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Living carbocationic polymerization

XXXIII. Living polymerization of isobutylene by tertiary hydroxyl/boron trichloride/electron pair donor systems

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ABSTRACT

Tert-alcohols in conjunction with BCl_3 plus strong electron pair donors (EDs), such as dimethyl sulfoxide (DMSO) and dimethyl acetamide (DMA), have been found efficiently to initiate the living polymerization of isobutylene (IB) in methyl chloride diluent yielding narrow molecular weight distribution (MWD) polyisobutylenes (PIBs). For example, the aliphatic diol 2,6-dihydroxy-2,4,4,6-tetramethylheptane/BCl_3/IB/DMA/-45°C system yields linear *tert*-chlorine telechelic $^{\underline{t}}Cl\text{-}PIB\text{-}Cl^{\underline{t}}$s with $\bar{M}_w/\bar{M}_n = 1.12$ at $\bar{M}_n = 2500$, and the aromatic triol 1,3,5-tri(2-hydroxyisopropyl)benzene/BCl_3/IB/DMA/-50°C system produces three-arm star *tert*-chlorine telechelic $^{\underline{t}}Cl\text{-}\underset{\underset{Cl^{\underline{t}}}{|}}{PIB}\text{-}Cl^{\underline{t}}$ with $\bar{M}_w/\bar{M}_n = 1.15$ at $\bar{M}_n = 2000$. Premixing experiments suggest that in the presence of excess BCl_3 the *tert*-alcohols are rapidly transformed to *tert*-chlorides, and that the latters are the true initiating species. Due to reversible termination the products are capped by *tert*-chlorines.

A. INTRODUCTION

Tert-alcohols, such as *tert*-butanol, 1,1-diphenyl ethanol, 2-phenyl-2-propanol, in conjunction with BCl_3 were found to initiate the polymerization of IB, however, these polymerizations have not been recognized to be living (1). Very recently we have demonstrated that these earlier systems were in fact living (see the preceding paper in this series, XXXII, in this issue).

Recently it was shown that the high reactivity of carbocations in IB polymerizations can be modulated by the addition of strong EDs, such as DMSO or DMA, and that side reactions caused by highly reactive cations can be suppressed or altogether eliminated by these additives (2,3). These beneficial effects were attributed to cation stabilization by

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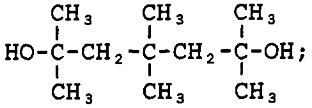
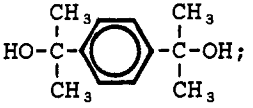
the EDs. 2-Chloro-2,4,4-trimethylpentane (TMPCl), an aliphatic *tert*-chloride, mimicking the end group of *tert*-chlorine capped PIB, has been shown to be an effective initiator in conjunction with BCl_3 plus DMSO or DMA, for living IB polymerization (3). This implies that in the presence of strong EDs the aliphatic *tert*-chlorine end groups that arise (4) are dormant only temporarily, i.e., termination is reversible.

The transformation of termination-dominant IB polymerization initiated by *tert*-OH/BCl_3 systems (1) to living systems by the use of strong EDs has already been described in a preliminary report (2). This paper concerns living polymerization of IB by the use of various *tert*-alcohols, e.g.,

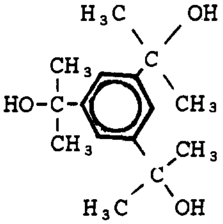


$HO-C(CH_3)_2-CH_2-C(CH_3)_2-CH_2-C(CH_3)_2-OH$;

TMHDiOH



DiCumOH



TriCumOH

in conjunction with BCl_3 plus DMSO or DMA as strong EDs.

B. EXPERIMENTAL

B.1. Materials

The syntheses of 1,3,5-tri(2-hydroxyisopropyl)benzene (tricumyl alcohol, TriCumOH) and 2,6-dihydroxy-2,4,4,6-tetramethylheptane (TMHDiOH) have been described (5). 1,4-Di(2-hydroxyisopropyl)benzene (dicumyl alcohol, DiCumOH) (The Goodyear Tire and Rubber Co.) was stirred with carbon black in methanol overnight, filtered, and recrystallized from methanol. The source and purification of CH_3Cl, IB and BCl_3 have been described (1,2). Methanol, anhydrous DMSO and DMA (Aldrich) were used as received.

