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Dilute Solution Properties of Model PMMA-*g*-PMMA's

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ABSTRACT: The dilute solution properties of some model graft poly(methyl methacrylates) (PMMA) with similar molecular weights and different branching levels were investigated. Variable-temperature size-exclusion chromatography (SEC) was used to obtain molecular weight distributions (MWD), intrinsic viscosities, branching parameters, average unperturbed chain dimensions, and information on hydrodynamic behavior. Number- and weight-average molecular weights determined by SEC with differential viscometry (DV) and low-angle laser light scattering (LALLS) compared favorably with those measured by membrane osmometry and static low-angle laser light scattering. SEC/DV accurately measured intrinsic viscosities quickly and conveniently. Combination of these results revealed that the PMMA-*g*-PMMA's containing up to 40 mass % of long-chain branching obeyed the universal calibration conditions. SEC/DV appears to be a viable method for determining branching distributions in such grafts and shows some potential as a tool for the measurement of unperturbed chain dimensions in these highly branched materials.

Introduction

The objective of this investigation was to evaluate the effect of long-chain branching on dilute solution properties of comb poly(methyl methacrylate) (PMMA-*g*-PMMA). Specifically, two main goals were to determine whether the universal calibration[1,2] is an appropriate way to obtain accurate molecular weight results for branched systems and to study the effect of branching on the hydrodynamic behavior of polymers having similar molecular weights. For these purposes, the PMMA-*g*-PMMA's used here were synthesized to obtain polymers with differing levels of branching but having similar molecular weights and high levels of molecular weight uniformity both in the chain backbone and the pendant branches.

Universal calibration approaches to size-exclusion chromatography were examined by differential viscosity detection and low-angle laser light scattering. SEC is typically conducted with a single, concentration-sensitive detector. This experiment can yield molecular weights after calibration by using polymer standards. However, SEC separates according to hydrodynamic volumes and not molecular weights. Therefore, in order to obtain an absolute molecular weight of an unknown, the standard used must have the same structure as the sample being tested; otherwise, SEC done in this manner only yields a molecular weight that is relative to the type of standard used. The dual detection instrument configuration involving SEC/LALLS is an established molecular weight determination technique widely regarded as yielding absolute molecular weights. SEC/DV, on the other hand, is a new technique based on universal calibration. The validity of using universal calibration to analyze highly branched polymers has not been clearly documented. Some light may be shed on this question by comparing the performance of the established SEC/LALLS system to the fairly new SEC/DV instrumentation. In addition, molecular weights obtained by membrane osmometry ($\bar{M}_n$) and static LALLS ($\bar{M}_w$) were used to provide reference values for the SEC experiments.

The hydrodynamic behavior of the branched polymers was investigated by examining intrinsic viscosity at various temperatures to study possible changes in conformation. The expected result of maintaining similar molecular weights of the branched polymers while varying the branching levels was to increase the coil density and decrease the hydrodynamic size of the polymer chains. Again, the results obtained here were compared to those obtained from SEC/DV.

Due to the ability of SEC/DV to fractionate small amounts of polymer and simultaneously obtain the intrinsic viscosities of these fractions, the potential exists to extend the utility of SEC/DV beyond molecular weight determinations. One possibility is to measure unperturbed dimensions of branched molecules. This was attempted by using the Stockmayer–Fixman equation, which allowed the extrapolation of results of intrinsic viscosity obtained in good solvent environments to Θ conditions where the unperturbed dimensions were calculated. These values were compared to theoretically derived quantities. Branching information such as branch index and distribution of branching usually accessible from SEC/LALLS was also obtained by using SEC/DV.

Background

Branching Index. Assuming Θ conditions, a *g* factor can be defined for a flexible polymer chain containing branches but having no loops. The branching index, *g*, is the ratio of the mean-square radius of gyration of a branched molecule to that of a linear molecule containing the same number of segments, *n*

$$\langle r_g^2\rangle_b = g\langle r_g^2\rangle_l = \frac{1}{6}na^2g \qquad (1)$$

where the subscripts b and l refer to branched and linear chains, respectively, and *a* is the unperturbed effective length of a segment. Expressions for *g* may be derived for different chain architectures.[3,4]

If

$$p = (f-1)m + 1 \qquad (2)$$

where *p* is the total number of subchains (portion of the molecule between two junction points or between a junction point and a dangling end), *f* is the number of branches emanating from a branch point, and *m* is the number of

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branch points, then[5]

$$g_{\mathrm{u}}(\text{comb}) = \frac{3p-2}{p^2} + \frac{1}{p^3}(f-1)^2 m(m^2-1) \tag{3}$$

$$g_{\mathrm{r}}(\text{comb}) = \frac{6}{p(p+1)(p+2)}\left[p^2 + \frac{1}{6}(f-1)^2 m(m^2-1)\right] \tag{4}$$

where u represents a uniform distribution and r stands for a random distribution of subchain lengths. With the definition of p given in eq 2, eqs 3 and 4 can be written in terms of f and m; thus, the number of branch points in a comb may be determined by assuming that all these points have the same functionality.

The numerical values of g are always less than 1, indicating that, under similar solution conditions, the average chain dimensions of a branched molecule will always be smaller than that of its linear counterpart having the same degree of polymerization.[3,6]

Second Virial Coefficient. The second virial coefficient, A_2, reflects the strength of polymer/solvent interactions. Its value is affected by solvent power, chain architecture, temperature, and molecular weight. For branched molecules, A_2 may be expressed as

$$A_2 = (N_{\mathrm{A}} n^2 \beta / 2M^2)(1 - Cz + ...) \tag{5}$$

where N_{A} is Avogadro's number and β is the binary cluster integral for a pair of segments and represents the effective excluded volume for one segment due to the presence of another segment in that space. β is generally larger in solutions where strong polymer/solvent interactions exist and decreases with loss of solvation. In eq 5 M is the polymer molecular weight and C is a constant that is a function of chain structure. For a comb branched molecule with a branch functionality of 3, C increases with an increasing number of branches, resulting in a decreasing second virial coefficient. The quantity z is defined as $(3/2\pi\langle r^2\rangle_0))^{3/2}\beta n^2$ where $\langle r^2\rangle_0$ is the mean square unperturbed end-to-end distance.[3,7,8]

Intrinsic Viscosity. The average molecular dimensions of a branched chain may be obtained directly from light scattering experiments or calculated indirectly from intrinsic viscosity experiments.[9] The latter method involves using theories of the frictional properties of polymer molecules to derive the following relationship for a nonlinear, random, flexible coil:

$$[\eta] = \frac{\Phi_0' \langle r_g^{\,2}\rangle^{3/2}}{M} \tag{6}$$

Here, $\Phi_0' = 6^{3/2}\Phi_0$, where Φ_0 is a universal constant having the value of 2.5×10^{23} (cgs) for linear, flexible, random coils.[3] The factor 6 arises from the relationship between the radius of gyration and end-to-end distance for a flexible linear chain. For a linear, flexible chain, eq 6 is often reformulated as

$$[\eta] = \Phi_0\left(\frac{\langle r^2\rangle_0}{M}\right)^{3/2} M^{1/2}\alpha_\eta^{\,3} = K_0 M^{1/2}\alpha_\eta^{\,3} \tag{7}$$

to obtain the unperturbed end-to-end distance where

$$K_0 = \Phi_0\left(\frac{\langle r^2\rangle_0}{M}\right)^{3/2} \tag{8}$$

is a constant for a given polymer independent of solvent and molecular weight. Since the chain expansion factor $\alpha_\eta = 1$ under Θ conditions, the measurement of intrinsic viscosities under this constraint should yield the unperturbed chain dimensions of a polymer molecule;[3,10-13] however, these experiments are often difficult. It is more convenient to use good solvents and extrapolate results to Θ conditions.[12,14-17] The simplest equation that has been found to be adequately accurate is the one proposed by Stockmayer and Fixman[18]

$$\frac{[\eta]}{M^{1/2}} = K + 0.51\Phi_0 B M^{1/2} \tag{9}$$

where B indicates long-range interactions. According to eq 9, the intercept of a plot of $[\eta]/M^{1/2}$ against $M^{1/2}$ should yield K from which the unperturbed chain dimensions may be calculated.

