Polymer Bulletin 34, 461–467 (1995)

Polymer Bulletin

^{13}C NMR characterization of unsaturated terminal structures in oligoisobutylenes

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Received: 3 November 1994/Revised version: 19 December 1994/Accepted: 2 January 1995

Summary

^{13}C NMR analysis revealed the existence of additional unsaturated terminal structures in oligoisobutylene samples, in addition to the well-known $-CH_2C(CH_3)=CH_2$ and $-CH=C(CH_3)_2$. Structure with a double bond between two quaternary carbons was detected both in commercial Oppanol B3 and in a oligoisobutylene (PIB) sample prepared by polymerization in CH_2Cl_2 with a high concentration of monomer in the presence of BCl_3 at −20°C. In the latter sample, another type of the structure with a double bond between quaternary carbon and methine carbon ($-CH=C(CH_3)-CH_2CH_3$) was found in a large amount.

Introduction

Until now only two types of unsaturated end structures in oligoisobutylene samples have been reported on the basis of ^1H and ^{13}C NMR spectra (1–7): $-CH_2C(CH_3)=CH_2$ (structure A) and $-CH=C(CH_3)_2$ (structure B). In ^1H NMR spectra structure A shows in the olefinic region the lines at 4.62 ppm and 4.82 ppm, while structure B gives a line at 5.12 ppm (8). Recently, we have found that oligoisobutylene samples prepared in CH_2Cl_2 (with high concentration of the monomer) in the presence of BCl_3 at −20°C exhibit in the olefinic region of ^1H NMR spectra, in addition to lines mentioned above, also a new line at 5.09 ppm, indicating a new type of double bond end structures (9). In this paper we report the results of ^{13}C NMR analysis both of this sample and of commercial Oppanol B3. In addition to conventional ^{13}C NMR spectra, also APT (APT-Attached Proton Test and DEPT (DEPT – Distorsionless Enhancement by Polarization Transfer) spectra (10,11) were measured. While APT spectra enabled us to determine whether the number of hydrogens attached to a given carbon is odd (one in our case) or even (zero or two), in DEPT spectra only the lines of carbons bonded to hydrogens are detected.

Experimental

Samples: Oligoisobutylene sample (PIB) ($\overline{M}_n = 2700$, $\overline{M}_w/\overline{M}_n = 1.3$) was prepared by polymerization of isobutylene in CH_2Cl_2 ([M] = 7 mol/l) at −20°C in the presence of BCl_3 for 168 h; details of the synthesis are given elsewhere (9). The polymerization product was dissolved in pentane, stirred for a few minutes and then washed several times with water;

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the organic layer was separated and dried with anhydrous sodium sulfate. Finally, the product was filtered, the solvent removed by evaporation (Rotovap) and dried in vacuo for 48 h at room temperature. Commercial oligoisobutylene Oppanol B3 (BASF, $\overline{M}_n \simeq 800$) was also studied (as received, without further purification).

NMR measurements: ^{13}C and ^{1}H NMR spectra were measured with a Bruker AC-300 spectrometer at 75.5 MHz and 300.1 MHz, respectively, and room temperature. In conventional ^{13}C NMR spectra 30° pulses were used with 9400 scans, spectral width 16129 Hz, acquisition time 1 s and relaxation delay 6 s. 20% (w/v) solutions of studied samples in $CDCl_3$ (Merck) were measured in 5 mm NMR tubes. Hexamethyldisiloxane, with a signal at 2.0 ppm from TMS in ^{13}C spectra and at 0.05 ppm in ^{1}H spectra, was used as an internal standard; all chemical shifts in the text, table and figures are referred to TMS.

