Synthesis and Aqueous Solution Characterization of Dihydrophilic Block Copolymers of Methyl Vinyl Ether and Methyl Triethylene Glycol Vinyl Ether

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ABSTRACT: Water-soluble dihydrophilic AB block copolymers of methyl vinyl ether (MVE) and methyl triethylene glycol vinyl ether (MTEGVE) were synthesized by living cationic polymerization, with copolymer molecular weights in the range 1500−13 900 with fairly narrow molecular weight distributions ($M_w/M_n < 1.29$). The MVE block length was fixed at 20 monomer units, and the MTEGVE block length was varied from 2 to 67 units. Aqueous solutions of these copolymers were studied using dynamic light scattering, dye solubilization, and turbidimetry to determine the effect of temperature on micellization and precipitation. The light scattering data for all of the block copolymers indicated that they were dispersed as single chains in water at room temperature, this was further confirmed by aqueous SEC experiments. Turbidimetry experiments showed that phase separation occurred upon heating aqueous solutions of MVE and MTEGVE homopolymers to 18 and 83.5 °C respectively. Micelles were formed on heating aqueous solutions of these block copolymers above 50 °C, which was expected due to the hydrophobic nature of the MVE block at this temperature. Dynamic light scattering studies gave hydrodynamic sizes of the block copolymers ranging from 8.1 to 31 nm. Variable temperature ^{1}H NMR spectroscopy (in D_2O) confirmed that the MVE block forms the micellar core and that micellization was reversible. The critical micellization temperatures determined by dye solubilization were found to increase with the MTEGVE content over a relatively small temperature range from 27 to 41 °C. The cloud points of these copolymers follow a similar trend and increase with the MTEGVE content, covering a wide range of temperatures from 26 to 79 °C.

Introduction

Continuing our work with water-soluble homopolymers[1] and block copolymers[2,3] synthesized by living cationic polymerization, we present a new family of diblock poly(vinyl ethers) where both constituent blocks are water-soluble. This is in contrast with most of the water-soluble block copolymers in the literature, which usually consist of one hydrophobic and one hydrophilic block, called amphiphilic copolymers. Throughout this report, the term *dihydrophilic* block copolymers is used to describe hydrophilic−hydrophilic block copolymers.

As far as we are aware, there are only two other examples of dihydrophilic block copolymers based on vinyl ethers. Copolymers of 2-methoxyethyl vinyl ether and 2-ethoxyethyl vinyl ether have been synthesized by Aoshima and co-workers,[4] and diblock copolymers of vinyl alcohol (*via* hydrogenolysis of a benzyl vinyl ether precursor) and methyl vinyl ether were synthesized by our group.[3] Some of the Pluronic PEO−PPO−PEO (PEO = poly(ethylene oxide); PPO = poly(propylene oxide)) triblock copolymers[5] can also be considered as dihydrophilic block copolyethers because low-molecular weight (MW) PPO segments are water-soluble at room temperature (although high-MW PPO's are water-insoluble at room temperature). There are no examples of ionizable dihydrophilic block poly(vinyl ethers) but there are a few examples of methacrylate-based block copolymers synthesized by anionic[6] and group transfer polymerization (GTP).[7]

Amphiphilic block copolymers often form micelles in aqueous solution at room temperature and may precipitate at elevated temperatures due to the inverse temperature solubility characteristics of aqueous polymer solutions. In contrast, dihydrophilic block copolymers should be molecularly dissolved as unimers at room temperature due to the water-solubility of both components. If the phase-separation temperatures of the two blocks of a dihydrophilic block copolymer are substantially different, then, as the temperature of the aqueous solution is increased, a unimer−micelle transition should occur first as one of the blocks precipitates, followed by macroscopic precipitation when the second block precipitates. This double transition has indeed been observed with aqueous solutions of the Pluronic PEO−PPO−PEO triblock copolymers, where the PPO precipitation temperature is much lower than that of the PEO.[8] We expect similar behavior for our dihydrophilic block copolymers whose component blocks precipitate at different temperatures. These copolymers may be suitable for applications similar to those of the Pluronic copolymers, including stabilization, dispersion, emulsification, and flocculation.

The monomers used in this study are methyl vinyl ether (MVE) and methyl triethylene glycol vinyl ether (MTEGVE), whose chemical structures are shown in Figure 1. We present here the synthesis of dihydrophilic block copolymers based on these two monomers by living cationic polymerization. The aqueous solution behavior of these novel block copolymers has been characterized using a variety of techniques.

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.

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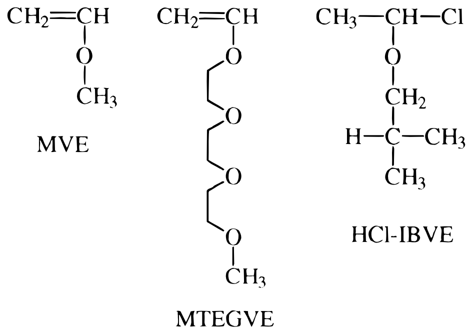

Figure 1. Chemical structures of methyl vinyl ether (MVE), methyl triethylene glycol vinyl ether (MTEGVE), and the HCl−IBVE adduct.

The gaseous MVE (bp = 5 °C) was supplied by GHC Gerling (99%) in a lecture bottle. Dichloromethane was purchased from Fisons. Acidic impurities were removed by washing with 10% aqueous sodium hydroxide and deionized water, followed by drying with anhydrous calcium chloride and calcium hydride at room temperature. Finally, the purified solvent was refluxed for 3 days over calcium hydride and distilled immediately prior to the polymerization. The initiator used was a 1.0 M solution of the hydrogen chloride adduct of isobutyl vinyl ether (HCl−IBVE) in *n*-hexane prepared from the reaction of isobutyl vinyl ether (Aldrich) with hydrogen chloride.[9] The hydrogen chloride adduct of MVE (HCl−MVE) which was used as an initiator for the MVE homopolymerization, was prepared in the same way. Tin(IV) chloride ($SnCl_4$) was used as the polymerization catalyst; it was purchased from Aldrich as a 1.0 M solution and used as received. Tetrabutylammonium chloride (nBu_4NCl) which was used as an "added salt" to enhance the livingness of the polymerization was also purchased from Aldrich. This salt was ground to a fine powder and dried under high vacuum for approximately 5 days. This salt was then transferred to a dry nitrogen glovebox for storage. Finally, it was dissolved in dry dichloromethane to give a 0.1 M solution.

Polymer Synthesis. The polymerizations were carried out in 250 mL round bottom flasks. The solvent was distilled immediately prior to the polymerization and transferred to the reaction flasks *via* glass syringes. The distillation and polymerization glassware were dried overnight at 150 °C and cooled under vacuum prior to use. MVE was purified immediately prior to its polymerization; the gas was passed through a column containing the drying agent, calcium hydride, into an evacuated glass bulb of known volume (7.5 L) and at a known pressure (approximately 63 mmHg). This gas was then condensed at −196 °C into a small flask which contained granular calcium hydride. The solidified monomer was allowed to melt at −78 °C and stirred for 1 h, before being allowed to evaporate back into the glass bulb. The gas was then condensed directly into the polymerization vessel on top of the frozen reaction solvent at −196 °C and allowed to warm up to the reaction temperature of −78 °C. This monomer solution was stirred for 1 h to allow complete mixing of the solution prior to the addition of salt, initiator, and catalyst.

