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An Overview of Size Exclusion Chromatography Applied to Polymers and Coatings

By Theodore Provder

The coatings technologies of waterborne, high solids, powder, and radiation curable coatings generally require high-molecular-weight latex polymers or strategically designed low-molecular-weight polymers, oligomers, and reactive additives. The design of these resin materials requires molecular weight distribution (MWD) information in the very high and very low-molecular-weight ranges which are accessible by size exclusion chromatography (SEC). In addition, there is a need for compositional distribution information as a function of molecular weight, particularly for oligomers; absolute MWD information, particularly for water-soluble polymers; and chain-branching information for high-molecular-weight polymers.

This overview discusses the SEC separation mechanism, molecular weight calibration methods including the use of hydrodynamic volume, data treatment methods, and polymer chain-branching determination. The use of molecular size sensitive detectors (viscometer, light scattering) and compositional sensitive detectors (UV-visible, IR) are discussed in the context of illustrative qualitative and quantitative examples. The practice of high-resolution SEC analysis of oligomers is discussed and illustrated with problem-solving examples.

INTRODUCTION

During the past several decades, new coatings technologies, such as high solids, powder, waterborne, and radiation curable coatings have been developed to meet the challenges of: (a) governmental regulations in the areas of ecology [volatile organic compounds (VOC) emissions]; (b) long-term increasing costs of energy, and petroleum-based solvents; (c) more active public consumerism; and (d) the continual need for cost-effective, high-performance coatings in a highly competitive and global business environment.

These new coatings technologies require the use of water as the major solvent with water-soluble or high-molecular-weight latex polymers or the use of strategically designed low-molecular-weight polymers, oligomers, and reactive additives that when further reacted produce high-molecular-weight and crosslinked polymers. Knowledge of the molecular weight and molecular-weight distribution (MWD) of the polymer components in a coatings system is essential for the optimization of polymer design for specific end-use properties.

Since its introduction many decades ago, gel permeation chromatography (GPC)[1], or size exclusion chromatography

(SEC), has become an important and practical tool for the determination of the MWD of polymers. Numerous studies have been published on the use SEC in plastics, elastomers, and coatings systems including several monographs [2-15]. With the advent of high-efficiency columns, the resolution in the lower-molecular-weight region (molecular weights in the range of 200 to 10,000) has been greatly improved and the speed of analysis increased. These features make high-performance SEC (HPSEC) an indispensable characterization tool for the analysis of oligomers and polymers used in environmentally acceptable coatings systems.

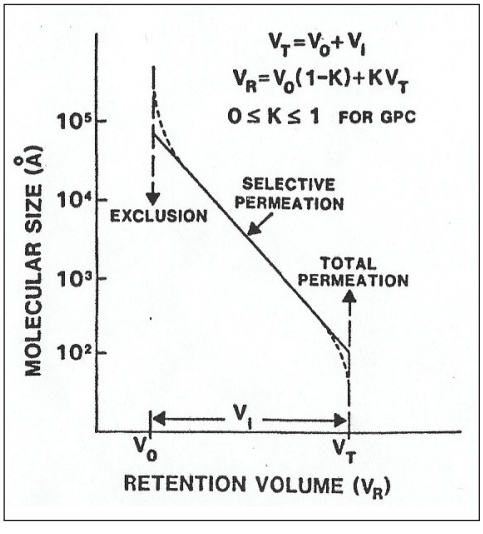
SEC SEPARATION MECHANISM

Size exclusion chromatography separates the polymer molecules by their molecular size or "hydrodynamic volume" in solution. The separation occurs as the polymer molecules elute through one or more columns packed with a porous support. Smaller molecules are retained in the pores to a greater degree than the larger molecules. As a result, the largest size molecule (or the molecule having the greatest hydrodynamic volume) elutes from the column first followed by the smaller molecules.

The volume of liquid at which a solute elutes from a column or the volume of liquid corresponding to the retention of a solute on a column is known as the retention volume (V_R) and is related to the physical parameters of the column, such as interstitial (void) volume (V_0), and internal pore volume. The dependence of molecular size in solution upon retention volume is schematically illustrated in *Figure 1*. The void volume V_0 corresponds to the total exclusion of solute molecules from the pores. The excluded solute molecules are significantly larger than the largest available size pores. Between V_0 and V_R the solute molecules are selectively separated based on their molecular size in solution.

Beyond the total column volume V_T, separation will not be achieved by a liquid exclusion chromatography mechanism. If molecules appear to separate beyond V_T they are being retained on the column support by an affinity mechanism. The fundamental aspects of the SEC separation mechanism have been treated theoretically by Casassa et al.[16-20], Giddings[21], and Yau et al.[22, 23]

FIGURE 1—Dependence of molecular size in solution upon retention volume



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These treatments are based on an equilibrium distribution of species between the mobile phase in the interstitial volume and the species in the pore volume of the column support.

Instrumentation

The essential components of the instrumentation are a solvent reservoir, a solvent delivery system (pump), sample injection system, packed columns, a detector(s), and a data processing system.

The heart of the instrumentation is the fractionation column where the separation takes place. The most common packing material used has been a semirigid crosslinked polystyrene gel. Developments in column technology have made the low efficiency, large particle size (37 to 75 μm) packing material obsolete. Currently, almost all the available SEC columns are packed with the high efficiency Microparticulate packings (< 10 μ.m). Some micro-particulate packings have been described by Majors[24]. A listing of such types of packing materials is included in an overview on SEC[25].

The concentration of the polymer molecules eluting from SEC columns is continuously monitored by a detector. The most widely used detector in SEC is the differential refractometer (DRI), which measures the difference in refractive index between solvent and solute. Other detectors commonly used for SEC are (1) functional group detectors: ultraviolet (UV) and infrared (IR) and (2) absolute molecular weight detectors: low angle laser light scattering (LALLS) and in-line continuous viscometers. Applications of these detectors to SEC analysis will be discussed later in the "Multiple Detector" section. Other detectors that have been used include the densimeter[26-34], the mass detector[35-41], and photodiode array UV-Visible spectrometer and multiangle laser light scattering (MALS)[42-44].

Calibration

To convert a chromatogram into a molecular weight distribution curve, a calibration curve relating molecular weight to retention volume is required. Narrow MWD standards (polydispersity, $\mathbf{M}_w/\mathbf{M}_n$, is usually less than 1.1) of the polymer of interest are used to generate retention volume curves. A one-to-one correspondence of peak retention volume with peak molecular weight, $\mathbf{M}_p$, is made. The peak retention volume is usually assigned to be $(\mathbf{M}_w \cdot \mathbf{M}_n)^{1/2}$ for narrow MWD polymers. By plotting log $\mathbf{M}_p$ versus retention volume a primary molecular weight calibration curve is generated. The disadvantage of this method is that quite often well-characterized narrow MWD polymer fractions of interest are not readily obtainable or require extensive laboratory effort for their generation.

There are other methods for generating absolute MWD curves without resorting to polymer fractionation. One of these methods uses broad MWD standards to generate the molecular weight calibration curve[45-57]. Other methods involve the use of

the hydrodynamic volume concept. Polymers having different chemical structures or polymers having the same chemical structures but different chain configurations (linear versus different types of branching) will have unique calibration curves. The SEC separation mechanism is based upon molecular size in solution (not molecular weight) or hydrodynamic volume. Therefore, if a parameter related to hydrodynamic volume is used to generate calibration curves, a common calibration curve for a variety of polymers will be obtained.

