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Liquid chromatography of polymers under limiting conditions of desorption II. Tandem injection and quantitative molar mass determination☆

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Abstract

Liquid chromatography under limiting conditions of desorption (LC LCD) is a method which allows molar mass independent elution of various synthetic polymers. A narrow, slowly moving zone of small molecules, which promotes full adsorption of one kind of polymer species within column (*an adsorli*) acts as an impermeable barrier for the fast moving macromolecules. The latter accumulate on the barrier edge and elute nearly in total volume of liquid within column. At the same time, transport of less adsorptive macromolecules is not hampered so that these are eluted in the size exclusion (SEC) mode. As result, polymers differing in their polarity and adsorptivity can be easily separated without molar mass interference. Three methods of barrier creation are discussed and compared. It is shown that a fraction of sample may elute unretained if the adsorli sample solvent is used as a barrier in connection with a narrow-pore column packing. One part of excluded macromolecules likely breaks-out from the adsorli zone and this results in partial loss of sample and distortion of the LC LCD peaks. This problem can be avoided if the adsorli zone is injected immediately before sample solution. Applicability of the LC LCD method for polymer separation has been demonstrated with a model mixture of poly(methyl methacrylate) (adsorbing polymer) and polystyrene (non adsorbing polymer) using bare silica gel as a column packing with a combination of tetrahydrofuran (a desorption promoting liquid – *a desorli*) and toluene (*adsorli*). It has been shown that the LC LCD procedure with tandem injection allows simple and fast discrimination of polymer blend components with good repeatability and high sample recovery. For quantitative determination of molar masses of both LC LCD and SEC eluted polymers, an additional size exclusion chromatographic column can be applied either in a conventional way or in combination with a multi-angle light scattering detector. A single eluent is used in the latter column, which separates the mixed mobile phase, system peaks and the desorli zone from the polymer peaks so that measurements are free from disturbances caused by the changing eluent composition. The resulting LC LCD × SEC procedure has been successfully applied to poly(methyl methacrylate) samples.

Keywords: Liquid chromatography of polymers; Polymer adsorption and desorption; Complex polymers

1. Introduction

Liquid chromatography of polymers under limiting conditions of desorption (LC LCD) is a novel method which couples entropic and enthalpic retention mechanisms [1]. LC LCD belongs to the family of procedures which work at the point of exclusion–adsorption transition. It employs the fact that large macromolecules, which are partially or fully excluded from the packing pores travel along an appropriate high-performance liquid chromatographic (HPLC) system with a higher average velocity than small molecules of low molecular liquids. The latter, slowly moving species promoting polymer adsorption (molecules of *an adsorli*) can act as a narrow "barrier", which efficiently hampers fast progression of macromolecules along the column. As result, polymer molecules transported by an eluent promoting polymer desorption (*a desorli*) accumulate on the edge of the adsorli barrier irrespectively of their molar masses and leave the LC

☆ First part of this series is ref. [1].

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LCD column in the form of a rather narrow band. At the same time, less adsorptive macromolecules may break-through the barrier, which is effective for the more adsorptive polymer, and freely elute in the size exclusion chromatography (SEC) mode. In this way, polymers of different adsorptivities can be mutually discriminated. Selected features of LC LCD, especially methods of the narrow adsorli barrier creation are discussed and compared in this contribution. Determination of absolute molar mass values for the LC LCD eluted polymer species using a multi-angle light scattering detector is also demonstrated.

2. Experimental

2.1. Chromatograph

The chromatograph consisted of following components. Model 510 isocratic pumps (Waters, Milford, MA, USA) were employed at the flow rates of 0.5 and 1 ml min^{-1}. The actual flow rate was checked by a burette. An autosampler MIDAS (Spark Holland, Emmen, The Netherlands) was applied for sample injection. Tandem injections were performed in the "μl pick-up injection mode" of the instrument. The volume of the adsorli barrier varied from 20 to 100 μl. Columns were kept at constant temperature in an air oven (Knauer, Berlin, Germany) or in a custom made oven with a duplex wall connected to a water thermostat. The temperature of experiments was 30 °C.

