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Critical assessment of size exclusion chromatography

Summary — Size exclusion chromatography (SEC) of synthetic polymers is assessed from the point of view of its both strong and weak points, advantages and drawbacks. Basic information on the SEC retention mechanism are presented together with the complexity of SEC systems and processes. Present stand of SEC instrumentation is outlined and the role of experimental conditions is described. The need of further development of SEC and of standardization of experimental conditions is demonstrated. The enthalpic interactions, leading to adsorption and enthalpic partition phenomena in the SEC columns are described. It is shown that the latter should be suppressed to obtain reliable SEC results. Alternatively, enthalpic interactions can be deliberately combined with the entropic partition (exclusion) basic SEC retention mechanism either to allow separation of complex polymers exhibiting multiple distributions in their molecular characteristics or to increase selectivity of separation.

Key words: size exclusion chromatography, separation mechanism, interlaboratory reproducibility, equipment influence, experimental conditions role.

SIZE EXCLUSION CHROMATOGRAPHY — ILLUSION AND REALITY

Molecular characterization of synthetic polymers is dominated by size exclusion chromatography (SEC) [called also gel permeation chromatography in case of lipophilic macromolecules and gel filtration chromatography in the case of hydrophilic (bio)polymers]. SEC belongs to the family of high performance liquid chromatography (HPLC) methods. Unlike other procedures of polymer HPLC, the SEC retention mechanism is based exclusively on the processes of the entropic partition while enthalpic interactions are suppressed or even fully eliminated. SEC is a fast, simple, and relatively cheap method noted for its high intralaboratory repeatability and low sample consumption.

SEC gives absolute data on molar mass both averages (*MMW*) and distributions (*MWD*) of numerous linear soluble polymers, on the long-chain branching, on the limiting viscosity numbers and sizes of macromolecules in solution, as well as on preferential solvation of polymer species in two-component solvents. Fractions of polymers showing relatively narrow molar masses can be produced, which are needed for various other physicochemical methods. SEC also furnishes valuable estimates on *MMW* and *MWD* of various copolymers or functionalized polymers.

All these attractive features lead to the notion that SEC is a concluded chapter of polymer science that does not need further development. However, SEC is troubled by many problems that should be solved or attenuated. For example, SEC exhibits a surprisingly poor interlaboratory reproducibility. Low separation selectivity and efficiency of SEC result in poor resolution of polymer species. This may lead to a wrong conclusion that the analyzed products of synthesis are "good", "narrow", "pure", *etc.* Also scientists like illusions... Only exceptionally, SEC gives absolute values of *MMW* and *MWD* for complex polymers, which show more than one distribution in their basic molecular characteristics that is in molar mass, chemical structure (composition) and/or physical architecture.

Selected problems of SEC are briefly discussed in this contribution with the aim to show that the method needs further development. It is also demonstrated that the standardization is needed for

— sample preparation,
— measurements,
— processing of results.

The specific standard procedures, a sort of "SEC good laboratory practice", should cover particular groups of polymers, for example the tetrahydrofuran soluble polymers, highly polar polymers, polymers soluble at elevated temperature (*e.g.* polyolefins), water soluble polymers, *etc.* It is also important to know that SEC is not yet in the stage of development when unqualified operators can run the instruments in the mode "switch-on, inject, switch-off".

SEPARATION MECHANISM

It is well accepted that the basic retention mechanism of SEC is steric exclusion of macromolecules from both the pores and the surface of the particles of column packing. Macromolecules are pulled into the packing pores to equalize their concentration with that in the interstitial volume. The species are partially squeezed to fit into the pores up to the point when the lost of conformational entropy outbalances the pulling force. Larger macromolecules find smaller volume of pores available and elute in front of smaller species. One speaks about entropic partition of polymers between two liquid phases of the same chemical nature. The processes based on the changes of mixing and conformational entropy are probably combined with the changes of orientation entropy of macromolecules. Moreover, long segments of large macromolecules can be selectively pulled into relatively narrow pores, which are unable to accommodate entire polymer species. This partial penetration of macromolecules can lead to an unexpected increase in retention volumes and also to the mechanical degradation of polymer species, especially in the area of ultra high molecular weights.

