NOTE

Automatic, Simultaneous Determination of Differential Refractive Index of a Polymer and Its Corresponding Monomer

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INTRODUCTION

The differential refractive index (dn/dc) of a polymer/solvent pair is an important parameter in situations involving refractometric concentration determination, light scattering determinations of absolute molar mass, and so forth. It is well known that the dn/dc can be different for a polymer and its corresponding monomer.

In this Note we present a rapid and accurate means of simultaneously determining the dn/dc for a monomer and a polymer and apply it to the case of acrylamide/polyacrylamide. Our motivation for developing this technique, instead of simply making separate determinations of dn/dc for the monomer and then the polymer, was based on concerns about the hygroscopic nature of the polyacrylamide (PAAm): PAAm normally contains 10–15% water by mass, and this is difficult to remove entirely and reliably. On the other hand, AAm is far less hygroscopic, so that if one commences with an accurate concentration of AAm in a polymerization reaction the concentration of AAm plus PAAm throughout the chain-growth polymerization reaction will remain constant; thus, the problem of an unknown amount of PAAm hydration starting from a "dry" powder is avoided.

The technique involves continuous measurement of the monomer and total monomer/polymer concentration while the polymerization of the monomer proceeds. This method will be useful whenever detectors can be found that can distinguish between the concentration of the monomer and polymer, and the polymer can be produced in a homogeneous monomer/solvent system. A refractometric detector (RI) detects both the monomer and polymer. In the monomers with double bonds or conjugation, such as AAm, there is a strong ultraviolet absorbance that is lost upon polymerization. This allows an ultraviolet spectrophotometer (UV) to monitor the disappearance of the monomer during a polymerization reaction. Another possible scheme for distinguishing the monomer from the polymer is via evaporative light scattering, in which the monomer and solvent can be stripped via passage through a heated drift tube from droplets containing the monomer, solvent, and polymer. Any standard chromatography pump can be used to deliver reacting liquid to the detectors. RI and UV detectors and a chromatography pump are standard devices in polymer characterization laboratories, so application of this technique will not normally require any investment in additional equipment.

EXPERIMENTAL

The PAAm polymerization reaction was repeated twice and was carried out as follows each time: 100 mL of water containing 0.020 g/mL of AAm (Aldrich 14,866-0) was heated to 60°C, and 0.0912 g of sodium thiosulfate ($Na_2S_2O_3$, Aldrich 21,726-3) and 0.1603 g of potassium persulfate ($K_2S_2O_8$, Aldrich 37,982-4) were added according to the redox couple initiation reaction described by Riggs and Rodriguez.[1] An ISCO isocratic HPLC pump continuously withdrew material from the reactor at a rate of 0.5 mL/min and pumped the liquid through a Shimadzu SPD-10AV UV operating at $\lambda = 245$ nm and then a Waters 410 RI operating at $\lambda = 930$ nm. A detailed study of online monitoring of the absolute molecular weight and reduced viscosity, in addition to
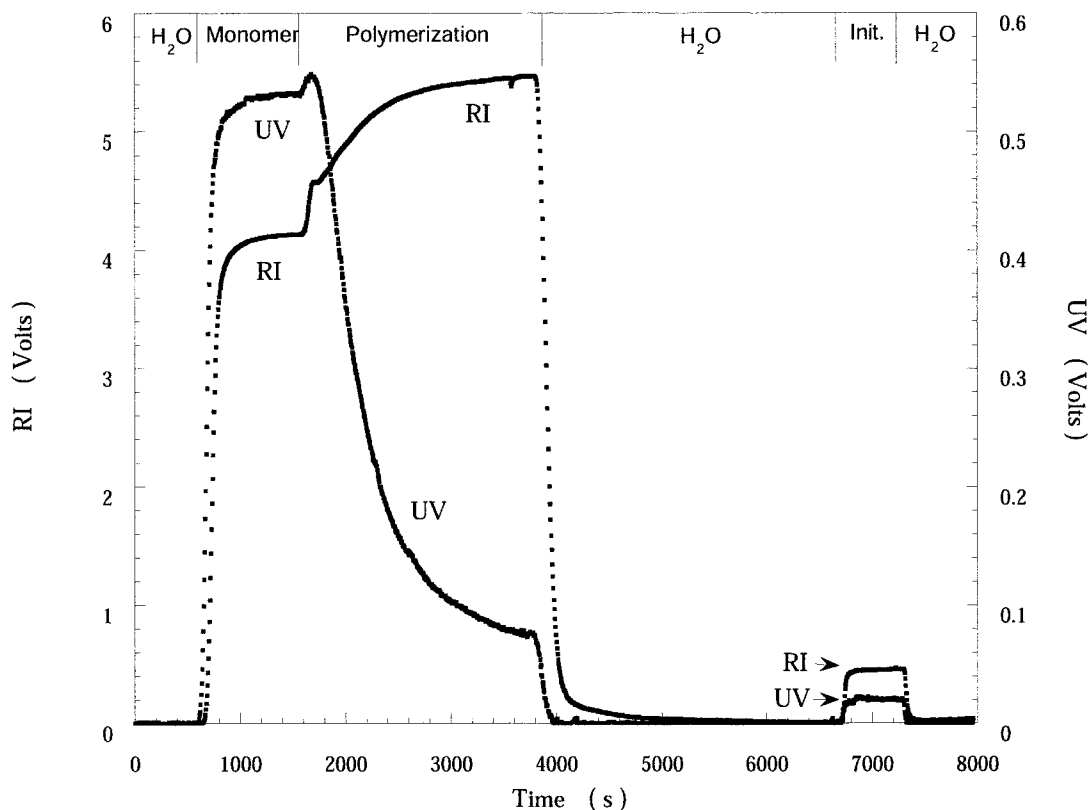
Figure 1 Raw data for experiment 1, showing the raw UV and RI detector signals. The solvent flowing through the detectors for each regime is labeled. The injection of pure initiator at the end for $\Delta V_{\text{UV,initiator}}$ and $\Delta V_{\text{RI,initiator}}$ for use in eqs. (2)–(4) is seen.

