Novel hydrophilic–hydrophilic block copolymers based on poly(vinyl alcohol)

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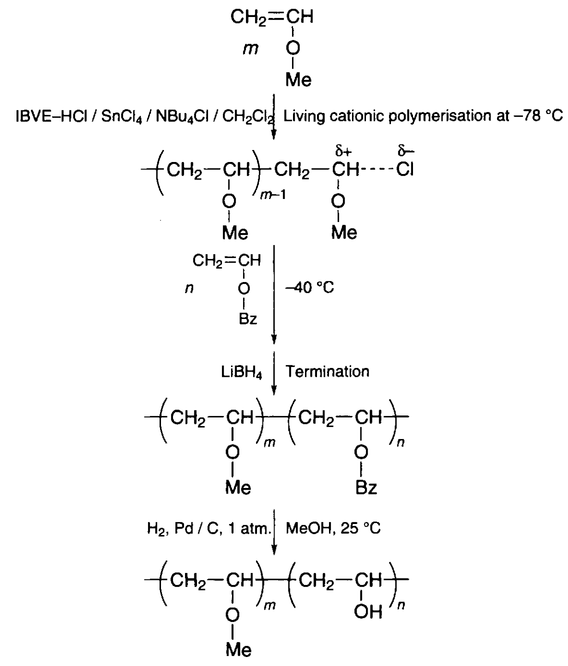
Novel, near-monodisperse poly(methyl vinyl ether–block–vinyl alcohol) copolymers are synthesised using living cationic polymerisation where the vinyl alcohol groups were protected using benzyl groups which were subsequently removed by catalytic hydrogenolysis under mild conditions; the resulting hydrophilic–hydrophilic block copolymers are water-soluble at room temperature and form micelles at temperatures above the cloud-point of the poly(methyl vinyl ether) block (*ca.* 29 °C).

Currently there is considerable academic and industrial interest in the synthesis of water-soluble (co)polymers with specific properties. Recently there have been many reports describing a wide range of hydrophilic–hydrophobic water-soluble or water-dispersible diblock copolymers.[1–3] However, there are very few examples of hydrophilic-hydrophilic water-soluble block copolymers. Aoshima and co-workers have reported the synthesis of poly(2-methoxy ethyl vinyl ether–block–2-ethoxy ethyl vinyl ether) copolymers[4] and Hoogeveen *et al.* have described the adsorption behaviour of methacrylate-based hydrophilic–hydrophilic diblock copolymers onto silica and titania particles.[5]

We have recently described the synthesis of near-monodisperse poly(methacrylic acid)[6] and poly(vinyl alcohol)[7] using 'group transfer' and living cationic polymerisation techniques respectively. In these syntheses the functional monomer was protected using either benzyl ester or benzyl ether groups, respectively. The use of benzyl protecting groups is well established in organic chemistry but this strategy has been apparently under-utilised in synthetic polymer chemistry. Here we describe the first examples of poly(methyl vinyl ether–block–vinyl alcohol) copolymers, synthesised using benzyl protecting groups. These novel block copolymers are structural isomers of the commercially successful poly(ethylene oxide–block–propylene oxide) 'Pluronic' copolymers.

Methyl vinyl ether (MVE) was polymerised in CH_2Cl_2 at −78 °C *via* living cationic polymerisation using the isobutyl vinyl ether–hydrogen chloride adduct (IBVE–HCl) as initiator, a tin(IV) chloride co-initiator and an added salt, tetrabutylammonium chloride as described by Higashimura and co-workers.[8] The resulting poly(methyl vinyl ether) homopolymers had molecular weights of *ca.* 4 000 g mol^{-1} as determined by end-group analysis of the initiator fragment using NMR (doublet at δ 0.9). Subsequent addition of benzyl vinyl ether at −40 °C led to block copolymer formation, Scheme 1. The benzyl vinyl ether content of the block copolymers was systematically varied from 9 to 48 mol%. The 'living' copolymers were terminated using a 2 mol dm^{-3} $LiBH_4$ solution in THF and inorganic residues were removed by extraction using first dilute HCl and then water. Finally, the CH_2Cl_2 solvent was removed under vacuum. GPC analysis (THF eluent, polystyrene standards) indicated low polydispersities for both homopolymers and block copolymers, with M_w/M_n values typically less than 1.20, Table 1. Copolymer compositions from NMR spectroscopy were in excellent



Scheme 1 Reaction scheme for the synthesis of the poly(methyl vinyl ether–block–vinyl alcohol) copolymers *via* living cationic polymerisation

Table 1 Copolymer compositions, molecular weights, polydispersities and yields for the poly(methyl vinyl ether–block–benzyl vinyl ether) copolymers synthesised by living cationic polymerisation. Synthesis conditions were: $[MVE]_o$ = 0.78 mol dm^{-3}; $[HCl\text{-}IBVE]_o = [SnCl_4]_o = [NBu_4Cl]_o$ = 10 mmol dm^{-3} in CH_2Cl_2 at −78 °C (MVE) and −40 °C (BzVE).

Sample	Comonomer feed ratio MVE:BzVE		M_n Theory	M_n* Expt.	M_w/M_n	Comonomer ratio in copolymer/mol%[a] MVE:BzVE	Yield (%)
		Homo	4500	4000	1.05		
1	90:10	Block	5700	4900	1.08	91:9	>99
		Homo	4500	3900	1.10		
2	80:20	Block	7100	6200	1.15	81:19	>99
		Homo	4500	3800	1.10		
3	70:30	Block	9000	7500	1.20	71:29	>99
		Homo	4500	3900	1.15		
4	52:48	Block	14300	12200	1.40	52:48	>99

[a] Determined by ^{1}H NMR spectroscopy

agreement with the expected values and copolymer yields were quantitative.

