Incorporation of a differential refractometer into a laser light-scattering spectrometer

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A new differential refractometer, which mainly consists of a laser light source, a position-sensitive detector, and a temperature-controlled refractometer cuvette has recently been developed. In comparison with a conventional differential refractometer, it has a different optical design so that the effect of laser beam drift can be greatly reduced. In our design, a very small pinhole is illuminated by the laser light and the illuminated pinhole is imaged to the detector by a lens located in the middle between the detector and the pinhole in a $2f$-$2f$ configuration. The cuvette is placed just before the lens. The pinhole, the cuvette, the lens, and the detector are mounted on a small optical rail. The refractometer can be easily incorporated into any laser light-scattering spectrometer, in which the laser, the thermostat, and the computer are shared. This not only reduces the total cost (at least ten times cheaper than a commercial differential refractometer), but also enables us to measure the specific refractive index increment and the scattered light intensity under the identical experimental conditions, such as wavelength and temperature. This novel refractometer has a wide linear detection range (± 0.035 RI units) with a resolution of 10^{-6} RI units, which is sufficient for determining the specific refractive index increment of most polymer solutions.

I. INTRODUCTION

The specific refractive index increment (ν) of a polymer solution is defined as $\lim_{C\to 0}[(n - n_0)/C]_{T,P,\lambda_0}$, or more precisely $\lim_{C\to 0}(\partial n/\partial C)_{T,P,\lambda_0}$, where n and n_0 are the refractive indices of the solution and the solvent, respectively, and C is the polymer concentration in the unit of g/ml. ν is not an intrinsic property of polymer. This is why the conditions of constant temperature T, pressure P, and a fixed wavelength of light in vacuum λ_0 are introduced in the definition.

ν is normally measured by using either a differential refractometer or an interferometer. In the refractometer, light is refracted at the boundary between the sample and a reference medium. Commonly, the beam displacement is directly measured and then converted to the refractive index increment by multiplying a calibrated constant which can be obtained by using solutions with an accurately known refractive index difference $(n-n_0)$.[1] In the interferometer, two light beams with identical geometrical paths transverse two different optical paths. One passes through the sample and the other through the reference medium. The method relies on the formation of interference between the two beams. The details can be found elsewhere.[2,3]

In polymer science, the measurement of ν has various applications.[4–10] Among them is the use of precise ν in the determination of the weight-average molecular weight M_w of a polymer in laser light scattering (LLS).[11]

In LLS experiments, an additional commercial refractometer or interferometer is not only costly, but also has the problem of wavelength correction if, for example, an Ar-ion laser is used in the light-scattering experiment while a lamp or a He-Ne laser is used in most of commercial differential refractometers. In the present work, we have successfully utilized a novel $2f$-$2f$ optical design in our differential refractometer to eliminate the problem of laser beam drifting and integrated it into an existing commercial laser light-scattering spectrometer.

II. EXPERIMENT

Refractometer: Figure 1(a) shows a schematic presentation of our newly developed refractometer. A small pinhole (P) with a diameter of 400 μm is illuminated with laser light. The illuminated pinhole is imaged to a position-sensitive detector (PD) (Hamamatsu S 3932) by a lens (L) located at an equal distance between the pinhole and the detector. The distance between the detector and the pinhole is four times the focal length ($f=100$ mm) of the lens, i.e., we have used a ($2f$-$2f$) design instead of a conventional ($1f$) design where a parallel incident light beam is used and the distance between the detector and the lens is only one focal length. A temperature-controlled refractometer cuvette (C) (Hellma 590.049-QS) is placed just in front of the lens. The cuvette is a flow cell and has a volume of ~ 20 μl, which is divided by a glass plate at $\sim 45°$ into two compartments. The pinhole, the cuvette, the lens, and the detector are rigidly mounted on a small optical rail. The refractometer has dimensions of only 40 cm in length, 15 cm in width, and 10 cm in height. The output voltage (-10 to 10 V) from the position-sensitive detector is proportional to the displacement of the light spot from the center of the detector which can be measured with an analog-to-digital data acquisition system. We carried out an absolute calibration of the detector by placing it on a

