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SYNTHESIS OF POLY(2-CHLORO ETHYL VINYLETHER) AND ITS DERIVATIVES

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ABSTRACT

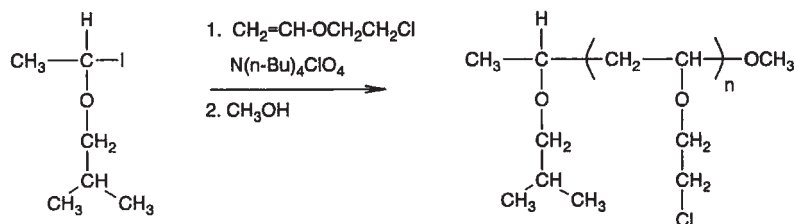
The cationic polymerization of 2-chloro ethyl vinyl ether (CEVE) is initiated by 1-iodo-1-(2-methylpropyloxy)ethane/ $(n\text{-Bu})_4\text{NClO}_4$. The monomer is consumed following first order kinetics. Molar masses are controlled by the ratio $[M]:[I]$. A rather narrow molar mass distribution is obtained. These observations and the linear conversion-molar mass relationship indicate the living nature of the CEVE polymerization. Poly(CEVE) was converted into poly(2-(1-pyrrolidonyl)-1-ethylvinylether) by the complete nucleophilic substitution of chlorine by the anion of pyrrolidone.

INTRODUCTION

Cationic polymerization of 2-chloro ethyl vinyl ether (CEVE) has already been studied in some detail. Important work was

published by Higashimura et al. on the initiation of CEVE by HI/I₂¹⁾ and by Deffieux et al. on the initiation by HI/ZnI₂²⁾ and 1-iodo-1-(2-methylpropyloxy)ethane ZnCl₂/ZnI₂ respectively^{3,4)}.

In this contribution we will describe the polymerization of CEVE initiated by 1-iodo-1-(2-methylpropyloxy)ethane/(n-Bu)₄NClO₄ according to the following scheme:



Another objective of this study is to synthesize a polyvinylether with pyrrolidone as polar side groups.

RESULTS AND DISCUSSION

Polymerization of CEVE was carried out in CH₂Cl₂ at -10°C by adding successively a solution of 1-iodo-1-(2-methylpropyloxy)ethane in n-hexane and a solution of (n-Bu)₄NClO₄. The monomer conversion was followed by gas chromatography with toluene as internal standard. Typical experimental data are given in TABLE 1.

The plot of ln(1-C) against the time (FIG. 1) is a straight line which indicates, that monomer consumption follows the first order kinetics.

The polymerization rate of CEVE is remarkable slower than that of e.g. isobutylvinylether (IBVE)^{1,2,6)}. However, the initiation is fast and only the chain growing is a slow reaction, which one can conclude from FIG. 3.

From earlier experiments with this initiating systems we know that the actual ion concentration is very low⁷⁾.

TABLE 1:

Polymerization of CEVE initiated by 1-iodo-1-(2-methyl-propyl-oxy)ethane (I) / $(n\text{-Bu})_4\text{NClO}_4$ (A) .

$[\text{CEVE}]_0 = 0,99 \text{ mol l}^{-1}$, $[\text{I}]_0 = 0,02 \text{ mol l}^{-1}$

$[\text{A}] = 0,02 \text{ mol l}^{-1}$, $T = -10^\circ\text{C}$

time	conversion (%)	$\ln(1-C)$
10 min	4,1	-0,042
75 min	9,5	-0,198
6 h	26,8	-0,312
19 h	58,0	-0,868
27 h	71,5	-1,255
44 h	88,0	-2,120

