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LIVING CARBOCATIONIC POLYMERIZATION. VII. LIVING POLYMERIZATION OF ISOBUTYLENE BY TERTIARY ALKYL (OR ARYL) METHYL ETHER/BORON TRICHLORIDE COMPLEXES

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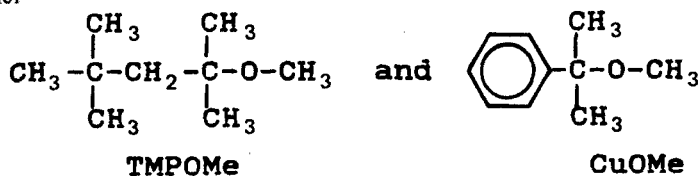
ABSTRACT

It has been discovered that the living polymerization of isobutylene (IB) can be induced by $\text{MeOR}^t/\text{BCl}_3$ initiating systems in CH_2Cl_2 or CH_3Cl at -10 and -30°C . Diagnostic proof for the living polymerizations are 1) proportionality of \bar{M}_n to polyisobutylene (PIB) formed and 2) independence of number of PIB chains of amount of PIB formed. By the use of aged $\text{C}(\text{CH}_3)_3\text{CH}_2\text{OMe}/\text{BCl}_3$ and $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{OMe}/\text{BCl}_3$ systems, initiation efficiency (I_{eff}) $\approx 100\%$ and \bar{M}_n is determined by the $[\text{monomer}]_0/[\text{initiator}]_0$ ratio. Polymerizations quenched by methanol yielded *t*-chloro end groups.

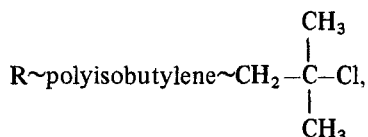
INTRODUCTION

In the course of our continuing investigation on living carbocationic polymerization of olefins [1], we have discovered that certain ethers, specifically MeOR^t ethers (where $\text{Me} = \text{CH}_3$ and $\text{R}^t =$ tertiary organic group) in conjunction with BCl_3 are efficient initiating systems for the living polymerization of isobutylene (IB) at relatively high temperatures, e.g., -30 to

-10°C . By the use of MeOR^t , we have prepared living polyisobutylenes (PIB) with one propagating center, and with certain di-*t*-ethers we have synthesized linear PIB's propagating at both extremities. This paper concerns the demonstration of living polymerization of isobutylene by an aliphatic and an aromatic *t*-ether



in conjunction with BCl_3 coinitiator, and the synthesis of ω -*t*-chloro polyisobutylenes:



where $\text{R} = \text{C}(\text{CH}_3)_3\text{CH}_2\text{C}(\text{CH}_3)_2-$ or $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2-$. A future communication will deal with telechelic products.

EXPERIMENTAL

Materials

The source and purity of the solvents, isobutylene, and BCl_3 have been described [2, 3].

2,4,4-Trimethyl-2-methoxy pentane (TMPOMe) was prepared by etherifying 2,4,4-trimethyl-2-pentanol obtained from 2,4,4-trimethyl-1-pentene [4]. Etherification of the alcohol was carried out as follows: In a 50-mL two-neck round-bottom flask equipped with condenser, dropping funnel, and magnetic stirring bar, under a dry N_2 atmosphere, was placed sodium hydride (Aldrich Chemical Co., 2.5 g, 0.1 mol) and then vacuum-distilled 2,4,4-trimethyl-2-pentanol (4.0 g, 0.03 mol) was added. The pasty mixture was allowed to react for 16 h. After the evolution of H_2 stopped, freshly distilled methyl iodide (Fisher Scientific Co., 4 mL, 0.06 mol) was added, and stirring was continued for 2 more hours. Then anhydrous diethyl ether (50 mL) was added to the paste, the suspension was filtered, and the solvent and the unreacted methyl iodide were evaporated

(Rotavap). Yield: 90% TMPOMe. The extent of etherification was analyzed by $^1\text{H-NMR}$ spectroscopy. The resonance at 3.0 ppm associated with $-\text{OCH}_3$ was quantitatively related to the sharp resonances at 1.33, 1.06, and 0.9 ppm associated with $-\text{CH}_2-$, $-\text{C}(\text{CH}_3)_2-$ and $-\text{C}(\text{CH}_3)_3$, respectively. According to this evidence, essentially pure ether was obtained. This compound has also been prepared by another route to much lower conversions [5].