Intrinsic viscosity values are dependent not only on the solvent used in the experiment but also on the temperature of the measurements. The temperature coefficient of the intrinsic viscosity is related to the changes in the unperturbed chain dimensions and the expansion factor in the following manner:

$$\frac{\mathrm{d}\ln[\eta]}{\mathrm{d}T} = \frac{\mathrm{d}\ln K_\theta}{\mathrm{d}T} + 3\frac{\mathrm{d}\ln\alpha}{\mathrm{d}T} \tag{10}$$

From the variation of intrinsic viscosity with temperature, it is then possible to detect any conformational changes in the polymer.

Determination of Long-Chain Branching in Polymers. The branching index defined in eq 1 can be used to determine the average branching in a polymer. This requires light scattering to measure both the radius of gyration of a branched molecule and its linear analogue of the same molecular weight. Alternatively, another relationship describing branching is

$$g^x = [\eta]_{\mathrm{b}}/[\eta]_{\mathrm{l}} \tag{11}$$

Although the derivation of this equation assumes Θ conditions, it is a reasonable approximation at non Θ conditions. This equation can be used to obtain branching information if intrinsic viscosities are determined on both the branched and linear polymers of the same molecular weight in the same solvent and at the same temperature. When it is not possible to obtain a linear analogue with the same molecular weight, the Mark–Houwink equation may be used to estimate its $[\eta]$. This route is contingent on the availability of the Mark–Houwink constants for the polymer/solvent/temperature combination of interest.

The expression for g^x is useful for the investigation of branching only if the architecture of the branched polymer is known since both the exponent x and the final equation required for g are dependent on the type of branching present in the polymer.[19-26] Values for x range from 0.5 to 1.5. For star branched polymers, it has been established that $x = 0.5$. For combs with many short branches x approaches 1.5. When the comb has a low branching frequency, then x is closer to 0.5. For randomly branched polymers, x ranges from 0.7 to 1.3 depending on the degree of branching.[7,19,22,27,28]

Distributions of branching may also be nonuniform. SEC with the appropriate detectors may be used to determine the amount of branching distributed across a MWD.

SEC/DV. SEC coupled with a viscosity detector provides a direct method of obtaining the branching factor g^x across a distribution since the intrinsic viscosity is measured on fractionated material.[21,29] The Viscotek DV measures intrinsic viscosity by detecting the difference in pressure, ΔP, between the solvent and the solution. This ΔP is proportional to the specific viscosity. When used in conjunction with a DRI detector, intrinsic viscosities are determined since SEC is conducted under dilute solution conditions.[30,31]

The importance of the information obtained by the coupling of SEC with intrinsic viscosity experiments in branching studies is underscored by the fact that, before on-line viscosity detectors, the study of branching via SEC was conducted through measurement of intrinsic viscosities after collection of effluent fractions as they eluted from the columns into microviscometers. With the improvement in chromatographic efficiency, however, the amount of sample injected has dramatically decreased so that this earlier procedure has been abandoned.[32-36] More recently, the universal calibration approach was used as the basis for obtaining the molecular weight and branching distribution without the use of an on-line viscometer.[27,28,37,38]

Several viscosity detectors have been developed for use in SEC in conjunction with a concentration-sensitive detector.[23,30,31,39-50] Park and Graessley reported that where there was a high branching frequency, both this characteristic as well as the molecular weight obtained were underestimated when only viscosity detection was used. In the other extreme, very small amounts of branching were difficult to detect due to the insensitivity of the concentration detector at the portion of the elution curves where the effect of the branching might be observed.[23]

Hamielec et al. tested the accuracy of a commercially available viscosity detector marketed by Viscotek in the molecular weight determination of some linear and branched polymers. They found that the weight-average molecular weights were in good agreement with the values from other experiments. Number-average molecular weights varied, however. It was postulated that the deviation in molecular weights from values determined by traditional means was due to peak broadening.[51]

Although the differential viscosity detector does yield intrinsic viscosities, an analysis of the separation mechanism reveals that g^x is not the quantity that one obtains directly. The branching index g^x is the ratio of intrinsic viscosities for a branched and linear molecule having the same molecular weight. SEC, however, does not separate on the basis of molecular weight but on hydrodynamic volume—molecules having the same hydrodynamic volume elute at the same retention volume; therefore, the g obtained is actually

$$g_v = \left(\frac{[\eta]_b}{[\eta]_l}\right)_v \tag{12}$$

where v indicates constant elution volume. The relationship between g^x and g_v was shown to be[23,52]

$$g^x = g_v^{\,a+1} \tag{13}$$

where the "a" was the Mark–Houwink exponent. Obtaining the Mark–Houwink exponent requires fractionation of a polymer and the determination of the intrinsic viscosities and molecular weights of each of these fractions. This may be achieved by the SEC/DV system, thus making it an ideal method for investigating branching in polymers.[14,52,53]

SEC/LALLS. Since its commercial introduction 18 years ago, the LALLS has been used as an on-line molecular weight detector for the SEC. In theory, the SEC can separate whole polymers into monodisperse fractions, i, so that $\bar{M}_i = \bar{M}_{i,n} = \bar{M}_{i,w}$. However, for a number of reasons, including mixing in the detector, a broader than ideal dispersion of molecular weights exists and $\bar{M}_i$ is closer to $\bar{M}_{i,w}$. For this reason, many investigators believe that SEC/LALLS can only give accurate $\bar{M}_w$'s while the other moments of molecular weight distribution from SEC are unreliable except for polymers having high uniformity in molecular weight.[8,29,54-58] Use of LALLS as an on-line detector assumes that the specific refractive index increment and the second virial coefficient have been accurately determined (separately) for the polymer/solvent system at some temperature and that these two quantities remain constant throughout the MWD. The $\partial n/\partial c$ is particularly sensitive to temperature, with a linear dependence.[59-63]

For branching investigations it was assumed that

$$g^x = \frac{[\eta]_b}{[\eta]_l} = \left(\frac{M_l}{M_b}\right)_v^{a+1} \tag{14}$$

In the application of SEC/DV to branching studies, the observed branching factor, g^x, is actually that which results at a particular elution volume rather than at a specific molecular weight. Equation 13 will thus be applicable with the exception that g^x is now couched in terms of molecular weights instead of intrinsic viscosities. Again, the Mark–Houwink exponent "a" is required for the calculation.[14,21,22,26,52-54,64] However, the use of SEC/LALLS data necessitates a more complex route for obtaining "a".[22,65,66]

