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Synthesis of Branched Poly(methyl methacrylate)s: Effect of the Branching Comonomer Structure

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ABSTRACT: Branched poly(methyl methacrylate)s have been prepared using conventional solution phase free radical polymerization of methyl methacrylate (MMA) in the presence of a branching divinyl comonomer with appropriate levels of dodecanethiol (DDT) chain transfer agent added to inhibit gelation. The branching comonomers employed were five ethylene glycol dimethacrylates with varying lengths of PEG chains, divinylbenzene (DVB), and ethylene glycol diacrylate (EGDA). Soluble branched polymers were obtained in good yield with a MMA/brancher mole ratio up to 100/15. The minimum mole ratio of DDT required to avoid gelation was evaluated. The isolated polymers were characterized by elemental analysis to determine the level of DDT incorporated, by ^{1}H NMR spectroscopy, to determine the molecular composition and in particular the level of brancher incorporated (both as a branch unit and as a pendant functionality), and by double detection SEC in order to evaluate the level of branching. The differing behaviors of the branchers are discussed with a focus on a comparison of ethylene glycol dimethacrylate (EGDMA), EGDA and DVB. The latter brancher has been shown to produce the most regularly branched material with the smallest molar mass distributions. In general, however, the latter are broad or very broad.

Introduction

As a result of the relatively high cost and the slow technological exploitation of dendrimers,[1] attention has turned recently to methodologies for preparing structurally less pure but more conveniently synthesized hyperbranched polymers. Considerable progress has been made in this context with step-growth polymers using AB$_x$ type monomers.[2,3] Generic routes to branched chain growth polymers, especially those derived from vinyl monomers, are few and far between. However, a very important advance in this area was disclosed in 1995 by Fréchet et al.,[4] who employed a vinyl monomer with an additional functional group capable of initiating the polymerization of other vinyl groups. Fréchet's self-condensing vinyl polymerization (SCVP) methodology has subsequently been expanded by other groups.[5−14] The announcement from our own laboratory in 2000[15] of a facile and generic route to branched vinyl polymers, employing conventional free radical polymerization of a vinyl comonomer with a difunctional comonomer in the presence of a free radical transfer agent to inhibit cross-linking and gelation, is also proving to be an important step forward. The method uses only cost-effective materials routinely available in polymer laboratories and to polymer manufacturers, and it holds out good promise in terms of scale-up and exploitation. We and our collaborators[16] have demonstrated clearly the branched nature of the products and the ability to produce good yields of soluble polymer at high conversion.

Most recently, we have reported on an in-depth study of the system methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) using dodecanethiol (DDT) as the radical transfer agent.[17] Careful structural analytical work using solution phase ^{1}H nuclear magnetic resonance (NMR) spectroscopy has enabled the branching process to be monitored at the molecular level, while dual detection size exclusion chromatography (SEC) has provided absolute molar mass distribution data demonstrating the increased density of the branched products relative to a linear broad molar mass poly(methyl methacrylate) (PMMA) reference polymer. In this system, we have shown that increasing the level of EGDMA, and simultaneously the level of DDT, results in increased branching and a broadening of the molar mass distribution. Furthermore, up to 15 mol % of the EGDMA can be employed while still producing completely soluble polymer at high conversion. It is also clear that branching arises via the reaction of one vinyl group in EGDMA to produce polymer chains containing pendent C=C bonds in the first instance, followed by the reaction of these pendent groups with additional MMA monomer units or other growing chains to produce a branched architecture.

We were somewhat surprised at the differential reactivity of the two vinyl groups in EGDMA under the conditions of our copolymerizations, but this made us realize how potentially important these relative reactivities are, and encouraged us to examine other difunctional comonomer species. The present paper reports on the branching copolymerization of MMA with divinylbenzene (DVB), EGDMA, diethylene glycol dimethacrylate (di-EGDMA), triethylene glycol dimethacrylate (tri-EGDMA), tetraethylene glycol dimethacrylate (tetra-EGDMA), poly(ethylene glycol) dimethacrylate 400 (PEG 400 dimethacrylate) and ethylene glycol diacrylate (EGDA).

Experimental Section

Materials. MMA, EGDMA, di-EGDMA, tri-EGDMA, tetra-EGDMA, PEG 400 dimethacylate, EGDA, DVB (∼80% grade), and DDT were used as supplied by the Aldrich Chemical Co. Azobis(isobutyronitrile) was used as supplied by the BDH Chemical Co. The solvents used (toluene, methanol, hexane, tetrahydrofuran (THF), chloroform, dichloromethane (DCM), and dimethyl sulfoxide (DMSO)) were of standard laboratory reagent grade. The linear, broad molar mass PMMA used as

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Table 1. Branched Copolymers of MMA Prepared Using Various Ethylene Glycol Dimethacrylate Branchers[a]

entry	branching agent	yield (%)	solubility (0.5 g/mL)	% S content	M_n	M_w	M_w/M_n
linear PMMA			soluble in all solvents		52 270	115 000	2.20
l-PMMA1		70	soluble in all solvents		27 920	37 770	1.35
l-PMMA2		70	soluble in all solvents		11 210	17 740	1.58
b-PMMA1	EGDMA	67	soluble in all solvents	2.3	21 940	58 170	2.65
b-PMMA2	Di-EGDMA	62	insoluble in DMSO and DCM	2.4	6570	18 190	2.76
b-PMMA3	tri-EGDMA	65	insoluble in DMSO	2.5	5870	20 210	3.44
b-PMMA4	tetra-EGDMA	61	insoluble in DMSO	2.2	6600	98 410	10.36
b-PMMA5	PEG 400 dimethacrylate	62	insoluble in all solvents	2.6			

[a] MMA, 5 g, 50 mmol; mole feed ratio MMA/brancher/DDT = 100/12/12; AIBN, 1 mol % of total C═C; T (°C) = 80; solvent, toluene (25 mL); time = 5 h. [b] Solvents tested: toluene, THF, $CHCl_3$, DCM and DMSO.

a reference sample in the SEC analyses ($\bar{M}_w = 111\,500$; $\bar{M}_w/\bar{M}_n = 2.2$) was from the Aldrich Chemical Co.

Synthesis of Branched Copolymers. The copolymerizations were carried out using a Carousel Reaction Station (Radley Discovery Technology, U.K.). The branching comonomer, DDT, AIBN (1 mol % of total C═C), and MMA (1.5 g, 15 mmol or 2.5 g, 25 mmol) were added successively to toluene (5 or 7.5 mL). The mixtures were degassed using a vacuum pump and then blanketed in nitrogen. The reaction vessels, each equipped with a condenser, were maintained at 80 °C for 5 h with magnetic stirring. Each product was isolated by precipitation into *n*-hexane 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 45 °C to yield the isolated polymers.

Characterization. Solubility Tests. Solubility tests were performed visually in test tubes placed in an ultrasonic bath for 10 min at room temperature. The solvents tested were toluene, THF, chloroform, DCM, and DMSO.

Elemental Microanalyses. These were carried out on a Perkin-Elmer 2400 analyzer by the Elemental Microanalytical Service available within the Department of Pure and Applied Chemistry at the University of Strathclyde.