B.2. Procedures

Polymerizations were carried out in a dry box under nitrogen in large ($\sim$75) mL test tubes or round bottom flasks, as described (2,3). Detailed concentration etc. data are given in the text and table or figure captions. PIB molecular weight determination has been described (4). The $\overline{M}_n$ of the three-arm star PIB sample was determined by VPO using a Knauer osmometer and toluene solvent. Number average end functionalities ($\overline{F}_n$) of PIBs prepared with DiCumOH and TriCumOH were determined by the well-established dehydrochlorination method (6). The *tert*-chlorine end groups of PIB samples prepared with TMHDiOH and TriCumOH were quantitatively converted into primary OH end groups and $\overline{F}_n$s were determined by IR spectroscopy (7,8). ^1H NMR spectra were taken by a Varian T-60 spectrometer using CCl_4 solvent.

C. RESULTS AND DISCUSSION

C.1. Demonstration of Living Polymerization of IB and Mechanistic Considerations

We selected TMHDiOH as initiator because the structure of the dication expected to form from this diol mimicks that of the growing $^{\oplus}$PIB$^{\oplus}$ dication. Table I and Figure 1 show the conditions and results of IB polymerization initiated by the TMHDiOH/BCl_3 system in the presence of DMA. DMA·BCl_3 complexes are more soluble in CH_3Cl than in $CH_3Cl/n\text{-}C_6H_{14}$ 40/60 v/v mixtures under similar conditions (3). After 10 minutes of premixing polymerization was started by the addition of IB and 10 mL samples were withdrawn from the charge to monitor conversion and molecular weight as a function of time.

TABLE I

Polymerization of IB by the TMHDiOH/BCl_3/DMA System

TMHDiOH = 0.0715 mole; BCl_3 = 0.896 mole; DMA = 0.071 mole; CH_3Cl = 1400 mL; V_o = 1750 mL; -45°C; 10 min premixing, then IB = 2.67 mole

Time min	W_p* g	Conversion %	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	I_{eff} %
20	52.7	25.5	820	1.36	90
40	99.9	56.7	1520	1.16	92
60	125.0	73.2	1860	1.15	94
100	151.7	91.1	2280	1.14	93
140	155.3	93.7	2360	1.14	92
180	159.3	96.7	2530	1.12	88
240	161.6	98.4	2590	1.12	87
Control experiments:					
1) IB = 0.024 mole; DMA = 0.001 mole; CH_3Cl = 25 mL, then added BCl_3 = 0.0128 mole					
30		no polymer			
2) IB = 0.024 mole; CH_3Cl = 25 mL, then added BCl_3 = 0.0128 mole					
30	0.1	6.5	102,000	1.85	

* g of PIB formed, calculated from conversions (obtained from aliquots)

Polymerization is slow by cationic standards (e.g., 56.7% conversion in 40 mins) indicating that the ED modulates the reactivity of the cations. The linear $\overline{M}_n$ versus W_p and the horizontal N (number of PIB moles formed) versus W_p plots shown in Figure 1 demonstrate living IB polymerization. Initiator efficiencies (I_{eff}) are close to 100% and the MWDs are narrow. Control experiments (see Table I) show that while in the absence of TMHDiOH and DMA a small amount of high molecular weight ($\overline{M}_n$ = 102,000) polymer is formed most likely by protogenic impurities, in the presence of DMA polymer is absent. This indicates that in the presence of DMA only controlled initiation by TMHDiOH (in fact by TMHDiCl, as it will be shown below) has occurred.

