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A new initiating system for the "living" polymerization of vinyl ethers leading to hydroxy-terminated polymers

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Summary

The reaction of trimethylsilyl iodide (TMSI) with 1,3-dioxolane (DXL) leads to the formation of 1-trimethylsiloxy-4-iodo-3-oxabutane. In combination with tetrabutyl ammonium triflate this compound can be used as an initiator for the polymerization of vinyl ethers. According to a living polymerization mechanism, the polymers are characterized by controlled molecular weights and narrow molecular weight distributions. The trimethylsiloxy head group originating from the initiation reaction is easily transformed into a primary hydroxyl function by hydrolysis.

Introduction

In 1984 Sawamoto and Higashimura have discovered that vinyl ethers can be polymerized by a living mechanism when initiated with a combination of hydrogen iodide and iodine (HIGASHIMURA, SAWAMOTO, 1984, SAWAMOTO et al, 1988a). Later, they have presented a number of variations of their initiating system (SAWAMOTO, HIGASHIMURA, 1988b).

Nuyken and co-workers have reported that analogous polymerization characteristics could be obtained with a combination of an α-iodo ether and a tetraalkylammonium salt with a non-nucleophilic counter ion (NUYKEN, KRONER, 1988). The α-iodo ether however, has also to be prepared from a vinyl ether and hydrogen iodide and has a limited shelf life.

It is known that trimethylsilyl iodide (TMSI) reacts with acetals to produce the corresponding α-iodo ether and trimethylsiloxane (JUNG et al, 1977, 1978)

$$(CH_3)_3SiI + ROCH_2OR \longrightarrow ROSi(CH_3)_3 + ROCH_2I$$

It was expected therefore, that the combination TMSI, an acetal and a tetrabutylammonium salt would act as an initiator for the polymerization of vinyl ethers. If the acetal is 1,3-dioxolane (DXL)(KEYSER et al, 1979), the TMS group is introduced as a head group, thus providing the possibility to prepare polymers with functional end groups.

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Results and Discussion

1. The reaction between TMSI and DXL.

Since the purpose of the living polymerizations is the synthesis of well defined polymers with narrow molecular weight distributions, it was necessary to know if the reaction of TMSI with DXL was fast and quantitative. This was checked by ^{1}H-NMR spectroscopy. Figure 1 shows the spectrum of an equimolar mixture of the two reagents in chloroform, two minutes after mixing at 20°C. It is clear that in this short period a nearly quantitative ring opening to 1-trimethylsiloxy-4-iodo-3-oxabutane has taken place.

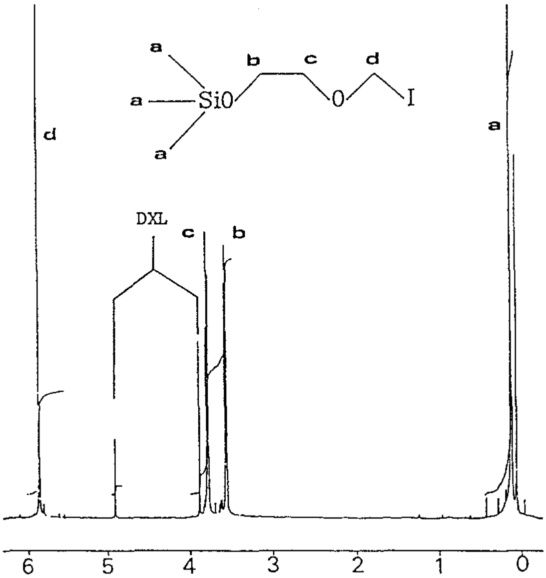


Figure 1 : 360 MHz ^{1}H-NMR spectrum of a mixture of TMSI and DXL in deuterated chloroform two minutes after mixing at 20°C.

2. Polymerization of n.butyl vinyl ether (n.BVE).

Polymerizations were carried out under dry nitrogen in methylene chloride at -40°C during one hour. As ammonium salt we chose tetrabutylammonium trifluoromethane sulfonate (TBAT). The sequence of addition was DXL, TMSI, TBAT and n.BVE. Table 1 gives a survey of the results obtained. The observation that the molecular weights of the obtained polymers are governed by the ratio of the initial monomer to initiator concentration, proves that a quantitative initiation reaction takes place. The GPC analysis of different polymers is shown in figure 2. It may be concluded that the system works perfectly, leading to polymers with the expected molecular weights and with narrow molecular weight distributions.

