Synthesis of Well-Defined, Semibranched, Hydrophilic−Hydrophobic Block Copolymers Using Atom Transfer Radical Polymerization

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ABSTRACT: A series of well-defined, semibranched hydrophilic−hydrophobic diblock and triblock copolymers have been synthesized in high yield under environmentally friendly conditions via atom transfer radical polymerization (ATRP). The hydrophilic block is based on methoxy-capped oligo(ethylene glycol) methacrylate (OEGMA), a branched analogue of PEO, and the hydrophobic component is a linear PPO block. In view of the commercial importance of linear, nonionic PEO−PPO type surfactants, we were interested in the aqueous solution properties of these related, semibranched POEGMA−PPO diblock and triblock copolymers. High conversions of POEGMA (>95%) and good control (high initiator efficiencies and low polydispersities) were routinely achieved within 16 h at 20 °C. The polymerization is first order with respect to monomer up to 95% conversion, which implies that the polymer radical concentration remains constant for the duration of the polymerization. As the PPO block length was fixed at 33 units, the hydrophilic−hydrophobic balance of the block copolymers was adjusted by varying the Dp of the POEGMA block; this was achieved simply by changing the monomer-to-macroinitiator ratio from 14 to 97. With linear PEO−PPO block copolymers the limiting surface tension is governed by the PPO block length. With the semibranched POEGMA−PPO copolymers a similar trend was also evident, since, for the fixed Dp of 33 for the PPO block, the surface tension curves are almost independent of both the length of the POEGMA block and the diblock/triblock copolymer architecture. Combined ^{1}H NMR and DLS studies indicated that the POEGMA−PPO copolymers are thermoresponsive, forming large, highly hydrated micelles reversibly at 20−60 °C. This is understandable since coronal branching should reduce micellar packing efficiency, leading to bigger, looser micellar aggregates.

Introduction

Ethylene oxide/propylene oxide-based (PEO−PPO−PEO) triblock copolymers are an important class of nonionic surfactants that have received increasing attention during the past two decades.[1] Synthesis involves sequential monomer addition using anionic ring-opening polymerization chemistry, which leads to narrow molecular weight distributions and well-defined block architectures. Because of their low toxicity, these copolymers have found widespread use in pharmaceutical applications; for example, they aid the absorption of poorly water-soluble drugs by wetting, deflocculation, or micellar solubilization.[2,3]

One of the most interesting aspects of their aqueous solution behavior is that micellization is strongly temperature-dependent. (The cmc can decrease by up to 3 orders of magnitude as the temperature is raised by about 20 °C.) In general, these PEO−PPO−PEO triblock copolymers are molecularly dissolved in dilute aqueous solution at low temperatures (<15 °C) since both blocks are soluble. At higher temperatures the PPO block gradually becomes hydrophobic and micelle formation occurs. This reversible aggregation behavior has been studied extensively using a wide range of methods over the past few years.[4−13]

PEO−PPO block copolymers can also self-assemble to form various normal and reverse phase liquid crystalline structures and polymorphs.[14−16] For a given copolymer, the most important parameters are the overall copolymer molecular weight, the PEO/PPO block ratio, and the solvent. Just above ambient temperature, highly concentrated aqueous solutions of PEO−PPO copolymer exhibit a dramatic increase in viscosity due to overlap of the micellar corona to yield a gel phase with long-range crystalline order.[17−20] It has been suggested that this thermoreversible gelation, together with the low toxicity of these copolymers, gives rise to applications in controlled drug delivery.[1] Since these gels are capable of solubilizing both water-soluble and oil-soluble solutes,[21] they can also be used as emulsifying, wetting, thickening, coating, dispersing, lubricating, and foaming agents.[22,23] Another interesting feature of PEO−PPO copolymers is their ability to adsorb at the air−water, solid−water, and oil−water interface. Because of their amphiphilic nature, these polymers are effective steric stabilizers for many colloidal dispersions.[22,23]

Following its discovery[24,25] in 1995, ATRP has been used extensively to synthesize functional polymers with a wide range of copolymer architectures, including blocks, grafts, stars, and hyperbranched polymers.[26,27] Since the propagating chain ends are generally believed to be radicals, ATRP is much more tolerant of monomer functionality than ionic polymerizations. Although termination is merely suppressed relative to propagation, relatively narrow molecular weight distributions can be achieved for styrenics, acrylates, and methacrylates.[28−30]

We have recently shown[31−33] that ATRP is particularly efficient in aqueous media under mild conditions, which augurs well for the synthesis of new water-soluble copolymers with well-defined architectures. In particular, a commercially available monomer, monomethoxy-capped oligo(ethylene glycol) methacrylate [OEGMA], can be polymerized to more than 95% conversion within 20−30 min at 20 °C in aqueous media. In the context

