Synthesis of Highly Branched Poly(methyl methacrylate)s Using the "Strathclyde Methodology" in Aqueous Emulsion

R. Baudry and D. C. Sherrington*

Department of Pure and Applied Chemistry, Westchem Graduate School of Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, Scotland, UK

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ABSTRACT: High-conversion copolymerizations of methyl methacrylate (MMA) and divinylbenzene (DVB) in aqueous emulsion have been carried out using sodium dodecyl sulfate as the emulsifier and potassium persulfate as the conventional free radical initiator. Various thiols have been investigated in order to inhibit cross-linking and hence favor the formation of branched products. Hexanethiol (HT) and benzylthiol (BT) have been found to be particularly effective. Use of appropriate levels of BT allow mole feed ratios of MMA/DVB up to 100/20 to be employed in producing highly branched products without cross-linking. Typically DVB/BT mole ratios of ≤ 1 ensure that cross-linking is avoided. Perhaps most remarkably of all no organic solvent is required in producing these branched products, whereas analogous polymerization feed compositions under bulk or aqueous suspension polymerization conditions lead inevitably to cross-linked products irrespective of the level of chain transfer agent used. The molar mass and branching architecture of the products have been characterized by ^{1}H NMR and MALS/SEC analyses, and the complete incorporation of DVB residues as branching units has been confirmed.

Introduction

Stimulated by the interest generated around dendrimers[1] and step-growth hyperbranched polymers,[2] a number of groups have been pursuing strategies aimed at producing generic syntheses of branched vinyl and other chain growth polymers. In this context we have recently developed a facile and generic synthetic methodology (the "Strathclyde methodology") for the high yielding synthesis of branched vinyl polymers using conventional free radical polymerization.[3−7] This complements the technique of "self-condensing vinyl polymerization" introduced by Frechet and co-workers[8−11] and the so-called "initiator-fragment incorporation radical copolymerization" reported by Sato and co-workers.[12−16] Indeed, we believe that our own approach offers broader scope in terms of scale-up and wider commercial exploitation. The methodology involves the simple free radical copolymerization of a vinyl monomer with a difunctional (or multifunctional) comonomer with cross-linking and network formation inhibited by use of appropriate levels of a stoichiometric free radical chain transfer agent, such as a thiol, or indeed a catalytic chain transfer agent.[17,18] Essential to this strategy, however, is the use of an organic solvent which dilutes the whole reaction medium and contributes to the inhibition of cross-linking. In addition, a solvent such as toluene has a small but significant free radical chain transfer capability. We have shown that if the degree of dilution of the reaction medium falls too low, it is extremely difficult to inhibit cross-linking and gelation,[5] even when using very high levels of a chain transfer agent. Interestingly, the use of a solvent in the commercial production of many commodity vinyl polymers would render such processes uneconomic. Adapting our branching methodology to solventless, or in effect bulk polymerization conditions, is therefore scientifically and technologically challenging. Remarkably, however, we have now found that solvent can be completely removed from our branched polymer synthesis without inducing cross-linking and gelation providing the polymerizations are carried out in aqueous emulsion,[19] and this paper reports our findings. Interestingly, Morbidelli et al.[20] have recently reported the synthesis of branched polystyrenes via copolymerization of styrene and divinylbenzene, some samples being prepared in the absence of solvent. However, high temperatures are involved (>300 °C), and the use of a continuous stirred tank reactor made the evaluation of conversion problematical.

* Corresponding author. E-mail: d.sherrington@strath.ac.uk.

Experimental Section

Materials. Methyl methacrylate (MMA) (99%), divinylbenzene (DVB) (tech., 80% mixture of isomers), dodecanethiol (DDT) (99%), thiolactic acid (95%), dibutyl sulfide (96%), triphenylmethanethiol (98%), benzylthiol (BT) (99%), sodium dodecyl sulfate (SDS) (98%), and potassium persulfate from the Aldrich Chemical Co. and hexanethiol (HT) (97%) from Lancaster were used as supplied. Benzoyl peroxide was recrystallized from $CHCl_3$/CH_3OH, and the water used was doubly distilled.

