Polymer Bulletin 9, 423–428 (1983)

**Polymer Bulletin**

# Polymerization of Vinylchloride by *t*-Butylmagnesiumchloride

## 1. Terminating End Group

**K.-F. Elgert, R. Henschel and R. Kosfeld**

Universität (GH) Duisburg, FB 6 Physikalische Chemie, 4100 Duisburg 1,
Federal Republic of Germany

***To Prof. Dr. H.-J. Cantow on his 60th birthday with our best wishes***

## SUMMARY

Vinylchloride can be polymerized in THF by t-butylmagnesiumchloride as an initiator. Polymers obtained are free of carbon double bonds. Leading t-butyl as well as terminating $-CH_2-CH_2Cl$ have been identified as end groups by C-13 nmr spectroscopy. According to the monomer/initiator ratio oligomers as well as high polymers have been prepared.

## INTRODUCTION

Structure and reactivity of Grignard reagents in ether solvents have been subject to intensive investigations by organic chemists. In contrast to these considerable efforts Grignard reagents found only limited application as catalysts in polymerisation reactions. Especially, t-butylmagnesiumchloride in THF has been used for polymerisation of poly(vinylchloride) (PVC) which was suggested to have the following structure (GUYOT et al. (1963), (1964))

$$(CH_3)_3C- (CHCl-CH_2-)_n\ CH=CH_2 \qquad (I)$$

generated by abstraction of chlorine from the ultimate monomer unit accompanied by formation of $MgCl_2$. The existence of a terminating carbon double bond as well as a leading t-butyl group should be easily revealed by C-13 nmr spectroscopy.

## RESULTS AND DISCUSSION

Polymerisations have been performed as described in the experimental section. The polyreaction under study is characterized by a fast initiation. The initially homogenous reaction mixture becomes cloudy at increasing conversions by precipitation of $MgCl_2$. Typical results are listed in Table 1.

Low yield of polymeric material of sample 1 and 2 in Table 1 indicate a considerable amount of termination. Grignard reagents exist in the well known Schlenk equilibrium

$$2\ R-Mg-Cl \rightleftarrows R_2Mg + MgCl_2 \qquad (II)$$

and

$$(R-Mg-Cl)_n \rightleftarrows n \cdot R-Mg-Cl \quad ; \qquad (III)$$

t-butylmagnesiumchlorid or its associates solvated by THF (PARIS et al. (1971)) can be easily recognized as the initiating species. Addition of $MgCl_2$ to a solution of the Grignard reagent shifts the equilibria in (II) and (III) to the left increasing the concentration of the active initiator.

Consequently, the monomer/initiator ratio as well as the molecular weight of the polymer are diminished. This is confirmed by sample 3 in Table 1. Full proportionality between the monomer/initiator ratio and the molecular weight cannot be expected since the concentration of the active catalyst depends on the actual position of the equilibria (II) and (III). Furthermore, molecular weights are influenced by the termination reaction rate. The entire mechanism is not completely understood at present time.

Typical C-13 nmr spectra of low and high molecular weight samples are shown in Fig. 1 and 2. Interpretation of the spectra is based on C-13 nmr spectra of 1-chloroalkanes (STOTHERS (1972)) and PVC (ELGERT et al. (1981)) aided by H-1 nmr spectra as well as by common homo and hetero decoupling techniques. Chlorine substituted carbons have been identified by extensive application of J-modulated spin echo (ELGERT et al. (1983)). Results are summarized in Table 2.

In contrast to the expected structure of the terminating end group in (I) no aliphatic carbon double bonds in the resonance region G between 110 and 150 ppm are recorded in Fig. 1 and 2. A leading t-butyl group according to (I) is detected in B in Fig. 1 and 2. Resonance signals of $-CH_3$ and $CH_2$ groups in A indicate several unknown by-products to an amount of 5 - 10%. Thus it is reasonable to explain the formation of $MgCl_2$ during polymerisation by rearrangement of the propagating species or termination by alkylation rather than by chlorine abstraction from the ultimate monomer unit.