Benoit and coworkers[58] first proved the experimental validity of this concept by generating calibration curves consisting of a plot of the product of the intrinsic viscosity, [η] and weight average molecular weight, $\mathbf{M}_w$, versus retention volume. With the commercially available polystyrene standards, such curves are readily generated. One can use experimental and/or mathematical techniques to obtain[59] secondary molecular weight calibration curves from the hydrodynamic volume calibration curve. *Figure 2* shows the schematic procedures for obtaining the secondary molecular weight calibration curve from on-line SEC/viscometer data.

Two refinements involving the use of hydrodynamic calibration curves are: (1) Rudin's equation[60], which accounts for the reduction of effective hydrodynamic volume of high-molecular-weight polymers with finite concentration; (2) Hamielec and Ouano's finding[61] that the hydrodynamic volume is the product of intrinsic viscosity and $\mathbf{M}_n$ instead of $\mathbf{M}_w$. This refinement is important when applying hydrodynamic volume considerations to molecular branching models for highly branched and heterogeneous polymers. Transformation of the raw chromatogram into various molecular weight averages, differential and cumulative distribution curves was described by Pickett[62]. To numerically fit the calibration curve, various approaches have been used, i.e., polynomial, Yau-Malone equation[63] and a sum of exponentials. Detailed discussion of these treatments can be found in Balke's book[64]. With all the calibration options available the primary molecular weight calibration curve is still the most widely used calibration method in the coatings industry.

Instrument Spreading Correction

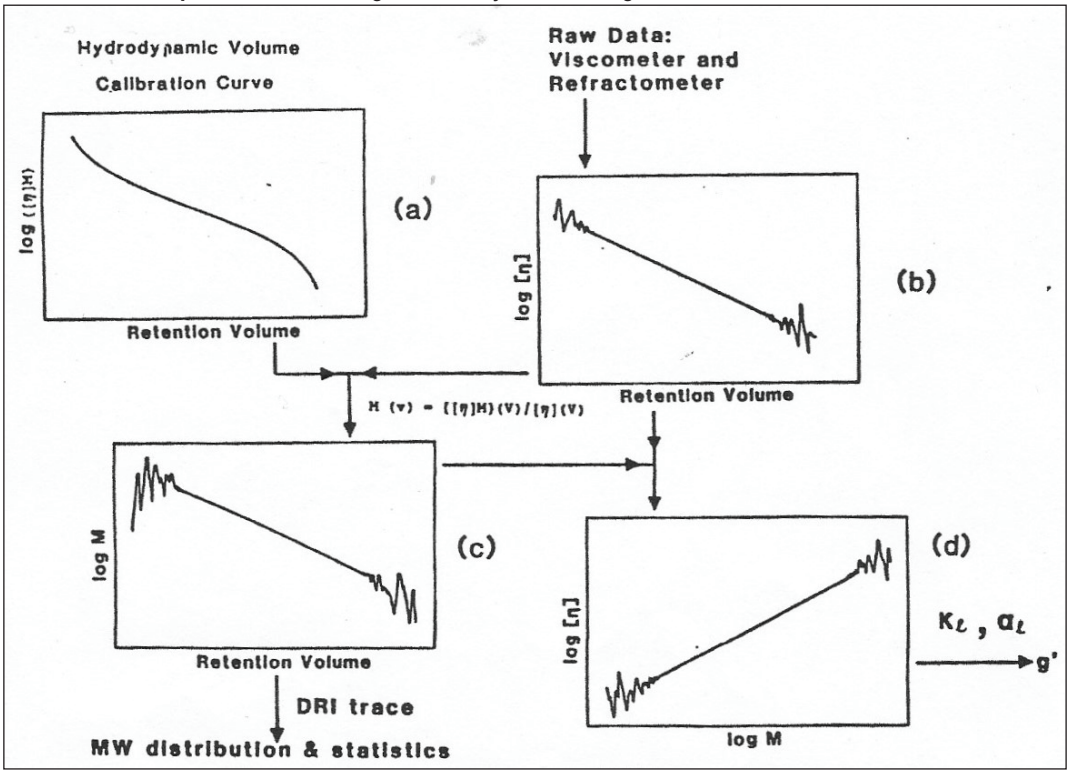
MWD curves calculated from SEC are generally broader than the true or absolute MWD curves due to instrumental spreading of the experimental chromatogram. Thus, the molecular weight averages calculated from the experimental chromatograms can be significantly different from the absolute molecular weight averages. The instrument spreading in SEC has been attributed to axial dispersion and skewing effects. Several computational procedures[65-76] have been reported in the literature to correct for these effects. In each method a specific shape for the chromatogram of an ideal monodisperse species or narrow MWD sample is assumed.

Tung[77] has shown that the normalized observed SEC chromatogram, F(v), at retention Volume v is related to the normalized SEC chromatogram corrected for instrument broadening, W(y), by means of the shape function G(v,y) through the relation

$$F(v) = \int_{-\infty}^{\infty} G(v-y)w(y)dy \qquad (1)$$

Provder and Rosen[68], applying Tung's equation and the method of molecular-weight averages in conjunction with a linear calibration curve, obtained corrected molecular-weight averages from the uncorrected values. The method of molecular

FIGURE 2—Schematic procedures for obtaining the secondary molecular weight calibration curve from on-line SEC/viscometer data



weight averages has been included in ASTM Test Method for Molecular Weight Averages and Molecular Weight Distribution of Polystyrenes by Liquid Exclusion Chromatography (Gel Permeation Chromatography-GPC) (D 3536,-76) to correct for instrument spreading effects. The relation of then-corrected molecular-weight averages, $\mathbf{M_n(c)}$, $\mathbf{M_w(c)}$, to the uncorrected molecular-weight averages $\mathbf{M_n(uc)}$, $\mathbf{M_w(uc)}$ are given by equations (2) and (3) below;

$$\mathbf{M_n(c)} = \mathbf{M_n(uc)} \cdot [X_1 \cdot (1+ X_2)], \quad (2)$$

$$\mathbf{M_w(c)} = \mathbf{M_w(uc)} / [X_1 \cdot (1- X_2)], \quad (3)$$

Where

$$X1 = 1/2\{[\mathbf{M_n(t)/M_n(uc)}] + [\mathbf{M_w(uc)/M_w(t)}]\} \quad (4)$$

$$X2 = (\Phi-1)/(\Phi+1) \quad (5)$$

$$\Phi = [\mathbf{M_n(t)} \cdot \mathbf{M_w(t)}] / [\mathbf{M_n(uc)} \cdot \mathbf{M_w(uc)}], \quad (6)$$

and $\mathbf{M_n(t)}$and $\mathbf{M_w(t)}$ are the true or experimentally determined molecular weight averages.

For the high-performance microparticulate organic gel columns, the need for instrument spreading corrections is minimum. However, for the porus silica columns the need to correct for instrument spreading still exists. Yau and coworkers[69] used the following equations to correct the spreading effect of the bimodal porous silica columns:

$$\mathbf{M_n} = D_1 \exp[(D_2\sigma)^2/2] /[\Sigma F(v)\exp(D_2v)] \quad (7)$$

$$\mathbf{M_w} = [\exp- (D_2\sigma)^2/2]\Sigma F(v)D_1\exp(-D_2v), \quad (8)$$

where σ^2 is the variance of the Gaussian instrument spreading function and a measure of peak broadening, and D1, D2 are the intercept and slope of the linear calibration curve. Hamielec et al.[70-71] extended these stuations to a nonuniform Gaussian spreading function and a nonlinear molecular weight calibration curve.