The benzyl groups were removed *via* catalytic hydrogenolysis (1 atm. H_2 gas) in methanol at room temperature for 7 d using a Pd/C catalyst.[9] During work-up the deprotected copolymers were treated with methanolic KOH in order to hydrolyse any benzyl esters which can sometimes result from aerial oxidation of the benzyl protecting groups. Proton NMR studies indicated that debenzylation was quantitative, with no evidence for any residual aromatic signals at δ 7–8 in the deprotected block copolymers, Fig. 1. These results were confirmed by FTIR spectroscopy: two very intense absorption associated with the benzyl groups (bands at 734 and 696 cm^{-1} due to the aromatic out-of-plane C–H bending modes) of the precursor blocks were completely absent in the IR spectra of the poly(methyl vinyl ether–block–vinyl alcohol) copolymers. It is interesting to compare this very high level of debenzylation (> 99%) with that obtained for poly(benzyl vinyl ether) homopolymers under the same conditions (only 20–25%).[7,10] In the latter case it is difficult to find a suitable hydrogenolysis solvent which is a good solvent for both the precursor and the deprotected poly(vinyl alcohol). In contrast, the methyl vinyl ether block is soluble in a wide range of organic solvents and thus aids debenzylation by preventing precipitation of the poly(vinyl alcohol) component. On the other hand, we were only able to achieve *ca.* 70–88% deprotection of the analogous poly(methyl triethylene glycol vinyl ether–block–benzyl vinyl ether) copolymers.[10] Even after attempted clean-up, the resulting poly(methyl triethylene glycol vinyl ether–block–vinyl alcohol) copolymers were heavily contaminated with catalyst residues. We believe that these two observations are connected: the triethylene glycol groups probably adsorb strongly onto the catalyst support and thus interfere with the heterogeneous debenzylation reaction.

Several groups have reported the use of dry HBr to remove benzyl groups from poly(benzyl vinyl ethers).[11–13] However, this reagent often leads to discolouration and reduced water-solubility of the resulting poly(vinyl alcohols).[7,10,11] In contrast, the poly(methyl vinyl ether–block–vinyl alcohol) copolymers obtained from our catalytic hydrogenolyses were white or pale yellow, depending on their vinyl alcohol content. The deprotected copolymers **1–4** (Table 1) dissolved readily in water at 25 °C to give optically clear solutions. Photon correlation spectroscopy studies at 20 °C on copolymers **2** and **3** gave very low counts, which suggests that these copolymers were molecularly dissolved as unimers. On heating these aqueous solutions, micellisation occurred near the cloud-point expected for poly(methyl vinyl ether) homopolymer (*ca.* 29 °C). Photon correlation spectroscopy measurements at 60 °C indicated micelle diameters in the range 20–30 nm, with a small fraction of larger aggregates. Copolymer **1**, which contains the lowest vinyl alcohol content, exhibited a cloud-point at *ca.* 39 °C in turbidimetry experiments. In contrast, copolymers **2–4** remained in solution up to 100 °C.

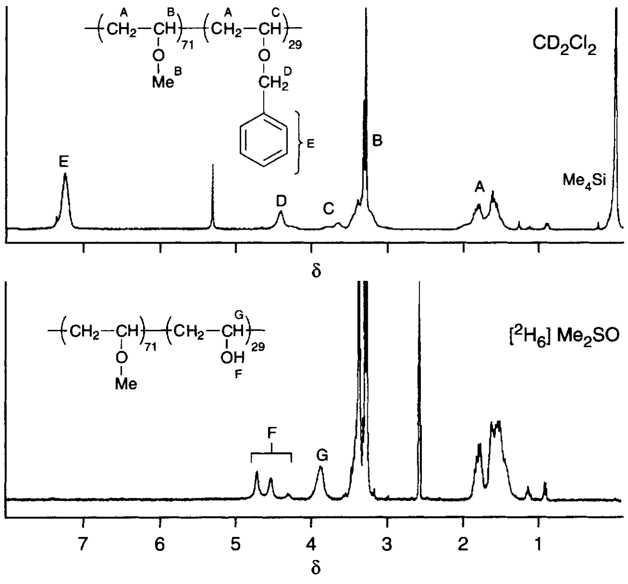


Fig 1 ^1H NMR spectra of (*a*) the poly(methyl vinyl ether–block–benzyl vinyl ether) precursor copolymer **3** (Table 1) in CD_2Cl_2 (CH_2Cl_2 peak at δ 5.3) and (*b*) the deprotected poly(methyl vinyl ether—block–vinyl alcohol) obtained after hydrogenolysis in $[^2H_6]Me_2SO$ (Me_2SO peak at δ 2.5)

Since debenzylation was achieved at room temperature, it seemed very unlikely that any significant chain scission of the block copolymers had occurred. In order to verify this, copolymers 1–3 were analysed by aqueous GPC at 27 °C (Pharmacia Biotech 'Superdex' 200 HR 10/30 GPC column and 0.25 mol dm^{-3} NaCl + 50 mmol dm^{-3} Tris buffer as eluent at pH 8.5). Their polydispersities were in the range 1.12 to 1.28, in good agreement with those of the precursor blocks given in Table 1. Thus the deprotected copolymers are indeed near-monodisperse, as expected.

Further characterisation of the aqueous solution properties of these hydrophilic–hydrophilic block copolymers is in progress. Potential applications, including use as novel surfactants, emulsifiers, stabilisers and dispersants, are currently being evaluated.

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