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Synthesis and characterization of aldehyde-capped polyisobutylenes

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Summary

The synthesis and characterization of linear mono- and ditelechelic polyisobutylenes (PIBs) carrying terminal primary aldehyde groups are described. The synthesis starts by chlorine terminated PIBs (PIB-Cl and Cl-PIB-Cl) prepared by inifering or living carbocationic polymerization. These starting materials were dehydrochlorinated to vinylidene ($\sim CH_2-C(CH_3)=CH_2$) terminated PIBs and hydroformylated with CO/H_2 in the presence of a rhodium catalyst. According to NMR (500 MHz) and GPC analyses, the transformations are selective and demonstrably quantitative. The structures of these novel polymers are:

$$(CH_3)_3C\sim\sim\sim PIB\sim\sim\sim CH_2\text{-}CH(CH_3)\text{-}CH_2\text{-}CHO \quad \text{and}$$

$$OCH\text{-}CH_2\text{-}CH(CH_3)\sim\sim\sim PIB\sim\sim\sim p\text{-}C_6H_4\sim\sim\sim PIB\sim\sim\sim CH(CH_3)\text{-}CH_2\text{-}CHO$$

In view of the rich chemistry of the aldehyde group, these materials are valuable intermediates.

Introduction

Since the discovery of the inifer technique (1) and the living polymerization of isobutylene (IB) (2) by Kennedy *et al.*, the synthesis of well-defined telechelic PIBs capped with various useful functional groups remained a main objective of various research groups. A comprehensive compilation of achievements in this area has recently become available (3). The availability of olefin-capped PIBs (4) led us to attempt the preparation of aldehyde-capped PIBs by hydroformylation (oxo process) (5).

Recently Di Serio *et al.* attempted the synthesis of aldehyde-capped PIBs by the use of a cobalt catalyst (6). However, the commercial PIB employed contained a large amount of internal double bonds of the type $\sim CH=CR_2$, so that a significant portion of the starting material was unreactive to hydroformylation and the conversion of double bonds was under 80%. Furthermore, hydroformylation was accompanied by hydrogenation of the formed aldehyde to alcohol so that the final product was a mixture of polymers with different functional endgroups: olefinic, aldehydic, and alcoholic. It is also documented that cobalt carbonyl-tertiary phosphine systems catalyze olefin hydrogenation as well as hydroformylation (7) resulting in saturated hydrocarbyl endgroups.

This paper concerns the syntheses and characterization of essentially pure aldehyde-capped PIBs. The syntheses were carried out according to Scheme 1.

Experimental

Materials. Rhodium(III) chloride hydrate (Aldrich), cycloocta-1,5-diene (Aldrich, 99%), potassium acetate (Aldrich, 99%), pentaerythritol (Aldrich, 98%), triethylphosphite (Eastman, 98%), *tris*(2,4-di-*t*-butylphenyl)phosphite (Irgafos 168) (Ciba Geigy), 2,4,4-trimethylpent-1-

