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Polymer Characterization Using Liquid Chromatography with Evaporative Light-Scattering Detection

G. Saunders, J. Watkins, and E. Meehan,
Polymer Laboratories, Inc., Amherst, Massachusetts

All forms of liquid chromatography (LC) require the use of a detector to determine the solute concentration eluting from the column. This applies not only to regular LC experiments employing a single detector but also to more-complex multiple detector or hyphenated techniques such as multidetector gel-permeation chromatography (GPC) and LC–mass spectrometry (MS). Several different types of concentration detectors have been used in LC methodologies, but most of them rely upon the analyte displaying a particular chemical property; for example, a UV detector requires the analyte to have a strong chromophore. However, not all detectors are suitable for all applications, and making the correct choice of concentration detector for a particular LC application is as critical to success as optimizing the separation itself.

The evaporative light-scattering detector is a relatively new development in LC detectors that has attractive features for a wide range of applications because the evaporative light-scattering detector does not rely on any specific properties of the analyte. The detector operates by nebulizing the sample and solvent leaving the LC column using an inert gas to form a fine plume of droplets. The plume passes through a heated chamber and the solvent is removed by evaporation, resulting in a cloud of tiny solute particles. At the end of the evaporator tube the particles enter a light-scattering chamber where a simple light-scattering mechanism is used to measure a response proportional only to the concentration of sample. In this way, evaporative light-scattering detectors are often referred to as mass detectors, as any material will give a response on an evaporative light-scattering detector providing it is less volatile than the solvent.

Evaporative light-scattering detectors have several advantages over more common LC concentration detectors — they give stable baselines, do not suffer from solvent effects, and always give a positive response. The following separations illustrate the application of evaporative light-scattering detectors in the analysis of polymers by LC, including GPC and interactive chromatography.

In the GPC analysis of polymer blends (and block copolymers), a problem that may be experienced with differential refractive index detection is the fact that dn/dc can be either positive or negative with respect to the solvent, or a polymer could be isorefractive with the eluent. To illustrate this problem, two polymers were selected to produce a model blend, polystyrene and polydimethylsiloxane. Both polymers are soluble in a range of solvents, but tetrahydrofuran and toluene were selected as possible eluents.

Approximate dn/dc values for these polymer solvent combinations are summarized in Table I.

Figures 1 and 2 illustrate the raw data chromatograms obtained from differential refractive index and evaporative light-scattering detectors for the individual polymers and a 50:50 blend of the two. The differential refractive index data strongly reflect the dependence of the response on dn/dc. The evaporative light-scattering, on the other hand, always gives a positive response for all solutes and permits quantification of the polymer blend as well as significantly increased sensitivity.

In many cases, the sample being analyzed may contain a range of analytes with a variety of chemistries, making detection with traditional differential refractive index and UV detectors unsuitable. This is illustrated by the analysis of a range of polymer additives by GPC. Such materials are used as stabilizers and antioxidants in commercial polymers such as PVC, PE, etc. For this application, UV detection cannot be employed because some of the additives do not contain a chromophore; furthermore, and as the additives are present in polymer formulation at very low concentrations, differential refractive index detection is often lacking in sensitivity for adequate quantitation. In this case, evaporative light-scattering detection is ideal because all compounds will give a positive response, and evaporative light-scattering sensitivity is much greater than differential refractive index (and slight-

Table I: dn/dc values for polystyrene and polydimethylsiloxane in tetrahydrofuran and toluene

Solvent	Polystyrene (dn/dc)	Polydimethylsiloxane (dn/dc)
Tetrahydrofuran	0.185 mL/g	0.000 mL/g
Toluene	0.096 mL/g	−0.089 mL/g

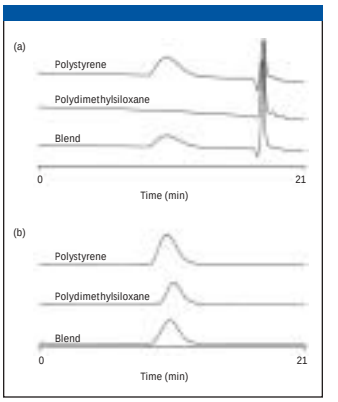

Figure 1: Chromatograms from the analysis of polystyrene and polydimethylsiloxane using evaporative light-scattering detection. Columns: two 300 mm × 7.5 mm, 5-µm d_p PLgel Mixed-C. Eluent: tetrahydrofuran. Flow rate: 1.0 mL/min. Detector: PL-ELS 1000.

