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Living carbocationic polymerization

XXXII. Living polymerization of isobutylene by tertiary alcohol/boron trichloride systems

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Abstract

Mono- and bifunctional tert-alcohols, i.e., cumyl alcohol (CumOH), 2,4,4-trimethyl-2-pentanol (TMPOH), 2,6-dihydroxy-2,4,4,6-tetramethylheptane (TMHDiOH), in conjunction with BCl_3 have been shown to be efficient initiating systems for the living polymerization of isobutylene (IB) in CH_3Cl or CH_2Cl_2 solvents in the -10° to -80°C range. The living nature of the polymerizations was demonstrated by linear $\bar{M}_n$ versus amount of polyisobutylene (PIB) formed (W_{PIB}) plots starting at the origin and corresponding horizontal number of PIB moles formed (N) versus W_{PIB} plots. Quenching with methanol produces tert-chlorine terminated PIBs. Quantitative dehydrochlorination of the latter products yields exo-olefin (isopropylidene) end groups. These experiments demonstrate that living carbocationic polymerizations have in fact been conducted in these laboratories long ago (1) without having been recognized as such.

Introduction

Living carbocationic polymerizations are now routinely effected by the use of tert-esters or -ethers in the presence of conventional Friedel-Crafts acids, such as $TiCl_4$, BCl_3(2-4). Part of our research is devoted to widen the scope of this field and to uncover new initiating systems. In the course of these investigations we have decided to explore initiation of living cationic polymerizations by tert-alcohols in conjunction with BCl_3. This decision appeared promising in view of the great structural similarity that exists between esters and ethers and alcohols, and particularly in light of our earlier discovery that tert-alcohols effect controlled polymerization of IB (1).

Thus this report concerns our research aimed to demonstrate living carbocationic polymerization of IB by the use of aliphatic and aromatic tert-alcohols in the presence of BCl_3, the formation of PIBs capped by tert-chlorine groups, and the synthesis by dehydrochlorination of exo-olefin capped PIBs. Specifically, this communication describes the synthesis of tert-chlorine ended PIBs by the use of the following aliphatic and aromatic alcohols (in the presence of BCl_3):

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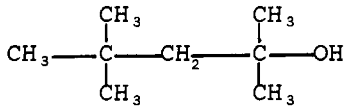
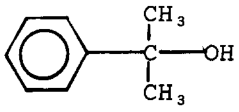
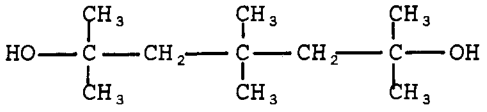


$CH_3-C(CH_3)_2-CH_2-C(CH_3)_2-OH$

TMPOH



CumOH



$HO-C(CH_3)_2-CH_2-C(CH_3)_2-CH_2-C(CH_3)_2-OH$

TMHDiOH

Experimental

A. Materials

2,4,4-trimethyl-2-pentanol (TMPOH) was prepared from 2,4,4-trimethyl-1-pentene according to Brown et al. (5). The synthesis of 2,6-dihydroxy-2,4,4,6-tetramethyl heptane(TMHDiOH) has been described (4). 2-phenyl-2-propanol (CumOH) (Aldrich Chem. Co.) was used as received. The purity of the chemicals was ascertained by ^1H NMR spectroscopy and GC analysis.

B. Polymerization and Characterization

Experiments have been carried out under dry nitrogen in a stainless steel dry box using large (60 mL) test tubes or round-bottom flasks (500 mL) equipped with a mechanical stirrer at -10° to -80°C. Both the "incremental monomer addition" (IMA) and "all monomer in" (AMI) techniques have been used (2). Charges were quenched by prechilled MeOH. Molecular weights were determined using a Waters high-pressure GPC instrument equipped with a Model 6000 A pump, differential refractometer R-401, UV absorbance detector Model 440, and five microstyragel columns (500, 10^3, 10^4, 10^5, 10^6). Flow rate: 1 mL/min. The calibration curve was made with narrow MWD ($M_w/\bar{M}_n \sim 1.1$) PIB standards. ^1H NMR spectra were obtained by a Varian T-60 NMR spectrometer.

