Use of Rapid Triple Detection Size Exclusion Chromatography To Evaluate the Evolution of Molar Mass and Branching Architecture during Free Radical Branching Copolymerization of Methyl Methacrylate and Ethylene Glycol Dimethacrylate

Greg Saunders

Polymer Laboratories Ltd., Church Stretton SY6 6AX, UK

Peter A. G. Cormack, Susan Graham, and David C. Sherrington*

Department of Pure & Applied Chemistry, University of Strathclyde, 295, Cathedral Street, Glasgow G1 1XL, UK

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ABSTRACT: A heavily branched poly(methyl methacrylate) (PMMA) has been prepared by free radical solution copolymerization of methyl methacrylate (MMA) with ethylene glycol dimethacrylate (EGDMA) in the presence of dodecanethiol (DDT) to inhibit network formation. A molar feed ratio MMA/EGDMA/DDT of 100/15/13 was employed. These conditions allow a high conversion to fully soluble branched products, and the evolution of molar mass and intrinsic viscosity was monitored by subjecting extracted samples of polymerization mixture to rapid triple detection size exclusion chromatographic (SEC) analysis using a PL-PMC device. These data showed that the global molar mass increased with reaction time, but the corresponding viscosity rise was far lower than would expected for linear macromolecules, hence demonstrating the formation of an increasingly densely branched architecture. ^{1}H NMR spectral and elemental S analysis of the finally isolated branched PMMA showed the composition to be in reasonable agreement with the molar feed ratio MMA/EGDMA/DDT and that ~95% of the incorporated EGDMA was present as doubly reacted branched segments. High-resolution SEC analysis of the finally isolated material confirmed the branched nature of the product across the whole of its molar mass range and that branching increases as the molar mass of individual macromolecules increases.

Introduction

Currently the synthesis and characterization of branched polymers are attracting significant research interest, not only from a fundamental point of view but also because the unusual physical properties[1−4] of these materials offers novel opportunities in terms of exploitation in useful products. Strategies and methodologies for generating branched step-growth polymers are relatively straightforward and well developed,[5,6] whereas generic routes to branched vinyl polymers and other chain growth species are fewer in number.[7,8] In this context we have reported a facile low-cost procedure employing conventional free radical copolymerization of a monofunctional comonomer with a difunctional (or polyfunctional) comonomer in the presence of a chain transfer agent, such as a thiol, to inhibit cross-linking.[9−11] Despite the apparent naivety of the approach, high conversions to yield fully soluble and processable branched products without a gel fraction are readily achievable, though of course the materials obtained are a complex mixture of macromolecules in terms of both molar mass and backbone architecture. Nevertheless, it is slowly becoming clear that these branched products can have very different properties to their linear analogues[12] and consequently seem likely to provide new opportunities for technological exploitation.

The quantitative characterization of the architecture of branched polymers is perhaps best developed in the case of model homopolymers with a narrow molar mass distribution and a unique architecture e.g. star and comb polymers prepared via living or controlled polymerization methodologies. Significant careful work on corresponding step-growth polymers has also been carried out. Very useful reviews in this context have been published by Roovers,[13] Small,[14] and Burchard.[15] The Zimm branching factor[16] or geometric factor, g, is one measure of the degree of branching where for polymers of equal molar mass:

$$g = \bar{s}^2(\text{branched})/\bar{s}^2(\text{linear})$$

$\bar{s}^2$ is the mean-square radius of gyration and can be obtained from light scattering data.