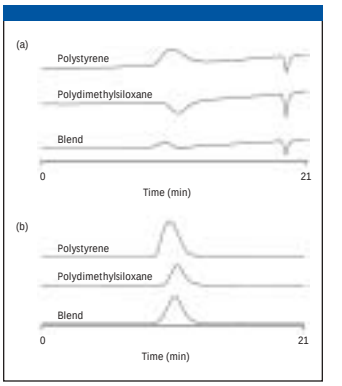

Figure 2: Chromatograms from the analysis of polystyrene and polydimethylsiloxane using differential refractive index detection. Columns: two 300 mm × 7.5 mm, 5-µm d_p PLgel Mixed-C. Eluent: toluene. Flow rate: 1.0 mL/min. Detector: differential refractive index.

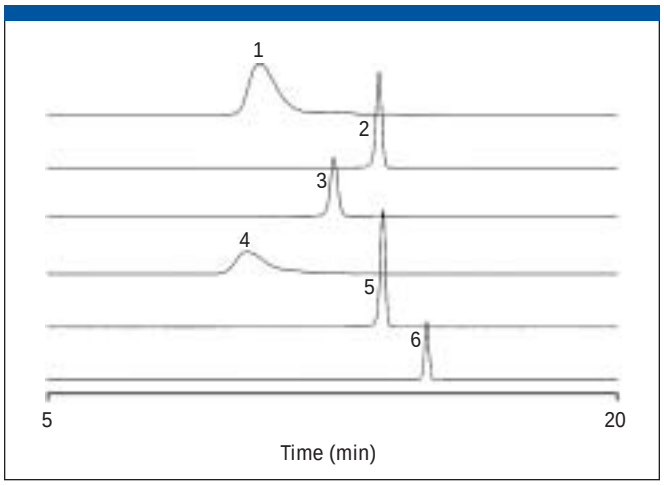

Figure 3: Overlay of chromatograms from six additives. Columns: two 300 mm × 7.5 mm, 5-μm d_p, 50 Å PLgel. Injection volume: 20 μL. Eluent: tetrahydrofuran and 0.1% DEA. Flow rate: 1.0 mL/min. Detector: PL-ELS 1000. Peaks: 1 = Chimasorb 944, 2 = Irgafos 168, 3 = Irganox 1010, 4 = Tinuvin 622, 5 = Tinuvin 770, 6 = Tinuvin 327.

ly greater than UV) detection. In addition the excellent baseline stability and lack of solvent interference peaks with the evaporative light-scattering permit easy peak integration.

Figure 3 shows an overlay of the chromatograms of the six additives. The two additives Chimasorb 944 and Tinuvin 622 are clearly shown to be polymeric, giving broad GPC peaks. Tetrahydrofuran was chosen as the eluent for the analysis with 0.1% diethanolamine added to minimize interactions between the samples and the column packing material.

Evaporative light-scattering detection is also an excellent choice for LC techniques which employ gradient elution. In the evaporative light-scattering detector, the solvent is evaporated during passage through the detector, so there is no baseline drift associated with changes in eluent composition. Increasingly, interactive gradient LC techniques are being applied to the analysis of polymers. An example is the analysis of low molecular weight polyethylene glycol. Polyethylene glycol is a hydrophilic water-soluble compound utilized in drug delivery systems as a viscosity modifier and as a precursor for the production of surfactants. The physical properties will be influenced by its molecular weight–to-oligomer distribution; therefore, it is essential that these parameters can be determined.

To obtain resolution of the individual oligomers in a low molecular weight polyethylene glycol, a gradient reversed phase method was used. Refractive index detectors cannot be used with gradient elution due to the changing refractive index of the solvent, and polyethylene glycol has little or no UV chromophore and so UV detection is not applicable. Although low molecular weight polyethylene glycols are semivolatile — diethylene glycol has a boiling point in the 243–246 °C range — they can be detected using the PL-ELS 1000 evaporative light-scattering detector.