Results and Discussion

Previous research in these laboratories has shown that both aliphatic and aromatic tert-alcohols in conjunction with BCl_3 are efficient initiators of IB polymerization (CH_2Cl_2, -50°C, high vacuum conditions) (1). Initiation was demonstrated to be controlled, chain transfer absent, however, termination was thought to be operational. A reexamination of these data in light of knowledge recently generated in regard to living carbocationic polymerizations (2,3) led us to conclude that the earlier systems in fact may have been truly living. Thus it was decided to carry out IB polymerizations by essentially the same type of initiating systems employed earlier, however, by using the diagnostic IMA technique. The IMA technique (i.e., incrementally adding monomer to an active system) provides a simple means to diagnose rapid living polymerizations (2) and has been routinely used for this purpose (2-4).

A. Orienting Experiments and Kinetic Investigations

Table I shows the results of some representative scouting experiments with the CumOH/BCl_3 combination. Polymerizations were rapid upon BCl_3 addition as judged by the appearance of cloudiness due to the precipitation of PIB. Evidently CumOH is an efficient initiator. Promisingly, the $\bar{M}_n$'s of products obtained in the presence of CumOH were much lower than those formed in the absence of this alcohol (controls) i.e., produced by adventitious protic initiation, and the initiator efficiencies ($I_{eff} = (100\ W_{PIB}/\bar{M}_n)/I_o$) were high.

TABLE I
Orienting Experiments Demonstrating the Activity of the $CumOH/BCl_3$ Initiating System*

[CumOH] mole/L	Solvent	Conv. %	$\bar{M}_n$ g/mole	$\bar{M}_w/\bar{M}_n$	I_{eff} %
----	CH_3Cl	3	----	----	----
$6.5x10^{-2}$	CH_3Cl	90	1100	2.9	81
$2.2x10^{-2}$	CH_3Cl	∿100	3550	2.2	80
$7.35x10^{-3}$	CH_3Cl	∿100	10550	2.1	83
----	CH_2Cl_2	40	39000	2.4	----
$6.58x10^{-2}$	CH_2Cl_2	80	950	2.8	84
$2.2x10^{-2}$	CH_2Cl_2	∿100	3700	2.6	79
$7.35x10^{-3}$	CH_2Cl_2	∿100	11320	2.0	82

*$[BCl_3] = 3.0 \times 10^{-1}$mole/L, [IB] = 1.17 mole/L, -30°C, total volume = 20 mL, quenched with prechilled MeOH 30 mins after CumOH addition

Figure 1 shows the M_n versus W_{PIB} plot obtained under conventional conditions using the $TMPOH/BCl_3$ system in CH_2Cl_2 at -10°C. The inset shows the corresponding N versus W_{PIB} plot.

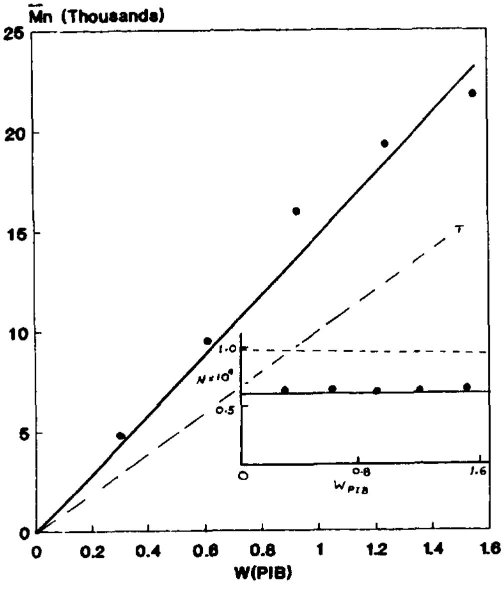


Figure 1. $\bar{M}_n$ and N, the number of PIB moles (inset) versus W_{PIB} weight of PIB formed in $TMPOH/BCl_3/IB/CH_2Cl_2/-10°C$ experiments. (AMI technique, 30 min.: [TMPOH] = 4.7×10^{-3} mole/L, $[BCl_3] = 2.4 \times 10^{-1}$mole/L. Total volume = 25 mL.) Broken line indicates theoretical (T) values.

