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Block copolymers of poly(vinyl ethers) and poly(ethylene glycol) by means of the living cationic polymerization of vinyl ethers

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Summary

If living poly(vinyl ethers) are terminated with a large excess of methanol, containing aqueous ammonia, well-defined products are obtained. If only a slight excess of methanol is used, aldehydes and coupling products are formed. However, termination with an excess of a hydroxy terminated polymer is cumbersome. According to a given reaction scheme, the termination with methanol in the presence of an anhydrous organic base, should give better results. With two equivalents of triethylamine with respect to the initiator only two equivalents of methanol are needed to give a clean reaction. With this recipe block copolymers of poly(vinyl ether) and poly(ethylene glycol) are prepared.

Introduction

In 1984 Higashimura and Sawamoto discovered the living cationic polymerization of vinyl ethers with hydrogen iodide as initiator and iodine as co-catalyst (1).
These authors also reported the synthesis of AB-block copolymers by sequential polymerization of two different vinyl ether monomers (2).
The synthesis of block copolymers in which a poly(vinyl ether) is coupled to a polyoxazoline has been described by Kobayashi et al (3).
Living poly(vinyl ethers) can be terminated by adding a large excess of methanol containing 5 vol% of aqueous ammonia (4). The reason for using this large excess was not clear. When methanol is used as terminator, the excess can be easily removed from the polymer via the evaporation of the solvent. However, if one adds an excess of a hydroxy-functional polymer instead of methanol, separation problems might occur. Therefore, the terminaton reaction was subjected to further study.

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Experimental

Materials

All solvents (toluene, hexane, dietyl ether) were dried on molecular sieves 4A. Triethylamine (TEA, Merck) and triethylene monomethyl ether (Aldrich) were dried on molecular sieves 4A. Ethyl vinyl ether (Aldrich) was dried on sodium and distilled before use. HI was obtained from a 57 % aqueous solution by dehydratation with phosphorus pentaoxide and stored at -78°C as hexane solution. ZnI_2 (Aldrich, 99,99 %) was used as received and dissolved in diethyl ether.

Polymerization

The polymerizations were carried out under dry nitrogen in a baked vessel. Firstly, the HI solution was added to the monomer solution for the initiation step. Then, ZnI_2 was added to start the propagation. The temperature was kept at 0°C. The living polymerization was terminated with methanol, containing 5 vol % of aquaous ammonia, or with a mixture of methanol and TEA, at > 90 % conversion (controled by GC analysis). The quenched reaction mixture was sequentially washed with a 10 % aqueous thiosulphate solution and with water and then the organic layer was evaporated to dryness under reduced pressure to give the polymer products.

Characterization

The molecular mass distribution of the polymers was determined by size exclusion chromatography in THF with ultrastyragel columns (1000, 5000 and 100 A, Waters). The Mn/Mw values were obtained using a calibration curve of polystyrene standards. ^{1}H-NMR spectra were recorded in $CDCl_3$ on a Bruker AC200.

Results and discussion

The polymerization of ethyl vinyl ether in toluene was initiated by HI/ZnI_2. The living polymer was terminated with a large excess of methanol (methanol/HI=500), containing 5 vol % of aqueous ammonia to neutralize the HI. The initiation, propagation and termination reaction proceeds according to scheme 1.

Scheme 1

$$CH_2{=}CH(OR) + HI \text{ --> } CH_3\text{-}CH(OR)I$$

$$CH_3\text{-}CH(OR)I + nCH_2{=}CH(OR) \text{ --}ZnI_2\text{--> } CH_3\text{-}CH(OR)\text{-}[CH_2\text{-}CH(OR)]_n\text{-}I$$

$$CH_3\text{-}CH(OR)\text{-}[CH_2\text{-}CH(OR)]_n\text{-}I + CH_3OH \text{ -->}$$

$$CH_3\text{-}CH(OR)\text{-}[CH_2\text{-}CH(OR)]_n\text{-}OCH_3 + HI$$

$$NH_4OH + HI \text{ ---> } NH_4I + H_2O$$

Fig. 1 shows the ^{1}H-NMR spectrum of the poly(ethyl vinyl ether) (PEtVE) in CDCl$_3$. The methoxy end-group of the acetal moiety of the polymer can easily be seen at 3.3 ppm. The results obtained are in full agreement with those of Higashimura and Sawamoto (5).