NMR Spectroscopy. ^1H NMR spectra were recorded on a 400 MHz Bruker DPX-400 spectrometer using $CDCl_3$ as the solvent in 5 mm NMR tubes. In all the spectra the signal of $CDCl_3$ was used as a reference.

Dual Detection Size Exclusion Chromatography (DT-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 Shimadzu CTO-6A column oven; (v) a set of three Styragel HR 2, HR 4 and HR 6 designation 7.8 × 300 mm GPC columns; (vi) two detectors connected in a serial configuration, a multiangle light scattering detector (mini-Dawn) operating at 690 nm 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 30 °C, and the flow rate was 1 mL/min. The samples were prepared for injection by dissolving 20 mg of polymer in 4 mL of HPLC grade THF; 0.2 mL of this mixture was then injected and data collected for 40 min. The dedicated Astra software package for Windows was used to collect and progress the signals transmitted from the detectors to the computer and to produce the molar mass distribution and molar mass vs elution volume plots.

The interferometer refractometer, Optilab DSP, was employed to carry out the d*n*/d*c* measurements in an off-line mode of operation. For each product analyzed, a series of sample dilutions were prepared. The highest concentration used in the analysis depended upon the sample but also on its corresponding RI response (usually in the range 1×10^{-3} to 3×10^{-3} g/mL). A stock solution, which was 5−10 times as concentrated as the highest sample concentration to be examined, was prepared, and a series of dilutions ranging from the highest sample concentration to 10% of this value were prepared by dilution of the stock solution. Typically five different samples (including the highest sample concentration) were prepared which were distributed evenly throughout the range of concentrations. The Optilab DSP was then flushed with the solvent in which the d*n*/d*c* value was to be determined (THF) to ensure that a representative and stable response was obtained. A glass syringe (10 mL) was filled with the solvent or sample solution and connected to the Optilab DSP using a syringe luer. The syringe was then placed in a syringe pump and the flow rate set at 1 mL/min. The software DNDC for Windows was used to collect and process the data. The d*n*/d*c* values measured were in the range of 6×10^{-2} to 10×10^{-2} mL/g.

Results and Discussion

Evaluation of SEC Data. At the outset it is important to realize that the synthetic methodology reported here involves a highly complex, kinetically controlled process, such that the resulting macromolecular products are, in general, a very complex mixture in terms of molar mass and also backbone architecture. It is not surprising therefore that the branched PMMAs produced in this work give rise to complex SEC data (see later). So much so, in fact, that in analyzing and discussing the data we have previously argued[17] that the most informative way of presenting these data is in terms of molar mass distribution curves and molar mass vs elution volume plots. The data have been derived from the output of both the refractive index and light scattering SEC detectors, with the necessary d*n*/d*c* data determined separately off-line. In this sense, therefore, the molar mass data can be regarded as "absolute" but is nevertheless limited to the capability of the Astra software. It is also important to appreciate that, for example, a molar mass datum point at a single SEC elution volume potentially still relates to a complex mixture of macromolecules of differing molar mass and branching architecture, all of which coincidentally possess very similar hydrodynamic volume.

As a basis for comparison of the data from our branched samples we have prepared a linear homopolymer of MMA (l-PMMA1) under identical conditions to those used in preparing the branched samples but in the absence of both a branching comonomer and DDT. A second linear homopolymer of MMA (l-PMMA 2) has been prepared similarly but in the presence of 1 mol % DDT relative to MMA. M_n, M_w, and M_w/M_n data for these two samples and a broad linear homopolymer of MMA obtained from the Aldrich Chem. Co. (linear PMMA) are shown in Table 1.

Ethylene Glycol-Based Dimethacrylate Branching Agents. The branching monomers EGDMA, di-EGDMA, tri-EGDMA, tetra-EGDMA, and PEG 400 dimethacrylate were each copolymerized with MMA in toluene using DDT as the transfer agent at a mole ratio MMA/brancher/DDT of 100/12/12. The ratio MMA/brancher was chosen from previous results[17] with the MMA/EGDMA system to be close to the limit above

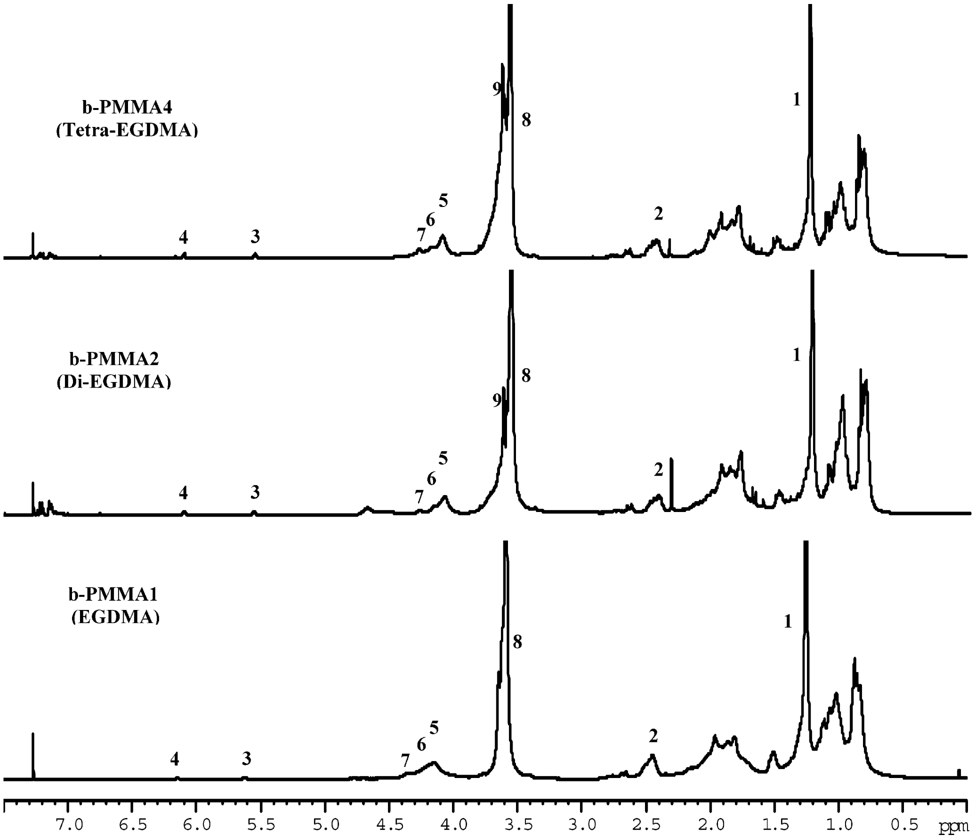

Figure 1. ^{1}H NMR spectra of branched copolymers b-PMMA1 (EGDMA), b-PMMA 2 (di-EGDMA), and b-PMMA 4 (tetra-EGDMA).

