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Determination Methods

Polymerization of Vinylchloride by *t*-Butylmagnesiumchloride

2. Structure of Oligomers by C-13 NMR

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SUMMARY

Vinylchloride has been polymerized in THF by t-butylmagnesiumchloride as an initiator. Saturated oligomers of DP=1-3 have been prepared and analyzed by joint HPLC and C-13 nmr spectroscopy. The structure of the oligomers confirm a regular head-to-tail enchainment of the monomer during initiation and propagation.

INTRODUCTION

In a preceeding paper (1) we reported the C-13 nmr spectra of poly(vinylchloride) polymerized by t-butylmagnesiumchloride. Polymers under study are saturated according to (2,3, 4). Additional methyl groups observed in the spectra (see part I in this series) indicate a termination reaction involving the t-butyl group. Furthermore, no decision could be made on the monomer enchainment as nmr spectroscopy of high polymers cannot distinguish between (I) and (II) for n>>1

$$R - (CHCl - CH_2)_n - X \qquad \text{(I)} \qquad\qquad R - (CH_2 - CHCl)_n - X \qquad \text{(II)}$$

$$R = -C(CH_3)_3 \qquad\qquad X = -CH_2-CH_2Cl$$

In high polymers end group concentrations are too low to be detected within a practically available signal/noise ratio. In mixtures of oligomeres C-13 resonance signals of long monomer sequences are overlapping with signals of short chain oligomers. To make any decision on the actual monomer enchainment it was necessary to analyze a series of corresponding oligomers.

RESULTS AND DISCUSSION

Mixtures of oligomers have been prepared by polymerisation of vinylchloride with t-butylmagnesiumchloride at ambient temperature in THF as described in the preceeding paper. The monomer/initiator ratio was 2. In the presence of $MgCl_2$ the yield of oligomers increased to 64%. Low temperatures at 220-270 K suppress sidereactions and polymerisations can be performed to 85% yield without addition of $MgCl_2$. Reactions were terminated with HCl.

Informations on monomer enchainment can be revealed only from propagating species which are quenched by HCl acidification of the reaction mixture. With respect to the suggested termination reaction a linear molecule, e.g. (III), has an ambiguous meaning on the monomer enchainment type.

$$R - CH_2 - CHCl - CH_2 - CHCl - R$$

(III)

$$R = -C(CH_3)_3$$

The following analysis concerns with oligomers of DP = 1-3. Except DP = 1 oligomers have been prepared from completely resolved HPLC fractions. C-13 nmr spectra of oligomers are shown in fig. 1-3. Interpretation of C-13 spectra were performed using

a) chemical shift parameters, derived from alkanes, 2,2-dimethylalkanes and chloroalkanes
b) H-1 nmr spectra with homo-decoupling
c) C-13 nmr spectra including broadband and hetero-decoupling
d) J-modulated spin echo (JMSE)

A version of JMSE (5) offers unique capabilities of detecting structural details. Under special experimental conditions (see EXPERIMENTAL) resonance signals of protonated carbons are blanked out and resonance signals of chlorine substituted carbons are observed separately. JMSE has been proven as a very powerful technique when proton nmr becomes extremely complicated for higher oligomers due to overlapping of signals. Common decoupling methods are restricted to lower oligomers. Additionally, chemical shift parameters can be applied only to spectra of molecules of different constitution. Spectra of diastereomers usually cannot be predicted by chemical shift parameters. Spectra shown in fig. 1-3 have been assigned to chloroalkanes:

1-chloro-3,3-dimethylbutane	IV
1,3-dichloro-5,5-dimethylhexane	V
threo-1,3,5-trichloro-7,7-dimethyloctane	VI
erythro-1,3,5-trichloro-7,7-dimethyloctane	VII

Chemical shifts are given in table 1. The identified chloroalkanes are vinylchloride oligomers which structures are given in fig. 4.