2-Phenyl-2-methoxy-propane (cumyl methyl ether, CuOMe). In a 250-mL one-neck round-bottom flask, equipped with a condenser and magnetic stirring bar, a solution of 2-phenyl-2-propanol (Lancaster Synthes, 20 g, 0.147 mol) in 60 mL methanol was placed, and concentrated sulfuric acid (Fisher, reagent grade, 0.007 mL) was added. After refluxing ($\sim 65^\circ\text{C}$) for 16 h, the charge was cooled to room temperature, *n*-pentane (100 mL) was added, and the mixture stirred for a few minutes. The organic layer was washed several times with water, separated, and dried with anhydrous sodium sulfate. Finally the product was filtered and the solvent removed (Rotavap). Yield: $\sim 100\%$. The extent of etherification was analyzed by $^1\text{H-NMR}$ spectroscopy. The resonance at 3.0 ppm associated with $-\text{OCH}_3$ was quantitatively related to the resonance in the range 7.0-7.6 ppm characteristic of aromatic protons and to the sharp resonance at 1.48 ppm associated with $-\text{CH}_3$. According to this evidence, essentially pure ether was obtained. An alternate, more involved route to this compound has been described [6].

Procedures

All the experiments were carried out under a blanket of dry nitrogen in a safety enclosure (dry box). General material handling techniques have been described previously [2, 3, 7]. Orienting experiments (reported in Table 1) were carried out in 60-mL test tubes with manual agitation. The test tubes were filled with solvent, IB, and initiator, and the BCl_3 was added last. After 30 min the reactions were quenched with prechilled MeOH and the products worked up. Details of the experimental technique are identical to those published earlier [7].

The incremental-monomer-addition (IMA) and the all-monomer-in (AMI) techniques have also been described in detail [7]. Characterization methods by GPC and $^1\text{H NMR}$ have been described [2, 3, 7].

Termination Studies

The end groups of representative PIB's have been analyzed by $^1\text{H-NMR}$ spectroscopy. To facilitate quantitative analysis the *t*-chloro end groups were

TABLE 1. Demonstration of Initiating Activity of Various MeOR^t/BCl₃ Systems under Various Conditions^a

R ^t	Concentration, mmol/L	Diluent	Temperature, °C	Yield, g	Conversion, %	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	<i>I</i> _{eff} , %
—	—	CH ₂ Cl ₂	-30	—	78	41 400	92 000	2.2	—
TMP	76	CH ₂ Cl ₂	-30	1.55	>98	3 900	6 600	1.7	26
TMP	23	CH ₂ Cl ₂	-30	1.38	>98	7 700	15 400	2.0	39
TMP	7.4	CH ₂ Cl ₂	-30	1.33	>98	16 900	37 200	2.2	53
—	—	CH ₂ Cl ₂	-30	—	78	41 400	92 000	2.2	—
Cu	77.3	CH ₂ Cl ₂	-30	1.53	>98	1 500	5 000	3.3	66
Cu	23	CH ₂ Cl ₂	-30	1.42	>98	4 650	14 400	3.0	66
Cu	7.43	CH ₂ Cl ₂	-30	1.48	>98 ^b	13 700	30 100	2.2	73

—	—	CH ₃ Cl	-30	13	62 800	111 800	1.78	—
Cu	77.3	CH ₃ Cl	-30	>98	960	2 900	3.0	104
Cu	23	CH ₃ Cl	-30	>98	3 600	8 600	2.3	83
Cu	7.43	CH ₃ Cl	-30	>98 ^b	14 700	29 000	1.9	68
—	—	CH ₂ Cl ₂	-10	70	31 000	77 500	2.5	—
Cu	23	CH ₂ Cl ₂	-10	>98	5 000	15 000	3.0	60
Cu	7.43	CH ₂ Cl ₂	-10	>98 ^b	12 000	36 000	3.0	75

^a[BCl₃] = 0.37 mol/L; [M] = 1.173 mol/L; t = 30 min; total volume = 20 mL.

^bConversion was ~100% after 1 min.

converted to $-\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$ end groups by the well-established method [8, 9].

RESULTS AND DISCUSSION

Orienting Experiments

Following our discovery of living carbocationic polymerization of isobutylene (and other olefins) by the use of *t*-organic ester/ BCl_3 complexes [1, 7], we postulated that *t*-ethers in conjunction with BCl_3 may also initiate such reactions. A search of the literature concerning ether/ BCl_3 complexes and their reactions [10-12] gave us further encouragement, particularly the information that BCl_3 -mediated cleavage of ethers occurs via cationic intermediates by S_N1 mechanisms under very mild conditions and gives the highest yields.

Thus a series of experiments was carried out to demonstrate the initiating activity of *t*-ether/ BCl_3 complexes for the polymerization of isobutylene. Table 1 summarizes experimental conditions and results. In these experiments neat BCl_3 was added to IB/MeOR^t solvent charges in large test tubes (for further details, see Experimental). Polymerizations were very rapid and could be judged by the appearance of cloudiness due to the precipitation of PIB in CH_2Cl_2 and CH_3Cl . After an arbitrary 30 min, the polymerizations were quenched by chilled MeOH.

