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Progress in the liquid chromatography of synthetic non-charged lipophilic macromolecules

Summary — A review with 30 refs. covering high-performance liquid chromatography (HPLC) as a tool to determine molecular properties (mainly *M* and *MWD*) of synthetic polymers, with particular reference to retention mechanisms (entropy-based size exclusion, and enthalpy-based adsorption, partition and phase separation). Further size-exclusion chromatography (SEC) for lipophiles (gel permeation chromatography) and biopolymers (gel filtration chromatography), coupled LC procedures (*e.g.*, isocratic compensation approach), HPLC under "critical" (weak enthalpic interactions) conditions (LCCC), (continuous) eluent gradient polymer LC (EGPLC), LC-like approaches including the full adsorption-desorption technique, and multidimensional HPLC of complex polymers are discussed. Instrumentation (*e.g.*, detectors), pumps, materials, and applications of analytical HPLC for polymers (evaluation of long chain branching, radius of gyration, limiting viscosity number, *etc.*) are also briefly reviewed.

Key words: high-performance liquid chromatography, retention mechanisms, enthalpy-and entropy-based retention mechanisms coupled liquid chromatography procedures, full adsorption-desorption method, instrumentation, analytical applications.

Utility properties of polymeric materials are dictated by molecular characteristics of macromolecules, their arrangement in the system, and the presence of various additives. The major macromolecular property data include the molecular weight (*M* or *MW*), chemical structure/composition (CC), and molecular architecture (MA). In man-made complex polymers, these data exhibit certain distribution and we speak about average values ($\overline{M}$ or *MMW*, *MCC* and *MMA*) and about their distributions (*MWD*, *CCD* and *MAD*). The average values of molecular characteristics can be determined by various conventional methods. For example, osmometry, light scattering measurements, viscosimetry, sedimentation and diffusion analyses provide information about polymer molecular weights, and spectrometry, especially IR and NMR, affords data on chemical composition and molecular architecture. Many, at least semiquantitative, information on molecular characteristics of polymers can be extracted from their mechanical/rheological properties. However, to assess the distributions of molecular property data, polymers must be separated by applying appropriate batch, chromatographic, and recently also mass spectrometric procedures. Analytical separation of macromolecules is presently dominated by liquid chromatography, mainly in the column arrangement.

Let us first elucidate the basic terms and retention mechanisms which are operative in HPLC of lipophilic electroneutral macromolecules.

RETENTION MECHANISMS IN LIQUID CHROMATOGRAPHY OF MACROMOLECULES

The major mechanisms utilized for selective retention of electroneutral macromolecules are: steric exclusion, adsorption, partition, and phase separation (precipitation/redissolution).

Steric (size) exclusion of macromolecules from the pores and the surface of column packing particles as well as from the column walls is the entropy driven process. Losses of conformational [1, 2] and possibly also orientational entropy [3] of macromolecules while they are progressing along the HPLC column are responsible for sample retention. The exclusion of macromolecules from the pores of column packing enforced by their exclusion from the outer surface of particles is the basis of size exclusion chromatography. The exclu-

sion from the walls of the (capillary) columns and from the outer surface of nonporous column packing particles is utilized in hydrodynamic chromatography of macromolecules.

The entropic chromatographic distribution constant K_S is

$$\log K_S = \frac{\Delta S}{R} \quad (1)$$

where: *R is the gas constant and ΔS is the entropy change connected with the interphase transfer of macromolecules.*

Adsorption, partition, and phase separation retention mechanisms are based on enthalpic interactions among the constituents of HPLC systems, *viz.*, polymeric sample, column packing, and mobile phase. These interactions are, however, necessarily accompanied by non-negligible entropy changes in polymer systems. The overall enthalpic distribution constant K_H is

$$\log K_H = \frac{-\Delta H}{RT} \quad (2)$$

where *T is temperature and ΔH is the enthalpy change.*

The extent of enthalpic interactions between the mobile phase and the column packing is qualitatively described by the strength of the mobile phase. Accordingly, we have strong and weak mobile phases. A mobile phase strongly interacting with the column packing suppresses enthalpic interactions between the analyte and the column packing. A strong liquid (mobile phase) which prevents adsorption of a given polymer on a given adsorbent (column packing) at a given temperature is called the desorli. A weak liquid which promotes adsorption of a given polymer on a given adsorbent at a given temperature is termed the adsorli.

