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New telechelic polymers and sequential copolymers by polyfunctional *ini*tiator-trans*fer* agents (inifers)

LI. Synthesis and characterization of anisole-terminated polyisobutylenes

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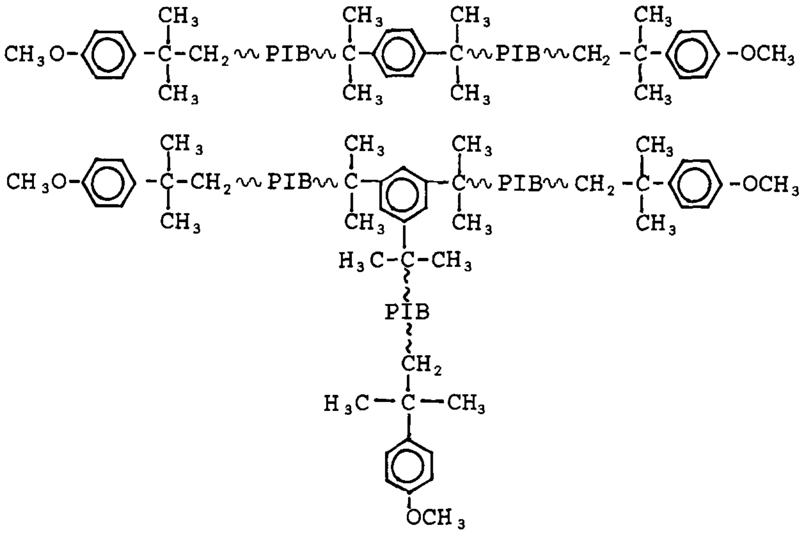
Summary

The synthesis and quantitative end group characterization of anisole-terminated polyisobutylenes are described. These new telechelic prepolymers consist of a linear or a three-arm star polyisobutylene (PIB) carrying exactly two or three anisole termini, respectively. The synthesis was accomplished by quantitative Friedel-Crafts alkylation of anisole by olefin- and/or tert.-chloro-telechelic PIB's, and characterization involved ^1H NMR and UV spectroscopy, GPC and Osmometry. According to charcterization research the linear and three-arm star anisole-terminated polyisobutylenes have the following structures:



Introduction

In the course of our fundamental studies on the derivatization of telechelic PIBs we became interested in the quantitative Friedel-Crafts functionalization of tert.-chloro- and isopropylidene-terminated PIBs. Thus we have explored the alkylation of anisole ($C_6H_5OCH_3$) with these prepolymers and prepared a series of new anisole-terminated PIBs. These materials may be of use, among other things, in the further structure characterization of PIBs by UV spectroscopy (PIB is transparent to UV but the anisole end groups are strong absorbers).

Experimental

A. Materials and Instruments

Anisole (Aldrich Chemical Co.) was used as received. Boron trifluoride etherate (Aldrich) was distilled under reduced pressure. Hexanes, acetone, methanol, methylene chloride, carbon tetrachloride, sodium sulfate (anhydrous), magnesium sulfate (anhydrous), pentane (Fisher Scientific Co.) cyclohexane (Fisher, spectroanalyzed) were high quality commercial products. The hexanes were freed from olefinic impurities by treatment with fuming sulfuric acid.

Molecular weights were determined by a Kanuer Vapor Pressure osmometer, Model No. 11.00 (Utopia Instrument Co.) and by a membrane osmometer (Mechrolab 503) in toluene at 40°C and 38°C, respectively. GPC eluograms were obtained by a Waters Associates 6000A high pressure instrument equipped with a Model 440 UV and a Model R401 differential RI detector, and five μ-Styragel columns of pore sizes of 10^6, 10^5, 10^4, 10^3 and 500 Å. A calibration curve was constructed by using well fractionated PIB samples of known molecular weights with $\bar{M}_w/\bar{M}_n = 1.1 - 1.3$.

^1H NMR spectroscopy was performed by a Varian Associates T-60 NMR spectrometer at room temperature, with CCl_4 solvent and TMS standard. High resolution ^1H NMR spectra were obtained on an XL-400 Varian instrument with $CDCl_3$ solvent.

Absorbances were measured by a Perkin Elmer 559A UV/VIS Spectrometer.