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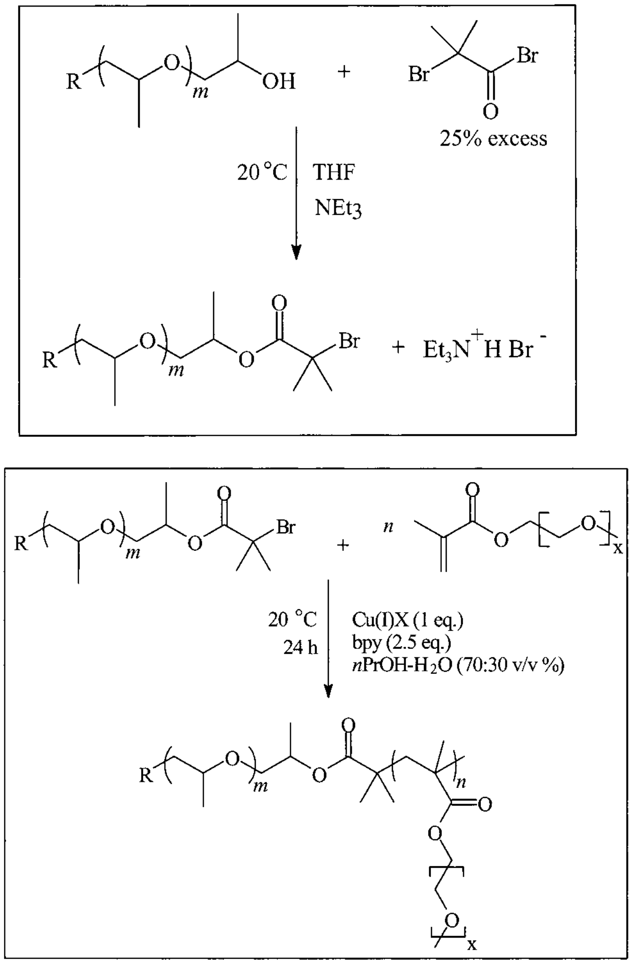

Figure 1. Reaction scheme for (a) the preparation of a PPO macroinitiator and (b) ATRP of OEGMA using the PPO macroinitiator.

of aqueous ATRP OEGMA appears to be a "model" hydrophilic monomer.[33,34]

Because of the commercial importance of PEO−PPO copolymers, we were interested in the synthesis and properties of related semibranched copolymers based on methoxy-capped oligo(ethylene glycol) methacrylate (OEGMA), which is a branched analogue of the linear PEO block (see Figure 1). As far as we are aware, there have been no previous reports addressing the effect of coronal chain branching on the micellization of hydrophilic−hydrophobic block copolymers. Intuitively, significant effects might be expected, since branching should reduce packing efficiency within the micelle corona, leading to bigger, looser micellar aggregates. In this initial paper we describe the facile synthesis of two new series of semibranched hydrophilic block copolymers via atom transfer radical polymerization (ATRP) in an aqueous alcohol milieu at room temperature.

Experimental Section

Materials. Unless otherwise stated, all chemicals were purchased from Aldrich and used without further purification. Monohydroxy-capped poly(propylene oxide) (MPPO) [^{1}H NMR ($CDCl_3$) indicated an M_n of 1940] and dihydroxy-capped poly(propylene oxide) (DPPO) [$M_n = 2000$, by ^{1}H NMR ($CDCl_3$)], each with a polydispersity of 1.18, were both kindly donated by Laporte Performance Chemicals (Hythe, UK).

Synthesis. The ATRP macroinitiators were synthesized by reacting either the MPPO (typically 20 g) or the DPPO with 2-bromoisobutyryl bromide (1.6 mL, 25% excess) and triethylamine (1.7 mL 25% excess) at room temperature in dry toluene or THF (100 mL) for at least 3 h, as shown in Figure 1a. The resulting reaction solution was filtered to remove the amine salt, stirred with activated carbon, dried with $MgSO_4$, and filtered, and the solvent was removed under vacuum. Both COSY and ^{1}H NMR spectroscopy were used to confirm the secondary hydroxy groups in the PPO precursors. The ^{1}H NMR spectra for the MPPO precursor and the PPO−Br initiator are shown in Figure 2. The degree of esterification was calculated by comparing the integrals from peak **d** (δ 1.8), corresponding to the two methyl groups adjacent to the ester group, with peaks characteristic of the PPO precursor (either **b**, **c**, or **e**).

