

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Living Carbocationic Polymerization. XLIX. Two-Stage Living Polymerization of Isobutylene to Di-*tert*-chlorine Telechelic Polyisobutylene

C. Charles Chen^{ab}, Jiaoshi Si^{bc}, J. P. Kennedy^b

^a Dow Chemical Co., Midland, Michigan ^b Institute of Polymer Science The University of Akron, Akron, Ohio ^c Xian Modern Chemical Research Institute, Shaanxi, Peoples Republic of China

To cite this Article Chen, C. Charles , Si, Jiaoshi and Kennedy, J. P.(1992) 'Living Carbocationic Polymerization. XLIX. Two-Stage Living Polymerization of Isobutylene to Di-*tert*-chlorine Telechelic Polyisobutylene', Journal of Macromolecular Science, Part A, 29: 8, 669 – 679

To link to this Article: DOI: 10.1080/10601329208052191

URL: <http://dx.doi.org/10.1080/10601329208052191>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIVING CARBOCATIONIC POLYMERIZATION. XLIX. TWO-STAGE LIVING POLYMERIZATION OF ISOBUTYLENE TO DI-*tert*-CHLORINE TELECHELIC POLYISOBUTYLENE†

C. CHARLES CHEN,‡ JIAOSHI SI,§ and J. P. KENNEDY*

Institute of Polymer Science
The University of Akron
Akron, Ohio 44325-3909

ABSTRACT

A two-stage process was developed for the living polymerization of isobutylene (IB) employing di-*tert*-alcohol initiators in conjunction with BCl_3 coinitiator in the first or initiation stage, followed by TiCl_4 coinitiator in the second or propagation stage; the process was shown to yield high molecular weight (up to $\overline{M}_n \approx 20,000$), narrow molecular weight distribution (MWD) $\overline{M}_w/\overline{M}_n = 1.1\text{--}1.2$ di-*tert*-chlorine telechelic polyisobutylenes ('Cl-PIB-Cl'). The initiation stage involves the homogeneous solution living polymerization of IB induced by the di-*tert*-alcohol/ BCl_3 combination in the presence of an electron donor such as *N,N*-dimethylacetamide in CH_3Cl solvent at -80°C and proceeds up to $\overline{M}_n < 5000$; this is followed by the propagation stage in which TiCl_4 and the bulk of IB plus a sufficient amount of *n*- C_6H_{14} are added to the charge to bring the solvent composition to $\text{CH}_3\text{Cl}/n\text{-C}_6\text{H}_{14}$ 60/40 v/v and the living polymerization is continued until high \overline{M}_n product is obtained. This two-stage process was developed because 1) it employs very

†For Paper XLVIII in this series, see T. Pernecker, J. P. Kennedy, and B. Iván, *Macromolecules*, 25(6), 1642 (1992).

‡Present address: Dow Chemical Co., Midland, Michigan 48640.

§Permanent address: Xian Modern Chemical Research Institute, Shaanxi, Peoples Republic of China.

inexpensive chemicals; 2) di-*tert*-alcohol/ BCl_3 combinations initiate living IB polymerization in CH_3Cl but the product after reaching $\overline{M}_n \approx 5000$ precipitates out of the CH_3Cl solution, and di-*tert*-alcohol/ TiCl_4 combinations do not initiate IB polymerization; and 3) di-*tert*-alcohol/ BCl_3 systems do not initiate (or only very slowly) the living polymerization of IB in $\text{CH}_3\text{Cl}/n\text{-C}_6\text{H}_{14}$ mixtures, whereas similar TiCl_4 -based systems do. The polymerization remains living during both stages although the propagating species and solvent polarity are profoundly altered. The livingness of the system has been analyzed by kinetic experiments and the structure of the 'Cl-PIB-Cl' product by routine spectroscopic means.

