in capped Pyrex tubes at  $-50 \pm 1^\circ C$ . The mixing sequence was

isobutylene solution-cumyl chloride-DtBP- $\text{BCl}_3$ . The total volume was 30 mL. The reactants were thermoequilibrated for 20 min before charging the polymerization tubes. Polymerizations were terminated by adding prechilled methanol. The polymer was transferred to preweighed aluminum dishes and the unreacted monomer and solvent was evaporated. The polymer was dried in a vacuum oven at room temperature and weighed. Great efforts were made to obtain well reproducible weight and molecular weight data.

Molecular weights were determined using a Waters high pressure GPC instrument, comprising a Model 6000A Pump; a series of 500,  $10^3$ ,  $10^4$ ,  $10^5$ , and  $10^6$  Å Styragel columns; and a R401 Differential Refractometer. The instrument was calibrated with polyisobutylene standards.

NMR spectra were recorded by a Varian 300 MHz spectrometer.

## RESULTS AND DISCUSSION

### Kinetic Studies

Investigations started by establishing conditions for the polymerization of isobutylene in terms of rates and molecular weights. Reasonable rates and molecular weights could be obtained by the use of 1.0 M IB, 1 to  $1.2 \times 10^{-3}$  M CC, and  $5.0 \times 10^{-3}$  M  $\text{BCl}_3$  in  $\text{CH}_2\text{Cl}_2$  solvent at  $-50 \pm 1^\circ\text{C}$  after 30 min of polymerization, and these conditions have been used throughout the experiments.

"Control" runs, i.e., runs in which CC and DtBP were omitted, were always carried out parallel to experiments and, depending on the temperature and time of polymerization, usually yielded 4-7% polymer. This small amount of PIB obtained was regarded acceptable and was attributed to unscavenged protic impurities. In the absence of DtBP but in the presence of CC, conversions invariably reached ~90% within a few minutes.

Figure 1 shows the results of a representative set of conversion/time experiments in which  $\text{BCl}_3$  was added to CC/IB charges in  $\text{CH}_2\text{Cl}_2$  containing various amounts of DtBP. Evidently the addition of even very small amounts of DtBP significantly reduces yields. The experiment carried out in the absence of DtBP resulted in 90% conversion (off scale, not shown), while that carried out in the absence of CC but in the presence of DtBP yield < 1% conversion. Polymerizations were very rapid and final yields were reached a few minutes after  $\text{BCl}_3$  introduction. There may be a slight upward drift in conversions with extended times; however, this effect, if it is real, is quite small. Since polymerizations were found to be complete within 10-20 min, further kinetic experiments were uniformly carried out for 30 min.

Figure 2 shows the effect of DtBP concentration on ultimate IB conversions, i.e., after 30 min of reaction. In the absence of DtBP the conversion was 90% (off scale, not shown) whereas in the absence

