ELSEVIER

PII: S0032-3861(97)10192-6

*Polymer* Vol. 39 No. 21, pp. 5127–5132, 1998
0032-3861/98/$ - see front matter

# Reconcentration of diluted polymer solutions by full adsorption/desorption procedure — 1. Eluent switching approach studied by size exclusion chromatography

**Son Hoai Nguyen**[a], **Dušan Berek**[a,*] **and Oscar Chiantore**[b]
[a]*Polymer Institute of the Slovak Academy of Sciences, 842 36 Bratislava, Slovakia*
[b]*Department of Inorganic, Physical and Materials Chemistry, University of Torino, 10125 Torino, Italy*
*(Revised 7 October 1997)*

A Full Adsorption–Desorption (FAD) procedure is proposed for the controlled reconcentration of diluted polymer solutions. In the first step, macromolecules are quantitatively trapped from their diluted solution onto an appropriate adsorbent. In the second step, polymer is released by a small amount of desorption promoting liquid.

The efficiency of this reconcentration process was tested with poly(methyl methacrylate) (PMMA), polytetrahydrofuran (PTHF), poly(ethylene oxide) (PEO) and polystyrene (PS). Bare nonporous silica packed into FAD minicolumns was used for reconcentration of dilute solutions of PMMA, PTHF and PEO in toluene and chloroform. Nonporous silica bonded with aliphatic $C_{18}$ groups was applied to reconcentrate PS solutions from dimethylformamide (DMF). The desorbing liquid was tetrahydrofuran for PMMA and PTHF, DMF for PEO and toluene for PS. The efficiency of reconcentration was tested by size exclusion chromatography that was coupled on-line with the FAD minicolumn. The efficiency of reconcentration was found to be very high in the case of medium polar and polar polymers PTHF, PMMA and PEO: full recovery of macromolecules was demonstrated by the SEC peak sizes and shapes. Consequently, agreement was found between the values of mean molar mass and polydispersity obtained for a series of polymer samples before and after the reconcentration procedure if the size of the FAD column was optimized. On the other hand, it was more difficult to effectively reconcentrate polystyrene which was not fully adsorbed on bare silica from the most common solvents. Agreement was obtained for molecular characteristics of PS before and after reconcentration from dimethylformamide on $C_{18}$ bonded silica for higher molar masses above *ca.* $9 \times 10^4$ g mol$^{-1}$. Very diluted solutions containing 5 mg of polymer per litre of solution could be easily treated in this way and no problems are anticipated even with more diluted systems.

The FAD procedure also allows ready exchange of the sample solvent and it can be used in various analytical methods, especially in multidimensional liquid chromatography of macromolecules where effluent from a column separating in the 'first dimension' is further separated in the 'second- and higher dimension' columns. The reconcentration of polymer mixtures including the selective reconcentration of one blend component and thus the preseparation of blends is also feasible. Preparative reconcentration based on the controlled full adsorption–desorption processes is also expected to be possible. In any case, the appropriate adsorbent and both adsorbing and desorbing liquid must be carefully chosen. © 1998 Elsevier Science Ltd. All rights reserved.

**(Keywords: reconcentration; adsorption/desorption; polymer mixtures)**

## INTRODUCTION

The reconcentration of dilute polymer solutions is often needed in science and technology. A controlled increase of polymer concentration is very important, e.g. in the analysis and molecular characterization of macromolecular substances. The starting samples may be either too dilute by their nature or are being diluted in a particular stage of their processing. Typical examples of the latter case are two-, three- or multidimensional column liquid chromatographic procedures. Here, the column effluent that was diluted in the course of the first stage of the separation process is injected into the second, third etc. column or column system for further treatment applying other separation mechanisms.

Partial evaporation of a solvent or solvent mixture from bulk solution by distillation is the most frequently used reconcentration procedure that is suitable particularly for preparative purposes. However, precision of the evaporation control is often rather limited and the process is impractical for continuous handling of small samples. Moreover, some macromolecules are rather sensitive and the evaporative reconcentration can lead to undesired oxidization/degradation processes. Very recently, an on-line solvent evaporator for coupled LC systems was proposed by Grob *et al.*[1]. An important drawback of this system was its time-consuming and complicated set-up. The procedure needs further optimizations in order to achieve higher recovery and to minimize zone broadening.