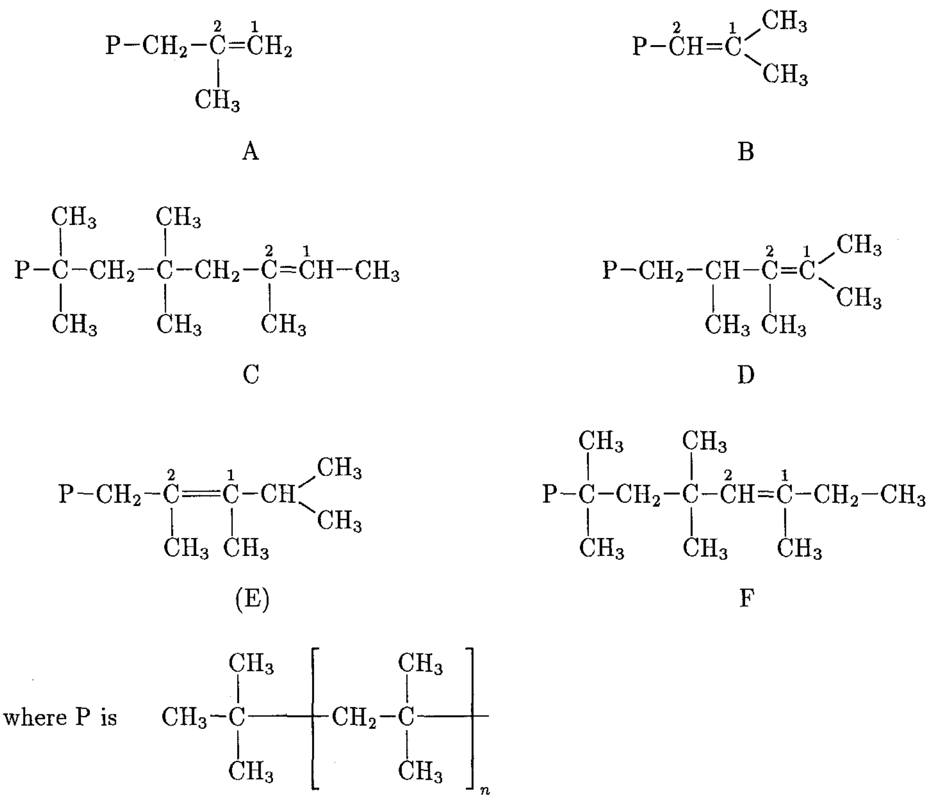
Results and Discussion

In Figure 1, the conventional, APT and DEPT ^{13}C NMR spectra of the olefinic region of a commercial Oppanol B3 sample in $CDCl_3$ are shown; in APT spectrum, the signals with a positive amplitude correspond to methylene or quaternary carbons, while the signals with negative amplitude correspond to methine carbons. The strongest pairs of the signals at 114.45 ppm and 143.8 ppm, and at 128.0 ppm and 135.55 ppm (CH) correspond to well-known structures A and B, respectively (see Scheme 1]). Their chemical shifts agree well with values reported in the literature (5–7) as well as with values observed in model olefins (12) (cf. Table 1). In Table 1, chemical shifts calculated by using the empirical parameters obtained by regression analysis of olefinic carbon shifts in substituted alkenes (11,13) are also shown for comparison. As is generally known, for tri- or tetrasubstituted

Table 1: ^{13}C NMR chemical shifts of the olefinic carbons measured in spectra of the oligoisobutylene samples compared with calculated values and values reported for model olefins

Structure	Chemical shift (ppm)					
	Measured		Calculated[a]		Model olefins[b]	
	C1	C2	C1	C2	C1	C2
A	114.45	143.8	110.5	142.9	113.8[c]	143.9[c]
B	128.0	135.55	127.5	139.2	130.0[d]	135.2[d]
C	122.8	133.8	121.5	135.8	–	–
D	121.5	133.3	123.5	139.3	123.1[e]	129.6[e]
E			126.1	139.6	–	–
F	129.8	140.3	133.5	137.3	–	–

[a] Calculated by using empirical parameters reported in refs 7 and 9
[b] Values taken from ref. 12
[c] $CH_2{=}C(CH_3)CH_2C(CH_3)_3$
[d] $(CH_3)_2C{=}CHC(CH_3)_3$
[e] $(CH_3)_2C{=}C(CH_3)CH_2CH_3$