INTRODUCTION

In the course of our fundamental studies on the mechanism of living carbocationic polymerizations (LC^+Pzn), we became interested in exploring the possibility of using di-*tert*-alcohols as initiators in conjunction with TiCl_4 as coinitiator for the synthesis of relatively high molecular weight and narrow molecular weight distribution (MWD) polyisobutylenes (PIB), specifically 'Cl-PIB-Cl'. The main impetus for this research came from the recent finding [1] that *tert*-alcohol/ BCl_3 combinations readily induce the efficient LC^+Pzn of IB. A further justification was that the principal ingredients required, i.e., TiCl_4 and 1,4-di-(2-hydroxyisopropyl)benzene (dicumyl alcohol, DiCumOH), are commercially available at low cost. It has been amply documented that both TiCl_4 and BCl_3 are efficient coinitiators of LC^+Pzn initiated by *tert*-chlorides, -esters, and -esters under essentially identical experimental conditions [2-6].

Surprisingly, we soon established that in contrast to the *tert*-alcohol/ BCl_3 system, *tert*-alcohol/ TiCl_4 combinations were completely inactive. This handicap has been overcome by a two-stage process in which the LC^+Pzn of a limited amount of IB was started by the *tert*-alcohol/ BCl_3 system in a relatively polar medium (CH_3Cl), and after a short initial phase the polymerization was continued by the addition of TiCl_4 in hexane plus the bulk of the monomer. The two-stage addition of the monomer, together with the modification of the solvent system from CH_3Cl to $\text{CH}_3\text{Cl}/n\text{-C}_6\text{H}_{14}$ and the concurrent change in the Friedel-Crafts acid coinitiator are essential requirements of the process dictated by the following circumstances: Although the *tert*-alcohol/ BCl_3 /IB/ $\text{CH}_3\text{Cl}/-80^\circ\text{C}$ system readily yields a living system, the PIB starts to precipitate from CH_3Cl when the \overline{M}_n reaches ~ 5000 g/mol [1, 2]. Although high molecular weight PIB is readily soluble in $\text{CH}_3\text{Cl}/n\text{-C}_6\text{H}_{14}$, 40/60 v/v mixtures even at -80°C , BCl_3 -based initiating systems are inactive in this medium; in contrast, TiCl_4 -based initiating systems readily yield homogeneous LC^+Pzn s in this solvent mixture.

This paper concerns a convenient two-stage homogeneous solution LC^+Pzn process for the synthesis of high molecular weight narrow MWD telechelic PIBs. The polymerization is induced by an inexpensive di-*tert*-alcohol initiator, e.g., DiCumOH, in conjunction with BCl_3 in CH_3Cl , and after a relatively brief initiation stage during which a small amount of IB is converted, the process is continued by the addition of TiCl_4 in hexanes and the bulk of the monomer. The switch from

BCl_3 to TiCl_4 and from a more polar to a less polar medium do not interfere with the living nature of the polymerizations, and the final products are the conventional 'Cl-PIB-Cl's.

EXPERIMENTAL

Materials

2,6-Dihydroxyl-2,4,4,6-tetramethylheptane (TMHDI₂OH) was synthesized as described [7]. The source and purification of 1,4-di(2-hydroxyisopropyl)benzene (dicumyl alcohol, DiCumOH), IB, BCl_3 , TiCl_4 , CH_3Cl , and hexanes have been described [1-3]. Anhydrous *N,N*-dimethylacetamide (DMA, Aldrich) was used as received.

Procedures

Experiments were performed in a stainless steel enclosure (dry box), purged with dried N_2 (Molecular Sieves and BaO), and kept under a slight positive N_2 pressure.

The experiments shown in Table 1 were carried out in large (~75 mL) test tubes. Methyl chloride was collected directly into the test tube, followed by addition of hexanes if necessary; the charging sequence of reagents is indicated in Table 1. Agitation was provided only during the mixing of reagents. After desirable periods of time, the reactions were quenched by prechilled MeOH.

The experiments described in Tables 2 and 3 were at larger scales, ranging from total IB charges of 110 to 570 g, carried out in round-bottom flasks of various sizes (3-5 L) equipped with overhead stirrers. Samples were withdrawn during the polymerizations by prechilled calibrated pipets. The trace of solution adhering to the outside of the pipet tip was rinsed back to the charge with solvent, while the content of the pipet was transferred quantitatively to a test tube (by thoroughly rinsing with hexanes) containing a few milliliters of MeOH for quenching. Additional experimental details were described in earlier reports [2, 3].