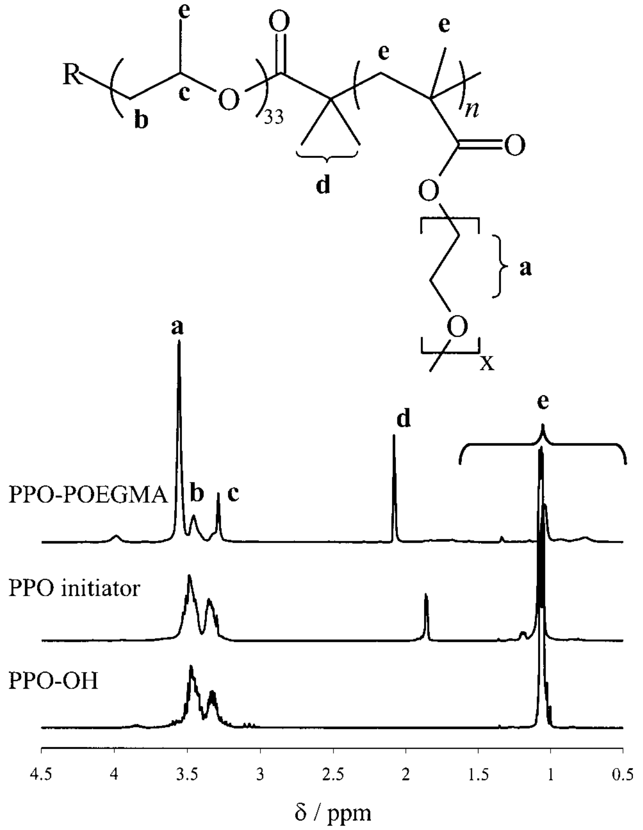

Figure 2. ^{1}H NMR spectra of the MPPO−OH starting material, a PPO−Br initiator, and an example of a PPO−POEGMA diblock copolymer.

ATRP syntheses were carried out at 20 °C. The initiator (typically 1.6 g) and OEGMA monomer (16.5 g for a Dp of 50) was dissolved in 16.5 mL of a 70:30 v/v % *n*PrOH:H_2O solution prior to degassing using a nitrogen purge. To this was added the bpy ligand (315 mg, 2.5 equiv) and Cu(I)Cl (80 mg, 1 equiv); see Figure 1b. The exotherm (typically 2 °C) was monitored and the reaction mixture stirred at room temperature for 24 h. The reaction solution was diluted with *n*PrOH and passed down a basic alumina column, and the solvent was removed under vacuum. Cleanup was achieved via three consecutive precipitations into *n*-hexane. Figure 2 shows the ^{1}H NMR spectra for (a) the monohydroxy-capped MPPO, (b) the PPO-based ATRP macroinitiator, and (c) the resulting PPO−OEGMA diblock copolymer. Kinetic data were obtained by removing aliquots at regular intervals and analyzing the monomer/polymer solutions by ^{1}H NMR in $CDCl_3$.

Copolymer Characterization. Molecular weight distributions were assessed using a GPC comprising of a Polymer Laboratories PL gel 3 μm Mixed "E" column with a Knauer K-2301 differential refractive index detector and THF eluent at a flow rate of 1 mL min^{-1}. A series of near-monodisperse PMMA homopolymers were used as calibration standards. ^{1}H NMR spectra were recorded using a 300 MHz Bruker AC-P spectrometer, in $CDCl_3$ for the PPO−POEGMA diblock and POEGMA−PPO−POEGMA triblock copolymers. Surface tension measurements were carried out using a Krüss K10ST surface tensiometer equipped with a platinum ring. All measurements were carried out at 20 °C. Reproducibility was checked by frequent determination of the surface tension of deionized doubly distilled water (72 mN m^{-1}). Dynamic light scattering measurements were carried out using a Brookhaven Instruments Corp. BI-200SM instrument equipped with a 50 mW laser operating at 532 nm and a 9000AT correlator. All measurements were carried out using 1.0% (w/v) copolymer solutions in the presence of 0−0.50 M NaCl, and the scattered light was detected at 90° to the incident beam. The data were fitted using the NNLS algorithm.

Results and Discussion

We recently described the atom transfer radical polymerization of various hydrophilic monomers in aqueous media.[31,33] In particular, we have shown that OEGMA can be polymerized with good control in water at room temperature using various ATRP initiators in combination with a Cu(I)/bpy catalyst. In the present study we sought to extend this fundamental study by using mono- or bifunctional PPO macroinitiators for the polymerization of OEGMA. Since these PPO-based macroinitiators are relatively hydrophobic, it was considered necessary to use an alcohol cosolvent to ensure dissolution. Complete solubilization of the macroinitiator is essential for high initiator efficiency. We found that the PPO macroinitiators could be molecularly dissolved in 70:30 1-propanol:H_2O mixtures. In our experience, addition of alcohol to an aqueous ATRP formulation solution invariably slows down the rate of polymerization significantly. Nevertheless, very high conversions of OEGMA (>95%) were routinely achieved within 16 h at 20 °C using the PPO macroinitiators.

It is well-known that PPO exhibits inverse temperature solubility behavior.[35] Although water-insoluble at 20 °C, the two PPO macroinitiators dissolved completely in cold water (<5 °C). Hence, the ATRP of OEGMA using a monofunctional PPO macroinitiator in the absence of any alcoholic cosolvent was investigated at approximately 5 °C. An exotherm of 10 °C was observed for this aqueous reaction, which is in marked contrast with the alcohol−water mixture syntheses where little or no exotherm was observed. In aqueous−alcohol mixtures at 20 °C the reaction required 16 h to reach high conversion (>95%), whereas in the low-temperature ATRP synthesis in aqueous media the OEGMA monomer was completely consumed within 3 h.