Emulsion Polymerizations. *General Procedure.* These were carried out as follows. The aqueous phase (500 g) comprised the SDS, the monomers, and the potassium persulfate. This was added to a five-necked jacketed glass reaction (1 L) fitted with a nitrogen bubbler, an overhead PTFE screw propeller stirrer, and a condenser. The mixture was stirred vigorously at 950 rpm while N_2 was bubbled through for 20 min. The flow of N_2 was reduced, and the stirrer speed was set to 950 rpm. The polymerization reaction was allowed to proceed for 65 °C for 5 h, heat being supplied by circulating appropriately thermostated hot water around the reactor jacket.

Synthesis of Linear Poly(methyl methacrylate)s, PMMA1−4. The aqueous phase (500 g) contained 0.25 g of SDS and 0.5−2 g of potassium persulfate (see Table 1). The organic phase was 50 g of MMA (0.5 mol).

^{1}H NMR ($CDCl_3$, 298 K) δ (ppm): 0.84, 1.00, and 1.20 (m, 3H, −C**H**$_3$), 1.42 and 1.80 (m, 2H, −C**H**$_2$), 3.58 (m, 3H, OC**H**$_3$).

Synthesis of Linear Poly(methyl methacrylate)s, PMMA5−10. The aqueous phase (500 g) contained 0.25 g of SDS and 0.5 g of potassium sulfate (0.44% relative to double bonds). The organic phase contained 40 g of MMA (0.4 mol) and 2 mol % (relative to MMA) of thiol (see Table 2).

Synthesis of Branched Poly(MMA-co-DVB), b-PMMA1−18. The aqueous phase (500 g) contained 0.25 g of SDS (*b*-PMMA1−14)

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Table 1. Emulsion Polymerization Synthesis of Linear PMMAs

sample	[initiator] (g/L)	transfer agent (2%)	conv (%)	M_n[a] (g/mol)	M_w[a] (g/mol)	M_w/M_n
PMMA1	1	none	98	249 000	817 000	3.3
PMMA2	2	none	~100	353 000	870 000	2.5
PMMA3	3	none	~100	237 000	704 000	3
PMMA4	4	none	~100	169 000	645 000	3.8
PMMA5	1	DDT	80	23 000	41 000	1.8
PMMA6	1	HT	99	7 500	17 000	1.6
PMMA7[b]	1	thiolactic acid				
PMMA8	1	BT	~100	6 400	12 000	1.8
PMMA9[c]	1	dibutyl sulfide	98			
PMMA10	1	triphenylthiol	22			
PMMA11[d]	3	DDT	~100	4 700	8 500	1.8

[a] MALS/SEC. [b] A macrogel was obtained. [c] PMMA9 was insoluble in THF. [d] Solution polymerization in toluene.

Table 2. Synthesis and Molecular Compositional Characterization of Branched PMMAs

			MALS/SEC ($\times 10^{-3}$ g/mol)						^{1}H NMR	
			crude polymer			purified polymer			crude polymer	purified polymer
sample	mole feed ratio MMA/DVB/BT	conv (%)	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n	mole ratio MMA/DVB/BT	mole ratio MMA/DVB/BT
b-PMMA1	100/2/4	98	3.3	37	19	4.2	44	10	100/1.5/4.0	100/2.0/4.0
b-PMMA2[a]	100/2/3	93								
b-PMMA3	100/5/10	88	2	8.8	10	4.6	12	2.6	100/4.5/9.0	100/4.0/7.0
b-PMMA4	100/5/9	87	1.9	10	5	3.9	12	3	100/4.5/8.5	100/4.5/7.0
b-PMMA5	100/5/8	96	1.6	19	12	1.9	20	10	100/4.5/7.5	100/4.0/6.5
b-PMMA6	100/5/7	96	2.4	72	30	7.6	81	11	100/4.5/6.5	100/3.5/4.5
b-PMMA7[a]	100/5/6	98								
b-PMMA8	100/10/20	84	1.1	3.1	3	1.4	4.2	3	100/10.0/18.5	100/8.5/12.5
b-PMMA9	100/10/18	74	1.3	4.6	3.4	2.9	6.6	2.3	100/10.0/16.5	100/8.5/11.0
b-PMMA10	100/10/16	90	1.3	7.1	5.6	4.8	19	2.3	100/9.0/14.5	100/8.0/10.0
b-PMMA11	100/10/14	89	1.6	16	10	3.9	17	4	100/9.5/13.0	100/8.0/9.0
b-PMMA12	100/10/12	88	7.1	160	97	7.1	160	22	100/9.5/11.5	100/9.0/10.0
b-PMMA13[a]	100/10/11	96								
b-PMMA14	100/15/21	93	0.85	8.5	10	7	14	2	100/13.5/19.0	100/12.5/16.0[b]
b-PMMA15	100/15/18	95	1.1	48	40	3.8	48	13	100/14.0/17.0	100/125/14.5
b-PMMA16	100/15/17	97	35.6	462	13					
b-PMMA17	100/20/24	80	1.8	46	24	13	74	6	100/18.5/22.0	100/14.5/14.5
b-PMMA18[a]	100/20/23	100								

