Polymer Bulletin 28, 117–122 (1992)

Polymer Bulletin

Cationic polymerization of selected α- and β-substituted vinyl ethers

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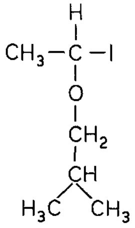
Summary

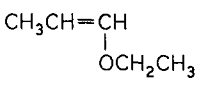
The cationic polymerization of various α- and β-substituted vinyl ethers, initiated by 1-iodo-1-(2-methylpropyloxy)ethane 1 and tetrabutylammonium perchlorate (TBAP) was investigated. The polymerization of 2,3-dihydrofuran (DHF, 3a) in CH_2Cl_2 at -40°C proceeds via opening of the ethylenic double bond and yields polymers with narrow molar mass distributions and high glass transitions. The number average of molar mass increased linearly with conversion. Under these conditions, a controlled polymerization of two propenyl ethers (1-ethoxypropene 2a and 2-methoxypropene 2b) and two other cyclic unsaturated ethers (3,4-dihydro-2H-pyran 3b and 5-methyl-2,3-dihydrofuran 3c) could not be achieved. Either transfer reactions or the decomposition of 1 prevented the formation of high molar mass polymers of these vinyl ethers.

Introduction

Recent studies in our laboratory have shown that isobutyl vinyl ether (IBVE) can be polymerized by an initiator-coinitiator system consisting of 1-iodo-1-(2-methylpropyloxy) ethane 1 and tetrabutyl ammonium perchlorate (TBAP)[1]. This type of polymerization is characterized by a spontaneous initiation, control of molar masses by the ratio [Monomer]/[Initiator], control of the end groups, narrow molar mass distributions, and a linear relationship between monomer conversion and molar mass of the polymer. Due to these characteristics this process is considered to be a "living polymerization", which is a useful pathway for the synthesis of macro initiators, telechelics, and block copolymers[2,3].

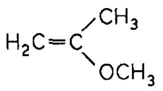


1

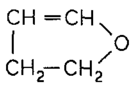


$CH_3CH{=}CH(OCH_2CH_3)$

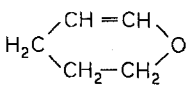
2a



2b



3a



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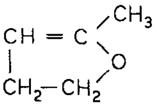

3c

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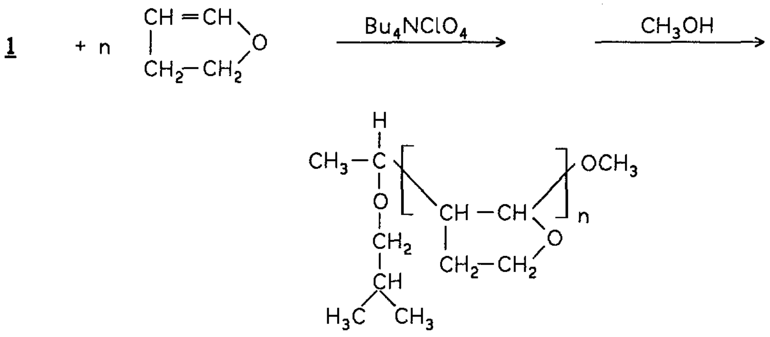
The monomers that have been found so far to undergo living cationic polymerization with 1/TBAP, are linear and unsubstituted alkyl vinyl ethers and 4-methoxy styrene[4]. Although α- and β-substituted vinyl ethers such as propenyl ethers (2) and cyclic unsaturated ethers (3) are known to give high molar masses via cationic polymerization[5-7], little is known about their behaviour under conditions which allow living polymerizations. Nevertheless, it was shown by Higashimura, that 1-ethoxypropene (2a) and 5-methyl-2,3-dihydrofuran (3c) give nearly perfect living polymers with HI/I_2 or HI/acetyl perchlorate initiator, respectively[8,9]. It was of interest, whether the initiator-coinitiator system 1/TBAP could be applied to this type of monomer.

