Synthesis and Aqueous Solution Properties of Amphiphilic Diblock Copolymers Based on Methyl Triethylene Glycol Vinyl Ether and Benzyl Vinyl Ether

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ABSTRACT: Water-soluble diblock copolymers of methyl triethylene glycol vinyl ether and benzyl vinyl ether were synthesized by living cationic polymerization, giving molecular weights in the range 13 400−17 300 and narrow molecular weight distributions ($M_w/M_n = 1.18-1.28$). The MTEGVE block length was fixed at 56 monomer units and the BzVE block length varied from 6 to 56 units. Aqueous solutions were studied by using dynamic light scattering and turbidimetry to determine the effect of block ratio on micellization and precipitation. Dynamic light scattering at room temperature in water revealed two intensity-average populations for all the copolymers, assigned as well-defined micelles and large aggregates. The hydrodynamic radii of the micelles ranged from 10.2 to 26.2 nm. Turbidimetry showed a cloud point of 83.5 °C for the MTEGVE homopolymer. The cloud points of the block copolymers decreased with increasing BzVE content and leveled off at higher BzVE contents. Selective removal of the benzyl group was achieved by catalytic hydrogenolysis, as a route to block copolymers with poly(vinyl alcohol) sequences. The maximum extent of deprotection was only 88%. Incomplete deprotection was attributed to the adsorption of the MTEGVE block onto the carbon support, thus blocking the catalyst sites.

Introduction

Poly(vinyl alcohol) (PVOH) is one of the most important synthetic water-soluble polymers. It is normally synthesized *via* the alcoholysis of poly(vinyl acetate) (PVAc).[1] Since vinyl acetate is invariably polymerized by free-radical methods, the precursor polymer inevitably has relatively high polydispersity (typically $M_w/M_n = 2-3$).[1,2] Unfortunately PVAc cannot be synthesized by living polymerization techniques.[3]

Other protected monomers, including *tert*-butyl vinyl ether,[4] trimethylsilyl vinyl ether,[5] and benzyl vinyl ether,[6] have been polymerized by nonliving cationic chemistry to give poly(vinyl ether) precursors to PVOH. With recent advances in living polymerization chemistry, it is now possible to polymerize a suitable protected monomer to give precursor polymers of narrow molecular weight distribution which could be subsequently converted to near-monodisperse PVOH. The feasibility of this route has been demonstrated by a number of research groups.[7−10]

We have recently examined the deprotection of benzyl vinyl ether (BzVE) homopolymers[11] and found that acetylation, followed by alkaline saponification as described by Fujii,[12] is a viable route to near-monodisperse PVOH. Attempted debenzylation *via* catalytic hydrogenolysis was incomplete. In contrast, we have recently described synthesis of water-soluble dihydrophilic block copolymers based on methyl vinyl ether and vinyl alcohol, synthesized via the catalytic hydrogenolysis of MVE-*block*-BzVE copolymers.[13] In this case, NMR confirmed quantitative debenzylation under mild conditions.

In this work we describe the synthesis of amphiphilic diblock copolymers based on methyl triethylene glycol vinyl ether and benzyl vinyl ether. In principle, debenzylation of these copolymers should produce novel dihydrophilic copolymers containing PVOH blocks; see Figure 1. These copolymers have also been characterized by using turbidimetry and dynamic light scattering to probe their micellar behavior in aqueous solution.

Experimental Section

Materials. MTEGVE (BASF) was stirred over calcium hydride and distilled under vacuum. It was kept over calcium hydride and distilled a second time immediately prior to use. Benzyl vinyl ether was synthesized by transetherification of ethyl vinyl ether and benzyl alcohol with mercuric acetate as catalyst.[11] The purified monomer was distilled from calcium hydride immediately prior to use. Toluene (Fisons) was refluxed for 3 days over sodium and distilled immediately prior to use. Ethyl acetate (Aldrich) was washed with 5% aqueous sodium carbonate followed by saturated sodium chloride and then dried over anhydrous potassium carbonate. It was then distilled twice from calcium hydride prior to use. 1-Isobutoxy ethyl acetate (*i*BuOEtAc) was prepared by reacting acetic acid with a 50 mol % excess of isobutyl vinyl ether (IBVE) at 60 °C for 3 h, distilled twice from calcium hydride, and dissolved in dry *n*-hexane to give a 0.5 M solution. Ethyl aluminium sesquichloride ($Et_{1.5}AlCl_{1.5}$) was purchased from Aldrich as a 0.9 M solution in toluene (97% purity) and used as received. Two hydrogenolysis catalysts, ruthenium (5%)/carbon and platinum(IV) oxide (Adam's catalyst), were purchased from Aldrich and a third, palladium (10%)/carbon, was purchased from Fluka.