[a] Gelation occurred. [b] Purified polymer = 77 wt %, residue from purification filtrate = 23 wt %, composition MMA/DVB/BT = 100/25/49.

or 0.5 wt % relative to the organic phase (*b-PMMA 14−18*) and 0.44 mol % of initiator (relative to total number of double bonds). The organic phase contained 40 g of MMA (0.4 mol) and various levels of DVB and BT (see Table 2 for molar feed ratios).

^{1}H NMR (acetone-d_6, 298 K) δ (ppm): 0.85, 1.06, and 1.22 (m, 3H, −C−**H**$_3$ from MMA), 1.45 and 1.85 (m, 2H, −C**H**$_2$ from MMA), 2.51 (m, 2H, C**H**$_2$) from benzylthiol), 3.02 (m, 2H, −C**H**− from DVB), 3.61 (m, 3H, OC**H**$_3$ from MMA), 6.98 (m, 4H, aryl**H** from DVB), 7.33 (m, 5H, aryl**H** from benzylthiol).

Solution Synthesis of Linear Poly(methyl methacrylate), PMMA-11. In a 50 mL three-necked flask equipped with stirrer and condenser, 3 g (30 mmol) of MMA, 0.121 g (0.6 mmol, 2% relative to MMA) of DDT, and 0.58 g (2.4 mmol, 2% relative to MMA) of benzoyl peroxide were added to 25 mL of toluene. The reaction mixture was degassed for 15 min by bubbling nitrogen. The polymerization was conducted at 85 °C for 5 h under nitrogen. The reaction mixture was then concentrated under vacuum and dissolved in dichloromethane, and the product was isolated by precipitation in diethyl ether and was collected by filtration on a Buchner funnel. The solvent and monomer residues were removed by evaporation to constant mass using a vacuum oven set at 40 °C to yield the isolated polymer. Yield: ~100%.

Latex Characterization. Particle size was determined by dynamic light scattering (Coulter N4 plus). Samples of latex were dried overnight at 130°C in an oven, and conversions were then determined gravimetrically. Samples of latex were also dried first by azeotropic distillation (toluene) and then overnight using a vacuum oven set at 40 °C. The crude polymer was then dissolved in dichloromethane and precipitated in *n*-hexane. The PMMAs were collected by filtration and dried to constant mass under vacuum at 40 °C.

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

Multiangle Light Scattering-Size Exclusion Chromatography (MALS/SEC). The instrument package was supplied by Optokem and comprised the following equipment: (i) a Jones Chromatography 760 series Solvent D-Gasser, (ii) a Waters 515 HPLC pump operating at room temperature, (iii) a Jasco AS-950 autosampler with 50 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 refractomer 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 10 mg of polymer in 1 mL of HPLC grade THF and filtered off with an Acrodisc 0.2 μm PTFE membrane. 0.2 mL of this mixture was then injected, and data were collector for 40 min. The wavelength used was 690 nm. The d*n*/d*c* value used was 0.089. 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.