Multiple Detectors

Most size exclusion chromatographs use a DRI as a detector to monitor the concentration curves of samples eluting from the columns. This type of detector is highly sensitive and versatile and can monitor exceedingly low sample concentrations in a variety of solvents. However, it has several disadvantages which prevent it from being a "universal detector." At low and intermediate molecular weights, the specific refractive index increment at a given sample concentration is dependent upon the molecular weight[78-79].

For homopolymers, this difficulty can be circumvented by constructing a response factor curve versus molecular weight. For multicomponent polymer systems, there is the additional complexity of the dependence of the specific refractive index increment upon the composition of the polymer. In principle, if the structural features of the polymer system were known, response factor curves for a given multicomponent system could be constructed from a knowledge of atomic and bond refractions[80]. However, this is a very impractical approach for real polymer systems.

Most coatings materials are complex multicomponent systems covering the low- to intermediate-molecular-weight range. The use of a differential refractometer detector in the practice of SEC provides useful routine screening information wilh regard to the approximate molecular-weight distribution of these samples.

However, little or no information can be inferred with regard to the compositional distribution as a function of molecular weight. To obtain this type of information on polymers in the past, SEC fractions have been collected and analyzed by infrared spectroscopy. In addition to being a tedious and time-consuming method, a rather crude analysis of compositional distribution as a funclion of molecular weight is obtained[81-82]. To get maximum benefit from the SEC technique in terms of obtaining absolute molecular-weight distributions and refined compositional distributions as a function of molecular weight, specific functional group detectors coupled on-line to the SEC are required.

SEC/DRI/UV/IR

There have been a number of studies reported in the literature concerning the use of online functional group detectors[83-101] for SEC. The following examples show how SEC with multiple detectors can be used in a qualitative manner. *Figure 3* shows an SEC/DRI/ IR/UV chromatogram for a copolymer of methyl methacrylate (MMA) and vinyl acetate (VA) (25/75). Comparison of the SEC/IR trace with the SEC/DRI trace shows the difference in the ratio of the low-retention volume to high-retention volume peaks.

The DRI detector has a different response to VA functionality than the MMA functionality at low-retention volumes (high-molecular weight). Although there are no UV active monomers present in the polymer, there is a UV detector response to the benzoyl peroxide initiator fragments attached to polymer chain ends. The difference in curve shape for the SEC/UV trace compared to the SEC/IR and SEC/DRI traces over the common retention volume range is indicative of a high degree of branching in this polymer.

This is to be expected because vinyl acetate is known to produce branched polymers when made by emulsion polymerization techniques as was this copolymer of vinyl acetate. From this type of analysis of chain end distributions, valuable information about polymer chain-branching can he obtained.

FIGURE 3—SEC/DRI/ IR/UV chromatogram for a copolymer of methyl methacrylate (MMA) and vinyl acetate (VA) (25/75)

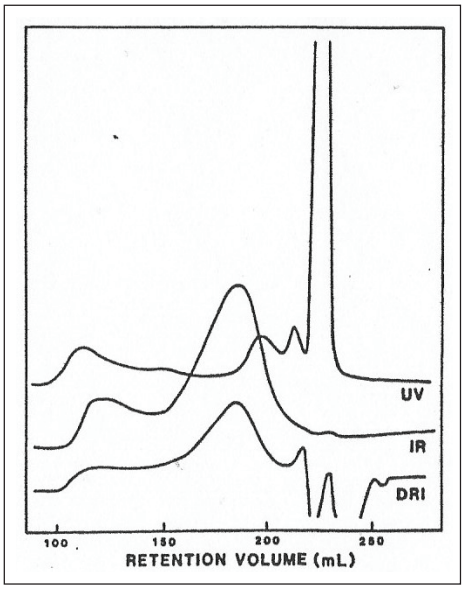


FIGURE 4—SEC/UV/IR chromatogram of a blend of a styrene/acrylic/acid terpolymer resin and a melamine resin

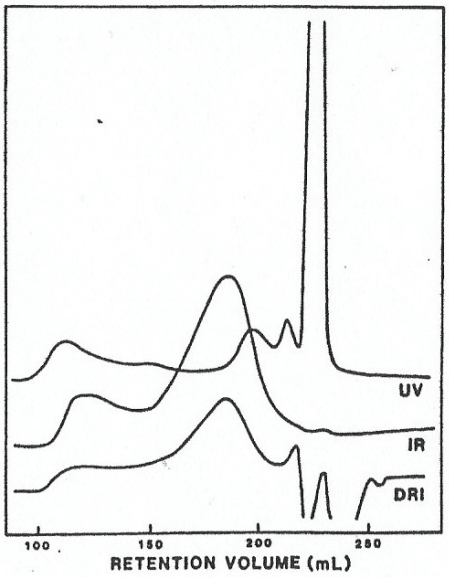


FIGURE 5— SEC/UV and SEC/IR chromatogram of poly(methyl methacrylate) (PMMA) samples

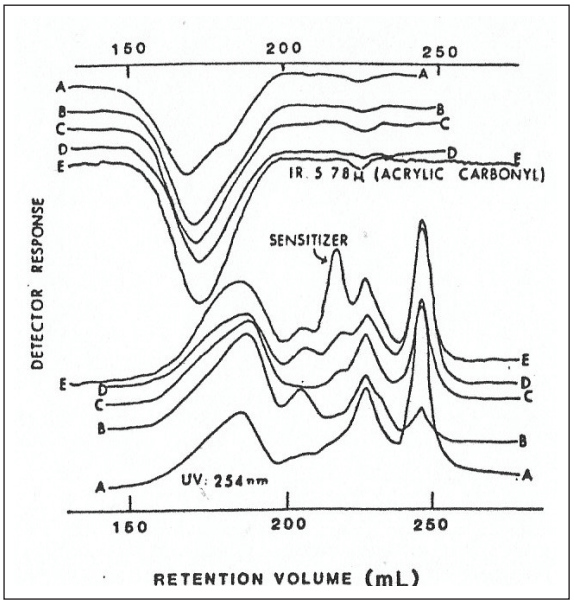


Figure 4 shows the SEC/UV/IR chromatogram of a blend of a styrene/acrylic/acid terpolymer resin and a melamine resin. It is seen that there are three distinct peaks in the SEC/UV trace for this blend. The SEC/UV/IR traces shows that the peak at ~ 185 ml corresponds to the polymer backbone; the middle peak at -205 ml is associated with the melamine resin; and the third peak at ~220 ml has a strong UV absorbing characteristic and is acidic in nature and may well be caused by reaction byproducts between catalyst, solvent, and monomers. The melamine resin is melt-blended with the terpolymer resin. This chromatogram indicates that physical mixing occurs. The SEC/IR/UV information shown in this example is quite helpful in establishing proper blending conditions.

