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Liquid chromatography of polymer mixtures applying a combination of exclusion and full adsorption mechanisms: 2. Eluent switching approach

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The molar mass and molar mass distribution of particular components of a polymer mixture can be determined by a combination of size exclusion chromatography (s.e.c.) and full adsorption/desorption (f.a.d.) modes. One component of a polymer mixture is retained on the surface of an appropriate sorbent using an appropriate eluent while another component is chromatographed in the conventional s.e.c. mode. In the next step the eluent is changed so that the previously retained polymer is desorbed and analysed in the s.e.c. mode. This idea is demonstrated with a mixture of polystyrene (PS) and poly(methyl methacrylate) (PMMA) using two different f.a.d. columns packed with a silica-based sorbent and a s.e.c. column packed with polystyrene gel. Using toluene as eluent, PMMA was retained on the f.a.d. silica gel packed column while PS was eluted in the typical s.e.c. mode and the molar mass and molar mass distribution of PS could be determined in the first step. After switching the eluent from toluene to tetrahydrofuran in the second step, PMMA was desorbed from the f.a.d. column and swept into the s.e.c. column where its molar mass and molar mass distribution could be determined as well.

(Keywords: liquid chromatography; polymer mixtures; separation)

INTRODUCTION

Classical methods of separation of polymer mixtures, namely selective precipitation from dilute solutions[1–3], selective extraction[4] and selective turbidimetric titration[5], are highly demanding in terms of time and labour. Moreover, the former two methods may be influenced by polymer occlusion, they consume rather a large amount of sample, and they do not provide any information about the molar mass (M) and molar mass distribution (MMD) of a polymer. Consequently, the separation of constituents in a mixture must be followed by determination of M and MMD.

The most elegant and straightforward method for separation of polymer mixtures is size exclusion chromatography (s.e.c.)[6]. However, the application of conventional s.e.c. procedures to polymer mixtures is possible only if the hydrodynamic volumes of particular constituents of multicomponent polymer systems are fairly different. Other chromatographic approaches can be applied to separation of polymer mixtures, e.g. Balke and Patel's 'orthogonal chromatographic procedures'[7], Mori's 'on–off elution method'[8], Pasch's 'liquid chromatography at the critical point of adsorption'[9] or Hunkeler *et al.*'s 'liquid chromatography under limiting conditions of solubility'[10,11].

Owing to the wide application of polymer mixtures, rapid determination of the M and MMD of their constituents becomes more and more important. We have shown[12] that particular components of some polymer mixtures differing in their polarity can be separated by liquid chromatography applying an active gel and a non-polar eluent. In this case, conditions are sought under which just one kind of macromolecule is eluted in the size exclusion mode while the other component is fully retained within the column packing. The proposed system is complicated by the necessity to analyse the retained component of the polymer mixture separately.

In this paper the above problem is solved by applying an on-line combination of full adsorption/desorption and size exclusion mechanisms (f.a.d./s.e.c.) for fast determination of the molecular characteristics of chemically different constituents of a polymer mixture. We propose the arrangement in which one column is used for temporary trapping of one constituent of a polymer mixture (full adsorption/desorption—f.a.d. column) while another column (or a set of columns) is used solely for a size exclusion chromatographic separation (s.e.c. column). In the first step, the more

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polar constituent is fully retained on the surface of the f.a.d. column packing using a non-polar eluent while the less polar constituent passes into the s.e.c. column where its M and MMD are determined. In the second step, the more polar constituent of a polymer mixture is desorbed from the f.a.d. column using an appropriate desorbing eluent. The desorbed polymer is carried directly into the s.e.c. column where its M and MMD are determined too.

This eluent switching method permits the separation of polymer mixtures, together with the determination of M and MMD of their components, in the same apparatus in two steps.