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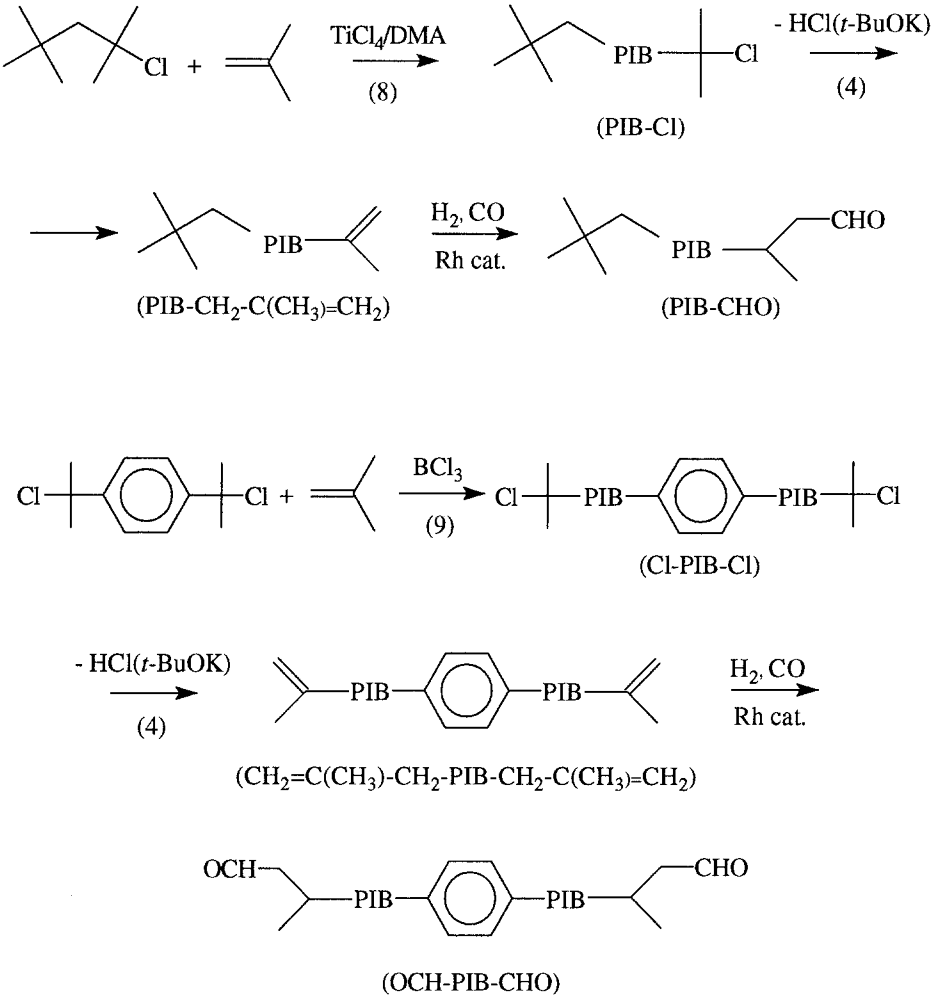
Scheme 1. Preparation of Aldehyde-Telechelic PIBs.



ene (Aldrich, 99%), *n*-butanol (Aldrich, anhydrous, 99%), acetone (EM Industries, GR), CO and H_2, 1:1 mol. mixture (Matheson Gas) were used as received. Toluene (EM Industries, GR) was dried by molecular sieves (Fisher, type 3A). The source and purity of other chemicals have been described (8,9).

Syntheses. Chlorine-terminated polymers were prepared by using 2-chloro-2,4,4-trimethylpentane/$TiCl_4$/N,N-dimethylacetamide (DMA) (8) and 1,4-*bis*(1-methyl-1-chloroethyl)benzene/BCl_3 (9) combinations, respectively. The syntheses and purification of α-*tert*-butyl-ω-(2-methylprop-2-enyl)polyisobutylene (PIB-CH_2-$C(CH_3)=CH_2$) and α,ω-di(2-methylprop-2-enyl)polyisobutylene ($CH_2=C(CH_3)$-CH_2-PIB-CH_2-$C(CH_3)=CH_2$) have been described (4). *Bis*(cycloocta-1,5-diene)-μ,μ'-diacetatodirhodium ($[Rh(1,5\text{-cod})Ac]_2$) was prepared from $RhCl_3 \cdot xH_2O$, cyclooctadiene and CH_3COOK (10). 4-Hydroxymethyl-2,6,7-trioxaphosphabicyclo[2,2,2]octane was synthesized from pentaerythritol and triethylphosphite (11).

Procedures. $\bar{M}_n$ and MWDs were determined (9) using THF solutions and a Waters high pressure GPC instrument equipped with RI and UV detectors and five μ-Styragel columns. The calibration curve was obtained with PIB standards.

^1H NMR spectra were recorded in standard 5 mm sample tubes at ambient temperature using a Bruker AM-500 spectrometer operating at 500 MHz. Sample concentrations were ~100 mg/mL in $CDCl_3$. TMS was used as an internal standard. The relaxation delay between 60^0 pulses was 20 sec. The number of acquisitions was 32.