The \bar{M}_n of PIBs was determined by GPC and the details have been described [3]. The *t*-Cl telechelic PIBs were quantitatively converted to isopropylidene-ended PIBs by a well-established dehydrochlorination method [8]. The number-average end functionalities (\bar{F}_n) were obtained from the ratio of the number of protons of olefinic end-groups relative to that of aromatic initiator fragment by using a Varian 200 MHz ^1H FT NMR instrument. The ^1H -NMR method was also used to determine the \bar{F}_n of primary hydroxyl telechelic PIBs, and independently confirmed by a FT-IR method [9]. The conversion of olefin end-groups to hydroxyl end-groups and their characterizations have been described [9, 10].

RESULTS AND DISCUSSION

Preliminary Experiments: Attempts to Initiate LC^+Pzn of IB by Di-*tert*-Alcohol/ TiCl_4 Combinations

A variety of alcohols, including DiCumOH, an inexpensive readily available di-*tert*-alcohol, and TMHDI₂OH, in conjunction with the moderately expensive BCl_3 plus an electron donor, such as DMA, are excellent initiators for the living polymer-

TABLE 1. Attempts to Initiate IB Polymerization with *tert*-Alcohol/TiCl₄/DMA Systems^a

Expt	1	2	3	4	DiCumOH				TMHDiOH										
					CH ₃ Cl/hexanes 60/40		CH ₃ Cl		CH ₃ Cl/hexanes 60/40		CH ₃ Cl								
					Conversion, %	\bar{M}_n	\bar{M}_w/\bar{M}_n	Conversion, %	\bar{M}_n	\bar{M}_w/\bar{M}_n	Conversion, %	\bar{M}_n	\bar{M}_w/\bar{M}_n	Conversion, %	\bar{M}_n	\bar{M}_w/\bar{M}_n			
1	Diol	IB	DMA	TiCl ₄	0														
2	Diol	IB	TiCl ₄	DMA	0														
Control	TiCl ₄ ^b	DMA	IB	—	95														
3	IB	DMA	Diol	TiCl ₄	0														
4	Diol	TiCl ₄ ^c	DMA	IB	0														
5	Diol	IB	TiCl ₄	—	46	50,000	2.1	88	30,000	1.8	15,000	1.24	85	8,000	1.45				
Control	IB	DMA	TiCl ₄	—	0			0					0						

^a[DiCumOH] = [TMHDiOH] = 1.3×10^{-2} M, [DMA] = 2.6×10^{-2} M for Experiments 1 and 2, and 3.8×10^{-2} M for Experiments 3, 4, and 5, [TiCl₄] = 0.1 M, [IB] = 0.51 M, solvent = 15 mL hexanes + 10 mL CH₃Cl or 25 mL CH₃Cl, 30 min, -80°C.

^b[TiCl₄] = 0.2 M.

^cDiol + TiCl₄ aged for 5 min prior to DMA addition.

TABLE 2. Scouting Experiments for Two-Stage Living Polymerization ($\sim 80^\circ\text{C}$)

Charging sequence	Experiment				
	1	2	3	4	5
BCl_3 phase					
DiCumOH (mol)	0.0114	0.0227	0.0273	0.10	0.12
CH_3Cl (mL)	800	1,600	1,600	2,000	1,900
$[\text{BCl}_3]$ (M)	0.5	0.5	0.5	0.5	0.5
[DMA] (M)	0.03	0.03	0.03	0.03	0.03
IB (mol)	<u>0.746</u>	<u>1.54</u>	<u>0.88</u>	<u>3.22</u>	<u>3.85</u>
\downarrow Time (min)	$\downarrow 120$	$\downarrow 120$	$\downarrow 60$	$\downarrow 90$	$\downarrow 90$
M_n /MWD	2,490/1.12	2,350/1.12	950/1.23		
TiCl_4 phase					
Hexanes (mL)	1,200	2,400	2,400	2,000	1,900
$[\text{TiCl}_4]$ (M)	0.011	0.017	0.021	0.050	0.063
IB (mol)	<u>0.598</u>	<u>2.836</u>	<u>4.373</u>	<u>1.900</u>	<u>2.125</u>
\downarrow Time (min)	$\downarrow 10$	$\downarrow 15$	$\downarrow 15$	$\downarrow 30$	$\downarrow 20$
M_n /MWD	3,920/1.11	7,530/1.12	4,870/1.14		
IB (mol)	<u>0.598</u>	$\downarrow 15$	$\downarrow 15$	<u>1.900</u>	<u>2.125</u>
M_n /MWD		10,050/1.12	8,490/1.14		
IB (mol)	$\downarrow 10$	$\downarrow 15$	$\downarrow 15$	$\downarrow 30$	$\downarrow 20$
M_n /MWD		11,290/1.10	11,050/1.12		
		$\downarrow 15$	$\downarrow 15$		
Final					
M_n /MWD	4,840/1.12	11,910/1.10	12,250/1.12	4,500/1.13	5,760/1.12
Conversion (%)	46.2	96	96.0	98.7	99.9
I_{eff} (%)	96.2	90.6	86.3	91.3	87.0

