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Synthesis of Branched Water-Soluble Vinyl Polymers via Oxyanionic Polymerization

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ABSTRACT: A range of new water-soluble branched vinyl polymers have been synthesized by the statistical copolymerization of 2-(dimethylamino)ethyl methacrylate [DMA] with ethylene glycol dimethacrylate [EGDMA] under oxyanionic polymerization conditions (potassium benzyl alkoxide initiator, anhydrous THF, 50 °C). Advantages of using such living polymerization chemistry include (i) the ability to control the primary chain length simply by adjusting the comonomer/initiator molar ratio and (ii) the reduced probability of cross-linking due to improved control over the molecular weight distribution. In this study the mean degree of polymerization of the primary chains was fixed at 50, and the proportion of EGDMA branching agent was varied systematically. Gel permeation chromatography analysis indicated that soluble, high molecular weight DMA−EGDMA statistical copolymers were produced in most cases. The degree of branching increased monotonically as the proportion of EGDMA comonomer was increased, with Mark−Houwink α values as low as 0.25 being obtained. Using higher levels of EGDMA led to lower comonomer conversions; this is believed to be due to the increased solution viscosity rather than copolymerizability problems. No macrogelation was observed even at relatively high levels of EGDMA brancher (up to 25 mol %). In principle, more than one brancher per primary chain should be sufficient to cause cross-linking and hence macrogelation. Thus, this anomalous result was attributed to the relatively high probability of intramolecular cyclization of the EGDMA comonomer occurring under oxyanionic polymerization conditions. It is likely that complexation between the EGDMA comonomer and the potassium cation enhances this cyclization side reaction.

Introduction

In 1997, Nagasaki and co-workers reported[1] the controlled homopolymerization of a tertiary amine methacrylate, 2-(diethylamino)ethyl methacrylate (DEA), using potassium ethoxide in THF at or above ambient temperature. Similarly, a potassium 4-vinylbenzyl alkoxide initiator led to the formation of well-defined, styrene-capped, DEA-based macromonomers (M_w/M_n < 1.30, with lower polydispersities being obtained at higher temperature); such selectivity is not possible using classical anionic polymerization. Recently, we extended[2] these macromonomer syntheses to include other tertiary amine methacrylates, such as 2-(dimethylamino)ethyl methacrylate (DMA), 2-(*N*-morpholino)ethyl methacrylate (MEMA), and 2-(diisopropylamino)ethyl methacrylate (DPA). In particular, styrene-capped DMA macromonomers have been used as reactive polymeric stabilizers for the synthesis of polystyrene latexes[3] and pH-responsive microgels.[4] The living character of this oxyanionic polymerization chemistry was demonstrated by synthesizing reasonably well-defined diblock or triblock copolymers.[5] Fluorescently labeled diblock copolymers were also synthesized using a pyrene-functionalized initiator and subsequently used to gain greater understanding of the molecular reorganization of surface-adsorbed micelles on planar surfaces.[6]

The present paper explores the synthesis of branched water-soluble polymers by modifying the route pioneered by Sherrington and co-workers for conventional radical polymerization.[7] In this approach a chain regulating agent such as a mercaptan is used to reduce the primary chain length. Provided that there is only one branching agent [e.g., ethylene glycol dimethacrylate (EGDMA) or divinylbenzene] per chain, macrogelation is suppressed and soluble branched polymers can be prepared.[8] Since oxyanionic polymerization has living character, the primary chain length can be controlled by simply adjusting the monomer/initiator molar ratio. Moreover, the relatively narrow molecular weight distributions that are inherent to living polymerizations should enable higher levels of branching agent to be tolerated without macrogelation, since there are significantly fewer higher molecular weight polymer chains in the distribution. Herein we examine the oxyanionic polymerization of a hydrophilic monomer, DMA, in the presence of EGDMA as a route to weakly basic polyelectrolytes with highly branched architectures (see Figure 1).

Experimental Section

THF was dried with sodium wire for 3 days and subsequently refluxed in the presence of sodium. It was distilled under nitrogen just prior to use. DMA (98%), EGDMA (98%), MMA (99%), benzyl alcohol (99.8%), potassium *tert*-butoxide (1.0 M in THF), potassium metal (98%; under mineral oil), AIBN (98%), and naphthalene (>99%) were obtained from Aldrich. All monomers were passed through basic alumina columns, stirred over calcium hydride for 24 h, stored at −9 °C, and distilled immediately prior to use. All other reagents were used as received. Polymerizations were carried out under dry nitrogen. Glassware was heated overnight at 150 °C before assembly and then further heated under vacuum to eliminate surface moisture. Liquid reagents were handled using standard Schlenk techniques.

Instrumentation. All ^{1}H NMR spectra were recorded using a 300 MHz Bruker Avance DPX300 spectrometer. A Polymer Laboratories PL-GPC50 integrated gel permeation chromatography (GPC) system was used to analyze the branched copolymers. Linear and branched DMA polymers were characterized by GPC. The setup was as follows: two 5 μm (30 cm) mixed "C" columns, a WellChrom K-2301 refractive index

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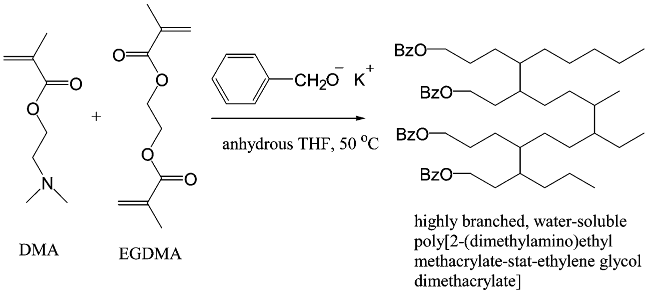