Results and Discussion

Synthesis of Model Linear PMMAs in Aqueous Emulsion. In the absence of any firm data on the efficiency of chain transfer agents in aqueous emulsion polymerization of MMA, the

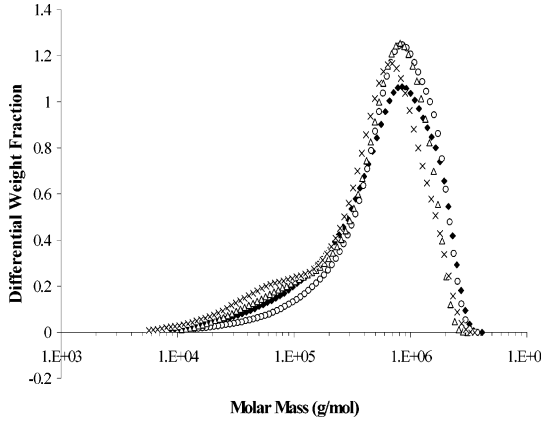

Figure 1. MALS/SEC molar mass distribution curves for linear PMMAs using different concentration of initiator: (◆) PMMA1: $[K_2S_2O_8] = 1$ g/L; (○) PMMA2: $[K_2S_2O_8] = 2$ g/L; (△) PMMA3: $[K_2S_2O_8] = 3$ g/L; (×) PMMA4: $[K_2S_2O_8] = 4$ g/L.

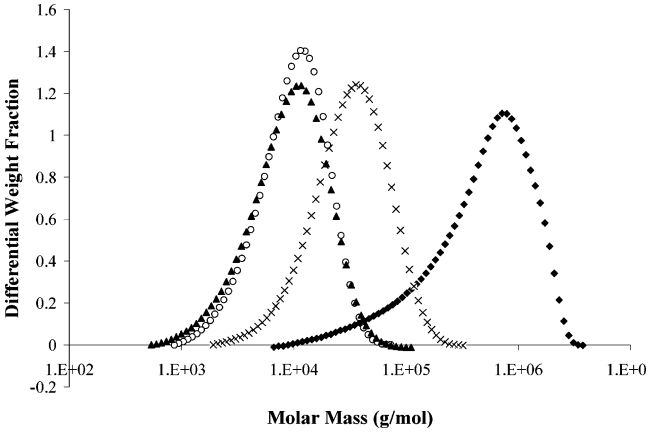

Figure 2. MALS/SEC molar mass distribution curves for linear PMMAs using different transfer agents: (◆) PMMA1: none; (×) PMMA5: 2 mol % DDT; (○) PMMA6: 2 mol % HT; (▲) PMMA8: 2 mol % BT.

behavior of the latter was first investigated in the absence of any branching comonomer. Samples PMMA1−4 (Table 1) were prepared in essentially quantitative yield without any chain transfer agent. The molar mass of the linear PMMAs is typically high, and although this falls with increase in the level of potassium persulfate used, the dependence is a weak one, and an initiator concentration of 1 g/L was chosen for use in synthesizing linear PMMAs in the presence of various transfer agents. The SEC molar mass distribution curves for PMMA1−4 (Figure 1) show remarkable similarity, with the observed change in M_n and M_w (Table 1) seemingly due to minor differences in the level of a small low molar mass fraction. Samples PMMA5−10 were prepared under the same conditions (see Experimental Section) but with 2 mol % (relative to MMA) of different chain transfer agents. For reasons of which we are unsure, the water-soluble transfer agent thiolactic acid yielded a macrogel, and further experimental work is needed to rationalize what might be happening in this system. Dibutyl sulfide also yielded PMMA9, which proved to be insoluble in THF (the SEC eluent), and again it is unclear why this is so. Triphenylmethanethiol gave rise to only a low level of isolated polymer, and the most likely explanation of this is that the thiolate radical formed in the transfer reaction is rather stable and reinitiates polymerization only slowly. Dodecanethiol (DDT), hexanethiol (HT), and benzylthiol (BT) all proved to be effective chain transfer agents while still allowing high conversion to polymer. The M_n and M_w data for the products obtained (Table 1) and the molar mass distribution curves (Figure 2) indicate that DDT is less effective than HT and BT in these emulsion polymerizations. One possible explanation of this is that the high level of hydrophobicity of DDT, relative to HT and BT, may inhibit its migration through the aqueous phase from the monomer droplets to the polymerizing particles. Alternatively, it could be that DDT has some surfactant-like character and resides at the interface of micellar particles with the potentially reactive thiol group essentially unavailable, being orientated toward the aqueous phase. From this preliminary study BT was chosen as the chain transfer agent in the synthesis of the branched PMMAs.

