Synthesis and Characterization of Branched Water-Soluble Homopolymers and Diblock Copolymers Using Group Transfer Polymerization

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ABSTRACT: Group transfer polymerization [GTP] was used to synthesize branched statistical copolymers by copolymerizing either 2-(dimethylamino)ethyl methacrylate) [DMA] or 2-(diethylamino)ethyl methacrylate) [DEA] with ethylene glycol dimethacrylate (EGDMA) in THF at 20 °C. Since GTP has reasonable "living" character, it allows good control over both the primary chain length and the molecular weight distribution compared to previous branched vinyl polymers synthesized using conventional radical polymerization. Using GTP allows a remarkably high proportion of EGDMA brancher to be copolymerized without causing macrogelation. This unexpected result is attributed to a significant amount of intramolecular cyclization occurring (in addition to intermolecular branching) in these syntheses. Branched diblock copolymers based on DMA and DEA were prepared by sequential monomer addition, with EGDMA being used to achieve branching in either the DMA block or the DEA block or in both blocks. The order of monomer addition was varied to examine whether branching affected the "living" character of the polymerization. There was some evidence for better blocking efficiencies if the first block was a linear homopolymer, rather than a branched block copolymer. ^{1}H NMR spectroscopy indicated that very high comonomer conversions (>99%) were obtained in all cases. The branched diblock copolymers were characterized in terms of their block compositions and primary chain lengths using ^{1}H NMR, and their molecular weight distributions were assessed by THF GPC using a light scattering detector to obtain absolute M_w values. The evolution of molecular weight with conversion was assessed by periodic sampling of the polymerizing solution. Dynamic light scattering (DLS) and surface tensiometry data obtained for dilute aqueous solutions of the branched block copolymers were compared to those obtained for a linear diblock copolymer. Similar surface tension profiles were obtained regardless of the block architecture, but DLS studies indicated that larger, more polydisperse micelles were obtained if the coronal block was branched.

Introduction

There is increasing interest in branched vinyl polymers, which have fundamentally different solution and melt behavior compared to their linear counterparts. Frechet and co-workers prepared branched vinyl polymers by self-condensing vinyl polymerization, in which the monomer also acts as an initiator.[1] This initial example involved cationic polymerization, but examples based on nitroxide-mediated polymerization,[2] atom transfer radical polymerization (ATRP),[3−5] and group transfer polymerization (GTP)[6,7] were subsequently reported. However, in each case synthesis of the appropriate monomer−initiator adduct was required prior to polymerization, which is a potential disadvantage for the commercialization of this approach.

Over the past five years the synthesis of branched copolymers using conventional radical copolymerization of monovinyl and divinyl monomers has been described in a series of papers.[8−12] Here a chain transfer agent (typically a thiol) was used to lower the primary chain length and hence suppress macrogelation. The resulting soluble branched polymers are of broad interest, since their preparation is facile and involves only inexpensive, commercially available reagents. Recently, we have shown[13] that this facile methodology can also be employed to prepare branched poly(methyl methacrylate) using an ethylene glycol dimethacrylate (EGDMA) brancher via either ATRP or GTP. These two techniques have imperfect "living" character; termination is merely suppressed (rather than eliminated) in ATRP, and GTP can suffer from "backbiting" termination, particularly under monomer-starved conditions. Nevertheless, in both cases the primary chain length is readily controlled by varying the monomer/initiator molar ratio; hence, such "living" polymerizations require no additional chain transfer agent. We have now extended these preliminary findings. Statistical copolymerization of a hydrophilic monomer, 2-(dimethylamino)ethyl methacrylate [DMA], with EGDMA was carried out using GTP, and the reaction solution was sampled periodically to examine the evolution of molecular weight and polydispersity. These results were then exploited to prepare a range of new water-soluble branched block copolymers via sequential monomer addition using a related second monomer, 2-(diethylamino)ethyl methacrylate [DEA]. Finally, the surface activity and micellar self-assembly behavior of these pH-responsive branched

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Table 1. Summary of the GPC and NMR Data Obtained for a Branched PDMA-*stat*-EGDMA Statistical Copolymer, a Branched PDEA-*stat*-EGDMA Statistical Copolymer, a Linear−Linear PDEA−PDMA Diblock Copolymer, Four Linear−Branched Diblock Copolymers in Which Either the PDMA or the PDEA Block Is Branched, and a Branched−Branched [PDEA-*stat*-EGDMA]−[PDMA-*stat*-EGDMA] Diblock Copolymer[a]

