

# Improved Accuracy and Precision in the Light-Scattering Characterization of Homo- and Copolymers in THF

D. HUNKELER,<sup>1</sup> T. SPYCHAJ,<sup>2</sup> S. ZHU<sup>3</sup>

<sup>1</sup> Laboratory of Polymers and Biomaterials, Swiss Federal Institute of Technology, CH-1015, Lausanne, Switzerland

<sup>2</sup> Polymer Institute, Technical University of Szczecin, ul. Pulaskiego 10, 70-322, Szczecin, Poland

<sup>3</sup> Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7

Received 31 October 1996; accepted 7 April 1997

**ABSTRACT:** A one-point method was developed for the estimation of weight-averaged molecular weights from light-scattering data. The method is based on the calculation of the second virial coefficient from theoretical predictions of the dependence of  $A_2$  on the molecular weight. The second virial coefficient is then regressed for a particular polymer–solvent combination from a series of preexisting measurements over a range of molecular weights. The one-point method is found to yield as accurate molecular weight estimates as obtained from a Debye plot using the conventional dilution technique. The variance in the estimation of the Rayleigh factor has also been found to be highly dependent on the measurement concentration. Therefore, the precision in the estimation of molecular weight can be improved by calculating molecular weights at or near the optimal concentration, which is itself molecular weight-dependent. The one-point method is demonstrated for poly(methyl methacrylate)s of various polydispersities in tetrahydrofuran. The molecular weight of polystyrene and polystyrene-*co*-acrylic acid were also estimated by the one-point method in THF. In the case of the polystyrene-*co*-acrylic acid, THF becomes a poorer solvent with increasing levels of acrylic acid in the copolymer, and the parameter ( $A_2M^{0.5}$ ) is found to vary with the copolymer composition, as is theoretically predicted. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1303–1316, 1997

**Key words:** light scattering; molecular weight characterization; second virial coefficient; one-point method; poly(methyl methacrylate); polystyrene; polystyrene-*co*-acrylic acid

## INTRODUCTION

In a previous article,<sup>1</sup> a one-point method was developed for the interpretation of light-scattering data. This algorithm, which can also be adopted to expedite data acquisition, was demonstrated for the characterization of polyacrylamides in saline solutions. It was shown that over

50% of the variance in light-scattering measurements is due to the estimation of the second virial coefficient from the dilution of a base sample. The remainder of the variance was accounted for in errors in a sample concentration, both in the preparation and purification of the dilute polymer solutions, slight imperfections in the optical alignment, and variations in the laser intensity. The one-point method estimates the molecular weight from a single concentration rather than from an extrapolation required for a Debye plot<sup>2,3</sup> or the double extrapolation characteristic of Zimm's method.<sup>4</sup> Due to the absence of Rayleigh factors

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Correspondence to: D. Hunkeler.

*Journal of Applied Polymer Science*, Vol. 66, 1303–1316 (1997)  
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from multiple concentrations, the second virial coefficient is calculated from preexisting data for a given polymer–solvent combination, which have regressed to yield a dependence of  $A_2$  on the weight-average molecular weight:

$$A_2 = \alpha M_w^\beta \quad (1)$$

The values of  $\alpha$  and  $\beta$  are available for several polymer–solvent systems, as is demonstrated in Table I. Therefore, given that the values of  $\alpha$  and  $\beta$  are established from the correlation of multiple sets of individual light-scattering measurements (often tens or hundreds), it is reasonable to expect that the accuracy in the estimate of the second virial coefficient is dramatically improved with the one-point method over the conventional dilution techniques (Debye plot). This has been experimentally observed.<sup>1</sup> More significantly, particularly for an analytical chemist, the precision in the estimate of the weight-average molecular weight increased over twofold.<sup>27</sup> The relationship between the second virial coefficient and the molecular weight is valid for linear polymers. For highly branched chains, the exponential dependence of  $A_2$  on the molecular weight increases. Strictly speaking, eq. (1) is valid for a uniform molecular weight sample. However, polymolecularity corrections have a minor influence on the second virial coefficient. For example, polymers with the most probable distribution have a value of  $A_2$  only 7% larger than that of a monodisperse sample of the same composition.<sup>1</sup>

It was the aim of the present article to demonstrate the one-point method for common organic polymers (styrene, methyl methacrylate) as well as for a copolymer with commercial significance (polystyrene-*co*-acrylic acid). Since the polydispersity of the molecular weight distribution is known to influence the second virial coefficient, a series of poly(methyl methacrylate)s (PMMA)s were synthesized with PDIs between 1.43 and 8.07 in order to evaluate the applicability of the one-point method for highly heterodisperse polymers.

## Second Virial Coefficient

Flory and Orofino<sup>28</sup> showed that, for high molecular weight polymers in good solvents, the second virial coefficient, normalized with respect to the molecular weight and intrinsic viscosity, is a constant:

$$\frac{A_2 M}{[\eta]} = \text{constant} \quad (2)$$

Flory and Orofino found this constant to have a value of 150 (dimensionless), while other authors' estimates have fallen in the 110–160 range,<sup>29–31</sup> if the intrinsic viscosity is expressed in units of dL/g. One would expect the ratio  $A_2 M/[\eta]$  to be dependent on the copolymer composition since the interaction potential of the various comonomer units will differ in a given solvent. If one combines eq. (2) with the Mark–Houwink–Sakurada equation, then the second virial coefficient can be expressed as

$$A_2 = CM^{\alpha-1} \quad (3)$$

This predicts that the dependence of the second virial coefficient on the molecular weight is related to the Mark–Houwink–Sakurada (MHS) exponent, as was demonstrated for a variety of polymer–solvent systems.<sup>1</sup> In a good solvent, the MHS exponent will be 0.7–0.8, and, hence, “ $\beta$ ” will have a value between –0.2 and –0.3, as is virtually universally observed (Table I). For systems in a theta solvent, the values of “ $a$ ” and “ $\beta$ ” revert to 0.5 and –0.5, respectively, as will be demonstrated later in this article.

