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Synthesis of poly(vinyl alcohol)s with narrow molecular weight distribution from poly(benzyl vinyl ether) precursors

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Summary

A series of poly(benzyl vinyl ether)s of low molecular weight (5000 to 15000 g mol^{-1}) and narrow molecular distribution ($\overline{M}_w / \overline{M}_n$ < 1.20) have been synthesised *via* the cationic polymerisation of benzyl vinyl ether. Acetylation with acetic anhydride/tin (IV) chloride leads to poly(vinyl acetate), which can be hydrolysed to near-monodisperse water-soluble poly(vinyl alcohol) with an isotacticity of approximately 47 %. This polymer was re-acetylated and its molecular weight distribution assessed to confirm that hydrolysis gives minimal chain scission.

Introduction

Poly(vinyl alcohol) (PVA) is one of the most important synthetic water-soluble polymers. It is widely used as a stabiliser in the suspension polymerisation of vinyl chloride (1) and the emulsion polymerisation of vinyl acetate (1,2), and its copolymers are important in the adhesives, food packaging, paper-making and cosmetics industries (2,3).

PVA is normally synthesised *via* the de-acetylation of poly(vinyl acetate) (PVAc) (1). Vinyl acetate is invariably polymerised by free-radical methods which give PVA having broad molecular weight distributions (typically $\overline{M}_w / \overline{M}_n$ = 2 - 3) (1,2). In principle, near-monodisperse samples might be obtained by fractionation but in practice this is time-consuming, tedious and rarely completely successful. Moreover, there is some evidence that, in the case of PVAs containing residual vinyl acetate groups, polymer fractions can have different compositions as well as molecular weights (4). PVAc cannot be synthesised by conventional living anionic or cationic polymerisation. Very recently Matyjaszewski et al. have described synthesis of low molecular weight PVAc of reduced polydispersity by so-called "living free-radical" polymerisation (5). However, as far as we are aware, de-acetylation to obtain near-monodisperse PVA has not yet been reported.

Other protected monomers have been used as precursors polymerisable cationically, including t-butyl vinyl ether, trimethylsilyl vinyl ether and benzyl vinyl ether (6-8). Polymerisation of a suitable protected monomer by appropriate cationic (9) or anionic (10) methods should yield a precursor polymer of narrow molecular weight distribution which could then be converted to near-monodisperse PVA. The feasibility of this route has been shown by both Sogah and Webster (11) and Risse and Grubbs, using "aldol-GTP" chemistry (12).

In a 1986 review (13) Higashimura *et al.* reported that the living cationic polymerisation of benzyl vinyl ether produced near-monodisperse polymer ($\overline{M}_w / \overline{M}_n$ = 1.18), which could be deprotected using dry HBr to give PVA. However, as far as we are aware, only this single example of rather low molecular weight (*ca.* 3200 g mol^{-1} by GPC *vs.* polystyrene standards) poly(benzyl vinyl ether) (PBzVE) was reported. We note that the PVA would have had a molecular weight of only *ca.* 1100 g mol^{-1} (approximately 20-25 vinyl alcohol units) due to the loss of the relatively massive benzyl group. Moreover, it was apparently assumed that no chain scission had occurred during the debenzylation step. Few synthetic details (e.g. reagent concentration, time *etc.*) were given and no indication of the extent of debenzylation.

We have recently been interested in the synthesis of water-soluble homopolymers and block copolymers with controlled structure and molecular weight (14-17). We have therefore re-examined the Higashimura route to near-monodisperse PVA. Prompted by a recent paper by Kobayashi and co-workers (18) we wish to report our own progress.

Experimental

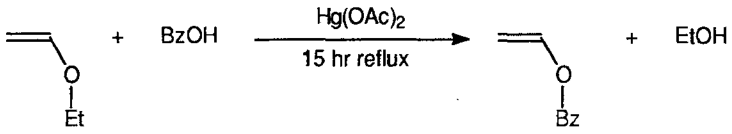
Materials

Zinc iodide (Aldrich; > 99.99% purity) was rapidly ground to a fine powder and dried under vacuum at room temperature for 48 h in the dark. This light-sensitive compound was subsequently handled in a nitrogen dry box under reduced light conditions. Toluene and hexane were dried and distilled from sodium and finally distilled from calcium hydride just before use. Diethyl ether was distilled twice from calcium hydride. Acetic anhydride (Aldrich; >99% purity) was used as received. Benzene was distilled from sodium and stored over 4A molecular sieves. Tin (IV) chloride (Aldrich; 99% purity) was used as received. Mercuric acetate was recrystallised from ethanol.