We are testing the application of adsorptive processes for polymer reconcentration using the Full Adsorption–Desorption (FAD) procedure. The solution to be reconcentrated is brought into contact with the appropriate adsorbent that retains macromolecules. In the next step, macromolecules are desorbed by changing the conditions e.g. by applying a liquid that promotes desorption of macromolecules (DESORbing LIquid—DESORLI). Alternatively,

---

[*] To whom correspondence should be addressed

macromolecules can be desorbed by changing temperature and, possibly also pressure. In any case both the adsorption and desorption must be as fast and quantitative as possible so that all macromolecules trapped by the adsorbent in the adsorption step are rapidly and quantitatively released in the desorption step. This means that the recovery of polymer is complete and, moreover, macromolecules are washed out of the adsorbent with the minimum volume of DESORLI. Both batch and dynamic i.e. flow-through or column arrangements can be applied. The latter generally give higher recoveries and are better suited to quantitative analytical work, although they can also be used for preparative or even for production purposes by applying large-scale adsorption–desorption equipment.

The FAD method is, in principle, similar to the solid phase extraction procedures that are applied to both analytical and preparative preseparation and preconcentration of low molecular substances. However, the adsorption of macromolecules substantially differs from that of small molecules: the adsorption equilibrium can be more effectively shifted in the case of macromolecules so that they are fully retained unless the surface of the adsorbent is saturated. As a result, the concentration of macromolecules in the supernatant may be negligible up to the saturation point[2,3] and, consequently, nearly 100% recovery of reconcentrated substance is anticipated when appropriate desorption conditions are applied.

On the other hand, the adsorption and desorption processes of macromolecules are often considered to be slow[2–4] and this could limit the feasibility of the proposed reconcentration procedures. We shall show that this is not necessarily the case and that the adsorption and desorption processes of macromolecules are often fast enough to be utilized for dynamic reconcentration.

### *Full adsorption–desorption/size exclusion chromatography coupling (FAD/SEC)*

The efficiency of the proposed reconcentration procedure was controlled on-line via size exclusion chromatography (SEC). The appropriate SEC system was directly attached to the FAD column so that the amount and molecular characteristics of desorbed polymer could be assessed.

Coupling of FAD/SEC was initially developed for the stepwise characterization of two-component polymer mixtures[5]. The scheme of the present FAD/SEC arrangement is shown in *Figure 1*. The dilute polymer solution to be reconcentrated is introduced into the FAD column by means of the injection valve V2 which can be provided with loops of different volumes. Pump 1 transports sample solvent through valve V3 into the FAD column.

The FAD column packing must be selected so that macromolecules are fully retained from the sample solvent under given experimental conditions (temperature, pressure). This is the most important restriction of the FAD reconcentration method since the choice of the appropriate FAD column packings is limited. Our recent studies[5] have revealed that nonporous FAD column packing gives much better results in the FAD/SEC analysis of polymer mixtures than the porous one where the adsorption and, especially, the desorption rate is controlled by the diffusion processes within the pores of the packing. Consequently, the desorbed polymer zone is broadened and even split when using a porous packing for FAD columns[5].

Another restriction concerns the initial sample solvent i.e. the ADSORption promotion LIquid (ADSORLI) that remains in the FAD column. This solvent is displaced by the DESORLI eluent together with macromolecules from the FAD column and may disturb further sample processing, e.g. further chromatographic separation of reconcentrated polymer solution. This problem is avoided by introducing the auxiliary solvent, a second ADSORLI into the FAD column through valves V1 and V3 after adsorption is accomplished but before the desorption step is started. This second ADSORLI is transported by pumping system 1 and also promotes adsorption of the polymer sample within the FAD column but does not disturb further sample processing. Eventually, the DESORLI flushes the FAD column when the V3 switching valve is operated so that macromolecules are eluted from the FAD column.