Hydroformylation. In a typical hydroformylation experiment, the components were introduced into a magnetically stirred 300 mL stainless steel reactor (Autoclave Engineers) by a catalyst injection syringe under nitrogen. In a model experiment, the 2,4,4-trimethylpent-1-ene (7.2 mL, 45 mmoles) was added to the reactor followed by the Irgafos 168 (0.39 g, 0.6 mmoles) and $[Rh(1,5\text{-cod})Ac]_2$ (0.03 g, 0.06 mmoles) each dissolved in toluene (30 mL). In the hydroformylation of olefin-ended PIBs, the polymer (40 g) was dissolved in toluene (60 mL) and introduced into the reactor, followed by Irgafos 168 (2.34 g, 3.6 mmoles) and $[Rh(1,5\text{-cod})Ac]_2$ (0.09 g, 0.17 mmoles) both dissolved in toluene (20 mL). The latter two form *in situ* the hydroformylation catalyst. The reactor was then flushed 3 times with synthesis gas (equimolar mixture of CO and H_2) and heated to 80 ^0C while the pressure was increased to 270 psi. For the first 4-6 hours, the reactor was vented to 200 psi and then recharged to 270 psi every half hour. The purpose of flushing is to prevent the buildup of CO or H_2 in case the molar ratio of the two gases is not exactly 1:1 (we have no analytical procedure for checking Matheson's specification). Excess CO would stop the hydroformylation while excess H_2 can lead to olefin isomerization and hydrogenation. The reaction with model olefin was run for 400 minutes. The conversion and selectivity were calculated by GC analysis. In several cases the aldehyde product was isolated by distillation. The hydroformylation of polymers was typically allowed to continue overnight to ensure 100% conversion. The higher the molecular weight of the polymer, the higher catalyst concentration and longer time should be used to obtain quantitative hydroformylation. For example, in the case of monofunctional PIB of $\bar{M}_n$=10,500 g/mole, the amount of catalyst was increased 3 fold (0.27 g) and reaction was allowed to proceed 48 hours.

The extraction of rhodium from the toluene solution of the polymer was carried out similarly to (12). To the reaction mixture, a 4-hydroxymethyl-2,6,7-trioxaphosphabicyclo-[2,2,2]octane solution in *n*-butanol (0.9 g, 5.5 mmoles in 30 mL) was added and the transparent solution stored overnight. Methanol used as the solvent for the cyclic phosphite in the original procedure was replaced by *n*-butanol because methanol precipitates the polymer, prevents the recovery of rhodium, and produces discolored (yellow) polymers. *n*-Butanol does not cause polymer precipitation, even if it is present in slight excess (up to 2-fold) to toluene. The solution was extracted 5 times with water, the polymer precipitated into acetone, and dried in vacuo at ambient temperature.

Results and discussion

A) Model Experiment.

In order to test the viability of the concept and the efficacy of the catalyst towards the anticipated olefinic endgroup, a series of model reactions was run in which 2,4,4-trimethylpent-1-ene was used as a low molecular weight model of the olefin-terminated PIB. The benefit of this procedure is that the catalyst activity and selectivity can be followed by monitoring conversion of the 2,4,4-trimethylpent-1-ene to aldehydic products by both NMR and GC techniques. The procedure used was similar to that of van Leeuwen and Roobeek (13).

In every case the selectivity to 3,5,5-trimethylhexan-1-al was excellent, ranging from ~100% to a low of 98%. A byproduct, when formed, was assumed to be traces of 2,2,4,4-tetramethylpentan-1-al. ^1H NMR spectroscopy (using $CDCl_3$) exhibited an aldehydic proton resonance at 9.75 ppm for the major product and at 9.45 ppm for the trace product.

B) Hydroformylation of Telechelic Polyisobutylenes.