Figure 5 shows the SEC/UV and SEC/IR chromatogram of poly(methyl methacrylate) (PMMA) samples[102] that were photopolymerized with different concentrations of photosensitizer (0.05×10^{-2} M, 0.08×10^{-2} M, 0.25×10^{-2} M. and 0.5×10^{-2} M). The photosensitizer used was 4,4' bis-(diethyl amino) benzophenone (DEABP). From the UV traces, it is seen that the photosensitizers are chemically bound to the polymer chains. The results also seem to indicate that a greater number of sensitizer fragments reside in the lower-molecular-weight regions. A considerable amount of free sensitizer can be detected by the UV detector (retention volume ~210 mL) when the initial concentration of the sensitizer is above 0.08×10^{-2} M.

The other auxiliary peaks beyond the retention volume of 200 ml could be due to some oligomeric components or solvent. The SEC/UV trace at retention volumes less than 200 ml are polymer chains having sensitizer fragments attached to the chain ends. Thus, the UV trace provides a distribution of polymer chain ends in these samples. Values of $\mathbf{M}_n$ and $\mathbf{M}_w$. can be calculated by means of the hydrodynamic volume approach. These results show that the molecular weight of PMMA decreases with increasing concentration of sensitizer. This is expected from the kinetics of conventional free-radical polymerization.

Earlier results of the same samples run on an SEC/DRI instrument did not show this systematic trend of molecular weights of PMMA as a function of DEABP concentration. The DRI detector picked up contribution from all the existing components that may not be PMMA, such as those which show up at retention volumes greater than 200 mL. These low-molecular-weight impurities distorted the chromatograms with respect to molecular-weight distribution calculations. Consequently, the calculated molecular weights and molecular-weight distrihutions would be erroneous. This illustrates one of the advantages of using the SEC/IR traces.

In addition, there are no negative peaks in the SEC/IR traces as there are in the DRI trace. The absence of these negative peaks allows much better definition of the low-molecular-weight baseline cut-off point. Also, the IR detector is not as sensitive to room temperature fluctuations as is the DRI and, therefore, the SEC/IR chromatogram baseline will have better longterm stability. The same considerations with regard to better baseline definition and longterm stability apply to the SEC/UV chromatograms.

The main problem with on-line IR detector is the spectral interference caused by the organic solvents used as eluents. This limitation prevented the dispersive IR detector from the widespread use in SEC characterization. With the advent of fourier transform IR (FTIR), the speed and sensitivity of obtaining spectra have been greatly improved. However, these advantages of FTIR did not alleviate the solvent interference problem when conventional flow-through cell technology is used.

A type of flow-through cell based on attenuated total reflectance (ATR) is commercially available. This cylindrical internal reflectance cell (CIRCLE) has been used mostly for HPLC (95) for on-line analysis. This accessory was tested for SEC on-line detection. With triglycine sulfate (TGS) as an IR detector, the concentration of effluent coming out of the SEC column was not high enough to obtain good spectra. Mathias[96] reported similar negative results for the use of a ClRCLE cell for aqueous SEC. Mercury cadmium telluride (MCT), which is a much more sensitive IR detector than TGS, might provide sufficiently improved signal-to-noise to make FTIR detection in SEC more viable.

Another way to reduce the solvent interference in a flow-through cell is to use deuterated solvents. However, this may not be practical. Supercritical fluid chromatography (SFC) has been

revitalized and developed into commercial instrumentation where pressurized CO_2 is used as the cluent. The combinalion of SFC and FTIR appears to be more promising than SEC/FTIR with respect to solvent interference problems.

Photodiode array detection, (PAD), has been used for UV-VIS detection in liquid chronrnlography. It can simultaneously monitor all wavelengths (190 to 600 nm) in the spectrum in contrast to the conventional single wavelength or slow wavelength-scanning UV-VIS detectors. The stored data can be retrieved for postrun data manipulations. In addition to the conventional chromatographic analysis, PAD provides additional data with regard to the spectral information contained in the sample. The features of PAD[103] can include:

(1) *Spectrum analysis*. This mode monitors spectral regions at various retention times across a peak or within a given analysis. The abilty to look at several (up to six) spectral regions across one peak provides an indication of peak purity. The ability to monitor several (up to six) different spectral regions within a chromatogram allows the analyst to compare various components to discern easily any spectral similarities or differences.

(2) *Spectrum index plot*. Spectral points of peak maxima, slope, and valley can be automatically plotted for spectral comparisons to help confirm peak identity and purity.

(3) *Three-dimensional plot*. Four angles can he chosen to display a 3-D plot of the chromatogram. The analyst can review 45° left and right, and 90° left and right, and be confident that all areas of the chromatograms have been displayed.

(4) *Contour plot*. This mode provides a topographical look at the chromatogram to provide still another view of the peak. The method of viewing the concentric rings of concentration shows areas of peak asymmetry and indicatess peak purity. PAD is useful for monitoring compositional heterogeneity as a function of molecular weight. *Figure 6* shows a contour plot of a Glycidal Methacrylate (GMA) acrylic copolymer, and *Figure 7* is the