The entropy based processes are too complicated to be *a priori* assessed in the quantitative way. They are also influenced by the hydrodynamic effects caused by the differences in the flow rate of eluent in dependence on its distance from the surface of column packing. Moreover, most meso- and macroporous SEC column packings exhibit complex geometry, which cannot be described by a simple model. Therefore the exact theory of SEC was not yet formulated and the method is not absolute. Each SEC column (system) must be calibrated by appropriate "standards" with known characteristics or molar masses of polymers in column effluent must be monitored with the "absolute" detectors.

Besides entropic partition, various enthalpic (interactive) retention mechanisms can be unwantedly active in the SEC column. These may affect retention volumes of polymers (V_R)

$$V_R = f(K) \approx \exp\left(\frac{-\Delta G}{RT}\right) = \exp\left(\frac{\Delta S}{R} - \frac{\Delta H}{RT}\right) \quad (1)$$

where: K — *distribution constant;* ΔG — *Gibbs function;* ΔS *and* ΔH — *the entropic and enthalpic contributions to retention volume, respectively;* T — *temperature;* R — *gas constant.*

Enthalpic contribution to V_R depends on the interaction energy (ε) between column packing and segments of macromolecules, which is affected by presence of small molecules of eluent.

Enthalpic retention mechanisms in polymer HPLC are adsorption, enthalpic partition, phase separation,

ion effects, and bio-affinity. For synthetic polymers the adsorption and enthalpic partition are most important.

Adsorption of macromolecules takes place on the surface of column packing or on the interface between mobile phase and the "liquid" immobilized on the column packing surface. Adsorption is controlled by the affinity between the molecules of eluent and the column packing, that is by the eluent strength. If the affinity is larger between segments of macromolecules and the column packing than between molecules of mobile phase and column packing, polymer species will be retained and their V_R will increase. Mobile phases, which strongly interact with the surface of column packing, may fully suppress adsorption of polymer sample.

Enthalpic partition of macromolecules takes place between the volumes of the stationary liquid within column packing and the mobile phase. The stationary liquid is usually chemically bonded to the column packing surface. Typically, it is the array of solvated alkyl (*e.g.* $C_{18}H_{37}$-) groups bonded on the surface of solid particles, *e.g.* of silica gel. The stationary phase can be created also by the solvated loops of free ends of macromolecules chains protruding over the surface of column packing formed by crosslinked polymers [*e.g.* poly(styrene/divinylbenzene) resins (PS/DVB)]. The extent of enthalpic partition of macromolecules depends on the difference in their solubilities within both phases. It is controlled by the solvating power (thermodynamic quality) of mobile phase toward separated macromolecules. If the mobile phase is a poorer solvent for polymer species than the solvated stationary "liquid", macromolecules are pushed into the latter and their retention volumes increase. If the mobile phase is (much) better solvent for polymer species than the solvated (bonded) groups on the column packing, enthalpic partition may be fully or partially suppressed.

If enthalpic retention mechanisms are efficiently eliminated, macromolecules are separated exclusively on the base of entropic and hydrodynamic processes. One speaks about ideal size exclusion chromatography. This situation is generally expected in the SEC analytical systems. Unfortunately, too often the unwanted enthalpic interactions affect retention volumes of analyzed polymers. This may lead to large errors in determined molar masses. The errors grow with increasing difference between effect of enthalpic retention of the analyzed polymer and of macromolecules used for calibration of SEC column.

SOURCE OF ERRORS IN SEC RESULTS

Let us briefly discuss particular components of the SEC instruments and some other factors from the point of view of their possible contributions to the errors in the SEC results.

Column packings

Following properties are important for a choice of the SEC column packing materials:

a) particle size and shape,

b) pore size, shape and volume,

c) mechanical stability,

d) feasibility of preparation of regular and stable bed of particles,

e) compatibility with eluents and eluent additives and feasibility of eluent changes,

f) enthalpic interactivity,

g) price.

The four parameters, namely a)—d), largely affect the selectivity and efficiency of separation, attainable by a packing material.

