Polymer Bulletin 15, 469–475 (1986)

Polymer Bulletin
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NMR-Spectroscopy

New Telechelic Polymers and Sequential Copolymers by Polyfunctional *Ini*tiator-Trans*fer* Agents (Inifers)

L. High Resolution ^{13}C NMR Spectroscopy of Telechelic Polyisobutylenes

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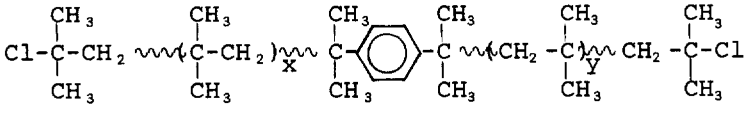
Abstract

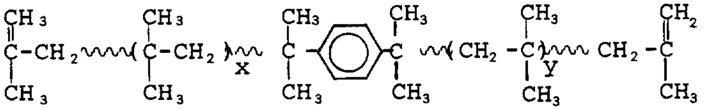
α,ω-Di-tert.-chloropolyisobutylenes (^{t}Cl-PIB-Cl^t) have been synthesized by the dicumyl chloride/BCl_3 inifer system and the detailed structure of the products has been thoroughly investigated by high resolution ^{13}C NMR spectroscopy. To facilitate spectroscopic quantitation the ^{t}Cl-PIB-Cl^t was dehydrohalogenated to α,ω-di(isopropylidene)polyisobutylene ($CH_2=C(CH_3)$-PIB-$C(CH_3)=CH_2$). According to this definitive analysis telechelic PIBs with essentially theoretical terminal functionalities (i.e., olefin and by implication tert.-chloro) can be prepared by the inifer technique; evidence for indanyl end groups has not been found. The $\bar{M}_n$s of olefin telechelic PIBs can be readily determined by ^{13}C NMR spectroscopy.

Introduction

It has been shown by various methods (1-5) that under suitable conditions linear and three-arm star telechelic PIBs can be prepared by the inifer technique. Indeed some of these products have recently become commercially available in research and development quantities (6). In view of the continued interest in these materials for a variety of purposes and applications, we decided to undertake a detailed structural analysis of the linear telechelic PIBs by high resolution ^{13}C NMR spectroscopy. Experimentally, we prepared the ^{t}Cl-PIB-Cl^t parent compound and in order to facilitate quantitation by NMR spectroscopy dehydrochlorinated it by treatment with base (7,8).



^{t}Cl-PIB-Cl^t



$CH_2=C(CH_3)$-PIB-$C(CH_3)=CH_2$

Experimental

The synthesis of ^{t}Cl-PIB-Cl^{t} has been described (1,4,). Dehydrochlorination conditions by base (i.e., tBuOK) has also been published (7).

The ^{13}C NMR spectra were obtained on a XL-400 Varian Spectrometer utilizing a 10 mm broad band probe. Most spectra were taken with PW = 90°, SW = 20 kHz and a 32K transform. In addition, T_1 and NOE values were obtained. All samples were in $CDCl_3$ at approximately 25% v/v solution.

Results and Discussion

Figure 1 shows the proton coupled and uncoupled 100 MHz ^{13}C spectrum of $CH_2{=}C(CH_3)$-PIB-$C(CH_3){=}CH_2$. The coupled spectrum clearly shows the methyl group (30.6 ppm) and methylene group (59.5 ppm) of the isobutylene chain as a quartet and triplet spin multiplet. The quaternary carbon of the isobutylene repeat unit is shown as a singlet (39.1 ppm). The deuterated chloroform solvent is the familiar triplet at ∿ 78 ppm from the transmitter frequency.