The extent of enthalpic interactions between the mobile phase and a polymeric sample is qualitatively described by the term thermodynamic quality. We distinguish good and poor solvents, and nonsolvents (precipitants). The thermodynamic quality of a solvent affects the size of macromolecules in the solution. The better the solvent, the larger the size of the polymer species of a given molecular weight.

The relation between the strength and the thermodynamic quality of mobile phases for a given column packing and polymer sample is rather ambiguous. For example, a strong mobile phase for a given column packing may be either a good or a poor solvent for a given polymeric sample, whereas a good mobile phase for a given polymer may be either strong or weak with respect to a given column packing. Both the strength and the quality of mobile phases can be controlled by mixing constituents of various polarities and/or by adjustment of temperature.

The combination of both the enthalpic and the entropic effects in the HPLC system gives

$$V_R \approx f(\log K) = f(\log K_H + \log K_S) = f\left(\frac{-\Delta H}{RT} + \frac{\Delta S}{R}\right) = f\left(\frac{-\Delta G}{RT}\right) \quad (3)$$

where V_R *is the sample retention volume, K is the overall distribution constant, and ΔG is the Gibbs function.*

Relations between entropy- and enthalpy-based retention of macromolecules can be elucidated by comparing the dependences of polymer retention volume on polymer size in the solution (Fig. 1). Macromolecules of constant composition and architecture, *i.e.*, linear homopolymers, and porous column packings, are considered. The extent of enthalpic interactions is controlled either by eluent strength or by temperature. Curve *a* represents the situation when enthalpic interactions are negligible ($\Delta H \approx 0$). We speak about the ideal size exclusion separation mechanism. Curve *b* indicates the presence of small enthalpic interactions. The entropy-based mechanism fully dominates, however. Curve *c* depicts the situation when enthalpic interactions have increased but the entropic retention mechanism still prevails. ΔH and ΔS terms in Eq. 3 may mutually compensate each other. In this case, the K value approaches 1; in most practical systems, K is slightly higher than unity (as evident from the course of curve *d*) and separation of macromolecules according to size is lost. This situation is often referred to as the "critical conditions" [4, 5], or "compensation conditions", or "exclusion-interaction transition" (see *e.g.* [5]). Curves *e* and *f* illustrate the situations when the ΔH term in Eq. 3 prevails respectively only slightly or fully.

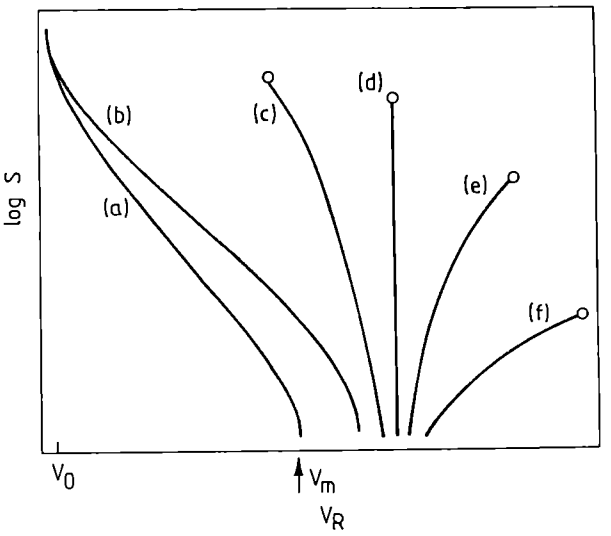

Fig. 1. Retention volume (V_R) vs. logarithm of size of macromolecules (S), also called calibration relationship; V_0 — interstitial volume, V_m — total volume of liquid in column; (○) — denotes situation when polymer species may be fully retained within column (for detailed explanation, see main text)

Let us present the major HPLC methods which utilize the above retention mechanisms for separation of multicomponent polymer systems whose constituents differ in *MW*, *CC*, and *MA*.

ENTROPIC LIQUID CHROMATOGRAPHY OF MACROMOLECULES: SIZE EXCLUSION CHROMATOGRAPHY (SEC)

The HPLC method in which analyte retention is fully or dominantly governed by entropic processes is called the size exclusion chromatography (SEC). The term gel permeation chromatography (GPC) is widely used for SEC of lipophilic macromolecules, whereas another term, *viz.*, gel filtration chromatography (GFC), has been coined for the exclusion-based HPLC applied to hydrophilic macromolecules, mainly biopolymers.