Previously, we have reported extensively on the preparation of branched PMMAs via conventional free radical polymerization in organic solvent using difunctional comonomers as the source of branching and DDT as an inhibitor of network formation.[3,5,7] From these results and the known similarity in reactivity ratios between MMA and styrene,[21] it was decided to exploit divinylbenzene (DVB) as the branching comonomer in our emulsion polymerizations. The data in Table 2 show the polymerization compositions explored, the conversion data, the compositions of the polymers obtained, and their molar mass characterization data. In all cases very good conversions were obtained, and representative examples were shown to have average particle diameters in the range 200−300 nm. The materials recovered simply by drying a sample of latex overnight at 130 °C typically displayed a low molar mass tail in their SEC molar mass distribution curves (for an example see Figure 3), which undoubtedly contains initiator and surfactant fragments but is primarily a MMA/DVB oligomer fraction. The samples recovered from reprecipitation (for an example, see Figure 3) show essentially complete removal of this fraction, and this is reflected in an upward shift in the computed M_n and M_w values for the purified vs the impure products.

The ^{1}H NMR spectra of all products (see Experimental Section) showed the presence of MMA and DVB segments and also benzylthioether terminal units. In all cases no signal was detected for pendent $-CH{=}CH_2$ groups from partially reacted DVB, and so all the latter from the feed is essentially incorporated as branching units. The resonances at 3.61 ppm ($-OCH_3$ from MMA), 6.98 ppm (4 aromatic H in DVB), and 7.33 ppm (5 aromatic H in $PhCH_2S-$) allowed the molar ratio MMA/DVB/BT to be determined for each product, and these are shown in Table 2. Overall, there is good correlation between the MMA/DVB feed ratios and the corresponding molar ratios found in the unpurified products as would be expected from the high conversions achieved. Typically, the levels of DVB found in the purified products are lower than the feed values, but clearly DVB is incorporated very efficiently. A similar trend is found with the MMA/BT ratios with the fall in the latter between the unpurified and purified samples being perhaps a little larger than is the case with the DVB. The purified polymer *b*-PMMA14 was obtained as ∼75 wt %, with the balance (the lower molar mass fraction) being recovered from the purification filtrate. Interestingly, ^{1}H NMR analysis of this fraction indicated a molar composition MMA/DVB/BT = 100/25/49. Summing the DVB components in the two fractions yields 15.5 (i.e., 12.5 × 0.75 + 25 × 0.25) and the corresponding sum for the BT component is 24.2 (i.e., 16 × 0.75 + 49 × 0.25), giving an overall molar composition MMA/DVB/BT = 100/15.5/ 24.2 which represents a respectable correlation with the feed values. These data suggest that both the DVB and the BT have high reactivity in these emulsion polymerizations and that the low molar mass component also contains substantially branched species.

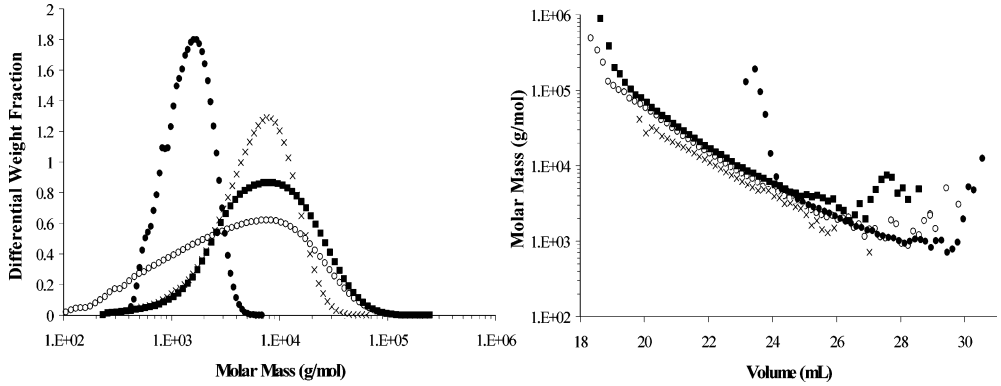

Figure 3. MALS/SEC molar mass distribution curves (left) and SEC molar mass vs elution plots (right) for (○) *b*-PMMA14 crude product, (●) *b*-PMMA14 higher molar mass purified product, (■) *b*-PMMA14 low molar mass fraction, and (×) PMMA11 (MMA/DDT 100/2 synthesized in toluene solution).