B. Synthesis

1. Binifer

1,4-Di(2-chloro-2-propyl)benzene (p-dicumyl chloride or "binifer") was prepared by chlorination of 1,4-di(2-hydroxyl-2-propyl)benzene (Goodyear Tire and Rubber Co.). The starting material was recrystallized in methanol, mp. = 140°-142°C. Chlorination was carried out by treating 100g recrystallized 1,4-di(2-hydroxyl-2-propyl)benzene with 1000 ml concentrated HCl at 0 °C. The mixture was stirred at 0°C for 3 hours, 1000 ml CH_2Cl_2 were added and stirred for 30 minutes. The organic layer was separated, dried with anhydrous K_2CO_3 for 15-20 hours at 0°C, filtered, and the solvent removed. The product was twice recrystallized from n-pentane or n-hexane, yield 75% mp. = 67°-69°C.

^1H NMR spectroscopy showed two sharp resonances, one between 7.0-7.5 ppm and the other between 1.0-2.0 ppm corresponding to the phenyl and methyl protons, respectively (1). Figure 1 shows the ^{13}C NMR spectrum together with assignments.

2. Synthesis of Polymers

The preparation and purification of linear and three-arm star telechelic PIBs with 2.0 or 3.0 tertiary chloro or isopropylidene end groups have been described (2-7).

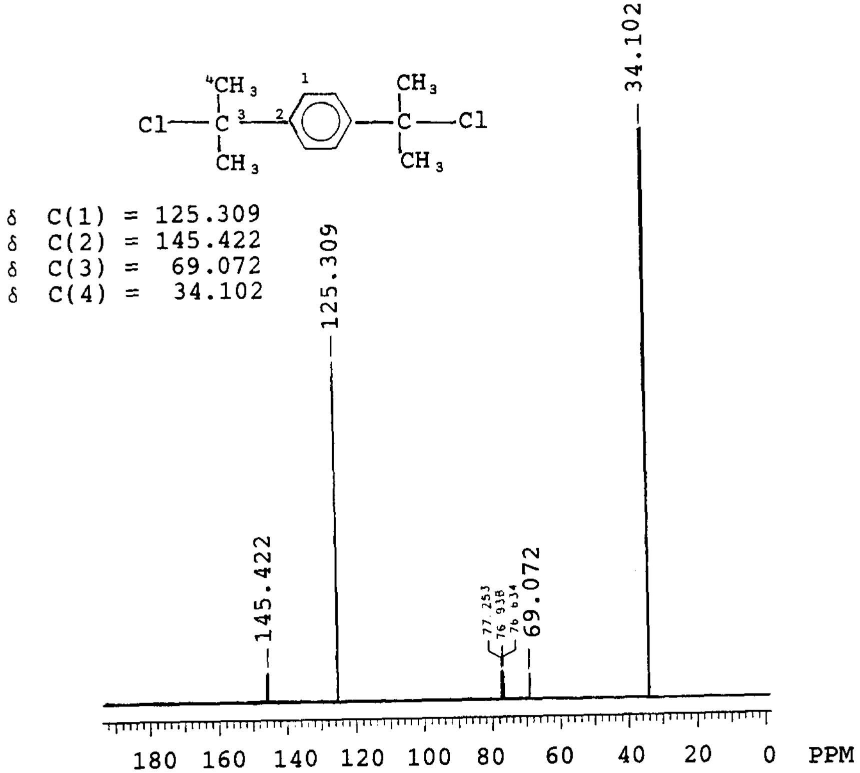


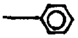
Figure 1. ^{13}C NMR spectra of 1,4-Di(2-chloro-2-propyl) benzene (p-dicumyl chloride or "binifer")