SEC is presently the most popular HPLC method for the determination of $\overline{M}$ and *MWD* of polymers. It may also provide further valuable information on separated macromolecules (*cf.* last section).

In SEC, the controlling separation parameter is the size of macromolecules in the solution. Unfortunately, the complicated entropic processes taking place in SEC columns (*e.g.*, pore exclusion, surface exclusion, hydrodynamic processes) cannot be assessed quantitatively *a priori*. Moreover, the pore geometry is too complicated for the behavior of polymer species to be predicted quantitatively. Therefore, size exclusion chromatography is inherently a non-absolute method. The molecular weights of the macromolecules in the effluent leaving SEC columns must be continuously monitored or the SEC system must be calibrated. The most straightforward calibration method includes injection of a series of narrow MWD "standards" of well-known *M*, measuring their retention volumes, and plotting calibration relationships similar to curve *a* in Fig. 1. Unfortunately, only a few appropriate polymer standards are readily available. In practice, polystyrenes, and poly(methyl methacrylate)s prepared by anionic polymerization are applied for organic mobile phases. Proteins and fractions of polysaccharides are utilized for aqueous eluents. The relation between *M* and the effective size of macromolecules in the solution depends on polymer-solvent interactions, *i.e.*, on the thermodynamic quality of the eluent. Therefore, values of *MMW* and *MWD* are only semiquantitative if calculated directly from the calibration curves obtained with standards differing in nature from samples investigated. This approximation is rather common in the literature and even the nature of calibration standards is often not given. Benoît *et al.* [6] have proposed the universal SEC calibration parameter called the polymer hydrodynamic volume, V_h. This is the product of the most abundant molecular weight in the polymer standard, *M*, and its limiting viscosity number in the eluent, $[\eta]$. Consequently, the plot of log $M[\eta]$ *vs.* V_R is called the SEC universal calibration curve. This approach is very useful because it allows to transfer data between various mobile phases and especially between macromolecules of various chemical nature and architecture. A problem appears when enthalpic interactions in systems are not negligible (curves *b* and *c*, Fig. 1). In this case, the transfer of data between different systems is impracticable [7].

Another weak point in the SEC calibration procedures is that V_R is related to the injected polymer concentration (c_i). The plots V_R *vs.* c_i are usually straight lines and for a given column packing, their slopes are related to polymer's *M* and to the thermodynamic quality of the eluent used for a polymer under study [8].

The general problem of SEC is that the size *vs.* hydrodynamic volume of macromolecules depends on all the three molecular characteristics of polymer *i.e.*, *MW, CC,* and *MA*. Therefore, SEC alone can only exceptionally produce data simultaneously on all these molecular characteristics. Similarly, *MMW/MWD* of a polymer cannot be determined if the macromolecules change their chemical structure and/or architecture together with their molecular weight and the functional dependence of these changes is unknown. Two or several separation mechanisms must be combined to assess the multiple distributions of molecular characteristics encountered in complex polymers (blends, copolymers, functionalized polymers). We speak about coupling of the HPLC separation mechanisms (see *e.g.* [5]). SEC usually represents an important component of such combinations.

Though size exclusion chromatography has become a routine method in many research and industrial laboratories, it still suffers from several serious drawbacks. The SEC data generally exhibit an excellent intra-laboratory repeatability but, at the same time also a surprisingly low inter-laboratory reproducibility [9], and are often misinterpreted and their information value is overestimated. It is evident that an appropriate standardization of SEC measurements should be introduced.

Chromatographic zones in the SEC columns are broadened, for example, owing to slow diffusion of big molecules, high viscosity of polymer solutions, and parasitic mixing processes. As a result, the *MWD* values calculated from SEC are overestimated. In the initial stage of SEC me- thod development various procedures were introduced to correct, at least partially, for the band broadening effects. They were, however, largely abandoned after better, highly efficient SEC column packings had been commercialized. To obtain high precision *MMW* data the band broadening correction, however, appears to be the necessary prerequisite [10]. Therefore future improvements anticipated in the SEC methodology will include also the re-introduction of corrections for both band broadening and concentration effects. These corrections are especially important for polymers with very high *M* and narrow *MWD*.