sample code	diblock copolymer architecture[b]	DEA (mL)	DMA (mL)	EGDMA (mL)	MTS (mL)	target DP (monomer + EGDMA)	DP (NMR)	M_w (GPC)	M_w/M_n (GPC)
VB436	branched PDMA-*stat*-EGDMA		9.0	1.0	0.25	44 + 4.3	50	70 400	2.14
VB442	branched PDEA-*stat*-EGDMA	11.0		1.0	0.25	45 + 4.3	49	90 000	2.16
VB421	linear PDEA−PDMA diblock	11.0	9.0		0.25	45/44	55/51	19 800*	1.23*
VB441	PDEA−[PDMA-*stat*-EGDMA]	11.0	9.0	1.0	0.25	45/[44 + 4.3]	55/60	200 000	2.17
VB423	[PDMA-*stat*-EGDMA]−PDEA	11.0	9.0	1.0	0.25	[44 + 4.3]/45	51/57	723 000	5.49
VB440	PDMA−[PDEA-*stat*-EGDMA]	11.0	9.0	1.0	0.25	44/[45 + 4.3]	51/48	124 000	2.27
VB425	[PDEA-*stat*-EGDMA]−PDMA	11.0	9.0	1.0	0.25	[45 + 4.3]/44	40/37	100 000	1.87
VB426	[PDEA-*stat*-EGDMA]−[PDMA-*stat*-EGDMA]	11.0	9.0	0.50 + 0.50	0.25	[45 + 2.2]/[44 + 2.2]	42/47	455 000	5.84

[a] All GTP syntheses were conducted at 20 °C in 150 mL of THF using 0.25 mL of MTS initiator and 50 mg of bibenzoate catalyst. The two asterisks for entry VB421 indicates that these data were obtained by conventional GPC calibration using PMMA standards, rather than using the light scattering GPC detector. [b] The first named block was polymerized first in all cases.

diblock copolymers were compared to those previously reported for an analogous linear PDMA−PDEA diblock copolymer.[14,15]

Experimental Section

General Protocols. Chemicals were purchased from Aldrich unless otherwise stated. To eliminate surface moisture, glassware and transfer needles were oven-dried overnight at 140 °C before use. The hot glassware was directly assembled from the oven, flamed out under high vacuum ($<10^{-4}$ Torr), and allowed to cool to room temperature. THF (Fisher) was initially dried over sodium wire and refluxed over potassium for 3 days and then stored over 4 Å molecular sieves at room temperature prior to use. Solvent transfer into the reaction vessel was achieved using a cannula. The 1-methoxy-1-trimethylsiloxy-2-methyl-1-propane (MTS) initiator was distilled and stored at −5 °C in a graduated Schlenk flask under dry nitrogen prior to use. The tetra-*n*-butylammonium bibenzoate (TBABB) catalyst was prepared as described previously[16] and stored under a dry nitrogen atmosphere. DMA, DEA, and EGDMA were each passed in turn through a basic alumina column, stirred over calcium hydride in the presence of 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH) inhibitor, and then stored below −25 °C prior to use. Each monomer was distilled under reduced pressure before transferring into the reaction vessel by cannula under dry nitrogen. Nitrogen was passed through both a silica column and a P_2O_5 drying column prior to use. All copolymerizations were carried out under dry nitrogen.

Synthesis of the Linear PDEA−PDMA Diblock Copolymer. DEA was homopolymerized first according to the following protocol. The solid catalyst (50−100 mg, 2 mol % based on initiator) was added from a sidearm under a nitrogen purge into a 250 mL three-necked round-bottomed flask. THF (100 mL) was then transferred into the flask via cannula before the addition of MTS (0.25 mL). This solution was stirred for 15 min, and then DEA monomer (11.0 mL) was added by cannula. In the meantime, a contact thermocouple was attached to the side of the reaction vessel to measure the change of temperature during monomer addition. It was observed that the reaction temperature increased to more than 40 °C. The reaction mixture was stirred until the solution temperature returned to room temperature (≈40−50 min). A 2.0 mL aliquot was extracted from the reaction mixture for GPC and NMR analyses. Then DMA monomer (9.0 mL) was added via cannula, and a second exotherm was recorded, indicating that a second-stage polymerization had occurred. The reaction mixture was stirred at room temperature until the exotherm had abated (≈1 h). After a second 2.0 mL aliquot was extracted for GPC and NMR analyses, the block copolymer was terminated with methanol (2 mL) prior to recovery using a rotary evaporator. The resulting linear diblock copolymer was dried under vacuum for 24 h and isolated in very high yield (>98%).

