Living Carbocationic Polymerization. Xxxvii. Asymmetric Telechelic Polyisobutylenes by Lactone/Bcl₃ Initiating Complexes

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LIVING CARBOCATIONIC POLYMERIZATION. XXXVII. ASYMMETRIC TELECHELIC POLYISOBUTYLENES BY LACTONE/BCl₃ INITIATING COMPLEXES

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ABSTRACT

A new family of initiating systems of carbocationic polymerization has been introduced comprising complexes of a lactone and a Lewis acid. It has been shown by model experiments that the true initiating species are the lactone/Lewis acid complexes. A series of these complexes has been investigated in scouting experiments of isobutylene polymerization to identify an initiating complex which facilitates the diagnosis of living polymerizations. The γ-tolyl-γ-valerolactone/BCl₃ complex has been found to yield high initiation efficiencies at low isobutylene conversions and therefore has been selected for detailed investigation. It has been demonstrated that this lactone in the presence of BCl₃ effects the living polymerization of isobutylene. A variety of lactone/BCl₃ complexes has been found to be efficient initiators for the polymerization of styrene, 4-methylstyrene, and 2,4,6-trimethylstyrene; however, under the conditions employed, these polymerizations were not living. The mode of

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forced termination by the addition of different quenching agents has been studied in model experiments using ester/Lewis acid complexes as model compounds. Forced termination has been found to result in a tertiary chlorine end group in model experiments as well as in functionalization experiments by adding the quenching agent at the end of the polymerization. Living polymerizations initiated by lactone/BCl_3 complexes have been shown to yield α,ω-asymmetric telechelic polyisobutylenes; that is, PIBs capped with an ester or acid group at the α-terminus and a tertiary chlorine at the ω-terminus. End-group characterizations have shown theoretical functionalities within experimental variations.

I. INTRODUCTION

tert-Esters in conjunction with Lewis acids (BCl_3, $TiCl_4$, etc.) were found to be effective initiators for the living carbocationic polymerization LC⁺Pzn of olefins (isobutylene, styrene, etc.) [1–8]. The present research concerns an extension of this concept to *tert*-cyclic esters (cyclic *tert*-lactones). The growing center in these polymerization systems is proposed to be analogous to those initiated by linear ester/Lewis acid complexes [1]. Justification for undertaking this research was the possibility of synthesizing α,ω-asymmetric telechelics, i.e., telechelic prepolymers carrying dissimilar terminal functions.

This paper presents evidence for the living carbocationic polymerization of isobutylene by lactone/boron trichloride initiating complexes and the synthesis of α,ω-asymmetric telechelic polyisobutylenes. The polymerization of 4-methylstyrene and 2,4,6-trimethylstyrene using lactone/boron trichloride initiating complexes has also been investigated.

II. EXPERIMENTAL

Materials

tert-Butanol (Malinckrodt, analytical grade), chloroform, deuterated (Aldrich, 99.8 atom% D), xanthone (Aldrich, 99%), (+, –)β-butyrolactone (Aldrich, analytical grade), 3,6-dihydro-4,6,6-trimethyl-2*H*-pyran-2-one (Aldrich (98%), 1,6-dioxaspiro[4.4]nonane-2,7-dione (Aldrich, 98%), and γ-phenyl-γ-butyrolactone (Aldrich, 97%) were used as received. Carbon tertrachloride (Aldrich, reagent grade), ethyl acetate,

methanol, and pyridine (Fisher Scientific, reagent grade) were refluxed over calcium hydride overnight and distilled under N_2. Methyl chloride and isobutylene (Linde Division, Union Carbide, commercial grade) were purified by passing the gases through a glass drying column (1 m long, 0.1 m in diameter) packed with anhydrous barium oxide and molecular sieves and condensed directly inside the dry box in a flask immersed in a low temperature bath ($\leq -30°C$). BCl_3 (Linde Division, Union Carbide) was condensed inside the dry box into a cooled culture tube. Methylene chloride (CH_2Cl_2) (Fisher Scientific, reagent grade) was dried over Molecular Sieves, then refluxed under N_2 over calcium hydride overnight and distilled. Subsequently, $\sim 1\%$ by volume Et_3Al was added and the mixture was refluxed overnight, then distilled freshly before experiment. 4-Methylstyrene (Mobil Chemical Co.) was extracted with 5% aqueous sodium hydroxide solution to remove the inhibitor, washed with distilled water until neutral, and dried over anhydrous calcium chloride, then distilled from calcium hydride under reduced pressure. 2,4,6-Trimethylstyrene (Aldrich, 95.2%) was purified by distillation from calcium hydride under reduced pressure.

γ-Phenyl-γ-valerolactone was synthesized by the method of Heiba et al. from acetic acid and α-methylstyrene under mild oxidative conditions using manganic acetate [9] and was purified by vacuum distillation (110°C/0.5 torr). The purity of the product (a clear colorless liquid solidifying at room temperature) was checked by FTIR [9] and NMR [10, 11] spectroscopy.

γ-Tolyl-γ-valerolactone was synthesized by the method of Heiba et al. [9] from acetic acid and α,p-dimethylstyrene. The α,p-dimethylstyrene was prepared according to D'Onofrio [12]. The crude lactone was distilled under reduced pressure (114–115°C/0.9 torr) to yield a clear, colorless oily liquid that solidified on standing. The purity of the product was checked by FTIR [9] and NMR [10,11] spectroscopy.

2,4,4-Trimethyl-2-pentyl acetate was synthesized according to Faust and Kennedy [1].

2,4,4-Trimethyl-2-pentyl 4-phenylbutyrate was synthesized by the reaction of 2,4,4-trimethyl-2-pentanol (*tert*-TMPOH) and 4-phenylbutyryl chloride by using the esterification procedure described by Faust and Kennedy [4]. The crude, 2,4,4-trimethyl-2-pentyl 4-phenylbutyrate ester was purified by vacuum distillation (110–112°C/0.25 torr). The starting materials were prepared as follows: *tert*-TMPOH was prepared according to Brown and Geoghagan [13] from 2,4,4-trimethyl-1-pentene, and the 4-phenylbutyryl chloride was obtained by the reaction of 4-phenylbutyric

acid and phosphorous trichloride in CH_2Cl_2 solution (20 h reflux) under a blanket of N_2 and was purified by vacuum distillation (71°C/0.25 torr).

Procedures

Polymerization experiments were performed in a stainless steel enclosure (dry box) under a N_2 atmosphere in culture tubes ($\sim$50 mL maximum volume) with Teflon-lined screw-caps immersed in a constant temperature bath. Thorough mixing of the polymerization systems was achieved by a Vortex mixer (turbomixing) during the addition of the Lewis acid, and the tube was replaced immediately in the constant temperature bath.

