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Synthesis of Mono and Difunctional Oligoisobutylenes

2. Structural Study of *α,ω*-Dichlorooligoisobutylenes Obtained by the Inifer Method

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SUMMARY

A complete quantitative structural analysis of α,ω-dichlorooligoisobutylenes is carried out. It appears that, in fact, two kinds of end groups are present : 70 % of these are separated from inifer by a "long" polyisobutylene chain ; the other 30 % are directly linked to the inifer molecule. These results were obtained by H-NMR analysis of the unsaturated oligomers resulting from a dehydrochlorination of the chlorinated oligomers.

INTRODUCTION

In the first part of this series (M. Tessier, 1981) we reported the synthesis of α-chloro and α,ω-dichlorooligoisobutylenes according to KENNEDY's classical inifer method (J.P. KENNEDY 1976, 1977, 1980 ; FEINBERG 1976).

When we tried to modify chlorine end groups in order to carry out block copolycondensations, we felt that the structure of the chain was probably more sophisticated than had been estimated from the first examination. However, the chemical modification of the end groups was successful and it was possible to prepare α-anhydride - (M. TESSIER, part 3) and α,ω-dianhydride - (M. TESSIER, part 4) oligoisobutylenes. The present article gives a complete structural analysis of α,ω-dichlorooligoisobutylenes.

EXPERIMENTAL

1. Purification of reactants and synthesis of α,ω-dichlorooligoisobutylenes have been described in part I(1).

2. Analysis of the polymers :

- Tonometric measures were carried out with a Knauer vapor pressure osmometer (Dampfdruck Osmometer) in methylene chloride as solvent.

- Gel permeation chromatography : G.P.C. chromatograms were obtained using Waters chromatograph (Pump 6000A ; injector U6K ; differential refractometer R401). Columns:µstyragel : set of 3 columns : 2 x 500 Å + 100 Å ; set of 4 columns : 10 Å + 2 x 500 Å + 100 Å. THF as solvent ; duty : 2 ml.min.$^{-1}$; record rate : 2 cm.min^{-1}.

- Chlorine titration by Schöniger's method.

- Infrared spectra : were registered on a Perkin-Elmer chromatograph (type 577).

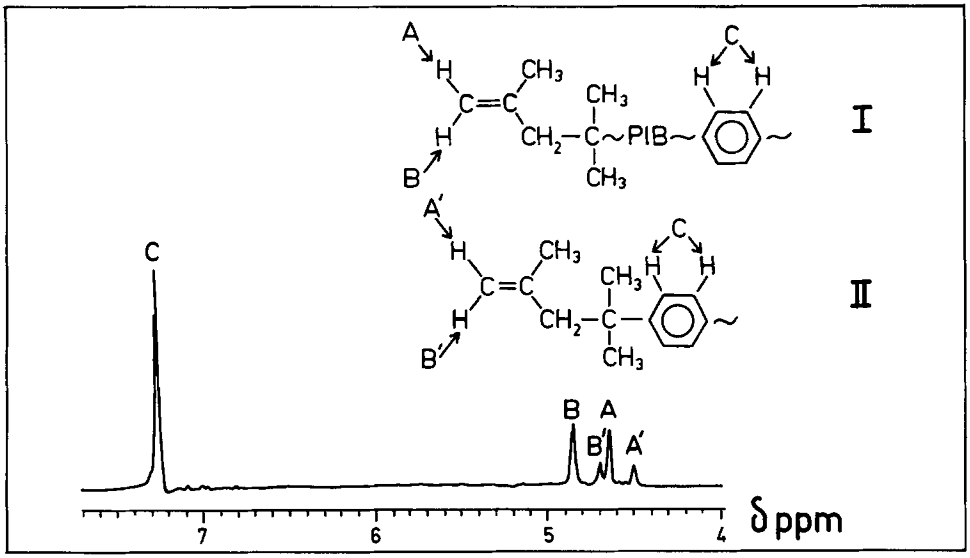


Fig. 1. ^{1}H-NMR spectrum of di(2-methyl-2-propenyl) oligoisobutylene end groups.

