Direct Synthesis and Stimulus-Responsive Micellization of Y-Shaped Hydrophilic Block Copolymers

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ABSTRACT: Two bifunctional atom transfer radical polymerization (ATRP) macroinitiators were synthesized via Michael addition of 2 equivalents of 2-hydroxyethyl acrylate to two commercial monoamine-capped poly(alkylene oxides), Jeffamine XTJ-506 and Jeffamine XTJ-507, followed by esterification using excess 2-bromoisobutyryl bromide. ^{1}H NMR and MALDI−TOF mass spectra (MALDI−TOF MS) were consistent with the expected structures for these two ATRP macroinitiators. A range of well-defined, Y-shaped, pH-responsive or thermoresponsive block copolymers was synthesized using these macroinitiators by polymerizing various hydrophilic methacrylic monomers via ATRP in methanol at 20 °C. The stimulus-responsive micellization of selected Y-shaped block copolymers in aqueous solution was investigated by ^{1}H NMR, dynamic light scattering (DLS), and surface tensiometry. For comparative purposes, their linear diblock copolymer counterparts were also synthesized, and their micellization properties in aqueous solution were investigated. DLS studies indicated that the nonlinear architectures of selected Y-shaped block copolymers usually resulted in micelles with differing dimensions to those formed by the corresponding linear diblock copolymers. DLS studies also confirmed that one of these new Y-shaped block copolymers exhibited "schizophrenic" thermoresponsive behavior in aqueous solution. Near-monodisperse spherical micelles were obtained at higher temperatures (above 45 °C), whereas polydisperse nonspherical micelles appear to be formed at lower temperatures (below 12 °C).

Introduction

The micellar self-assembly of amphiphilic block copolymers in aqueous solution is of considerable academic interest. Potential commercial applications include personal care and cosmetics products, pharmaceutics, coatings, rheology modifiers, colloidal stabilization, and the synthesis of nanomaterials.[1−5] Fundamental parameters such as critical micelle concentration (cmc), micelle aggregation number (N_{agg}) and micelle hydrodynamic radius (R_h), micelle shape, and colloidal stability are influenced by the solution pH, temperature, copolymer concentration, polymer−solvent interactions, block compositions, and copolymer molecular weights.[6−9] Recent research has revealed that the block copolymer architecture also plays an important role in determining micelle properties.[1,2,10−13] For example, asymmetric star-shaped (AB_2 or AB_3 type) block copolymers exhibit fundamentally different micellization behavior compared to that found for the corresponding linear AB diblocks.[10−13] Asymmetric AB_2 type block polymers are sometimes referred to as "miktoarm star"[10−16] or "Y-shaped" block copolymers. Pispas et al.[11] compared the micellization properties of Y-shaped block copolymers comprising polyisoprene (I) and polystyrene (S) in organic solvents to linear I−S diblock copolymers of the same molecular weight and composition. Light scattering and viscometric studies indicated that "the presence of only one graft chain per molecule can change considerably the micellar characteristics of complex block copolymers". In *n*-decane (which is a good solvent for polyisoprene but a nonsolvent for polystyrene), the N_{agg} and R_h of the micelles both increase in the order I_2S < S_2I < SI. Although the difference between S_2I and SI was relatively small, the area of the core−shell interface per copolymer chain increased in the order SI < S_2I < I_2S. Of more relevance to our own work, Yun et al.[12] investigated the aqueous solution properties of amphiphilic AB, A^1A^2B, and A_2B block copolymers using fluorescence spectroscopy and light scattering, where A is polyisobutylene and B is poly(methyl vinyl ether) and the superscripts denote molecular weight asymmetry at a constant molecular weight and block composition. It was found that the cmc values measured at 23 °C increased in the order A_2B < A^1A^2B < AB. Below 25 °C, both N_{agg} and R_h increased in the order AB < A^1A^2B < A_2B.

Y-shaped block copolymers have been typically synthesized via living anionic[10,11,14−16] or cationic polymerization.[12] For example, Gnanou and co-workers[16] synthesized styrene-functionalized polystyrene-*block*-[poly(ethylene oxide)]$_2$ (PS−PEO_2) macromonomers using anionic polymerization in combination with protecting group chemistry. These copolymers were used as reactive surfactants in emulsion polymerization[16] and also as steric stabilizers for dispersion polymerization.[17] Recently, the same group reported the synthesis of polystyrene-*block*-[poly(*tert*-butyl acrylate)]$_2$ (PS−P*t*-BA_2) Y-shaped block copolymers by atom transfer radical polymerization (ATRP) using a multistep route, again relying on protecting group chemistry.[18] Subsequent acid hydrolysis resulted in the removal of the *tert*-butyl protecting groups and the formation of amphiphilic PS−PAA_2 Y-shaped block copolymers. In a recent review article, Haddleton et al. briefly mentioned the

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synthesis of an poly[2-(dimethylamino)ethyl methacrylate]-*block*-poly(methyl methacrylate)-*block*-(poly[2-(dimethylamino)ethyl methacrylate])$_2$ (PDMA−PMMA−PDMA$_2$, ABA$_2$ type) block copolymer that also involved ATRP in combination with protecting group chemistry.[19] More recently, Zhao et al.[20] reported the synthesis of ABC mikto three-arm star terpolymers by combining three different controlled/"living" polymerization techniques: ring-opening polymerization (ROP), ATRP, and nitroxide-mediated radical polymerization (NMRP). This approach involved using a trifunctional initiator bearing a suitable hydroxyl group for ROP, an ATRP initiator, and a NMRP initiator. These miktoarm star terpolymers were obtained via a three-step synthesis: first ROP of ϵ-caprolactone (CL), followed by ATRP of methyl methacrylate (MMA); after removal of the bromine end groups using tri(*n*-butyl) tin hydride, the NMRP of styrene gave the target PCL−PMMA−PS 3-miktoarm star terpolymers.

Stimulus-responsive *linear* diblock copolymers have been extensively studied both in our laboratory[21−26] and also by other research groups.[27,28] In a recent communication we reported the first examples of stimulus-responsive *nonlinear* block copolymers.[29] Herein we describe further examples of such copolymers, particularly those that exhibit either pH- or thermoresponsive properties. Two commercially available monoamine-capped statistical copolymers of ethylene oxide (EO) and propylene oxide (PO), Jeffamine XTJ-506 and Jeffamine XTJ-507, were employed for the synthesis of the ATRP macroinitiator precursors, and all reactions were carried out under mild conditions. Moreover, our synthetic strategy was designed to avoid protecting group chemistry and to be reasonably atom efficient. The pH- and/or thermoresponsive micellization of these Y-shaped double-hydrophilic block copolymers in aqueous solutions were investigated using dynamic light scattering (DLS), surface tensiometry and ^{1}H NMR spectroscopy. Finally, various corresponding linear diblock copolymers were also synthesized as reference materials, and their micellization properties in aqueous solution were investigated for comparative purposes.

Experimental Section

Materials. Jeffamine XTJ-506 (JM1000-NH$_2$), a monoamine-capped statistical copolymer of ethylene oxide (EO) and propylene oxide (PO) [EO/PO molar ratio = 19/3] with M_n = 1000 g mol^{-1} and M_w/M_n = 1.10 (M_w = weight-average molecular weight; M_n = number-average molecular weight; M_w/M_n = molecular weight polydispersity index), and Jeffamine XTJ-507 (JM2005-NH$_2$), a monoamine-capped statistical copolymer of PO and EO [PO/EO molar ratio = 29/6] with M_n = 2200 g mol^{-1} and M_w/M_n = 1.08, were both donated by Huntsman Chemicals (UK). Poly(ethylene oxide) (PEO$_{23}$-OH) with an M_n of 1000 (DP$_n$ = 23) and a M_w/M_n of 1.10 and poly(propylene oxide) (PPO$_{33}$-OH) with an M_n of 1940 (DP$_n$ = 33) and a M_w/M_n of 1.06 were both donated by Cognis Performance Chemicals (Hythe, UK); these two precursors were each converted into the corresponding ATRP macroinitiators (PEO$_{23}$-Br and PPO$_{33}$-Br) by esterification with excess 2-bromoisobutyryl bromide (Aldrich, 98%) using previously reported protocols.[30] Glycerol monomethacrylate (GMA) was kindly donated by Röhm (Germany). 2-Hydroxyethyl methacrylate (HEMA) and 2-hydroxyethyl acrylate (HEA) were donated by Cognis Performance Chemicals (Hythe, UK). 2-(*N*-Morpholino)ethyl methacrylate (MEMA) was purchased from Polysciences. 2-Methacryloyloxyethyl phosphorylcholine (MPC) monomer (99.9% purity) was a gift from Biocompatibles (Farnham, Surrey, UK). 2-(Diethylamino)ethyl methacrylate (DEA, 99%), 2-(dimethylamino)ethyl methacrylate (DMA, 98%), 2,2′-bipyridine (bpy, ≥99%), copper(I) bromide (CuBr, 99.999%), 2-bromoisobutyryl bromide (98%), triethylamine (TEA, 99%), 1,3-propane sultone (98%), iodomethane (CH$_3$I, 99.5%), and phenothiazine (≥98%) were all purchased from Aldrich. All monomers were passed through silica columns prior to their use in either Michael addition reactions or polymerizations. Other chemicals were used without further purification.