The apparatus shown in *Figure 1* can be used also for the reconcentration and separation of polymer blends: in the

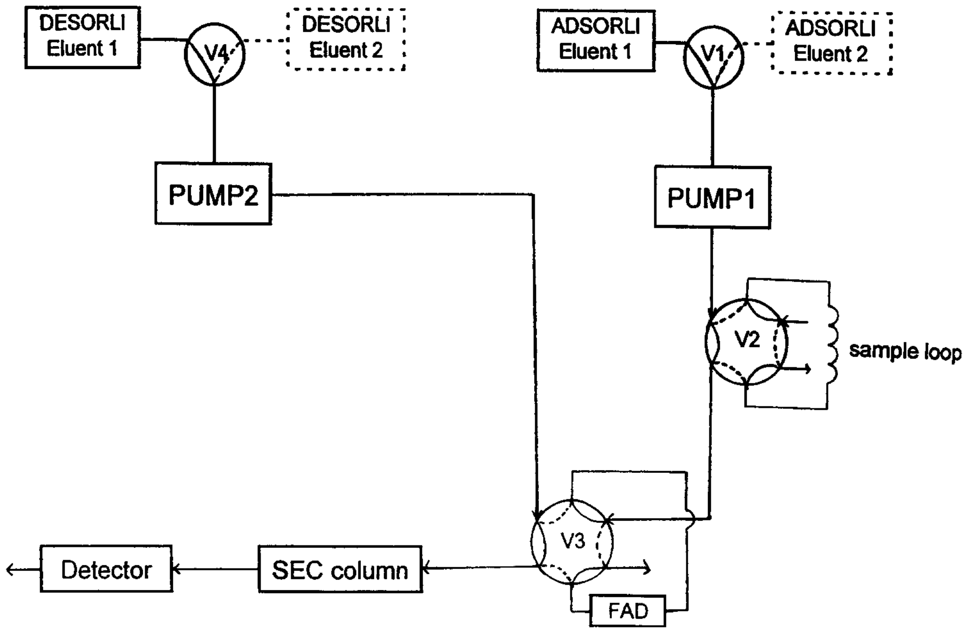

**Figure 1** The scheme of FAD/SEC assembly used for reconcentration studies of diluted polymer solutions. See text for details

first step both constituents of a binary blend are trapped by the FAD column from the ADSORLI eluent. In the second step, the FAD column is flushed out by the eluent that acts as an ADSORLI for one constituent of polymer blend but as a DESORLI1 for another constituent. Finally, the remainder of the polymer blend is desorbed from the FAD column by another appropriate (stronger) DESORLI2. Similarly, multicomponent polymer mixtures can be reconcentrated and discriminated in the course of a stepwise desorption.

In the present study, the DESORLI simultaneously served as the SEC eluent. In order to suppress the negative effect of the sample solvent that leaves the FAD column together with polymer, the sample solvent adsorption promoting strength can be reduced by adding a small quantity of DESORLI. Alternatively, the downsizing of the FAD column can reduce or even delete the effect of the sample solvent zone[6]. The minimum size of the FAD column is, however, dictated by its sample capacity.

When it is not necessary to change the sample matrix, one can abandon the auxiliary solvent and even work with one single pumping system, as is done in the initial FAD/SEC study[5].

Desorption processes can also be initiated by (sudden) changes of temperature. In this case, pumping system 2 and valve V2 can be omitted. However, the use of FAD systems that are highly sensitive to temperature changes may bring additional problems due to viscous heat dissipation within the LC packed columns[7]. Moreover, the temperature controlled desorption process may be difficult to carry out repeatedly and rapidly enough so the stop-flow procedure would have to be applied.

We have limited our present study to desorption by means of solvent changes.