Polymer Synthesis. All polymerizations were carried out in 250-mL round-bottomed flasks. The distillation and polymerization glassware and syringes were dried overnight at 150 °C and cooled under vacuum prior to use. The solvent, monomers, and ethyl acetate were distilled immediately prior to the polymerization and transferred to the reaction flasks *via* glass syringes. In a typical polymerization 50 mL of toluene and 4.9 mL of EtAc (50 mmol, 0.88 mM final concentration) were syringed into the reaction flask containing 5 mL of MTEGVE (25.3 mmol, 0.444 M final concentration) at 0 °C. Subsequently 0.9 mL of the 0.5 M *i*BuOEtAc initiator solution (0.45 mmol, 7.95 mM final concentration) followed by 1.0 mL of the 0.9 M $Et_{1.5}AlCl_{1.5}$ catalyst solution (0.9 mmol, 15.8 mM final concentration) was added. After 1 h 3.5 mL of BzVE (25.5

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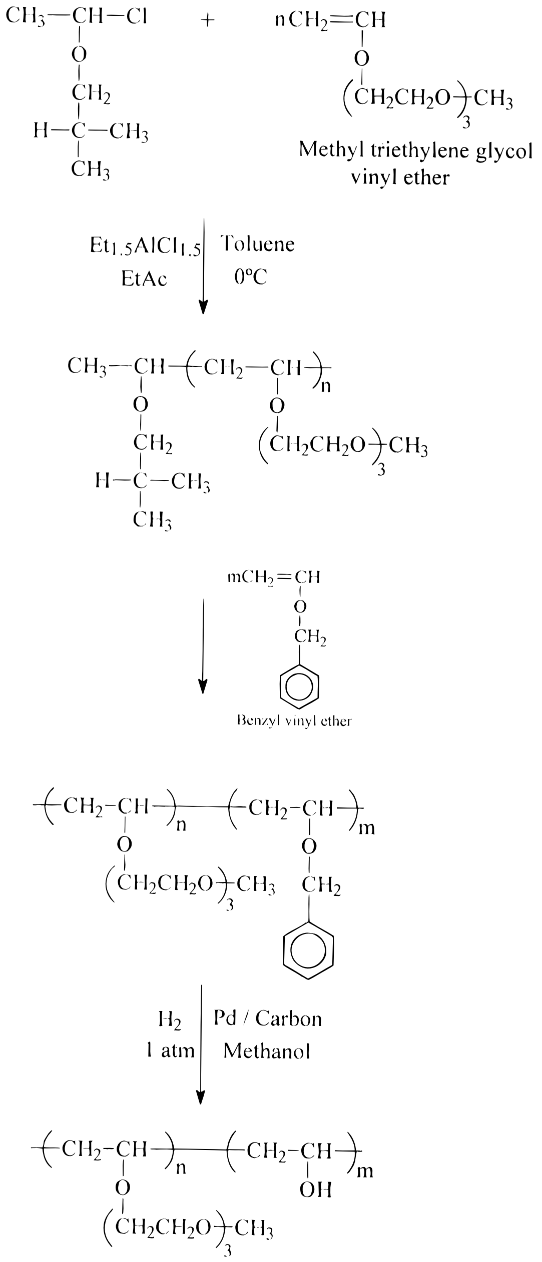

Figure 1. Reaction scheme for the synthesis of the MTEGVE-*block*-BzVE copolymers via living cationic polymerization, followed by catalytic hydrogenolysis.

mmol, 0.44 M; for the synthesis of an equimolar block) was added and left to polymerize for 24 h at 0 °C. The polymerization was terminated by using 1.0 mL of a 2.0 M solution of $LiBH_4$ in THF.