Synthesis of the JM1000-Based Bifunctional ATRP Macroinitiator (JM1000-Br$_2$). JM1000-NH$_2$ (20.0 g, 0.02 mol), HEA (13.9 g, 0.12 mol, HEA/NH$_2$ molar ratio = 6.0), doubly distilled water (1.0 g), and phenothiazine (10.0 mg) were added to a 100 mL one-necked round-bottomed flask. The reaction solution was stirred at 20 °C for 5 days. ^{1}H NMR studies indicated that this Michael addition went to completion. The resulting bishydroxy-functionalized JM1000 was precipitated from cold diethyl ether at −10 °C and recrystallized from diethyl ether three times prior to drying under vacuum overnight (yield: 19.3 g, 78%). ^{1}H NMR (in CDCl$_3$): δ 4.14 (4H, COOCH_2CH$_2$OH), δ 3.73 (4H, COOCH$_2$CH_2OH), δ 3.67−3.17 (89H, OCH_2CH_2O and OCH_2CH(CH$_3$)O), δ 2.78 (5H, NCH_2), δ 2.43 (4H, CH_2COO), δ 1.12−0.86 (9H, OCH$_2$CH(CH_3)O).

The resulting bishydroxy-functionalized JM1000-(OH)$_2$ (10.0 g, 0.0074 mol) was added, along with triethylamine (2.99 g, 0.03 mol) and anhydrous THF (100 mL), to a dried 250 mL one-necked round-bottomed flask immersed in an ice bath. This solution was stirred for 30 min, and 2-bromoisobutyryl bromide (6.90 g, 0.03 mol) was then added dropwise to the flask via syringe over 1 h. The reaction mixture was stirred at 20 °C for a further 48 h. The resulting insoluble amine hydrobromide salt was removed by filtration, and most of the THF was removed by rotary evaporation prior to dissolution in water at pH 9 and repeated extraction with dichloromethane. This solution was dried using magnesium sulfate, and the solvent was removed under vacuum. The resulting JM1000-Br$_2$ macroinitiator was purified by recrystallization from cold diethyl ether followed by drying under vacuum (yield: 10.2 g, 82%). ^{1}H NMR (CDCl$_3$): δ 4.38−4.25 (8H, COOCH_2CH_2OCO), δ 3.81−3.18 (85H, OCH_2CH_2O and OCH_2CH(CH$_3$)O), δ 2.78 (5H, NCH_2), δ 2.43 (4H, CH_2COO), δ 1.91 (12H, C(CH_3)$_2$Br), δ 1.16−0.90 (9H, OCH$_2$CH(CH_3)O).

Synthesis of JM2005-Based Bifunctional ATRP Macroinitiator (JM2005-Br$_2$). JM2005-NH$_2$ (20.0 g, 0.01 mol), HEA (7.0 g, 0.06 mol), doubly distilled water (1.0 g), and phenothiazine (10.0 mg) were added to a 100 mL one-necked round-bottomed flask. The reaction solution was stirred at 50 °C for 4 days. ^{1}H NMR studies indicated that the Michael addition went to completion. Most of the unreacted HEA was removed under vacuum at 70 °C for 5 h, and the residual HEA was removed by passing the crude product through a silica column using dichloromethane as an eluent. The solvent was removed under vacuum to yield the bishydroxy-functionalized JM2005 (yield: 18.1 g, 82%). ^{1}H NMR (CDCl$_3$): δ 4.19 (4H, COOCH_2-CH$_2$OH), δ 3.77 (4H, COOCH$_2$CH_2OH), δ 3.67−3.16 (132H, OCH_2CH_2O and OCH_2CH(CH$_3$)O), δ 2.78 (5H, NCH_2), δ 2.47 (4H, CH_2COO), δ 1.34−0.71 (94H, OCH$_2$CH(CH_3)O).

The resulting bishydroxy-functionalized JM2005 (10.0 g, 0.0036 mol), triethylamine (1.45 g, 0.014 mol), and anhydrous THF (100 mL) were charged to a dried 250 mL one-necked round-bottomed flask immersed in an ice bath. This solution was stirred for 30 min, and 2-bromoisobutyryl bromide (3.22 g, 0.014 mol) was then added dropwise to the flask via syringe over 1 h. The reaction mixture was stirred at 20 °C for a further 48 h. The resulting insoluble hydrobromide amine salt was removed by filtration, and most of the THF was removed by rotary evaporation prior to dissolution in water at pH 9 and repeated extraction with dichloromethane. This organic solution was dried using magnesium sulfate and passed through a silica column. The solvent was removed under vacuum to yield the JM2005-Br$_2$ macroinitiator (yield: 8.8 g, 72%). ^{1}H NMR (CDCl$_3$): δ 4.33 (8H, COOCH_2CH_2OCO), δ 3.73−3.06 (128H, OCH_2CH_2O and OCH_2CH(CH$_3$)O), δ 2.78 (5H, NCH_2), δ 2.43 (4H, CH_2COO), δ 1.91 (12H, C(CH_3)$_2$Br), δ 1.34−0.71 (98H, OCH$_2$CH(CH_3)O).

ATRP Protocol for the Synthesis of JM1000-Based Y-Shaped Block Copolymers. A typical ATRP synthesis using the JM1000-Br_2 macroinitiator was as follows. JM1000-Br_2 (1.00 g, 0.74 mmol, 1.48 equiv) and DMA (2.32 g, 14.8 mmol, 14.8 equiv, target DP_n of 10 per PDMA branch) were dissolved in methanol (4 mL). After purging with nitrogen for 30 min, the Cu(I)Br catalyst (53.0 mg, 0.37 mmol, 0.37 equiv) and bpy ligand (115.0 mg, 0.74 mmol, 0.74 equiv) were added to this stirred solution under nitrogen. The reaction mixture immediately became dark brown and progressively more viscous, indicating the onset of polymerization. After 5 h, ^{1}H NMR analysis indicated that 98% of DMA had been polymerized. The reaction solution turned blue on exposure to air, indicating aerial oxidation of the Cu(I) catalyst. The resulting copolymer was diluted with methanol and passed through a silica column to remove the spent ATRP catalyst. The copolymer solution was dried under vacuum to remove the solvent. Yield: 3.01 g, 93%. Similar protocols were used for the polymerization of DEA, MEMA, HEMA, and GMA.

Synthesis of Acidic Y-Shaped Block Copolymers. Acidic Y-shaped copolymers were prepared by esterification of JM1000−$(HEMA_{10})_2$ and JM1000−$(GMA_{10})_2$ using a two molar excess of succinic anhydride (relative to the hydroxyl group of HEMA units) in anhydrous pyridine. A typical synthesis was as follows: In a 100 mL dried flask, JM1000−$(HEMA_{10})_2$ (3.00 g, 14.5 mmol HEMA units) and succinic anhydride (2.90 g, 29 mmol) were dissolved in 30 mL of anhydrous pyridine. The reaction solution was stirred at 20 °C for 24 h. The final mixture was precipitated three times into a 1:1 *n*-hexane/THF mixture before drying under vacuum. Yield: 3.65 g, 82%.

ATRP Protocol for the Synthesis of JM2005-Based Y-Shaped Block Copolymers. A typical ATRP synthesis using the JM2005-Br_2 macroinitiator was as follows. JM2005-Br_2 (1.00 g, 0.36 mmol, 0.72 equiv) and DMA (2.26 g, 14.4 mmol, 14.4 equiv, target DP of 20 per PDMA branch) were dissolved together in methanol (4 mL). After purging with nitrogen for 30 min, the Cu(I)Br catalyst (51.0 mg, 0.36 mmol, 0.36 equiv) and bpy ligand (112.0 mg, 0.72 mmol, 0.72 equiv) were added to this stirred solution under nitrogen. The reaction mixture immediately became dark brown and progressively more viscous, indicating the onset of polymerization. After 5.5 h, ^{1}H NMR analysis indicated that 97% of DMA had been polymerized. The reaction solution turned blue on exposure to air, indicating aerial oxidation of the Cu(I) catalyst. The resulting copolymer was diluted with methanol and passed through a silica column to remove the spent ATRP catalyst. The copolymer solution was dried under vacuum to remove the solvent. Yield: 2.90 g, 91%. Similar ATRP protocols were used for the polymerization of MPC and GMA.

