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Liquid Chromatography of Polymers

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I. INTRODUCTION

A. Overview of Liquid-Phase Chromatography

Modern high-performance liquid chromatography (HPLC) is a versatile analytical technology that can provide a range of essential information about the soluble components of plastics, including the base polymer, the formulated resin, and the additives. All modes of HPLC use a column packed with materials to separate species in a complex mixture. In some modes of HPLC the separation is based on differences in chemical composition or selectivity. The mode of HPLC that is most familiar to polymer analysts is gel permeation chromatography (GPC). It is also termed size-exclusion chromatography (SEC).

As suggested by the names, the mechanism of separation in GPC/SEC is based on apparent size differences among the sample components in solution. This makes it especially useful for characterizing polymers. This chapter focuses primarily on the use of GPC and to a lesser extent on HPLC in plastics analysis. While gas chromatography (GC) is also used extensively for characterizing monomers and some polymers, it is beyond the scope of this review.

B. Molecular-Weight Distribution of Polymers

Monomers, the building blocks of polymers, have a single molecular weight. As low-molecular-weight organic compounds, they are monodisperse. Typical monomers include styrene, ethylene, and phenol. At the onset of polymerization these molecules combine to form oligomers such as dimers, trimers, tetramers, and so on. Ultimately, the growing chains of molecules reach sufficient size to be termed polymers. At this stage not every molecule contains the exact same number of monomer units. This results in a distribution of chain lengths or molecular weights. Depending on the type and conditions of polymerization, this molecular-weight distribution can be very narrow or quite broad. For example, a condensation, or step-growth polymer such as a polyester, poly(ethyleneterephthalate), will have a narrow distribution of molecular weights. Conversely, a free-radical polymerization of an olefin such as ethylene may produce a polyethylene polymer with a very broad distribution of chain lengths and molecular weights.

Both the molecular-weight distribution and the average molecular weight are among the most important determinants of the polymer performance. This encompasses the physical properties of the polymer as well as its processability [1]. Consequently, it is vital to be able to accurately measure molecular weights and molecular-weight distributions for many purposes. These uses include controlling the kinetics of the polymerization to achieve a desired distribution, ensuring the quality and consistency of incoming materials that will be formulated and fabricated, evaluating competitive materials and diagnosing an undesired change in performance.

The widespread use of gel permeation chromatography is due to its ability to accurately and reproducibly determine polymer molecular-weight distributions and to distinguish subtle differences between closely related samples. Figure 1 shows the slight shifts in molecular-weight distribution of a polypropylene sample at various points in the injection-molding process, especially before and after the gate. The profiles for the pellet and the sample taken from the runner are offset for ease of comparison.

C. Composition and Chemical Structure

While polymer molecular-weight average and distribution have a major influence on behavior, many other factors are also very significant. The structure of the polymer chain, polymer chemical composition, and the additive packages may all play a key role. For example, a polymer chain structure that is linear will have very different thermal and processability characteristics than one that is branched. Of course the chemical composition of the monomer or the use of two or more monomers to produce a copolymer or terpolymer will often account for greater differences than a

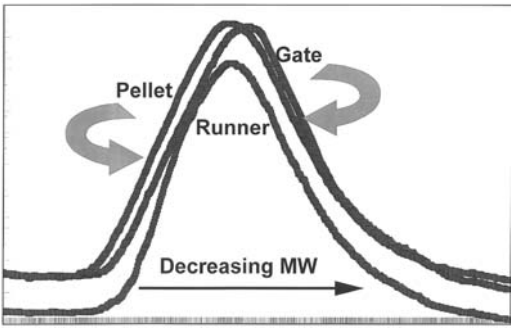


Figure 1 Injection molding effects. Solvent: 1,2,4-trichlorobenzene. Temperature: 140°C. Columns: Styragel HT6, HT5, HT4, and HT3. The shift in the molecular-weight distribution of the "Gate" sample may be due to melt shear-induced reduction of the largest molecules after passing through the mold gate.

slight shift in molecular-weight distribution between two samples of the sample polymer type. The vital role of additives is also well known.

In addition to molecular weight and distribution, modes of HPLC can also be used to characterize polymer structure, polymer composition, and additives. Sections II.D. and III.B describe the use of multiple-detector GPC for measuring branching and other aspects of polymer structure, while Secs. II.F and III.C contain brief examples of additive and copolymer analysis by HPLC.

D. Gel Permeation Chromatography

GPC is the most predictable mode of HPLC. The separation is based on the size of the sample in solution, not the molecular weight. There must not be any interaction with the column packing material (adsorption, partition, etc.), as there is in other modes of HPLC. GPC column packings are particles of cross-linked gel that contain surface pores. The sizes of these pores are controlled and vary from small to large. They act as a molecular filtration system. The most widely used gels are styrene/divinylbenzene copolymers for organic solvent-soluble polymers and acrylate gels for water-soluble polymers.

In practice, the polymer is dissolved in a suitable solvent and a small sample of the dilute polymer solution is injected into a solvent (usually the same as the polymer solvent) that is being pumped through the columns. For most applications, several columns of varying pore size are connected in

series. When the column packing porosity range is chosen properly, the largest polymer molecules in the distribution will fit into only a few of the pores and will pass through the columns primarily in the interstitial volume between the packing particles. They will elute sooner than the smaller polymer molecules that can fit into more of the pores and therefore be retained in the columns longer. The solvent path out of the column is through one or more detectors that can sense the presence of the polymer fractions as they elute. The detector signal is then recorded as a chromatogram showing the distribution of the various size components in the sample, proceeding from largest to smallest. The amount of each fraction corresponds to the height of the peak.

The schematic separation shown in Fig. 2 represents the molecular-weight (MW) distribution of the polymeric gum base used in chewing gum, followed by the lower-MW components in decreasing order of size. A similar example could be a chromatogram of PVC with a mixture of plasticizers, antioxidants, and UV stabilizers.

One of the original techniques for using GPC was simply to superimpose the chromatograms of two or more samples and display regions of difference in the distribution. This was used to explain differences in behavior, Fig. 3, or to establish acceptance envelopes for incoming materials, Fig. 4. Note the detail of the oligomeric region of the uncured phenolic resin in Fig. 4. Also, recall that since GPC is performed with dilute solutions of the polymer sample, this type of analysis is only suitable for thermosetting resins and elastomers before they are cured.

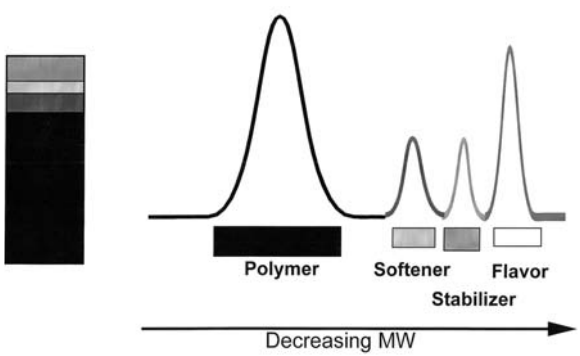


Figure 2 GPC example: chewing gum. The chromatogram is not to scale—the stabilizer and flavor peaks would probably be much smaller and would consist of one or more monodisperse peaks instead of the distribution shown to illustrate the size separation concept.

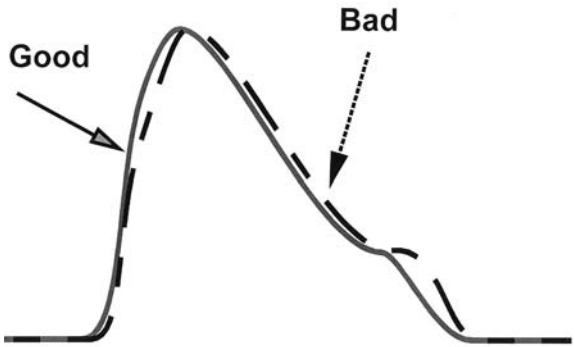


Figure 3 Comparison of results. Many differences in properties or processability of polymers can be explained by comparing molecular-weight regions. In this example the bad sample has slightly less high-molecular-weight and more low-molecular-weight content than the good sample.

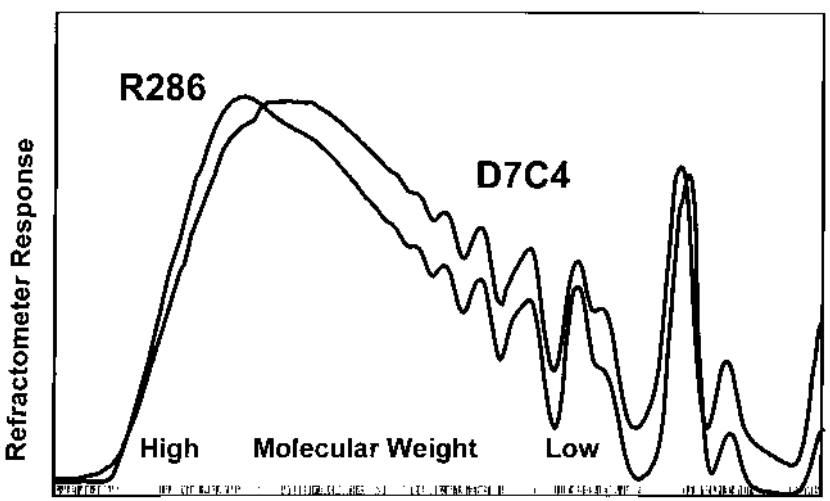


Figure 4 Phenolic resins from different vendors. GPC is useful for incoming quality control, technical support, and competitive analysis. Differences in the molecular-weight distributions of these two phenolic resins could correspond to acceptable and unacceptable processability or performance.

With an understanding of the influence specific molecular-weight regions have on behavior, this can be a very useful way to use GPC information. However, for many purposes it is desirable, if not essential, to be able to quantify the molecular-weight values.

E. Polymer Characterization: Molecular-Weight Values

In order to assign numerical values to the GPC chromatogram, it is divided into a number of vertical slices and treated statistically, Fig. 5. When a mass-sensitive detector is used in the GPC system, the height of each slice, H_i corresponds to the number of molecules present in that slice. The retention time (or volume) of that slice is assigned a molecular weight value, M_i, which is obtained from a calibration curve, such as that shown in Fig. 6. Calibration methods are discussed in Sec. II.B.

Once values for H_i and M_i are assigned to each slice, the summations indicated in Fig. 5 are performed to obtain the various molecular-weight averages that describe the molecular-weight distribution. The values are statistical moments of the distribution, while PD, the polydispersity, is an indication of the narrowness of the distribution.

