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# Liquid Chromatography of Polymer Mixtures Applying Combination of Exclusion and Full Adsorption/Desorption Mechanisms 3. Role of Adsorption Column and Adsorbing Eluent

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Full adsorption/desorption plus size exclusion chromatography (FAD/SEC) is a useful procedure for the analysis and molecular characterization of complex polymer systems. The constituents of polymer mixture are selectively adsorbed and retained within a properly designed FAD column using an appropriate adsorption-promoting eluent. The retained polymers are then successively and selectively desorbed into an adjacent SEC column in which separation according to the size of macromolecules takes place. The FAD/SEC procedure was tested in model binary polymer mixtures of polystyrene plus poly(methyl methacrylate) and polystyrene plus poly(vinyl acetate). The role of both the FAD column size and the eluent applied for polymer adsorption was elucidated. It was shown that after the desorbing eluent was introduced, the zone of original adsorption-promoting eluent leaving the FAD column together with the desorbed polymer may affect the resulting SEC retention volumes. Therefore, it was necessary to optimize both above experimental parameters, that is, FAD column size and the strength of adsorption-promoting eluent to obtain precise data on both molar mass and molar mass distribution of polymer constituents.

**Keywords:** Liquid chromatography, polymer mixtures, separation, full adsorption/desorption, size exclusion combination

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## INTRODUCTION

Molecular characterization and analysis of complex polymer systems such as polymer mixtures, copolymers and functionalized macromolecules requires liquid chromatographic separation methods that couple two or even several separation mechanisms. Recently we have proposed and tested two such couplings, namely the combination of full adsorption with size exclusion (FA/SEC) [1] and of full adsorption–desorption with size exclusion (FAD/SEC) [2]. We have demonstrated the ability of both coupled procedures to effectively separate two component polymer mixtures and to simultaneously determine the molar mass ( $M$ ) and molar mass distribution (MMD) of one [1] or both [2] constituents of mixture.

FA/SEC [1] is based on the selective retention of one component of a polymer mixture within the SEC column while the second component is freely eluted. This coupling is applicable to the separation of polymer mixtures which constituents differ in their chemical or physical structure and, consequently, in their adsorption properties. The appropriate column packing plus eluent system must be identified in which one polymer is fully adsorbed while another one is not retained on the basis of interactive mechanisms. We have tested this approach with polystyrene (PS) plus poly(methyl methacrylate) (PMMA) systems using bare silica gel as the column packing and toluene as the eluent. Toluene is a good solvent for both polymers; however, the more polar PMMA is fully adsorbed on the silica surface while PS is eluted in the SEC mode. The mobile phase from which the given polymer is fully adsorbed on the surface of a given adsorbent (SEC column packing) is termed an adsorption-promoting mobile phase.

We have shown [1] that the SEC packing can accommodate relatively large amounts of the fully adsorbed polymer prior to the elution characteristics of the nonretained polymer are affected. As a result, many analyses of the nonretained polymer, PS, could be carried out without interference from the adsorbed polymer, PMMA. The  $M$ /MMD values for PS were found to be in good agreement with the data measured without the presence of PMMA. Periodically, the SEC column was flushed with a small volume of polymer desorption-promoting mobile phase, tetrahydrofuran (THF) in the above case, to release the adsorbed PMMA and to regenerate the column packing for a new series of analyses.

Evidently, the molecular characteristics of polymer adsorbed in the SEC column could not be determined with the above FA/SEC coupled procedure. To solve this problem, a column and eluent switching method was developed which is called full adsorption/desorption (FAD)/SEC coupling [2]. In this case, two columns are used in an online arrangement: an FAD column packed with silica serves for the selective temporary retention of one component (PMMA) of the polymer mixture from the adsorption-promoting mobile phase (toluene) while the other polymer (PS) is not adsorbed and passes into the adjacent SEC column packed with polystyrene gel to be characterized in the conventional way. After the SEC separation of PS has been accomplished; the SEC column is equilibrated with the desorption-promoting mobile phase (THF) which is switched into the FAD column to desorb PMMA and carry it into the SEC column for characterization.