Scheme 1: Unsaturated structures in oligoisobutylenes

olefins somewhat larger deviations between measured and calculated values may exist (11), as demonstrated for C1 carbon in structure A and C2 carbon in structure B. However, Figure 1 shows the presence of additional lines in ^{13}C NMR spectra of Oppanol B3: A pair of stronger lines at 121.5 ppm and 133.3 ppm, and a second pair of weaker lines at 122.8 ppm (methine carbon) and 133.8 ppm indicate the presence of additional two types of unsaturated structures. In DEPT spectra ($\theta = \pi/4$ and $3\pi/4$) (Fig. 1c) the lines at 121.5 ppm and 133.3 ppm were not detected (similarly to those at 128.0 ppm, 133.8 ppm and 143.8 ppm), thus confirming that they correspond to quaternary carbons. On the basis of the comparison with chemical shifts observed in model olefins and with calculated chemical shift values we assigned the weaker lines to structure C and stronger lines to structure D containing the double bond between two quaternary carbons. In the latter case a similar structure E cannot be excluded. The finding that Oppanol B3 contains a relatively large amount ($\sim$ 20%, determined from integrated line intensities in conventional ^{13}C NMR spectrum) of unsaturated structures with the double bond between two quaternary carbons is also corroborated by the fact that only lines corresponding to structures A and B have been detected in the olefinic region of its ^{1}H NMR spectrum (Fig. 2a).

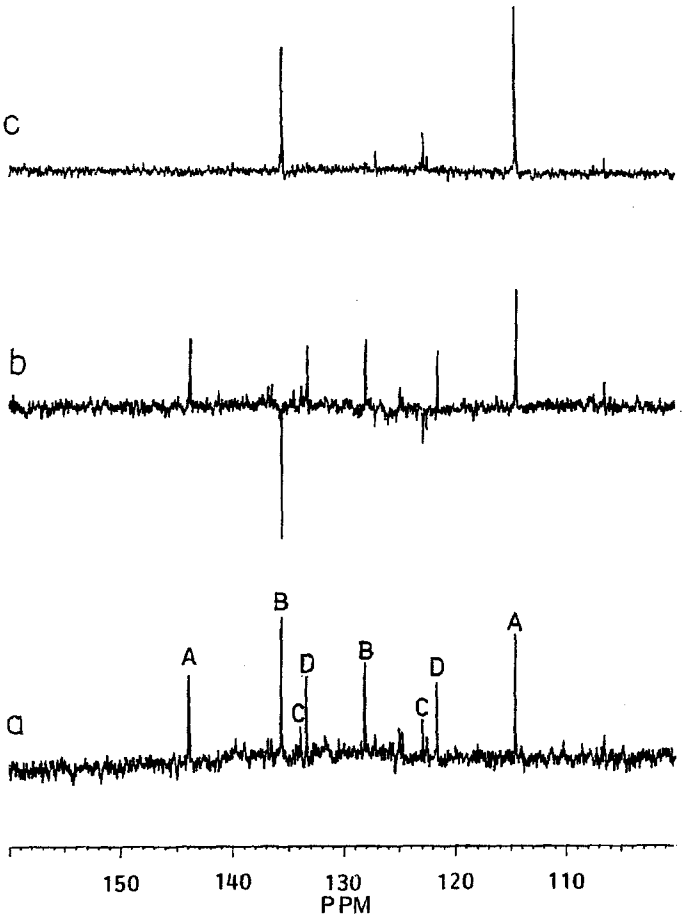


Figure 1: The olefinic region in 75.5 MHz ^{13}C NMR spectra of Oppanol B3 in $CDCl_3$ at room temperature: (a) conventional spectrum, (b) APT spectrum, (c) DEPT ($\theta = \pi/4$) spectrum.