When polymerization temperatures were higher than the boiling point of solvent or monomer or both, polymerizations were carried out in pressure tubes (thick-wall Pyrex glass tubes of $\sim$50 mL volume) equipped with a crimp cap with neoprene rubber liner previously extracted with CH_2Cl_2 and hexane. Polymerization charges were filled in the tubes at a temperature below the boiling point of the solvent and monomer, the tubes were closed with a crown cap crimper, and the bath temperature was raised to the required level. The Lewis acid was added to the charges by piercing the neoprene liner by a syringe while vortex mixing, and the tubes were replaced in the constant temperature bath. After the desired polymerization times, the quenching agent was added to the polymerization charge by a syringe. The pressure tubes were cooled below the boiling point of volatiles before opening the tubes for workup.
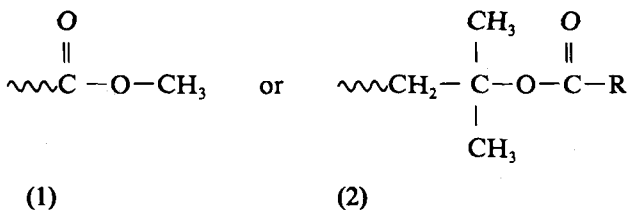
Model Experiments

In model experiments the lactone/Lewis acid complex was prepared at a desired temperature. Complex formation was allowed to proceed for a predetermined time (typically 10–60 min) and then additional reagents (e.g., stoichiometric amount of monomer) were added, or the complex was quenched by various reagents. Experiments were carried out by using several solvents; deuterated chloroform, carbon tetrachloride, or methylene chloride allowed sampling the solution directly for NMR measurements. With other solvents or solvent mixtures (e.g., methyl chloride, methyl chloride/hexane mixtures), first the solvents were evaporated under a hood and then the sample was dissolved in deuterated chloroform or carbon tetrachloride for NMR or FTIR measurements. When necessary (e.g., to remove organic acid decomposition products), the products

were first purified by dissolving in ether and extracting the saturated aqueous sodium bicarbonate solution and washing with distilled water.

NMR spectroscopy was performed by using a Varian T60 MHz NMR spectrophotometer and carbon tetrachloride or deuterated chloroform solutions, and tetramethylsilane (TMS) as internal standard.

FTIR spectroscopy was performed by using a Beckman FTIR instrument and carbon tetrachloride solutions or NaCl disks.

$$\begin{array}{ccc} \overset{\displaystyle O}{\underset{\displaystyle \|}{}} & & \overset{\displaystyle CH_3}{\underset{\displaystyle |}{}} \quad \overset{\displaystyle O}{\underset{\displaystyle \|}{}} \\ \text{\small\raise1pt\hbox{$\wedge\!\wedge\!\wedge$}} C - O - CH_3 & \text{or} & \text{\small\raise1pt\hbox{$\wedge\!\wedge\!\wedge$}} CH_2 - \underset{\displaystyle \underset{\displaystyle CH_3}{|}}{C} - O - C - R \\[2em] (1) & & (2) \end{array}$$

The (1) and (2) end functions were quantitated by the stretching frequencies of the esters at 1740 and 1727 cm^{-1}. Figure 1 shows the calibration curves obtained with methyl butyrate and 2,4,4-trimethyl-2-pentyl 4-phenylbutyrate for the quantification of
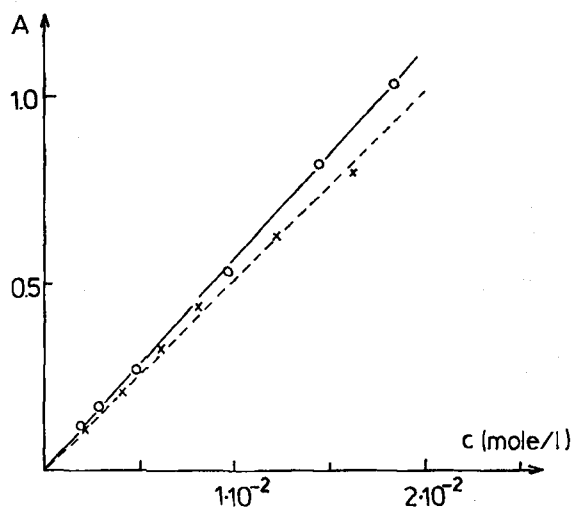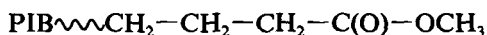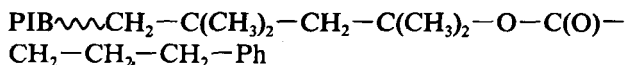

FIG. 1. Calibration curves for ester end-group determination. ($\times$) methyl butyrate ($\nu = 1740$ cm^{-1}); ($\bigcirc$) 2,4,4-trimethyl-2-pentyl 4-phenylbutyrate ($\nu = 1727$ cm^{-1}).

$$PIB\text{\wedge\wedge\wedge}CH_2-CH_2-CH_2-C(O)-OCH_3$$

and

$$PIB\text{\wedge\wedge\wedge}CH_2-C(CH_3)_2-CH_2-C(CH_3)_2-O-C(O)-$$
$$CH_2-CH_2-CH_2-Ph$$

respectively.

The overall error of this end group analysis is estimated to be $\sim$15% due to a $\pm$10% error in molecular weight determination by GPC and $\pm$5% in quantitative IR spectroscopy.

Molecular weights were determined by a Waters high pressure GPC instrument (Model 6000A Pump) equipped with a series of ultra-Styragel columns (100, 500, 10^3, 10^4, 10^5A), a differential refractometer (Model 2401), and a UV absorbance detector (Model 440) by using tetrahydrofuran (THF) solvent and a 1 mL/min flow rate. The calibration curves for polyisobutylenes (PIB) and for polystyrenes (PSt) were prepared by using a series of well-fractionated polymer standards. Molecular weight measurements of poly(α-methylstyrene), poly(2,4,6-trimethylstyrene), and poly(4-methylstyrene) were based on polystyrene calibration. The error of molecular weight determination is estimated to be $\pm$10%.

III. RESULTS AND DISCUSSION

A. Polymerization of Isobutylene

1. Scouting Experiments

Preliminary polymerization experiments by the use of a variety of lactone/BCl₃ complexes have proven that, with the exception of β-butyrolactone, these complexes are true initiators. In the absence of BCl₃, lactones did not initiate polymerization. In polymerization experiments performed in the absence of lactones (control experiments), BCl₃ produced low conversions (8–10%) and high molecular weight PIB, most likely due to initiation by protic impurities [1]. The concentration of protic impurities as calculated from the results of control experiments was found to be 2–8 $\times$ 10^{-4} M.