The above-described FAD/SEC coupling presents a potentially useful tool for molecular characterization of not only binary polymer mixtures but also more complex polymer systems like copolymers, functionalized and chemically modified macromolecules, and multi-component polymer blends containing macromolecules that differ only slightly in their chemical nature or in their physical structure: All but one constituents of a complex polymer system must be fully adsorbed in the appropriate FAD column from which they are successively and selectively desorbed by stepwise changes of either eluent composition or temperature and further separated in the adjacent SEC column(s). Instead of SEC, a variety of other separation methods can be applied based, for example, on the adsorption or solubility mechanisms and on their combinations such as LC at the point of exclusion—adsorption transition, that is, either LC at the critical adsorption point [3], or LC under limiting conditions of adsorption, further precipitation liquid chromatography (gradient polymer elution chromatography) [4], LC under limiting conditions of solubility [5], and other emerging “multi-dimensional” procedures [6].

FAD/SEC coupling can be also applied to the study of some features of dynamic and quasi dynamic polymer adsorption on solid surfaces, the FAD principle itself can be utilized for the reconcentration of diluted polymer solutions including reconcentration of diluted column effluents in both multidimensional and preparative LC of macromolecules [7].

Our recent results [2], however, indicate that the FAD/SEC system and,

especially, both the FAD column and eluents must be readily optimized to obtain results of adequate precision and repeatability. The peculiarities of the FAD/SEC coupling including its optimization and applications will be described in future publications. The present work shows the role of both FAD column size and the adsorption-promoting eluent.

## EXPERIMENTAL

The FAD/SEC assembly is schematically shown in Figure 1. The valves  $V_1$ ,  $V_2$  and  $V_3$  were common six-port three-way devices from Rheodyne (Cotati, CA, USA) and Knauer (Berlin, Germany). The pump was a Waters Model 510 (Milford, MA, USA) and the detector was Model DDL-21 evaporative light scattering instrument (Cunow, Cergy Pontoise, France).

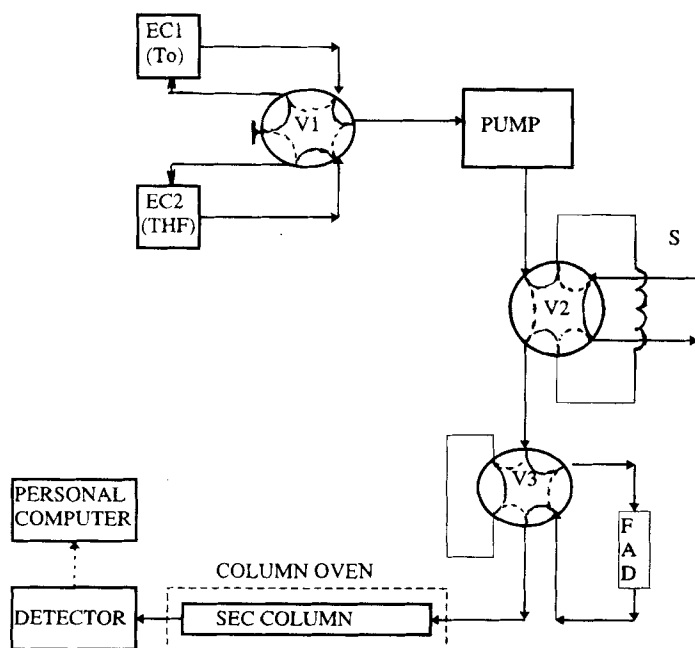


FIGURE 1 The principal scheme of the FAD/SEC assembly: EC1, EC2 – eluent containers of the adsorption-promoting (toluene or 5 and 10 wt% mixture of THF) or desorption-promoting (THF) eluent respectively,  $V_1$ ,  $V_3$ —switching valves,  $V_2$  – sample injection valve with loop S (– in position “a”, --- in position “b”)

The SEC data were collected and processed by means of Waters Maxima/Baseline PC-based Data Acquisition System (Milford, MA, USA). The data acquisition rate was 1 pt/s.

