Living Carbocationic Polymerization of Isobutylene Using Blocked Dicumyl Chloride or Tricumyl Chloride/TiCl₄ Pyridine Initiating System

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LIVING CARBOCATIONIC POLYMERIZATION OF ISOBUTYLENE USING BLOCKED DICUMYL CHLORIDE OR TRICUMYL CHLORIDE/TiCl₄/PYRIDINE INITIATING SYSTEM

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ABSTRACT

Living polymerization of isobutylene was achieved using an initiation system based on either 1,3-di(1-chloro-1-methylethyl)-5-*tert*-butylbenzene (*tert*-butyl-dicumyl chloride) or 1,3,5-*tris*(1-chloro-1-methylethyl)benzene (tricumyl chloride) in conjunction with $TiCl_4$ and pyridine in hexanes/methyl chloride (60/40, v/v) cosolvents. $TiCl_4$/pyridine was found to yield narrow molecular weight distribution (MWD ≈ 1.1) and quantitative initiation efficiency ($I_{eff} > 90\%$). The living nature of the polymerization system was demonstrated by the linearity of molecular weight vs conversion plots and first-order kinetic plots up to about 90% monomer conversion. If polymerization was allowed to proceed further, a departure from first-order kinetics and a broadening of the molecular weight distribution was observed to occur. The living polymerization was investigated as a function of temperature, reaction time, and the concentration of $TiCl_4$/pyridine. Polymerization rates were observed to increase with decreasing temperature and/or increasing concentration of $TiCl_4$/pyridine. Number-average molecular weights of the polyisobutylenes ranged from 5,000 to 100,000 under the conditions employed.

INTRODUCTION

The term "living polymerization" describes any chain growth polymerization which proceeds in the absence of kinetically significant chain termination or chain transfer processes. Synthetic utility of living polymerizations is manifest in the ability to perform macromolecular engineering, i.e., to achieve fine control of the polymer molecular weight and molecular weight distribution (MWD), and to form well-defined block copolymers and end-functionalized (telechelic) polymers.

Living polymerization was first described by Ziegler [1] and Abkin and Medvedev [2], and was later caused to be generally recognized by Szwarc et al. [3] who successfully polymerized styrene and butadiene using sodium naphthalide in tetrahydrofuran. Since this discovery, anionic living polymerizations have been extensively used for both kinetic and mechanistic studies and for complex and difficult preparative procedures. However, the development of living cationic polymerization has lagged far behind the anionic counterpart, since propagating carbocations tend to undergo transfer or termination reactions due to their inherent instability under conventional cationic polymerization conditions.

In spite of these problems, in the late 1970s Higashimura et al. [4, 5] produced relatively long-lived propagating carbocations in nonpolar solvents using oxygenated olefins such as p-methoxystyrene and isobutyl vinyl ether and the Lewis acid, I_2. In these early systems, I_2 served as both initiator and coinitiator, and initiation was slow.

"Quasiliving" cationic polymerization was achieved by Faust, Fehervari, and Kennedy in 1980 for the polymerization of isobutylene (IB) [6] and α-methylstyrene [7] using a monomer starvation technique. This method yielded a linear increase in the number-average molecular weight (M_n) of the polymer with weight of monomer added. This result was thought to be due to the reversibility of chain transfer and termination reactions under the conditions employed, allowing for reinitiation of growing chains.

It was not until 1984 that Higashimura et al. [8] reported the first well-defined, truly living cationic polymerization process, in this case for vinyl ether polymerization in nonpolar solvents using hydrogen iodide/iodine (HI/I_2) as the initiating system. The addition of HI was the key factor, allowing for fast initiation and producing polymers of narrow molecular weight distribution. Thereafter, Higashimura et al. [9] reported that living polymerization of vinyl ethers could be attained under otherwise conventional cationic polymerization conditions (organoaluminum halide coinitiator) by the addition of a Lewis base or an electron donor (ED), such as ethyl acetate, to the polymerization mixture.

The living carbocationic polymerization of IB was first reported by Kennedy et al. upon discovery that IB could be polymerized by *tert*-alkyl and *tert*-aryl esters [10] and ethers [11] in conjunction with Lewis acids such as BCl_3 or $TiCl_4$. Kaszas et al. [12] later reported that living carbocationic polymerization of IB, producing products of narrow MWD, could also be achieved by the addition of certain EDs, i.e., dimethylsulfoxide (DMSO), dimethylacetamide (DMA), ethyl acetate, etc., to a variety of *tert*-alkyl (or aryl) chloride, ether, or alcohol/Lewis acid systems. The authors observed that DMSO and DMA were most effective in bringing about the desired effects. They also demonstrated that, in the presence of suitable EDs, undesirable side reactions, such as uncontrolled initiation by protic impurities and

intramolecular alkylation of aromatic initiators, leading to indanyl structures, could be suppressed or totally eliminated. Later, a detailed mechanism for the living carbocationic polymerization of IB initiated by *tert*-alkyl (or aryl) ester or ether/ BCl₃ or TiCl₄ complexes was proposed by Kaszas et al. [13]. According to their mechanism, the function of an ED, whether formed *in situ* [10, 11] or added externally [9, 12], is to stabilize the active carbocations.