which cross-linking becomes difficult to suppress. The results obtained are shown in Table 1. In the case of the first four copolymers each polymerization mixture remained as an isotropic solution after 5 h, whereas the copolymerization reaction employing PEG 400 dimethacrylate gelled. The latter product, b-PMMA5 once isolated as a solid, proved to be insoluble in all solvents tested and was clearly cross-linked. The EGDMA based product b-PMMA 1 was readily soluble in all the solvents examined, but b-PMMA 2−4 proved to be very poorly soluble in DMSO with some evidence that the limited solubility decreased further as the length of the brancher increased. Somewhat anomalously b-PMMA-2 also showed poor solubility in DCM. Overall however the isolated yields of branched copolymers were satisfactory ~65% and no attempt was made to further optimize these. The elemental microanalytical data indicated good incorporation of sulfur from the DDT transfer agent. The ^{1}H NMR spectra (Figure 1) confirm this with the multiplet at 1.3 ppm corresponding to the methylene H atoms (H^1) in the $-(CH_2)_9-$ group and the broad signal at 2.5 ppm corresponding to the $-CH_2-S-$ methylene H atoms (H^2) (Figure 2). All the spectra show clear evidence for unreacted pendent methacrylate groups with the vinylic H atom resonances at 5.7 (H^3) and 6.2 (H^4) ppm. We have previously assigned the signals at 4.1, 4.2, and 4.35 ppm in MMA/EGDMA copolymers respectively to methylene H atoms (H^5) in fully reacted (branching) EGDMA residues and to methylene H atoms (H^6) and (H^7) in pendent unreacted EGDMA residues[17] (Figure 2), though the 4.2 ppm signal is often overlapped by the 4.1 ppm signal. The spectrum of b-PMMA 1 prepared here with MMA/EGDMA is consistent with our previous assignment. The spectra of b-PMMA 2 and b-PMMA 4 (Figure 1) prepared respectively with MMA/di-EGDMA and MMA/tetra-EGDMA are similar to that of b-PMMA 1 but include a signal at ~3.65 ppm a little downfield from the signal at 3.6 ppm the latter being characteristic of the methoxy H atoms (H^8) in the predominant MMA residues. We assign the 3.65 ppm resonance to the

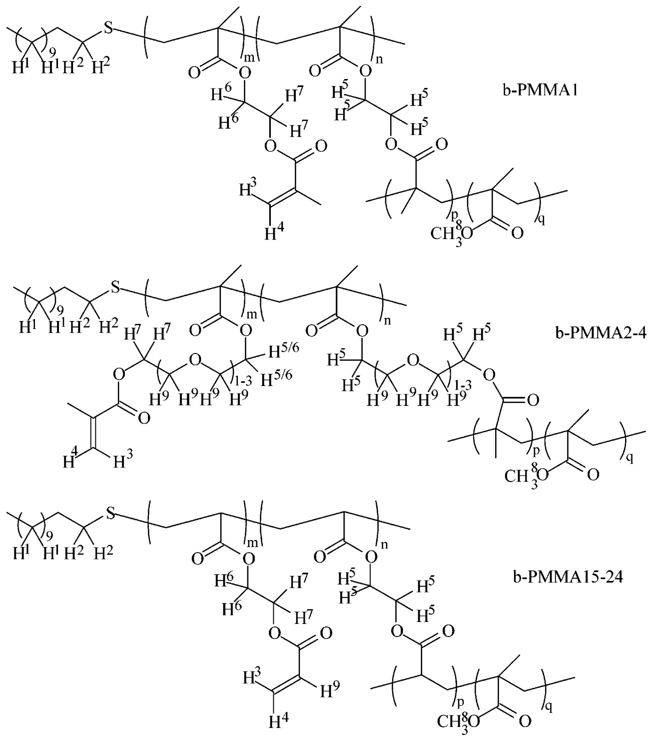

Figure 2. Structures of branching units and pendent unreacted methacrylate residues in branched copolymers b-PMMA 1−4 and b-PMMA 15−24.

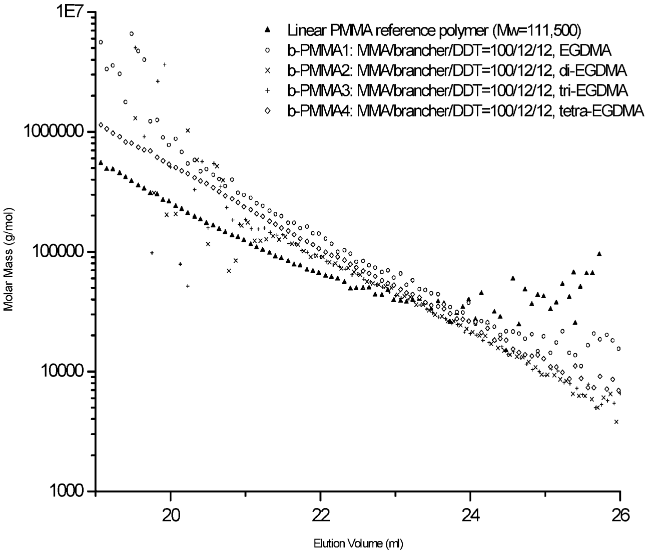

Figure 3. SEC molar mass vs elution volume plots for branched PMMAs prepared using different ethylene glycol based dimethacrylates as brancher.

$-CH_2\ OCH_2-$ methylene H atoms (H^9) in the oligo(ethylene oxide) branching groups in b-PMMA 2−4 (Figure 2). The small aromatic multiplets ~7.2 ppm in the spectra of b-PMMA 2 and b-PMMA 4 (Figure 1) arise from trapped toluene which seems to be associated with the EO residues in these copolymers. Overall therefore the ^{1}H NMR data indicate that di-EGDMA, tri-EGDMA, and tetra-EGDMA behave similarly to EGDMA in terms of branching.

The SEC chromatograms of b-PMMA 1−4 are broad as expected and the corresponding M_n M_w and M_w/M_n data are shown in Table 1. Comparing these data with the corresponding ones from the in-house prepared linear polymers l-PMMA 1 and l-PMMA 2 superficially, it seems that b-PMMA 1 is not too dissimilar to l-PMMA 1 and that b-PMMA 2 is not too different from l-PMMA 2. In the case of b-PMMA 3 and 4, the increased breadth of the molar mass distribution is however more obvious. The raw M_n and M_w data do not however convey the full picture. The corresponding molar mass vs elution volume curves (Figure 3) are perhaps more informative. In all cases at any given elution volume, e.g., 22 mL, the molar masses of the copolymers b-PMMA 1−4 are all larger than that of the linear PMMA sample. SEC theory dictates that all of these samples have the same hydrodynamic volume, and so the copolymers must have a higher segment density i.e., they are all branched, as indicated from their ^{1}H NMR spectra. In this instance b-PMMA 1 is on average the most branched, followed by b-PMMA 4. b-PMMA 2, and b-PMMA 3 are on average less branched. However, it is important not to overinterpret these data which are likely to be highly convoluted because of the complexity of the samples. In a given copolymer, macromolecules with different molar masses, and at the same time different degrees of branching, are likely to have similar hydrodynamic volumes and hence elute simultaneously.