EXPERIMENTAL

A liquid chromatography system was used, comprising a Waters model 510 pump (Millipore Co., Milford, USA) and a model PK 1 injector valve with a 10 μl loop (Institute of Chemical Processes Fundamentals, Czechoslovak Academy of Sciences, Prague, Czech Republic). A model DDL-21 evaporative light scattering device (Cunow, Cergy Pointoise, France) was employed as detector. The data were collected on-line using a Waters Maxima/Baseline PC Based Data Acquisition System (Millipore Co., Milford, USA). The rate at which the work station took readings from the detector was one point per second.

Chromatographic measurements were performed with a system consisting of two columns connected in series. First, the adsorbing (f.a.d.) column was packed with a bare silica gel sorbent. Approximately 0.1 g of material was dry packed into a stainless steel column with an i.d. of 3 mm and a length of 30 mm. Two types of sorbents were used: SGX-500 with 50 nm pore size and 10 μm particle size (Tessek Co., Prague, Czech Republic)—column f.a.d. 1; and non-porous spherical silica with a particle size from 5 to 15 μm prepared in this laboratory—column f.a.d. 2. Next, the s.e.c. column, 300 × 7.5 mm, was packed with polystyrene-based gel (PL-gel, Mixed B, 10 μm, Polymer Laboratories, London, UK).

Narrow polystyrene (PS) standards with average molar masses of 666, 2.6×10^3, 10.1×10^3, 17.5×10^3, 37×10^3, 97.2×10^3, 233×10^3, 498×10^3, 1.2×10^6, 2×10^6 and 6.77×10^6 g mol^{-1} (polydispersity 1.06–1.20) were obtained from Pressure Chemicals Co., USA. Narrow poly(methyl methacrylate)s (PMMA) with molar masses of 16×10^3, 31×10^3, 65×10^3, 103×10^3, 169×10^3, 294×10^3, 461×10^3 and 613×10^3 g mol^{-1} were obtained from Rohm (Darmstadt, Germany) and with molar masses of 1200×10^3 and 5100×10^3 g mol^{-1} from Institute Sadron CNRS (Strasbourg, France). Broad samples of PS with molar masses of 15×10^3 and 350×10^3 g mol^{-1}, prepared at the Polymer Institute by radical polymerization, were also used. Generally, the injected concentration was 0.5 mg ml^{-1}.

The s.e.c. column and column systems consisting of f.a.d. 1/s.e.c. or f.a.d. 2/s.e.c. were calibrated with narrow PS or PMMA using either toluene or tetrahydrofuran (THF) as eluent. Corresponding calibration curves were considered in the calculation of M and MMD of the broad polymer samples.

Analytical grade toluene from Lachema (Brno, Czech Republic) and tetrahydrofuran from Merck (Darmstadt, Germany) were used as mobile phases at a flow rate of 1 ml min^{-1}. The accuracy of flow rate was checked by a burette. It was found to be +1.0%.

RESULTS AND DISCUSSION

It was shown[12] that PMMA was fully retained within a column packed with silica gel with 50 nm pore diameter when toluene was used as eluent at ambient temperature. On the other hand, the retained macromolecules are quantitatively desorbed by THF[12]. Thus, toluene could be used as an 'adsorbing' eluent for PMMA and THF as a 'desorbing' eluent for this polymer in combination with a silica column packing. Both toluene and THF were s.e.c. eluents for PS with silica-based column packings. Therefore, we tested our eluent switching procedure with a polymer mixture containing PS and PMMA using a silica f.a.d. column and toluene and THF as eluents.

The scheme of the chromatographic assembly for the f.a.d./s.e.c. method is shown in *Figure 1*. Initially the valves V_1 and V_3 were in position 'a', i.e. toluene was transported through both f.a.d. and s.e.c. columns. PMMA was retained with the f.a.d. column and PS was separated in the s.e.c. column, so that the M and MMD of PS could be determined in the conventional way. After the analysis of PS was complete, the f.a.d. column was disconnected by switching the valve V_3 from position 'a' to 'b'. Simultaneously, the eluent was changed into THF by switching the valve V_1 from position 'a' to 'b' and the s.e.c. column was re-equilibrated by flushing it with approximately three volumes of THF. Then the valve V_3 was switched from 'b' to 'a' position and the adsorbed PMMA was flushed by THF into the s.e.c. column in order to determine values of M and MMD.