Since the hydrodynamic volume, and hence the radius of gyration of a macromolecule in solution, is a major factor in controlling the intrinsic viscosity (IV), in some circumstances a more convenient branching factor is g' where for polymers of equal molar mass:

$$g' = \text{IV(branched)/IV(linear)}$$

In practice

$$g' = g^{\beta}$$

where the exponent $\beta \sim 0.5-1.0$ and depends on the type of branching (regular star, regular comb, randomly branched, etc.) and the solvent used. The parameter g' is still generally accepted as a good qualitative indicator of the degree of chain branching.[17]

Most of the characterization data we have generated so far for these systems have been obtained from

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

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analysis of the products isolated at high conversion, with much less information available on the evolution of parameters such as molar mass and degree of branching during polymerization.[18] We have now undertaken process monitoring of a typical solution free radical copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) in the presence of dodecanethiol (DDT). We have chosen a reaction composition that has been shown previously to produce branched products, but it should be emphasized that quite broad reaction compositions do yield soluble branched products using this methodology.[10,11] Monitoring was via use of rapid multidetector flow injection size exclusion chromatographic (SEC) analysis. The instrumentation employs a SEC column of relatively low resolving range and power to allow rapid near real-time monitoring of the polymerization mixture during the reaction. The latter coupled with high-resolution SEC analysis of the final product offers a detailed picture of the evolution of the molar mass and backbone architecture of the macromolecules formed during the reaction.

Experimental Section

Materials. Methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDMA), dodecanethiol (DDT), and azobis(isobutyronitrile) (AIBN) were all purchased from Aldrich and used without purification. Toluene and *n*-hexane were of standard laboratory grade and were used without purification.

Synthesis of Branched PMMA Using a Molar Feed Composition of MMA/EGDMA/DDT of 100/15/13. MMA (5 g, 50 mmol), EGDMA (1.49 g, 7.5 mmol), DDT (1.32 g, 6.5 mmol), and AIBN (0.11 g, 0.65 mmol/1 mol % total monomer) were added to toluene (25 mL) in a three-necked-round-bottomed flask fitted with a reflux condenser. The reaction mixture was degassed with stirring for ~15 min with a stream of N_2 from a needle pierced through a septum. The vessel was then brought to 80 °C in an oil bath. A constant flow of N_2 was maintained throughout the reaction. After 5 h the reaction mixture was allowed to cool; the product precipitated into cold *n*-hexane (10 times the volume of the reaction solvent) and was collected by filtration on a Buchner funnel. The solvent and monomer residues were removed by evaporation using a vacuum oven set at 40 °C to yield the isolated, soluble polymer.

During the polymerization small samples of the reaction mixture were removed by syringe every 15 min and cooled to terminate polymerization prior to analysis.

Rapid Multidetector Flow Injection SEC Analysis. Each sample of polymerization reaction mixture was diluted accurately to nominally ~1 mg of sample per mL of eluent (tetrahydrofuran, THF) before 100 μL was injected for analysis. A Polymer Laboratories PL-PMC (process monitoring and control) device was used for the analyses.

The instrumentation consisted of a PL Rapid F (150 × 7.5 mm) SEC column, a PL-RI 50 differential refractometer, a PL-BV 400 four capilliary bridge viscometer, and a Precision Detectors PD-2020 dual angle (15° and 90°) light scattering detector. The eluent from the SEC column was passed first through the light scattering detector, and then the stream split equally and passed in parallel through the other two detectors. The eluent was THF delivered at 1.0 mL min^{-1} at ambient temperature at 0.7 MPa. A narrow molar mass linear polystyrene (195 900 g mol^{-1}) of known intrinsic viscosity, concentration, and refractive index increment, d*n*/d*c*, was used as a calibrant to generate the following detector constants: interdetector delay (viscosity) = −0.05 min, interdetector delay (light scattering) = 0.26 min, *K*(concentration) = 4229.6, *K*(light scattering 15°) = 143 661, *K*(light scattering 90°) = 38 619.4, and *K*(viscometer) = 0.80. Concentrations were calculated using a d*n*/d*c* = 0.094 obtained from analysis of the final product (see below).