The fact that copolymer b-PMMA 5 prepared using PEG 400 dimethacrylate could not be prepared as a branched, rather than a gelled, product under the same conditions used for the other copolymers is significant. This tends to suggest that it is more difficult to inhibit cross-linking when using longer branchers, and additional experiments using this group of branchers tends to support this view. This also prompted us to examine DVB providing a short potentially much more rigid branching unit.

DVB as Branching Agent. Copolymers with different MMA/DVB/DDT mole feed ratios were prepared under standard conditions in toluene. The results are shown in Table 2. (Note: The mole ratio of DVB is quoted as if the commercially sourced material was 100% DVB; in practice the grade used contained ~55% *m*-DVB, ~25% *p*-DVB and ~20% *m*- and-*p*-ethylstyrene.) Using a MMA/DVB mole ratio of 100/1 produced an insoluble cross-linked product as expected. However use of DDT in a 1/1 mole ratio with DVB yielded soluble copolymers up to a MMA/DVB mole ratio of 100/15. However using a mole feed ratio of MMA/DVB/DDT of 100/5/3 yielded a cross-linked insoluble copolymer. Typically the yields of isolated fully soluble branched copolymers are high (80−50%) though these do seem to fall as the level of DDT used increases. No further attempts were made to improve the recoveries. Overall the pattern of behaviour seen is very similar to that already reported for the MMA/EGDMA system.[17] The elemental microanalytical data for C, H and S % were used to compute the % of oxygen by difference. The % S was then used to calculate the content of DDT residues in the product, the % oxygen gave the MMA content and the DVB content was calculated as the balance. Bearing in mind the likely uncertainties in this methodology, there is a surprisingly good correlation (Table 2) between the expected and found contents of both DVB and DDT. Overall from these data there is evidence that the brancher content is consistently a little higher than the content of chain transfer agent residues, although the ^{1}H data (not recorded here) suggests the balance to be slightly the other way. The latter evaluation however is also subject to error because of the overlapping of signals from the DDT and MMA residues. Overall, therefore, the relatively good correlation between the DVB and DDT feeds and the corresponding experimentally determined copolymer compositions contrasts with the situation which arises in the MMA/EGDMA/DDT system.[17] In the latter case, EGDMA residues are consistently incorporated more efficiently than are the DDT fragments. The chain transfer constant of styrene to DDT is reported to be 15, whereas the corresponding figure for MAA is 0.7.[18] Hence presumably the styrenic (and hence the DVB) radical reacts more efficiently with DDT than does the MMA (and hence the EGDMA) radical. (Note: we have not been able to find chain transfer constants for DVB and EGDMA directly.) This no doubt accounts for the improved efficiency of incorporation of DDT residues when DVB is the brancher but may also be a factor in the more uniform rate of branching which seems to occur (see ^{1}H NMR data to follow) when using this brancher.

A typical ^{1}H NMR spectrum of b-PMMA 9−13 is shown in Figure 4 in this instance b-PMMA13 prepared with the highest level of DVB. The DDT residues are clearly visible in the signals at 1.3 and 2.5 ppm, and the broad aromatic H signals due to the DVB residues are manifest at ~7 ppm. What is remarkable, however, is the complete absence of any signals due to pendent unreacted vinyl groups. The spectra of the other copolymers confirmed this picture. This result is quite different from that found with the ethylene glycol-based dimethacrylate branchers. It suggests that the two polymerizable groups in DVB are of similar reactivity

Table 2. Branched Copolymers of MMA Prepared Using DVB as Brancher[a]

entry	feed ratio (mol) MMA/DVB/DDT	appearance of reaction mixture	yield (%)	solubility (0.5 g/mL)	DVB content[c] (wt %) expected	DVB content[c] (wt %) found	DDT content[c] (wt %) expected	DDT content[c] (wt %) found	M_n	M_w	M_w/M_n
b-PMMA8	100/1/0	gel	68	insoluble	1	4.6	0	0			
b-PMMA9	100/1/1	viscous solution	79	soluble[b]	1	6.3	1	2.3	5520	62 080	11.20
b-PMMA6	100/2/2	fluid solution	77	soluble[b]	2	3.5	2	2.8	7395	97 690	13.20
b-PMMA10	100/5/5	viscous solution	69	soluble[b]	5	6.4	5	5.8	10 160	130 200	12.81
b-PMMA11	100/8/8	viscous solution	61	soluble[b]	8	9.5	8	8.6	9180	111 110	12.10
b-PMMA12	100/12/12	viscous solution	51	soluble[b]	12	13.7	12	12.7	12 680	102 700	8.09
b-PMMA13	100/15/15	viscous solution	49	soluble[b]	15	16.5	15	13.2	13 020	84 750	6.50
b-PMMA14	100/5/3	gel	66	insoluble	5	8.0	3	3.7	-	-	-

[a] MMA, 2.5 g, 25 mmol; AIBN, 1 mol % of total C=C; T (°C) = 80); solvent: toluene (7.5 mL); time = 5 h. [b] Products soluble in THF, toluene, chloroform and DCM. All products insoluble in DMSO. [c] DDT content (±0.5%) calculated from elemental microanalytical % S; MMA content from 0%; DVB by difference (±2.0%).

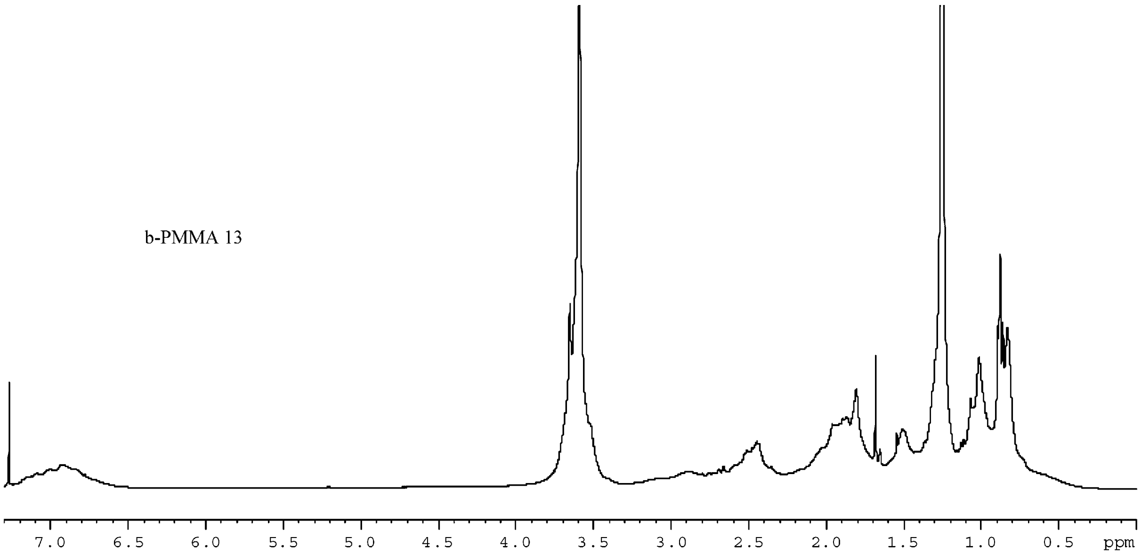

Figure 4. ^{1}H NMR spectrum (CDCl$_3$) of b-PMMA 13 (MMA/DVB/DDT = 100/15/15).

and certainly that both are consumed more readily than the two polymerizable groups in, e.g., EGDMA. Overall, the branching process involving DVB seems to be a smoother, more regular process than that involving MMA with EGDMA (and EGDA, see later) in the sense that both of the DVB vinyl groups seem to be used efficiently and concurrently in generating branching units. In the copolymerization of DVB isomers with styrene it is generally accepted that the first vinyl group in DVB is more reactive than the second (arguably because the radical formed from addition to the first vinyl group is more resonance stabilized than the radical arising from addition to the second, the first vinyl group no longer being available for participation in resonance stabilisation).[19,20] However, no analogous data seems available in the literature for copolymerization of DVB with MMA, though the evidence here is that any reactivity difference seems small. Care is required, however, because of the high chain transfer constant of styryl radical to DDT mentioned above, and this may play an important role in determining net relative reactivity.