Two silica-based packings were used in the FAD column of different sizes, viz. a spherical silica gel with 50-nm pores and 10- $\mu\text{m}$  particles prepared in this laboratory from the narrow-pore silica gel Tessek SGX (Prague, Czech Republic) by a proprietary pore-widening procedure, and a nonporous spherical silica with 10- $\mu\text{m}$  particles prepared from Silpearl TLC silica gel (Kavalier Co., Votice, Czech Republic). All FAD columns were dry packed. The mass of the sorbent in the FAD column was determined by weighing (except for column FAD3). The information on FAD columns used are summarized in Table I.

The SEC column packed with polystyrene gel was purchased from Polymer Laboratories (Shropshire, UK). Narrow polystyrenes (PS) with molar masses from 666 to  $1.2 \times 10^6$  g/mol were obtained from Pressure Chemicals Co. (Pittsburgh, PA, USA). The  $M$  values of the narrow PS are given in ref. [2]. The samples of poly(methyl methacrylate)s (PMMA) with  $M$  from  $1.6 \times 10^4$  to  $5.1 \times 10^6$  g/mol were donated by Rohm (Darmstadt, Germany) and by the Institut Charles Sandron CNRS (Strasbourg, France). Their molar mass and tacticity data are given in ref. [8]. The broad poly(vinyl acetate) (PVAC) with weight average molar mass  $5.00 \times 10^5$  g/mol and a  $M_w/M_n$  value of 2.5 was obtained from Polysciences Inc. (Warrington, PA, USA).

Analytical grade toluene was from Lachema (Brno, Czech Republic) and tetrahydrofuran (THF) from Merck (Darmstadt, Germany).

The experimental FAD-SEC procedure comprised three steps (Fig. 1):

TABLE I Characteristics of FAD columns

FAD Column	Column Length (mm)	Column i.d. (mm)	Column Volume ( $\mu\text{L}$ )	Type of Sorbent	Mass of Dry Sorbent (g)	Column Efficiency $N$ (theoretical plates)
FAD1	30	3	212	SGX-500 50 nm 10 $\mu\text{m}$	0.112	7000
FAD2	30	3.3	256	nonporous SI 5-15 $\mu\text{m}$	0.291	1200
FAD3	150	3.3	1283	nonporous SI 5-15 $\mu\text{m}$	—	1600
FAD4	20	1.5	35	nonporous SI 5-15 $\mu\text{m}$	0.046	—

- (i) The entire system was equilibrated with the adsorption-promoting eluent (valve  $V_1$  in position "a") of low polarity from container 1 (pure toluene or toluene plus either 5 or 10 wt% THF mixture). Two-component polymer mixtures of PS plus PMMA or of PS plus PVAC were dissolved in toluene and injected via valve  $V_2$  (in position "a") into FAD. The more polar constituent of the polymer mixture, that is, either PMMA or PVAC, was retained within the FAD column while the less polar PS was eluted into the SEC column and characterized in usual way.
- (ii) Valve  $V_1$  was set into position "b" and SEC column was equilibrated with the desorption-promoting eluent of higher polarity (pure THF) from container 2. The FAD column was kept in the adsorption - promoting eluent (valve  $V_3$  in position "b").
- (iii) Valve  $V_3$  was switched into position "a" and THF was introduced into the FAD column to desorb the retained polymer (PMMA or PVAC) and carry it into the SEC column where it was characterized in the exclusion mode.

