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HPLC and C-13 NMR Spectroscopy of Polymers

2. Oligomers of Poly (Vinylchloride)

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Summary

Vinylchloride oligomers have been prepared by t-butyllithium in THF at 280 K. Constitutional and configurational structures of oligomers have been determined by joint HPLC and C-13 nmr spectroscopy. C-13 nmr spectra of diastereomeric oligomers of DP = 4 have been analyzed and assigned.

Introduction

In a preceeding paper we reported the fractionation and characterisation of styrene oligomers by HPLC and C-13 nmr spectroscopy(1). We extended this technique to polar vinylchloride oligomers and to HPLC in a reversed phase system. The object of the present study is the structure of vinylchloride oligomeres prepared by t-butyllithium. As the polymer is suggested to be linear (2,3) oligomers can be used as standards for future investigations of vinylchloride oligomers starting with a t-butyl group.

Results and Discussion

Oligomers have been prepared by polymerisation of vinylchloride by t-butyllithium (2,3). The initial monomer/initiator ratio was 3. Due to the proposed mechanism of the polyreaction the following oligomers up to DP = 4 are to be expected in low yield:

1-chloro-3,3-dimethylbutane	I
1,3-dichloro-5,5-dimethylhexane	II
threo-1,3,5-trichloro-7,7-dimethyloctane	III
erythro-1,3,5-trichloro-7,7-dimethyloctane	IV
ribo-1,3,5,7-tetrachloro-9,9 dimethyldecane	V
xylo-1,3,5,7-tetrachloro-9,9-dimethyldecane	VI
arabino-1,3,5,7-tetrachloro-9,9-dimethyldecane	VII
lyxo-1,3,5,7-tetrachloro-9,9-dimethyldecane	VIII

I-IV are identical structures of oligomers, which have been determined for oligomers prepared by t-butylmagnesiumchloride. (5). **II**, **III** and **IV** have been isolated and identified in the system under study. Thus, the following analysis is concerned only with the diastereomeric isomers of 1,3,5,7-

tetrachloro-9,9-dimethyldecane (= TCDMD). From subsequent fractions the isomers RM and MM can be isolated in sufficient purity. Fig. 1a and 1b show the spectra of the ribo-isomer MM and the mixture of the diastereomeric oligomers, respectively.

The interpretation of C-13 nmr spectra were performed using

a) chemical shift parameters, derived from 2,2-dimethylalkanes and 1-chloroalkanes
b) C-13 broad band decoupled nmr spectra
c) J-modulated spin echo (4)
d) spectra of DP = 1-3 as demonstrated in (5) and
e) concentration ratio of **III** and **IV**

It was not possible to assign the C-13 spectra in Fig. 1b completely by chemical shift parameters, which are too inaccurate to predict chemical shift differences smaller than 1 ppm. The signals of the terminating $-CH_2-CH_2Cl$ group are overlapping. Separation and identification of these signals becomes successful by application of the J-modulated spin echo (4) as the carbons are different by chlorine substitution. A unique feature of this technique is the selective observation of protonated and chlorine substituted carbons even in the case of overlapping resonance signals. Assignment and chemical shifts of the 4 stereoisomers under study are given in Table 1. For chemical shifts of oligomers **I-IV** see (5). Fischer projections of the molecules are shown in Fig. 3.

In terms of macromolecular stereochemistry the corresponding pairs of TCDMD diastereomer and the configurational monomer enchainment are

V = ribo-TCDMD ≡ MM
VI = xylo-TCDMD≡ RR
VII = arabino-TCDMD ≡ RM
VIII = lyxo-TCDMD ≡ MR