Therefore we have examined the possibility of living cationic polymerizations of some α- and β-substituted vinyl ethers with the 1/TABP initiator.

Polymerization of 2,3-Dihydrofuran (DHF, 3a)

The polymerization of DHF was initiated by addition of a certain amount of 1 to a precooled solution of DHF and TBAP in CH_2Cl_2 (see scheme 1). The polymerization proceeded without an induction period. It was stopped by pouring the reaction mixture into a precooled solution of 10 vol.-% aqueous ammonia in methanol. The colourless polymers were filtered and dried in high vacuum.

Scheme 1



We have found that the MWD and the $\overline{M}_n$ of the resulting polymers depend on the ratio of coinitiator and initiator, i. e. [TBAP]/[1]. Table 1 shows some of the results.

Table 1: Polymerization of DHF in CH_2Cl_2 at -40°C

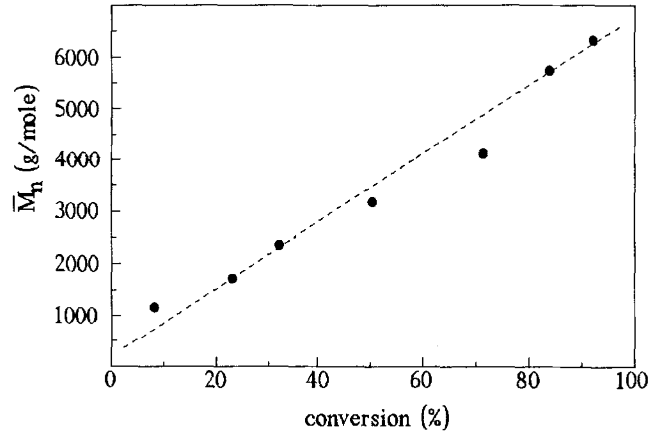
time [h]	[DHF] [mole·l^{-1}]	[1] [mole·l^{-1}]	[TBAP] [mole·l^{-1}]	conv. [%]	$\overline{M}_n$ $^{a)}$ [g·mole^{-1}]	$\overline{M}_n$ $^{b)}$ [g·mole^{-1}]	$\overline{M}_w/\overline{M}_n$
7	1.0	0.01	0.01	72	5170	3920	1.87
5	1.0	0.01	0.03	92	6570	6330	1.37
4	1.0	0.01	0.05	90	6430	7260	1.26

a) $\overline{M}_n$ calculated

b) $\overline{M}_n$ determined by GPC, polystyrene calibration

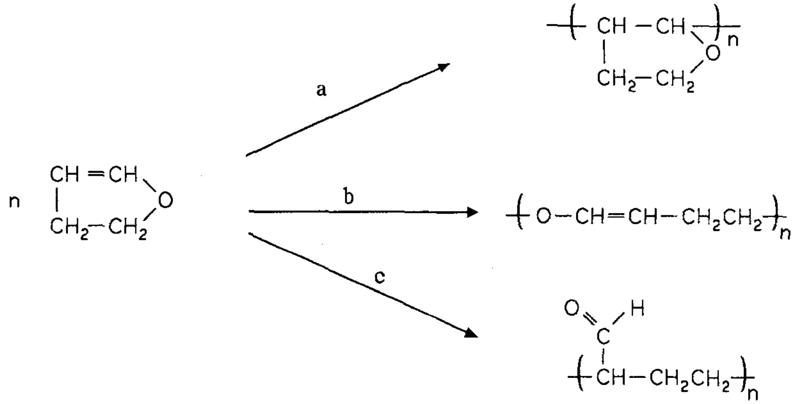
At a ratio [TBAP]/[1] ≤ 1 the MWD of the polymers was rather broad and the molar mass of the polymers could not be controlled by [DHF]/[1]. Under these conditions the polymerizations stopped at conversions C < 85%. At an increasing ratio [TBAP]/[1] however, the MWD decreased and a linear relationship between conversion and molar mass could be achieved (see figure 1).