In testing the above f.a.d./s.e.c. procedure we first studied the adsorbing/desorbing properties of two different silica sorbents packed in f.a.d. columns 1 and 2. To minimize possible effects of deterioration of the FAD column on the overall efficiency of the liquid chromatography system, we used small f.a.d. columns. The adsorbing capacity of the f.a.d. columns was checked by repeated injections of dilute solutions of PMMA ($M = 416 \times 10^3$ g mol^{-1}) in toluene. The results are shown in *Figure 2*. Breakthrough of PMMA was

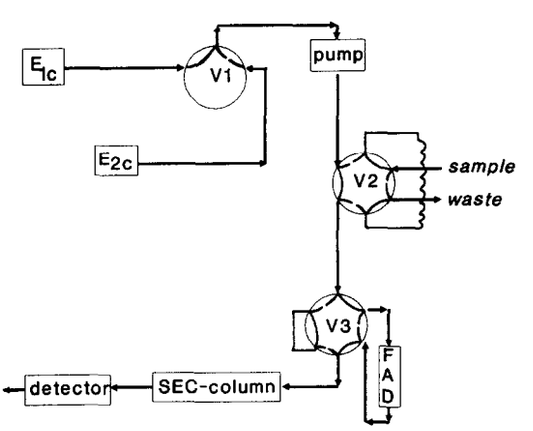

Figure 1 Scheme of the f.a.d./s.e.c. assembly: E_{1c}, E_{2c}, eluent containers for toluene and THF respectively; V_1, low pressure valve in position 'a' (—) and 'b' (– –); V_2, sample injecting valve; V_3, switching valve in position 'a' (—) and 'b' (– –)

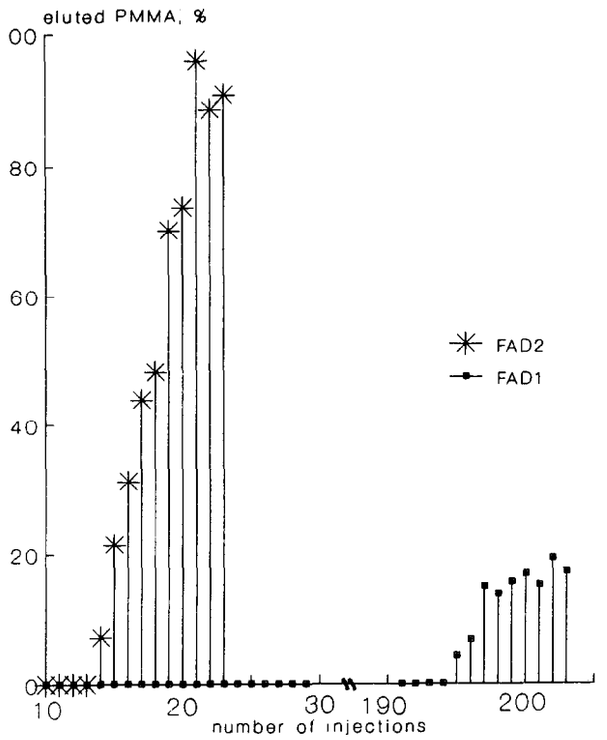

Figure 2 Dependence of percentage of eluted PMMA on the number of injections. 10 μl portions of PMMA ($M = 461 \times 10^3$ g mol^{-1}) solution, each containing 0.005 mg of polymer, were repeatedly injected into the f.a.d. 1 and f.a.d. 2 columns. Toluene was used as eluent. The amount of eluted PMMA was determined from the peak area after appropriate calibration