In the presence of ester/BCl₃ complexes, initiation by protic impurities was shown to be negligible [1, 4]. This observation was confirmed by the following set of experiments, designed to simulate polymerization condi-

tions using ester/BCl₃ initiating complexes. Thus, control experiments were performed by adding ethyl acetate or triphenylmethyl acetate to investigate initiation by protic impurities in the presence of ester/BCl₃ complexes which themselves do not initiate isobutylene polymerization. In the presence of the triphenylmethyl acetate/BCl₃ complex, polymer was absent after 2 h at $-30°C$ (3×10^{-3} M triphenylmethyl acetate and 0.25 M BCl₃ were added to a 1 M solution of isobutylene in CH₂Cl₂). In the presence of the ethyl acetate/BCl₃ complex, the conversion was only ~2% after 1 h at $-30°C$ (5.6×10^{-3} M ethyl acetate and 5×10^{-2} M BCl₃ were added to a 1 M solution of isobutylene in CH₃Cl). In light of these experiments and considerations presented earlier [1, 4], it can be concluded that initiation by adventitious impurities is absent under the conditions employed.

Lactone/BCl₃ initiating complexes produced intermediate to high conversions, and the molecular weights were a function of the initial lactone concentration. Data are listed in Table 1. Initiation efficiencies were calculated from conversion and molecular weight data:

$$I_{\text{eff}} = W_p \times 10^3 / \bar{M}_n [I]_0 V$$

where W_p is the weight of polymer obtained, $\bar{M}_n$ is the number-average molecular weight, $[I]_0$ is the initial lactone concentration, and V is the volume.
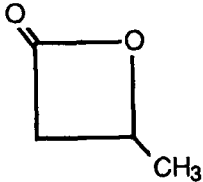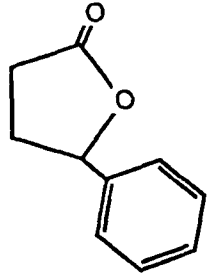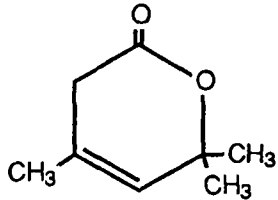
Based on the results of these preliminary experiments, the γ-tolyl-γ-valerolactone/BCl₃ complex proved to be the most efficient initiating system among the lactone/BCl₃ complexes. It produced relatively high initiation efficiencies over a wide lactone concentration range, and therefore this lactone was selected for further studies.

2. Kinetic Studies

In typical polymerization experiments the concentration of the γ-tolyl-γ-valerolactone was ∿$3.6 \times 10^{-3}M$, which produced close to 100% initiation efficiencies during the early stages of polymerization. This initiator concentration was sufficiently high to yield low molecular weight polymers and was still significantly higher than the concentration of adventitious protic impurities ($2-8 \times 10^{-4}M$).
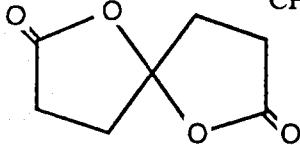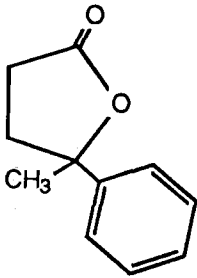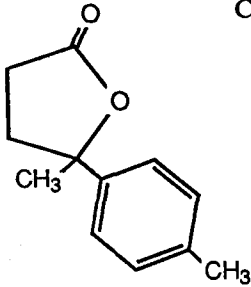
Living polymerization was demonstrated by the use of the γ-tolyl-γ-valerolactone/BCl₃ complex and isobutylene in CH₃Cl solution at -40, -30, and $-20°C$. Aliquots were quenched at different conversions and the number of moles of polymers [P] were determined as a function of the

TABLE 1. Orienting Experiments Using Lactone/BCl_3
Complex Initiators[a]

	Solvent	$[I]_0$, mol/L	Conversion, %	I_{eff}, %
β-Butyrolactone	CH_2Cl_2	1.12×10^{-3}	2–5	—
		5.6×10^{-2}		

γ-Phenyl-γ-butyrolactone

	Solvent	$[I]_0$, mol/L	Conversion, %	I_{eff}, %
	CH_3Cl	1.12×10^{-3}	22.1	16.2
		5.6×10^{-3}	28.1	14.8
		5.6×10^{-3}	51.7	33.4
		2.8×10^{-2}	16	4.7
		2.8×10^{-2}	54.1	11.9
		5.6×10^{-2}	25.9	5.0
		5.6×10^{-2}	69.8	9.8
		1.12×10^{-1}	100	9.8
	CH_2Cl_2	2.55×10^{-3}	88.5	24.4
		5.10×10^{-3}	78.2	12.4
		2.55×10^{-2}	72.2	13.2
		5.10×10^{-2}	82.2	14.6
		1.02×10^{-1}	72.9	5.8

3,6-Dihydro-4,6,6-trimethyl-2H-piran-2-one

	Solvent	$[I]_0$, mol/L	Conversion, %	I_{eff}, %
	CH_3Cl	9.846×10^{-4}	24.1	29.7
		9.800×10^{-4}	65.7	70.0
		4.923×10^{-3}	40.9	24.3
		5.003×10^{-3}	28.1	24.2
		5.003×10^{-3}	63.4	40.3
		4.900×10^{-3}	79.3	30.0
		2.462×10^{-2}	32.7	13.4
		2.517×10^{-2}	60.2	16.3
		2.450×10^{-2}	64.5	14.1
		4.923×10^{-2}	73.2	14.0
		4.900×10^{-2}	64.5	14.1

(continued)

TABLE 1. (continued)