The SEC column both alone and connected with an FAD column was calibrated with a series of PS and PMMA in the usual way. The FAD-SEC procedure was tested with model mixtures containing PS ( $15 \times 10^3$  g/mol) plus PMMA ( $31 \times 10^3$  g/mol) and PS ( $360 \times 10^3$  g/mol) plus PMMA ( $461 \times 10^3$  g/mol) and PS ( $491 \times 10^3$  g/mol) plus PVAC ( $500 \times 10^3$  g/mol).

## RESULTS AND DISCUSSION

A comparison of SEC calibration curves without and with the FAD column [2] revealed important effects of the FAD columns. The overall retention volumes increased because of the volume of liquid within the FAD column and the inherent SEC separation ability of the FAD column when it was packed by macroporous silica gel particles. This indicated the advantage of small FAD columns over larger ones, as well as the preference of non-porous particles over macroporous packings. At the same time, we observed SEC peak broadening and even peak splitting for test polymer probes (more polar constituent of the polymer mixture analyzed in the second step) in the case of FAD columns packed with macroporous silica

gel. These phenomena were probably caused either by the limited polymer desorption and diffusion rate or by overload effects [9] that dramatically influenced the overall separation efficiency of FAD-SEC systems and lead to lower  $M_w$  values and higher polydispersity for polymer probes. This further illustrated the preference of non-porous over macroporous FAD column packing.

Evidently, the optimum FAD column must:

- (i) Minimally contribute to SEC retention volumes, as well as to band broadening, skewing and splitting caused by mixing and diffusion.
- (ii) Fully retain one polymer constituent while the other polymer passes unretained.
- (iii) Rapidly and quantitatively release the adsorbed polymer constituent so that the sample recovery approaches 100%.

These requirements were investigated. The efficiency expressed as the number of theoretical plates per meter ( $N$ ) of FAD columns was determined in THF in the usual way applying *n*-hexane as probe and using  $N = 5.545 (V_R/w_{1/2})^2$ , where  $V_R$  is the retention volume and  $w_{1/2}$  is the peak width of *n*-hexane at the half of its height. The characteristics of FAD columns 1–4 are given in Table I. The determination of  $N$  for the micro-column FAD4 was not feasible with the injection valve and detector used. It is evident that the FAD columns packed with nonporous silica exhibited lower efficiency than that ones packed with macroporous silica gel. However, the influence of FAD columns packed with nonporous silica on the overall separation efficiency of the system for macromolecules was not as pronounced as in the case of porous silica gel. This is evident from the  $M_w/M_n$  data determined for unretained PS probes in toluene, when FAD1 or FAD2 columns were connected with the SEC column [2].

The  $M$  and MMD values of single polymers determined using the SEC column and SEC plus FAD2 or SEC plus FAD4 column systems are given in Table II. The best agreement of data obtained is achieved by using SEC plus the FAD4 column system. The effect of the FAD4 column on the SEC calibration curve is shown in Figure 2. The shift is small and roughly corresponds to the volume of FAD column plus connecting capillaries and valve  $V_2$ . The advantages of using small FAD4 column will be even more obvious when eluent switching procedure will be applied for the characterization of the second constituent of the polymer mixture.

The adsorption capacity of the FAD columns was evaluated by repeated



TABLE II Molar mass values of single polymers determined using an SEC column and the SEC plus FAD column system

Polymer <sup>a</sup>	Column System	Eluent	$M_n \times 10^{-3}$ (g/mol)	$M_w \times 10^{-3}$ (g/mol)	$M_w/M_n$	Reference
PS 15	SEC	toluene	14.3	11.2	1.27	2
	FAD2/SEC		15.9	12.4	1.2	2
	FAD4/SEC		16.0	12.8	1.25	this work
PS 350	SEC	toluene	358	202	1.77	2
	FAD2/SEC		355	204	1.74	2
	FAD4/SEC		360	204	1.76	this work
PS 498	SEC	toluene	486	421	1.15	2
	FAD2/SEC		486	395	1.23	2
	FAD4/SEC		487	406	1.20	this work
PMMA 31	SEC	THF	31.6	25.3	1.25	2
	FAD2/SEC		28.7	23.1	1.28	2
	FAD4/SEC		31.3	25.1	1.25	this work
PMMA 461	SEC	THF	436	305	1.43	2
	FAD2/SEC		440	299	1.47	2
	FAD4/SEC		437	314	1.40	this work
PVAC 500	SEC	THF	574	238	2.41	this work
	FAD4/SEC		577	240	2.40	this work

<sup>a</sup> Number following polymer abbreviation is  $M \times 10^{-3}$  g/mol.