## Light-scattering Theory

For optically isotropic polymers, the relationship between the Rayleigh factor and the weight-average molecular weight is given by<sup>4</sup>

$$\frac{Kc}{R_\theta} = \frac{1}{M_w P(\theta)} + 2A_2 c + 3A_3 c^2 + \dots \quad (4)$$

where  $M_w$  is the weight-averaged molecular weight;  $c$ , the mass concentration;  $A_3$ , the third virial coefficient;  $R_\theta$ , the excess Rayleigh factor;  $P(\theta)$ , the particle-scattering function; and  $K$ , an optical constant defined, for monochromatic polarized light, as<sup>2</sup>

$$K = \frac{2\pi^2 n^2}{\lambda^4 N_a} \left( \frac{dn}{dc} \right)^2 (1 + \cos^2 \theta) \quad (5)$$

where  $n$  is the refractive index of the solvent at the incident wavelength ( $\lambda$ );  $N_a$ , Avogadro's number;  $dn/dc$ , the specific refractive index increment, and  $\theta$ , the measurement angle.

From wide-angle measurements, or for scattering bodies larger than  $\lambda/20$ , the particle function is required. For a flexible coil,  $P(\theta)$  can be expressed, at low angles, as

$$P(\theta) = 1 + \frac{16\pi^2}{3\lambda^2} \langle S^2 \rangle \sin^2(\theta/2) \quad (6)$$

where  $\langle S^2 \rangle$  is the mean-square radius of gyration. Clearly, the particle-scattering function reduces to unity at low angles.

### One-point Method

By combining eqs. (1) and (4) and recognizing that interactions involving more than two polymers coils (third and higher virial coefficients) are extremely unlikely in dilute solutions, one obtains an expression which permits the estimation of the weight-average molecular weight from a single concentration:

$$\frac{Kc_0}{R_\theta} = \frac{1}{M_w P(\theta)} + 2\alpha M_w^\beta c_0 \quad (7)$$

In a previous publication,<sup>1</sup> it was demonstrated that the variance in the measurement of the Rayleigh factor was highly dependent on the polymer concentration. This optima was also observed to be molecular weight-dependent. Therefore, the recommended procedure for the one-point method is to repeat the measurement of the Rayleigh factor only at the concentration where the variance in the measurement is lowest ( $c_0$ ) and to regress the weight-average molecular weight from eq. (7).

Interestingly, it was shown that the precision in the estimate of the weight-average molecular weight was improved over the dilution technique even if the calculation was not performed at the optimal concentration.<sup>28</sup> This is due to the fact that the estimation of parameters from a Debye plot [eq. (4)] does not satisfy one of the principal requirements of linear regression: constant variance of all points. Therefore, data in which one has high confidence (low variance) are averaged with low certainty estimates (high variance). To accommodate nonconstant variances, weighted least-squares analyses are usually advocated. For light scattering, this would involve replicate measurements at all concentrations and a molecular weight regression where each concentration is weighted according to the reciprocal of its variance. While this could certainly be facilitated with

the data acquisition software supplied with current photometers, it is not a common practice. As a practical approximation of the weighted least-squares analysis, we have, therefore, proposed to place complete weighting on the concentration where there is the highest confidence.<sup>27</sup> This has been shown to be a reasonable approximation, given the strong dependence of the variance in the measurement of the Rayleigh factor as a function of the polymer solution concentration.<sup>1</sup>

Our previous publications related to the one-point method were limited to water-soluble polymers.<sup>1,27</sup> In this article, the generality of the method will be established by analyzing data on organically soluble polymers such as polystyrene and PMMA as well as for commercial copolymers. For the latter, we selected polystyrene-*co*-acrylic acid, which is commonly applied as a coating in floor finishes.

## EXPERIMENTAL

### Light-scattering Characterization

Weight-average molecular weights and second virial coefficients were regressed from Debye plots obtained on a Chromatic KMX-6 low-angle laser light-scattering photometer. A cell length of 15 mm and a field stop of 0.2 were employed, with a corresponding average scattering angle of 4.8°. The refractive index increment of the solvent was determined using a Chromatix KMX-16 laser differential refractometer at 25°C. Both instruments were equipped with helium–neon lasers operating at a wavelength of 632.8 nm. For PMMA in tetrahydrofuran (THF), the  $dn/dc$  was measured to be 0.0842. For polystyrene in THF, the  $dn/dc$  was 0.1905.

Polymer solutions were clarified by filtration through 0.45  $\mu\text{m}$  cellulose–nitrate membranes (Millipore). A 0.22  $\mu\text{m}$  membrane of the same type was used for the clarification of the degassed THF.

Polystyrene standards were purchased from TSK (Tosoh Corp., Tokyo, Japan). Additionally, commercial samples of polystyrene were supplied by Dow Chemicals (Midland, MI, U.S.A.) and Polysar (Sarnia, Ontario, Canada).

### Synthesis of PMMA

The PMMAs investigated herein were synthesized specifically for this study. As the data have not been previously published, a full accounting

**Table I** Values of the Parameters  $\alpha$  and  $\beta$  in the Expression  $A_2 = \alpha M^\beta$  for Several Polymer–Solvent Systems