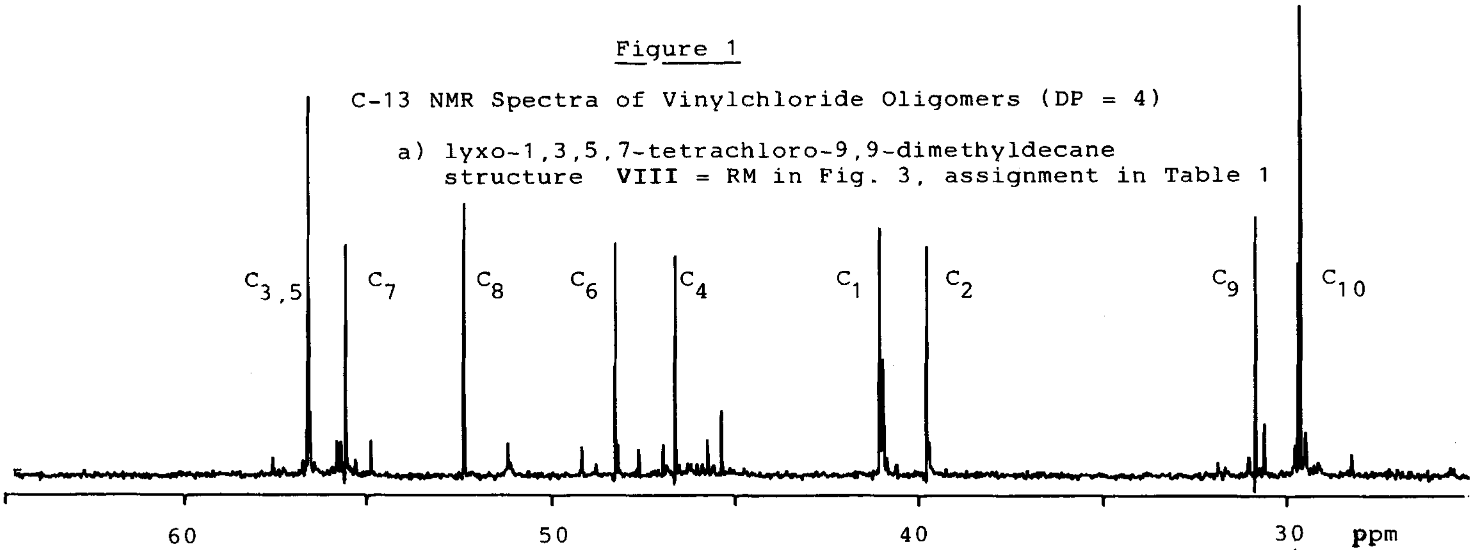
Relative concentrations of **III** and **IV** are equivalent to diad probabilities R and M, resp.. The syndiotactic monomer enchainment has been determined to R = 0.58. According to Bernoullian statistics triad probabilities can be calculated. Observed and predicted values are in good agreement as given in Table 2. The results are derived from a completely resolved part of the spectrum as shown in Fig. 3. As a result, the sequence of 4 monomer units can be described quantitatively, even for MR and RM which are found indistinguishable in polymer spectra.

In contrast to the t-butylmagnesiumchloride system no polymeric termination product has been found. Propagation and dehalogenation of the monomer by the catalyst are competing reactions. Results given here and in (1) clearly demonstrate the great potential of joint HPLC and C-13 nmr. Limiting factors are the resolution of the chromatograms and of the C-13 nmr spectra.