2.2. Detection

Similar to other liquid chromatographic methods, which couple entropic (exclusion) and enthalpic (adsorption) retention mechanisms, the eluent strength must be carefully adjusted also in LC LCD. The most convenient way to do so consists in application of mixed solvents eluents. However, due to preferential solvation of macromolecules by one eluent component, system peaks appear on chromatograms monitored with the non-specific detectors [2]. Moreover, LC LCD eluting macromolecules partially overlap with the adsorli barrier. Therefore, refractive index detectors (RID) cannot be directly used for sample detection. Evaporative light scattering detector (ELSD) (Model PL 1000 from Polymer Laboratories, Church Stretton, Shropshire, UK), which does not respond to volatile solvent molecules was used in this work. Still, due to problems with quantitative processing of the ELSD response [3,4] this detector was used only for determination of polymer retention volumes. The shapes and positions of desorli barrier zones were monitored by a density detector (DDS 70, Chroma, Graz, Austria).

A multi-angle light scattering instument (MALS) (DAWN DSP from Wyatt Corporation Technology, Santa Barbara, CA, USA) was used in the two dimensional arrangement LC LCD × SEC. Polymer species eluted from the LC LCD column were on-line introduced into the SEC column flushed with pure tetrahydrofuran (THF) (Fig. 1).

The SEC column allowed an exchange of the original environment of polymer species (LC LCD eluent plus adsorli zone) for THF so that a MALS/RID (Model 410, Waters, Milford, MA, USA) combination could be employed. Data from the light scattering measurements were processed with help of software ASTRA (Wyatt Corporation Technology, Santa Barbara, CA, USA). For calculation of molar masses, dn/dc values 0.192 and 0.084 ml g^{-1} for PS and PMMA in THF, respectively, were used [5]. Experimental data were independently processed also with the Clarity (DataApex, Prague, Czech Republic) PC software applying calibration with polystyrene standards.

Peaks of *n*-hexane were monitored by an RID Model 198 (Knauer, Berlin, Germany).

2.3. Stationary and mobile phases

Bare silica gels were chosen for this study to avoid extensive enthalpic partition and interphase adsorption of macromolecules in favor of bonded stationary phases [6]. Thus, adsorption of macromolecules onto surface silanols of silica gel was anticipated the main enthalpic retention mechanism coupled with the exclusion retention mechanism. Narrow pore (6 nm) spheroidal silica gel Silpearl (Glasswork, Votice,

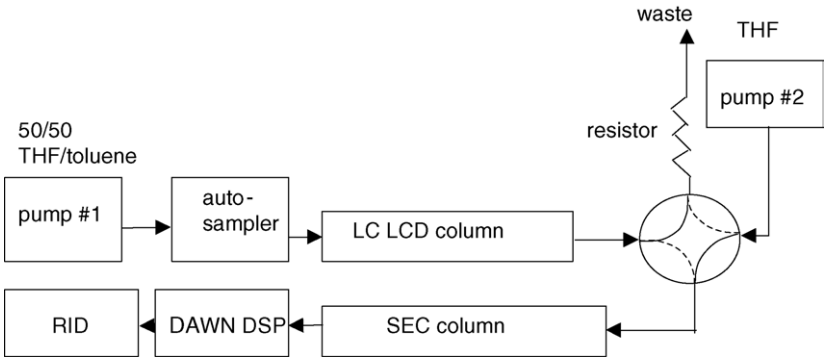

Fig. 1. Scheme of a two-dimensional LC LCD/SEC chromatograph. Resistor was a capillary with a pressure drop similar to that of the SEC column.

Table 1
Specifications of columns used

Column	Column packing (particle diameter)	Column dimensions (mm)	Pore diameter (nm)	Column efficiency N_T (m^{-1})	V_M (ml)	V_0 (ml)
#1	Silpearl (7 μm)	250 × 4	6	11800	2.92	2.02
#2	Silpearl (10 μm)	300 × 7	6	25400	9.04	5.80

Czech Republic) with particle diameters 7 and 10 μm, was applied in experiments. It was expected that in this way the effect of size exclusion within the LC LCD column would be suppressed and the resulting peaks would be better focused. Sorbents were packed into stainless steel columns of two different dimensions (see Table 1) in this laboratory. The column efficiencies N_T and total volumes of mobile phase within column V_M were determined with RID by injection of 20 μl solution of *n*-hexane (1 vol.%) in toluene into columns flushed by toluene. The column #1 was poorly packed and it exhibited a rather low efficiency. With this column, little influence of column quality on results obtained and thus robustness of the LC LCD method is demonstrated. Interstitial volumes of columns, V_0, were assessed by means of high molar mass polystyrene 498 kg mol^{-1}, which was fully excluded from the column packing pores in the THF eluent.