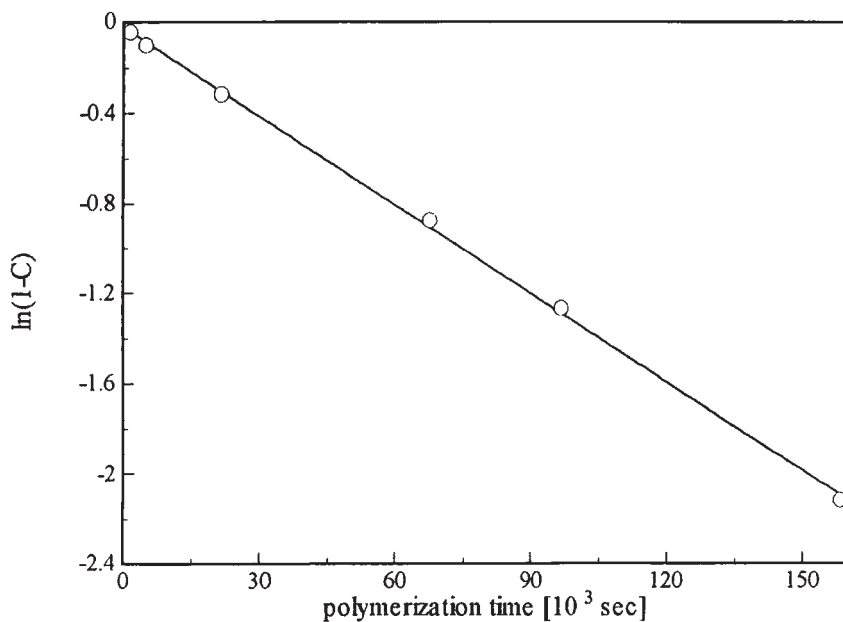


FIG. 1: Polymerization of CEVE with 1-iodo-1-(2-methyl-propyloxy)ethane / $(n\text{-Bu})_4\text{NClO}_4$ in CH_2Cl_2 at -10°C .

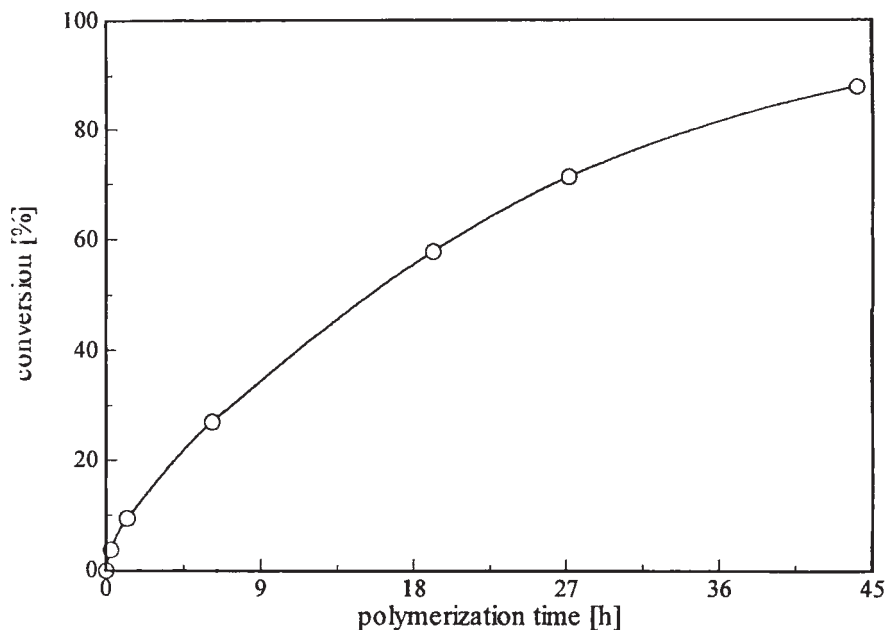


FIG. 2: Polymerization of CEVE with 1-iodo-1-(2-methyl-propyloxy)ethane/ $(n\text{-Bu})_4\text{NClO}_4$ in CH_2Cl_2 at -10°C .