Overall, however, a picture emerges from the use of DVB as the brancher, relative to EGDMA, in MMA copolymerizations of a more regular branching process in which pendent vinyl groups are consumed smoothly throughout the conversion process such that their stationary concentration remains low. To some extent this is counterintuitive since DVB might be expected to provide much more rigid branching points than does, e.g., EGDMA. However, this relatively rigid conformation may actually offer a favorable opportunity for reaction and branching, and minimize the interaction between converging polymer chains.

The SEC chromatograms for copolymers b-PMMA 9–13 show that all the products have a broad molar mass distribution with strong evidence that the distributions are multimodal. The calculated M_n, M_w and M_w/M_n data are shown in Table 2, confirming the breadth of the molar mass distributions. However, the changes in M_w/M_n as the DVB and DDT feeds are increased are not large (see EGDA as brancher Table 3) particularly bearing in mind that the mole ratio MMA/DVB is increased from 100/2 to 100/15. Much more substantial broadening of the distributions are seen in the MMA/EGDMA system as the EGDMA and DDT feeds are increased,[17] and the more internal uniformity in the MMA/DVB series of copolymers seems to be a reflection of the better balance between the reactivity of the brancher and the DDT, compared to that in the MMA/EGDMA system, and the more regular nature of the whole conversion process. The molar mass vs elution volume plots Figure 5 show clearly that the copolymers b-PMMA 9–13 have higher molar mass at all elution volumes than the linear PMMA reference. At a given elution volume, i.e., hydrodynamic volume, the copolymers are on average denser and hence branched. The densest, and hence most highly branched, are b-PMMA 12 and b-PMMA 15, not surprisingly from the high MMA/DVB mole ratios, 100/12 and 100/15 respectively,

Table 3. Gelation Limit of the System MMA/EGDA/DDT = 100/15/x[a]

entry	feed ratio (mol) MMA/EGDA/DDT	appearance of reaction mixture	yield (%)	solubility[b] (0.5 g/mL)	content of DDT (wt %)[c]		M_n	M_w	M_w/M_n
					expected	found			
b-PMMA15	100/15/15	fluid solution	60	soluble	29.0	17.0	5280	15 550	2.94
b-PMMA16	100/15/14	fluid solution	62	soluble	27.0	18.5	6140	21 900	3.56
b-PMMA17	100/15/13	fluid solution	61	soluble	25.0	14.0	7845	44 550	5.68
b-PMMA18	100/15/12	fluid solution	71	soluble	22.8	17.0	7144	59 300	8.30
b-PMMA19	100/15/11	fluid solution	68	soluble	21.0	6.8	8137	87 400	10.74
b-PMMA20	100/15/10	fluid solution	84	soluble	19.7	16.7	5030	159 700	31.76
b-PMMA21	100/15/9	fluid solution	78	soluble	17.1	13.8	6830	206 300	30.21
b-PMMA22	100/15/8	fluid solution	72	soluble	15.6	11.6	6019	133 800	22.24
b-PMMA23	100/15/7	gel	70	insoluble	13.6	8.5			
b-PMMA24	100/15/6	fluid solution	74	soluble	12.7	5.8	15 840	3 774 000	238.17
b-PMMA25	100/15/5	gel	77	insoluble	9.4	9.8			

[a] MMA, 1.5 g, 15 mmol; AIBN, 1 mol % of total C═C; *T* (°C) = 80; solvent, toluene (7.5 mL); time 5 h. [b] Solubility tests carried out in toluene, THF, chloroform, DCM, and DMSO. All products insoluble in DMSO. [c] Determined from elemental microanalytical % S.

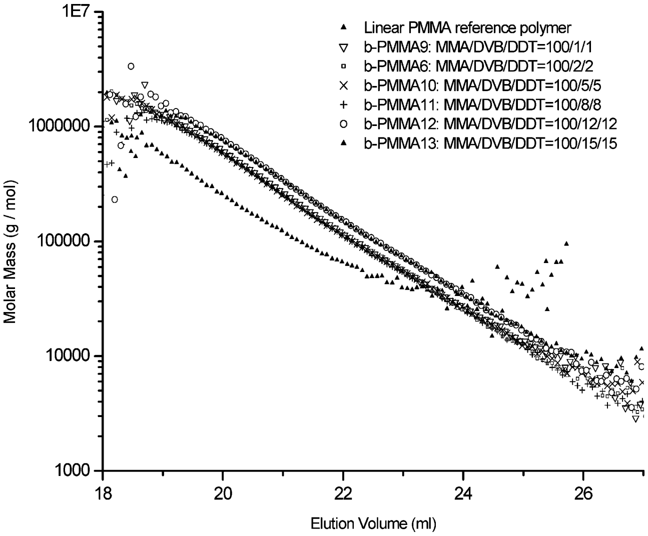

Figure 5. SEC molar mass vs elution volume plots for branched PMMA's prepared using DVB as brancher.

used in synthesizing these copolymers. It is important to note however that the variation in branching density seen here with the MMA/DVB series of copolymers is considerably lower than that seen in the following MMA/EGDA series.

EGDA as Branching Agent. EGDA was selected as a branching agent for PMMA because it offers potentially contrasting behavior to that of dimethacrylates as a result of the known differences in reactivity ratios between methacrylates and acrylates.[21] We have previously reported on the use of low levels of tripropylene glycol triacrylate[16] as a branching agent but here we report on the use of much higher levels of EGDA and hence potentially on much higher levels of branching. Copolymers with a mole ratio MMA/EGDA of 100/15 were prepared under standard conditions in toluene with the level of DDT transfer agent progressively reduced to determine the critical conditions when gelation could not be inhibited. This parallels our earlier study with EGDMA as brancher.[17] The results are summarized in Table 3. Good recovery of copolymers was achieved in all cases and reaction mixtures remained as isotropic fluid solutions until the MMA/DDT mole ratio was reduced to ~100/6. The polymers b-PMMA 15−22 isolated as dry powders from fluid solutions were subsequently completely soluble (0.5 g mL^{-1}) in toluene, THF, chloroform and DCM but were insoluble in DMSO; these materials are branched (see later). b-PMMA 23 and b-PMMA 25, which were obtained as gels, were insoluble in all solvents tested and are undoubtedly cross-linked. b-PMMA 24 prepared with a mole ratio MMA/EGDA/DDT of 100/15/6 is apparently a soluble material. However, the SEC-derived data for this copolymer (Table 3 and Figure 8, discussed later) suggest this species is more likely to be a microgel.

