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A new asymmetric-telechelic polyisobutylene prepared by the *cis*-2-pinanol/BCl_3, initiating system

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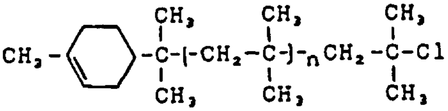
SUMMARY

A new asymmetric-telechelic polyisobutylene (PIB):

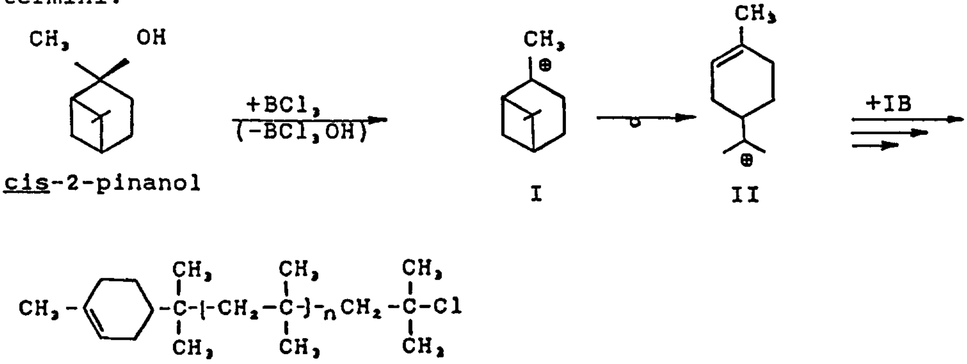


has been prepared by the polymerization of isobutylene (IB) using the novel cis-2-pinanol/BCl_3 initiating system in CH_3Cl diluent in the -30 to -50°C range. The molecular weight range explored was $\overline{M}_n$ = 1000-35,000. The polymerization most likely involves the in situ formed 2-pinanyl chloride.

INTRODUCTION

Asymmetric telechelic prepolymers are of great interest as they allow selective end-group derivatization. However, the synthesis of these materials is usually very difficult. In the course of our systematic studies directed toward the synthesis of telechelic IB prepolymers the idea arose to investigate the possibility of isobutylene polymerization by the cis-2-pinanol/BCl_3 initiating system. cis-2-Pinanol is commercially available and relatively inexpensive.

It was theorized that this strained tert-alcohol in the presence of the strong acid BCl_3 will yield the 2-pinanol cation intermediate I which will rapidly rearrange (1,2) to the aliphatic tert-cation II, the true initiating entity. Propagation and termination were anticipated to proceed by the conventional BCl_3-mediated route (3,4) leading to tert-chloride termini:



cis-2-pinanol

I

II

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*Visiting scientist, permanent address: Department of Applied Chemistry, L. Kossuth University, H-4010 Debrecen 10, Hungary tert-Alcohols, both aromatic and aliphatic, in conjunction with BCl_3 have been found to be efficient initiating systems for the polymerization of IB in CH_3Cl or CH_2Cl_2 solvents in the -10 to -50°C range (3,4). Thus initiation of IB polymerization by cis-2-pinanol in the presence of BCl_3 was anticipated.

EXPERIMENTAL

Materials

cis-2-Pinanol (Morton-Thiokol, Inc., 96% purity) was purified by sublimation. The source and purification of BCl_3, isobutylene, CH_3Cl, tetrahydrofuran, methanol, and potassium tert-butoxide have been described (5,6).

Procedures

Polymerizations were carried out in a stainless steel dry box under a dry N_2 atmosphere using large test tubes (∿75 mL) or round bottom flasks (7). Both the "incremental monomer addition" (IMA) and conventional "all monomer in" (AMI) techniques (5) have been used. Charges were quenched by prechilled methanol.

Molecular weights were determined by a Waters high pressure GPC instrument equipped with dual RI and UV detectors and five μ-Styragel columns. The calibration curve was constructed of PIB standards (8).

^1H NMR spectra were obtained by a Varian T-60 Spectrometer using CCl_4 solutions (∿30% w/v) and a TMS standard at room temperature (5), and by a Varian Gemini-200 Spectrometer using $CDCl_3$ solutions (∿15% w/v).

The quantitative dehydrochlorination method has been described (6).

RESULTS AND DISCUSSION

A. Kinetic studies

Orienting experiments have shown that cis-2-pinanol in the presence of BCl_3 initiates the polymerization of IB under a variety of conditions. Subsequently the system was systematically explored by the use of both the AMI and IMA (5) techniques.