Figure 1. Reaction scheme for the statistical copolymerization of 2-(dimethylamino)ethyl methacrylate [DMA] with an ethylene glycol dimethacrylate branching agent [EGDMA] in THF at 50 °C using a potassium benzyl alkoxide initiator.

detector operating at 950 ± 30 nm, a Precision detector PD 2020 light scattering detector operating at 685 nm and 20 mW (with two scattering angles of 90° and 15°, respectively), and a BV400RT viscosity detector. THF containing 2% triethylamine was employed as an eluent at 30 °C using a flow rate of 1.0 mL min^{-1}. Molecular weights of the branched polymers were determined by the triple detection method using PL Cirrus Multi online software (version 2.0) supplied by Polymer Laboratories. A series of near-monodisperse linear PMMA standards (purchased from Polymer Labs) were used to construct the calibration curve. The refractive index increments (d*n*/d*c*) of the branched copolymers were determined in THF using an Optilab differential refractometer operating at 633 nm.

DMA Homopolymer Synthesis via Conventional Free Radical Bulk Polymerization. DMA monomer (15.0 g, 0.095 mol) was introduced into a dry 100 mL Schlenk flask together with a magnetic stir bar. After purging with nitrogen for 30 min, 0.15 g of AIBN (0.913 mmol) initiator was added to this flask under nitrogen. The flask was then immersed to a preheated oil bath at 70 °C. After ≈1.5 h, ^{1}H NMR analysis indicated that more than 90% of the DMA had been polymerized. (The vinyl signals between δ 5.5 and 6.0 were compared to that of the CH_3 group at δ 0.5−1.5.) The crude homopolymer was then dissolved in a small amount of THF and precipitated into a large excess of *n*-heptane to remove any unreacted DMA monomer. The purified DMA homopolymer was dried under vacuum to remove traces of solvent and characterized by THF GPC using PMMA standards (see entry 1 in Table 1).

Preparation of Potassium Naphthalene Complex. Potassium metal (0.39 g, 0.010 mol) in mineral oil was placed in a preweighed round-bottomed flask along with a magnetic stirrer and dried under nitrogen after washing four times with anhydrous *n*-pentane. After addition of THF (30 mL), a 2-fold molar excess of naphthalene (5.12 g, 0.040 mol) was added under a nitrogen atmosphere. The suspension was stirred until all the potassium had reacted to produce a dark green complex.

Branched Copolymers via Statistical Copolymerization of DMA with EGDMA. THF (80 mL) was introduced into a dry 250 mL Schlenk flask together with a magnetic stir bar. Benzyl alcohol (0.072 mL, 0.70 mmol) was added to this flask via syringe, and this solution was heated to 50 °C prior to titration using a freshly prepared potassium−naphthalene complex. When the color of this solution became slightly green and persisted for 3 min, the appropriate amounts of DMA (5.60 mL, 33.2 mmol) and EGDMA (0.35 mL, 1.75 mmol) were added to the flask using a double-tipped needle. The polymerizing solution was stirred for 3 h before quenching with methanol. The final reaction solution was passed through a basic alumina column and then precipitated into excess *n*-heptane three times to remove the excess naphthalene. The copolymer was then dried under high vacuum to give a slightly yellow solid. Overall yields usually exceeded 90% (entry 6 in Table 1). Aliquots for kinetic analysis were removed from the polymerizing solution using a degassed syringe after appropriate intervals and analyzed without further purification.

Polymerizations using the potassium *tert*-butoxide initiator were carried out as follows. Potassium *tert*-butoxide (1.25 mL of a 1.0 M solution in THF; Aldrich) was added to a 100 mL flask that contained 50 mL of dry THF. Freshly distilled monomer was then added to this initiator solution, and the same protocol as that described for the potassium benzyl alkoxide syntheses was employed.

Statistical Copolymerization of DMA with MMA by Oxyanionic Polymerization. THF (100 mL) was introduced into a dry 250 mL Schlenk flask together with a magnetic stir bar. Benzyl alcohol (0.15 mL, 1.40 mmol) was added to this flask via syringe, and this solution was heated to 50 °C prior to titration using a freshly prepared potassium−naphthalene complex. When the color of this solution became slightly green and persisted for 3 min, the appropriate amounts of DMA (9.40 mL, 56.0 mmmol) and MMA (1.46 mL, 14.0 mmol) were added to the flask using a double-tipped needle. The polymerizing solution was stirred for 30 min before quenching with methanol, ^{1}H NMR studies indicated a monomer conversion of more than 99%. (The vinyl signals between δ 5.5 and 6.0 were compared to that of the CH_3 group at δ 0.5−1.5.) The final reaction solution was precipitated into excess *n*-heptane three times to remove the excess naphthalene. The resulting DMA_{40}−MMA_{10} statistical copolymer was then dried under high vacuum to give a slightly yellow solid. The overall isolated yield exceeded 90% (9.2 g).

Homopolymerization of MMA by Oxyanionic Polymerization. THF (100 mL) was introduced into a dry 250 mL Schlenk flask together with a magnetic stir bar. Benzyl alcohol (0.22 mL, 2.0 mmol) was added to this flask via syringe, and the resulting solution was heated to 50 °C prior to titration using a freshly prepared potassium−naphthalene complex. When the color of this solution became slightly green and persisted for 3 min, the appropriate amount of MMA (10.4 mL, 100 mmol, target Dp = 50) was added to the flask using a double-tipped needle. The polymerizing solution was stirred for 2 h before quenching with methanol. The final reaction solution was precipitated into excess *n*-heptane three times to remove the excess naphthalene. The resulting poly(methyl methacrylate) was then dried under high vacuum to give a white solid in an overall yield of more than 90% (9.1 g).