There are other techniques for determining the various molecular-weight averages. Number average, Mn, can be obtained by membrane osmometry or end-group analysis. Weight average, Mw, is determined by

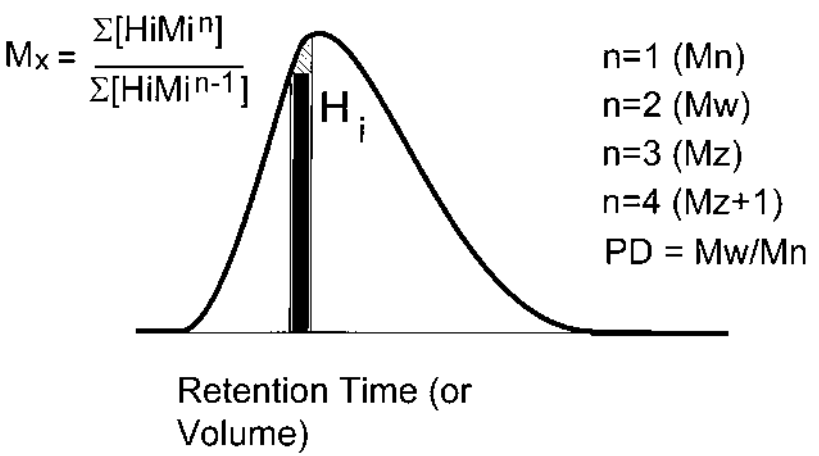


Figure 5 A number of molecular-weight averages are calculated from the distribution curve to fully define the distribution.

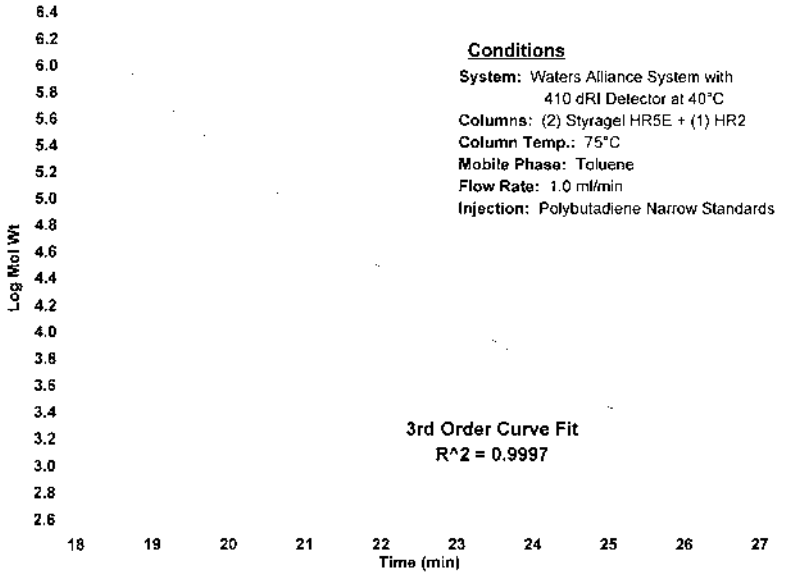


Figure 6 Polybutadiene calibration. The curve is developed for a specific column set with the same solvent and at the same conditions that will be used to characterize unknown samples.

light scattering, while Z and $Z + 1$ averages, M_Z and M_{Z+1} are measured by ultracentrifugation. GPC is unique in that all of these averages can be obtained in a single analysis.

The value in determining the different molecular-weight averages is related to the influence that various molecular-weight fractions have on properties and behavior. For example, additional high-molecular polymer chains may change the flexibility of the polymer to a much greater extent than the same number of low-molecular chains in the material. Raising the molecular weight to a higher power in the calculation of Mz than in the calculation of Mn reflects the greater influence of these longer chains. Mz is related to elongation and flexibility, while Mn is related to brittleness and flow properties. The region of the molecular-weight distribution where each of these molecular-weight averages occurs is shown in Fig. 7. MP is the only chromatographic value in the figure, corresponding to the peak molecular weight.

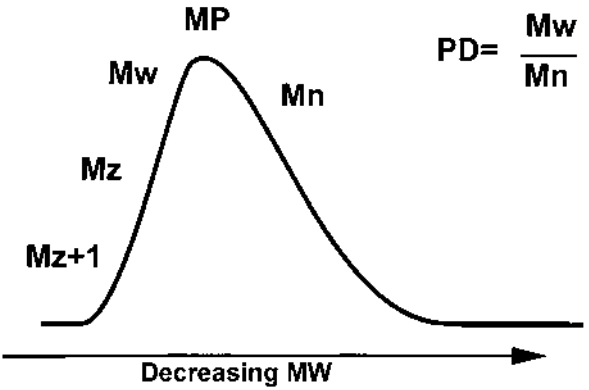


Figure 7 The calculated molecular-weight values correspond to regions of the full distribution. The peak molecular weight, Mp, is not calculated but read directly from the chromatogram. The polydispersity, PD, is the ratio of the weight-average to number-average molecular-weight, an indication of the broadness of the molecular-weight distribution.

F. Structure–Property Correlations

The relationship between certain molecular-weight averages and properties extends beyond the brief examples mentioned in the preceding section. Various studies and correlations have been published [2–5].

Weight-average molecular weight, Mw, is related to characteristics such as tensile strength and impact resistance. The actual relationship may be the consequence of molecular weight and structure contributing to the balance of amorphous and crystalline regions, which in turn influence physical behavior. This is shown in a study of three polypropylene samples that were characterized by GPC, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and melt rheometry. Molecular-weight values and intrinsic viscosity were determined by GPC. Enthalpy of melting, a measure of crystallinity, was determined by DSC. Tan δ, the ratio of loss modulus to storage modulus, a measure of amorphous content at glass transition, was measured by DMA, and zero-shear melt viscosity was measured by melt rheometer. The results appear in Tables 1 and 2.

The most apparent correlation is between the rheology and the GPC measurements. The samples had a broad range of melt flow index values, the amount of material that will flow through a standard oriface in 10 min under a fixed combination of temperature and pressure. Higher melt flow index values indicate a greater tendency to flow. The most frequently

Table 1 Correlating GPC and Rheology

Sample melt flow [g/10 min]	Mn $\times 10^3$	Mw $\times 10^3$	Intrinsic viscosity (solution) (η)	Zero shear viscosity (melt) [Pa.S]
30	26	201.4	1.26	2,960
10	44	275.5	1.47	3,990
1.8	69	328.6	1.76	41,800

When comparing the same type of polymer, molecular weight and flow properties may correlate very strongly, as shown for these polypropylene samples.

reported molecular-weight values, number average, Mn, and weight average, Mw, decreased as melt flow index increased. Lower-molecular-weight polymers contain shorter polymer chains that will entangle less often in flowing conditions and therefore have less resistance to flow. Hence the higher melt flow index samples had lower dilute solution viscosity and melt viscosity values with decreasing molecular weights. The intrinsic viscosity was determined with a GPC system containing a viscometer detector. More information is given in Secs. II.D and III.B.

As suggested above, the influence of molecular weight on various mechanical properties may, in some instances, actually be attributed to differences in the degree of crystallinity, which, in turn, is related to chain length. Longer polymer chains may be less mobile and therefore sterically inhibited from alligning as many chain segments into ordered, crystalline regions as the shorter polymer chains. This simplified mechanistic model is supported by the values listed in Table 2. Enthalpy of melting shows more

Table 2 Correlating GPC and Thermal Analysis

Sample melt flow [g/10 min]	Mn $\times 10^3$	Mw $\times 10^3$	Enthalpy of melting ΔHm[a] [J/g]	tan δ @ Tg[b]
30	26	201.4	99.5	0.053
10	44	275.5	96.7	0.061
1.8	69	328.6	95.4	0.072

Thermal and thermal mechanical properties are related to crystallinity, which in turn can be influenced by molecular weight.

[a] Increases with higher crystallinity (less amorphous).

[b] Increases with lower crystallinity (more amorphous).

crystallinity with the lower-molecular-weight samples, while tan δ, a measure of toughness contributed by the amorphous region of the polymer, also shows more crystallinity (less amorphous material) at the lower molecular weight.

Any such analysis is valid only for a closely related set of samples of the same polymer type. Otherwise, factors such as chemical composition of the polymer, differences in degree of branching, or presence of additive packages can overshadow the contributions of shifts in molecular weight. In addition, the history of the sample may also account for a difference in behavior. Recall in Fig. 1, the shift in the MW distribution toward the lower range due to the melt shear imparted to the resin during the injection-molding operation. This also suggests the utility of monitoring molecular-weight profiles to estimate the amount of regrind that can be used without impairing performance.

II. CHROMATOGRAPHY PRACTICES

A. System Configuration

All HPLC systems, including GPC, employ a pumping system to deliver a steady flow rate of solvent through the columns and detectors. There is also some means of introducing the sample solution into the flowing solvent before it enters the columns, as well as a data handling device. The components may be modular or incorporated into an integrated system. Manufacturers of GPC systems are listed in Appendix E. Whatever the configuration, the pumping system is the key to the performance of the system. It must be a sophisticated fluid manager capable of delivering flow accurately, reproducibly, and smoothly. The significance of flow precision is illustrated in Sec. III.A.

The most basic GPC system consists of a basic, single solvent delivery system, a sample injection device, columns, and a differential refractometer detector. The sample injection mechanism can be a simple, single-sample, manually activated valve or an autosampler for unattended processing of multiple samples. A basic modular system with autosampler is shown schematically in the top section of Fig. 8.

Numerous variations and enhancements are available for many of the system components. Solvent delivery systems that operate with multiple solvents to produce programmable changes in composition during the course of the analysis are used often. This enables the system to also perform HPLC analysis of additives or oligomeric resins such as phenolics and epoxies. For these applications it is also necessary to use additional detectors, such as the photodiode array (PDA) detector indicated in the middle

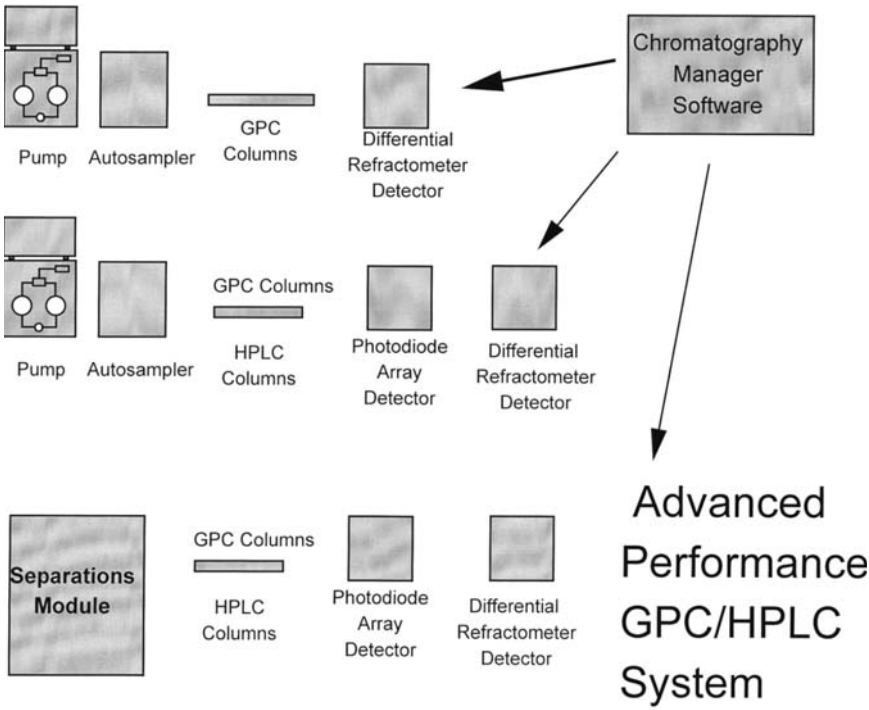


Figure 8 Primary components of modern GPC/HPLC instruments.

system of Fig. 8 (see Secs. II.D and F). Manufacturers of complete HPLC systems are listed in Appendix E.