Linear AM gel 7.8 mm × 305 mm (American Polymer Standards Corporation, Mentor, OH, USA) SEC column was applied with the THF eluent at the flow rate of 0.5 ml min^{-1}.

Analytical grade THF (Slavus, Bratislava, Slovakia), was chosen as a medium effectivity desorli for poly(methyl methacrylate)s (PMMA) in combination with bare silica gel. In fact, a weak adsorption of PMMA in THF was observed with the non-modified silica gels [7,8]. The retention volumes of PMMA probes in THF were slightly increased in comparison with the non adsorbed PS of the same hydrodynamic volume. Analytical grade toluene (Slavus, Bratislava, Slovakia), which prevented elution of PMMA from the bare silica gel was chosen as an efficient adsorli [8]. It should be noted, that both THF and toluene are well miscible, thermodynamically similarly good solvents for PMMA [9], and the deterioration of the mixed solvents quality due to a cononsolvency effect is improbable. Both solvents were dried in conventional way and distilled before use. THF was stabilized immediately after distillation with 0.02 wt.% of butylated *p*-crezol. The LC LCD eluent composition range was identified in the previous work [1] for PMMA and bare silica gel. It included eluents containing from 50 to at least 60 wt.% THF. Below 50 wt.% of THF, the eluent approached its "critical composition" that is it did not elute PMMA in the exclusion mode any more. On the other hand, it was anticipated that eluent containing well over 60 wt.% of THF would be too strong so that a barrier of toluene could not efficiently hamper fast elution of PMMA from bare silica gel. Generally, the strenght of the LC LCD eluent should be kept as low as possible, still preserving SEC elution of polymer under study. A 50/50 (w/w) mixture of THF/toluene was used in all present experiments. Mixed eluents were prepared by weighing solvents with a precision better than 0.1%.

2.4. Polymers, injected solutions

Poly(methyl methacrylate)s prepared by anionic polymerization and exhibiting medium polydispersity and low stereoregularity with the most abundant molar masses (*M*) ranging from 6.5 to 1600 kg mol^{-1} were employed. They were gifts of Dr. W. Wunderlich (Röhm, Darmstadt, Germany) and Dr. J. Herz (Institut Sadron, CNRS, Strasbourg, France). Polystyrene standards used for SEC column calibration and for LC LCD × SEC experiments were from Pressure Co, (Pittsburgh, PA, USA) and their molar masses ranged from 0.9 to 2000 kg mol^{-1}. In the LC LCD experiments, samples were dissolved and injected either in pure toluene or in eluent. In the latter case, the sample solution was immediately preceded with a zone of toluene adsorli barrier with a volume up to 100 μl. This kind of tandem injections was applied also in some experiments, in which sample was dissolved in adsorli that is in pure toluene (see Section 3). For conventional SEC measurements, samples were dissolved in THF. The standard injected sample volume was 50 μl. Concentration of solutions was nearly 1 mg ml^{-1}. For separation of polymer mixtures, samples were prepared by mixing original polymer solutions.

3. Results and discussion

As mentioned, the principle of the LC LCD procedure consists in the action of a barrier made of a solvent, which is an adsorli for a given polymer on a given column packing and at given temperature. At the same time, eluent is a desorli. The barrier must efficiently block fast progression of macromolecules and its position within column must be well defined. There are three possibilities to create an adsorli barrier

(i) an adsorli is used as sample solvent [1,10,11];
(ii) a zone of adsorli is introduced into column just before sample, which is dissolved in eluent;
(iii) a combination of (ii) and (i) is employed that is the sample is dissolved in an adsorli and injected immediately behind a zone of pure adsorli.