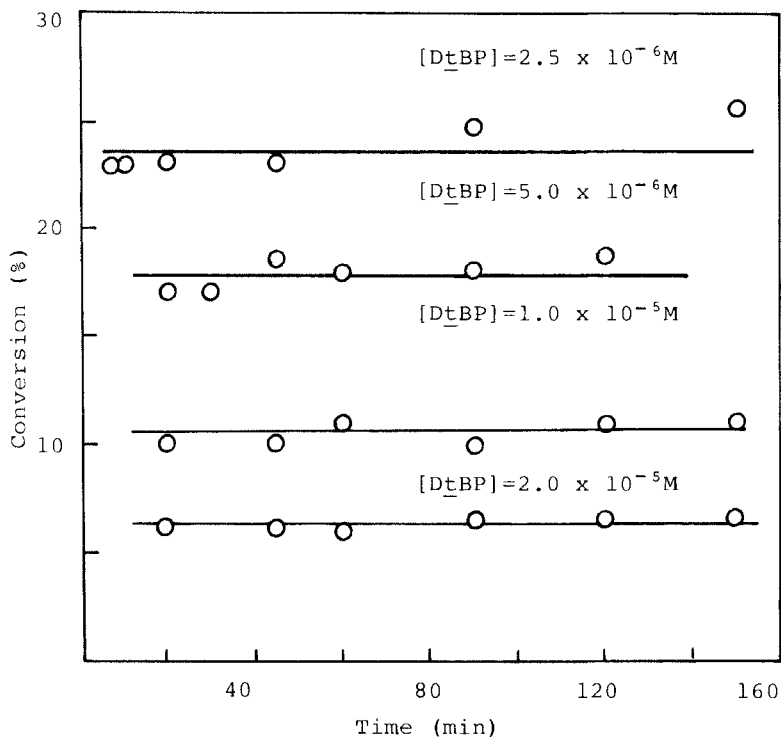


FIG. 1. Isobutylene conversion versus time plots at different DtBP concentrations. ( $[IB] = 1.0 \text{ M}$ ,  $[BCl_3] = 5.0 \times 10^{-3} \text{ M}$ ,  $[CC] = 1.2 \times 10^{-3} \text{ M}$ ,  $\text{CH}_2\text{Cl}_2$  diluent,  $-50 \pm 1^\circ\text{C}$ .)

of CC but in the presence of  $[DtBP] > 5 \times 10^{-6} \text{ M}$ , conversions were  $< 1\%$ . Evidently DtBP strongly reduces PIB yields even in the presence of  $\sim 10^{-6} \text{ M}$  DtBP, i.e., with  $[CC]/[DtBP] \approx 1000$ . The polymerization cannot be completely suppressed even in the presence of large stoichiometric excesses of DtBP; the yields level off at  $\sim 2\%$  with  $[DtBP] \approx 5 \times 10^{-3} \text{ M}$  and some low molecular weight product is formed.

These results are reminiscent to those obtained under similar conditions with  $\alpha\text{MeSt}$  [8, 9]. Evidently initiation by the CC/ $\text{BCl}_3$  system is not blocked by the hindered pyridine base, and a small measure of propagation proceeds even in the presence of relatively vast quantities of the proton trap.

Concurrently with the yields, the molecular weights of PIB's obtained in the above experiments have also been determined. Figure 3 shows these data (numbers in Fig. 3 are molecular weight dispersities, MWD).

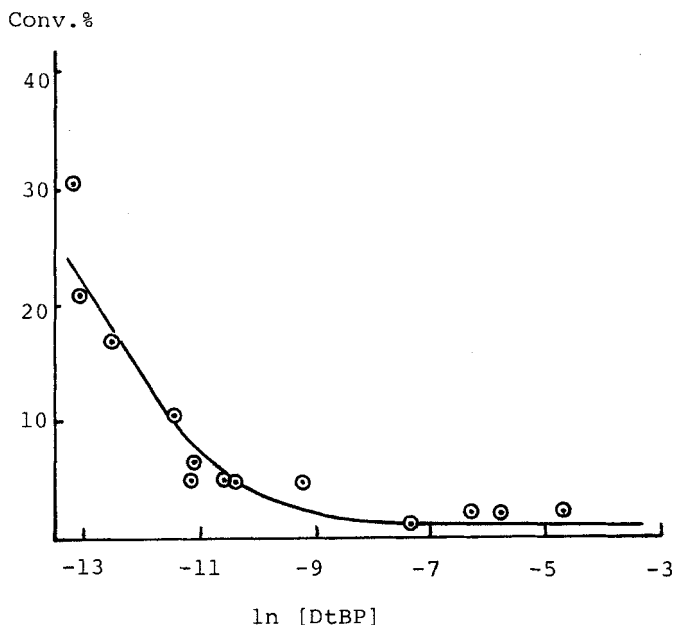


FIG. 2. Isobutylene conversion as a function of DtBP concentration. ( $[IB] = 1.0 \text{ M}$ ,  $[BCl_3] = 5.0 \times 10^{-3} \text{ M}$ ,  $[CC] = 1.0 \times 10^{-3} \text{ M}$ ,  $CH_2Cl_2$  diluent,  $-50 \pm 1^\circ \text{C}$ , 30 min.) Experimental points  $\odot$  and calculated line [14].