Encouraged by these data experiments have been carried out by the IMA technique rigorously to diagnose living polymerizations. Figures 2 and 3 show the $\bar{M}_n$ versus W_{PIB} plot and the inset the N versus W_{PIB} plot obtained with the CumOH/BCl_3 system under various conditions (see legends). The I_{eff}s were consistently high (80 - 85%). The MWDs exhibit a narrowing tendency with increasing $\bar{M}_n$. According to these results the CumOH/BCl_3/IB/CH_3Cl or CH_2Cl_2/-30 to -80°C systems are truly living.

Figures 4-6 show similar data for the TMHDiOH/BCl_3 initiating system. According to this evidence this aliphatic tert-diol also yields living polymerizations in CH_2Cl_2 at -10° and -30°C, or in CH_3Cl at -40°C.

B. Structure Characterization and End Group Quantitation

The structure of the products have been characterized by dual detection (RI and UV) GPC and ^1H NMR spectroscopy. GPC traces of PIBs obtained by the CumOH/BCl_3 system (not shown) exhibited the expected UV absorption due to the phenyl head-group. The ^1H NMR spectra of the products obtained upon quenching with CH_3OH showed the phenyl head group and the $-CH_2C(CH_3)_2Cl$ tail group, and are essentially identical to those published earlier (2,3). The structure of the products obtained by the aliphatic initiators have similarly been characterized and the spectra obtained were the same as those published earlier (4,6).

The structures were further quantitatively characterized by dehydrochlorination with potassium tert-butoxide followed by quantitative ^1H NMR spectroscopy. This well-known now routinely used method showed that the end product is exclusively the isopropylidene ($-CH_2C(CH_3)=CH_2$) capped product. The ^1H NMR spectra were identical to those published earlier (7).

Conclusions

On the basis of the data gathered in this research we are confident that tert-alcohols in conjunction with BCl_3 readily initiate the living polymerization of IB. In view of the great similarity of the systems used in this research and those by Nguyen and Kennedy (1), living polymerizations must have prevailed in the earlier work also, however, this crucial fact was not recognized at that time.

In regard to the mechanisms, we think that the earlier proposed mechanism (1) is in general valid, except that termination is absent (after all, the polymerization is living); termination can of course be forced to occur by quenching with CH_3OH.

These results have interesting implications in regard to H_2O (i.e., "H_2O"/BCl_3) initiated IB polymerizations: In view of the great similarity between the propagating entities in H_2O and tert-alcohol-initiated IB polymerizations (most likely both involve $-CH_2C^{\oplus}(CH_3)_2 \cdots BCl_3OH^{\ominus}$ ion pairs) we postulate that both polymerizations are living in nature. Experiments have been carried out to substantiate this postulate (i.e. by adding BCl_3 to charges containing IB and CH_3Cl saturated with water at -40°C), however, the GPC traces obtained were bimodal, unsuitable for quantitative analysis. A visual examination of the GPC traces nonetheless indicated $\bar{M}_n$ growth with increasing conversion. This evidence may be construed to suggest living