Further progress, not only in SEC but also in other procedures of polymer HPLC, includes instrumentation, materials, data processing and unconventional applications. Important new developments represent the combinations of exclusion and interactive separation mechanisms operated within a single chromatographic column-eluent system or in a cascade arrangement including column and/or eluent switching which is called two- and multidimensional HPLC of macromolecules.

ENTHALPIC LIQUID CHROMATOGRAPHY OF MACROMOLECULES: INTERACTIVE LIQUID CHROMATOGRAPHY

As mentioned, the entropic retention mechanism is effective in each chromatographic technique dealing with macromolecules, even if a nonporous column packing is applied. The term enthalpic interaction liquid chromatography (or interactive HPLC) of macromolecules is used to describe the procedures in which the non-exclusion mechanisms dominate. Inspection of the "calibration relationship" (Fig. 1, *f*) reveals that the isocratic interactive HPLC is feasible practically only for separation of macromolecules with lower molecular weights like oligomers ($M < 10^4$ g/mol). Isocratic interactive HPLC also allows a polymeric constituent to be selectively separated and independently molecularly characterized, from oligomeric constituents — provided the high polymer is eluted in the entropic mode and the oligomers are eluted in the enthalpic mode. Similarly, two chemically different oligomers can often be discriminated if they exhibit different enthalpic interactivities with the column packing. Further HPLC approaches which include enthalpic interactions are discussed in the following sections.

COUPLED LIQUID CHROMATOGRAPHIC PROCEDURES

An important group of HPLC procedures for separation of polymer mixtures represent those in which at least two different separation mechanisms are intentionally combined, coupled within the same chromatographic column [11].

As evident from the preceding sections, the general problem that complicates the separation of many complex polymer systems involves the interference of molecular weights with chemical compositions or molecular architecture of the constituents. To solve this problem, separation methods must be introduced which either suppress or increase the effect of one molecular characteristics on the polymer retention volume. Usually polymer's M is the suppressed characteristic. It follows from Eq. 3 and Fig. 1 that, in the entropy driven separations (curves *a—c*), polymer V_R decreases as M is increased. On the contrary if the separation is dominated by enthalpic processes (curves *a* and *f*), V_R increases. When in Eq. 3, the ΔH-term is fully compensated by the ΔS-term [4, 5], the resulting curve is the "calibration curve" (Fig. 1, *d*) in which V_R does not depend on M. Such a compensation can be attained either in a macroscopically homogeneous mobile phase or in a heterogeneous mobile phase applied in the column, *i.e.*, by creating a "barrier" impermeable to macromolecular species.

In the isocratic compensation approach, the weak ("critical") enthalpic interactions (adsorption or partition) in the HPLC system are utilized. We speak about the HPLC of macromolecules under critical conditions (LCCC). Column packing is used which exhibits enthalpic interactivity toward eluted macromolecules. Eluent strength is adjusted by mixing two or more liquids and/or by temperature so that macromolecules are just slightly, critically retained within the column.

LCCC can be used for the separation and independent characterization of binary polymer mixtures, further for the characterization of block, graft and stereoregular polymers, as well as for the determination of oligomer functionality. For example, in the case of polymer mixtures, block and graft copolymers, one kind of polymer chains (A) is eluted irrespectively of its M. Another kind of polymer chains (B) in polymer mixtures, block and graft copolymers elutes under SEC conditions and its molecular characteristics can be independently determined because, to a first approximation, the A chains can be neglected. This LCCC column can be on-line connected with an SEC column, or with a different LCCC column, to determine molecular characteristics of the chains A. Similarly, the nature and the number of functional groups in oligomers can be assessed if their macromolecular chains are eluted independently of their molecular weight [12].

The "critical" liquid chromatography is very attractive for the characterization of many complex polymers. Unfortunately, elution of macromolecules under critical conditions suffers from several serious drawbacks, especially from extensive band broadening and reduced sample recovery (*cf.* Fig. 1) [13, 14]. These and other weak points of LCCC have been overlooked by Pasch (for review see [15]) and an unfounded optimism has been created. Further research in the area of LCCC is needed to make the compensation approach more reliable. The possible alternatives of LCCC represent the "barrier methods" or the "local gradient approaches" in which entropic/exclusion and enthalpic mechanisms are combined dynamically. The latter approaches are called the liquid chromatography under limiting conditions of adsorption, or desorption, or solubility [11].