3. Alkylation of Anisole with Telechelic PIBs

A representative alkylation has been carried out as follows: To a solution of 75 ml anisole and 25 ml n-hexane containing 15g telechelic PIB stirred at 45-48°C in a 500 ml two neck flask fitted with condenser, dropping funnel, magnetic stirring bar, and nitrogen inlet-outlet, were rapidly added 9 ml freshly distilled BF_3-OEt_2 (9 mole % of anisole). The solution was stirred for 48 hours. After the alkylation was over the solvent and unreacted anisole were removed by distillation under reduced pressure. The anisole-modified PIB was washed many times (at least 10 operations) by shaking with methanol to remove unreacted anisole. The washings were followed by UV spectroscopy to ascertain the quantitative removal of the anisole. Thus shaking in methanol, discarding the washing liquid, adding fresh methanol and resuming the washings was continued until the methanol used for washings was free of anisole by UV spectroscopy. After the unreacted anisole was quantitatively removed the PIB was dissolved in n-hexane, washed with water, separated, and the organic layer was dried for ∿ 12 hours over anhydrous Na_2So_4. Finally the n-hexane was removed by rotavap and the product was dried in a vacuum oven at 70°C for 7 days.

Results and Discussion

Anisole was quantitatively alkylated by linear and three-arm star t-chloro and isopropylidene-terminated PIBs and the number of anisole termini were determined by a variety of methods, i.e., UV and ^{1}H NMR (both 60 and 400 MHz) spectroscopies, GPC, VPO and membrane osmometry.

Figure 2 shows the ^{1}H-NMR spectra together with assignments of the linear α,ω-dianisole-terminated PIB and the starting α,ω-diisopropylidene-terminated PIB. Similarly Figure 3 shows the ^{1}H-NMR spectra and assignments of the tri-arm-star trianisole-terminated PIB and three-arm star isopropylidene-telechelic PIB. The key resonance at 3.78 ppm is associated with the protons of the $-OCH_3$ group in anisole. This resonance is also present in the anisole-capped polymer at 3.73 ppm and indicates the presence of $-OCH_3$ end groups in the polymer.

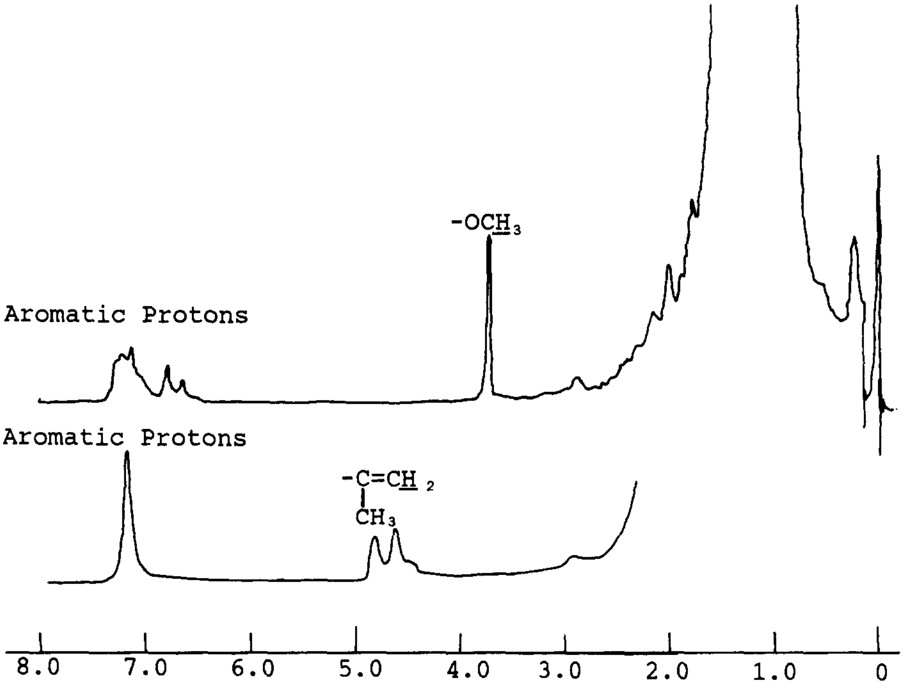


Figure 2. ^{1}H NMR spectra of α,ω-dianisole-PIB and α,ω-diisopropylidene-PIB precursor

End-group quantitation ($\bar{F}_n$ measurement) has been carried out by two independent methods: ^{1}H NMR spectroscopy (absolute) method), and UV spectroscopy coupled with $\bar{M}_n$ determination.