Some of the other components commonly found in GPC systems are column heater compartments and solvent degassers. The column heater is often used, even for polymers that are soluble at room temperature, to reduce solvent viscosity and ensure uniform column operating conditions, despite any fluctuations in room temperature. The solvent degasser is located before the pump intake. Degassing prevents noisy signals caused by intermittent outgassing in the refractive index detector. In all systems the data management system is essential. It can range from a simple strip-chart recorder or integrator to a computer-based software package that can control the system as well as processing the data and reporting the results. See Sec. II.E.

The lower system schematic in Fig. 8 shows a module in which the pumping system and autosampler have been integrated into a single Separations Module. This unit, the 2690 Separations Module, is the basis

of high-performance HPLC and GPC Alliance Systems that combine the high performance and capacity of the solvent and sample management with the flexibility of detector choices according to the ways the system is to be used. It can be used for single-solvent (isocratic) GPC work or for up to four solvent gradient separations of additives and oligomers. It offers the option of integral solvent degassing. A number of design enhancements incorporated into the 2690 significantly improve GPC performance associated with traditional gear-driven dual reciprocating-head pumps. The two heads are independently microprocessor controlled, producing extremely smooth, precise flow that contributes to exceptionally reproducible molecular-weight values. See Sec. III.A. Figure 9 is a photo of a basic Alliance HPLC/GPC System using a refractive index detector, while Fig. 10 depicts the major internal configuration of this system.

Figure 9 A versatile integrated solvent and sample management module configured with modular refractive index detector for performing basic GPC.

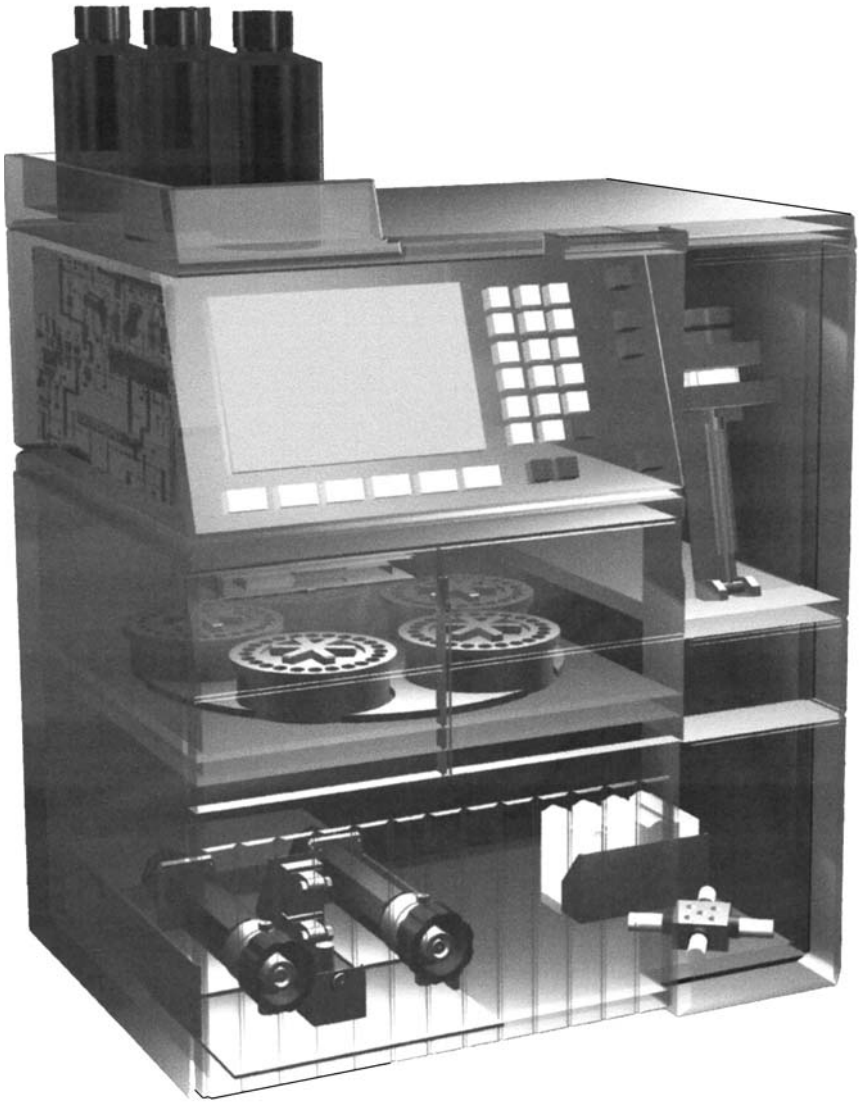


Figure 10 The primary components of the system shown in Fig. 9 include the control panel (upper left), injection mechanism (upper right), autosampler carousels (mid-level), independently driven dual reciprocating solvent delivery pistons (lower left), and degasser/solvent select module (lower right).

In order to perform GPC of polyolefins and other polymers that are only soluble at elevated temperatures, a completely integrated system is used to ensure that solvent, injector, columns, and detector are all maintained at temperature to preserve solubility and provide greatest reproducibility. Such systems are produced by Polymer Laboratories and Waters Corp. The Waters Alliance GPC 2000 System is shown in Fig. 11. It features the same innovative flow management design as the 2690 Separations Module, plus a precise dual-temperature-zone injector and the option of single detection with integral differential refractometer or dual detection with refractometer and viscometer. See Secs. III.B and III.D. The autosampler can agitate the samples by spinning to ensure complete solubility and homogeneity and also filter the samples. This is especially useful for samples prepared from filled materials or elastomers that may contain gels. The agitation and filtration operations take place in the pre-injection zone, which is thermally isolated and independently controlled relative to the holding positions in the autosampler. They can be at the same temperature or the pre-injection zone temperature can be set higher than the holding positions. This enables the samples to be injected at temperature without impairing sample stability while in the queue. The benefits of the integrated system and the sample processing capabilities can also be applied to ambient soluble polymers.

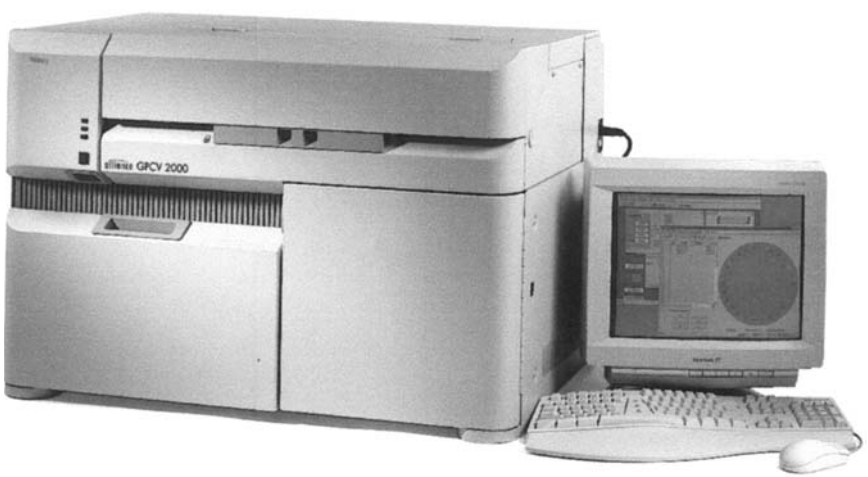


Figure 11 A completely integrated, automated GPC system capable of analyzing samples ranging from those soluble at ambient conditions to those which are only soluble at temperatures up to 180°C.

B. Column Conventions: Selection and Calibration

To ensure that a representative molecular-weight distribution is obtained, it is critical to choose the correct columns. This refers to the correct packing pore sizes to maximize the resolution in the molecular-weight range of concern. The solvent must also be considered. GPC is a separation technique based on the size of the polymer in solution, and the solvent will influence the conformation of the polymer in solution. The solvents that are most suitable for specific polymers are listed in the Appendix.

Column designations are related to the pore size of the packing, but the numerical grades are not the actual pore size. Instead, they are the nominal size (in solution) of the smallest polymer molecule that will be excluded by that column. That is, all polymers of that size and larger will not fit into even the largest pores and will be excluded by the column. So a 10^3 Å column will exclude all polymer chains in the sample that have an effective size in solution of 10^3 Å or greater.

For convenience, the organic soluble polymer molecular-weight ranges corresponding to the specific column designations have been tabulated in Table 3.

The breadth of molecular-weight ranges for any one column is a consequence of the variety of polymer types that are characterized by GPC. Furthermore, the process of producing the porous, cross-linked packings results in a narrow but finite distribution of pore sizes. Typically, three or more columns representing a range of pore sizes are used in series to provide adequate resolution and ensure that the full molecular-weight range of the samples is evaluated.

Table 3 Organic Soluble Polymer Molecular-Weight Ranges Corresponding to the Specific Column Designations

MW range	Column (Å)
100–1000	50
250–2500	100
1000–18K	500
5000–40K	10^3
10K–200K	10^4
50K–1M	10^5
200K–> 5M	10^6
500K–~ 20M	10^7

For example, to analyze a low-molecular-weight material such as an uncured epoxy resin, a suitable column set would be one each of 10^3, 500, 100, and perhaps a 50. For a medium-molecular-weight PVC sample a likely column set would contain a 10^3, 10^4, and 10^5. Choosing individual pore sizes targeted at the molecular-weight range of the polymer provides the highest resolution. If the molecular-weight range is not known or is very broad, there are also mixed-bed, or "linear" columns that contain blends of packings to provide an extended range of use, over several orders of magnitude of molecular weight. The trade-off is a loss of resolution within any specific polymer molecular-weight range, so multiple columns are also needed with these mixed bed types to achieve the necessary resolution.

For some applications mixed-bed columns are combined with individual-pore-size columns for optimum utility. Using two mixed-bed columns plus a 500 Å provides extra pore volume at the low-molecular-weight "tail" of the distribution and ensures that all polymer chains will be well resolved from any low-molecular-weight additive or impurity peaks that may appear at the end of the chromatogram.

There are other factors to consider when choosing a column, especially the particle size of the packing materials, the column dimensions, and the solvent in which the column is packed. For GPC of polymers in organic solvents, columns are commercially available prepacked in some of the most frequently used solvents. Particle size influences the ruggedness and resolving power of the columns, while column length can also affect resolving power and diameter relates directly to solvent consumption.