However, the GPC analysis for the PPO_{33}−$POEGMA_{30}$ diblock copolymer prepared by aqueous ATRP indicated a multimodal distribution. This is partly due to significant PPO macroinitiator contamination (around 30%), but the copolymer itself was unexpectedly rather polydisperse, with an M_w/M_n of around 1.5. Thus, although the rate of polymerization of OEGMA in aqueous ATRP at 0 °C is greater than that in the aqueous alcohol milieu at 20 °C, the initiator efficiency is less than 70% in the former case, and inferior control over the molecular weight distribution is achieved. In view of this, the low-temperature aqueous ATRP syntheses were abandoned.

A summary of the block compositions and polydispersities of a series of PPO−POEGMA diblocks prepared in 70:30 1-propanol−water at 20 °C are presented in Table 1. Clearly, the ATRP of OEGMA using the PPO-based macroinitiator proceeds to high conversion and with good control (high initiator efficiency and low polydispersities) under these conditions. In this study we elected to fix the PPO chain length (Dp = 33) and to vary the chain length of the POEGMA block systematically (target Dp = 14−100). Very similar results were obtained for the POEGMA−PPO−POEGMA triblock copolymers synthesized using the bifunctional PPO macroinitiator (see Table 2). Again, the central PPO block was fixed at a Dp of 33, and the overall Dp of the two outer POEGMA blocks was systematically varied from 33 to 97. The copper catalyst was easily removed by alumina chromatography in alcohol to produce colorless diblock or triblock copolymers in very high yields.

Table 1. Summary of Molecular Weights, Polydispersities and Compositions of Various PPO−POEGMA Diblock Copolymers Synthesized Using Atom Transfer Radical Polymerization at 20 °C in (2.5:1) *n*PrOH:H_2O[a]

poly ID	target Dp[b]	exptl Dp (NMR)	exptl M_n (NMR)	M_n (GPC)	M_w/M_n (GPC)	OEGMA conv % (NMR)
KV64	15	14	7 700	8 900	1.32	>99
KV84	22	22	11 000	10 800	1.27	>99
KV125[c]	30	28	13 400	5300	1.55	>99
KV65	30	31	14 700	14 200	1.18	98
KV72	44	43	19 600	18 100	1.28	>99
KV137	50	58	25 700	21 500	1.19	>99
KV82	80	75	32 600	19 300	1.18	92
KV176	100	93	40 000	32 600	1.13	92

[a] Conditions: 20 °C, 16 h, $[M]_0 = 50$ w/v %, MPPO−Br:Cu(I):bpy molar ratio was 1:1:2.5. [b] Calculated from the POEGMA/macroinitiator molar ratio. [c] H_2O at 0 °C (bimodal trace).

Table 2. Summary of Molecular Weights, Polydispersities and Compositions of Various POEGMA−PPO−POEGMA Triblock Copolymers Synthesized Using Atom Transfer Radical Polymerization at 20 °C in (2.5:1) *n*PrOH:H_2O[a]

poly ID	target Dp[b]	exptl Dp (NMR)	exptl M_n (NMR)	M_n (GPC)	M_w/M_n (GPC)	OEGMA conv % (NMR)
KV81	30	33	15 500	12 400	1.23	>99
KV136	50	54	24 000	17 700	1.16	>99
KV80	48	56	24 800	18 000	1.13	>99
KV178	76	74	32 200	29 800	1.19	>99
KV85	100	97	41 600	21 500	1.12	>99

[a] Conditions: 20 °C, 16 h, $[M]_0 = 50$ w/v %, Br−PPO−Br:Cu(I):bpy molar ratio was 1:1:2.5. [b] Calculated from the POEGMA/macroinitiator molar ratio.

The new copolymers were characterized by ^1H NMR and GPC. The degree of polymerization of POEGMA was calculated by comparing signal **a** at δ 3.5−4.0 from POEGMA with signals **b** or **c** from the PPO macroinitiator at δ 3.4 or δ 3.25, respectively (see Figure 2). The results obtained are recorded in Tables 1 and 2. It is worth noting that the experimental Dp determined by ^1H NMR is in very good agreement with the theoretical Dp's for these materials. In most cases very high conversions were obtained; in the few cases where the monomer conversion was incomplete, the experimental Dp agreed with the target Dp if the conversion was taken into account.