Important and fast developing new methods for HPLC of complex polymers involve the continuous eluent gradient which can be applied to the retention control of polymer species and to the separation of macromolecules according to their composition. An experiment in the eluent gradient polymer (high performance) liquid chromatography (EGPLC) also called the gradient polymer elution chromatography (GPEC) (the term trade-marked by Waters), usually starts with a retention promoting (retaining) mobile phase (*e.g.*, with an adsorption promoting liquid, an adsorli, or with a precipitant). A sample dissolved and injected in an adsorli or in a poor solvent is retained near the HPLC column inlet. Subsequently, a mobile phase is introduced together with a progressively increased amount of a displacer (*e.g.*, a desorli or a good solvent). If both the column packing and the gradient conditions are chosen correctly, macromolecules are separated according to differences in retentivity. EGPLC in the precipitation—redissolution mode was pioneered by Glockner [16] whereas the adsorption—desorption EGPLC was proposed by Inagaki *et al.* [17] in the TLC arrangement and independently by Teramachi [18] in the experimentally more feasible column ar-

rangement. Most EGPLC experiments involve narrow-pore column packings. Therefore, different velocities of eluent molecules and macromolecules play an important role in polymer elution and EGPLC can be included into the coupled HPLC methods. Continuous gradient elution can also be carried out on nonporous or gigaporous column packings where exclusion may be neglected. In this case, the EGPLC separations, mainly those dealing with oligomers, should be included into common interactive liquid chromatographic procedures. EGPLC retention volumes of macromolecules often do not depend on M if the retention mechanism is adsorption or partition and narrow pore column packings are applied [19]. In these cases, EGPLC can separate macromolecules exclusively according to their chemical composition. A very high selectivity and efficiency of separation can be attained which allows multicomponent polymer blends to be effectively separated in short EGPLC columns. Polymers leaving EGPLC can be on-line characterized by SEC in the two-dimensional approach. The M-independent retention in adsorption and partition driven EGPLC can be explained, *e.g.*, by considering the critical conditions [20] or the barrier mechanism [21]. In the former case, each constituent of a polymer mixture is eluted just within its "critical eluent" composition. In the latter case, fast moving macromolecules find the impermeable mobile phase composition, "a barrier" on which they are accumulated irrespectively of their M. Each polymer composition has its own "barrier mobile phase" composition which is similar to the critical mobile phase composition. In addition to the independence of V_R from polymer M, this coupled separation mechanism explains also the high EGPLC separation selectivity.

As shown by Chang *et al.* (for review see [22]), macromolecules can be very selectively separated also by adjusting the column temperature (temperature gradient interaction chromatography — TGIC). In principle, the critical conditions concept is applied; however, the column temperature is changed either continuously or in small increments so that just one fraction of a polymer mixture is eluted at a temperature. By applying this approach even "narrow-*MWD* samples" were separated into a series of fractions. In the case of a polymer mixture, one constituent has been eluted and characterized by applying the SEC mode, whereas another component was eluted at a different temperature and independently characterized according to the TGIC mode without interference.

LIQUID CHROMATOGRAPHY-LIKE APPROACHES: FULL ADSORPTION—DESORPTION METHOD

The liquid chromatography-like approaches employ full retention and consequent stepwise complete elution of polymer samples. All three enthalpic retention mechanisms can be applied for non-charged synthetic polymers but the most effective seems to be the adsorption desorption approach. We speak about the full adsorption—desorption method (FAD) (for review see [23]). In this overview we have included the FAD method into the liquid chromatographic methods for two reasons. FAD utilizes the HPLC equipment and it can be advantageously on-line combined with other HPLC methods, especially with SEC to allow full molecular characterization of polymer mixtures.

FAD resembles the solid phase extraction procedures applied to low-M substances. However, the experimental conditions (adsorbent, mobile phase, temperature) can be relatively easily established, under which the sample is fully retained in the full adsorption—desorption column. In the next step, the mobile phase composition is abruptly altered so that one constituent of a polymer mixture is quantitatively displaced from the FAD column. FAD represents a simple, fast and efficient method for the discrimination of many complex polymer systems including polymer mixtures containing a very small amount (~1%) of macromolecular additives [24].