Figure 1:
$\overline{M}_n$-conversion plot for poly(DHF) obtained with 1 and TBAP in CH_2Cl_2 at -40°C; $[M]_0$= 1.0 mole · l^{-1}, [1] = 0.01 mole · l^{-1}, [TABP] = 0.03 mole · l^{-1}



Formally, the cationic polymerization of cyclic unsaturated ethers can proceed via at least three modes: the opening of the ethylenic double bond, the scission of the C-O bond and another mode of C-O bond scission followed by an isomerization (see scheme 2).

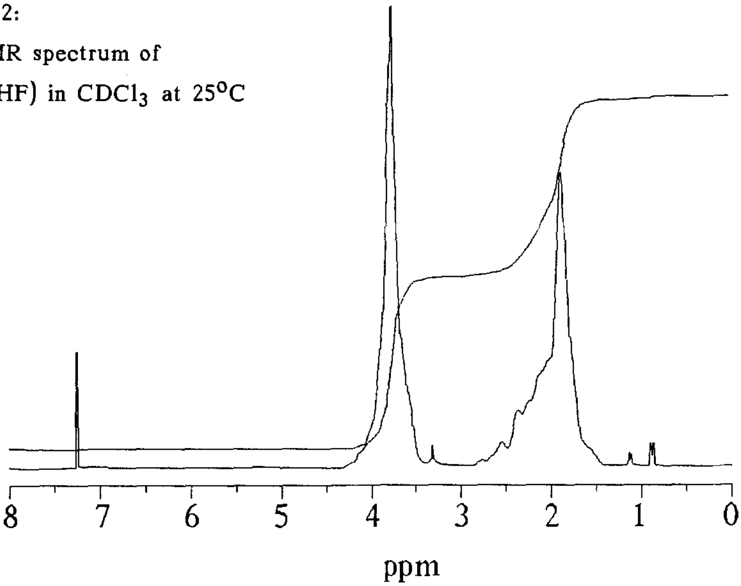
Scheme 2



The ^{1}H-NMR spectrum of poly(DHF) (figure 2) shows two broad peaks of equal area at 4.8 and 2.0 ppm, respectively. The resonance signals at 1.1 and 0.9 ppm clearly prove the incorporation of the initiator 1 as well as the signal at 3.3 ppm proves the existence of the terminating methoxy group. The ^{13}C-NMR spectrum shows four broad areas, corresponding to the four carbon positions of a 2,3-disubstituted THF ring. Neither the

NMR nor the IR spectra of poly(DHF) obtained with [TBAP]/[1] > 1 gave any evidence of a C-O bond scission. Analysis by DSC showed a glass transition at 117°C. These analytic data prove that the polymerization proceeds via opening of the ethylenic double bond (scheme 2a). Polymerizations with [TABP]/[1] ≤ 1 however, led to products which show some weak resonances in the area between 5.5 and 4.8 ppm. This indicates a termination via ring opening (scheme 2b) under these conditions.

Figure 2:
^{1}H-NMR spectrum of
poly(DHF) in $CDCl_3$ at 25°C



Polymerization of 3,4-dihyro-2H-pyran (DHP, 3b)

After successful polymerization of DHF with 1/TBAP, it was of interest, whether DHP, a cyclic six-membered unsaturated ether, can be converted into polymer using the same initiator system. Addition of the initiator 1 to a solution of 3b and TBAP in CH_2Cl_2 at -40°C, gives rise to a very slow reaction, indeed. This reaction was completed after six days and an orange oil could be isolated. Analysis by GPC showed only oligomers with a degree of polymerization ≤ 7. Both ^{1}H-NMR and IR spectra showed signals characteristic of the olefinic double bond. Thus, an efficient transfer reaction must take place which provides formation of high molar mass polymers.