Polymer	Solvent	Temperature (°C)	$\alpha \cdot 10^3$ (mL/g)	$\beta$ (dimensionless)	Reference
Acrylamide	0.02M Na <sub>2</sub> SO <sub>4</sub>	22	8.18	-0.211	1
Acrylonitrile	Dimethylformamide	20	49.4	-0.24	5
Acrylonitrile	Dimethylformamide	20	24.3	-0.22	6
Acrylonitrile	Dimethylformamide	35	27.4	-0.24	7
1-Butene	Toluene	45	—	-0.25 → -0.32	8
Isobutene	Benzene	40	0.75	-0.12	9
Isobutene	Cyclohexane	25	—	-0.264	10
Isobutene	<i>n</i> -Heptane	—	14.9	-0.28	11
Isobutene	Isooctane	25	—	-0.394	10
<i>m</i> -Chlorostyrene	Butanone	30	1.54	-0.17	12
<i>m</i> -Chlorostyrene	Toluene	35	26.5	-0.33	12
<i>o</i> -Chlorostyrene	Toluene	—	5.22	-0.23	13
Dimethylsiloxane	Toluene	25	—	-0.256	10
Ethylhexylacrylate	Toluene	37	4.5	-0.25	14
Ethylene	1,2-Dichloro-benzene	—	6.3	-0.15	15
Ethylene	<i>p</i> -Xylene	105	26.2	-0.24	16
Ethylene oxide	Methanol	—	37.9	-0.32	1
<i>p</i> -Methoxystyrene	Butanone	25	—	-0.20	17
<i>p</i> -Methoxystyrene	Toluene	30	—	-0.40	17
MMA	Acetone	—	3.51	-0.221	1
MMA	Butyl acrylate	—	—	-0.34	1
MMA	Dioxane	—	—	-0.32	1
MMA	Nitroethane	—	0.67	-0.257	18
MMA	THF	—	6.62	-0.242	1
MMA	THF	22	8.15	-0.246	This work
MMA (high PDI)	THF	22	5.49	-0.212	This work
<i>o</i> -Methylstyrene	Toluene	30	38.9	-0.38	19
Polyester <sup>a</sup>	3,5-Bis(trifluoromethyl)phenol	65	—	-0.158	10
Propylene (isotactic)	1-Chloronaphthalene	125	4.3	-0.16	20
Propylene (isotactic)	1-Chloronaphthalene	135	16.5	-0.27	20
Propylene (atactic)	Benzene	25	3.2	-0.20	20
Propylene (atactic)	Chlorohexane	25	20.0	-0.26	20
Styrene	Benzene	30	—	-0.26	10
Styrene	Butanone	—	2.73	-0.247	1
Styrene	Butanone	—	—	-0.22	21
Styrene	Dichloroethane	—	—	-0.298	21
Styrene	THF	22	7.09	-0.223	This work
Styrene	THF	30	—	-0.28	10
Styrene	Toluene	—	12.41	-0.269	1
Styrene	Toluene	—	—	-0.22	22
Styrene	Toluene	30	—	-0.264	10
Styrene (comb)	Toluene	30	—	-0.22	9
Styrene (comb)	Toluene	30	4.6	-0.22	23
Styrene (comb)	Toluene	30	2.1	-0.146	23

of the experimental conditions and characteristics of the polymers obtained is reported.

The MMA monomer was purchased from Fisher Scientific and was purified by washing with a 10 wt % aqueous KOH solution to remove

the inhibitor. It was subsequently washed with deionized water, dried successively with anhydrous sodium sulfate, and 4 Å molecular sieves and then distilled under reduced pressure while collecting the middle fraction (30°C).<sup>32</sup> Azobisiso-

**Table I** (Continued from the previous page)

Polymer	Solvent	Temperature (°C)	$\alpha \cdot 10^3$ (mL/g)	$\beta$ (dimensionless)	Reference
Styrene- <i>co</i> -acrylic acid	THF	22	—	-0.57	This work
Styrene (26.4 mol %)- <i>co</i> - <i>p</i> -Methoxystyrene	Toluene	25	2.0	-0.115	24
Styrene (53 mol %)- <i>co</i> - <i>p</i> -Methoxystyrene	Toluene	25	2.4	-0.135	24
Styrene (75.6 mol %)- <i>co</i> - <i>p</i> -Methoxystyrene	Toluene	25	2.3	-0.145	24
Vinylacetate	Trichlorobenzene	—	5.94	-0.33	25
Vinylbromide	THF	25	—	-0.36	10
<i>N</i> -Vinylcarbazole	Dioxane	—	4.26	-0.27	26

<sup>a</sup> *p*-Hydroxybenzoic acid (30 mol %)-*co*-6-hydroxy-2-naphthoic acid.

butyronitrile (AIBN) was purchased from Eastman Kodak and was recrystallized from methanol prior to use.

Bulk polymerizations of MMA were carried out in 3 mm o.d. Pyrex ampules. The samples were degassed using three freeze-thaw cycles using liquid nitrogen and a reduced pressure of  $10^{-4}$  mmHg prior to polymerization. The ampules were then filled with 99.999% N<sub>2</sub> to reduce the gas bubbling produced during the polymerization. Polymerizations were carried out by submersing the ampules in a temperature-controlled oil bath (HAAKE, Fisher Scientific) for predetermined periods. Temperature control was always to within  $\pm 0.1^\circ\text{C}$ . Upon removing the ampules, the reaction was quenched in liquid nitrogen. The conversion of monomer to polymer was verified by gravimetry.<sup>32</sup>

PMMA were prepared through nonisothermal polymerizations so as to investigate the utility of the one-point method for highly polydisperse samples. A glass ampule was withdrawn from the oil bath after a predetermined time, prior to reaching complete conversion, and then immersed in the same bath at a different temperature. We generally investigated steps from 50–80, 50–90, 70–90, and 80–90°C or vice versa.<sup>33</sup> Table II lists the properties of the PMMA synthesized herein.

#### Synthesis of Polystyrene-*co*-Acrylic Acid

All polymer samples were synthesized via a bulk free-radical polymerization in either a 0.4 or 1.4 L

continuous stirred tank reactor. Technical-grade monomers were used as received. Styrene was purchased from Aldrich Chemical Co. (Milwaukee, WI) while glacial acrylic acid was obtained from Rohm and Haas Canada Inc. (Toronto, Ontario, Canada). Polymerizations were carried out following the degassing and purging of the monomer feed with UHP-grade nitrogen. In all cases, the reaction temperature exceeded 200°C. Primary radicals were generated through the thermal initiation of the styrene monomer or through a combination of thermal and chemical initiation. *Tert*-butyl hydroperoxide (Aldrich Chemical Co., Milwaukee, WI) was employed as the chemical initiator. The experimental conditions<sup>34,35</sup> and additional synthetic details were described in preceding publications.<sup>35,36</sup> The GPC characterization of the polydispersity of these polystyrene-*co*-acrylic acids was previously reported.<sup>37</sup>

