Liquid Chromatography of Synthetic Polymers under Limiting Conditions of Insolubility. I. Principle of the Method

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A novel liquid chromatographic procedure is presented. It is based on differences in the transport velocities of the fast-moving, pore-excluded macromolecules and slow-progressing, pore-permeating small molecules of an auxiliary liquid. A barrier of small molecules selectively decelerates certain kind of macromolecules while other kind remains unhindered. As a result, polymers of different nature are efficiently separated. In this new approach, the barrier is formed by a zone of a non-solvent injected immediately before the sample solution. The resulting method is denoted liquid chromatography under limiting conditions of insolubility.

Keywords: liquid chromatography, macromolecule, polymer, barrier polymer HPLC

Liquid chromatographic characterization of complex synthetic polymers, which exhibit more than one distribution in their molecular characteristics, requires purposeful combination of entropic (exclusion) and enthalpic (interaction) retention mechanisms. Such combinations are often designated as coupled procedures in high-performance liquid chromatography of polymers (polymer HPLC) [1]. Typical examples include liquid chromatography under critical conditions and eluent gradient polymer HPLC [1—4]. A new approach to coupling retention mechanisms is represented by a group of barrier polymer HPLC methods. The latter procedures utilize different mobility of small molecules of eluent or other appropriate low-molar-mass auxiliary compound compared to large species, macromolecular sample components, when traveling along HPLC column packed with particles of suitable porosity. Progress of small molecules is slow because they penetrate practically all pores of column packing. On the contrary, transport of macromolecules is much faster under otherwise identical conditions, since they are partially or fully excluded from the pores. This velocity difference enables creation of slowly moving “barrier” of small molecules, which may be impermeable for certain kinds of macromolecules and efficiently hinders their rapid progression along the column. Other kinds of macromolecules may elute from the same column unhindered and thus can be separated from the decelerated species. The resulting separation methods are called Liquid Chromatography under Limiting Conditions (LC LC) [5—12]. Typical features of the so far evaluated LC LC procedures are peak-focusing due to the accumulation of macromolecules on the barrier edge, which allows injection of extremely large sample volumes – even above 15% of the total column volume [10, 11]; robustness in terms of low sensitivity toward eluent composition and temperature changes [9, 11], and resulting user-friendliness; and applicability in a broad polymer molar-mass range from a few thousands to at least several millions g mol$^{-1}$ [9, 10, 12]

Two methods can be applied in LC LC to block a fast transport of macromolecules:

i) Mobile phase prevents elution of polymer species but sample solvent promotes their elution. In this case, eluent itself represents a continuous barrier because interacting macromolecules cannot leave the zone of their initial solvent in the course of their transport along the column [5—7, 9, 10, 12];

ii) Eluent promotes elution of sample solution but the latter is preceded by a defined, narrow or broad zone of appropriate kind of small molecules, hindering fast elution of macromolecules [9, 11, 12].

The barrier zone can be injected together with macromolecules as sample solvent [9] or independently – just before sample introduction [12].
In the first case, the eluent barrier has constant composition so that a sample break-through is not possible. On the contrary, elution-preventing (narrow) barrier zone is diluted during column passage. As a result, sample break-through may appear.

Various enthalpic retention mechanisms can be employed to create the barrier effect. So far, three LC LC procedures were tested. When Liquid Chromatography under Limiting Conditions of Solubility (LC LCS) [5, 7] is used, eluent is a weak non-solvent for macromolecules, which are injected in a thermodynamically good solvent. Liquid Chromatography under Limiting Conditions of Adsorption (LC LCA) [8—11] is based on the use of eluent promoting adsorption, desorli. If polymer species were dissolved and injected in eluent they would stay trapped within column. However, desorption-promoting liquid, desorli, is employed as sample solvent. In the third procedure, Liquid Chromatography under Limiting Conditions of Desorption (LC LCD) [9, 11, 12], desorli is an eluent and a narrow zone of desorli creates barrier for macromolecules.