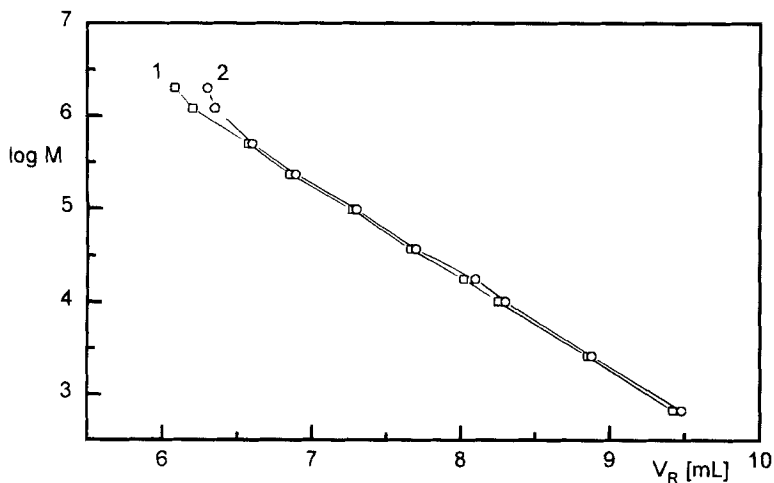


FIGURE 2 Calibration curves for PS in toluene. Column system: 1. SEC; 2. SEC + FAD4.

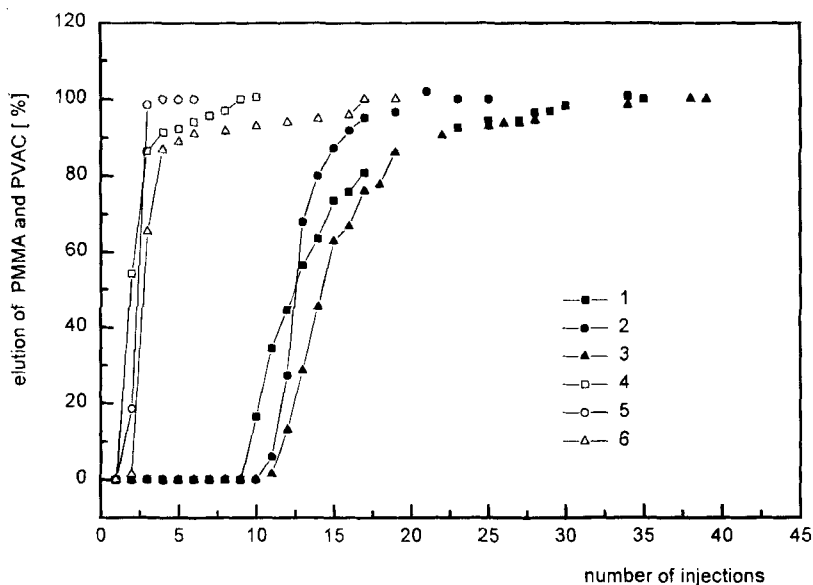


FIGURE 3 Dependence of percentage of eluted PMMA  $31 \times 10^3$  g/mol (1,4), PMMA  $461 \times 10^3$  g/mol (2,5) and PVAC  $500 \times 10^3$  g/mol (3,6) on the number of injections. 10  $\mu$ L of solution of PMMA or PVAC were repeatedly injected into FAD2 (1-3) or FAD4 (4-6) columns. Toluene was used as the eluent.