Synthesis of Branched Statistical Copolymers. A soluble branched PDMA-*stat*-EGDMA statistical copolymer with a target degree of polymerization of 45 was synthesized by GTP using EGDMA as a branching agent with a DMA/EGDMA molar ratio of 44.0/4.3 according to the following protocol. The solid GTP catalyst (≈50 mg) was added from a sidearm under nitrogen purge into a 250 mL three-necked round-bottomed flask. THF (150 mL) was then transferred into the flask via cannula before the addition of MTS initiator (0.25 mL). DMA (9.0 mL) and EGDMA (1.0 mL) were transferred into another Schlenk tube containing a stir bar and stirred for 20 min at 20 °C. After this initiator solution was stirred for 15 min, the DMA/EGDMA comonomer mixture was transferred by cannula into the flask. The reaction mixture was stirred for 24 h. During this reaction period, a series of 3 mL aliquots of the reaction mixture were extracted via syringe at various time intervals for GPC and NMR analyses. These samples were quickly transferred into bottles containing a few drops of methanol (for GPC) or D_2O (for NMR) and shaken to terminate the polymerization. For the final product in the reaction flask, the reaction was quenched by adding methanol (2.0 mL). THF solvent was removed with a rotary evaporator. Finally, the recovered PDMA-*stat*-EGDMA statistical copolymer was dried on a vacuum line at room temperature for 24 h. The same protocol was used for the synthesis of a branched PDEA-*stat*-EGDMA statistical copolymer using an almost identical DEA/EGDMA molar ratio of 45.0/4.3. The resulting soluble branched copolymers were characterized by NMR and GPC.

Synthesis of Branched Diblock Copolymers. The protocol used for the synthesis of the branched−linear [PDMA-*stat*-EGDMA]−PDEA diblock copolymers was the same as that used for the branched PDMA-*stat*-EGDMA copolymer (see above), except that DEA monomer was added at the end of the DMA copolymerization. The reaction solution was again terminated by addition of methanol. The effect of varying the order of monomer addition was also examined by preparing the identical branched diblock copolymer in reverse sequence, i.e., by synthesizing the linear PDEA block first, followed by the branched PDMA block. The same general protocol was used for the synthesis of branched−linear [PDEA-*stat*-EGDMA]−PDMA diblock copolymers. A summary of all the synthesized copolymers, including their NMR and GPC data, is listed in Table 1. Finally, a branched−branched [PDEA-*stat*-EGDMA]−[PDMA-*stat*-EGDMA] diblock copolymer was also synthesized by the same general method. In this case, a DEA/EGDMA comonomer mixture was polymerized first, followed by a DMA/EGDMA comonomer mixture. The total amount of EGDMA branching agent used in this branched−branched synthesis was the same as that employed in the linear−branched copolymer syntheses to prevent the solution viscosity becoming too high during the second-stage polymerization. The following quantities of materials were used in each synthesis of the soluble branched polymers: 9.0 mL of DMA, 11.0 mL of DEA, 1.0 mL of EGDMA, 0.25 mL of MTS initiator, 50 mg of GTP catalyst, and 150 mL of THF.

Molecular weights and molecular weight distributions of each statistical copolymer and diblock copolymer were deter-

mined using gel permeation chromatography (GPC). The GPC setup comprised a Viscotek LC pump, a refractive index detector, either mixed "E" and mixed "D" (for linear copolymers), or two mixed "B" columns (for the branched copolymers; all columns were ex. Polymer Labs), and calibration was carried out for the linear diblock copolymer using a series of linear poly(methyl methacrylate) calibration standards (ex. Polymer Labs). The GPC eluent was HPLC grade THF stabilized with BHT at a flow rate of 1.0 mL min^{-1}. A refractive index detector was used to analyze the linear diblock copolymer, whereas a three-angle mini-DAWN (Wyatt Corp.) light scattering detector was used to characterize the branched statistical copolymers and diblock copolymers. A mean d*n*/d*c* value of ≈0.089 was estimated for these copolymers in THF using an Optilab differential refractometer instrument (Wyatt Corp.).

Surface tension measurements were carried out at 20 °C using a Kruss K10ST surface tensiometer equipped with a platinum ring for the linear−linear, linear−branched, branched−linear, and branched−branched diblock copolymers. Initially, 0.3% aqueous copolymer solutions were prepared at pH 2, and the solution pH was varied by the addition of KOH. The surface tension of pure water (≈71 mN m^{-1}) was checked periodically between measurements.

Dynamic light scattering studies of the block copolymer micelles in aqueous solution were conducted using an ALV/CGS-3 compact goniometer system (Malvern, UK) equipped with a 22 mW He−Ne laser operating at $\lambda_0 = 632.8$ nm, an avalanche photodiode detector with high quantum efficiency, and an ALV/LSE-5003 multiple tau digital correlator electronics system. All measurements were performed on 0.50% w/v aqueous copolymer solutions at 20 °C using a fixed scattering angle of 90°, and the data were fitted using second-order cumulants analysis.

All ^{1}H NMR spectra were recorded in $CDCl_3$ using a Bruker 300 MHz NMR instrument. The mean degrees of polymerization of the PDMA-*stat*-EGDMA and PDEA-*stat*-EGDMA statistical copolymers were estimated from their NMR spectra by comparing the methoxy signal at 3.6 ppm due to the MTS initiator fragment to the signal at 4.0 ppm due to the oxymethylene protons.