MULTIDIMENSIONAL HPLC OF COMPLEX POLYMERS

The basic strategy for multidimensional HPLC of complex polymers includes successive separation of sample according to particular characteristics. Each step is performed in a different HPLC system (column packing, eluent, temperature) in such a way that the effect of all but one characteristic feature is eliminated or at least strongly suppressed. Coupled HPLC procedures are applied for this purpose. Multidimensional HPLC is complicated by extensive dilution of samples within each column and by the associated detection problems. The reconcentration steps between each column pair should be considered. So far, only two dimensional separations were attempted and a typical assembly is schematically shown in Fig. 2 [25]. The combination of

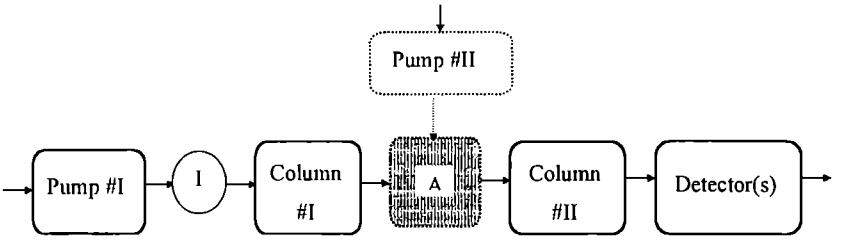

Fig. 2. Schematic representation of a two-dimensional HPLC system; I is sample injector. A is the sample storage, re-injection and reconcentration device which can also be used for sample matrix/eluent exchange; pump II and device A are redundant in some 2D-HPLC systems.

LCCC with SEC allowed some block copolymers to be at least semiquantitatively characterized [26]; the reversed approach, *viz.*, a combination of SEC with LCCC showed a potential for the independent characterization of *M* and tacticity distribution in stereoregular polymers [27, 28]. Multidimensional HPLC of complex polymers is only in its initial stage and a fast development of the methodology is anticipated.

INSTRUMENTATION AND MATERIALS

Pumping systems are being improved to produce highly constant flow rates at high pressures. This is rather important in all HPLC procedures, however, the constant flow is crucial in the HPLC of macromolecules because the retention volumes, together with corresponding sample concentrations in the effluent, represent the primary data used for the calculation of molecular characteristics. Volumeters are rarely used in modern HPLC and, instead, the time scale is applied. Therefore, the flow rate drift may badly affect the precision of results. The short term flow rate changes, pulsations, often make sample detection impossible.

Detectors

Differential refractometers and UV photometers with increased sensitivity and baseline stability have been developed. Two or more various detectors are sometimes used on-line to produce not only data on overall polymer concentration, but also on composition and/or architecture of macromolecules (hyphenated detection). "Absolute" detectors have been introduced to continuously monitor the molecular weights of the analytes leaving the column. They include viscometric detectors and devices measuring the intensity of the light scattered by macromolecules in effluents. The attempts to continuously measure osmotic pressure within column effluent so far has not led to a commercial apparatus. Strong NMR instruments can cope with a low polymer concentration in HPLC column effluents and thus afford information about the chemical structure and architecture of the separated macromolecules.

An interesting detection principle proposed already in the 1960s has been commercialized only recently. It involves nebulizing of the effluent, evaporating of the eluent from the droplets, and monitoring the light scattered by the resulting stream of fine "solid" particles. These "evaporative light scattering detectors" are highly sensitive devices to measure the mass of the polymer in the effluent. They are subject to vivid innovations to decrease the dependence of their response on polymer's *M* and chemical compositions as also on the eluent nature.

Interfaces were developed to remove the mobile phase from the effluent being continuously deposited on a germanium disk. The composition of the resulting polymer layer is measured by infrared spectroscopy. Fractions leaving the SEC column can be further separated and characterized by the soft ionization mass spectrometric methods, *e.g.*, by matrix assisted laser desorption ionization MS or electrospray MS devices.

