One-Pot Synthesis of Branched Poly(methacrylic acid)s and Suppression of the Rheological “Polyelectrolyte Effect”

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ABSTRACT: A novel synthesis of branched poly(methacrylic acid)s (PMAAs) is reported via conventional solution free radical polymerization of MAA with divinylbenzene (DVB) as the branching comonomer. Controlled levels of dodecanethiol (DDT) have been used successfully to inhibit network formation and gelation. Quantitative methylation of the branched polymers has been achieved using trimethylsilyldiazomethane, and subsequent ^{1}H NMR spectroscopic analysis of both the acid polymers and their methyl esters has allowed quantification of their molecular composition. Characterization of the branched architecture was carried out using dual detection size exclusion chromatography (DDSEC) and was confirmed by ^{1}H NMR spectroscopic analysis. A pH dependence study of the dilute solution reduced viscosity of the branched poly(methacrylic acid)s in 10 vol % MeOH/H_2O has shown almost complete suppression of the polyelectrolyte effect which we attribute to the branched architecture of these macromolecules.

Introduction

Recently, branched synthetic polymers have become increasingly attractive since the physical properties (e.g., solubility, melt and solution viscosity, etc.) of these macromolecules can be very different from those of their linear analogues.[1−4] Not surprisingly, therefore, the synthesis of polymers with branched architectures has become a strategically important topic. Indeed, a number of elegant strategies have been demonstrated for the synthesis of dendrimers[5−7] and hyperbranched polymers.[8−10] Most of these are applicable to step-growth macromolecules, and far fewer are available for chain-growth polymers. Furthermore, most approaches are applicable only for certain monomer types, may require specialist reagents or catalysts, or involve lengthy stepwise procedures. Making large-scale quantities available for extensive physicochemical studies has therefore been a problem and arguably has slowed the more widespread technological exploitation of materials with these novel architectures. A significant step forward in the case of branched vinyl polymers came with the introduction of the “self-condensing vinyl polymerization” (SCVP) methodology from Frechet’s group in 1995.[11] However, this approach has its limitation in that a chemically functional (co)monomer is required to generate the branching segments. In 2000, our group reported a one-pot versatile synthesis of high molar mass branched vinyl polymers using conventional free radical polymerization.[12] The strategy involves polymerization of a vinyl monomer in the presence of a bifunctional (or higher[13,14]) comonomer with a controlled level of chain transfer agent added to inhibit cross-linking and thence gelation. The procedure employs only low-cost regulatory approved materials that are routinely available in both academic and industrial laboratories. Since then, the synthesis of low molecular weight dendrimer-like oligomers has also been reported using a similar strategy involving a catalytic chain transfer species.[15] We have now disclosed further results from our own laboratory[16,17] and from collaborations with other colleagues[13,14] that lead us to believe that the strategy offers an excellent prospect for scale-up. The potential is very real for the provision of large quantities of a wide range of branched vinyl polymers for extensive physicochemical characterization and technological evaluation.

Polyelectrolytes are an important class of synthetic macromolecules and continue to be widely investigated. It is known that linear poly(methacrylic acid) chains can behave almost in a rodlike manner at certain pHs corresponding to extensive ionization. It has been suggested that charge repulsion is responsible for this so-called “polyelectrolyte effect” and the sharp rise in solution viscosity associated with this.[18,19] It occurred to us that in principle we had in our hands a very facile synthetic route to branched poly(methacrylic acid)s, and along with other research groups we felt that these species might offer interesting novel behavior. Theoretical studies have been carried out on such macromolecules,[20] and recently Muller’s group have reported on their very elegant studies relating the topology of branched polyelectrolyes to their physical characteristics.[21] The materials described by this group are well-defined in terms of molar mass, molar mass distribution, and backbone architecture because controlled free radical methodology (ATRP) has been used in their synthesis. The only drawback with this approach is that methacrylic acid protected as its *tert*-butyl ester must be used in the self-condensing polymerization along with 2-(2-bromopropionyloxy)ethyl acrylate as the source of branching. The branched polyelectrolyte is then generated by cleavage of the *tert*-butyl ester groups. In contrast, the results we now report involve a facile one-pot polymerization of methacrylic acid itself. However, the polymers we produce are very complex in terms of both molar mass distribution and backbone architecture. Nevertheless, these display very interesting solution rheology behavior.