Tables I and II show the conditions and results of isobutylene polymerizations initiated by the cis-2-pinanol/BCl_3 system in CH_3Cl at -40°C. Conversions are incomplete which is most likely due to the depletion of the initiating species (see Mechanistic Speculations). While the $\bar{M}_n$'s increase with increasing [IB], they are higher than expected from [IB]/[cis-2-pinanol] and the N's (the number of PIB moles formed) are lower than [cis-2-pinanol]. The $\bar{M}_w/\bar{M}_n$'s are ∿2.0. According to the results of IMA experiments the polymerizations are not living. Polymer was not obtained when isobutylene was introduced after 30 minutes to a premixed solution of cis-2-pinanol and BCl_3 in CH_3Cl. This result suggest that cis-2-pinanol was converted to inactive product(s). This may also be the reason for the relatively low initiator efficiencies (I_{eff} = 20-30%).

Table III and Figure 1 show conversion versus time and N versus time plots obtained with the cis-2-pinanol/BCl_3/IB/CH_3Cl/-40°C system by using the conventional AMI technique. These results indicate slow polymerization and the formation of constant $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ PIB's. The $\bar{M}_n$ and M_w/M_n (∿2.0) values

TABLE I

Isobutylene Polymerization by the *cis*-2-Pinanol/BCl_3 Initiating System

(Total volume: 25 mL; CH_3Cl; -40°C; 30 min; [*cis*-2-pinanol] = 5.6×10^{-3} mole/L; [BCl_3] = 0.252 mole/L)

[IB] mole/L	Conv. %	$\overline{M}_n$ g/mole	$\overline{M}_w/\overline{M}_n$	I_{eff}* %	N x 10^5 mole
All monomer in (AMI) conditions					
0.24	4	900	2.20	11	1.5
0.48	9	2,100	2.10	21	2.9
0.71	14	3,350	2.15	29	4.1
0.96	18	6,510	1.95	26	3.7
1.19	21	10,400	2.03	24	3.4
1.43	23	13,000	1.85	25	3.5
1.67	25	18.700	1.90	22	3.1
1.91	26	24,100	1.70	21	2.9
2.39	26	34,900	1.64	18	2.5
Incremental monomer addition (IMA);cumulative [IB]shown;30 min.					
0.96	18	6,510	1.95	26	3.7
1.91	23	9,490	2.25	46	6.5
2.88	21	9,520	2.25	63	8.9

$$\text{* Initiator efficiency (\%)} = \frac{W_p(g)}{\overline{M}_n(g/mole)I_o(mole)} \times 100$$

TABLE II

Isobutylene Polymerization by the *cis*-2-Pinanol/BCl_3 Initiating System

(Total volume: 25 mL; CH_3Cl; -40°C; 30 min; [*cis*-2-pinanol] = 14.8×10^{-3} mole/L; [BCl_3] = 0.252 mole/L)

[IB] mole/L	Conv. %	$\overline{M}_n$ g/mole	$\overline{M}_w/\overline{M}_n$	I_{eff} %	N x 10^{-5} mole
All monomer in (AMI) conditions					
0.24	18	820	2.01	20	7.5
0.48	17	1,100	1.96	28	10.4
0.48*	36	1,800	1.85	36	169.0
0.71	19	2,100	1.85	24	9.0
0.96	24	3,900	1.96	22	8.3
0.96**	7	-	bimod.	-	-
0.96***	<1	-	-	-	-
1.19	28	4,900	2.10	26	9.5
1.43	31	6,800	2.13	25	9.1
1.67	32	9,200	2.10	22	8.1
1.91	32	12,300	2.09	19	7.0
Incremental monomer addition (IMA);cumulative [IB]shown;30 min.					
0.48	17	1,100	1.96	28	10.4
0.96	20	1,870	2.86	39	14.4
1.31	23	2,000	3.21	57	21.1

* Larger scale experiment at -50°C: Total volume 500 mL; 120 min

** [*cis*-2-pinanol] = 0, average of 6 experiments

*** IB was introduced into the premixed solution of *cis*-2-pinanol and BCl_3

together with the rate profile suggest a transfer or termination dominated polymerization.