While SEC/LALLS is valuable in studies described above, its use in conjunction with a concentration-sensitive differential refractive index (DRI) detector introduces accompanying problems. The LALLS detector is most sensitive to high molecular weight materials. The DRI detector on the other hand lacks sensitivity on both peripheries of the chromatogram. The decreased resolution at high and low molecular weight may cause large errors in $\bar{M}_w$ and $\bar{M}_n$. A solution suggested for this problem is to electronically enhance the signal to noise ratio where needed.[8,52,57,67,68] In addition, axial dispersion and accurate knowledge of dead volume between detectors are pertinent problems. In spite of these shortcomings, variations in the molecular weights determined by SEC/LALLS are typically less than previously obtained by other methods.[49,57,69-73]

Multidetection SEC. In order to have complete information on the MWD of a polymer, not only dual detection but multidetection is desirable. This may be achieved by separately running SEC/LALLS and SEC/DV experiments. An excellent combination involves three detectors—concentration, viscosity, and light scattering—connected in tandem on a SEC. For this configuration, one must be especially careful with the dead volume and axial dispersion.[14,27,50,53,70,71,74] So far, the authors are aware of only one such combined instrument reported in the literature.[75]

Experimental Section

In this section the procedures used in this investigation of the PMMA graft homopolymers will be detailed.

Materials. This investigation required the synthesis of model branched polymers having well-defined branching and uniform molecular weight distributions in all topological parts. This was achieved by the synthesis of PMMA-*g*-PMMA through combination of the macromonomer technique with anionic polymerization.[76,77] The methacryloyloxy-terminated macromonomer was synthesized via group-transfer polymerization, yielding products with a narrow distribution of molecular weights. These macromonomers formed the graft part of the polymer to produce a uniform distribution of branch molecular weights. The backbone was generated via anionic polymerization, which also yields a narrow molecular weight distribution. This combination of synthetic methods should provide model branched polymers having both controlled molecular weight in the branches and the backbone portions. The details of the synthesis may be found

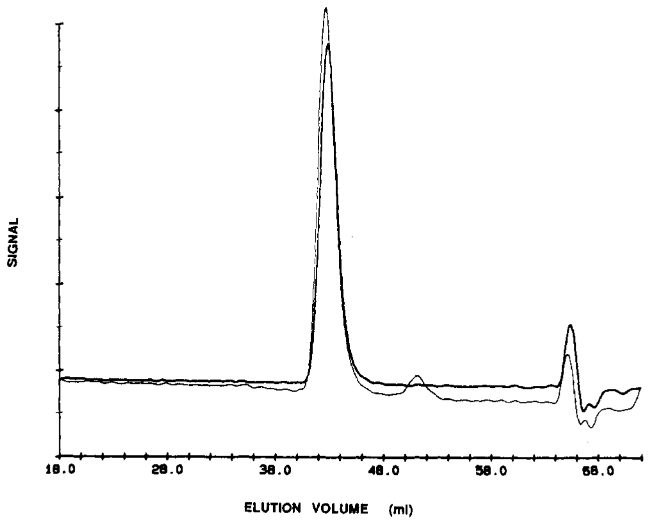

Figure 1. Concentration chromatograms of PMMA-g-PMMA A before (fine trace) and after (bold trace) removal of unincorporated macromer.

elsewhere.[78-80] Three samples of PMMA-g-PMMA's with different levels of branching produced in the above manner were used in this study.

In order to determine branching for the polymer, a linear analogue of the same molecular weight was required. A PMMA SEC standard with uniform molecular weight was obtained from American Polymer Standards Corp. for this purpose. The specifications from the source indicated that this standard had a $\bar{M}_w$ of 251 000 g/mol and a $\bar{M}_n$ of 239 100 g/mol. The intrinsic viscosity at 30 °C in THF was given as 0.7 g/dL, and the Mark-Houwink exponent "a" was 0.69.[81]

Removal of Unincorporated Macromonomer. The graft polymers obtained after synthesis contained a small amount of unincorporated macromonomer, which does not significantly affect SEC analysis since the signal due to the unincorporated material and its concentration may be eliminated in the data processing step of the experiment. In the other experiments, however, the presence of the linear macromonomers having a much lower molecular weight than the graft polymer would have led to erroneous results. Removal of the unincorporated material was therefore necessary. This was achieved by using steps based on fractional precipitation.[82] The most effective procedure involved making a ca. 1 w/v % solution of the polymer in tetrahydrofuran (THF). Nonsolvent was slowly added to this solution with agitation. Either methanol or hexane was used as nonsolvent, with hexane being more effective. Nonsolvent addition was terminated before the turbidity end point, judged by difficulty in dissipating the cloudiness of the solution following addition of a nonsolvent aliquot. At this point, the solution was allowed to ripen for several hours. More nonsolvent was subsequently added until precipitates were visible. The solution was allowed to stand at room temperature in order to allow sedimentation of the precipitate. (When methanol was utilized as the nonsolvent, 20 min of centrifuging was necessary to facilitate the separation of the precipitate from the supernatant liquid.) This method yielded a thick film of the graft PMMA, which was reprecipitated. This was achieved by making up a 5 w/v % solution of the material in THF and slowly adding this solution to approximately 10 times its volume of hexane in a Waring blender at a moderate blending speed. The resulting flakes were dried at about 40 °C under vacuum for at least 6 h. The procedure detailed above allowed the fractionation of large quantities of polymer at one time, eliminating the need to pool samples from several fractionations, as would be the case if preparative-scale SEC were utilized. For this investigation, approximately 10 g of polymer was fractionated with a yield of roughly 75%. Success of the procedure is demonstrated in the SEC chromatogram in Figure 1, where no change in the peak position for the branched material before and after fractionation was observed. All the experiments conducted below, except for the determination of the number of branches, utilized the PMMA's from which the unincorporated macromonomer had been removed.

Vapor Phase Osmometry (VPO). The absolute number-average molecular weight of the macromonomer was determined by using a Wescan Model 233 vapor-phase osmometer. The experiment was conducted in HPLC-grade, unstabilized THF at 30 °C and in HPLC-grade toluene at 63 °C. Molecular weight was obtained by using the multistandard calibration.[83] The concentrations of macromonomer solutions used ranged from 1×10^{-3} to 7×10^{-3} g/mL.

Membrane Osmometry (MO). The absolute number-average molecular weights of the PMMA-g-PMMA's were measured by using a Wescan Model 231 membrane osmometer. The measurements were done with RC 52 and RC 51 regenerated cellulose membranes, which have lower molecular weight cut-off limits of 20 000 and 10 000 g/mol, respectively. Experiments were conducted at 30 °C in HPLC-grade toluene. Seven solutions with concentrations ranging from 2×10^{-3} to 8×10^{-3} g/mL were used. They were filtered through MSI Teflon membrane filters having pore diameters of 0.5 μm prior to the measurements.

Static Low-Angle Laser Light Scattering (LALLS). The weight-average molecular weights and second virial coefficients of the PMMA-g-PMMA's were measured by using the Chromatrix KMX-6 LALLS photometer in the static mode. The experiments were conducted at room temperature in unstabilized, HPLC-grade THF by using solutions ranging in concentration from 1×10^{-3} to 5×10^{-3} g/mL. The solutions were filtered through an Acrodisc CR 0.2-μm filter as it was pumped at 0.2 mL/min by a Sage syringe pump through the 15-mm Teflon sample cell.