Apparently the  $\bar{M}_n$  of PIB is quite sensitive toward the presence of DtBP ( $\bar{M}_n \sim 7 \times 10^4$  in the absence of the base, off scale, not shown). While these observations can be readily explained (see below), these  $\bar{M}_n$  data were quite unexpected in view of our previous experience [8, 9] with  $\alpha\text{MeSt}$  and " $H_2O$ "/ $BCl_3$  in which system  $\bar{M}_n$ 's initially increase (MWD narrows) and then remain constant (constant MWD) with increasing DtBP concentration.

The parallel effect of DtBP concentration on yields and molecular weights of PIB is shown in Fig. 4 which is a plot of  $\bar{M}_n$  versus % conversion at various DtBP concentrations. The linear part of the plot can be smoothly extrapolated to the origin, indicating the absence of chain transfer to monomer in the presence of DtBP. The plot deviates from linearity beyond  $\sim 40\%$  conversion, suggesting the gradual appearance of chain transfer to monomer at higher conversions and/or low [DtBP]. At  $\sim 90\%$  conversion  $\bar{M}_n \sim 7 \times 10^4$ , and  $\sim 20\%$  of the product may be due to chain transfer to monomer.

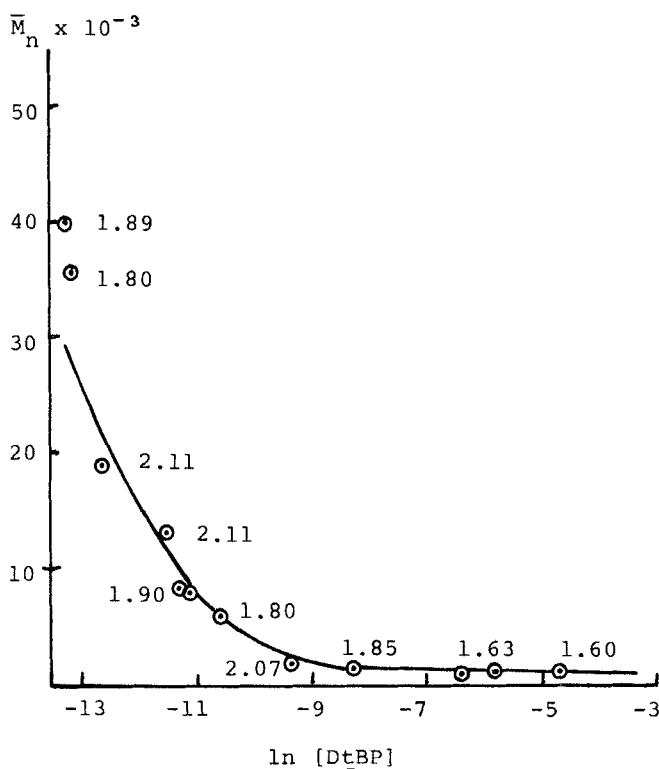


FIG. 3. Polyisobutylene  $\bar{M}_n$  versus DtBP concentration. ( $[IB] = 1.0 \text{ M}$ ,  $[BCl_3] = 5.0 \times 10^{-3} \text{ M}$ ,  $[CC] = 1.0 \times 10^{-3} \text{ M}$ , 30 min,  $CH_2Cl_2$  solvent,  $-50 \pm 1^\circ C$ .) Numbers beside curve are  $\bar{M}_w/\bar{M}_n$ . Experimental points  $\odot$  and calculated line [14].