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Table 1. Synthesis and Molecular Compositional Characterization of Branched Poly(methacrylic acid)s

sample	feed ratio MAA/DVB/DDT (mol)	yield (g/%)	polymer composition (mol) MAA/DVB/DDT		
			^{1}H NMR spectra		elemental microanalytical data acid polymers
			acid polymers	methyl ester polymers	
PMAA	100/0/0	4.3/86			
PMAA1	100/2/1	5.0/95	100/4.9/6.3	100/6.1/5.3	100/1.5/3.0
PMAA2	100/5/4	4.1/69	100/5.9/6.3	100/5.7/5.0	100/3.0/3.7
PMAA3	100/25/20	6.1/86	100/31/28	100/36/39	100/26/19.5

Experimental Section

Materials. Methacrylic acid (MAA) (99%), divinylbenzene (DVB) (tech., 80% mixture of isomers), and dodecanethiol (DDT) (98%+%) were used as supplied from the Aldrich Chemical Co., and azobis(isobutyronitrile) (AIBN) was used as supplied from the BDH Chemical Co. The solvents employed (methanol, ethanol, toluene, *n*-hexane, tetrahydrofuran, chloroform, and dimethyl sulfoxide) were of standard laboratory reagent grade. The linear, broad molecular weight poly(methyl methacrylate) used as a reference sample in the SEC analyses ($M_\mathrm{w} = 101\,500$ and $M_\mathrm{w}/M_\mathrm{n} = 1.6$) was supplied by the Aldrich Chemical Co. as was the TMS-diazomethane (2.0 M in hexanes).

Polymer Syntheses. *Synthesis of Linear Poly(methacrylic acid) (PMAA).* MAA (5 g, 58 mmol) and AIBN (0.095 g, 0.58 mmol) were added to EtOH (25 mL) in a three-necked round-bottomed flask equipped with a condenser. The temperature of the reaction mixture was maintained at 75 °C for 5 h under nitrogen with magnetic stirring. At the end of this period the reaction mixture was left to cool to room temperature, and then the products were isolated by precipitation into diethyl ether (10 times the volume of the reaction mixture). The PMAA was collected by filtration on a Buchner funnel, and the solvent and monomer residues were removed by evaporation to constant mass using a vacuum oven set at 45 °C. Yield 4.3 g (86%).

^{1}H NMR (d_6-DMSO) δ (ppm): 0.9 (b) $-\mathrm{C}\mathbf{H}_3$ from PMAA; 1.7 (b) $-\mathrm{C}\mathbf{H}_2$ from PMAA; 1.9 $-\mathrm{C}\mathbf{H}_3$ from MAA; 5.6 and 5.9 $\mathbf{H}_2\mathrm{C}{=}$ trace residual MAA; 12.3 (b) $-\mathrm{CO_2}\mathbf{H}$. FT-IR: v(O−H) (cm^{-1}): 3400 (b); v(C−H): 2920; v(C=O): 1685.

Synthesis of Branched Polymers (PMAA1−3). MAA (5 g, 58 mmol), DVB, DDT, (see Table 1 for molar feed ratios), and AIBN (1% of total mol C=C) were added successively to EtOH (25 mL) in a three-necked round-bottomed flask equipped with a condenser. The temperature of the reaction mixture was maintained at 75 °C for 5 h under nitrogen with magnetic stirring. At the end of this period each reaction mixture was left to cool to room temperature, and then the products were isolated by precipitation into *n*-hexane (diethyl ether in the case of PMAA2) (10 times the volume of the reaction mixture). Polymers PMAA1−3 were then isolated and dried as was PMAA. See Table 1 for yields.