	Solvent	$[I]_0$, mol/L	Conversion, %	I_{eff}, %
1,6-Dioxaspiro[4.4]nonane-2,7-dione				
	CH$_3$Cl	9.690×10^{-4}	25.0	53.2
		1.024×10^{-3}	7.9	31.1
		4.657×10^{-3}	86.8	50.0
		4.845×10^{-3}	71.3	38.7
		5.119×10^{-3}	29.6	36.1
		2.423×10^{-2}	100	13.6
		2.560×10^{-2}	91.5	13.1
		4.845×10^{-2}	89	8.3
		5.119×10^{-2}	73.1	71.5
γ-Phenyl-γ-valerolactone				
	CH$_3$Cl	2.776×10^{-3}	10.3	29.4
		2.776×10^{-3}	12.5	32.6
		5.551×10^{-3}	9.02	22.7
		5.551×10^{-3}	16.9	32.8
		2.776×10^{-2}	20.6	13.4
		2.776×10^{-2}	53.4	25.5
		5.551×10^{-2}	88.6	25.2
γ-Tolyl-γ-valerolactone				
	CH$_3$Cl	1.018×10^{-3} [b]	23.3	53.9
		1.018×10^{-3}	38.8	87.1
		2.036×10^{-3}	19.1	73.8
		2.036×10^{-3}	28.4	90.6
		3.600×10^{-3}	13	82.0
		3.600×10^{-3}	31.3	78.0
		3.600×10^{-3}	56.3	107
		7.200×10^{-3}	37.3	49.2
		7.200×10^{-3}	56.3	77.5
		1.800×10^{-2}	100	50.3
		3.600×10^{-2}	100	38.2

[a][IB] = 0.934 M, −30°C.
[b][IB] = 0.5 M.

amount (weight) of polymer formed. The molecular weight distribution of polymers was relatively broad, ranging between $\bar{M}_w/\bar{M}_n = 1.3$–$4.3$, but continuously decreasing with increasing monomer conversion. $\bar{M}_n$ and [P] versus weight of polymer (W_p) plots were constructed based on conversion and molecular weight data as illustrated in Figs. 2 and 3. The solid lines show the theoretical values assuming instantaneous initiation. At -20 and $-30°C$ the experimental data show good agreement with the theoretical values, indicating living polymerizations. At low conversions the slightly lower number of polymer chains and the correspondingly higher than theoretical molecular weights are due to incomplete initiation.
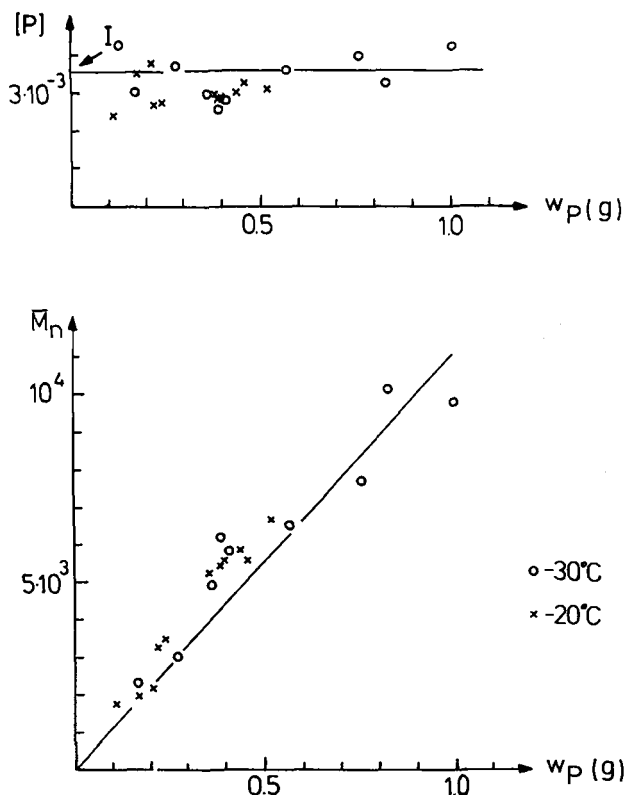

FIG. 2. Demonstration of living polymerization of isobutylene in CH_3Cl solution at -20 and $-30°C$. [IB] $= 0.934\,M$, [I]$_0 = 3.6 \times 10^{-3}\,M$ [BCl$_3$] $= 3.42 \times 10^{-2}\,M$.
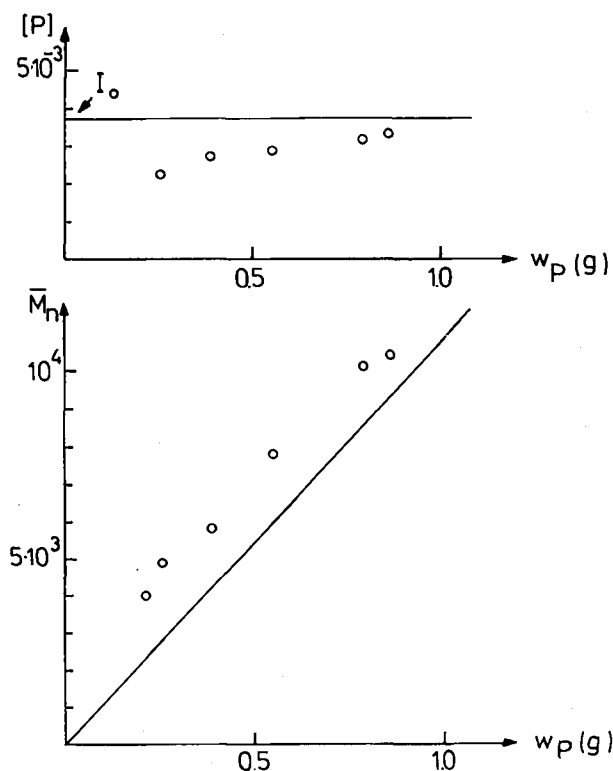
FIG. 3. Demonstration of living polymerization of isobutylene in CH_3Cl solution at $-40°C$. [IB] $= 0.934\,M$, $[I]_0 = 3.6 \times 10^{-3}\,M$, $[BCl_3] = 3.42 \times 10^{-2}\,M$.

At $-40°C$, lower than 100% I_{eff} were obtained even at moderate to high monomer conversions (cf. Fig. 3). The number of moles of polymers increased continuously throughout the polymerization and approached the number of moles of initiator added to the system at higher monomer conversion.

According to this evidence, the polymerization is living at temperatures at least up to $-20°C$. At $-10°C$ in CH_3Cl, polymerization was found to be nonliving due to chain transfer to monomer.