## RESULTS

Figures 1 and 2 illustrate the dependence of the second virial coefficient on the molecular weight for polystyrene and PMMA, respectively. Both polymers were characterized in THF. The second virial coefficient on molecular weight scales to the  $-0.223$  power for polystyrene and the  $-0.246$  power for PMMA. These agree reasonably well with the literature values in Table I. However, the primary significance of data such as in Figures 1 and 2 is to illustrate that, while the second virial coefficient

**Table II** Properties of the PMMAs Synthesized Herein

Temperature Profile (°C)	Initiator Concentration (wt %)	Reaction Time (min)	Conversion (%)	Polydispersity
60	0.1	100	14.25	2.12
60	0.1	180	36.67	1.77
60	0.1	201	51.77	1.80
60	0.1	220	79.50	1.74
60	0.1	260	86.74	1.81
60	0.5	30	17.70	1.72
60	0.5	80	28.18	1.90
60	0.5	100	32.78	1.79
60	0.5	135	87.92	2.67
60	0.5	201	89.90	3.38
80	0.3	20.05	23.13	1.60
80	0.3	32.5	44.92	1.79
80	0.3	37.5	63.81	2.87
80	0.5	10	13.95	1.96
80	0.5	27.5	67.40	2.80
80	0.5	40	94.87	2.61
50–80	0.5	150	20.17	2.01
50–80	0.5	185	29.82	2.01
50–80	0.5	220	60.72	2.60
50–80	0.5	225	57.92	2.67
50–80	0.5	227.5	83.57	3.03
50–80	0.5	237.5	93.98	2.94
<b>50–70–90</b>	0.3	240	28.32	2.34
<b>50–70–90</b>	0.3	255	31.31	2.10
<b>50–70–90</b>	0.3	270	48.16	1.70
<b>50–70–90</b>	0.3	275	71.80	2.33
<b>50–70–90</b>	0.3	320	94.58	1.86
80–90	0.3	10	10.53	1.93
80–90	0.3	20	23.12	1.71
80–90	0.3	30	41.15	2.47
80–90	0.3	33	67.44	3.71
80–90	0.3	36	89.38	2.27
80–50	0.3	15	13.47	1.78
80–50	0.3	32	31.34	1.69
80–50	0.3	70	42.31	8.07
80–50	0.3	90	53.64	5.90
80–50	0.3	110	75.66	6.26
80–50	0.3	300	86.75	6.06
90–80	0.5	6	19.76	1.69
90–80	0.5	10	28.00	1.50
90–80	0.5	15	35.97	1.66
90–80	0.5	20	45.72	1.98

estimates are collectively reasonable, individual data are quite spurious. This is evident in the vertical deviation from the regressed lines in Figures 1 or 2. Indeed, a preceding publication has

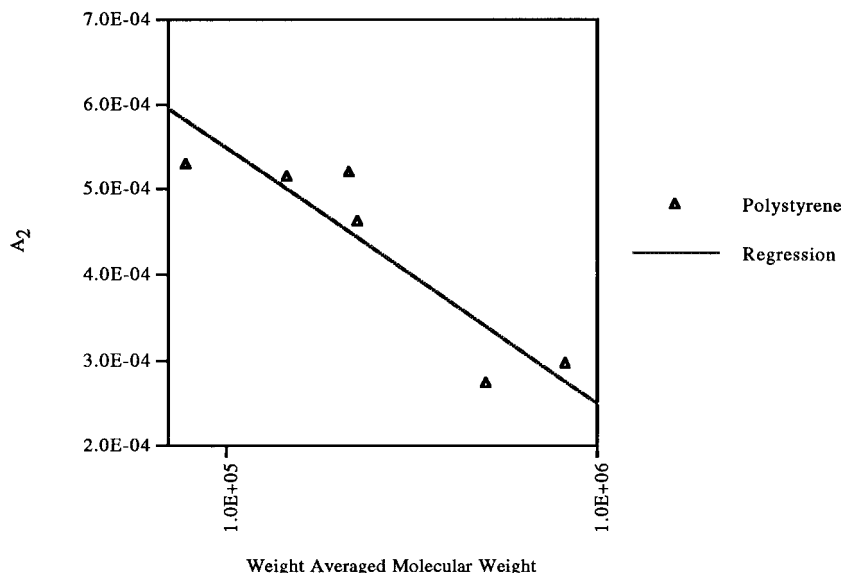
shown that the error in molecular weight predictions can be as high as 25% using measurements of  $A_2$  from a dilution technique, even for moderate molecular weight samples.<sup>27</sup> The irreproducibility

**Table II** (Continued from the previous page)

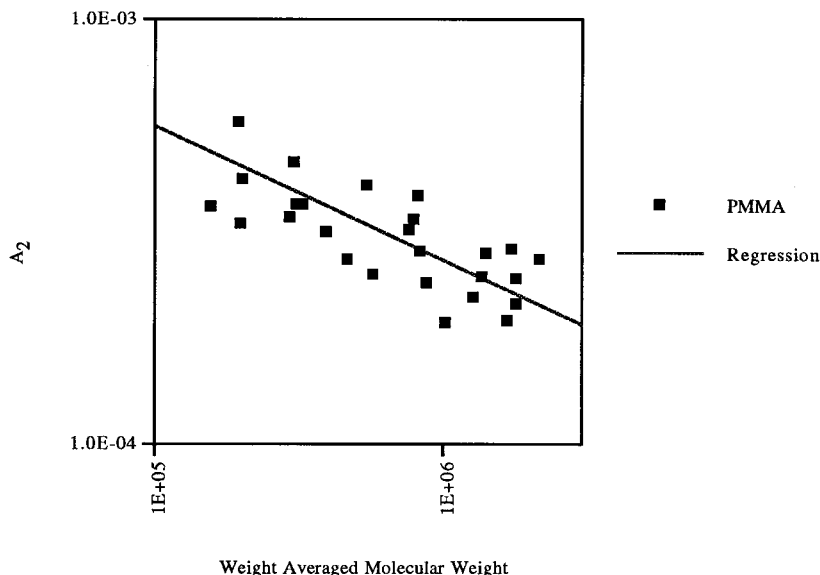
Temperature Profile (°C)	Initiator Concentration (wt %)	Reaction Time (min)	Conversion (%)	Polydispersity
90-70	0.5	8	16.81	1.58
90-70	0.5	12	27.40	1.59
90-70	0.5	19	39.78	1.43
90-70	0.5	28	59.71	2.29
90-70	0.5	43	83.24	—
90-70	0.5	290	92.18	—
<b>90-70-50</b>	0.5	5	11.77	1.53
<b>90-70-50</b>	0.5	13	30.23	1.63
90- <b>70</b> -50	0.5	25	57.19	4.68
90-70- <b>50</b>	0.5	60	78.42	4.59
90-70- <b>50</b>	0.5	180	83.42	4.46