^{1}H NMR spectra for linear PDMA homopolymer and the corresponding linear−branched PDMA−[PDEA-*stat*-EGDMA] diblock copolymer (VB440) were recorded (spectra not shown). The methoxy signal at δ 3.6 due to the MTS initiator fragment was used to estimate the mean degree of polymerization of the PDMA, which was calculated to be 51 (see Table 1). The block composition of the linear−branched PDMA−[PDEA-*stat*-EGDMA] copolymer was calculated by comparing the peak integral of the six dimethylamino protons due to the DMA residues at δ 2.3 to that of the oxymethylene protons of the DEA residues at δ 4.0. Thus, the mean degree of polymerization of the PDEA-*stat*-EGDMA block in this copolymer was estimated to be 48 (see Table 1). The degree of polymerization of the PDEA-*stat*-EGDMA statistical copolymer was also estimated using the same end-group analysis method: in this case the peak integrals of the methoxy protons at δ 3.6 due to MTS were compared to those due to the oxymethylene protons of the DEA and EGDMA comonomers at δ 4.0.

Results and Discussion

Group transfer polymerization [GTP] was used to synthesize branched statistical copolymers and diblock copolymers by copolymerizing DMA and/or DEA with EGDMA in THF at 20 °C. The "living" character of these syntheses was assessed by GPC and ^{1}H NMR spectroscopy; the aqueous solution properties of the resulting branched polymeric surfactants were assessed by dynamic light scattering and surface tensiometry studies.

Homopolymer Syntheses. The first two entries in Table 1 refer to branched PDMA-*stat*-EGDMA and PDEA-*stat*-EGDMA copolymers prepared via GTP. The statistical copolymerization of DMA with EGDMA was

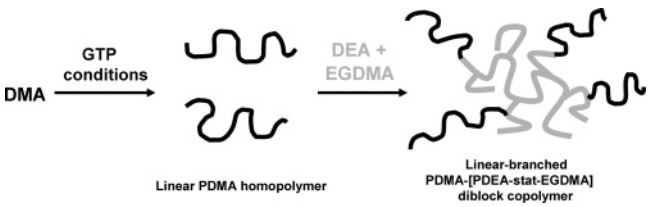

Figure 1. Schematic representation of the synthesis of a linear−branched PDMA−[PDEA-*stat*-EGDMA] diblock copolymer via group transfer polymerization using 2-(dimethylamino)ethyl methacrylate [DMA] as the first monomer, 2-(diethylamino)ethyl methacrylate [DEA] as the second monomer, and ethylene glycol dimethacrylate as a branching agent in the second-stage polymerization.

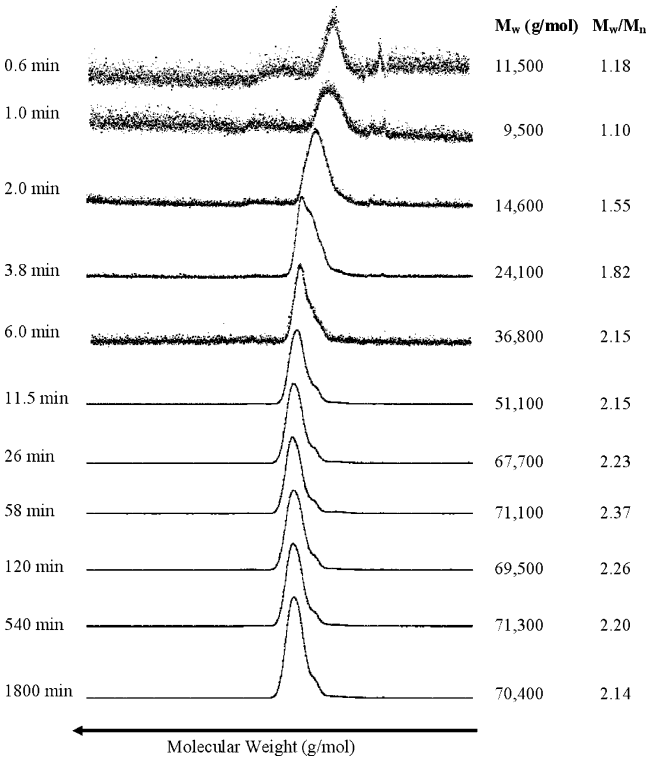

Figure 2. Evolution of GPC chromatograms (obtained using the light scattering detector) with time for the statistical copolymerization of DMA with the bifunctional EGDMA branching agent via GTP (VB436, see Table 1).