Purification and Drying. The solution of the terminated polymer was diluted with 150 mL of dichloromethane and washed with 0.1 M aqueous HCl (3 × 50 mL) and subsequently with deionized water (3 × 50 mL) to remove the catalyst residues. The solvents were removed under vacuum at room temperature for 24 h. The final monomer conversion was determined by gravimetry.

Hydrogenolysis. Poly(benzyl vinyl ether), homopolymer or block copolymer (0.50 g), was dissolved in a suitable solvent (40 mL) in a one-necked 250 mL round-bottomed flask fitted with a tap and a balloon. To this was added the catalyst, e.g., 10% palladium on activated charcoal (0.125 g, typically one quarter of the mass of polymer used), under a nitrogen atmosphere with stirring. The system was purged with dry nitrogen by repeated filling and deflating of the balloon. Hydrogen was then added to the balloon in a similar manner. The balloon was refilled with hydrogen twice a day until the reaction was complete. At the end of the reaction the catalyst was removed by centrifugation at 12 000 rpm followed by filtration through a 0.45 μm syringe filter. The solvent was then removed under reduced pressure. (In the case of dimethyl formamide, the solution was dialyzed by using benzoylated dialysis tubing (molecular weight cutoff 2800) against water for 5 days before freeze drying from this solution.)

Characterization in Organic Solvents. SEC. Molecular weights and molecular weight distributions (MWDs) were determined by size exclusion chromatography (SEC) using a single Polymer Laboratories PL-Mixed 'E' column (void volume = 4.75 mL; total permeation volume = 9.0 mL). The injection volume was 20 μL of a 6 wt % (co)polymer solution in THF. The mobile phase was tetrahydrofuran (THF, flow rate 1 mL min^{-1}) delivered by using a Perkin-Elmer Series 10 liquid chromatograph. The refractive index signal was measured by using a Perkin-Elmer LC-25 RI detector. Calculations were based on a linear calibration obtained using four narrow MW polystyrene standards (Mp = 580, 5050, 10 100, and 30 300) supplied by Polymer Laboratories.

^{1}H NMR Spectroscopy. A Bruker AC-P 250 MHz instrument was used to acquire the proton NMR spectra of polymer solutions in either $CDCl_3$, CD_2Cl_2, or DMSO-d_6 with TMS as a reference.

Characterization in Water. All experiments were performed by using 1% w/w polymer solutions in double-distilled deionized water which were prepared at least 24 h prior to analysis, filtered through 0.2 μm Phenomenex syringe filters, and stored at 5 °C.

Dynamic Light Scattering. The hydrodynamic radii of the polymers in aqueous solution were measured by using a Malvern PCS 4700 spectrometer equipped with a 40 mW He–Ne laser operating at 633 nm and a Series 7032 Multi-8 correlator. The scattered light was detected at 90° and the data fitted by using the CONTIN algorithm. The temperature of the sample was kept at 24 ± 0.1 °C.

Cloud Points. Cloud points were determined by monitoring optical density at 500 nm of a stirred, 1% w/w polymer solution with increasing temperature, using a Lambda 2S UV/vis spectrometer.

Results and Discussion

Homopolymerization of Methyl Triethylene Glycol Vinyl Ether. We have recently reported the homopolymerization of MTEGVE and its block copolymerization with IBVE by living cationic polymerization.[14] The homopolymerization of related alkyl oligo(ethylene glycol) vinyl ether monomers has been studied by other workers.[15–18]

Synthesis of block copolymers requires an initiator capable of polymerizing both monomers, and the *i*BuO-EtAc/$Et_{1.5}AlCl_{1.5}$/EtAc initiating system was selected. MTEGVE homopolymerization experiments using this initiating system in toluene at 0 °C showed that the polymerization is complete within 50 min. The number-average molecular weight (M_n), as determined by SEC, increased linearly with conversion and all the experimental points lay close to the theoretical line, confirming the living nature of the polymerization. The polydispersity values decreased during the course of the reaction, from 1.60 down to 1.30 at complete conversion. These results are in good agreement with the data published by Aoshima *et al.*[15] The rate of polymerization is greater than those from typical alkyl vinyl ethers, such as IBVE. Nakamura *et al.*[17] suggested that there may be an intramolecular activation of the growing end by the pendant oxyethylene groups, thus increasing the effective charge on the carbon center and making the chain end more reactive. This may also account for the relatively broad MWDs.