Therefore we assume that reversible termination plays an important role in this type of polymerization.

The agreement of calculated and observed molar masses is not perfect (TABLE 2). FIG. 4 shows clearly a linear molar mass-conversion relationship, which points to a living system.

REACTION OF POLY(CEVE) WITH PYRROLIDONE

Since 2-(1-pyrrolidonyl)ethyl vinyl ether (PEVE) could not be polymerized with the initiating systems applied for CEVE⁶⁾ we have tried to synthesize poly(PEVE) by

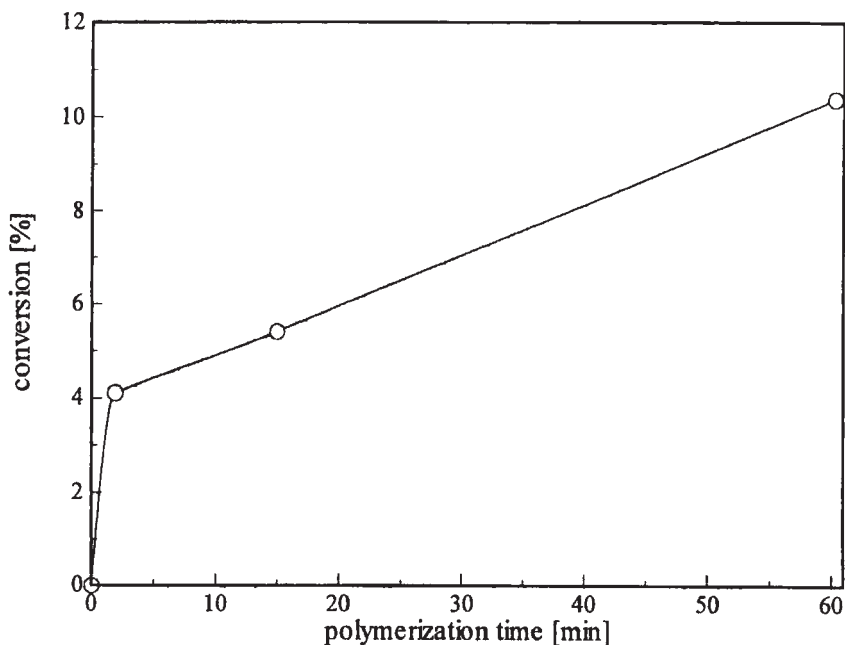


FIG. 3: Polymerization of CEVE with 1-iodo-1-(2-methylpropyloxy)ethane/ $(n\text{-Bu})_4\text{NClO}_4$ in CH_2Cl_2 at -10°C , first 60 min.

TABLE 2:

Polymerization of CEVE, initiated by 1-iodo-1-(2-methylpropyloxy)ethane/ $(n\text{-Bu})_4\text{NClO}_4$ in CH_2Cl_2 at -17°C ; $[M]_0 = 1,0 \text{ mol l}^{-1}$, $[I]_0 = 0,03 \text{ mol l}^{-1}$, $[A] = 0,023 \text{ mol l}^{-1}$

t	C %	$M_n(\text{GPC})^1)$	$M_n(\text{calc.})$	M_w/M_n
5 min	5,4	470	324	1,40
20 min	8,1	520	420	1,38
1 h	12,3	620	569	1,32
4 h	28,4	970	1140	1,34
9 h	47,3	1430	1811	1,28
18 h	70,7	2050	2642	1,26
27 h	77,2	2480	2873	1,21