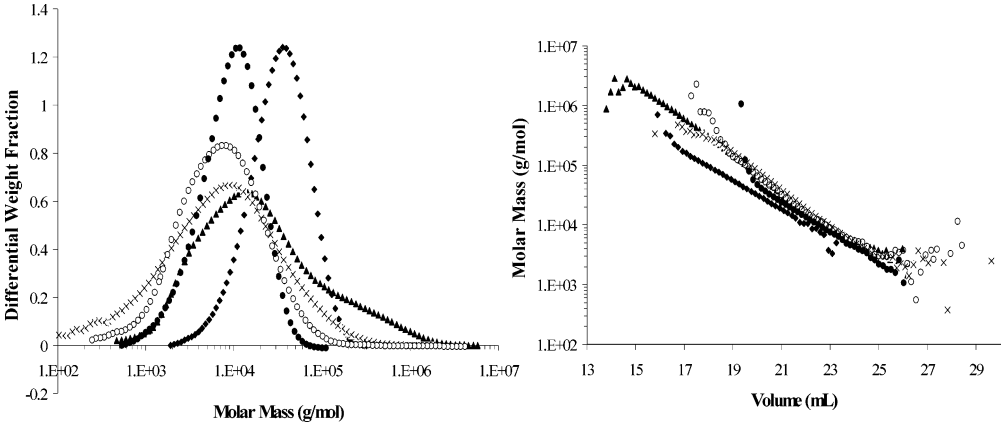

Figure 4. MALS/SEC molar mass distribution curves (left) and SEC molar mass vs elution plots (right) for (◆) PMMA5 MMA/DDT = 100/2, (●) PMMA8: MMA/BM = 100/2 (○), *b*-PMMA4: MMA/DVB/BT = 100/5/9, (×) *b*-PMMA5: MMA/DVB/BT = 100/5/8, and (▲) *b*-PMMA6: MMA/DVB/BT = 100/5/7.

The control linear polymer PMMA-8 prepared with a mole ratio MMA/BT of 100/2 has a M_w of 12 000. All of the branched samples (Table 2) were prepared using higher levels of BT, most of them with substantially higher levels. Despite this, in most cases the M_w values are higher than the control. Likewise, the polydispersity (M_w/M_n) data are substantially higher than that of the control. These factors are consistent with these samples having a branched architecture.

Looking in more detail at the polymerization compositions and corresponding polymer compositions, it is remarkable that soluble branched products are obtained with MMA/DVB feed mole ratios as high as 100/20 (i.e., on average one branch every six monomer segments) in the absence of any organic solvent. If such feed compositions were to be employed in bulk, i.e., without dispersion in an aqueous continuous phase with the aid of surfactants, then, almost irrespective of the level of chain transfer agent used, cross-linking and gelation would occur.[5] Indeed, when analogous polymerization mixtures are used in aqueous suspension rather aqueous emulsion poymerizations, then it is impossible to use such high levels of brancher without causing cross-linking, again irrespective of the level of chain transfer agent used.[22] In the present aqueous emulsion polymerizations therefore there seems to be some special factors that allow high branching levels to be achieved and cross-linking to be suppressed, even without the diluting effect of an organic solvent. These factors may be associated with the complex physicochemical migration processes involving polymerization components known to occur in emulsion polymerizations. The idealized model for emulsion polymerizations differs markedly from those of solution and bulk polymerizations in that only one active free radical is present at any one time in each polymerizing particle.[19] This may be an important or contributing factor, but at present we are unclear why this might be so. Another factor may involve local or microenviromental partitioning effects of the relatively hydrophobic DVB residues within the growing particles which results in cross-linking being disfavored. At this stage we also do not know how general this result might be and whether it might be limited to the MMA/DVB system. Our suspicion is that it is not limited to this comonomer combination.