## EXPERIMENTAL

The FAD/SEC assembly described above (*Figure 1*) and used in this work consisted of two Knauer model 64 pumps (Pump1 and Pump2), of a six-port three-way injection valve V2 (Knauer, Berlin, Germany) and of three switching valves V1, V3, V4 (Rheodyne, Cotati, CA, USA). The detector was either a differential refractometer from Knauer Model 198 or an evaporative light scattering detector model DDL 21 (Cunow, Cergy Pointoise, France). Different volumes of sample loops between 20 and 4000 μl were used. Thus, injected volumes were very different, however, the total mass of polymer samples was kept constant to avoid concentration effects in SEC and to prevent FAD column overloading. Various FAD columns were applied. We report on the results obtained with the FAD column designated FAD2 (30 × 3.3 mm), FADs (45 × 2 mm) and FAD7 (30 × 3.3 mm). The former two FAD columns were packed with bare nonporous spheroidal silica of 10 μm particle size. This packing was prepared in our laboratory by agglutination of a highly pure spheroidal mesoporous silica gel Silpearl (Kavalier Votice, Czech Republic) for 2 h at 1200°C. The resulting material still contained a small amount of micropores below 1 nm and its surface was rather uneven, probably because of $SiO_2$ crystallization at high temperature. The FAD7 column was packed with the same nonporous silica as FAD2 and FAD5 columns, however, the material was bonded with aliphatic $C_{18}$ groups to a high degree of coverage forming the 'polymeric phase'[8]. The SEC columns were purchased from Polymer Laboratories (Shropshire, UK) ('Linear mixed B', polystyrene/divinylbenzene gel, 300 × 7.5 mm) or supplied by Jordi Assoc. (Bellingham, MA, USA) (Mixed Bed Linear DVB, divinylbenzene gel, 250 × 10 mm). Medium broad poly(methylmethacrylate)s (PMMA) of low stereoregularity were from Röhm (Darmstadt, Germany) and narrow polytetrahydrofurans (PTHF) were from Polymer Laboratories. Narrow polystyrene (PS) samples were kindly provided by Institute Charles Sadron CNRS (Strasbourg, France) and narrow polyethyleneoxide (PEO) samples were from Toso (Shinnanyo, Japan). The polymer samples were dissolved in the ADSORLI solvents to obtain model diluted polymer solutions. The same polymer solutions were used for calibration of the FAD/SEC system using the DESORLI eluents i.e. under conditions when macromolecules were not retained by FAD columns. The SEC data were collected and

**Table 1** Molar mass characteristics of PMMA reconcentrated from diluted solutions using FAD/SEC procedure

| ADSORLI/ DESORLI | Injection volume (μl) | PMMA2.75K | | | PMMA31K | | |
|---|---|---|---|---|---|---|---|
| | | $M_w \times 10^{-3}$ | $M_n \times 10^{-3}$ | $M_w/M_n$ | $M_w \times 10^{-3}$ | $M_n \times 10^{-3}$ | $M_w/M_n$ |
| THF | 20 | 3.80 | 3.33 | 1.14 | 26.9 | 20.5 | 1.31 |
| TO/THF | 20 | 3.67 | 3.22 | 1.14 | 27.5 | 21.3 | 1.29 |
| | 100 | 4.07 | 3.55 | 1.15 | 27.7 | 22.0 | 1.26 |
| | 500 | 4.26 | 3.73 | 1.14 | 31.2 | 25.6 | 1.22 |
| | 1000 | 4.01 | 3.51 | 1.14 | 28.6 | 22.6 | 1.27 |
| | 2000 | 3.75 | 3.26 | 1.15 | 29.3 | 24.2 | 1.21 |
| | 4000 | 3.89 | 3.38 | 1.15 | 26.7 | 20.0 | 1.34 |

| ADSORLI/ DESORLI | Injection volume (μl) | PMMA83.6K | | | PMMA461K | | |
|---|---|---|---|---|---|---|---|
| | | $M_w \times 10^{-3}$ | $M_n \times 10^{-3}$ | $M_w/M_n$ | $M_w \times 10^{-3}$ | $M_n \times 10^{-3}$ | $M_w/M_n$ |
| THF | 20 | 103 | 50.0 | 2.06 | 418 | 269 | 1.55 |
| TO/THF | 20 | 102 | 50.5 | 2.02 | 429 | 290 | 1.48 |
| | 100 | 105 | 53.7 | 1.96 | 427 | 283 | 1.51 |
| | 500 | 107 | 53.0 | 2.02 | 433 | 267 | 1.62 |
| | 1000 | 104 | 49.2 | 2.11 | 399 | 251 | 1.59 |
| | 2000 | 102 | 49.1 | 2.08 | 404 | 253 | 1.60 |
| | 4000 | 109 | 55.0 | 1.98 | 390 | 261 | 1.49 |