Within the range of complete resolved fractions and the sensitivity of the concentration detectors of the HPLC system no constitutional isomers, e.g. (VIII) and (IX), have been observed

$$R - CHCl - CH_3 \qquad R - CH_2 - CHCl - CHCl - CH_3$$

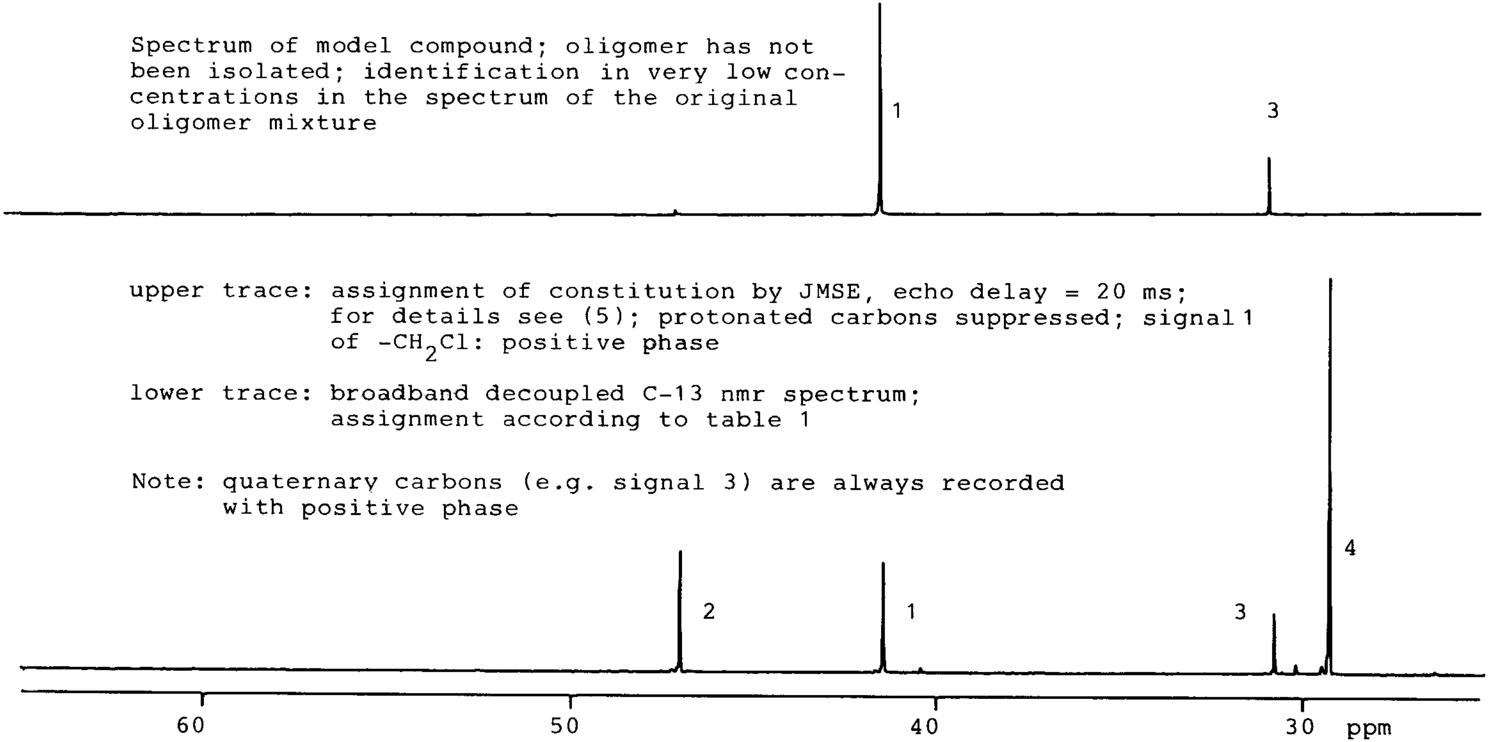
(VIII) (IX)

$$R = -C(CH_3)_3$$

As the elution of the oligomers is assumed to be effected by molar mass rather than by stereochemical and constitutional isomerism these results confirm a regular head-to-tail enchainment of the vinylchloride monomer.