^{1}H NMR (d_6-DMSO) δ (ppm): 0.9 (b) $-\mathrm{C}\mathbf{H}_3$ from PMAA and incorporated DDT; 1.24 $-(\mathrm{C}\mathbf{H}_2)_9$ from incorporated DDT; 1.6 (m) $-\mathrm{C}\mathbf{H}_2$ from PMAA and incorporated DVB, and $\mathrm{S}{-}\mathrm{CH_2}{-}\mathrm{C}\mathbf{H}_2$ from incorporated DDT; 1.83 $-\mathrm{C}\mathbf{H}_3$ from trace residual MMA; 2.5 $-\mathrm{C}\mathbf{H}_2{-}\mathrm{S}$ from incorporated DDT; 5.6 and 5.9 $\mathbf{H}_2\mathrm{C}{=}$ from trace residual MAA; 7.0 (m) from incorporated DVB; 12.3 (b) $-\mathrm{CO_2}\mathbf{H}$. FT-IR: v(O−H) (cm^{-1}): 3400 (b); v(C−H): 2927 and 2854 from incorporated DDT; v(C=O): 1696.

Esterification of Branched Polymers. Polymer (50 mg) was placed in a glass vial containing MeOH (0.2 mL) and the vial agitated via a mechanical shaker until a homogeneous solution resulted. Toluene (0.2 mL) was added at this point and again the vial agitated. The TMS−diazomethane reagent was added dropwise until the yellow color was just apparent. The resulting solution was evaporated and the solid residue dried to constant mass using a vacuum oven set at 45 °C.

^{1}H NMR (d_6-DMSO) δ (ppm): 0.9 (b) $-\mathrm{C}\mathbf{H}_3$ from PMMA and incorporated DDT; 1.27 $-(\mathrm{C}\mathbf{H}_2)_9$ from incorporated DDT; 1.76 (m) $-\mathrm{C}\mathbf{H}_2$ from PMMA and incorporated DVB and $\mathrm{S}{-}\mathrm{CH_2}{-}\mathrm{C}\mathbf{H}_2$ from incorporated DDT; 2.5 $-\mathrm{C}\mathbf{H}_2{-}\mathrm{S}$ from incorporated DDT; 3.6 $-\mathrm{OC}\mathbf{H}_3$ from PMMA, 7.0 (m) from incorporated DVB. FT-IR: v(C−H): 2991, 2949, and 2854; v(C=O): 1724.

Polymer Characterization. *Solubility Tests.* Solubility tests were performed in test tubes placed in an ultrasonic bath for 10 min at room temperature. The solvents tested were deionized water, methanol, toluene, tetrahydrofuran, chloroform, and dimethyl sulfoxide.

Elemental Microanalyses. The Elemental Micro-analytical Service available within the Department of Pure and Applied Chemistry at the University of Strathclyde carried out these analyses using a Perkin-Elmer 2400 analyzer.

NMR Spectroscopy. ^{1}H NMR spectra were recorded on a 400 MHz Bruker DPX-400 spectrometer using d_6-DMSO as the solvent in 5 mm NMR tubes. In all the spectra the residual hydrogen signal in d_6-DMSO was used as a reference.

FT-IR Spectroscopy. The polymer sample was ground into fine particles and a single particle placed between two diamond plates in a compression cell. FT-IR absorbance/transmission spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using 4 cm^{-1} resolution and 16 scans.

Dual Detection Size Exclusion Chromatography (*DD-SEC*). The instrument package was supplied by Optokem and comprised the following equipment: (i) a Jones Chromatography 7600 series Solvent D-Gasser, (ii) a Waters 515 HPLC pump operating at room temperature, (iii) a Waters 717 plus autosampler with 96 or 48 position sample racks, (iv) a column oven, (v) a set of three Styragel HR 2, HR 4, and HR 6 designation 7.8 × 300 mm GPC columns, and (vi) two detectors connected in a serial configuration: a multiangle light scattering detector (mini-Dawn) supplied by Wyatt Technology and an interferometer refractometer detector (Optilab DSP) supplied by Wyatt Technology.

THF was the mobile phase, the column oven temperature was set to 40 °C, and the flow rate was 1 mL/min. The samples were prepared for injection by dissolving 5 mg of polymer in 1 mL of HPLC grade THF; 0.2 mL of this mixture was then injected, and data were collected for 40 min. The wavelength used was 690 nm. Astra for Windows was used to collect and process the signals transmitted from the detectors to the computer and to produce the molar mass distribution and molar mass vs elution volume plots.

Viscosity Sample Preparation. PMAA or PMAA1−3 (50 mg) was added to a 50 cm^3 volumetric flask that contained methanol (5 mL). This was mechanically shaken until a homogeneous solution resulted, and the solution was made to volume with deionized water. Several solutions of each polymer were prepared each with a different pH. The solution pH was adjusted by titration of small aliquots of NaOH (0.015 M), which were added before the solutions were made to volume. The pH was measured using a Jenway 3015 pH meter with combined pH electrode.