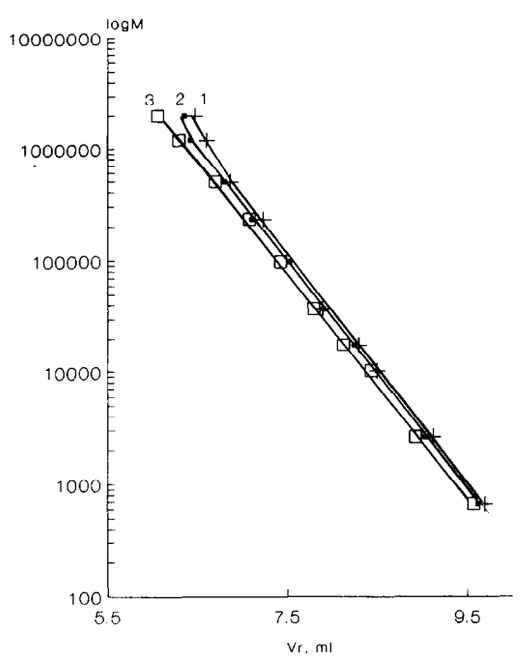

Figure 3 Calibration curves for PS injected into f.a.d. 1 + PL-gel (1), f.a.d. 2 + PL-gel (2) and PL-gel (3) columns in toluene

observed after 194 and 13 injections for f.a.d. 1 and f.a.d. 2, respectively. The maximum amount of PMMA which was still fully trapped by the f.a.d. columns (critical amount) corresponded to about 9.7 mg and 0.22 mg of PMMA per g of dry sorbent in columns f.a.d. 1 and f.a.d.

Table 1 Molar mass values determined using the s.e.c. column and the system of f.a.d. plus s.e.c. columns

			Molar mass characteristics		
Sample[a]	Column	Eluent	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
PS 15	s.e.c.	Toluene	14.3	11.2	1.27
	f.a.d. 2/s.e.c.		15.9	12.4	1.28
PS 17.5	s.e.c.	Toluene	17.0	14.1	1.20
	f.a.d. 1/s.e.c.		16.6	13.0	1.27
	f.a.d. 2/s.e.c.		17.1	14.8	1.16
PS 498	s.e.c.	Toluene	486	421	1.15
	f.a.d. 1/s.e.c.		518	236	2.20
	f.a.d. 2/s.e.c.		486	395	1.23
PS 350	s.e.c.	Toluene	358	202	1.77
	f.a.d. 2/s.e.c.		355	204	1.74
PMMA 31	s.e.c.	THF	31.6	25.3	1.25
	f.a.d. 2/s.e.c.		28.7	23.1	1.28
PMMA 461	s.e.c.	THF	436	305	1.43
	f.a.d. 2/s.e.c.		440	229	1.47

[a] Number following polymer abbreviation is $M \times 10^{-3}$ g mol^{-1}

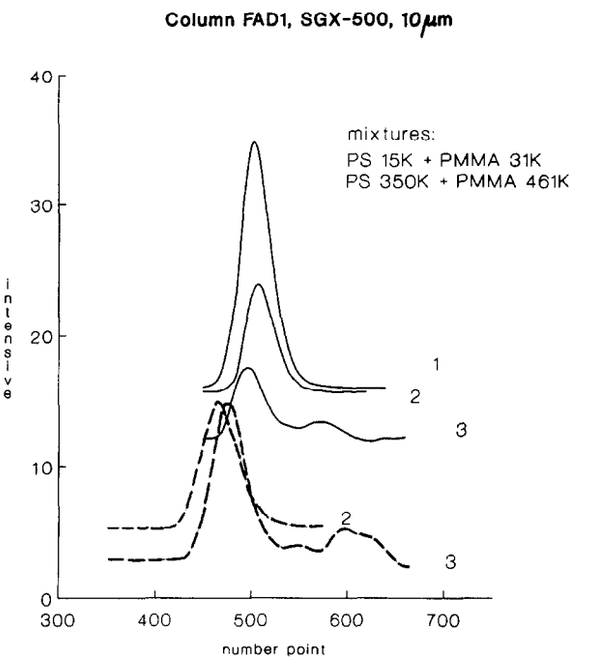

Figure 4 Chromatograms of mixtures of PS and PMMA obtained with the f.a.d. 1/s.e.c. system of columns. (1) THF, both polymers eluted; (2) toluene, PS eluted and PMMA retained; (3) eluent switching from toluene to THF, PMMA desorbed and eluted