TABLE III

Time conversion and time-N (the number of PIB moles formed) data for a *cis*-2-pinanol/BCl_3/IB/CH_3Cl/-40°C experiment using AMI technique. ([*cis*-2-pinanol] = 14.8 x 10^{-3} mole/L; [BCl_3]= 0.252 mole/L; [IB] = 0.96 mole/L. Total volume: 25 mL)

Time min	Conv. %	N x 10^5 mole	$\overline{M}_n$ g/mole	$\overline{M}_w/\overline{M}_n$	I_{eff} %
8	9	3.2	3,790	1.86	9
10	11	3.7	4,000	1.93	10
15	14	4.7	4,000	2.01	13
20	18	6.4	3,800	1.89	17
30	25	8.3	4,030	2.12	23
45	31	11.1	3,750	1.97	30

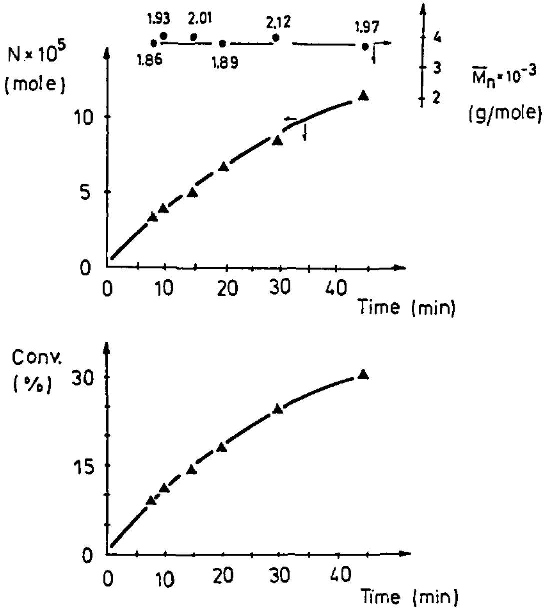


Figure 1. Time-Conversion and time-N (the number of PIB moles formed) plots for a *cis*-2-pinanol/BCl_3 /IB/ CH_3Cl/-40°C experiment using the AMI technique [*cis*-2-pinanol] = 14.8x 10^{-3} mole/L; [BCl_3] = 0.252 mole/L; [IB] = 0.96 mole/L. Total volume: 25 mL. The numbers show $\overline{M}_w/\overline{M}_n$ values

Table IV and Figure 2 show the effect of *cis*-2-pinanol concentration on $\overline{M}_n$, $\overline{M}_w/\overline{M}_n$, I_{eff}, conversions and N. The $\overline{M}_n$ decreases while the conversion and the N increase with increasing [*cis*]-2-pinanol] suggesting a transfer-dominated polymerization.

The essential absence of chain transfer to monomer is indicated by the nature of the end group of the PIB formed: According to ^1H NMR spectroscopy (see Section B) the terminal group is $-CH_3C(CH_3)_2Cl$ and not $-CH_2C(CH_3)=CH_2$ which would arise by $H^{\oplus}$ expulsion during chain transfer to monomer. Also, according to earlier studies *tert*-alcohol/BCl_3 initiated IB

TABLE IV

Isobutylene Polymerization by the cis-2-pinanol/BCl_3 Initiating System

(Total volume: 25 mL; CH_3Cl; -40°C; 30 min; [IB]=0.96 mole/L; [BCl_3] = 0.252 mole/L)

Conventional AMI conditions

[cis-2-pinanol] x 10^3 mole/L	Conv. %	$\bar{M}_n$ g/mole	$\bar{M}_w/\bar{M}_n$	I_{eff} %	N x 10^5 mole
5.6	18	6,510	1.95	26	3.7
7.9	23	5,810	1.90	27	5.3
10.5	25	4,970	1.98	26	6.8
14.8	25	4,030	2.12	23	8.3
18.4	27	3,600	2.00	22	10.1
21.0	30	3,150	2.10	24	12.8
28.0*	56	2,300	1.80	47	1,309.0

