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Synthesis of Well-Defined Branched Copolymers by Quaternization of Near-Monodisperse Homopolymers

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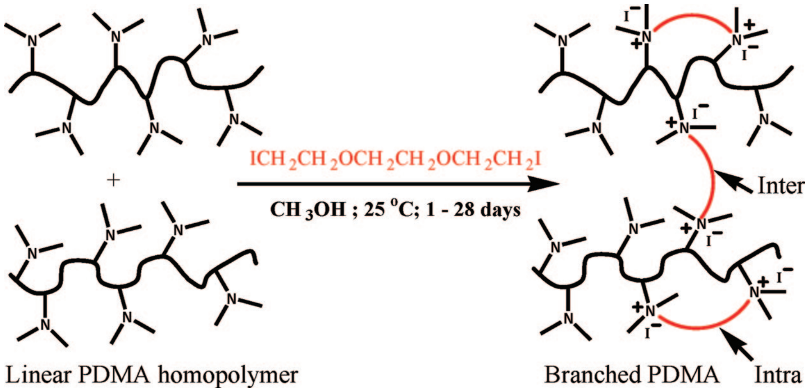
ABSTRACT: We report the synthesis of water-soluble cationic branched copolymers by quaternization of near-monodisperse poly[2-dimethylamino)ethyl methacrylate] chains using bis(2-iodoethoxy)ethane. This model system is very useful for exploring the relative propensities for *intermolecular* branching and *intramolecular* cyclization. At polymer concentrations higher than the critical overlap concentration (c^*), intermolecular branching is preferred over intramolecular cyclization; however, below c^*, intramolecular cyclization is much more likely than intermolecular branching. These results allow some rationalization of the apparently contradictory literature data on branched copolymers prepared by living radical copolymerizations.

Introduction

Free radical copolymerization of a monovinyl monomer with a relatively small amount of a divinyl monomer usually leads to gelation.[1–5] Important technological examples of such formulations include contact lenses.[4] There are many early literature examples of such copolymer gels[2–4] and the concept of avoiding gelation by using chain transfer agents to reduce the primary chain length has been recognized for many years.[5] Recently, Sherrington and co-workers at Strathclyde University reported a facile route to *soluble* branched copolymers based on the free radical copolymerization of monomers such as methyl methacrylate with either diacrylates or dimethacrylates in the presence of an alkanethiol.[6–12] This chain transfer agent substantially reduces the molecular weight of the primary chains. Hence gelation is eliminated provided that less than fully reacted one branching comonomer is incorporated per primary chain. As far as we are aware, this body of work was the first to demonstrate that gelation could be avoided even at very high monomer conversions.

The "Strathclyde" approach to branched copolymers has been recently extended to include (pseudo-) living polymerizations, such as atom transfer radical polymerization (ATRP).[13–21] In principle, ATRP offers much better control over both the primary chain length and polydispersity and hence over the branching process. Using this technique, Bannister and co-workers reported detailed GPC and NMR studies of a copolymerizing solution of 2-hydroxypropyl methacrylate (HPMA) and ethylene glycol dimethylacrylate (EGDMA) and showed that, although the *onset* of branching occurred at around 70% conversion, *significant* degrees of branching were only obtained above 90% conversion.[15] Thus, to a zeroth-order approximation, the linear primary chains were formed first, followed by latent branching. Moreover, branching copolymerizations conducted under ATRP conditions conform quite closely to classical gelation theory: soluble branched copolymers are obtained when the brancher/initiator molar ratio is less than unity, whereas insoluble copolymer gels are invariably obtained for brancher/initiator molar ratios exceeding unity.[14,15] In contrast, branched copolymer syntheses conducted using reversible addition−fragmentation transfer (RAFT) copolymerization typically lead to *nonideal* behavior: significantly more than one brancher per chain can be employed without causing gelation, even at very high conversions (>98%).[22] Similarly anomalous behavior was reported by us for methacrylic branched copolymers prepared by group transfer polymerization and oxyanionic polymerization.[23,24] Very recently, we suggested that this apparent discrepancy simply indicates that intramolecular cyclization occurs to a substantially greater extent in *nonideal* branching copolymerizations.[18] In the present work, we introduce a model system to gain a better understanding of the branching process (see Scheme 1). Our results confirm that, as predicted by Flory,

Scheme 1. Reaction Scheme for the Post-Polymerization Quaternization of Poly[(2-dimethylamino)ethyl methacrylate] (PDMA) Homopolymer with Bis(2-iodoethyoxy)ethane (BIEE) in Methanol



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intramolecular cyclization is much more favored in *dilute* solution compared to more concentrated solution. This observation allows rationalization of much of the apparently conflicting literature on branched copolymer syntheses conducted under (pseudo)-living conditions (i.e., ATRP and RAFT) using the ‘Strathclyde’ route.

