NOTE

Refractive Index Increment (*dn/dc*) Using GPC for the *α*-Methyl Styrene/Methyl Methacrylate Copolymer at 670 nm in Tetrahydrofuran

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Although much work has been published about the *dn/dc* values for homopolymers, including α-methyl styrene (AMS) and methyl methacrylate (MMA)[1,2] there has been little in the way of published work to determine the *dn/dc* values for copolymers. It is generally accepted that the *dn/dc* value for a homopolymer is almost entirely dependent on the monomer and weakly dependent on (or independent of) molecular weight.[2]

Copolymers may be very different, however. Because molecular weight and composition can be closely linked (especially for systems with depropagating monomers like AMS and to a lesser extent MMA), some correlation may be present. Another factor that affects molecular weight, besides the reaction conditions, is the feed fraction of monomers. Will this have an effect on the *dn/dc* values obtained?

From the *Polymer Handbook*[2] there is a historical recording of *dn/dc* values primarily at wavelengths below 633 nm, with new data appearing for 633 nm He–Ne lasers, but with none at the wavelength that current equipment uses: 670 nm. Another incentive to embark on this work is to show whether the assumption of a *linear* relationship between *dn/dc* and copolymer composition is valid[2–6] and whether the relationship works better for the mole or weight fraction composition.

To determine the *dn/dc* of the copolymers and of the two homopolymers, a GPC setup, including a Waters solvent/sample delivery system (Waters, Milford, MA) with an in-line degasser (model AF), 515 HPLC pump, and 717plus autosampler, was used. The detectors on the system were from Viscotek (Houston, TX), contained in the TDA 302 quad detector package that incorporates RALS/LALS (670 nm), differential refractive index (DRI), viscometer, and UV (model 2501) detectors. The analysis software OmniSEC v2.0 (Viscotek) was included with the detectors.

The samples analyzed in this study were produced by free-radical polymerizations at temperatures ranging from 100 to 140°C. Consequently, the AMS content in the copolymer reached a maximum of about 20%. To produce a polymer with a higher AMS content we would have to greatly sacrifice both yield and molecular weight, making the polymer undesirable for practical applications.

To determine *dn/dc* it is possible to use this equipment along with the following expression based on the DRI response:

$$RI_i = \frac{RI_{cal}C_i}{n_0}\frac{dn}{dc} \qquad (1)$$

where RI_{cal} is the calibration constant for the RI detector, established by analyzing samples of known *dn/dc* and known concentrations; RI_i is the measured response from the detector; C_i is the sample concentration; and n_0 is the refractive index of the solvent. Because we already have the RI_{cal}, and we know C_i and n_0, then the *dn/dc* can be calculated for the sample. Alternatively, the *dn/dc* can be calculated by plotting the RI_{area} (integrated from the RI signal) versus C_i. Because RI_{area} is assumed directly proportional to the refractive index of the sample in solution, the slope of this line will be *dn/dc*. For the work discussed here, this second technique was used.

In our study the objective was to assess the validity of this method using samples of polymer with realistic compositions of MMA and AMS. For each sample that has a given copolymer composition, a variety of concentrations must be made. Each solution, at a different polymer concentration while having the same copolymer composition, was sent through the detectors mentioned above, where a full analysis was done. For example, from Table I, sample 2-1 had five subsequent solutions made at varying concentrations of the same polymer. When using the OmniSEC software for *dn/dc* analysis (using the second method mentioned above), precision must be used while integrating the DRI signal because this is the primary source of data for the *dn/dc* calculation.

Previously published data for the homopolymers[1,2] indicated that at 633 nm the *dn/dc* for MMA is 0.083 mL/g, whereas that for AMS is 0.2056 mL/g. The values of Table I were obtained for the homopolymers and copolymers.

From Table I, it can be seen that the *dn/dc* values for the two homopolymers are not significantly different from the

TABLE I
dn/dc **Values for AMS/MMA Copolymers**

Sample	Mole fraction AMS[a]	M_W[b] (g/mol)	PDI	*dn/dc* (mL/g)
2–1	0.204	131,063	1.47	0.1045
2–2	0.206	121,724	1.50	0.1080
3–1	0.105	95,849	1.40	0.0916
3–2	0.096	96,677	1.42	0.0910
4–1	0.153	389,582	1.49	0.0985
4–2	0.114	348,629	1.57	0.0932
5–1	0.147	388,780	1.76	0.0970
6–1	0.042	254,556	2.13	0.0872
6–2	0.041	255,612	1.54	0.0900
AMS_{STD}	1.000	72,000	~1	0.1924
MMA_{STD}	0.000	100,000	~1	0.0843

[a] Mole fraction AMS = copolymer composition.
[b] M_W = weight-average molecular weight.

published values (6.4% difference for AMS and 1.5% difference for MMA).