TABLE 3. Demonstration of Two-Stage Living Polymerization of IB^a

Incremental IB addition mL (g)	Time, min	No.	Volume, mL	Samples				
				PIB yield, g	IB conversion, %	M_n , g/mol	M_w/M_n	
BCl ₃ , 56 (40.3)	90	1	14.4	0.257	39.4	1,760	1.13	
TiCl ₄ , 80 (57.6)	105	2	14.6	0.276	98.9	3,900	1.12	
	120	3	13.2	0.425	71.2	6,590	1.12	
	135	4	12.0	0.490	90.2	8,210	1.13	
	150	5	11.0	0.476	95.6	8,860	1.11	
	165	6	9.7	0.441	100.0	9,140	1.11	
	70 (50.4)	180	7	9.0			11,190	1.11
75 (54.0)	195	8	9.0	0.573	94.9	13,400	1.11	
	210	9	9.0	0.601	99.5	13,870	1.11	
	225	10	9.0	0.603	99.9	13,890	1.11	
	240	11	8.0	0.609	85.0	16,060	1.14	
	255	12	7.0	0.603	96.2	17,700	1.15	
	270	13	7.0	0.651	104.0	18,600	1.14	

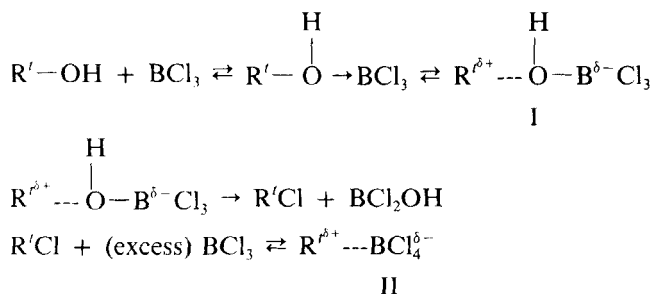
^aProcedure: 800 mL CH₃Cl, 1.886 g (9.72×10^{-3} mol) DiCumOH, 2.3 mL (2.47×10^{-2} mol) DMA, 56 mL (40.33 g) IB, and finally 30 mL (0.40 mol) BCl₃ were charged; after 90 min of stirring, Sample 1 was withdrawn. After sampling, 4.5 mL (0.041 mol) TiCl₄ in 1200 mL hexanes (-80°C) was added; after 15 min of stirring, Sample 2 was withdrawn, and 80 mL (57.6 g) IB was added. Thereafter, sampling occurred every 15 min. After Samples 6 and 10, incremental amount of IB were added, as indicated.

ization of IB [1, 6]. Against this background, experiments have been carried out to investigate under what conditions could the very inexpensive TiCl₄ also be used to the same end. Surprisingly, we found that under the conditions in which BCl₃ efficiently coiniciates the LC⁺Pzn of IB, TiCl₄ is completely inactive. The beneficial effect on EDs mediating LC⁺Pzn has been amply demonstrated [6, 11, 12]; in this research we used DMA for this purpose.

Table 1 summarizes the conditions and key results obtained. Polymerization occurred in only five experiments. A detailed examination of the circumstances of these experiments leads us to conclude that polymerizations were largely due to initiation by traces of adventitious moisture and not to the di-*tert*-alcohols. In regard to the first positive experiment (Row 3 in Table 1), this conclusion is self-evident since diol was absent. In the other positive experiments (Experiment 5), the diols were present but DMA, a potent proton scavenger [11], was absent; that initiation was due to moisture is indicated by the relatively low conversions (particularly in the mixed CH₃Cl/*n*-C₆H₁₄ solvent) and by the absence of the UV active aromatic fragment in the product. Initiation by moisture usually occurs rapidly in the presence of TiCl₄, and conversions increase with increasing solvent polarity [3]. That EDs (e.g., DMA) inhibit adventitious protic initiation is well documented [11]

and is also borne out by the absence of polymerization in Experiments 3 and 4. However, this effect diminishes as the concentration of TiCl_4 increases; this is shown by comparing the results obtained in the two control experiments.