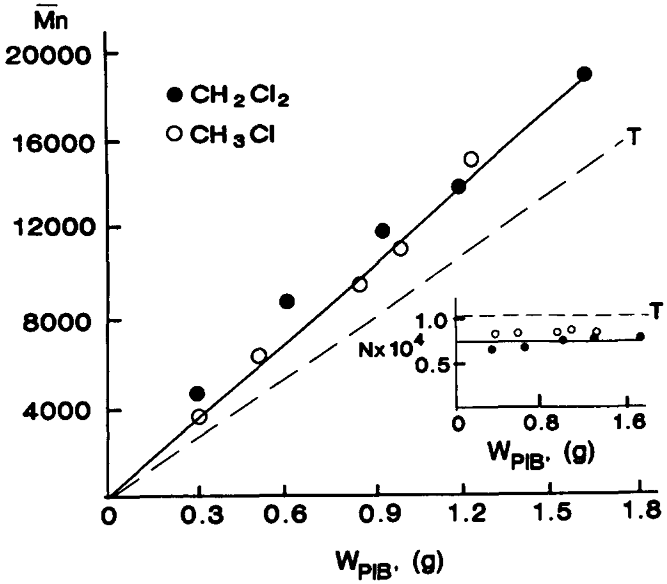


Figure 2. $\overline{M}_n$ and N, the number of PIB moles (inset) versus W_{PIB} weight of PIB formed in CumOH/BCl_3/IB/-30°C experiments. (IMA technique, 30 mins. time interval: CH_3Cl (O), CH_2Cl_2 (●), [CumOH] = 5.73 x 10^{-3} mole/L, [BCl_3] = 1.58 x 10^{-1} mole/L, total volume = 20 mL) Broken line indicates theoretical (T) values.

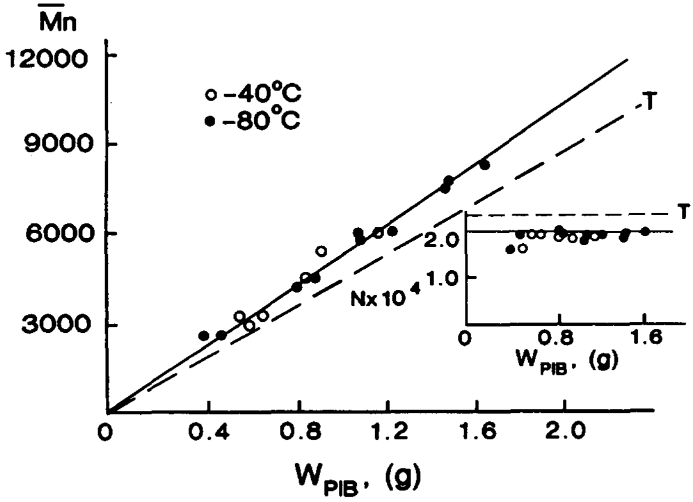


Figure 3. $\overline{M}_n$ and N, the number of PIB moles (inset) versus W_{PIB} weight of PIB formed in CumOH/BCl_3/IB/-40°C and -80°C experiments. (IMA technique, 30 mins. and 45 mins. time interval at -40°C and -80°C respectively: 30 mins. interval (O), 45 mins. interval (O), [CumOH] = 4.9 x 10^{-3} mole/L, [BCl_3] = 4.7 x 10^{-2} mole/L). Broken line indicates theoretical (T) values.

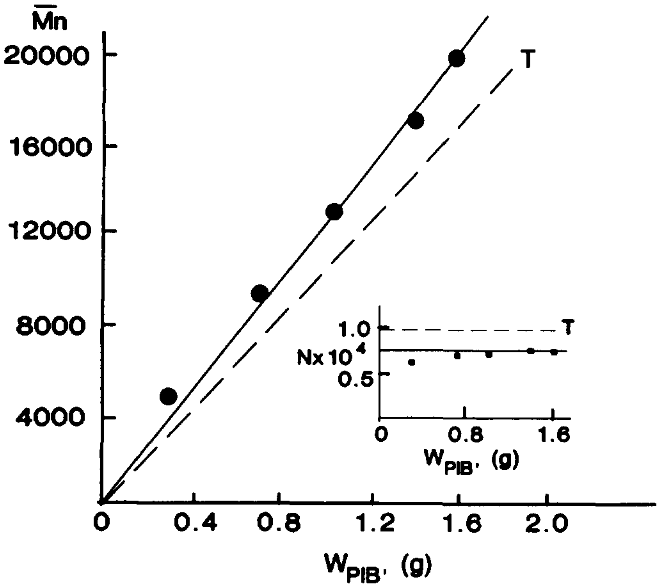


Figure 4. $\overline{M}_n$ and N, the number of PIB moles (inset) versus W_{PIB} weight of PIB formed in TMHDiOH/BCl$_3$/IB/CH$_2$Cl$_2$/-30°C experiments. (IMA technique, 30 mins. time interval: [TMHDiOH] = 4.68 x 10^{-3} mole/L, [BCl$_3$] = 2.4 x 10^{-1} mole/L. Total volume = 25 mL). Broken line indicates theoretical (T) values.