TABLE 1
Polymerization of n.BVE with TMSI and DXL as initiating system$^{(a)}$.

	$[I]_o$ (mol/l)	$\frac{[nBVE]}{[TMSI]}$	$M_n^{(b)}$ (theor.)	M_n (VPOM)	$M_w/M_n^{(c)}$ (GPC)
a	0.017	60	4006	3925	1.2
b	0.025	40	2106	1970	1.2
c	0.05	20	1306	1216	1.3

(a) In dichloromethane solution at -40°C. [nBVE] = 1.0 mol/l, [TBAT] = [TMSI]

(b) M_n(theor.) = [(conv.%/100)x([n.BVE]/[TMSI])]xMW(n.BVE)+106
The additional value of 106 originates from end groups after termination (see text).

(c) Calibrated on polystyrene standards.

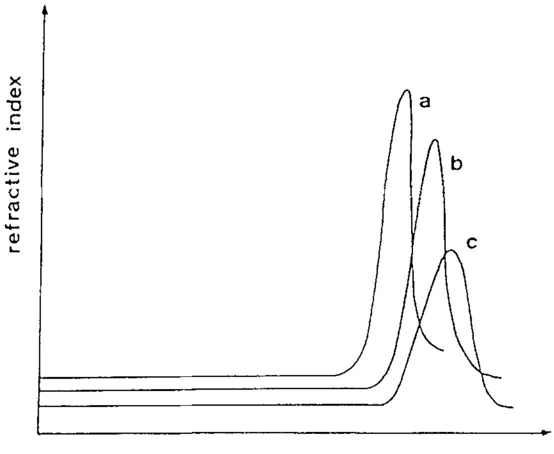
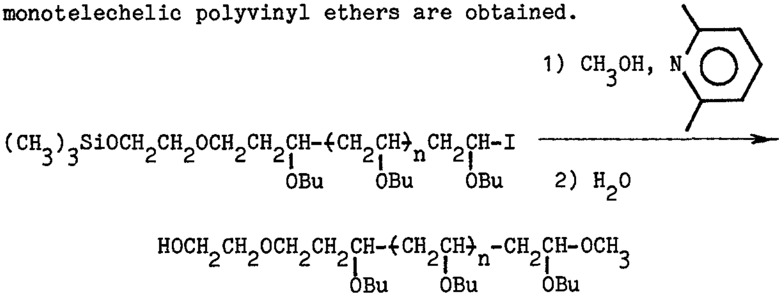


Figure 2 : GPC analysis of poly(n.butyl)vinyl ether with different molecular weights. a,b,c: see table 1.

3. Characterization of the polymer end groups.

The living polymerization of the vinyl ether is terminated by addition of methanol. Hereby, the active propagating centres are converted to acetal functions (SAWAMOTO et al, 1988b). The protons produced by the acetal formation are trapped by adding a non nucleophilic amine such as lutidine. Due to the nature of the initiating species the polymers possess a trimethylsiloxane group as head group. This type of group can be easily hydrolyzed to the corresponding silanol and alcohol function (EABARN, 1960). In the present case, hydrolysis of the trimethylsiloxane leads to the formation of a primary alcohol as head group. In this way, monotelechelic polyvinyl ethers are obtained.



$$(CH_3)_3SiOCH_2CH_2OCH_2CH_2\underset{OBu}{CH}-(CH_2\underset{OBu}{CH})_nCH_2\underset{OBu}{CH}-I \xrightarrow[2)\ H_2O]{1)\ CH_3OH,\ N}$$

$$HOCH_2CH_2OCH_2CH_2\underset{OBu}{CH}-(CH_2\underset{OBu}{CH})_n-CH_2\underset{OBu}{CH}-OCH_3$$

The ^1H-NMR signal originating from the methylene group adjacent to the hydroxyl function is covered by the signals of the polymer protons. Reaction with trichloroacetyl isocyanate leads to the