GPC analyses of some of the crude diblocks indicated low levels (typically <5%) of contamination by the PPO macroinitiator. This could be easily removed by extraction with *n*-hexane. Figure 3 shows the GPC traces of a crude diblock copolymer contaminated with PPO macroinitiator, the same diblock after three extractions with *n*-hexane, and the original PPO macroinitiator. Clearly, the *n*-hexane extraction is successful in removing the unreacted macroinitiator. The polydispersities for the purified copolymers were relatively narrow, ranging from 1.09 to 1.32.

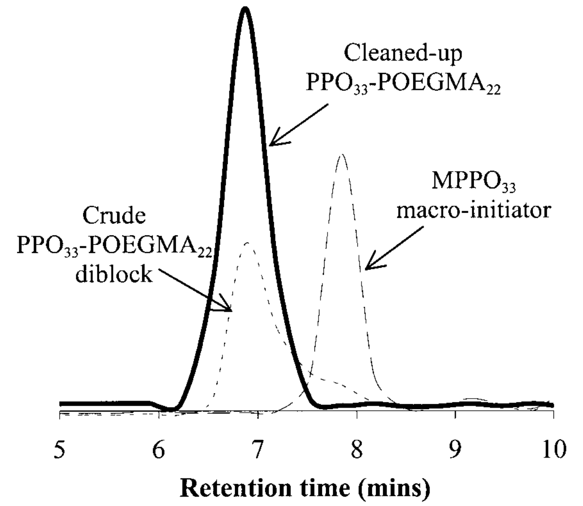

Figure 3. Typical GPC traces for a $MPPO_{33}$ macroinitiator, overlayed with the crude $PPO_{33}-POEGMA_{22}$ diblock copolymer and the same diblock copolymer after cleanup.

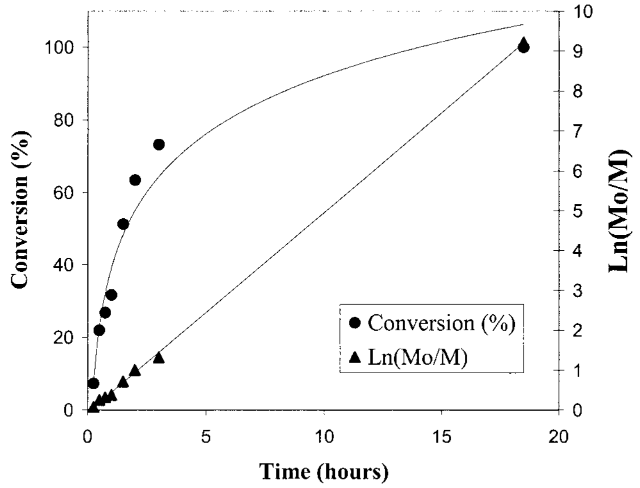

Figure 4. Kinetic plot for the ATRP of OEGMA using a PPO macroinitiator in nPrOH:H_2O 70:30 v/v % at 20 °C; $[M]_0 = 50$ w/v %, OEG-Br:Cu(I)Cl:bpy 1:1:2.5. The target Dp was 41.

To assess the living character of ATRP in aqueous alcohol solution, we studied the kinetics of the homopolymerization of OEGMA using a monofunctional macroinitiator (see Figure 4). From the conversion vs time plot, it is evident that the rate of polymerization is relatively slow, with 95% conversion requiring 16 h at 20 °C. As a comparison, the homopolymerization of OEGMA in purely aqueous media at 20 °C under otherwise identical conditions gave conversions of more than 95% in less than 30 min.[34] These observations are consistent with a report by Matyjaszewski and coworkers, who found that the rate of ATRP of n-butyl acrylate depends markedly on the solvent polarity, with higher rates being observed in more polar solvents such as ethylene carbonate.[36]

A linear semilogarithmic plot of monomer concentration vs time is shown in Figure 4, which suggests that this polymerization is first order with respect to monomer for the duration of the polymerization. The living character of this system is also supported by the linear M_n vs conversion plot shown in Figure 5.

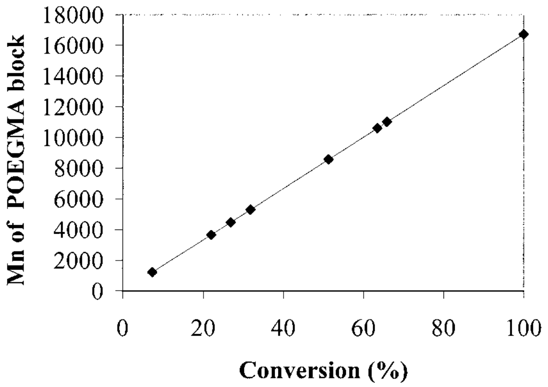

Figure 5. Evolution of molecular weight with conversion for the same experiment as in Figure 4.

