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Living cationic polymerization of isobutyl vinyl ether, 2

Telechelics by controlled chain termination and their application to the synthesis of blockcopolymers

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Summary

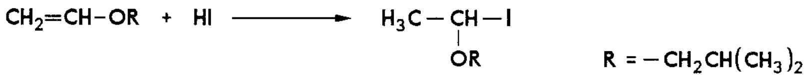
Living cationic polymerization of isobutyl vinyl ether (IBVE), initiated by 1-iodo-1-(2-methylpropyloxy)-ethane (1) and tetraalkylammonium perchlorate yields polymers of well defined molar masses and end groups. The controlled introduction of end groups was confirmed by a model reaction and was then applied to introduce an azo initiator function. The resulting polymeric initiator was used for the synthesis of a blockcopolymer.

Introduction

The controlled synthesis of telechelics is one of the most promising fields in modern polymer chemistry. Telechelics are polymers or oligomers with at least one functional group at the end of each polymer chain. The essentials in the synthesis of telechelics are: 1) control of the molar mass and 2) control of the end groups. Although the cationic polymerization of vinyl compounds seemed to be too complex for this type of polymers, the activity in this field increased remarkably since 1980[1-3]. In 1984 Higashimura and coworkers[4,5] showed that it is possible to synthesize telechelic poly(isobutyl vinyl ether) (PIBVE) with the initiator systems HI/I_2 and HI/ZnI_2. A big step towards a controlled synthesis of telechelic poly(vinyl ethers) was the discovery of $HI/R_4N^+ClO_4^-$ as initiator system[6,7]. The main advantage of this new initiator system is the absence of side reactions. The nucleophilic substitution of the end group (iodide or perchlorate) allows a great variety of reactions, including the introduction of end groups which can react as initiators for radical polymerization. These polymeric initiators can be applied in the synthesis of blockcopolymers[8].

Living cationic polymerization of IBVE

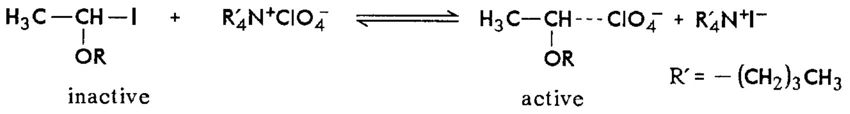
Addition of HI to IBVE yields 1-iodo-1-(2-methylpropyloxy)-ethane (1) :



$$CH_2{=}CH{-}OR + HI \longrightarrow H_3C{-}\underset{\overset{|}{OR}}{CH}{-}I \qquad R = -CH_2CH(CH_3)_2$$

1

Compound 1 is not able to initiate the polymerization of IBVE, but can be activated by iodine[4], zinc iodide[5] or tetraalkylammonium perchlorate [6,7]:



$$\underset{\text{inactive}}{H_3C{-}\underset{\overset{|}{OR}}{CH}{-}I} + R'_4N^+ClO_4^- \rightleftharpoons \underset{\text{active}}{H_3C{-}\underset{\overset{|}{OR}}{CH}\cdots ClO_4^-} + R'_4N^+I^- \qquad R' = -(CH_2)_3CH_3$$

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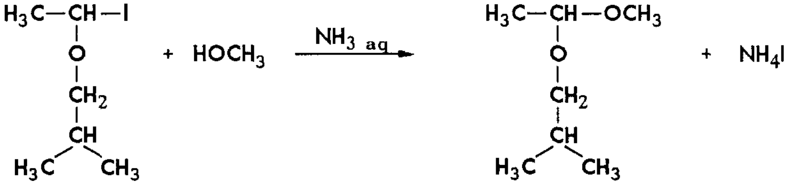
This type of polymerization is characterized by[9] :

- control of molar masses by $[M]/[I]$
- narrow molar mass distribution $\overline{M}_w/\overline{M}_n < 1.25$
- end group control
- linear relationship between monomer conversion and molar masses

It is therefore claimed to be a living polymerization. A typical polymerization procedure is described in part 1 of this series of papers[9].