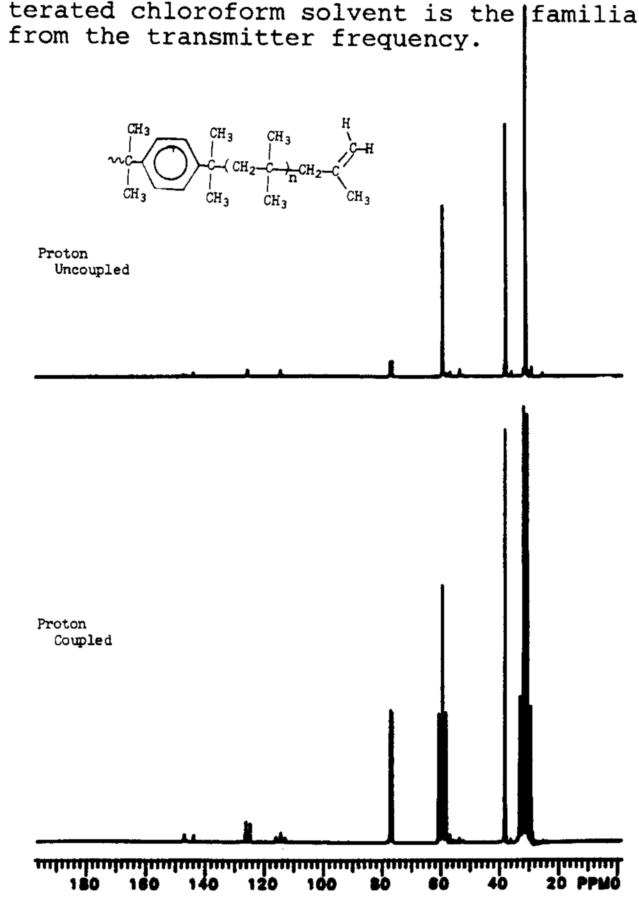


Figure 1. ^{13}C NMR Spectra of $CH_2{=}C(CH_3)$-PIB-$C(CH_3){=}CH_2$ (Sample 1 of Table I)

The minor but significant peaks across the spectrum are associated with the inifer residue in the polymer and the olefinic end groups.

The uncoupled spectrum confirms the spin multiplet patterns as each collapses to a single resonance.

It should be noted that all carbon chemical shifts (δ_C) are with reference to the transmitter frequency and can be converted to tetramethylsilane reference by (δ_C - 1.31 ppm).

Figure 2 shows the proton coupled and uncoupled spectra of the inifer residue and end group carbons of $CH_2{=}C(CH_3)$-PIB-$C(CH_3){=}CH_2$ at a much higher amplitude. These spectra are at approximately X50 in gain from spectra in Figure 1.

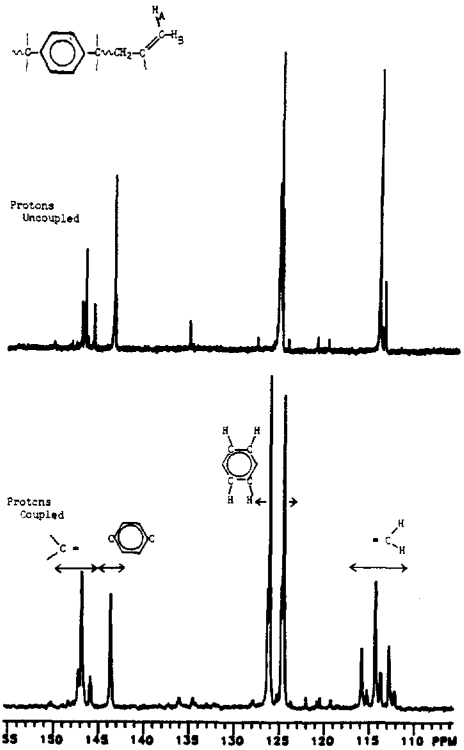


Figure 2. ^{13}C NMR Spectra of the Aromatic and Olefinic Carbon Regions of Figure 1

The coupled spectrum shows clearly at least two triplet patterns centered at about 114 ppm that represent two chemically shifted olefin carbon nuclei with two directly bonded protons. These resonances represent the terminal carbon of the olefinic end groups. When the protons are uncoupled at least three chemically shifted olefinic carbons can be distinguished. The two multiple peaks shown at 125 ppm are the four symmetrical carbons of the inifer residue; the two main peaks represent the spin-splitting of the single proton bonded to each of the four carbons.

The resonance at 144 ppm which does not exhibit spin multiplicity due to directly bonded protons, is assigned to the 1 and 4 carbons of the phenyl ring of the inifer residue attached to the polymer chain. The peaks grouped at 147 ppm, which also show no directly bonded proton multiplicity, are due to the vinyl carbons (-C=) of the olefinic end groups. This group also shows chemically shifted olefinic end groups, as does the terminal olefinic carbon (see above), most likely representing end groups with probably less than four isobutylene repeat units in an arm.

The other minor peaks present in the spectra vary in amplitude due to the time and method of drying the polymer and are believed to be due to impurities (solvent residues, etc.).

Figure 3 represents the spectra of the terminal olefinic carbons with protons coupled and uncoupled. The coupled spectrum again clearly illustrates the triplet due to the primary bonded proton. Superimposed on this carbon is the quartet-like fine structure expected to arise from a β-methyl group. This structure is further corroborated by the spectrum of the model compound 1-isopropenyl-4-isopropylbenzene shown in Figure 4. In addition, the coupled spectrum shows several slightly