The rate of polymerization has been determined at $-30°C$ gravimetrically. The rate of propagation has been found to be consistent with

$$-d[M]/dt = k_p[M_n^+][M]$$

where [M] is the concentration of the monomer, $[M_n^+]$ is the concentration of the growing centers, k_p is the rate constant of the propagation, and t is time. Thus k_p was determined based on the equation $\ln([M]_0/[M]) = k_p[M_n^+]t$ and assuming $M_n^+ = I_0$. The slope of the $\ln([M]_0/[M])$ versus t plot, shown in Fig. 4, yields $k_p = 9.44 \times 10^{-3}$ mol/L $\cdot$ s, calculated by linear regression, with correlation coefficient $r = 0.991$. These result are in good agreement with kinetic data obtained with various linear ester/ BCl_3 complexes in CH_3Cl solution at $-30°C$ [7], where the propagation rate was also shown to be first order in monomer. Values of apparent propagation rate constants ranged between 1.1×10^{-3} and ~ 10–20 mol/ L$\cdot$s, depending on the structure of the ester. The k_p value determined for the γ-tolyl-γ-valerolactone/BCl_3 initiating system is comparable to those of 2,4,4-trimethyl-2-pentyl isobutyrate/BCl_3 $(k_p = 2.1 \times 10^{-3}$ mol/L$\cdot$s) and 2,4,4-trimethyl-2-pentyl phenylacetate/BCl_3 $(k_p = 0.74$ mol/ L$\cdot$s)[7].

It is of interest to emphasize that k_p remains constant during the

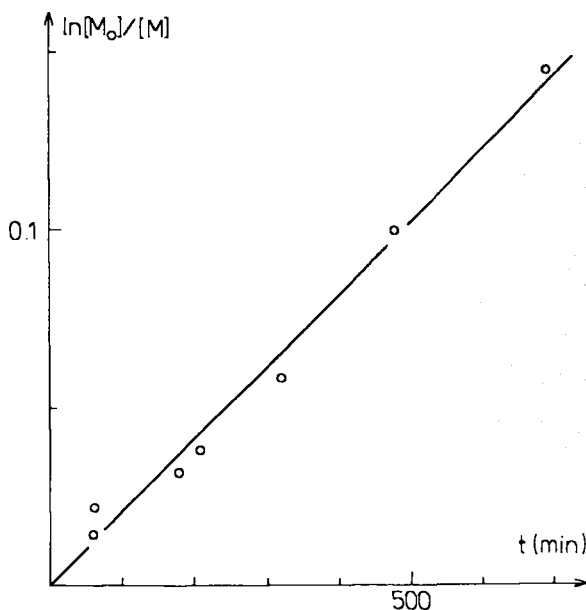FIG. 4. Determination of apparent k_p in isobutylene polymerization initiated by the γ-tolyl-γ-valerolactone/BCl_3 complex. $[IB] = 0.937 M$, $[I]_0 = 3.61 \times 10^{-3} M$, $[BCl_3] = 3.42 \times 10^{-2} M$; in CH_3Cl at $-30°C$. $k_p = 9.44 \times 10^{-3}$ mol$\cdot$ L$^{-1}\cdot$s^{-1}.

experiments (i.e., 2–13 h), indicating that the nature of the growing centers did not change during the polymerizations.

In conclusion, kinetic studies of isobutylene polymerization initiated by the γ-tolyl-γ-valerolactone/BCl₃ complex has shown living polymerization up to −20°C. It has been found that the polymerization follows the rate equation $-d[M]/dt = k_p[M_n^*][M]$, and that propagation is first order in monomer.

B. Polymerization of Styrene Derivatives by γ-Tolyl-γ-valerolactone/BCl₃ Complex

Complexes of linear esters with BCl₃ were found to be efficient initiators for the living polymerization of styrene [4], 4-methylstyrene [5], and 2,4,6-trimethylstyrene [6]. Thus, investigations have now been carried out with 4-methylstyrene, 2,4,6-trimethylstyrene, and the γ-tolyl-γ-valerolactone/BCl₃ imitating complex.

The polymerization of 4-methylstyrene initiated by the γ-tolyl-γ-valerolactone/BCl₃ complex at −30°C exhibited slow initiation relative to the rate of propagation and chain transfer to monomer. Propagation rates were too high for intermittent sampling, therefore polymerizations were carried out by using the incremental monomer addition technique [1]. Experimental details and data are compiled in Table 2. According to the [P]/[I]₀ ratio (number of polymer chains per initiator molecule), the first monomer addition yields [P]/[I]₀ = 0.43, showing that initiation is slow relative to the rate of propagation. The [P]/[I]₀ ratio exceeds unity

TABLE 2. Polymerization of 4-Methylstyrene Initated by γ-Tolyl-γ-valerolactone/BCl₃[a]

W_p	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	[P]/[I]₀
0.473	24,600	69,400	2.82	0.43
0.916	22,400	57,000	2.54	0.91
1.367	20,900	60,000	2.87	1.46
1.817	21,600	55,700	2.58	1.88
2.313	27,700	67,000	2.42	1.86

[a]Incremental monomer addition method, 0.5 mL monomer increments introduced at 10 min time intervals, [I]₀ = 3.583 × 10⁻³ M, [BCl₃] = 0.239 M CH₃Cl, −30°C.

after the third monomer addition, which indicates chain transfer to monomer.

Living carbocationic polymerization of 2,4,6-trimethylstyrene was shown to occur by using linear tertiary ester/BCl$_3$ initiating systems [6]. In line with these findings it was anticipated that the γ-tolyl-γ-valerolactone/BCl$_3$ complex would give similar results. Contrary to these expectations, the results showed continuous deactivation of the growing centers through chain transfer to monomer. Figure 5 shows the results. Similar results have been obtained by reducing the time between the addition of monomer increments from 20 to 10 min or decreasing the polymerization temperature to $-40°$C.

C. Model Experiments

Efforts have been made to gain insight into the structure of the initiating species (lactone/Lewis acid complexes) by model experiments. Thus lactone/BCl$_3$ complexes have been prepared under polymerization conditions but in the absence of monomer, and they were subsequently decomposed by the addition of different nucleophiles or by heating (heat quenching).

The original lactone was consistently recovered upon the addition of pyridine to various lactone/BCl$_3$ systems:
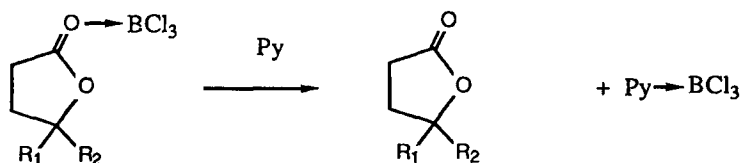
where Py is pyridine, R$_1$ is H or CH$_3$ and R$_2$ is phenyl or tolyl. Figure 6 shows the ^{1}H-NMR spectrum of the product obtained in a typical model experiment with γ-tolyl-γ-valerolactone/BCl$_3$. Quenching the complex with saturated aqueous NaHCO$_3$ at room temperature or by heating to room temperature also gave the original lactone. According to these model experiments, the mixing of *tert*-lactones with BCl$_3$ does not induce chemical transformations, which in turn suggests that the initiating species are, in fact, lactone/Lewis acid complexes. Quenching studies involving lactone/BCl$_3$ complexes with an alcohol have been described elsewhere in more detail [14].