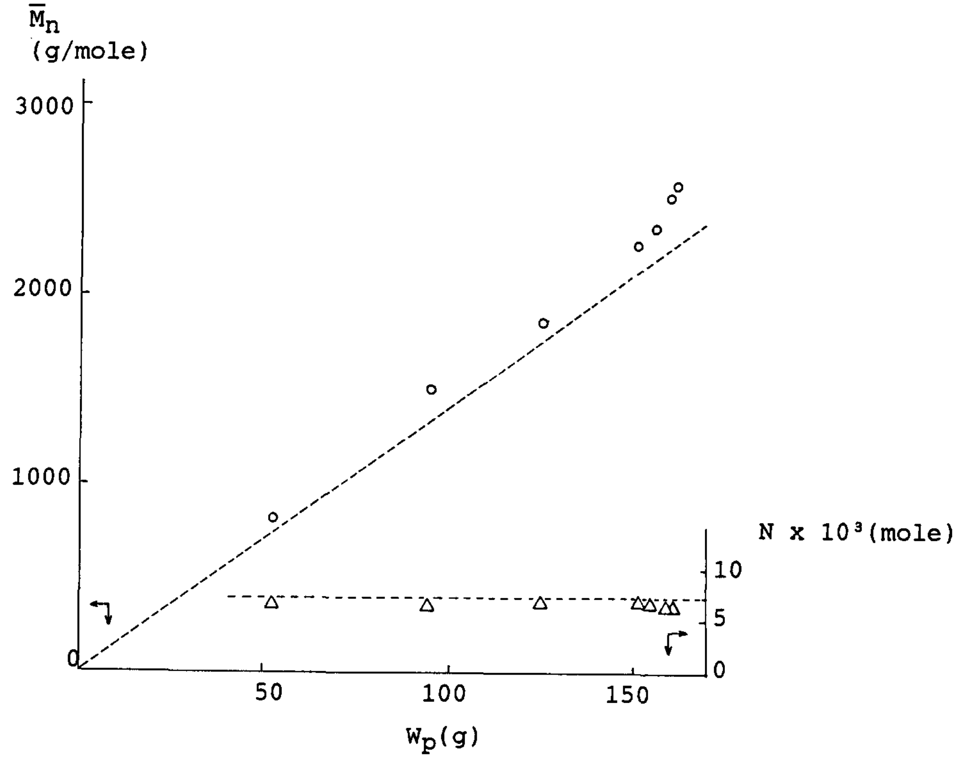


Figure 1. Living Polymerization of IB by the TMHDiOH/BCl_3/DMA System. Conditions as in Table I. Dotted lines show Theoretical Values

TMHDiOH is only partially soluble in CH_3Cl at -45°C and the initial charge containing all the components except IB and BCl_3 is heterogeneous. Upon BCl_3 addition, however, the charge becomes immediately homogeneous, indicating the transformation of TMHDiOH to a soluble product. It is a matter of record that the reaction of <u>tert</u>-alcohols and BCl_3 quantitatively yields <u>tert</u>-chlorides and boron-containing compounds in the -10 ∿ -80°C range (9,10). Thus most likely the addition of BCl_3 to the insoluble TMHDiOH transforms it into the corresponding soluble <u>tert</u>-dichloride TMHDiCl, and polymerization is most likely initiated by the ionization of TMHDiCl by the excess BCl_3. Similarly to our earlier conclusions (3,4) these polymerizations are visualized to involve reversible termination $\sim\sim^{\oplus}C(CH_3)_2\ BCl_4^{\ominus} \rightleftharpoons \sim C(CH_3)_2Cl + BCl_3$. As a consequence, these products are capped by <u>tert</u>-chlorine end groups.

According to these data TMHDiOH is an effective initiator in conjunction with BCl_3 plus DMA for the living polymerization of IB, and the system produces narrow MWD ($\bar{M}_w/\bar{M}_n$ = 1.12) PIBs at -45°C.

Table II shows the conditions and results of IB polymerizations initiated by the DiCumOH/BCl$_3$ system in the presence of DMSO. Polymerizations were carried out at -65°C to avoid undesirable indanyl ring formation that occurs at temperatures higher than $\sim$-65°C even in the presence of strong EDs (3).

TABLE II

Polymerization of IB by the DiCumOH/BCl$_3$/DMSO System

DiCumOH = 3.09 x 10^{-4} mole; BCl$_3$ = 6.6 x 10^{-3} mole; DMSO = 6.2 x 10^{-4} mole; CH$_3$Cl = 25 mL; -65°C; 15 min premixing

Sample	Time min	W_p g	Conversion %	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	I_{eff} %
a) AMI (all monomer in) technique, IB = 0.5 mL						
1	30	0.229	47	840	1.56	89
2	60	0.339	76	1050	1.49	104
b) IMA (incremental monomer addition) technique, 3 x (0.5 mL IB/15 min)						
3		0.147	42		multimodal	
4		0.242	34		multimodal	
5		0.375	28	1074	2.0	110

Similarly to TMHDiOH, DiCumOH is also insoluble in CH$_3$Cl. Upon BCl$_3$ addition most of the initiator dissolved, however, a few DiCumOH crystals were still present even after 20 mins in the charge possibly due to insufficient stirring in the test tubes. Polymerization was also found to be slow by cationic standards (conversion was only 47% in 30 minutes). The product recovered after 60 minutes showed essentially theoretical $\overline{M}_n$ (I_{eff} = 100% within what is considered to be experimental error) and relatively narrow MWD.