While we do not know with certainty why TiCl_4 is totally inactive under the conditions in which BCl_3 yields efficient LC^+Pzn , some cautious speculations to explain the observations are warranted: We are quite confident that initiation in *tert*-alcohol/ BCl_3 systems involves the following set of transformations [3, 14]:



Propagation occurs by the complexes I and/or II and most likely involves stretched polarized bonds (dipoles) indicated by --- [14]. Evidently this sequence of reactions does not occur with TiCl_4 . The reaction $\text{R}'\text{-OH} + \text{TiCl}_4 \rightarrow \text{R}'\text{-OTiCl}_3 + \text{HCl}$ may occur; however, the alkoxides may be too stable for initiation [15].

It must also be kept in mind that DiCumOH and TMHDiOH are insoluble or at best sparingly soluble in CH_3Cl or $\text{CH}_3\text{Cl}/n\text{-C}_6\text{H}_{14}$ mixtures. These and similar alcohols are excellent initiators (rather initiator-precursors) in conjunction with BCl_3 because they are very rapidly converted upon contact with this Friedel-Crafts acid even at -80°C to the corresponding *tert*-chlorides, the true initiating species. Thus, for example, when BCl_3 is added to a suspension of DiCumOH in CH_3Cl , the alcohol virtually instantaneously dissolves and the system becomes homogeneous, i.e., the insoluble alcohol is converted to the soluble chloride [14].

Living IB Polymerization by a Two-Stage Process Employing BCl_3 and TiCl_4

The BCl_3 or Initiation Stage

In line with the above facts and teachings [1, 12], we postulated that the LC^+Pzn of IB could be achieved with *tert*-alcohol/ TiCl_4 combinations provided initiation could be induced by BCl_3 plus a small amount of IB. After the initiation phase with BCl_3 , we theorized that propagation could be sustained by the addition of TiCl_4 plus the bulk of the monomer. In order to get reasonable rates, the BCl_3 stage should be carried out in CH_3Cl . This stage can be continued as long as the PIB molecular weight is below the precipitation limit in this system (e.g., $\overline{M}_n < 5000$). Once the polymerization is in progress, both BCl_3 and TiCl_4 could be present because either coinitiator is able to sustain the living process [1, 6, 12].

Table 2 shows the conditions and results of five representative two-stage experiments. The DiCumOH (white suspension in CH_3Cl) immediately dissolved upon BCl_3 addition. Then the DMA was added to the charge and finally the IB. After 90–120 min of stirring (see Table 2), a sample was withdrawn to ascertain \overline{M}_n and

the MWD (expressed by $\overline{M}_w/\overline{M}_n$). In line with earlier information [1], it was assumed that I_{eff} 's are 100% under these conditions. As indicated by the data, the \overline{M}_n 's were safely below $\overline{M}_n \approx 5000$ and the systems were homogeneous.

The TiCl_4 or Propagation Stage

According to earlier experience, LC^+Pzn can be readily achieved with TiCl_4 -based systems in $\text{CH}_3\text{Cl}/n\text{-C}_6\text{H}_{14}$ 40/60 v/v mixtures at -80°C [3, 5]. TiCl_4 -based initiating systems are very sensitive to adventitious protic initiation, but initiation by moisture is of little significance in relatively nonpolar media at -80°C [3]. BCl_3 -based initiating systems are far less reactive than TiCl_4 -based systems in $\text{CH}_3\text{Cl}/n\text{-C}_6\text{H}_{14}$ 40/60 v/v mixtures.

Keeping these facts in mind, TiCl_4 in hexanes solution and the desired amounts of monomer were added to the charges as outlined in Table 2. The amount of hexanes was calculated to bring the $\text{CH}_3\text{Cl}/n\text{-C}_6\text{H}_{14}$ ratio to 40/60 v/v. From this point forward, samples were withdrawn for \overline{M}_n and $\overline{M}_w/\overline{M}_n$ analysis, and further IB increments were added at various times. After quenching, the final \overline{M}_n , $\overline{M}_w/\overline{M}_n$, and I_{eff} were determined. These data are shown in Table 2.

