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Application of the "Strathclyde Route" to Branched Vinyl Polymers in Suspension Polymerization: Architectural, Thermal, and Rheological Characterization of the Derived Branched Products

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ABSTRACT: Copolymerizations of methyl methacrylate (MMA) and ethyl acrylate (EA), both monofunctional monomers, with ethylene glycol diacrylate (EGDA) as the brancher (a difunctional monomer) have been carried out via free-radical solvent-free suspension polymerization using 2,2′-azobis-(isobutyronitrile) (AIBN) as the source of radicals, in the presence of a chain transfer agent (CTA) to avoid cross-linking and produce only branched polymers. Investigation of various CTAs led to the choice of 1-dodecanethiol (DDT) mainly due to its low volatility and hydrophobicity. Typically, EGDA/DDT mole ratios of ≤ 0.7 ensure that cross-linking is avoided. The molar mass and the branching architecture of the polymers have been characterized by MALS/SEC and the thermal and rheological behavior by DSC and melt rheology, respectively. The results confirm earlier indications from solution and emulsion polymerizations of the versatility of the "Strathclyde methodology" in producing branched polymers, in this instance in the form of free-flowing spherical particulates and have allowed demonstration of the differences in the thermal and rheological behavior of the branched products relative to their linear analogues.

Introduction

As a result of the relatively high cost and slow technological exploitation of dendrimers, branched and hyperbranched polymers have received considerable attention.[1] They present a more economic and facile way of producing architecturally complex molecules that exhibit, to a lesser extent, some of the unique bulk and solution properties associated with dendrimers such as lower solution and melt viscosities, increased solubility, and higher functional group density. Possible applications of these polymers range from rheological modifiers to applications in nanotechnology and in the field of biomaterials.[2−5]

In 1952, Flory[6] described a polycondensation approach, which marked the beginning of branched and hyperbranched polymer synthesis. It was not until 1995 that Fréchet et al.[7] further extended branching methodologies to vinyl monomers by introducing the concept of self-condensing vinyl polymerization (SCVP), which coupled with features such as end-group control and living polymerization has allowed other groups to further develop this methodology.[8−13] Other generic routes to (hyper)branched chain growth polymers, especially those derived from vinyl polymers, have since been developed; however, these are relatively few in number.[14−20] In this context a facile and generic route to branched vinyl polymers employing conventional free radical polymerization was announced from our own laboratory in 2000.[21] The strategy involves copolymerizations of a vinyl comonomer with a difunctional (or multifunctional) comonomer in the presence of a free radical transfer agent or catalytic chain transfer species to inhibit cross-linking and gelation. The "Strathclyde methodology" has proven to be versatile. We have since gone some way to rationalizing this process and introducing some design criteria[22−24] and employed this in targeting the synthesis of branched versions of some technically useful linear polymers.[25,26] Other groups have employed a similar or related strategy in controlling the synthesis of branched vinyl polymers using conventional free radical polymerization,[27−30] and indeed there has been some useful work in modeling these branching conventional free radical polymerizations.[31] The approach of using a difunctional comonomer to yield branched products has also been adapted by a number of groups employing controlled free radical polymerization methodologies. In principle, and indeed in practice, this offers the prospect of producing branched species with a more regular backbone architecture and distribution of architectures. Emphasis here has been on atom transfer polymerization (ATRP)[32−46] and reversible addition−fragmentation transfer polymerization (RAFT).[47−51] Gao and Matyjaszewski[52] have recently summarized this area in a comprehensive review on controlled radical polymerization of monomers in the presence of cross-linkers to yield polymer structures varying from stars to gels.

Our own group has also demonstrated that the "Strathclyde methodology" can be employed very successfully in conventional free radical aqueous emulsion polymerization,[53] and others have emphasized the potential technological importance of this.[29,30] These processes avoid the use of organic solvent diluent and so are challenging in terms of avoiding cross-linking. Another preferred industrial process employing conventional free radical chemistry is aqueous suspension polymerization,[54] and again these are solventless reactions. This paper describes our application of the "Strathclyde methodology" in producing branched polymers in suspension polymerization. The specific objectives of the work were (i) to demonstrate that this approach can be successfully carried in aqueous suspension in the absence of any solvent, (ii) to carry this out in a laboratory scale reactor but

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Table 1. Suspension Polymerization Synthesis of Linear P(MMA-*co*-EA)s

	composition (molar ratio)						MALS/SEC		
entry	CTA	MMA	EA	CTA	AIBN	recovery (%)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
L1[a]	TPMT	97	3	1	0.15				
L2	TPH	97	3	1	0.15	90	14 000	260 000	18.6
L3	4HTP	97	3	1	0.15	91	35 600	479 000	13.5
L4	BzM	97	3	1	0.15	88	12 200	22 000	1.8
L5	ET	97	3	1	0.15	97	80 000	191 000	2.4
L6	BT	97	3	1	0.15	89	15 000	26 500	1.8
L7	HT	97	3	1	0.15	88	13 400	23 100	1.7
L8	OT	97	3	1	0.15	89	12 300	23 000	1.9
L9	DDT	97	3	1	0.15	87	12 400	22 600	1.8
L10	DDT	97	3	0.22	0.15	82	50 000	85 000	1.7
L11	DDT	97	3	0.5	0.15	89	23 600	41 300	1.8
L12	DDT	97	3	0.7	0.15	85	19 100	31 900	1.7
L13	DDT	97	3	0.8	0.15	85	15 800	27 700	1.8
L14	DDT	97	3	0.9	0.15	83	14 300	25 600	1.8
L15	DDT	97	3	2	0.15	85	6 200	12 100	2.0

[a] No high-quality spherical polymer particulates were recovered.

otherwise employing conditions closely analogous to those that might be employed on a technological scale and yielding free-flowing spherical particulate (beaded) non-cross-linked melt processable branched product, (iii) to characterize the branching architecture using our in-house instrumental facility, (iv) to investigate the thermal behavior of the products (notably any influence of branching on T_g), and (v) to evaluate any effect of branching on the melt rheology of the products, since the latter is a potentially important factor in the technology of processing such products.