Table 2 Molar mass characteristics of components of polymer mixtures determined by f.a.d./s.e.c. procedure

Column	Sample[a]		$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
f.a.d. 1 plus s.e.c.	PS 15	mixture 1	16.4	11.5	1.43
	PMMA 31		23.6	6.5	3.7
	PS 350	mixture 2	335	144	2.32
	PMMA 461		217	110	2.0
f.a.d. 2 plus s.e.c.	PS 15	mixture 1	14.5	10.8	1.34
	PMMA 31		27.0	20.8	1.3
	PS 350	mixture 2	325	184	1.77
	PMMA 461		432	262	1.65
	PS 15		13.1	9.2	1.4
	PMMA 31	mixture 3	31.6	25.0	1.26
	PMMA 461		419	279	1.50

[a] Number following polymer abbreviation is $M \times 10^{-3}$ g mol^{-1}

2, respectively. The amount of PMMA fully trapped by porous silica gel was almost 44 times higher than that with non-porous silica. The outer surface area of non-porous silica was, however, about 160 times smaller than the surface area of SGX-500 and the above result indicates that only a small part of the inner surface of silica was accessible for PMMA macromolecules with $M = 461 \times 10^3\ g\,mol^{-1}$ as is also evident from the corresponding s.e.c. calibration curve[12]. On the other hand, after the breakthrough point had been reached, the adsorbing capacity of non-porous silica for further portions of PMMA was rather low and approached zero after 24 injections. In any case both columns f.a.d. 1 and f.a.d. 2 had sufficient adsorption capacity to catch all the PMMA contained in the sample in a sufficiently large quantity to be detected easily.

The calibration curves for PS in toluene measured with the s.e.c. column and with systems of column f.a.d. 1/s.e.c. and f.a.d. 2/s.e.c. are shown in *Figure 3*. The calibration curves for s.e.c. and s.e.c. plus f.a.d. 2 systems are practically parallel except for the highest M of PS where probably additional effects such as excessive hydrodynamic degradation of macromolecules on the column end fittings may take place. In the case of s.e.c. plus the f.a.d. 1 system, the porous structure of SGX-500 used as the f.a.d. 1 column packing may slightly influence the course of a calibration curve. SGX-500 selectively separates polystyrene in the molar mass range from $\sim 3 \times 10^3$ to $\sim 2 \times 10^6\ g\,mol^{-1}$ (ref. 12).

Further, we compared the results obtained with the s.e.c. column both alone and in combination with f.a.d. 1 or f.a.d. 2 columns from the point of view of separation efficiency. To avoid adsorption, PSs were injected in toluene while PMMAs were injected in THF. Qualitatively, the Gaussian shapes of peaks were not distorted but the quantitative data expressed in terms of M and MMD were affected to an extent which somewhat exceeded the expected experimental errors—especially in the case of f.a.d. 1 packed with the porous sorbent. As seen from *Table 1*, the polydispersity coefficients M_w/M_n calculated for PS were higher when the f.a.d. 1/s.e.c. system was used, compared with the situation when the f.a.d. 2/s.e.c. combination or lone s.e.c. column was employed.

The effect of the f.a.d. column packing was even more pronounced in the case when an adsorption/desorption process was introduced, i.e. when PMMA was the polymer sample and eluent switching was applied with porous SGX-500 as the f.a.d. column packing. The corresponding peaks of desorbed PMMA were distorted, especially in the range of high retention volumes (*Figure 4*), and the resulting M_w and mainly M_n values for PMMA were incorrect (*Table 2*). Probably the desorption process was slowed down by the porous structure of SGX-500 so that the zone of PMMA transported into the s.e.c. column was excessively broadened.

The above problems were suppressed when non-porous silica was used as the f.a.d. column packing. Typical chromatograms obtained with the f.a.d. 2 column are shown in *Figure 5* and corresponding M_n, M_w and M_w/M_n data are collected in *Table 2*. One can see that the agreement of the results obtained for binary and ternary mixtures of PS and PMMA using the proposed procedure with the f.a.d. 2/s.e.c. system with the data measured for single polymers with a lone s.e.c. column is remarkably good. Still, the results indicate the necessity to further optimize the properties of f.a.d. columns.

