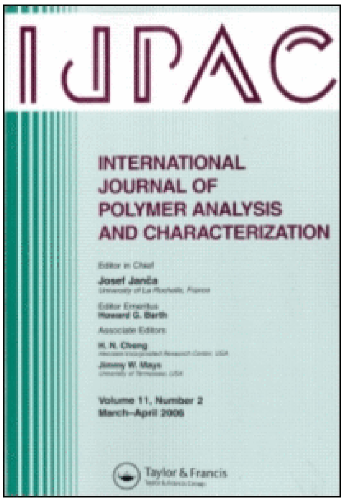

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Senak, Larry , Wu, Chi San and Smith, Terry E.(2001) 'A Simple Measurement of Polymer Specific Refractive Index Increments with an LED-Based Differential Refractometer', International Journal of Polymer Analysis and Characterization, 6: 5, 393 — 401

To link to this Article: DOI: 10.1080/10236660108033956

URL: http://dx.doi.org/10.1080/10236660108033956

Int. J. Polym. Anal. Charact.,
2001 Vol. 6, pp. 393–401
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A Simple Measurement of Polymer Specific Refractive Index Increments with an LED-Based Differential Refractometer

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(Received 9 June 1999; In final form 22 November 1999)

An inexpensive LED based differential refractometer has been used to obtain specific refractive index increment (*dn/dc*) values for six different polymers. The polymers examined by this technique were: dextran, poly(*N*-vinyl pyrrolidone), poly(maleic anhydride/methyl vinyl ether), poly(vinyl caprolactam), poly(methyl methacrylate), and polystyrene. Polymers were examined in solvents of polarities ranging from water to toluene. Differences between the *dn/dc* measurements of the LED refractometer and measurements made at 632.8 nm are within variability previously noted for such measurements, varying from 0–6%. The effect of such differences in *dn/dc* on M_w ranged from 0–6%.

Keywords: Specific refractive index increments; Light scattering; Size exclusion chromatography; Absolute molecular weight

INTRODUCTION

Absolute molecular weight characterization of polymers and biopolymers by light scattering has evolved into the technique of preference for most laboratories and a variety of instrumental configurations are currently commercially available for such studies. Typical instrumentation includes low-angle laser light scattering (LALLS), multi-angle laser light scattering (MALLS), and dual-angle light scattering, as well

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as light scattering combined with viscosity and refractive index detection. With the exception of the latter technique, the light scattering experiments may be performed either in a "batch mode" or combined with SEC fractionation.

The Rayleigh light scattering technique as practiced is, of course, based upon the light scattering equation presented by Zimm[1]

$$R_{\theta\to 0}/K^*c = MP(\theta) - 2A_2cM^2P^2(\theta) \qquad (1)$$

where R_θ is the Rayleigh ratio, c is polymer concentration, K^* is the optical constant, $P(\theta)$ is the scattering factor, A_2 is the second virial coefficient, and M is the molecular weight.

From the light scattering experiment, the absolute weight average molecular weight of the polymer, and root-mean-square radius, as well as the second virial coefficient (a measure of polymer solvent interaction) may be obtained.

Crucial to the success of this experiment is the evaluation of the K^* term in the Rayleigh equation, known as the polymer optical constant, which is defined by

$$K^* = 2\pi^2 n_0^2 (dn/dc)^2 \lambda_0^{-4} N_A^{-1} \qquad (2)$$

where: n_0 is the solvent refractive index at incident radiation, λ_0 is the wavelength of incident light (632.8 nm), N_A is Avogadro's number, and (dn/dc) is the differential refractive increment of the polymer at incident wavelength.

Of these parameters, only the value of the specific refractive index increment (srii) (dn/dc) is not always readily obtainable from the literature. For MW measurements where literature values of dn/dc were not available, workers have traditionally used values obtained off-line from a laser-based differential refractometer (typically using a wavelength of 632.8 nm), or values that have been back-calculated from SEC/light scattering software. By this method the DRI detector used in conjunction with the LS/DRI chromatography configuration must be carefully calibrated. This calculation (where software packages offer such an option) assumes complete sample recovery from the SEC column.[2]

There are two weaknesses with the latter approach. First, the light employed by the SEC/LS differential refractometer is either of a broad wavelength range or not a direct match for the laser light scattering detector, for instance a Waters 410 refractometer operating at 933 nm. It should be noted, however, that Cheng and Zhao[3] had previously reported *dn/dc* values in good agreement with the literature using values obtained with an HPLC refractive index detector by assuming that the dependence of *dn/dc* of all polymers upon wavelength chosen are nearly the same. Secondly, complete mass recovery from the SEC column is not always an assumption easily made. Several workers have utilized HPLC detectors "off-line" to evaluate *dn/dc* values for various polymers.[4, 5] The experimental technique for such analyses may often be laborious and time consuming.

