Automated Batch Characterization of Polymer Solutions by Static Light Scattering and Viscometry

ROLAND STRELITZKI, WAYNE F. REED

Physics Department, Tulane University, New Orleans, Louisiana 70118, USA

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ABSTRACT: Using a programmable mixing pump, light scattering flow chamber, refractive index detector, and single capillary viscometer, the batch (unfractionated) characterization of polymers in solution has been automated. Three different schemes to produce polymer concentration gradients were used, and values for weight average mass M_w , root mean square radius of gyration $\langle S^2 \rangle^{1/2}$, second virial coefficient A_2 , and intrinsic viscosity $[\eta]$ were determined for a broad distribution sample of poly(vinyl pyrrolidone) (PVP) and a narrow fraction of poly(ethylene oxide) (PEO). High concentration experiments on the PVP also allowed determination of the third virial coefficient A_3 . The method has several advantages over traditional manual methods in terms of accuracy, sample preparation, and amount of labor required. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2359–2368, 1999

Key words: automated light scattering; automated viscometry; PVP [poly(vinyl pyr-rolidone)]; molecular weight; third virial coefficient

INTRODUCTION

Static light scattering (SLS) provides a useful means of characterizing the equilibrium properties of polymer and colloid solutions. The weight average molecular weight M_w , the scattering form factor P(q), and the second virial coefficient A_2 can be determined by making a series of SLS measurements at a number of angles on dilute polymer solutions at varying concentrations. Higher virial coefficients also can be determined at sufficiently high polymer concentrations.

Capillary viscometry provides a simple means of measuring the reduced viscosity η_r of a solution containing polymers and colloids. The intrinsic viscosity $[\eta]$ is the limit of η_r at zero concentration and shear rate. $[\eta]$ is related to the hydrodynamics of a polymer and provides a useful basic characterization.

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Currently, size exclusion chromatography (SEC), coupled to SLS, concentration, and viscosity detectors, provides a powerful means of determining the detailed properties of polymer populations and subpopulations in terms of molar mass distributions, dimensions, and viscosity.^{1,2} There are several contexts in which separation of polymer solutions by SEC is not possible or desirable, and for which so-called batch (or unfractionated) characterization is called for: (1) A_2 and higher virial coefficients are to be determined. SEC, because it operates at very low polymer concentration, does not allow such determinations. (2) The polymers are too large to be separated by the SEC columns and merely elute in the void volume. (3) The polymers might damage expensive SEC columns, or it is not known which columns can be used to separate the polymers. (4)Time-dependent processes are occurring in the polymer solution; that is, it is not in equilibrium. SEC is exclusively an equilibrium technique. Time-dependent static light scattering (TDSLS) has recently become an important technique in

Correspondence to: W. F. Reed.

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studying processes such as phase separation, gelation, aggregation, depolymerization, and polymerization. $^{3-9}$

This work combines elements of SEC and TDSLS methodologies to automate the batch characterization of polymer solutions. Traditional batch characterization involves a labor intensive sequence of preparing solutions of several concentrations, filtering or centrifuging them to remove dust and other scattering impurities, using several scattering cells, and manually gathering scattering data on each sample. The automated technique presented here (i) reduces sample preparation to one stock polymer concentration, (ii) determines the correct polymer concentration by using an online concentration detector, (iii) uses the same scattering chamber for all concentrations, (iv) provides many more concentration points for increased accuracy, (v) simultaneously provides information on polymer viscosity, (vi) uses less polymer sample, and (vii) is less labor intensive. As in SEC with a refractive index (RI) detector, the error in M_w in the current automated method is linear in the differential refractive increment dn/dc, whereas in traditional batch determinations without an RI detector, the error varies as (dn/dc).²

LIGHT SCATTERING

The well-known Zimm approximation¹⁰ allows determination of weight average molecular mass M_w , second and third virial coefficients A_2 and A_3 , respectively, and particle shape factor P(q). Zimm has shown that to second order in concentration c (g/cm³), the quantity Kc/I(q, c), where I(q, c) is the excess Rayleigh scattering ratio, can be approximated by

$$\frac{Kc}{I(q, c)} = \frac{1}{MP(q)} + 2A_2c + [3A_3Q(q) - 4A_2^2MP(q)(1 - P(q))]c^2 \quad (1)$$