TABLE III The breakthrough / saturation amounts of adsorbed polar constituents (PMMA or PVAC) of polymer mixture on FAD columns

FAD Column Lx i.d. (mm)	Adsorbed Polymer ( $\times 10^3$ g/mol)	Eluent Composition (% vol.)	The Amount of Adsorbed Polymer (mg / g adsorbent)
FAD2, 30 $\times$ 3.3	PMMA 31	Toluene	0.19; 0.17*
FAD2, 30 $\times$ 3.3	PMMA 461	Toluene	0.19; 0.17; 0.17*
FAD2, 30 $\times$ 3.3	PVAC 500	Toluene	0.17
FAD2, 30 $\times$ 3.3	PMMA 461	To:THF = 90:10	0.08
FAD2, 30 $\times$ 3.3	PMMA 461	To:THF = 85:15	0 (breakthrough)
FAD4, 25 $\times$ 1.5	PMMA 31	Toluene	0.11
FAD4, 25 $\times$ 1.5	PMMA 461	Toluene	0.11
FAD4, 25 $\times$ 1.5	PVAC 500	Toluene	0.11

\*parallel measurements

injections of 10- $\mu$ L portions of toluene solutions of PMMA or PVAC with a concentration of 0.5 mg/mL. The adsorption capacity of the FAD columns nos. 2 and 4 is compared in both Figure 3 and Table III. The micro FAD column no. 4 is still able to trap the amount of PMMA that is necessary for the following SEC analysis. The shapes of the adsorption isotherms of various polymers measured under static conditions show that the adsorption capacity of sorbents increases with increasing molar mass of the polymer probe [10]. The maximum amount of a given polymer adsorbed ( $A$ ) using adsorbent plus solvent system obeys the equation

$$A = a M^b$$

where  $a$  and  $b$  are constants assuming positive values for a given system [10]. The breakthrough curves (Fig. 3), however, indicate slightly lower adsorption capacities of the FAD columns for lower  $M$  of polymers. The adsorption capacity for PVAC was slightly higher than that of PMMA, but the quantitative comparison of data was not possible because the polydispersities of both probes were rather different. The adsorption capacity for columns FAD 2 and 4 was not fully proportional: The amount of adsorbent within column 2 was 5.5 times larger than within column 4 but the maximum amount of polymers trapped by columns was seven times higher in the case of FAD 2. Evidently, it was necessary to check the adsorption capacity of a given FAD column for a given polymer plus eluent system before each application. One would need further experimental material to explain the above results, as well as the differences in the shapes of the "saturation curves" in Figure 3.

The  $M$  data for selected mixtures of PS plus PMMA and PS plus PVAC using the FAD/SEC procedure (eluent switching approach) are collected in Table IV. One can see that the  $M$  data obtained for PMMA (more polar constituent of polymer mixtures) with SEC plus FAD2 column system are systematically slightly lower than the values measured for a single PMMA when the FAD step was not included (using the SEC column alone or SEC plus FAD column system and THF as eluent) (Table III). This indicates that the polymer zone was slightly retarded in the SEC column when the FAD step was introduced. The extent of this retardation depended on the size of the FAD column and was most pronounced for the large FAD 3 column (data are not given), while it was negligible for the micro FAD 4 column (Tables III and IV).