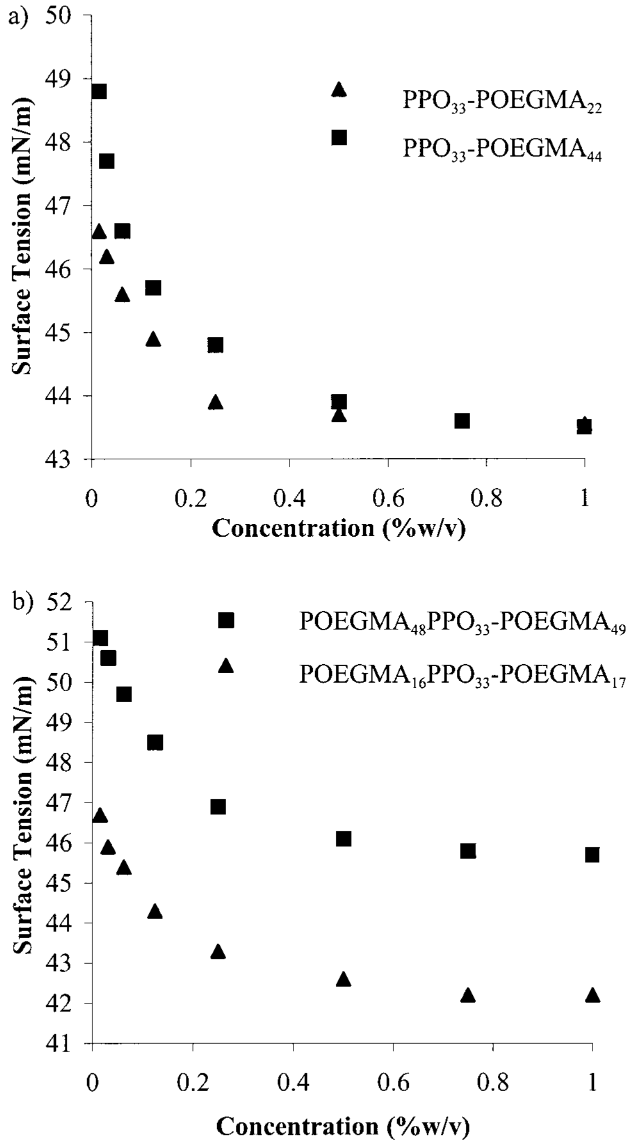

Figure 6. Surface tensiometry curves as a function of copolymer concentration for (a) diblock copolymers $PPO_{33}-POEGMA_{22}$ and $PPO_{33}-POEGMA_{44}$ and (b) triblock copolymers $POEGMA_{48}-PPO_{33}-POEGMA_{49}$ and $POEGMA_{16}-PPO_{33}-POEGMA_{17}$.

The surface activities of these semibranched POEGMA–PPO copolymers (see Figure 6) were compared with data reported previously for the commercial linear PEO–PPO (Pluronic) materials. In general, the limiting surface tensions for Pluronics are in the 33–43 mN m^{-1} range.[37] It is well-documented that for Pluronics the limiting surface tensions mainly depend on the PPO block length.[38] Triblock copolymers which differ only in the number of EO units per chain usually present similar surface tension vs copolymer concentration curves, which is not the case for hydrocarbon-EO based surfactants.[39]

Another characteristic feature of Pluronics is the reduction in the critical micelle concentration (cmc) with increasing temperature. This decrease can be more than 3 orders of magnitude over a relatively narrow temperature range of 15−40 °C.[38] This is due to the progressive dehydration of the PPO blocks. At ambient temperature the PPO blocks have only weak hydrophobic character and low surface activity, but at higher temperatures this hydrophobicity increases due to the loss of hydrogen-bonded water molecules, therefore increasing the surface activity.[35]

All of the new OEGMA-based semibranched block copolymers had limiting surface tensions just above 40 mN m^{-1} at 20 °C. In addition to the PPO blocks, the methacrylate backbone of the POEGMA blocks also makes a contribution to the overall hydrophobic character. However, it is also likely that the branched nature of the POEGMA residues prevents the efficient adsorption of the PPO block at the air−water interface. Temperature differences may also partly account for the observed differences between the linear Pluronics and the semibranched POEGMA−PPO block copolymers of the present study.

In Tables 1 and 2, the average Dp of the PPO block is fixed at 33 and the Dp of the POEGMA block(s) is systematically varied from 14 to 97. The surface tension curves for the two diblocks studied (with POEGMA Dp's of 22 and 44, respectively) are almost identical, despite the doubling of the POEGMA block length. This suggests that the surface activities of these copolymers do not depend significantly on the Dp of the hydrophilic POEGMA block(s). It is also apparent that the limiting surface tension is almost independent of the copolymer architecture; over the concentration range explored the limiting surface tensions of PPO_{33}−$POEGMA_{22}$ (KV84) and $POEGMA_{48}$−PPO_{33}−$POEGMA_{49}$ (KV85) differed by less than 5 mN m^{-1}. Similar observations have been reported in the Pluronic literature.[38]

One of the characteristic features of Pluronics is that their micellization behavior is strongly temperature dependent in aqueous media. Such micelles typically have mean diameters of around 10 nm, with PPO cores and hydrated PEO coronas. Micelle size decreases at higher temperature, due to gradual dehydration of the PPO cores. There is also some experimental data which suggest that the PEO coronas contract at elevated temperatures.[40] This dehydration leads to the reduction of the hydrated spherical micelles to give more compact, hydrophobic aggregates at higher temperatures.