Synthesis of benzyl vinyl ether

Scheme 1

Monomer synthesis



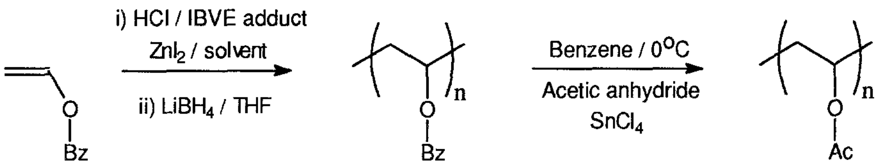
The monomer synthesis was based on a modification of a transetherification procedure described by Watanabe and Conlon (19) (see Scheme 1). Thus, mercuric acetate (10 g) was added to a solution of benzyl alcohol (100 ml) in ethyl vinyl ether (1000 ml) in a two-neck flask. This reaction mixture was heated at reflux for 10 h, before being treated with a further portion of mercuric acetate (5 g). After cooling, the solution was washed with 10 % potassium carbonate solution and then dried over anhydrous potassium carbonate. The solution was concentrated under reduced pressure and stirred over sodium. Vacuum distillation yielded two fractions: first unreacted ethyl vinyl ether and then the crude product. The monomer was further purified by distillation from $LiAlH_4$. (overall yield: 69.3 g; 53.5 %).

Polymerisation

In view of the light sensitivity of the ZnI_2, all polymerisations were carried out under dry nitrogen using baked-out, darkened glassware. Freshly distilled BzVE monomer (2-10 ml) was added to 50 ml toluene. The polymerisation was initiated by addition of an iso-butyl vinyl ether hydrochloride initiator adduct as a 1 M solution in hexane (20), to give the initiator concentration needed for the desired molecular weight. This was followed by sufficient ZnI_2 co-catalyst as an 0.1 M solution in diethyl ether to give a 1:1 ratio to the initiator (see Scheme 2). Polymerisation was terminated by the addition of $LiBH_4$ in THF. The quenched mixture was washed with aqueous sodium thiosulfate and water to remove initiator residues. Finally the poly(benzyl vinyl ether) (PBzVE) was isolated by precipitation into excess methanol.

Scheme 2

Polymerisation and acetylation



Acetylation of poly(benzyl vinyl ether)

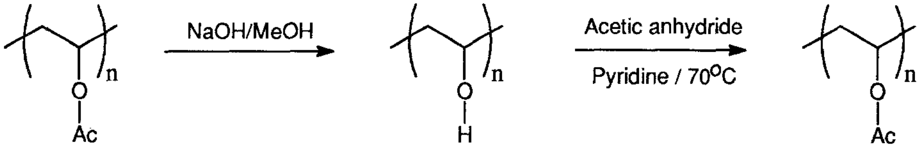
To 1.5 g PBzVE dissolved in 20 ml benzene was added a mixture of acetic anhydride (10 ml) and benzene (10 ml). The solution was cooled to 0°C and tin (IV) chloride (0.8 ml) was added (see Scheme 2). The reaction was allowed to proceed for one hour and then terminated by the addition of water. The benzene layer was washed with aqueous sodium hydrogen carbonate solution and water, dried over anhydrous sodium sulfate and precipitated into hexane. This acetylation was repeated on the partially acetylated PBzVE to maximise acetylation (21).

Hydrolysis and re-acetylation of poly(vinyl alcohol)

Hydrolyses were carried out according to a procedure described in the patent literature (22). PVAc (0.45 g) was dissolved in 3.0 ml of a 96:4 v/v % methanol/water solution at room temperature. Cyclohexane (0.55 ml) was added and the reaction mixture was heated to 50 °C. NaOH (4.7 mg, dissolved in methanol) was then added and the hydrolysis carried out for approximately 1 h at 50 °C. According to Watts, the above procedure yields PVAs which contain low levels of residual vinyl acetate groups to aid water solubility (22).

Scheme 3

Hydrolysis and re-acetylation



Re-acetylation was based on a method reported by Yuki *et al.* (23). PVA (1g) was suspended in 10 ml of dry pyridine at room temperature. After the polymer was swollen, acetic anhydride (5 ml) was added and the reaction mixture heated to 60-70 °C (see Scheme 3). This temperature was maintained for 1- 2 hours after the polymer had dissolved. The resulting PVAc was isolated by repeated precipitation from methanol into water.

Instrumentation

Molecular weight distributions were assessed by gel permeation chromatography (GPC) in THF at room temperature using polystyrene calibration standards. Our GPC system consists of a Perkin Elmer Series 10 LC pump, a Perkin Elmer LC-25 RI detector and a Knauer variable wavelength UV detector with 2 x 30 cm Polymer Laboratories 5 μm "mixed-bed D" columns. Proton nmr spectra obtained using a Bruker AC-250 MHz instrument.