Results and Discussion

Background. Although oxyanionic polymerization can be used to polymerize nitrogen-containing monomers such as DMA, it is not normally considered to be applicable to conventional (nonfunctional) methacrylic monomers such as methyl methacrylate.[1,9,10] According to Nagasaki and co-workers, the only monomers that undergo oxyanionic polymerization are those that contain a suitable heteroatom such as DMA.[1] This is apparently because the heteroatom (in this case nitrogen) complexes with the potassium counterion and makes the oxyanionic species more reactive toward polymerization. Our earlier attempted oxyanionic polymerization[2] of nonfunctional monomers such as methyl methacrylate at ambient temperature gave induction periods, rapid uncontrolled polymerizations, and broad molecular weight distributions ($M_w/M_n > 2.0$). Thus, one of our initial concerns in the present study was whether DMA would actually copolymerize efficiently with the EGDMA branching agent under oxyanionic polymerization conditions. One obvious option would have been to synthesize a branching agent containing an appropriate nitrogen heteroatom; for example, *N*-ethyldiethanolamine could be reacted with excess methacryloyl chloride to produce a new dimethacrylate branching agent that should be amenable to oxyanionic copolymerization with DMA. Fortunately, our exploratory experiments confirmed that the EGDMA branching agent copolymerized readily with DMA. This observation is perhaps not too surprising since Nagasaki and co-workers have had some limited success in using methacrylic monomers that contain oxygen heteroatoms.[11]

Table 1. Summary of Reaction Conditions, Molecular Weights, and Polydispersities for the Synthesis of Branched Copolymers by the Statistical Copolymerization of 2-(Dimethylamino)ethyl Methacrylate (DMA) with Ethylene Glycol Dimethacrylate (EGDMA) at 50 °C Using Either Potassium Benzyl Alkoxide or Potassium *tert*-Butoxide in Anhydrous THF[a]

entry no.	target structure (subscript = Dp)	EGDMA (mol %)	time (h)	conv (%)	d*n*/dc	EGDMA (mol %)	Dp[b]	M_n	M_w	M_w/M_n	α
1	PDMA (AIBN initiator)*	0	0.5	80	0.081			131 000	216 000	1.65	0.61
2	Bz-DMA_{50}	0	0.5	100			56	8 600	10 100	1.18	0.59
3	*t*-Bu-DMA_{50}	0	0.5	100				9 300	14 400	1.55	0.58
4	*t*-Bu-DMA_{46}−$EGDMA_{4.0}$	8	3.0	99		11		30 600	146 000	4.79	0.35
5	Bz-DMA_{49}−$EGDMA_{1.0}$	2	3.0	>99.9	0.082	3	51	31 500	45 000	1.42	0.55
6	Bz-$DMA_{47.5}$−$EGDMA_{2.5}$	5	3.0	>99	0.083	6	44	37 000	54 000	1.45	0.41
7	Bz-DMA_{46}−$EGDMA_{4.0}$	8	3.0	98	0.082	10	46	71 500	152 000	2.13	0.37
8	Bz-DMA_{45}−$EGDMA_{5.0}$	10	3.0	96	0.080	14	44	114 000	329 000	2.89	0.33
9	Bz-$DMA_{42.5}$−$EGDMA_{7.5}$	15	3.0	95	0.079	21	48	210 000	751 000	3.58	0.30
10	Bz-$DMA_{37.5}$−$EGDMA_{12.5}$	25	3.0	90	0.079	33	43	633 000	3 890 000	6.14	0.25
11	Bz-DMA_{30}−$EGDMA_{20.0}$	40	3.0	81							

[a] The first three entries refer to DMA homopolymerizations only and are included for comparative purposes. Other symbols are defined in the main text. [b] Entry 1 is a linear PDMA homopolymer synthesized by conventional bulk free radical polymerization using AIBN initiator at 70 °C.

Homopolymer Syntheses. In our preliminary experiments two initiators, potassium *tert*-butoxide and potassium benzyl alkoxide, were employed for the oxyanionic homopolymerization of DMA. The results are summarized in Table 1. Although the commercial availability of potassium *tert*-butoxide suggests that it might be the preferred reagent, relatively high polydispersities ($M_w/M_n > 1.50$) were always obtained with this initiator, which is consistent with our earlier study.[5] The DMA homopolymer obtained with this initiator had an M_n of 9300, as determined by the triple detection method. In contrast, DMA homopolymer obtained using the potassium benzyl alkoxide initiator had a much lower polydispersity ($M_w/M_n = 1.18$), and its M_n of 8600 was closer to the theoretical value expected from the monomer/initiator molar ratio ($M_n = 7850$). Therefore, polymerizations initiated by potassium benzyl alkoxide have significantly better living character than those initiated by potassium *tert*-butoxide. Moreover, the former initiator produces polymers with terminal aromatic groups, which allows end group analysis by ^{1}H NMR to obtain the mean degree of polymerization of the primary chains. Both initiators gave very fast polymerizations, with all the DMA monomer being consumed within 0.5 h according to ^{1}H NMR studies (as judged by the complete disappearance of the vinyl signals). The Mark−Houwink α exponents of the two linear DMA homopolymers were found to be 0.58 and 0.59, respectively. However, these values were not particularly reliable due to the relatively narrow polydispersities and low molecular weights of these homopolymers. To obtain a more accurate Mark−Houwink exponent, DMA was polymerized in the bulk at 70 °C using an AIBN initiator to obtain a linear, polydisperse homopolymer with an M_n of 131 000 and an α exponent of 0.61 (see Table 1).