In a typical polymerization CH_2Cl_2 (100 mL) and nBu_4NCl (13 mL, 1.3 mmol; final concentration of 11.2 mM) were syringed into the reaction flask containing MVE (1.5 g, 25.8 mmol; final concentration of 0.22 M) and were left to equilibrate at −78 °C. Subsequently 1.0 M HCl−IBVE adduct initiator solution (1.3 mL, 1.3 mmol, final concentration 11.2 mM) followed by the 1.0 M tin(IV) chloride catalyst solution (1.3 mL, 1.3 mmol; final concentration 11.2 mM) were transferred into the reactor. After 1 h, the temperature was raised to −20 °C and MTEGVE (5.0 mL, 26 mmol, 0.22 M; for the synthesis of the equimolar diblock) was syringed into the reaction flask and left to polymerize for 2 h at −20 °C. The polymerization was terminated using a 5% solution of ammonia (aqueous 0.88 M) in methanol.

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 evaporated under prolonged vacuum at room temperature for 24 h. The final monomer conversion was determined by gravimetry.

Characterization in Organic Solvents. (a) SEC. Molecular weights and molecular weight distributions (MWD's) 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 tetrahydrofuran (THF). The mobile phase was THF (flow rate 1 mL min^{-1}) delivered using a Perkin-Elmer Series 10 liquid chromatograph. The refractive index signal was measured using a Perkin-Elmer LC-25 RI detector. Calculations were based on a linear calibration obtained using four narrow MW (580, 5050, 10 100 and 30 300) polystyrene standards supplied by Polymer Laboratories.

(b) ^{1}H NMR Spectroscopy. A Bruker AC-P 250 MHz instrument was used to acquire the proton NMR spectra of polymer solutions in $CDCl_3$ using tetramethylsilane (TMS) as a reference.

Characterization in Water. All the experiments were performed using 1% (w/w) polymer solutions in doubly-distilled deionized water which were filtered through 0.2 μm Phenomenex syringe filters.

(a) Dynamic Light Scattering. The hydrodynamic size of the polymers in aqueous solution were measured 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 measurements were performed at an angle of 90°, and the data were fitted using the CONTIN algorithm. The temperature of the sample was controlled to ± 0.1 °C.

(b) Aqueous SEC. Aqueous SEC was performed using a Polymer Laboratories PL Aquagel-OH 60 column or a Pharmacia Biotech "Superdex" 200 HR 10/30 column and a ERC-7515A refractive index detector. The eluent was 0.25 M NaCl + 50 mM Tris buffer in doubly-distilled deionized water, delivered using a Polymer Laboratories LC1120 HPLC pump (flow rate = 1 mL min^{-1}). The MW calibration curve was constructed using four narrow MW (1080, 10 600, 32 600, and 73 400) poly(ethylene glycol) standards supplied by Polymer Laboratories.

(c) Dye Solubilization. A 20 μL aliquot of a 0.4 mM solution of the nonionic dye 1,6-diphenyl-1,3,5-hexatriene (DPH) in THF was transferred to 2 mL of a 1% (w/w) aqueous copolymer solution using a 25 μL syringe, resulting in minimal dilution of the polymer solution with final aqueous concentrations of DPH and THF of 4 μM and 1% (v/v), respectively. The solutions were kept in the dark for at least 10 min before the start of the experiment. The absorbance at 356 nm was recorded as a function of temperature, from 0 to 70 °C (heating rate, approximately 2 °C min^{-1}) using a Perkin Elmer Lambda 2S UV/vis spectrometer.

(d) Cloud Points. A 2.5 mL aliquot of a 1% (w/w) polymer solution was transferred to a 10 mm path length quartz cuvette containing a small magnetic stirring bar. The cuvette was placed in the sample compartment of the Lambda 2S UV/vis spectrometer, and stirring was initiated using a miniature magnetic stirrer. A small temperature probe was immersed in the upper part of the solution, which was heated slowly from 15 to 95 °C. The optical density at 500 nm and the temperature were monitored.

Results and Discussion

Homopolymerization of Methyl Vinyl Ether. MVE has been previously polymerized using the hydrogen iodide/iodine initiating system reported by Miyamoto *et al.* in 1984.[10] Low-MW polymers with narrow MWDs ($M_w/M_n = 1.10$; $M_n = 2500$) were obtained. This polymerization showed all of the typical characteristics of a living system. The ability to form block copolymers with this monomer was shown by the synthesis of methyl vinyl ether-*block*-cetyl vinyl ether[11] (M_n <3500)

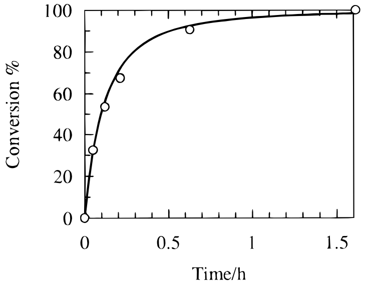

Figure 2. Conversion *vs* time curve for the polymerization of MVE in CH_2Cl_2 at −78 °C; $[MVE]_0 = 0.22$ M; $[HCl-IBVE]_0 = [SnCl_4]_0 = [nBu_4NCl]_0 = 11.2$ mM.

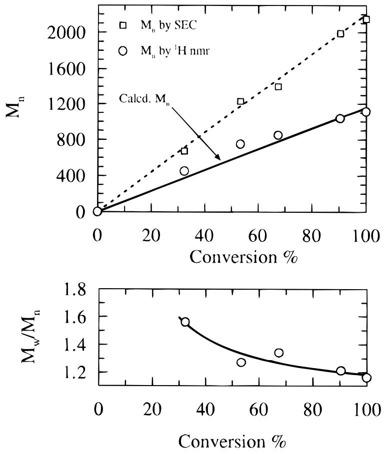

Figure 3. Variation of M_n and M_w/M_n with conversion for the polymerization of MVE in CH_2Cl_2 at −78 °C: $[MVE]_0 = 0.22$ M; $[HCl-IBVE]_0 = [SnCl_4]_0 = [nBu_4NCl]_0 = 11.2$ mM. The solid straight line indicates the calculated molecular weight for living polymers from the monomer/initiator mole ratio. The dashed straight line indicates the line of best fit for the M_n values derived from SEC.

and methyl vinyl ether-*block*-*p*-methoxystyrene[12] ($M_n = 2500$) using the HI/ZnI_2 initiating system. Both of these systems gave poly(methyl vinyl ether)s with good control over the MW and narrow MWD's. More recently, Ohmura *et al.*[13] have reported the living polymerization of MVE by the HCl−IBVE adduct/$SnCl_4$/nBu_4NCl initiating system. MVE polymers with $M_n = 3000$ and polydispersities of $M_w/M_n = 1.04-1.07$ were prepared in dichloromethane at −78 °C.