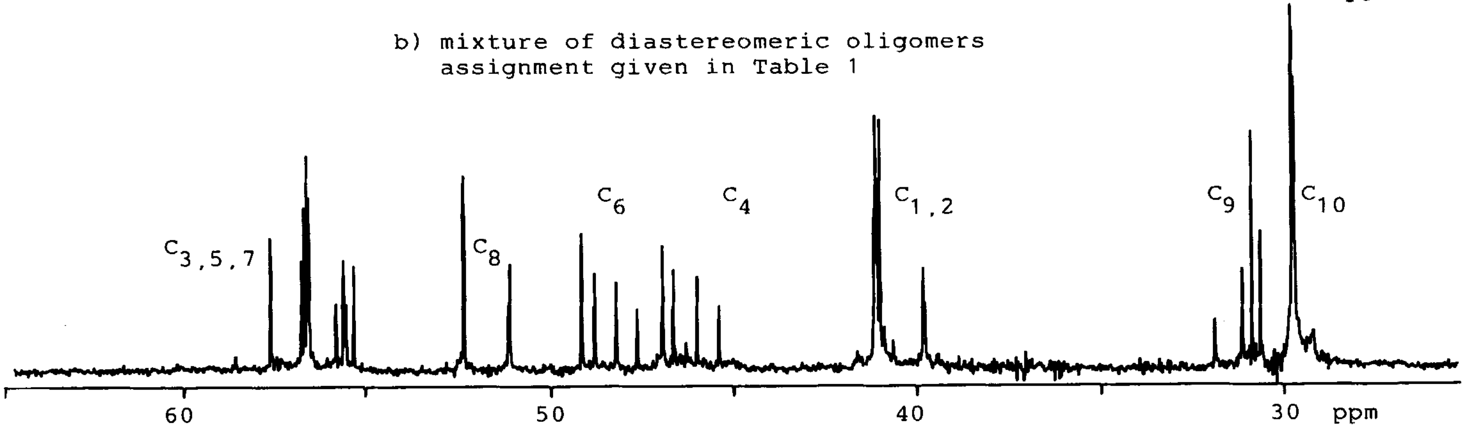
Figure 1

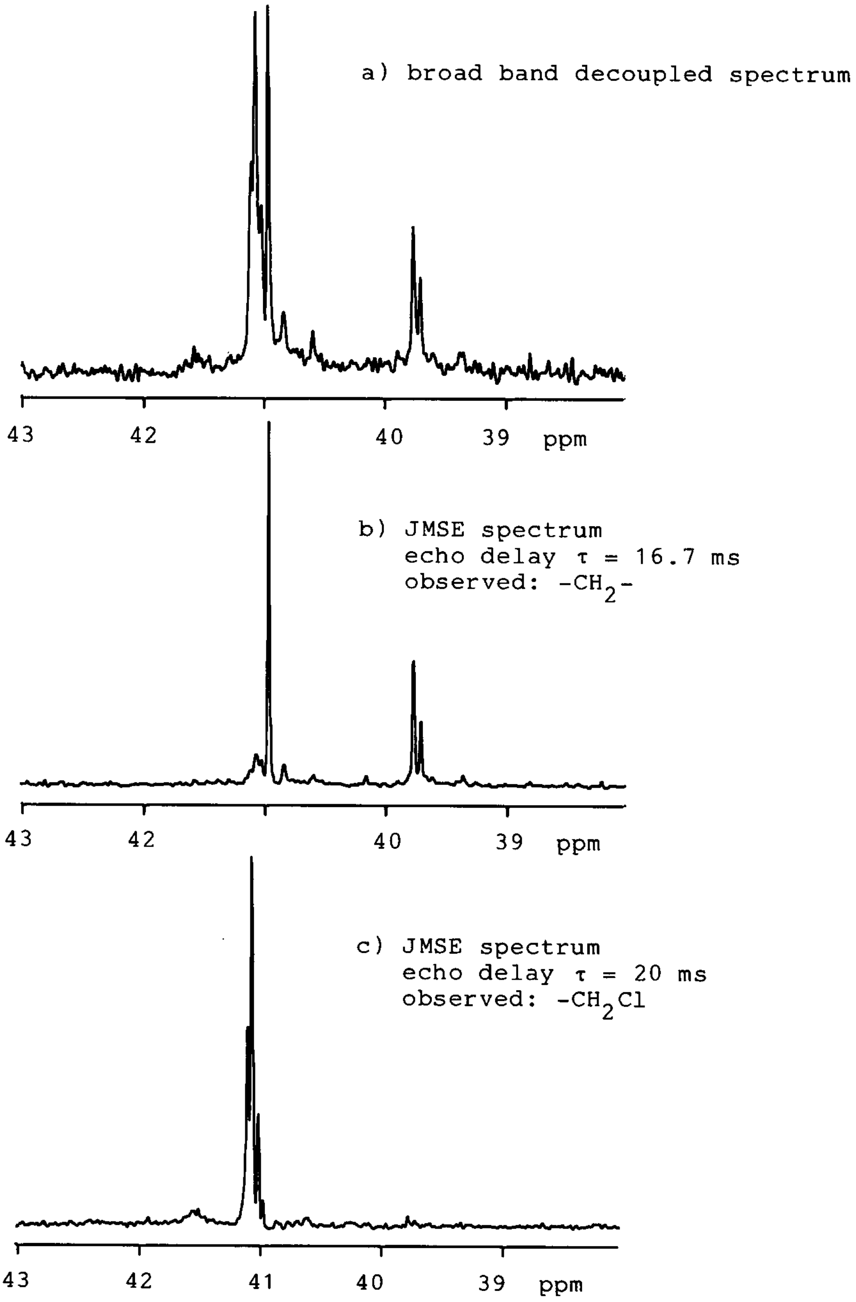
C-13 NMR Spectra of Vinylchloride Oligomers (DP = 4)