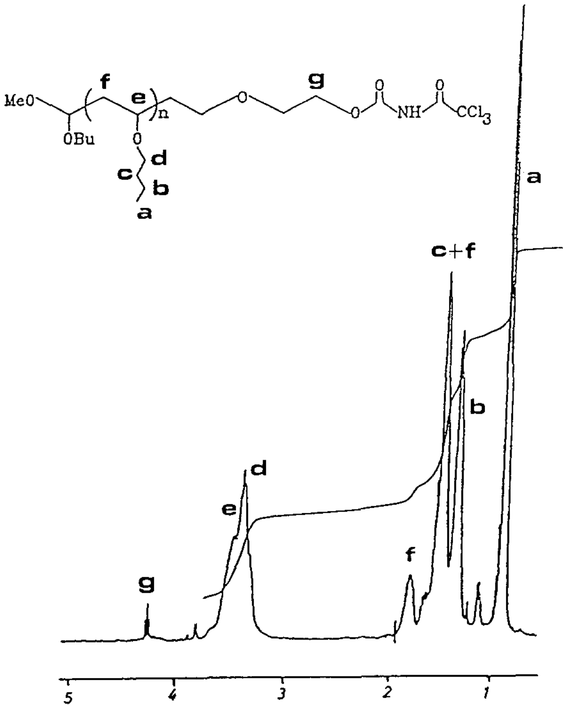


Figure 3 : 360 MHz ^1H-NMR spectrum of primary alcohol terminated poly(n.butyl) vinyl ether after reaction with trichloroacetyl isocyanate in deuterated chloroform.

quantitative formation of the corresponding urethane function (GOODLETT, 1965). After this derivatization the terminal methylene group of the polymer can be detected as a triplet at $\delta = 4.25$ ppm. The ^{1}H-NMR spectrum of the modified polymer is shown in figure 3.

Conclusion

The combination of TMSI and DXL leads to a fast and quantitative formation of 1-trimethylsiloxy-4-iodo-3-oxabutane. In the presence of tetrabutylammonium triflate, this compound can be used as an initiator for the living polymerization of vinyl ethers. The resulting polymers are characterized by controlled molecular weights and narrow molecular weight distributions, confirming the living polymerization mechanism. Hydrolysis of the TMS group originating from the initiator system, leads to a primary alcohol functionalized monotelechelic polyvinyl ether.

Experimental Part

Tetrabutylammonium trifluoromethanesulfonate (TBAT) was prepared as follows. To a solution of 472 mg of tetrabutylammonium iodide in 5 ml of dichloromethane, 361 mg of silver trifluoromethanesulfonate was added. The mixture was stirred during 12 hours under nitrogen atmosphere. After sedimentation, the precipitated silver iodide was removed by filtration and the solvent evaporated under vacuo. 0.5 g of TBAT was obtained.

The polymerization of n.butyl vinyl ether (n.BVE) proceeded as follows. 196 mg of TBAT was dissolved in 8.55 ml of dichloromethane under dry conditions. The solution was cooled at -40°C. 0.035 ml of DXL was added, followed by 0.071 ml of TMSI ($[I]_o = 0.05$ mol/l). After 5 minutes stirring, 1.34 ml of n.BVE ($[M]_o = 1$ mol/l) was injected. Polymerization proceeded during 50 minutes and was terminated with 0.040 ml of methanol. The mixture was neutralized by adding 0.280 ml of lutidine.

Purification. After termination, 30 ml of dichloromethane was added to the mixture. The solution was washed with 50 ml of a 10% solution of sodium thiosulfate in water. After isolation of the organic phase, the solvent was evaporated and the residual product was dissolved in ether. An excess of sodium sulfate was added followed by filtration and evaporation of the solvent under vacuo. 0.64 g of poly(n.butyl)vinyl ether with a molecular weight of 1216 (VPOM) and a dispersity of 1.3 (GPC) was obtained.

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References

EABARN C.: Organosilicon Compounds, Butterworths Sci. Publ. Ed. Academic Press, 301 (1960).

GOODLETT V.W.: Anal. Chem. 37, 431 (1965).

HIGASHIMURA T. and SAWAMOTO M.: Adv. Polym. Sci. 62, 49 (1984).

JUNG M.E., MAZUREK M.A. and LIM R.L.: Synthesis, 588 (1978).

JUNG M.E., ANDRUS W.A. and ORNSTEIN P.L.: Tetrahedron Lettres, 4175 (1977).

KEYSER G.E., BRYANT J.D. and BARRIO J.R.: Tetrahedron Lettres 35, 3263 (1979).

MIYAMOTO M., SAWAMOTO M. and HIGASHIMURA T.: Macromolecules 17, 265 (1984).

NUYKEN O. and KRONER H.: Polymer Preprints 29, 87 (1988).

SAWAMOTO M., AOSHIMA S. and HIGASHIMURA T.: Makromol. Chem., Makromol. Symp. 13/14, 513 (1988a).

SAWAMOTO M., KAMIGAITO M. and HIGASHIMURA T.: Polym. Bulletin 20, 407 (1988b).

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