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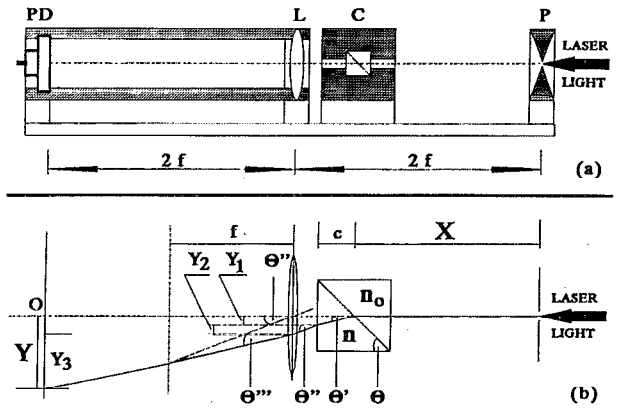

FIG. 1. (a) Schematic of differential refractometer. P: pinhole; C: differential refractometer cuvette; L: lens ($f=10$ cm); and PD: position-sensitive detector. All components are rigidly mounted on a 40 cm long optical rail. (b) Light path, where one compartment of C contains solvent with refractive index n_0 and the other contains solution with slightly different refractive index $n=n_0+\Delta n$. The cuvette and angel θ', θ'', and θ''' are enlarged so that the light path can be clearly shown. The angles of θ', θ'', and θ''' are actually very small ($\sim 0.01°$).

high precision translation stage. The calibration result shows that the detector has a very good linear response within ± 9.5 V.

Basic principles: Figure 1(b) shows a light path, where θ', θ'', θ''', and the cuvette have been artificially enlarged so that the details can be seen. If both the compartments are filled with a solvent (i.e., $n=n_0$), the illuminated pinhole will be imaged at point O. However, if the solvent in one of the compartments is replaced by a dilute polymer solution with a slightly different refractive index (i.e., $n=n_0+\Delta n$), the light will be bent first by the glass plate, then by the cuvette wall, and finally by the lens. The image is shifted away from point O at a distance of Y. In Fig. 1(b)

$$Y=Y_1+Y_2+Y_3$$
$$=\cot(\theta')+(2f-X-c)\tan(\theta'')+2f\tan(\theta''') \quad (1)$$

and

$$\tan(\theta'')=f\tan(\theta''')+\cot(\theta')$$
$$+(2f-X-c)\tan(\theta''), \quad (2)$$

where $c=5\pm 0.1$ mm, $X=155.0\pm 0.5$ mm in our present setup and $\theta=45°$. By using Snell's law, we have

$$n_0\sin(90°-\theta)=(n_0+\Delta n)\sin(90°-\theta-\theta') \quad (3)$$

and

$$(n_0+\Delta n)\sin(\theta')=\sin(\theta''), \quad (4)$$

where θ', θ'', and θ''' are actually very small because Δn is in the order of 10^{-4} RI units, which allows us to approximate $\sin(\theta')\cong\theta'$, $\sin(\theta'')\cong\theta''$, $\tan(\theta')\cong\theta'$, $\tan(\theta'')\cong\theta''$ and $\tan(\theta''')\cong\theta'''$. By using Eqs. (2)–(4), we can rewrite Eq. (1) as

$$Y=K\cdot\Delta n, \quad (5)$$

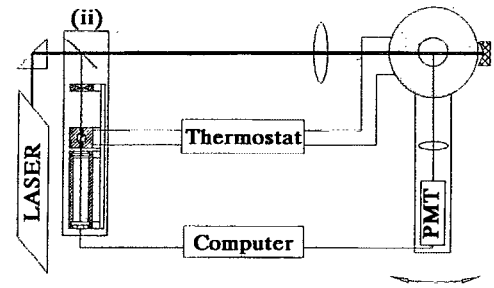

FIG. 2. Schematic of the incorporation of our differential refractometer into a laser light-scattering spectrometer.

where $K=[X+c(1-1/n_0)]\tan(90°-\theta)$. For a given optical setup and solvent, X, c, θ, n_0, and hence K are constants. Equation (5) shows our signal is proportional to the refractive index increment Δn, and the larger the value of X, the higher the sensitivity ($Y/\Delta n$), which means that the cuvette should be as close as possible to the lens in the experimental setup.