1) calibrated with polystyrene standards

2) calc. from $M_n = M_M ([M] / [I]) \cdot C + M_{\text{Head}} + M_{\text{End}}$

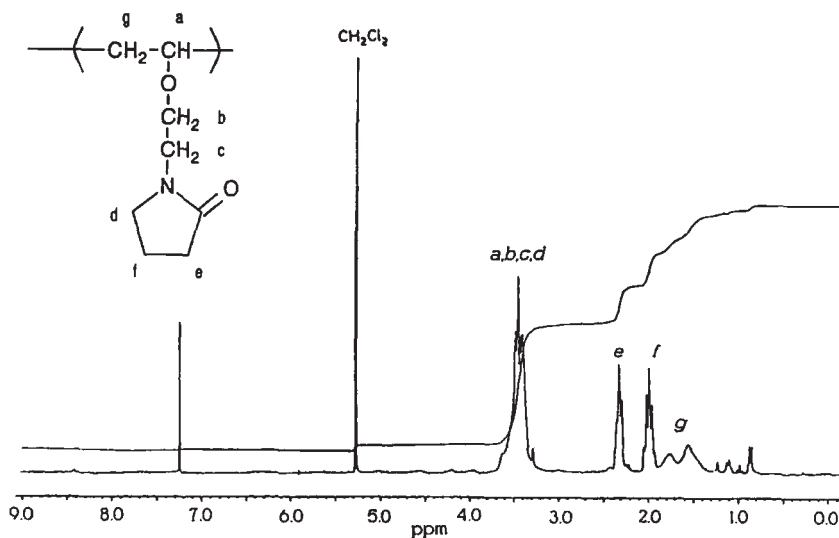


FIG. 5: ^1H NMR of poly(2-(1-pyrrolidonyl)ethyl vinyl ether) in CDCl_3 .

poly(CEVE) belong to the protons e, f of the pyrrolidone ring. Equation [1] can be used for a quantitative calculation of the degree of substitution.

$$5 \times I_{\text{CEVE}} = I_{\text{A}} - (I_{\text{p}}/2) \times 7 \quad [1]$$

I_{CEVE} = Integral of one proton of CEVE

I_{A} = Integral of the region 3,9-3,2 corresponding with 7 protons of a substituted unit (a,b,c,d) and 5 protons of an unsubstituted chlorinated unit (a,b,c)

I_{p} = integral over 2 protons of the pyrrolidone ring (the signals at 2.0 or 2,3 representing 2 protons each).

The calculation revealed that the substitution of the chlorine was 100%. This result is supported by elemental analysis which does not show any residual chlorine. The molar mass of poly(PEVE) according to GPC (560 g mol^{-1}) was much lower than the calculated value of 3360 g mol^{-1} (by taking into consideration of the molecular weight of the poly(CEVE) adduct as $M_n = 2350 \text{ g mol}^{-1}$). However, we believe that this is due to the higher polarity of the product poly(PEVE) compared with the poly(CEVE) adduct and therefore the elution time is extended. This view is strongly supported by the molar mass determined via ^1H NMR : 3240 g mol^{-1} which is close to the calculated value of 3360 g mol^{-1} .

EXPERIMENTAL PART

INSTRUMENTS

IR: Digilab FTS-40 (FT-IR); ^1H NMR: Bruker AC 250 (250 MHz); ^{13}C NMR: Bruker AC 250 (62,5 MHz); GPC: Waters 510, Waters 590 RI, THF; DSC: Perkin Elmer DSC 7; GC: Varian GC 3700, column CP Sil 5CB; Cryostate: Lauda UK 8 DW.

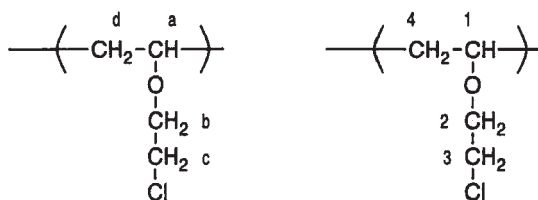
CHEMICALS

Solvents were dried and freshly distilled before use. Isobutylvinylether (Fluka) and 2-chloroethyl vinylether (Fluka) were dried over CaH_2 and freshly distilled before use. Tetrabutylammonium perchlorate (Fluka) was dried for 24 hrs under high vacuum conditions and stored under argon. 1-Iodo-1-(2-methylpropyl-oxy)ethane was synthesized as described in the literature⁷⁾.