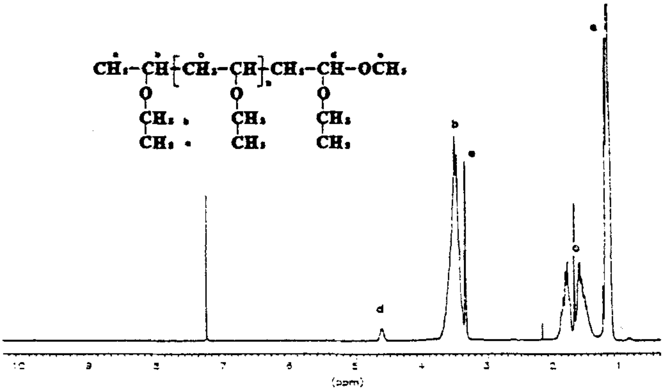


Fig.1. ^{1}H-NMR spectrum (CDCl$_3$) of the methanol terminated PEtVE. [CH$_3$OH]/[HI]=500, [NH$_4$OH]/[HI]=12.5, [H$_2$O]/[HI]=25.

In order to use hydroxy containing polymers as terminating agents, it is necessary to lower the ROH/initiator ratio. Therefore, in a first experiment, methanol was added to the living polymer in a molar ratio of 2:1, with respect to the active centre. Also the ratio between the aqueous base and the initiator was lowered (see Fig. 2). In Fig. 2 it can be seen, that under those conditions the ^{1}H-NMR spectrum of the polymer is quite similar to the one of Fig. 1. However, additional peaks appear at 2.6 and 9.8 ppm which are probably caused by the presence of an aldehyde group.

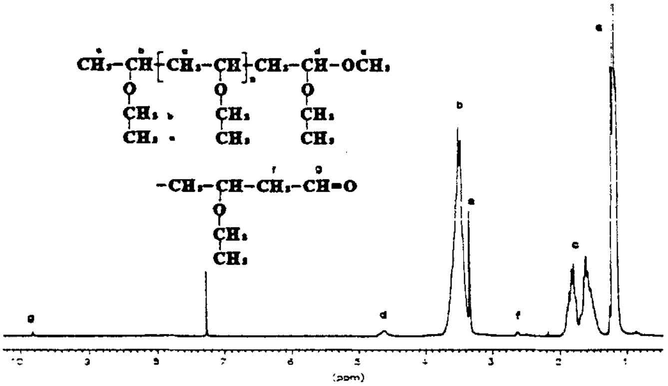
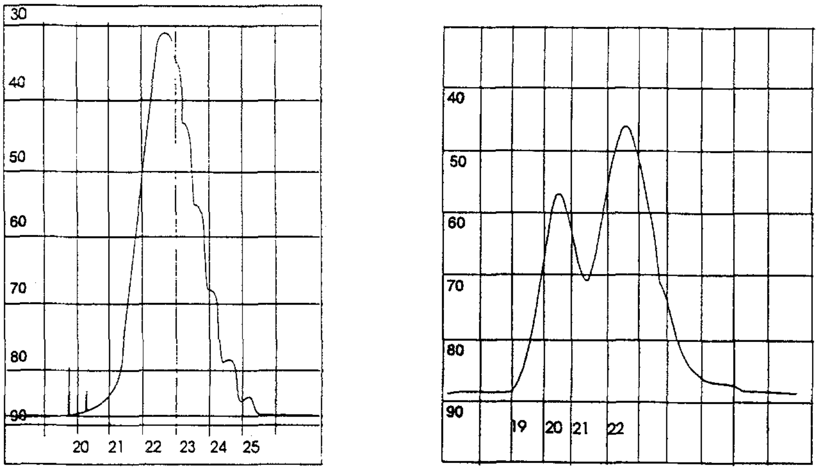


Fig. 2. ^{1}H-NMR spectrum of the methanol terminated PEtVE. [CH$_3$OH]/[HI]=2, [NH$_4$OH]/[HI]=2, [H$_2$O]/[HI]=4.

An aldehyde group can easily be formed by splitting off an alcohol from a hemiacetal [7] (see reaction scheme 2). A hemiacetal can be formed by acid hydrolysis of an acetal [5] or by a direct reaction of the living polymer with water [2] or ammonia [3]. These reactions are well-known from the chemistry of low molcular weight acetals.

A more pronounced difference between the two polymers terminated with a large and a small excess of methanol was noticed in the molecular mass distribution. The GPC curve, depicted in Fig.3, shows a bimodal molecular mass distribution in which the high molecular peak can be a polymer dimer, according to the molecular mass. The poly-dispersity (Mw/Mn) shows a shift from 1.12, in the case of a large excess of the termination agent, to 1.32 in this experiment.