All three LC LC procedures were applied for the fast and efficient separation of model polymer blends, while LC LCA was successfully engaged also in discrimination of minor (1%) macromolecular constituents from a major (99%) polymer matrix [10].

There were doubts concerning applicability of phaseseparation (precipitation) retention mechanism in the ii) arrangement, whether a narrow (experimentally feasible) zone of a non-solvent can efficiently decelerate insoluble macromolecules, and also whether HPLC systems can be identified, in which a possible creation of micro-phased system in the course of polymer precipitation would prevent application of the barrier LC LC principle.

To answer the above questions, experiments were performed using a series of narrow-molar-mass-distribution polystyrenes (PS) (Pressure, Pittsburgh, PA, USA) as precipitating polymers and a broad-molar-mass-distribution poly(vinyl acetate) (PVAC) (Polysciences, Warrington, PA, USA) as a non-precipitating polymer. Toluene and tetrahydrofuran (THF), which are good solvents for both polymers, and methanol, used as a selective non-solvent for PS were applied as mobile phase and barrier components. Methanol and toluene were purchased from Slavus (Bratislava, Slovakia), and THF from POCH (Gliwice, Poland). They were of analytical grade, distilled immediately before their use. THF was stabilized with 0.01 mass % of 2,6-di-tert-butyl-p-cresol. Narrow-pore (6 nm) spherical silica gel (10 μm particles) from Kavalier (Vo- tice, Czech Republic) was home-packed into columns of various sizes. Column dimensions did not affect the elution mode. The pumping system Knauer 64 (Knauer, Berlin, Germany) worked at the elution rate 1 mL min⁻¹ at ambient temperature. Eluents, toluene and THF, as well as mixed eluents toluene—methanol and THF—methanol containing 20 mass % of methanol were pre-thermostated in a water bath. The actual flow rate was checked by a burette and the sample retention volumes were corrected accordingly. Columns were kept at 30 ± 0.1°C in a custom-made oven connected with a water bath thermostat. A tandem of two six-port two-way injection valves from Rheodyne 7725i (Cotati, PA, USA) and Valco (VICI, Houston, TX, USA) provided with the loops of various sizes was used for injection of methanol barrier zone immediately followed by a polymer solution. Samples were dissolved in eluent. Detector was an evaporative light-scattering device from Eurosep (Cergy-Saint-Pontoise, France), Model DDL 21. The peak retention volumes, \( V_R \), were calculated from retention times of the peak apexes applying corrections for the actual flow rate. The retention volume of methanol was determined by an independent experiment using a refractive index detector ERC 7515A (ERMA, Tokyo, Japan).

Typical results for eluents toluene and toluene—methanol (20 mass % of methanol) are shown in Figs. 1—3. The elution tendencies were identical for the second mixed eluent THF—methanol (20 mass % of methanol).

It was found that the LC LC procedure using small-volume non-solvent barriers with narrow-pore column packing created well-defined polymer peaks. Moreover, the LC LC retention volumes of polystyrenes were independent of their molar masses in the entire molar-mass area under the study conditions, starting from 4 up to 498 kg mol⁻¹. They were similar to \( V_R \) of the non-solvent, methanol, while polymers injected in the same eluent but without methanol...
barrier eluted in the SEC mode, mostly in the interstitial volume of column. Finally, the LC LC technique with a barrier made of a narrow zone of appropriate non-solvent allowed fast and easy separation of polymers with similar molar masses differing in their solubility. Polymer, which is soluble in the non-solvent for another polymer, easily breaks through and elutes in the exclusion mode.

In this way, queries mentioned above were responded positively. As a result, new coupled-polymer HPLC procedure Liquid Chromatography under Limiting Conditions of Insolubility (LC LCI) was formulated. The detailed study on the role of experimental conditions and on applications of LC LCI is in progress in our laboratory.

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