Scheme 1 helps to visualize the transformations that lead to aldehyde-telechelic PIBs. The first step is the synthesis of PIB-Cl or Cl-PIB-Cl (8,9). According to GPC analysis, the starting chlorine-terminated materials were $\overline{M}_n$=10,600 g/mole and $\overline{M}_w/\overline{M}_n$= 1.12 in the case of the monofunctional polymer, and $\overline{M}_n$=1,650 g/mole and $\overline{M}_w/\overline{M}_n$= 1.12 for the difunctional one. The second step is regioselective dehydrochlorination. According to ^{1}H NMR spectra, the endgroups are *exo* double bonds (δ(=CH_2) 4.64, 4.85). The small signal observed at 5.15 ppm could be assigned to the proton of ~$CH=CR_2$ (14). The internal double bond content was estimated to be ~5% of the total amount of double bonds in both cases.

The third step is hydroformylation which gives the desired aldehyde-terminated products. Figure 1 shows a ^{1}H NMR spectrum of a representative hydroformylated polymer, specifically, α,ω-dioxopolyisobutylene (OCH-PIB-CHO). The signal of the aromatic initiator fragment is at 7.24 ppm (4,15) and it overlaps with the signal due to $CHCl_3$ in the $CDCl_3$ NMR solvent. The aldehyde proton gives a triplet centered at 9.74 ppm ($^3J_{H,H}$2 Hz) which is expected from the structure -CH_2-CHO. Additional aldehyde signals, as well as the signals of vinylidene protons (=CH_2) of the starting material (4.64 and 4.85) ppm, are absent in the spectrum. Evidently, the process is highly selective and virtually quantitative, and yields the primary aldehyde terminus with functionality very close to 2.0 (or 1.0 in the case of monofunctional polymer), as shown by Scheme 1.

These conclusions are confirmed by the good agreement between the experimental molecular weight ($\overline{M}_n$=2,500 g/mole) determined by GPC, and that calculated ($\overline{M}_n$=2,800 g/mole) from the ratio between the integral intensity of the aldehyde proton signal and of the aliphatic protons (0.8-2.5 ppm) assuming $\overline{F}_n$=2.0 ($\overline{F}_n$- number average terminal functionality). The increased molecular weight of the polymer relative to that of the starting material ($\overline{M}_n$= 1,650 g/mole) is most likely due to the loss of a low molecular weight portion during precipitations.

The set of resonances in the 2.1-2.5 ppm range is assigned to the CH_2 protons in the α position, and CH protons in the β position, relative to the aldehyde group: PIB-CH(CH_3)-CH_2-CHO (upon comparison with isovaleraldehyde (16)). The pattern of these signals is due not only to spin-spin interaction, but also to the chirality of the CH carbon which renders the two neighboring protons diastereotopic. Thus the product is a racemic mixture of two enantiomers.

The signal at 5.15 ppm is due to the proton of the internal double bond (~$CH=CR_2$) and its intensity does not change after hydroformylation. Obviously, under the conditions employed, this type of double bond is unreactive to the oxo process. This conclusion is similar to that made in (6) for the cobalt assisted hydroformylation. The material with trisubstituted double bonds is a minor contaminant (~5%).

The aldehyde group is very reactive and can undergo various side reactions, such as aldol condensation, Tishchenko reaction, cyclooligomerization, and polymerization (17). All these reactions involve the coupling of aldehyde molecules, and the products should have $\overline{M}_n$ at least twice as high as the starting materials. Hence the molecular weight of products could be a sensitive indicator for these reactions.

In contrast to low molecular weight polymers, higher molecular weight polymers ($\overline{M}_n$>5,000 g/mole) can be quantitatively isolated by precipitation and they give highly reproducible $\overline{M}_n$ and MWD values after every functionalization step (Figure 2). This evidence, together with NMR spectroscopic analysis, indicate that the entire reaction sequence shown in Scheme 1 is essentially free from side reactions.

In summary, hydroformylation was demonstrated to produce essentially pure aldehyde-capped PIBs, specifically α-*tert*-butyl-ω-oxopolyisobutylene and α,ω-dioxopolyisobutylene.