Table 1. Block Copolymerization of MTEGVE and BzVE Using the Initiating System *i*BuOEtAc/$Et_{1.5}AlCl_{1.5}$/EtAc in toluene at 0 °C; $[MTEGVE]_o = 0.444$ M; $[iBuOEtAc]_o = 7.95$ mM; $[Et_{1.5}AlCl_{1.5}]_o = 15.8$ mM; $[EtAc]_o = 0.88$ M

	copolymer comp,[a] mol %					
sample	theoretical MTEGVE: BzVE	exptl MTEGVE: BzVE		M_n (theory)	M_n (SEC)	M_w/M_n
			homo	10 600	12 700	1.20
CF305	90:10	91:9	block	11 500	13 500	1.28
			homo	10 600	12 500	1.26
CF306	80:20	82:18	block	12 600	13 400	1.27
			homo	10 600	12 500	1.27
CF307	70:30	74:26	block	13 900	13 600	1.28
			homo	10 600	12 600	1.26
CF308	60:40	64:36	block	15 600	14 700	1.24
			homo	10 600	11 800	1.36
CF304	50:50	53:47	block	18 200	17 300	1.18

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

Homopolymerization of Benzyl Vinyl Ether. The living nature of the polymerization of benzyl vinyl ether was established in a similar fashion. Aoshima *et al.*[19] have previously studied the homopolymerization of BzVE under similar conditions using $EtAlCl_2$ as the catalyst to produce polymers with narrow MWD. In our syntheses the slightly weaker Lewis acid, $Et_{1.5}AlCl_{1.5}$, was used, because this was found to be the most effective initiator to induce the living polymerization of MTEGVE.[14] Polymerizations were much slower and complete monomer conversion required approximately 17 h. The M_n values were found to increase linearly with conversion and a second addition of monomer at 100% conversion led to a new polymerization which also had living characteristics. The MWD became narrower (M_w/M_n approached 1.20) during the course of the polymerization. These polydispersities are slightly larger than those published by Aoshima *et al.*[19] ($M_w/M_n = 1.10-1.15$) for the polymerization of BzVE using $EtAlCl_2$.

Block Copolymerization. Although both sequences of polymerization are feasible, it was decided that the MTEGVE monomer should be polymerized first, followed by the BzVE monomer. With this block sequence any homopolymer impurity arising from premature termination of MTEGVE chains would be water-soluble and less likely to affect the aqueous solution properties of the copolymer (reversing the block sequence might lead to a small amount of water-insoluble PBzVE homopolymer impurity, which would be expected to form large aggregates in aqueous solution and so interfere with dynamic light scattering measurements).

A series of block copolymers was synthesized with a constant MTEGVE block length and varying BzVE block length. The MTEGVE was polymerized first to give an M_n of 10 600 (Dp = 56) followed by the addition of BzVE, $M_n = 800-7500$ (Dp = 6−56 monomer units). The polymerizations were quantitative (yields close to 100%), allowed good molecular weight control, and resulted in products with satisfactorily narrow molecular weight distributions. Table 1 lists the range of block copolymers synthesized along with their molecular weights, polydispersities, and compositions.

Characterization in Organic Solvents. Table 1 shows that the homopolymer samples taken from each copolymerization experiment have relatively broad MWDs ($M_w/M_n = 1.20-1.36$), as determined by SEC, which is probably due to the highly reactive MTEGVE monomer. The M_n value of each homopolymer was consistently 2000 above the expected value of 10 600 (using polystyrene calibration standards). A systematic error is probably incurred by the use of polystyrene calibration standards. Figure 2 shows two typical SEC traces of diblock copolymers CF308 and CF304, along with their corresponding homopolymers. It is clear that both the homopolymers and the block copolymers are unimodal and there is no significant tailing to low molecular weight. This is consistent with efficient block copolymer formation.