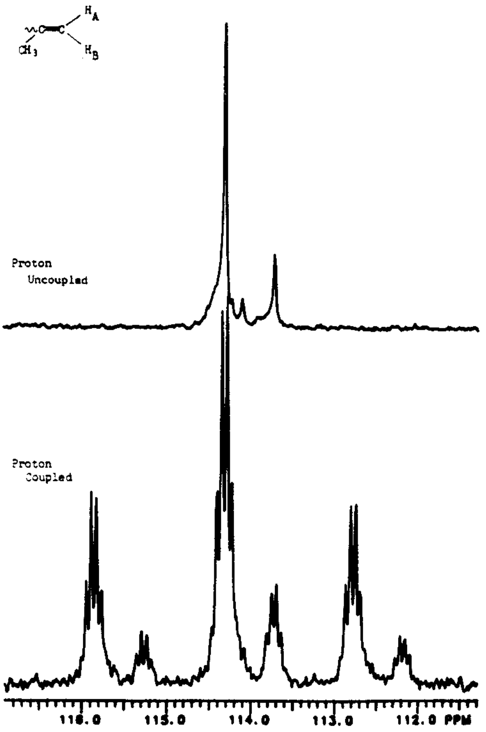


Figure 3. ^{13}C NMR Spectra of the Olefinic Carbon Region of Figure 1

shifted structurally similar olefinic groups. Indeed, three and possibly four different peaks are seen in the uncoupled carbon spectrum indicating the presence of PIB arms consisting of three, four, and many isobutylene repeat units.

Figure 4 shows spectra of 1-isopropenyl-4-isopropylbenzene with protons coupled and uncoupled. The coupled spectrum shows the triplet of the terminal olefinic carbon (∿ 116 ppm). These resonances are similar to those seen for the end group of the telechelic diolefin PIB. Other expected multiplet patterns are shown which readily identify this molecule (quartet at 22 and 24 ppm, doublet at 34, 126, and 127 ppm, singlets at 139, 143, and 148 ppm). Significantly, the asymmetry of the substituents on the phenyl ring helps to identify the expected chemical shift region for the phenyl carbons of the inifer residue in the polymer as seen in Figure 2. Only one major doublet pattern is evident for the phenyl carbons, which indicates the minor doublet resonance in the phenyl carbons region of the polymer are indeed, slightly chemically shifted inifer fragments similar in amplitude to difference seen in the terminal olefinic region.

Figure 5 shows the amplified 100 MHz ^{13}C NMR spectra of the olefinic carbon of 1-isopropenyl-4-isopropylbenzene. The coupled spectrum clearly shows the triplet-like spin multiple pattern (J_{CH} = ∿156H_2)expected for on olefinic carbon nucleus carrying two hydrogens. On a much narrower sweep width the two terminal vinyl proton appear as slightly chemically shifted peaks, so that the triplet is really two overlapping spin doublets with nearly equivalent J-values. Superimposed on this triplet-like multiplet is a quartet-like multiplicity (J_{CCCH} = ∿6H_Z) indicative of a nearby β-methyl group. The single resonance seen in the proton-uncoupled spectrum clearly shows that the multiplicity of the coupled spectrum is a result of protons bonded to carbons. The chemical shift (δ_C = 111.62 ppm) indicates an unsaturated carbon, thus the spectra unambiguously represent the terminal olefinic carbon of an isopropenyl fragment.

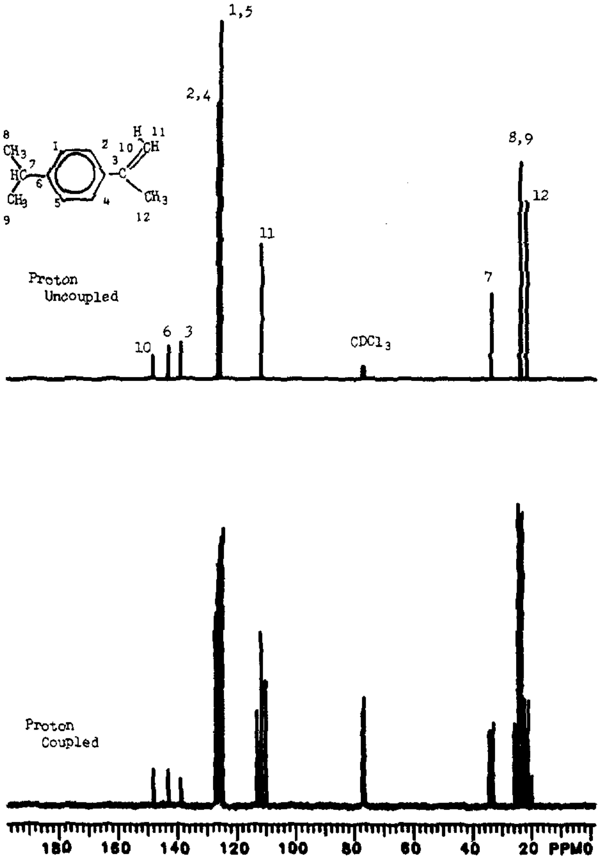


Figure 4. ${}^{13}C$ NMR Spectra of 1-Isopropenyl-4-Isopropylbenzene

Figure 6 shows the 100 MHz ${}^{13}C$ NMR spectra of two isopropylidene-polyisobutylenes with $\bar{M}_n$ = 1500 and 4200. Based on the assignments for the carbon resonances of the aromatic inifer residue and the olefin end group in Figures 1, 2, and 3, we would expect a linear decrease in the intensity of these resonance areas with increasing molecular weight, as compared to the carbon resonances of the methyl, methylene and quaternary carbons of the isobutylene repeat unit. The two spectra clearly demonstrate this effect.