Branched Copolymer Synthesis. EGDMA is widely employed as a cross-linker to prepare hydrogels, and it is also suitable for the synthesis of branched polymers by conventional radical polymerization.[7] Although EGDMA does not contain a nitrogen heteroatom, our initial attempt to make DMA-based branched copolymers using this comonomer with the potassium *tert*-butoxide initiator was quite encouraging (see Table 1 and Figure 2). The overall target degree of polymerization was 50 (i.e., 46 DMA and 4 EGDMA units), and more than 99% conversion was achieved after 3 h at 50 °C. Compared to the corresponding linear DMA homopolymer, this statistical copolymer has a significantly higher molecular weight ($M_w = 30\,600$) and a much higher polydispersity ($M_w/M_n = 4.79$). More importantly, the Mark−Houwink α exponent of this DMA−EGDMA copolymer was only 0.35, which is substantially lower than that obtained for linear DMA homopolymer prepared in the absence of any EGDMA (α = 0.58−0.61, depending on the synthesis method). This low α value is consistent with a highly branched copolymer architecture.

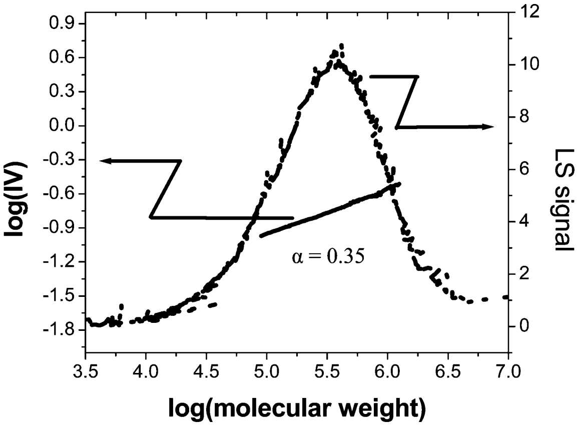

Figure 2. Mark−Houwink plot and light scattering signal of the branched poly[2-(dimethylamino)ethyl methacrylate-*stat*-ethylene glycol dimethacrylate] [DMA_{46}−$EGDMA_{4.0}$] copolymer obtained by oxyanionic polymerization using the potassium *tert*-butoxide initiator (see entry no. 4 in Table 1).

On the basis of the preliminary results obtained above, a series of polymerizations using the preferred potassium benzyl alkoxide initiator were carried out to obtain more systematic information (see Table 1 and Figure 3). For the homopolymerization of DMA in the absence of any EGDMA, the reaction solution became slightly yellow within a few minutes of addition of DMA. In contrast, the polymerizing solution became milky immediately on addition of the DMA/EGDMA mixture and gradually became transparent with a slightly yellow coloration over a period of a few minutes. This initial solution turbidity persisted longer when higher levels of EGDMA were used, with up to 25 min being required for the 25 mol % EGDMA polymerization to become transparent (see entry 10 in Table 1). Soluble branched copolymers were obtained for entries 5−10. However, at 40 mol % EGDMA, some macrogelation was observed (see entry 11 in Table 1).

The formation of linear DMA homopolymer in the absence of any EGDMA is very fast under oxyanionic

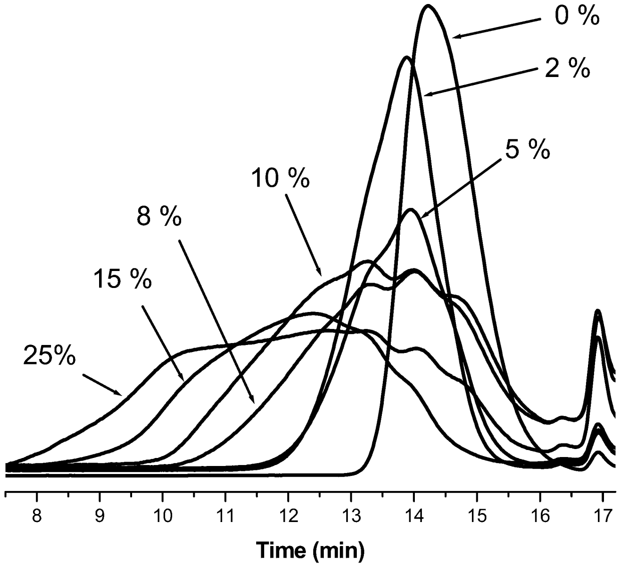

Figure 3. Gel permeation chromatography traces for branched copolymers obtained from the statistical copolymerization of 2-(dimethylamino)ethyl methacrylate [DMA] with varying proportions of ethylene glycol dimethacrylate [EGDMA] brancher. See Table 1 for detailed polymerization conditions.

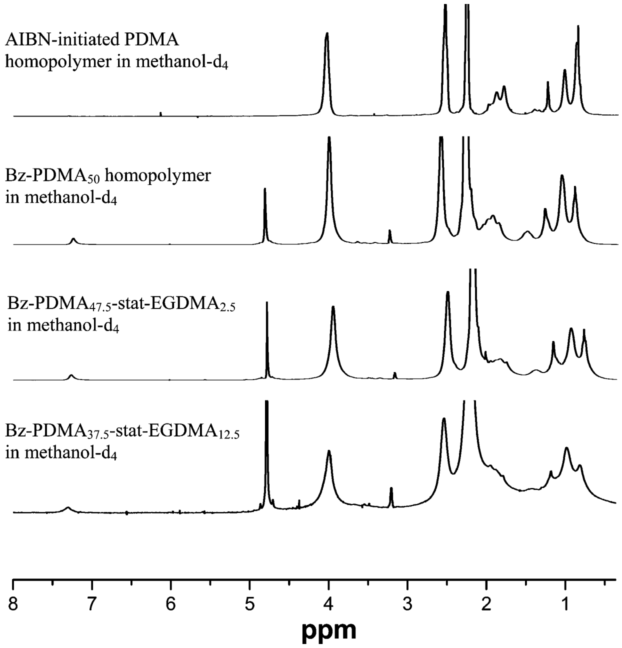

Figure 4. Typical ^{1}H NMR spectra (methanol-d_4) recorded for two linear poly[2-(dimethylamino)ethyl methacrylate] samples (upper two spectra) and two branched poly[2-(dimethylamino)ethyl methacrylate-*stat*-ethylene glycol dimethacrylate] samples (lower two spectra). Note the presence of the aromatic benzyl signal at 7.0−7.5 ppm in the spectra of the three polymers that were prepared by oxyanionic polymerization. This end group was used to calculate the mean degrees of polymerization of the primary chains in each case.