Upon discovery of a new, simplified method for the sulfonation of *tert*-alkyl chloride-terminated polyisobutylene (PIB) [14, 15], we became interested in preparing a series of telechelic PIB ionomers with narrow polydispersity. We elected to explore variations of the method of Kaszas [12], i.e., the use of an external ED, and so several of these compounds were used and their effects on the MWD were examined. It was observed that pyridine consistently yielded PIBs with the most narrow MWD among the several electron donors studied. Thus, the living polymerization of IB using an initiation system based on either the difunctional initiator, 1,3-di(1-chloro-1-methylethyl)-5-*tert*butylbenzene [*tert*-butyl-dicumyl chloride (*t*-Bu-*m*-DCC)], or the trifunctional initiator, 1,3,5-*tris*(1-chloro-1-methylethyl)benzene [tricumyl chloride (TCC)], in conjunction with TiCl₄/pyridine has been well characterized in our laboratory and applied to the synthesis of telechelic ionomers [14, 15] with narrow MWDs, and the synthesis of poly(styrene-*b*-isobutylene-*b*-styrene) [16] by a sequential monomer addition technique. This paper describes in detail the living polymerization of IB, using the *t*-Bu-*m*-DCC or TCC/TiCl₄/pyridine initiating system, and its usefulness for the synthesis of narrow-polydispersity, well-defined PIB with the desired M_n.

EXPERIMENTAL

Materials

t-Bu-*m*-DCC, which is blocked against ring alkylation, was prepared from 5-*tert*-butyl isophthalic acid (Amoco Chemical Co.). The procedure of Wang et al. [17] was followed to produce first the ethyl ester of the starting dicarboxylic acid and then 1,3-di(1-hydroxy-1-methylethyl)-5-*tert*-butylbenzene (dicumyl alcohol) by reaction of the ester with methylmagnesium bromide. The experimental procedure for chlorination of dicumyl alcohol is described below.

TCC was synthesized using a modification of the procedure of Santos et al. [18]. In accordance with the published method, the starting material, 1,3,5-triisopropylbenzene (Aldrich Chemical Co.), was brominated using N-bromosuccinimide (NBS) and a free radical source such as benzoyl peroxide. The tricumyl bromide thus obtained was then reacted with *tert*-BuO⁻K⁺ to produce triisopropenyl benzene, which was subsequently hydrochlorinated by reaction with HCl gas to yield the final product (tricumyl chloride). Among the several steps in this synthesis, the bromination reaction was the most difficult due to the occurrence of a nearly explosive exotherm as the reaction commenced. As described in detail below, a small amount of added water, in conjunction with NBS, leads to a large decrease in the exotherm, rendering greater control over the reaction, yet still allowing almost quantitative conversion (yield: 96%). The other reactions in the sequence, dehydrobromination and chlorination, were accomplished according to published methods.

Hexanes were freshly distilled over CaH$_2$ before use. Anhydrous pyridine and TiCl$_4$ (Aldrich) were used as received. IB and methyl chloride (Linde Division, Union Carbide Corp.) were dried before use by passing the gas through a column packed with BaO and CaCl$_2$. Anhydrous methanol was used as received.

Instrumentation

GPC was performed using a Waters Associates system consisting of a high-pressure 6000A pump, four μ-Styragel columns of pore sizes 10^5, 10^4, 10^3, and 10^2 Å, a differential refractometer model 410 (RI), and a tunable absorbance detector model 484 (UV) operating at 37°C. A calibration curve was produced using commercial PIB standards (American Polymer Standard Corp.).

Procedures

Synthesis of 1,3-Di(1-chloro-1-methylethyl)-5-*tert*-butylbenzene [*tert*-Butyl-dicumyl Chloride (*t*-Bu-*m*-DCC)]

The starting compound, 5-*tert*-butyl isophthalic acid, was readily converted to the corresponding alcohol (*t*-Bu-*m*-DCOH) using the procedure of Wang et al. [17]. *t*-Bu-*m*-DCC was obtained by hydrochlorination of the *t*-Bu-*m*-DCOH at ice water temperature in the presence of calcium chloride as a water scavenger. A typical procedure was as follows: To a 1000-mL three-necked round-bottomed flask, equipped with gas inlet and outlet tubes, mechanical stirrer, and external ice/water cooling bath, were charged 50 g *t*-Bu-*m*-DCOH (0.2 mol), 50 g CaCl$_2$, and 500 mL methylene chloride. HCl gas was generated in a separate reactor by addition of concentrated sulfuric acid to solid NaCl. The gas was passed through a column packed with anhydrous CaCl$_2$ and then bubbled continuously into the solution with stirring for 10 h. The alcohol is not soluble in methylene chloride but was observed to slowly go into solution as it reacted. The reaction progress was monitored using ^{1}H NMR to observe the disappearance of the hydroxyl proton resonance at 2.85 ppm. Excess HCl and MeCl$_2$ were vacuum stripped, and the product was twice recrystallized from hexanes to yield colorless needles (mp = 68°C). Yield: 44.6 g (81.3%). ^{1}H NMR (ppm): 1.34 (methyl, s, 9H), 2.04 (methyl, s, 12H), 7.55 (aromatic, s, 2H), 7.63 (aromatic, s, 1H).