Given that the available data pertain to values up to 20% AMS content, models using the data will be applicable only for this composition range. Initial investigations of the data show a linear trend between *dn/dc* and the square of the mole fraction of AMS in the copolymer (MFAMS). Modeling efforts have included many different models that take into account both MFAMS and the molecular weight of the polymer. Most exhibited curvature in the model predictions, some with a quadratic and others with a cubic dependency. Included in these modeling efforts is the simple weighted average model, where the *dn/dc* is predicted by the mole fraction of the mono-

mers in the copolymer and the *dn/dc* values of the two homopolymers. This weighted-average model was not successful either. Once a model that appeared linear was obtained, using MFAMS and the molecular weight, it turned out that the parameter for the molecular weight term was potentially zero. This indicates that the dependency of *dn/dc* on molecular weight (at least for the range used here) is insignificant.

For the simple $y = mx^2 + b$ model, the following [eq. (2)] was obtained from linear regression while setting the intercept to zero:

$$\frac{dn}{dc} = C_1(MFAMS^2) + C_2 \qquad (2)$$
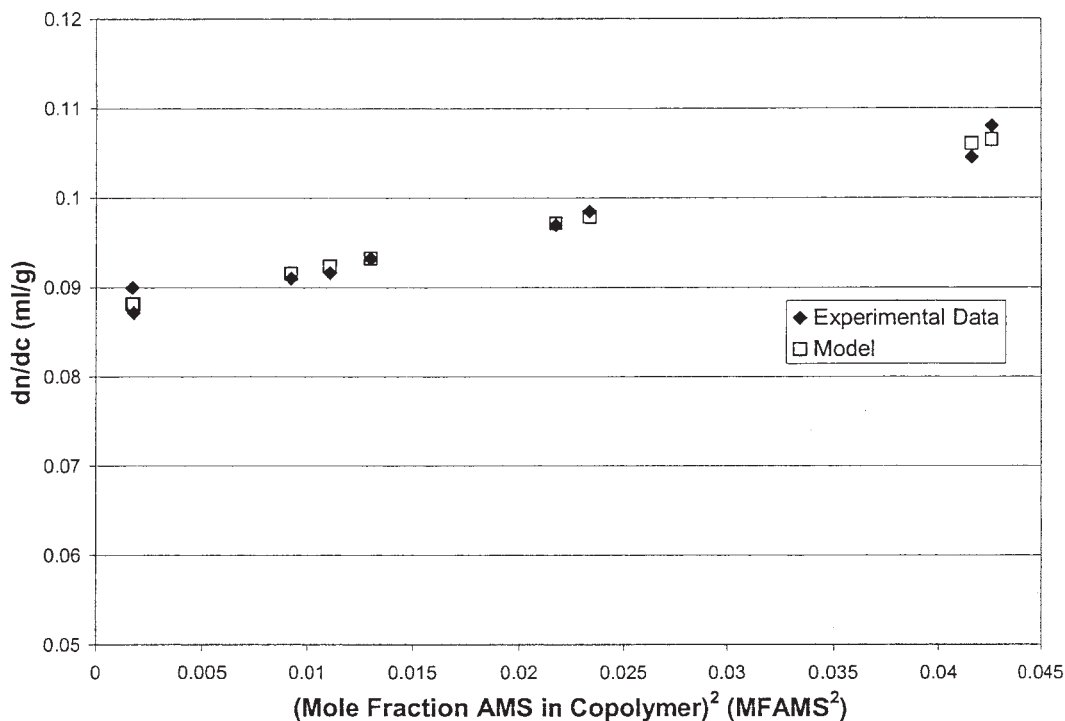
Figure 1 *dn/dc* model versus experimental data.

where $C_1 = 0.449 \pm 0.396$ and $C_2 = 0.087 \pm 0.061$.

The R^2 value for this regression is 0.973. Residual analysis does not show any significant patterns, although the error is not centered about zero. This is mainly imparted by two data points at higher MFAMS values, indicating that at higher MFAMS there is the potential for curvature and that eq. (2) may not be as useful for AMS compositions much above 20%.

Figure 1 shows the experimental data plotted against the model. There is good agreement and, like all the other models attempted, the dependency on MFAMS is significant. From this analysis is would appear that dn/dc is almost entirely independent of molecular weight for the range in consideration and dependent alone on the mole fraction of AMS in the copolymer.

Our study has included only one copolymer system, a system that we are currently working with for other research purposes. The MMA/AMS system is well behaved in that there are no issues with dissolving the polymer in THF (i.e., no gel portion). The main advantage of this type of analysis is that it is expedient and simple. However, from the parameter uncertainty, it is recommended that more data for the system be analyzed. To be certain that this GPC technique is in fact accurate and reliable more copolymer systems using wider ranges of composition with more data points will need to be studied.

References

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