It is evident that the system remained living after switching from BCl_3 to TiCl_4 and reducing the polarity of the medium. The TiCl_4 concentrations used in these experiments ($1.7\text{--}6.3 \times 10^{-2} M$) were decidedly lower than those usually used ($0.1 M$) in LC^+Pzn , possibly because substituting the TiCl_4 by BCl_3 effected the ionization of the *tert*-alcohol and the complexation with DMA.

A reviewer queried whether we could replace the two-step process by a single-step process using all the ingredients (solvents, alcohol, IB, DMA, BCl_3 , and TiCl_4) in the starting charge and adding the calculated amount of hexanes somewhat later to prevent polymer precipitation from the CH_3Cl medium. Indeed, we tried using various $\text{BCl}_3/\text{TiCl}_4$ mixtures in the starting charge, and we obtained very rapid polymerization and a broad MWD product, most likely due to uncontrolled initiation by moisture. We also tried to slow down the polymerizations by adding hexanes (i.e., 40/60 $\text{CH}_3\text{Cl}/\text{hexanes}$ v/v) to the above mixed $\text{BCl}_3/\text{TiCl}_4$ charge before adding the IB; in this case we obtained slow initiation and low I_{eff} (60–80%). These experiments were carried out under the following conditions: $\text{TMHDiOH} = 9.2 \times 10^{-3} M$, $\text{BCl}_3 = 2.69 \times 10^{-2} M$, $\text{IB} = 1.03 M$, $\text{DMA} = 2.39 \times 10^{-2} M$, $\text{CH}_3\text{Cl}/\text{hexanes} = 40/60$ v/v, and the TiCl_4 concentration varied from 1.46×10^{-2} to $14.59 \times 10^{-2} M$. Much more experimentation will be needed to work out a satisfactory one-step mixed-coinitiator-based living polymerization process.

Demonstration of Living Polymerization with Two-Stage Process

After the parameters needed for two-stage living polymerizations were established, an experiment was carried out specifically to demonstrate livingness by an extended diagnostic IMA run [2]. Table 3 shows the procedure, reagent concentrations, and results. The polymerization was initiated by the addition of precooled BCl_3 to a $\text{DiCumOH}/\text{DMA}/\text{IB}$ charge at -80°C .

After a suitable period of stirring, a sample was withdrawn and analyzed to ascertain that initiation was complete and that a living polymerization was in prog-

ress. Then TiCl_4 in hexanes solution and further IB were added, and sampling was continued every 15 min. Further aliquots of monomer were introduced after the 6th and 10th samples.

Figure 1 is a diagnostic plot of \bar{M}_n versus W_p (g PIB formed), with the inset showing N (the number of moles of PIB formed) versus W_p . Since the charge composition was continuously changing because of the addition of several IB increments and withdrawal of samples, W_p was calculated from the PIB yield (g) per 10^{-4} mol DiCumOH. The diagnostic \bar{M}_n versus W_p plot is rectilinear and shows no intercept, and the N versus W_p plot is horizontal. According to this evidence, living polymerization prevailed within experimental error up to $\bar{M}_n \approx 20,000$. The I_{eff}