All modern SEC column packings are composed from spherical microparticles. They create a dense bed of packing. The arrangement of particles within the bed is affected by the technology of column packing process. This process is carefully optimized by the column producers for each packing material. The mechanical stability of bed depends on the stability of packing particles, the packing bed density and the swellability of particles. Gel particles may de-swell in eluent, which is a poor solvent or nonsolvent for their building macromolecules. Typical example is dimethyl formamide as eluent for some PS/DVB gels. As a result, the voids are formed within the gel bed, the peaks are broadened and column efficiency drops. Therefore, it is necessary to consult column manual before changing the eluent nature. The rearrangement of packing particles may by caused also by mechanic strokes and sudden changes of pressure within a column.

Excessively widened and skewed peaks may be interpreted as broad and non-symmetrical molar mass distribution of a sample. Therefore, it is necessary to check occasionally the column efficiency using appropriate low molar mass probes or better, the well characterized narrow or broad molar mass polymeric reference materials.

The resistance toward diffusion of macromolecules into the pores and back into the mobile phase (solute mass transfer) codetermines efficiency of separation process. It depends on the size of particles and on the pore geometry. The smaller particles of column packing, the higher the column efficiency. However, with decreasing particle size the flow resistance of column increases, and consequently also experimental problems connected with the flow rate instability may become more significant. Also the mechanical degradation of ultra-high molar mass species due to shearing raises with decreasing particle size.

Depending on the eluent and polymer analyzed, 5 μm or 10 μm particles are applied for oligomers and polymers of medium — high molar mass. Larger, even 20 μm packing particles are used for charac-

terization of ultra-high molar mass polymers at low flow rates.

Pore geometry is optimized by column producers. The aim is to prepare an open pore structure with the maximum large pore volume allowed by necessary mechanical stability of particles.

Presently, most SEC separations of lipophilic synthetic polymers is performed with PS/DVB column packings. Some commercial PS/DVB packings exhibit surprisingly high interactivity toward polar macromolecules. Probably various polar components of the polymerization system are built into the matrix of the gel and interact with the polar separated macromolecules, especially if eluent is not strong enough. The same phenomenon is expected also for other kinds of the SEC column packings.

In the improperly chosen SEC system, a fraction of sample may stay fully retained within the column packing. Evidently, the retained part of sample is not considered in molar mass calculation. Moreover, the retained species deteriorate column efficiency and usually further increase the enthalpic interactivity of a column. Effective sizes of pores are changed and even retention volumes of non-interacting samples can be altered. One speaks about SEC column history.

Highly polar acidic or basic substances are often added to the eluents in order to suppress polar interactivity of the SEC column packings. These additives may, however, attack the instrument and also complicate quantitative detection of a sample.

It seems that in order to suppress enthalpic retention mechanisms described above, the SEC systems: sample-mobile phase-column packing should be as similar as possible and the binary interactions sample-eluent, eluent-column packing and sample-column packing should be alike.

Important drawbacks of SEC represent intrinsically low both efficiency and selectivity of separation. Efficiency of SEC is affected by relatively slow diffusion rate of macromolecules, as well as by various parasitic mixing processes, which lead to the chromatographic zone broadening.

Limited selectivity of SEC separation is proper to the exclusion retention mechanism. Retention volumes of polymer species are situated within a relatively narrow slice between the interstitial volume (V_0) and the total volume (V_M) of a liquid in the column, that is within the pore volume of column packing. Moreover, the polymer molecular weight area subject to SEC separation spans at least over two decades for hypothetical column packing with uniformly sized pores. The real SEC column packings usually show relatively broad pore size distribution, which results in further broadening of separated molar mass area.

Low selectivity of SEC columns has especially serious consequences when "universal", "linear" SEC columns are applied. These contain mixtures of packing materials with various pore sizes to separate polymer species in the broad range of their molar masses and to produce linear or quasi-linear calibration dependences log M *vs.* V_R or log V_h *vs.* V_R, where M is the most abundant molar mass present in the narrow molar mass distribution polymer "standards" used for calibration and V_h is the hydrodynamic volume of macromolecules defined as product of molar mass and limiting viscosity number of the calibration standard in eluent. Broadening the area of molar mass covered with the "universal" SEC columns facilitates analyses of unknown samples and linearity of calibration dependences simplifies data processing. However, the universal columns further reduce the actual separation selectivity of the system. As a result, bimodality of *MWD* in analyzed polymer samples is often masked and even the presence of macromolecular admixtures remains undiscovered so the SEC data may be wrongly interpreted.