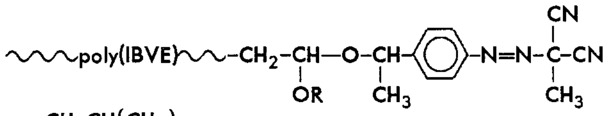
Nucleophilic substitution of the labile end group (I^- or ClO_4^-) by an alcoholate yields poly (vinyl ether)s bearing acetal end groups. The quantitative character of this substitution was clearly demonstrated by the reaction of 1 with methanol, yielding 1-methoxy-1-(2-methylpropyloxy)ethane (2). The ^1H-NMR- and ^{13}C-NMR-spectra of the acetal (2) show, that it equilibrates slowly with the two symmetrical acetals, 1,1-dimethoxy-ethane and 1,1-di-(2-methylpropyloxy)ethane. Due to the high volatility of the 1,1-dimethoxy-ethane, the elemental analysis of the mixture of the three acetals does not fit very well.



1

2

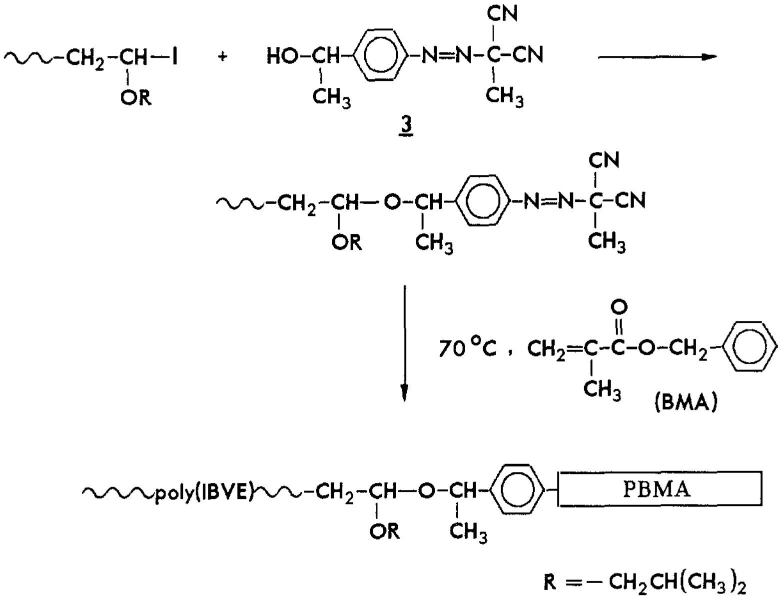
This type of reaction was also successfully applied to the synthesis of polymers bearing an azo initiator as the end group :



$R = -CH_2CH(CH_3)_2$

Polymeric azo initiator and block copolymerization

Nucleophilic substitution of the labile end group by the alcoholic azo compound 1-(4-(1-(1,1-dicyanoethyl)azo)phenyl)ethanol (3) yields a polymeric initiator, which can be applied to radical block copolymerization:



A PIBVE having a $\overline{M}_n$ = 12600 was terminated by addition of an excess of **3**. The resulting product was dispersed in methanol several times to separate the polymer from unreacted **3**. The UV-curve (254 nm) of the gel permeation chromatogram (GPC) of the polymer clearly indicates the presence of the azo end group within the polymer (Figure 1 , curves 1a and 1b).

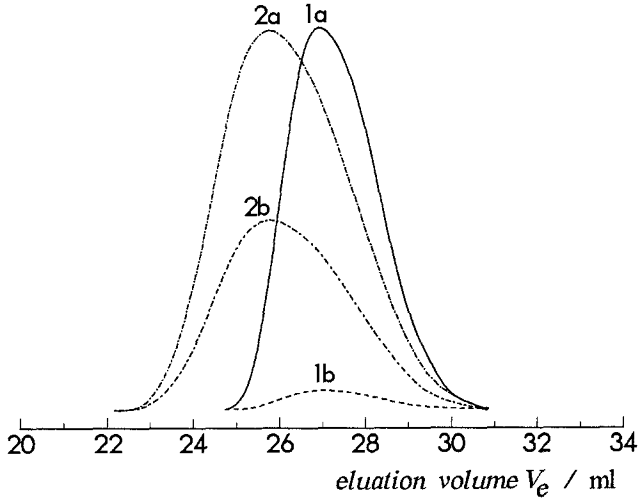


Figure 1 : GPC spectrum of the macroazo initiator (curves 1a and 1b) and the blockcopolymer (curves 2a and 2b)
Index a marks the refractometer, index b the UV-detector