Synthesis of Y-Shaped Cationic and Zwitterionic Copolymers Based on JM2005. A Y-shaped cationic JM2005−$(MeDMA_{20})_2$ block copolymer [MeDMA: methyl iodide-quaternized 2-(dimethylamino)ethyl methacrylate] was prepared as follows: In a 100 mL dried flask, JM2005−$(DMA_{20})_2$ (3.00 g, 13 mmol DMA units) was dissolved in 30 mL of THF, and then CH_3I (3.77 g, 26 mmol) was added into the reaction solution and stirred at 20 °C for 24 h. The solvent and residual CH_3I were removed under vacuum. ^{1}H NMR studies indicated that this quaternization reaction was essentially complete, with little or no evidence for any signals due to unreacted DMA residues. Yield: 4.72 g, 97%.

A Y-shaped zwitterionic JM2005−$(SBMA_{20})_2$ block copolymer (SBMA stands for "sulfobetaine methacrylate") was prepared as follows: In a 100 mL dried flask, JM2005−$(DMA_{20})_2$ (3.00 g, 13 mmol DMA units) was dissolved in 30 mL of THF, and then 1,3-propane sultone (3.17 g, 26 mmol) was added into the reaction solution and stirred at 20 °C for 24 h. The solvent and residual 1,3-propane sultone were removed by centrifugation and washed three times using THF (30 mL). ^{1}H NMR studies indicated that this quaternization reaction was essentially complete, with little or no evidence for any signals due to unreacted DMA residues. Yield: 4.17 g, 86%.

Synthesis of PEO_{23}−DEA_{10} and PEO_{23}−DEA_{20} Linear Diblock Copolymers. These two diblock copolymers were obtained by the ATRP of DEA using the PEO_{23}-Br macroinitiator in 50% methanol at 20 °C using [DEA]:[PEO_{23}-Br]:[CuBr]:[bpy] relative molar ratios of 10:1:0.3:0.6 for the PEO_{23}−DEA_{10} diblock and 20:1:0.6:1.2 for the PEO_{23}−DEA_{20} diblock. Polymerizations were terminated after 98% conversion, as judged by ^{1}H NMR studies. The reaction solution turned blue on exposure to air, indicating aerial oxidation of the Cu(I) catalyst. The resulting copolymer was diluted with methanol and passed through a silica column to remove the spent ATRP catalyst. The copolymer solution was dried under vacuum to remove solvent. THF GPC analyses using poly(methyl methacrylate) standards indicated that narrow molecular weight distributions were obtained (PEO_{23}−DEA_{10}: $M_{n,cal}$ = 3100, $M_{n,NMR}$ = 3650, $M_{n,GPC}$ = 6200, M_w/M_n = 1.21; PEO_{23}−DEA_{20}: $M_{n,cal}$ = 4900, $M_{n,NMR}$ = 5600, $M_{n,GPC}$ = 8400, M_w/M_n = 1.23), and ^{1}H NMR studies ($CDCl_3$) enabled the mean degrees of polymerization of the DEA blocks to be calculated by end group analysis using the PEO block as an end group.

Similar ATRP protocols were used for the synthesis of PPO_{33}−GMA_{20} and PPO_{33}−GMA_{40} linear diblock copolymers, with [GMA]:[PPO_{33}-Br]:[CuBr]:[bpy] relative molar ratios of 20:1:0.5:1 being used for the PPO_{33}−GMA_{20} diblock and 40:1:1:2 for the PPO_{33}-*b*-GMA_{40} diblock. The following ^{1}H NMR and DMF GPC results were obtained: PPO_{33}−GMA_{20}: $M_{n,cal}$ = 5300, $M_{n,NMR}$ = 5800, $M_{n,GPC}$ = 11 600, M_w/M_n = 1.25; PPO_{33}−GMA_{40}: $M_{n,cal}$ = 8500, $M_{n,NMR}$ = 9300, $M_{n,GPC}$ = 16 800, M_w/M_n = 1.22.

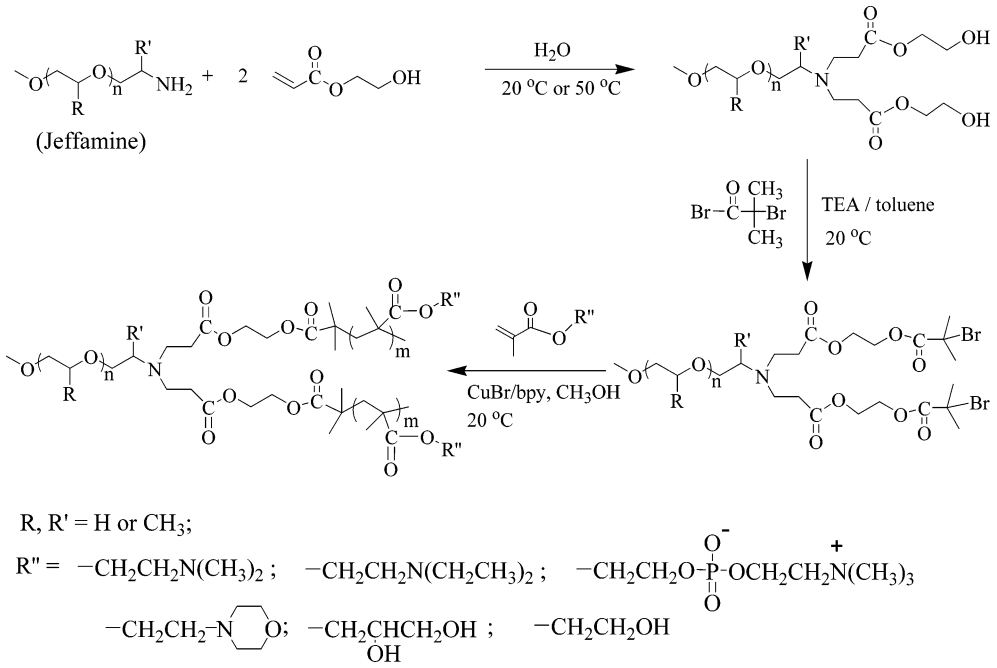
Characterization. ^{1}H NMR spectra were recorded using a Bruker Avance DPA 300 spectrometer operating at 300 MHz using $CDCl_3$ for tertiary amine methacrylate-based block copolymers and d_5-pyridine for the hydroxylated and acidic block copolymers. For all Y-shaped copolymers and their linear diblock counterparts, M_n values were calculated using the poly(alkylene oxide)-based macroinitiator as an "end group", which was based on δ 3.7−3.2 (89H, OCH_2CH_2O and $OCH_2CH(CH_3)O$) for JM1000-based copolymers and δ 3.8−3.0 (128H, OCH_2CH_2O and $OCH_2CH(CH_3)O$) for JM2005-based copolymers. In these calculations it was assumed that the macroinitiator efficiency was 100%, that chain transfer was negligible, and that every copolymer chain contained a macroinitiator end group.

MALDI−TOF mass spectrometry was performed on a Bruker Daltonics OmniFLEX spectrometer with a nitrogen laser operating at a wavelength of 337 nm at a pressure of 10^{-5} Torr. Samples were prepared from THF solution by mixing 2.0 mg/mL copolymer solution and 10.0 mg/mL 2,5-dihydroxybenzoic acid (DHB, Aldrich, 98%, used as matrix) in a 2:1 volume ratio. The mixture was introduced onto the surface of a 49 point (7 × 7) array (Bruker Daltonics Ltd.) using a glass pipet and allowed to dry in the open air. No salt was added to any of the samples. The acceleration voltage was 19 kV, the laser delay time was 1 s, and the laser scan rate was 0.5 s. C_{60} was used as a calibration standard, and M_n values were determined in the linear mode.

The molecular weight and molecular weight distribution of the two Jeffamine precursors and their corresponding macroinitiators and the three tertiary amine methacrylate-based Y-shaped block copolymers were determined using a GPC setup consisting of a Perkin-Elmer LC pump and an Agilent 1100 series refractive index detector and either a PLgel 3 μm, 300 × 7.5 mm mixed "E" or a 5 μm, 300 × 7.5 mm mixed "D" column (Polymer Labs). The GPC eluent was HPLC-grade THF stabilized with BHT and 2.0 vol % TEA, at 20 °C and a flow rate of 1.0 mL min^{-1}. The molecular weights and polydispersities of the HEMA-based and GMA-based Y-shaped block copolymers were assessed using a DMF GPC setup comprising a Polymer Laboratories PLgel 5 μm mixed "B" column and a refractive index detector. The GPC eluent was HPLC-grade DMF stabilized with 0.01 M LiBr. A flow rate of 1.0 mL/min was used, and the column temperature was set at 70 °C. A series of near-monodisperse poly(methyl methacrylate) calibration standards (Polymer Labs) were used for both types of GPC measurements.

