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SYNTHESIS OF AMPHIPHILIC POLY(2-(1-PYRROLIDONYL)-ETHYLVINYLETHER-*b*-ISOBUTYLVINYLETHER)

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Abstract

Block copolymers consisting of isobutyl vinyl ether (IBVE) and 2-(1-pyrrolidonyl)-ethylvinylether (PEVE) were synthesized by the nucleophilic substitution of poly(2-chloroethylvinylether-*b*-isobutylvinylether) (poly(CEVE-*b*-IBVE)) by the anion of pyrrolidone. The poly(CEVE-*b*-IBVE) was obtained by sequential polymerization of CEVE and IBVE initiated by 1-iodo-1-(2-methylpropyloxy)ethane/tetrabutylammonium perchlorate. The molar mass and the composition of the block copolymer can be controlled, because the polymerization shows the characteristics of a living polymerization.

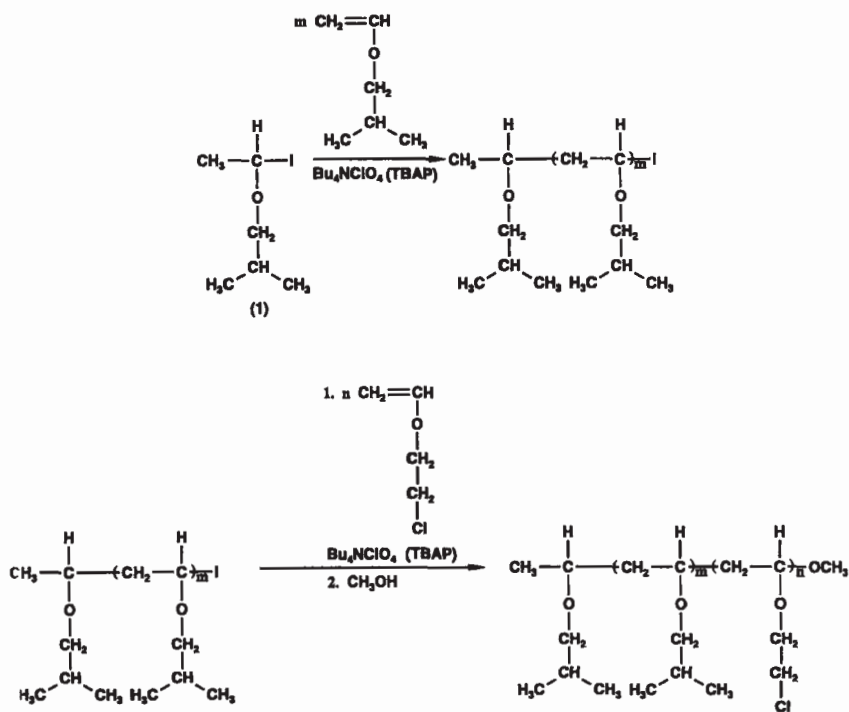
Introduction

From earlier studies we know that the polymerization of CEVE with the initiator system 1-iodo-1-(2-methylpropyloxy)ethane(1)/tetrabutylammonium perchlorate (TBAP) shows the characteristics of a living polymerization¹⁾. Furthermore, we have shown that the water soluble poly(2-(1-pyrrolidonyl)ethylvinylether) (PPEVE) is obtained by a complete nucleophilic substitution of the chlorine in poly(2-chloroethylvinylether) (PCEVE) by the anion of pyrrolidone¹⁾. It was our interest to synthesize an amphiphilic block copolymer via poly(IBVE-*b*-CEVE) as intermediate which can be converted into poly(IBVE-*b*-PEVE) by the nucleophilic substitution already successfully applied for PCEVE. Although several block copolymers of various vinyl ethers have been synthesized already²⁻⁵⁾, none of them has been prepared by 1-iodo-1-(2-methylpropyloxy)ethane(1)/tetrabutylammonium perchlorate (TBAP)

as initiator. Since this initiator system has several advantages over HI/I_2 and HI/ZnI_2 (no side reactions, no discolouration, control of molar mass up to high value,...) it may open an attractive route to new block copolymers with controlled sequences. The „one step“ nucleophilic substitution replacement would allow the synthesis of a great variety of polymers which are not obtainable by sequential addition of monomers.