For the synthesis of the block copolymers an initiator capable of polymerizing both MVE and MTEGVE was required. Our initial MVE homopolymerization experiments using the HCl−IBVE adduct/$SnCl_4$/nBu_4NCl initiating system are described below. Figure 2 shows the conversion *vs* time plot for the polymerization of MVE using the HCl−IBVE/nBu_4NCl/$SnCl_4$ initiating system at −78 °C in dichloromethane. This experiment indicates that the polymerization is complete within 90 min. These data compare well with the results presented by Ohmura *et al.*[13] from their polymerization of MVE. The M_n *vs* conversion curve shown in Figure 3 presents two sets of M_n data for the MVE homopolymer: one determined from SEC and one from ^{1}H NMR spectroscopy. The polydispersities are also shown in the lower part of this figure; they are reasonably narrow and decrease from 1.56 to 1.16 with increasing conversion, suggesting minimal chain transfer/deactivation reactions. The M_n values obtained from SEC appear to be approximately twice the expected MW based on the monomer/initiator molar ratio. On the other hand, the M_n values determined from end-group analysis by ^{1}H NMR spectroscopy lie close to the expected MW.[14] The discrepancy between the MW's derived from SEC and the expected values may be due to hydrodynamic size effects. This would not be surprising in view of the expected hydrodynamic differences between poly(MVE) (PMVE) and polystyrene calibration standards. This result could also be explained if dimerization of these PMVE chains had occurred during the termination step. Each homopolymer sample would then contain two IBVE end groups, so the SEC would therefore give twice the expected size for the homopolymers, whereas end-group analysis by ^{1}H NMR spectroscopy would still give the expected MW values. The partial dimerization of poly(ethyl vinyl ether) chains during the termination reaction has been observed by Loontjens *et al.*[15] These workers showed that, when the concentration of the terminating reagents was dramatically reduced, a bimodal molecular weight distribution was observed by SEC. The SEC traces for our MVE homopolymers are unimodal and narrow, this suggests that either no dimerization has occurred or that there has been quantitative dimerization of the PMVE chains. However, complete dimerization seems very unlikely under these conditions. We conclude that end-group analysis by ^{1}H NMR spectroscopy is a more reliable method for the determination of M_n than SEC analysis on the basis of polystyrene calibration.

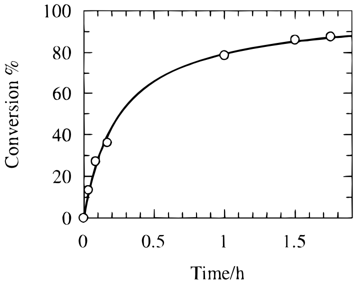

Figure 4. Conversion *vs* time curve for the polymerization of MTEGVE in CH_2Cl_2 at −20 °C: $[MTEGVE]_0 = 0.63$ M; $[HCl-IBVE]_0 = [SnCl_4]_0 = [nBu_4NCl]_0 = 11.24$ mM.

Homopolymerization of Methyl Triethylene Glycol Vinyl Ether. The HCl−IBVE/nBu_4NCl/$SnCl_4$ initiating system was examined for the polymerization of MTEGVE. Attempts to polymerize MTEGVE with this initiating system at −78 °C yielded no polymer. Increasing the temperature to −20 °C, however, induced polymerization of the MTEGVE, resulting in polymers with polydispersities as low as 1.10 at 86% conversion. Figure 4 shows the conversion *vs* time curve for the polymerization of MTEGVE at −20 °C in dichloromethane. This plot indicates that the polymerization proceeds to 80% conversion within the first 60 min and reaches 87.5% within 105 min. Figure 5 shows the M_n values and polydispersities determined by SEC as a function of conversion for the homopolymerization of MTEGVE, for the same reaction. The M_n was found to increase linearly with conversion, which is an indication of the livingness of this system. All of the points lie close to the line of expected MW. In the same reaction the polydispersities decrease from 1.19 to 1.10 with increasing conversion. These low polydispersity values compare well with the range of 1.15−1.20 obtained with the HI/I_2 initiating system for the polymerization of ethyl(oligoethylene glycol) vinyl ethers[16] and the polydispersity of 1.11 found for the *i*BuOEtAc/$Et_{1.5}AlCl_{1.5}$/EtAc initiating system for the polymerization of methoxyethyl vinyl ether.[17] As already discussed, the polymerization reaction starts to slow down dramati-

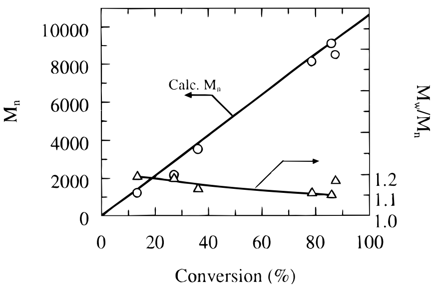

Figure 5. Variation of M_n (○) and M_w/M_n (△) with conversion for the polymerization of MTEGVE in CH_2Cl_2 at −20 °C; $[MTEGVE]_0 = 0.63$ M; $[HCl{-}IBVE]_0 = [SnCl_4]_0 = [nBu_4NCl]_0 = 11.2$ mM. The straight line indicates the calculated molecular weight for living polymers from the monomer/initiator mole ratio.

cally as the monomer conversion reaches ~80%. At the same time the polydispersity index starts to broaden: at 86% monomer conversion the polydispersity was measured at 1.10, but as the conversion proceeded to 87.5%, a distinct broadening of the MWD raised the polydispersity to 1.17 (see Figure 5). Along with this increase in the polydispersity index at 87.5% monomer conversion, there is a small decrease in the observed M_n. The incomplete monomer conversion in these experiments is most likely the result of termination rather than chain transfer reactions. The increase in polydispersity is also consistent with a chain transfer/deactivation process. Further addition of monomer at this point induced a second-stage polymerization. However, a bimodal distribution was observed, presumably due to “homopolymer” contamination. The polymerization of MTEGVE under these conditions does not lead to a truly living polymerization process, however, it will be shown later that the synthesis of low-MW MTEGVE (in the block copolymerization with MVE) with an M_n less than 5000 can be achieved with relatively low polydispersities and complete monomer conversion.

In summary, it has been demonstrated that the HCl−IBVE/$nBu_4NCl/SnCl_4$ initiating system can lead to the living polymerization of both MVE and MTEGVE (up to 85% conversion). Although in our previous work[2] the iBuOEtAc/$Et_{1.5}AlCl_{1.5}$/EtAc initiating system gave reasonably monodisperse MTEGVE polymers with 100% monomer conversion within 30 min, we decided to use the HCl−IBVE/$nBu_4NCl/SnCl_4$ initiating system for the block copolymerization of these two monomers due to its suitability for the polymerization of MVE.

Block Copolymerization. For the block copolymerizations, we elected to polymerize MVE first, due to the incomplete conversion of the MTEGVE monomer. If this latter monomer had been polymerized first, it would probably have caused reduced blocking efficiency, resulting in homopolymer contamination, and may also have produced tapered block copolymers. However, by polymerization of the MVE monomer first, any homopolymer impurity in the block copolymer would be PMVE rather than PMTEGVE. The precipitation temperature of the PMTEGVE homopolymer is 83.5 °C,[2] while that of the PMVE homopolymer is around 34 °C.[18] Thus having PMVE as a homopolymer impurity may be detrimental in the aqueous solution studies at elevated temperatures. For example, light scattering from PMVE homopolymer aggregates is likely to be more significant than that from the much smaller block copolymer micelles.

A series of dihydrophilic block copolymers were synthesized with a constant MVE block length and varying MTEGVE block length. The MVE was polymerized first to give an M_n of 1100 ($D_p = 19$) followed by the addition of MTEGVE, $M_n = 380{-}12\,750$ ($D_p = 2{-}67$ monomer units). A single statistical copolymer consisting of 13 MVE units and 15 MTEGVE units was also synthesized simply by premixing these comonomers prior to polymerization. The results from all these copolymerizations are summarized in Table 1.