Poly(CEVE)

The polymerization of 2-chloroethyl vinylether (CEVE) was carried out in methylene chloride under argon at -10°C in the presence of xylene as internal standard (for

quant. determination of conversion by GC). 1-Iodo-1-(2-methylpropyl-oxy)ethane and $(n\text{-Bu})_4\text{NClO}_4$ (see Table 1) were added to CEVE to initiate the polymerization. After complete conversion of CEVE the polymerization was quenched with methanol/aqu. NH_3 . The polymer solution was then washed with $\text{Na}_2\text{S}_2\text{O}_3$ (10% solution in water) and with water. The solution was dried over sodium sulfate. Then the solvent was removed in vacuum and the residue was redissolved in toluene. Insoluble salts were filtered off. After removal of the solvent the polymer was dried in vacuum and characterized.



^1H NMR (CDCl_3) δ (ppm): 3,9-3,4 ($\text{H}^{\text{a}}, \text{H}^{\text{b}}, \text{H}^{\text{c}}$); 2,0-1,4 (H^{d})

^{13}C NMR (CDCl_3) δ (ppm): 73,6 (C^1); 68,7 (C^2); 43,7 (C^3); 41-39 (C^4)

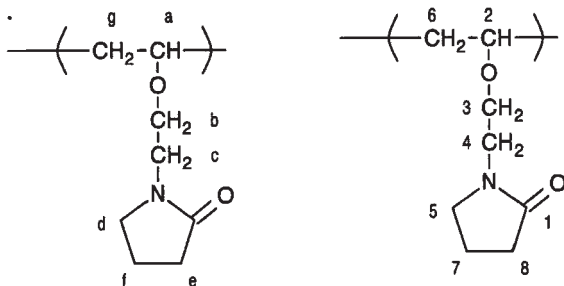
Poly(2-(1-pyrrolidonyl)ethyl vinyl ether)

1,11 g (13 mmol) pyrrolidone, 0,05 g (0,15 mmol) tetrabutylammoniumbromide and 1,35 g (12 mmol) potassium t-butylate were dissolved in 15 ml dimethylformamide (DMF) and stirred at room temperature for one hour. Then 1 g of poly(CEVE) ($M_n = 2350 \text{ g mol}^{-1}$) dissolved in 10 ml toluene was added slowly. This mixture was heated up to 70°C and stirred for 16 hrs at this temperature. After cooling to room temperature the mixture was filtered. The precipitate was washed with toluene and DMF. Then the filtrate was dropped into diethylether at -60°C . The precipitate was washed several time with cool diethylether (-60°C), redissolved in a small portion of CH_2Cl_2 and cleared off by centrifugation. After

separation of the solvent an oily product was received.

Yield: 0,7 g (50%)

IR (film) cm^{-1} : 2926, 2878 (CH); 1689, 1681 (CO); 1118, 1097 (COC).



^1H NMR (CDCl_3) δ (ppm): 3,9-3,3 ($\text{H}^a, \text{H}^b, \text{H}^c, \text{H}^d$), 2,3 (H^e), 1,95 (H^f), 1,9-1,4 (H^g)

^{13}C NMR (CDCl_3) δ (ppm): 174,8 (C^1); 73,5 (C^2); 65,9 (C^3); 48,3 (C^4); 42,6 (C^5); 41-38 (C^6); 30,5 (C^7); 17,7 (C^8)

Elemental analysis: ($\text{Mn} = 3240 \text{ g/mol} = 20 \text{ repeat units} + \text{head} + \text{end}$)

calc. (%): C:61,98 H:8,60 N:8,65 O:20,76 Cl:0,0

found: C:60,67 H:8,58 N:7,13 O:23,53 Cl:0,0

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