In regard to the ^{1}H NMR studies, we have integrated the aromatic proton regions from 6.5 to 8.0 ppm versus the $-OCH_3$ protons from 3.5 to 4.0 ppm in the anisole end groups. The averages of four to six integrations have been taken. The results are compiled in Table I.

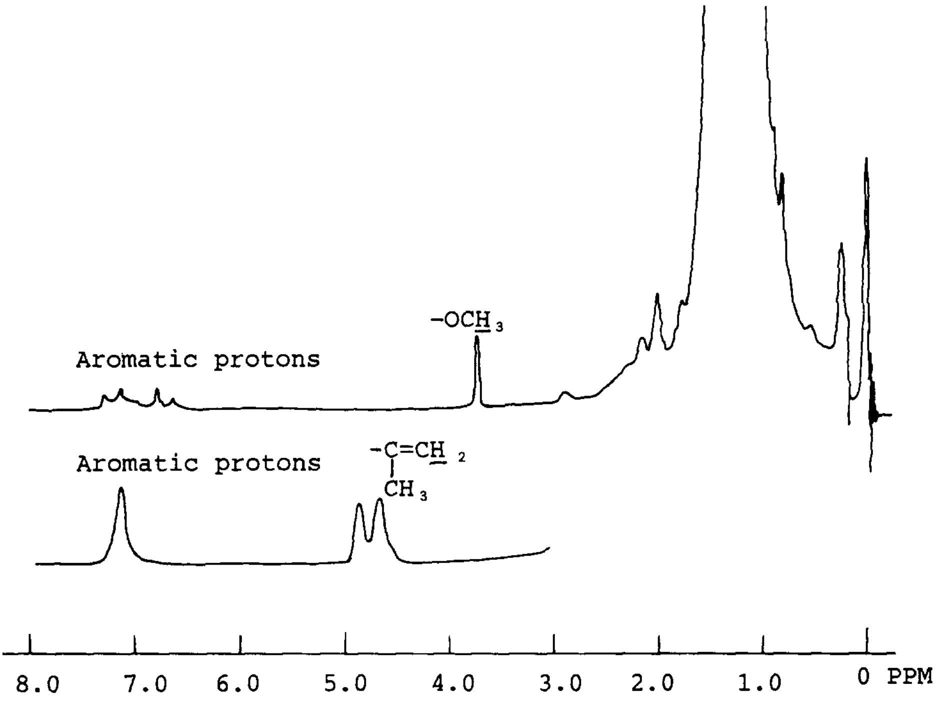


Figure 3. ^1H NMR spectra of trianisole-PIB and triisopropylidene-PIB Precursor

TABLE I
Synthesis and Characterization of Linear and Tri-arm Star Anisole Terminated PIBs

Starting Material	$\overline{M}_n$		Anisole Functionality, $\overline{F}_n$	
	GPC	Osmometry	NMR	UV
$CH_2=(CH_3)CCH_2\text{-}PIB\text{-}CH_2C(CH_3)=CH_2$	5,360	5,000* (VPO)	2.0	1.99
$CH_2=(CH_3)CCH_2\text{-}PIB\text{-}CH_2C(CH_3)=CH_2$	12,740	11,000	2.0	1.95
$CH_2=(CH_3)CCH_2\text{-}PIB\text{-}CH_2C(CH_3)=CH_2$	15,980	14,000	2.0	1.98
$Cl^{\underline{t}}\text{-}PIB\text{-}Cl^{\underline{t}}$	57,425	55,000	-	1.93
$CH_2=(CH_3)CCH_2\text{-}\underset{\overset{\vert}{CH_2C(CH_3)=CH_2}}{PIB}\text{-}CH_2C(CH_3)=CH_2$	-	14,000	3.0	2.96
$CH_2=(CH_3)CCH_2\text{-}\underset{\overset{\vert}{CH_2C(CH_3)=CH_2}}{PIB}\text{-}CH_2C(CH_3)=CH_2$	-	17,500	3.0	2.94
$Cl^{\underline{t}}\text{-}\underset{\overset{\vert}{Cl^{\underline{t}}}}{PIB}\text{-}Cl^{\underline{t}}$	-	85,150	-	1.93

To carry out UV quantitation of anisole end groups first a calibration plot of anisole in cyclohexane at 269 nm has been constructed. Figure 4 shows the absorbance (ε) versus concentration (c) plot. The $\overline{F}_n$ values have been obtained by determining the anisole concentration by the use of this calibration plot and the $\overline{M}_n$ of the individual samples. The results are shown in Table I.