High-Resolution SEC Analysis of Final Product. A solution of the final product was prepared accurately at nominally ~2 mg mL^{-1} in THF, and the sample injection volume was again 100 μL. The instrumentation was essentially as before but with 2 × PLgel 5 μm MIXED-C (300 × 7.5 mm) columns replacing the PL Rapid F column, operated at 1.0 mL min^{-1}, giving a constant pressure of 5 MPa. This produced sufficient resolution to allow slice-by-slice analysis of the SEC chromatogram. The same linear narrow molar mass polystyrene calibrant was employed to generate the following detector constants: interdetector delay (viscosity) = −0.06 min, interdetector delay (light scattering) = 0.25 min, *K*(concentration) = 4230.6, *K*(light scattering 15°) = 141 158, *K*(light scattering 90°) = 38 099.9, and *K*(viscometer) = 0.83.

Results and Discussion

Synthesis of Branched PMMA. We have previously reported extensively on the synthesis of branched PMMAs employing EGDMA as the branching comonomer.[10,11] In the present study the feed ratio MMA/EGDMA/DDT was selected as 100/15/13 from previous experience to maximize the level of branching achieved in the final product while excluding the complication of cross-linking. The synthesis proceeded as previously and a high conversion to branched polymer achieved. Exact quantification of the yield was not undertaken because of the real-time monitoring (~20 samples) by SEC being carried out. The chemical structure of the final product was confirmed by ^{1}H NMR and FTIR spectroscopy along with elemental microanalysis. Using the ^{1}H NMR spectral assignments, we have previously reported the ratio of MMA/EGDMA/DDT in the final product was estimated to be ~100/20/17 with the content of EGDMA and DDT apparently being higher than the feed values. However, the rather broad and overlapping signals mean that the error in this estimation is significant, and the data are perhaps better interpreted as indicating that there is good incorporation of both EGDMA and DDT residues consistent with the feed levels employed. The % of EGDMA residues present as doubly reacted branching units is ~95%; i.e., ~5% of unreacted pendent methacrylate groups remain from EGDMA units. The elemental microanalytical datum for sulfur is 2.25, which corresponds to ~90% of the expected value for full incorporation of the feed DDT.

In principle, the exact chemical compositions of the macromolecules isolated at different times during the polymerization and with different molar masses might differ substantially since the products are copolymers of MMA and EGDMA, with in addition some of the latter incorporated as branching units and some as pendent partially reacted species. Furthermore, most polymer chains will be terminally functionalized with a $C_{12}H_{25}S$ residue from the DDT transfer agent. Such compositional variations are potentially an important factor of course since these changes could be reflected in changes in the refractive index increment, d*n*/d*c*, which in turn could influence significantly the interpretation of refractive index and light scattering SEC detector outputs. Furthermore, accounting for such changes as a function of elution time during SEC analysis would be very challenging. In fact, in the present system MMA and EGDMA are electronically very similar and hence have very similar chemical reactivity. Indeed, reactivity ratio data would suggest that a statistical incorporation of these segments is very likely. Also, the transfer constant for DDT would suggest that this is consumed smoothly during the reaction. Overall therefore there is good reason to expect

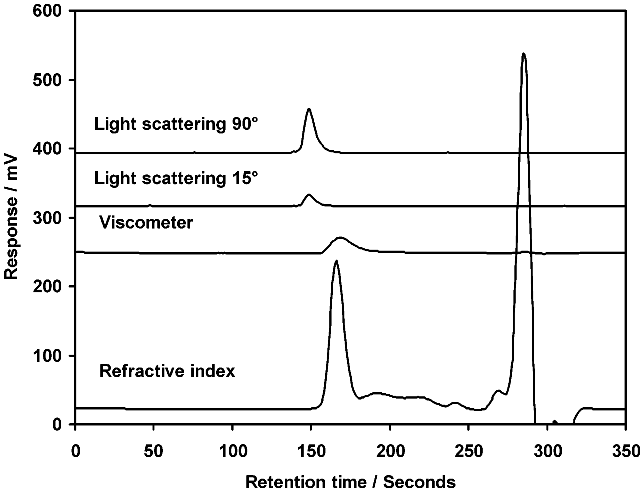

Figure 1. Typical detector outputs from rapid low-resolution TD-SEC analysis a sample withdrawn during branching copolymerization of MMA and EGDMA.