Although the linear PPO block is identical in both sets of copolymers, it is clearly difficult to compare the new semibranched copolymers directly with traditional Pluronic-type copolymers. For example, it is unlikely that, for a fixed PPO block length, the direct comparison of an POEGMA block with that of a linear PEO block of the same Dp would be instructive, since the branched block would contain at least 7 times more EO residues than the linear counterpart. On the other hand, a comparison based on the total number of EO units in the branched and linear copolymers also seems too simplistic, since this neglects the hydrophobic character of the methacrylate backbone of the branched copolymers.

It is well-documented in the Pluronic literature that the longer the hydrophobic PPO block, the lower the cmc and cmt (critical micelle temperature) of the copolymer. Also, micelle formation becomes more difficult if the copolymer is too hydrophilic, although the effect of varying the PEO block length on the cmc and cmt is less pronounced than variation of the PPO block length.[41]

Regardless of whether we use the Dp of the POEGMA block or the total number of EO residues to compare the POEGMA−PPO copolymers to Pluronics, we always observe a much lower cmt. For example, a 1.0% (w/v) solution of KV85 [$POEGMA_{48}$−PPO_{33}−$POEGMA_{49}$] has a cmt below 20 °C. For Pluronics with a similar PPO block length, the cmt's are always above 31 °C, regardless of the Dp of the PEO block.[41] For a cmt of 20 °C a PPO block length of at least 55 units would be required for the Pluronic copolymer. This suggests that the semibranched POEGMA−PPO have a greater tendency to form micelle structures than their linear Pluronic counterparts.

^{1}H NMR and DLS experiments were carried out on a 1.0% aqueous solution of $POEGMA_{48}$−PPO_{33}−$POEGMA_{49}$ triblock copolymer (KV85). DLS studies indicated the formation of large, reversible, hydrated micelles (D_H > 94 nm) at all temperatures between 20 and 60 °C. The branched nature of the hydrophilic outer blocks of these copolymers apparently prevents efficient packing in the micelle coronas. Furthermore, some authors have explained the very high degree of hydration of EO units (the hydration number of P94 [PEO_{24}−PPO_{47}−PEO_{24}] in water is 1.4 g of H_2O per gram of copolymer).[42] Presumably this is partly due to hydrogen bond formation with the ether oxygen.

From the ^{1}H NMR results shown in Figure 7, it is clear that the apparent degree of polymerization of the PPO block decreases with increasing temperature. The apparent degree of polymerization of the PPO block in the absence of salt was 33. This is identical to the real degree of polymerization obtained from ^{1}H NMR in $CDCl_3$, indicating negligible dehydration of the PPO micelle cores under these conditions. However, at 0.10 M Na_2SO_4 the apparent degree of polymerization of the PPO blocks is 6.7, which suggests an 80% reduction in the degree of hydration of the micelle cores. The micelle core becomes extensively dehydrated at 60 °C with 0.50 M salt (complete disappearance of PPO signals at δ 1.55). However, under these conditions the POEGMA corona is partially salted out and the micelles become colloidally unstable as judged by DLS.

DLS studies show that the intensity-average micelle diameter decreases at higher temperatures at low salt concentration ($\leq$0.1 M Na_2SO_4). This behavior is also true for Pluronics: at temperatures up to 50 °C, a dramatic increase in the hydrodynamic diameter is observed, perhaps indicating a large increase in the micelle aggregation number.[42] For KV85 this effect was only observed after the addition of 0.2−0.5 M Na_2SO_4. As the temperature was increased from 25.5 to 40 °C, the hydrodynamic micelle diameter became progressively smaller, presumably due to the dehydration of the PPO cores observed by ^{1}H NMR spectroscopy.

In our experience, thermoresponsive block copolymers usually form hydrated micelles when heated above the cloud point of the less hydrophilic block.[43] These observations, which are based on variable temperature ^{1}H NMR studies, appear to be very general and independent of both the block structure and the polymerization