Once the column set has been chosen and assembled, it must be calibrated to enable calculation of the molecular-weight and polydispersity values. As noted in Sec. I.E, calibration enables assignment of molecular-weight values to each retention-time slice of the raw chromatogram. There are several ways to perform a calibration. The simplest is to use a relative calibration based on a set of well-characterized polymer standards, each with as narrow a molecular-weight distribution as possible.

The ideal standards are monodisperse, with $Mw/Mn = 1$. There are polymer standards that are polymerized specifically for this use, such as anionically polymerized polystyrene. They have dispersity of < 1.10 and cover molecular weights ranging from monomer to $> 10{,}000{,}000$. Other narrow standards available for organic solvent GPC include poly(methylmethacrylates), polyisoprenes, polybutadienes (Fig. 6), and poly(THF), while poly(ethylene oxides), poly(ethylene glycols), and pullulans (polysaccharides) are used for aqueous GPC.

Polystyrene is the most frequently used narrow standard for organic GPC analysis. A series of the narrow standards of known molecular weight

are analyzed using the same conditions that will be employed with the samples, especially flow rate, injection volume, and concentration. Then a plot of log MW versus retention time (or volume) is generated with a polynomial fit, usually third (Fig. 6) or fifth order. The values are taken from this curve to calculate the molecular-weight averages of the samples.

This conventional narrow standard calibration procedure yields "relative" molecular-weight values because the averages obtained are relative to the calibration polymer. For example, if polyethylene molecular weights are determined with a calibration curve produced with polystyrene narrow standards, the results would be incorrect for polyethylene. For many purposes relative molecular-weight values are adequate, since the results obtained with an unknown sample may be compared to preestablished acceptable relative values. If narrow standards of the same polymer as the unknown sample are available, then it is possible to calculate "absolute" values.

Other calibration techniques that enable determination of "absolute" molecular-weight values include broad standard calibration [6] and universal calibration [7]. The broad standard approach uses a polymer of the same type as the sample for which the various molecular-weight averages have been characterized by alternative methods such as membrane osmometry, light scattering, and ultracentrifugation. These molecular-weight averages are entered into the software and the broad standard is chromatographed by the same conditions used for the samples. The software does a Simplex search routine, fitting the broad standard chromatogram to the given molecular-weight averages.

The resulting broad standard calibration curve will consist of the data points for each average. If only number- and weight-average molecular-weights are available, the resulting calibration curve will consist of these two points plus the peak molecular-weight, or a three-point calibration curve. This is in contrast to a typical nine-point minimum that is common with narrow standard calibration. However, for the QC lab regularly testing the same polymer in the same molecular-weight range as the broad standard, this is sufficient to produce absolute molecular-weight values.

Modern GPC systems incorporating viscometry detection together with the differential refractometer are able to generate universal calibration curves and from them determine absolute molecular-weight values. In 1967 Benoit and co-workers introduced the concept of universal calibration. Instead of plotting the log molecular-weight M versus retention time, the log of the product of intrinsic viscosity [η] times molecular-weight M is plotted versus retention time. This product, [η]M, is related to the hydrodynamic volume of the polymer in solution.

The hydrodynamic volume is the reciprocal of density, so the plot of log (volume/mass) versus time becomes independent of the polymer type, enabling construction of the universal calibration curve, Fig. 12. This concept is applicable to all random-coil polymers, the most commonly used synthetic polymers. Other conformations, such as rods, spheres, or globular, may not comply with the universal calibration approach.

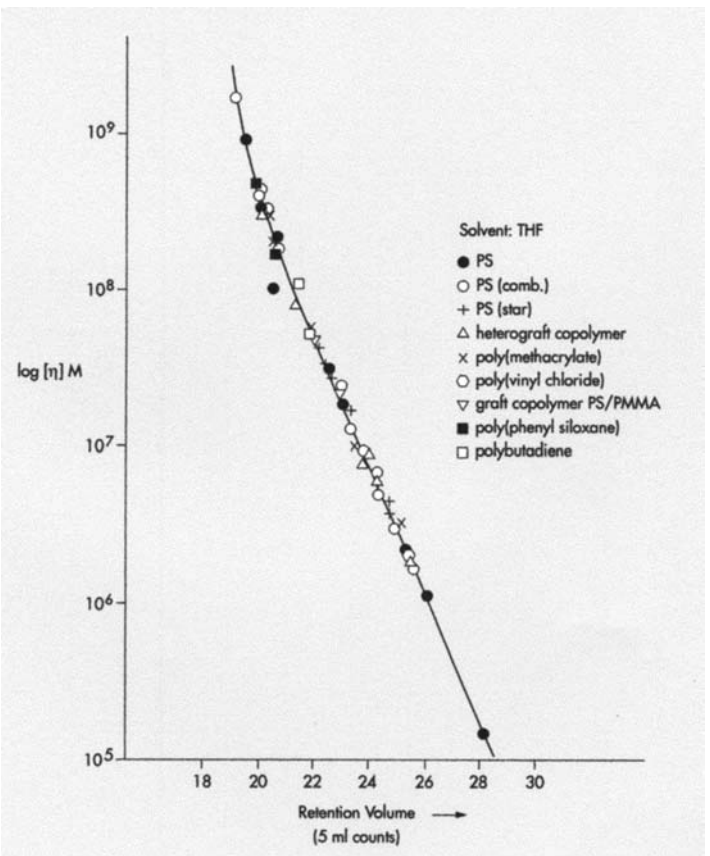


Figure 12 The universal calibration curve makes it possible to determine the absolute molecular-weight values for a polymer even if standards of the same chemical composition are not available.

C. Sample Handling and Solvent Considerations

GPC analysis is a dilute solution procedure. Among the most frequently used solvents for characterizing synthetic organic polymers, tetrahydrofuran (THF) is probably the most common. Toluene is also popular, especially for elastomers. Appendix A–D contains an extensive list of solvent/polymer combinations plus information about the solvents. Depending on the effectiveness of the solvent that is being used, the molecular-weight range of the polymer, and its crystallinity, preparation of the standard and sample solutions will take time. This usually requires a few hours. Gentle stirring or shaking can be used, but high-speed mixing, ultrasonic, or microwave dissolution should not be used without first determining if it causes shear degradation or other damage to the polymer. Polyolefins and some other classes of polymers are soluble only at elevated temperatures. They are also listed in Appendix C.

The appropriate polymer concentration is somewhat a function of the molecular-weight. It must be high enough to produce a good detector signal but low enough to avoid column overload and resulting concentration-related viscous effects that can skew the results. The ranges shown in Table 4 are based on experience with typical analyses in which the sample injection size is 100 μL per 7.8 mm ID × 30 cm column in a set. Concentrations are mass/volume, so 0.10% is 1.0 mg/mL.

In GPC, the solvent in which the standards and sample are dissolved should be identical to the mobile-phase solvent in which the analysis will be performed. In most cases filtration is the only step needed to prepare the mobile phase. Organic solvents should be vacuum filtered through a 0.45-μm fluorocarbon filter, while acetate-type filters are used with aqueous mobile phases. In some cases mobile-phase additives are required. When polar solvents such as N,N-dimethyformamide, N,N-dimethylacetamide, and *n*-methyl pyrrolidone are used to analyze polar polymers such as poly-

Table 4 Polymer Concentrations

MW range	Concentration range (%)
> 1,000,000	0.007–0.02
500K–1,000,000	0.02–0.07
100K–500K	0.07–0.10
50K–100K	0.10–0.13
10K–50K	0.13–0.16
< 10K	0.16–0.20

urethanes or polyimides, a dipole interaction can occur, causing artificial shoulders to appear on the high-molecular-weight end of the distribution. This interaction is eliminated by adding 0.05 M lithium bromide to the solvent.

Salts are also used in aqueous GPC because the methacrylate-based gel packing has a net anionic charge. This can cause ion exclusion with anionic samples and ion adsorption with cationic samples instead of the simple size-exclusion separation mechanism that is essential for valid GPC. Sodium nitrate is the preferred salt for minimizing these ionic interferences

D. Detection Options

There are a number of detection options, some used primarily for GPC and others that have use for GPC as well as other modes of HPLC. The differential refractometer, viscometer, and light-scattering detectors are associated mostly with GPC, while absorbance detectors such as the UV/visible or photodiode array (PDA) are widely used in all HPLC modes, including GPC. The UV/visible and PDA are especially useful for characterizing polymers and oligomers with chromophoric groups and for HPLC analyses of additives. Mass spectrometry is also used for some analyses. This is described in Sec. II.F.

The most popular GPC detector is the differential refractometer. It is a concentration-sensitive detector that measures the difference in refractive index (ΔRI) between the eluent (the flowing solvent) and the sample solution. It is a universal detector that will respond to any polymer with a significant refractive index difference from the solvent. So another consideration when selecting a solvent, besides being a good solvent for the polymer, must be a refractive index that will provide a significant ΔRI. The solvent/polymer combinations listed in the Appendix fulfill this criterion.

Two additional detectors specific to GPC are the viscometer and the light-scattering detectors. They are used to complement the information provided by the differential refractometer, since they respond to molecular-weight and structural characteristics of the polymer, while the refractometer responds primarily to mass. The viscometer determines viscosity by measuring differences in the pressure drop as the solvent and sample solutions flow through capillaries. Determination of absolute molecular-weight information with the viscometer and refractometer was mentioned in Sec. II.B. Having the viscometer detector in line with the refractometer also makes it possible to calculate the intrinsic viscosity [η] across the molecular-weight distribution and to obtain information about long-chain branching. See Sec. III.B.

Light scattering, coupled with the refractometer, is another powerful mode of advanced GPC detection. A laser beam is scattered by the dissolved polymer molecules as they flow through a cell. The intensity of scattered light is proportional to the size of the scattering molecules. Measuring the intensity at various angles enables very accurate determination of weight-average molecular-weight, Mw. Light-scattering detection also provides information about the polymer radius of gyration and branching. See Sec. III.B.

Absorbance detection, either UV/visible or photodiode array, has broad but specific applicability, especially for styrenic polymers, epoxies, phenolics, polycarbonates, polyurethanes, aromatic polyesters, and many additives. When other HPLC modes are used, additional separating capability is sometimes achieved by changing the solvent composition during the analysis (gradient elution). For this work the UV or PDA detector is essential, since the RI detector would drift excessively as the composition, and therefore the refractive index, changes. See Sec. II.F.

The PDA can monitor the separation at hundreds of wavelengths simultaneously in the range from 190 to 800 nm. This makes it possible to generate the actual UV spectra of polymers and additives and evaluate the chemical composition distribution. Block SBR copolymers are distinguishable from random copolymers [8]. Spectral libraries can be created for known polymers and additives to assist identification and deformulation of unknowns.

E. Data Reduction

A wide variety of choices exist for processing the GPC data, extending from simple integrators to powerful computer-based systems. Most integrators will process only one sample chromatogram at a time and offer little or no flexibility in presenting information.