conversion, for the PAAm polymerization is currently underway in our laboratory.

Before starting the polymerization reaction, pure water was pumped through the system to stabilize the RI and UV. Then the unreacted monomeric material from the reactor was withdrawn until the instruments were stabilized. Subsequently, the persulfate/thiosulfate powders were added to the reactor, and monitoring was continued until no further change in the UV was detected. Raw signals for the reaction are given in Figure 1. When the persulfate/thiosulfate powders are added there is a small, sharp increase in RI voltage, corresponding to the change in the solution index of refraction these powders cause, and a very small change in the UV voltage. These changes were verified by adding an identical amount of persulfate/thiosulfate after the reaction was completed and the detectors restabilized with pure water. They are visible in Figure 1.

RESULTS AND DISCUSSION

The RI signal in volts [$V_{\text{RI}}(t)$] is related to the concentration of a component at time t [$C(t)$] via the RI calibration factor CF (in refractive index units per volt of output, 7.514×10^{-4} Δn/volt in this case) and the component's dn/dc.

$$C(t) = \text{CF}\frac{V_{\text{RI}}(t)}{dn/dc} \qquad (1)$$

Let C_0 represent the initial monomer concentration in the reactor. After the initiator is added at time t_0, the RI voltage will be

$$V_{\text{RI}} = \frac{C_0}{\text{CF}}\left\{f_m(t)\left.\frac{dn}{dc}\right|_m + (1 - f_m(t))\left.\frac{dn}{dc}\right|_p\right\}$$
$$+ \Delta V_{\text{RI,initiator}}H(t - t_0) \quad (2)$$

where $\Delta V_{\text{RI,initiator}}$ is the increase in RI voltage due to the addition of the initiators persulfate/thiosulfate, $H(t - t_0) = 1$ for $t \geq t_0$ and $H(t - t_0) = 0$ for $t < t_0$ (the Heaviside step function), and $f_m(t)$ is the fraction of the initial monomer remaining at time t. The $f_m(t)$ is derived from the UV voltage $V_{\text{UV}}(t)$ by