Characterization in Organic Solvents. (a) SEC Analysis. The MW's and polydispersities of both of the homopolymer samples and the block copolymers were determined by SEC. Homopolymer samples were taken from the reaction vessel for SEC analysis before addition of the second monomer. The M_n values obtained from SEC were higher than those expected, probably due to the use of polystyrene calibration standards as discussed earlier. The exceptions were two block copolymers which contained the highest proportion of MTEGVE, since polystyrene is a more suitable calibration standard for PMTEGVE.[2] All further M_n values quoted will be those derived from NMR spectroscopy. Polydispersities ranged from 1.14 to 1.29 and increased with increasing MTEGVE content due to the side reactions associated with the polymerization of this monomer. The SEC traces of all of the block copolymer samples, along with their corresponding homopolymers, and the single statistical copolymer (GM61) are shown in Figure 6. With the exception of block copolymers CF345 and CF347, all of the homopolymer and block copolymer SEC traces were narrow and showed no “tailing” to low molecular weight. These data confirm living polymerization of the MVE monomer and efficient blocking with the MTEGVE monomer. Copolymers CF345 and CF347 show a low-MW tail in the copolymer SEC trace. This suggests the presence of homopolymer contamination, which may be caused by the highly reactive nature of the alkyl(oligoethylene glycol) vinyl ether monomers, which have been shown to polymerize much more rapidly than nonfunctionalized alkyl vinyl ethers.[16] Alternatively the presence of impurities in the MTEGVE monomer will also produce homopolymer contamination.

Since the homopolymerization of MTEGVE to M_n = 10 700 ($D_p = 56$) proceeded to only 90% conversion (see Figure 4), we expected similarly incomplete conversion

Table 1. Block Copolymerization of Methyl Vinyl Ether and Methyl Triethylene Glycol Vinyl Ether in CH_2Cl_2 at −78 and −20 °C, Respectively $[MVE]_0 = 0.22$ M; $[HCl{-}IBVE]_0 = [SnCl_4]_0 = [nBu_4NCl]_0 = 11.2$ mM]

sample	theoretical compsn (D_p) MVE:MTEGVE	compsn by ^1H NMR (D_p) MVE:MTEGVE	M_n (theory)	M_n (SEC)	M_n (^1H NMR)	M_w/M_n	yield (%)
CF348	20:0	19:0	1,260	2,150	1,200	1.16	>99
CF352	20:2	19:2	1,540	2,900	1,580	1.14	>99
CF351	20:5	19:5	2,100	3,200	2,160	1.20	>99
CF350	20:10	20:8	3,000	4,300	2,780	1.18	>99
CF349	20:20	19:17	4,960	6,400	4,440	1.29	>99
CF347	20:39	20:34	8,580	6,800	7,730	1.29	88.5
CF345	20:78	19:67	16,000	12,700	13,950	1.25	86.5
GM61	19:19	13:15	4,700	5,600	3,700	1.14	>99

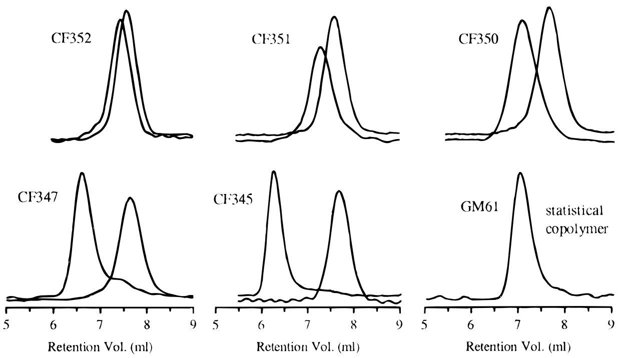

Figure 6. SEC traces obtained from the block and statistical copolymerizations of MVE and MTEGVE with their corresponding homopolymers in CH_2Cl_2 at −78 and −20 °C, respectively: $[MVE]_0 = 0.22$ M; $[HCl{-}IBVE]_0 = [SnCl_4]_0 = [nBu_4NCl]_0 = 11.2$ mM. Conversions and polydispersity ratios are indicated in Table 1.

for the block copolymers. However, with the exception of samples CF347 and CF345, block copolymer yields were quantitative (as determined by gravimetry and confirmed by SEC). Copolymer samples CF345 and CF347 had a lower conversion, probably due to the incomplete polymerization of the MTEGVE monomer. These results suggest that at low degrees of polymerization ($D_p < 20$), MTEGVE proceeds to 100% conversion.

(b) ^{1}H NMR Spectroscopy. The number-average molecular weight can be determined using end-group analysis by ^{1}H NMR spectroscopy. Ohmura *et al.*[13] used this method for the determination of PMVE with MW's up to 3500. Figure 7 shows the ^{1}H NMR spectrum of both MVE and MTEGVE homopolymers and also a typical diblock copolymer. In a similar way, end-group analysis was used to determine the M_n of our homopolymer samples by ratioing the residual IBVE initiator fragment at δ 0.85 to the characteristic MVE methyl peak at δ 3.2−3.5. The initiator peaks at δ 0.85 and δ 1.1 are due to the two methyl peaks on the isobutyl vinyl ether side group (Y) and the single chain-end methyl group (X), respectively. The peak at δ 0.85 has twice the integral of the end methyl peak at δ 1.1, so the former was chosen to provide increased accuracy. The MW's of the diblock copolymers were established in a similar manner by measuring the integral ratio of the initiator peak and the peaks at δ 3.8−3.5 due to the MTEGVE units in the polymer. The results are summarized in Table 1 and show a satisfactory agreement with the expected values.

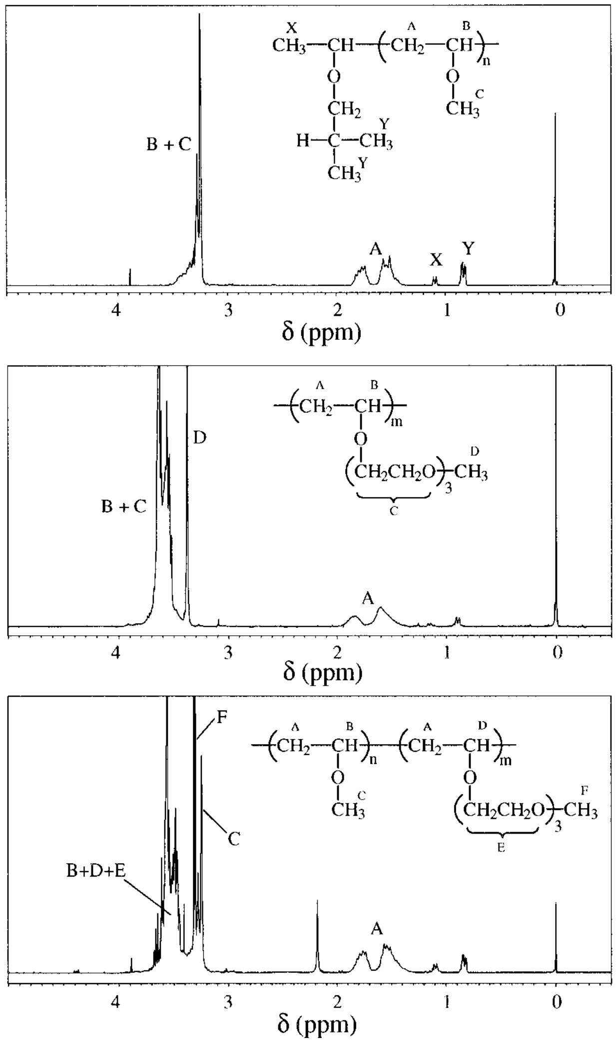

Figure 7. ^{1}H NMR spectra of MVE and MTEGVE homopolymers and a typical MVE-*block*-MTEGVE diblock copolymer in $CDCl_3$.