a) lyxo-1,3,5,7-tetrachloro-9,9-dimethyldecane
structure **VIII** = RM in Fig. 3, assignment in Table 1



b) mixture of diastereomeric oligomers
assignment given in Table 1





a) broad band decoupled spectrum

b) JMSE spectrum
echo delay τ = 16.7 ms
observed: $-CH_2-$

c) JMSE spectrum
echo delay τ = 20 ms
observed: $-CH_2Cl$

Figure 2

C-13 NMR Spectrum of 1,3,5,7-tetrachloro-9,9-dimethyldecane

Expanded resonance region from 38 - 43 ppm

Table 1

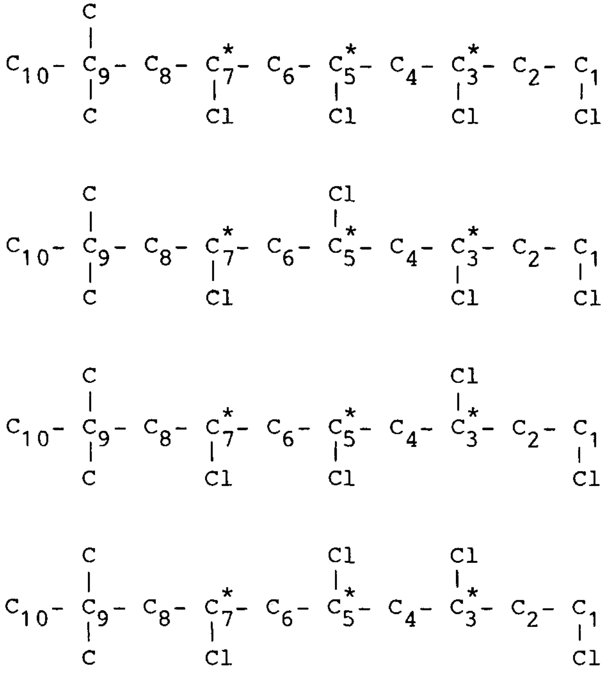
C-13 Chemical Shifts of Vinylchloride Oligomers
(Degree of Polymerisation = 4)

Carbon	V = MM	VI = RR	VII = MR	VIII = RM
1	41.09a)	41.13	41.09a)	41.03
2	40.97a)	39.78	40.97a)	39.72
3	55.82	57.63	56.78	56.62
4	45.36	46.92	45.97	46.62
5	55.60	56.71	56.56	56.62
6	47.63	49.15	48.79	48.20
7	55.54	56.58	55.33	55.63
8	51.13	52.33a)	51.10	52.33a)
9	30.81a)	31.05a)	30.81a)	31.05a)
10	29.87a)	29.84a)	29.87a)	29.84a)

a) signal not completely resolved

Figure 3

Structure of Vinylchloride Oligomers
(Degree of Polymerisation = 4)



$$\mathrm{C_{10}-\underset{C}{\overset{C}{C_9}}-C_8-\underset{Cl}{C_7^*}-C_6-\underset{Cl}{C_5^*}-C_4-\underset{Cl}{C_3^*}-C_2-\underset{Cl}{C_1}}$$

V

$$\mathrm{C_{10}-\underset{C}{\overset{C}{C_9}}-C_8-\underset{Cl}{C_7^*}-C_6-\overset{Cl}{C_5^*}-C_4-\underset{Cl}{C_3^*}-C_2-\underset{Cl}{C_1}}$$