Using computers and commercially available GPC software, calibration, molecular-weight averages and distributions, and structural information are determined quickly and easily. These packages can process chromatograms from the various detectors and present the information in multiple, user-selectable formats. Multiple calibration procedures are supported. GPC software is available from Polymer Laboratories, Polymer Standards Service, Viscotek, and Waters Corp. Some packages have enough flexibility to enable the user to automate the entire procedure in a ''run and report'' mode or to integrate specific chromatograms manually if desired.

In addition, the most advanced software will also control the instrumentation and archive the raw data and results in a relational database that links instrumentation records with operating conditions, data processing,

and reporting methods. User-designed reporting for standard or custom purposes is also integrated into the software. Statistical options permit tailored information retrieval for tracking and trending purposes. Workstations may be operated independently or as elements of a network within the laboratory or throughout the operations of multinational corporations.

F. HPLC of Polymers and Additives

Modes of HPLC other than GPC can be used to evaluate polymer mixtures, copolymer composition, and to analyze additives. As indicated in Fig. 8 and in Secs. II.A and II.D, for this work a number of changes are made to the system, especially the type of column and detection methods. The mechanism of separation is no longer exclusion, in which no adsorptive interaction between the sample components and the column packing material is tolerable. Instead, there is deliberate adsorptive interaction between the samples and the column packing in order to achieve separations based on differences in chemical composition of the sample components, independent of molecular size, Sec. III.C.

HPLC columns usually contain packings based on porous silica particles, often with organic chemical groups bonded to the surface. The solvents used with these bonded-phase packings range from nonpolar to aqueous phases, depending on the characteristics of the sample. Solvent composition is often programmed during the analysis to further regulate the separation.

In GPC instrumentation the pumping system delivers a single eluent throughout the analysis. It may be a single solvent, a blend of solvents, or a solvent plus an additive, Sec. II.C, but the composition remains constant. Solvent programming, also termed gradient elution, in HPLC requires more capability from the solvent delivery system to ensure precise flow and reproducible solvent composition profiles.

While RI detectors are used for isocratic HPLC, the other detectors, viscometer and light scattering, are not generally suitable for HPLC. As noted in Sec. II.D. absorbance detectors, either UV/visible or photodiode array (PDA), are much more useful. Table 5 and Fig. 13 show the HPLC of a polymer additive mixture. The reproducibility of 12 consecutive injections shown in Fig. 13 demonstrates exceptional reproducibility of the analysis, especially considering that both the solvent composition and solvent flow rates were programmed for this work.

Depending on the nature of the work, other detection techniques that can be employed in conjunction with absorbance detection, or alone, include mass spectrometry (MS) and evaporative light scattering, Sec. III.C. While MS has been used to characterize polymers for a number of years, the

Table 5 Chromatographic Conditions for Polymer Additive Analysis by Gradient HPLC

System: Waters Alliance System with 996 PDA detector
Column: Symmetry C8, 3.9 × 150 mm
Column Temperature: 50°C
Solvent program: 70% acetonitrile (ACN)/water to 100% ACN in 5 min
Flow program: Initially 2.0 mL/min, at 6.0 min ramped to 3.0 mL/min in 0.2 min
Injection volume: 10 µL of standard additive mixture
Reproducibility study: 12 duplicate injections

The separation was performed using a packing material with a nonpolar C8 bonded phases. The column temperature was set above ambient to ensure reproducible conditions. Analytical HPLC injection volumes are typically an order of magnitude smaller than GPC injection volumes.

utilization of MS as an HPLC detector is a more recent development. An example of this use is shown in Table 6 and Figs. 14 and 15. The data system is able to extract ion and adsorbance spectra from the total chromatogram, Fig. 14. Closer examination of electron ionization spectrum in Fig. 15 shows the correspondence of fragments with the parent molecule and likely pathways to the dominant ions, enabling definitive identification of the Irganox 1076 (Ciba Specialty Chemicals, Additives Division, Tarrytown, NY).

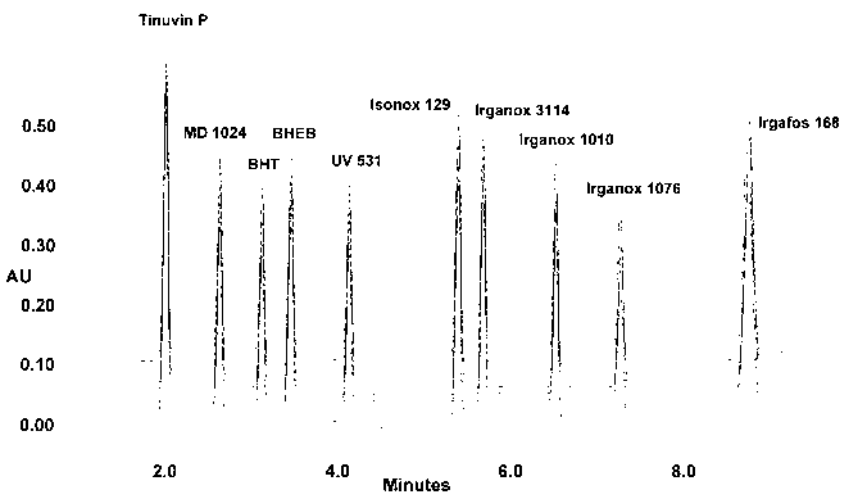


Figure 13 Polymer additive analysis by HPLC of a synthetic mixture of antioxidants and UV stabilizers (Alliance reproducibility study). An analysis of this type could be used to deformulate a competitive material.

Table 6 Chromatographic Conditions for Polymer Additive Analysis by LC/MS

LC conditions
Gradient conditions:
Solvent A: water
Solvent B: acetonitrile
Gradient: 80% to 100% B in 5 min, holds for 10 min
Column: Waters Symmetry C8 (3.0 mm × 150.0 mm) at 50°C
Flow rate: 0.6 mL/min
The LC/MS system used is a Waters Integrity system consisting of:
ThermaBeam mass detector
Waters 996 photodiode array detector
Waters 2690 separations module
Millennium 2010 data system

The gradient program in this work is less complex than that listed in Table 5. Use of MS and photodiode array detection provides extensive information about the sample.

For the multifunctional plastics analysis laboratory, the most versatile, basic chromatography instrument would be an HPLC system containing a PDA detector plus an RI detector and a supply of HPLC and GPC columns. This would enable the system to be configured for GPC analyses and yet still provide enough solvent-delivery flexibility to perform the more complex operations that are associated with additive analyses. All of the detection enhancements, viscometry and light scattering for GPC as well as mass spectrometry for HPLC, could also be accommodated as dictated by budget and analytical requirements. The only limitation would be the analysis of polyolefins and other polymers that are not soluble at room temperature. Here a dedicated, integrated GPC system is required, as noted in Secs. II.A and III.D.

III. CHROMATOGRAPHY RESULTS

A. Design Influences on Performance

The primary purpose of GPC is to accurately and reproducibly characterize polymeric materials, typically a complex mixture and distribution of closely related components. Therefore it is essential that the GPC system is able to reliably delineate differences that, although very slight, may be quite significant. For this to occur, the pumping system must deliver the solvent accurately, precisely, and uniformly. Flow fluctuations during an analysis or from one analysis to the next will seriously impair the quality of the results

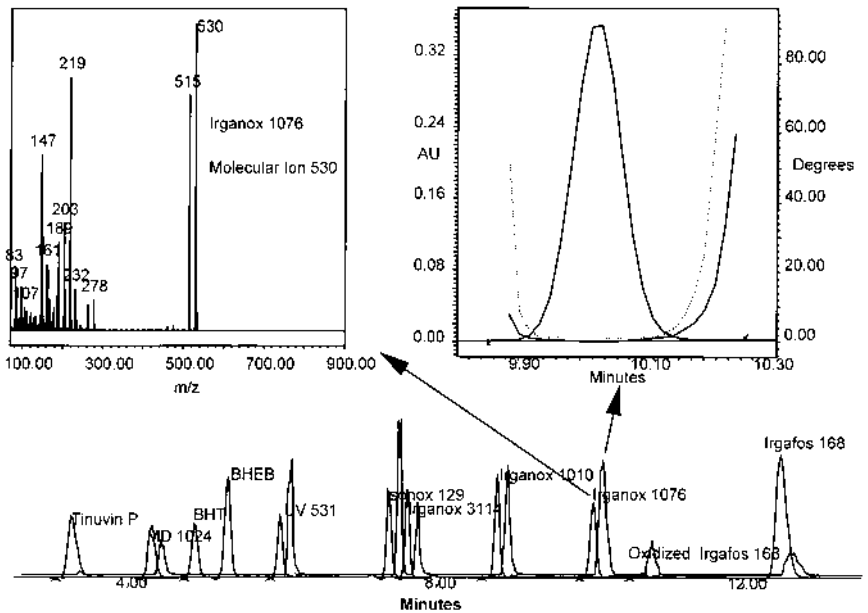


Figure 14 Additive analysis results. The chromatogram is an overlay of the MS and PDA responses. Each response curve contains extraordinary amounts of information. The mass spectrum, upper left, and a spectral measure of peak purity, upper right, have been extracted from the chromatogram. — TMD: total ion chromatogram from 100 to 700 amu. . . . PDA: extracted chromatogram at 230 nm.

and dependability of the information. In the extreme, these fluctuations may mask any true differences between samples.

The critical dependence on the flow characteristics arises from the calibration procedure that is the basis for quantitating the GPC chromatograms, Sec. II.B. Recall that calibration involves chromatographing a series of narrow-dispersity standards of known molecular-weight and plotting their log molecular-weight versus elution time. Although the time scale is used, GPC is actually a volumetric effect. The assumption is made that the flow rate remains constant throughout the analysis and from analysis to analysis, enabling time and volume to be used interchangeably. Any variation in the volume of solvent being delivered will cause the particular molecular-weight fraction to elute at a different time and shift the calibration curve. The error is magnified because of the log scale used for the molecular-weight, Fig. 6.

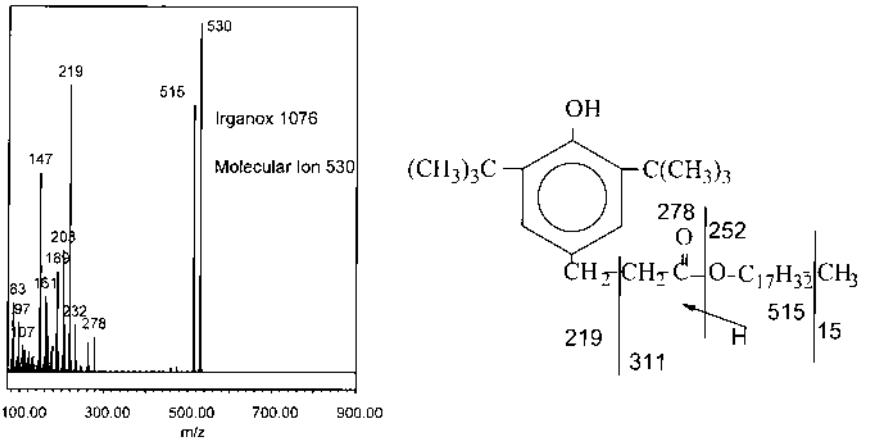


Figure 15 The classical electron impact mass spectra produced enable definitive compound identification, Irganox 1076 in this example. Electron impact mass spectra are interpretable as well as library-searchable.