The refractometer with its present dimension can be easily incorporated with any LLS spectrometer where the laser, the thermostat, and the computer are shared. Therefore, the total cost of the refractometer is greatly reduced (at least ten times cheaper than a commercial differential refractometer). Figure 2 shows the incorporation. One optical glass plate placed in the laser light path at 45° is used to reflect $\sim 4\%$ of the laser light, which is used as a light source in the refractometer. In this way, we are able to do LLS and the ν measurement simultaneously at identical wavelength and temperature.

Samples: Sodium chloride (NaCl) (Merck, analytical grade) and double-distilled water were used for calibrating the refractometer. Sodium chloride was dried overnight in a vacuum oven at 110 °C before being dissolved in doubly distilled deionized water. Polystyrene standard ($M_w=6\times 10^5$ g/mol) and toluene (analytical grade) purchased from Pressure Chemical and Baker, respectively, were used without further purifications.

III. RESULTS AND DISCUSSION

Figure 3 shows that the fluctuation of V as a function of time (t) is less than $\pm 3\times 10^{-4}$ V, which corresponds to the root-mean-square (rms) noise: $\sim 1.63\times 10^{-4}$ V. It will be shown later that this rms noise corresponds to a change of $\pm 10^{-6}$ RI units in the measured refractive index difference (Δn), which is sufficient for determining the value of ν for most dilute polymer solutions since Δn for dilute polymer solutions is normally in the range of 10^{-4} to 10^{-3} RI units. It should be noted that the RMS noise in the present ($2f$-$2f$) design is at least five times lower than that in a conventional ($1f$) design. In the (2f-2f) design, the detector and the pinhole (acting as a light source) are placed at the exact imaging positions along the optical axis of the lens. This configuration is *optically* equivalent to placing the detector directly behind the pinhole, so that laser beam drifting is eliminated.

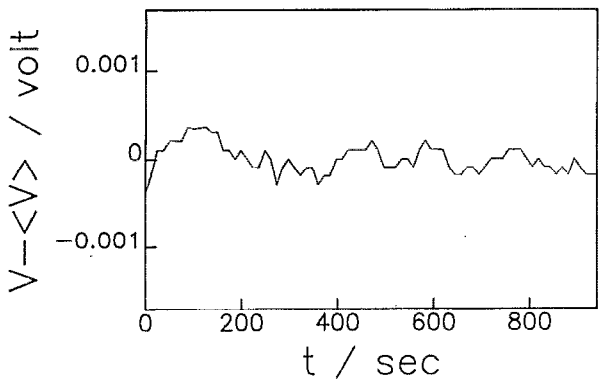

FIG. 3. Fluctuation of the output voltage (V) around the average value ($\langle V \rangle$) in our ($2f$-$2f$) design, which is caused mainly by the detector itself and not by the laser beam drift (see text for the detail).

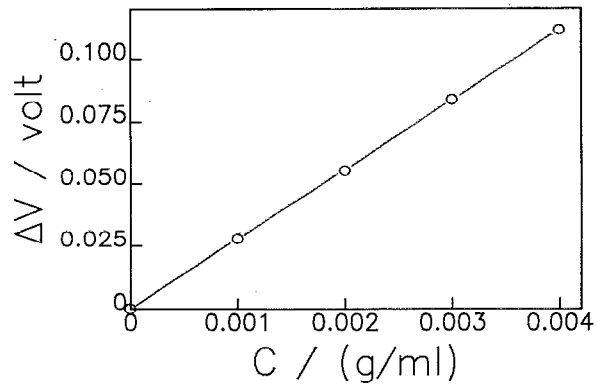

FIG. 5. Plot of the output voltage (ΔV) vs polymer concentration (C) for polystyrene in toluene at $\lambda_0=632$ nm and 25 °C. The circles represent the measured data and the line a least-squares fit. $\Delta V/C=27.9$ V/(g/ml).

Figure 4 shows a calibration of the refractometer where we used a set of NaCl solutions with known Δn. The calibration shows that the output voltage ΔV is proportional to Δn, i.e.,

$$\Delta n=(3.92\pm0.01)\times10^{-3}\Delta V, \tag{6}$$

where Δn and ΔV are in the units of RI and volts, respectively. In terms of the good linear range (±9.5 V) of the position sensitive detector, the measurable range of the refractometer will be at least ±0.035 RI units.