Experimental Section

Materials. 2-(Dimethylamino)ethyl methacrylate (DMA), 1,2-bis-(2-iodoethoxy)ethane (BIEE), and 1-methoxy-1-trimethylsiloxy-2-methyl-1-propane (MTS) were each purchased from Aldrich. THF (Fisher) was initially dried over sodium wire and refluxed over potassium for three 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 MTS initiator was distilled under vacuum 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[25] and stored under a dry nitrogen atmosphere prior to use. DMA monomer was passed through a basic alumina column, stirred over calcium hydride and then stored below −25 °C prior to use. DMA was distilled under reduced pressure before being transferred 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 other chemicals were purchased from Fisher or Aldrich at the highest available purity and were used as received.

Synthesis of Linear Poly[2-(dimethylamino)ethyl methacrylate] Homopolymer. 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. The solid catalyst (10 mg) 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 (0.20 mL). This solution was stirred for 15 min, and then DMA monomer (8.36 mL) was added by cannula. The resulting polymerization exotherm was monitored using a contact thermocouple attached to the side of the reaction vessel. The reaction mixture was stirred until the exotherm had abated (typically within 40−50 min). The polymer was terminated with methanol (2 mL) prior to recovery using a rotary evaporator. The resulting linear poly[2-(dimethylamino)ethyl methacrylate] (PDMA) homopolymer was dried under vacuum for 24 h and isolated in very high yield (>98%).

Synthesis of Branched PDMA Polymers via BIEE Quaternization. A typical protocol for the synthesis of PDMA-based branched polymer was as follows: 0.50 g of PDMA homopolymer was dissolved in 0.50 g (0.56 mL) of CD_3OD, and BIEE was then added at various BIEE/PDMA molar ratios. Samples were periodically withdrawn and immediately analyzed by aqueous GPC (quenched by dilution with the aqueous GPC eluent) and ^{1}H NMR (quenched by dilution with CD_3OD) to assess the polymer molecular weight distribution and monomer conversions.

Characterization of Branched Quaternized PDMA. All ^{1}H NMR spectra were recorded in either D_2O, or CD_3OD using a 250 MHz Bruker ACF-250 spectrometer. The molecular weights and polydispersities of the PDMA homopolymer and various branched quaternized polymers were determined by aqueous GPC at 35 °C using Polymer Laboratories Aquagel-OH 40 and Aquagel-OH 30 columns. The eluent was a pH 3.0 buffer solution comprising 0.30 M NaH_2PO_4 and 1.0 M acetic acid at a flow rate of 1.0 mL min^{-1}. The dn/dc was determined to be 0.253 for this particular eluent using stock solutions of known polymer concentration (assuming 100% recovery). The acidity of the eluent ensures that any unquaternized DMA units are protonated, so the polymer chains have maximum cationic charge density. This GPC protocol has been previously shown to be appropriate for the characterization of cationic methacrylic polymers.[26] Near-monodisperse poly(2-vinylpyridine) standards were used for calibration purposes. The data were analyzed using PL Cirrus GPC software (version 2.0, triple detection method) supplied by Polymer Laboratories.

Results and Discussion

Our model system involves quaternization of a near-monodisperse PDMA homopolymer using a bifunctional reagent, bis(2-iodoethoxy)ethane [BIEE].[27,28] This *postpolymerization* reaction leads to random branching of the PDMA chains. In essence, this situation is therefore very similar to that reported by Li and Armes for the statistical *copolymerization* of HPMA with a disulfide-based dimethacrylate comonomer: cleavage of the disulfide bonds in this latter system confirmed that the highly branched copolymer chains simply comprised randomly linked near-monodisperse primary chains.[14] In the present work,^{1}H NMR analysis confirmed that the mean degree of polymerization of the PDMA chains was approximately 89, while THF GPC analysis indicated an M_n of 11 800 and an M_w/M_n of 1.06 for this homopolymer precursor.