Column set FAD5/SEC. Injected PMMA amount was the same, viz. 0.02 mg processed using a Waters Maxima/Baseline PC-based Data Acquisition System (Milford, MA, USA). The data acquisition rate was one point per second.

The ADSORLI sample solvent/eluent was analytical grade toluene for PMMA and PTHF or dimethylformamide (DMF) for PS. Analytical grade trichloromethane stabilized with 1% of ethanol was used as an auxiliary eluent in some experiments. It is an ADSORLI for PMMA, PTHF and PEO but a DESORLI for PS with the bare silica sorbent. Tetrahydrofuran (THF) was used as the DESORLI eluent for PMMA and PTHF, while toluene served as the DESORLI for PS and DMF as the DESORLI for PEO.

## RESULTS AND DISCUSSION

The reconcentration results for PMMA, PTHF and PS samples are given in *Tables 1–3*. It is evident that the effective reconcentration of dilute solutions of poly(methylmethacrylate)s and poly(tetrahydrofuran)s can be easily obtained with bare silica gel as FAD column packing: the molar masses measured with an on-line SEC column are in a good agreement for starting, nonreconcentrated solutions and for reconcentrated samples (*Tables 1 and 2*). The 200 × sample reconcentration was tested with PMMA and the 100 × sample reconcentration was tested with PTHF. More diluted samples can probably also be successfully treated in this way.

A limiting polymer molar mass presumedly exists for each system under which full adsorption is not possible and this fact presents a limitation of the FAD reconcentration procedure. Nevertheless, even very low molar mass PMMA and PTHF, namely 2750 and 6000, respectively, could be effectively reconcentrated using bare silica sorbent. The situation is, however, more complicated with PS. This polymer has a low affinity towards a bare silica surface when applying common solvents of low polarity such as toluene. Therefore, the 'reversed system' has to be used, i.e. silica bonded with $C_{18}$ aliphatic groups in combination with highly polar solvent, dimethylformamide. Even under these conditions, polystyrene samples with molar masses below $9 \times 10^4$ could not be effectively reconcentrated (*Table 3*). Evidently, in the case of both PS34K and PS60K, only the largest macromolecules were trapped within the FAD column so that the higher apparent molar mass was determined. The recovery of PS15K was only about 5% and the SEC measurement could not be done at all. This result also indicates another limitation of the present reconcentration procedure: it will be difficult to find the appropriate FAD column packings for nonpolar and possibly also for highly polar polymers. Conversely, sample solvents also present a restriction of the FAD reconcentration procedure: only samples dissolved in appropriate ADSORLI solvents can be considered for reconcentration with the FAD columns available.

The exchange of the sample matrix was tested with PMMA31K. The sample solvent was toluene that is an ADSORLI for PMMA not only with bare silica but, surprisingly, also with some polystyrene-divinylbenzene

**Table 2** Molar mass characteristics of PTHF reconcentrated from diluted solutions using FAD/SEC procedure

| ADSORLI/ DESORLI | Injection volume (μl) | PTHF6K | | | PTHF283K | | |
|---|---|---|---|---|---|---|---|
| | | $M_w \times 10^{-3}$ | $M_n \times 10^{-3}$ | $M_w/M_n$ | $M_w \times 10^{-3}$ | $M_n \times 10^{-3}$ | $M_w/M_n$ |
| THF | 20 | 5.49 | 4.06 | 1.35 | 229 | 173 | 1.32 |
| TO/THF | 20 | 5.53 | 4.10 | 1.35 | 228 | 177 | 1.29 |
| | 100 | 5.42 | 3.97 | 1.38 | 229 | 176 | 1.30 |
| | 200 | 5.38 | 3.93 | 1.37 | 228 | 173 | 1.32 |
| | 500 | 5.47 | 3.96 | 1.38 | 227 | 175 | 1.30 |
| | 1000 | 5.27 | 3.84 | 1.37 | 230 | 178 | 1.29 |
| | 2000 | 5.25 | 3.78 | 1.39 | 222 | 170 | 1.31 |