Polymerization of 1-ethoxypropene (EP, 2a)

The polymerization of EP in CH_2Cl_2 proceeded without any induction period. We found a linear relationship between ln (1- C) and reaction time (see figure 3). Thus, the consumption of this β-substituted vinyl ether follows the same first order kinetics as IBVE [1]. In contrast to IBVE, however, the MWD was rather broad and the molar masses could not be controlled by [Monomer]/[Initiator]. The ^{1}H- and ^{13}C-NMR spectra of the polymers showed the expected signals of a regular head-to-tail structure of poly(EP). However, additional signals between 5 and 6 ppm, indicate a certain amount of olefinic protons. Thus, efficient transfer reactions, e. g. the proton transfer to monomer or the elimination of ethanol in connection with proton transfer, yielded terminal olefinic end groups of the polymers.

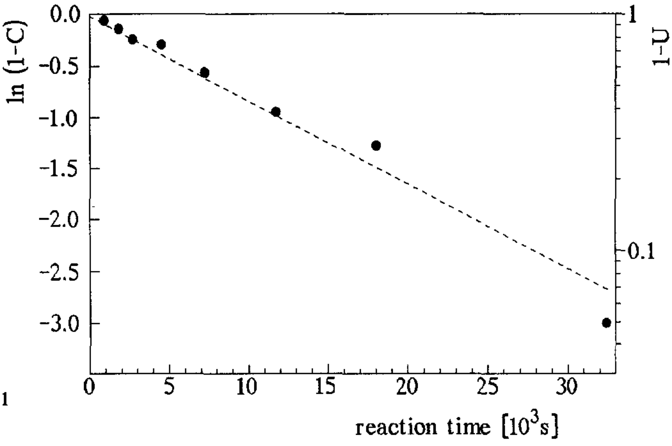


Figure 3:
Kinetics of the polymerization of **2a** with 1/TBAP in CH_2Cl_2 at -40°C
$[\mathbf{2a}]_0 = 0.5$ mole·l^{-1};
[1] = 0.005 mole·l^{-1};
[TBAP] = 0.005 mole·l^{-1}

Polymerization of 2-methoxypropene (**2b**) and 5-methyl-2,3-dihydrofuran **3c**).

In contrast to the β-substituted vinyl ethers described above, these two α-substituted monomers could not be polymerized by 1/TBAP. At the addition of the initiator 1 to the precooled solution of the monomer and TBAP, an exothermic reaction took place. In both CH_2Cl_2 and toluene, the reaction mixture turned into a deep brown colour, which disappeared after washing with an aquous solution of $Na_2S_2O_3$. This indicated clearly the decomposition of 1 in accompanied by the formation of I_2.

Experimental part

Instruments: ^{1}H-NMR, ^{13}C-NMR: Bruker AC 250; GC: Varian GC 3500, fused silica column CPSil 5 CB; GPC: Waters model 590, eluent THF, polystyrene standards; IR: Digilab FTS-40; DSC: Perkin Elmer DSC 7; Kryostat: Lauda UK 8 DW.

Chemicals: All solvents were dried and freshly distilled before use. The monomers were purified by distillation over CaH_2. The coinitiator tetrabutylammonium perchlorate was dried in high vacuum several hours before use.

1-iodo-1-(2-methylpropyloxy)ethane (1):
The synthesis and characterization of 1 are described in the literature$^{1)}$.

Polymer characterization:

Poly(DHF): ^{1}H-NMR (in $CDCl_3$, δ in ppm vs. TMS): 3.50-4.30, 3.30, 1.45-2.80, 1.10, 0.87
^{13}C-NMR (in $CDCl_3$, δ in ppm vs. TMS): 78-86, 65-70, 41-49, 25-32, 19.5
IR (KBr, ν in cm^{-1}): 2968, 2941, 2870, 1452, 1063, 922

Poly(EP): ^{1}H-NMR (in $CDCl_3$, δ in ppm vs. TMS): 3.30-3.80, 2.95-3.30, 2.50-2.70, 1.65-2.10, 1.40-1.60, 1.05-1.25, 0.60-1.05
^{13}C-NMR (in $CDCl_3$, δ in ppm vs. TMS): 79-85, 62-69, 35-42, 15-17, 9-13

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Accepted February 5, 1992 C