TABLE IV Molar mass data of polymer mixture constituents determined by the FAD/SEC procedure

Column System	Polymer Mixtures <sup>a</sup>	$M_w \cdot 10^{-3}$ (g/mol)	$M_n \cdot 10^{-3}$ (g/mol)	$M_w/M_n$	Reference
FAD2+SEC	PS 15	14,5	10,8	1,34	2
	+ PMMA 31				
	PS 350	27	20,8	1,3	
	+ PMMA 461				
	PS 15	325	184	1,77	
	+ PMMA 461				
	PS 15	13, 1	9,2	1,4	
	+ PMMA 31				
	PMMA 461	31,6	25,0	1,26	
+ PMMA 461					
FAD4+SEC	PS 15	16,1	12,9	1,25	this work
	+ PMMA 31				
	PS 350	31,2	25,4	1,23	
	+ PMMA 461				
	PS 15	358	202	1,77	
	+ PMMA 461				
	PS 498	440	316	1,39	
	+ PMMA 461				
	PVAC 500	490	405	1,21	
+ PVAC 500					
		580	240	2,42	

<sup>a</sup> Number following polymer abbreviation is  $M \times 10^{-3}$  g/mol.

In the case of FAD columns packed with nonporous silica, this retardation can be caused by the

- (i) slow desorption and mixing processes within FAD column
- (ii) presence of the zone of adsorption-promoting eluent in the SEC column that is eluted from the FAD column almost simultaneously with the desorbed macromolecules.

The important role of the adsorption-promoting eluent zone was shown in the following experiment. The FAD column was substituted with an empty capillary with a similar volume to that of the FAD column. The capillary was filled with pure adsorption-promoting eluent. When PMMA samples were injected so that they passed the capillary before entering the SEC column, we observed a similar increase in their retention volumes as in the case of the FAD/SEC system. The tentative explanation of this phenomenon involves the attractive interaction of polymers also with the SEC column packing in the presence of the adsorption-promoting eluent.

Macromolecules are adsorbed near the entrance of the FAD column. A volume of adsorption-promoting eluent from the FAD column and connecting capillary enters into the SEC column just before the zone of desorbed polymer during the desorption step. Macromolecules, however, travel along the SEC column faster than the eluent zone and pass it. In other words, macromolecules desorbed from the FAD column will for some time accompany the zone of the adsorption-promoting eluent. This might be responsible for the raise of retention volumes of macromolecules.

In the next experiment, we equilibrated the SEC column with toluene and injected toluene solutions of PMMAs. Surprisingly, polymers were fully retained within the SEC column. The explanation involving the high value of the second virial coefficient  $A_2$  of PMMA in toluene responsible for polymer retention within the PS gel packed SEC column [11] does not seem to be feasible: The value of  $A_2$  for PMMA in toluene is about the same as in THF where no extra retention is observed. A reasonable explanation of this phenomenon may involve the presence of some components of the PS gel polymerization system, for example, initiator, suspension stabilizer, etc. To suppress these adsorption effects, the adsorption-promoting eluent was modified by adding 5 or 10% wt of THF, that is, PMMA was adsorbed in the FAD column from toluene plus THF 95/5 or 90/10 wt/wt, respectively. The addition of 5% of THF slightly decreased retention volumes of PMMA but some delay in polymer elution was still observed. However, "normal"  $V_R$  values as measured without the presence of any adsorption-promoting eluent zone were found with the 90/10 toluene/THF. This means that 10% of THF in toluene effectively suppressed the adsorptive interactions between the PS column packing and the PMMA probes within the zone of the eluent released from the FAD column. The 90/10 toluene/THF mixture also eluted PMMA samples from the SEC column without adsorptive retention when used as the eluent. However, 10 wt % of THF in toluene did not substantially change the adsorption of PMMA on the silica packing.

Another possibility to suppress polymer retention in SEC column caused by the presence of the adsorption-promoting eluent zone is the application of a miniaturized FAD column which releases a small volume of adsorption-promoting eluent. This approach was successfully tested using the micro FAD column no. 4 with a total volume of about 35  $\mu\text{L}$  containing only about 0.05 g of sorbent. A typical chromatogram obtained using the SEC/FAD approach with the FAD4 column is shown in Figure 4, and the corresponding