Evidently both TMPOMe and CuOMe are efficient initiators in conjunction with BCl_3 coinitiator for the polymerization of isobutylene in polar (CH_3Cl , CH_2Cl_2) diluents in the -10 to -30°C range. The results of control experiments carried out in the absence of *t*-ethers (using only BCl_3) are completely in line with earlier experience [1, 7, 13]: conversions were rather high ($\sim 78\%$) in CH_2Cl_2 , indicating the presence of copious protic impurities which, short of high-vacuum drying, are very difficult to remove [14]. However, even in these runs, conversions went to completion in the presence of *t*-ethers. In contrast to those in CH_2Cl_2 , conversions of the controls in CH_3Cl were much lower ($\sim 13\%$), which is again in line with earlier experience [1, 7, 13].

Conversions rose rapidly and were invariably $\sim 100\%$ in the presence of *t*-ethers. It was ascertained in several runs that $\sim 100\%$ conversions were attained after 1 min (Table 1). Most encouragingly, the molecular weights were determined by the $[\text{IB}]/[\text{MeOR}^t]$ ratio and were independent of temperature. Also, $^1\text{H-NMR}$ analysis of low- \bar{M}_n PIB's did not show unsaturated end groups, suggesting the absence of H^\oplus expulsion, i.e., chain transfer to monomer.

Closer scrutiny of these scouting results and those published earlier (Table

I in Ref. 7) show great similarities and lead to similar conclusions; for example, in regard to the negligible effect of moisture or protic impurities in these systems [7]. Also, in regard to differences between aliphatic and aromatic ether (ester [7]) initiators, we found that the aliphatic TMPOMe gives much lower initiator efficiencies (I_{eff}) than the aromatic CuOMe ($I_{eff} = 66\text{-}100\%$).

Experimental Proof for the Living Polymerization of Isobutylene in the Presence of $\text{MeOR}^t \cdot \text{BCl}_3$ Complexes

Linear \bar{M}_n versus amount-of-polymer-formed plots starting from the origin indicate living (transferless and terminationless) polymerizations. If the rate of initiation is much faster than that of propagation, \bar{M}_w/\bar{M}_n will approach 1.0. Systematic kinetic experimentation demonstrates the living nature of $\text{MeOR}^t/\text{BCl}_3/\text{IB}$ polymerization systems under our experimental conditions. Because of the very rapid polymerizations, we were unable to use the classical technique (i.e., adding initiator to a monomer charge followed by removing a series of aliquots as a function of time for conversion and molecular weight analysis) but were compelled to use the incremental monomer addition (IMA) technique as developed for $\text{MeCOOR}^t/\text{BCl}_3$ systems [1, 7] and described in the next paragraph. Figures 1 and 2 show the results of four series of experiments.

Figure 1 summarizes results with the $\text{TMPOMe}/\text{BCl}_3$ system. Plot 1a shows the correlation between \bar{M}_n and PIB produced as obtained by the IMA technique, i.e., a series of tubes was filled with the same TMPOMe/IB charges, and at zero time BCl_3 coinitiator was added to all the tubes. After 30 min the reaction in the first tube was quenched, and a quantity of IB was added to the remaining four charges. After another 30 min the reaction in the second tube was quenched and a quantity of IB was added to the remaining three charges, etc. Plot 1b shows the results obtained in essentially the same experiment, except with "aged" initiating system. Thus a series of five tubes was charged with $\text{MeOR}^t/\text{BCl}_3$ and stored at -30°C for 30 min ("aging"). At zero time a quantity of IB was added to all five reactors. After 30 min the reaction was quenched in the first reactor and the same quantities of IB were added to the remaining four tubes. After an arbitrary 30 min the reaction was quenched in the second tube and, at the same time, the same quantities of IB were added to the remaining three tubes, etc.

The linear \bar{M}_n versus PIB-formed plots starting at the origin demonstrate living polymerizations up to $\bar{M}_n \approx 20\,000$. The solid lines are "theoretical," i.e., indicate \bar{M}_n expected at 100% conversions under the experimental conditions employed. In Series 1a, higher-than-expected \bar{M}_n was obtained, most likely because the rate of initiation with unaged $\text{TMPOMe}/\text{BCl}_3$ systems was