All three approaches were applied in this work. The (i) approach is simple and straightforward. A usual six-port two-way injection valve can be used for sample introduction. However, there is a danger of partial break-out of polymer species from the injected sample solution. Macromolecules, which manage to escape from the zone of their initial adsorli solvent and reach the desorli eluent are further eluted in

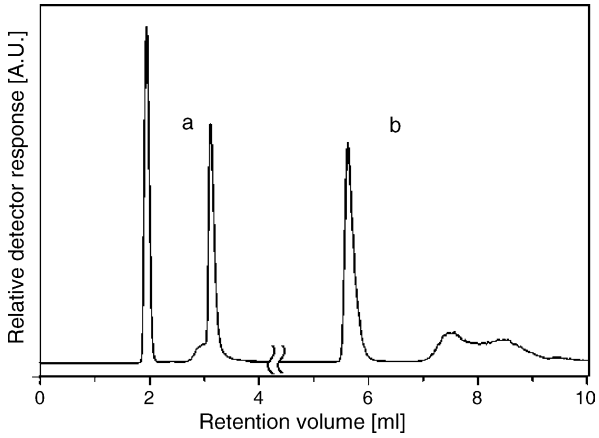

Fig. 2. Typical chromatograms of PMMA 294 kg mol^{-1} which broke-out from the adsorli zone and eluted partially in the SEC and in the LC LCD modes. The LC LCD peaks are skewed. Sample was injected in toluene adsorli (a) column #1 and (b) column #2.

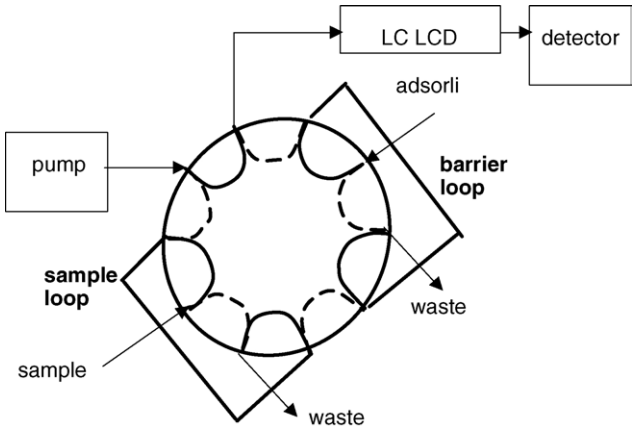

Fig. 4. Scheme of an experimental arrangement for the tandem injection mode using one 10-port two-way valve equipped with two loops.

the SEC mode. This may happen to an important fraction of macromolecules from the front part of the sample solution, which is extensively mixed with eluent. The break-out process takes place especially in the initial stage of sample elution and results in appearance of a second polymer peak on chromatogram, which exhibits lower retention volume. Moreover, the sample peaks eluted in the LC LCD mode may be distorted (Fig. 2).

In this way a part of sample is lost and the LC LCD peaks are difficult to interpret. If the LC LCD method is used for separation of two polymers with different adsorptivities, the breaking-out fraction of more interactive species interferes with the peak of less adsorptive macromolecules. The break-out phenomenon seems to be especially important with the narrow pore column packings. The very fast moving pore excluded macromolecules likely quit the zone of the adsorli solvent easier than the pore permeating species. The break-out of sample molecules was not observed when 10 nm and macroporous packings were applied [1,11]. As mentioned, the narrow pore LC LCD column packings are especially preferred when the main task is a direct separation of polymer species differing in their adsorptivities. The excluded, non-adsorptive polymer is eluted in the interstitial volume of the LC LCD column and its retention volume differs well from the retention volume of the adsorptive species, which travel behind the small molecules of adsorli that is near the total volume of liquid within column. As result, well chosen narrow pore columns produce slim both SEC and LC LCD peaks. Moreover, the focusing of LC LCD peaks in the narrow pore columns is not disturbed by the exclusion processes, which may take place in the desorli eluent. The focused polymer peaks are especially welcome in separation of multicomponent polymer blends and copolymers applying a series of adsorli barriers with different strenghts. Work in this direction is in progress in our laboratory. The break-out problem can be solved by the tandem sample injection approaches (ad ii and iii). Tandem injection (ad ii) must be applied also if the injected polymers exhibit limited solubility in pure adsorli. Two six-port two-way valves (Fig. 3) or a 10-port two-way valve (Fig. 4) or an appropriate autosampler are to be used for sample and barrier zone introduction in the (ii and iii) modes.

The tandem injections of pure adsorli and sample dissolved in eluent (ii) using autosampler in the μl pick-up injection mode produced single peaks with retention volumes independent of polymer molar masses (Fig. 5).