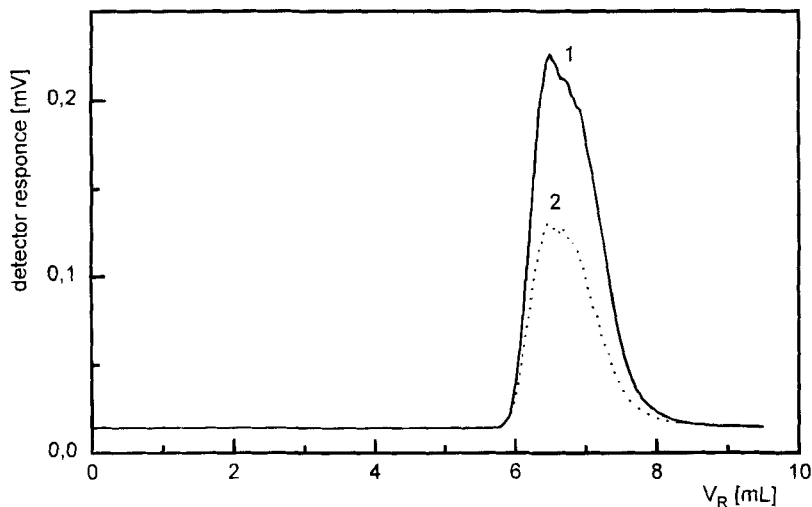


FIGURE 4 Typical chromatogram of PVAC  $500 \times 10^3$  g/mol obtained with the SEC plus FAD4 column system. 1. PVAC injected alone, eluent THF; 2. PVAC injected in a mixture with PS and adsorbed within the FAD4 column. Subsequently desorbed with THF and eluted from the SEC column.

*M* data for some selected polymer mixtures are collected in Table IV.

The above observations have again confirmed the necessity to optimize both the FAD column size and the adsorption-promoting eluent. The adsorption processes must be evaluated in the dynamic system. Both the (full) adsorption and the (full) desorption thresholds must be defined and experimentally identified. These two thresholds must be considerably different for the FAD and SEC columns to get both effective separation and precise characterization of constituents of a polymer mixture.

## CONCLUSIONS

The prerequisite for a successful application of full adsorption/desorption plus size exclusion coupling (FAD/SEC) is the careful optimization of not only the adsorbent within the FAD column but also both the FAD column size and adsorption promoting eluent: The FAD column should be of a

minimum tolerable size from the point of view of its sample capacity and the adsorption promoting eluent must allow effective adsorption and trapping of polymer(s) within the FAD column but, at the same time, it must not lead to adsorption within the SEC column.

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### **References**

- [1] Jančo, M., Prudskova, T. and Berek, D. (1995). *J. Appl. Polym. Sci.*, **55**, 393.
- [2] Jančo, M., Prudskova, T. and Berek, D. (1995). *Polymer*, **36**, 3295.
- [3] Belenkii, B. G., Valchikhina, M. D. Vakhtina, I. A., Gankina, E. S. and Tarakanov, O. G. (1976). *J. Chromatogr.*, **129**, 115.
- [4] Glöckner, G. (1992). *Gradient HPLC of Copolymers and Chromatographic Cross-Fractionation*, (Springer-Verlag, Berlin).
- [5] Hunkeler, D., Macko, T. and Berek, D. (1991). *Polym. Mater. Sci. Eng.*, **65**, 581.
- [6] Berek, D. (1996). *5th Latin American Polymer Symposium*, Mar del Plata p. 37.
- [7] Nguyen, S.H. and Berek, D. submitted to *Polymer*.
- [8] Berek, D., Jančo, M., Kitayama, T. and Hatada, K. (1994). *Polym. Bull.*, **32**, 629.
- [9] Mori, S., Uno, Y. and Suzuki, M. (1986). *Anal. Chem.*, **58**, 303.
- [10] Lipatov, Yu and Sergeeva, L. M. (1974). *Adsorption of Polymers*, (Wiley and Sons, New York).
- [11] Hobson, C. Polymer Laboratories Ltd., private communication.