Configurational monomer sequences are identified in D and F of Fig. 2. Corresponding resonance signals of -CHCl- and $-CH_2-$ are recorded between 54-58 ppm and 44-48 ppm, respectively. Chemical shifts for -CHCl- are in excellent agreement with assignments reported earlier from radically prepared PVC (ELGERT et al. (1981)). Quantitative analysis of signal intensities results in a syndiotactic enchainment R = 0.6 of the PVC backbone chain. From triad probabilities a slight deviation from Bernoullian statistics is calculated to $d = 2 \cdot R(1-R)/MR = 0.96$. A regular head-to-tail enchainment of the monomer is highly probable. Limitations in the nmr analysis of high polymers are obvious as the end group concentrations are to low to be detected. For n >> 1 there is no appreciable distinction between (IV) and (V)

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

(IV) (V)

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

## Table 1

### Polymerisation of Vinylchloride

| Sample | $RMgCl$[a] \|mmol · $l^{-1}$\| | $M_o$[b] \|mol · $l^{-1}$\| | $MgCl_2$[c] \|mol · $l^{-1}$\| | Yield \|%\| | $\bar{M}_{LS}$[d] |
|---|---|---|---|---|---|
| 1 | 50 | 8 | - | 39.4 | 5400 |
| 2 | 5 | 8.3 | - | 22.3 | 46300 |
| 3 | 5 | 8.1 | 0.1 | 36.0 | 29000 |

[a] concentration of Grignard reagent

[b] concentration of monomer, vinylchloride

[c] addition of t-butylmagnesiumchloride

[d] molecular weight determined by LALLS, see Experimental

## Table 2

### Structural Assignment of C-13 NMR Spectra of PVC

| Resonance signals[a] | Carbon | |
|---|---|---|
| A 0-29 | $-CH_3$, $-CH_2-$ | by-products of uncertain structure<br>termination and alkylation |
| B 29-32 | $-C(CH_3)_3$ | t-butyl group of initiator |
| C 39-45 | $-CH_2-CH_2Cl$ | terminating end group |
| D 45-50 | $-CH_2$ | PVC backbone chain, configurational sequences |
| E 65, 55 | $-CH_2-$, $-CH-$ | short chain PVC |
| F 55-62 | $-CHCl-$ | PVC backbone chain, configurational sequences |
| G 110 - 150 | $-CH=CH-$ | aliphatic carbon double bounds |