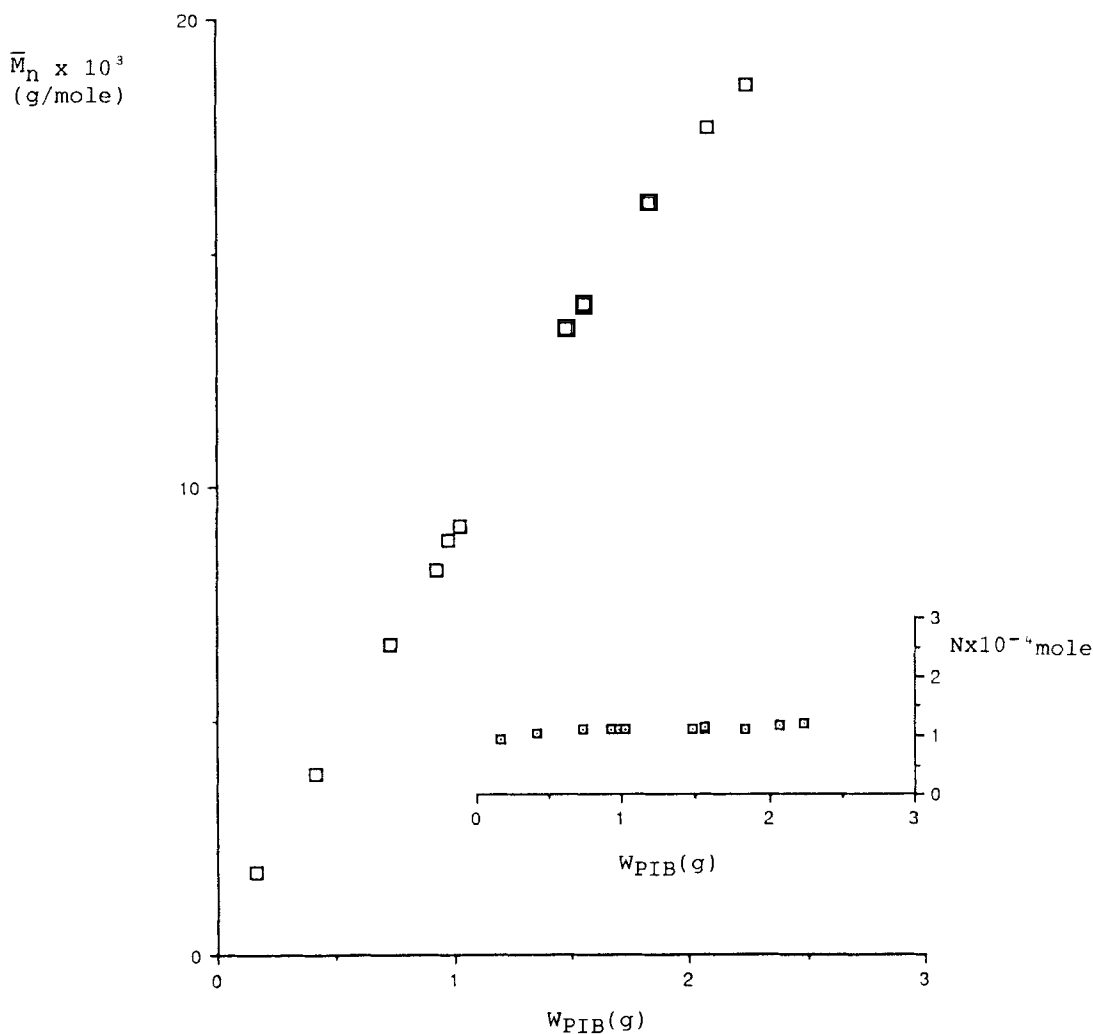


FIG. 1. Two-stage living polymerization of IB by DiCumOH/ $\text{BCl}_3/\text{TiCl}_4/\text{DMA}$. Conditions as in Table 3: $W_{\text{PIB}} = \text{PIB yield per } 1.0 \times 10^{-4} \text{ mol initiator}$. $N = W_{\text{PIB}}/\bar{M}_n$.

data were consistently 10–20% higher than the theoretical values, probably because of some unidentified systematic operational or analytical error (most likely due to the GPC values).

Structure Determination of 'Cl-PIB-Cl'

The structures of the products obtained in living polymerization of IB induced by various initiators (e.g., *tert*-ethers, -esters, -chlorides, -alcohols) in conjunction with BCl_3 or TiCl_4 have been determined [1, 2, 4, 6, 16]. These products were found invariably to contain initiator fragments that became incorporated into the polymer as a result of controlled initiation and of *tert*-chlorine end-groups ($\sim\text{CH}_2\text{C}(\text{CH}_3)_2\text{Cl}$) that arose by reversible quasiliving termination [12, 17, 18]. Thus we expected and found evidence for the incorporation of the aromatic dicumyl fragment ($-(\text{CH}_3)_2\text{C}-\text{C}_6\text{H}_{14}-\text{C}(\text{CH}_3)_2-$) when DiCumOH was used as the initiator, and for the presence of *tert*-chlorine end-groups when either the aromatic or aliphatic di-*tert*-alcohol was used.