Viscosity Measurements. The reduced specific viscosity of each of these solutions was calculated from flow times recorded using a number 1 Ubbelohde viscometer, 10 vol % MeOH/deionized water solution being run as a reference between each sample. Six efflux times were measured for each solution. The temperature was maintained at 25 ± 0.2 °C using a water bath.

Results and Discussion

Polymer Synthesis and Molecular Structure. Details of the linear PMAA and the three branched polymers (PMAA1−3) synthesized are shown in Table 1. The polymersations were carried out in solution in ethanol at 30 wt %. With PMAA1−3 branching was

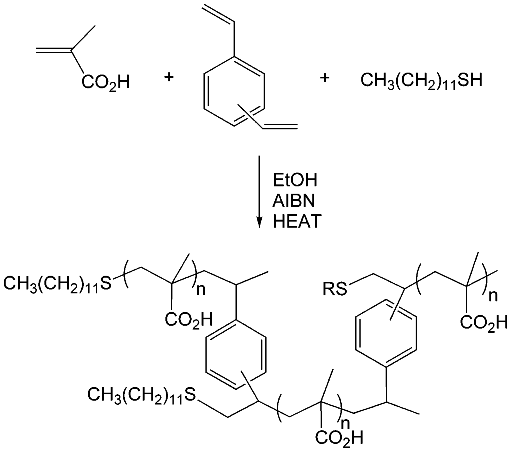

Figure 1. Direct one-pot synthesis of branched poly(methacrylic acid)s using divinylbenzene as the branching comonomer.

induced by the use of DVB as a comonomer (Figure 1). In each case reaction mixtures remained isotropic with no obvious gelation or phase separation, this being achieved with PMAA1−3 by the use of DDT as a transfer agent. All samples were obtained in good yield, and bearing in mind the usual losses during isolation, the corresponding conversions seem close to quantitative.

Each product is soluble in ethanol, methanol, and DMSO as well as in methanol/H_2O mixtures. In addition, PMAA is soluble in H_2O, and PMAA3 is soluble in THF. Appropriate solutions of PMAA1−3 were completely isotropic, and these products are therefore not cross-linked. The incorporation of the branching comonomer, DVB, is clearly apparent with a broad signal at $\delta = 7.0$ ppm in the ^{1}H NMR spectrum of each polymer arising from the aromatic hydrogen atoms in the DVB segments. In each case there are also very small broad resonances centered on $\delta = 5.3$ and 5.75 ppm, which can be assigned to the CH_2 hydrogen atoms in pendent unreacted vinyl groups derived from DVB residues in which only one vinyl group has undergone polymerization. We have previously investigated in some detail the presence of pendent unreacted vinyl groups from difunctional comonomers in the synthesis of branched poly(methyl methacrylate)s and shown that the proportion of nonpolymerized groups can vary quite widely.[17] With the present materials PMAA1−3, only the relevant signals in the spectrum from PMAA3 prepared using a MAA/DVB mole ratio of 100/25 are sufficiently intense to allow quantification of the level of unreacted pendent groups which corresponds to ~8% of the total DVB feed. Overall, therefore, most DVB is incorporated as branching units.

The ^{1}H NMR spectra and elemental microanalytical data (C, H, and S) of the samples also in principle allows evaluation of the molecular composition of the branched polymers, most conveniently expressed as the mole ratio MAA/DVB/DDT. Unfortunately, however, neither of these analyses is without its difficulties and limitations, as indicated by the spread of data shown in Table 1. The ^{1}H NMR spectral analysis of PMAA1−3 is limited in accuracy since the MAA content is evaluated from the weak and broad $-CO_2H$ hydrogen signal. In addition, the DDT incorporated is estimated from the $(CH_2)_9$ signal which falls close to the other $-CH_2-$ signals from the polymer backbone. The DDT data are therefore almost certainly an overestimation. This situation is also true of the data derived from the ^{1}H NMR spectra of corresponding methylated polymers PMAA1−3M (see below). In principle, use of the DVB aromatic hydrogen resonance and that of the $-OCH_3$ ester hydrogen resonance in the methylated polymers PMMA1−3M should allow clarification of the MAA/DVB ratios. However, these samples were prepared only on a very small scale (primarily for SEC analysis; see below), and to prevent precipitation of the incipient methyl esters, it was necessary to use a tailored mixture of MeOH and toluene as solvent. Residues of the latter appear in the ^{1}H NMR spectra and introduce a significant error in integrating the DVB aromatic signals.