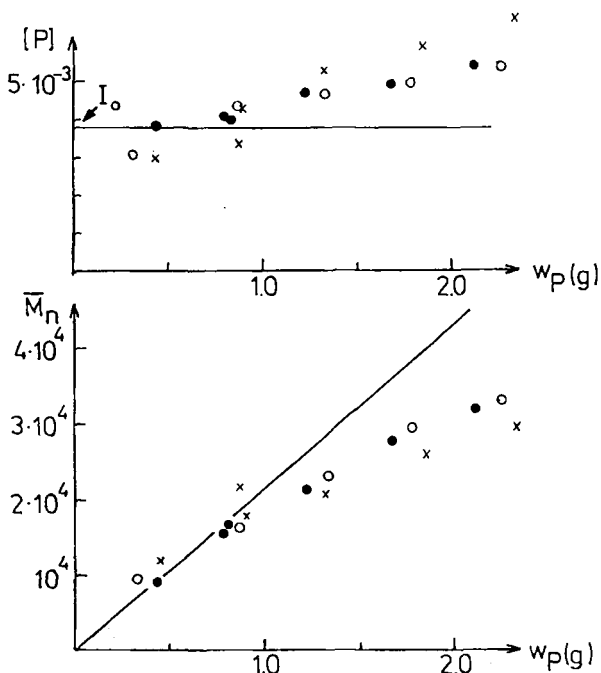Further model experiments have been designed to provide information

FIG. 5. Polymerization of 2,4,6-trimethylstyrene by IMA method by using γ-tolyl-γ-valerolactone/BCl$_3$ initiating complex in CH$_3$Cl. [I] = 3.61 $\times$ 10^{-3} M, [BCl$_3$] = 3.42 $\times$ 10^{-2} M; IMA method using 0.5 mL monomer increments. ($\bigcirc$) $-30°$C, 10 min between monomer additions; ($\bullet$) $-30°$C, 20 min between monomer additions; ($\times$) $-40°$C, 10 min between monomer additions.

in regard to functionalization of polymers produced by lactone/Lewis acid complexes. The results of model experiments using lactone/Lewis acid complexes give information only in regard to the initiation step and the identity of the initiating species. The 2,4,4-trimethyl-2-pentyl 4-phenylbutyrate/BCl$_3$ complex is considered a suitable model of the living polymer complex since it mimics the PIB chain end and the initiator residue in the polymer, while the stabilizing effect of the five-membered lactone structure is absent.

Model studies with this complex showed that the addition of nucleophiles as quenching agents (i.e., pyridine, methanol, 1/1 mixture of pyridine and methanol, *tert*-butanol, ethylene glycol, diethylaminoethanol, ethyl acetate, acetonitrile, xanthone) quantitatively produces a
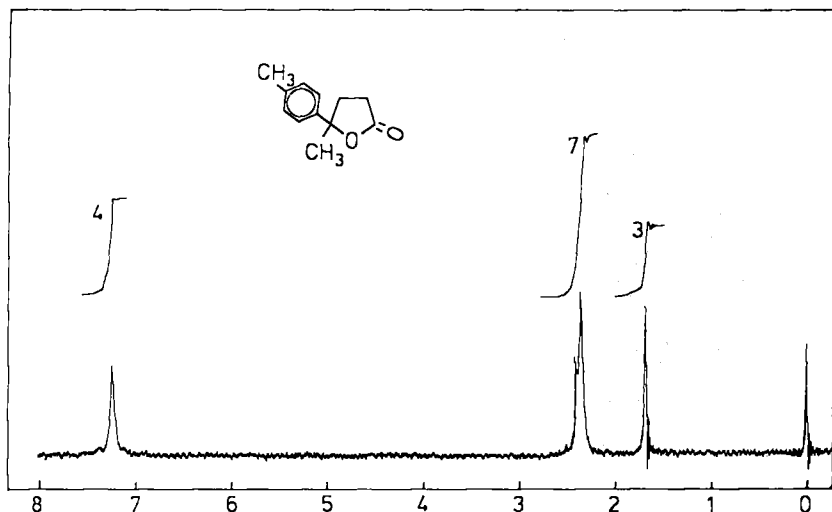
FIG. 6. ¹H-NMR spectrum of the product obtained in the model experiment with the γ-tolyl-γ-valerolactone/BCl₃ complex, pryidine quenching. 3C$\underline{H}_3$, 1.65 ppm; 3C$\underline{H}_3$Ph, 2.45 ppm; 4C$\underline{H}_2$, 2.3-2.5 ppm; 4Ph, 7.25 ppm. Experimental conditions: [γ-tolyl-γ-valerolatone], 1.18×10^{-2} M, [BCl₃], 0.239 M; quenched with [Py], 0.952 M after 20 h in CH₃Cl at $-10°C$.

tertiary alkyl chloride, 2-chloro-2,4,4-trimethyl-pentane (TMPCl). The ¹H-NMR spectrum of the decomposition products shows a corresponding shift of the alkyl resonances in the TMP group (2CH₂ : $1.85 \rightarrow 1.95$, and 6CH₃ : $1.55 \rightarrow 1.7$ ppm). Alcohols as quenching agents also lead to tertiary chlorine end groups. The acid residue is simultaneously esterified with primary alcohols, which is indicated by the appearance of the corresponding resonances in the ¹H-NMR spectrum of the decomposition products (e.g., 3CH₃O : at 3.6 ppm with methanol as quenching agent). Upon quenching the complex with tertiary alcohols, the acid residue is converted to the corresponding acid (tertiary esters are not formed in acidic media).

Based on these model experiments, it is concluded that quenching the living polymerization of isobutylene initiated by lactone/BCl₃ complexes yields tertiary chlorine end groups, and linear, α,ω-asymmetric telechelic PIBs are produced. Depending on the nature of the quenching agent, the α-terminus is an acid or ester, and the ω-terminus is a tertiary chlorine.

D. Preparation of α,ω-Asymmetric Telechelic Polyisobutylenes

Under living polymerization conditions, lactone/BCl$_3$ initiating complexes provide an excellent method for the introduction of a versatile acid or ester group, since the acid group is attached at the α-terminus of the linear polymer as part of the initiator residue, due to the cyclic structure of the lactone. As shown by model studies, quenching by alcohols, pyridine, etc. produces a tertiary chlorine at the ω-terminus. Therefore, the living polymerization of isobutylene initiated by lactone/BCl$_3$ complexes produces α,ω-asymmetric telechelic PIBs.