FIGURE 6—Contour plot of a Glycidal Methacrylate (GMA) acrylic copolymer

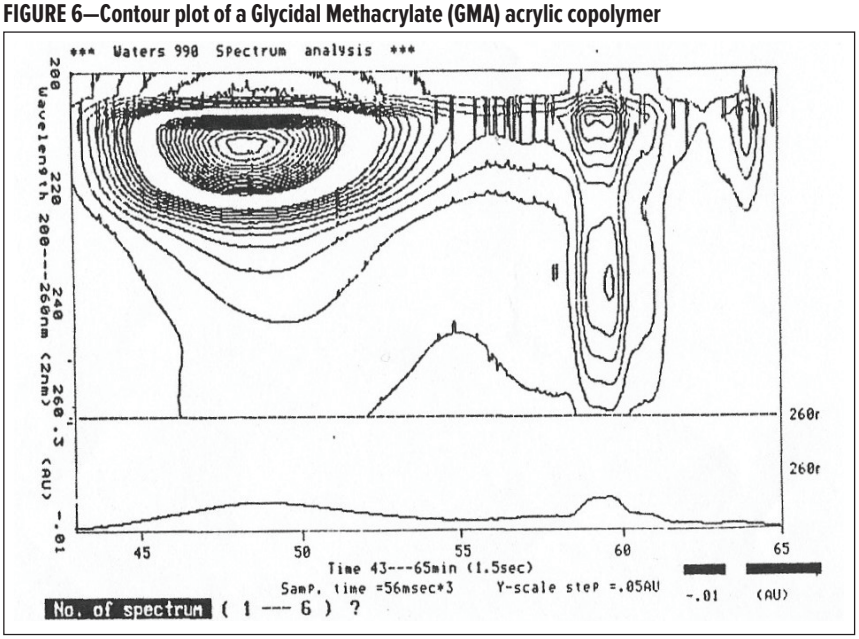


FIGURE 7—Spectrum index plot of an acrylic copolymer

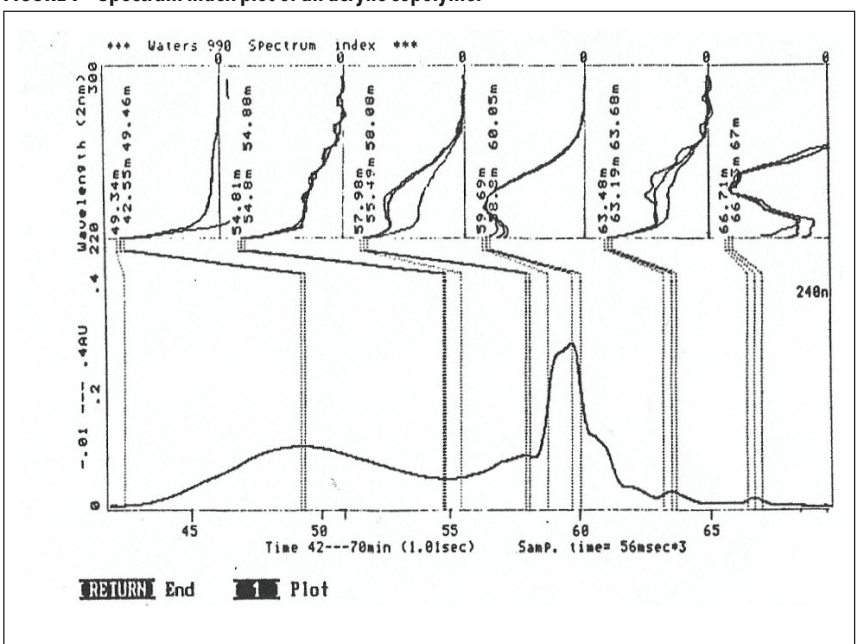
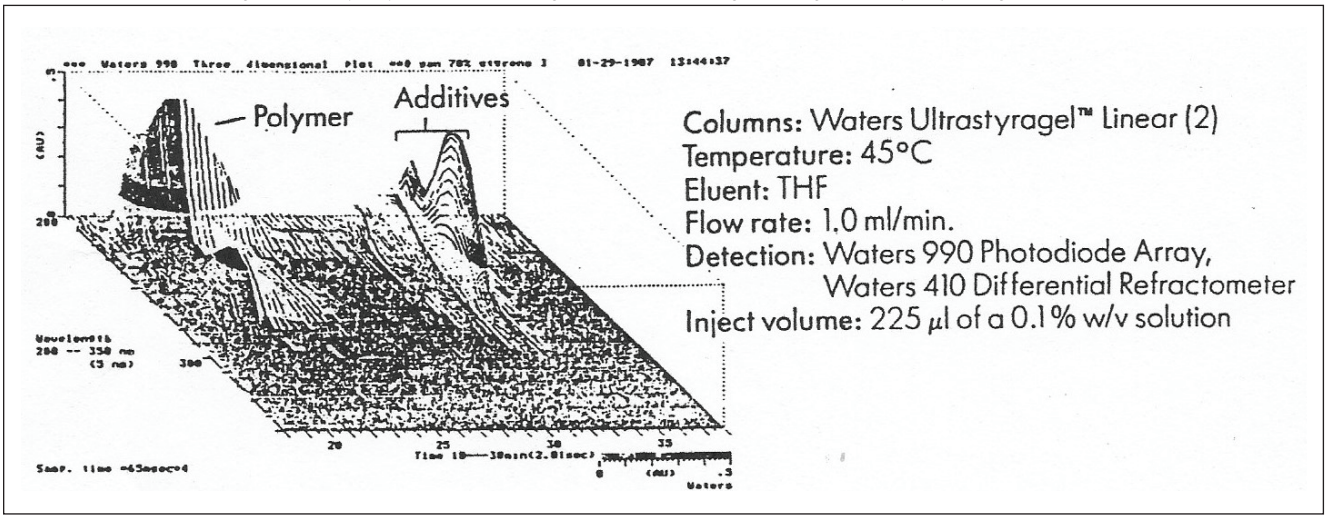


FIGURE 8—Photodiode array detection (PAD) estimate of the styrene content of a styrene acrylonitrile (SAN) copolymer



corresponding spectrum index plot. *Figure 8* shows an example of using PAD to estimate the styrene content of a styrene acrylonitrile (SAN) copolymer[104].

Although there are severe limitations in the use of the DRI detector, and there are many favorable attributes for functional detectors, the DRI detector is still the most widely used detector in the coatings field due to its simplicity.

Quantitative Compositional Molecular-Weight Distribution Considerations

The previous examples demonstrated that crucial qualitative information can he obtained about the composition of components in multicomponent copolymers and blends. Coatings systems typically contain three to six components with some present as minor constituents. To quantitatively determine compositional heterogeneity and/or distribution as a function of molecular weight is a rather formidable task for such complicated systems.

In addition, there are some complexities associated with using multiple detectors for determining the compositional heterogeneity of copolymers, as discussed by Mori and Suzuki[97] and Bressau[101]. These complexities include accounting for: (a) dead volume corrections, (b) hyperchromic shifts of copolymer detection wavelengths, (c) variance of monomer component absorptivity in the homopolymer to the copolymer, (d) validity of the copolymer molecular-weight scale or hydrodynamic volume calibration approach, and (e) mismatch of detector sensitivities in either the low or high-molecular-weight ranges of the chromatogram.

To experimentally determine the individual response factors, generally the homopolymers of the components are monitored by the appropriate detector at several concentrations[84,87]. The slope of the detector response (area under the appropriate SEC/detector trace) versus concentration (grams), which should be linear, is then the response factor for that component.

When the total polymer response is known as a function of retention volume, the molecular-weight distribution can he obtained in the usual manner with the appropriate molecular-weight calibration curve. The molecular-weight calibration curve can be obtained: (a) by using the Runyon[87] copolymer molecular-weight scale approach, or (b) by using a hydrodynamic volume approach if the Mark-Houwink constants for the polymer of interest are known or can be determined, or (c) by using a hydrodynamic volume approach in conjunction with an on-line viscometer detector.

SEC/LALLS/MALS

One of the absolute molecular-weight detectors finding increasing usage is the low angle laser light scattering (LALLS) detector[105-109]. The unique features of SEC/LALLS include: (a) simultaneous generation of the absolute molecular-weight calibration curve and generation of the absolute molceular weight distribution by using a DRI detector in conjunction with a LALLS detector, (b) beng an excellent detector for aqueous SEC because it can generate an absolule molecular calibration curve, (c) its use for high temperature measurement, especially for polyolefins, and (d) being sensitive to very high-molecular-weight polymers, e.g., microgel. LALLS detection can sense a high-molecular-weight component that sometimes escapes detection with an IR or DRI detector.