polymerization conditions at 50 °C: no vinyl signals are observed by ^{1}H NMR after only 15−20 min, which indicates complete consumption of the DMA monomer on this time scale. In contrast, a progressive decrease in the rate of polymerization with increasing proportions of EGDMA was observed in the branched copolymer syntheses (see Table 1). At low or zero EGDMA contents, the statistical copolymerization of DMA with EGDMA was essentially complete within 3 h at 50 °C as judged by ^{1}H NMR. However, a systematic reduction in final conversion was observed above 8 mol % EGDMA. For example, at an EGDMA content of 40 mol %, the overall comonomer conversion was only 80% after 3 h (entry 11 in Table 1). There are two possible explanations for the reduced conversions obtained at higher levels of EGDMA branching agent. First, the viscosity of the polymerizing solution is obviously significantly higher for the high molecular weight branched copolymers compared to the relatively low molecular weight linear homopolymer; this is likely to retard the rate of polymerization. Second, the copolymerizability of EGDMA with DMA may be less favored at higher levels of EGDMA.

To explore the second hypothesis, we decided to test the statistical copolymerization of DMA with a methacrylic comonomer that did not contain a nitrogen heteroatom. Thus, DMA was copolymerized with methyl methacrylate (MMA) under oxyanionic polymerization conditions in the absence of any EGDMA brancher. Targeting a degree of polymerization of 50, 20 mol % MMA was successfully copolymerized with DMA to give the desired DMA−MMA statistical copolymer at very high conversion (at least 99%) within 0.5 h at 50 °C. GPC analysis of this copolymer indicated an M_n of 9100 and a polydispersity of 1.18. Lascelles et al.[2] had previously reported that the homopolymerization of MMA under oxyanionic polymerization conditions at 20 °C had poor living character: an induction period of 10 min was observed, followed by rapid, uncontrolled polymerization to produce poly(methyl methacrylate) with a high polydispersity ($M_w/M_n > 2.0$). However, we felt that it was prudent to repeat this control experiment at the same temperature used for the statistical copolymerization of DMA with MMA in case this higher polymerization temperature improved the living character of the MMA polymerization.[1] At 50 °C, poly(methyl methacrylate) with an M_n of 13 100 (target $M_n = 5000$) and an M_w/M_n of 1.74 was obtained at almost 100% conversion. The relatively high polydispersity again indicated poor living character, and the high M_n suggested poor initiator efficiency under these conditions. Thus, although oxyanionic polymerization does not allow the controlled homopolymerization of MMA,[2] it can nevertheless tolerate relatively high proportions of MMA comonomer in statistical copolymerizations. This suggests that the slower, less complete copolymerizations observed for the DMA/EGDMA branched copolymer syntheses are most likely simply due to the increased solution viscosity, rather than copolymerizability problems.

All copolymers were purified by several precipitations from THF solution using excess *n*-heptane. This ensured complete removal of the excess naphthalene as judged by ^{1}H NMR. Once this aromatic impurity was removed, ^{1}H NMR could be used to calculate the mean degree of polymerization of the primary chains of the DMA−EGDMA branched copolymers: the integrated signal due to the five aromatic protons of the terminal benzyl group was compared to that of the methylene groups of the methacrylic backbone. A typical ^{1}H NMR spectrum is shown in Figure 4. For comparison, the ^{1}H NMR spectrum of the DMA homopolymer prepared by normal radical polymerization using AIBN as initiator is also shown in Figure 4. As expected, there is no aromatic signal at 7−8 ppm for the AIBN-initiated DMA homopolymer. The calculated degree of polymerization (Dp) for the branched DMA−EGDMA copolymer synthesized using the potassium benzyl alkoxide initiator is shown in Table 1. The calculated Dp values all lie between 44 and 56. Given the experimental errors involved (e.g., accurate dispensing of small volumes of initiator solution in the oxyanionic polymerization syntheses as well as the uncertainties involved in NMR integration), these values are in reasonably good agreement with the target Dp of 50. Actually, when due allowance is made for the incomplete conversions, the experimental Dp values are generally closer to the theoretical values. If the EGDMA comonomer had not copolymerized properly with the DMA, the molecular weights and polydispersities obtained by GPC should be similar to those of the linear DMA homopolymer obtained by oxyanionic polymerization in the absence of any EGDMA. However, it is evident from Table 1 that all the polymers prepared in the presence of EGDMA have much higher molecular weights and significantly broader molecular weight distributions; this suggests that branched DMA−EGDMA copolymers have been produced as expected.