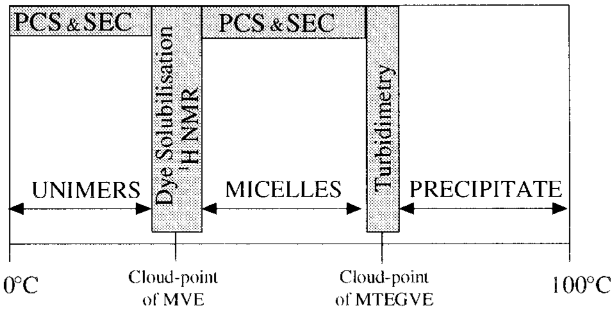

Figure 8. Simplified phase diagram of the expected phase transitions for the MVE-*block*-MTEGVE copolymers and the experimental techniques used to examine them.

Characterization in Aqueous Solution. These dihydrophilic MVE−MTEGVE block copolymers are expected to undergo two thermal transitions in aqueous solution. This is illustrated in the simplified phase diagram shown in Figure 8, where the experimental techniques used to examine the phase transitions are also indicated. Below the precipitation temperature of the MVE homopolymer, both blocks are water-soluble and the copolymer should exist in solution as molecularly dissolved chains (unimers). Above the precipitation temperature of the MVE block and below that of the MTEGVE, the chains should self-assemble to form micelles with the now-insoluble MVE units forming the micellar core and the water-soluble MTEGVE units forming the solvated corona. At the precipitation temperature of the MTEGVE homopolymer the copolymer should precipitate because both blocks become insoluble. The transition temperature between unimers and micelles is known as the critical micellization temperature (cmt), and the transition temperature between micelles and precipitate is the cloud point. In reality, the cmt's and cloud points will depend on copolymer composition and also the degree of polymerization of each block. These transition temperatures were determined for each copolymer using various methods. Dye solubilization and NMR techniques were used to examine the first transition (micellization), while turbidimetry was employed to determine the cloud points. Photon correlation spectroscopy (PCS) was used to determine the particle size above and below the cmt. Finally, aqueous SEC was used to examine the copolymer size at room temperature.

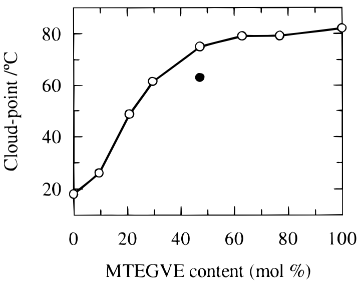

Figure 9. Cloud-points determined by turbidimetry: Effect of increasing the MTEGVE mole percent (○) at constant MVE length (20 units). The solid data point corresponds to a statistical copolymer comprising 13 MVE and 15 MTEGVE units (GM61).

These dihydrophilic MVE-*block*-MTEGVE copolymers are not dissimilar to the Pluronic PEO−PPO−PEO triblock copolymers. MVE is a structural isomer of PPO, and these two blocks are the least water-soluble components in the respective families of block copolymers. The PEO and MTEGVE are both very water-soluble, and the pendant group on the MTEGVE is a trimer of ethylene oxide. However, only a general comparison can be made between these two block copolymer systems, due to the differences in the structures of the respective monomer units, on the one hand, and the different block copolymer architecture (diblock *vs* triblock) on the other.

(a) Cloud Points. Figure 9 shows the cloud points of the copolymers plotted against the molar fraction of MTEGVE units in the copolymer. The data point corresponding to 100% MTEGVE is a homopolymer of M_n = 10 000, which we have previously shown to undergo phase separation at 83.5 °C.[2] The data point corresponding to zero MTEGVE units is the MVE homopolymer, which has a M_n = 1200 by NMR spectroscopy and has approximately 19 MVE units. The cloud point of this latter homopolymer is 18 °C, which is somewhat lower than the literature value of 34 °C. On the other hand, an MVE homopolymer synthesized in our laboratory using the same method with an M_n = 4000 (i.e., 69 MVE units, determined by ^{1}H NMR spectroscopy) had a cloud point of 29.5 °C,[3] which is slightly lower than the literature value. The HCl−IBVE initiating system used in our syntheses confers a single hydrophobic isobutyl vinyl ether unit onto the polymer chain end. We believe that this IBVE residue lowers the cloud points of both of our MVE homopolymers. Supporting this explanation is the fact that the cloud point decreases with increasing chain length. This terminal hydrophobic unit comprises only 1% of the total number of monomer units in the case of the longer homopolymer (M_n = 4000) but corresponds to 5% of the units in the case of this shorter homopolymer (M_n = 1200) and so has a more pronounced effect on the precipitation temperature. To confirm this end-group effect, an identical MVE homopolymer was synthesized with 20 MVE units initiated using a HCl−MVE adduct. This resulted in a homopolymer in which all of the monomer units, including the initiator residue, were MVE. The cloud point of this polymer was observed at 42 °C, which is somewhat higher than the expected value of 34 °C; this is probably due to the relatively low MW of this polymer. These results are summarized in Table 2.

The cloud points of the dihydrophilic block copolymers, shown in Figure 9, increase with the number of units of the more hydrophilic MTEGVE component, from 26 to 79 °C. It is interesting that block copolymers, having only a small range of MTEGVE units from 2 to 17 (10−47 mol %), exhibit a relatively wide range of cloud points from 26 to 75 °C. Also included in Figure 8 is a single point (filled circle) for a statistical copolymer (sample GM61) comprising 13 MVE units and 15 MTEGVE units. The cloud point of this statistical copolymer is 63 °C, i.e., 12 °C lower than that of the corresponding block copolymer (CF349) of similar comonomer content. This indicates that this block copolymer is much more stable in aqueous solution than the statistical copolymer. This is probably due to micellization of the block copolymer, since the hydrophobic units (i.e., MVE block above its cloud point) can effectively “hide” from the aqueous solution by forming micelles (see next section).

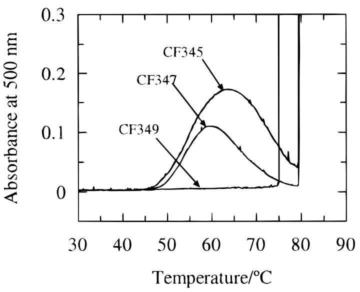

Figure 10. Absorbance at 500 nm as a function of temperature for three MVE-*block*-MTEGVE copolymers, CF345, CF347, and CF349. Homopolymer contamination is indicated by a slight increase in the optical density prior to complete precipitation for both CF345 and CF347. As a comparison, CF349 shows no homopolymer contamination.