Specific Refractive Index Increments ($\partial n/\partial c$). The $\partial n/\partial c$'s required for both the static LALLS experiments and SEC/LALLS measurements were obtained by using the Chromatrix KMX-16 laser differential refractometer haivng a He-Ne laser operating at 633 nm. Experiments were conducted at 25 and 45 °C in unstabilized, HPLC-grade THF for the PMMA-g-PMMA's and the linear PMMA standard. The solutions used ranged in concentration from 4×10^{-3} to 10×10^{-3} g/mL. For the 45 °C experiments, the solutions were maintained in a thermostat for 30 min to assure that there was no temperature gradient in the contents of the volumetric flask. They were then corrected to volume by the addition of solvent, also at 45 °C. These precautions were taken to assure that the concentration used in the calculations was that which was obtained at the temperature of the experiment. It was crucial that the solvent used in the reference cell of the refractometer be as close in temperature to that of the solution as possible.

Size-Exclusion Chromatography (SEC). SEC on both the fractionated and unfractionated form of the polymer was conducted on a Waters 150C ALC/SEC equipped with a differential refractive index detector connected in parallel to a Viscotek Model 100 differential viscosity detector and in series to a Chromatix KMX-6 LALLS. Experiments using the SEC/DV were conducted in two modes, one where the LALLS was off-line and one with the LALLS on-line.

Five-column-resolution repacked Permagel columns ranging in specified pore diameters from 100 to 10^5 Å were connected in series to an Ultrastyragel column having a pore diameter of 10^6 Å. The polymers used to construct the universal calibration curve were Polymer Laboratories narrow distribution polystyrene standards having molecular weights of 1250, 2150, 2950, 5000, 9200, 22 000, 34 500, 52 000, 68 000, 120 000, 170 000, 500 000, and 1 130 000 g/mol. Branched and linear PMMA solutions having concentrations of approximately 2×10^{-3} g/mL were used. These were prepared by using unstabilized, degassed HPLC-grade THF. The solutions were filtered through MSI Teflon membrane filters having pore diameters of 0.5 μm prior to injection. An injection volume of 300 μL was used with a flow rate of 1 mL/min. Experiments were conducted at 30, 35, 40, and 45 °C, with a calibration curve generated and the detector lag times calculated at each temperature.

At temperatures above 30 °C, the viscometer and the LALLS were heated. Aside from the heaters available on the LALLS that controlled the temperature of sample flow cell, an auxiliary strip heater was used to prevent thermal gradients in the cell.

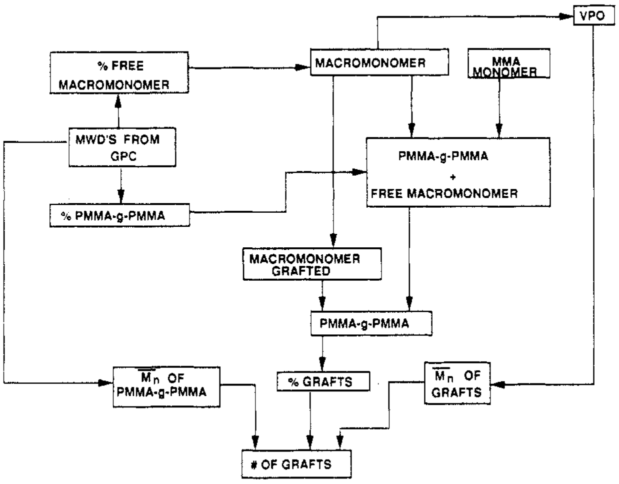

Figure 2. Algorithm for stoichiometric branching calculation.

At elevated temperatures, solution preparation was completed in the heated injection compartment of the chromatograph to ensure the correct concentration at the higher temperature.

Intrinsic Viscosity, [η]. Intrinsic viscosity experiments were carried out in Cannon CUU 50 Ubbelohde capillary viscometers where THF solution flow times of more than 100 s were obtained. Measurements were done for the linear and branched PMMA solutions with concentrations ranging from 2×10^{-3} to 8×10^{-3} g/mL at temperatures ranging from 25 to 45 °C at 5° intervals (±0.02 °C). Flow times of the solutions were measured until five consecutive readings that varied by less than 0.1% were obtained.

Results and Discussion

Vapor Phase Osmometry. The molecular weight for the PMMA macromonomer was determined to be 7000 ± 100 g/mol in experiments in THF and toluene, at different temperatures. The proximity in results in the different solvents was expected for samples in which no anomalous behavior such as association existed.

Stoichiometric Determination of Branching. The number of branches on the comb PMMA's were determined stoichiometrically by combining information from synthesis, SEC, and the VPO. The assumption made here was that all of the macromonomer charged in the synthesis was recovered either as free, unincorporated macromonomer by fractionation or as branches on the remaining PMMA-*g*-PMMA. A diagram of the algorithm used in the branching calculations is shown in Figure 2. The right-hand portion shows the final step in the reaction where a known amount of macromonomer and MMA monomer were combined to produce the comb PMMA. The resulting product was a mixture of the unincorporated macromonomer and the PMMA-*g*-PMMA.

As shown in the left-hand side of Figure 2, the next step required use of the molecular weight distributions obtained from SEC to determine the proportion of graft PMMA and free macromonomer in the product. To do this, the SEC/DV was used to calculate a cumulative molecular weight and differential molecular weight distribution of the comb PMMA as shown in Figure 3. The data here for comb PMMA C are representative of what was obtained for all three comb PMMA's. The molecular weight of unincorporated macromonomer was determined from the SEC/DV-derived MWD. The corresponding molecular weight on the cumulative distribution was read from an alignment of the abscissas of both plots and the percentage of macromonomer was revealed from the ordinate of the cumulative distribution plot. These experiments were conducted three times and averaged. It was concluded that the residual macromonomer was of the order of 3%, 5%, and 6%, ±1% for the three samples that are designated A–C, respectively.

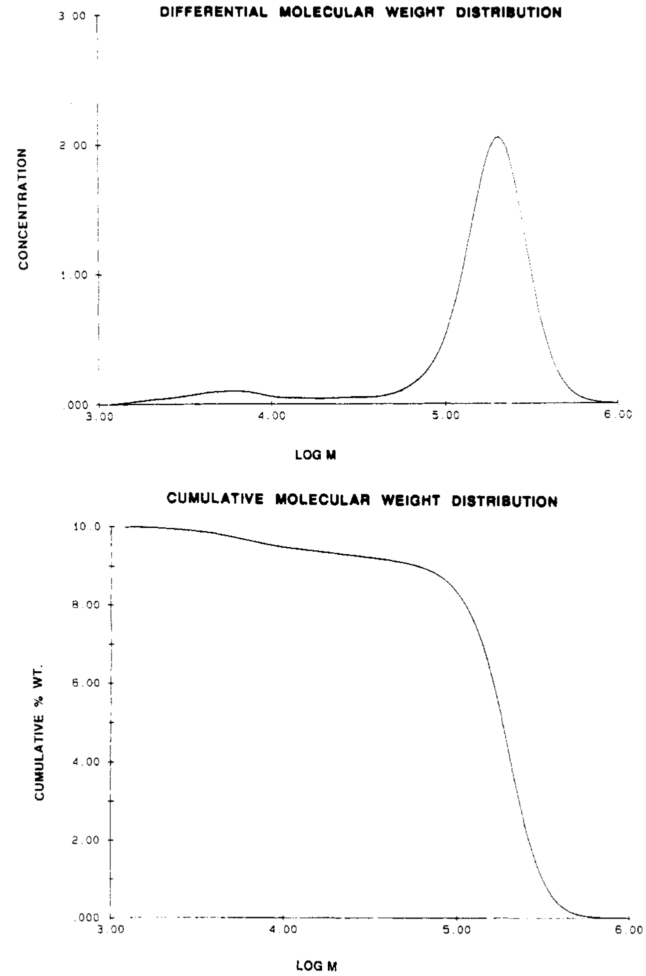

Figure 3. Molecular weight distribution and cumulative molecular weight distribution for PMMA-*g*-PMMA C used for branching calculations.