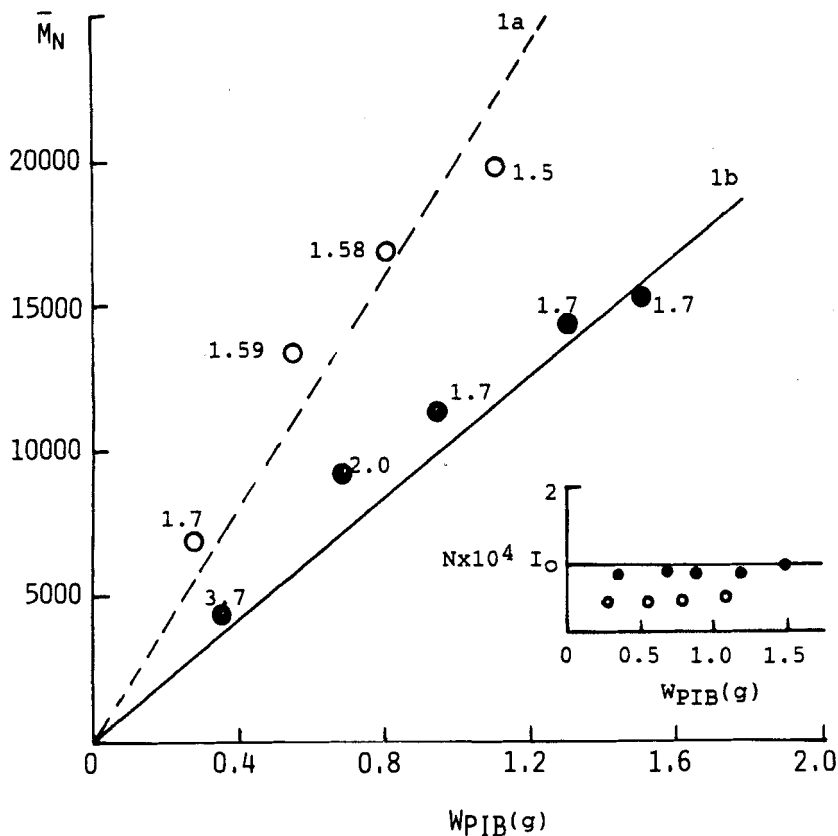


FIG. 1. \bar{M}_n and N (number of PIB chains, see inset) versus W_{PIB} (weight of PIB formed) in the TMPOMe/ BCl_3 /IB/ CH_2Cl_2 / $-30^\circ C$ system by the IMA technique. (a) Without aging (○), (b) TMPOMe/ BCl_3 aging for 30 min (●). [TMPOMe] = 4.89 mmol/L, [BCl_3] = 155 mmol/L. Total volume = 20 mL. Numbers indicate \bar{M}_w/\bar{M}_n values. The solid lines are theoretical plots.

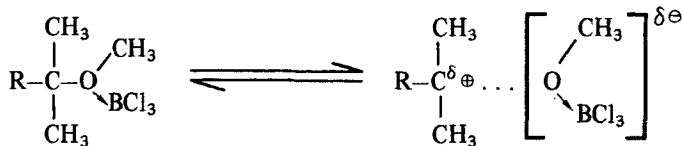
relatively low; $I_{eff} = \sim 60\%$, i.e., the monomer was consumed before all the TMPOMe had disappeared by the initiation reaction. In Series 1b, with the aged initiating system, theoretical results were obtained, and the charged [IB]/[TMPOMe] ratio indeed controlled the \bar{M}_n . The I_{eff} in these experiments was $\sim 100\%$. Significant differences are noted between the I_{eff} and \bar{M}_w/\bar{M}_n results obtained with aged and unaged initiating systems, i.e., higher

I_{eff} and broader molecular weight distributions occur with aged systems. The reason for these discrepancies is obscure at the present.

The horizontal plots of the number of PIB chains versus PIB formed (inset in Fig. 1) further corroborate these conclusions. The horizontal plots indicate that the number of PIB chains (i.e., active sites) remain unchanged during the runs, which in turn suggests living systems. The horizontal line obtained for Series 1a is much below the theoretical $N = 1.0$ line due to the relatively lower I_{eff} in these runs. The line for Series 1b is within experimental error of unity.

The breadth of the molecular weight distributions ($\overline{M}_w/\overline{M}_n$) in Fig. 1 gradually decrease with each monomer addition, which is the expected behavior for living systems. Again, similar phenomena have been described for the $\text{MeCOOR}^t/\text{BCl}_3$ systems [1, 7].

Figures 2 and 3 show the results of experiments with $\text{CuOMe}/\text{BCl}_3$ in CH_2Cl_2 and CH_3Cl diluents at -30°C . In these systems, close to theoretical results were obtained by the IMA technique and aging was unnecessary. Evidently the aromatic system is more reactive than the aliphatic one because the rate of ion formation is facilitated by resonance stabilization by the aromatic ring:



where $\text{R} = (\text{CH}_3)_3\text{C}-\text{CH}_2-$ or C_6H_5- , i.e., the equilibrium is further to the right with CuOMe than with TMPOMe .