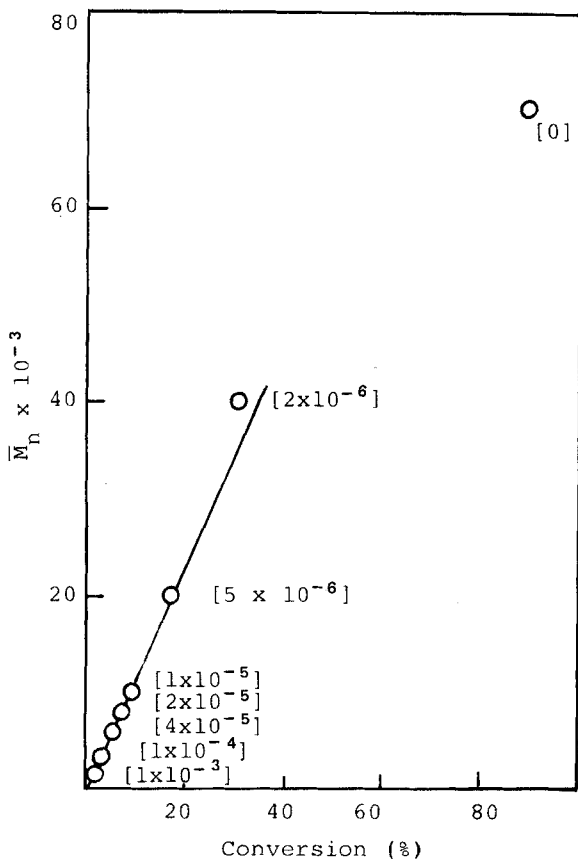


FIG. 4. Polyisobutylene  $\bar{M}_n$  versus conversion at various DtBP concentrations. ( $[IB] = 1.0 \text{ M}$ ;  $[BCl_3] = 5.0 \times 10^{-3} \text{ M}$ ,  $[CC] = 1.0 \times 10^{-3} \text{ M}$ ,  $\text{CH}_2\text{Cl}_2$  solvent,  $-50 \pm 1^\circ \text{C}$ .) The numbers in brackets are  $\bar{M}$  of DtBP.



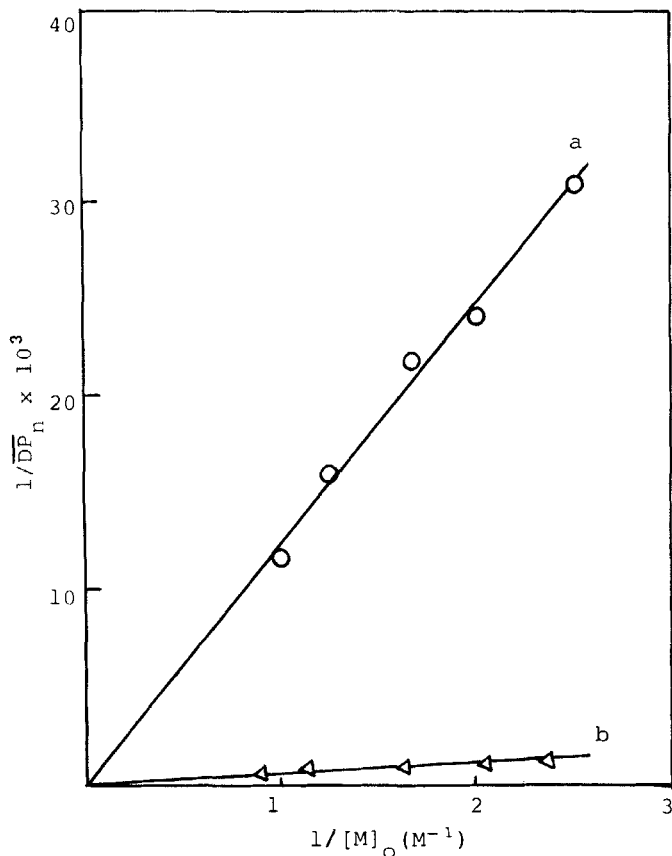


FIG. 5. Mayo plots (a,  $[BCl_3] = 5.0 \times 10^{-3} M$ ,  $[CC] = 1.0 \times 10^{-3} M$ ,  $[DtBP] = 1.0 \times 10^{-5} M$ ,  $CH_2Cl_2$  diluent, compensating solvent cyclohexane,  $-50 \pm 1^\circ C$ , b, data from Ref. 10).

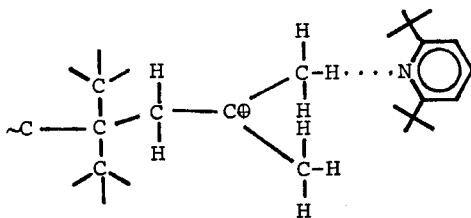
The absence of chain transfer to monomer in the  $CC/BCl_3/IB$  systems in the presence of DtBP is confirmed by the Mayo ( $1/\overline{DP}_n$  versus  $1/[M]_0$ ) plot (Line a) displayed in Fig. 5. The absence of an intercept indicates the absence of chain transfer to monomer over a wide range of monomer concentrations at 4-10% conversions in the presence of DtBP.