[a] resonance region in Fig. 1 and 2, chemical shift in ppm

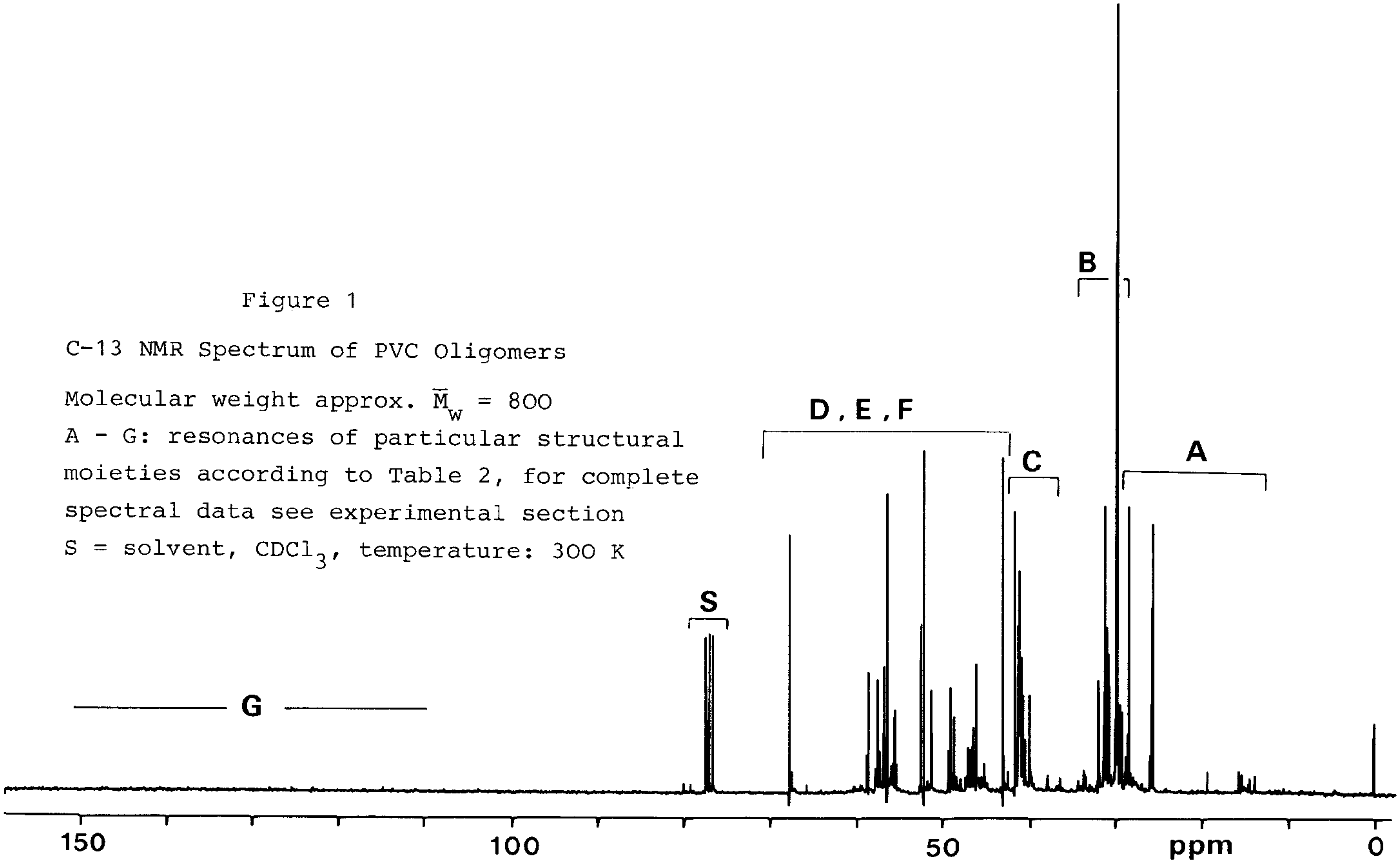

Figure 1

C-13 NMR Spectrum of PVC Oligomers

Molecular weight approx. $\overline{M}_w$ = 800

A - G: resonances of particular structural moieties according to Table 2, for complete spectral data see experimental section