By combining data on the amount of reactants and the yield from the synthetic procedure with the percentages of graft polymer and free macromonomer (as calculated from the MWD's), the quantities of graft polymer and unincorporated macromonomer in the product were determined. The amount of macromonomer successfully grafted was the difference between the amount charged and the amount recovered as unincorporated macromonomer. This step is shown in the middle of Figure 2. The mass fraction of the comb polymer comprised of these branches resulted from ratioing the amount of incorporated macromers to the total amount of PMMA-*g*-PMMA. The number-average molecular weight of the PMMA-*g*-PMMA was also obtained from the SEC/DV MWD. This, together with the number-average molecular weight of the macromonomer obtained by VPO and the mass fraction of grafts present in the polymer, was used to calculate the average number of branches, m

$$m = (\text{mass fraction of branches in PMMA-}g\text{-PMMA}) \times (\bar{M}_n \text{ of PMMA-}g\text{-PMMA})/\bar{M}_n \text{ of branch} \quad (15)$$

The results are given in Table I.

Membrane Osmometry. The results from membrane osmometry are given in Table I. These results are absolute molecular weights and were used for comparison with the SEC results. Considering that the desired molecular weight in the synthesis was about 250 000 g/mol, the results

Table I
Molecular Weights of PMMA's Containing Different Branching Levels

	no. of	mass %	$\bar{M}_n \times 10^{-5}$				$\bar{M}_w \times 10^{-5}$				$A_2 \times 10^4$,
sample	branches	graft	MO	GPC	GPC/DV(LALLS)	GPC/DV	static LALLS	GPC	GPC/DV(LALLS)	GPC/DV	(mol cm^3)/g^2
A	2 ± 0.4	5.4	2.81	1.81	2.14	2.37	2.95	2.30	2.60	2.84	3.1
B	7 ± 1.4	24.0	2.15	1.52	1.79	2.03	2.33	1.76	2.05	2.33	2.9
C	13 ● 2.6	39.9	2.49	1.67	1.95	2.15	2.66	1.95	2.24	2.52	2.4

Table II
Temperature-Dependent $\partial n/\partial c$'s[a] Used in LALLS Calculations

	temp, °C				
sample	25	30	35	40	45
A	0.0823	0.0813	0.0803	0.0793	0.0783
B	0.0811	0.0808	0.0805	0.0803	0.0800
C	0.0791	0.0794	0.0796	0.0799	0.0801

[a] Errors in $\partial n/\partial c$ are less than 5%.

demonstrate very good molecular weight control.

Low-Angle Laser Light Scattering. The results obtained from static LALLS are also shown in Table I. These weight-average molecular weights are regarded as the most accurate molecular weights determined and will be used as the reference values for comparison with SEC numbers. Inspection of the results from membrane osmometry and light scattering indicates a relatively small polydispersity, as expected from the synthetic route used. In addition to molecular weights, LALLS also yielded second virial coefficients, A_2. A decrease in A_2 with increasing branching agrees with theory, which predicted a decrease in polymer/solvent interaction as the density of polymer segments within a coil increases.[3]

Specific Refractive Index Increment. Because SEC/LALLS was applied between 30 and 45 °C, $\partial n/\partial c$'s for these temperatures were needed. The $\partial n/\partial c$'s were measured only at two temperatures, 25 and 45 °C. On the basis of $\partial n/\partial c$ proportionality to temperature in the literature, values for intermediate temperatures were interpolated. The $\partial n/\partial c$'s obtained at the two temperatures where experiments were conducted are given in Table II. The value of the temperature coefficient is of the magnitude expected—on the order of 10^{-4}–10^{-5} mL^{-1} g^{-1} °C^{-1}.[74]

The optical constant K needed in the LALLS experiment was calculated by using these $\partial n/\partial c$'s and the solvent refractive indices at the various temperatures. The refractive index for THF at 25 °C used was 1.4036 cm^{-1}. It was obtained by using the Cauchy dispersion relationship

$$\nu = \xi + \xi'/\lambda_0^2 \tag{16}$$

where ν is the specific refractive index increment, and ξ and ξ' are constants relating refractive index at any wavelength λ_0 to the value at a reference $(\lambda_0)_{\text{ref}}$. The equation was used to interpolate data at 633 nm from literature values of refractive indices obtained at two other wavelengths.[84] The change in refractive index with temperature also had to be considered, and the temperature coefficient for this change was taken to be −0.0004/°C.[85]

Molecular Weights from Size-Exclusion Chromatography. As discussed in the Introduction, SEC with dual detectors may be used to obtain absolute molecular weight distributions, which are inaccessible by conventional SEC. Results obtained for $\bar{M}_n$ and $\bar{M}_w$ from the SEC/DV and SEC/LALLS were evaluated by comparing them with the numbers measured separately on the MO and on the LALLS.

SEC/DV. The molecular weights at 30 °C obtained for the two modes of SEC/DV experiments are shown in Table I together with the $\bar{M}_n$ and $\bar{M}_w$ obtained on the SEC in separate experiments where no viscosity detector was used and whose calibration was based on the molecular weight of linear PMMA standards. The results from the first mode of instrument configuration where the LALLS was on-line are indicated by SEC/DV(LALLS). The results obtained for the second series are given in the column SEC/DV—the designation for the instrument configuration without the LALLS on-line. These values from the SEC/DV experiment are averages of two experiments. The numbers were reproducible to within 2%. A survey of the numbers and comparison with the absolute molecular weights in Table I indicate that calibration based on *linear* molecular weight standards was *not* suitable for the *branched* polymers. The molecular weights obtained in this way underestimate the more accurate values by 30–35%. For the SEC/DV with the LALLS on-line, the $\bar{M}_n$'s still fell below the values provided by the membrane osmometer, although there was about a 10% improvement in the accuracy compared to that obtained by calibration with molecular weights of linear standards. The best results were obtained without the LALLS connected, in which case the values fell short from 5 to 15%.

Weight-average molecular weights gathered from the SEC experiment using calibration with linear PMMA standards deviated from the absolute values by about 25%. Inspection of the $\bar{M}_w$'s obtained by SEC/DV shows that, with the LALLS on-line, the deviations of the measured values from the absolute $\bar{M}_w$'s from static LALLS experiments were about 12–15%. When the LALLS was removed as a detector, results were in excellent agreement with static LALLS numbers, with deviations being less than 4%, well within the limits of the experimental error. Again, these findings confirm the problems associated with using linear standards to calibrate a SEC when branched samples are investigated. The larger deviation in results from the absolute values in both the $\bar{M}_n$'s and the $\bar{M}_w$'s when the LALLS was on-line may be due to unknown dead volume in the connections between the detectors. This might be affecting the data at the larger elution volumes resulting in a bigger error in the $\bar{M}_n$'s than in the $\bar{M}_w$'s.