Result and Discussion

Poly(2-chloroethylvinylether-b-isobutylvinylether) (poly(CEVE-b-IBVE)) was synthesized according to the following scheme.



The polymerization of IBVE was started with **1**/TBAP. The monomer conversion was followed by GC with toluene as internal standard. After the conversion of IBVE the temperature was raised and the second monomer (CEVE) was added. The rate of polymerization of CEVE is lower compared to the rate of IBVE (see also¹⁾).

Tab.1 shows that the calculated and observed molar masses are similar, indicating that both monomers react in a living manner. It is interesting to mention that the GPC spectrum of the block copolymer shows only one peak. This is an additional prove for the existence of the block copolymer.

Tab. 1: Block copolymerization of IBVE and CEVE with 1/TBAP
 Solvent: CH₂Cl₂; [IBVE] = 1.0 mol l⁻¹; [CEVE] = 0.8 mol l⁻¹

Experiment	1	2
IBVE-polymerization		
[Initiator] mol l ⁻¹	0.036	0.036
[Bu ₄ NClO ₄] mol l ⁻¹	0.024	0.013
temperature °C	-40	-30
conversion %	95.3 ^{a)}	92.6 ^{b)}
CEVE-polymerization		
[Initiator] mol l ⁻¹	0.031	0.031
[Bu ₄ NClO ₄] mol l ⁻¹	0.019	0.022 ^{b)}
temperature °C	-15	-10
conversion %	67.1 ^{c)}	87.3 ^{c)}
\bar{M}_n (GPC) g/mol	4150	4830
\bar{M}_n (calc. ^{d)} g/mol	4720	5270
$\frac{\bar{M}_w}{\bar{M}_n}$	1.39	1.34

- a) Conversion of IBVE after one hour (exp. 1) or after 2.5 hour (exp. 2)
 b) Addition of an extra portion of TBAP with the CEVE-solution
 c) Conversion of CEVE after 24 hour (exp. 1) or after 44 hour (exp. 2)
 d) calc. from $\bar{M}_n = M_{M1} \times [M_1]_0/[I] \times C_1 + M_{M2} \times [M_2]_0/[I] \times C_2 + M_{Head} + M_{End}$
 C = conversion (C₁ = 100 %)

The composition of the block copolymer can be determined by the ¹H-NMR-spectra of poly(IBVE-*b*-CEVE) (Fig. 1). The spectrum contains an independent signal of one unit, the signal at 0.9 ppm corresponds with six protons of IBVE (i) and the area between 3.9-3.0 ppm corresponds with five protons of a CEVE-unit (a,b,c) and three protons of an IBVE-unit (d,e). Therefore it is possible to calculate the composition of the block copolymer on the basis of the following relation:

$$X_{CEVE} = \frac{I_{CEVE}}{I_{CEVE} + I_{IBVE}}$$

$I_{IBVE} = i/6$; i area of signal at 0.9 ppm

$I_{CEVE} = (A - I_{IBVE} \times 3)/5$, A area of signal between 3.9-3.0 ppm

$X_{CEVE} = n/[n + (m + 1)]$, mol fraction CEVE

n = number of repeating units of CEVE

m = number of repeating units of IBVE

(+1 due to the initiator unit)

As one can see from table 2, the composition of the block copolymers based on ¹H-NMR are nearly equal to the calculated composition based on the conversion data in table 1.