Results and discussion

The details of selected benzyl vinyl ether polymerisations at a fixed monomer/initiator ratio are summarised in Table 1. A significant fraction of the monomer always remained unpolymerised; polymer yields ranged from 26 % up to 83 % depending on the reaction conditions. Given these relatively low conversions it is not surprising that the molecular weight was always significantly lower than the target, 24400 g mol^{-1}, expected from quantitative polymerisation.

Although we have yet to establish good control over the molecular weight it is noteworthy that: (i) the molecular weight could be varied from 5800 up to 15900 g mol^{-1} (as measured by GPC using polystyrene standards) depending on the reaction conditions; (ii) polymers of reasonably narrow molecular weight distribution ($\overline{M}_w / \overline{M}_n \leq 1.20$) were usually obtained. This latter observation suggests that the reaction has some living character, although it is slow.

Table 1
Reaction conditions and polymer properties for the polymerisation of benzyl vinyl ether

Sample No	Solvent	Monomer volume /ml[a]	Reaction temp/ °C	Reaction time/ min	Yield/ %	$\overline{M}_n$ /g mol^{-1} (Expt.)[b]	$\overline{M}_w / \overline{M}_n$ (Expt.)[b]
1	Toluene	2.0	-40	60	26	5800	1.09
2	Toluene	2.0	-40	120	43	9600	1.19
3	Toluene	2.0	-15	60	52	10300	1.32
4	Toluene	5.0	-40	60	45	7900	1.11
5	Toluene	10.0	-40	30	81	11700	1.20
6	Toluene	10.0	-40	60	83	15900	1.18
7	CCl_4	2.0	-20	60	60	11700	1.18
8	CH_2Cl_2	2.0	-40	60	43	7500	1.21

a: Solvent volume was 50 ml in all cases
b: "Polystyrene equivalent", derived from GPC calibrated with PS standards. The initiator concentration was chosen so that the theoretical $\overline{M}_n$ for complete reaction was always 24400 g mol^{-1}

Longer reaction times led to higher polymer yields under the same synthesis conditions (compare samples 1 and 2 and 5 and 6). Higher monomer concentration increased the polymer yield within a given reaction time (compare samples 1, 4 and 5). Higher reaction temperatures also led to improved yields but with an increase in polydispersity (compare samples 1 and 3). Although only a limited number of experiments were carried out, it seems that chlorinated solvents such as CCl_4 and CH_2Cl_2 probably offer some improvement in polymer yield compared to similar syntheses in toluene. These solvents are currently being investigated in more detail.

In classical organic chemistry it is well known that benzyl ethers and benzyl esters can be cleaved under relatively mild conditions (24). Such selectivity has been recently utilised in synthetic polymer chemistry. For example, we have recently reported an improved synthesis of near-monodisperse poly(methacrylic acid) based on the hydrogenolysis of poly(benzyl methacrylate) precursors (14). In later work the selectivity of this deprotection reaction was confirmed by synthesis of poly(methacrylic acid-*b*-methyl methacrylate) block copolymers (15).

In view of this initial success we anticipated that the benzyl protecting group might be useful in PVA syntheses. In principle hydrogenolysis of vinyl ether copolymers containing benzyl groups should leave other vinyl ether comonomer(s) intact. Unfortunately we were unable to deprotect the homopolymers by hydrogenolysis (*e.g.* 1 atm. H_2 with a Pd/C catalyst at room temperature for 40 h removed only 20-25 % of the benzyl groups (25)).

Initial hydrolysis experiments were also disappointing: the dry HBr/toluene reaction favoured by Higashimura's group (13) produced highly coloured PVAs which were only partially water-soluble. Use of $(CH_3)_3SiI$ in CH_2Cl_2 under literature conditions (26) resulted in quantitative removal of the benzyl groups (confirmed by nmr spectroscopy). However, these PVAs were presumably cross-linked since they were completely insoluble even in boiling water. On the other hand, the acetylation/hydrolysis method described by Fujii (21) in his studies on polydisperse PBzVEs worked well in our hands (see Scheme 2).

Typical ^1H nmr spectra of a PBzVE before and after debenzylation are shown in Figure 1, together with the spectrum obtained after deacetylation. The relative areas of the proton signals in the spectrum of pristine PBzVE are consistent with the expected values. In debenzylated and acetylated material, a comparison of the integral arising from the aromatic benzyl protons at δ 7.0-7.5 with that due to the methyl protons of the acetyl group at δ 1.8-2.0 indicates more than 95 % debenzylation (or acetylation). The near-quantitative disappearance of the acetyl proton signal after alkaline alcoholysis of the PVAc confirmed the formation of PVA containing less than 9.0 mol % of residual acetyl and benzyl groups (see Figure 1c). We estimated the isotactic content as approximately 47 % by ^1H nmr (6c).