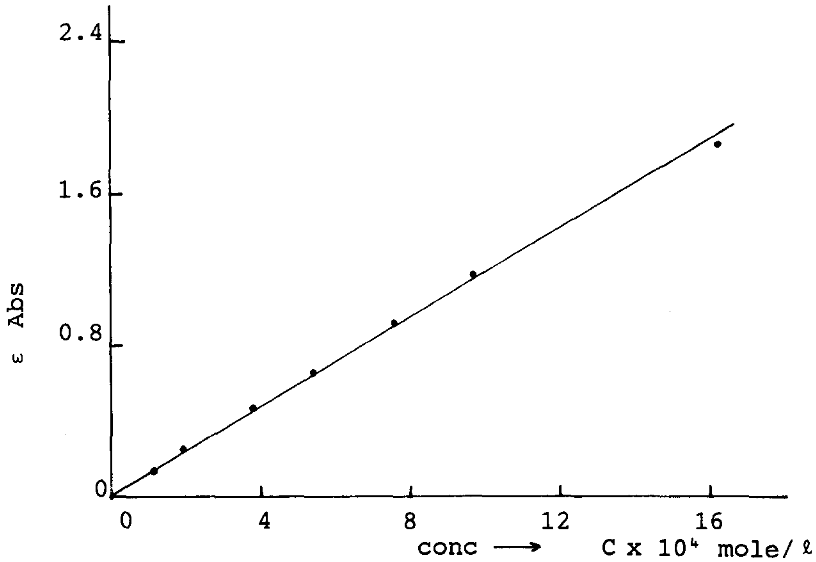


Figure 4. UV calibration curve to determine anisole concentration at (269 nm)

Figure 5 shows the 400 Mhz ^{1}H NMR spectrum of the lowest $\overline{M}_n$ product ($\overline{M}_n$ = 5360). The sharp CH_3O- resonance at ∿3.7 ppm indicates essentially pure para substitution of the anisole. The sharp resonances at 7.15 ppm are due to protic impurities in the $CDCl_3$ solvent.

According to these data the target materials, whose formula is shown in the Abstract have been obtained.

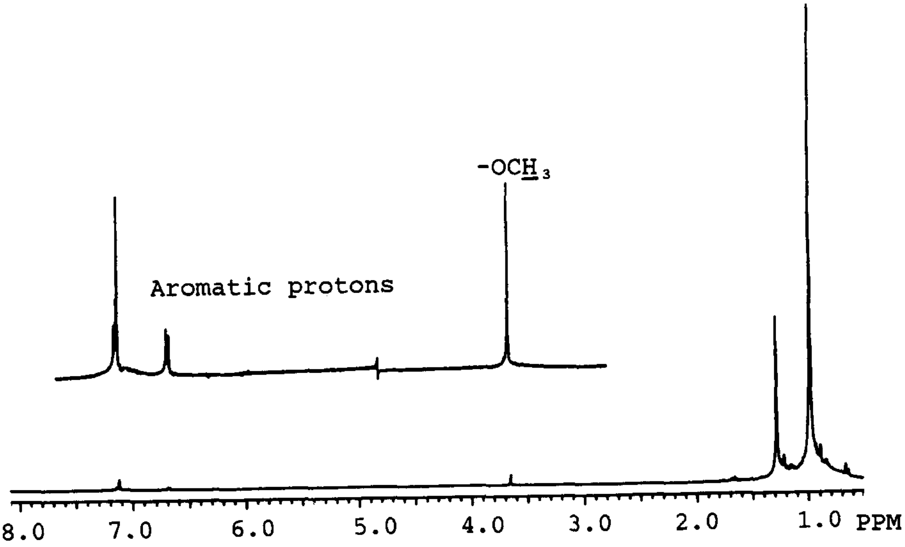


Figure 5. $\underline{4}$00 MHz ^{1}H NMR spectrum of α,ω-dianisole-PIB $\overline{M}_n$ = 5360

Acknowledgement

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