This equation forms the basis of the well-known Zimm plot, which, at low concentrations and for $q^2 \langle S^2 \rangle \ll 1$, can be written for a polydisperse polymer population, as

$$\frac{Kc}{I(q,c)} = \frac{1}{M_w} \left(1 + \frac{q^2 \langle S^2 \rangle_z}{3} \right) + 2A_2 c \qquad (2)$$

which directly permits determination of M_w , A_2 , and the *z*-averaged mean-square radius of gyration $\langle S^2 \rangle_z$. *K* is an optical constant, given for vertically polarized incident light by

$$K = \frac{4\pi^2 n^2 (dn/dc)^2}{N_A \lambda^4} \tag{3}$$

where *n* is the solvent index of refraction, λ is the vacuum wavelength of the incident light, dn/dc is the differential refractive index for the polymer in the chosen solvent, and *q* is the usual scattering wavevector $q = (4\pi n/\lambda)\sin(\theta/2)$, where θ is the scattering angle.

Typically, A_2 has been determined by SLS measurements on a series of concentrations for a set of scattering angles. The precision of these measurements has usually been low because few concentration points are generally used. Measurements of A_3 for polymers are much rarer, due to the fact that, according to eq. (1), a quadratic fit in concentration must be performed on a limited number of concentration points.

VISCOSITY

Total solution viscosity is given by

$$\eta = \eta_s [1 + [\eta]c + k_p [\eta]^2 c^2]$$
(4)

where η_s is the pure solvent viscosity, $[\eta]$ is the intrinsic viscosity of the polymer, and k_p is a constant related to the hydrodynamic interactions between polymer chains, usually around 0.4 for neutral, coil polymers.¹¹ The intrinsic viscosity is the extrapolation to zero concentration and zero shear rate of the reduced viscosity η_r . η_r can be computed directly from the voltage of a single capillary viscometer (a differential pressure transducer) at every point *i*, without the need of an instrumental calibration factor, in terms of the viscometer baseline voltage V_b and the concentration at point *i*, c_i ,

$$\eta_{r,i} = \frac{V_i - V_b}{c_i V_b} \tag{5}$$

This is because the output of the viscometer is directly proportional to the pressure drop across the capillary of radius R and length L, which in turn is directly proportional to the total solution viscosity via Poisseuille's equation

$$\eta = \frac{\pi R^4 P}{8LQ} \tag{6}$$

where Q is the flow rate through the capillary (in cm³/s). The average shear rate in the capillary is

$$\dot{\gamma}_{\rm ave} = \frac{8Q}{3\pi R^3} \tag{7}$$

In the method presented here it is possible to extrapolate η_r to c = 0, although the average shear rate will remain finite at about 860 s⁻¹ for Q = 1 ml/min and R = 0.0254 cm. Fortunately, shear effects diminish with diminishing c. It is also noted that it is currently standard practice in SEC coupled to viscometric detectors to approximate $[\eta]$ by the values of η_r determined at finite (but low) c and shear rate.

METHODS AND MATERIALS

A programmable mixer (ISCO 2360) was used to form a time-dependent concentration gradient of polymer. A single stock solution of polymer and a reservoir of solvent was used. An ISCO 2350 SEC pump was used to withdraw the mixed solution from the mixing chamber of the mixer. A Waters 410 refractometer (RI) was used as the concentration detector. The concentration at time t was determined according to

$$c(t) = \frac{(V_{\rm RI}(t) - V_{\rm RI,base})CF}{(dn/dc)}$$
(8)

where CF is the refractometer calibration factor $(\Delta n/\text{Volt})$, and $V_{\text{RI,base}}$ is the baseline voltage of the refractometer when pure solvent is flowing.

The home-built capillary viscometer has been previously described.¹² The basic design of the home-built light scattering flow chamber has also been recently discussed and analyzed.¹³ In this work, up to seven angles were used (39°, 56°, 73°, 90°, 107°, 124°, and 141°) and the light source was a 25-mW vertically polarized, circularized diode laser operating at 677 nm. The optical fibers used for detection were removably inserted into the scattering chamber using threaded chucks.