$$f_m(t) = \frac{V_{\text{UV}}(t) - \Delta V_{\text{UV,initiator}}H(t - t_0)}{V_{\text{UV}}(0)} \qquad (3)$$
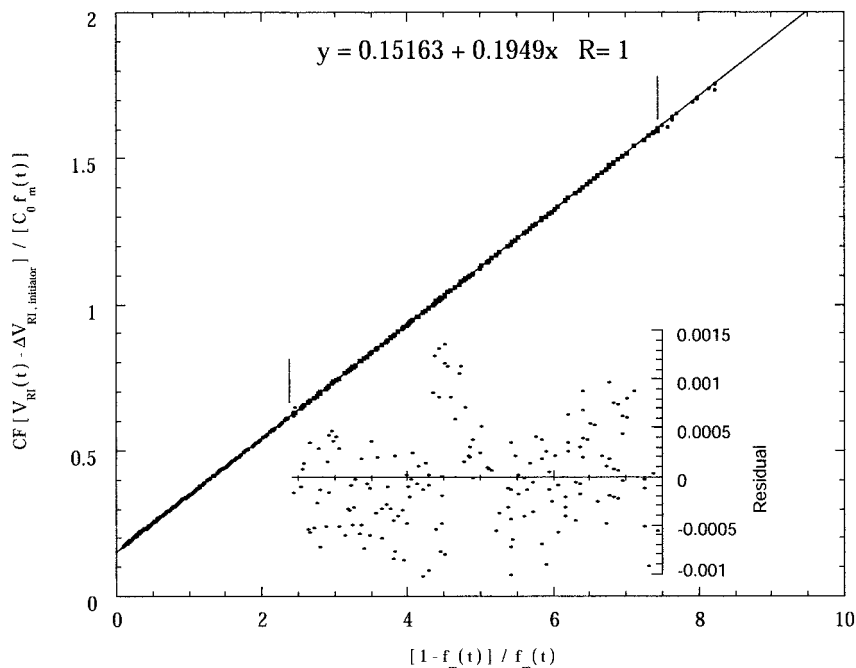
Figure 2   Data from Figure 1 plotted according to eqs. (3) and (4). There is a linear fit over the region for which the residuals are displayed. As noted, if the fit were over the entire linear regime, the variation in the dn/dc values for AAm and PAAm would be 1 and 0.2%, respectively.

where $V_{UV}(0)$ is the UV voltage when pure unreacted monomer flows before the addition of the initiator and $\Delta V_{UV,initiator}$ is the change in the UV signal when the initiators are added. The following expression then permits the convenient determination of dn/dc for the monomer and polymer:

$$\frac{CF[V_{RI}(t) - \Delta V_{RI,initiator}]}{C_0 f_m(t)} = \frac{dn}{dc}\bigg|_m$$

$$+ \frac{dn}{dc}\bigg|_p \frac{[1 - f_m(t)]}{f_m(t)} \quad (4)$$

Figure 2 is a plot of the above function; the voltages were taken from Figure 1, including $\Delta V_{RI,initiator}$ and $\Delta V_{UV,initiator}$. Both these latter voltages can be seen in the steps at the end of the Figure 1 data. The value of $CF = 7.514 \times 10^{-4}$ (Δn/volt) was used. From the slope and intercept for AAm and PAAm, respectively, are at $T = 35°C$ and $\lambda = 930$ nm. Also shown in the plot are the residuals $r(t)$, which are defined as

$$r(t) = \frac{y_{exp}(t) - y_{calc}(t)}{y_{calc}(t)} \quad (5)$$

The random nature of the residuals, with values on the order of 0.1%, attests to the linearity of each detector and the absence of any significant changes in the RI and UV signals due to changes in the initiators, which

justifies the use of the $\Delta V_{RI,initiator} H(t - t_0)$ and $\Delta V_{UV,initiator} H(t - t_0)$ terms in eqs. (2) and (3), respectively. If the data in Figure 2 are fitted over the entire data range, the deviation of the values of dn/dc for AAm and PAAm are less than 1 and 0.2%, respectively, which place upper limits on the random error for a given experiment.