It is of interest to compare the slopes of the two Mayo plots shown in Fig. 5. In general the slope of a Mayo plot reflects the rate constant ratio of termination over propagation  $k_t/k_p$ . The slope of Plot 5a

constructed with data obtained in polymerizations carried out in the presence of DtBP is  $\sim 25$  times larger than that of Plot 5b obtained earlier [10] in a set of similar (though not identical) inifer experiments in the absence of DtBP;  $k_t/k_p = 1.28 \times 10^{-2}$  and  $5.0 \times 10^{-4}$  with and without DtBP, respectively. Evidently termination is much enhanced in the presence of DtBP which is further evidence for the existence of terminative proton entrapment by this hindered base. In line with these considerations it is proposed that the slope of Plot 5a reflects  $(k_{t,Cl} + k_{t,DtBP})/k_p$ , where the nominator is the sum of rate constants of termination by chlorination  $k_{t,Cl}$  and termination by DtBP  $k_{t,DtBP}$ .

### Termination by DtBP in Isobutylene Polymerization

Proton NMR spectroscopy holds the clue as to the nature of termination of isobutylene polymerization by DtBP.  $^1H$  NMR spectra of low molecular weight PIB's ( $\bar{M}_n \approx 500$ ) prepared for this purpose in the presence of DtBP revealed the presence of only the exo endgroup  $CH_2=C(CH_3)CH_2\sim$  characterized by resonances at 4.72 and 4.92 ppm (absence of resonance at  $\sim 5.1$  ppm indicates the absence of endo endgroup  $(CH_3)_2C=CH\sim$ ). Evidently DtBP is able to abstract protons from  $-CH_3$  groups flanking the propagating polyisobutylene carbocations; however, it is unable to interact with the sterically less accessible  $-CH_2-$  protons:



Indeed a thorough search through the literature on DtBP has shown that equilibria of the type



have been postulated and investigated [11-13].

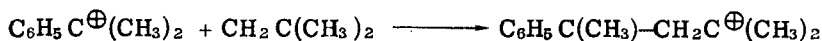
The Mechanism of Isobutylene Polymerization by the  $C_6H_5C(CH_3)_2Cl/BCl_3$  Initiating System and the Effect of DtBP

In view of the findings presented in the previous sections and on the basis of extensive mechanistic information available relative to  $RCI/BCl_3$ /isobutylene systems in general [1-6], the following mechanism is proposed for the polymerization of isobutylene in the presence of cumyl chloride initiator:

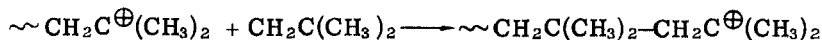
Ion generation:



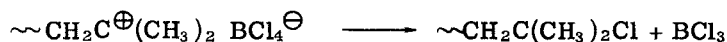
Cationation:



Propagation:

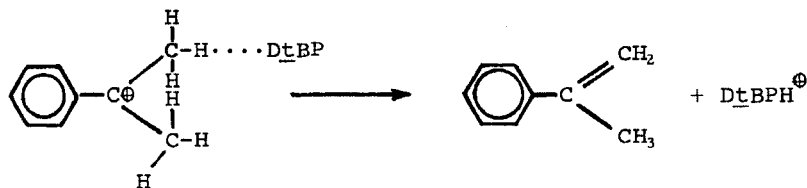


Termination:



Chain transfer to the monomer is absent [1].