VI

$$\mathrm{C_{10}-\underset{C}{\overset{C}{C_9}}-C_8-\underset{Cl}{C_7^*}-C_6-\underset{Cl}{C_5^*}-C_4-\overset{Cl}{C_3^*}-C_2-\underset{Cl}{C_1}}$$

VII

$$\mathrm{C_{10}-\underset{C}{\overset{C}{C_9}}-C_8-\underset{Cl}{C_7^*}-C_6-\overset{Cl}{C_5^*}-C_4-\overset{Cl}{C_3^*}-C_2-\underset{Cl}{C_1}}$$

VIII

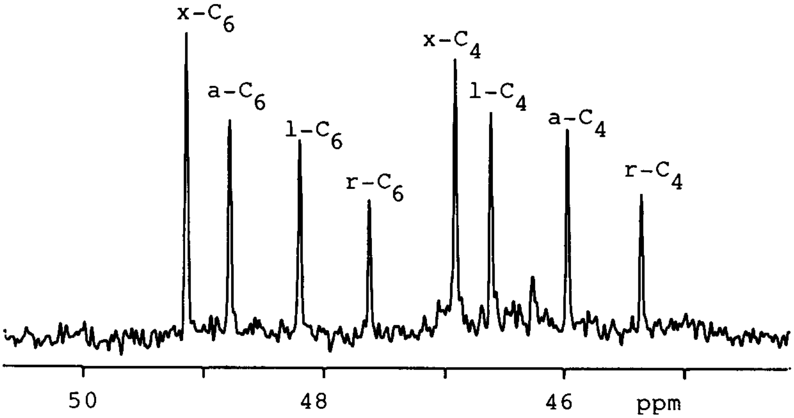


Figure 4

C-13 NMR Spectrum of 1,3,5,7-tetrachloro-9,9-dimethyldecane Expanded resonance region of C_4 and C_6 from 45 - 50 ppm for assignment see Table 1, quantitative results are given in Table 2;x = xylo-, a = arabino-, l = lyxo- and r = ribo-1,3,5,7-TCDMD

Table 2

Normalized Signal Intensities[a]

Carbon	V = MM	VI = RR	VII = MR	VIII = RM
3	0.17	0.33	0.25	0.25a)
4	0.17	0.34	0.23	0.25
5	0.18	0.34	0.24	0.24a)
6	0.17	0.34	0.26	0.24
7	0.15	0.33	0.26	0.25
calc.:[c]	0.18	0.34	0.24	0.24

a) for assignment of carbon C_3 - C_7 see Table 1

b) 0.5*observed signal intensity (overlapped signals)

c) calculated according to Bernoullian statistics, R = 0.58

Experimental

Vinylchlorid dried over KOH was condensed at 240 K to a 200 ml hexane solution of the initiator precoooled in a thick-walled reaction vessel. The concentration of t-butyllithium was 1.5 $\mathrm{mol \cdot l^{-1}}$. After mixing the polymerisation was finished at 280 K within 8 hours. Reactions were terminated by addition of HCl. Oligomers were achieved from the hexane solution by evaporation of the solvent. The yield was 10%.

C-13 nmr spectra were recorded at 75.47 MHz in $CDCl_3$. The chromatographic equipment comprised 2 reversed phase columns (21x250 mm). Acetonitrile/water (88/12%) was used as an isocratic eluent. This system provides fractionation of oligomers up to DP = 8. Spectroscopical as well as chromatographic details are given in (5).

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References

1.) K.-F. Elgert, R. Henschel, H. Schorn and R. Kosfeld, Polymer Bulletin, 4, 105 (1981)

2.) M. Kudrna, V. Jisova, M. Kolinsky, J. Polym. Sci., 15, 2367 (1977)

3.) V. Jisova, M. Kolinsky and D. Lim, J. Polym. Sci., A-1, 8, 1525 (1970)

4.) K.-F. Elgert and R. Kosfeld, J. Magn. Res., in preparation

5.) K.-F. Elgert and R. Kosfeld, Polymer Bulletin, **10**, 175 (1983)

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