Materials

Polystyrene-co-divinyl benzene and partially also silica gel based column packings are commonly used in permeation chromatography of lipophilic polymers while various hydrophilic resins, mainly poly(metha)crylates, polysaccharides and poly(vinyl alcohol), are applied in gel filtration chromatography of water soluble polymers [27]. Bare and chemically bonded silica gels are frequently applied in the coupled HPLC of macromolecules. The most important species bonded to silica gels are aliphatic C_{18}, C_8 and C_4 and further amino, nitrilo, and glyceryl groups divided from the silica surface by *n*-propyl spacers. Hybrid inorganic/organic polymer packings are likely to be introduced to allow fine column retentivity adjustments. As a rule, column packings are prepared in the form of small spherical particles (3—10 μm) with narrow size distributions. Larger particles (>20μm) are applied for the separation of ultra-high-*M* polymers to diminish their degradation by shearing. Small particles of column packings reduce the diffusion path lengths of analytes and offer increased separation efficiency. This means that broadening of chromatographic bands is reduced. However, the smaller the packing particles, the larger the pressure drop within the column and the larger the experimental problems. A reasonable compromise must be sought for. Evidently, some separation efficiency must be sacrificed when the particle size is increased. Pore sizes of the SEC column packings have been optimized to produce linear log *M vs.* V_R or universal calibration relationships log *M* [η] *vs.* V_R. The overall progress in packing technology resulted in highly efficient, selective, stable — and expensive — SEC columns. A general drawback to many SEC packings including PS/DVB, lies in their surprisingly high polar interactivity that results in full or partial retention of many polymers from eluents that are unable to effectively suppress adsorption effects [29]. A modern trend in enthalpic HPLC of small molecules represents monolithic columns [30]. Rods prepared of organic polymers or silica gel possess larger flow-through channels (1—2 μm) and smaller separation pores. The control of bimodal pore structure is very demanding and preparation of monoliths with separation (macro)pores suitable for SEC of polymers may be somewhat problematic. Moreover, the volume of separation pores is rather low. Monolithic columns which exhibit decreased flow resistance and fast mass transfer show a potential for interactive HPLC of both synthetic and biological macromolecules.

SEC eluents are subject to many requirements. The GPC field is dominated by tetrahydrofuran and chlorinated benzenes, whereas in GFC aqueous solutions are mainly used as eluents. Various single and mixed liquids are often applied and some exotic solvents are tested in various modes of SEC, to attain good sample solubility and detectability and to suppress adsorption of analyzed macromolecules within the column.

Fast and ultra-fast HPLC of polymers

SEC mobile phase flow rates are usually about 1 mL /min. Depending on the total volume of the packing bed, the conventional SEC analysis takes 10 to 30 min. The velocity of the EGPLC analysis, generally run in short columns, depends also on the steepness of gradient. Some specific applications, *e.g.* combinatorial material research approach need increased sample throughputs. Columns are miniaturized and mobile phase flow rates are increased to complete at least a semiquantitative analysis in 1—5 min. Petro *et al.* [30] have reported on the application of monolithic columns at flow rates as high as 20 mL/min which allowed to curtail the analysis time below one minute.

Data processing

Several sophisticated software products have been introduced to allow fast data acquisition and processing to obtain *MMW* and *MWD* or long chain branching characteristics. Special software products allow also to treat the data from the "absolute" (light scattering, viscometric) detectors. Future progress is likely to include computerized corrections of SEC data for the effects of both instrumental peak broadening and injected polymer concentration.

APPLICATIONS OF ANALYTICAL HPLC OF POLYMERS

Applications of analytical SEC include mainly the determination of the size of macromolecules and separation of macromolecules from small molecules. As mentioned before, average *M* and *MWD* are the most important products of polymer SEC. Further information rendered by SEC includes long chain branching characteristics, limiting viscosity numbers, constants in the Mark—Houwink viscosity law, and radii of gyration of macromolecules in the solution. The recent unconventional SEC applications tend to assess various secondary data which only indirectly depend on the original sizes of macromolecules in the solution, *e.g.*, evaluation of degradation, complexation (aggregation, association, micellization), polymer—solvent interactions, preferential solvation of macromolecules, and estimation of diffusion rates of macromolecules in porous media. "Inverse" SEC attains semiquantitive, but for soft gels indispensable, information on the pore size distribution of particulate materials.

Knowledge of *M* and *MWD* enables the processability of polymeric materials and their basic utility properties to be estimated. The kinetics of polyreactions — building up, chemical transformations and destruction of macromolecules — can be efficiently evaluated from changes in *M*. Certainly, some of the above-mentioned information can be considered semiquantitative only, similarly as the *MMW* and *MWD* data for copolymers calculated directly from the SEC chromatograms. Nevertheless, these information are very useful for polymeric materials both synthesis and application research.