The Effect of Diluent on the Living Polymerization of Isobutylene

In view of our previous experience [7], it was of interest to compare the living polymerization of IB in CH_2Cl_2 and CH_3Cl . Figure 4 shows the results. Similarly to the earlier observations [7], the polymerization in CH_2Cl_2 by the IMA technique invariably gave theoretical results, whereas the rates in CH_3Cl were somewhat lower. The less than 100% conversions obtained in CH_3Cl can be increased to 100% by not quenching the system after the arbitrary 30 min but letting the heterogeneous systems "live" longer. The line in Fig. 4 shows the increase in yield in a representative experiment. These observations are essentially identical to those made earlier with $\text{MeCOOR}^t/\text{BCl}_3$ systems [7].

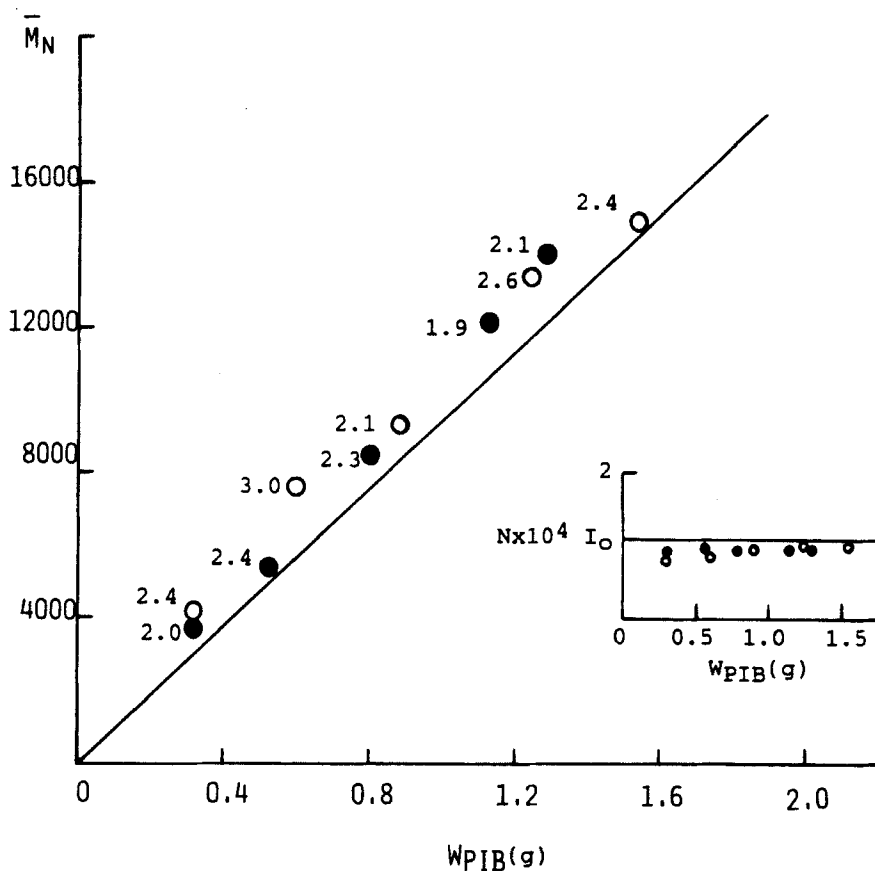


FIG. 2. \bar{M}_n and N (number of PIB chains, see inset) versus W_{PIB} (weight of PIB formed) in the CuOMe/BCl₃/IB/-30°C system by the IMA technique. (a) CH₃Cl (●), (b) CH₂Cl₂ (○). [CuOMe] = 5.76 mmol/L, [BCl₃] = 155 mmol/L. Total volume = 20 mL. Numbers indicate \bar{M}_w/\bar{M}_n values. The solid lines are theoretical plots.

Mechanistic Studies

For reasons identical to those developed for the MeCOOR^f/BCl₃ system (i.e., to gain deeper insight into the details of undesirable chain transfer to monomer processes) [7], a series of experiments was carried out with the CuOMe/BCl₃/IB/CH₂Cl₂ system by various techniques at -30 and -10°C. First we compared the data obtained at -30 and -10°C by