Table 2. Effect of the Type of Initiator Residue and Degree of Polymerization on the Cloud Points of MVE Homopolymers in Aqueous Solution

initiator fragment	no. of MVE units	cloud point (°C)
IBVE	19	18
IBVE	69	29.5
MVE	20	42

The SEC analyses of CF347 and CF345 indicate the presence of some low-MW impurity, which was attributed to homopolymer contamination. This contamination was also revealed in turbidimetry experiments. The absorbance *vs* temperature curves for these two copolymer samples, shown in Figure 10, show a small increase in the optical density starting at approximately 48 °C (typically, for complete precipitation the absorbance reaches a maximum of 3.0). For comparison the data for CF349 are also shown; there is no increase in the optical density of this block copolymer until 75 °C, where complete precipitation occurs. However, this temperature of 48 °C is higher than the precipitation temperature of the MVE homopolymer, suggesting that the precipitating impurity may be a short block copolymer consisting of 20 MVE units and 5−8 MTEGVE units. Alternatively, the precipitating species may indeed be true homopolymer, which has been stabilized by the block copolymer in solution. This would delay the onset of precipitation of any homopolymer impurity. The optical densities of the solutions of CF345 and CF347 each reach a maximum of approximately 0.2 before returning to zero before complete precipitation; this may be a result of either solubilization of the precipitate into the core of the forming micelles or creaming of the precipitate.

Aoshima *et al.*[19] has investigated a similar system of statistical copolymers comprising water-soluble meth-

Table 3. Variation of Hydrodynamic Radius (R_h) MVE-*block*-MTEGVE Copolymers at Constant MVE Length (19 Units) with Increasing MTEGVE Length (0−67 Units) at 17 and 50 °C

					R_h (nm)		
						at 50 °C	
sample	comonomer ratio (D_p)[a] MVE:MTEGVE	MTEGVE content (mol %)[a]	M_n[a]	R_g (theory) (nm)	at 17 °C (nm)	$R_h^{micelle}$	$R_h^{aggregate}$
CF351	19:5	21	2 160	1.4		8.1[b]	36.7[b]
CF350	20:8	29	2 780	1.5		8.1	
CF349	19:17	47	4 440	1.7	2.4	9.2	121
CF347	20:34	63	7 730	2.0	2.5	30.8	107
CF345	19:67	78	13 950	2.6	3.7	18.4	

[a] As determined by ^{1}H NMR spectroscopy. [b] Measured at 40 °C.

oxyethyl vinyl ether units and the marginally water-soluble ethoxyethyl vinyl ether units. The copolymer molecular weight was fixed at 20 000. The cloud points of the respective homopolymers were 70 and 20 °C. The cloud points of these statistical copolymers increased more or less linearly with the mole fraction of methoxyethyl vinyl ether monomer. The nonlinearity of our cloud point data (Figure 8) most likely arises from the micellization of our block copolymers as well as from the increase in total MW with the MTEGVE content. The MVE length was kept constant in our copolymers, while the overall degree of polymerization was kept constant by the Japanese group.

(b) Dynamic Light Scattering. The hydrodynamic radii of our dihydrophilic block copolymers as measured by dynamic light scattering at 17 and 50 °C are shown in Table 3. At 50 °C the copolymers were expected to be micellar because this temperature is well above the cloud point of the MVE homopolymer. Light scattering was possible at 50 °C for most of the copolymers since their cloud points were above this temperature. We chose the lower temperature of 17 °C because this is below the cloud point of MVE homopolymer; therefore, the copolymers should exist as unimers at this temperature. The measured hydrodynamic radii of our block copolymers at 17 °C were between 2.4 and 3.7 nm. These values are consistent with a random coil configuration of chains. The theoretical radii of gyration (R_g) for a given degree of polymerization were calculated assuming a square root dependence on the degree of polymerization,[20] correcting for the tetrahedral angle of carbon and using the PMVE stiffness factor of 2.23.[21] These values, also given in Table 3, are in reasonable agreement with our light scattering data. We were unable to determine the unimer size of the smaller block copolymers (CF351 and CF350), probably due to a combination of their low degree of polymerization and the relatively low power of our 40 mW He−Ne laser. These data suggest that at 17 °C the block copolymers exist as molecularly dissolved unimers. This was confirmed by aqueous SEC experiments, where the observed MW's corresponded closely to the unimer mass (see later).

Table 3 also shows the hydrodynamic radii of the block copolymers, at 50 °C. The cloud points of CF351 and CF352 were below 50 °C, so light scattering studies of these copolymers were not possible at this temperature. Thus, the light scattering experiments reported for CF351 were performed at 40 °C. Data analysis using the CONTIN algorithm revealed the presence of two intensity-average populations, the smaller size being presumably that of well-defined micelles and the larger size probably attributed to non-equilibrium micellar aggregates. The former population is approximately 90%, except for sample CF347 for which the "micelle" population was only 61%. On the other hand, the volume-average intensities indicated more than 99% micelles. The measured micelle sizes are clearly larger than the corresponding unimer sizes at 17 °C (also the number of counts detected by the correlator at 50 °C was much higher than at 17 °C). This suggests micellization has occurred, which was expected based on the basis of solubility characteristics of the MVE units. Copolymer CF351 did not form stable micelles at 40 °C. During the light scattering measurement its micellar radius increased as a function of time. After 10 min at 40 °C its hydrodynamic radius was 8.1 nm, but within 15 min this radius had increased to 12.5 nm. After 1 h the measured hydrodynamic radius was 27.3 nm. The value stated in Table 3 is the value obtained after 10 min of equilibration. All of the other block copolymers formed stable micelles; i.e., their sizes did not change with time. This may imply gradual precipitation of CF351 at 40 °C, below the cloud point determined by turbidimetry of 48 °C. The measured hydrodynamic radii of these copolymers in water increased with increasing MTEGVE chain length, with the exception of copolymer CF347, which has an anomalously large hydrodynamic radius. The relatively large micelle size measured for this copolymer sample may be a result of homopolymer impurity, as discussed in the previous section. During the PCS experiment, such impurities would affect the micellar size and give anomalous results.

(c) Aqueous SEC. Aqueous SEC was used to determine the aggregation state of our dihydrophilic block copolymers at room temperature using a Pharmacia Superdex column. This experiment can also be performed at elevated temperatures to examine the micellization process. Indeed, Malmensten *et al.*[22] have looked at the aqueous SEC traces of Pluronic triblock copolymers as a function of temperature in order to follow the micellization process and hence obtain an estimate of the cmt value. However, in the present work we were restricted to working at 27 °C. The MW data obtained from the aqueous SEC of our block copolymers at room temperature were close the SEC values obtained in THF. This suggests that the copolymers are molecularly dissolved under these conditions, which is consistent with the light scattering. Figure 11 shows the aqueous SEC traces of copolymers CF349 and CF350 and two narrow molecular weight PEG calibration standards for comparison. These traces clearly indicate that the block copolymers are unimodal and have low molecular weights consistent with molecularly dissolved polymers.