If the quenching agent is methanol, a methyl ester will arise at the α-terminus. Figure 7 shows the NMR spectrum of $\bar{M}_n = 4700$ polymer purified by preparative GPC. The resonances of the 4-phenyl and 3-methyl protons, respectively, are distinctly detectable, and their intensity ratio is 4 : 3. Figures 8 and 9 show IR spectra of polymers of $\bar{M}_n = 4300$ and a $\bar{M}_n = 8200$. The position of the C=O stretching frequency is at 1740 cm^{-1}, corresponding to the methyl ester group, and the number-average terminal functionalities, based on the C=O calibration, are 1.1 and 1.15, respectively.
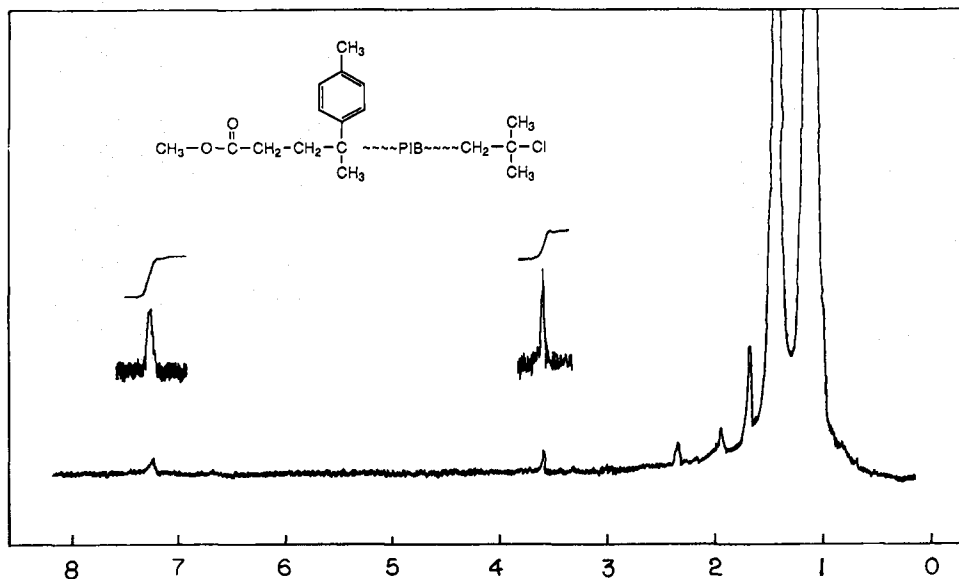
FIG. 7. ^{1}H-NMR spectrum of PIB prepared by using the γ-tolyl-γ-valerolactone/BCl$_3$ initiating complex and methanol quenching. $\bar{M}_n = 4700$. 3C$\underline{H}_3$O, 3.6 ppm; 4Ph, 7.25 ppm.
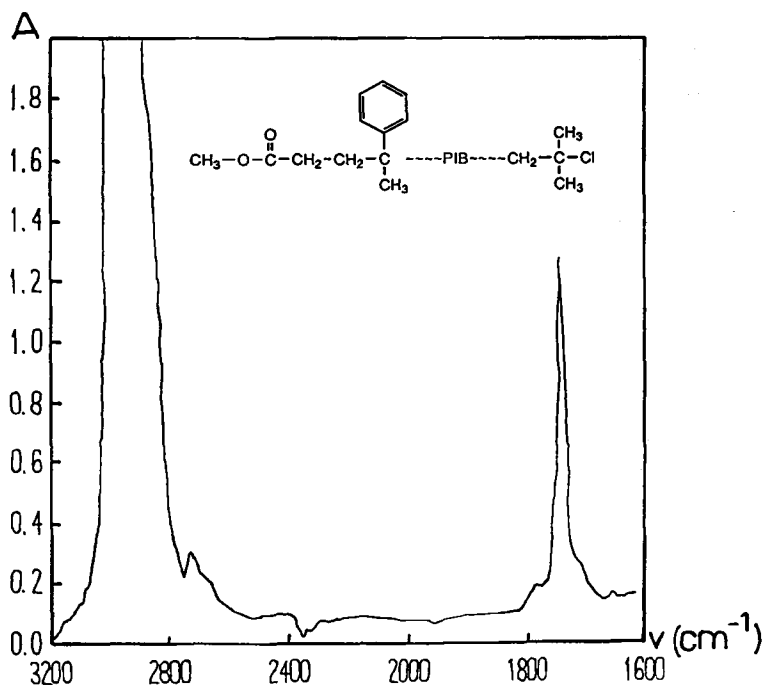
FIG. 8. IR spectrum of α,ω-asymmetric telechelic polyisobutylene prepared by using the γ-tolyl-γ-valerolactone/BCl_3 initiating complex and methanol quenching. $\overline{M}_n = 4300$.

With pyridine as quenching agent, the α,ω-asymmetric telechelic PIB carries a carboxylic acid group at the α-terminus and a tertiary chlorine at the ω-terminus. Figure 10 shows the NMR spectrum of a polymer prepared by using pyridine as a quenching agent, and Fig. 11 shows the corresponding IR spectrum. The presence of the initiator residue is shown by the phenyl resonance in the NMR spectrum and by the C=O absorption in the IR spectrum at 1711 cm^{-1}, corresponding to the carboxylic acid group.

The chlorine content has been determined by elemental analysis, on the basis of which we calculate $\overline{F}_n = 0.987$ and 1.11 for asymmetric telechelic PIB samples purified by preparative GPC ($\overline{M}_n = 4700$ and 4500). The chlorine has also been determined by using a newly developed chlorine analysis method [15], which also yielded $\overline{F}_n = 1.15$ for an
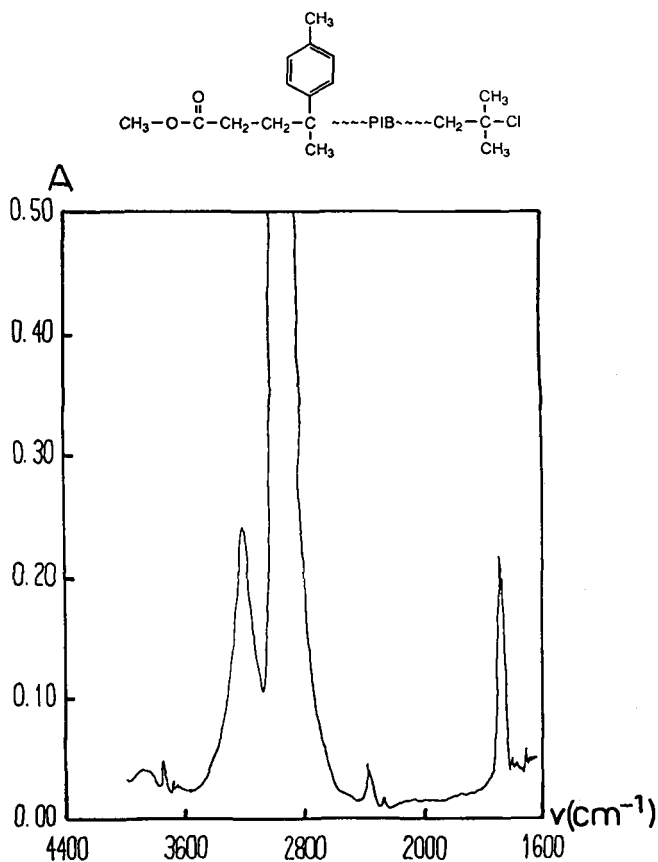
FIG. 9. IR spectrum of α,ω-asymmetric telechelic polyisobutylene prepared by using the γ-tolyl-γ-valerolactone/BCl$_3$ initiating complex and methanol quenching. $\overline{M}_n$ = 8200.