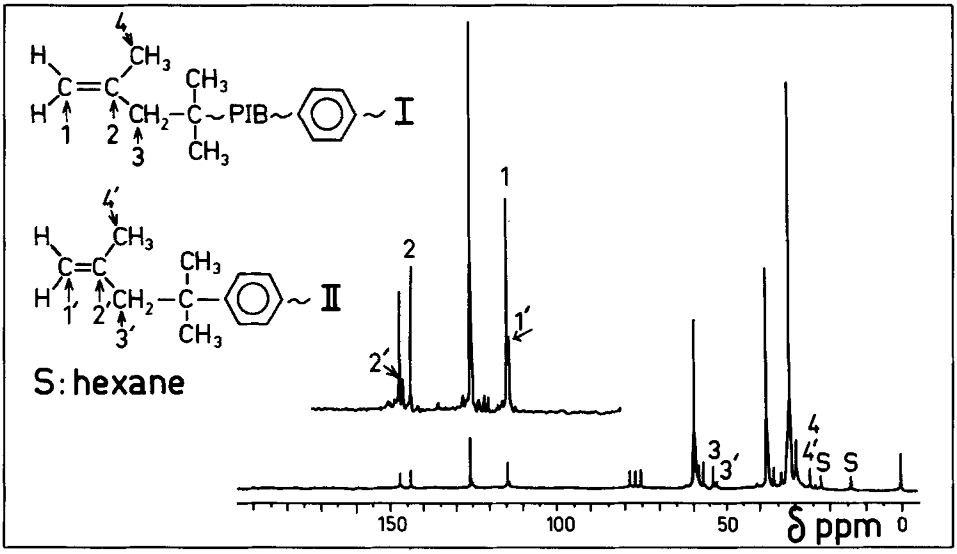


Fig. 2. ^{13}C-NMR spectrum of α, ω - di(2-methyl-2-propenyl) oligoisobutylene end groups.

NMR spectra :

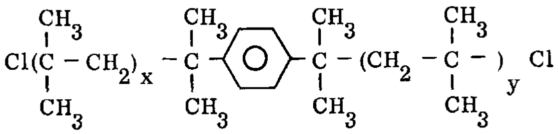
^1H-NMR : These were registered on a spectrometer Brücker 250 MHz by impulsion and Fourier transformation. TMS is the reference for chemical shifts.

^{13}C-NMR : These were registered on Jeol and Brücker spectrometers at 25 and 62 MHz by impulsion and Fourier transformation. TMS or solvent is the reference for chemical shifts.

RESULTS and DISCUSSION

1. Preparation of α,ω-dichlorooligoisobutylene :

This was prepared as reported in the first article of this series (M. TESSIER 1981) by reaction of di(2-chloro-2-isobutyl)-4,4' benzene (inifer molecule) with isobutylene. In a preliminary approximation the resulting α,ω-dichlorooligoisobutylene can be described by the following formula :



x and y are integers $\gg$ 1.
We obtained oligoisobutylenes with a molecular weight ranging from 1085 to 1750 and a dispersity index between 1.3 and 1.6 (Gel permeation chromatography).

2. Molecular weights :

These were determined by several methods ; results are reported in table 1. Agreement between the values obtained by the different methods is very satisfactory.

Table 1

Values of $\overline{M}_n$ of three different α,ω-dichlorooligoisobutylenes.

Chlorine % (weight)	$\overline{M}_n$ From chlorine content	$\overline{M}_n$ (Tonometry)
7.6 ± 0.1	935 ± 15	1030 ± 100
5.1 ± 0.1	1390 ± 30	1480 ± 100
4.9 ± 0.1	1450 ± 30	1330 ± 100

3. Infrared spectrum : (wave numbers : cm^{-1})

A band ranging from 2850 to 3000 corresponds to ν(aliphatic C - H) ; δCH (scissoring of CH_2 and asymmetric swinging of CH_3) gives a band at 1460. Two peaks at 1360 and 1380 correspond to the swinging of twin CH_3. Around 1220 a broad band results from out of plane CH bending of CH_2. A weak absorption at 580 cm^{-1} overlaps the C - Cl vibration. All these bands are present both in α-chloro- and α,ω-dichlorooligoisobutylene. In the dichlorinated oligomer a band at 825 cm^{-1} corresponds to the out of plane vibrations of benzenic C - H ; these C - H belong to the 1,4-disubstituted phenyl ring of the inifer.

^{13}C-NMR spectroscopy of chlorinated oligomers.

Chemical shifts and attributions have been published in part 1. Methyl groups of chain appear at 31.2 ppm and methyl groups of end units ($ClC(CH_3)_2$ -) at 35.2 ppm.