Computation of the composition of the polymers PMAA1−3 from elemental microanalytical data (C, H, and S%) also has significant limitations. In principle, the DDT content can be evaluated from the S%, the MAA content from the O% (the latter obtained indirectly as the balance of C, H, and S%), and thence the DVB content from C%. In practice, this method is satisfactory when the S% is large enough to be analyzed accurately; indeed, the data for PMAA3 (MAA/DVB/DDT = 100/26/19.5) are in close agreement with the feed values. However, when the S% is low and subject to a proportionately large error, this method becomes very insensitive. Overall, the high conversions achieved in the polymerizations, and a realistic evaluation of the analytical data, suggest that the polymer compositions cannot differ very much from the feed data.

Methylation of Branched Polymers. Since poly(methacrylic acid)s are not soluble in THF, the mobile phase used routinely in our SEC analytical instrument, it was decided to methylate each sample to allow us to use our own dual detector system. We have previously shown that there is good correlation between the SEC behavior of poly(acrylic acid)s and their methylated derivatives.[22] Since that early work the introduction of TMS−diazomethane as a quantitative methylating agent has considerably facilitated this type of derivatization procedure and indeed improved the safety of the methodology enormously. With the present poly(methacrylic acid) samples the only practical difficulty was the significant shift in solubility properties between the polyacids and their methyl esters. As indicated above, use of methanol alone as the solvent caused premature precipitation of the methylated product and as a result incomplete methylation. Using a methanol/toluene mixture as described in the Experimental Section solved this problem completely; indeed, the yellow color of the TMS−diazomethane reagent allows the reaction to be carried out almost as a titration. Both the ^{1}H NMR and FT-IR spectra confirmed that each methylation was essentially quantitative. The $-CO_2H$ resonance ($\delta = 12.3$ ppm) in the ^{1}H NMR spectra is replaced completely by the $-OCH_3$ resonance ($\delta = 3.6$ ppm), and in the FT-IR spectra the carbonyl band shifts from 1690 to 1724 cm^{-1}.

SEC Analysis. The dual detector system utilized on our instrument might be described as yielding "absolute" molar mass data, and we have previously explained our analytical procedure and our position with regards to the significance of these data.[16] Suffice to say here that the procedure we prefer generates differential weight fraction vs molar mass curves and molar mass vs elution volume relationships. In evaluating branching, the SEC data are compared with an appropriate broad molar mass linear polymer, in this case a poly-

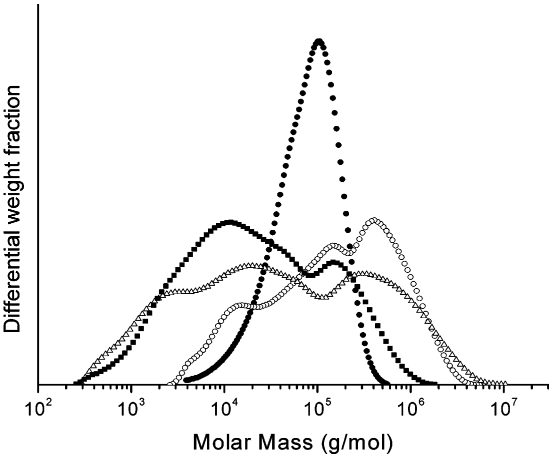

Figure 2. SEC molar mass distribution curves for (●) linear PMMA control, (△) PMAA1M, (■) PMAA2M, and (○) PMAA3M.