It is evident that even the low selectivity SEC gives very valuable information on the tendencies of many building and degradation reactions of macromolecules in the course of scouting measurements, which include also ultra-fast high-throughput analyses. These semi-quantitative data are certainly important for initial optimization of polyreactions, for example in the combinatorial material science, but they definitively should not be used in the precise calculations of polymerization kinetics parameters, and so on. Increased selectivity of separation is necessary to acquire the high precision/accuracy comprehensive information on molecular characteristics of polymers.

Pumps and detectors

Numerous different pumping systems are available on the market. Both short term and long term flow stability, as well as pump resetability represent important requirements for high precision and accuracy of SEC measurements. Pulseless eluent flow is needed for a successful operation of some types of detectors. It seems that the optimum solution may be the pumping system equipped with two pistons, each driven by its own, computer controlled motor. The flow rate can be independently checked by the internal standards or by the (broad) reference polymeric materials.

Besides retention volumes, concentration of sample in the column effluent is the most important primary information obtained from conventional SEC. It is furnished by the flow — through concentration or mass detectors. Sensitivity, linearity of response and compatibility with sample and eluent belong to the important requisites of majority of the detectors.

Unfortunately, most polymers do not contain appropriate chromophores and therefore the application of photometers as detectors is rather limited. Differential refractometers (RI detectors) are the most important detectors in conventional SEC. Unfortunately, they exhibit

relatively low sensitivity. Due to preferential solvation effects, the signals of differential refractometers must be corrected when mixed mobile phases are applied, especially in the lower molar mass area. The base line (in)stability of RI detectors necessitates their careful thermostating. RI detectors "see" peaks of air dissolved in sample solution, peaks of low molar mass impurities, as well as system peaks due to local excess of one eluent component if mixed mobile phases are applied. The system peaks are caused by preferential solvation of sample by one eluent component, by the selective displacement of one eluent component from the column packing, by preferential evaporation from the sample solution or by preferential adsorption on the walls of sample container and syringe. The peaks of air and other impurities as well as the system peaks often interfere with the low molar mass fractions of polymers, especially if linear SEC column of low selectivity is applied. The base line and peak limit setting become uncertain. The errors in the molar mass values, mainly in the number averages caused by these phenomena may be very large, even several hundred of percent.

Important progress brought evaporative light scattering detectors (ELSD) and interfaces which allow deposition of the column effluent on an appropriate surface, for example on a germanium disk. After evaporation of a solvent, ELSD monitors intensity of light scattered by "dry" particles of polymer, which are created by nebulization of the column effluent and following evaporation of solvent from the microdroplets. The intensity of scattered light depends on the mass concentration of polymer in the effluent. The film produced by an interface can be subject of infrared measurement.

Both above approaches allow working with continuous or local eluent gradients. Sensitivity of ELSD is generally 10—20 times higher than that of RI detectors. Still, further improvements of both detector types are needed. For example the linearity of ELSD response is limited and it depends on the nature of both polymer and mobile phase. The films created by the present interphase devices are often uneven.

Viscometric and light scattering detectors were developed for continuous monitoring of sample molar masses in eluents. Various approaches to flow through viscometers and light scattering detectors were elaborated. Multi-capillary viscometers are preferred over single-capillary instruments while the "bridge" arrangement seems to be optimal. Light scattering detectors work either at a low (7°) or at right angle. Alternatively, simultaneous measurements at several angles (up to 18) are applied with an advantage. It is expected that a few new viscometric and light scattering detectors soon appear on the market — after expiration of present patent rights — and that prices of these very useful instruments will drop. In spite of several attempts, the construction of flow through osmometer was not yet successful.

Very attractive is coupling of SEC with mass spectrometry (MS), especially with the matrix assisted laser desorption ionization (MALDI) and electrospray ionization (ESI) mass spectrometry. Progress in appropriate matrices and interfaces for MALDI and in the data interpretation concerning both MS techniques is very fast and the expected drop in instrument prices will likely broaden the applications of both techniques.