in the estimation of dilute solution properties such as second virial coefficients and intrinsic viscosities from dilution techniques has motivated the development of this and other<sup>38</sup> one-parameter methods. Figure 3 plots the  $A_2$ - $M_w$  dependence for PMMA synthesized under nonisothermal conditions. For these PMMAs, which have a larger range of polydispersities, the scatter in the measurement of the second virial coefficient is larger than for the samples with PDIs close to that of the most probable distribution (Fig. 2), as would be predicted theoretically.

Figure 4 presents a plot of the second virial coefficient as a function of molecular weight for a series of polystyrene-co-acrylic acids, characterized in THF, with compositions varying from 0 to 100 mol % styrene. Interestingly, the data fall on a single line with moderate scatter. The second virial coefficient scales with the molecular weight to the  $-0.57$  power. This value is reasonable given that THF is a poor solvent for the styrene-acrylic acid copolymers, particularly those rich in acrylic acid. Therefore, one would predict an MHS exponent of 0.5 and a corresponding inverse square-



**Figure 1** Second virial coefficient as a function of the weight-average molecular weight for a series of polystyrene measured in THF. The polydispersities of the samples ranged from 1.04 to approximately 2.5.

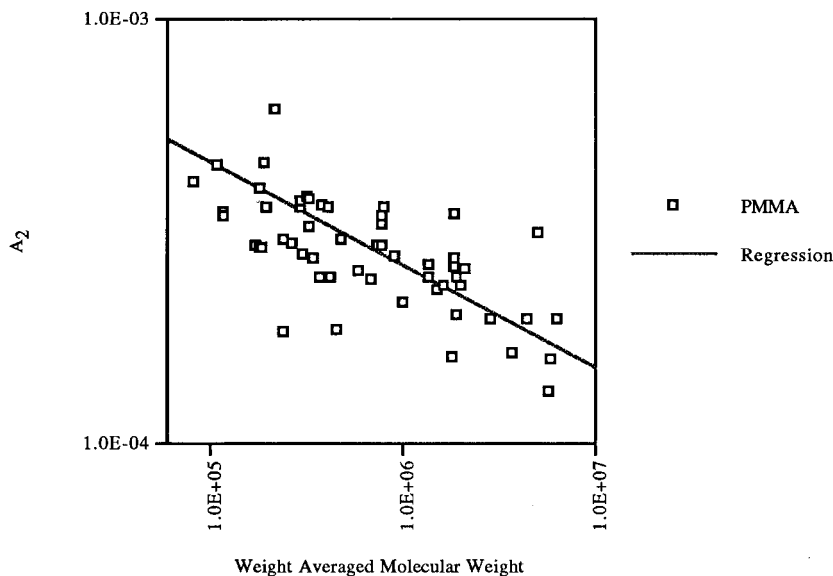


**Figure 2** Second virial coefficient as a function of the weight-average molecular weight for a series of isothermally synthesized PMMAs with polydispersities between 1.53 and 4.68. All polymer samples were dissolved in THF.

root dependence of  $A_2$  on  $M_w$ . The observed  $-0.57$  power dependence is within the experimental errors of this expected value.

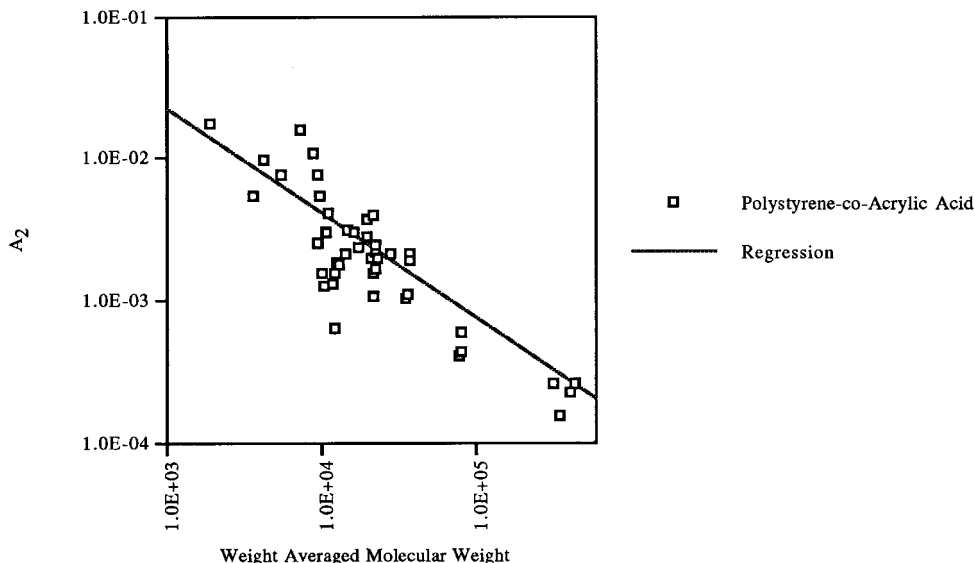
Figure 5 presents a plot of the normalized second virial coefficient ( $A_2M/[\eta]$ ) as a function of the copolymer composition. For this plot, the in-

trinsic viscosity of the polystyrene-*co*-acrylic acid was represented by its MHS equation ( $[\eta] \sim M^{0.5}$ ). As expected, the normalized second virial coefficient ( $A_2M^{0.5}$ ) is a function of the copolymer composition, with a moderately curvilinear dependence observed. A previous dilute solution charac-



**Figure 3** Second virial coefficient as a function of the weight-average molecular weight for a series of PMMAs, synthesized under nonisothermal conditions, with polydispersities between 1.43 and 8.07. All polymer samples were dissolved in THF.