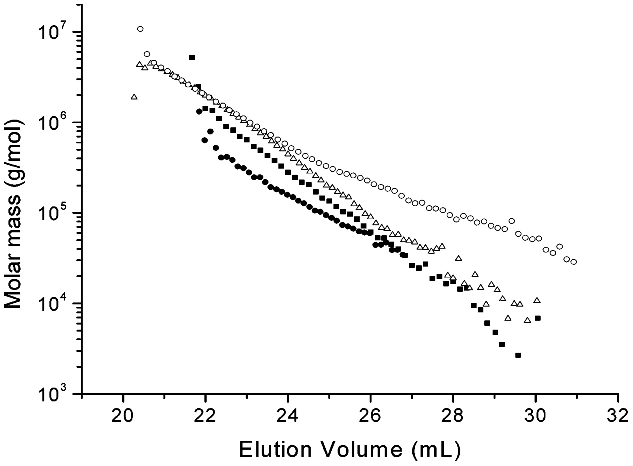

Figure 3. SEC molar mass vs elution volume plots for (●) linear PMMA, (△) PMAA1M, (■) PMAA2M, and (○) PMAA3M.

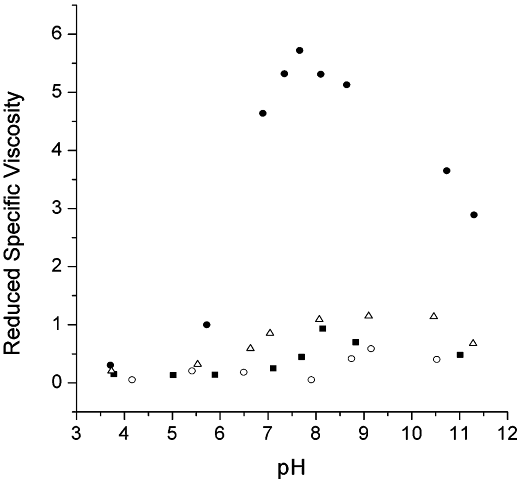

Figure 4. Dilute solution (10 vol % MeOH/H_2O) reduced viscosity pH dependence of (●) linear PMAA control, (△) PMAA1, (■) PMAA2, and (○) PMAA3.

(methyl methacrylate) (PMMA) ($M_w = 101\,500$, $M_w/M_n = 1.6$).

The differential weight fraction vs molar mass curves for methylated polymers PMAA1−3M and a linear PMMA reference are shown in Figure 2. The latter displays a typical monomodal distribution with peak molar mass $\sim 10^5$. In contrast, the branched samples are at least bimodal with a much broader molar mass distribution: PMAA1M, $M_w = 300\,100$, $M_w/M_n = 55$; PMAA2M, $M_w = 81\,800$, $M_w/M_n = 13.7$; and PMAA3M, $M_w = 368\,600$, $M_w/M_n = 8.8$.

However, we have shown previously that such broad molar mass distribution curves are characteristic of the materials produced using this polymerization methodology and reflect that these are mixtures, complex both in terms of molar mass and backbone architecture.[16,17] We have also shown with branched poly(methyl methacrylate)s prepared similarly that as the level of difunctional (branching) comonomer employed is increased the molar mass distribution curve shifts to higher molar mass. This is the case here as well in moving from PMAA2M to PMAA3M with a shift in the DVB employed from a mole ratio MAA/DVB = 100/5 to 100/25. Interestingly, the data for PMAA1M prepared using a mole ratio MMA/DVB of only 100/2 seems anomalous since the molar mass distribution curve seems to straddle those of the other two samples. However, we have also shown previously that the level of radical transfer agent, DDT, employed is also important. For a fixed level of branching comonomer, the molar mass distribution curves broaden and shift to higher molar mass as the level of transfer agent used is reduced.[17] In the case of PMAA1M the mole feed ratio DVB/DDT was 2/1 whereas for PMAA2M it was 5/4; the lower ratio of DDT employed in the former polymerization, and hence the much reduced rate of radical transfer, seemingly gives rise to higher molar mass primary chains and ultimately to a shift in the molar mass distribution curve which extends beyond that of the PMAA2M sample.

The relative level of branching (as opposed to molar mass) is shown more clearly in the corresponding molar mass vs elution volume curves (Figure 3). The curves for all three branched polymers lie significantly above that of the linear PMMA reference sample, indicating that at any given elution volume, e.g. 23 mL, the samples elute with same hydrodynamic volume, but the corresponding molar masses increase in the series PMMA (reference) < PMAA2M < PMAA1M ≈ PMAA3M. This indicates that branching increases in this series as well with the polymer coils becoming more dense and compact.