As shown in Scheme 1, quaternization of the PDMA chains using BIEE can lead to either *intermolecular* branching or *intramolecular* cyclization.[29] Intermolecular branching leads to statistical coupling between two or more PDMA primary chains, leading to a branched, quaternized polymer whose molecular weight is approximately equal to the sum of the primary chains. In contrast, intramolecular cyclization occurs *within the same polymer chain* and involves no significant increase in molecular weight (other than the relatively small additional mass of the BIEE reagent). Clearly, cyclization should be favored at *lower* polymer concentrations, whereas branching is more likely to occur at *higher* polymer concentrations. This insight is important both in the context of the present work and also for the interpretation of literature data. It is noteworthy that the monomer concentrations utilized in branched copolymer syntheses vary significantly depending on the nature of the polymerization chemistry. For example, anionic copolymerizations have been conducted at monomer concentrations of about 6% w/v,[23,24] which is significantly lower than the monomer concentrations typically utilized for ATRP chemistry (45−50% w/v).[14,15] Given that essentially all the monomer is eventually converted into polymer, and that significant branching only occurs at a relatively late stage, the effective polymer concentration during branching is, to a first approximation, simply determined by the initial monomer concentration. Thus the *monomer* concentration can be used to assess whether the primary polymer chains generated for a given target degree of polymerization will be below, near or above their critical overlap concentration (c^*) when latent branching finally occurs.

^{1}H NMR and aqueous GPC were used to monitor the extent of BIEE quaternization of the PDMA chains at a PDMA concentration of 47.0% w/v (see Figures 1 and 2). The mean degree of quaternization was calculated by comparing the signal at 3.7 ppm due to the four pairs of oxyethylene protons (Figure 1, signals g and h) to that at 4.2 ppm due to the two pairs of oxyethylene protons on the PDMA chains (Figure 1, signal c). Light scattering GPC chromatograms obtained after various reaction times are shown in Figure 2. Significant branching only occurs when 82% of the iodoethyl groups on the BIEE brancher have reacted with the PDMA chains, with a large increase in polymer molecular weight only occurring above 97% conversion with respect to BIEE (see Table 1). Thus this latent branching behavior is very similar to that previously reported for the branching copolymerization of a methacrylic monovinyl monomer with a methacrylic divinyl monomer under ATRP conditions.[14,15] For the GPC data shown in Figure 2 and Table 1, there are *two* BIEE molecules per PDMA chain and gelation does eventually occur when the degree of quaternization exceeds 99.9%. However, if intermolecular branching had occurred

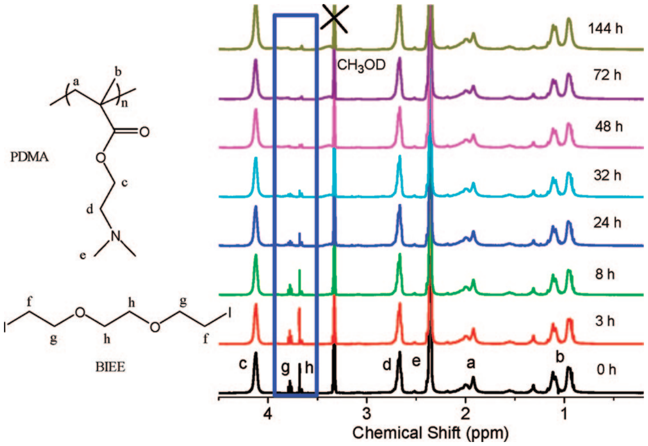

Figure 1. Evolution of ^{1}H NMR spectra recorded during post-polymerization quaternization of PDMA with BIEE at 25 °C. Conditions: 47% w/v PDMA in CD_3OD; BIEE:PDMA molar ratio = 2.0.

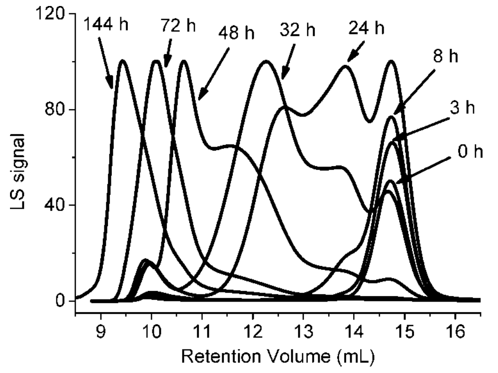

Figure 2. Light scattering GPC chromatograms recorded during the post-polymerization quaternization of PDMA with BIEE at 25 °C. Conditions: 47% w/v PDMA in d_4-methanol; BIEE:PDMA molar ratio = 2:1.