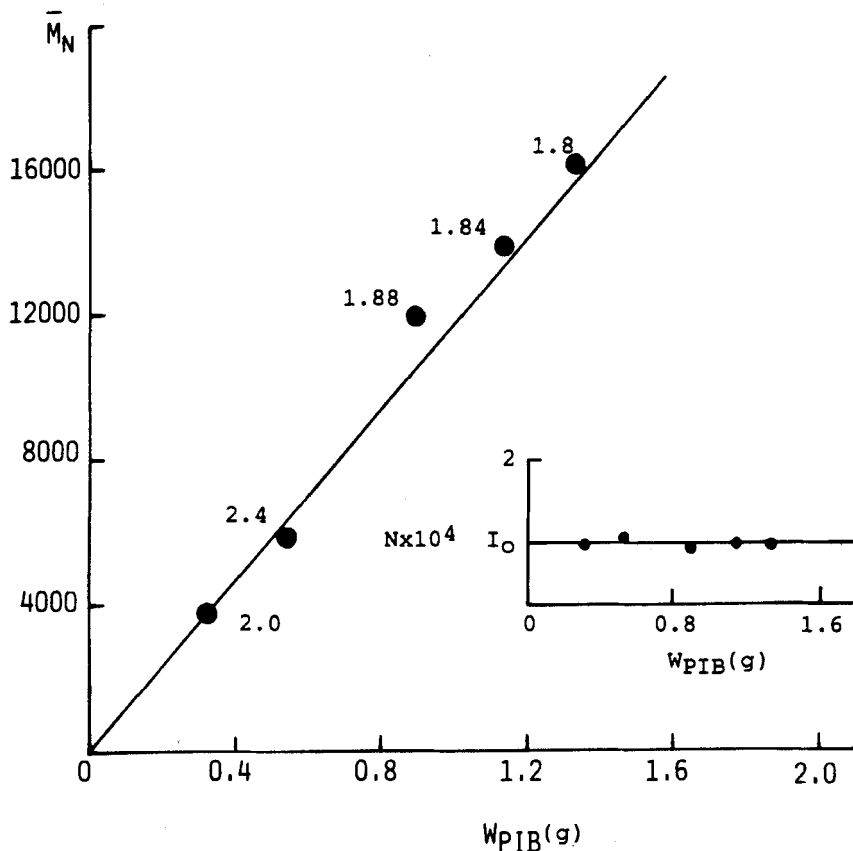


FIG. 3. \bar{M}_n and N (number of PIB chains, see inset) versus W_{PIB} (weight of PIB formed) in the CuOMe/ BCl_3 /IB/ CH_3Cl / $-30^\circ C$ system by the IMA technique: $[CuOMe] = 3.46 \text{ mmol/L}$, $[BCl_3] = 99 \text{ mmol/L}$. Total volume = 25 mL. Numbers indicate \bar{M}_w/\bar{M}_n values. The solid lines are theoretical plots.

the IMA technique. Figure 5 shows the results of experiments carried out at $-10^\circ C$. The only difference between these results and those obtained with the $MeCOOR^t/BCl_3$ system under the same conditions [7] is that the deviation from the theoretical line in the \bar{M}_n plot for the $-10^\circ C$ experiment becomes significant after the second or third monomer addition, rather than after the first increment as in the $MeCOOR^t/BCl_3$ system [7]. In line with

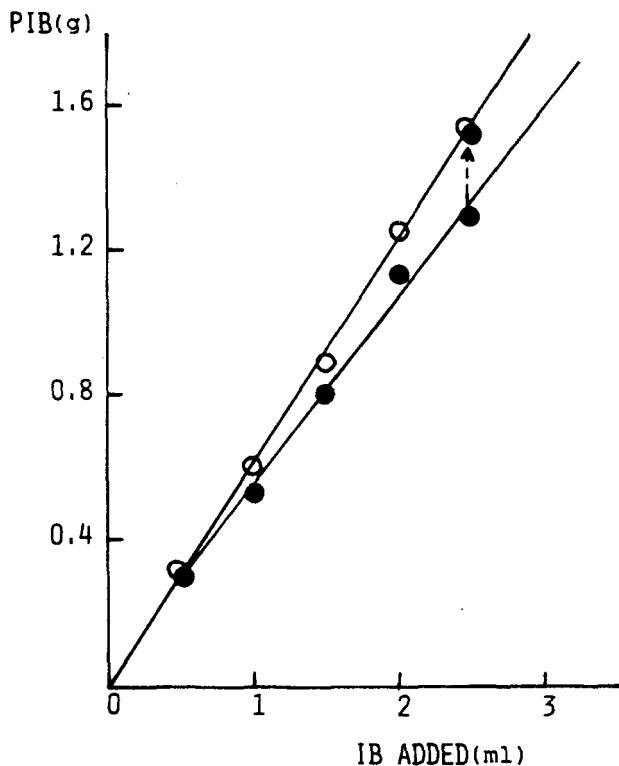


FIG. 4. The weight of PIB formed versus the cumulative amount of IB added in CH_2Cl_2 (○) and CH_3Cl (●) at -30°C , 30 min between monomer additions. $[\text{CuOMe}] = 5.76 \text{ mmol/L}$, $[\text{BCl}_3] = 155 \text{ mmol/L}$. Total volume = 20 mL.

our earlier analysis, therefore, we carried out a series of experiments in which the same amounts of BCl_3 were added to a series of five reactors containing an increasing amount of monomer at -10°C (AMI technique). Gratifyingly, essentially theoretical \bar{M}_n values were obtained even at -10°C by this technique. These results are further corroborated by the N plots shown in the inset of Fig. 5.