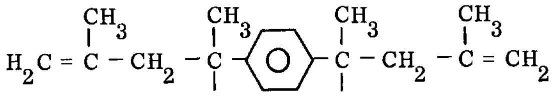
4. Titration of aromatic protons :

U.V. and ^{13}C-NMR spectra show the presence of aromatic protons due to the inifer, but allow only qualitative determination. From H-NMR spectroscopy it was possible to obtain a quantitative description of the structure and to show that two kinds of end groups are present. This has important consequences for the chemistry of these oligomers.

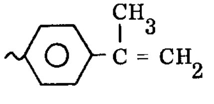
In order to reach this determination α,ω-dichlorooligoisobutelene was transformed into α,ω-di(2-methyl-2-propenyl) oligoisobutylene by dehydrochlorination. This was carried out by heating a solution of the dichlorinated oligomer in THF, in the presence of tert. BuOK, under inert atmosphere. Figure 1 shows the part of the ^{1}H-NMR spectrum corresponding to the aromatic and vinylidenic protons, in the case where the unsaturated unit is far from the phenyl ring (1) and where it is immediately bonded to the isopropyl group of the inifer.

In both cases a singulet, corresponding to aromatic protons (C), is present at 7.25 ppm. Two doublets are present in the area ranging from 4.50 to 4.90 ppm : one (A) at 4.65 and 4.85 ppm, the other (B) at 4.50 and 4.70 ppm ; they are relative to methylenic protons and correspond to an AB pattern with $J_{AB} \leqslant 5$ MHz.

This interpretation of H-NMR spectrum is confirmed by that of a model molecule : 1,4-bis (1,1,3-trimethyl-3-butenyl) benzene :



The doublet relative to the methylenic protons of this compound gives two peaks at 4.4 and 4.7 ppm.

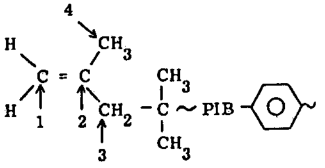
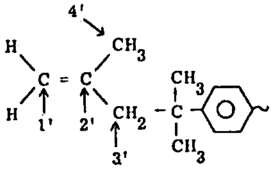
There is no peak close to 5.02 and 5.35 ppm corresponding to the chemical shifts of the methylenic protons in α-methyl or 1,4-diisopropylbenzene ; there are thus no  groups in the oligomer.

Integration of the whole spectrum shows that there is only one aromatic ring per chain.

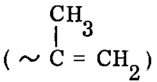
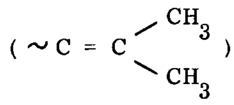
In addition to the qualitative analysis of the unsaturated oligomer by ^{1}H-NMR, we recorded its ^{13}C-NMR spectrum which is reported in figure 2. Attributions and chemical shifts of the end groups are given by table 2 and fit the conclusions drawn from ^{1}H-NMR study.

Table 2

Attributions and chemical shifts of the ^{13}C-NMR spectrum of the end groups of α,ω-di(2-methyl-2-propenyl) oligoisobutylene.

End groups	Attribution	δ p.p.m.
	C_1	114.30
	C_2	143.75
	C_3	53.65
	C_4	25.65
	C'_1	113.7
	C'_2	146.25
	C'_3	52.75
	C'_4	24.45

CONCLUSION

Macroscopic analysis of the α,ω-dichlorooligoisobutylenes prepared according to Kennedy fits the results reported by this author. However, a thorough analysis of the structure shows that two kinds of end groups are present : 2-chloro-2-butyl groups, separated from the benzenic ring by several monomer units, and 4-(3-chloro-1,1,3,3-tetramethyl-1-propyl)phenyl groups (m = 1 in the general formula). The contribution of the second type of groups is close to 30 %. In part 3 and 4 of this series (M. TESSIER part 3 and 4) we will see that the behaviour of these two types of end groups towards chemical modification differs to some extent. The presence of 4-(3-chloro-1,1,3,3- tetramethyl-1-propyl) phenyl units is responsible for such disturbing side reactions as the formation of indane rings.
It is worth underlining that the dehydrochlorination technique that we used results in the formation of exo double bonds  $(\sim \overset{CH_3}{\overset{|}{C}} = CH_2)$ only, and that no endo double bonds  $(\sim C = C\begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix})$ were formed.

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