The impact of flow fluctuation on the accuracy of molecular-weight calculations can be shown by analyzing a known sample at a slightly different flow rate than the flow rate used to develop the calibration curve. Dow 1683 is a well-characterized polystyrene introduced a number of years ago by the research department at Dow Chemical Company (Midland, MI, USA). Many investigators have used it as a reference material during studies of various polymer characterization techniques. The accepted molecular-weight values for this material are Mn = 100,000 and Mw = 250,000.

A sample of Dow 1683 was analyzed at 1.0 mL/min, the same flow rate that was used to construct the calibration curve. Then it was analyzed again at 0.95 mL/min and quantitated with the 1.0-mL/min calibration curve (Table 7).

The use of the log molecular-weight scale versus time (volume) for calibration results in about a 10-fold magnification of any flow error. This general relationship is shown in Fig. 16. Hence the emphasis on using the most precise solvent delivery system possible. It is still good practice to periodically bracket samples with narrow-distribution calibration standards and compare them to the calibration curve to monitor the condition of the system and columns.

A manufacturer of medical devices found that product made from a new batch of resin differed from that fabricated from the resin he had been using. The resin supplier claimed the batches were identical. Comparison of

Table 7 Analysis of a Sample of Dow 1683 (at the same flow rate used to construct the calibration curve)

	Accepted values	Values at 1 mL/min	Values at 0.95 mL/min
Number avg., Mn	100,000	98,457	43,264
Weight avg., Mw	250,000	246,501	108,143

the two batches with an Alliance GPC system revealed slight but reproducible differences, Fig. 17. To ensure that these subtle changes were not due to fluctuations in system operation, each sample was analyzed five times. All 10 molecular-weight distributions are included in the display. The tables show the extraordinary reproducibility of the analyses. The ability to compare the entire distributions by overlaying the composite chromatograms enabled the manufacturer to identify the likely causes of changes in processability and product performance.

In addition to flow precision, flow smoothness is also essential. Flow smoothness results in a very stable, low-noise baseline signal from the RI detector. Detector sensitivity is governed by the ratio of the signal that is produced to the baseline noise. With lower noise it is possible to reduce the scale of operation and still obtain a good signal for quantitation. Reducing

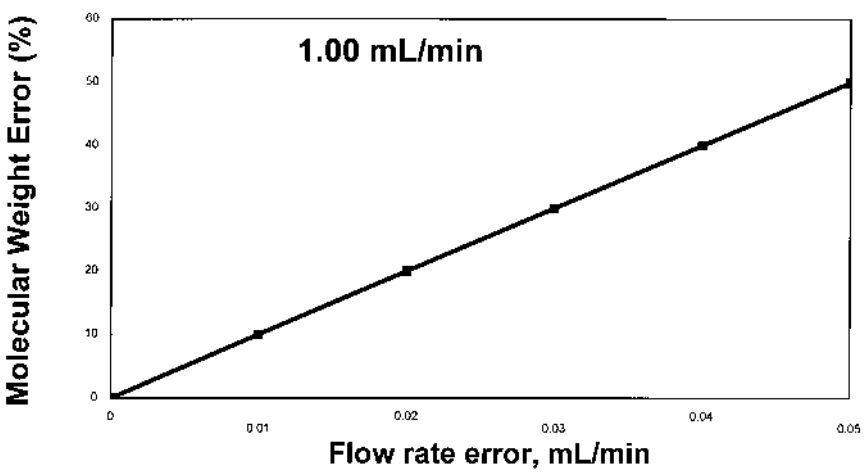
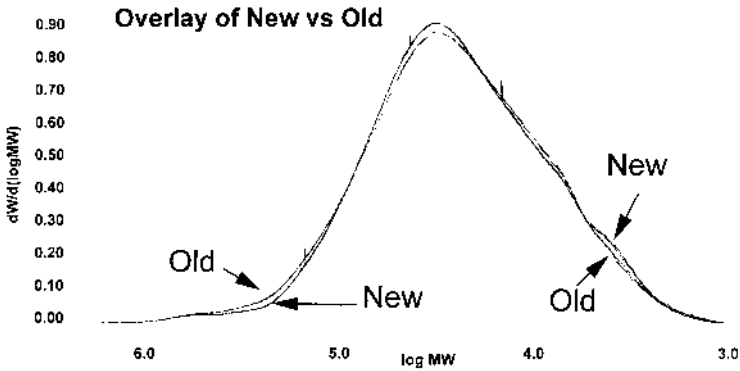


Figure 16 Effect of pump flow rate precision. Each 1% error in GPC flow rate results in a 10% error in molecular-weight value.



Polyether Amide-New	Average N=5	%RSD N=5
PeakApex Rt	18.923 min	0.113 %
Mn	14,855	0.564 %
Mw	44,177	1.119 %
Mz	150,880	4.990 %
Mw/Mn	2.974	1.084 %

Polyether Amide-Old	Average N=5	%RSD N=5
PeakApex Rt	18.952 min	0.066 %
Mn	14,953	1.296 %
Mw	40,061	1.039 %
Mz	154,462	3.440 %
Mw/Mn	2.679	1.363 %

Figure 17 Alliance narrow-bore GPC (medical, pastic-grade polyether amide). Very subtle differences in the molecular-weight distributions are determined reliably with modern, high-performance instrumentation. Each chromatogram is actually an overlay of five consecutive analyses.

the scale of operation involves using 4.6-mm-ID instead of 7.8-mm-ID columns. Flow rates and injection volumes are reduced proportionately, lowering solvent consumption by about two-thirds. The polyether amide medical-grade resin, Fig. 17, is soluble only at room temperature in a very expensive solvent, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). Being able to operate with only one-third the amount of HFIP that would have been necessary with a conventional GPC system was a very significant economic benefit to this laboratory.

An interlaboratory comparison of GPC results provides another demonstration of the exceptional reproducibility provided by the modern high-performance instrumentation. Three polycarbonate resins were independently analyzed by two laboratories, one in the United States and the other in Europe. The conditions each used were similar but not identical (Table 8). This work was also done with 4.6-mm-ID narrow-bore columns and absorbance detection, Sec. II.D, photodiode array in the United States and tunable UV (TUV) in Europe. The most significant difference in the setup between the two labs was the column sets that were used. Polystyrene

Table 8 Conditions for Analyzing Three Polycarbonate Samples in Two Laboratories

	US Lab	Europe Lab
Calibration	PS Stds. in Me_2Cl_2	PS Stds. in Me_2Cl_2
Columns 4.6 × 300 mm	HR 2, 3, & 4	HR 3 & 4
Injection	25 μL	25 μL
Concentration	0.15%	0.10%
Flow rate	350 μL/min	350 μL/min
Detection	PDA @ 239 nm	TUV @ 254 nm

The conditions were chosen independently. Methylene chloride was the solvent used in both locations.

standards were used for calibration, so the results in Fig. 18 and Table 9 are relative molecular-weights, Sec. II.B.

Each laboratory performed all analyses in triplicate, with precision of molecular-weights less than 1% for virtually every value. The exceptional agreement between labs proves that using a highly reproducible system for calibration and analysis will ensure consistent results within and between labs, even if the operating conditions between labs are not identical.

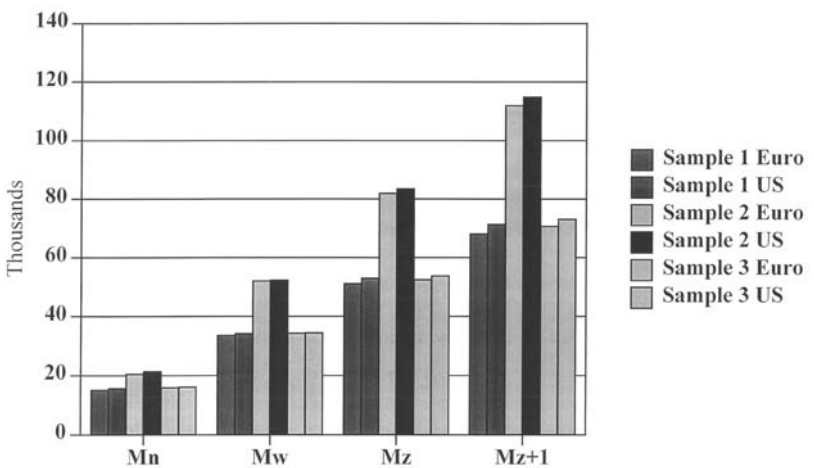


Figure 18 Alliance GPC interlaboratory results (polycarbonates). Reproducibility within labs and accuracy of results, as measured by the agreement between labs, was exceptional, despite slightly different operating conditions.

Table 9 Alliance GPC Interlab Results (Polycarbonates)

	Mn	Mw	Mz	Mz + 1
Sample 1 Euro	15,144	33,607	51,142	68,104
Sample 1 US	15,628	34,145	52,980	71,360
Sample 2 Euro	20,482	52,033	81,931	111,986
Sample 2 US	21,257	52,330	83,426	114,851
Sample 3 Euro	15,878	34,300	52,536	70,647
Sample 3 US	16,124	34,398	53,782	73,078

Nevertheless, for best results the operating conditions and column sets should be as similar as possible, and each system must be calibrated under the exact conditions at which it will be used to analyze samples. It should also be noted that all of the results reported by the European lab were very slightly lower than those from the United States. Slight differences in factors such as procedure, data reduction parameters, or the difference in detector absorbance wavelengths might have caused this consistent bias, rather than random variability.

B. Structural Determination

Depending on monomer chemistry and polymerization conditions, polymer chains may be linear, resembling a long, randomly coiled strand of repeating units, or they may be branched, with side chains extending off the main, linear backbone. For some polymers, branching has as much influence on processability and properties as molecular-weight averages, if not more. GPC with multiple detectors, Secs. II.B and II.D, can be used to determine whether a polymer is linear or branched, and if branched, the degree of branching.

When an on-line viscometer is used together with the refractive index detector to generate the intrinsic viscosity [η] in order to build the universal calibration curve, Sec. II.B, the intrinsic viscosity [η] can also be used to determine the presence and degree of branching. This is done by plotting the log of [η] versus log molecular-weight for each slice of the distribution. This plot is called the viscosity law plot, or the Mark-Houwink plot. It is described by the equation

$$[\eta] = KM^{\alpha}$$

in which K is the intercept and α is the slope, also known as the Mark-Houwink constant [9]. If the polymer is linear, the viscosity will increase

linearly with molecular-weight and the slope will remain constant. However, if there is any long-chain branching, [η] will not increase linearly with molecular-weight and may even approach a constant value. Corresponding α values will decrease in the branched region of the distribution.