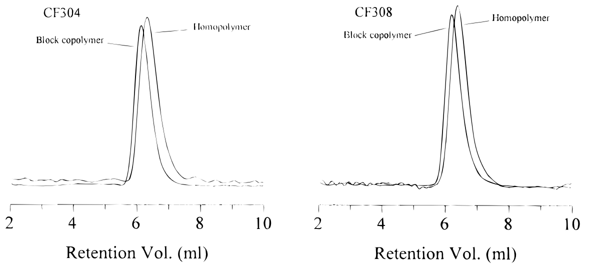

Figure 2. Typical SEC traces obtained from the block copolymerization of MTEGVE and BzVE with their corresponding homopolymers in toluene at 0 °C, samples CF304 and CF308; $[MTEGVE]_o = 0.444$ M; $[iBuOEtAc]_o = 7.95$ mM; $[Et_{1.5}AlCl_{1.5}]_o = 15.8$ mM; $[EtAc]_o = 0.88$ M. Conversions and polydispersity ratios are indicated in Table 1.

Table 2. Variation of the Hydrodynamic Radii (R_h) on 1 w/w % Aqueous Solutions of MTEGVE-*block*-BzVE Copolymers at Constant MTEGVE Length with Increasing BzVE Molar Fraction, at 24 °C

sample	copolymer comp,[a] (%) MTEGVE:BzVE	M_n	hydrodynamic radii (R_h), nm $R_h^{micelle}$	$R_h^{aggregate}$
CF305	91:9	13 500	10.2	45
CF306	82:18	13 400	14.1	79
CF307	74:26	13 600	17.0	81
CF308	64:36	14 700	19.5	86
CF304	53:47	17 300	26.2	115

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

The comonomer compositions of the block copolymers were determined by ^{1}H NMR spectroscopy. The spectrum of the copolymer was, as expected, the sum of those of the two homopolymers and the comonomer ratio was found from the ratio of the aromatic peaks at δ 7.0−7.5 from the PBzVE and the peaks at δ 3.3 and 3.5 from PMTEGVE. The values are in agreement within experimental error with those expected from the initial comonomer feed.

Characterization in Aqueous Solution. When dissolved in aqueous media, these block copolymers were expected to form micelles, with the insoluble BzVE units forming the micellar core and the water-soluble MTEGVE units forming the solvated corona. Photon correlation spectroscopy (PCS) was used to determine micelle radii at room temperature, while turbidimetry was employed to determine the effect of varying the hydrophilic block length on the cloud points.

Dynamic Light Scattering. Light scattering studies were carried out on the MTEGVE-*block*-BzVE copolymers in 1% w/w solutions at 24 °C. These copolymers have a constant hydrophilic MTEGVE block length, with a varying hydrophobic BzVE block length. Table 2 summarizes the results of light scattering experiments on aqueous solutions. Analysis of the light scattering data using the CONTIN algorithm revealed two intensity-average populations. The intensity-average contributions to the light scattering from the small size population were above 70% in all cases, whereas the number- and volume-average contributions were each greater than 97%. The smaller sized population revealed by CONTIN is presumably well-defined micelles, with the larger species being due either to impurities or to large, nonequilibrium aggregates.

The formation of nonequilibrium aggregates has been discussed by Stejskal *et al.*[20] who considered that it arises from the phase separated structure of diblock copolymers in the solid state, which may be partly preserved when selective solvents are used for dissolution. To overcome this problem the copolymer should first be dissolved in a small volume of a nonselective solvent so that the large aggregates are broken up and every copolymer chain is molecularly dissolved (unimers). Water is then added slowly so that the hydrophobic units associate to form the core of the micelles. Light scattering measurements on a 1% aqueous solution of CF308 prepared by dissolving 100 mg of this copolymer in THF (0.4 mL) followed by addition of water (9.6 mL) gave an average hydrodynamic size of 19 and 87 nm (CONTIN). There is very little difference between the hydrodynamic sizes obtained by direct dissolution into water (see Table 2) and the THF/water mixture: this suggests that the large aggregates are not a result of residual bulk state morphology.