The molecular weights determined by using SEC/DV confirmed the trends seen by Hamielec et al. where it was found that the use of the Viscotek detector led to an underestimation of the $\bar{M}_n$ while giving the correct $\bar{M}_w$.[51] This is surprising; theoretically, the viscosity detector should yield the correct $\bar{M}_n$ and not $\bar{M}_w$ since its operation is based on universal calibration from which $\bar{M}_n$ is the quantity that is obtained directly.[69]

The SEC/DV experiments were also conducted at elevated temperatures. The main purpose of raising the temperature was to investigate the change in hydrodynamic volume of such branched polymers in dilute solution. This change should also be indicated by the variation in intrinsic viscosities. The molecular weights calculated at these higher temperatures should not deviate from those obtained at lower temperatures. Indeed, the results in Table III (taken with the LALLS on-line) indicate that this is the case with variation in molecular weights at the different temperatures within 5%.

Table III
Results from Variable-Temperature SEC/DV(LALLS)

	$M \times 10^{-5}$, g/mol							
	30 °C		35 °C		40 °C		45 °C	
sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$
A	2.144	2.596	2.077	2.542	2.072	2.518	2.170	2.658
B	1.786	2.052	1.726	2.007	1.780	2.021	1.902	2.237
C	1.946	2.242	1.837	2.171	1.920	2.160	2.051	2.407

Table IV
Results from Variable-Temperature SEC/LALLS

	$M \times 10^{-5}$, g/mol							
	30 °C		35 °C		40 °C		45 °C	
sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$
A	2.593	2.828	2.694	2.930	2.840	3.031	2.910	3.048
B	2.162	2.287	2.159	2.303	2.196	2.318	2.271	2.438
C	2.544	2.656	2.486	2.637	2.484	2.670	2.460	2.618

Table V
Variable-Temperature Intrinsic Viscosities from Capillary Viscometry

sample	25 °C	30 °C	35 °C	40 °C	45 °C
linear	71.12 ± 7.46	70.73 ± 7.61	73.03 ± 7.66	73.25 ± 7.72	73.66 ± 7.78
A	61.98 ± 6.42	62.00 ± 10.68	63.05 ± 6.00	62.82 ± 6.29	65.77 ± 6.97
B	51.82 ± 5.85	54.93 ± 10.52	52.31 ± 3.93	53.81 ± 4.65	56.49 ± 5.46
C	54.97 ± 4.27	57.52 ± 10.43	57.84 ± 5.68	57.87 ± 5.32	60.05 ± 5.43

SEC/LALLS. Results for the SEC/LALLS experiments are shown in Table IV for all temperatures. Again, the numbers given in the table are averages of duplicate runs and were reproducible to within 2%. As expected, the molecular weights did not vary significantly with temperature. They were also in excellent agreement with the absolute molecular weights obtained from MO and static LALLS. Compared to the results obtained from SEC/DV, SEC/LALLS was the more accurate method for obtaining both the $\bar{M}_n$ and the $\bar{M}_w$ of such branched polymers.

While SEC/LALLS afforded the more accurate molecular weights, its use required more experiments and greater care when compared to the SEC/DV. One needs to measure A_2 separately by static LALLS if the system under investigation is one that involves a new polymer/solvent combination for which no literature values are available. It is also necessary to measure $\partial n/\partial c$ accurately at the same temperature and wavelength that correspond to the LALLS experiment. SEC/LALLS is more sensitive to errors in $\partial n/\partial c$ than to errors in A_2's. As a test, different A_2's were entered as constants in the data processing of these data. It was found that a 4-fold increase in A_2 resulted in a 3% increase in the $\bar{M}_n$ and a 2% increase in the $\bar{M}_w$. These differences are within the limits of experimental error of the experiment. On the other hand, when the $\partial n/\partial c$ was in error by 15%, the $\bar{M}_w$ obtained was higher by 40%. These results are consistent with previous findings.[57]

Intrinsic Viscosities. Intrinsic viscosities were obtained by using capillary viscometers and SEC/DV. The values obtained from SEC/DV were compared with the numbers from the capillary viscometry, which will be considered the more precise values.

Capillary Viscometry. The results of viscometry for the linear PMMA and the PMMA-*g*-PMMA's at the different temperatures are shown in Table V. These values were obtained by taking the average of the $[\eta]$ results from the double extrapolation of reduced viscosity and inherent viscosity. In all cases, there was little discrepancy in the two values. In Table V, the difference in hydrodynamic behavior of linear and branched PMMA's is demonstrated.

Table VI
$[\eta]$ Results from SEC/DV(LALLS)

	$[\eta]$, dL/g			
sample	30 °C	35 °C	40 °C	45 °C
linear	0.698	0.720	0.734	0.733
A	0.614	0.644	0.675	0.652
B	0.530	0.552	0.566	0.562
C	0.570	0.588	0.610	0.608

The linear PMMA had a higher intrinsic viscosity than any of the three branched polymers, even in some cases where the PMMA-*g*-PMMA's had higher molecular weights. PMMA-*g*-PMMA C had slightly higher $[\eta]$'s than PMMA-*g*-PMMA B, in spite of its having about twice the number of branches as sample B. The difference in the molecular weights of samples B and C is not large enough to explain the higher intrinsic viscosity for sample C.

The effect of temperature on changes in hydrodynamic behavior of branched materials is illustrated by the hydrodynamic volumes of the polymers at the temperatures where they have the smallest and largest $[\eta]$'s. The maximum change in hydrodynamic volume at these temperatures for linear PMMA was 4%, while for the branched PMMA's the variation ranged from 8 to 10%. It is interesting to note that the maximum changes in hydrodynamic volumes were significantly higher in the branched systems compared to those of the linear PMMA. The addition of two branches almost doubled the increment in hydrodynamic volume over the 20° increase in temperature.

SEC/DV. Intrinsic viscosities were also determined from data obtained on the differential viscosity detector. A slight temperature dependence of the differential pressure transducer sensitivity was noted and considered in the calculations. The results from the intrinsic viscosity measurements are shown in Table VI. These values were reproducible to within 5%. For the branched systems, the values of intrinsic viscosities from the SEC/DV were within about 3% of those obtained using capillary viscometry. This suggests that SEC/DV provides a quick and reliable method of determining $[\eta]$'s for branched polymers of this type.

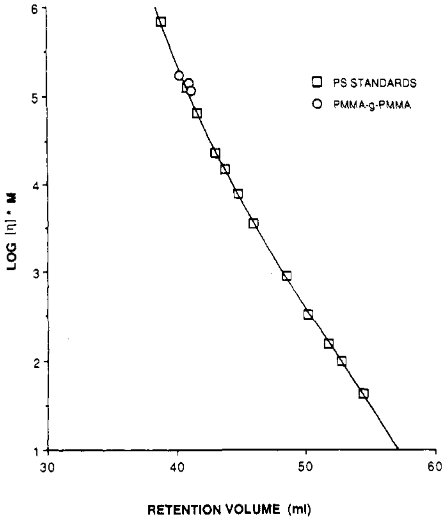

Figure 4. Universal calibration curve for polystyrene standards (from SEC/DV) and PMMA-*g*-PMMA (obtained independently).