Experimental Section

Materials. Methyl methacrylate (MMA) (99%), ethyl acrylate (EA) (99%), ethylene glycol diacrylate (EGDA) (90%), 1-dodecanethiol (DDT) (99%), triphenylmethanethiol (TPMT) (98%), 1-butanethiol (BT) (99%), ethanethiol (ET) (99%), 1-octanethiol (OT) (98%), 1-hexanethiol (HT) (97%), benzyl mercaptan (BzM) (99%), thiophenol (TPH) (99%), and 2,2′-azobis(isobutyronitrile) (AIBN) (97%) from Aldrich Chemical Co. were used as supplied. The solvents used (toluene, tetrahydrofuran (THF), dichloromethane (DCM), dimethyl sulfoxide (DMSO), and chloroform) were of standard laboratory reagent grade. The water used was deionized and doubly distilled.

Suspension Polymerizations. *General Procedure*. These were carried out as follows in a 1 L round-bottomed-flask reactor coupled to a five-necked flange fitted with a condenser, overhead stirrer, thermometer probe, nitrogen supply, and a stopper. The stirrer speed was set to 550 ± 10 rpm. The aqueous phase (300 g of water with 0.3 wt % of poly(acrylic acid)) was purged by bubbling nitrogen through it for ~30 min while heating to 40−50 °C, after which the organic phase (100 g) was added, comprising the monomers, the CTA and AIBN as the source of radicals. The reactor was placed in a water bath, and polymerizations were allowed to proceed under nitrogen at 80 °C until completion (typically 1 h), after having observed the Trommsdorff−Norrish effect[55,56] with a small rise in temperature (ca. 5 °C). The reaction mixture was then heated to 90 °C to destroy initiator residues and minimize residual monomer content. The polymers were recovered in the form of good quality beads (approximately 200−800 μm) via simple filtration through a 75 μm nylon mesh, washed with ca. 1 L of deionized water, and placed to dry in a vacuum oven at 40 °C until constant weight (typically 6 days).

Polymer Characterization. *Solubility Tests*. Solubility tests were performed visually in sealed vials left overnight at room temperature. The solvents tested were THF, toluene, DMSO, DCM, and chloroform.

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

Nuclear Magnetic Resonance Spectroscopy (*NMR*). ^{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 of 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 versus elution volume plots. Each polymer was analyzed three times, and the M_n and M_w data were averaged.

Differential Scanning Calorimetry (*DSC*). The instrument used was a TA Instruments DSC Q1000, with all data being processed with TA Instruments Universal Analysis 200 software. The appropriate method used in the analysis of all samples was found as follows: The sample (ca. 2−4 mg) was weighed in a crimped aluminum pan, and analysis was preformed under a flow of nitrogen (20 mL/min) through the following steps: 1. Equilibrate at 25.0 °C. 2. Isothermal for 1.00 min. 3. Ramp 10.0 °C/min to 200.0 °C 4. End of cycle 1. 5. Isothermal for 1.00 min. 6. Ramp 10.0 °C/min to 30.0 °C. 7. End of cycle 2. 8. Isothermal for 1.00 min. 9. Ramp 10.0 °C/min to 350.0 °C 10. End of cycle 3. 11. End of method. The glass transition temperature, T_g, of the polymers was taken as the midway point of the incline generated by the heat flow change for this transition on the third step.

Rheology (*Oscillatory Measurements*). The polymers were tested, under a constant flow of nitrogen, using a TA Instruments CSL^{2}500 controlled stress rheometer using parallel plate geometry (2 cm diameter), with the gap set at 250 μm. Assuming the density as 1000 kg m^{-3}, the amount of sample loaded was 0.12 g. The linear viscoelastic region was determined for all

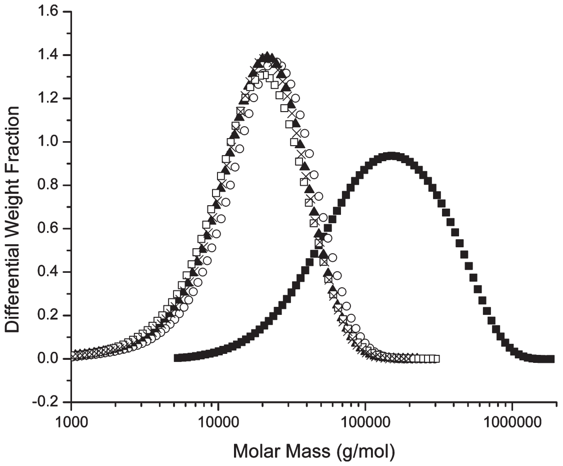

Figure 1. MALS/SEC molar mass distribution curves for linear polymers using different alkyl thiol transfer agents keeping the comonomer/CTA at 100/1: (■) L5: ET; (○) L6: BT; (×) L7: HT; (▲) L8: OT; (□) L9: DDT (see Table 1 for polymerization feed compositions).

polymers tested and at 1 rad s^{-1} was found to extend beyond 10% strain (2.5 mrad displacement). This value was therefore chosen as the set strain for subsequent experiments, wherein the frequency was varied between 0.1 and 100 rad s^{-1}. For each polymer, the temperature was set at 10 deg intervals in the range 180−220 °C. At each temperature, the storage and loss moduli were determined, and the magnitude of the complex viscosity was calculated.