Dilute Solution Viscosity Behavior. The reduced specific viscosity pH dependences of dilute solutions (~0.1 wt %) of samples PMAA and PMAA1−3 in 10 vol % MeOH/water are shown in Figure 4. The linear polymer, PMAA, behaves as expected from previous results in the literature,[18,19] showing a sharp rise in the solution viscosity at ~pH = 6, rising rapidly to a maximum ~pH = 7.5, before falling less steeply as the pH is further increased. This is in keeping with the model (Figure 5a) in which the highly coiled undissociated polyacid at low pH exhibits low viscosity. As the carboxylic acid groups become ionized with increase in pH, the macromolecule unfolds to assume a highly extended conformation, driven by the repulsive forces of the like charges bound to the polymer chain. As the conformation extends, the viscosity rises to a maximum. Beyond this point a further increase in pH simply increases the ionic strength of the medium, and the bound charges become increasingly shielded. The overall repulsion within individual macromolecules declines slowly, the polymer starts to fold again, and the viscosity falls.

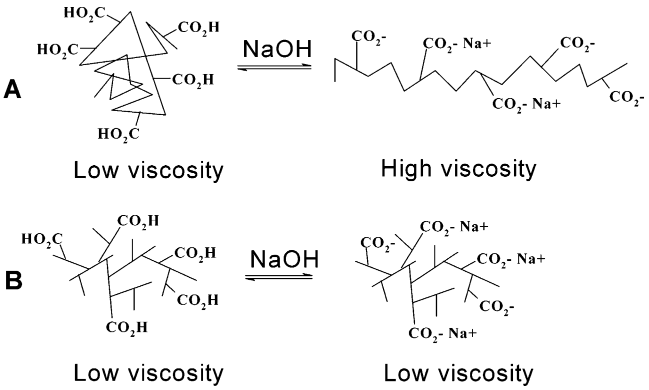

Figure 5. Schematic representation of (A) linear poly(methacrylic acid) coil expansion on ionization and (B) absence of coil expansion with branched poly(methacrylic acid).

In the case of all three branched polymer samples, PMAA1−3, the viscosity/pH dependence is quite different. While each sample does show an increase in viscosity as the pH is increased, with a suggestion of a maximum and a decline at the highest pH, the effect is a very small one.

Indeed, in comparison to the behavior of linear PMAA the so-called pH effect on viscosity is all but eliminated in these branched polymers. This can be rationalized in terms of a modified model (Figure 5b) in which the branched polyacid at low pH is in an unionized coiled conformation with similarly low viscosity to that of a linear polyacid. As the pH is increased and the acid groups become progressively ionized, bound like charges start to repel each other as before, but the branched backbone architecture of the polymer precludes any significant expansion of the polymer coil, with the hydrodynamic volume becoming essentially pH independent. The latter is manifest as only a minimal increase in the dilute solution viscosity as the pH is raised. While this model seems plausible we have been surprised at the low level of difunctional comonomer DVB, i.e., branching, that seems to give rise to this suppression of this pH-dependent polyelectrolye effect and also to the relative similarity of the polymers prepared with MAA/DVB (brancher) feeds of 100/2, 100/5, and 100/25. Similar suppression of the polyelectrolyte effect has been reported before in the case of hyperbranched polyesters with terminal carboxylic acid groups at high added salt concentration.[23]

We have considered whether hydrophobic forces may also be playing a role since the DVB and the C_{12} aliphatic hydrocarbon groups derived from the thiol transfer agent incorporated into these branched polyacids undoubtedly introduce hydrophobic character, and hydrophobic effects can be important at higher polymer solution concentrations when interpolymer chain interactions can contribute.[24,25] We did prepare a linear copolymer with a mole feed ratio of MAA/styrene of 100/5, the styrene residues being a hydrophobic mimic of DVB. Interestingly, this copolymer proved to be insoluble in 10 vol % MeOH/water, and so it was not possible for us to run the control viscosity measurements. The fact that this linear copolymer with ∼5 mol % styrene is insoluble in 10 vol % MeOH/water has made us realize that the solubility of the (branched) MAA/DVB copolymer with ∼25 mol % DVB in this solvent mixture is itself remarkable, and we can only conclude that it is highly branched backbone architecture of this species that is responsible for this.

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