Table VII
Unperturbed Radii of Gyration for PMMA's

		$\langle r_g^2\rangle_0 \times 10^{12}$ cm^2			
sample	theoretical	30 °C	35 °C	40 °C	45 °C
linear	35.4	5.11	5.00	5.03	4.73
A	10.7	2.40 ± 0.28	1.93 ± 0.74	1.85 ± 0.21	2.12 ± 0.16
B	6.53	1.83 ± 0.16	1.87 ± 0.06	1.90 ± 0.01	2.11 ± 0.16
C	6.83	2.24 ± 0.28	2.04 ± 0.09	1.12 ± 0.21	1.95 ± 0.21

Universal Calibration. Some investigators have suggested that universal calibration breaks down for some branched polymers. This assertion was evaluated by using the accumulated data. The intrinsic viscosities obtained from capillary viscometry and the number-average molecular weight obtained by MO were multiplied to get a hydrodynamic volume, which is the ordinate of the universal calibration curve. The retention volume at the peak of the SEC chromatogram located the abscissa point in each case. The results are shown in Figure 4 overlaid on a universal calibration curve that was obtained by using polystyrene standards at the same temperature. *Excellent agreement is shown, especially considering that the data points for the graft PMMA's came from three independent sources. This shows that the universal calibration does work for these well-defined, but highly branched, systems, a significant finding.*

Unperturbed Chain Dimensions. Results of theoretical calculations of unperturbed chain dimensions are shown in Table VII. These values were obtained by using eq 4 in conjunction with the unperturbed end-to-end distance calculated when the hindered rotor model is assumed. It is observed that there was a 3-fold decrease in the radius of gyration of PMMA when two branches were added. While the difference in the number of repeat units from sample A to sample B was only 23%, the change in the radius of gyration was 39%. This indicated a significant decrease in size due to the increase in branching content from 5 to 20 mass %. The volume appeared to be buffered at this branching level as the addition of about six more branches caused only a 4% decrease in dimensions despite a 13% difference in the number of repeat units between samples B and C.

The ability of the SEC/DV system to fractionate the polymer and to provide the intrinsic viscosity and molecular weight of each fraction was used to get unperturbed chain dimensions at conditions away from the Θ condition. The Stockmayer–Fixman equation shown in eq 9 was applied with a value of Φ_0' assumed to be 3.7×10^{24} for $[\eta]$'s in mL/g. This value was obtained by multiplying the Φ_0 given by Yamakawa[3] by $6^{3/2}$ so that the unperturbed dimension obtained is the radius of gyration. The constant K in the Stockmayer–Fixman equation may be applied to nonlinear polymers if couched in terms of the radius of gyration instead of unperturbed end-to-end distance.[10]

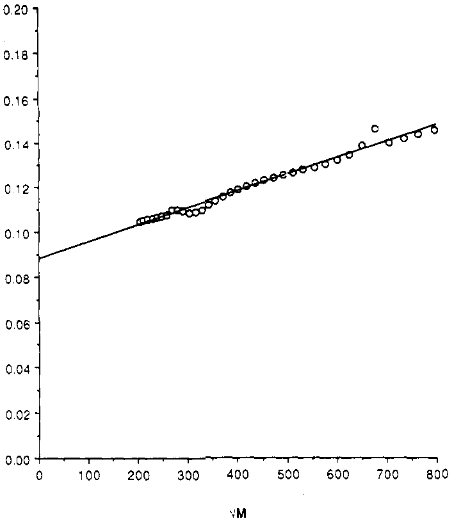

Figure 5. Stockmayer–Fixman plot of PMMA-*g*-PMMA B obtained from SEC/DV.

Using the calculated data for intrinsic viscosities and molecular weights from SEC/DV at four temperatures, the ratio of the intrinsic viscosity to the square root of molecular weight was plotted against the square root of the molecular weight. The Stockmayer–Fixman equation predicts that a straight line will result. The intercept of this line is equal to K as defined by eq 8. To convert eq 8 from one based on the unperturbed end-to-end distance to one that is a function of radius of gyration, the following relationship was used

$$K_0 = 6^{3/2}\Phi_0\left(\frac{\langle \bar{r}^2{}_g\rangle_0}{M}\right)^{3/2} \tag{17}$$

where M ideally should be the absolute weight-average molecular weight of the polymer.

A graph that was typical of the results appears as in Figure 5. There was some curvature observed in the plots. This behavior has been observed by others in similar measurements employing good solvents. The calculations were done for duplicate runs on the SEC and the average values of these two runs are given in Table VII. While the results were in the right order of magnitude when compared to theoretically calculated quantities, the radii of gyration calculated underestimated these values by 3–4.5 times for the branched materials and up to 7 times for linear PMMA. These results indicate that this technique may be viable but fails in our case due to the insensitivity of the detectors used at the low and high molecular weight ends of the distribution. Better agreement might be obtained if the signal at the ends of the distribution could be selectively enhanced electronically as was done by Hamielec et al. for SEC/LALLS.[8]

Branching Index. The branching index g^x may be calculated from the intrinsic viscosity experiments done in capillary viscometers, the SEC/DV experiments, and indirectly through the SEC/LALLS experiments. A table of g values at a fixed number of grafts randomly placed along the backbone may be generated using eq 4. This equation was chosen because although the molecular weights of the grafts of the samples used were fairly uniform, their placement on the backbone was not, leading

Table VIII
g^x's from Capillary Viscometry

sample	25 °C	30 °C	35 °C	40 °C	45 °C	average
A	0.862	0.870	0.864	0.858	0.896	0.870 ± 0.015
B	0.723	0.768	0.729	0.735	0.767	0.744 ± 0.022
C	0.755	0.813	0.785	0.791	0.795	0.788 ± 0.021

Table IX
g^x's from SEC/DV(LALLS)

sample	30 °C	35 °C	40 °C	45 °C	average
A	0.880	0.894	0.920	0.889	0.896 ± 0.015
B	0.759	0.767	0.771	0.767	0.766 ± 0.022
C	0.817	0.817	0.831	0.829	0.824 ± 0.021

to a backbone subchain polydispersity.

Capillary Viscometry. The g^x factors based on results from capillary viscometry for the three comb PMMA's at the different temperatures are given in Table VIII. These were generated by taking the ratio of the intrinsic viscosity of the branched PMMA's to those of the linear PMMA standard. Some error may be introduced here since M_l was not exactly equal to M_b. The number of branches obviously remained constant over the small temperature ranges of this study; thus, the average values of all the branching indices at all the temperatures appear in Table VIII. The standard deviations are shown with the averages in this table.

To determine the average number of branches, an $x = 0.7$ for g^x was chosen for PMMA-*g*-PMMA A and B. This choice yielded g factors corresponding to 2 and 7 branches, respectively. This agrees with the stoichiometrically determined values. The method used to determine branch frequency here does not appear to be appropriate for sample C—the most highly branched sample in the series.

In the literature, there is not agreement concerning the exponent recommended for different polymer architectures in eq 4. The difficulty encountered may be an indication of the sensitivity of the method to a match between the molecular weights of the linear and branched analogs. The g^x could be underestimated or overestimated due to this source of error.