Recently, several groups working with poly(styrene-*block*-ethylene oxide) have found that these copolymers form micelles in aqueous solution.[21,22] Xu *et al.*[22] studied PS−PEO diblock copolymers and found that there were larger aggregates in addition to a small population of well-defined micelles. The fraction of these aggregates was very small compared to the micelle population (only 3−13% of the volume-average distribution). These workers suggested that the larger population may be due to aggregation of the PEO block sequence. Even at room temperature, aqueous solutions of PEO can form large, weakly bound thermodynamically-reversible association complexes.[23] Xu *et al.* suggested that the hydrophilic PEO chains in the micelle coronas associate to create clusters consisting of 20−30 micelles. MTEGVE contains three ethylene oxide units per monomer residue so a similar phenomenon may be responsible for the large population in our copolymer solutions. The hydrodynamic radii of the MTEGVE homopolymer (M_n by SEC = 12 700) were measured to determine if any aggregation was occurring. The measured hydrodynamic radius was 2.0 nm (as measured using the cumulants analysis), which is in agreement with a molecularly-dissolved polymer. However, the polydispersity was rather broad, suggesting some agregation. It is noteworthy that our block copolymers were synthesized by using an initiator that contained a single hydrophobic monomer unit of isobutyl vinyl ether. The IBVE initiator residue is attached to the hydrophilic end (MTEGVE) of the block copolymer. It is possible that this single hydrophobic unit may be at least partially responsible for the formation of the larger aggregates observed in the PCS experiments. In summary, all the MTEGVE-*block*-BzVE copolymers assemble to form both micelles and larger aggregates. The data also confirm that block copolymers bearing a greater number of hydrophobic BzVE units have a larger hydrodynamic size.

Cloud Points. Phase separation of MTEGVE homopolymer (M_n by SEC = 12 700) in aqueous solution has been previously observed at 83.5 °C.[14] This is higher than the cloud points of the homopolymers of the methyl mono- and di(ethylene glycol) vinyl ethers (70 and 80 °C, respectively) and lower than the cloud point for the methyl tetra(ethylene glycol) vinyl ether homopolymer (M_n = 20 000) (95 °C).[15] This trend is in agreement with the expectation that the water solubility of the copolymer should increase with the number of pendant oxyethylene units.

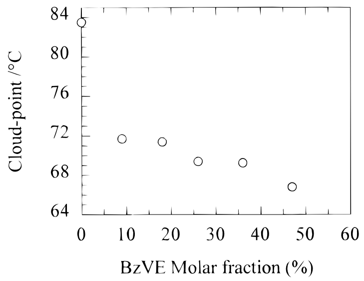

Figure 3. Cloud points of 1 w/w % aqueous solutions of MTEGVE-*block*-BzVE copolymers as determined by turbidimetry. Effect of increasing the BzVE molar fraction while maintaining a constant MTEGVE block length.

The cloud points of 1 w/w % aqueous solutions of our copolymers were measured by turbidimetry at a wavelength of 500 nm. The phase separation for each block copolymer was quite sharp and reversible. The effect of polymer structure on the cloud points was investigated. Figure 3 shows the cloud points of copolymers with constant MTEGVE block length and increasing length of the BzVE block. The precipitation temperature of the block copolymer is reduced as the number of BzVE units increases, which can be attributed to the hydrophobic nature of BzVE. The decrease in the cloud points of the block copolymers is more pronounced at low BzVE contents and levels off at higher BzVE contents. Aoshima *et al.*[24] investigated statistical copolymers with water-soluble methoxyethyl vinyl ether units (cloud point 70 °C) and marginally water-soluble ethoxyethyl vinyl ether units (cloud point 20 °C). The overall copolymer molecular weight was fixed at 20 000. These copolymers cannot form micelles and the cloud points increased more or less linearly with the mole fraction of methoxyethyl vinyl ether units. The nonlinearity of our cloud point data (Figure 3) most likely arises from micellization, which shields the hydrophobic BzVE units from the solvent. Similar hydrophilic−hydrophobic MTEGVE-*block*-IBVE copolymers show an almost identical dependence of the phase separation temperature on the IBVE chain length.[14]

Hydrogenolysis of Benzyl Vinyl Ether Residues. It is well known that benzyl ethers and benzyl esters can be selectively cleaved under relatively mild conditions by catalytic hydrogenolysis.[25] Such selectivity has been utilized recently in synthetic polymer chemistry.[26,27] We thus anticipated that the benzyl protecting group might be a useful route to PVOH by the catalytic hydrogenolysis of poly(benzyl vinyl ether) homopolymers. Unfortunately, the extent of deprotection was very low (27%) and the resulting copolymer was insoluble in water.[25]