sampled periodically, and the aliquots were analyzed by GPC and NMR. The evolution of the molecular weight distribution with reaction time is shown in Figure 2. On the basis of the monomer/initiator molar ratio and assuming no branching, the degree of polymerization expected for the primary chains under these conditions was ≈44, which corresponds to an M_n of around 7200. Thus, it is clear that branching occurs in the early stages of this polymerization, since even the first sample has a relatively high M_w of 11 500. (The poor signal-to-noise ratios observed in the first two chromatograms are due to the insensitivity of the light scattering detector toward low molecular weight polymers.) The M_w values increase monotonically with reaction time, and the molecular weight distribution remains essentially unimodal (with some evidence for a low molecular weight shoulder) during this particular polymerization. The polydispersity, which is a crude measure of the width of the molecular weight distribution, reaches a maximum value of 2.37 after 58 min, which corresponds to almost complete monomer conversion (>99%). Thereafter, the polydispersity decreases

slightly to reach 2.14 after 30 h, with the M_w remaining almost unchanged at around 70 000 over the same time period. Very similar results, including a maximum in polydispersity of 2.24 and a final M_w of around 90 000, were obtained for the branched copolymerization of DEA with EGDMA (data not shown).

In contrast, multimodal chromatograms (and usually much higher final polydispersities) have been reported for the branching copolymerization of methyl methacrylate with EGDMA using conventional free radical copolymerization.[8−12] It appears that "living" polymerizations allow the synthesis of more uniform branched polymers. Presumably, this is because the intrinsic molecular weight distribution obtained in the absence of any branching agent is much narrower: typical polydispersities for GTP syntheses are around 1.10,[14,15] whereas conventional free radical polymerizations lead to polydispersities of at least 1.50 and usually greater than 2.0. The much tighter control over the chain length distribution provided by GTP means that there are fewer higher molecular weight chains present and therefore a much reduced probability of more than one branching agent per primary chain, which is believed to lead to macrogelation.[13] However, there are also other unidentified factors involved in these GTP syntheses since it is possible to incorporate remarkably high levels of EGDMA brancher (significantly more than one brancher per chain) without observing macrogelation. This is most likely related to the known propensity of EGDMA to undergo intramolecular backbiting or cyclization, in addition to intermolecular branching.[17] Our current hypothesis is that this intramolecular side reaction is much more likely to occur for the anionic enolate chain ends obtained in GTP, rather than the radical chain ends that are characteristic of conventional radical polymerization (or ATRP). In summary, although the branched statistical copolymers and diblock copolymers prepared in this study are apparently highly branched since they contain a high proportion of EGDMA branching agent, it is likely that most of the copolymerized EGDMA is not actually involved in intermolecular branching. In future work this hypothesis will be tested by evaluating alternative bifunctional and multifunctional methacrylic branching agents.

Selected NMR spectra recorded after periodic sampling of the PDMA-*stat*-EGDMA copolymerization are shown in Figure 3. Conversions were estimated from the NMR spectra shown in Figure 2 by comparing the integrated vinyl signals at δ 5.5 and δ 6.2 with that due to the azamethylene protons of DMA monomer/copolymer at δ 2.6. The vinyl signals at δ 5.5−6.2 due to residual DMA monomer are clearly visible initially, but after 26 min these signals disappear, indicating very high conversions (>99%). This also confirms that the concentration of unreacted pendent vinyl groups originating from the copolymerized EGDMA units is also very low (<1%). This is consistent with the relatively high final M_w obtained for this branched copolymer. In contrast, significant levels of unreacted pendent vinyl groups have been reported for branched methacrylic copolymers prepared using conventional free radical polymerization.[8−12]

Regardless of the precise fate of the EGDMA branching agent, it is clear that the "living" character of these GTP statistical copolymerizations does not appear to be unduly compromised by the addition of this bifunctional comonomer. It is also noteworthy that conventional GTP