^{13}C NMR spectra of PIB in $CDCl_3$ are shown in Figure 3. From this figure it is clear that, in addition to the expected structures A and B, the polymer also contains structures D (or E); however, no signals corresponding to structures C were found in the spectra. Contrary to ^{13}C NMR spectra of Oppanol B3, a new pair of strong lines at 129.8 ppm and 140.3 ppm was detected in PIB. Its APT spectrum confirms that the line at 140.3 ppm corresponds to methine carbons, thus proving the existence of another type of unsaturated structure with a double bond between the quaternary carbon and methine carbon. On the basis of the comparison with calculated chemical shifts, we assigned these two lines to structure F (cf. Scheme 1 and Table 1). As already mentioned, this structure exhibits a line at 5.09 ppm in ^1H NMR spectrum (Fig. 2b; cf. also ref. 9). The line at

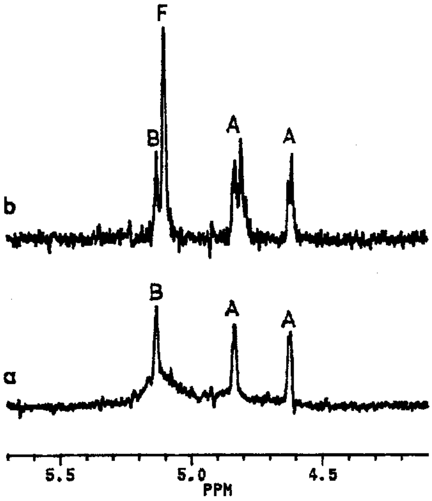


Figure 2: The olefinic region in 300.1 MHz ^1H NMR spectra of Oppanol B3 (a) and PIB (b) in $CDCl_3$ at room temperature.

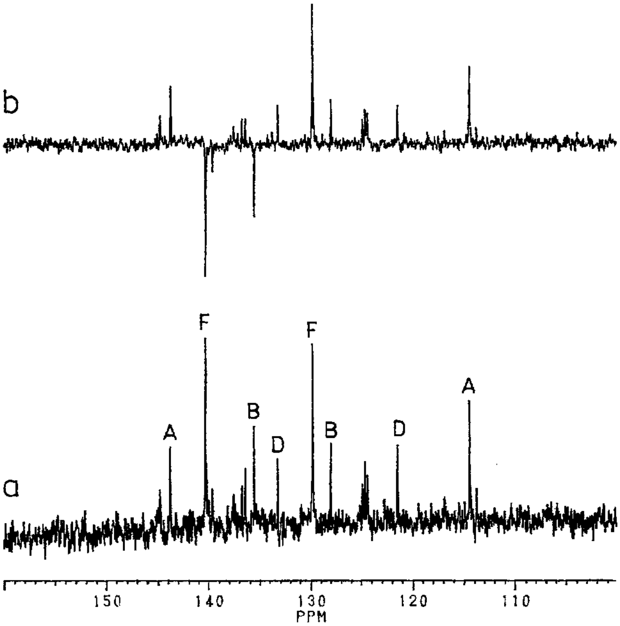
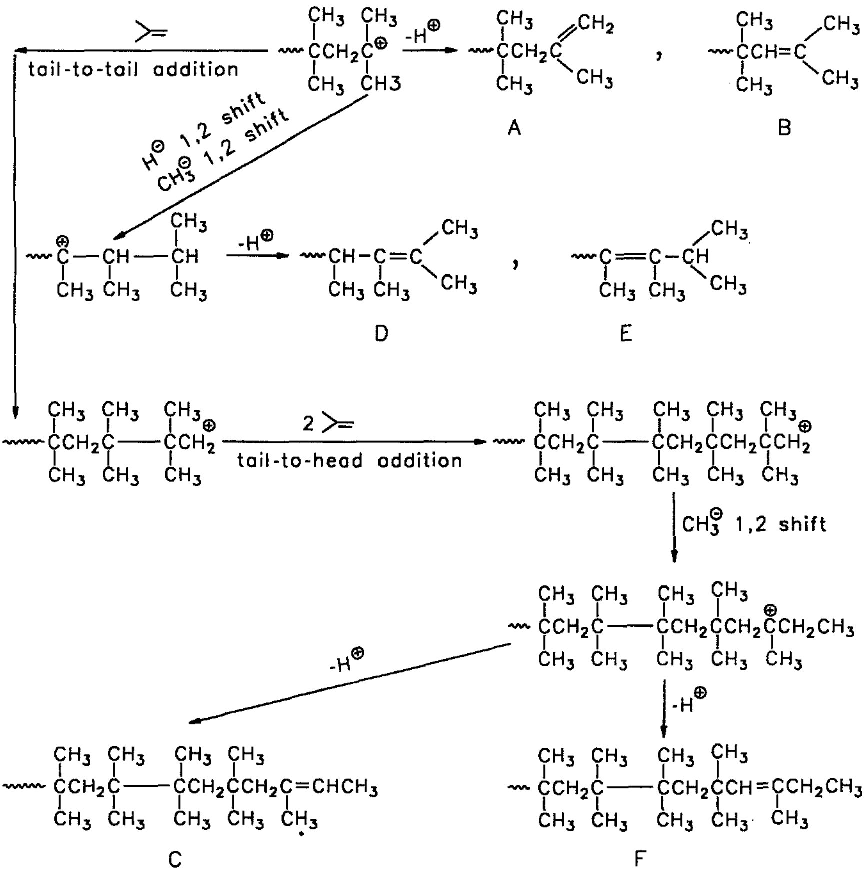