S = solvent, $CDCl_3$, temperature: 300 K

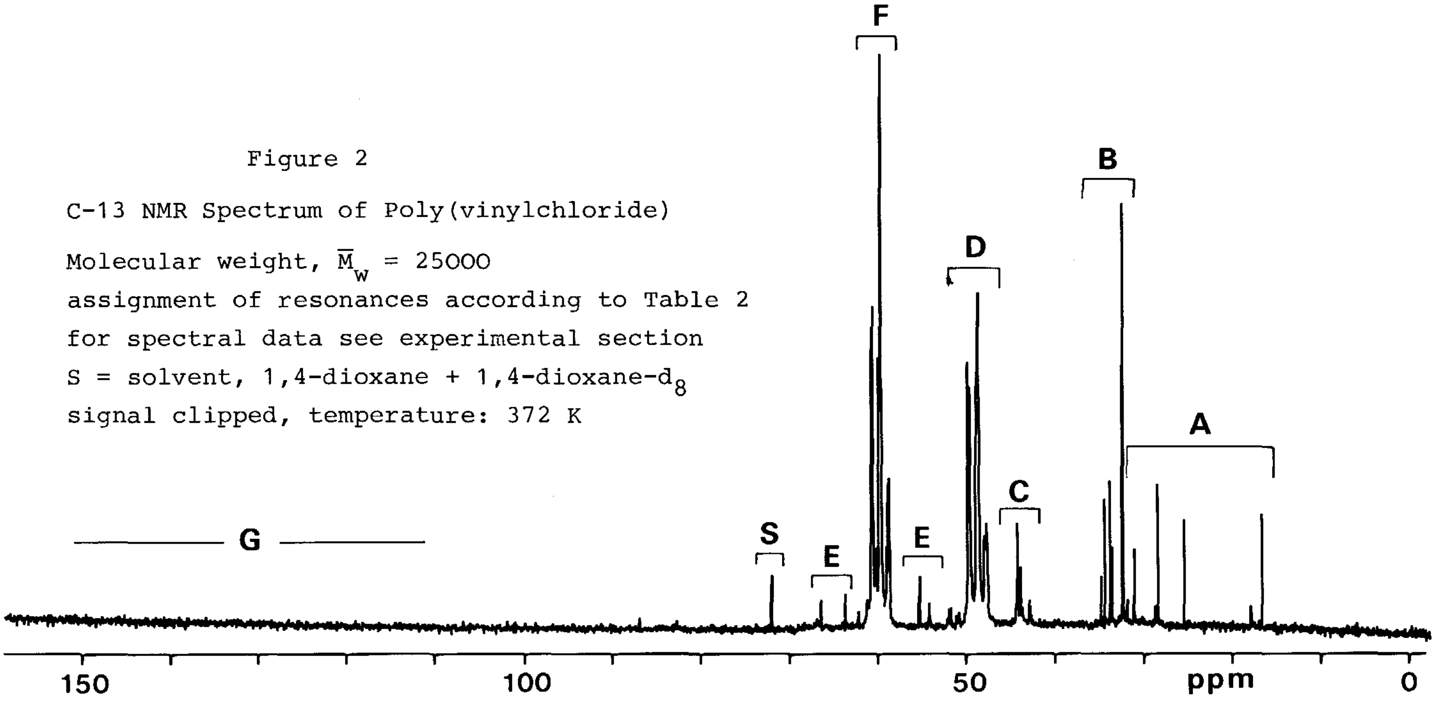

Figure 2

C-13 NMR Spectrum of Poly(vinylchloride)

Molecular weight, $\overline{M}_w$ = 25000

assignment of resonances according to Table 2

for spectral data see experimental section

S = solvent, 1,4-dioxane + 1,4-dioxane-$d_8$

signal clipped, temperature: 372 K

Furthermore, the analysis of oligomer mixtures in Fig. 1 is hindered by overlapping of resonance signals. Any desired decision on the enchainment of the trailing monomer units can be derived only from C-13 nmr spectra of isolated oligomers. Corresponding investigations have been started and will be delt with in a subsequent paper.

## EXPERIMENTAL

The initiator was prepared from dried t-butylchloride and excess Mg of commercial grade (Merck-Schuchardt, 99%) by common techniques. THF was freshly destilled over $LiAlH_4$. The concentration of the Grignard solution was 2 mol · $l^{-1}$. Vinylchloride was dried over KOH and condensed at 240 K to a 250 ml THF solution of the initiator precooled in a thick-walled reaction vessel. After mixing the polymerisation was completed at 300 K within 12 hours. Polymerisation in the presence of $MgCl_2$ have been initiated by a suspension of $MgCl_2$ in the Grignard solution. Reactions were terminated by addition of HCl. Polymers as well as oligomers were isolated and purified by precipitation from THF solutions.

Characterisation with respect to the molecular weight has been achieved by joint gel permeation chromatography (GPC) and low angle laser light scattering (LALLS). To GPC 4 columns were applied ($10^5$ Å, $10^4$ Å, $10^3$ Å, $10^2$ Å). Molecular weight determinations by LALLS (Chromatix, KMX-6) at 300 K are based on a refractive index increment dn/dc = 0.101.

C-13 nmr spectra were recorded by a Bruker WM 300 at 75.473 MHz under software control according to the WM 300 Software Manual (release 810515, programm 3: power gated decoupling). Programm variables were set as follows: D1 = 60s, S1 = 14H, D2 = 0.01 s, S2 = 5H, PW = 18.5 µs, SW = 12.13 kHz and S = 1000 scans; sensitivity enhancement by Gauss multiplication, GB = 0.15, LB = -1.5. Spectra are broadband decoupled and referenced to TMS = o ppm.

## ACKNOWLEDGEMENT

The financial support of the Arbeitsgemeinschaft Industrieller Forschungsgemeinschaften (AIF), Köln, is gratefully acknowledged. The authors are indebted to Thyssen Niederrhein AG, Duisburg, for providing with laboratory rooms.

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*Received January 21, accepted January 24, 1983*