CONCLUSION

A novel procedure for determination of molar mass and molar mass distribution of constituents of polymer mixtures was proposed and tested. It utilizes the size exclusion chromatographic mechanism for the analysis of molecular characteristics and the full adsorption/desorption mechanism for the on-line separation of

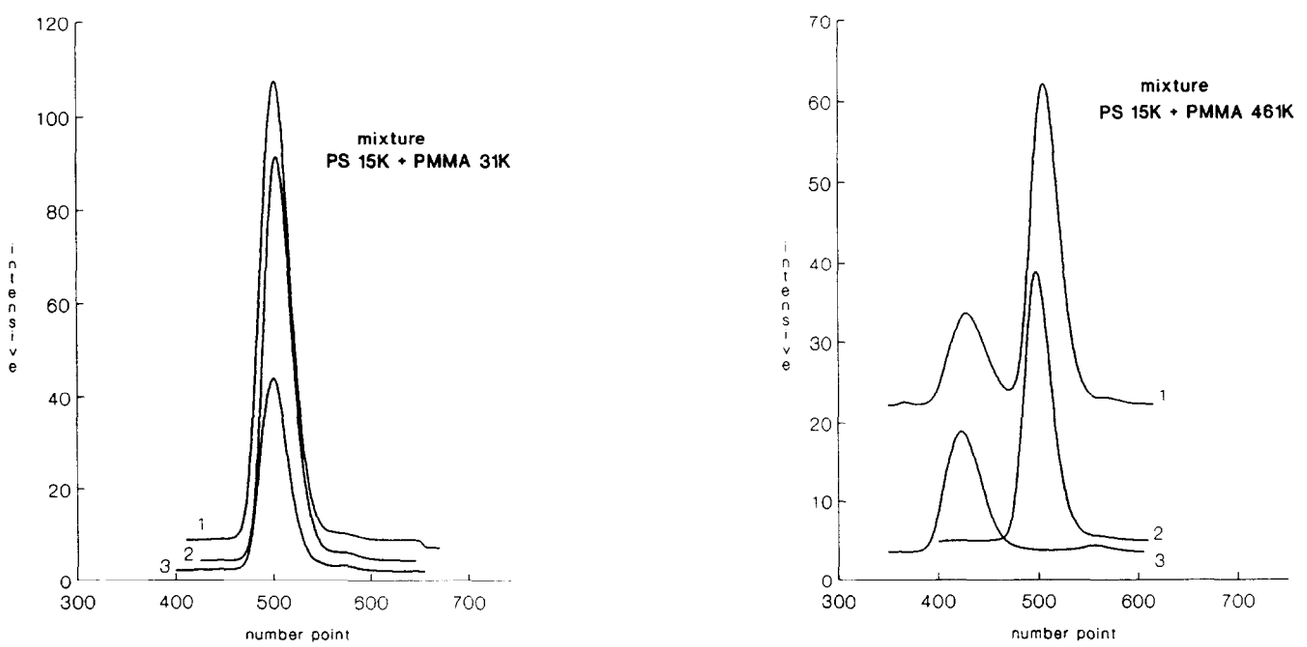

Figure 5 Chromatograms of mixtures of PS and PMMA obtained with the f.a.d. 2/s.e.c. system of columns. (1) THF, both polymers eluted; (2) toluene, PS eluted and PMMA retained; (3) eluent switching from toluene to THF, PMMA desorbed and eluted

particular constituents of a polymer mixture. Eluent switching allows successive analyses of both constituents in the same column system. A non-porous column packing was found to be advantageous for the adsorption columns. The procedure is fast, selective and reliable, and sample consumption is as low as in the case of a conventional s.e.c. analysis. No special equipment including detectors is needed. The method, however, is limited to polymer mixtures for which an appropriate selective column packing and an adsorbing/desorbing eluent pair can be found.

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