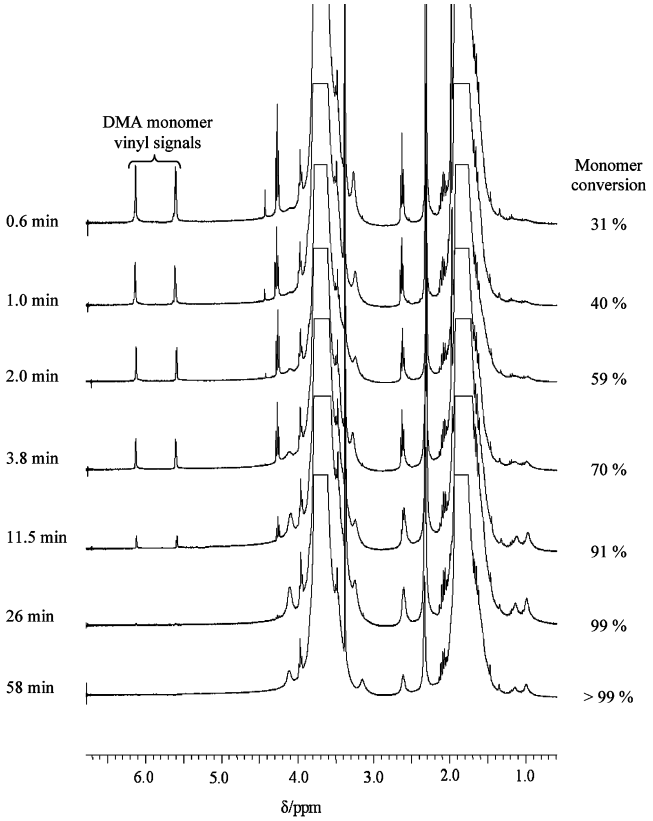

Figure 3. Evolution of ^{1}H NMR spectra with conversion for the statistical copolymerization of DMA with the EGDMA branching agent via GTP. Each spectrum was recorded on the reaction solution in THF after termination of the polymerization by addition of methanol. Note the disappearance of the vinyl signals, indicating that essentially all of the pendent vinyl groups due to the EGDMA comonomer had reacted within 1 h.

is usually limited to producing polymers with DP's less than 1000. Using this simple branching methodology, this upper limit can be easily extended by at least an order of magnitude, albeit at the expense of control over the molecular weight distribution. In contrast, such high molecular weights are typically not observed for branched polymers prepared using the self-condensing vinyl polymerization route.

Finally, it is noticeable that the branched PDEA-*stat*-EGDMA copolymer entry in Table 1 (VB442) has a somewhat higher M_w than that observed for the analogous branched PDMA-*stat*-EGDMA copolymer entry (VB436). We do not have a satisfactory explanation for this observation at the present time, although it may be related to small differences in the final monomer conversions in these syntheses. Clearly further investigations will be required to understand why the final molecular weights and polydispersities of these branched copolymers appear to be relatively sensitive to the reaction conditions.

Diblock Copolymer Syntheses. The target degrees of polymerization (DP) for the PDEA and PDMA blocks in the various copolymer syntheses ranged from 44 to 49 (see Table 1). The actual degree of polymerization of the first PDEA block of the linear PDEA−PDMA diblock copolymer was determined by end-group analysis[15] using ^{1}H NMR. Thus, the integrated methoxy signal at δ 3.6 due to the MTS initiator fragment was compared to the integrated oxymethylene proton signal at δ 4.0 in order to calculate the mean DP of the PDEA block,

Table 2. Summary of the Hydrodynamic Radii and Polydispersities Obtained from 0.30 % Aqueous Solutions of Diblock Copolymer Micelles at 20 °C Using Dynamic Light Scattering

sample code	diblock copolymer architecture	solution pH	hydrodynamic radius (nm)	polydispersity
VB421	linear PDEA−PDMA	7.6	24	0.05
VB441	PDEA−[PDMA-*stat*-EGDMA]	7.6	32	0.24
VB423	[PDMA-*stat*-EGDMA]−PDEA	7.3	47	0.41
VB440	PDMA−[PDEA-*stat*-EGDMA]	7.6	17	0.10
VB425	[PDEA-*stat*-EGDMA]−PDMA	7.5	20	0.08
VB426	[PDEA-*stat*-EGDMA]−[PDMA-*stat*-EGDMA]	7.3	59	0.35