**Figure 4** Second virial coefficient as a function of the weight-average molecular weight for a series of polystyrene-co-acrylic acids. All polymer samples were dissolved in THF.

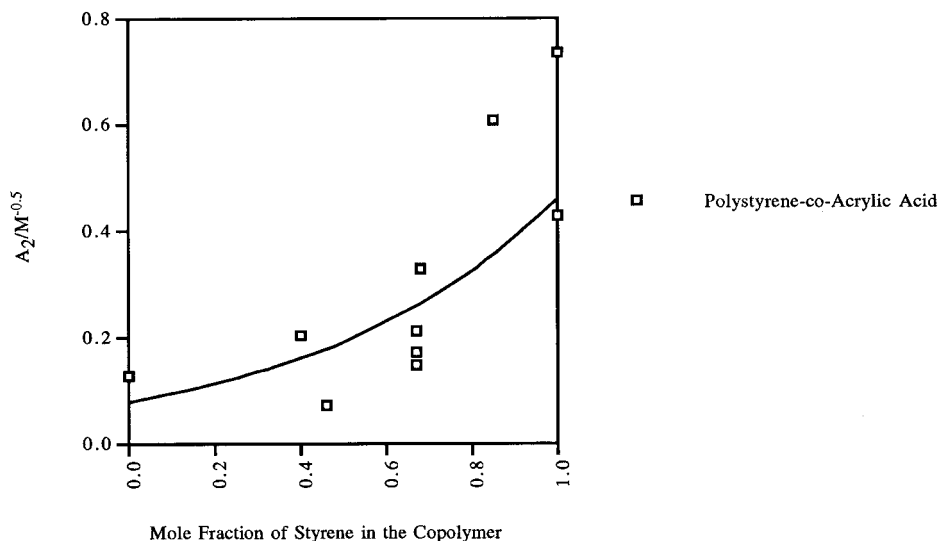
terization of acrylic acid copolymers also found the solvency to be highly sensitive to the mol fraction of acrylic acid groups.<sup>39,40</sup>

**DISCUSSION**

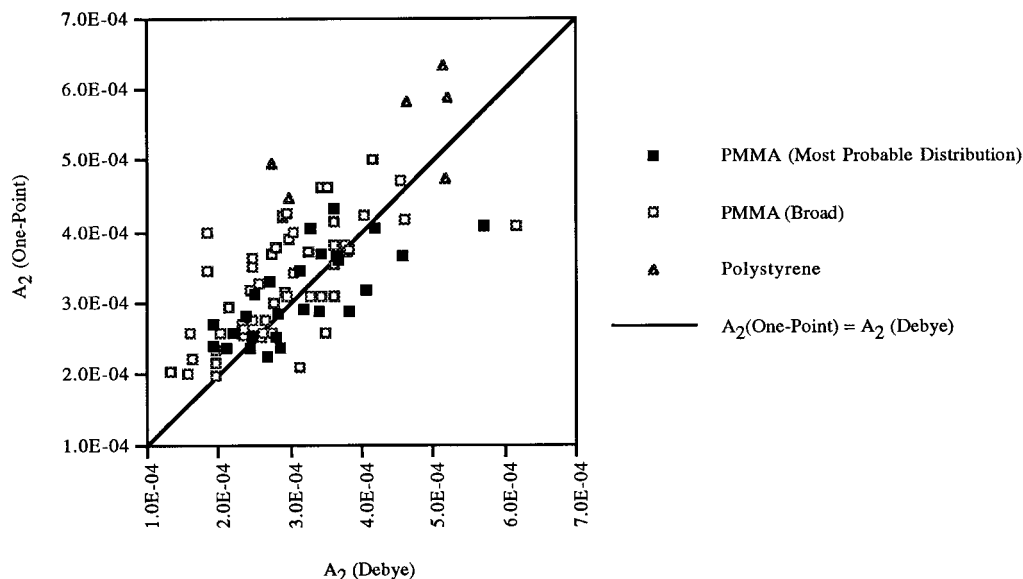
**Obtaining Precise Estimates of  $A_2$ : Measurement vs. Prediction**

Figure 6 shows a plot of the estimated second virial coefficient obtained from the scaling law ( $A_2$

$= \alpha M_w^\beta$ ) compared with those measured from a Debye plot. Clearly, the physical prediction of  $A_2$  is consistent with the data obtained from the experimental dilution measurements. The accuracy of the dilution technique is not in question. Indeed, light scattering is, along with an analytical ultracentrifuge, the standard method for the characterization of polymer standards. However, as the data in Figures 1–4 demonstrate, while the accuracy of the Debye and Zimm plots may