The absolute Rayleigh scattering ratios were determined according to

$$I(t) = \frac{(V(t) - V_{\text{solvent}})}{(V_{\text{toluene}} - V_{\text{dark}})} F_{\text{(toluene, solvent)}} I_{\text{toluene}}$$
(9)

where

$$F(1, 2) = \frac{D + 2R \tan(\theta_{A,1})}{D + 2R \tan(\theta_{A,2})}g$$
 (10)

and g is a reflection loss given by

$$g = \frac{\left(1 - \left|\frac{n_1 - n_c}{n_1 + n_c}\right|^2\right)}{\left(1 - \left|\frac{n_2 - n_c}{n_2 + n_c}\right|^2\right)}$$
(11)

where n_c is the index of refraction of the fiber optic core material.

The detectors were first equilibrated by flowing pure solvent through them prior to the experiments. Calibration factors for the RI and SLS must be known prior to the experiments or determined afterwards. Up until this point, the procedure is the same as for equilibrating a typical SEC system without the columns. After equilibration of the detectors was achieved, the programmable mixer was programmed to provide the desired series of concentrations. These concentrations can take the form of a stepped ramp, a continuous ramp, or a higher resolution continuous ramp based on solution recirculation. Data are collected from the detectors via a 12 bit A/D board in the bus of a microcomputer. Software was written for data collection and analysis. Concentrations, reduced viscosity, and apparent M_w and $\langle S^2 \rangle_z$ can be quickly computed and displayed in real time.

If step ramps are used, then it is not necessary to know the dead volume between the detectors, because the plateau values of each can be used for each concentration step. If a continuous ramp is used, however, the dead volumes must be carefully determined. This problem is similar to that in SEC, and the consequences of erroneously determined dead volumes can introduce substantial errors in analysis.¹⁴ The difference with respect to SEC, however, is that in SEC, one has little control over the peak width of the material fractionated by the column, whereas in the current technique, one has a wide choice in making the gradient steep or gradual. The advantage of continuous ramps over step ramps is that less time and sample are required, and a continuum of



Figure 1 Raw data from TDSLS at one angle (90°), RI, and viscometer, using a stepped concentration gradient.

concentration points is obtained. The interdetector dead volumes were obtained by using an SEC injection value to inject 10 μ L of polymer solution into the flowing solvent train and measuring the time of arrival of the material at each detector.

The polymers used in this work were unfractionated samples of poly(vinyl pyrrolidone) (PVP) from Sigma Chemical Co. (St. Louis, MO) with a nominal mass of 360 kD ($M_z/M_w \sim 2.7$, $M_w/M_n \sim 2.5$, by SEC measurements in our laboratory), as well as a narrow molecular weight poly(ethylene oxide) (PEO) standard of 51.5 kD from American Polymer Standards Corp. (Mentor, OH). The dn/dc was 0.173 for PVP and 0.141 for PEO. The solvent used in all experiments was aqueous 0.1M NH₄NO₃ with 0.5 g/L NaN₃ sodium azide added as an antibacterial agent.

RESULTS AND DISCUSSION

Figure 1 shows raw data for the RI, viscometer, and a selected scattering angle (90°) for the PVP using a stepped concentration gradient with a flow rate of 0.5 mL/min. The lag time in reaching the plateau is due entirely to the mixing pump efficiency, because all the detectors respond instantaneously to the material flowing through them. The periodic fluctuations in the viscometer signal are due to the pulsations of the pump and can be smoothed by different techniques.

Figure 2 shows data obtained using a programmed, continuous gradient on the same PVP at a flow rate of 1 mL/min. Here, the concentration went up to 0.008 mg/mL, which is high



Figure 2 Raw data from TDSLS at one angle (90°), RI, and viscometer, using a continuous concentration gradient, up to a maximum concentration of 0.008 g/cm³. The maximum in the TDSLS is clearly seen, and can be used, via eq. (12) to compute A_3 . The results of A_3 computed this way and by direct fit are compared in Table I.

enough for A_3 effects to become pronounced. In fact, it can be seen that the scattering intensity reaches a maximum value, then decreases, as is expected for positive values of A_2 and A_3 .