Results and Discussion

Synthesis of Model Linear Poly(MMA-*co*-EA)s in Suspension Polymerization. In the absence of any firm data on the efficiency of chain transfer agents in suspension polymerization of MMA and EA, their behavior was first investigated in the absence of any branching comonomer. Samples L1−L9 (Table 1) were prepared with good recoveries (80−90%). In this context "recovery" is defined as the mass percent of product relative to the comonomer feed mass that is recovered as dry free-flowing spherical particulates with a modestly broad particle size distribution centered around 500 μm. Excluded is any amorphous product adhering to the reactor walls or stirrer. Keeping the comonomer/CTA mole ratio constant at 100/1, a comonomer/initiator mole ratio of 100/0.15 was chosen for use in synthesizing the linear polymers in the presence of various transfer agents. Triphenylmethanethiol (L1) was the only CTA tested that failed to produce any recoverable polymer. This result comes in good agreement with similar experiments preformed in emulsion polymerization within our group.[53] The explanation for this is most likely the high stability of the thiolate radical formed in the transfer process, which fails to reinitiate polymerization in an effective way. Thiophenol (L2) and 4-hydroxythiophenol (L3), two water-soluble CTAs, produced polymers with high M_w and very high polydispersities, proving these to be poor CTAs for this system, probably due to their loss into the aqueous phase. Polymers L5−L9 were all produced with linear aliphatic CTAs with 2, 4, 6, 8, and 12 carbons, respectively. The MALS/SEC data for L5 prepared using ethanethiol (ET) as the CTA (Table 1 and Figure 1) are quite different from the corresponding data for the other aliphatic CTAs with the high M_w and rather broader molar mass distribution, suggesting that ET is a poor CTA in this system. In fact, this thiol has a low boiling point (∼35 °C), and so, at the temperature of the polymerization, it seems that most of this thiol is lost to the vapor phase. For the remaining alkyl thiols, BT, HT, OT, and DDT, and also benzyl mercaptan, the molar masses of the corresponding linear polymers are much lower, and the molecular weight distributions overlap substantially (Figure 1), clearly indicative of the effectiveness of these as CTAs in this system. Of these, DDT was chosen as the transfer agent for further work because of its low volatility and its hydrophobic character (likely to maximize partition into the organic phase even at low concentrations) and to allow comparison with our earlier solution phase studies where DDT was used extensively as the chain transfer agent.[22−24] Linear copolymers L10−L15 (Table 1) were therefore synthesized varying the amount of DDT, allowing a better understanding of the transfer process as well as providing linear polymers with a range of M_w values. In practice, the latter fell rapidly to ∼12 000 with a mole ratio of DDT of 2 (L15, Table 1), and all attempts to use higher values than this, as used in the syntheses of the branched polymers (Tables 2 and 3), led to collapse of the aqueous suspension and aggregation of the amorphous polymeric products. No spherical particulates were recovered from these polymerizations. We assume that this was because the M_w of the products and the associated T_gs were simply too low (see later).

Synthesis of Branched EGDA Copolymers in Suspension Polymerization. From previous work in our laboratory,[23] ethylene glycol diacrylate, EGDA, was chosen as the branching comonomer since levels of up to 15 mol % relative to total comonomer feed were previously and successfully incorporated when copolymerized with MMA via free radical *solution* polymerization using appropriate levels of CTA, without cross-linking and gelation. However, when investigating analogous suspension polymerizations, it was anticipated that the incorporation of the branching monomer EGDA might be more restricted. The main reason for this is that suspension polymerization is mechanistically identical to bulk polymerization, where the benefit of solvent dilution, which tends to favor branching over cross-linking, is not present. Interestingly, however, in earlier work, we have found that in emulsion polymerization *without the incorporation of an organic solvent* branched polymers have been successfully synthesized with surprisingly high levels of branching, up to 20% of divinylbenzene relative to MMA, again without inducing cross-linking and gelation.[53] Different free radical mechanisms operate in bulk (suspension) and emulsion polymerization, and this seems to be relevant with respect to the occurrence of branching versus cross-linking. In an idealized model for emulsion polymerization, only one radical is present at any one time in each polymerizing particle, a condition that is not so in either bulk/suspension or solution polymerization. This factor may well be important in some way for the different behavior in branching polymerization. However, the exact relevance of this to the issue of branching versus cross-linking remains unclear. Be this at it may, we have now successfully synthesized two series of branched copolymers in aqueous suspension via the "Strathclyde methodology" with different low levels of EGDA incorporation, 0.5 and 1 mol % relative to the monofunctional monomers (Tables 2 and 3, respectively), without inducing cross-linking and gelation.