^{1}H NMR spectra of the branched DMA−EGDMA statistical copolymers recorded in d_4-methanol suffered from poor spectral resolution due to severe peak overlap problems (see Figure 4). Thus, the copolymers were dissolved in 0.1 M DCl in D_2O (spectra not shown). In this solvent mixture, an NMR signal at 4.0−4.5 ppm was assigned to the two oxymethylene protons of the DMA residues, while the signal at 3.3−3.7 ppm is due to the two azamethylene protons of the DMA residues and also the two oxymethylene protons of the EGDMA residues. Peak integration and comparison of these signals allowed estimation of the EGDMA contents of the DMA−EGDMA branched copolymers. The results are summarized in Table 1. Perhaps surprising, the EGDMA contents estimated from this NMR analysis are always somewhat higher than the values expected from the comonomer feed ratios. At first sight this suggests that there is no copolymerizability problem with the EGDMA comonomer under oxyanionic polymerization conditions, which is consistent with the conclusion that the reduced monomer conversions observed at higher levels of EGDMA are simply due to retarded rates of polymerization caused by the relatively high solution viscosities. However, it should be emphasized that the NMR peak integration errors increase at higher EGDMA contents due to the progressively poorer spectral resolution.

Although the EGDMA content of the branched copolymers varies significantly, the presence of this comonomer has little or no effect on the differential refractive index increments (d*n*/d*c*) determined in THF (see Table 1). Increasing the EGDMA content of the comonomer feed led to a monotonic increase in the M_w values and polydispersities obtained by light scattering GPC analysis (see Figure 3 and Table 1). The highest M_w value obtained for these soluble DMA−EGDMA statistical copolymers was 3.89×10^6 (with a corresponding polydispersity of 6.14). These results are generally comparable to those reported by Sherrington and co-workers[7] for branched poly(methyl methacrylate)s prepared by conventional radical polymerization, who reported M_w values in the range of 1.55×10^4−3.77×10^6. However, the polydispersities reported by Sherrington and co-workers are appreciably higher, typically ranging from 2.65 to 32, with one example of up to 238. Presumably, the generally lower polydispersities achieved in the present study are attributable to the living character of the oxyanionic polymerization, which allows much better control over the molecular weight distribution. This hypothesis is supported by the results reported by Muller and co-workers, who used self-condensing vinyl polymerization (either group transfer polymerization[12] or atom transfer radical polymerization,[13,14] both of which have living character[15,16]) to make branched polymers. Their polydispersities range from 1.6 to 6.24, which are comparable to our data and are significantly narrower than Sherrington's data.

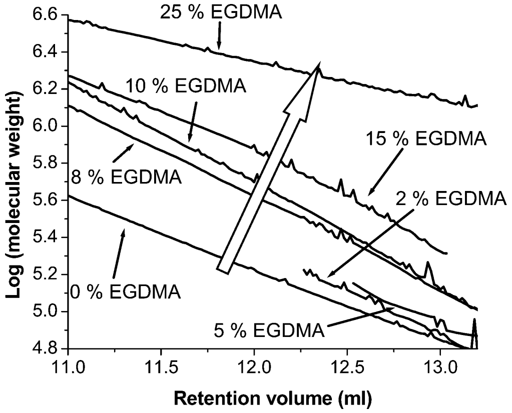

Figure 5. Relationship between log(molecular weight) and retention volume for a series of branched DMA−EGDMA statistical copolymers obtained by oxyanionic polymerization at varying EGDMA brancher contents (mol %). See Table 1 for detailed polymerization conditions.

It is well known that branched polymers have more compact structures in solution compared to linear polymers of the same molecular weight, since higher levels of branching lead to smaller hydrodynamic volumes. GPC analysis is only sensitive to changes in hydrodynamic volume. This means that linear polymer chains of a given molecular weight cannot be distinguished from higher molecular weight branched chains, since these species could in principle elute at the same retention volume.[7] Figure 5 shows the relationship between log(molecular weight) and retention volume for the branched DMA−EGDMA statistical copolymers prepared by oxyanionic polymerization. The M_w data were determined by light scattering and hence are absolute values. From Figure 5, we can see that, for a given retention volume, each of the branched DMA−EGDMA statistical copolymers have higher molecular weights than the linear polydisperse DMA homopolymer prepared using the AIBN initiator. Moreover, the molecular weight increases monotonically with increasing EGDMA brancher content. These results strongly suggest a systematic increase in the degree of branching of these DMA−EGDMA copolymers with increasing EGDMA content.

Branched polymers are always less viscous compared to the equivalent linear homopolymers, which leads to lower Mark−Houwink α values for branched polymers. Figure 6 shows the Mark−Houwink plots obtained for the branched DMA−EGDMA statistical copolymers prepared by oxyanionic polymerization. The calculated α values lie in the 0.25−0.55 range (see Table 1). Higher levels of EGDMA brancher lead to a monotonic decrease in α, with the lowest α value being 0.25. In contrast, α is typically 0.6−0.8 for linear homopolymers adopting a random coil conformation in a good solvent;[17] this is exemplified by an α value of 0.61 obtained for PDMA homopolymer in THF (see entry 1 in Table 1). For most

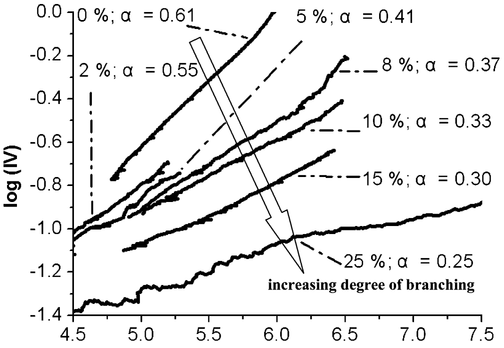

Figure 6. Mark−Houwink plots for a series of branched DMA−EGDMA statistical copolymers prepared by oxyanionic polymerization at varying EGDMA brancher contents (mol %). See Table 1 for detailed polymerization conditions. A polydisperse linear DMA homopolymer (entry no. 1 in Table 1) synthesized by conventional radical polymerization is included as a reference.