SEC/DV. SEC/DV can be used to provide the average number of branches in graft polymers by using the intrinsic viscosities of both linear and branched polymers of the same chemical composition. One can take advantage of the fractionation capabilities of the SEC to compare intrinsic viscosities of the branched and linear analogues at the same elution (and hydrodynamic) volume. This then leads to a capability to calculate the branching frequency throughout the molecular weight distribution of the graft polymers. These results will be discussed below.

Branching Factors. As already discussed, one of the results obtained from SEC/DV is the intrinsic viscosity of a polymer solution calculated as a best fit over the entire MWD. Thus, the average g factor may also be calculated from these findings to give the average number of branches present in the graft polymers. The g^x quantities for the three comb PMMA's are given in Table IX for data taken from 30 to 45 °C. An average g^x (across the temperature range) was obtained and tabulated in the last column of the table. For PMMA-*g*-PMMA A, if $x = 0.5$, the calculated g is for combs with between two and three grafts. For PMMA-*g*-PMMA B, with $x = 0.7$ a branching index corresponding to combs with six branches results. These findings coincide with those obtained from capillary viscometry. Again, the results for PMMA-*g*-PMMA C were nebulous.

Branching Distribution. The branching distributions were obtained by using eq 13. The results shown in Table X for one experiment with PMMA-*g*-PMMA A at 30 °C are representative of observations for the three polymers in this study. The constant elution volume at which the calculations were valid was dictated by matching elution volumes found in the results from the linear PMMA. With elution volumes rounded off to the second decimal point, an agreement to within ±0.02 was considered to be sufficient. The first datum fell at about 40.26 mL and the last point at 43.79 mL. The intrinsic viscosities of the branched and linear polymers at the matching elution volumes were ratioed and were equal to $g^{1.69}$. The exponent 1.69 was equal to $1 + a$ as shown in eq 13 where "a" is the Mark–Houwink exponent of the linear PMMA used. A check on the sample chromatogram shown in Figure 6 reveals that a small portion of both the high and low molecular weight portion of the chromatogram was not included in the calculations. The fact that the whole chromatogram was not used does not detract from the purpose of determining the branching distribution—to give an idea of how the frequency of branching changed as the molecular weight varied across the distribution.

Table X
g^x Distribution of PMMA-*g*-PMMA A from SEC/DV(LALLS)

$V_{\mathrm{el\,(br)}}$, mL	$[\eta]$, dL/g	log M	$V_{\mathrm{el\,(lin)}}$, mL	$[\eta]$, dL/g	$g^{1.69\,a}$
40.26	0.688	5.431	40.25	1.143	0.424
40.34	0.672	5.412	40.36	1.116	0.425
40.68	0.608	5.338	40.68	1.037	0.406
41.02	0.545	5.263	41.00	0.965	0.381
41.10	0.530	5.245	41.11	0.941	0.379
41.35	0.486	5.189	41.33	0.897	0.355
41.44	0.472	5.170	41.44	0.875	0.352
41.52	0.458	5.152	41.54	0.854	0.349
41.77	0.421	5.096	41.76	0.814	0.328
41.86	0.409	5.077	41.87	0.794	0.326
42.19	0.369	5.002	42.19	0.739	0.309
42.28	0.360	4.984	42.30	0.721	0.309
42.53	0.334	4.928	42.52	0.687	0.296
42.61	0.326	4.909	42.62	0.670	0.296
42.86	0.300	4.853	42.84	0.638	0.279
42.95	0.292	4.835	42.95	0.623	0.278
43.28	0.263	4.760	43.27	0.579	0.264
43.37	0.256	4.742	43.38	0.565	0.263
43.62	0.237	4.686	43.60	0.539	0.250
43.70	0.231	4.667	43.70	0.526	0.249
43.79	0.225	4.649	43.81	0.514	0.248

[a] Value obtained by using eq 11 with $a = 0.69$.

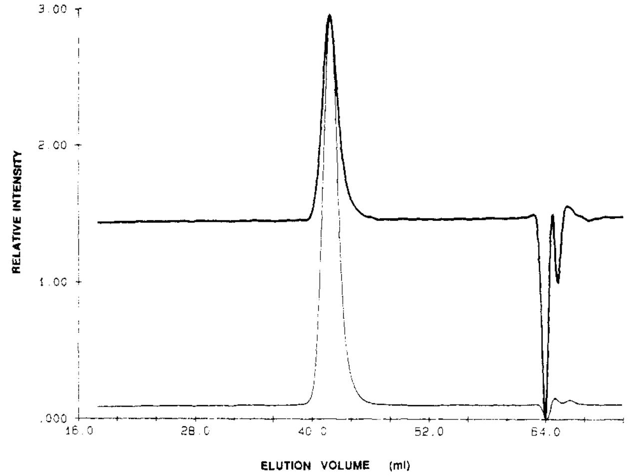

Figure 6. SEC dual chromatogram of PMMA-*g*-PMMA A; bold trace for DRI signal and fine trace for DV signal.

The distributions of branching for PMMA-*g*-PMMA A obtained from duplicate experiments at 30 °C are found in Figure 7. It is clear that, as the molecular weight

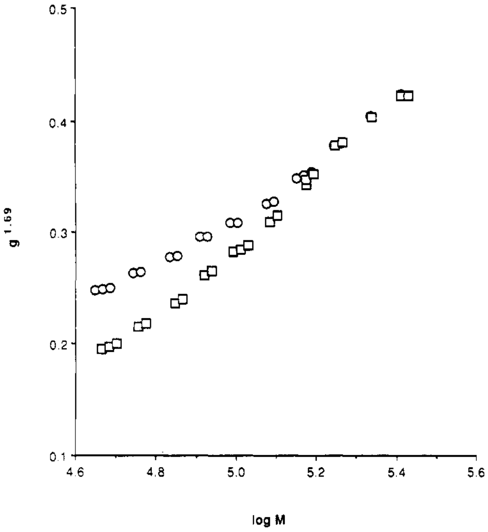

Figure 7. Branching distribution for PMMA-*g*-PMMA A from SEC/DV. Results shown are for duplicate experiments.

increased across the distribution, the branching decreased. This trend could be due to the mechanism of macromer addition to the backbone where the macromer kinetics differ from the monomer. This speculation will require further investigation. This same trend was observed for PMMA-*g*-PMMA B and C. The gaps in the plot are due to the fact that matches in the elution volumes of the linear and branched polymers were not always found. However, the trend was still clear.

Summary and Conclusions

In summary, it was shown that SEC/DV, which is based on the hydrodynamic volume fractionation assumption is an appropriate way to determine absolute molecular weights and molecular weight distributions for long-chain branched systems having comb architectures. The universal calibration curve was shown to be valid for graft homopolymers containing up to 40 mass % of long-chain branching. However, the multidetector setup appears to require more hardware and software refinements to eliminate errors caused by dead volume between detectors and axial dispersion, both of which led to the underestimation of molecular weights. With awareness of these problems, SEC/DV offers a favorable alternative to the more tedious SEC/LALLS.

The intrinsic viscosities obtained at each increment of the elution volume were used to calculate unperturbed chain dimensions with an accuracy that was found to depend on the sensitivity of both the DRI and DV detectors.

Other branching parameters such as the branching index and branching frequency may be obtained directly from data provided by SEC/DV. The accuracy of these characterizations was found to depend on both the software and hardware of the analyses. Moreover, branching theory advances are desirable in order to provide better foundations for experimental findings such as these reported.

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