Dynamic light scattering (DLS) studies were performed using a Brookhaven Instrument Corp. BI-200SM goniometer equipped with a BI-9000AT digital correlator and a solid-state

Scheme 1. Synthetic Route for the Poly(alkylene oxide)-Based Y-Shaped Block Copolymers from the Commercial Jeffamine Precursors Using Atom Transfer Radical Polymerization (ATRP)



laser (125 mW, λ = 532 nm). Unless stated otherwise, all measurements were performed at a fixed scattering angle of 90°. The intensity-average hydrodynamic diameter, $\langle D_h \rangle$, and polydispersity index, $\langle \mu_2/\Gamma^2 \rangle$, of the micelles were evaluated by cumulants analysis of the experimental correlation function. All copolymers readily dissolved in doubly distilled water under stirring at room temperature. Either 0.1 M NaOH or 0.1 M HCl solution was used for adjusting the solution pH of the pH-responsive copolymers. After adjusting to the desired copolymer concentration and/or solution pH, all copolymer solutions were stirred for a further 30 min to ensure that the micellar self-assembly had reached its equilibrium structure. The solutions were filtered through a Millipore Teflon filter (0.20 μm pore size) prior to measurements.

Surface tensiometry measurements were carried out using a Kruss K10ST surface tensiometer using the platinum ring method at 20 °C. The platinum ring was flamed using a Bunsen burner prior to measurement to ensure complete wetting by the aqueous solution. After adjusting the solution pH, the solutions were stirred for at least 30 min at room temperature prior to measurements. Each copolymer solution was measured in triplicate, with typical reproducibilities being within 0.5 mN m^{-1}.

Results and Discussion

The general synthetic route used for the preparation of the poly(alkylene oxide)-based, stimulus-responsive Y-shaped block copolymers is presented in Scheme 1. Advantages of this approach include the mild conditions used in each step, the use of cheap, readily available starting materials (the Jeffamine precursors), and the avoidance of protecting group chemistry, which is inherently atom inefficient.

Synthesis of Poly(alkylene oxide)-Based ATRP Macroinitiators. The addition of a small quantity of water (5.0 wt % relative to JM1000) catalyzed the Michael addition of the HEA to the JM1000-NH_2 Jeffamine precursor.[31] The desired bifunctional ATRP macroinitiator (JM1000-Br_2) was obtained by esterification of this bishydroxy-functionalized JM1000-$(OH)_2$ with excess 2-bromoisobutyryl bromide. Integral analysis of ^{1}H NMR indicates that complete esterification was achieved (see Figure 1).

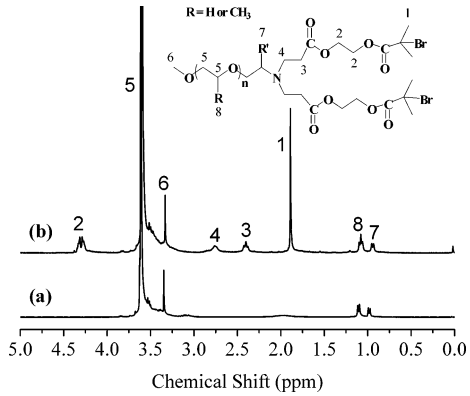


Figure 1. ^{1}H NMR spectra of (a) the JM1000-NH_2 precursor and (b) the corresponding JM1000-Br_2 ATRP macroinitiator.

A very high degree of esterification for this macroinitiator was also confirmed by MALDI−TOF studies. The calculated mass increase for the JM1000-Br_2 macroinitiator compared to that for the JM1000-NH_2 precursor was 532 g mol^{-1}, which is close to the actual mass increase of 534 g mol^{-1} observed experimentally (see Figure 2). THF GPC analyses (vs PMMA standards) of this JM1000-Br_2 macroinitiator indicated an M_n of 2100 and an M_w/M_n of 1.10 (see Figure 3).

The same synthetic route was also employed for the second Jeffamine precursor, JM2005-NH_2. This is also a monoamine-capped statistical copolymer, but it contains 29 PO and 6 EO units, so it is PO-rich rather than EO-rich. Its aqueous solution properties are therefore very similar to those of homopoly(propylene oxide), which exhibits thermoresponsive behavior.

Michael addition to the JM2005-NH_2 precursor was monitored by ^{1}H NMR studies by comparing the integrals of the reacted HEA residues at δ 4.07 [COOCH_2] to those due to the unreacted HEA at δ 4.18 [COOCH_2] (see Figure S1b, Supporting Information). To ensure that accurate conversions were obtained, the integral of the reacted HEA residual peak at δ 2.37 [CH_2COO] was also compared to the integrated peak due to the

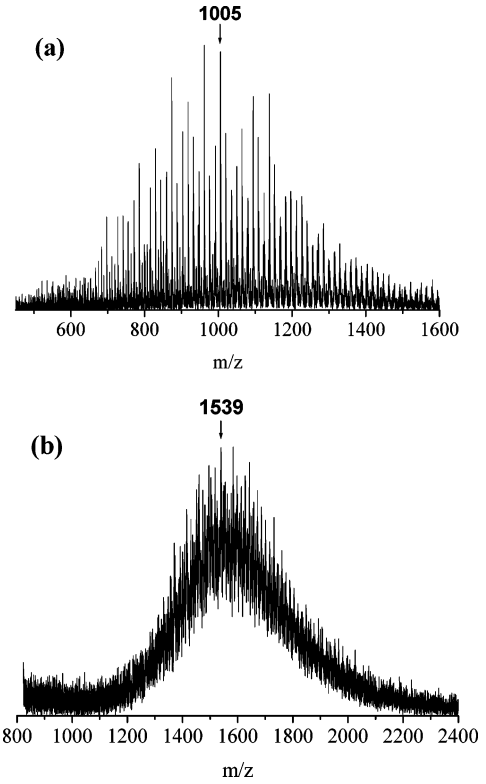


Figure 2. MALDI−TOF mass spectra of (a) the JM1000-NH_2 precursor and (b) the corresponding JM1000-Br_2 ATRP macroinitiator.

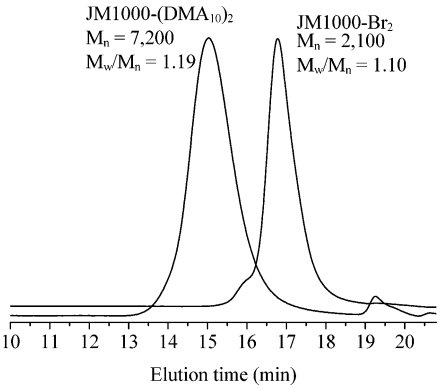


Figure 3. THF GPC traces obtained for the JM1000-Br_2 macroinitiator and the corresponding JM1000−$(DMA_{10})_2$ Y-shaped block copolymer.

JM2005 residues at δ 1.05 [$CH_2(CH_3)CHO$] (see Figure S1b). These two methods gave similar conversions within experimental error.

It is noteworthy that the rate of Michael addition of HEA to the JM2005-NH_2 precursor was significantly slower than for the JM1000-NH_2 precursor. Initially, the Michael addition reaction was conducted under the same conditions as that of JM1000-NH_2 mentioned above. However, ^{1}H NMR studies indicated that only 78% conversion was achieved after 15 days at 20 °C. To achieve higher conversions, the reaction mixture was stirred in an oil bath at 50 °C. After 4 days, ^{1}H NMR studies indicated that essentially complete conversion was achieved (see Figure S1b). The unreacted excess HEA was removed by a two-step purification: first under vacuum at 70 °C for 5 h (see Figure S1c, Supporting Information) and then passing the copolymer solution through a silica column using dichloromethane as an eluent. ^{1}H NMR studies confirmed that purified bishydroxy-functionalized JM2005-$(OH)_2$ was obtained (see Figure S1d, Supporting Information).

^{1}H NMR studies indicated complete esterification of the bishydroxy-functionalized JM2005-$(OH)_2$ using excess 2-bromoisobutyryl bromide to produce the target bifunctional ATRP macroinitiator, JM2005-Br_2 (see Figure S1e, Supporting Information). Very high degrees of functionalization were also indicated by MALDI−TOF studies (see Figure S2, Supporting Information): the experimentally observed mass increase for JM2005-Br_2 macroinitiator compared to that for the JM2005-NH_2 precursor was 535 g mol^{-1}, which is close to the calculated mass increase of 532 g mol^{-1}.