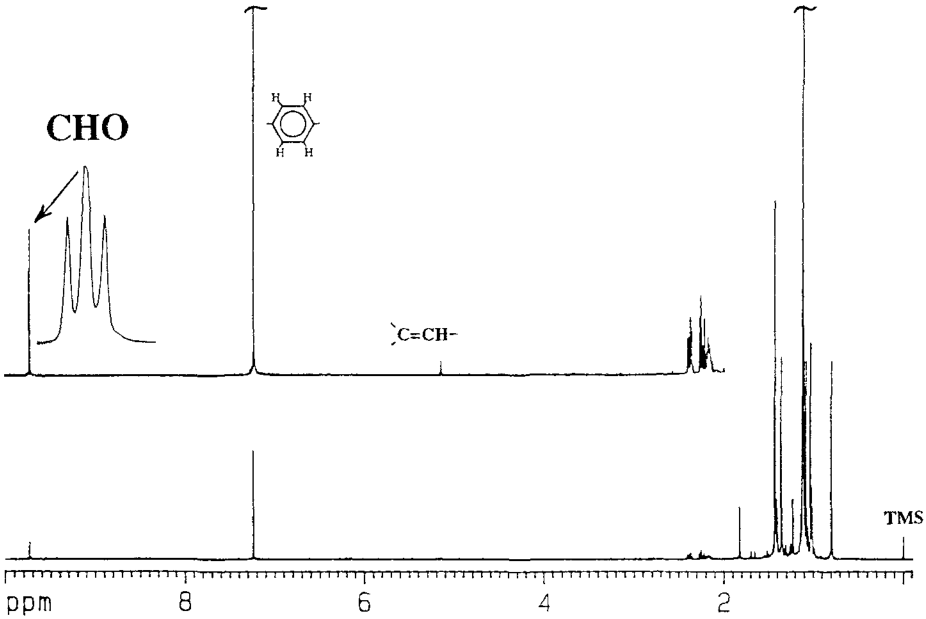


Figure 1. ^{1}H NMR (500 MHz, 10 %w/v in CDCl$_3$) spectrum of α,ω-dioxopolyisobutylene (OCH-PIB-CHO), $\bar{M}_n$=2,500 g/mole (See Scheme 1).

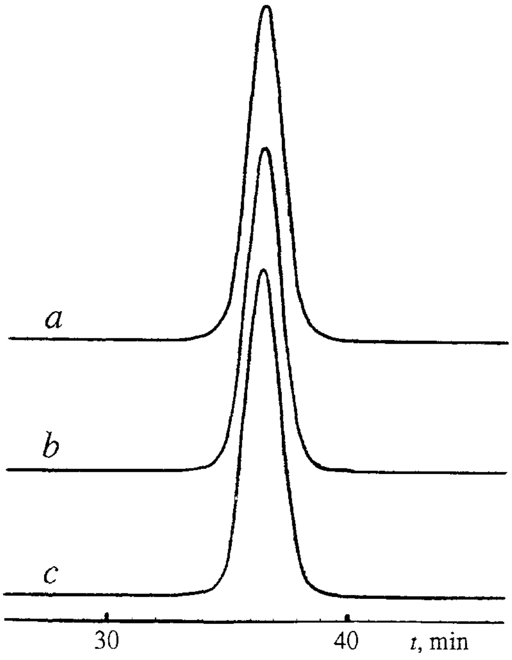


Figure 2. GPC (RI detector) traces of

a - PIB-Cl; $\bar{M}_n$=10,600 g/mole, $\bar{M}_w/\bar{M}_n$=1.12.
b - PIB-CH$_2$-C(CH$_3$)=CH$_2$; $\bar{M}_n$=10,500 g/mole, $\bar{M}_w/\bar{M}_n$=1.11.
c - PIB-CHO; $\bar{M}_n$=10,500 g/mole, $\bar{M}_w/\bar{M}_n$=1.12.
(See Scheme 1)

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