After the calibration, we tested the refractometer by measuring the specific refractive index increment of polystyrene in toluene at 25 °C ($\nu^{25\,°C}_{PS/toluene}$). The choice of this pair of polymer and solvent is simply because it has been extensively studied and there exists an abundance of measured values. In the *Polymer Handbook*,[12] the average values of ν at $\lambda_0=436$ and 546 nm for polystyrene in toluene at 25 °C are (0.112 ± 0.001) ml/g and (0.110 ± 0.001) ml/g, respectively. However, the listed ν at $\lambda_0=632.8$ nm ranges from 0.101 to 0.110 ml/g.

Figure 5 shows a plot of the output voltage (ΔV) versus polymer concentration (C). The circles represent the measured data and the line, a least-squares fit of

$$\Delta V=(27.6\pm0.2)C, \tag{7}$$

where ΔV and C are in units of volts and g/ml, respectively. After combining Eqs. (6) and (7), we get $\nu=\Delta n/C=(\Delta n/\Delta V)(\Delta V/C)=0.109\pm0.001$ ml/g. Since the listed values of ν at $\lambda_0=632.8$ nm are scattered, it is improper to directly compare our measured ν with the listed values. Therefore, we extrapolated the listed values of ν at $\lambda_0=436$ and 546 nm to a new one at 632.8 nm by using the known relationship of $\nu\propto1/\lambda^2$. The extrapolated value of ν at $\lambda_0=632.8$ nm and 25 °C is 0.109 ± 0.001 ml/g, which is identical to our measured ν.

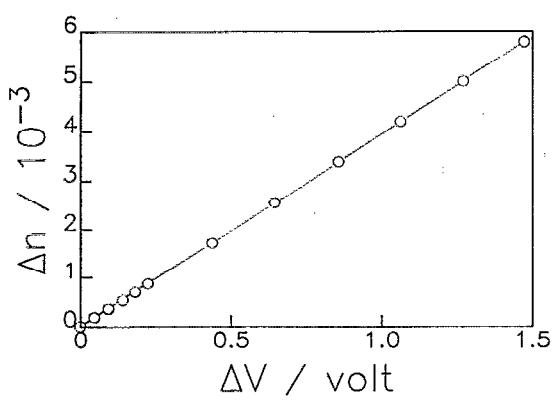

FIG. 4. Refractometer calibration curve obtained by using a set of NaCl solutions ranged from 0.1 to 3.5 g NaCl/100 g water, which corresponds to a range of Δn from $\sim2\times10^{-4}$ to $\sim6\times10^{-3}$ RI units. The circles represent the measured data and the line a least-squares fit. $\Delta n/\Delta V=3.92\times10^{-3}$ V^{-1}.

Finally, we incorporated the refractometer with our present LLS spectrometer where an Ar-ion laser ($\lambda_0=488$ nm) is used as a light source. As we know, ν at $\lambda_0=488$ nm is not available in the *Polymer Handbook*. Again, our testing results showed that $\nu(^{25\,°C,488\ nm}_{PS/toluene})$ is identical as the extrapolated value of 0.111 ml/g. This clearly demonstrated that our new refractometer performs well as we have expected.

In the testing process, we noted that if we average the output signal over a 10–15 min period, the experimental noise will be reduced so that we should be able to determine the correct ν by using *only one dilute polymer solution*. We have noticed that the error of using only one concentration is no more than $\pm1\%$, which is acceptable in most of LLS experiments.

We have successfully demonstrated that, with our present design, the differential refractometer can be incorporated with a normal existing laser light-scattering spectrometer, wherein the laser, the thermostat, and the computer are shared. This will not only reduce the total cost of the refractometer, but also enables us to make the specific refractive index increment measurement and the light scattering measurement simultaneously under identical experimental conditions, such as wavelength and temperature. Our ($2f$-$2f$) design has been tested and proven to function well. With this design, our refractometer has achieved a resolution of 10^{-6} RI units. In addition, we have shown

that an inexpensive position sensitive detector can be satisfactorily used as the detector in a differential refractometer.

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