Linearity of detector response on sample concentration is usually good except for mentioned, otherwise very attractive evaporative light scattering detectors. However, the relatively low sensitivity of differential refractometers may make "invisible" the extreme parts of SEC chromatograms that is the regions of retention volumes, where the highest and the lowest molar mass fractions do elute. An instable base line may cause large error in the calculated data. The base line drift may be brought about, for example, by temperature or pressure variations or by mobile phase composition changes, for example due to gradual saturation of eluent by air or moisture — especially in case of differential refractometers. The base line drift may be hidden within the sample peak. *Vice versa*, the long tail of low molar mass fraction in the sample may be considered a base line irregularity. Coupled detection and especially combinations of concentration detectors with the "absolute" detectors, that is with the devices continuously monitoring light scattering and/or viscosity of effluent as well as with the mass spectrometers, can help in diagnosis/deleting problems with the concentration detectors.

Mobile phases

The importance of specific physicochemical parameters of SEC mobile phases is well recognized. The ability of eluent to dissolve sample, its viscosity, refractive index/UV transparency, boiling point — together with health effects and price belong to them. These parameters are well considered by most SEC system operators.

Somewhat overlooked is the mobile phase purity — moisture absorbed from air, residues and impurities coming from production/purification processes, oxidation products formed during storage/application, purposefully added auxiliary compounds, as stabilizers, *etc.* Already minute amounts of admixtures in eluent may strongly affect its SEC behavior. Impurities in an eluent together with low molar mass impurities in sample may form additional peaks at chromatograms. As mentioned, peaks of low molecular impurities, together with peaks of dissolved gases and with system peaks may interfere with the low molar mass tail of a sample. Consequently, the values of number average molar mass (M_n) can be affected. These latter phenomena are rather frequent and their influences on M_n data increase with decreasing column selectivity. Impurities in an eluent may change solubility of polymer sample (eluent quality) and also

eluent strength. Consequently, enthalpic partition and adsorption of macromolecules can be affected.

Typical example is tetrahydrofuran (THF) rapidly absorbing the moisture from air. Water is an efficient nonsolvent for majority of synthetic polymers and a very strong additive concerning polar sites or the column packing. The azeotropic mixture THF/water contains about 4.5 wt. % of water and its boiling point differs only about 3 °C from the boiling point of pure THF.

Sample concentration and injected volume effects

It is known that SEC retention volumes of polymeric samples increase with rising sample concentration. The dependences of V_R on injected polymer concentration are usually linear and their slopes (k_c) increase with both polymer molar mass and thermodynamic quality of mobile phase for polymer sample. The dependence of k_c on thermodynamic quality of eluent may cause mutual shifts of universal calibration dependences of different polymers. At a certain low molar mass (usually in the oligomer range of a few kg/mol) and in a thermodynamically poor (theta) eluent k_c approaches zero. Similarly, k_c diminishes for macromolecules excluded from the packing pores.

Concentration effects influence also the width of polymer peaks. Increased viscosity of concentrated sample solution decreases the diffusion rate and decelerates the mass transfer of macromolecules. Large difference between viscosities of mobile phase and sample solution may cause flow disturbances of sample zone ("viscous fingering"). As a result, the chromatographic zone is broadened and deformed. At the same time, the molar mass dependence of k_c may bring about some peak sharpening for broad molar mass distribution samples because the low retention volumes (for higher M) increase more due to the concentration effects than the high retention volumes. It depends on the particular system which influence eventually prevails.

To reduce the role of injected polymer concentration one should:

— Inject the lowest possible polymer concentration. This requirement may be not feasible for some SEC systems, due to low sensitivity of detectors, especially of refractometers.

— Use eluents of nearly equal thermodynamic quality for calibration "standards" and for polymer analyzed. Unfortunately, enthalpic partition of macromolecules mentioned in previous section may severely complicate the work with poor or even with theta solvents as eluents.

— Introduce corrections of V_R for injected concentration. The existing procedures for such corrections are, however, rather cumbersome and therefore practically not used.