Figure 4 shows the oligomeric profile of polyethylene glycol 400 where peak 1 is the diethylene glycol of molecular weight 106. In order to assess the sensitivity and limits of detection for this method, reduced injection volumes were chromatographed, which gave on-column loads in the 10–100 μg range of total sample (see Figure 5). Even with a total on-column load of 5 μg, some of the individual oligomers are still clearly visible.

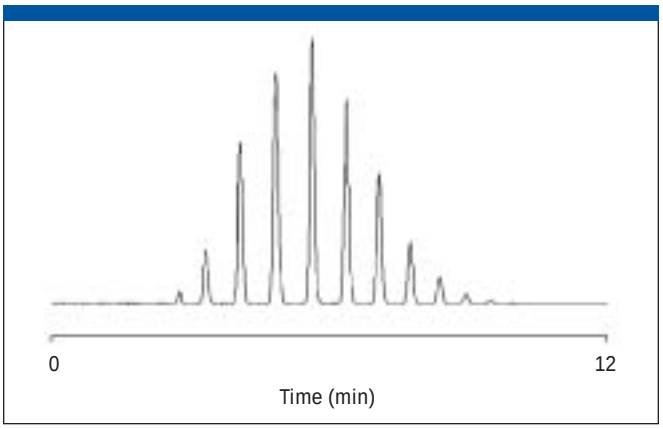

Figure 4: Oligomeric profile of polyethylene glycol 400. Peak 1 is the diethylene glycol of MW 106. Sample: polyethylene glycol 400 (1 mg/mL water) where M_w/M_n = 1.05. Column: 150 mm × 4.6 mm, 5-μm d_p, 100 Å PLRP-S. Eluent A: 1:99 (v/v) acetonitrile–water. Eluent B: 100% acetonitrile. Gradient: 10–30% B in 15 min. Flow rate: 1.0 mL/min.

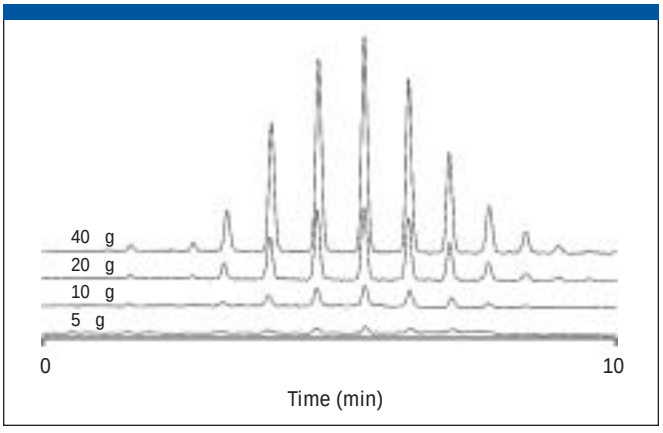

Figure 5: Analysis of the sample from Figure 4 with reduced injection volumes and on-column loads of 10–100 μg of total sample. Sample: polyethylene glycol 400 (1 mg/mL water) where M_w/M_n = 1.05. Column: 150 mm × 4.6 mm, 5-μm d_p, 100 Å PLRP-S. Eluent A: 1:99 (v/v) acetonitrile–water. Eluent B: 100% acetonitrile. Gradient: 10–30% B in 15 min. Flow rate: 1.0 mL/min.

This paper illustrates the application of evaporative light-scattering detection for the analysis of polymers by GPC and interactive LC techniques. The benefits of the evaporative light-scattering detection over other more traditional techniques such as differential refractive index and UV detection, namely insensitivity to sample chemistry and eluent composition, make evaporative light-scattering an ideal detection method for polymer analysis.

Polymer Laboratories, Inc.
Amherst Fields Research Park, 160 Old Farm Road,
Amherst, MA 01002
tel. (413) 253-9554, fax (413) 253-2476
http://www.polymerlabs.com