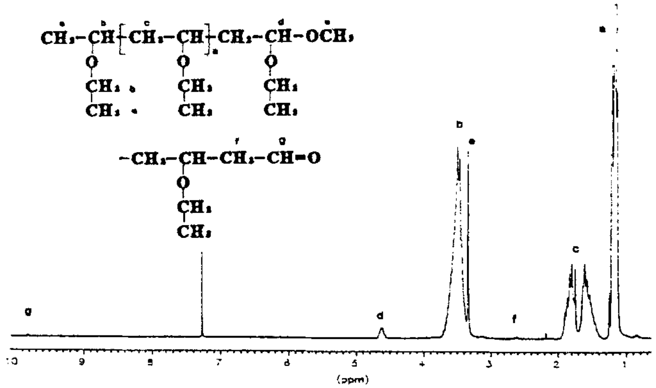
A. $[CH_3OH]/[HI]=500$, $[NH_4OH]/[HI]=12.5$, $[H_2O]/[HI]=25$

B. $[CH_3OH]/[HI]=2$, $[NH_4OH]/[HI]=2$, $[H_2O]/[HI]=4$

Fig. 3. GPC curve of the methanol terminated PEtVE.

Another series of experiments was performed with and without aqueous ammonia. The methanol to HI ratio was 10. From the ^{1}H-NMR spectra in fig. 4 it can be seen that the aldehyde formation increases in the absence of a base. The GPC spectrum (not shown here) indicates a broadening of the MMD.

A. $[NH_4OH]/[HI]=2$
$[H_2O]/[HI]=4$



B. No aqueous base.

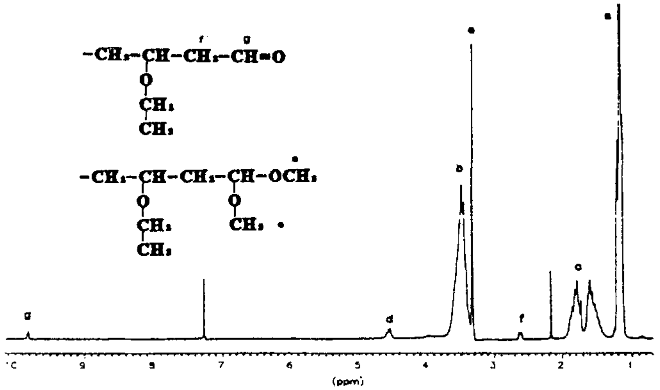


Fig. 4. ^{1}H-NMR spectrum of the methoxy terminated PEtVE. [CH3OH]/[HI]=10.

Furthermore, Fig. 4 B shows that more than one equivalent of methanol is build-in (see peak at 3.3 ppm). This is possible by an exchange reaction in which ethanol from the acetal is replaced by methanol [8]. GC analysis reveals that the polymer solution contains CH_3I, which is formed during the termination reaction. HI can give, in a Sn_2 reaction with the methanol terminated polymer, CH_3I and a hemiacetal [6]. Two hemiacetals can couple to give a dimer by splitting off water [9]. Water, under acid conditions (HI), can hydrolyse acetals into hemiacetals which are rapidly converted into aldehydes [7]. Thus reactions [1] and [4] are the desirable ones. But, under acid conditions, several other reactions can occur, which are well-known for the low molecular weight acetals. Although we didn't prove the dimer formation reaction [9], one can speculate that hemiacetals and aldehydes react with oneself or with each other or with the living polymer. All side-reactions can occur if the termination reactions [1] and [4] are relatvely slow. All reactions are summarized in scheme 2.

SCHEME 2

$PCH(OR)...I + CH_3OH \longleftrightarrow PCH(OR)OCH_3 + HI$ [1]

$PCH(OR)...I + H_2O \longleftrightarrow PCH(OR)OH + HI$ [2]

$PCH(OR)...I + NH_4OH \longleftrightarrow PCH(OR)OH + NH_4I$ [3]

$HI + NH_4OH \longrightarrow NH_4I + H_2O$ [4]

$PCH(OR)OCH_3 + H_2O \longleftrightarrow PCH(OH)OCH_3 + ROH$ [5]

$PCH(OR)OCH_3 + HI \longleftrightarrow PCH(OR)OH + CH_3I$ [6]

$PCH(OR)OH \longleftrightarrow PCHO + ROH$ [7]

$PCH(OR)OCH_3 + CH_3OH \longleftrightarrow PCH(OCH_3)_2 + ROH$ [8]

2 polymer chains ---> coupling products [9]

According to scheme 2 it appears to be important to avoid water, although it remains necessary to neutralize HI. Because a hydroxy containing base might give also a hemiacetal with the living polymer, water-free TEA was selected as a base. Experimental conditions were sought to use the lowest $[CH_3OH]/[HI]$ ratio as possible. Fig. 5 shows the ^1H-NMR spectrum of a product which is prepared by adding, after the polymerization, two equivalents of TEA and two equivalents of methanol. There are no aldehyde peaks at 2.6 and 9.8 ppm and the GPC spectrum shows no broadening (Mn/Mw=1.12).