All samples B2−B14 and B16−B22 were obtained with good recovery of high-quality spherical particulates, and bearing in mind handling losses in recovering the polymer including adherence of some polymer to the reactor walls and stirrer, these seem to indicate high conversion. The polymers B1 and B15 were aggregated material, and these polymers were cross-linked. This indicates that the level of DDT employed had reached the minimum value possible for

Table 2. Suspension Polymerization Synthesis of 0.5% Branched P(MMA-*co*-EA-*co*-EGDA)s

	composition (molar ratio)						MALS/SEC			DSC
entry	MMA	EA	EGDA	DDT	AIBN	recovery (%)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	T_g (°C)
B1[a]	97	3	0.5	0.9	0.15	88				
B2	97	3	0.5	1.0	0.15	85	14 000	110 000	7.9	100
B3	97	3	0.5	1.1	0.15	86	12 000	81 000	6.8	100
B4	97	3	0.5	1.2	0.15	88	9 200	66 000	7.2	97
B5	97	3	0.5	1.3	0.15	86	9 300	47 000	5.1	98
B6	97	3	0.5	1.4	0.15	85	7 200	41 000	5.7	96
B7	97	3	0.5	1.5	0.15	81	8 000	34 000	4.3	92
B8	97	3	0.5	1.6	0.15	85	7 900	30 000	3.8	97
B9	97	3	0.5	1.7	0.15	79	7 200	30 000	4.2	94
B10	97	3	0.5	1.8	0.15	88	5 700	27 000	4.7	94
B11	97	3	0.5	1.9	0.15	86	7 000	26 000	3.7	88
B12	97	3	0.5	2.0	0.15	87	6 900	22 000	3.2	86
B13	97	3	0.5	2.1	0.15	90	6 800	22 000	4.6	85
B14	97	3	0.5	2.2	0.15	85	4 200	18 000	4.3	80

[a] Although high-quality spherical beads were recovered these were insoluble in the solvents tested.

Table 3. Suspension Polymerization Synthesis of 1% Branched P(MMA-*co*-EA-*co*-EGDA)s

	composition (molar ratio)						MALS/SEC			DSC
entry	MMA	EA	EGDA	DDT	AIBN	recovery (%)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	T_g (°C)
B15[a]	97	3	1	1.0	0.15					
B16	97	3	1	1.5	0.15	82	6 600	200 000	30.3	94
B17	97	3	1	2.0	0.15	84	4 800	78 000	16.3	91
B18	97	3	1	2.5	0.15	86	6 000	36 000	3.0	86
B19	97	3	1	3.0	0.15	84	3 400	20 000	5.9	76
B20	97	3	1	3.5	0.15	84	2 500	15 000	6.1	70
B21	97	3	1	4.0	0.15	85	1 100	12 000	10.9	69
B22	97	3	1	5.0	0.15	84	2 900	9 000	3.1	54

[a] During polymerization the suspension system collapsed due to a formation of a block of aggregated polymer on the stirrer shaft which proved to be insoluble in the solvents tested.

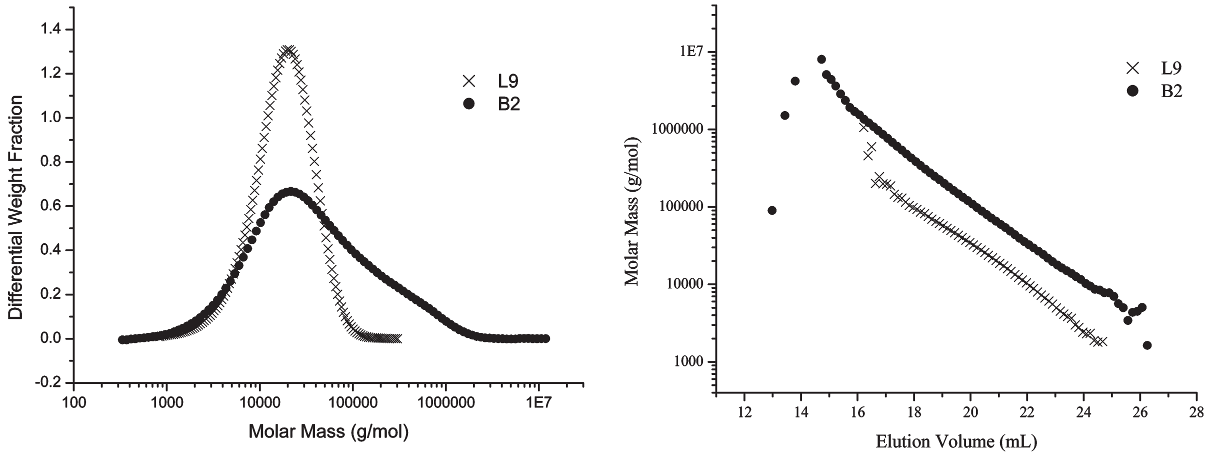

Figure 2. MALS/SEC molar mass distribution curves (left) and molar mass versus elution plots (right) for (×) L9 and (●) B2 (see Tables 1 and 2 for corresponding polymerization feed compositions).

branching to be favored over cross-linking. When attempting to synthesize a branched copolymer using a poor CTA, such as thiophenol, the result was always the formation of an insoluble cross-linked material in all the solvents tested, even when the mole ratio brancher(EGDA)/CTA(TPH) was 0.5/2.5, i.e., even when the content of TPH was much higher than that of DDT used to produce branched polymers shown in Table 2.