*Larger scale experiment at -30°C: Total volume 1000 mL; time 120

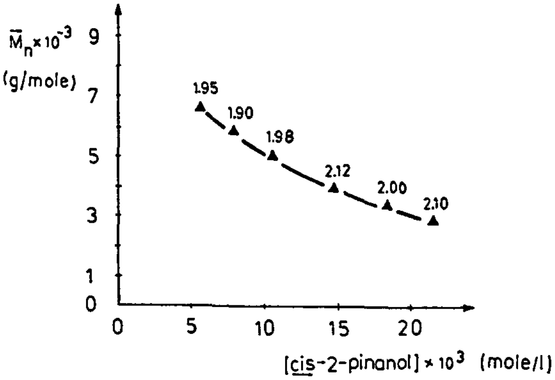
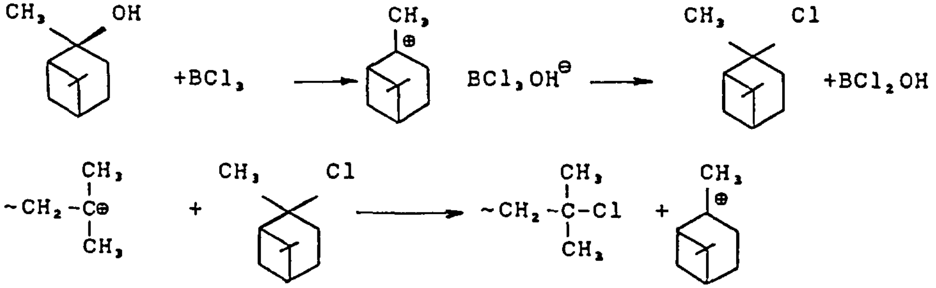
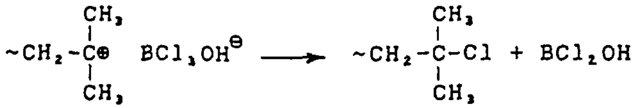


Figure 2. $\bar{M}_n$ versus [cis-2-pinanol] plot for cis-2-pinanol/BCl_3/IB/CH_3Cl/-40°C experiments. (Total volume: 25 mL; polymerization time: 30 min; [IB] = 0.96 mole/L; [BCl_3] = 0.252 mole/L; AMI technique. The numbers are $\bar{M}_w/\bar{M}_n$ values)

polymerizations are transfer-free and termination is present (3). In the system under investigation, however, chain transfer may occur by 2-pinanyl chloride formed *in situ* during initiation from 2-pinanol (see also Section C. Mechanistic Speculations):



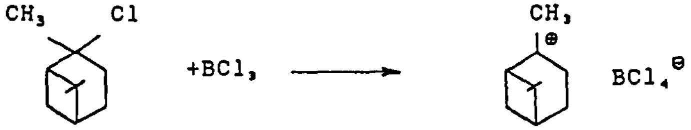
The rate of this process will depend on the 2-pinanyl chloride concentration and the rate of termination will depend on concentration of the growing ion pair:



$$\sim CH_2-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}}\ \ BCl_3OH^{\ominus} \longrightarrow \sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Cl + BCl_2OH$$

Both the [2-pinanyl chloride] and [$BCl_3OH^{\ominus}$] will increase with increasing [<u>cis</u>-2-pinanol].

Alternatively, according to the Wondraczek-Kennedy-Storey model (10) the <u>tert</u>-chlorine end group may also arise by termination by the $BCl_4^{\ominus}$ with the simultaneous regeneration of the BCl_3 coinitiator:



$$\sim CH_2-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}}\ \ BCl_4^{\ominus} \longrightarrow \sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Cl + BCl_3$$

The rate of termination by either model will increase with increasing [<u>cis</u>-2-pinanol] and will thus reduce $\overline{M}_n$'s.

B. End Group Determination

The structure of relatively low $\overline{M}_n$ (i.e., $\overline{M}_n$ = 1500-3000) samples prepared in the range from -30° to -50°C has been investigated by ^{1}H NMR spectroscopy. Figure 3 shows the spectrum of a representative PIB sample obtained in this research together with assignments. The broad resonance at 5.3 ppm is assigned to the olefinic proton in the cyclohexene ring (11) and indicates the expected head group. The absence of even weak resonances at high amplification (i.e., the absence of $>C=CH_2$ protons) at 4.58 and 4.78 ppm indicates that chain transfer to monomer is essentially absent. The rest of the observed resonances have been assigned in line with earlier detailed analyses (6,7,12).