The elemental microanalytical data (Table 3) show that as the feed ratio of DDT falls so does the content of DDT residues in the product copolymer. Though there is some scatter in the data, the incorporation of DDT residues is always lower than the feed values. Examination of the ^{1}H NMR spectra of the soluble branched products (Figure 6) confirms the presence of DDT residues with the resonance at 1.25 ppm due to the methylene H atoms (H^1) of the $-(CH_2)_9-$ chain. Integration of this signal and that of the H atoms (H^8) in the methoxy groups of the MMA residues at 3.6 ppm allows calculation of the MMA/DDT ratio in copolymers. The overlap of the signal at 1.25 ppm with other backbone H signals means that the accuracy in this calculation is limited. Nevertheless the data derived (Table 4) show the same trend as that derived from the S % data (Table 3), though the level of incorporation of DDT residues from the ^{1}H NMR data seems much closer to the feed values.

As is the case with EGDMA residues, EGDA residues are incorporated as fully reacted branching points and pendent unreacted acrylate groups. The signal at 4.2 ppm corresponds to the methylene H atoms (H^5) in branching EGDA residues, and those at 4.25 and 4.35 ppm to the methylene H atoms (H^6) and (H^7) respectively in pendent acrylate groups (Figures 6 and 2). The latter are accompanied by the vinyl H atom signals at 6.45, 6.15, and 5.9 ppm corresponding to H atoms (H,^{9} H^4 and H^3) respectively The MMA/total EGDA content can be calculated by appropriate integration of the signals from the (H^5−H^7) atoms relative to that of the (H^8) atoms in the methoxy groups of the MMA residues. These data are shown in Table 4. Likewise integration of the (H^3, H^4, and H^9) signals relative to the (H^5−H^7) signals allows the percentage of all incorporated EGDA residues that are unreacted pendent species to be computed (Figures 6 and 2). Again these data are shown in Table 4. Interestingly the level of incorporation of (all) EGDA residues is fairly consistent in all copolymers b-PMMA 15−24 at a MMA/EGDA ratio ~100/13. Though there is some scatter in the data, it seems that the proportion of EGDA residues incorporated that remain as pendent rather than branching groups increases as the level of DDT used is decreased. In principle reducing

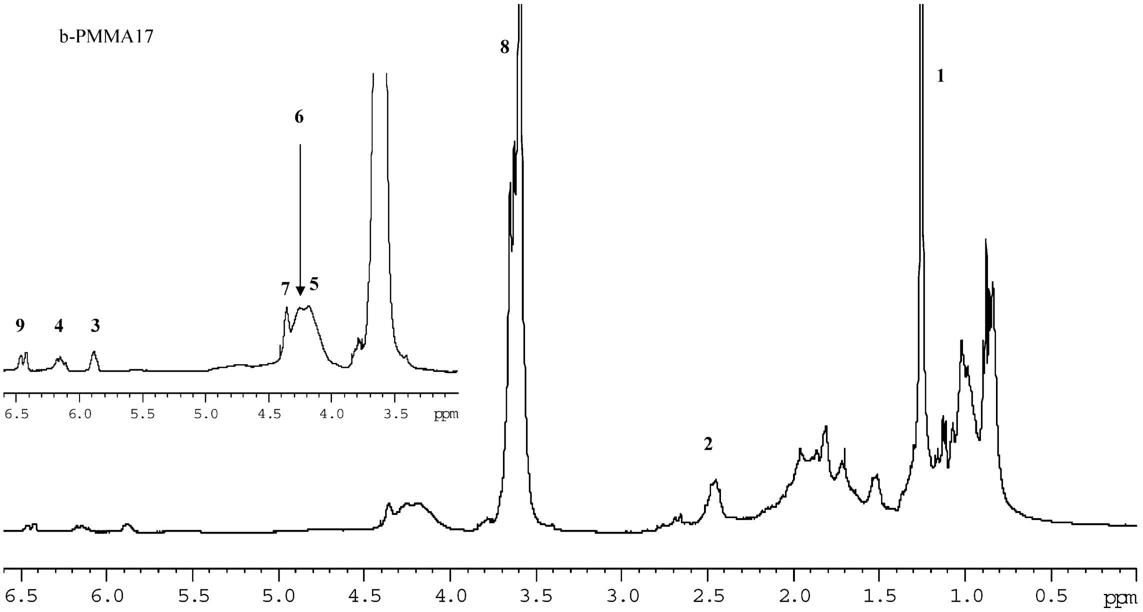

Figure 6. ^{1}H NMR spectrum CDCl$_3$) of b-PMMA17 (MMA/EGDA/DDT = 100/15/13).

Table 4. Composition of Branched MMA/EGDA Copolymers Deduced from ^{1}H NMR spectra

entry	feed ratio (mol) MMA/EGDA/DDT	incorporation ratio (mol) MMA/DDT	incorporation ratio (mol) MMA/EGDA	pendent EGDA (%)	branching ratio (mol) MMA/EGDA	N_c[a]
b-PMMA15	100/15/15	100/10.8	100/13.0	16.0	100/10.9	1.01
b-PMMA16	100/15/14	100/11.5	100/14.8	28.5	100/10.6	0.92
b-PMMA17	100/15/13	100/10.0	100/13.0	30.7	100/9.0	0.90
b-PMMA18	100/15/12	100/9.9	100/12.9	25.0	100/9.7	0.98
b-PMMA19	100/15/11	100/9.8	100/13.6	25.6	100/10.1	1.03
b-PMMA20	100/15/10	100/10.6	100/12.1	26.6	100/8.9	0.84
b-PMMA21	100/15/9	100/9.5	100/12.7	16.6	100/10.6	1.12
b-PMMA22	100/15/8	100/8.7	100/12.9	35.0	100/8.4	0.97
b-PMMA24	100/15/6	100/6.3	100/12.4	36.6	100/7.9	1.25

[a] N_c = branching EGDA/incorporated DDT (mol/mol).

the level of DDT relative to EGDA in the feed will increase the probability of cross-linking. However, since the proportion of EGDA which actually forms branches also falls as the DDT feed is reduced, the tendency to cross-link is not as pronounced as it might have been. This result also suggests that the dodecanethiol radical shows a greater reactivity toward acrylate groups than does methyl methacrylate radical toward acrylate groups. Data in the literature certainly indicate that a given thiol shows greater reactivity toward acrylate radicals than toward methacrylate radicals.[22]