Injected volume of sample solution (v_i) affects both the position and width of chromatographic peaks. This way the SEC data may be influenced by v_i applied. Important effects of v_i were observed above $V_t/v_i \sim 10^2$, where V_t is total volume of the column packing.

Temperature effects

As typical for entropy driven process, SEC retention volumes intrinsically do not depend on temperature. An exception represents the vicinity of theta point where macromolecules extensively change their sizes with temperature. Temperature variations may also strongly affect the enthalpic interactions within a column and the viscosity of mobile phase. As mentioned, the temperature changes deteriorate the detector base line, especially at differential refractometers and affect the actual volume of the column effluent. Therefore, it is advisable to use a column thermostat and to work with a prethermostated eluent. Poor sample solubility often requires an application of elevated temperature. This is typical for polyolefins, polyesters and many polyamides. Chromatographic experiments at high temperature bring many additional problems and it is to be hoped that the new generation of high-temperature SEC instruments will show an improved performance.

Instrument operation, data acquisition and processing

In many laboratories, the operation mode of SEC instrument is similar to UV or IR spectrometers ones. The instruments are commonly accessible and they are switched on/off for any (single) measurement. Usually, columns are not thermostated. Calibration dependences and column efficiencies, as well as intralaboratory reproducibility are checked only rarely. The basic experimental conditions especially injected concentration are not kept constant. The eluents are neither purified before use nor protected from oxygen and moisture absorption. An identical column packing, usually PS/DVB linear column is used for any analyzed polymer, which is soluble in the eluent available (usually tetrahydrofuran) and irrespective of the sample molar mass. A sample loop of the same volume is often used for columns of fairly different sizes. The injected concentrations usually vary.

Surprisingly, even in spite of this situation the short-term, intralaboratory repeatability of SEC measurements may be good. However, the recent round robin tests organized under auspices of IUPAC, in which participants did not apply prescribed, nearly identical experimental conditions, showed a very large data scatter, the MMW values easily differed several hundred of percents. It is evident that the SEC systems and experimental conditions should be standardized. The standardization was attempted in the past, however, the standard sets of experimental conditions differed in particular countries. The data obtained under recommended standard conditions should be appropriately designated.

Even the highly automated and computerized SEC data acquisition systems often need skilled operators. For example, the operator should decide where to situate the base line and the peak limits, especially if sample contains a broad spectrum of macromolecules. Typically those are samples showing an extended and not well-marked tail at low molar mass area. Computer may consider such long and low tail just as a base line perturbance. Frequent changes of mobile phase nature and temperature of instrument belong to further sources of erroneous SEC results.

It seems that skilled and specialized operators supervising a series of continuously running instruments, one for each mobile phase, belong to the important prerequisite for obtaining accurate SEC data.

COUPLED AND TWO-DIMENSIONAL TECHNIQUES

As shown, the unwanted enthalpy based retention of macromolecules can badly affect the results of SEC. On the other hand, exclusion mechanism can be deliberately and in the controlled way combined with enthalpic retention mechanisms. In any case, the entropic effects, especially the changes in conformational entropy of macromolecules are always present. The combination of entropic and enthalpic retention mechanisms within the same column leads to coupled procedures of polymer HPLC.

The most common coupled procedure is polymer HPLC under critical conditions. It is based on the mutual compensation of exclusion (entropic partition) of macromolecules, which reduces their retention volumes when their molar masses increase, with either adsorption or enthalpic partition that is with enthalpic retention mechanisms, which increase sample retention volumes of samples with growing molar masses. The successful compensation of ΔS and ΔH contributions results in independence of polymer V_R on its molar mass [see equation (1)]. This allows to practically eliminate the effect of one constituent of a complex polymer, for example a block in the block copolymers, a component in polymer blends or one part of the functionalized macromolecules on the overall elution behavior of polymer species. As a result, both parts of a complex polymer can be independently characterized successively using different experimental conditions (column packing, eluent, temperature).

Other important coupled procedures apply continuous or stepwise eluent gradient. Coupled procedures form an important part of two(multi) dimensional polymer HPLC, in which fractions of polymer sample obtained in the first column working with coupled retention mechanism are transported into the second or further column(s) for subsequent separation. First column separates macromolecules exclusively or at least prevailingly according to one characteristic while the last column, usually SEC system, accomplishes the characterization of sample.