The molar mass distribution curves and corresponding molar mass vs elution volume plots for unpurified polymer *b*-PMMA14, and its higher and lower molar mass fractions are shown in Figure 3 together with data for a broad linear PMMA control with similar molar mass and molar mass distribution. The resolution of the distribution curve of the unpurified sample into the distributions of the two separate fractions is clearly evident. The corresponding molar mass vs elution volume plots for the unpurified and higher molar mass purified samples of *b*-PMMA14 both lie to the upper right of the plot for the linear PMMA control, hence confirming the branched architecture of these samples. In addition, the plot for the low molar mass fraction, though lying very much to higher elution volumes, also lies above right to the data for the control. Again, this indicates that the species present are branched in keeping with the ^{1}H NMR data showing a significant content of DVB segments in this fraction.

Similar molar mass distribution curves and corresponding molar mass vs elution volume plots for samples *b*-PMMA4−7 prepared with a MMA/DVB mole ratio of 100/5, for samples

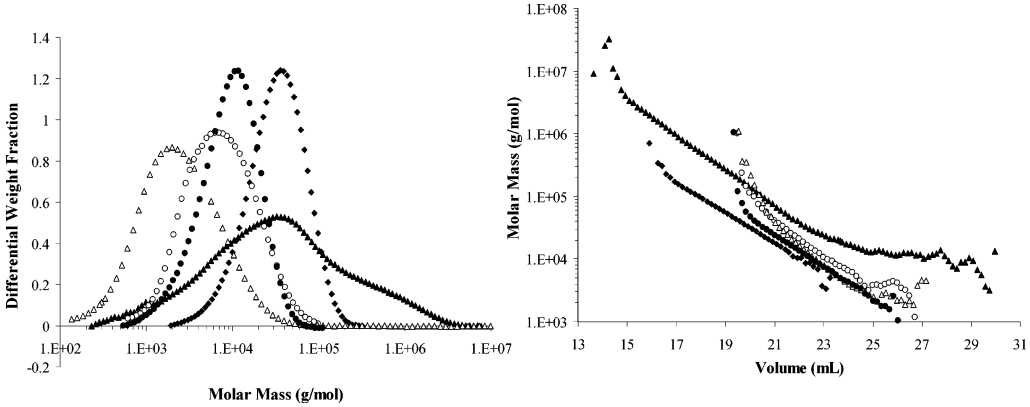

Figure 5. MALS/SEC molar mass distribution curves (left) and SEC molar mass vs elution plots (right) for (◆) PMMA5: MMA/DDT = 100/2, (●) PMMA8: MMA/BM = 100/2, (△) *b*-PMMA8: MMA/DVB/BT = 100/10/20, (○) *b*-PMMA10: MMA/DVB/BT = 100/10/16, and (▲) *b*-PMMA12: MMA/DVB/BT = 100/10/12.