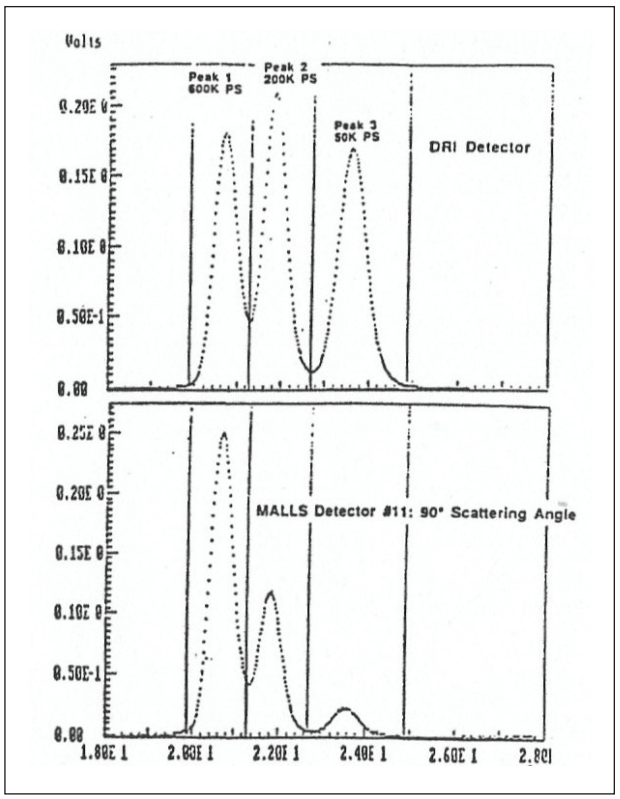
SEC/LALLS also has been used for the detection of shear degradation of polymers in SEC columns[110], simultaneous calibration of molecular-weight separation and column dispersion[111], measurement of Mark-Houwink parameters[112], determination of molecular weight and compositional heterogeneity of block copolymers[113], and in obtaining branching information in homopolymers and copolymers[114-124].

However, in using SEC/LALLS the analyst needs to be aware of some data analysis considerations: (a) specific refractive index increment, dn/dc, varies with molecular weight for low-molecular-weight polymers and is dependent on the composition of the copolymers; (b) virial coefficients depend on molecular weight; (c) transient noise spikes caused by bleeding of packing materials or elution of dust particles can occur; (d) there can be a sensitivity mismatch between LALLS and DRI (e.g., inadequate sensitivity in low-molecular-weight regions and detection of microgel in high-molecular-weight regions); (e) instrumental peak broadening can occur in the scattering cell; and (f) SEC/LALLS provides only qualitative indications of polymer chain branching.

The multiangle laser light scattering (MALS) detector DAWN® commercialized by Wyatt Technology[125] measures the intensity of light scattered at 15 angles simultaneously for the determination of absolute molecular weights and sizes, as well as important information about particle structures and distribution.

Figure 9 shows an example of SEC/MALS responses from DRI and MALS detectors for a three component polystyrene (PS) mixture[149]. It is seen that like LALLS, MALS is more sensitive to higher-molecular-weight components. *Figure 10* shows the variations of scattering intensities with angular position and retention volume. The radius of gyration (r_g) can be obtained from the angular dissymmetry[125].

FIGURE 9—SEC/MALS responses from DRI and MALS detectors for a three component polystyrene mixture



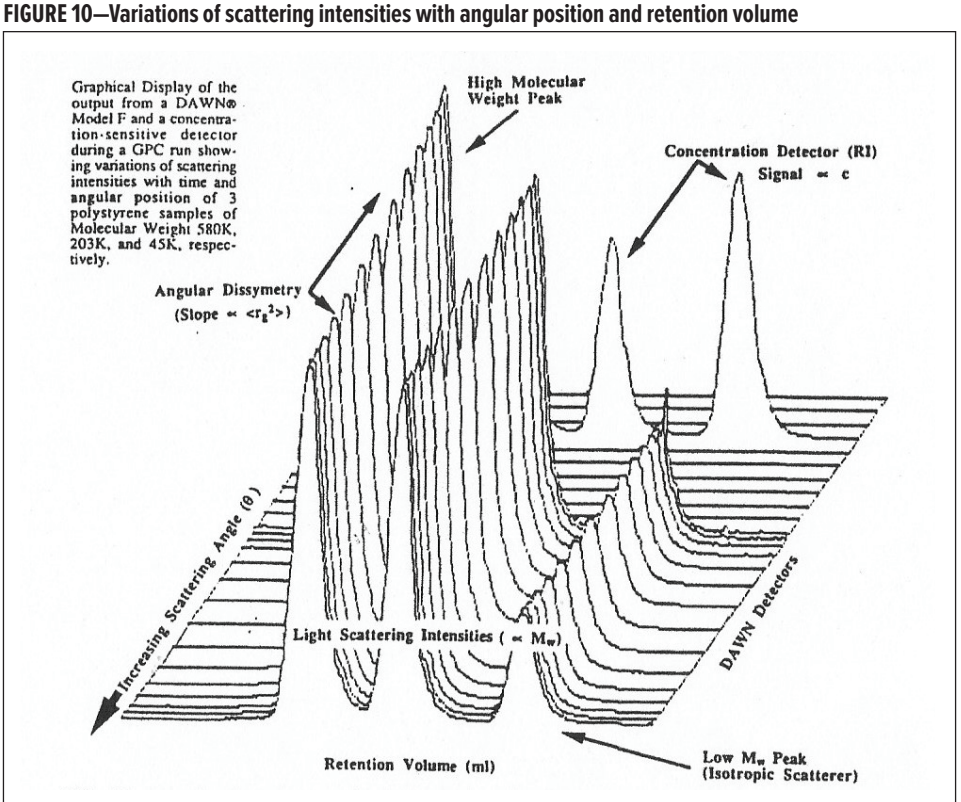
SEC/Viscometer

Another on-line SEC detector that can provide both absolute molecular-weight statistics as well as branching information is the viscosity detector. A discrete viscometric technique[126-135] involving the coupling of a Ubbelohde-type viscometer to measure the efflux time of each fraction was reported in early 1970. The disadvantage of this type of viscometer is that it is not a truly continuous detector.

With the speed and reduced column volumes and lower sample concentrations associated with modern high-performance SEC, this type of viscosity detector is not practical. In 1972, Ouano[136] developed a unique on-line viscometer which used a pressure transducer to monitor the pressure drop across a capillary continuously. Lesec[137-139] and coworkers described a similar and simpler on-line viscosity detector. In the authors' laboratory, a differential transducer has been used to monitor the pressure drop across a section of capillary tubing as the polymer fractions elute from the SEC column. The experimental apparatus and performance evaluation were described previously[140-141].

In 1984, the first commercially available continuous viscosity detector for SEC was introduced by Viscotek[142-143]. The main component is the Wheatstone bridge configuration consisting of four balanced capillary coils. Abbott and Yau[144] described the design of a differential pressure transducer capillary

FIGURE 10—Variations of scattering intensities with angular position and retention volume



viscometer, which is comprised of two capillary tubes, one for eluting sample solution and one for eluting solvent. The advantage of this device is that the measured signal is independent of flow rate and temperature fluctuations. A commercial viscosity detector was introduced by Millipore Waters Chromatography. This detector is based on the work reported in the literature by Lesec and coworker, and by Kuo, Provder, Koehler, et al.[140,141,145] The performance characteristics of the hardware and evaluation of the software were the subjects of two published papers[146,147].

Like SEC/LALLS, the viscosity detector is sensitive to high-molecular-weight fractions as shown in *Figure 11* for a three-component PS mixture. It is seen that the viscometer is more responsive to the higher-molecular-weight component. The usefulness of SEC/Viscometer detection is exemplified by the study of branched polymers.