Enthalpic retention mechanisms can be used also for augmenting of the selectivity of polymer separation according to their molar masses. Isocratic enthalpy dominated separations, in which retention volumes increase with the molar masses of macromolecules are, however, feasible only in the area of low molar masses, below about 10 kg/mol. Above this limit, V_R increases very rapidly with sample molar mass and eventually macromolecules are fully retained in the column.

Increased selectivity of isocratic polymer separation in the high molar masses area can be obtained applying temperature gradient (temperature gradient interaction chromatography) or by controlled isocratic, isothermal combination of enthalpic and exclusion retention mechanisms in the vicinity of critical conditions above "SEC excluded" sample molar mass (enthalpy assisted SEC). The latter, novel methods apply the rapid decrease in the enthalpic interactions with sample M above its pore exclusion limit.

The common problem of all coupled procedures in polymer HPLC is a possible incomplete sample recovery. The danger of the full retention for a fraction of sample, usually that with the highest molar mass, increases with increasing extent of enthalpic interactions between column packing and polymer species. Sample recovery problem is more distinct in coupled procedures than in "pure" SEC. Enthalpic interactions are the part of the separation process and therefore they cannot be suppressed or oven removed.

CONCLUSIONS

Size exclusion chromatography is a marvellous method. At present, it is routinely (maybe too routinely!) applied in majority of polymer research laboratories and production units. SEC is a simple, fast, repeatable and relatively inexpensive analytical tool. Measurements are not labor-intensive and sample consumption is low. Due to above features, SEC practically substituted classical methods of molecular characterization of the polymers. In combination with the flowthrough light scattering and viscometry, as well as with infrared and mass spectrometries, SEC can provide detailed information about many various polymer species.

SEC gives the data of good to very good precision (high intralaboratory repeatability). On the other hand, SEC results suffer from limited to very low accuracy (low interlaboratory reproducibility). Standardization of sample preparation, experimental conditions of measurements, and data processing is needed which would be enforced by increased experience of operators. Selectivity of SEC separation is generally low. This is especially evident when the "linear" (universal) columns are used. Low selectivity of SEC further deteriorates results of high speed, high sample throughput procedures.

SEC data for complex polymers showing multiple distributions of their molecular characteristics and the

data produced by the fast or ultra-fast procedures can be considered only as semi-quantitative, appropriate mainly for assessment of tendencies. For detailed molecular characterization of complex polymers, coupled and two-dimensional procedures of polymer HPLC should be used instead of SEC alone. So far the former methods, however, are slow, work-intensive and not universal. Therefore, their applications are limited to a few special cases.

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W kolejnym zeszycie ukażą się następujące artykuły:

— Telecheliczne oligomery otrzymane z tlenku etylenu i kwasu fosforowego. Struktura oraz przekształcanie w polimery glinoorganiczne (*j. ang.*)

— Badania oksyetylenowanych żywic fenolowych. Cz. I. Charakterystyka powierzchni i właściwości powłok na podłożach metalicznych (*j. ang.*)

— Otrzymywanie nowego akrylanu poliorganosiloksanowego i właściwości zawierających go kompozycji akrylanowych utwardzanych promieniowaniem UV (*j. ang.*)

— Wpływ modyfikacji rezolowej żywicy fenolowo-formaldehydowej produktami chemicznej degradacji poli(tereftalanu etylenu) na jej właściwości

— O przyczynach efektu wielokrotnego topnienia występującego po izotermicznej krystalizacji jednorodnych kopolimerów etylen/1-okten (*j. ang.*)

— Biodegradacja folii z polietylenu modyfikowanego skrobią. Badanie zmian struktury nadcząsteczkowej polietylenu

— Mieszaniny polimerowe PET/ PE-LD i PET/PP z dodatkiem nowego kompatybilizatora

— Ocena przepływu w formie wtryskowej polimeru z napełniaczem płytkowym jako znacznikiem

— Osłabione wiązania w stanach przejściowych procesu degradacji polimerów jako prawdopodobne miejsca pękania makrocząsteczek (*j. ang.*)