Figure 3 shows raw data obtained for a recirculation experiment, in which the polymer at its initial maximum concentration was diluted by using the mixing pump (starting at about 5000 s), but the solution exiting from the detector stream was reintroduced into the sample reservoir, thus reducing the total amount of polymer used for the



Figure 3 Raw data from TDSLS at one angle (90°), RI, and viscometer, where a recirculation of the initial polymer stock solution is used. Recirculation starts at about 5000 s. No further solvent was added after 10,200 s.

experiment. The data shown are for PEO, but several similar recirculation experiments were also performed for PVP. This reduces the total amount of material needed for a determination by more than a factor of 10. Recirculation also permits reaching lower concentrations with a smoother gradient for the current mixer, because its mixing resolution between the two reservoirs is 1%.

Figure 4(a) shows the resulting Zimm-type plot resulting from stepped data, such as in Figure 1. Five angles from 56–124° were used for this determination. The fitting parameters are shown on the figure. Figure 4(b) shows the Zimm plot resulting from a continuous dilution gradient, such as from the low concentration portion of the data in Figure 2. Figure 5 shows the *Kc/I* versus *c* behavior at $\theta = 90^{\circ}$ for high concentration data on PVP, such as in Figure 2. The nonlinear behavior is clearly visible.

Figure 6 shows the results at $\theta = 90^{\circ}$ for the narrow fraction PEO. $q^2 \langle S^2 \rangle$ is so small that there is no angular dependence of the scattering from PEO. The measured value of 52,500 g/mol is in excellent agreement with the value of 51,500 given by the manufacturer for use of this polymer as a molecular weight standard.

Figure 7 shows the results of the viscometer analysis for an experiment reaching 0.008 g/cm³ for PVP. Values for M_w , A_2 , A_3 , $\langle S^2 \rangle^{1/2}$ [determined by eq. (1)], and $[\eta]$ and the parameter k_p [determined by eq. (4)] from many separate experiments for PVP are summarized in Table I. Also shown in Table I are the results of the narrow weight PEO for several independent runs. A_3 in Table I is also determined from the concentration c_m , at which the maximum in the scattering occurs (e.g., in Fig. 2), via the expression found by taking the derivative of I versus c

$$A_{3} = \frac{1}{3M_{w}c_{m}^{2}}$$
(12)

The values of A_3 determined in this way are in good agreement with those determined by directly fitting the whole Kc/I according to eq. (1).

Discussion of A_2 and A_3

For hard spheres of diameter d, the second and third virial coefficients A_2 and A_3 are given by

$$A_2 = \frac{2\pi d^3 N_A}{3M^2}$$
(13)

and

$$A_3 = \frac{5MA_2^2}{8}$$
(14)

The equivalent hard-sphere diameter for PVP from the above value is d = 487 Å, which gives a ratio of 0.624 for the effective hard radius to $\langle S^2 \rangle_z^{1/2}$. This value is typical for coil polymers.¹⁵

The computed value of A_3 , using the experimental value of A_2 from Table I for PVP, is 0.0495 cm^6 mol/g³, whereas the measured value is 0.0186. This leads to an overestimation according to the above formula for A_3 compared with the experimental value of 2.66. It has long been recognized¹⁶ that the hard sphere model overestimates the ratio of A_3/A_2^2 . Narrow-weight fractions of polystyrene in toluene, for example, consistently showed that A_3 , according to the above formula, overestimated the measured value by a factor of 1.88.¹⁷ Independent measurements¹⁸ vielded overestimation factors ranging from 1.89 to 4.06. Similar determinations for polyisobutylene in cyclohexane¹⁹ led to overestimation factors ranging from 1.35 to 2.28, and those for polystyrene in benzene²⁰ ranged from 1.27 to 2.51. The current overestimation value of 2.66 is in line with these values. A recent lattice-model Monte Carlo study²¹ concludes that the overestimate factor is universal for long chains and is equal to 2.08.