Figure 12 shows the log [η] versus log $\mathbf{M}_w$ plots for two randomly branched polyvinyl acetate samples obtained from the SEC/viscometer technique. The deviation from linearity in the high-molecular-weight region can be clearly seen. Upon comparing the intrinsic viscosity with that of the linear counterpart at the same molecular weight, the branching index g' can he obtained as a function of molecular weight. It also was concluded that the sample in *Figure 12b* is more branched than the sample in *Figure 12a*. In addition, the SEC/viscometer coupling can provide absolute molecular-weight averages, bulk intrinsic viscosity, and Mark-Houwink parameters from a single SEC experiment[145]. Also, SEC/viscometer detection has been used to estimate polymer tacticity[148] and the determination of the radius of gyration (r_g)[149] as well as determination of absolute $\mathbf{M}_n$ [150]. Yau[149] also reported combining an on-line osmometer with a viscometer for GPC detection to determine absolute $\mathbf{M}_n$, polymer branching, and conformation.

An analyst using a SEC/viscometer should be aware of the following operational parameters that can produce errors in the data: (a) flow variations caused by pump pulsations, temperature fluctuations, and restrictions in SEC columns as well as in the

FIGURE 11—HPGPC DRI/VISC detector responses versus retention volume

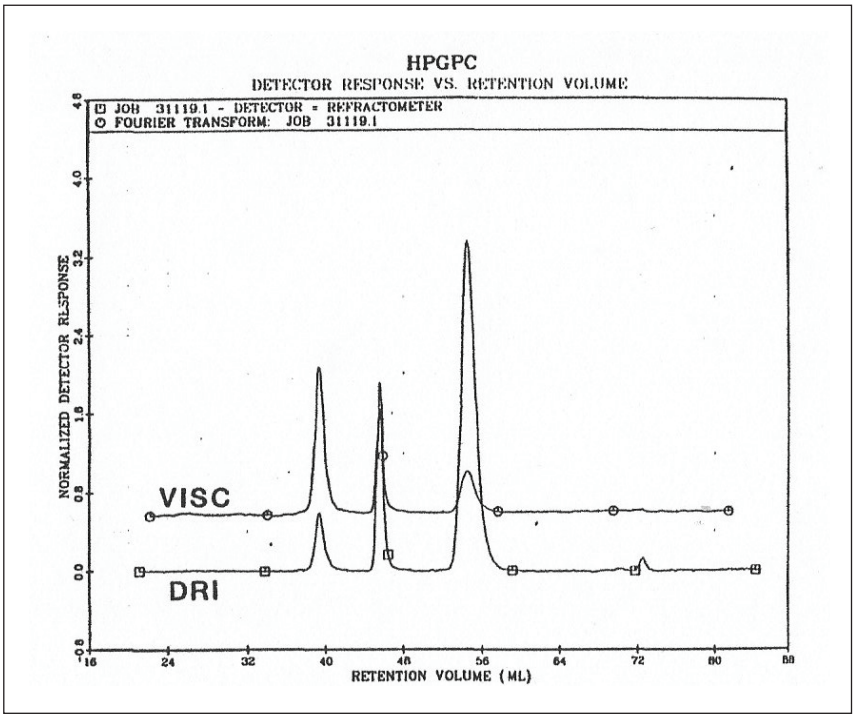


FIGURE 12—Log [η] versus log $\mathbf{M}_w$ plots for two randomly branched polyvinyl acetate samples

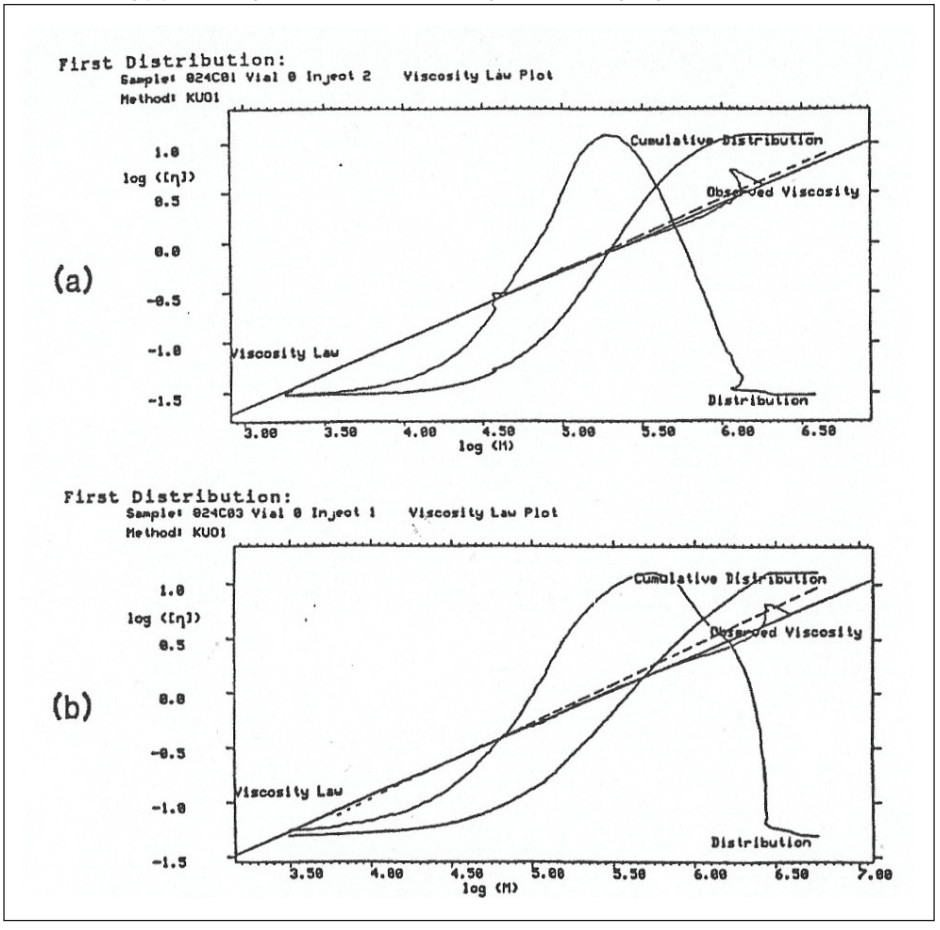


FIGURE 13—HPSEC chromatograms of two high solids polyester resin samples

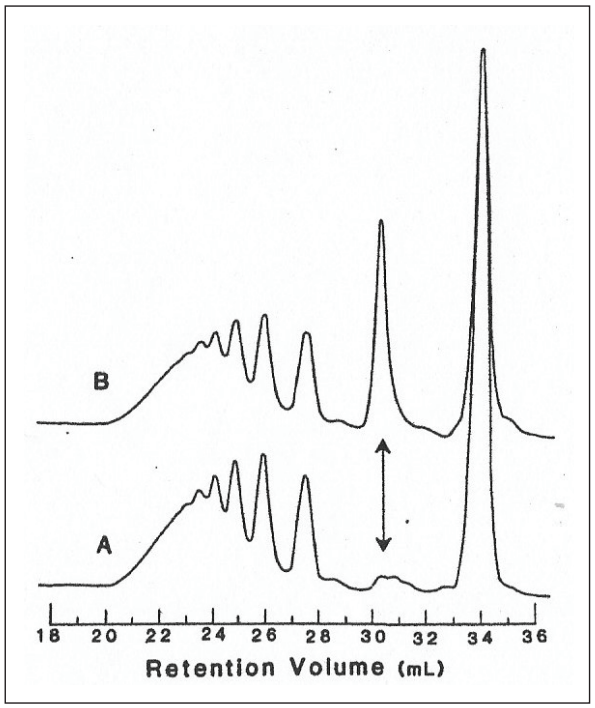
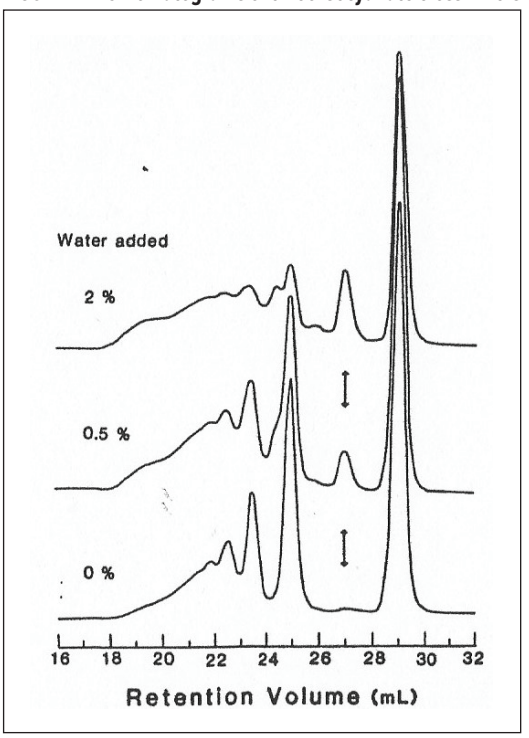