We had previously attempted to analyze our samples using a Polymer Laboratories PL Aquagel OH-60 column at both low and high temperatures, covering a temperature range from 20 to 50 °C.[23] Unfortunately, this latter column appeared to interact strongly with the copolymers at all temperatures, leading to either

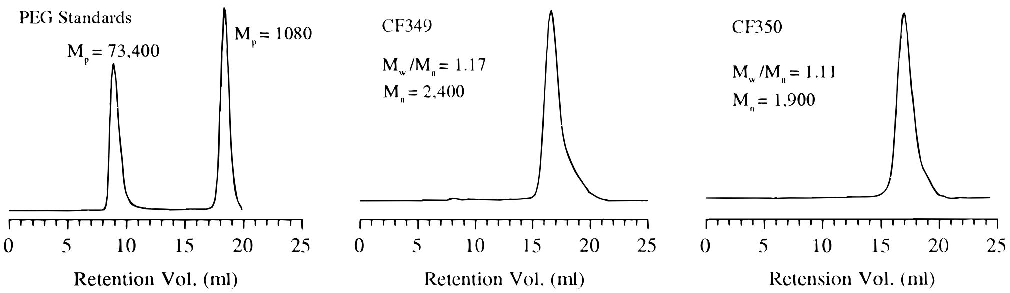

Figure 11. Aqueous SEC traces of MVE-*block*-MTEGVE copolymers CF349 and CF350 indicating that these copolymers are unimodal, with molecular weights consistent with molecularly dissolved unimers. Two narrow molecular weight distribution PEG calibration standards are also shown for comparison. Eluent, 0.25M NaCl + 50 mM Tris buffer at 27 °C; copolymer concentration, 1%.

very broad peaks or no elution at all. We tried to solve this polymer–column interaction problem by adding some of the copolymer sample under analysis to the mobile phase. This method is known as eluent SEC[24] and alleviates the sample adsorption problem by saturating the column with block copolymer from the mobile phase. The presence of the block copolymer sample in the mobile phase (at a concentration of typically 0.1% (w/w)) also facilitates the detection of micelles in samples with high critical micelle concentrations (cmc's). Unfortunately, eluent SEC did not result in the proper elution of our block copolymer samples at any temperature, probably due to the strong interaction between the copolymers and the stationary phase in combination with the exchange between the injected polymer sample and the polymer adsorbed onto the stationary phase.

The superior characteristics of the Pharmacia column compared to the Polymer Laboratories column can be attributed to the chemical nature of its stationary phase. The "Superdex" material of the Pharmacia column is extremely hydrophilic since it is based on dextran covalently bound to highly cross-linked porous agarose gel. Thus, the adsorption effects were eliminated and fractionation occurred solely on the basis of hydrodynamic volume.

(d) Dye Solubilization. The light scattering results above suggest that a unimer–micelle transition occurs between 17 and 50 °C. Thus, solubilization of a water-insoluble nonionic dye, (1,6-diphenyl-1,3,5-hexatriene, DPH) was used to determine the cmt for each copolymer. This dye has been used previously for the accurate determination of cmc's of both small surfactants[25] and amphiphilic block copolymers[2] and also for the cmt's and cmc's of Pluronic triblock copolymers.[8] Iodine[26] and benzopurpurine[27] have also been used as UV–vis absorbing probe molecules for the determination of cmt and cmc values, respectively.

Figure 12 shows the absorption spectrum of a 4 μM solution of DPH in THF, as well as a 1% (w/w) solution of CF350 at 10 °C and the same copolymer solution containing 4 μM DPH. There is no characteristic absorption of DPH in the copolymer solution at this temperature, because the environment is not hydrophobic enough. In fact, the dye is probably only suspended (as opposed to molecularly dissolved) in the solution, which would account for the long tail in the spectrum in the low-wavelength region due to light scattering. In contrast, there are three characteristic peaks at 338, 356, and 374 nm in the spectrum of the DPH/THF solution. Figure 13a shows how the absorbance at 356 nm of an aqueous solution of CF350 containing 4 μM DPH varies with temperature. The block copolymer solutions containing DPH were kept at 10 °C in the dark for a minimum of 10 min prior to examination. The temperature was then raised at approximately 2 °C min^{-1}, and the increase in absorbance at 356 nm was monitored. This increase indicates that solubilization of the hydrophobic dye is occurring, presumably into the core of the forming micelles. The absorbance levels off when all of the dye has been solubilized. The increase in absorbance at the onset of micellization was not very sharp. This has also been observed in the Pluronic PPO–PEO triblock copolymers[26] and is probably a result of polydispersity and composition effects in the copolymer samples. Thus, the cmt's were estimated by

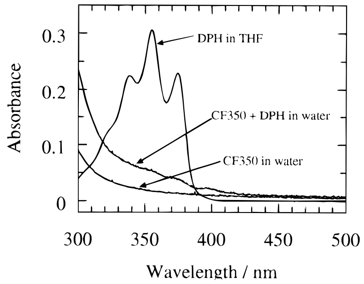

Figure 12. UV–vis absorption spectra at 10 °C of (i) 4 μM solution of DPH in neat THF; (ii) 4 μM solution of DPH in water containing 1% (w/w) CF350; (iii) 1% (w/w) CF350 in water in the absence of DPH.

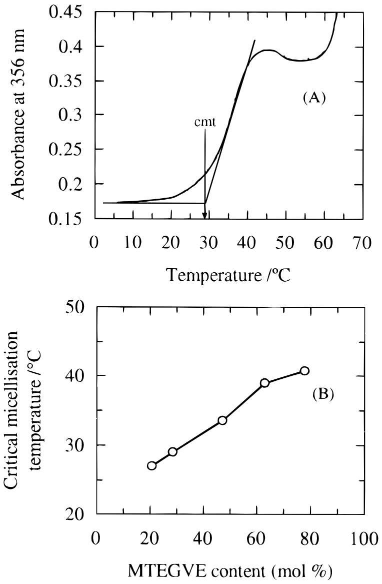

Figure 13. (A) Optical density at 356 nm for an aqueous 4 μM DPH solution containing 1% (w/w) copolymer (CF350) as a function of temperature. The cmt of this copolymer was determined as illustrated. (B) Critical micellization temperatures for all the MVE$_{20}$-*block*-MTEGVE$_n$ copolymers with constant MVE length with increasing MTEGVE block length.

taking the first differential of the absorption *vs* temperature curve as shown in the same figure.

The cmt's of all of the block copolymer samples were found to lie between 27 and 41 °C, which encompasses the precipitation temperature of the MVE homopolymer. These values are plotted in Figure 13b. The cmt's of these block copolymers increase with the number of hydrophilic MTEGVE units and level off around 40 °C for polymers containing 32 MTEGVE units. This suggests that micelle formation becomes more difficult as the size of the more hydrophilic block increases. Block copolymers with longer hydrophilic sequences are more soluble in water which would require a higher temperature for their micellization. For comparison, the cmt's of "Pluronic" PEO−PPO−PEO triblock copolymers have been investigated by Alexandridis *et al.*[8] Triblock copolymers with constant PPO chain length (30 monomer units) with an increasing PEO chain length (2 × 13, 2 × 18, and 2 × 76 units) have been investigated. These block copolymers show an increase in their cmt's from 31.5 to 50 °C, respectively.

The cloud point measurements confirmed that block copolymers CF347 and CF345 contained traces of homopolymer contamination. This contamination could also affect the dye solubilization experiments because the hydrophobic dye would partition into the precipitated homopolymer before the onset of micellization. This would result in an underestimation of the cmt for these two block copolymers.