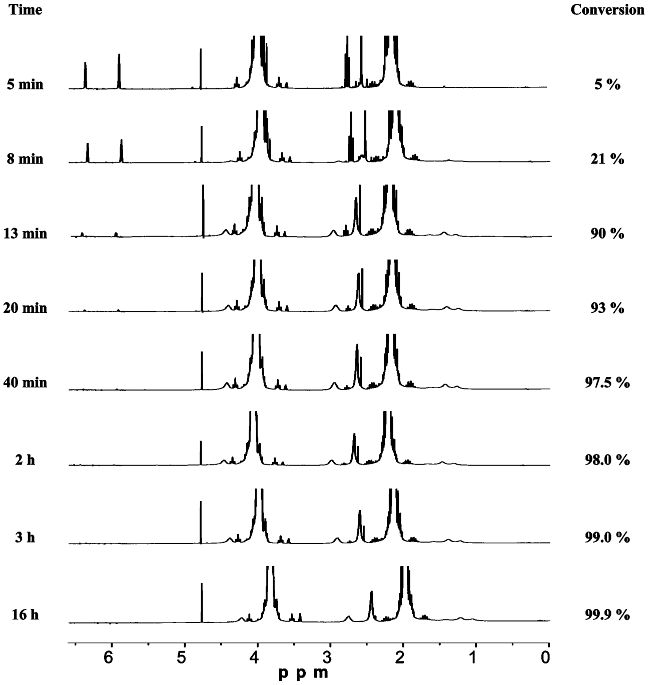

Figure 7. ^{1}H NMR spectra recorded during the synthesis of a Bz-DMA$_{46.5}$−EGDMA$_{3.5}$ branched copolymer by oxyanionic polymerization.

branched polymers, literature values of α normally lie the range of 0.20−0.50,[14] although α values as low as 0.08 have been claimed for branched polymers prepared by self-condensing vinyl polymerization.[17]

Kinetic Studies. To monitor the oxyanionic polymerization of the branched copolymers, aliquots for kinetic analysis were removed from the polymerizing solution using a degassed syringe after appropriate intervals. The samples were then analyzed by ^{1}H NMR, together with triple detection THF GPC. A typical series of ^{1}H NMR spectra are shown in Figure 7 for a branched copolymer with a final target composition of DMA$_{46.5}$−EGDMA$_{3.5}$ (7 mol % EGDMA; entry not shown in Table 1). Compared with the homopolymerization of DMA, an induction period of 2−3 min was observed, since no copolymer was formed initially and the monomer conversion was only 5% after 5 min. However, rapid copolymerization then occurred, since the monomer conversion reached 90% after 13 min. Thereafter, the rate of copolymerization became much slower. On the basis of our earlier discussion, this is more likely to be due to the relatively high solution viscosity rather than due to copolymerizability problems associated with the EGDMA comonomer under oxyanionic polymerization conditions. The evolution of the GPC chromatograms for the same branched DMA$_{46.5}$−EGDMA$_{3.5}$ statistical copolymer is shown in Figure 8. Initially, the polydispersity is relatively narrow, but after 8 min (21%) it has increased significantly, indicating the early onset of branching during this copolymerization.

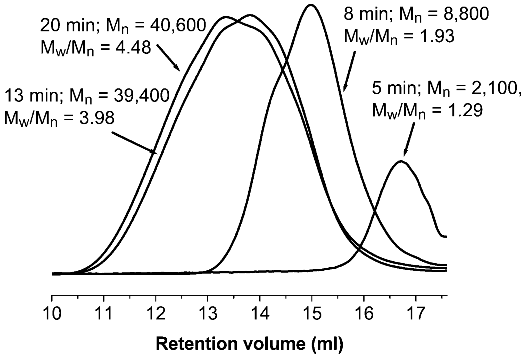

Figure 8. GPC chromatograms obtained after various reaction times during the synthesis of a Bz-DMA$_{46.5}$−EGDMA$_{3.5}$ branched copolymer via oxyanionic polymerization.

Compared to conventional free radical polymerization,[7] oxyanionic polymerization syntheses under branching conditions can tolerate remarkably high levels of EGDMA (up to 25 mol %) without macrogelation being observed. Sherrington and co-workers recently reported[8] similar results for branched methacrylic copolymers prepared by either group transfer polymerization or atom transfer radical polymerization using EGDMA comonomer. We believe that these observations are related to the known propensity for EGDMA to undergo intramolecular cyclization, in addition to intermolecular branching.[18] According to Nagasaki and co-workers,[1,11] a prerequisite for the controlled oxyanionic polymerization of methacrylates is that the monomer contains a suitable heteroatom such as nitrogen. This heteroatom apparently coordinates to the potassium cation and leads to a more reactive oxyanion, which is capable of attacking the vinyl group of the methacrylic monomer.[1] Although nitrogen heteroatoms give the best results, oxyanionic polymerization is also known for methacrylic monomers that contain an oxygen heteroatom.[11] Thus, it is likely that the second oxygen heteroatom of the EGDMA comonomer coordinates with the potassium cation, as shown in Figure 9. If such complexation occurs, it will ensure that the unreacted pendent methacrylic group of the EGDMA is in close proximity to the propagating enolate anion chain end. Thus, such complexation is likely to favor formation of a nine-membered ring via intramolecular cyclization, rather than intermolecular branching. Although this tentative hypothesis is based on literature precedent rather than direct experimental evidence, it is consistent with the unexpected observation that remarkably high amounts of EGDMA can be copolymerized with DMA without causing macrogelation. It is worth noting that Macosko and co-workers have reported experimental evidence for some degree of intramolecular cyclization occurring during the free radical copolymerization of MMA with EGDMA.[18] Thus, the complexation hypothesis outlined above is invoked to explain why intramolecular cycliza-

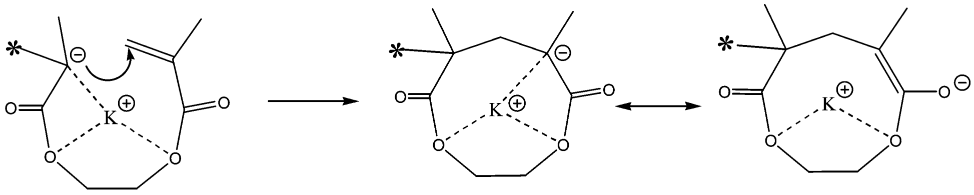

Figure 9. Suggested interaction between the potassium cation and the EGDMA branching agent during oxyanionic polymerization. If this complexation occurs, it should favor intramolecular cyclization, as opposed to intermolecular branching. The asterisk indicates the rest of the polymer chain.