Figure 1

C-13 NMR Spectrum of 1-chloro-3,3-dimethylbutane



Spectrum of model compound; oligomer has not been isolated; identification in very low concentrations in the spectrum of the original oligomer mixture

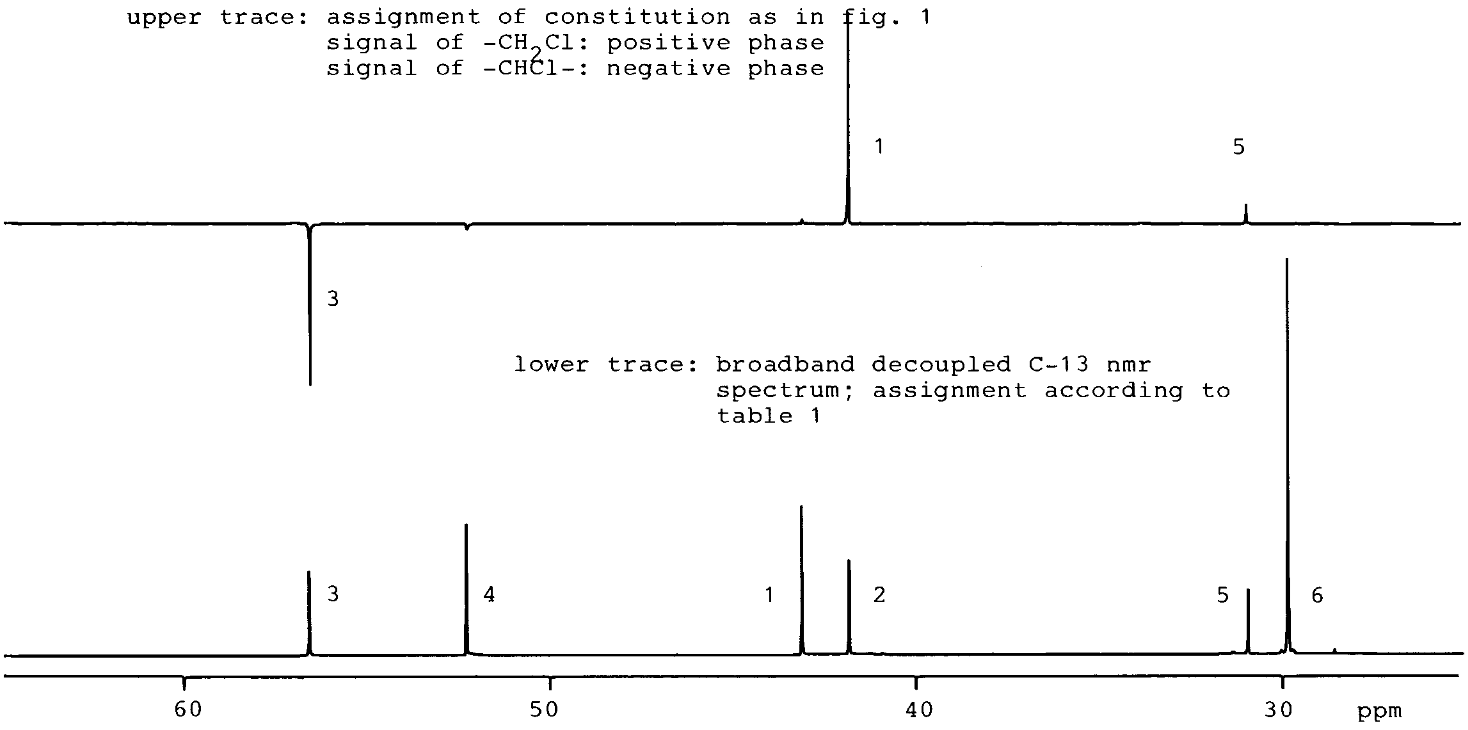
upper trace: assignment of constitution by JMSE, echo delay = 20 ms; for details see (5); protonated carbons suppressed; signal 1 of $-CH_2Cl$: positive phase

lower trace: broadband decoupled C-13 nmr spectrum; assignment according to table 1