Similarly to earlier investigations [7], the absence of second-order chain transfer to monomer has been experimentally demonstrated in the $\text{CuOMe}/$

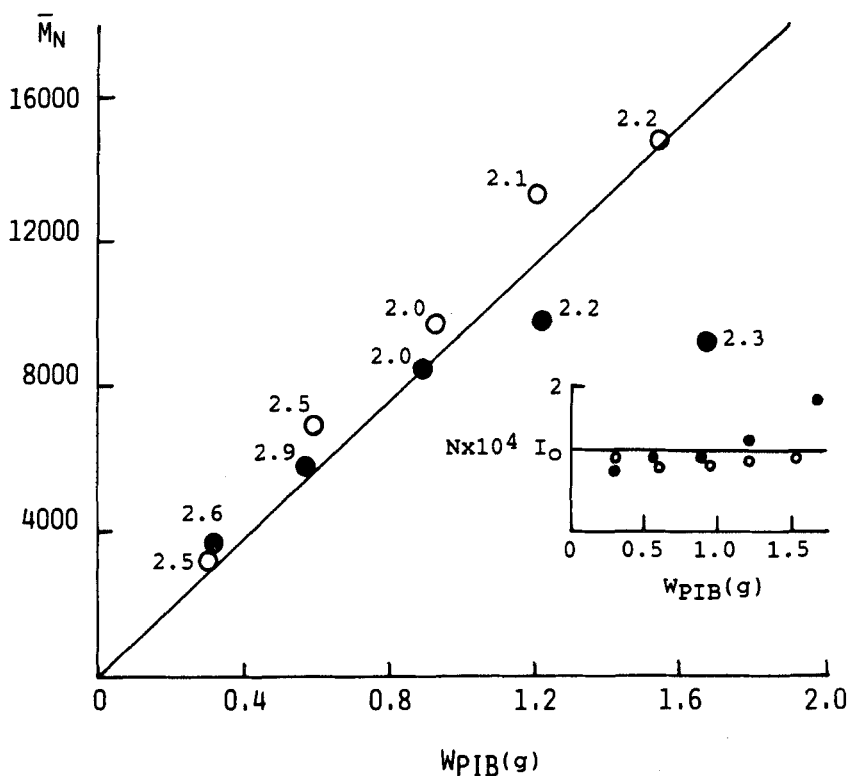


FIG. 5. \bar{M}_n and N (number of PIB chains, see inset) versus W_{PIB} (weight of PIB formed) in the CuOMe/BCl₃/IB/CH₂Cl₂ system by the IMA technique at -10°C (●) and with the AMI technique at -10°C (○). [CuOMe] = 5.76 mmol/L, [BCl₃] = 155 mmol/L. Total volume = 20 mL. Numbers indicate \bar{M}_w/\bar{M}_n values. The solid lines are theoretical plots.

BCl₃/IB/CH₂Cl₂/-10°C system. Table 2 shows the conditions and results of a series of experiments carried out to this end, and Fig. 6 shows the corresponding Mayo plot. The virtual absence of an intercept in Fig. 6 indicates $k_{tr,M}/k_p \approx 0$, i.e., chain transfer to monomer is negligible [7]. According to these findings, truly living, i.e., terminationless and transferless, isobutylene polymerizations can be readily accomplished even at -10°C under the right conditions (AMI technique). These conclusions and the underlying analysis are essentially identical to those derived for the MeCOOR^t/BCl₃ system [7].

TABLE 2. Polymerization of Isobutylene at Various Monomer Concentrations^a

[M], mol/L	Yield, g	Conversion, %	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	I_{eff} , %
0.282	0.3338	>98	3 080	7 600	2.4	94
0.564	0.6467	>98	7 100	17 900	2.5	79
0.846	0.9604	>98	11 900	24 850	2.0	70
1.128	1.2881	>98	13 300	28 400	2.1	84
1.58	1.5977	>98	14 900	32 900	2.2	93

^a[CuOMe] = 5.76 mmol/L; [BCl₃] = 0.155 mol/L; CH₂Cl₂; temperature = -10°C; *t* = 30 min; total volume = 20 mL.