Synthesis of 1,3,5-*Tris*(1-bromo-1-methylethyl)benzene [Tricumyl bromide (TCB)]

To a 1000-mL three-necked round-bottomed flask, equipped with a 66-cm Allihn condenser, magnetic stirrer, and dry nitrogen inlet tube, were charged 15 g 1,3,5-triisopropylbenzene (0.073 mol), 43 g N-bromosuccinimide (0.24 mol), 3.0 g benzoyl peroxide (0.012 mol), 10 g distilled (DI) water, and 350 mL CCl$_4$ freshly distilled from CaH$_2$. The solution was degassed by purging with nitrogen for 30 min and slowly heated to reflux. As the solution started to reflux, succinimide began to appear as an orange-colored precipitate. The charge was further refluxed for 15 min, cooled to room temperature, and refrigerated overnight, during which time the balance of the solid succinimide separated from the solution. The cold solution was freed of succinimide by filtration, and the CCl$_4$ was removed using a

rotary evaporator. The product was recrystallized from hexanes (mp = 75–76°C). Yield: 31.2 g (96%). ^{1}H NMR (ppm): 2.21 (methyl, s, 18H), 7.76 (aromatic, s, 3H).

Living Polymerization of IB

Near-monodisperse di-arm linear and three-arm star-branched PIBs were prepared using a modification of the method of Kaszas et al. [12]. A blocked dicumyl chloride initiator was used for the preparation of di-arm, linear PIB, since the utilization of the "nonblocked" p-dicumyl chloride initiator leaves open the possibility for undesirable aromatic ring alkylation after one monomer addition [12].

In our preparative procedures, a one-to-one ratio of pyridine/initiator chloride functionality was used, and the $TiCl_4$/pyridine ratio was held constant at 5:1. A representative polymerization procedure, conducted under a dry N_2 atmosphere within a glove box equipped with an integral cold-temperature bath, was as follows: Into a 2000-mL three-necked round-bottomed flask, equipped with mechanical stirrer, were charged 1.714 g (0.0056 mol) TCC, 1.328 g (0.0168 mol) pyridine, and 600 mL hexanes. The flask was immersed into the cold-temperature bath (−50°C), and first 400 mL methyl chloride and then 83 mL IB (1 mol) were condensed into a chilled graduated cylinder and transferred into the flask. With vigorous stirring, 31.872 g $TiCl_4$ (0.168 mol) was rapidly injected into the flask to commence polymerization. Before addition of the $TiCl_4$, the mixture was completely homogeneous; upon $TiCl_4$ addition, an immediate precipitation was observed, believed to be a complex of pyridine with $TiCl_4$ (stoichiometry unknown), and this precipitate persisted throughout the reaction. As far as could be observed, the product PIB was completely soluble in the cosolvents system. The polymerization was terminated by injection of an excess (50 mL) of prechilled methanol. The reactor was removed from the glove box, placed in a fume hood, and allowed to warm to room temperature with stirring to insure smooth evaporation of MeCl. Additional hexanes (400 mL) were added to the solution, which was then washed with 5 wt% aqueous HCl solution three times, washed with deionized water three times, and dried over $MgSO_4$. The polymer was isolated by evaporating the hexanes.

RESULTS AND DISCUSSION

Living polymerization of IB using t-Bu-m-DCC or TCC/$TiCl_4$/pyridine initiating system was found to yield near-monodisperse PIB with a well-defined structure. The hexanes/MeCl (60/40, v/v) cosolvents system yielded complete solubility of the product PIB. $TiCl_4$ coinitiator was employed, since BCl_3 is unable to coinitiate polymerization in the relatively nonpolar medium. Except where otherwise noted, the Lewis acid was always added as the last component, and always to the full complement of monomer. A GPC chromatogram of a representative PIB produced using this system is shown in Fig. 1. A typical plot of M_n versus conversion, shown as Fig. 2, is linear and passes through the origin, which is a necessary condition for living polymerization behavior, indicating the absence of chain transfer.