Average molecular weight determinations were also made by vapor phase osmometry (VPO) and gel permeation chromatography (GPC) and a comparison of the $\bar{M}_n$'s obtained by these methods is shown in Table I. Acceptable agreement of the $\bar{M}_n$'s is seen.

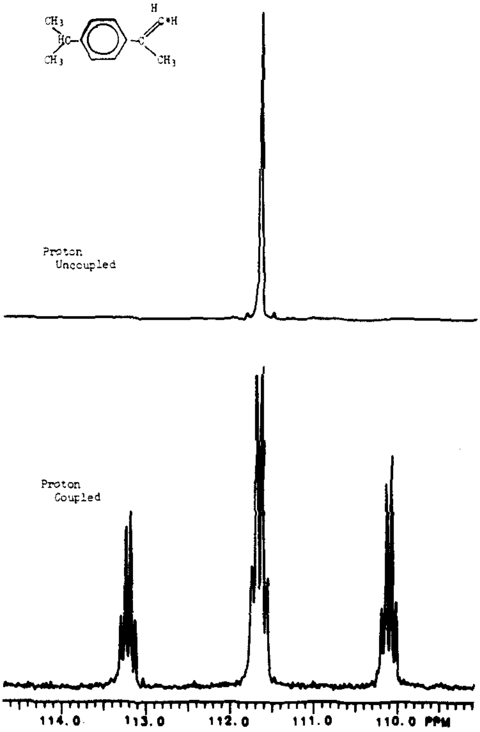


Figure 5. ^{13}C NMR Spectra of the Olefinic Methylene Carbon of 1-Isopropenyl-4-Isopropylbenzene

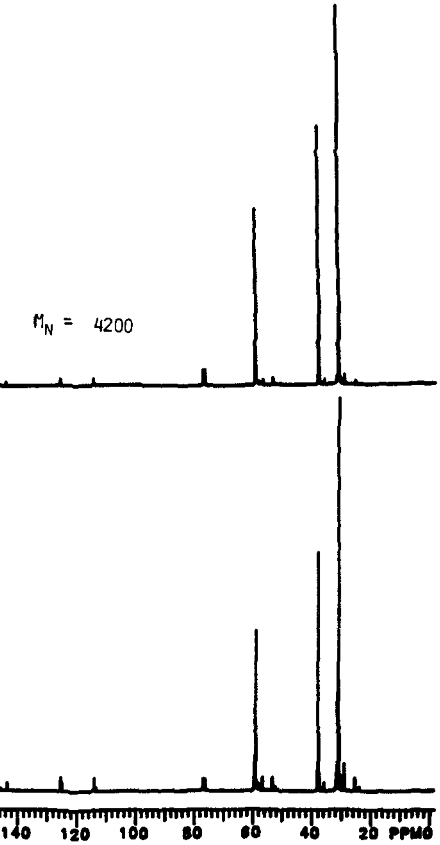


Figure 6. ^{13}C NMR Spectra of $CH_2=C(CH_3)$-PIB-$C(CH_3)=CH_2$ of $\overline{M}_n$ = 4200 and 1500

TABLE I

Comparison of Average Molecular Weights of
α,ω-di(isopropylidene)polyisobutylenes
Determined by ^{13}C NMR

	$\overline{M}_n$			
Sample	NMR	VPO	GPC	($\overline{M}_w/\overline{M}_n$)
1	4200	4000	4500	(1.9)
2	1500	1600	2200	(2.0)

Conclusions

According to high resolution ^{13}C NMR spectroscopy, ^{t}Cl-PIB-Cl^{t} is quantitatively dehydrohalogenated by published methods (7,8) and the product is $CH_2=C(CH_3)$-PIB-$C(CH_3)=CH_2$. There is no evidence for indanyl end groups in the polymer (9). The $\overline{M}_n$'s of reasonably low molecular weight telechelic PIBs can be readily determined by ^{13}C NMR spectroscopy.

Acknowledgement

Financial support by the NSF (Grant DMR-84-18617)is gratefully acknowledged.

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Accepted May 13, 1986