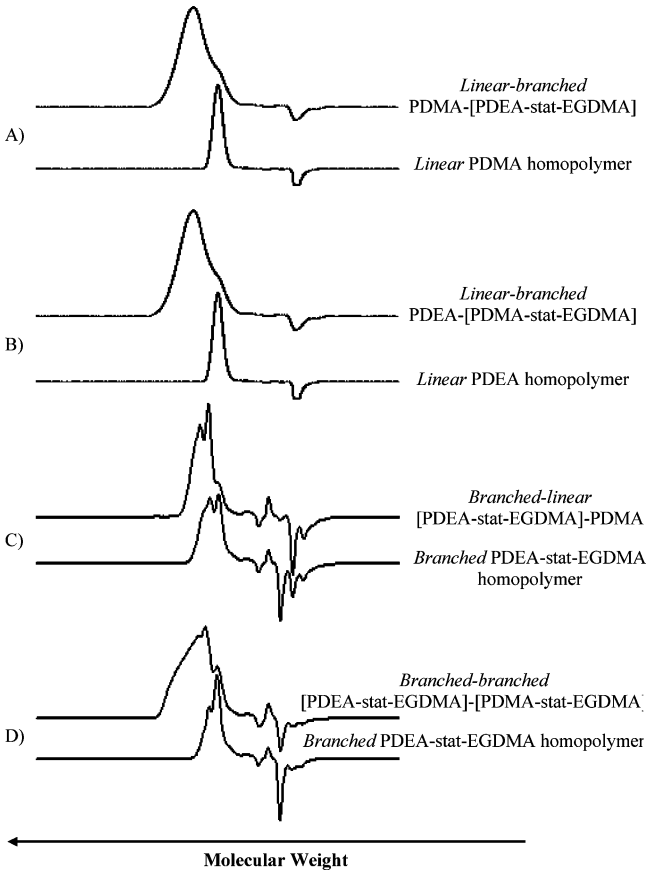

Figure 4. GPC chromatograms (refractive index detector) of branched diblock copolymers prepared by GTP via sequential monomer addition of two tertiary amine methacrylates. The upper pair of chromatograms labeled (A) was obtained for a linear PDMA homopolymer before and after chain extension using a DEA/EGDMA comonomer mixture (VB440, see Table 1). The pair of chromatograms labeled (B) was obtained for a linear PDEA homopolymer before and after chain extension using a DMA/EGDMA comonomer mixture (VB441). The pair of chromatograms labeled (C) was obtained for a branched PDEA-*stat*-EGDMA copolymer before and after chain extension using DMA alone (VB425). The lower pair of chromatograms (D) was obtained for a branched PDEA-*stat*-EGDMA copolymer before and after chain extension using a DMA/EGDMA comonomer mixture (VB426).

which was estimated to be 55. This value was then used to estimate a DP of 51 for the PDMA component of the block copolymer by comparing the integrated oxymethylene proton signal at δ 4.0 to that of the six dimethylamino protons in the DMA residues at δ 2.2−2.3. Reasonably good agreement was observed between the target [based on the (monomer + comonomer)/initiator molar ratios] and the experimental block lengths determined by NMR. A similar approach was used to obtain the experimental DP's for the branched copolymers.

Figure 4 shows the GPC chromatograms recorded after the first and second stage polymerizations in selected branched block copolymer syntheses. In these studies a refractive index detector was preferred, since this is more sensitive to lower molecular weights than the light scattering detector and is therefore better suited for the detection of the first block if it has a linear architecture. The upper pair of chromatograms (labeled A; see VB440 in Table 1) represents linear PDMA homopolymer (prepared in the absence of any EGDMA brancher) and the corresponding linear−branched PDMA−[PDEA-*stat*-EGDMA] diblock copolymer obtained after addition of a mixture of DEA and EGDMA comonomers to this reaction solution. The first chromatogram is relatively narrow and unimodal (M_n = 6200; M_w/M_n = 1.16), as expected for a near-monodisperse homopolymer prepared by GTP. The second chromatogram comprises a broad high molecular weight peak with a low molecular weight shoulder. The latter feature corresponds to the original linear PDMA homopolymer, which suggests that a small degree of termination occurred, possibly via backbiting. Very similar results were obtained for the second pair of chromatograms (labeled B; see VB441), in which DEA was polymerized first to give a linear homopolymer (M_n = 8100; M_w/M_n = 1.15), followed by a second-stage branching copolymerization of DMA and EGDMA. In the third pair of chromatograms (labeled C; see VB425), the order of branching has been reversed. This time it is the *first* block that is branched (i.e., DEA was copolymerized with EGDMA), followed by linear polymerization of the DMA monomer. Thus, the first chromatogram is already broad, bimodal, and of high molecular weight, but nevertheless there is a significant shift to higher molecular weight during the second-stage polymerization. Again, there is some evidence for premature termination. Finally, the fourth pair of chromatograms (labeled D; see VB426) was recorded during the synthesis of a branched−branched diblock copolymer, i.e., where EGDMA is added to both the first stage and the second stage polymerization.[18] Once again, a significant increase in molecular weight is observed after addition of the second batch of comonomers. In summary, chain extension predominates over premature termination in these branched block copolymerizations, and there is some evidence for better blocking efficiencies if the first block has a linear architecture.

We have previously reported the synthesis of the analogous linear PDMA−PDEA diblocks via GTP and shown that these copolymers can act as pH-responsive polymeric surfactants.[14,15] Dynamic light scattering studies indicated molecular dissolution at low pH (pH < 4), with micellar self-assembly occurring at around pH 7.5 (see Table 2). The linear diblock copolymer formed near-monodisperse micelles, as expected.[15] The two diblock copolymers with branched PDEA core-forming blocks formed fairly compact, relatively well-defined micelles (VB440 and VB425), whereas the two diblock copolymers with branched PDMA coronal chains formed relatively large, polydisperse micelles (VB441

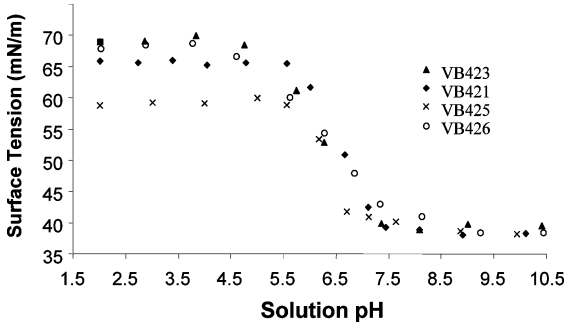

Figure 5. Variation of surface tension with solution pH for 0.30% aqueous solutions of selected tertiary amine methacrylate-based diblock copolymers (see Table 1).

and VB423). The branched−branched diblock copolymer (VB 426) also formed large polydisperse micelles. Thus, micellar self-assembly appears to be more sensitive to branching in the coronal block than the core-forming block.