Specific polymerization conditions and recorded data for the synthesis of linear and three-arm star PIBs are listed in Tables 1–3 for polymerizations at −30,
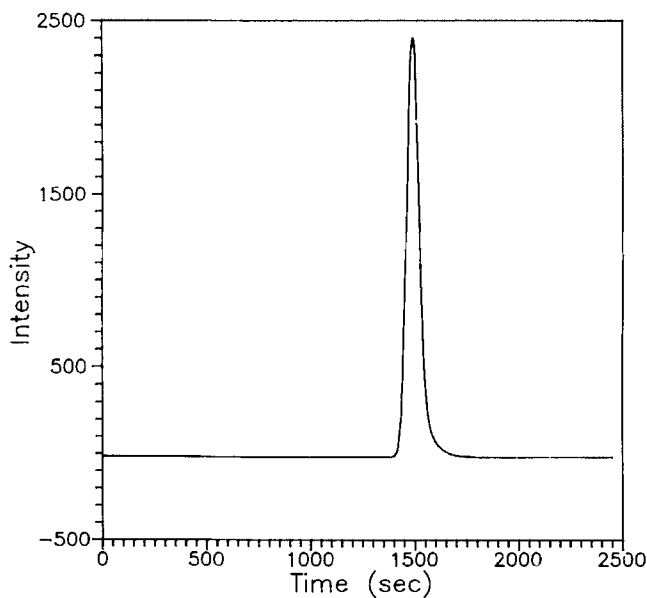
FIG. 1.   A typical GPC chromatogram of PIB obtained using the TCC/TiCl$_4$/pyridine initiating system and hexanes/methyl chloride (60/40, v/v) cosolvents.
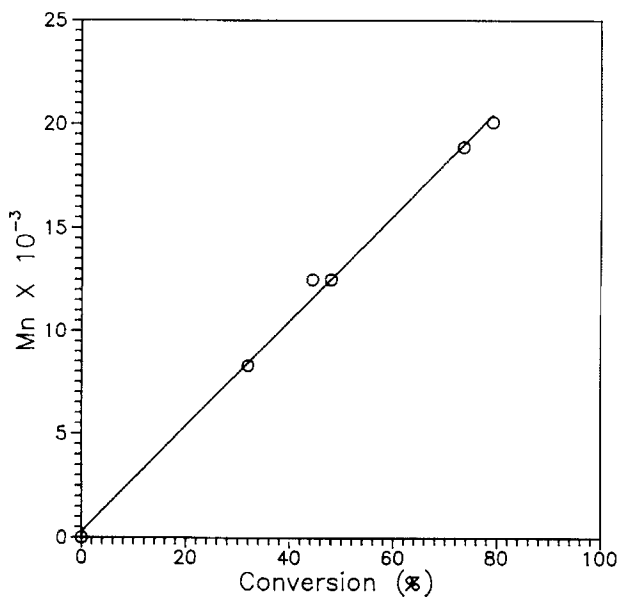

FIG. 2. M_n vs conversion for the living polymerization of isobutylene in hexanes/methyl chloride (60/40, v/v) cosolvents at $-50°C$, initiated by TCC/TiCl$_4$/pyridine (Sample 3, Table 2).

TABLE 1. Polymerization of IB Using TCC/TiCl$_4$/Pyridine Initiating System at −30°C[a]

Sample	M_n stoich.	[TCC] × 10^2	[IB]	Total reaction volume, mL	M_n obtained	MWD	Conversion, %	I_{eff}, %	Reaction time, min
1	20,000	3.13	1.11	800	6,800	1.10	32.3	95	30
2	10,000	0.56	1.00	35	10,700	1.18	88.2	82.4	30
3	10,000	0.8	1.03	350	7,200	1.07	60	83.3	30
4	5,000	1.14	1.03	350	5,400	1.18	100	93	30

[a]M_n stoich. = weight of IB/mol TCC, [pyridine] = 3 × [TCC], [TiCl$_4$] = 5 × [pyridine], solvent = hexanes/MeCl (60/40, v/v). M_n and MWD were calculated by GPC.

−50, and −80°C, respectively. In most cases, 1 M IB was used and the concentrations of other components were calculated therefrom; specific concentrations of all components are listed in the tables. Near-monodisperse PIBs (MWD ≈ 1.1) with various number-average molecular weights (5000 ≤ M_n ≤ 100,000) were obtained depending on the reaction conditions employed and the time allowed for reaction. Using our initiating system, I_{eff} was consistently greater than 90% regardless of the reaction temperature and the monomer conversion. This suggests that the rate of propagation is significantly slower than the rate of initiation, as would be desired for the preparation of near-mondisperse polymers from a living polymerization.