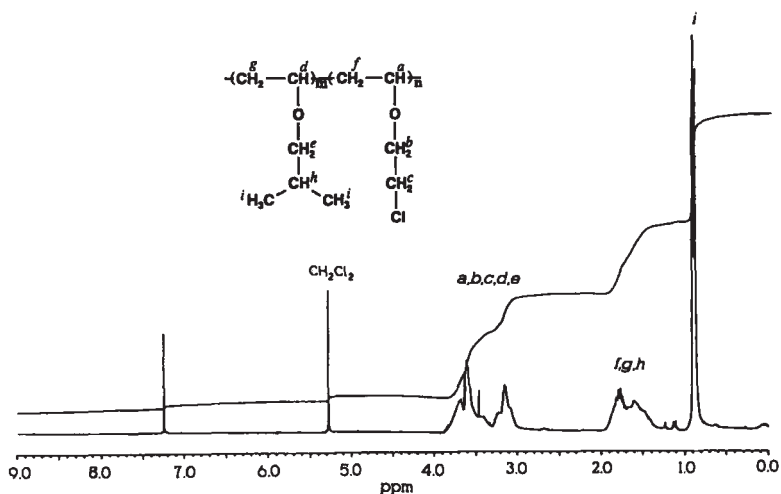


Fig. 1. $^1\text{H-NMR}$ -spectrum of poly(IBVE-b-CEVE) in CDCl_3

Reaction of poly(IBVE-b-CEVE) with the anion of pyrrolidone

Since the initiating systems which was used for the polymerization of IBVE and CEVE⁶⁾ do not polymerize 2-(1-pyrrolidonyl)ethylvinylether (PEVE), it was necessary to take a detour. Therefore we synthesize poly(IBVE-b-PEVE) by reacting of poly(IBVE-b-CEVE) with the anion of pyrrolidone according to the following scheme.

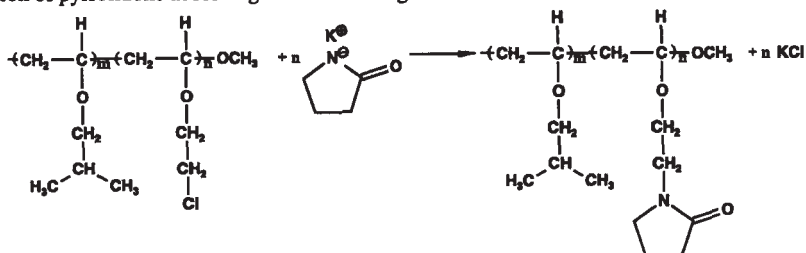


Figure 2 shows the $^1\text{H-NMR}$ -spectrum of the resulting product.

The signals at 2.0 ppm and 2.3 ppm are absent in the precursor (see Fig. 1). These signals belong to the protons of the pyrrolidone (g,h). The degree of the substitution can be calculated by the following equationation.

$$5 \times I_{\text{CEVE}} = I_A - (I_P/2) \times 7 - 3 \times I_{\text{IBVE}}$$

I_{CEVE} = Integral of one proton of CEVE

I_A = Integral of the region 3.9 - 3.0 ppm;

corresponding with seven protons of a substituted unit (a-d) and five protons of the

Tab. 2: Composition of the block copolymers of IBVE and CEVE determined by $^1\text{H-NMR}$

Experiment	$X_{\text{IBVE}}(\text{calc}^{\text{a}})$	$X_{\text{IBVE}}(^1\text{H-NMR})$	$X_{\text{CEVE}}(\text{calc}^{\text{b}})$	$X_{\text{CEVE}}(^1\text{H-NMR})$
1	62.4	60.1	37.6	39.9
2	56.1	54.2	43.9	45.8

a) based on complete conversion of IBVE

(+1; because of the initiator unit)