Recently, a commercially available refractometer has been introduced that operates at 589 nm, based on an LED light source and using a dual photodiode as a sensor. This instrumentation was designed for the determination of percent solids of dilute polymer solutions, upto about 2%. This report demonstrates the applicability of this instrument as an off-line method in the determination of polymer *dn/dc* for a range of polymers and copolymers that include poly(methyl vinyl ether/maleic anhydride) (PMVE/MA), poly(vinyl caprolactam) (PVCa), poly(methyl methacrylate) (PMMA), poly(vinyl pyrrolidone) (PVP), dextran, and polystyrene in solvent systems that span polarity from aqueous mobile phases to toluene. This instrument is, as in the case of most commercial differential refractometers used in LC analysis, not specific to the wavelength of light employed by the light scattering detector.

EXPERIMENTAL

The solvents used in this study including water, methanol, stabilized tetrahydrofuran, and toluene were purchased from Aldrich Chemical Co. Inc. (Milwaukee, WI). Poly(vinyl pyrrolidone) (PVP K-30 molecular weight grade) has been characterized by the Fikentscher *K*-value, which is related to the relative viscosity at 25°C.[6] Poly(MVE/MA) and PVCa were obtained from International Specialty Products (Wayne, NJ). Poly(ethylene oxide), PMMA, and polystyrene were obtained from Polymer Laboratories (Amherst, MA). Dextran was purchased from Fluka Chemical Corp. (Ronkonkoma, NY). All chemicals were of the finest commercial grade and used without further purification. Molecular weight data obtained from manufacturer's values are listed in Table I.

An Atago DD-7 differential refractometer (Tokyo, Japan) was used for this study. This instrument operating at 589 nm is an LED based dual-photodiode refractometer capable of measuring refractive index upto 1.50 n_D and solution concentrations up to 2%. The unit is capable of differentiating a 0.001% solution concentration, ± 0.005% for an aqueous sucrose solution. This level of sensitivity is within the typical range SEC sample concentrations. The refractometer utilizes quartz sample and reference cells of 45° design with a 10-mm path length for each of the respective flow cells. The flow cell volume is 0.2–0.3 mL. The temperature range of operation is ambient to 35°C (The instrument is not capable of cooling the measurement cells). Samples are introduced to the dual flow cells and pushed out to a waste drainage tube with syringes.

With disposable plastic syringes, the solvent and solution were introduced into the respective sample and reference cells of the DRI detector, which is set in the "count mode", and operated at 35°C to ensure thermal equilibrium regardless of the laboratory ambient temperature. (While temperature may have either a positive or negative effect upon *dn*/*dc*, such effects are usually less than

TABLE I A comparison of specific refractive index increments (*dn*/*dc*) obtained with the Atago-DD-7 refractometer and with 632.8 nm laser-based instruments

Sample	M_w *m*/*g.values*	*Solvent*	*dn*/*dc* *mL*/*g* *Atago* *589 nm*	*dn*/*dc* (632.8 *nm*) *mL*/*g*	% *Difference*
PVP	6×10^4	water	0.176	0.178[a]	1%
dextran	7×10^4	water	0.149	0.147[c]	1%
P(MVE/MA)	2.7×10^6	pH 9 buffer	0.227	0.226[a]	1%
PVCa	2×10^4	H_2O/MeOH 1:1 containing 0.1 M $LiNO_3$	0.176	0.173[b]	2%
PMMA	6×10^4	THF	0.088	0.083[c]	6%
polystyrene	2×10^5	THF	0.185	0.185[c]	0%
polystyrene	2×10^5	toluene	0.103	0.110[c]	6%

[a] Measured with Chromatix KMX-16.
[b] Measured with Wyatt Optilab.
[c] Reported in Chromatix app. note KMX-16.[7]

5×10^{-4} mL/g/C°. For a polymer with a *dn*/*dc* of 0.150 mL/g, the maximum variation for such an effect would be about 3%.[7] For this reason, values of *dn*/*dc* obtained at 35°C can be used in ambient experiments with reasonable confidence. The literature values of the polymers in this report were all obtained at a wavelength of 632.8 nm and at 25°C, hence the refractometer is calibrated against the value of a PEO standard at the same wavelength and temperature). The instrument was then zeroed, a polymer solution from 0.1 to 1.0% made with the appropriate solvent was introduced into the cell, and its count response measured. (Measurement of *dn*/*dc* at several concentrations will assure the absence of concentration effects for a given sample.) This methodology does not possess one advantage of SEC on-line *dn*/*dc* measurements, namely, the size exclusion of low-molecular-weight impurities from the sample. For this reason, if such species are suspected to be present in a sample, it would be prudent to treat the sample by dialysis before determination of *dn*/*dc*.