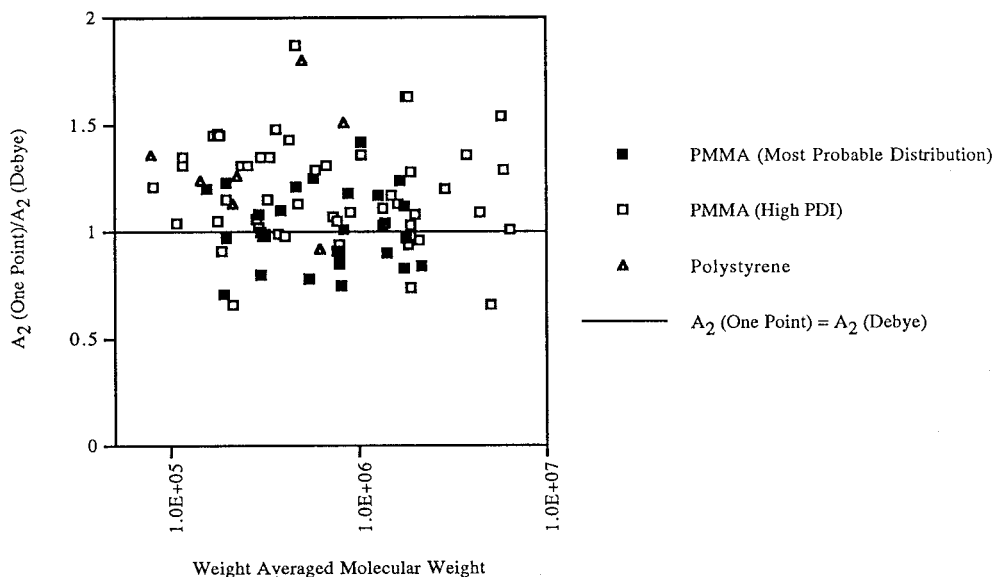
**Figure 5** Plot of the normalized second virial coefficient ( $A_2M/[\eta]$ ) as a function of the copolymer composition for polystyrene-co-acrylic acid in THF. The intrinsic viscosity in this theta solvent is proportional to the molecular weight to the 0.5 power.



**Figure 6** The estimated second virial coefficient obtained from the scaling law ( $A_2 = \alpha M_w^\beta$ ) compared with those experimentally measured from a Debye plot. All measurements were made in THF at room temperature.

be satisfactory, the precision ( $\pm 10\%$  under optimal conditions) could be improved upon. It is for this reason that the one-point method will be further evaluated herein. Figure 7 plots the ratio of the second virial coefficient estimated by the one-point method relative to that measured

experimentally with a Debye plot as a function of the polymer molecular weight. The one-point method for the PMMAs with the most probable distribution is essentially equal (2% larger) to that calculated from a Debye plot. However, when  $A_2$  for very broad MMAs is regressed from



**Figure 7** The ratio of the second virial coefficient regressed from the One-point Method relative to that measured from the dilution procedure (Debye plot) as a function of the polymer molecular weight.

the one-point method, the second virial coefficient is overpredicted, on average by 26%, compared to that measured from the dilution technique. These polydispersity-related effects are normal and can be expected according to theoretical treatments.<sup>1</sup>

It is important to note that the one-point method is not advocated as a tool to reduce the data acquisition. While it can be used in a highly precise manner for such purposes,<sup>1</sup> it is the authors' belief that the primary utility of the one-point method is in the verification of the calculations from the Debye or Zimm plots. Indeed, a previous publication showed<sup>27</sup> that the one-point method is less sensitive to errors in sample preparation and measurement, and, therefore, disagreement between calculated molecular weights from the one-point method and the dilution technique is an excellent metric to alert the experimentalist to potential errors in the measurement or sample preparation.

### Optimal Concentration for Light-scattering Measurements and Calculations

Equation (7) provides the basis for the calculation of the weight-average molecular weight from the measurement of the Rayleigh factor at a given concentration. The estimate of  $M_w$  requires an iterative solution of eq. (7), utilizing the values of  $\alpha$  and  $\beta$  for the specific polymer-solvent system at hand (Table I). In a previous application of the one-point method to water-soluble polymers,<sup>1,27</sup> the precision of the molecular weight estimate was found to be highly sensitive to the concentration used to calculate the molecular weight from eq. (7). In this article, we sought to investigate the effect of the measurement concentration on the accuracy of the molecular weight prediction. Table III presents molecular weight estimates for selected PMMAs as a function of the concentration used for the one-point regression. The accuracy, as measured by the difference in the predicted  $M_w$  by the one-point method compared to that obtained for the dilution technique, is also tabulated. The average deviation observed between the one-point method and the estimate from a Debye plot is 4.9%, with many samples within 2%. This is well within the random errors inherent in light-scattering measurements. Upon closer examination of Table III, one can observe that the agreement between the one-point method and the dilution technique is quite good

for all measured concentrations for most of the samples (#1, 3, 6, 7, 8). However, for other samples, such as #2, 4, and 5, the precision of the one-point method is reduced at higher concentrations. This was also observed for water-soluble polymers in a previous publication<sup>27</sup> and is caused by the measurement variance in the estimation of the Rayleigh factor, which is highly concentration-dependent.<sup>1</sup> Therefore, while the one-point method can be applied, with quite reasonable accuracy, at any concentration suitable for measurement of a Debye or Zimm plot, the accuracy can be improved when operating in a specific concentration range. We have previously referred to this as the "optimal" concentration, although it is, in effect, a range, as is demonstrated in Table IV. Figure 8 is a plot of the "optimal" concentration for the one-point method, as a function of the molecular weight of the polymer. As expected, the optimal concentration decreases as the molecular weight increases. Table IV summarizes the optimal concentrations for the measurement of the weight-average molecular weights of PMMAs in THF by light scattering. Insufficient data were collected for polystyrene homo- or copolymers to construct analogous tables for these systems.

### Example: Calculation of Molecular Weights Using the One-point Method

#### Calculation of Optical Constants

The refractive index of THF is 1.407, while the specific refractive index increment of PMMA in THF is 0.0842. Given that the wavelength of a helium-neon laser is 632.8 nm, the optical constant ( $K$ ) can be calculated, at low angles, from eq. (5) to yield a value of  $5.819 \times 10^{-8}$ .

#### Selection of an Optimal Concentration

If we are measuring a PMMA with an expected molecular weight of approximately 300,000 daltons, Table IV indicates that the optimal concentration for regression with the one-point method is 0.4 mg/mL.