MALS/SEC. As a control material and linear equivalent, copolymer L9 prepared with a mole ratio MMA/EA/EGDA/DDT/AIBN of 97/3/0/1/0.15, with a M_w of 22 600 was used to demonstrate the branching nature of the branched copolymers synthesized (Tables 2 and 3). This sample was chosen to achieve reasonable correlation of data over a similar SEC elution volume range. The levels of DDT used in the branched copolymers in order to prevent gelation are higher than that of the control (except for branched polymer B2). Nevertheless, it was possible to produce branched copolymers with M_w values higher than that of the control. Likewise, the polydispersity (M_w/M_n) data (Tables 2 and 3) are consistent with that of polymers possessing a randomly branched architecture with the M_w/M_n values, seemingly indicating a directional trend in breadth and polydispersity on moving from the 0.5% branched series B2–B14 to the 1% branched series B16–B22. The broad molar mass distributions of the branched copolymers versus that of the control are obvious in Figures 2, 3, and 4, left. Perhaps the clearest way to visualize the branching effect is when the control L9 is compared with branched copolymer B2 prepared using a MMA/EA/EGDA/DDT/AIBN mole

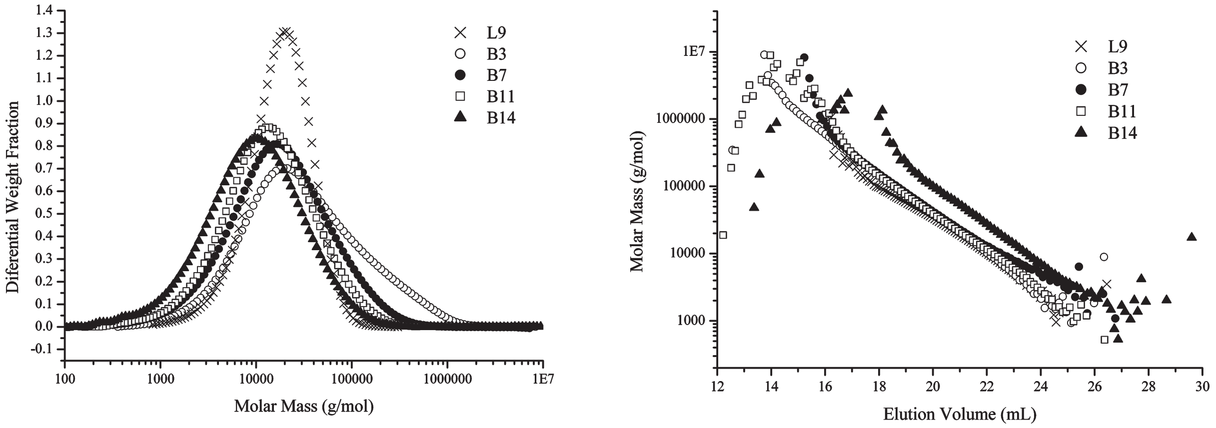

Figure 3. MALS/SEC molar mass distribution curves (left) and molar mass versus elution plots (right) for (×) L9, (○) B3, (●) B7, (□) B11, and (▲) B14 (see Tables 1 and 2 for corresponding polymerization feed compositions).

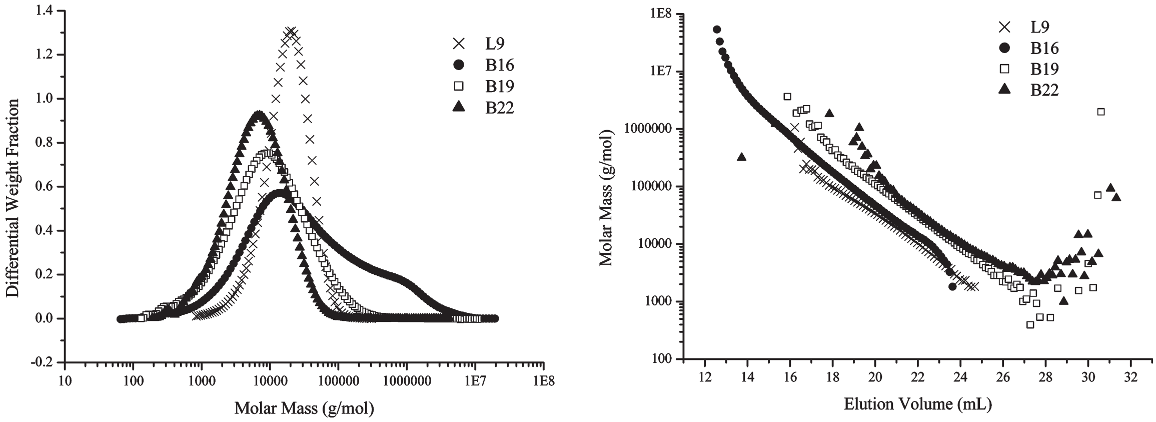

Figure 4. MALS/SEC molar mass distribution curves (left) and molar mass versus elution plots (right) for (×) L9, (○) B3, (●) B16, (□) B19, and (▲) B22 (see Tables 1 and 3 for corresponding polymerization feed compositions).