HPLC methods based on enthalpic interactions and entropy—enthalpy coupled procedures produce data on chemical composition including oligomer functionality and molecular architecture (stereoregularity) of macromolecules. Multidimensional HPLC methods are anticipated to fully characterize complex polymer systems.

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KALENDARZ IMPREZ

18—20 marca 2002 r. Meksyk (Mexico-City), Meksyk. **„ACHEMAMERICA 2002 – 1st International Exhibition and Congress on Chemical Engineering, Environmental Protection and Biology"**.

Organizatorzy: DECHEMA — Gesellschaft fur Chemische Technik und Biologie e.V. + AIChE — American Institute of Chemical Engineers + IMIQ Instituto Mexicano de Ingenieros Quimicos.

Informacje: DECHEMA, Theodor-Heuss-Allee 25, D-60486 Frankfurt am Main (Dr. Christiana Hirche). Tel.: ++49(0)69/7564-277, fax: ++49(0) 69/7564-272; http://www.dechema.de + http://www.acheamerica.de.

22—25 marca 2002 r. Zurich, Szwajcaria. **„European Thermoforming Conference 2002".**

Organizator: Society of Plastics Engineers (SPE), Thermoforming Division, Antwerpen, Belgium.

Informacje: SPE-European Member Bureau, Bistkapellei 44, BE-2180 Antwerpen, Belgium. Mrs. Yetty Pauwels, tel.: +32 3 541 77 55/fax: +32 3 541 84 25; e-mail:spe-europe@pi.be.

27—29 maja 2002 r. Lyon-Villeurbanne, Francja. Sympozjum europejskie **„7th European Symposium on Polymer Blends"**.

Organizator: Centre Nationale de la Recherche Scientifique, Laboratoire des Matériaux Macromoléculaires, Lyon.

Tematyka: termodynamika mieszania, zmiany morfologii podczas mieszania i przetwarzania, środki kompatybilizujące, mieszanie reaktywne, materiały, zależność struktura-właściwości, nowe kierunki rozwoju, strategie i zastosowania przemysłowe mieszanin.

Informacje: Secreatariat 7th European Symposium on Polymer Blends, Laboratoire des Matériaux Macromoléculaires, Bat. Jules Verne, INSA Lyon; 20 Avenue Albert Einstein, 69621 Villeurbanne Cedex, France. Fax: 33(0) 4 72 43 85 27, e-mail: polymerblends@insa-lyon.fr; http://www.insa-lyon.fr/polymerblends/index.htm.

27—31 maja 2002 r. Dniepropietrowsk, Ukraina. **„The Second Ukrainian-Polish Conference — Polymers for Special Applications".**

Organizatorzy: Department of Plastics Materials Processing and Photo-polygraphic Materials Technology of Ukrainian State Chemical-Technology University, Dniepropetrovsk, Ukraina + Department of Polymer Chemistry of Radom Technical University, Radom, Polska.

Informacje: Dr Jerzy Borycki, Radom Technical University, tel.: +48-48-361 75 61, 361 75 70, fax: +48-48-361 75 68, e-mail: borycki@kinx.man.radom.pl + Dr. Tatiyana Hohlova, Dniepropetrovsk, Gagarina Av. 8, Department of Plastic Materials Processing; e-mail: polymer@dicht.dp.ua.

3—7 czerwca 2002 r. Paryż, Francja. **„EUROOLAST 2002 — 12 th International Exhibition of Plastics, Rubber and Composite Materials"**.

Organizator: Reed Exhibition Companies, Reed Exhibitions France, Paris przy współpracy promotorów: ACDI (Association of Manufacturers, Distributora and Importers of Equipment for the Plastic Materials Industry), AFIM (French Association of Mould, Model and Mock-up Makers), AFICEP (The French Association of Rubber Syndicate).

Prezentacje: surowce i układy rozdzielcze, maszyny przetwórcze, formy i narzędzia, urządzenia peryferyjne, jednostki centralne, aparatura i urządzenia do badań laboratoryjnych i inne.

Uzupełnienie wystawy stanowią konferencje i referaty w poszczególnych sektorach.

Informacje: „Europlast 2002", Reed Exhibitions France: 70, rue Rivay, F-925 32 Levallois Cedex, France. Tel.: +33 01 55 21 34 38, fax: +33 01 55 21 34 29, e-mail: stéphanielauretti@reedexpo.fr; http://www.europlast-paris.com + http://plastibase.com.

cd. na str. 798