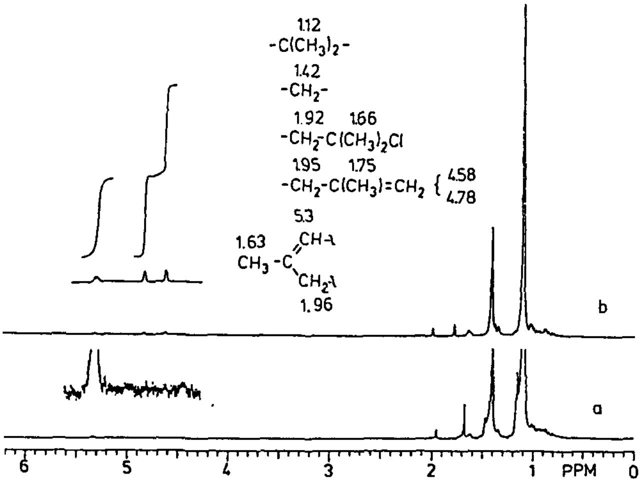


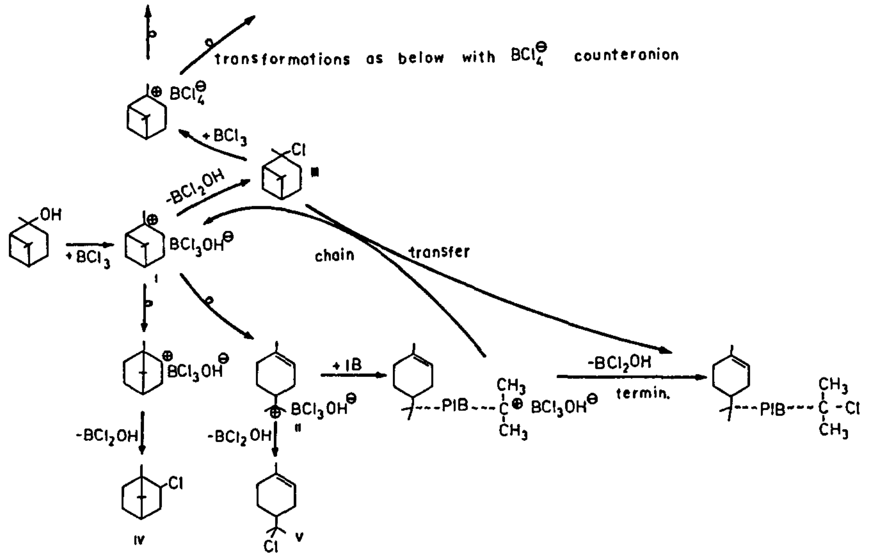
Figure 3. ^{1}H NMR spectrum of a typical PIB before (a) and after dehydrochlorination (b)($\overline{M}_n$= 2100 see Table II, entry 4). The numbers are resonances in ppm

Subsequently the PIB sample was dehydrochlorinated and analyzed (6). Figure 3b shows the spectrum. The appearance of resonances at 4.58 and 4.78 ppm indicates the presence of the external unsaturation $\geq C=CH_2$. Integration of the two types of olefinic protons gave close to theoretical values, i.e., $=CH-/=CH_2 = 0.50 \pm 0.005$. This fact quantitatively proves the asymmetric telechelic structure shown in the Introduction.

C. Mechanistic Speculations

Scheme 1 summarizes a plausible mechanism of polymerization of IB initiated by the cis-2-pinanol/BCl$_3$ system. The first step is probably the formation of an intimate ion pair I. The resulting carbenium ion I is severely hindered and is unable to initiate the polymerization of IB because of steric compression. The strained tert-cation I is rapidly rearranged to the sterically relatively unencumbered tert-aliphatic cation II the true initiating entity. Species I may also collapse to 2-pinanyl chloride III, a highly reactive unstable species (14), or rearrange and collapse to bornyl chloride IV. These reactions of the 2-pinanyl cation are based on accepted mechanisms (1,2,13,14). The collapsing of the initiating ion pair II may produce α-terpenyl chloride V which is inactive with respect to initiation in the presence of BCl$_3$ in CH$_3$Cl (15).

Propagation may occur by II or by a similar ion pair which differs only in the nature of the associated counteranion i.e., $BCl_4^{\ominus}$. The operational presence of an in situ chain transfer mechanism must also be considered: The propagating cations may readily interact with III which thus will function as an in situ chain transfer agent. Indeed this mechanism resembles an in situ minifer process with the difference that III is only a monofunctional chain transfer agent and not



Scheme 1. Proposed Mechanism of cis-2-Pinanol/BCl$_3$ Initiated Polymerization of Isobutylene

simultaneously an initiator as well (the true initiator is of course the cis -2-pinanol) (16). Unfortunately the data on hand are insufficient to assess quantitatively the extent of chain transfer to III because the rates of the competing processes yielding IV or V are unknown.

ACKNOWLEDGEMENT

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