The above method has been applied to a poly(ethylene oxide) standard with a *dn*/*dc* value of 0.132 mL/g ($\lambda_0 = 632.8$ nm, 25°C) obtained from Ref. [8]. Four concentrations were used, each of which was used to calculate an instrument constant from:

$$\text{inst. const.} = dn/dc\,(\text{sample conc.})/\#\text{counts} \tag{3}$$

The four concentrations of PEO standards used were 1.0116, 0.5027, 0.252 and 0.1008% (w/v) which resulted in instrument constant values of 1.32×10^{-6}, 1.31×10^{-6}, 1.33×10^{-6} and 1.32×10^{-6}, respectively. Calibration using the results of all the four concentrations of PEO resulted in an average instrument constant of 1.32×10^{-6}.

Utilizing the aforementioned instrument constant, PVP, poly(MVE/MA), PVCa, PMMA, and polystyrene were evaluated in the appropriate solvent systems. PVP was analyzed in aqueous 0.1 M $LiNO_3$. Poly (MVE/MA) was solublized in a pH 9, 0.1 M Tris buffer/0.2 M $LiNO_3$. PVCa was solublized in a mixed mobile phase of water/methanol 1/1 v/v made 0.1 M with $LiNO_3$. PMMA and polystyrene were studied in stabilized THF, and the polystyrene *dn*/*dc* was also examined in toluene.

Alternatively, several concentrations of a polymer with a known *dn*/*dc* may be evaluated against the same series of concentrations of an unknown polymer. Plotting the number of counts against concentration will generate two different slopes dependent upon the relative *dn/dc* of the respective polymers. Applying the ratio of these slopes to the value of the known *dn/dc* will allow evaluation of the unknown *dn/dc* value.

SEC/Light scattering experiments were performed with a Wyatt Technologies DAWN DSP MALLS detector (Santa Barbara, CA) coupled to a Waters 590 solvent delivery system and Waters 410 refractometer (Milford, MA). The column employed for the aqueous measurements was a Shodex linear OH-Pak SB80-MHQ column (Tokyo, Japan), while the column employed for organic solvents was a Polymer Laboratories PL-Gel Mixed C column (Amherst, MA). The software used for data analysis was Wyatt Technologies ASTRA version 4.2.

RESULTS AND DISCUSSION

The differential refractometry results are presented in Table I, along with the solvent employed, the sample MW, and a reference *dn/dc* value obtained from off-line *dn/dc* measurements at 632.8 nm.

These results have been essentially verified by the comparison of slopes of lines obtained by plotting refractometer counts against concentration for both the known PEO and the "unknown" samples to provide a ratio between the two. These plots are displayed in Figure 1. This method provided a *dn/dc* for PVP of 0.176 mL/g, in excellent agreement with the value obtained using the instrument constant method. This result is not surprising since the two calibration schemes are essentially the same. This plot also attests to the linear response of the detector over the concentration range studied.

The data presented in Table I generally display good agreement between *dn/dc* values obtained from the Atago instrument and those obtained from refractometry performed at 632.8 nm, with variation usually from 0 to 6%. The largest difference in these values was noted for the PMMA sample dissolved in THF and the polystyrene sample, which was dissolved in toluene. The larger differences in these samples are due primarily to their relatively low *dn/dc* values (where relatively small differences are magnified). Additionally, the difference in the