Polymerizations carried out by IMA technique (Expts. 3-5) gave constant and low conversions in spite of the successive addition of fresh monomer increments (increasing monomer concentrations). Similar observations have been made in other IB polymerizations in the presence of EDs (2-4, 11) which was accounted for by interaction between IB and the Lewis acid (4,11). The initially multimodal GPC traces became monomodal which may suggest slow dissolution of the DiCumOH initiator in the charge. After a sufficiently long time essentially theoretical molecular weights can be reached (see sample 5 in Table II).

The initiation mechanism is probably similar to that proposed for the TMHDiOH/BCl$_3$ initiated IB polymerization, i.e., the insoluble DiCumOH is first transformed to the soluble corresponding <u>tert</u>-chloride (DiCumCl), although apparently much slower than that observed in the case of the TMHDiOH/BCl$_3$ system, and polymerization starts by the ionization of DiCumCl by the excess BCl$_3$.

Next we have turned our attention to the TriCumOH/BCl$_3$/DMSO or DMA systems because undesirable indanyl ring formation is not possible with tricumyl initiators. Table III and Figure 2 show the results. According to the data in Figure 2 both systems yield living polymerizations.

TABLE III

Polymerization of IB by the TriCumOH/BCl /DMSO and DMA Systems

TriCumOH = 7.9×10^{-4} mole; BCl_3 = 9.5×10^{-3} mole; CH_3Cl = 25 mL; IB = 4.26×10^{-2} mole; -50°C, 10 min premixing; for addition sequences see text

Sample	Time min	W_p g	Conversion %	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	I_{eff} %
a) DMSO = 7.1×10^{-4} mole;						
1	60	1.71	63.1	2600	1.66	83
2	60	1.71	62.5	2420	1.65	89
3	180	2.37	90.1	3480	1.42	86
4	180	2.40	91.0	3100	1.52	98
b) DMA = 7.1×10^{-4} mole;						
5	60	1.08	35.1	1380	1.37	98
6	60	1.12	37.5	1540	1.39	92
7	180	2.00	75.0	2900	1.24	87
8	180	2.13	81.1	3230	1.20	83
9	180	2.09	79.5	3200	1.20	82
c) TriCumOH = 0.1595 mole; BCl_3 = 1.72 mole; CH_3Cl = 2500 mL; DMA = 0.152 mole; -50°C; 10 min premixing, then IB = 254 g						
10	240	282	96	1920	1.15	92

TriCumOH is only partially soluble in CH_3Cl at -50°C but readily dissolves upon BCl_3 addition. Most likely, the TriCumOH + BCl_3 reaction rapidly yields the corresponding TriCumCl which is soluble under the above conditions. Polymerizations are relatively slow and the addition sequence (after 10 minutes premixing IB was added last in experiments 1,3,5,7, 8 and 10, while BCl_3 was added last in experiments 2,4,6 and 9) does not seem to affect the results. The polymerizations are slower and the MWDs are narrower in the presence of DMA than with DMSO, perhaps because the solubility in CH_3Cl of DMA·BCl_3 is higher than that of DMSO·BCl_3. After the dissolution of TriCumOH upon BCl_3 addition in the presence of DMSO a slight precipitate appears (DMSO·BCl_3 complexes?) which persists throughout the polymerization.

The last set of data in Table III (sample 10) shows the results of a relatively large scale experiment (282 g PIB obtained of $\overline{M}_w/\overline{M}_n$ = 1.15 at I_{eff} = 92%).

C.2. Structure and Endgroup Determination

Spectroscopic studies showed that the PIBs obtained in these studies carry $-CH_3C(CH_3)_2Cl$ end groups. Figure 3 shows the ^1H NMR spectrum of a representative telechelic ^{t}Cl-PIB-Cl^t sample prepared by the TMHDiOH/BCl_3/DMA system (sample No. 1 in Table I). The $\overline{M}_n$ was calculated to be 840 g/mole by correlating the signals corresponding to the end group protons a) and b) with the main chain protons (c) and d); this value is in good agreement with $\bar{M}_n$ = 820 g/mole obtained by GPC. These results indicate essentially theoretical end-functionality ($\bar{F}_n$ = 2.0 ± 0.1).