As expected, macromolecules accumulated right behind the adsorli zone. In spite of adsorli zone broadening, the

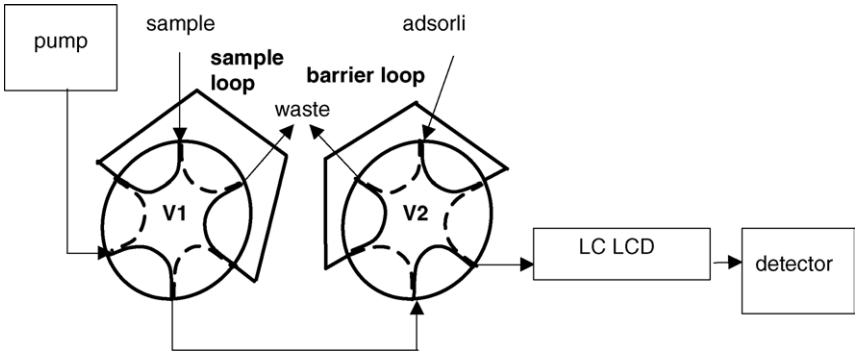

Fig. 3. Scheme of an experimental arrangement for the tandem injection mode using two six-port two-way valves.

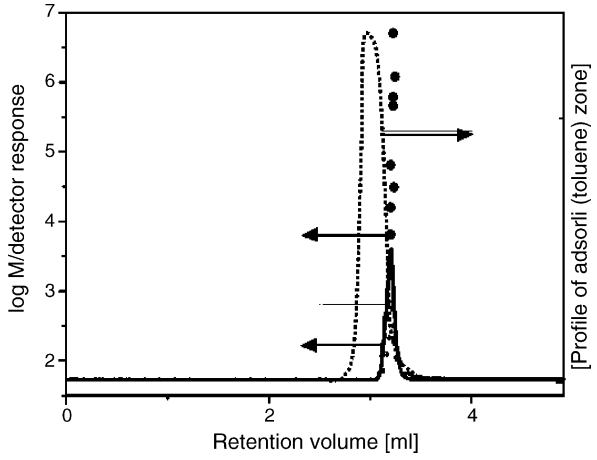

Fig. 5. Molar mass independent elution of eight PMMA samples with different molar masses in the LC LCD mode from column #2. Polymer species eluted irrespective of their molar masses (full circles, left axis) after injected barrier zone, which is depicted by the dotted line (right axis). The adsorli zone 100 μl was injected immediately before the polymer sample dissolved in eluent. Its profile was monitored with help of the density detector. The figure shows also focused LC LCD peaks of PMMA.

front parts of polymer peaks were steep but their tails were slightly broadened (Fig. 6). Still, the obtained LC LCD peaks can be considered well focused. After the LC LCD elution of PMMA had been completed, additional pulses of desorli THF were introduced into column. In contrast with our observation done in liquid chromatography under limiting conditions of adsorption (LC LCA) [12,13], no PMMA was eluted by two large (2 ml) THF pulses (Fig. 6). In LC LCA, eluent is an adsorli and sample solvent is a desorli. Macromolecules cannot leave their initial solvent and accumulate within the front part of the desorli zone. However, it was revealed [12] that a large fraction of polymer is pulled from the desorli zone into the narrow pores of packing which are in equilibrium with the adsorli eluent. These macromolecules remain trapped within the LC LCA column and can be partially released by large additional pulses of desorli [12,13]. Evidently, LC LCD is less susceptible to this kind of unwanted adsorption because the column packing, especially its narrowest pores are in equilibrium with the desorli eluent [12].

Fig. 6 illustrates also a relatively low importance of column efficiency in LC LCD. The sample band broadening in the more efficient but much larger column #2 seems to be comparable to that in column #1. This is surprising because both the usual sample zone dispersion and the adsorli zone spreading should be reduced in the column exhibiting high efficiency. In any case, a short and efficient LC LCD column is a choice for a simple separation of two-component polymer blends. It is expected, however, that length and diameter of the LC LCD column must be increased for separation of more complex polymer samples such as, for example, copolymers.