b) based on the conversion given in table 1

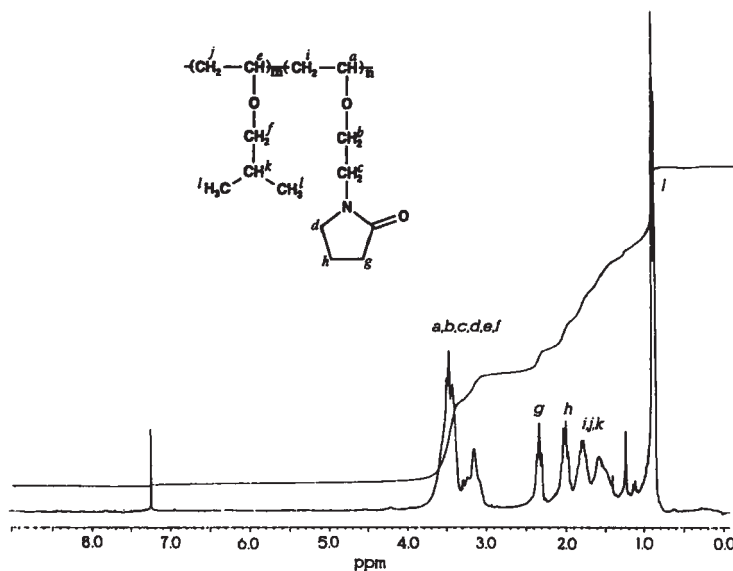


Fig. 2: $^1\text{H-NMR}$ -spectrum of poly(IBVE-*b*-PEVE) in CDCl_3

unsubstituted CEVE-unit (if existing; a-c: see Fig. 1) and the three proton of the IBVE-unit (e,f)

I_p = Integral of two protons of the pyrrolidone (g or h)

I_{IBVE} = Integral of one proton of IBVE

(Integral of 0.9 ppm divided by six)

The calculation shows that the degree of substitution of the chlorine was 100 %. The result is supported by elemental analysis which does not show any residual chlorine.

The molar mass of poly(IBVE-*b*-PEVE) measured by GPC was smaller instead of greater than the precursor ($\bar{M}_n(\text{calc.}) = 4930 \text{ g/mol}$, $\bar{M}_n(\text{GPC}) = 1240 \text{ g/mol}$, $\bar{M}_n(\text{precursor}) = 4150$

g/mol). The reason for this result is the higher polarity of the product compared with the precursor, therefore the elution time of the GPC is extended. If one determines the molar mass via $^1\text{H-NMR}$, one gets a value of 5310 g/mol, which is close to the calculated value of 4930 g/mol.

Experimental Part

Instruments

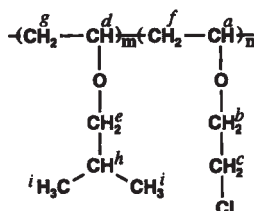
IR: Digilab FTS-40; $^1\text{H-NMR}$: Bruker AC 250 (250 MHz); $^{13}\text{C-NMR}$: Bruker AC 250 (62,5 MHz); GPC: Waters 510, UV and RI detector; calibration with polystyrene standards, elution with THF; GC: Varian GC 3700, column CP SIL 5CB, Chrompack 9000, Column CP SIL 5CB; Cryostate: Lauda UK 8 DN; Elemental analysis: Ilse Beetz, Kronach;

Chemicals

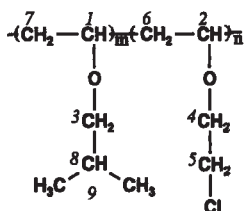
Toluene was distilled over sodium before use. CH_2Cl_2 was refluxed over CaH_2 and freshly distilled before each experiments. Isobutyl vinyl ether and 2-chloroethyl vinyl ether were dried over CaH_2 and freshly distilled before use. Tetrabutylammonium perchlorate was dried for 24 hrs under high vacuum conditions and stored under argon. 1-Iodo-1-(2-methylpropoxy)ethane was synthesized as described in the literature⁷⁾. The other chemicals were used as received.