Table 1. Summary of the Synthesis Parameters and Molecular Weight Data Obtained for Copolymers Synthesized by Atom Transfer Radical Polymerization (ATRP) Using the JM1000-Br_2 Macroinitiator at a [Monomer]:[JM1000-Br_2]:[CuBr]:[Bpy] Relative Molar Ratio of 20:1:0.5:1 in 50 % Methanol at 20 °C

target copolymer	reaction time (h)	conv[a] (%)	$M_{n,NMR}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
JM1000−$(DEA_{10})_2$	5.0	98	5200	8400[b]	1.23
JM1000−$(DMA_{10})_2$	5.0	98	4650	7200[b]	1.19
JM1000−$(MEMA_{10})_2$	5.0	96	5000	7400[b]	1.16
JM1000−$(HEMA_{10})_2$	4.5	99	4650	13100[c]	1.18
JM1000−$(GMA_{10})_2$	4.0	100	5900	12800[c]	1.20

[a] Determined from ^{1}H NMR studies. [b] Determined using THF GPC (vs poly(methyl methacrylate) standards). [c] Determined using DMF GPC (vs poly(methyl methacrylate) standards).

Synthesis of Y-Shaped Block Copolymers Using the JM1000-Based ATRP Macroinitiator. A series of hydrophilic methacrylic monomers were polymerized via ATRP using the JM1000-Br_2 macroinitiator to obtain a range of Y-shaped block copolymers, including pH-responsive examples (see Table 1). Since the JM1000 block is relatively short, it was considered important to restrict the degrees of polymerization (DP_n) targeted during ATRP in order to maintain a reasonable hydrophilic−hydrophobic balance for these new polymeric surfactants. However, high catalyst concentrations can lead to high radical concentrations being generated in the early stages of the polymerization, which can lead in turn to unwanted termination and reduced control. For example, for the ATRP of DMA in 50% methanol at a [DMA]:[JM1000-Br_2]:[CuBr]:[bpy] relative molar ratio of 20:1:1:2 (i.e., a mean DP_n of 10 for each DMA block), GPC analysis at 90% conversion (achieved within 1 h at 20 °C) indicated an M_n of 4200 and an M_w/M_n of 1.37, with a pronounced low molecular weight tail. This suggested that significant radical coupling occurred in the early stages of this polymerization. In contrast, at a [DMA]:[JM1000-Br_2]:[CuBr]:[bpy] relative molar ratio of 20:1:0.5:1 under the same conditions, the DMA conversion reached 98% after 5 h, and a significantly lower polydispersity of 1.19 was obtained (see Figure 3). The relatively high M_n value of 7200 obtained by THF GPC analysis is due in part to the calibration error incurred using poly(methyl methacrylate) standards. This interpretation is supported by the fact that the M_n value calculated from end-group analysis using ^{1}H NMR was in reasonable agreement (within experimental error) with the M_n expected on the basis of the target degree of polymerization. Thus, ATRP can be reasonably well controlled even at relatively low target degrees of polymerization, provided that lower catalyst concentrations are employed.

Acidic Y-shaped copolymers were readily obtained by esterification of the JM1000-$(HEMA_{10})_2$ and JM1000-

Scheme 2. Synthesis of Acidic Y-Shaped JM1000−($SEMA_{10}$)$_2$ Block Copolymer (SEMA: 2-Succinyloxyethyl Methacrylate) via Esterification of Hydroxyl Groups of 2-Hydroxyethyl Methacrylate (HEMA) Residues of JM1000−($HEMA_{10}$)$_2$ Using Succinic Anhydride in Anhydrous Pyridine at 20 °C

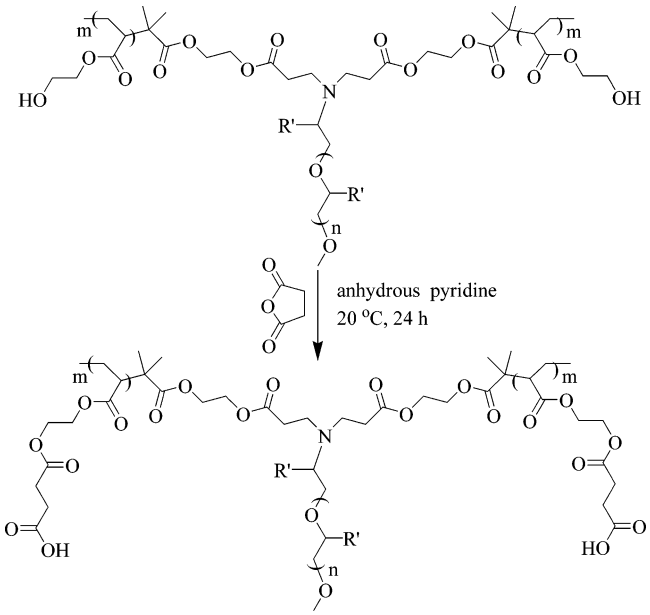


Table 2. Summary of the Synthesis Parameters and Molecular Weight Data Obtained for Copolymers Synthesized by Atom Transfer Radical Polymerization (ATRP) Using the JM2005-Br_2 Macroinitiator at a [Monomer]:[JM2005-Br_2]:[CuBr]:[Bpy] Relative Molar Ratio of 40:1:1:2 in 50 wt % Methanol at 20 °C

target copolymer	reaction time (h)	conv[a] (%)	$M_{n,NMR}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
JM2005−(GMA_{20})$_2$	4.0	100	8900	17100[b]	1.28
JM2005−(DMA_{20})$_2$	5.5	97	9400	10700[c]	1.26
JM2005−(MPC_{20})$_2$	3.0	100	15300		
JM2005−($SBMA_{20}$)$_2$[d]			15700		
JM2005−($MeDMA_{20}$)$_2$[d]			16300		

[a] Determined from ^{1}H NMR studies. [b] Determined using DMF GPC (vs poly(methyl methacrylate) standards). [c] Determined using THF GPC (vs poly(methyl methacrylate) standards). [d] Derived from JM2005−(DMA_{20})$_2$ after more than 95% conversion.

(GMA_{10})$_2$ Y-shaped block copolymers using succinic anhydride, as shown in Scheme 2.[32] From the ^{1}H NMR spectra (see Figure S3, Supporting Information), the signal assigned to the HEMA residues at δ 3.9 disappeared, and a new signal assigned to the 2-succinyloxyethyl methacrylate (SEMA) residues at δ 2.8 was observed, indicating that very high degrees of esterification were achieved (>95%).[33]

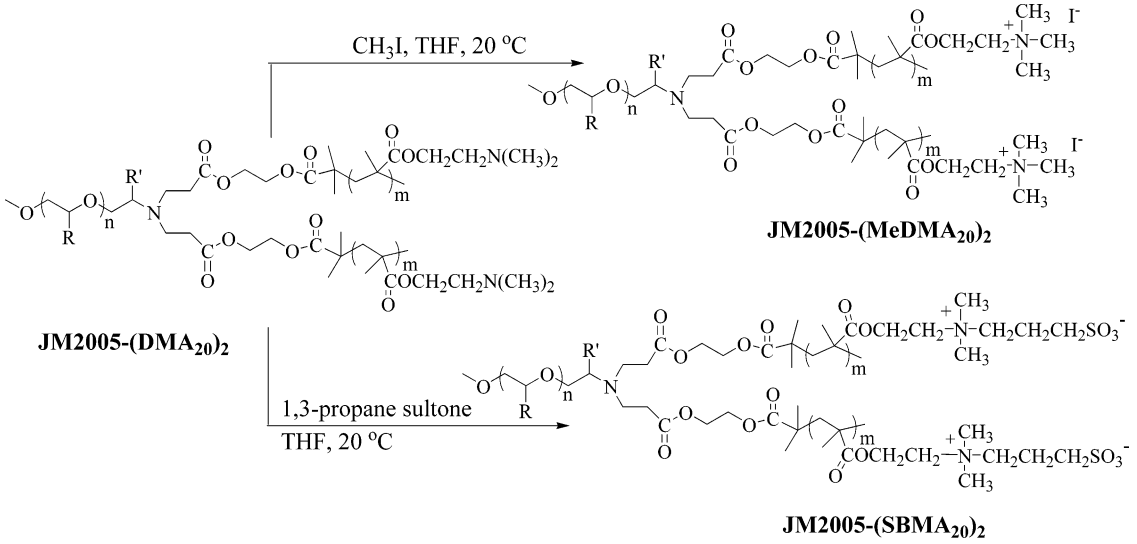
Synthesis of the Thermoresponsive Y-Shaped Block Copolymers Using the JM2005-Based ATRP Macroinitiator. The various thermoresponsive Y-shaped copolymers synthesized via ATRP of a series of hydrophilic methacrylic monomers are summarized in Table 2. The molecular weights of JM2005-(GMA_{20})$_2$, JM1000-($HEMA_{10}$)$_2$, and JM1000-(GMA_{10})$_2$ obtained by DMF GPC are much larger than those calculated by ^{1}H NMR studies. This is attributed to the calibration error.[34−36] Cationic Y-shaped JM2005-($MeDMA_{20}$)$_2$ block copolymers were readily prepared by quaternization of the tertiary amine groups of a JM2005-(DMA_{20})$_2$ block copolymer using CH_3I in THF (see Scheme 3). ^{1}H NMR studies indicated that a very high degree of quaternization (almost 100%) was achieved after 24 h at 20 °C. Moreover, a Y-shaped thermoresponsive schizophrenic JM2005-($SBMA_{20}$)$_2$ block copolymer was similarly prepared by quaternization of a JM2005-(DMA_{20})$_2$ block copolymer using 1,3-propane sultone in THF at 20 °C (see Scheme 3). Again, ^{1}H NMR studies indicated complete consumption of the tertiary amine groups within 24 h.[37]