A typical example for discrimination of poly (methyl methacrylate) and polystyrene of similar molar masses on the LC LCD principle is shown in Fig. 7. Polystyrene is less adsorptive than PMMA and it elutes in the SEC mode from bare silica gel in toluene eluent [8]. Therefore, polystyrene species were not retained by the toluene zone and left the LC LCD column in its interstitial volume. It should be noticed that the widths of polystyrene and PMMA peaks eluted from the low efficiency column #1 were comparable at their half heights regardless the latter polymer appeared at much higher retention volume. The peak of PMMA was even narrower than the peak of polystyrene at the base line though even smallest polystyrene molecules present in the sample were well excluded from the packing pores and therefore the pore permeation effects were hardly possible.

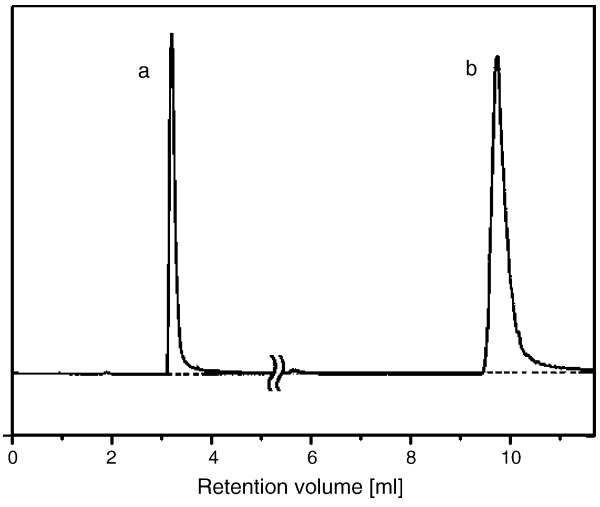

Fig. 6. Focused chromatogram of PMMA 294 kg mol^{-1} eluted in the LC LCD mode (full lines). Tandem injection with a 50 μl barrier of toluene was applied. The detector traces are also shown (dotted lines) due to injection of 2 ml THF zones after the LC LCD experiment had been finished. (a) Column #1 and (b) column #2.

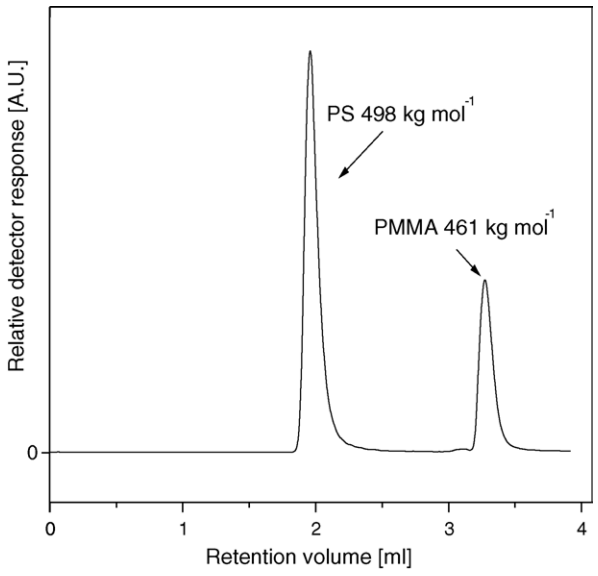

Fig. 7. Separation of a model polymer blend under LC LCD conditions. PS 498 kg mol^{-1} eluted in the SEC mode (peak with lower retention volume) while PMMA 461 kg mol^{-1} eluted in the LC LCD mode, after the adsorli barrier, column #1.

Table 2
Comparison of molar masses of a polymer sample determined by conventional SEC applying universal calibration with polystyrene standards (a), SEC/MALS (b), and by the LC LCD × SEC/MALS combination (c)

Sample designation	$\bar{M}_w$ (kg mol^{-1}) (a)	$\bar{M}_n$ (kg mol^{-1}) (a)	$\bar{M}_w$ (kg mol^{-1}) (b)	$\bar{M}_n$ (kg mol^{-1}) (b)	$\bar{M}_w$ (kg mol^{-1}) (c)	$\bar{M}_n$ (kg mol^{-1}) (c)
PMMA 65000	65 ± 3.0	53 ± 3.3	66.9 ± 3.4	63.8 ± 3.5	65.4 ± 2.6	60.1 ± 2.4

As known, separation of polymer blends can be accomplished, for example, by liquid chromatography under critical conditions (LC CC) [14,15], by eluent and temperature gradient polymer HPLC [15,16], by liquid chromatography under limiting conditions of adsorption [12,17], as well as by the full adsorption–desorption procedure (FAD) [18]. LC CC is presently the most popular approach but it is very sensitive to variation of experimental conditions [19,20]. Except for FAD with nonporous column packings, all above methods may suffer from limited sample recovery. As mentioned above, LC LCD can possibly help solve this problem [12].