In view of the possibility of termination by proton abstraction from  $-CH_3$  groups flanking the propagating polyisobutylene carbocation, the possibility of proton abstraction from the initiating cumyl cation also arises:



This possibility was examined by determining the initiation efficiency ( $I_{eff}$  = moles of polyisobutylene formed per mole of cumyl chloride

TABLE 1. Initiator Efficiency in the Cumyl Chloride/ $\text{BCl}_3$ /Isobutylene System in the Presence of DtBP ( $[\text{BCl}_3] = 5 \times 10^{-3} \text{ M}$ ,  $[\text{CC}] = 1 \times 10^{-3} \text{ M}$ , total volume 30 mL, 30 min,  $-50 \pm 1^\circ \text{C}$ )

$[\text{IB}]$ ( $\text{M}$ )	$[\text{DtBP}]$ ( $\text{M}$ )	PIB mol <sup>a</sup> $\times 10^5$	$I_{\text{eff}}^b$
1.0	0	2.0	0.67
1.0	$2.5 \times 10^{-6}$	1.6	0.53
1.0	$5.0 \times 10^{-6}$	1.5	0.50
1.0	$1.5 \times 10^{-5}$	2.0	0.67
1.0	$5.0 \times 10^{-5}$	1.7	0.57
1.0	$1.0 \times 10^{-4}$	2.5	0.83
1.0	$4.0 \times 10^{-4}$	2.2	0.73
0.2	$1.0 \times 10^{-5}$	2.5	0.83
0.5	$1.0 \times 10^{-5}$	2.1	0.70
0.6	$1.0 \times 10^{-5}$	2.2	0.73
0.8	$1.0 \times 10^{-5}$	1.7	0.60

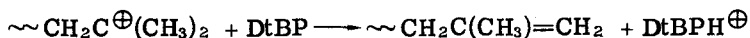
<sup>a</sup>  $\text{g PIB}/\bar{M}_n$ .

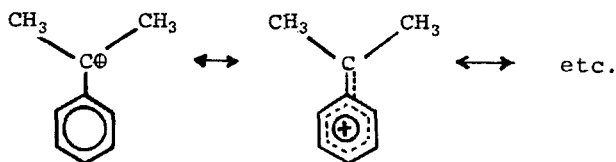
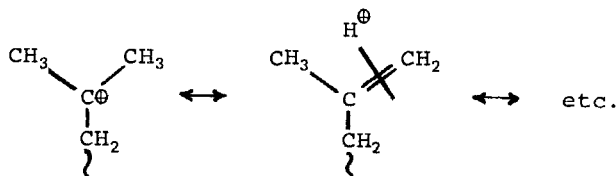
<sup>b</sup>  $I_{\text{eff}} = \text{moles of PIB}/\text{moles of CC}$ .

input). According to the data in Table 1,  $I_{\text{eff}}$  is constant with  $0.67 \pm 0.15$  over a wide range of DtBP concentrations, indicating that 1) the above possibility may be neglected at least under the experimental conditions used, and 2) chain transfer to cumyl chloride is unimportant. If chain transfer to cumyl chloride were important,  $I_{\text{eff}}$  would be close to 1.0. Further it could be argued that proton abstraction by DtBP occurs more readily from  $\sim \text{CH}_2\text{C}^\oplus(\text{CH}_3)_2$  than from  $\text{C}_6\text{H}_5\text{C}^\oplus(\text{CH}_3)_2$  because of the more acidic H's (hyperconjugation) in the former than in the latter cation as shown on the following page.

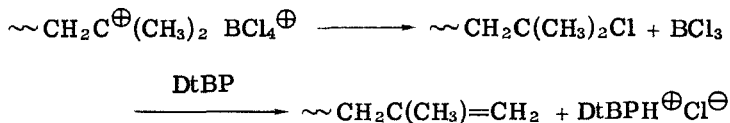
The reason why  $I_{\text{eff}}$  is somewhat less than unity may be due to the presence of some cumyl cation-consuming impurities and/or to a very small extent of chain transfer to monomer whose operational effect remains undetected by kinetic experiments (i.e., Mayo plots).

In the presence of DtBP the same basic mechanism holds except DtBP induces an additional termination step:





The possibility of termination by chlorination followed by HCl abstraction has been considered:



However, the consequences of this mechanism are inconsistent with the data: If dehydrochlorination by DtBP did occur, the yield and  $\bar{M}_n$  of polyisobutylene would be independent of DtBP concentration. This, however, is contrary to observations (cf. Figs. 1-4).

#### ACKNOWLEDGMENTS

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