Since molecular weight and conversion are proportional to one another (Fig. 2), and because it appears that an effective concentration of growing chains is

TABLE 2. Polymerization of IB Using TCC/TiCl$_4$/Pyridine Initiating System at −50°C[a]

Sample	M_n stoich.	[TCC] × 10^3	[IB]	Total reaction volume, mL	M_n obtained	MWD	Conversion, %	I_{eff}, %	Reaction time, min
1	30,000	1.96	1.05	1,700	23,300	1.11	78	101	150
2	25,000	2.35	1.05	170	14,700	1.08	56	95	15
3	25,000	2.35	1.05	1,700	20,400	1.13	80	102	150
4	25,000	2.23	1.00	35	20,200	1.13	79	98	180
5	20,000	2.80	1.00	100	18,500	1.08	—	—	180
6	15,000	3.92	1.05	1,700	7,100	1.06	50	106	30
7	15,000	3.92	1.05	1,700	11,500	1.06	71	93	45
8	15,000	3.92	1.05	1,700	14,100	1.04	99	105	60
9	10,800	5.88	1.13	1,700	11,800	1.05	104	95	40

[a]M_n stoich. = weight of IB/mol TCC, [pyridine] = 3 × [TCC], [TiCl$_4$] = 5 × [pyridine], solvent = hexanes/MeCl (60/40, vol/vol). M_n and MWD were calculated by GPC.

TABLE 3.   Polymerization of IB Using t-Bu-m-DCC or TCC/TiCl$_4$/Pyridine Initiating System at $-80°C^a$

Sample	M_n stoich.	[B-DCC] $\times 10^3$	[IB]	Total reaction volume, mL	M_n obtain.	MWD	Conversion, %	I_{eff}, %	Reaction time, min
1	20,000	3.7	1.32	100	19,400	1.08	95	98	180
2	18,000	3.92	1.26	1,700	19,300	1.06	104	93	40
3	15,000	3.92	1.05	1,700	16,200	1.07	105	97	30
4	13,600	4.32	1.05	1,700	11,400	1.10	87	104	15
5	9,400	6.26	1.05	1,700	10,300	1.07	102	94	15
6	4,400	13.37	1.05	1,700	5,100	1.15	118	103	15
	[TCC] $\times 10^3$								
7	100,000	0.67	1.20	2,500	94,600	1.10	96	101	390^b
8	50,000	1.34	1.20	2,500	49,500	1.09	96	97	180^b
9	27,000	1.73	0.83	1,500	24,600	1.12	95	105	40
10	20,000	2.80	1.00	300	20,300	1.04	106	104	60

^aM_n stoich. = weight of IB/mol B-DCC or TCC. B-DCC = t-Bu-m-DCC, [pyridine] = 2 × [B-DCC] = 3 × [TCC], [TiCl$_4$] = 5 × [pyridine], solvent = hexanes/MeCl (60/40, vol/vol). M_n and MWD were calculated by GPC.
^{b}Incremental monomer addition technique.

established early and remains invariant, we can assume, as a first approximation, a simple, pseudo-first-order kinetic expression for the rate of polymerization, r_p:

$$r_p = k_p[\text{R}^+][\text{M}] = k_p[\text{I}]_0[\text{M}] \tag{1}$$

where k_p = apparent rate constant for polymerization
[R$^+$] = constant concentration of growing chains
[I]$_0$ = initial concentration of initiator

Integration of Eq. (1), and substitution of the definition of the conversion, p, in terms of the initial monomer concentration, [M]$_0$, and the number-average degree of polymerization, $\overline{DP}_n$,

$$p = [\text{I}]_0\overline{DP}_n/[\text{M}]_0 \tag{2}$$

yields the function below, which, if linear when applied to polymerization data, is both a necessary and sufficient condition for living polymerization behavior [19].

$$-\ln(1 - p) = k_p[\text{I}]_0 t \tag{3}$$

Molecular weight was monitored as a function of time by removing aliquots at regular intervals for GPC analysis. As shown in Fig. 3, when the data were plotted according to Eq. (3), living behavior was indeed observed until about 90% conversion. After that point, the plot was observed to deviate from linearity due either to
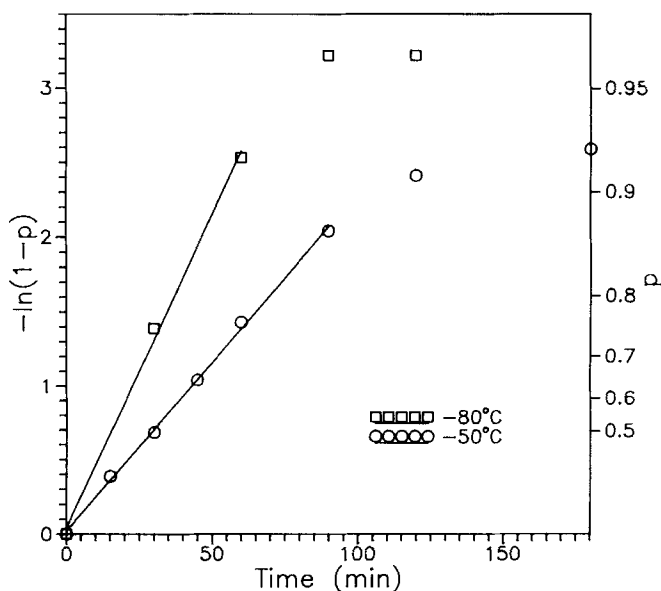
FIG. 3.   -Ln $(1 - p)$ vs time for the living polymerization of isobutylene in hexanes/methyl chloride (60/40, v/v) cosolvents, initiated by $TCC/TiCl_4$/pyridine at two different temperatures (Sample 5, Table 2; Sample 1, Table 3).