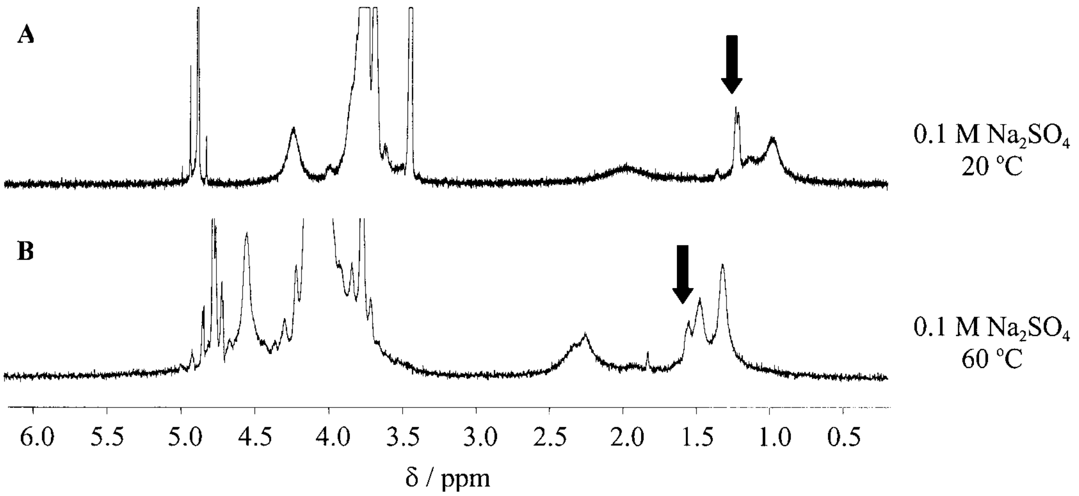

Figure 7. ^{1}H NMR spectra of a POEGMA$_{48}$−PPO$_{33}$−POEGMA$_{49}$ triblock copolymer in D$_2$O in the presence of 0.10 M Na$_2$SO$_4$: (A) at 20 °C (apparent Dp of PPO block is 33) and (B) at 60 °C (apparent Dp of PPO block is 6.7).

chemistry. Examples include diblock copolymers based on poly(methyl vinyl ether) prepared by living cationic polymerization[44] and 2-(dimethylamino)ethyl methacrylate (DMA)-based diblock copolymers synthesized by either group transfer polymerization (GTP)[45,46] or oxyanionic polymerization.[47] Furthermore, we have found that if the more hydrophilic block is branched, the degree of dehydration of the micelle cores is reduced, presumably due to inefficient chain packing in the micelle corona. For example, in the case of POEGMA−PDMA diblock copolymers synthesized by GTP,[45] dynamic light scattering studies confirm that micelles are formed at 65 °C, but ^{1}H NMR studies indicate little, if any, dehydration of the PDMA block in the micelle cores. In contrast, if the branched POEGMA block is replaced by a linear PEO block, partial dehydration of the PDMA block occurs at elevated temperature.[47] We have observed similar effects with pH-responsive block copolymers, which normally give fully dehydrated micelle cores.[48,49] However, only partially dehydrated micelle cores are observed by ^{1}H NMR if the linear PEO block in the micelle corona is replaced by a branched POEGMA block.[33,45,50] In summary, there is abundant experimental evidence from the micellization behavior of stimuli-responsive block copolymers to support our observations of highly hydrated PPO−core micelles in the present study.

Conclusions

A new series of well-defined, hydrophilic−hydrophobic diblock and triblock copolymers have been synthesized in high yield under environmentally friendly conditions. The hydrophilic block is based on POEGMA, a branched analogue of PEO, and the hydrophobic component is PPO, so the resulting semibranched copolymers are analogues to the well-known Pluronic-type PEO−PPO nonionic surfactants.

Since these PPO-based macroinitiators are relatively hydrophobic, they are not water-soluble at 20 °C. Hence, it was necessary to use a solvent mixture of 70:30 1-propanol:H$_2$O in order to ensure molecular dissolution. Although the polymerization was predictably slower in the presence of alcohol, kinetic studies show that the ATRP of OEGMA using the PPO-based macroinitiator proceeds to high conversion and with high initiator efficiency and low polydispersities. The linearity of the semilogarithmic plot of monomer concentration vs time suggests that this polymerization is first-order with respect to monomer up to 95% conversion, which implies that the polymer radical concentration remains constant for the duration of the polymerization.

As discussed previously, although the linear PPO block is common to both sets of copolymers, it is clearly difficult to compare the new semibranched copolymers directly with traditional linear Pluronic-type copolymers. However, our results show that the former copolymers have slightly lower surface activities, probably because the branched POEGMA blocks prevent efficient adsorption of the PPO block at the air/water interface.

It has been well documented for Pluronics that the limiting surface tension depends almost entirely on the PPO block length. With our semibranched copolymers a similar trend is also evident, as the surface tension curves are almost independent of both the length of the POEGMA block and the diblock/triblock copolymer architecture. Combined ^{1}H NMR and DLS studies indicate that the POEGMA−PPO copolymers are thermoresponsive, forming large, highly hydrated micelles reversibly at 20−60 °C. This is understandable since branching should reduce packing efficiency within the micelle corona, leading to bigger, looser micellar aggregates.

In future work we will examine whether the degree of branching imparted by the POEGMA block leads to qualitatively different phase behavior (micellization, gelation) in concentrated aqueous solution compared to linear Pluronic-type copolymers.

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References and Notes

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