Table 1. Evolution of the Molecular Weight and Polydispersity During Post-Polymerization Quaternization of PDMA homopolymer (M_n = 11 800, M_w/M_n = 1.06 by THF GPC vs PMMA standards, RI signal; DP = 89 based on ^{1}H NMR analysis) with BIEE[a]

no.	time (h)	convn (%)	M_n	M_w	M_w/M_n
1	0	0	14 200	14 400	1.01
2	3	9	14 300	14 700	1.03
3	8	36	15 700	17 100	1.09
4	24	82	21 100	31 700	1.50
5	32	90	24 800	51 500	2.08
6	48	97	31 300	151 800	4.85
7	72	99.0	42 000	888 300	21.1
8	144	99.9	76 000	7 500 000	98.7

[a] Conditions: BIEE:PDMA molar ratio = 2.0; 47% w/v PDMA in methanol at 25°C.

exclusively, then in principle only *one* BIEE molecule should be required per PDMA chain for gelation. This suggests that up to 50% of the BIEE is consumed (wasted) in cyclization side-reactions under the conditions described in Figure 1.

In practice, quaternization of the PDMA chains using BIEE in methanol is quite slow: normally a few days are required to obtain highly branched copolymers at 25 °C (see Table 1). In view of this, we conducted a control experiment in which a methanolic solution of BIEE was monitored by ^{1}H NMR spectroscopy for more than 1 week at 25 °C. No spectral changes were observed, which confirmed that BIEE neither decomposes nor reacts with methanol on the time-scale of these branching quaternization reactions. Faster rates of quaternization can be readily achieved by using higher BIEE/PDMA molar ratios (See Table 2, Table S1, and Figure S1, Supporting Information). However, reactions under these conditions require judicious termination at lower conversions to avoid gelation.

Table 2. Evolution of Molecular Weight and Polydispersity for a Series of Branched PDMA Copolymers Obtained in the Presence of Increasing Amounts (mol %) of BIEE Branching Agent at 25°C[a]

entry no.	BIEE:PDMA molar ratio	M_n	M_w	M_w/M_n
1	0.00	14 200	14 400	1.02
2	1.05	16 500	18 700	1.13
3	1.74	18 400	22 900	1.24
4	3.55	24 800	43 600	1.76
5	5.36	31 400	100 900	3.21
6	7.10	36 500	2 227 300	61.02

[a] Conditions: PDMA concentration = 47% w/v; reaction time = 18 h.

Table 3. Evolution of the Molecular Weight and Polydispersity for a Series of Branched PDMA Polymers Obtained in the Presence of Increasing Amounts (mol %) of BIEE[a]

no.	BIEE:PDMA molar ratio	convn (%)	M_n	M_w	M_w/M_n
1	0	0	14 200	14 400	1.01
2	4.45	>99	17 700	20 850	1.18
3	8.9	>99	21 600	28 900	1.34
4	17.8	>99	36 100	89 500	2.48
5	26.7	>99	92 500	938 500	10.15
6	35.6	>99	cross-linked gel		

[a] Conditions: 7.3% w/v PDMA in methanol; reaction time = 28 days at 25°C.

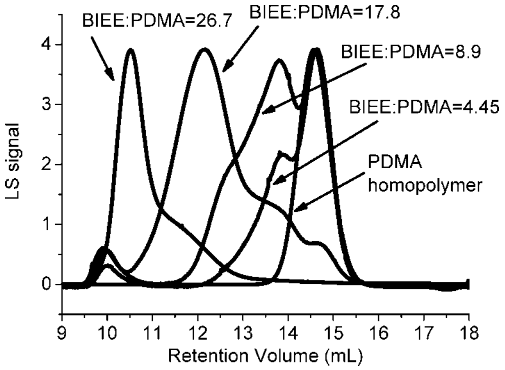

Figure 3. Light scattering GPC traces for the series of branched copolymers obtained in the presence of increasing amounts (mol %) of BIEE branching agent (see Table 3). PDMA concentration: 7.3% w/v. Time: 28 days at 25 °C.