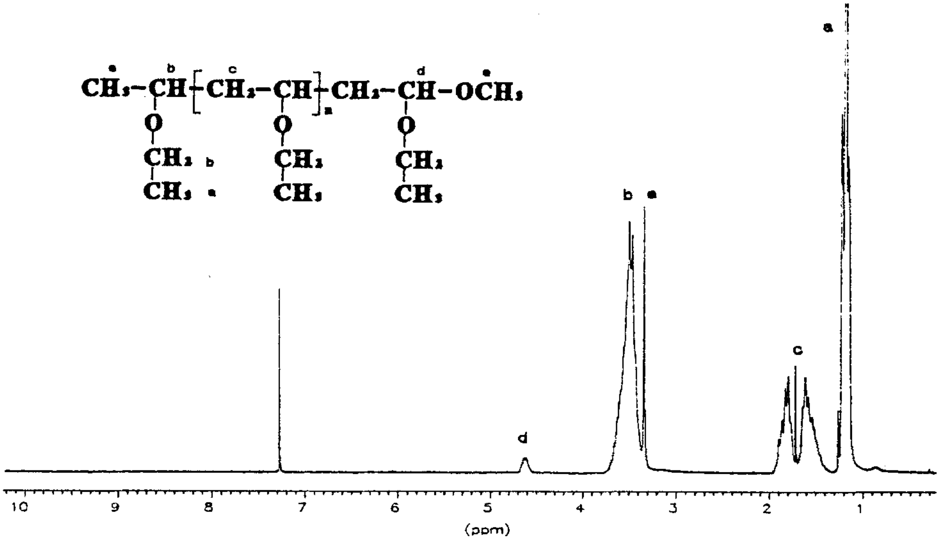


Fig. 5. ^1H-NMR spectrum of PEtVE-b-OCH3. Termination with $[CH_3OH]/[HI]=2$ AND $[TEA]/[HI]=2$.

A block copolymer in which living PEtVE was terminated with triethylene glycol monomethyl ether was made according to the procedure described above. Thus, the living polymer was treated at 0°C with two equivalents of TEA and ten equivalents of triethylene glycol monomethyl ether in this case. A precipitate, which appeared to be Et$_3$NHI, was filtered off. The ^{1}H-NMR spectrum (Fig. 6) shows no aldehyde peak. The dispersity was narrow (Mw/Mn=1.10).

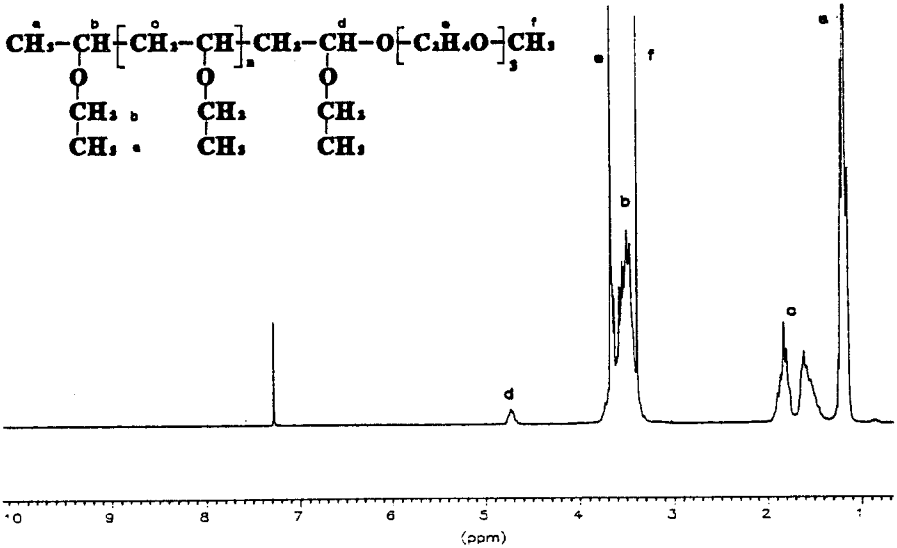


Fig. 6. ^{1}H-NMR spectrum of PEtVE-b-PEG
[PEG]/[HI]=10, [TEA]/[HI]=2.

CONCLUSIONS

During the termination of the living PEtVE with a slight excess of aqueous ammonia containing methanol, aldehydes and coupling products are formed. The initially formed acetals are hydrolyzed in the presence of water under acid conditions (HI). When water is avoided and HI is trapped by two equivalents of triethylamine well-defined products can be prepared with only 2 equivalents of methanol per initiator molecule. Under similar conditions well defined block copolymers are prepared in which living PEtVE was terminated by triethylene glycol monomethyl ether.

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