chain transfer and/or termination, and a distinct broadening of the MWD was observed in the GPC chromatogram (low molecular weight tail on the high-elution-volume side of the main polymer peak); however, the polymers remained mono-modal. This phenomenon was observed even at $-80°C$. Thus, conversion of the polymerization, and hence rate of propagation and time of reaction, are very important parameters in living cationic polymerization. Unlike living anionic polymerizations, which can be carried to essentially quantitative monomer conversion, living cationic polymerizations, as carried out under these conditions, must be terminated before total monomer depletion. This causes the polymerization rate to be a very critical variable and demands that close attention must be given to the time of reaction for each temperature and initiator concentration.

Polymerization rates were observed to increase with decreasing temperature. Apparent rate constants for propagation were extracted from the plots in Fig. 3, yielding a value of $k_p = 9 \times 10^{-2}$ L/mol·s at $-80°C$ and $k_p = 5 \times 10^{-2}$ L/mol·s at $-50°C$. Figure 4 shows explicitly the increase in the molecular weight as a function of time at two different temperatures. It may be noted that the molecular weight of PIB increased more rapidly at $-80°C$ than at $-50°C$, and at longer times both polymerizations produced PIBs quite close to the stoichiometric M_n of 20,000 ($M_{n \text{ stoich.}}$ = g IB/mole initiator). As reaction temperature was elevated further, the molecular weight increase with time became even less rapid, and as can be seen in Fig. 5 for a polymerization at $-30°C$, the apparent rate constant for propagation was only 1×10^{-2} L/mol·s at this temperature.

From the foregoing, it would thus appear that living cationic polymerization, under these conditions, displays a negative apparent activation energy for the rate
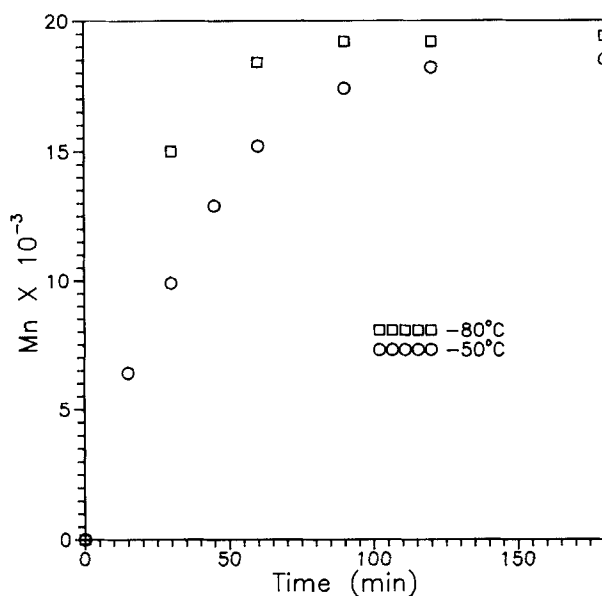
FIG. 4. M_n vs time for the living polymerization of isobutylene in hexanes/methyl chloride (60/40, v/v) cosolvents, coinitiated by $TiCl_4$/pyridine at two different temperatures (Sample 5, Table 2; Sample 1, Table 3).
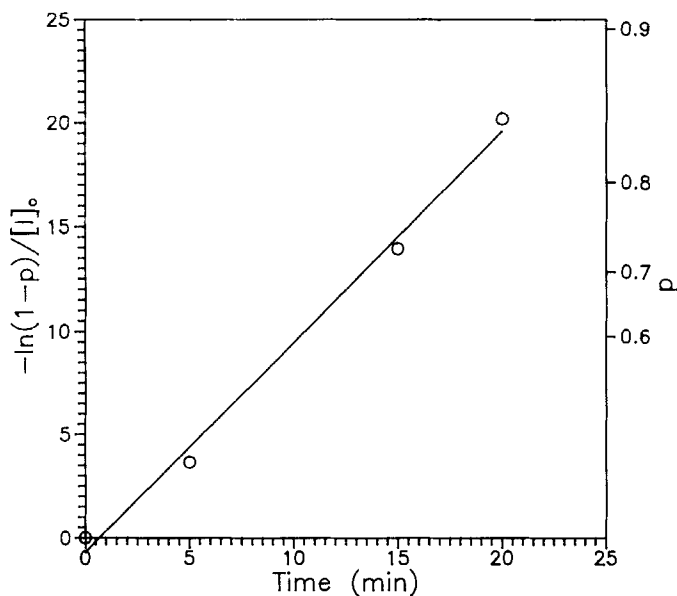
FIG. 5. M_n vs time for the living polymerization of isobutylene in hexanes/methyl chloride (60/40, v/v) cosolvents at $-30°C$, initiated by $TCC/TiCl_4$/pyridine (Sample 2, Table 1).