pH-Responsive Micellization of a Y-Shaped JM1000-(DEA_{10})$_2$ Block Copolymer. It is known that DEA homopolymer is a weak polybase with a pK_a of approximately 7.3.[38] DEA homopolymer dissolves in acidic aqueous solution as a cationic polyelectrolyte due to protonation of its tertiary amine groups, but it becomes insoluble above pH 7−8. However, the EO-dominated JM1000 blocks remain permanently hydrophilic, regardless of the pH and solution temperature. Thus, it was expected that micellization of the Y-shaped JM1000-(DEA_{10})$_2$ copolymer would occur in basic aqueous solution. The ^{1}H NMR spectra of the JM1000-(DEA_{10})$_2$ copolymer recorded in D_2O at pH 2 and 10 are presented in Figure S4 of the Supporting Information. At pH 2, all the expected NMR signals for the JM1000 and the protonated DEA residues are observed, indicating that both blocks are molecularly dissolved under these conditions. However, at pH 10 only the signal due to the JM1000 block at δ 3.53 can be detected, indicating that the deprotonated DEA blocks are no longer solvated in basic aqueous solution.

The micellization behavior of a 2.0 mg/mL aqueous solution of the Y-shaped JM1000-(DEA_{10})$_2$ copolymer was investigated using DLS studies (see Figure 4). In acidic aqueous solution the light scattering intensity is very low, indicating that no colloidal aggregates were formed. On increasing the solution pH, the light scattering intensity increased dramatically at around pH 7.3, which corresponds to the pK_a of the DEA residues.[19] This indicates that micellar self-assembly occurs. Indeed, near-monodisperse micelles with a D_h of 45 nm and a μ_2/Γ^2 of 0.05−0.08 were detected from pH 7.4 to pH 11.3. In view of the above ^{1}H NMR studies the nonsolvated DEA blocks most likely form the micelle cores. The copolymer surface activity also depends on the solution pH (see Figure 5). Above pH 7, the DEA block is relatively hydrophobic and hence strongly adsorbed at the air−water interface; thus, high surface activity (low surface tension) is observed. Below pH 7, the DEA residues become protonated and copolymer desorption from the interface occurred, resulting in much lower surface activity (higher surface tension).

To understand the effect of copolymer architecture on the micellization behavior, the aqueous solution properties of the linear PEO_{23}−DEA_{10} and PEO_{23}−DEA_{20} diblock copolymers were also studied for direct comparison with the Y-shaped JM1000-*b*-(DEA_{10})$_2$ copolymer. Similar pH-dependent micellization and surface activity behavior were observed for the linear PEO_{23}−DEA_{10} and PEO_{23}−DEA_{20} diblock copolymers, as expected.[39] However, in basic aqueous solution, the PEO_{23}−DEA_{20} copolymer had a larger D_h of 53 nm and the PEO_{23}−DEA_{10} copolymer had a smaller D_h of 33 nm. Thus, the nonlinear JM1000−(DEA_{10})$_2$ copolymer forms micelles of intermediate diameter (45 nm). This is presumably due to the branched nature of the Y-shaped copolymer, which hinders the aggregation and leads to lower micelle aggregation numbers than its linear counterparts. This interpretation was supported by surface tensiometry studies. The surface activity of the

Scheme 3. Synthesis of Y-Shaped JM2005−$(MeDMA_{20})_2$ [MeDMA: Methyl Iodide-Quaternized 2-(Dimethylamino)ethyl Methacrylate] and JM2005−$(SBMA_{20})_2$ Block Copolymers [SBMA: Sulfobetaine Methacrylate] via Quaternization of the Tertiary Amine Groups of JM2005−$(DMA_{20})_2$ Using Methyl Iodide and 1,3-Propane Sultone, Respectively



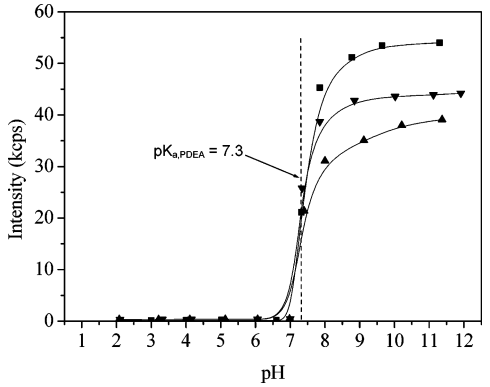


Figure 4. Variation of light scattering intensity with solution pH for 2.0 mg/mL aqueous solutions of the JM1000−$(DEA_{10})_2$ Y-shaped copolymer (■) and the PEO_{23}−DEA_{10} (▲) and PEO_{23}−DEA_{20} (▼) linear diblock copolymers.

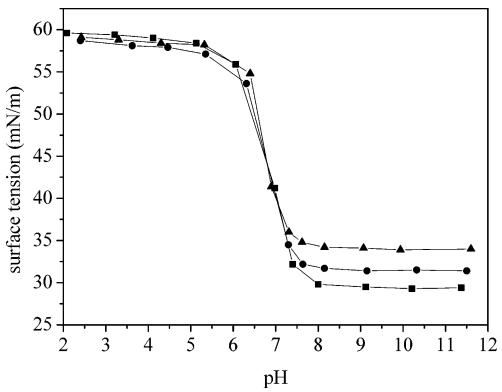


Figure 5. Variation of surface tension with solution pH for 2.0 mg/mL aqueous solutions of the Y-shaped JM1000−$(DEA_{10})_2$ block copolymer (▲) and the PEO_{23}−DEA_{10} (■) and PEO_{23}−DEA_{20} (●) linear diblock copolymers at 20 °C.

Y-shaped JM1000−$(DEA_{10})_2$ block copolymer in basic aqueous solution is lower than either the PEO_{23}−DEA_{10} or the PEO_{23}−DEA_{20} linear diblock copolymers under the same conditions (see Figure 5). Again, this difference is most likely due to the less efficient interfacial adsorption of the Y-shaped block copolymer due to its branched nature.

The self-assembly behavior of the carboxylic acid-based Y-shaped JM1000−$(SEMA_{10})_2$ block copolymer was complementary to that of the JM1000−$(DEA_{10})_2$ copolymer: very low light scattering intensity of a 5.0 g/L aqueous solution of Y-shaped JM1000−$(SEMA_{10})_2$ block copolymer indicated that this Y-shaped copolymer was molecularly dissolved at or above pH 7. On lowering the solution pH to approximately 5, the light scattering intensity increased significantly. Relatively large, polydisperse aggregates ($\langle D_h \rangle$ = 120 nm and μ_2/Γ^2 = 0.36−0.42) were observed between pH 4.3 and pH 1.8, indicating that the neutral hydrophobic SEMA blocks formed ill-defined aggregates or compound micelles at low pH, rather than regular "core−shell" micelles.[3b]

Thermoresponsive Micellization of the Y-Shaped JM2005−$(GMA_{20})_2$ Block Copolymer. The JM2005-based Y-shaped block copolymer exhibited thermoresponsive micellization due to the inverse temperature solubility behavior of the PO-rich JM2005 block. Like poly(propylene oxide), this JM2005 block is water-soluble at low temperature but precipitates from solution at higher temperature, whereas the GMA, MPC, and the MeDMA blocks are all permanently hydrophilic regardless of the solution temperature. Thus these Y-shaped block copolymers were expected to dissolve molecularly in water below 20 °C but form micelles at higher temperatures. The thermoresponsive micellization of a 5.0 g/L aqueous solution of the Y-shaped JM2005−$(GMA_{20})_2$ block copolymer was investigated by DLS studies. For comparative purposes, the thermoresponsive micellization behavior of 5.0 g/L aqueous solutions of the linear PPO_{33}−GMA_{20} and PPO_{33}−GMA_{40} diblock copolymers were also investigated. As shown in Figure 6, the critical micellization temperature (cmt) of the Y-shaped JM2005−$(GMA_{20})_2$ block copolymer is 42 °C, which is significantly higher than the cmt values of 28 and 35 °C observed for the linear PPO_{33}−GMA_{20} and PPO_{33}−GMA_{40} diblock copolymers, respectively. According to DLS studies, these Y-shaped JM2005−$(GMA_{20})_2$ copolymer micelles had a $\langle D_h \rangle$ = 18 nm and a μ_2/Γ^2 = 0.06 above 42 °C, which are smaller than those of the micelles obtained with either the PPO_{33}−GMA_{20} ($\langle D_h \rangle$ = 21 nm and μ_2/Γ^2 = 0.04 above