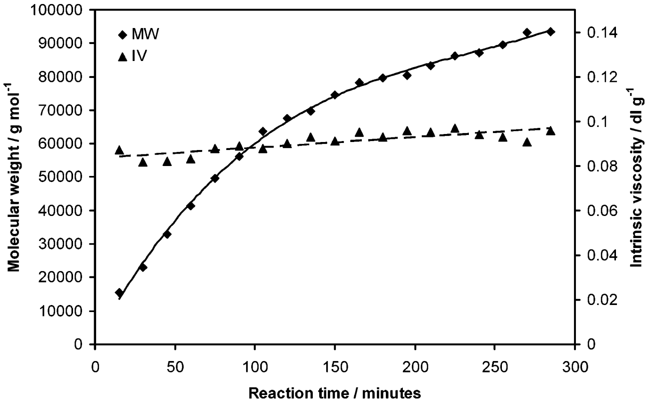

Figure 2. Variation of global molar mass and intrinsic viscosity of samples withdrawn progressively during branching copolymerization of MMA and EGDMA.

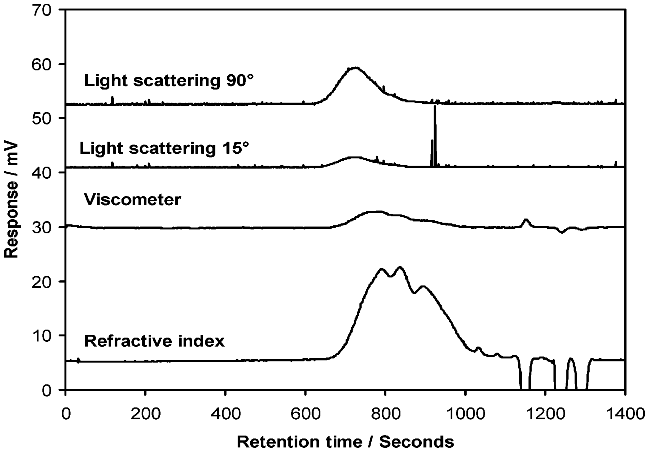

Figure 3. High-resolution TD SEC detector outputs for the final product recovered from the branching copolymerization of MMA and EGDMA.

that the average chemical composition of the complex molar mass and architectural mixture of macromolecules generated in this particular polymerization would not vary much during reaction and across the molar mass distribution. However, this would not of course necessarily be the case with other monomer/brancher combinations. In the following interpretation of the SEC data it will be assumed that chemical compositional variations are small, allowing a common value for d*n*/d*c* to be used in evaluating the data.

Evolution of Molar Mass and Branching Architecture during Polymerization. A typical overlaid and offset multidetector low-resolution chromatogram of one of the samples withdrawn during the polymerization is shown in Figure 1. In each trace, the signal at ~150 s corresponds to the excluded polymer and the other signals are due to monomers and solvent.

The duration of the analytical cycle is of course remarkably short relative to conventional SEC (see Figure 3). The sharpness of the polymer signals relative to those in Figure 3 are due to the deliberately chosen low resolving range of the rapid SEC column (4000 g mol^{-1} polystyrene equivalent). The polymer molecules produced in the synthesis are too large to be fully resolved and hence elute as a single, sharp peak at the exclusion volume of the column. On the basis of the flow injection analysis of the excluded polymer peaks, it is possible to compute from the total area of each peak what we shall refer to as "global" molar mass and intrinsic viscosities of each of the samples analyzed during polymerization; i.e., no slice-by-slice calculation is attempted in analyzing the signals from each sample. These global parameters are a reflection of all components in the sample, with the molar mass data tending numerically toward M_w. As indicated earlier, we have assumed with good background evidence that there is no major change in chemical composition with reaction time. In addition, since in the evaluation of the rapid low-resolution TD-SEC data no slice-by-slice analysis was carried out, use of the fixed d*n*/d*c* value of 0.094 obtained from the high-resolution analysis of the final product was thought to be justified. Figure 2 shows the plots of global molar mass and intrinsic viscosities as a function of the time of sampling from the polymerization reaction.