Poly(IBVE-b-CEVE)

The thermostated polymerization apparatus equipped with a thermostated dropping funnel, a 3-way tap, a thermometer, a septum and a stirring bar was carefully dried before use (heated to 150°C for 12 hrs, cooled under dry argon). Then the apparatus was filled with IBVE, toluene as internal standard (for quant. determination of conversion by GC) and a solution of TBAP in CH_2Cl_2 . The polymerization was started by the addition of prechilled solution of **1** in hexane. The reaction temperature was kept constant with a cryostate. Samples were taken through the septum during polymerization. After the conversion of IBVE (see table 1) the system was heated and a certain amount of CEVE was added. The progress of polymerization was followed by GC. After the conversion of CEVE the polymerization was quenched with methanol/aqu. NH_3 . Diethylether was added to the polymer solution. Then the polymer solution was 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. After removal of the solvent in vacuum the polymer was dried and characterized.



$^1\text{H-NMR}$ (CDCl_3) δ (ppm): 3.9-3.0 ($\text{H}^a, \text{H}^b, \text{H}^c, \text{H}^d, \text{H}^e$), 2.0-1.4 ($\text{H}^f, \text{H}^g, \text{H}^h$), 0.87 (H^i)



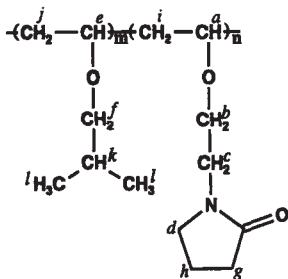
$^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 75.5 (C^1), 73.6 (C^2), 68.8 (C^3 , C^4), 43.6 (C^5), 42-39 (C^6 , C^7), 28.9 (C^8), 19.6 (C^9)

Poly(IBVE-*b*-PEVE)

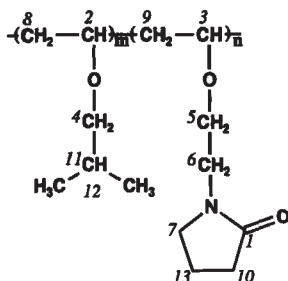
1,11 g (13 mmol) pyrrolidone, 0,05 g (0,15 mmol) tetrabutylammoniumbromide and 1,35 g (12 mmol) potassium *t*-butylate were dissolved in 15 ml dimethylformamide (DMF) and stirred at room temperature for one hour. Then 1 g of poly(IBVE-*b*-CEVE) ($\bar{M}_n = 4380$ g/mol; composition 47 mol % CEVE, 53 mol % IBVE) dissolved in 10 ml toluene was added slowly. This mixture was heated 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 reduced in vacuum. The oily product was redissolved in diethylether and washed with a saturated aqueous NaCl-solution and with water. After drying with Na_2SO_4 the solvent was removed in vacuum. Then the polymer was redissolved in diethylether and cleared off by centrifugation. After removal of the solvent in vacuum the polymer was dried and characterized.

Yield: 0.68 g (56 %)

IR (film) cm^{-1} : 2953, 2926, 2878 (CH); 1689, 1681 (CO); 1111, 1097 (COC)



$^1\text{H-NMR}$ (CDCl_3) δ (ppm): 3.9-3.0 (H^a , H^b , H^c , H^d , H^e , H^f), 2.33 (H^g), 1.98 (H^h), 1.9-1.4 (H^i , H^j , H^k), 0.87 (H^l)



^{13}C -NMR (CDCl_3) $\delta(\text{ppm})$: 174.8 (C^1), 75.7 (C^2), 73.6 (C^3 , C^4), 66.1 (C^5), 48.3 (C^6), 42.9 (C^7), 42-38 (C^8 , C^9), 30.7 (C^{10}), 28.9 (C^{11}), 19.5 (C^{12}), 18.0 (C^{13})

Elemental analysis: ($\bar{M}_n = 4380$ g/mol, 47 mol % PEVE, 53 mol % IBVE +endgroup)

calc. (%): C: 66.97 H: 10.37 O:18.41 N: 4.24 Cl: 0.0

found: C: 66.75 H: 10.26 O:18.83 N: 4.16 Cl: 0.0

Acknowledgement

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