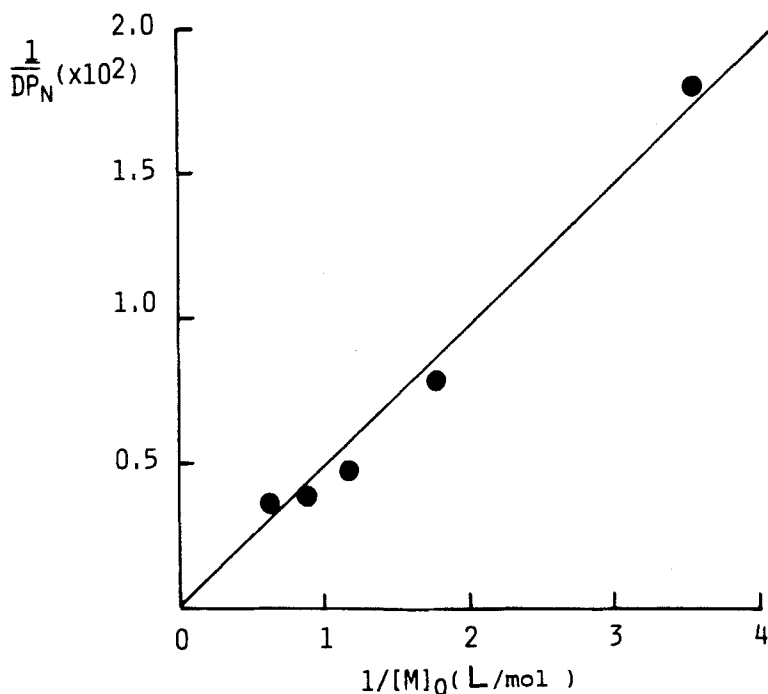
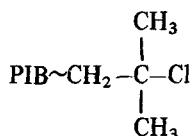


FIG. 6. $1/\bar{DP}_n$ versus $1/[M]_0$ plot for the CuOMe/BCl₃/IB/CH₂Cl₂/-10°C system: [CuOMe] = 5.76 mmol/L, [BCl₃] = 155 mmol/L. Total volume = 20 mL.

Termination Studies

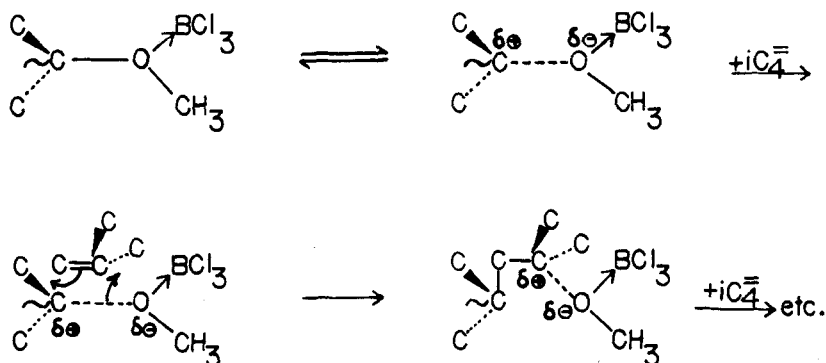
We have examined by $^1\text{H-NMR}$ spectroscopy the structure of the end groups of PIB produced by the living $\text{CuOMe}/\text{BCl}_3$ initiating systems after quenching with methanol. Interestingly, but not surprisingly in light of our earlier discoveries with the $\text{MeCOOR}^t/\text{BCl}_3$ systems [7], the end groups had the following structure:



CONCLUSIONS AND MECHANISTIC SPECULATIONS

As a sequel to our studies with $\text{MeCOOR}^t/\text{BCl}_3$, we have discovered that $\text{MeOR}^t/\text{BCl}_3$ systems also give rise to living polymerization of isobutylene. The molecular weights of PIB are controlled by the $[\text{IB}]/[\text{MeOR}^t]$ ratio; the \bar{M}_w/\bar{M}_n ratios are somewhat broader than those for Poisson distributions, most likely due to rapid propagation relative to initiation and various other effects (e.g., insufficient stirring, heterogeneous systems). Protic impurities (moisture) have a negligible effect, and the living polymerizations can be carried out in conventionally dried systems under N_2 .

We postulate that polymerization is induced by BCl_3 -etherate complexes which give rise to the true initiating entity:



Complexation of the ether oxygen with BCl_3 is viewed as weakening the $\text{R}^f \cdots \text{O}$ bond (indicated by the dashed line) and facilitating monomer incorporation; however, the state of ionization (ionicity) of the active species is obscure. That polymerizations are very fast in polar diluents would indicate some degree of charge separation. The nature of the organic groups on the ether oxygen will largely determine the rate of the above equilibration and the position of the equilibrium. Much more experimentation is needed to elucidate the mechanism of this most useful living polymerization system.

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