For block copolymerization the polymeric initiator was dissolved in toluene and benzyl methacrylate (BMA) was added. Then this solution was heated to 70 °C for 16 hours. The resulting polymer was precipitated into methanol, filtered, redissolved in CH_2Cl_2 and precipitated again into methanol. The raw product showed a bimodal molar mass distribution, which changed into monomodal after a washing procedure with hexane/diethylether, since unblocked PIBVE was separated. The block copolymer showed a higher UV absorption than the original polymeric initiator, due to the benzyl side groups in the PBMA blocks (Figure 1, curves 2a and 2b). The average molar mass of the block copolymer was determined to be $\overline{M}_n = 19600$ ($\overline{M}_w/\overline{M}_n = 1.75$).

A possible explanation of the relatively low degree of polymerization of the PBMA segments may be the limited diffusion of monomer (BMA) into the random coils of IBVE during the polymerization, since BMA is a "bad" solvent for PIBVE. Furthermore, the limited diffusion of BMA to the generated macroradicals is propably responsible for the fairly high amount (approx. 40%) of unblocked PIBVE which was found. However, formation of homo-PBMA was not observed. This is surprising, since a low molar mass radical [$*C(CN)_2CH_3$] is also formed during the decomposition of the macroinitiator. This means either that $*C(CN)_2CH_3$ is not an active radical or, more likely, that termination occurs via combination. Thermally induced polymerization was excluded by a model polymerization of BMA in the absence of an initiator.

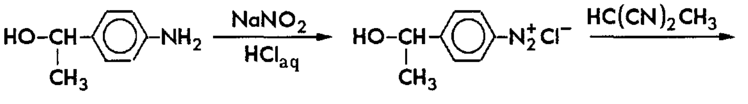
The thermogram of the macroazoinitiator (PIBVE, terminated by **3**, $\overline{M}_n = 12600$) shows a glass transition (T_g) at - 25°C. Homo - PBMA (synthesized by radical polymerization, $\overline{M}_n = 35000$) shows a $T_g = 48°C$ (Lit.10): 54°C). A physical mixture of both homopolymers, formed by coprecipitation from toluene is opaque and both glass transitions are detectable. However, the polymer obtained from the macroazoinitiator and BMA shows only one T_g at + 7°C, which is close to the value calculated from the Gordon-Taylor equation11) ($T_g = -3°C$). This result is surprising and probably due to the hindered phase separation of the two blocks.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (1)$$

with T_g = T_g of copolymer,
T_{gi} = T_g of homopolymer i,
w_i = weight fraction of monomer units i in the copolymer.

Synthesis and properties of the terminating agent (3)

The first step in the synthesis of 1-(4-(1-(1,1-dicyanoethyl)azo)phenyl)ethanol (**3**) was the diazotation of 1-(4-aminophenyl)ethanol followed by coupling of the diazonium salt with methylmalonodinitrile.



3

The decomposition kinetics of **3** were studied by DSC. The thermogram of **3** shows an endothermic peak at 75°C, which indicates the melting point of the sample. An exothermic peak with a maximum at 139°C results from the decomposition of the compound. An analysis of this peak can be used to determine the activation energy E_A of the decomposition of the pure substance without influence of a solvent12). From the DSC data the activation energy for the decomposition of **3** was determined to be 140 $kJ \cdot mol^{-1}$ (Table 1).