asymmetric telechelic PIB of $\overline{M}_n$ = 4700. Both values are in agreement with the theoretical value of 1.0 within the limits of experimental error.

The results of polymer end group analysis prepared by the γ-tolyl-γ-valerolactone/BCl$_3$ initiating complex indicate that this initiating system provides a simple, direct route for the synthesis of α,ω-asymmetric telechelic polyisobutylenes, specifically α-methoxycarbonyl,ω-*tert*-chloro-polyisobutylenes, and α-carboxyl,ω-*tert*-chloro-polyisobutylenes.
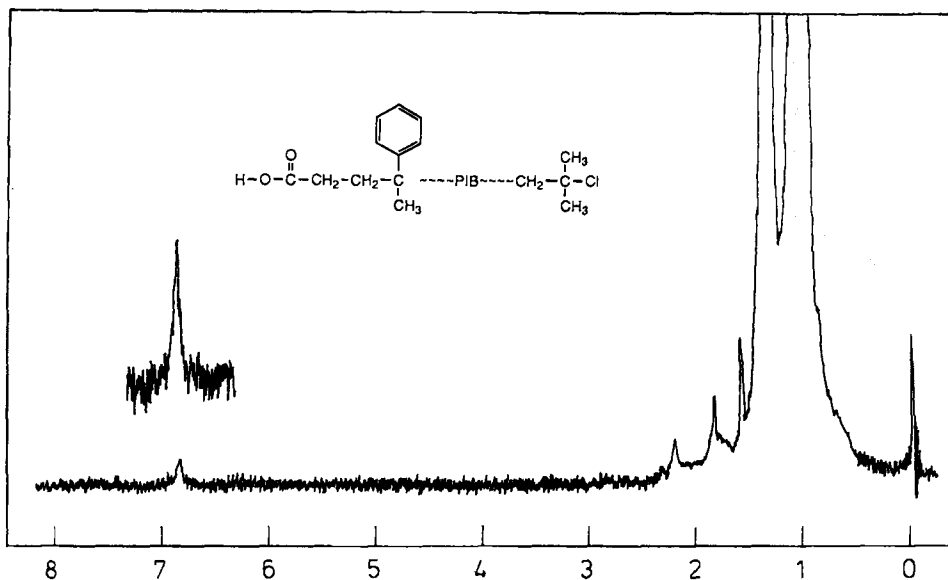
FIG. 10. ¹H-NMR spectrum of PIB prepared by using the γ-tolyl-γ-valerolactone/BCl_3 initiating complex and pyridine quenching. $\overline{M}_n = 4500$

IV. CONCLUSIONS

Lactone/BCl_3 complexes were found to be efficient initiators in the polymerization of isobutylene, 4-methylstyrene, and 2,4,6-trimethylstyrene. The polymerization of isobutylene was found to be living up to $-20°C$; the polymerization of styrene derivatives was accompanied by varying degrees of chain transfer to monomer.

Model experiments using lactone/BCl_3 complexes have shown that these complexes are the true initiating species. Kinetic studies on isobutylene polymerization showed that transformation of the living centers during polymerization did not occur.

Living polymerization of isobutylene initiated by lactone/BCl_3 complexes and quenched with pyridine or methanol yielded α,ω-asymmetric telechelic polyisobutylenes.
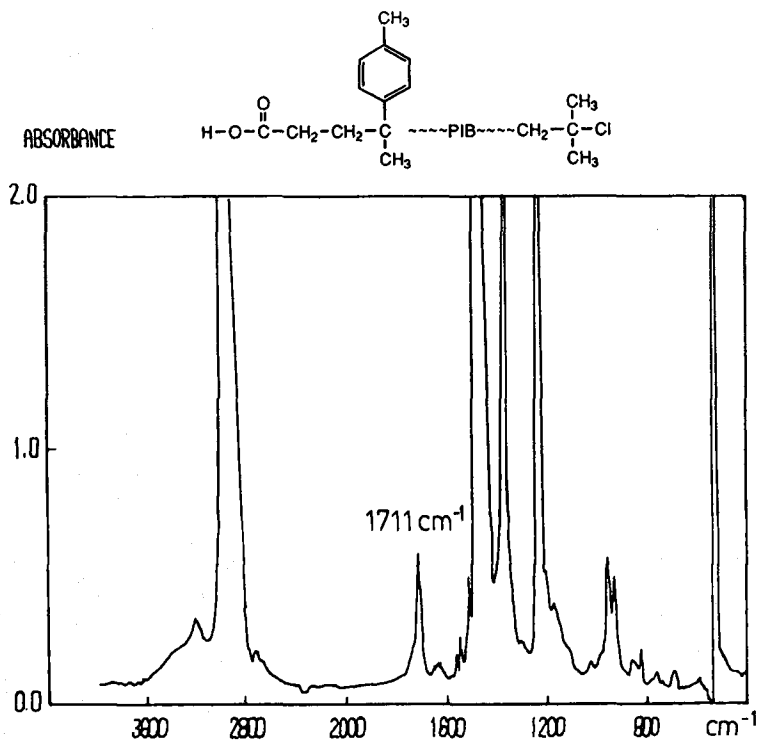
FIG. 11. IR spectrum of α,ω-asymmetric telechelic polyisobutylene prepared by using the γ-tolyl-γ-valerolactone/BCl$_3$ initiating complex and pyridine quenching. $\overline{M}_n = 4500$.

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