It is noted that water at room temperature is a good solvent for the PVP used, as judged by the large positive value of A_2 . Hence, the conditions here are far from the Θ point, where values of A_3 remain positive even as A_2 approaches zero.^{22,23} It is also interesting to point out that an earlier work reports measurements of A_3 for PVP when associated with negatively charged micelles of sodium dodecyl sulfate (SDS).24 This association gives a large electrostatic excluded volume to the PVP/SDS complex, making A_3 very large, >0.5cm⁶ mol/g³. The authors of that work were unable to measure A_3 of neutral PVP, however, because the resolution of their apparatus was insufficient. A recent work gives approximations for electrostatically based A₃ in polyelectrolytes.²⁵ Detailed measurements of the electrostatic enhancement of A_2 in PVP/SDS aggregates were recently made and analyzed via combined electrostatic persistence length and electrostatic-excluded volume theories.²⁶



Figure 4 (a) The Zimm plot resulting from a stepped gradient data, such as in Figure 1. (b) The Zimm plot resulting from the low concentration range of a continuous concentration gradient data, such as in Figure 2.



Figure 5 The Kc/I versus *c* data resulting from the full concentration range of data, such as in Figure 2.

Discussion of Intrinsic Viscosity

For a coil polymer at the Θ point, the intrinsic viscosity is given by

$$[\eta] = \frac{\Phi_v}{M} \left(\sqrt{6} \langle S^2 \rangle^{1/2} \right)^3 \tag{15}$$

where $\Phi_v = 2.56 \times 10^{23}$. Using the values from Table I yields $[\eta] = 345 \text{ cm}^3/\text{g}$, more than double



Figure 6 The Kc/I versus c data at $\theta = 90^{\circ}$ for narrow fraction PEO. The result is independent of angle for this low-mass polymer.



Figure 7 η_r versus *c* for a typical run. The intercept gives intrinsic viscosity $[\eta]$ and the slope gives k_p .

the measured value. Two problems are immediately apparent. First, by virtue of a nonzero A_2 , the PVP is not at the Θ point, and second, the $\langle S^2 \rangle^{1/2}$ from Table I is a *z*-averaged value, whereas *M* from Table I is a weight averaged value. Hence, for a polydisperse population, $[\eta]$ by eq. (15) will necessarily be an overestimate. Using the relation⁹ $\langle S^2 \rangle^{1/2}$ (Å) = $0.73M^{0.45}$ yields $\langle S^2 \rangle^{1/2} = 301$ Å for $M_w = 646,300$. This gives a value of $[\eta] = 159$ by eq. (15), which is in excellent agreement with the value of 154 in Table I.

The interaction factor for polymer coils k_p was measured to be 0.34, which is in excellent agreement with typical values for neutral, coil polymers.

Comments on Systematic and Random Errors

Systematic errors occur because of incorrect values of dn/dc and the refractometer calibration factor CF [eq. (7)], as well as stray light in the light scattering chamber. A method for assessing the stray light error was recently presented.¹³ Table II shows the effect on the different parameters from errors in dn/dc and CF.

The values for the parameters in Table I were obtained by unweighted least-squares fits to the scattering and viscosity data. The error bars appearing in Table I are based only on the average and standard deviation from multiple experiments. The random errors inherent in each experiment are due to the baseline fluctuations of each detector. Weighted fits could be performed according to standard procedures where the weight for

Sample	M_w (g/mol)	$\begin{array}{c} A_2 \\ (\mathrm{cm}^3 \ \mathrm{mol/g^2}) \end{array}$	$\begin{array}{c} A_3 \\ (\mathrm{cm}^6 \ \mathrm{mol/g^3}) \end{array}$	$\langle S^2 angle_z^{1/2}$ (Å)	$\left[\eta\right]_{w}$ (cm ³ /g)	k_p
PVP	$646,300 \pm 5\%^{a}$	$3.50 imes 10^{-4} \pm 7\%^{ m a}$	$0.0186 \pm 8\%^{ m b} \ 0.0181 \pm 5\%^{ m c}$	$390 \pm 6\%^{\mathrm{a}}$	$154 \pm 8\%^{\mathrm{a}}$	$0.34~\pm~3\%^{ m b}$
PEO	52,500 for dn/dc = 0.141	0.0022	_	Below detection limit	71	—

Table I Summary of Polymer Characterization Parameters for PVP and PEO

Error bars represent standard deviations over number of measurements stated, but do not include fitting errors or systematic experimental errors.