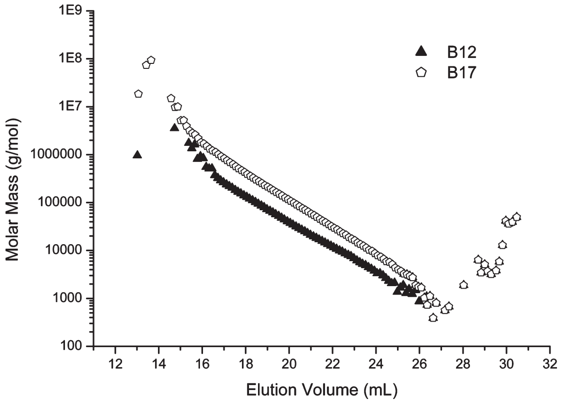

Figure 5. MALS/SEC molar mass versus elution volume plots of branched polymers B12 and B17 (see Tables 2 and 3 for corresponding polymerization feed compositions).

ratio of 97/3/0.5/1/0.15, where the only difference lies in the inclusion of the brancher EGDA in the polymerization composition. The molar mass distributions show a broader distribution for B2 and a shift toward higher M_w when compared to L9 (Figure 2, left). The elution volume versus molar mass plot also demonstrates the branching effect since at any given elution volume B2 always has a larger M_w than L9 (Figure 2, right).

With regard to the molar mass versus elution volume plots, those of the branched polymers in both series (0.5 and 1% mole feed ratio of EGDA) all lie to the upper right with respect to the plot for the linear analogue, confirming the branched nature of these samples (Figures 2, 3, and 4, right). Further indication is obtained when comparing in the same way polymers B12 and B17 (0.5 and 1% EGDA, respectively). Here, the plot for polymer B17 also lies to the upper right of the plot for B12 indicating, as expected, a higher branching level in B17 than in B12 (Figure 5).

One of the standard metrics indicative of branching is the Zimm branching or contraction parameter *g*. This is defined simply as the ratio of the mean-square radius of gyration of the branched polymer in solution to that of the analogous linear polymer of the same molar mass.[57] Since the branched polymer is anticipated to be more compact than the linear one, the *g* factor for a linear polymer is unity and the *g* value falls as the degree of branching increases. Light scattering data enables the root-mean-square (rms) radius of gyration of a polymer in solution to be measured, and so in principle a combination of a MALS detector and a SEC instrument enables the radii to be measured across the whole molecular weight distribution of a broad molecular weight sample. However, the scattering from low mass polymers is weak, and so unfortunately with our instrumentation meaningful data could not be obtained for macromolecules with rms radii ≤10−15 nm, as indeed has been reported by others.[58] This limitation applies to many of the samples prepared in the present work, but examination of appropriate high molecular weight samples is instructive. Linear polymer L3 and branched sample B16 have the highest M_w values in their respective groups, and their corresponding rms radii data across their molecular weight distributions are shown in

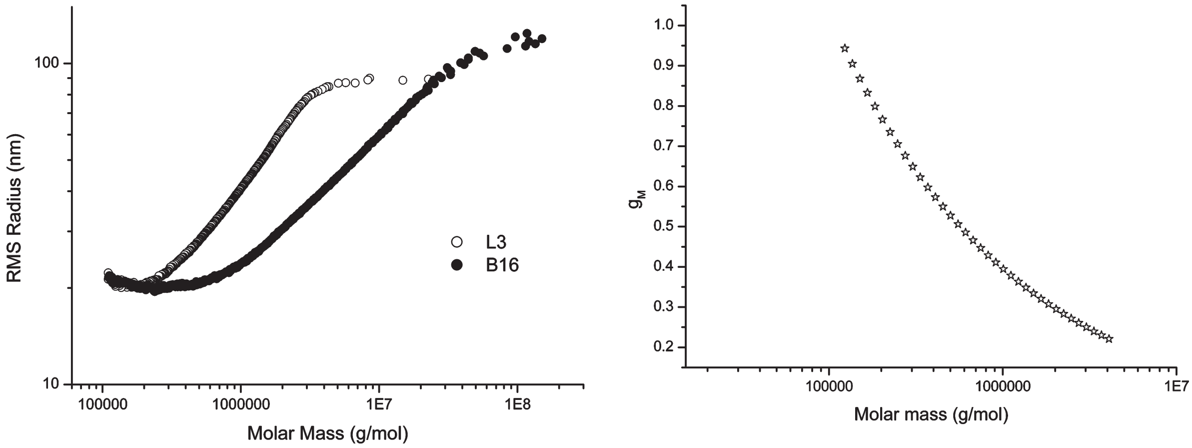

Figure 6. MALS/SEC rms radius versus molar mass curves (left) for (○) L3 and (●) B16 and branching ratio plot (right) calculated via the radius method.

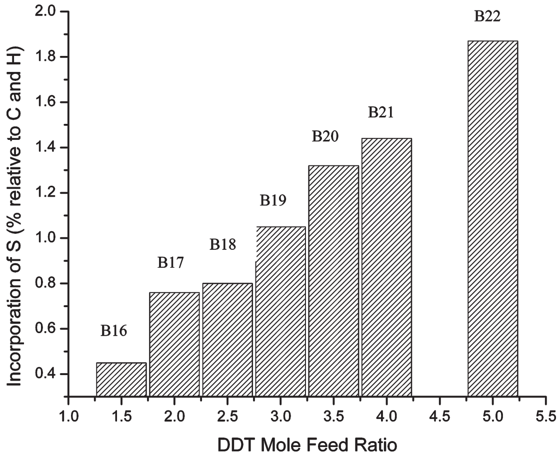

Figure 7. Incorporation of the CTA DDT in branched polymers B16−B22 (see Table 3 for corresponding polymerization feed compositions).