The compositional data in Table 4 derived from ^{1}H NMR spectra also provide a valuable opportunity to estimate the number of branching units (i.e., potential cross-links) per primary chain, N_c. The number of primary chains is likely to be controlled by the level of DDT reacted, i.e., the DDT residues incorporated at chain ends. The number of branches is indicated by the level of EGDA reacted via both vinyl groups. The ratio (moles of doubly reacted EGDA)/(moles of DDT incorporated) is therefore an estimate of N_c, and these data are shown in Table 4. The mean-field theory of Flory and Stockmayer (FS)[23,24] predicts gelation to occur when $N_c = 0.5$ for a narrow molar mass polymer, though of course their model has been further refined subsequently. Ide and Fukuda[25] more recently have deduced a value of N_c close to 1.0 for nitroxide-controlled free radical polymerization of styrene with 4,4^1-divinylbiphenyl, and have suggested that this close agreement with theory is consistent with the formation of a rather homogeneous gel network relative to that formed in a conventional free radical process. Our own values of N_c (as approximated here) are typically around unity and suggest that if N_c rises significantly beyond unity, gelation will ensure. The experimental limit found here for producing soluble (branched) polymer is MMA/EGDA/DDT feed = 100/15/8 and any further reduction in DDT yields a gel. Though we cannot make the necessary ^{1}H NMR spectral analyses of these gels the ratio of (moles of doubly reacted EGDA)/(moles of DDT incorporated) will amost certainly be much larger than unity. Copolymer b-PMMA 24 is interesting in that $N_c \sim 1.25$, and this is consistent with this material being largely a microgel, rather than a branched product.

The reactivity and compositional features of the MMA/EGDA series of copolymers are reflected in the molar mass distributions and branching architectures of these copolymers as revealed by their SEC behavior (Figures 7 and 8). The chromatograms in Figure 7 show that as the feed ratio of DDT is decreased the overall copolymer molar mass increases, and the molar mass distribution becomes progressively broader and increasingly multimodal. The corresponding M_n M_w and M_w/M_n data derived from the chromatograms (Table 3) confirm the above visual observation. Interestingly, the M_n figure remains relatively constant for the series as the M_w figure, and hence the M_w/M_n figure, rises progressively as the DDT feed is reduced. This is indicative of an increase in branching as the DDT feed is reduced. The effect is similar but more dramatic than

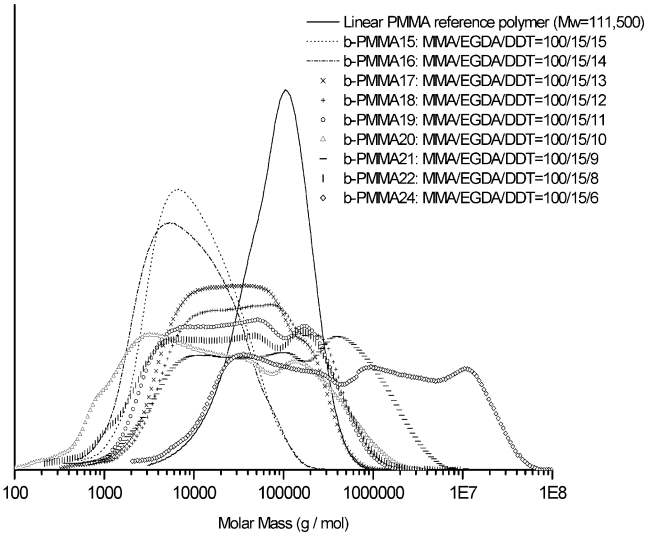

Figure 7. SEC molar mass distribution curves for branched PMMAs prepared using EGDA as brancher.

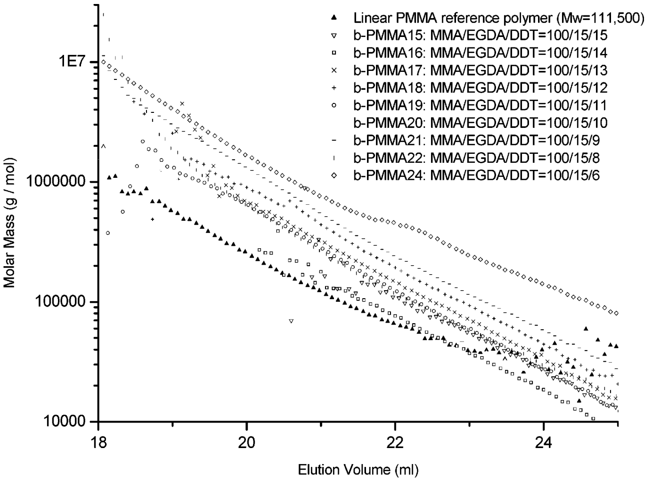

Figure 8. SEC molar mass vs elution volume plots for branched PMMAs prepared using EGDA as brancher.

the trends seen with the other branching comonomers EGDMA and DVB. In the case of b-PMMA 24 prepared using MMA/EGDA/DDT = 100/15/6, the molar mass curve extends nominally to $\sim 10^8$ g mol^{-1}, which in fact lies far beyond the resolution limit of the SEC columns employed and again this suggests that this material contains microgel. Similar distribution curves have been seen before[17] using EGDMA as brancher with the feed MMA/EGDMA/DDT = 100/5/2 and 100/15/10 i.e., when apparently soluble copolymers were produced with DDT $\ll$ brancher.

The corresponding architectures of the copolymers b-PMMA15−22 are indicated in the molar mass/elution curves in Figure 8. In all cases, the curves lie above that for the broad molecular weight linear PMMA reference polymer at all elution volumes. This indicates that for a given hydrodynamic volume b-PMMA 15−22 all have more dense coils than the corresponding linear macromolecule, and so all are branched. Furthermore, as the level of DDT used decreases the plots in Figure 8 move further and further from that of the linear PMMA reference indicating that the copolymer coil density rises systematically i.e., the average degree of branching rises. In some cases, e.g., b-PMMA 18 and 21, the slopes of the curves change significantly across the elution volume axis (i.e., molar mass range) suggesting that the average degree of branching changes, and these changes correlate with the multimodal molar mass distributions seen in the chromatograms. This very complex picture is consistent with our earlier findings using low levels of a diacrylate brancher with PMMA where we were able to fractionate a copolymer sample into various molar mass fractions and demonstrate some systematic variation in the level of branching across the molar mass range.[16] The molar mass/elution curve for copolymer b-PMMA 24 (Figure 8) is remarkable in that it lies so far above the curves for all of the other samples. We believe that this adds weight to our case that this species is largely microgel, and indeed it appears to be microgel across the whole molar mass range.

On balance therefore EGDA behaves more similarly to EGDMA than it does to DVB as a branching agent. The two vinyl groups seem to show a differential reactivity with significant incorporation of pendent unreacted acrylate groups. A more careful comparison of copolymers produced under very similar conditions is therefore worthwhile.