The slope of the Mark-Houwink curve for a branched polymer will still be linear at low molecular-weights when there is no long-chain branching. This linear region can be extrapolated into the high-molecular-weight region to enable determination of the branching index, g', which is defined by the ratio of intrinsic viscosities at a specific slice or molecular-weight point:

$$g' = \frac{[\eta]_{\text{branched}}}{[\eta]_{\text{linear}}}$$

The divergence of the viscosity law plot from linear and subsequent decline in g' for a lightly branched polyethylene is shown in Fig. 19. The work was done with an integrated GPC system that can maintain all zones at the temperature needed to keep the sample in solution. In this presentation the molecular-weight scale is high to low. This is a user preference that is chosen in the software. In addition to the degree of branching indicated by

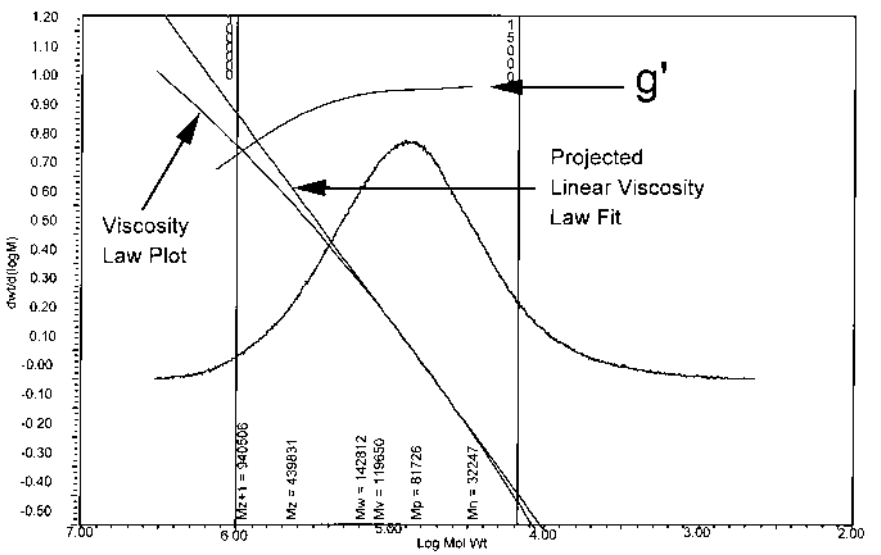


Figure 19 Molecular-weight distribution and branching information for a low-density polyethylene heavy-wall trash bag. The decrease in branching index, g', indicates that the higher-molecular-weight fractions have significant long-chain branching.

g', the software is also capable of calculating how often branches occur along the backbone. This is known as branching frequency, λ, and is determined using the Zimm-Stockmayer equation [10].

Light scattering and viscometry detectors are molecular-weight-dependent detectors. As such, they respond more strongly to higher-molecular-weight fractions than RI detectors. Conversely, the RI detectors are more sensitive to low-molecular-weight regions of the distribution. Light scattering is especially useful for determining the conformation of polymers in solution, the radius of gyration, and whether there is agglomeration or aggregation of polymer chains. Branching information is also provided by light-scattering detectors.

C. Compositional Determination

Analysis of polymer blends and alloys often requires the ability to separate two or more types of polymers or copolymers with varying monomer ratios. Size separation is less useful than other HPLC modes in which the separation is based on differences in chemical composition, Sec. II.F.

Polymer separations by HPLC are usually optimized by changing the solvent composition during the analysis. This is termed solvent programming or gradient elution. Since the refractive index of the solvent changes significantly during the gradient, differential RI detection cannot be used. Absorbance detectors are very popular for this work, providing the polymers being analyzed contain UV absorbing (chromophoric) groups. The evaporative light-scattering detector (ELSD) is a general-purpose detector that is compatible with gradient HPLC of polymers.

In an evaporative light-scattering detector the eluent leaving the column is mixed with a gas and forced through a nozzle to form a mist of uniform droplets that passes into a heated chamber. As the droplets are carried through this heated chamber or "drift tube" by the gas stream, the solvent evaporates, leaving a fine dispersion or cloud of sample particles. The particles travel through a laser light beam, scattering the light. The scattered light is detected in response to the presence of the sample.

One scheme for separating polymer mixtures by HPLC is based on a selective precipitation–redissolution model [11]. It has been used with the evaporative light-scattering detector to monitor the separation of a three-polymer mixture (Fig. 20). Solvent programming was used. The author suggests that this technique can be used to determine chemical composition of copolymers, but no examples are shown.

A subsequent study by another investigator used gradient elution to control the separation of a series of polymethyl methacrylate/butyl acrylate copolymers with varying monomer ratios. Elution times increased linearly

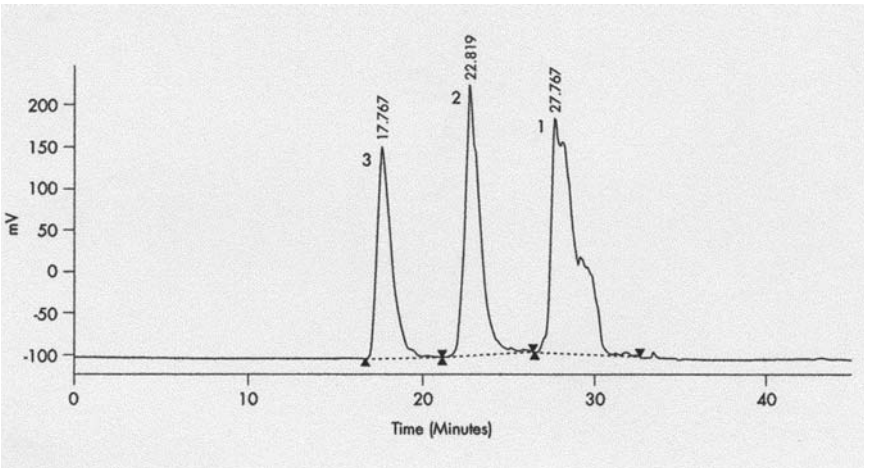


Figure 20 Chromatogram of poly(methyl methacrylate) 3, poly(styrene) 2 and poly(butadiene) 1. Chromatographic conditions: 30-min. linear gradient, 100% methanol to 100% tetrahydrofuran at 1 mL/min. NovaPak Cyano-Propyl 3.9 × 75 mm, 4-μm column at 30°C, evaporative light-scattering detector.

with butyl acrylate content. Monomer ratios were determined with an HPLC/mass spectrometer employing an electron ionization interface [12]. MS of polymers has been practiced for many years, but using the technique on-line to combine it with the separating power of HPLC makes it possible to examine the composition of more complex samples.

The monomer mass spectra were similar to those produced by pyrolysis GC/MS (Fig. 21). The MS detector was calibrated for the amount of butyl acrylate present and was used to determine the amount of this monomer present in unknown polymers. Linear relationships were observed between ion intensity/concentration and ions characteristic of both methyl methacrylate ($m/z = 100$) and butyl acrylate ($m/z = 127$). The peak compositions in Fig. 21 range from methyl methacryate homopolymer, A, to butyl acrylate homopolymer, F, in 20% butyl acrylate increments.

D. Analysis of High-Temperature Soluble Polymers

More polyolefins are produced and used worldwide than any other polymer group. All polyolefins, whether linear or branched, amorphous or crystalline, homopolymer or copolymer, are soluble only at elevated temperatures (Figs. 1 and 19). This imposes extra demands on instruments that are used

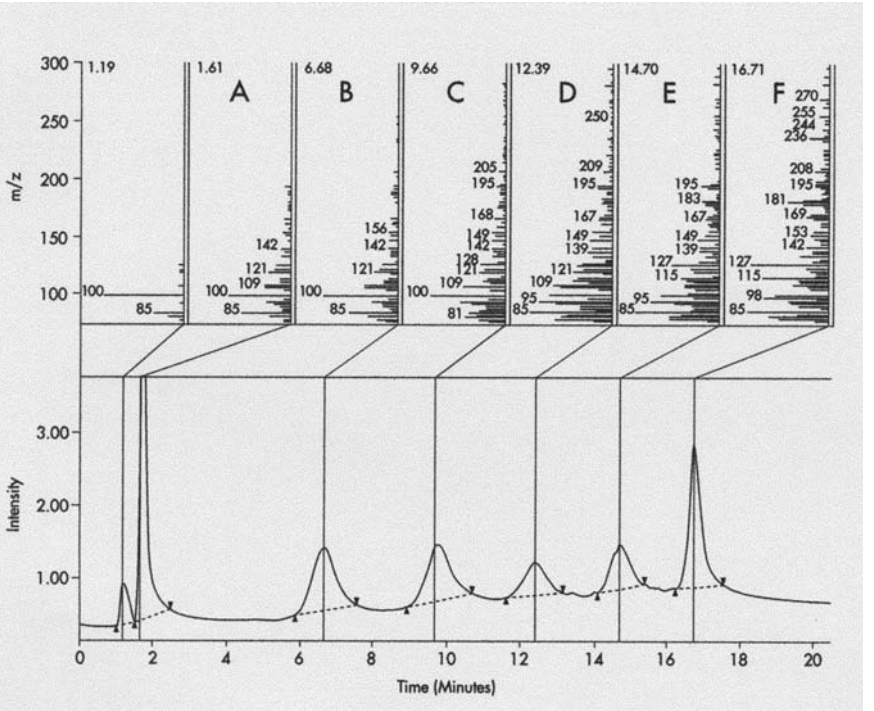


Figure 21 HPLC/MS spectrum index plot of pMMA/BA copolymers. Mass spectra extracted from the total ion chromatogram show the progression from polymethyl methacrylate homopolymer (A) to polybutyl methacrylate homopolymer (F) in 20% butyl acrylate increments.

to determine polyolefin molecular-weight values by GPC. The most common conditions for this work are to dissolve the sample in either TCB or ODCB and operate the instrument with injector, column, and detectors at 135–145°C (Appendixes A and C).

The most dependable approach to controlling temperature throughout the analytical instrument is to integrate all components into a self-contained system such as the Waters Alliance GPC 2000 (Fig. 11). In this way, the modules and connecting tubing can be maintained at the desired temperatures without concern for cold spots that might cause the sample to precipitate and possibly plug the system. Considering that some of the organic solvents used for high-temperature GPC are hazardous, safety features such as flow and pressure monitors, leak sensors, and spill containment can be readily incorporated into an integrated system with greater reliability than

in an open, modular configuration. A unique user interface based on an on-board computer produces real-time displays of detector signals and system operating conditions as well as facilitating setup, documentation, reporting, and archiving of results.

These same considerations apply to other important polymer groups that must be dissolved at elevated temperature. They include polyacetals, polyvinylidene fluoride, polyetherketone (PEK), polyetheretherketone (PEEK), polyether sulfone, polyimide, and imide copolymers. Traditionally polyamides and polyesters also were analyzed at elevated temperature, but HFIP will dissolve them at room temperature (Fig. 17).

IV. NATIONAL AND INTERNATIONAL STANDARDS FOR POLYMER LIQUID CHROMATOGRAPHY

ASTM Methods (U.S.)