Figure 3: The olefinic region in 75.5 MHz ^{13}C NMR spectra of the PIB in $CDCl_3$ at room temperature: (a) conventional spectrum, (b) APT spectrum.

5.10 ppm was already detected earlier during the study of the effect of $AlCl_3$ on the PIB synthesis and it was assigned to terminal structure $-\overset{2}{C}(CH_3)=\overset{1}{C}H(CH_3)$ (8). However, the presence of such structure in the PIB investigated can be excluded because both calculated chemical shifts (C1=115.5 ppm, C2=151.2 ppm) and chemical shifts found for the corresponding model olefin (12), $(CH_3\overset{1}{C}H=\overset{2}{C}(CH_3)-C(CH_3)_3)$, C1=114.8 ppm and C2=143.9 ppm, are markedly different from the values observed for PIB, especially for methine carbon. From Figure 3 it is evident that the lines corresponding to structure F are the strongest in the spectrum. From integrated line intensities we estimated that in PIB the amount of structures F is ~ 40% (estimated error ±5%) of the total unsaturated structures, while the content of each of structures A, B and D is ~ 20 ± 5%; these values agree well with those determined from ^1H NMR spectra (9).

The formation of oligoisobutylene with various unsaturated end groupings, terminal double bond (A), trisubstituted (B,C,F) and tetrasubstituted (D or E) double bonds, is depicted in Scheme 2. From this Scheme one can see that the assumption of the tail-to-



Scheme 2

head addition as generally accepted for polyisobutylene synthesis makes it possible to explain the formation of unsaturated terminal structures A, B and D (or E) only. Since branching of polyisobutylene is very improbable (14), the tail-to-tail addition is assumed to explain the terminal structures C and F. Thermal depolymerization data have shown (15) that about 2% of monomeric units in the polyisobutylene are linked tail-to-tail. After the tail-to-tail addition, the tail-to-head addition is easy for sterical reasons. Also the comparison of measured and calculated ^{13}C NMR chemical shifts (as shown in Table 1) indicates that the tail-to-tail addition is followed by tail-to-head addition (for structures analogous to C and F, but with the tail-to-tail addition followed directly by unsaturated and grouping, the difference between measured and calculated chemical shifts is significantly larger).

On the basis of ^1H NMR analysis it was reported that the type of the Lewis acid ($AlCl_3$, BF_3) and the time of contact between Lewis acid and polymer can affect the unsaturated terminal structures in isobutylene polymerization, e.g. by a rearrangement in the termination step, again assuming the tail-to-tail addition (8). A model study with the triisobutylene/$AlBr_3$/DBr system has also indicated that isomerization can occur during polymerization (16). We assume that the formation of unsaturated terminal structures C, D and F is also due to these reasons.

Acknowledgement

We would like to thank Dr. M. Suchopárek for the help with DEPT measurement.

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