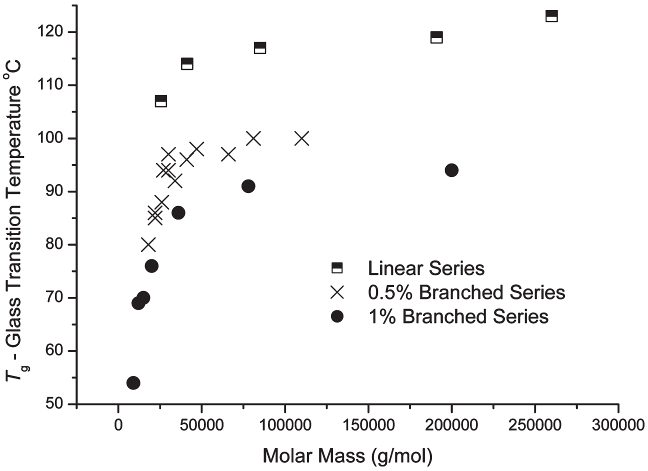

Figure 8. M_w dependence of the T_g for linear and branched polymers in Tables 1, 2, and 3.

Figure 6 (left). Clearly, at all slices of the molecular weight distributions where overlap occurs the radii of the linear polymer chains are larger than those of the branched polymer chains. The corresponding values for *g* computed from the instrumental software are shown in Figure 6 (right). At the low molecular weight end the value is ~0.95 where indeed there may be some linear chains; thereafter, *g* falls to ~0.25 at the highest comparable molecular weight slice. This is strong evidence that the branched sample is indeed branched and that branching increases as the molecular weight of individual chains increases. Again this is consistent with the observations of others.[58]

Elemental Microanalysis. Microanalytical data gives an insight into the level of incorporation of the transfer agent in the polymer backbone, and to some extent the efficiency of the transfer process. We found from the samples analyzed a linear relationship between the level of thiol in the polymer feed and the percentage of sulfur found in the resultant polymers (Figure 7).

Thermal Analysis: DSC. The glass transition temperature (T_g) of linear polymers is generally believed to be associated with the onset of long-range segmental motion of the polymer chain segments.[59−61] For linear polymers, the effect of end groups on the T_g diminishes with an increasing degree of polymerization. However, with dendritic polymers, the number of end groups is directly proportional to the degree of polymerization, and therefore the effect of end groups on the fractional free volume (i.e., available molecular space) and T_g can be significant, even at high degrees of polymerization. Although a model that accounts for the free volume of end groups in dendrimers has been developed by Wooley et al.,[62] to our knowledge there is no model that completely predicts the T_g of randomly branched systems. Since our materials are relatively lightly branched compared to dendrimers, it seems likely that the influence of end groups on T_g is small. Furthermore, since each sample in effect contains macromolecules with a distribution of backbone architectures our discussion will focus primarily on a qualitative rationalization of the other competing effects on T_g. Also, since in a broad molecular weight sample the M_w value is a better indicator than the M_n value of where the mass of a sample is focused; bulk, thermal, and mechanical properties are better correlated with M_w than they are with M_n. All of the experimentally determined T_g data are therefore plotted as a function of M_w in Figure 8. Factors of potential significance are the M_w itself, whether and to what extent a sample is branched, the molecular structure of the branched point, and average chain length between branch points. These factors are of course inter-related. The data in Figure 8 show that the two series of branched samples and the linear analogues have a dependence on M_w typical of most polymers; i.e., as M_w rises initially so does T_g until a plateau value is reached which is usually regarded as the point at which the

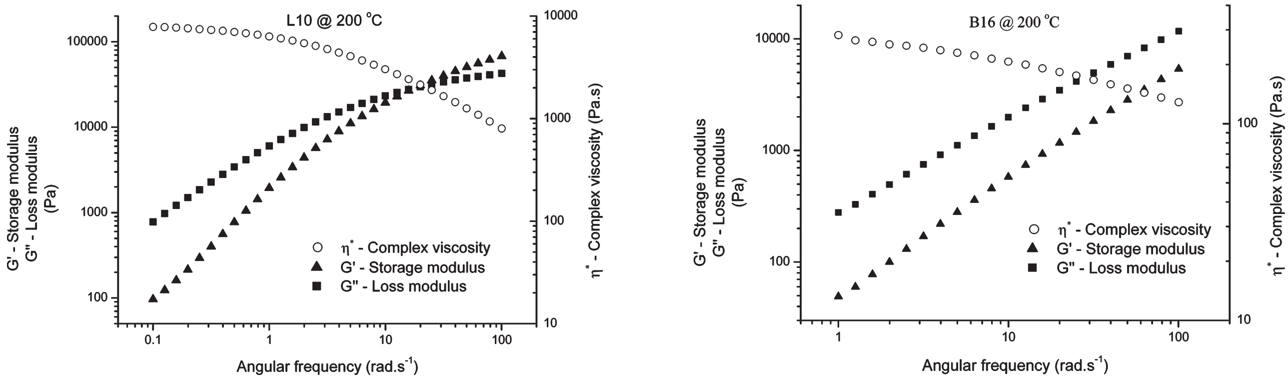

Figure 9. Rheological data obtained from oscillatory experiments with linear polymer L10 and branched polymer B16.