Note: quaternary carbons (e.g. signal 3) are always recorded with positive phase

Figure 2

C-13 NMR Spectrum of 1,3-dichloro-5,5-dimethylhexane

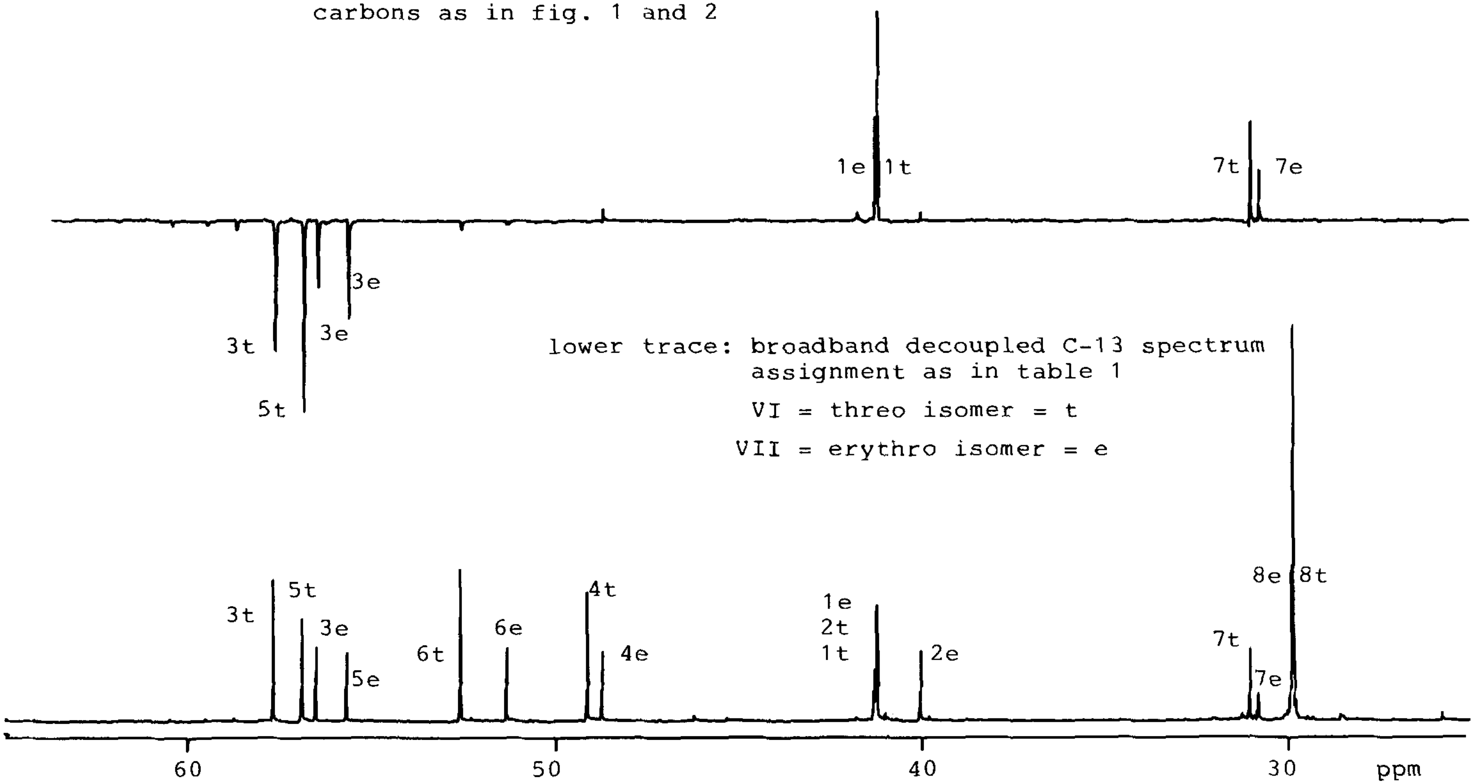


upper trace: assignment of constitution as in fig. 1
signal of $-CH_2Cl$: positive phase
signal of $-CHCl-$: negative phase

lower trace: broadband decoupled C-13 nmr spectrum; assignment according to table 1