of polymerization. This is similar to the behavior of conventional isobutylene poly-
merization observed under a variety of conditions, but for a seemingly different
reason. As discussed by Kaszas et al. [13], the mechanism of ED-mediated living
cationic polymerization of isobutylene is governed by an equilibrium reaction be-
tween the *tert*-alkyl chloride chain end and its active, ionized form. The proposed
mechanism of living polymerization of IB using the TCC/TiCl$_4$/pyridine initiating
system, based upon the ideas given by Kaszas et al., is shown in Fig. 6. As shown,
the rate of propagation depends on the position of the equilibrium between (III)
and (IV). At lower temperatures, the equilibrium shifts in favor of (III), which
causes more rapid polymerization due to an increase in the concentration of actively
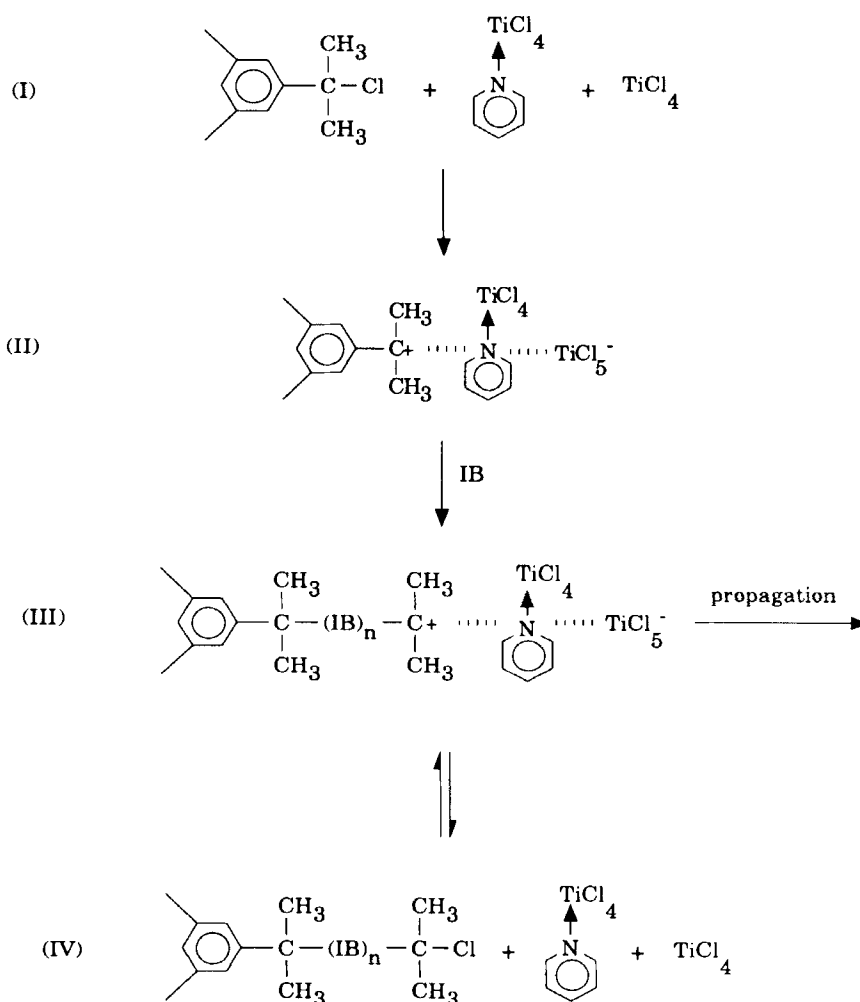growing chains.

FIG. 6.   Proposed mechanism for the living polymerization of isobutylene in hexanes/
methyl chloride cosolvents, initiated by *t*-Bu-*m*-DCC or TCC/TiCl$_4$/pyridine.

Due to the fact that the apparent activation energy for polymerization is negative, and because polymerizations designed to produce higher molecular weight PIBs necessarily possess lower concentrations of growing chains, from a practical standpoint, high molecular weight PIB ($M_n \geq$ 20,000) can be obtained in reasonable times only at relatively low temperatures ($\leq -50\,°C$). As illustrated in Table 1, Sample 3, PIB with $M_n \leq$ 10,000 can be prepared at $-30\,°C$ in about 30 min. However, in the case of a polymerization designed to produce higher molecular weight PIB, i.e., $M_{n\,\text{stoich.}}$ = 20,000 (Table 1, Sample 1), PIB with M_n of only 6,800 was obtained, because only 32% conversion was achieved in 30 min reaction time. By comparison, when a similar polymerization ($M_{n\,\text{stoich.}}$ = 18,000) was carried out at $-80\,°C$, quantitative conversion was achieved in 40 min, as shown in Table 3 (Sample 2).

Solvent polarity is another significant variable which impacts the ability to achieve relatively high molecular weight PIB. Using a more polar reaction medium would cause polymerization to proceed faster due also to a shift toward Species (III); however, the nonpolar PIB product may then precipitate, leading to broadening of the molecular weight distribution and/or low monomer conversions. Thus, the cosolvent mixture should be adjusted, from a consideration of the target molecular weight, to contain the maximum amount of polar cosolvent while maintaining complete solubility of the product PIB.