Table 1 : Kinetics of the decomposition of $\underline{3}$

T / K	388	393	398	403	408	413	418	423
$10^2 \cdot k/\mathrm{s}^{-1}$	1.00	2.06	3.70	6.51	10.81	16.93	25.51	37.68

Experimental part

The instuments used in this work were : ^{1}H-NMR, ^{13}C-NMR : Bruker AC 250; Bruker AC 500; UV-spectrometry : Varian Cary 219; DSC : Perkin Elmer DSC 7; GC : Varian GC3500, fused silica column CPSil 5 CB; GPC : Waters model 590, THF as eluent, polystyrene standards; Kryostat : Lauda UK 8 DW.

Solvents and Chemicals : All solvents were dried and freshly distilled before use, IBVE (Fluka) was purified by distillation over sodium hydride. The coinitiator tetra-n-butylammonium perchlorate (Fluka) was dried in high vacuum before use. The preparation of dry HI and the polymerization procedure of IBVE is described in detail in the literature$^{9)}$.

Benzyl methacrylate (BMA): 10.8 g (0.1 mole) benzylalcohol were mixed with 50 ml triethylamine and 50 ml diethyl ether and cooled to 0°C. Then 10.4g (0.1 mole) methacrylic chloride, dissolved in 30 ml diethylether were added dropwise. After stirring the reaction mixture at room temperature for 30 minutes, the precipitated triethylamino hydrochloride was separated by filtration. The ether phase was washed with water and dried over Na_2SO_4. After solvent evaporation the product was distilled under reduced pressure. Colorless liquid; b.p. = 30 - 35°C / 10 torr; yield 14g (80%)

^{1}H-NMR ($CDCl_3$, δ in ppm vs TMS) : 7.34 m (5H), 6.17 d (1H, $^2J_{gem}$= 1.2 Hz), 5.57 d (1H, $^2J_{gem}$ = 1.2 Hz), 5.24 s (2H), 1.97 s (3H)

IR (neat, $\tilde{\nu}$ in cm^{-1}) : 2980 (C-H), 1730 (C=O), 1640 (C=C), 1295 (C-O)

1-Iodo-1-(2-methylpropyloxy)-ethane ($\underline{1}$) :

The synthesis and characterization of $\underline{1}$ is described in the previous paper of this series$^{9)}$.

1-Methoxy-1-(2-methylpropyloxy)-ethane ($\underline{2}$) :

10 ml of a 0.38 molar solution of $\underline{1}$ in hexane were poured into a tenfold excess of methanol containing 5 vol% aqueous ammonia solution (25%) at -78°C. The mixture was stirred and allowed to warm up to room temperature. Then its volume was reduced to 50 ml by careful evaporation in vacuum. 100 ml diethylether were added to the solution and then the mixture was washed with an aqueous solution of $Na_2S_2O_3$ (5 wt.%) and water. The ether phase was dried over Na_2SO_4 and the solvent removed in vacuo. The remaining raw product was distilled under reduced pressure to give 470 mg (94%) of $\underline{2}$, b.p. 36-40°C/20 torr.

$C_7H_{16}O_2$ (132.2) : calc. 63.64 % C, 12.12 % H,
determ. 65.23 % C, 12.14 % H

^{1}H-NMR (Bruker AC 250, $CDCl_3$, δ in ppm vs. TMS) : 4.59 m (1H), 3.16 m (1H), 1.82 m (2H), 1.27 d (3H), 0.89 m (6H). An analysis of the 500 MHz spectra of this sample clearly proves the existence of three acetals (see text).

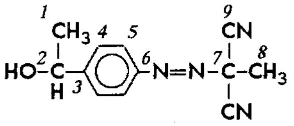
^{13}C-NMR ($CDCl_3$, δ in ppm vs. TMS) : 100.5 ($-O-\underline{C}H(OCH_3)$), 72.2 ($-O-\underline{C}H_2-$), 53.3 ($-O-\underline{C}H_3$), 28.6 ($-\underline{C}H(CH_3)_2$), 19.4 ($-CH(\underline{C}H_3)_2$), 19.2 ($CH-\underline{C}H_3$)

1-(4-(1-(1,1-dicyanoethyl)azo)phenyl)ethanol (3) :