As anticipated, the concentration of PDMA chains is clearly a key parameter in determining the relative probabilities of intermolecular branching and intramolecular cyclization in the BIEE quaternization of PDMA.[29] The experiments summarized in Figure 1 and Table 1 were conducted at 47.0% w/v PDMA. Lowering this PDMA concentration to 7.3% w/v clearly favors intramolecular cyclization, since a remarkable 26.7 BIEE molecules per PDMA chain can now be tolerated without causing gelation (see Table 3, Figure 3). Under these conditions it is obvious that the vast majority of the BIEE must be consumed in such cyclization side-reactions (see Table S2 and Figures S2, S3, and S4). This lower PDMA concentration was chosen because it is comparable to the relatively dilute solution conditions utilized in the synthesis of branched copolymers using either group transfer or oxyanionic copolymerization of DMA with EGDMA; see below.[23,24]

The critical overlap concentration, c^*, of a polymer is related to the molecular volume, V_m, and the radius of gyration, R_g, by the equation $c^* = (V_m/N_a)/R_g^3$. Thus

$$c^* = \frac{\frac{V_{\mathrm{m}}}{N_{\mathrm{a}}}}{R_{\mathrm{g}}^{\,3}} = \frac{\frac{M\times N}{d\times N_{\mathrm{a}}}}{\left(\frac{b\times(2N)^{0.6}}{\sqrt{6}}\right)^3} = \frac{M\times N}{d\times N_{\mathrm{a}}\times\left(\frac{b\times(2N)^{0.6}}{2.45}\right)^3}$$

where N_a is Avogadro's constant, N = mean degree of polymerization, $R_g = b \times ((2N)^{0.6})/(6^{0.5})$, and, taking the literature value for poly(methyl methacrylate), b is 0.65 nm. On the basis of the known molecular weight of the linear PDMA chains and assuming good solvent conditions, *c** is estimated to be around 10% w/v for our model system. Thus, when BIEE quaternization is conducted at a polymer concentration of 47% w/v PDMA (i.e., well above *c**), at least 50% of the reacting BIEE leads to intermolecular branching. Conversely, on reducing the PDMA concentration to 7.3%, which is just below *c**, the majority of the BIEE is consumed by intramolecular cyclization, since most of the PDMA coils do not interpenetrate each other in dilute solution.

According to the literature, ATRP syntheses of branched copolymers are normally conducted in more concentrated solution (e.g., 45% w/v,[14] 54% w/v,[15] or bulk[16]), which in each case corresponds to a polymer concentration well above *c**. Thus, near-ideal behavior is both expected and typically observed under these conditions. In contrast, the RAFT syntheses of branched vinyl copolymers described in the literature are usually conducted at relatively low concentrations, typically around 20% w/v,[22] which is quite similar to our estimated *c** values of 13−19% w/v for these formulations (Table 4). For example, Perrier's group reported that 1.74 branchers per chain could be employed without causing gelation, even at very high conversions (>98%).[22] This observation suggests that a significant degree of cyclization occurs under these synthesis conditions. Moreover, Taton and co-workers reported that, when acrylic acid was copolymerized with *N,N′*-methylenebisacrylamide [MBA] using RAFT chemistry at 20% w/v comonomer concentration, no gels were observed when using up to 2.5 MBA branchers per primary chain. Furthermore, up to 3.6 branchers per chain could be tolerated without inducing gelation for RAFT copolymerization of acrylamide with MBA at a comonomer concentration of 10 w/v %,[30] which is comparable to our estimated *c** of around 5% w/v for such a formulation. Finally, syntheses of branched PDMA−EGDMA copolymers prepared using oxyanionic copolymerization[24] or group transfer copolymerization[23] were typically conducted at about 6% w/v concentration, which is much lower than the *c** value of about 15% w/v calculated for such syntheses. In both cases strongly nonideal behavior was observed: up to 12.5 EGDMA brancher units per primary PDMA chain could be incorporated without causing gelation.

Thus there is clearly a strong correlation between increasingly nonideal behavior (i.e., suppression of the gel point) and the monomer concentration [M] utilized for these nonlinear copolymerizations. On the basis of our results obtained with the BIEE/PDMA model system, intramolecular cyclization is strongly favored when the monomer/polymer concentration is comparable to or lower than *c**, thus relatively high proportions of divinyl comonomer can be incorporated without causing macroscopic gelation. Similar concentration-dependent effects were reported by Macosko and co-workers for classical nonlinear copolymerizations conducted using conventional free radical chemistry.[31] The influence of both intramolecular cyclization and unequal monomer reactivities in determining the extent of branching/cross-linking for *nonliving* chain copolymerizations has been reviewed by Dusek.[29] Very recently, Gao and Matyjaszewski[32] investigated the effect of varying the monomer concentration on the relative degree of intermolecular branching/cross-linking compared to intramolecular cyclization. ATRP copolymerization of methyl acrylate and ethylene glycol diacrylate led to macroscopic gelation when conducted at higher monomer concentration (66% w/v), whereas the same formulation used at lower monomer concentration (11% w/v) produced soluble, branched copolymer. This difference was ascribed to enhanced intramolecular cyclization under dilute conditions. Gao and Matyjaszewski did not interpret their results in terms of a critical overlap concentration, but their experimental data are certainly consistent with the results reported herein with our model system.