It was found that the rate of polymerization is also affected by the ratio of $TiCl_4$/pyridine as shown in Fig. 7. When a one-to-one ratio of $TiCl_4$/pyridine was used, only low molecular weight PIB with insignificant conversion was obtained. The rate of polymerization was observed to become faster as the $TiCl_4$/pyridine ratio was increased. The most obvious reason for this behavior is that pyridine
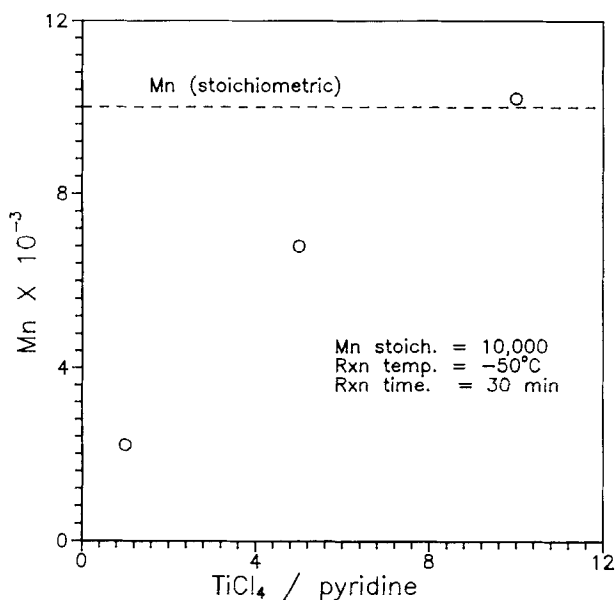

FIG. 7. M_n vs [$TiCl_4$]/[pyridine] for the TCC initiated living polymerization of IB in hexanes/methyl chloride (60/40, v/v) cosolvents at $-50\,°C$. [Pyridine] = 3 × [TCC].

complexes strongly with $TiCl_4$, and unless the latter is present in excess, it is not available to coinitiate the polymerization. It is conceivable that this behavior is also partly due to a shift in the equilibrium to the active propagating species (III) brought about by a higher excess of $TiCl_4$. Similar behavior was observed by Kaszas et al. [12].

CONCLUSIONS

Living polymerization of IB was achieved using blocked dicumyl chloride or tricumyl chloride/$TiCl_4$/pyridine initiating system in hexanes/methyl chloride (60/ 40, v/v) cosolvents. Externally added pyridine was found to serve as a very effective electron donor to moderate the reactivity of growing carbocations. Number-average molecular weight vs conversion plots were found to be linear and to pass through the origin. Near-monodisperse PIBs (MWD $\approx$ 1.1) with various number-average molecular weights (5,000 $\leq M_n \leq$ 100,000) were obtained depending on the reaction conditions employed and the time allowed for reaction. I_{eff} was consistently greater than 90% regardless of the reaction temperature and the monomer conversion, suggesting that the rate of initiation is rapid relative to rate of propagation.

The living nature of the polymerization system was demonstrated by the linearity of pseudo-first-order kinetic plots (first order in monomer, invariant concentration of growing chains) up to a monomer conversion of about 90%. Past this point, first-order kinetics were no longer observed and a broadening of the molecular weight distribution occurred. Examination of the GPC chromatograms showed that broadening occurred in the form of a low molecular weight tail on the high-elution-volume side of the main polymerization peak; this phenomenon was observed even at $-80°C$. Thus it is recommended that the polymerization be quenched before quantitative conversion of the monomer occurs in order to obtain near-monodisperse PIB with a well-defined structure. It is good practice to adjust the initial monomer/initiator stoichiometry upward such that the target molecular weight can be achieved and the polymerization terminated at around 85–95% conversion. This is an extremely important concept in the synthesis of block copolymers, where quantitative blocking efficiency must be obtained. It is often convenient to run scouting experiments prior to conducting block copolymerizations to foresee the trend of the increase in conversion with time.

Polymerization rates were observed to increase with decreasing temperature. It is proposed that the mechanism of living polymerization of isobutylene using this initiating system is governed by an equilibrium reaction between the dormant *tert*-alkyl chloride chain end and its active, ionized form. At lower temperatures the equilibrium shifts in favor of the active, ionized form, which causes more rapid polymerization due to an increase in the concentration of actively growing chains. It was observed that relatively high molecular weight PIB ($M_n \geq$ 20,000) was obtained in reasonable times only at lower temperatures ($\leq -50°C$) due to the apparent negative activation energy for polymerization. Solvent polarity was found to be an important consideration when designing high molecular weight PIB due to the possibility of precipitation of PIB in relatively polar media. Finally, the rate of polymerization was observed to become faster as a larger excess of $TiCl_4$/pyridine was used.

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