6.8 g (30 mmol) 1-(4-aminophenyl)ethanol were dissolved in a mixture of 25 ml water and 25 ml conc. HCl and then cooled to -5°C. A solution of 3.4 g (50 mmol) $NaNO_2$ in 40 ml water was added dropwise, keeping the temperature below -5°C. The solution of the formed diazonium salt was then added to a precooled (-10°C) mixture of 4 g methylmalonodinitrile in 60 ml ethanol and 40 g sodium acetate in 100 ml water. After complete addition, the reaction mixture was allowed to warm up to room temperature and stirred for another 10 min. The reaction product was then extracted with diethylether. The organic phase was dried over Na_2SO_4 and the solvent was removed carefully in vacuo. The raw product was purified by column chromatography (silica gel, diethylether/pentane 2:1). Yellow needles; m.p. 75°C; yield 5.7 g (50%)

$C_{12}H_{12}N_4O$ (228.3) : calc. 63.07 % C, 5.29 % H, 24.63 % N
determ. 63.83 % C, 5.27 % H, 23.98 % N

^{1}H-NMR (in $CDCl_3$, δ in ppm vs. TMS)
7.84 m (2H , ^3J = 8.5 Hz) ; 7.47 m (2H , ^3J = 8.5 Hz) ; 4.36 q (1H , ^3J = 6.4 Hz) 3.25 s (3H) ; 1.52 s (1H) ; 1.43 d (3H , ^3J = 6.4 Hz)
^{1}C-NMR (in $CDCl_3$, δ in ppm vs TMS)
150.3 (C^6) ; 149.1 (C^3) ; 127.1 (C^4) ; 124.1 (C^5) ; 112.9 (C^9) ; 79.1 (C^2) ; 56.7 (C^7) 24.8 (C^1) ; 23.7 (C^8)



IR (KBr) ; $\tilde{\nu}$ in cm^{-1}
3300 (O-H st) ; 2976 (C-H st) ; 1604 (ar C-C st) ; 1448 (N=N st) ; 1115 ($-CH_3$) 845 (ar C-H δ oop)
UV (CH_2Cl_2) : $\varepsilon = 14300\ cm^{-1}\cdot mol^{-1}\cdot l$ (λ = 297 nm)

Polymerization of IBVE

The polymerization procedure is described in the previous paper of this series$^{9)}$.

Functionalization of PIBVE

50 mmol IBVE in 50 ml CH_2Cl_2 were polymerized with 0.4 mmol 1 and 0.4 mmol TBAP as initiator. At 95 % conversion (determined by GC) a solution of 0.5 g 3 and 0.5 ml aqueous ammonia (25%) in 5 ml CH_2Cl_2 were added. Then the solvent was removed in vacuum and 100 ml diethyl ether were added. The organic phase was dried with Na_2SO_4, filtered and concentrated to about 10 ml. The resulting viscous solution was dispersed dropwise in 300 ml methanol. The polymer precipitated from the yellow (due to an excess of 3) methanolic phase. This procedure was repeated until the methanolic phase remained colourless. Polymer yield : 4.5 g slightly yellow viscous oil (90%).

Block copolymerization

0.7 g azo terminated PIBVE ($\overline{M}_n$ = 12600, $\overline{M}_w/\overline{M}_n$ = 1.2) and 2.0 g BMA were dissolved in 30 ml toluene. The solution was degassed by several freeze thaw cycles. Then the mixture was heated to 70°C and kept at this temperature for 16 h. The resulting polymeric raw product was isolated by precipitation into methanol. The product was dissolved in CH_2Cl_2 and precipitated again in methanol. Unblocked PIBVE was extracted with a mixture of hexane and diethylether (2:1). Yield 1.0 g copolymer, $\overline{M}_n$ = 19600, $\overline{M}_w/\overline{M}_n$ = 1.75

^{1}H-NMR (in $CDCl_3$, δ in ppm vs. TMS) : 7.2 , 6.8 , 4.25 , 4.0 , 3.5 , 3.15 , 1.8 , 1.6 , 0.9

^{13}C- NMR (in $CDCl_3$, δ in ppm vs. TMS) : 174 , 158 , 130 , 121 , 115 , 76 , 74 , 66 , 63 , 41 , 29 , 20

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