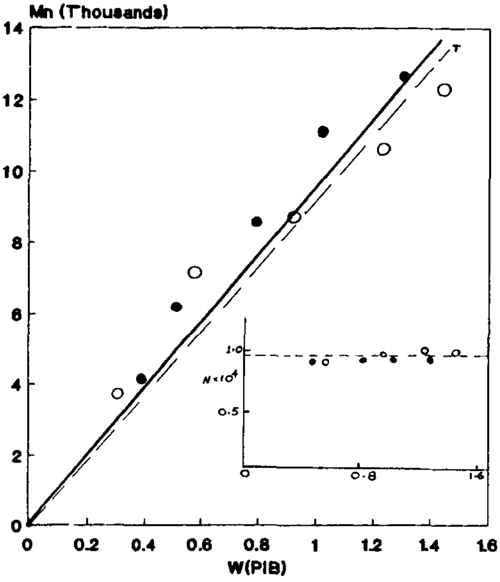


Figure 5. $\overline{M}_n$ and N, the number of PIB moles, (inset) versus W_{PIB}, weight of PIB formed in TMHDiOH/BCl$_3$/IB/CH$_2$Cl$_2$/-10°C experiments. (IMA technique, 15 mins. time interval (O), AMI technique 30 mins. (O),[TMHDiOH]= 4.68 x 10^{-3} mole/L, [BCl$_3$] = 2.4 x 10^{-1} mole/L. Total volume = 25 mL.) Broken line indicates theoretical (T) values.

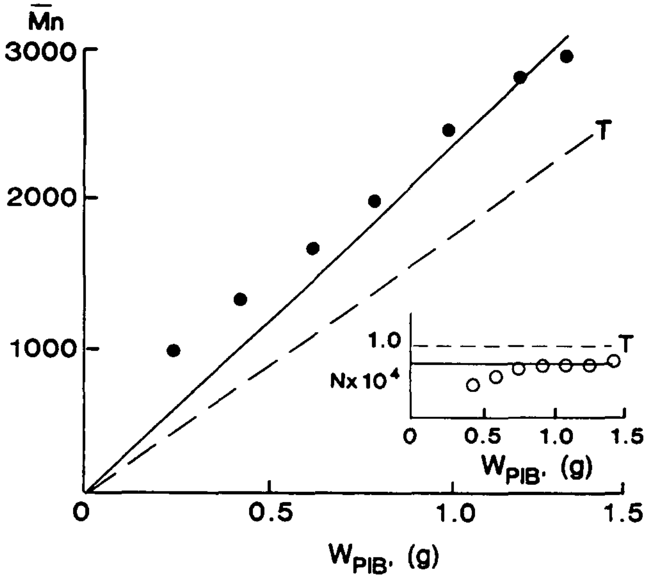


Figure 6. $\bar{M}_n$ and N, the number of PIB moles (inset) versus W_{PIB} weight of PIB formed, in TMHDiOH/BCl_3/CH_3Cl/ -40°C experiments. ([TMHDiOH] = 0.11 mole/L, [BCl_3] = 0.64 mole/L, [IB] = 1.0 mole/L, total volume = 235 mL in 500 ml flask equipped with mechanical stirrer. A series of samples were withdrawn at 10 min intervals immediately followed by addition of 0.12 mole IB each time). Broken line indicates theoretical (T) values.

polymerizations. Bimodality may be due to complex interactions between H_2O + BCl_3 + IB which, among other species and depending on conditions, will yield tert-butyl chloride, a singularly inefficient initiator (8). The H_2O in our system has originated not only from the moisture in the solvent but also from traces of moisture in the other chemicals used including the N_2 atmosphere in the dry box. Direct proof for the living nature of the H_2O/BCl_3/IB system would require quantitative studies by the use of super-dry chemicals under high-vacuum conditions.

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