#### Molecular Weight Regression

If, for the concentration selected in step 2, the average value of the excess Rayleigh factor was  $7.40 \times 10^{-6}$ , at a concentration of  $4.756 \times 10^{-4}$

**Table III Value and Accuracy of the Molecular Weight Estimates for Selected PMMAs in THF as a Function of the Concentration Used for the One-point Regression**

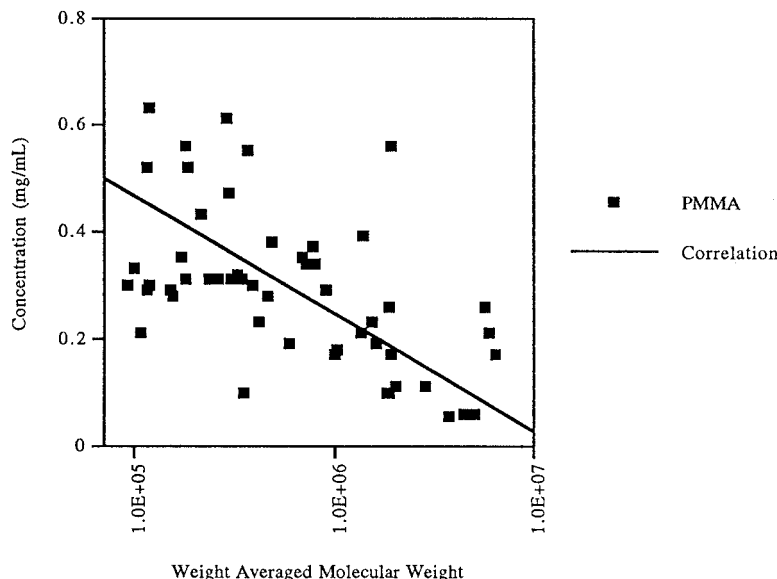
Polymer	Concentration Used for One-point Regression (mg/mL)	Weight-average Molecular Weight Estimated by the One-point Method (daltons) ( <b>A</b> )	Weight-average Molecular Weight Estimated from a Debye Plot (daltons) ( <b>B</b> )	Difference Between the One-point and Debye Estimates ( <b>A</b> - <b>A/B</b> ) 100%
1	0.1800	103,000	100,000	3.0
	0.2475	98,100		1.9
	0.3300	100,000		0.0
	0.5657	112,000		12.0
	1.9800	114,000		14.0
2	0.3073	181,000	179,000	1.1
	0.4225	177,000		1.1
	0.5633	187,000		4.5
	0.9657	195,000		8.9
	3.3800	209,000		16.8
3	0.1946	301,000	295,000	2.0
	0.2675	297,000		0.6
	0.4756	291,000		1.3
	0.7133	284,000		1.0
	2.1400	300,000		1.7
4	0.3727	772,000	784,000	1.5
	0.5125	758,000		3.3
	0.6833	755,000		3.7
	1.1714	752,000		4.1
	4.1000	679,000		13.3
5	0.1818	1,040,000	1,010,000	3.0
	0.2222	1,070,000		5.9
	0.5000	1,040,000		3.0
	0.6670	1,150,000		13.9
	2.0000	1,350,000		33.7
6	0.1836	1,890,000	1,860,000	1.6
	0.2563	1,830,000		1.6
	0.3727	1,790,000		3.8
	0.5857	1,900,000		2.2
	0.2050	1,810,000		2.7
7	0.0600	4,410,000	4,390,000	0.5
	0.1055	4,490,000		2.3
	0.2109	4,530,000		3.2
8	0.0962	6,440,000	6,370,000	1.1
	0.1683	6,340,000		0.5
	0.3367	6,450,000		1.3
Average deviation ( <b>1</b> - <b>A/B</b> ) 100%	N/A	N/A	N/A	4.9

g/mL, then eq. (7) reduces, for a low-angle measurement, to

$$\frac{5.89 \times 10^{-8}(4.756 \times 10^{-4})}{(7.40 \times 10^{-6})} = \frac{1}{M_w}$$

$$+ 2(8.15 \times 10^{-3})(4.756 \times 10^{-4})M_w^{-246} \quad (8)$$

From the preceding equation, the weight-averaged molecular weight can easily be determined, by iteration, to be 291,000, which agrees quite nicely with



**Figure 8** Plot of the “optimal” concentration for the one-point method as a function of the molecular weight for PMMAs in THF.

the value of 295,000 estimated from a Debye plot (Table III, Sample 3). All the data in Table III were regressed using the preceding algorithm.

## CONCLUSIONS

A one-point method was extended to organic polymers and copolymers and was found to improve the precision in molecular weight estimation. This involves calculating the value of the second virial coefficient based on a regression from aggregated measurements rather than using the dilution data of a single sample, as the Debye and Zimm methods do. The one-point method is adaptable to low-angle and wide-angle photometers. It is applicable only to systems where some preexisting light-scattering data are available so that the correlation of the dependence of the second virial coefficient on molecular weight can be established.

**Table IV** Optimal Concentration for Light-scattering Characterization and Regressions, for PMMA in THF, Using the One-point Method

Molecular Weight Range ( $10^3$ daltons)	Optimal Concentration (mg/mL)
100–500	$0.4 \pm 0.1$
500–2000	$0.2 \pm 0.1$
2000–7000	$0.15 \pm 0.1$

Nonetheless, while this is a restriction, there are 26 polymers presented herein for which sufficient data exist. Furthermore, the one-point method can be used as a supplemental computational procedure to compliment rather than to displace the conventional Zimm and Debye plots. It is also able to identify spurious data obtained using the conventional dilution technique.<sup>1</sup>

The dependence of the second virial coefficient on molecular weight was not found to significantly differ as the polydispersity of PMMA samples was increased, in agreement with theoretical predictions. The normalized second virial coefficient ( $A_2M/[\eta]$ ) was, however, observed to increase with the acrylic acid level in a polystyrene-*co*-acrylic acid.

We are particularly indebted to Lisa Morine for performing the light-scattering characterization of the polystyrene and polystyrene-*co*-acrylic acid samples. We would also like to express our thanks to Mary Ann Barban and Brian Thomas for their assistance in the data aggregation and regression, respectively, and to Christian Maier for his assistance in the copolymerizations.

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