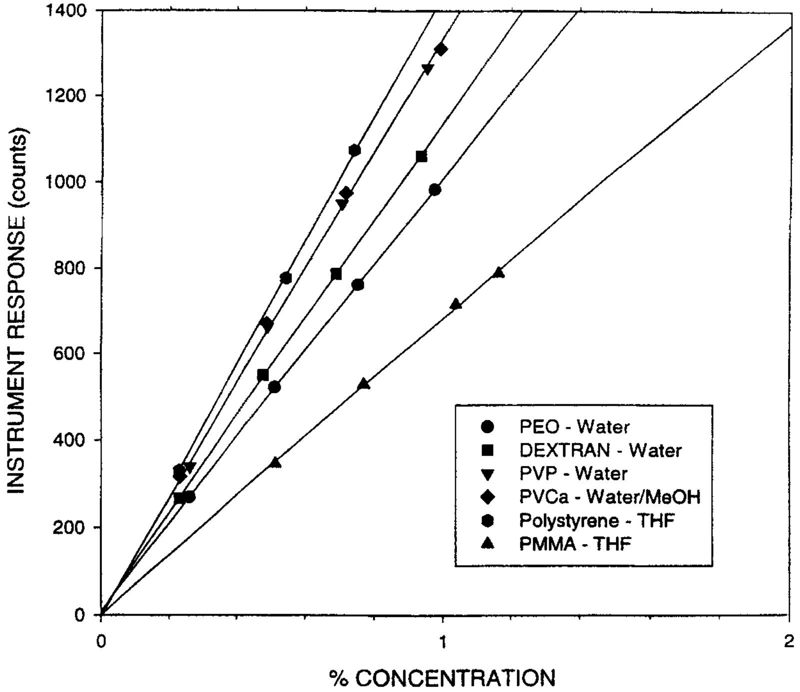

FIGURE 1 Instrument response as a function of concentration for a series of polymer-solvent systems at 35°C.

toluene–polystyrene solution is a result of toluene being a more difficult solvent with which to zero the Atago instrument, as toluene (1.491 n_D) is near the limit of the refractive index range specified for this instrument (1.50 n_D).

When considering wavelength dependence for the LED refractometer measurements, it is important to note that Cheng and Zhao[3] have shown that any small difference in *dn*/*dc* values are as likely to be attributable to experimental variation of wavelength dependence. It is well known that the *dn*/*dc* will increase as wavelength decreases. This behavior is reasonably well described by

$$(dn/d\rho_2)_{T,P,\lambda} = K_1 + K_2 1/\lambda^2 \tag{4}$$

where ρ_2 is the partial density of the polymer, n is the specific refractive index, λ is the wavelength, and both K_1 and K_2 are constants.[5]

TABLE II A comparison of M_w values obtained by SEC/MALLS using specific refractive index increments (*dn*/*dc*) obtained with the Atago DD-7 refractometer and with 632.8 nm laser-based instruments

Sample	*Mobile phase*	M_w *(Atago)*	M_w *(632.8 nm)*	*% Difference*
PVP K-30	aqueous 0.1M $LiNO_3$	4.98×10^4	4.92×10^4	1%
poly (MVE/MA)	pH9 buffer	2.71×10^6	2.75×10^6	1%
PVCap	H_2O/MeOH	1.85×10^4	1.88×10^4	2%
Polystyrene	THF	2×10^5	2×10^5	0%

Inspection of Eq. (4) as well as collected *dn*/*dc* data[8-10] indicates such differences in specific refractive increment for most polymers are generally small. More importantly, inspection of the same data indicates that given the equivalent solvent, these wavelength dependencies are nearly constant for most solutes.[3] A judicious choice of a calibration standard for the refractometer will then generally ensure the quality of subsequent measurements of various polymers.

As the *dn*/*dc* term is squared in the optical constant equation (Eq. (2)), it is a useful exercise to determine the effects of the *dn*/*dc* on the M_w values of the four polymers measured with the MALLS that were evaluated with both 632.8 nm *dn*/*dc* values, and the values obtained with the Atago DD-7 refractometer. These MW values are presented in Table II.

A comparison of data presented in Table II demonstrates good agreement in M_w values obtained by light scattering based upon the different *dn*/*dc* values found in Table I. These differentials in M_w range from 3 to 6% for the polymers studied. Such variation is typical of laboratory to laboratory differences in such molecular weight measurements regardless of the molecular weight characterization instrumentation employed.

CONCLUSIONS

Although the Atago DD-7 differential refractometer used in this study is designed specifically for the determination of percent solids for polymers at dilute concentrations, it represents a relatively inexpensive and rapid means of determining the *dn*/*dc* of polymers in solution, and may be used when a laser-based instrument is not available. With this instrumentation, the *dn/dc* may be measured by a simple manual calculation. No other elaborate instrumentation or accessories (such as an autosampler, fixed-injection loops, pumps, or special software) are needed for the measurement. To date, no greater than 6% discrepancy in the final M_w measurement has been observed resulting from differences between measurements made with this refractometer and those made at 632.8 nm.

Acknowledgments

The authors would like to gratefully acknowledge E. G. Malawer and R. Mininni for their gracious support of this work, and to International Specialty Products for permission to publish this work.

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