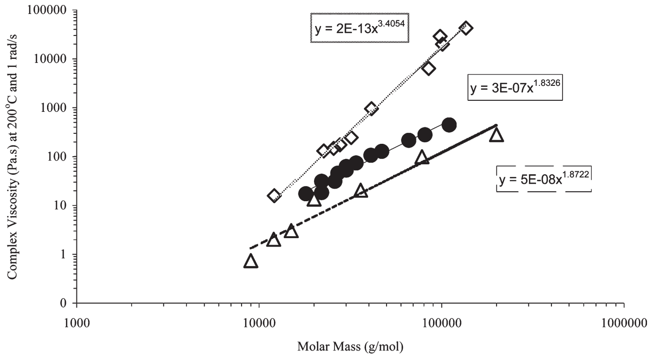

Figure 10. Complex viscosity (measured at 200 °C and 1 rad s^{-1}) versus M_w for linear polymers (◇), 0.5% branched copolymers (●), and 1% branched copolymers (△).

fully entangled macromolecular state, as opposed to the oligomeric state, is achieved. Comparison of T_g values in the plateau region is therefore more rational and avoids artifacts associated with differences of M_w values. In this region it seems clear that the linear polymer controls have the highest T_g values, typically ~20 °C higher than those of the 0.5% EGDA branched samples, which in turn are higher than those of the 1% EGDA branched series. Cooperative segmental rotation is in simple terms as intramolecular process, but the ease or onset of this is of course dependent on the "space" or free volume around any given macromolecule. Branched macromolecules can be regarded as more globular than linear analogues and as such might be viewed as having more free volume.[63] The ease or onset of segmental rotation also depends on the degree of entanglement of a given macromolecule with its neighbors, and again branched polymers can be viewed as likely to be less entangled than their linear counterparts. The respective plateau T_g values of the linear 0.5% EGDA branched samples, and the 1% EGDA branched samples are consistent with these two factors. However, in the branched polymers it could be argued that the branch point themselves might act as "anchor points" tending to restrict segmental rotation, particularly if the molecular structure of the branched point is sterically restricted, and the number of branch points is high. In fact, the branch points in the present samples all have an acrylate rather than a methacrylate structure and as such are less locally sterically hindered than the segments of the main methacrylate backbone. In addition, the level of branching is low in both series, a restriction imposed by the requirements of the suspension polymerization synthetic chemistry. Overall, therefore, and in case of the present branched samples, the nature and abundance of the branched points do not seem to introduce significant "anchor points" and in particular do not override their main influence of increasing the globular nature of the macromolecules and their free volume, while simultaneously reducing entanglements in these materials relative to their linear analogues.

Rheology. The rheological properties of polymer melts are known to depend on three underlying molecular structural parameters: molecular weight, molecular weight distribution, and molecular architecture (branching). Figure 9 shows two sets of data typified (left) by L10 in the case of the linear polymers in this study and (right) B16 in the case of the branched polymers, each derived from rheological oscillatory experiments. Note that the vertical axis in Figure 9 for L10 covers the range 0−100 000 Pa while that for B16 extends only to 10 000 Pa. The curves for B16 are typical of those for all the branched polymer samples. For both samples at low frequencies, the loss (or viscous) modulus component dominates and changes in approximately a linear fashion with frequency. The storage (elastic) modulus has approximately a quadratic relationship with the frequency for L10 but nearly linear for B16. Overall, the magnitude of the complex viscosity is approximately constant (Newtonian plateau) in both cases although as the frequency increases, some shear thinning (i.e., the complex viscosity decreases with frequency) is observed with the storage modulus increasing at a faster rate than the loss modulus. In some cases, at a critical frequency (different for each polymer and temperature), the values of the two moduli cross, as is the case here for the linear sample L10.

To allow a better and broader comparison of the melt behavior of all the linear and branched polymers, the molar mass (M_w) dependence of the shear rate viscosity is plotted in Figure 10. The viscosity data were obtained from the complex modulus at 1 rad s^{-1} at a temperature of 200 °C. While these values are not necessarily equal to the values of the zero shear rate viscosity, η_0 (which were not always attainable experimentally with sufficient accuracy), they are useful as comparators. In this double-logarithmic plot, the linear copolymers demonstrate the anticipated type of molar mass dependence, showing a slope of ~3.4, consistent with that of a well-entangled polymer.[64] However, for any given molar mass the complex viscosity values of the branched polymer samples are always lower than those of the linear analogues, and the slopes of the lines for both sets of branched polymers are only 1.8−1.9, suggesting only partial entanglement. This behavior has been observed before for dendrimers[65,66] and other hyperbranched polymers.[64,67] In addition, at any given molar mass all the data for the 1% branched samples lie below those of the corresponding 0.5% branched samples, again consistent with the higher level of branching in the former samples.

Conclusions

The use of EGDA in copolymerizations with MMA and EA allows the facile synthesis via suspension polymerization of soluble branched copolymers in the form of free-flowing spherical particulates provided that the molar ratio of EGDA/DDT remains ≤0.7 to avoid network formation and, hence, insoluble and non-melt-processable copolymer. The "Strathclyde methodology" has therefore been shown to be effective in aqueous suspension polymerization without the incorporation of a diluting solvent and produces branched polymer directly in a physical form suitable for subsequent processing. This is an important result since suspension polymerization is a key technology for the production of commodity vinyl polymers and copolymers and is a process that can be readily scaled up from a successful laboratory procedure. This augurs well for the potential exploitation of the "Strathclyde methodology" in both small- and large-scale syntheses of branched vinyl polymers. Melt rheology data have been used to complement MALS/SEC and DSC data and bring further insight with regards to the polymers prepared using this methodology and in particular substantiate the branching nature of polymers when compared with their linear counterparts. The rheological data presented also show that, at similar M_{w}, branched polymers display lower viscosities compared to a linear analogue or to polymer with fewer branches. As a consequence, the potential of branched polymers acting as rheological modifiers is demonstrated.

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