Surface tension vs pH studies (see Figure 5) on the linear PDEA−PDMA diblock copolymer revealed low surface activity in acidic solution but high surface activity at around neutral pH, as expected. Despite their much higher molecular weights and significantly greater polydispersities, broadly similar surface tensiometry results were obtained for the linear−branched, branched−linear, and branched−branched diblock copolymers.

Conclusions

1. The "living" character of these GTP polymerizations does not appear to be unduly compromised by the addition of the bifunctional EGDMA comonomer. Surprisingly high proportions of EGDMA can be incorporated without leading to macroscopic gelation.

2. GTP allows reasonably good control over both the target molecular weight of the primary chains and the molecular weight distribution. Higher conversions and lower polydispersities are obtained compared to branched copolymers prepared by conventional radical polymerization.

3. Sampling of these GTP syntheses indicates that branching occurs at a relatively early stage in the polymerization. The evolution of molecular weight with conversion is monotonic, and there is some evidence for a maximum in polydispersity at higher conversions.

4. The first examples of linear−branched water-soluble block copolymers are described. The order of monomer addition appears to have relatively little effect on the living character of these polymerizations. Some degree of premature termination is observed, but chain extension is reasonably efficient (at least 80−90%) if the first block has a linear architecture.

5. Addition of the EGDMA branching agent during polymerization of both the first and the second monomer has produced the first example of a soluble branched−branched diblock copolymer.

6. Despite their much higher molecular weight, the branched diblock copolymers exhibit broadly similar aqueous solution properties to those of the low molecular weight linear PDMA−PDEA diblock copolymers reported earlier. Micellization occurs above approximately pH 7, leading to the formation of large, relatively polydisperse aggregates if the coronal block is branched but smaller, less polydisperse aggregates if the core-forming block is branched. Surface tension data indicate significant adsorption at the air−water interface in alkaline media, but only relatively weak surface activity at low pH, as expected.

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References and Notes

(1) Frechet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *269*, 1080.
(2) Hawker, C. J.; Frechet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763.
(3) Weimer, M. W.; Frechet, J. M. J.; Gitsov, I. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 955.
(4) Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 1079.
(5) Matyjaszewski, K.; Gaynor, S. G. *Macromolecules* **1997**, *30*, 7042.
(6) Simon, P. F. W.; Müller, A. H. E.; Pakula, T. *Macromolecules* **2001**, *34*, 1684.
(7) Simon, P. F. W.; Müller, A. H. E. *Macromolecules* **2001**, *34*, 6206.
(8) O'Brien, N.; McKee, A.; Sherrington, D. C.; Slark, A. T.; Titterton, A. *Polymer* **2000**, *43*, 245.
(9) Costello, P. A.; Martin, I. K.; Slark, A. T.; Sherrington, D. C.; Titterton, A. *Polymer* **2002**, *43*, 245.
(10) Slark, A. T.; Sherrington, D. C.; Titterton, A.; Martin, I. K. *J. Mater. Chem.* **2003**, *13*, 2711.
(11) Isaure, F.; Cormack, P. A. G.; Sherrington, D. C. *J. Mater. Chem.* **2003**, *13*, 2701.
(12) Isaure, F.; Cormack, P. A. G.; Sherrington, D. C. *Macromolecules* **2004**, *37*, 2096.
(13) Isaure, F.; Cormack, P. A. G.; Graham, S.; Sherrington, D. C.; Bütün, V.; Armes, S. P. *Chem. Commun.* **2004**, 1138.
(14) (a) Bütün, V.; Billingham, N. C.; Armes, S. P. *Chem. Commun.* **1997**, 671. (b) Lee, A. S.; Gast, A. P.; Bütün, V.; Armes, S. P. *Macromolecules* **1999**, *32*, 4302.
(15) Bütün, V.; Billingham, N. C.; Armes, S. P. *Polymer* **2001**, *42*, 5993.
(16) Dicker, I. B.; Cohen, G. M.; Farnham, W. B.; Hertler, W. R.; Laganis, E. D.; Sogah, D. Y. *Macromolecules* **1990**, *23*, 4034.
(17) Landin, D. T.; Macosko, C. W. *Macromolecules* **1988**, *21*, 846.
(18) In this branched−branched block copolymer synthesis (VB426) the EGDMA brancher was distributed equally between the two branched blocks but maintained at the same overall level. Thus, on average there were 2.2 EGDMA units per DEA block (overall DP = 45 + 2.2) and 2.2 EGDMA units per DMA block (overall DP = 44 + 2.2). In contrast, there were 4.3 EGDMA units per branched block (DMA or DEA) in the four linear−branched block copolymer syntheses (see Table 1).

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