This PVA is completely water-soluble but, like commercial polymers, it is insoluble in THF. Since this material was not analysable with our GPC, we re-acetylated it using acetic anhydride/pyridine (see Scheme 3). Derivatisation yielded THF-soluble PVAc which we could then characterise. A typical gel permeation chromatogram for an as-synthesised PBzVE ($\overline{M}_w / \overline{M}_n = 1.11$) is shown in Figure 2(a). The corresponding traces for PVAc and reacetylated PVA samples derived from this polymer are also depicted for comparison (see Figures 2(b) and 2(c)). There is no appreciable broadening of the molecular weight distribution curves of these latter two polymers.

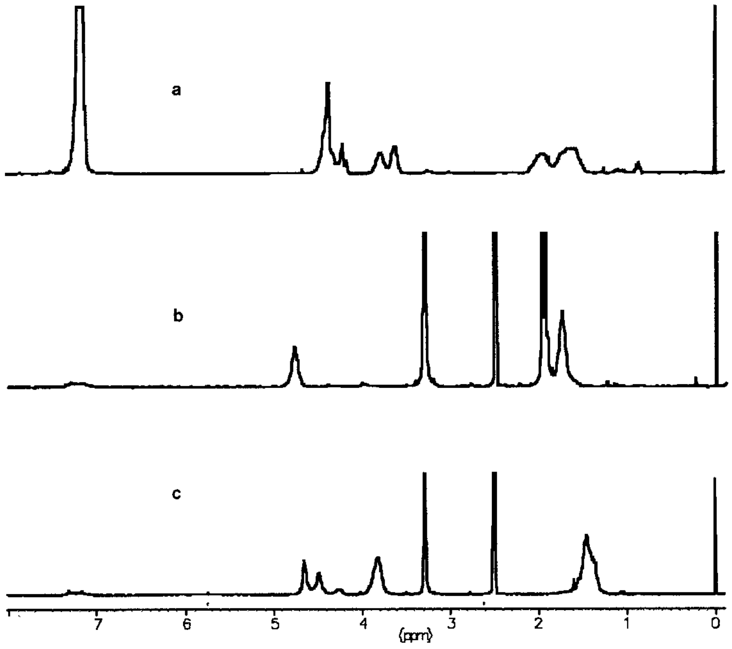


Figure 1: ^{1}H nmr spectra of (a) PBzVE in $CDCl_3$; (b) PVAc produced by acetylation of the same sample,; (c) PVA produced by deacetylation of the same sample, in d_6 DMSO

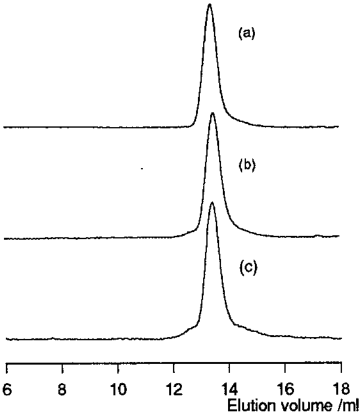


Figure 2: Gel permeation chromatograms of (a) PBzVE; (b) PVAc produced by acetylation of the same sample; (c) PVAc produced by acetylation, hydrolysis and reacetylation of the same sample

In most recent work we have prepared poly(isobutyl vinyl ether-*b*-benzyl vinyl ether) block copolymers of narrow molecular weight distribution ($\overline{M}_w / \overline{M}_n = 1.14$) by sequential monomer addition (27). In view of the incomplete benzyl vinyl ether polymerisation we elected to polymerise the isobutyl vinyl ether monomer first. We anticipate that these block copolymers will be easily derivatised to give novel block copolymers containing PVAc or PVA sequences.

Conclusions

Benzyl vinyl ether can been polymerised via cationic polymerisation to give a series of low molecular weight (5800 to 15900 g mol^{-1}) polymers of low polydispersity. The effects of solvent, reaction temperature, reaction time and monomer concentration on polydispersity and yield have been investigated and suggest that the polymerisation is living, at least in the sense of producing low polydispersity, but slow.

These precursor polymers can be readily acetylated using acetic anhydride/tin (IV) chloride to produce PVAcs. The degree of acetylation is typically greater than 95 %, as measured by nmr. Subsequent hydrolysis, using alcoholic NaOH yields water-soluble PVAs with the same narrow molecular weight distribution. Re-acetylation, followed by GPC analysis in THF confirmed that essentially no chain scission had occurred during hydrolysis. Thus this is an attractive synthetic route to near-monodisperse PVAs. We anticipate that its extension to sequential polymerisation with other vinyl ether monomers will produce novel block copolymers.

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