Clearly as the reaction proceeds there is steady growth in both the global molar mass and intrinsic viscosity of the assembly of macromolecules being formed. However, the intrinsic viscosity increases at a far lower rate than the molar mass. The intrinsic viscosity is related inversely to the polymer molecular density. This indicates that the macromolecules being generated are of increasing compactness and density with the latter arising as a result of the average level of branching in each macromolecule increasing. We have shown previously[10] that the level of pendent methacrylate groups in EGDMA residues which remain unreacted gradually decreases as the reaction proceeds, and this is consistent with the level of branching rising along with the growth in molar mass.

High-Resolution Multidetector SEC Analysis of Final Branched PMMA Product. The overlaid and offset multidetector high-resolution chromatograms of the finally isolated branched PMMA are shown in Figure 3 where the polymer peaks are clearly seen to be much broader and more complex than those in Figure 1. As before in evaluating these data, we have assumed that no significant chemical composition changes occur across the molar mass distribution, and a single d*n*/d*c* value was again used in manipulating the data. The latter therefore are taken as reflecting only the molar mass and architectural content of the undoubtedly highly complex product. In the case of this high-resolution TD-SEC experiment slice-by-slice analysis of the detector outputs is carried out, and so we accept that

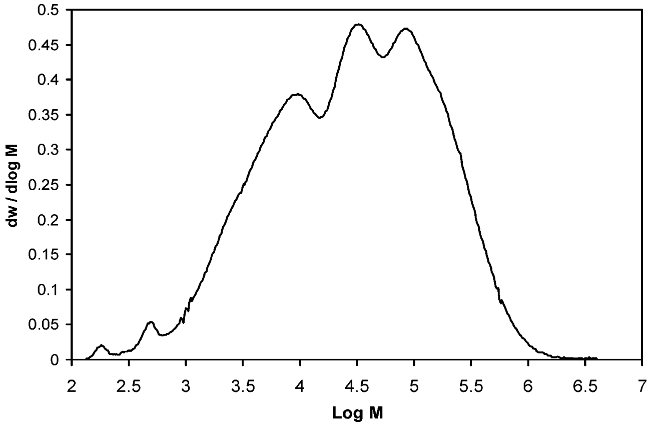

Figure 4. Molar mass distribution curve for the final product recovered from the branching copolymerization of MMA and EGDMA computed from the three high-resolution SEC detector outputs.

Table 1. Size Parameters[a] of Final Branched PMMA Product Calculated from High-Resolution TDC-SEC Analytical Data[a]

M_p	32700	M_z	382000	PDI	13.2
M_n	6600	M_{z+1}	1080000	IV$_w$ (dL g^{-1})	0.078
M_w	87500	M_v	41800	R_{gw} (nm)	47.7

[a] M_p = peak molar mass; M_n = number-average molar mass; M_w = weight-average molar mass; M_z = z-average molar mass; M_{z+1} = $(z + 1)$-average molar mass; M_v = viscosity-average molar mass; IV$_w$ = weight-average intrinsic viscosity; R_{gw} = weight-average radius of gyration. Molar mass units: g mol^{-1}.