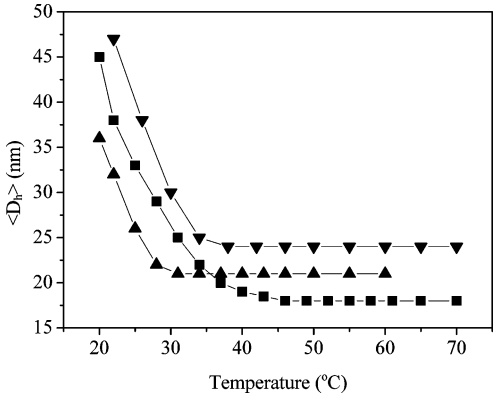


Figure 6. Variation of hydrodynamic diameter (D_h) and light scattering intensity with solution temperature for 5.0 mg/mL aqueous solutions of the Y-shaped JM2005−$(GMA_{20})_2$ block copolymer (■) and the PPO_{33}−GMA_{20} (▲) and PPO_{33}−GMA_{40} (▼) linear diblock copolymers.

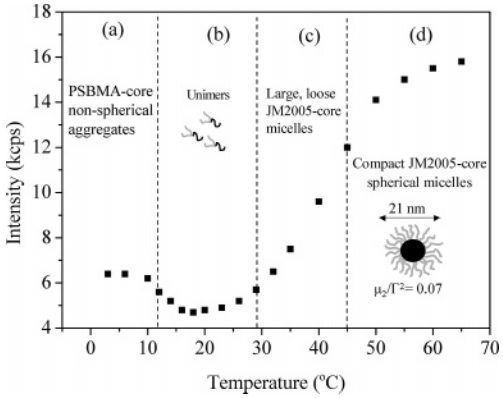


Figure 7. Variation of light scattering intensity with solution temperature for a 10.0 mg/mL aqueous solution of the JM2005−$(SBMA_{20})_2$ Y-shaped block copolymer.

28 °C) or PPO_{33}−GMA_{40} ($\langle D_h \rangle$ = 24 nm and $\mu_2/\Gamma^2 = 0.06$ above 35 °C) linear diblock copolymers.

Similar phenomena were also observed for the micellization of amphiphilic graft copolymers comprising hydrophobic backbones and hydrophilic side chains in aqueous solution:[40] the hydrophobic backbones collapsed to form the micelle cores, and the hydrophilic side chains formed the micelle coronas. On increasing the graft density, repulsion between the side chains strongly hindered micelle formation. As a result, micelles with lower aggregation numbers were formed in aqueous solution. Thus, the aggregation number and $\langle D_h \rangle$ of micelles formed by graft copolymers are usually lower than those of micelles formed by linear diblock copolymers. Y-shaped JM2005−$(GMA_{20})_2$ block copolymers can be regarded as having architectures that are intermediate between linear diblock copolymers and graft copolymers. Thus the branched nature of the coronal PGMA chains in the Y-shaped copolymer presumably leads to less efficient micellar self-assembly, a higher cmt, and a lower micelle aggregation number; this interpretation is consistent with the relatively weak scattering intensity obtained for these copolymer micelles.

Schizophrenic Thermoresponsive Micellization of the Y-Shaped JM2005−$(SBMA_{20})_2$ Block Copolymer. It is well-known that PSBMA homopolymer is thermoresponsive in aqueous solution.[41−44] Provided that the background electrolyte concentration is sufficiently low, PSBMA is water-insoluble below 20 °C due to the attractive interchain and intrachain electrostatic interactions between the anionic and cationic charges on the pendent sulfobetaine groups. Above approximately 20 °C, PSBMA becomes water-soluble.[41−44] Though often exhibited by hydrophobic polymers in organic solvents (e.g., the classical polystyrene/cyclohexane system), such UCST behavior is rather unusual for water-soluble polymers. As discussed above, the Y-shaped JM2005−$(GMA_{20})_2$ block copolymer exhibits a cmt at around 40 °C due to the inverse temperature solubility (or LCST) behavior of the PO-rich block. Thus, so-called "schizophrenic" micellization behavior was anticipated for the Y-shaped JM2005−$(SBMA_{20})_2$ block copolymer.[26] At sufficiently low temperature the desolvated PSBMA blocks should collapse to form micelle cores, with the hydrophilic PO-rich JM2005 blocks forming the micelle coronas. At intermediate temperatures (in this case, 12−30 °C) both the JM2005 and the PSBMA blocks should become hydrophilic, leading to molecular dissolution of the copolymer. Above the cloud point of the JM2005 block, inverted micelles with JM2005-based cores and SBMA-based coronas blocks should be produced.

Variable temperature DLS studies of the micellization behavior of a 10.0 g/L aqueous solution of the Y-shaped JM2005−$(SBMA_{20})_2$ block copolymer confirm the above expectations and are shown in Figure 7. Below 12 °C, the PSBMA blocks collapsed to form large PSBMA-core micelles, with a $\langle D_h \rangle$ of around 85 nm and a relatively high μ_2/Γ^2 of 0.38 (see Figure 7a), with relatively strong scattering intensities being observed. On increasing the solution temperature (see Figure 7b), the light scattering intensity decreased but remained higher than that obtained for the copolymer in a good solvent, suggesting that the copolymer was molecularly dissolved in a marginal solvent. On further increasing the solution temperature to around 30 °C (see Figure 7c), the light scattering intensity increased significantly, indicating that the JM2005 blocks collapsed to form large, loose JM2005-core micelles; the size of these micelles decreased with increasing solution temperature. Above 45 °C (the cmt for the inverted micelles), near-monodisperse JM2005-core micelles of almost constant size were formed ($\langle D_h \rangle$ = 21 nm and μ_2/Γ^2 = 0.07). The cmt observed for these inverted micelles is only slightly higher than that of JM2005−$(GMA_{20})_2$ copolymer micelles (cmt of 42 °C). Very similar observations were recently reported by Weaver et al.[26] for a linear SBMA−(2-*N*-(morpholino)ethyl methacrylate) diblock copolymer. Unpublished neutron scattering data obtained in collaboration with Gast and Stancik suggest that the near-monodisperse micelles observed above 50 °C by Weaver et al. are indeed spherical, as expected, but that the polydisperse SBMA-core micelles formed below 20 °C are actually wormlike, rather than spherical. To investigate this possibility in the present work, variable-angle DLS studies were undertaken on the two types of micelles formed by the Y-shaped JM2005−$(SBMA_{20})_2$ copolymer. If near-monodisperse spherical micelles are formed, little or no angular dependence was expected, whereas a strong angular dependence is normally characteristic of anisotropic (e.g., wormlike) particles. The $\langle D_h \rangle$ values for the JM2005-core micelles were almost constant at 50 °C (ranging from 20 to 22 nm for scattering angles of 30−120°). In contrast, the $\langle D_h \rangle$ values for the PSBMA-core micelles formed at 3 °C ranged from approximately 170 nm at 30° to 59 nm at 120°. This is a significant variation that was observed

in three separate experiments, and it suggests that these polydisperse micelles have nonspherical morphologies. Clearly, further work will be required to determine whether these micelles are actually wormlike, but this is beyond the scope of the present study. Finally, it is noteworthy that this JM2005−$(SBMA_{20})_2$ block copolymer is only the third report of a "schizophrenic" thermoresponsive copolymer; moreover, it is the first *nonlinear* example.

Conclusions

The commercial monoamine-capped poly(alkylene oxides), Jeffamine XTJ-506 and Jeffamine XTJ-507, were used to synthesize two new bifunctional ATRP macroinitiators via Michael addition of 2 equivalents of 2-hydroxyethyl acrylate, followed by esterification using excess 2-bromoisobutyryl bromide. The chemical structures of these macroinitiators were confirmed by both ^{1}H NMR and MALDI−TOF studies.