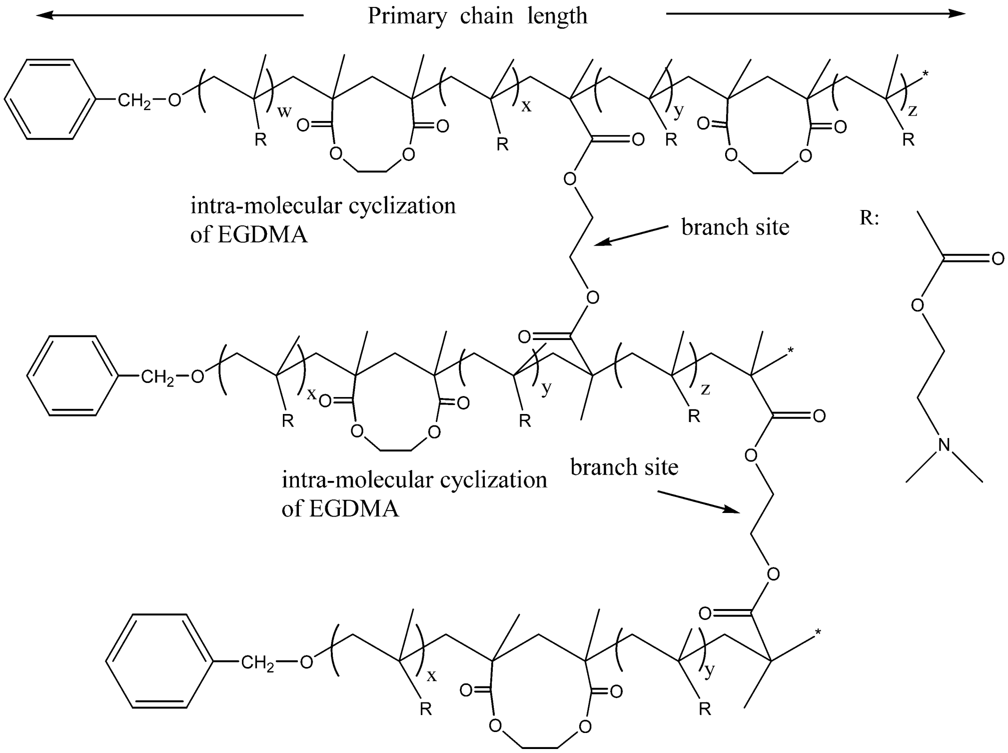

Figure 10. Chemical structure proposed for the branched DMA−EGDMA statistical copolymers prepared via oxyanionic polymerization. Each branched copolymer comprises near-monodisperse primary chains randomly linked by the EGDMA brancher.

tion is much more prevalent in oxyanionic polymerizations compared to conventional free radical polymerizations, rather than to rationalize the occurrence of intramolecular cyclization per se.

On the other hand, if most of the EGDMA acted as a branching comonomer and the two vinyl groups polymerized independently, a significant proportion of pendent vinyl groups should be observed in the ^{1}H NMR spectrum of the branched copolymer. Figure 4 shows the ^{1}H NMR spectrum of Bz-PDMA$_{37.5}$-*stat*-EGDMA$_{12.5}$. The total conversion is only 80%. However, after purification only very weak vinyl signals were observed, which is consistent with our hypothesis that most of the EGDMA copolymerizes intramolecularly under oxyanionic polymerization conditions rather than acting as a branching agent. Thus, the likely chemical structure of the branched DMA-*stat*-EGDMA copolymers obtained via oxyanionic polymerization under the conditions described in this work is shown in Figure 10.

Conclusions

EGDMA was used as a branching agent to synthesize a series of DMA-based polyelectrolytes with highly branched architectures via oxyanionic polymerization. Potassium *tert*-butoxide and potassium benzyl alkoxide were evaluated as initiators in these syntheses: the latter initiator proved more useful since it led to lower polydispersities in homopolymerizations conducted in the absence of any EGDMA and also provided a convenient NMR label for end group analysis. Copolymerization of DMA with EGDMA led to the formation of soluble branched copolymers with relatively high molecular weights and low polydispersities, as judged by GPC. ^{1}H NMR studies confirmed that these branched copolymers contained few, if any, pendent vinyl groups. The slower rate of copolymerization (compared to DMA homopolymerization) appears to be due to the increased solution viscosity rather than copolymerizability problems associated with the EGDMA brancher. This is supported by the observation that relatively high proportions of methyl methacrylate, which contains no heteroatom, can be statistically copolymerized with DMA under oxyanionic conditions without losing any living character. The α exponents of these branched DMA−EGDMA statistical copolymers were significantly lower than those of the corresponding linear polymers and decreased systematically according to the level of EGDMA branching agent employed. Surprisingly large amounts of EGDMA comonomer could be incorporated without producing macrogelation. Presumably this is because this branching agent tends to form intramolecular rings, rather than intermolecular branch sites, under the oxyanionic polymerization conditions employed in these syntheses.

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