The main problem was the lack of a compatible solvent for both the precursor PBzVE and the PVOH. Ideally both the precursor and the deprotected polymer should be soluble throughout the hydrogenolysis. This presents a special problem since PVOH is soluble in relatively few solvents, e.g., water, dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), and *N*-methylpyrrolidone (NMP). It is also swollen in pyridine. Unfortunately, basic solvents retard hydrogenolysis by poisoning the metal catalyst and alcohols; esters or carboxylic acids are typically selected for catalytic hydrogenolysis.[28] However, both PBzVE and PVOH homopolymer are insoluble in such solvents. The hydrogenolysis of MTEGVE-*block*-BzVE should reduce the problem as it allows us to choose a solvent that is good for both blocks. Thus, after formation of the PVOH block sequence, the MTEGVE block will still be soluble and help to prevent precipitation of the derivatized copolymer.

Hydrogenolysis reactions were carried out in a number of solvents with a range of different catalysts with the aim of maximizing the degree of debenzylation. As a model, the most hydrophobic copolymer CF304 ($MTEGVE_{53}$-*block*-$BzVE_{47}$) was treated at room temperature with 1 atm of H_2 using the 10% palladium/carbon catalyst for a reaction time of 7 days in various solvents. It was expected that this copolymer would be the most difficult to deprotect due to the relatively high proportion of benzyl (and ultimately vinyl alcohol) units. A large number of polar solvents was used; the degree of debenzylation was higher than 25% only in methanol or glacial acetic acid. NMR spectroscopy of the copolymer deprotected in glacial acetic acid showed 77% debenzylation, but there was some reduction in the MTEGVE integral and it is likely that the ether linkages in the MTEGVE block were cleaved in this solvent. Hydrogenolysis in methanol gave 70% deprotection without the loss of any MTEGVE units.

Carbon catalyst residues were removed by centrifugation at 12 000 rpm for 1 h, followed by ultrafiltration (0.45-μm filters). In all cases there was some residual catalyst in the copolymers, evidenced by their black color. Even ultrafiltration using 0.2-μm filters did not remove all of these small particles. In a further experiment, the hydrogenolysis of CF304 in methanol was analyzed at various reaction times. It was found that hydrogenolysis reaches a limit of 70% within 4 days and that longer reaction times do not significantly increase the degree of deprotection. With the observation of catalyst contamination, this suggests that the copolymer is adsorbing onto the Pd/C catalyst during the reaction, effectively blocking the catalyst surface. In this regard, it is noteworthy that the hydrogenolysis products of MVE-*block*-BzVE copolymers did not show any discoloration, indicating the absence of catalyst residues.[13] These results suggest that the triethylene glycol groups in the MTEGVE block may be responsible for absorption onto the catalyst surface.

Other hydrogenolysis catalysts were investigated: Hydrogenolysis of sample CF304 in methanol and ethyl acetate using a 5% Ru/C produced no measurable debenzylation. On the other hand, hydrogenolysis using a platinum(IV) oxide catalyst gave degrees of debenzylation comparable to those obtained by using the Pd/C catalyst, but the final copolymers were contaminated with catalyst residues. It was hoped that a higher degree of deprotection might be obtained when block copolymers with shorter benzyl sequences were investigated. Surprisingly the extent of debenzylation was not significantly affected by the overall benzyl chain length. The highest degree of debenzylation (88.5%) was found for sample CF371, which contained 26 mol % BzVE residues. Presumably, even at low benzyl contents, adsorption of the triethylene glycol sequences onto the catalyst surface is significant enough to prevent the quantitative deprotection of the benzyl groups.

Conclusions

Amphiphilic diblock copolymers of methyl triethylene glycol vinyl ether (hydrophilic) and benzyl vinyl ether (hydrophobic) with different comonomer compositions and molecular weights were synthesized by living cationic polymerization. Although the polymerizations of both monomers were near-quantitative, with good control over both molecular weight and copolymer composition, the polydispersities were limited by the high reactivity of the MTEGVE monomer. Light scattering studies show that these copolymers aggregate to form micelles in aqueous solution at room temperature. These micelles were accompanied by a very small population of larger aggregates. Cloud point data also suggested micellization, which is favored by increasing BzVE block length. Catalytic hydrogenolyses of MTEGVE-*block*-BzVE copolymers using precious metal catalysts were partially successful. Incomplete deprotection is attributed to adsorption of the ethylene glycol units onto the carbon catalyst support, blocking the catalyst sites.

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