A wide range of new stimulus-responsive Y-shaped block copolymers were prepared via ATRP of various hydrophilic methacrylates using these two bifunctional macroinitiators under mild conditions. This new synthetic route is a significant improvement on literature syntheses of Y-shaped copolymers, since it avoids protecting group chemistry and also allows access to stimulus-responsive copolymers. Polymerization of tertiary amine- or hydroxy-functional methacrylates is both straightforward and high-yielding. Acidic Y-shaped copolymers can be easily obtained by reacting the hydroxy-functional copolymers with succinic anhydride under mild conditions. Moreover, quaternization of 2-(dimethylamino)ethyl methacrylate-based Y-shaped copolymers allows access to nonlinear cationic or sulfobetaine-based copolymers.

The nonlinear architecture of selected stimulus-responsive Y-shaped block copolymers resulted in the formation of micelles that differed from those formed by the corresponding linear diblock copolymers. Moreover, DLS studies confirmed that one of these Y-shaped block copolymers [JM2005−$(SBMA_{20})_2$] exhibited "schizophrenic" thermoresponsive behavior in aqueous solution, since two types of micelles were obtained on varying the solution temperature. Near-monodisperse spherical JM2005-core micelles were obtained at higher temperatures whereas polydisperse, nonspherical PSBMA-core micelles appear to be formed at lower temperatures.

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Supporting Information Available: ^{1}H NMR spectra of (a) the Jeffamine JM2005-NH_2 precursor, (b) the reaction mixture of 2-hydroxyethyl acrylate (HEA) and JM2005-NH_2 after Michael addition at 50 °C for 4 days (>98% conversion based on the assigned peaks), (c) the crude JM2005-$(OH)_2$ product after removal of HEA under vacuum at 70 °C for 5 h, (d) the purified JM2005-$(OH)_2$ after removal of the residual HEA monomer using column chromatography, and (e) the JM2005-Br_2 macroinitiator; MALDI−TOF mass spectra of (a) the JM2005-NH_2 precursor and (b) the corresponding JM2005-Br_2 ATRP macroinitiator; ^{1}H NMR spectra of (a) the JM1000−$(HEMA_{10})_2$ Y-shaped block copolymer and (b) the corresponding acidic Y-shaped block copolymer, [JM1000−$(SEMA_{10})_2$]; ^{1}H NMR spectra obtained for the JM1000−$(DEA_{10})_2$ Y-shaped block copolymer dissolved in $CDCl_3$, DCl/D_2O (at pH 2), and NaOD/D_2O (at pH 10). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Förster, S.; Plantenberg, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 688.
(2) Riess, G. *Prog. Polym. Sci.* **2003**, *28*, 1107.
(3) Maaey, J. A.; Winnik, M. A.; Manners, I. *J. Am. Chem. Soc.* **2001**, *123*, 3147.
(4) Sohn, B.; Choi, J.; Yoo, S.; Yun, S.; Zin, W.; Jung, J.; Kanehara, M.; Hirata, T.; Teranishi, T. *J. Am. Chem. Soc.* **2003**, *125*, 6368.
(5) Jaramillo, T. F.; Bacck, S. H.; Cuenya, B. R.; McFarland, E. W. *J. Am. Chem. Soc.* **2003**, *125*, 7148.
(6) A brief review of schizophrenic block copolymers. Armes, S. P.; Liu, S. In *Self-Assembly*; Robinson, B. H., Ed.; IOS Press: Amsterdam, The Netherlands, 2003; pp 260−268.
(7) Forder, C.; Patrickios, C. S.; Armes, S. P.; Billingham, N. C. *Macromolecules* **1996**, *29*, 8160.
(8) Zhang, L.; Eisenberg, A. *J. Am. Chem. Soc.* **1996**, *118*, 3168.
(9) Thurmond, K. B.; Kowalewski, T.; Wooley, K. L. *J. Am. Chem. Soc.* **1997**, *119*, 6656.
(10) Ramzi, A.; Prager, M.; Richter, D.; Efstratiadis, V.; Hadjichristidis, N.; Young, R. N.; Allgaier, J. B. *Macromolecules* **1997**, *30*, 7171.
(11) Pispas, S.; Hadjichristidis, N.; Potemkin, I.; Khokhlov, A. *Macromolecules* **2000**, *33*, 1741.
(12) Yun, J.; Faust, R.; Szilágyi, L. S.; Kéki, S.; Zsuga, M. *Macromolecules* **2003**, *36*, 1717.
(13) Sotiriou, K.; Nannou, A.; Velis, G.; Pipas, S. *Macromolecules* **2002**, *35*, 4106.
(14) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211.
(15) Reutenauer, S.; Hurtrez, G.; Dumas, P. *Macromolecules* **2001**, *34*, 755.
(16) Gibanel, S.; Forcada, J.; Heroguez, V.; Schappacher, M.; Gnanou, Y. *Macromolecules* **2001**, *34*, 4451.
(17) Gibanel, S.; Heroguez, V.; Forcada, J.; Gnanou, Y. *Macromolecules* **2002**, *35*, 2467.
(18) Francis, R.; Lepoittevin, B.; Taton, D.; Gnanou, Y. *Macromolecules* **2002**, *35*, 9001.
(19) Bon, S. A. F.; Ohno, K.; Haddleton, D. M. *ACS Symposium Series 780*; McCormick, C. L., Ed.; American Chemical Society: Washington, DC, 2001; Chapter 9, p 148.
(20) He, T.; Li, D.; Sheng, X.; Zhao, B. *Macromolecules* **2004**, *37*, 3128.
(21) Bütün, V.; Billingham, N. C.; Armes, S. P. *J. Am. Chem. Soc.* **1998**, *120*, 11818.
(22) Bütün, V.; Billingham, N. C.; Armes, S. P. *Macromolecules* **2001**, *34*, 1503.
(23) Liu, S.; Billingham, N. C.; Armes, S. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2328.
(24) Liu, S.; Armes, S. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1413.
(25) Liu, S.; Armes, S. P. *Langmuir* **2003**, *19*, 4432.
(26) Weaver, J. V. M.; Bütün, V.; Armes, S. P. *Chem. Commun.* **2002**, 2122.
(27) Arotcarena, M.; Heise, B.; Ishaya, S.; Laschewsky, A. *J. Am. Chem. Soc.* **2002**, *124*, 3787.
(28) Dai, S.; Ravi, P.; Tam, K. C.; Mao, B. W.; Gan, L. H. *Langmuir* **2003**, *19*, 5175.
(29) Cai, Y. L.; Burguiere, C.; Armes, S. P. *Chem. Commun.* **2004**, 802.
(30) Jankova, K.; Chen, X. Y.; Kops, J.; Batsberg, W. *Macromolecules* **1998**, *31*, 538.
(31) Pardo, L.; Osman, R.; Weinstein, H.; Rabinowitz, J. R. *J. Am. Chem. Soc.* **1993**, *115*, 8263.
(32) Li, Z.; Liu, G.; Law, S.; Sells, T. *Biomacromolecules* **2002**, *3*, 984.
(33) Bories-Azeau, X.; Armes, S. P.; van den Haak, H. J. W. *Macromolecules* **2004**, *37*, 2348.
(34) Beers, K. L.; Boo, S.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 5772.
(35) Robinson, K. L.; Khan, M. A.; de Paz Báñez, M. V.; Wang, X. S.; Armes, S. P. *Macromolecules* **2001**, *34*, 3155.
(36) Save, M.; Weaver, J. V. M.; Armes, S. P.; Mckenna, P. *Macromolecules* **2002**, *35*, 1152.

(37) Bütün, V.; Bennett, C. E.; Vamvakaki, M.; Lowe, A. B.; Billingham, N. C.; Armes, S. P. *J. Mater. Chem.* **1997**, *7*, 1693.
(38) Bütün, V.; Billingham, N. C.; Armes, S. P. *Polymer* **2001**, *42*, 5993.
(39) Vamvakaki, M.; Billingham, N. C.; Armes, S. P. *Macromolecules* **1999**, *32*, 2088.
(40) Müller, A. H. E.; Cai, Y. L.; Hartenstein, M.; Gradzielski, M.; Zhang, M.; Mori, H.; Pergushov, D. V. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2004**, *45* (2), 267.
(41) Schulz, D. N.; Peiffer, D. G.; Agarwal, P. K.; Larabee, J.; Kaladas, J. J.; Soni, L.; Handwerker, B.; Garner, R. T. *Polymer* **1986**, *27*, 1734.
(42) Xue, W.; Huglin, M. B.; Khoshdel, E. *Polym. Int.* **1999**, *48*, 8.
(43) Lowe, A. B.; Armes, S. P.; Billingham, N. C. *Chem. Commun.* **1996**, 1555.
(44) Lowe, A. B.; Armes, S. P.; Billingham, N. C. *Macromolecules* **1999**, *32*, 2141.

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