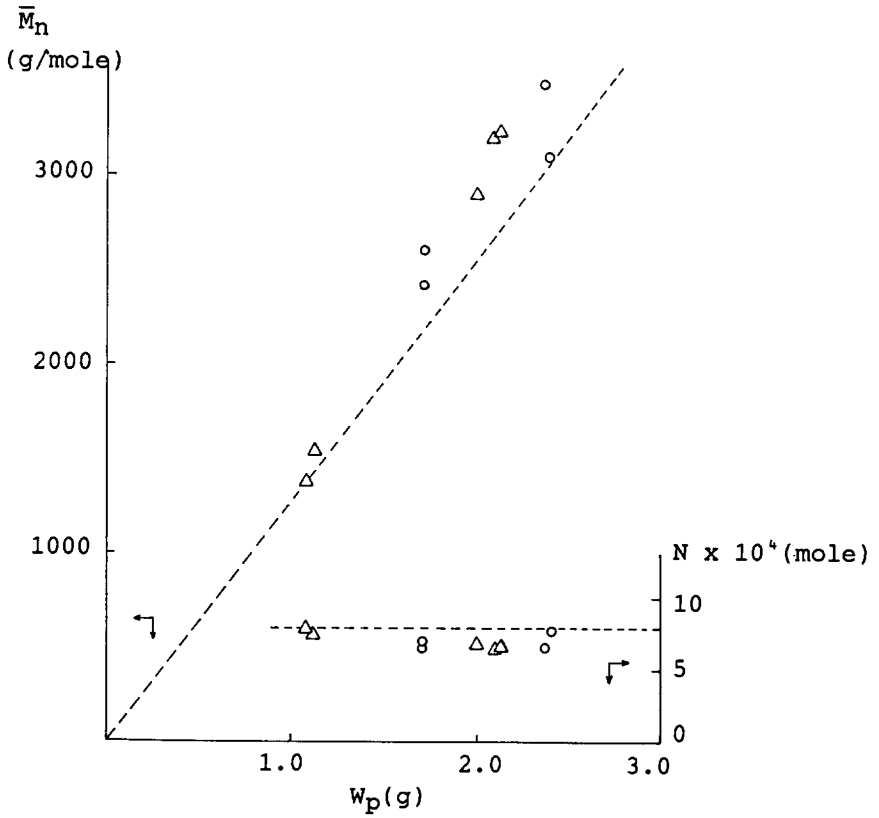


Figure 2. Polymerization of IB by TriCumOH/BCl_3/DMSO (O) and TriCumOH/BCl_3/DMA (Δ). Conditions as in Table III. Dotted lines show theoretical values

End group functionality was independently quantitated after converting the terminal *tert*-chlorines to primary hydroxyls by our routine method (7). According to these results also $\bar{F}_n$ = 2.0 ± 0.1.

Quantitative end group analyses were also performed on three-arm star PIBs by the use of both dehydrochlorinated and hydroxylated samples according to (6) and (8), respectively, and end-functionality was found to be $\bar{F}_n$ = 3.0 ± 0.1 in both cases.

In line with considerations as to the initiation mechanism presented in the previous section, and the revised polymerization mechanism of living IB polymerizations initiated by *tert*-esters, -ethers or -chlorides in the presence of EDs (2,3, 4), the formation of the tert-chloride end groups is most likely due to reversible termination: $\sim CH_2^{\oplus}C(CH_3)_2BCl_4^{\ominus} \rightleftarrows \sim CH_2C(CH_3)_2Cl + BCl_3$.

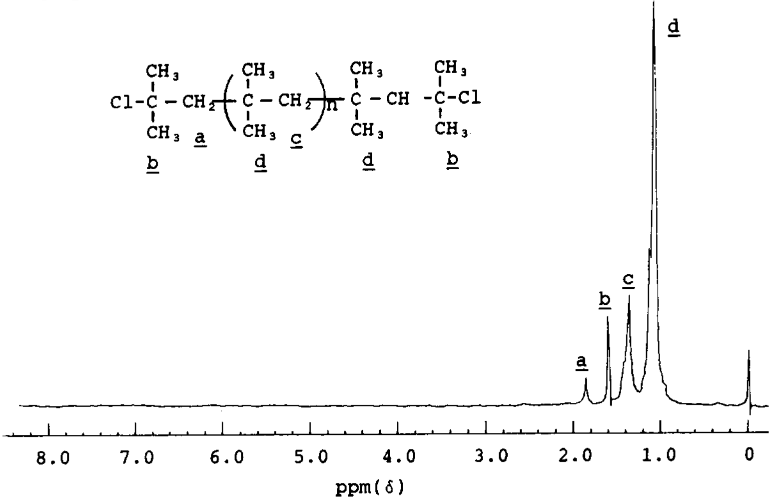


Figure 3. ^{1}H NMR Spectrum of a Representative Telechelic ^{t}Cl-PIB-Cl^t (Sample #1, Table I). Synthesis Conditions as in Table I

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