^a Average of ten measurements.

^b Average of three measurements.

^c From maximum in scattering versus concentration and eq. (12).

each light scattering point *i*, is $\sigma_{Kc/I,i}^2$, which is given by

$$\sigma_{Kc/I,i}^{2} = \left(\frac{K\sigma_{c}}{I_{i}}\right)^{2} + \left(\frac{Kc_{i}}{I_{i}}\right)^{2} \left(\frac{\sigma_{I}}{I_{i}}\right)^{2}$$
(16)

where σ_c and σ_I are the standard deviations in the concentration and intensity, which are directly proportional to the standard deviations in the voltage fluctuations of the refractometer and light scattering, $\sigma_{V,\text{LS}}$ and $\sigma_{V,\text{RI}}$, respectively. The weighting factors for each point Kc/I_i , are thus

$$\sigma_{Kc/I,i}^{2} = (Kc/I)_{i}^{2} \left[\frac{\sigma_{V,\text{LS}}^{2}}{(V_{\text{LS},i} - V_{\text{LS},b})^{2}} + \frac{\sigma_{V,\text{RI}}^{2}}{(V_{\text{RI},i} - V_{\text{RI},b})^{2}} \right]$$
(17)

In the least-squares minimization of χ^2 for an arbitrary polynomial fit in the concentration of the order N to a function y_i , these factors enter as²⁷

$$\chi^{2} = \sum_{i} \left[\frac{1}{\sigma_{i}^{2}} \left(y_{i} - \sum_{j=0}^{N} a_{j} c^{j} \right) \right]^{2}$$
(18)

Determination of $\sigma_{V,\text{LS}}$ and $\sigma_{V,\text{RI}}$ requires that a large enough sample for meaningful statistics be collected at fixed polymer concentrations. The stepped-gradient method in this work is ideal for

collecting such data, because multiple measurements are made at each concentration. In contrast, the continuous gradient method does not allow such statistics to be gathered, so that, as an approximation, $\sigma_{V,\text{LS}}$ and $\sigma_{V,\text{RI}}$ can be taken as the standard deviation of the baseline voltage fluctuations.

For viscosity, the weighting factors are given in terms of the viscometer and RI detector voltages by

$$\sigma_{\eta,i}^{2} = \eta_{r,i}^{2} \left[\left(\frac{\sigma_{v,\text{visc}}}{V_{\text{visc},i} - V_{\text{visc},b}} \right)^{2} + \left(\frac{\sigma_{V,\text{RI}}}{V_{\text{RI},i} - V_{\text{RI},b}} \right)^{2} \right]$$
(19)

The data were subjected to the random error analysis just outlined. The result was that voltage fluctuations contribute on the order of about 1% error to the final values for M_w , etc. In other words, random errors are basically insignificant compared to possible run-to-run stochastic errors, which are seen to range from 3 to 8% in Table I. Possible sources of run-to-run error include baseline drift in each detector, stray light in the light scattering detector, imperfect polymer/solvent mixing within the system (including dead-time effects), and sample heterogeneity for the inexpensive, highly polydisperse PVP.

Table II Effects on Polymer Parameters of RI Calibration and dn/dc

	M_w	$\langle S^2 angle_z$	A_2	A_3	$[\eta]$
dn/dc CF	$(dn/dc)^{-1}$ CF ⁻¹	No effect No effect	$(dn/dc)^2$ No effect	$(dn/dc)^3$ CF^{-1}	${dn/dc\over { m CF}^{-1}}$

CONCLUSIONS

Automated data acquisition for batch characterization of polymers in solution has been demonstrated by using coupled light-scattering, refractometric, and viscometric detectors. The method has yielded reproducible values of M_{w} , $\langle S^2 \rangle^{1/2}$, A_2 , A_3 , and $[\eta]$ for a broad mass distribution sample of PVP and a narrow mass fraction of PEO. Controllable dilution is provided by a programmable mixing pump operating in one of three modes, step gradients, continuous gradients, and recirculating continuous gradients. The latter method reduces the amount of material used by over an order of magnitude and provides smoother concentration gradients. The for method should be useful for increased accuracy, labor savings, and the potential for robotic automation of polymer solution characterization.

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