(e) Variable Temperature ^{1}H NMR Studies. NMR spectroscopy in D_2O was used to examine the temperature dependence of micellization. This technique is complementary to the dye solubilization method described in the previous section. The dye solubilization technique provides information on the micellization process, i.e. cmc and cmt values, while ^{1}H NMR spectroscopy (in D_2O) indicates which block sequence in the copolymer is forming the micellar core. ^{1}H NMR spectroscopy has been used previously to determine the cmt's of Pluronic triblock copolymers. Wanka *et al.*[28] observed the disappearance of the fine structure of both the methylene and the methyl groups of the PPO segments in the copolymer ^{1}H NMR spectra. This allowed the reasonably accurate determination of cmt's which were in good agreement with values determined by dye solubilization methods. Alternatively, Nivaggioli *et al.*[29] compared the longitudinal relaxation times of the methylene signal from PEO and the methyl signal of PPO to determine the onset of micellization and also found a good correlation with the values obtained by dye solubilization methods.

Figure 14 shows the ^{1}H NMR spectra of block copolymer CF349 as a 1 (w/w) % solution in D_2O at five different temperatures from 20 to 60 °C. In addition, a repeat spectrum at 20 °C was recorded after the solution had cooled from 60 °C back down to the starting temperature. This latter experiment confirms that the micellization was reversible, as expected. The NMR spectra in Figure 14 cover only the range between δ 3.0 and 5.0. The two peaks at δ 3.2 belong to characteristic protons of MTEGVE and MVE. The larger peak (A) downfield belongs to the MTEGVE block and is due to the terminal methoxy protons. The smaller peak (B) upfield is characteristic of the MVE methoxy protons. At 20 °C all of the NMR peaks are relatively sharp, which suggests that this block copolymer is dissolved as well-solvated unimers in agreement with the light scattering data. With increasing temperature the methoxy peak at δ 3.2 due to the MVE block starts to broaden at around 40 °C until, at 60 °C, a very broad peak is obtained. It is noteworthy that, over the same temperature range, the MTEGVE peaks remain relatively sharp. These observations suggest that the degree of solvation of the MVE units is significantly reduced at higher temperatures, while the MTEGVE units remain well-solvated. This observation is consistent with the onset of micellization with the now-hydrophobic MVE block located in the micelle core and a well-solvated corona of the MTEGVE block. In addition to this, a cmt of around 40 °C is reasonably consistent with that found by dye solubilization. For this particular copolymer, the dye solubilization measurements indicated an onset of micellization at 34 °C (taken to be the cmt) and completion of micellization at 48 °C. To summarize, the temperature dependence of the line width of the MVE peak gives a reasonable but crude estimate of the cmt. It is worth noting that the MVE peak always remains visible, even at the highest temperature of 60 °C, which suggests that the MVE units remain partially solvated. The presence of water in the micellar core has been predicted theoretically by Hurter *et al.*[30] in their modeling of the temperature-induced micellization of Pluronics. In contrast, examination of hydrophobic−hydrophilic block copolymers of isobutyl vinyl ether and methyl triethylene glycol vinyl ether (IBVE-*block*-MTEGVE) by ^{1}H NMR spectroscopy in D_2O did not reveal any peaks assignable to the hydrophobic IBVE block sequence.[23] This suggests that this latter system has a much more hydrophobic core which completely excludes the aqueous solvent.

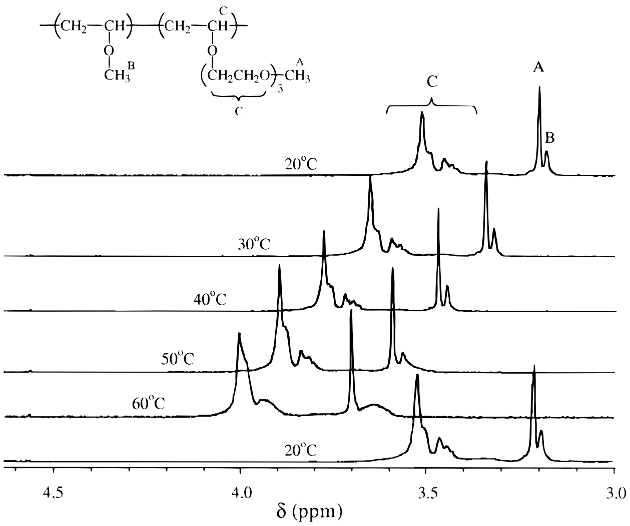

Figure 14. ^{1}H NMR spectra of the MVE_{19}-*block*-$MTEGVE_{17}$ block copolymer (CF349) in D_2O as a function of temperature from 20 to 60 °C. Note that the spectrum of the original cooled sample is identical to the original spectrum at 20 °C. This confirms the reversibility of the micellization process.

Bulk copolymer CF349 is a viscous liquid (block copolymers with 17 or more MTEGVE units were "liquids" at room temperature, whereas those copolymers containing less than 17 units were "pastes"). This is due to the low MW and the low T_g (glass transition temperature) of this copolymer. The fluid state of this bulk copolymer prompted us to consider whether the broad MVE signal at 60 °C could be due to the mobility of the MVE segments. To test this hypothesis, we studied copolymer CF349 *in the absence of solvent* at different temperatures using solution ^{1}H NMR techniques. At 20 °C, the ^{1}H NMR spectrum was very broad and the peak assignments were very difficult, but on raising the temperature to 60 °C (reducing the viscosity of the polymer), copolymer NMR peaks could be resolved, albeit with broad line-widths. This result indicates that the broadening observed for the methoxy signal of the copolymer in D_2O at 60 °C (Figure 14) could be due to the fluidity of the MVE block in the micelle core and/or its reduced solvation in the micellar core.

Conclusions

A series of dihydrophilic MVE-*block*-MTEGVE copolymers have been synthesized by living cationic polymerization. Each block copolymer had the desired MW and composition with reasonably narrow MWD's ($M_w/M_n < 1.29$). The aqueous solution behavior of these block copolymers was investigated using dynamic light scattering, turbidimetry, dye solubilization, and ^{1}H NMR spectroscopy. The cloud points of the block copolymers as determined by turbidimetry were found to vary over a wide range of temperatures (18−84 °C) and increased with an increase in the length of the more hydrophilic MTEGVE block. Dynamic light scattering was used to measure the hydrodynamic radius of the block copolymers below and above the cmt. This technique confirmed the existence of unimers at 17 °C and the formation of micelles at 50 °C. Aqueous SEC also confirmed the existence of unimers in water at room temperature. The block copolymer which contained only 5 MTEGVE units did not form stable micelles. Block copolymers with longer MTEGVE block lengths formed stable micelles with hydrodynamic radii from 8.1 to 31 nm. Dye solubilization was used to determine the critical micellization temperatures of the block copolymers. As expected, the cmt's increased with increasing MTEGVE block length and ranged from 27.5−41 °C. Homopolymer contamination in the more hydrophilic copolymers probably reduced their measured cmt's. Variable temperature ^{1}H NMR spectroscopy studies confirmed the reduced solvation and/or mobility of the MVE block sequence, with no significant changes being observed for the MTEGVE block sequence. These observations are consistent with the MVE block being located in the micellar core and the MTEGVE block forming the solvated corona.

The micellization of these copolymers in aqueous solution at elevated temperature implies that they will act as polymeric surfactants in water similar to the commercially available Pluronic PEO−PPO−PEO triblock copolymers. Thus, we hope that our copolymers will find analogous applications as the Pluronics and be used as dispersants, emulsifiers, detergents, foaming and antifoaming agents, and lubricants.

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