The analytical methods have been described in detail [8, 19, 20]. In this work the products were analyzed by 200 MHz ^1H FT NMR spectroscopy by relating quantitatively the four aromatic protons in the polymer with the four $-\text{C}(\text{CH}_3)=\text{CH}_2$ protons obtained from the two $\sim\text{CH}_2\text{C}(\text{CH}_3)_2\text{Cl}$ end-groups after dehydrochlorination [8]. Subsequently the $-\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$ end-groups were converted by quantitative hydroboration/oxidation to $-\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$ end-groups [10]. These end groups were then independently quantitated by ^1H NMR ($-\text{CH}_2\text{OH}$ versus aromatic internal standard protons) and FT-IR spectroscopy; for the latter method the \bar{M}_n of the products was determined by VPO and GPC [9]. These methodologies together with detailed analyses of the spectra have been described [8–10]. The products obtained in this research were invariably $\text{Cl}(\text{CH}_3)_2\text{-CCH}_2\text{-PIB-CH}_2\text{C}(\text{CH}_3)_2\text{Cl}$ with the number-average end functionalities $\bar{F}_n = 2.0 \pm 0.1$.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (Grant 89-20826) and by the Goodyear Tire and Rubber Co.

REFERENCES

- [1] C. C. Chen, G. Kaszas, J. E. Puskas, and J. P. Kennedy, *Polym. Bull.*, **22**, 463 (1989).
- [2] R. Faust and J. P. Kennedy, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 1847 (1987).
- [3] G. Kaszas, J. E. Puskas, and J. P. Kennedy, *Makromol. Chem., Macromol. Symp.*, **13/14**, 473 (1988).
- [4] M. K. Mishra and J. P. Kennedy, *J. Macromol. Sci.—Chem.*, **A24**(8), 933 (1987); *Polym. Bull.*, **17**, 7 (1987).
- [5] G. Kaszas, J. E. Puskas, and J. P. Kennedy, *Polym. Bull.*, **18**, 123 (1987).

- [6] G. Kaszas, J. E. Puskas, C. C. Chen, and J. P. Kennedy, *Ibid.*, 20, 413 (1988).
- [7] B. Wang, M. K. Mishra, and J. P. Kennedy, *Ibid.*, 17, 213 (1987).
- [8] J. P. Kennedy, V. S. C. Chang, R. A. Smith, and B. Iván, *Ibid.*, 1, 575 (1979).
- [9] V. S. C. Chang and J. P. Kennedy, *Ibid.*, 9, 518 (1983).
- [10] B. Iván, J. P. Kennedy, and V. S. C. Chang, *J. Polym. Sci., Polym. Chem. Ed.*, 18, 3177 (1980).
- [11] G. Kaszas, J. E. Puskas, J. P. Kennedy, and C. C. Chen, *J. Macromol. Sci.-Chem.*, A26(8), 1099 (1989).
- [12] G. Kaszas, J. E. Puskas, C. C. Chen, and J. P. Kennedy, *Macromolecules*, 23, 3909 (1990).
- [13] R. Feld and P. L. Cowe, *The Organic Chemistry of Titanium*, Butterworths, London, 1965, Chapters 2 and 3.
- [14] H. A. Nguyen and J. P. Kennedy, *Polym. Bull.*, 6, 47 (1981).
- [15] W. Gerard, *The Organic Chemistry of Boron*, Academic Press, New York, 1961, pp. 22-31.
- [16] M. K. Mishra, C. C. Chen, and J. P. Kennedy, *Polym. Bull.*, 22, 455 (1989).
- [17] J. P. Kennedy, T. Kelen, and F. Tudos, *J. Macromol. Sci.-Chem.*, A18(9), 1189 (1982).
- [18] J. E. Puskas, G. Kaszas, J. P. Kennedy, T. Kelen, and F. Tudos, *Ibid.*, A18(9), 1229 (1982).
- [19] J. P. Kennedy and R. A. Smith, *J. Polym. Sci., Polym. Chem. Ed.*, 18, 1523 (1980).
- [20] A. Fehervari and J. P. Kennedy, *J. Macromol. Sci.-Chem.*, A15(2), 215 (1981).

Received October 15, 1991

Revision received January 6, 1992