There are two main sources of systematic error. The first is the calibration factor CF, which was used in eq. (4). Our estimate of its error is 0.1%, based on the use of NaCl solutions[2] to determine CF. The other source of error is in determining the concentration of AAm for the experiment. The error in the weighing procedure itself was less than 0.025% (based on a conservative ± 0.5 mg error in weighing 2000 mg of AAm). The purity of the AAm is >99%, according to the manufacturer, with no mention of water being a part of the impurity component. A conservative error estimate for the impurity is thus 1%. The experiment was repeated under identical conditions to assess the run to run errors. The values for dn/dc of monomer and polymer with their corresponding random errors are given in Table I for each of the two experiments.

The final values of AAm and PAAm, including random, run to run, and systematic errors, are

$$\frac{dn}{dc}\bigg|_{AAm} = 0.1509 \pm 0.0026$$

Table I   Values of *dn/dc* for AAm and PAAm for Two Experiments with Final, Average Values, and Errors

Expt. No.	*dn/dc* of AAm	*dn/dc* of PAAm
1. With random errors	0.1502 ± 0.0015	0.1928 ± 0.0004
2. With random errors	0.1516 ± 0.0015	0.1949 ± 0.0004
Average with run to run, systematic, and random errors	0.1509 ± 0.0026	0.1939 ± 0.0027

$$\frac{dn}{dc}\bigg|_{\text{PAAm}} = 0.1939 \pm 0.0027$$

Kulicke et al.[3] provided a compilation of *dn/dc* values for PAAm in water and other solvents. Figure 3 shows a plot of *dn/dc* values for PAAm in pure water at $T = 25°C$ versus the wavelength. Also shown is the value of *dn/dc* from the current work. The reported values show wide discrepancies, and Kulicke et al.[3] stated that the varying degrees of hydration of the
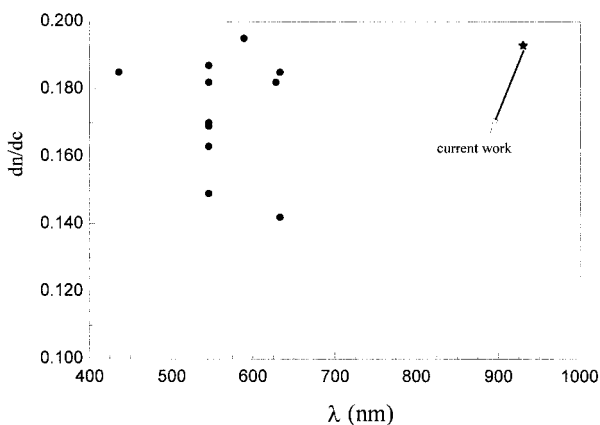
Figure 3   Literature values of *dn/dc* for PAAm vs. wavelength from the compilation of values given in Kulicke et al.[3] (★) The value of *dn/dc* from this work.

PAAm may have caused this. If water is present in the PAAm and not taken into account when the concentration is computed, this will lead to underestimates of *dn/dc*. The majority of the *dn/dc* measurements in Brandrup and Immergut[2] are significantly below our value, strengthening the argument that the various reporting authors had unknown degrees of hydration in their PAAm sample.

The data in Figure 3 are not accurate enough to determine the wavelength dependence of *dn/dc*, because the error in the values of *dn/dc* at each wavelength appear far higher than any wavelength dependence itself.

Finally, we recall that when using *dn/dc* for determinations of weight average molecular mass (M_w) by light scattering in batch mode, the error in the M_w varies as $(dn/dc)^{-2}$ whereas in flow mode (e.g., in size exclusion chromatography) with an RI detector the error in the M_w varies as $(dn/dc)^{-1}$. Figure 3 illustrates the large discrepancies that can result in the M_w determinations, depending on which literature value is used for *dn/dc*.

REFERENCES

1. Riggs, J. P.; Rodriguez, F. J Polym Sci Part A-1 1967, 5, 3167.
2. Brandrup, J.; Immergut, E. H., Eds. Polymer Handbook, 3rd ed.; Wiley: New York, 1989.
3. Kulicke, W. M.; Kniewske, R.; Klein, J. Progr Polym Sci 1982, 8, 373.