D 1996-92: Determination of Phenolic Antioxidants and Erucamide Slip Additives in Low Density Polyethylene Using Liquid Chromatography (LC)

D3016-78(1992): Use of Liquid Exclusion Chromatography Terms and Relationships

D5296-92: Molecular Weight Averages and Molecular Weight Distribution of Polystyrene by High Performance Size-Exclusion Chromatography

D5524-94: Determination of Phenolic Antioxidants in High Density Polyethylene Using Liquid Chromatography

D5815-95: Determination of Phenolic Antioxidants and Erucamide Slip Additives in Linear Low-Density Polyethylene Using Liquid Chromatography (LC)

D5910-96: Determination of Free Formaldehyde in Emulsion Polymers by Liquid Chromatography

D6042-96: Determination of Phenolic Antioxidants and Erucamide Slip Additives in Polypropylene Homopolymer Formulations Using Liquid Chromatography (LC)

DIN Method (Germany)

DIN 55672-1: Gelpermeationschromatographie (GPC)

ISO (International Organization for Standardization)

Draft International Standard ISO/DIS 13885: Binders for paints and varnishes-Gel permeation chromatography (GPC) with tetrahydrofuran (THF) as eluent—draft under consideration, 1997

Draft International Standard ISO/DIS 16014: Plastics—Determination of average molar masses and molar mass distribution of polymers using size exclusion chromatography. Part 1: General Principles. Part 2: Measurement at lower temperatures. Part 3: Measurement at higher temperatures—draft under consideration, 1999

JIS (Japan Industrial Standards)

JIS K0124: General Rules for Analytical Methods in High Performance Liquid Chromatography

APPENDIX A: ORGANIC SOLVENTS FOR GPC

Solvent/full name	Boiling point (°C)	Comments
THF (tetrahydrofuran)	66	Highly flammable peroxides may form
Toluene	111	Highly flammable
DMF (N,N′-dimethylformamide)	153	Strong irritant/toxic (0.05 M LiBr added to minimize polar effects)
DMAC (N,N′-dimethylacetamide)	166	Same as DMF
HFIP (1,1,1,3,3,3-hexafluoro-2-propanol)	58	Very expensive, corrosive vapors
TCB (1,2,4-trichlorobenzene	213	Toxic; 1.0 g/4 L of an antioxidant should be added
ODCB (orthodichlorobenzene)	173	Somewhat toxic, also needs antioxidant
NMP (*n*-methyl pyrrolidone)	202	Strong irritant/toxic (0.05 M LiBr added as for DMF)
$CHCl_3$ (chloroform)	61	Known carcinogen
CH_2Cl_2 (methylene chloride)	40	Toxic, possible carcinogen
DMSO (dimethyl sulfoxide)	189	Nontoxic

Several other solvents and solvent blends are used occasionally, such as decalin, (for polyolefins), xylene, (for amorphous polypropylene), *m*-cresol, and trifluoroethanol (for certain nylons and polyesters), etc. These are the solvents used most often as eluents in GPC analysis.

APPENDIX B: SOLVENT SELECTION FOR ROOM-TEMPERATURE ORGANIC SOLUBLE POLYMERS

Polymer	Solvent	Column temp. (°C)
Acrylonitrile/methylmethacrylate	THF	40
Cellulose acetate	THF	40
Cellulose acetate/butyrate	THF	40
Cellulose acetate/propionate	THF	40
Cellulose triacetate	THF	40
Diallyl phthalate	THF	40
Ethyl cellulose	THF	40
Epoxy resins	THF	40
Phenolic resins	THF	40
Polyglycolic acid	THF	40
Polyester alkyd resins	THF	40
Polymethylmethacrylate and other acrylics and acrylates	THF	40
Polypropyleneglycol	THF	40
Polystyrene	THF	40
Polystyrene/acrylonitrile (SAN) (low ACN)	THF	40
Polysulfone	THF	40
Polyurethane (some)	THF	40
Polyvinylacetate	THF	40
Polyvinylbutyral	THF	40
Polyvinylcloride	THF	40
Polyvinylchloride/acetate	THF	40
Polyvinylidenechloride	THF	40
Polyvinylformal	THF	40
Thermosetting polyesters	THF	40
Rosin acids	THF	40
Polybutadiene	Toluene	75
Polychloroprene (neoprene)	Toluene	75
Polydimethylsiloxane (silicone oils and rubber)	Toluene	75
Polyisobutylene (butyl rubber)	Toluene	75
Polyisoprene (natural rubber, chlorinated rubber)	Toluene	75
Styrene/butadiene rubber (SBR)	Toluene	75
Styrene/isoprene (SI)	Toluene	75

APPENDIX B: CONTINUED

Polymer	Solvent	Column temp. (°C)
Acrylonitrile/butadiene styrene (ABS)	DMF[a] with 0.05 M LiBr	85
Acrylic/butadiene/acrylonitrile (ABA)	DMF[a] with 0.05 M LiBr	85
Acrylic/butadiene/acrylonitrile (ABA)	DMF[a] with 0.05 M LiBr	85
ABS/polycarbonate	DMF[a] with 0.05 M LiBr	85
Carboxymethylcellulose	DMF[a] with 0.05 M LiBr	85
Polyacrylonitrile	DMF[a] with 0.05 M LiBr	85
Polybutadiene/acrylonitrile	DMF[a] with 0.05 M LiBr	85
Polystyrene/acrylonitrile (SAN) (high ACN)	DMF[a] with 0.05 M LiBr	85
Polyurethane (most)	DMF[a] with 0.05 M LiBr	85
Melamine/formaldehyde	HFIP with 0.05 M NATFA (trifluoroacetic acid, sodium salt)	35
Nylon (all nylons plus most other polyamides)	HFIP with 0.05 M NATFA	35
Polyethylene terephthalate (PET)	HFIP with 0.05 M NATFA	35
Polybutylene terephthalate (PBT)	HFIP with 0.05 M NATFA	35

[a]In most cases, DMAC may be substituted for DMF, again with the 0.05 M LiBr.

APPENDIX C: SOLVENT SELECTION FOR ELEVATED TEMPERATURE ORGANIC SOLUBLE POLYMERS

Polymer	Solvent	Column/injector temp. (°C)
Chlorinated polyethylene	TCB[a]	135–145
Ethylene/propylene diene monomer (EPDM)	TCB	135
Polyethylene	TCB	135–145
Polyethylene/ethyl acrylate	TCB	135–145
Polyethylene/vinyl acetate (EVA)	TCB	135
Polyethylene/methacrylic acid	TCB	135–145
Polyphenylene oxide	TCB	135
Poly-4-methyl pentene	TCB	135
Polypropylene	TCB	135–145
Ultra-high-molecular-weight PE (UHMWPE)	TCB	145
Polyamide-imide	NMP with 0.05 M LiBr	100
Polyether-imide	NMP with 0.05 M LiBr	100
Polyether sulfone	NMP with 0.05 M LiBr	100
Polyimide	NMP with 0.05 M LiBr	100
Polyvinylidene fluoride	NMP with 0.05 M LiBr	100
Polyacetals	DMF with 0.05 M LiBr	145
Polyetherketone (PEK)	1 : 1 TCB/Phenol	145
Polyetheretherketone (PEEK)	1 : 1 TCB/Phenol	145
Starch	DMSO	50–100
Cellulose	DMF with 6 M LiCl	85

[a]In most cases, ODCB may be substituted for TCB.

APPENDIX D: SOLVENT SELECTION FOR WATER-SOLUBLE POLYMERS WITH METHACRYLATE GEL COLUMNS

Polymer	Class	Eluent
Polyethylene oxide	Neutral	0.10 M $NaNO_3$
Polyethylene glycol	Neutral	0.10 M $NaNO_3$
Polysaccharides, Pullulans	Neutral	0.10 M $NaNO_3$
Dextrans	Neutral	0.10 M $NaNO_3$
Celluloses (water-soluble)	Neutral	0.10 M $NaNO_3$
Polyvinyl alcohol	Neutral	0.10 M $NaNO_3$
Polyacrylamide	Neutral	0.10 M $NaNO_3$
Polyvinyl pyrrolidone	Neutral, hydrophobic	80% 0.10 M $NaNO_3$/20% acetonitrile
Polyacrylic acid	Anionic	0.10 M $NaNO_3$
Polyalginic acid/alginates	Anionic	0.10 M $NaNO_3$
Hyaluronic acid	Anionic	0.10 M $NaNO_3$
Carrageenan	Anionic	0.10 M $NaNO_3$
Polystyrene sulfonate	Anionic, hydrophobic	80% 0.10 M $NaNO_3$/20% acetonitrile
Lignin sulfonate	Anionic, hydrophobic	80% 0.10 M $NaNO_3$/20% acetonitrile
DEAE dextran	Cationic	0.80 M $NaNO_3$
Polyvinylamine	Cationic	0.80 M $NaNO_3$
Polyepiamine	Cationic	0.10% TEA
n-Acetylglucosamine	Cationic	0.10 M TEA/1% acetic acid
Polyethyleneimine	Cationic, hydrophobic	0.50 M sodium acetate/0.50 M acetic acid
Poly(*n*-methyl-2-vinyl pyridinium)I salt	Cationic, hydrophobic	0.50 sodium acetate/0.50 M acetic acid
Lysozyme	Cationic, hydrophobic	0.50 acetic acid/0.30 M sodium sulfate
Chitosan	Cationic, hydrophobic	0.50 acetic acid/0.30 M sodium sulfate
Polylysine	Cationic, hydrophobic	5% ammonium biphosphate/ 3% acetonitrile (pH = 4.0)
Peptides	Cationic, hydrophobic	0.10% TFA/40% acetonitrile
Collagen/gelatin	Amphoteric	80 : 20 0.10 M $NaNO_3$/CH_3CN

Note that in the many cases where sodium nitrate is shown, many workers have used acetate, sulfate, sodium chloride, etc. Sodium nitrate tends to minimize ionic interferences very consistently for neutral and anionic compounds. These various eluents are used because the methacrylate-based gel packing for aqueous GPC has overall anionic charges, which can cause ion exclusion for anionic samples and ion adsorption for cationic samples if run in water alone.

APPENDIX E: MANUFACTURERS OF GEL PERMEATION CHROMATOGRAPHY AND HPLC SYSTEMS

Chromatography, gel permeation
- Alltech Associates Inc.
- Gilson Inc.
- Hitachi Instruments Inc.
- Polymer Laboratories Inc.
- Shimadzu Scientific Instruments Inc.
- Waters Corp.

Chromatography, LC, Complete Systems
- Alltech Associates Inc.
- Beckman Instruments Inc.
- Bioanalytical Systems Inc.
- Dionex Corp.
- Gilson Inc.
- Hitachi Instruments Inc.
- Jasco Inc.
- Perkin-Elmer Corp.
- Polymer Laboratories Inc.
- Shimadzu Scientific Instruments Inc.
- Thermo Separation Products Inc.
- Varian Instruments
- Waters Corp.

Source: *'97–'98 Lab Guide*, published by ACS Publications, American Chemical Society.

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