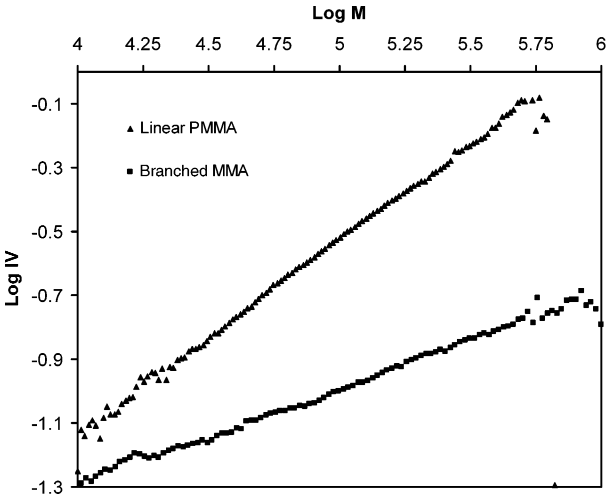

Figure 5. Variation of intrinsic viscosity with molar mass across the full molar mass range of the final product recovered from branching copolymerization of MMA with EGDMA and a broad molar mass linear PMMA model.

if any errors are introduced by making this assumption, these are likely to be more significant than before.

The corresponding molar mass distribution calculated from the triple detector outputs is shown in Figure 4. This has the characteristic multimodal shape which we have reported before[10,11] and seems to be a growing feature of the distributions displayed by branched polymer samples and which undoubtedly require further investigation. Calculation of the molar mass averages, polydispersity index (PDI), weight-average intrinsic viscosity (IV$_w$), and weight-average radius of gyration (R_{gw}) yields the data shown in Table 1. Figure 5 shows the Mark−Houwink plots[19] for a normal linear broad molar mass PMMA (M_n = 61 500, M_w = 104 000, PDI = 1.7) and for the final branched PMMA product. The branched sample has lower intrinsic viscosity than the linear control at all molar mass values, suggesting a more dense and compact structure for the former. Most importantly, the compact branched structure is confirmed by the corresponding Mark−Houwink α value which is significantly depressed (0.32) relative to that of the linear control (0.56).

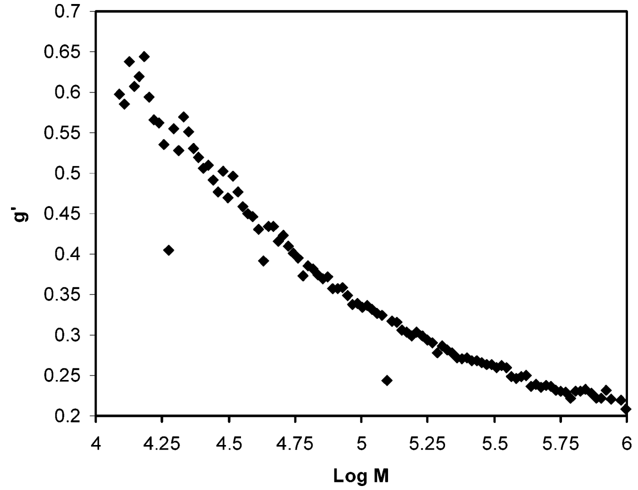

Figure 6. Variation of the Zimm branching factor with molar mass across the full molar mass range of the final product recovered from the branching copolymerization of MMA and EGDMA.

For a linear polymer the Zimm branching factor g' = 1, and for a given molar mass the more branched the polymer the smaller is g'. A plot of g' as a function of each molar mass slice (log M) of the final branched PMMA product is shown in Figure 6. These data show that the sample is branched across the whole of its molar mass distribution and that branching increases as the molar mass increases. This picture is consistent with the results of the polymerization process monitoring study and with our earlier findings of how g' falls with an increase in the molar mass of a lightly branched PMMA synthesized using tripropylene glycol diacrylate.[18] It suggests either that the higher molar mass species contain a larger fraction of the branching comonomer, EGDMA, in the present case, or most likely that fewer of these segments remain with pendent unreacted methacrylate residues.

Conclusions

The PL-PMC device, in effect a rapid multidetector SEC instrument employing a low-resolution column, allows facile monitoring of a polymerization reaction and in particular allows the evolution of molar mass and branching architecture to be conveniently characterized. Together with ^{1}H NMR spectral analysis and high-resolution SEC characterization of the final branched product, a fairly comprehensive picture of the branched structure of the polymer can be obtained both as a function of time during its synthesis and across the whole molar mass range of the final product.

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