Typical values of molar mass averages for a selected PMMA sample are compared in Table 2. They represent mean values of two measurements and were obtained by means of conventional SEC applying universal calibration (a) or with MALS detector. In the latter case, polymer was injected either directly into the SEC column (b) or into the 2D-LC system LC LCD column #1 plus SEC (Fig. 1) (c).

Repeatability of results for various PMMAs was better than 4% and agreement of *b* and *c* sets of values was good. Surprisingly, the $\bar{M}_w/\bar{M}_n$ values obtained by conventional SEC were higher than those monitored with MALS, likely because $\bar{M}_n$ values from the conventional SEC were lower. The results confirm applicability of LC LCD × SEC combination for molecular characterization of dissimilar polymers with comparable molar masses. Chromatograms of PMMA 294 kg mol^{-1} obtained with either SEC alone or with the LC LCD × SEC arrangement are shown in Fig. 8. The positions of chromatograms monitored for the LC LCD × SEC system were corrected for the volume of the LC LCD column. The results demonstrate a surprisingly small influence of the LC LCD column on the widths of SEC peaks obtained with the LC LCD × SEC system.

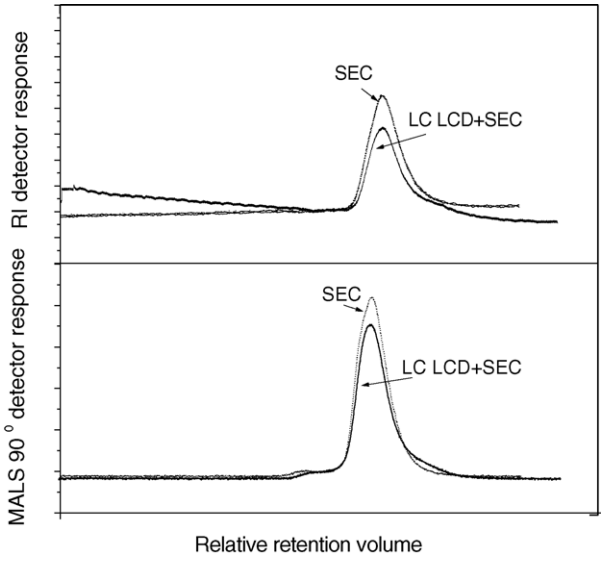

Fig. 8. Chromatograms of PMMA 294 kg mol^{-1} eluted from the SEC column alone and from the same SEC column on line attached to the LC LCD column #1. The traces were monitored by both RI concentration detector and MALS detector at 90°.

The general tendencies observed with the sample injection mode ad (iii) were identical with the (ii) one. It can be concluded that the (iii) mode of injection represents a sort of barrier enforcement. Its advantage is that a single set of sample solutions in pure adsorli solvent can be used in experiments with various eluents, during system optimization. Otherwise, a new series of sample solutions must be prepared for each eluent.

4. Conclusions

Liquid chromatography under limiting conditions of desorption (LC LCD) produces narrow peaks of polymers eluting irrespectively of their molar masses and with high recovery behind the barrier zone of the appropriate adsorli. In this way, LC LCD can quantitatively discriminate macromolecules differing in their adsorptivities without molar mass interference. Narrow pore LC LCD column packings are preferred because the SEC effects are suppressed and separation of polymer species with different nature is more efficient. However, these columns are rather vulnerable toward parasitic phenomena when the desorli zone is generated by sample solvent. In this case, one part of sample may elute unretained in the SEC mode.

It is demonstarted that the latter problem can be avoided applying a tandem injection. A separate adsorli zone is injected immediately before sample dissolved in eluent or in adsorli solvent. Tandem injection also simplifies eluent and barrier composition optimization.

Polymers discriminated by means of LC LCD can be further characterized employing an on-line SEC column flushed with a single solvent. The SEC column separates macromolecules from both the adsorli zone and the accompanying LC LCD eluent so that polymer species can be detected with a differential refractometer and their molar mass can be determined by a multi-angle light scattering photometer.

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