FIGURE 14—Chromatograms of three isocyanate crosslinkers



connecting tubing; (b) mismatch between the flow rate setting and actual delivered flow rate that can cause concentration errors; (c) finite dead volume between detectors that can produce a data offset between the DRI and the viscometer detector; (d) sensitivity mismatch between the viscometer and the DRI detectors in the high- and low-molecular-weight regions.

Oligomer Applications

The emergence of new coatings technologies such as high solids, powder, waterbome, and radiation curable coatings as a response to governmental regulations has led to the development of resin systems where the measurement of the oligomer and low-molecular polymer MWD is critically important to control the properties of these coatings systems.

The HPSEC technique, using high-efficiency columns, provides the necessary resolution in the low-molecular-weight region of interest for the above coatings systems. The high-efficiency columns result from the use of high-pore volumes and narrow particle-size distribution of microparticulate packing materials. The efficiency of a column is measured by plate count. For a typical HPSEC column with 10 μm or less, particle packing the plate count is usually on the order of 40,000 plates/meter in contrast to about 1500 plates/meter for conventional columns (37-75 μm particles).

The ability of a column to separate two adjacent peaks is expressed by the specific resolution, R_s, as derived by Bly[151]. For oligomer and small molecule applications, R_s values are usually obtained from various pairs of n-alkanes as reported in the literature[152-154] for a variety of HPSEC columns from various vendors.

The effect of operational variables (e.g., flow rate, particle size, column length, temperature, mobile phase, etc.) has been studied by various groups[155-158]. In general, the column-plate height decreases (efficiency increases) with decreasing flow rate until an optimum flow rate is achieved in accordance with the Van Deemter equation[159].

Consequently, to obtain high resolution, the flow rate should be kept as low as possible. For practical purpose, using THF as the mobile phase, the flow rate is usually set at 1 ml/min. The column efficiency also depends on the particle size of the packings as shown by Vivilecchia and coworkers[156]. Kato et al.[158] showed the effect of flow rate, particle size, and column length on the column-plate count.

With the advent of high-efficiency columns, HPSEC has become an indispensable characterization and problem-solving tool for oligomer analysis in environmentally acceptable coatings systems[153,160,161]. Specific applications include (a) quality control of supplier raw materials, (b) guiding resin synthesis and processing and (c) correlating oligomer distribution with end-use properties. Following are two examples:

(1) *Figure 13* shows the HPSEC chromatograms of two polyester resin samples. Sample A had good "shelf-life stability," while the Sample B was unstable over a two-week period. It is seen from the chromatograms that the peak, which eluted at retention volume ~30.5 mL, was present in excessive amounts for Sample B as compared to A. The component(s) under this peak for Sample B crystallized on standing, causing haze, and then precipitated. Identification of the presence and the amount of the component(s) under this peak helped resin chemists to control and eliminate the instability problem.

In powder coatings, some of the most frequently used curing agents are blocked isocyanate crosslinkers. It is well known that the level of moisture present in the coreactants will affect the MWD and properties of the resulting crosslinker. This is due to the high reactivity of the N = C = 0 functionality.

(2) *Figure 14* shows the chromatograms of three isocyanate crosslinkers made

with different amounts of added water present in the reactor. The one with 0% water added was a control. The other two samples were made with 0.5 and 2% of water being deliberately added as a co-reactant. The weight percent was based on the weight of one of the major coreactants. It is seen from the chromatograms that the molecular-weight distribution of the isocyanate crosslinkers made in the presence of added water is different from that of the control sample. In addition to the building up of the molecular weight, the level of the component eluted at retention volume ~27 ml is increasing with the amount of water added. A previous study showed that the presence of this component in excessive amounts was one of the reasons why this type of isocyanate crosslinker is overly reactive.

FUTURE TRENDS AND NEEDS

In the area of column technology, the development of the columns for ultra-high-molecular-weight ranges (MW > 10^6) are needed. There is a need for enhanced SEC/viscometer sensitivity for oligomers and small molecules. For SEC/UV, diode-array spectrometry providing a simultaneous multiwavelength scan will be advantageous for providing detailed compositional information for polymers with UV active chromophores. Using Fourier transform infrared (FTIR) detection for on-line polymer composition determination and identification would expand SEC capability to a significantly greater extent.

Current literature available for the application of FTIR to SEC in an on-line mode is limited[162-164]. In addition to the high cost of the FTIR detection, the main obstacle is the availability of a suitable flow-through cell to overcome mobile phase spectral interference and low solute concentration. For complex polymers, the technique of orthogonal chromatography[165-167] or cross-fractionation chromatography[168-175] should he explored. For oligomers, supercritical fluid chromatography (SFC)[176-180] has a significant potential. Chromatographic methods for gel content determination now are more feasible with LALLS and viscometric detectors and should be reexamined[181-185].

In the future, significant progress on the detection problem in compositional analysis will be made. There is still a need for improved analysis capability in the ultra-high-molecular-weight range. Improvements in detector sensitivity, column technology, and the application of chemometrics to SEC analysis will facilitate progress in this area. In addition, advancements occurring in thermal field flow fractionation (ThFFF)[186-197] show great promise. This overview covers only nonaqueous SEC. For the theory, practice, and applications of aqueous SEC, the reader is referred to the literature [198-208].

SUMMARY

A review of the SEC separation mechanism, molecular-weight calibration methods, and instrument spreading correction methods has been given. In addition, examples were shown for the application of multiple detectors to the determination of absolute molecular-weight distribution of polymers, compositional distribution as a function of molecular weight of copolymers, and branching information for nonlinear polymers.

Examples also were shown where HPSEC can be used for guiding polymer synthesis and processing, correlating oligomer distribution to end-use properties, and monitoring the quality of supplier raw materials. HPSEC has become an indispensable characterization and problem-solving tool for the analysis of oligomers and polymers in the plastics rubber, and coatings industries. The information generated by means of the HPSEC technique has significantly aided polymer chemists and coatings formulators to tailor-make coatings systems to meet specific end-use properties. ❄

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