Figure 3

C-13 NMR Spectrum of 1,2,3-trichloro-7,7-dimethyloctane



upper trace: assignment of chlorine substituted carbons as in fig. 1 and 2

lower trace: broadband decoupled C-13 spectrum assignment as in table 1

VI = threo isomer = t

VII = erythro isomer = e

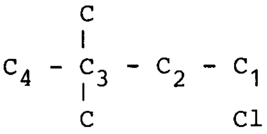
Table 1

Chemical Shifts in C-13 NMR Spectra of Vinylchloride Oligomers

Carbon	Oligomer IV	Oligomer V	Oligomer VI	Oligomer VII
1	42.41	43.03	41.21	41.27
2	46.96	41.64	41.17	39.99
3	30.75	56.37	57.63	56.46
4	29.24	52.15	49.10	48.69
5	-	30.88	56.85	55.64
6	-	29.80	52.53	51.31
7	-	-	30.94	30.70
8	-	-	29.82	29.86

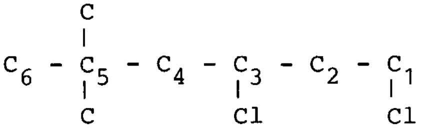
Figure 4

STRUCTURE OF VINYLCHLORIDE OLIGOMERS



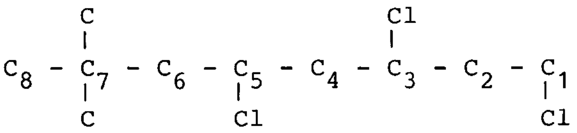
$$C_4 - \underset{C}{\overset{C}{C_3}} - C_2 - \underset{Cl}{C_1}$$

IV



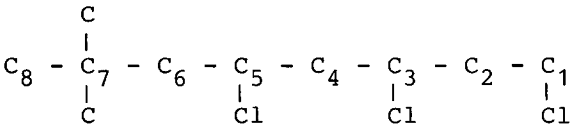
$$C_6 - \underset{C}{\overset{C}{C_5}} - C_4 - \underset{Cl}{C_3} - C_2 - \underset{Cl}{C_1}$$

V



$$C_8 - \underset{C}{\overset{C}{C_7}} - C_6 - \underset{Cl}{C_5} - C_4 - \overset{Cl}{C_3} - C_2 - \underset{Cl}{C_1}$$

VI



$$C_8 - \underset{C}{\overset{C}{C_7}} - C_6 - \underset{Cl}{C_5} - C_4 - \underset{Cl}{C_3} - C_2 - \underset{Cl}{C_1}$$

VII

Further studies to elucidate the structure of higher oligomers which have been generated by termination are in progress and will reported in a subsequent paper.

EXPERIMENTAL

The chromatographic equipment comprised a Dupont Preparative HPLC system provided with 2 Dupont ODS columns (21x250 mm). Sample injections of 20% (w/v) polymer solutions were made through a Rheodyne valve set to a loop volume of 20 ml. For recording elution curves refractive index monitors were used (Knauer Differentialrefraktometer and Multiref 902B, Optilab). Fractions have been accumulated by a FOXY (ISCO Corp.) fraction collector. The freshly destilled aceotrop of acetonitrile and water (9:1) was used as an isocratic solvent. The chromatographic system was operated at ambient temperature at a flow rate of 20 ml/min. After evaporation of the solvent oligomers were dissolved in $CDCl_3$ for nmr analysis.

C-13 nmr spectra were recorded by a BRUKER WM 300 at 75.47 MHz according to the Software Manual (release 810515) program 3: power gated decoupling. Program variables were set as required: D1 = 60 s, S1 = 14 H, D2 = 0.01 s, S2 = 5H, PW = 15.5 us, SW = 12.13 kHZ, and NS = 25 scans. JMSE spectra were controlled by program 19: J-modulated spin echo. The following variables have been used: D1 = 60 s, S1 = 13H, D2 = 0.001 s, S2 = 5H, P1 = 17.5 us, P2 = 35 us, SW = 12.13 kHZ, NS = 1024 scans and VD = 8,10,12 and 20 ms. Chemical shifts observed at 300 K are referenced to TMS = 0 ppm.

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