We do not claim that, for a given target DP (and hence *c**), the polymer concentration is the *sole* factor that determines the extent of intermolecular branching relative to intramolecular cyclization. Obviously, other parameters such as reaction temperature, monomer type, branching comonomer and the precise nature of the copolymerization chemistry (radical, cationic, anionic, living radical, etc) are likely to affect the precise extent of cyclization in any given branched copolymer synthesis. Nevertheless, we believe that the model system described herein provides considerable insight and, moreover, allows apparently conflicting literature data to be rationalized.

Finally, we note that our results also have implications for the synthesis of shell cross-linked micelles. We have previously reported that various PDMA-based AB diblock and ABC triblock copolymer micelles can be readily cross-linked in aqueous solution using BIEE to quaternize the tertiary amine groups.[33–38] It is difficult to estimate the local concentration of the PDMA chains in such micelles, but we suggest that this is relatively high and most likely well above c*. Our model system data obtained at 47% w/v indicates that up to 50% of the BIEE may be wasted in such cross-linking reactions due to the

Table 4. Summary of Synthesis Conditions, Final Monomer Conversions, and Corresponding Estimated *c Values for Various Literature Syntheses of Branched Copolymers Conducted under (Pseudo)-Living Conditions[a]**

reaction mechanism (ref)	monomer type	DP	[M] (% w/v)	*C** (%)	final convn (%)	no. of branchers per chain
ATRP[14]	HPMA	50	45	14	>99	0.95
ATRP[15]	HPMA	50	54	14	>99	1.0
ATRP[16]	MMA	100	bulk	6	80	0.5
ATRP[17]	MMA	100	20	6	88	1.0
ATRP[19]	MA	50	54	8	~100	0.9
RAFT[22]	MMA	35	20	13	97	1.74
RAFT[22]	MMA	22	20	19	96.5	1.13
RAFT[30]	Am	81	10	5	>97	3.6
anionic[24]	DMA	50	6	15	90	12.5
GTP[25]	DMA	50	6	15	>99	4.3

[a] If c* is much less than the monomer concentration [M], then approximately ideal branching behavior is observed. However, if c* is comparable to (or greater than) [M], then non-ideal behavior is observed: more than one branching comonomer per chain can be tolerated without inducing gelation, because a significant proportion of the brancher is consumed via intramolecular cyclization. Key: HPMA, 2-hydroxypropyl methacrylate; MMA, methyl methacrylate; MA, methyl acrylate; Am, acrylamide; DMA, 2-(dimethylamino)ethyl methacrylate. See individual references for details of each branching divinyl comonomer.

formation of intramolecular cycles. Thus the target degree of cross-linking based on the initial BIEE/PDMA molar ratio is likely to be a significant overestimate of the actual degree of cross-linking achieved. Similar considerations should apply to other cross-linking chemistries such as carbodiimide coupling, esterification, Michael addition, etc.[39,40]

Conclusions

In summary, the synthesis of water-soluble cationic branched copolymers by quaternization of near-monodisperse poly[2-dimethylamino)ethyl methacrylate] chains using bis(2-iodoethoxy)ethane was reported. This model system is very useful for exploring the extent to which intermolecular branching is preferred over intramolecular cyclization as a function of polymer concentration and allows apparently contradictory literature data on branched copolymers prepared by living radical copolymerizations to be rationalized. Our results also have implications for the synthesis of shell cross-linked micelles.

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Supporting Information Available: Two additional tables of data obtained for BIEE quaternization at high (47% w/v) and low (7.3% w/v) PDMA concentration and four additional figures (three sets of GPC data and one set of ^{1}H NMR spectra) obtained under various conditions, i.e. varying BIEE/PDMA molar ratios, reaction times, and PDMA concentrations. This information is available free of charge via the Internet at http://pubs.acs.org

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