Comparison of EGDMA, DVB, and EGDA Branching Comonomers. Potentially the more interesting materials of those studied are the species produced with high levels of branching comonomer, i.e., employing a mole ratio MMA/brancher of 100/15. In the case of EGDMA and EGDA, data are available for products with this target composition prepared in the presence of varying levels of DDT transfer agent. Significantly for the MMA/EGDMA system gelation occurs when the MMA/EGDMA/DDT mole ratio is reduced from 100/15/15 to 100/15/10[17] whereas for the MMA/EGDA system gelation is not seen until the MMA/EGDA/DDT mole ratio is reduced to 100/15/7. Also the product from the reaction involving MMA/EGDMA/DDT = 100/15/15 contains ~4 mol % of all incorporated EGDMA residues as pendent unreacted methacrylate groups whereas the analogous product from MMA/EGDA/DDT = 100/15/15 contains 16 mol % of its incorporated EGDA residues as pendent unreacted acrylate groups. These data are consistent with the idea that the average value for the number of branching units per primary chain, N_c reaches the critical value of ~1 (beyond which gelation occurs) at a mole ratio MMA/EGDMA/DDT = 100/15/10 for the EGDMA brancher whereas the critical value is not reached until the mole ratio MMA/EGDA/DDT = 100/15/7 for the EGDA brancher. The different rates of incorporation of pendant methacrylate groups (from EGDMA) and acrylate groups (from EGDA) arise from MMA-derived radicals being more reactive toward methacrylate monomers than acrylate monomers, and is in agreement with typical reactivity ratio data for these monomer groups.[21] The present results with EGDA are also in agreement with those reported by Costello and co-workers[16] using tripropylene glycol diacrylate as the brancher.

A direct comparison of the three branchers EGDMA, EGDA, and DVB is possible with the SEC data for materials prepared under identical conditions with the mole feed ratio MMA/brancher/DDT = 100/15/15. The M_n data for the MMA/DVB copolymer (b-PMMA 13) the MMA/EGDMA copolymer (b-PMMA−X) (note that this copolymer is reported in ref 17) and the MMA/EGDA copolymer (b-PMMA-15) are, respectively, 13 020, 4159, and 5280; the M_w data are 84 750, 383 600, and 15 550; and the M_w/M_n data are 6.50, 92.20, and 2.94. These

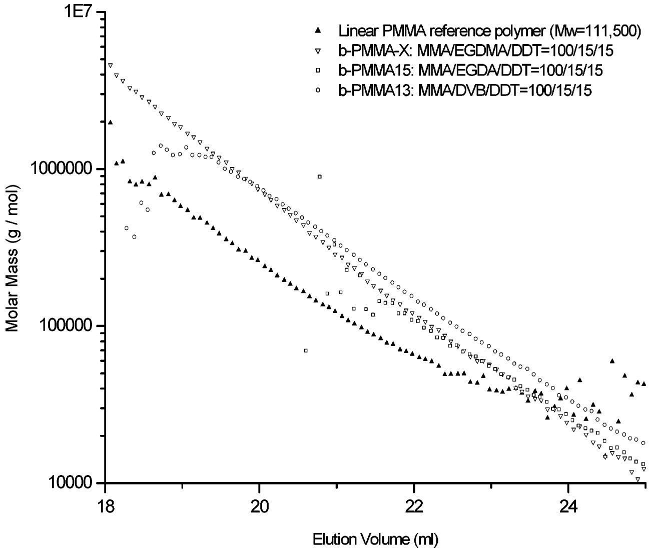

Figure 9. SEC molar mass vs elution volume plots for branched PMMAs prepared using EGDMA, EGDA and DVB as branchers with MMA/brancher/DDT = 100/15/15.

results indicate the molar mass distribution for the MMA/EGDMA copolymer is broader and the individual M_w figure higher than the corresponding data for the MMA/EGDA copolymer. This is consistent with EGDMA being incorporated more effectively as a brancher than EGDA. Interestingly, though the MMA/DVB copolymer also shows a less broad molar mass distribution than the MMA/EGDMA copolymer, the individual M_n datum is higher for the MMA/DVB product. This difference almost certainly arises because of the more regular incorporation of DVB residues as a result of the concurrent and efficient consumption of both vinyl groups in this brancher (note that MMA/DVB copolymers show no evidence of pendent unreacted vinyl groups) and suggests a somewhat more uniform and more highly branched architecture in this copolymer. Crucially as well the corresponding molar mass vs elution volume data (Figure 9) show the MMA/DVB copolymer to have the highest polymer coil density at all elution volumes, except at ∼20 mL. This confirms that DVB provides optimal branching under these conditions and in addition the breadth of the molar mass distribution curve is relatively narrow compared with that of many other samples. This reinforces the view from the analysis of ^{1}H NMR spectra earlier, which showed an absence of any pendent unreacted vinyl groups; that branching occurs relatively smoothly, and regularly, in the MMA/DVB/DDT system with both vinyl groups showing comparable reactivity. Since the DVB grade used is a mixture (∼55% *m*-DVB, ∼25% *p*-DVB, and ∼20% ethylstyrene isomers) this system is particularly complex and at the very least the reactivities of both *p*- and *m*-DVB need to be considered. The relevant reactivity ratios with MMA were calculated from the Alfrey and Price equation[21] to be $r_{\mathrm{MMA}} = 0.41$, $r_{m\mathrm{-DVB}} = 0.61$; $r_{\mathrm{MMA}} = 0.62$, $r_{p\mathrm{-DVB}} = 1.3$. Hence it seems plausible that the *p*-DVB isomer is more favorably incorporated at the early stages of the copolymerization with the *m*-DVB isomer becoming progressively more involved as conversion proceeds. Indeed it is tempting to suggest that the combination of *p*- and *m*-DVB in the commercial mixture may fortuitously contribute to producing a rather regular branching process. As mentioned earlier the short relatively rigid nature of the PVB-derived branching unit may also contribute in this respect. The results suggest that copolymers synthesized separately with pure *p*-DVB and pure *m*-DVB would make a very useful comparative study.

Conclusions

Use of ethylene glycol based dimethacrylates, EGDA, and DVB in copolymerizations with MMA allows the facile synthesis of soluble branched copolymers in moderate to good yields, providing gelation is inhibited by use of appropriate levels of DDT chain transfer agent. Soluble non-cross-linked copolymers with a mole ratio MMA/brancher up to 100/15 are readily prepared using this approach. The ethylene glycol-based dimethacrylates tend to give rise to gelation more easily as the PEG chain is lengthened; e.g., with PEG 400 dimethacrylate inhibition of gelation is difficult. Both EGDMA and EGDA give rise to branched copolymers containing pendent unreacted methacrylate and acrylate groups respectively, with the EGDA showing a higher tendency for this. In contrast, DVB yields products with no detectable (by ^{1}H NMR spectroscopy) pendent unreacted vinyl groups. Overall the least effective branching agent is EGDA and the most effective is DVB. The latter in particular provides rather smooth and regular branching chemistry with products having the lowest molar mass distributions. In practice the three branching agents provide a broad spectrum of opportunity in terms of the backbone architectures and molar mass distributions that can be made available to would-be PMMA users. The methodology described is generic, one-pot and exploits only regulatory approved starting materials available at low cost. In this respect, it avoids the need for speciality functional monomers, such as those used in self-condensing vinyl polymerization,[4−14] and the polymerizable chain transfer agents recently reported by Yamada et al.[26] in exploiting addition−fragmentation reactions for the production of branched vinyl polymers. The methodology provides a means of making a wide variety of branched vinyl polymers available, potentially on a large scale, and the prospects for technological exploitation look good.

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