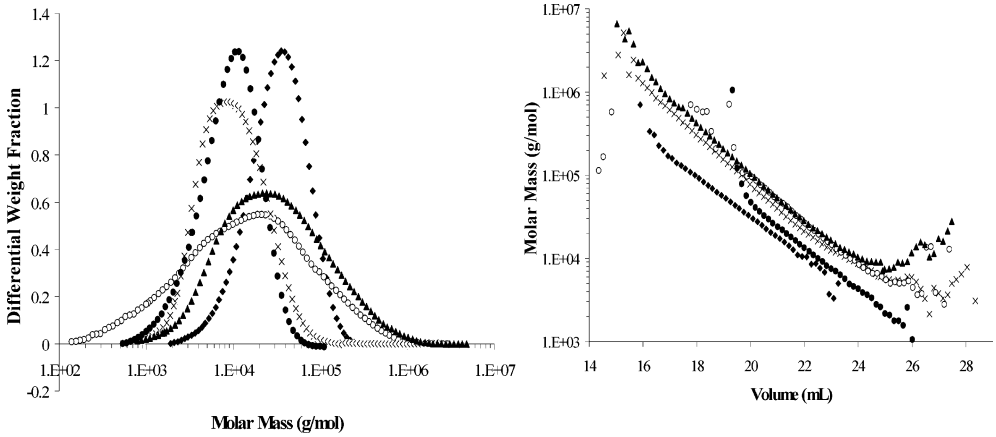

Figure 6. SEC molar mass distribution curves (left) and SEC molar mass vs elution plots (right) for (◆) PMMA5: MMA/DDT = 100/2, (●) PMMA8: MMA/BM = 100/2, (×) *b*-PMMA14: MMA/DVB/BT = 100/15/21, (○) *b*-PMMA15: MMA/DVB/BT = 100/15/18, and (▲) *b*-PMMA17: MMA/DVB/BT = 100/20/24.

b-PMMA8−12 prepared with MMA/DVB of 100/10, and for samples *b*-PMMA14−17 prepared with MMA/DVB of 100/15 or 100/20 are shown in Figures 4−6, respectively, along with data for two linear control samples, PMMA5 and PMMA8. For each group of samples the results are similar, the trends discussed below being increasingly manifest as the mole feed ratio of MMA/DVB is increased from 100/2 to 100/20. First, for a given MMA/DVB ratio as the level of chain transfer agent, BT, is reduced, the molar mass distribution of the products broadens and shifts to higher molar mass. In addition, the corresponding molar mass vs elution volume plots lie above right to the lines for the two linear controls, with the plots migrating further from the linear control data as the level of transfer agent is reduced. Second, as the level of brancher in the feed is increased from MMA/DVB = 100/2 to 100/20, the level of BT required to produce soluble branched polymer as opposed to insoluble cross-linked material also increases. Thus, for MMA/DVB mole feed ratios rising from 100/2 to 100/20 the minimum MMA/BT mole feed ratios required to avoid gelation rises from ∼100/4 to ∼100/24. Beyond a MMA/DVB ratio of 100/20, it proved impossible to produce soluble polymer irrespective of the level of BT used. To a good approximation therefore in the MMA/DVB range up to 100/20 the synthesis of branched polymer is achievable when the DVB/BT mole feed ratio is ≤1. This is consistent with the mechanistic picture we have deduced for similar branched polymerizations in organic solvents where we have shown that the average number of branching units per primary polymer chain, N_C, can be evaluated from analysis of appropriate ^{1}H NMR spectra of products.[7] The number of primary polymer chains is controlled by the level of transfer agent used (BT in the present polymerizations) and the number of branches by the level of fully reacted brancher incorporated (∼100% DVB in these polymers). It seems therefore that the same control mechanism is operating in the present organic solventless emulsion polymerizations, and control over branching vs cross-linking can be exercised as it can be in solution polymerization. As the DVB/BT mole feed ratio rises toward unity, the possibility of incorporation of more than one branching unit per primary polymer chain rises with the prospect of forming some microgel, and eventually with DVB/BT feeds beyond unity macrogelation becomes inevitable.

The MALS/SEC data for the purified branched polymers *b*-PMMA12,-15, and -17, which have relatively high levels of branching units (experimentally determined MMA/DVB mole ratios respectively of 100/8.5, 100/12.5, and 100/14.5) can be compared with the linear control polymer PMMA1. This allows computation of the respective mean-square radii of gyration at given molar masses,[23,24] and from these data the corresponding Zimm branching factors, *g*, can be calculated.[25] For molar mass slice 200 000 the *g* value is ∼0.38 for all three samples, falling to ∼0.30 at 500 000 and ∼0.24 at mol 700 000. These data confirm the highly branched nature of these products and are consistent with high content of DVB residues found in each of these.

Conclusions

Use of appropriate levels of benzylthiol chain transfer agent allows complete conversion of MMA/DVB mixtures to branched

products under aqueous emulsion conditions. Mole feed ratios of MMA/DVB up to 100/20 can be used to produce highly branched products without cross-linking, providing the DVB/BT mole ratio is ≤1. Remarkably, the branched products are formed in absence of any additional organic solvent whereas similar reaction mixtures employed under bulk or aqueous suspension conditions lead inevitably to cross-linked products irrespective of the level of transfer agent used.

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References and Notes

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