**Table 3** Molar mass characteristics of PS reconcentrated from diluted solutions in DMF using FAD/SEC procedure

| ADSORLI/ DESORLI | Injection volume (μl) | PS92K | | | PS350K | | |
|---|---|---|---|---|---|---|---|
| | | $M_w \times 10^{-3}$ | $M_n \times 10^{-3}$ | $M_w/M_n$ | $M_w \times 10^{-3}$ | $M_n \times 10^{-3}$ | $M_w/M_n$ |
| TO | 20 | 87.3 | 66.6 | 1.31 | 329 | 184 | 1.79 |
| DMF/TO | 20 | 87.0 | 65.9 | 1.32 | 336 | 186 | 1.81 |
| | 200 | 83.4 | 64.7 | 1.29 | 338 | 186 | 1.82 |
| | 500 | 88.6 | 66.6 | 1.33 | 336 | 190 | 1.77 |
| | 1000 | 87.8 | 67.5 | 1.30 | 327 | 180 | 1.82 |
| | 2000 | 85.1 | 64.5 | 1.32 | 339 | 188 | 1.80 |

| ADSORLI/ DESORLI | Injection volume (μl) | PS34K[a] | | | PS60K[a] | | |
|---|---|---|---|---|---|---|---|
| | | $M_w \times 10^{-3}$ | $M_n \times 10^{-3}$ | $M_w/M_n$ | $M_w \times 10^{-3}$ | $M_n \times 10^{-3}$ | $M_w/M_n$ |
| TO | 20 | 29.8 | 19.6 | 1.52 | 56.2 | 36.6 | 1.53 |
| DMF/TO | 20 | 47.7 | 37.0 | 1.29 | 81.7 | 61.1 | 1.34 |
| | 1000 | 51.0 | 40.1 | 1.30 | 83.1 | 62.7 | 1.33 |
| | 2000 | 48.6 | 37.1 | 1.31 | 80.5 | 60.2 | 1.34 |

Column set FAD7($C_{18}$nonporous SG) + SEC, injected amount was 0.01 mg

[a] Recovery (%) of PS34K and PS60K was 30 and 60, respectively

**Table 4** Matrix solvent change of toluene by trichloromethane for PMMA31K

| Procedure | ADSORLI/DESORLI | Injection volume ($\mu$l) | $M_w \times 10^{-3}$ | $M_n \times 10^{-3}$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| SEC | THF | 20 | 30.1 | 23.3 | 1.29 |
| FAD/SEC | TO/THF | 20 | 29.7 | 23.0 | 1.29 |
| Matrix eluent change | TO/$CHCl_3$/THF | 20 | 30.2 | 23.1 | 1.31 |
|  | TO/$CHCl_3$/THF | 2000 | 28.9 | 22.2 | 1.30 |

Other conditions were the same as in *Table 1*

**Table 5** Molar mass characteristics of PMMA and PEO reconcentrated from diluted solutions in $CHCl_3$ using FAD/SEC procedure

| Procedure | Eluent or DESORLI | Polymer sample or mixture | Injection vol. ($\mu$l) | $M_w \times 10^{-3}$ | $M_n \times 10^{-3}$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| SEC | THF | PMMA31K | 20 | 29.9 | 22.1 | 1.35 |
|  | THF | PMMA613K | 20 | 571 | 310 | 1.84 |
|  | DMF | PEO45K | 20 | 43.4 | 35.9 | 1.21 |
|  | THF | PMMA613K | — | 589 | 317 | 1.86 |
|  |  | > mixture | 1000 | — | — | — |
|  | DMF | PEO45K | — | 41.1 | 32.8 | 1.25 |
| Reconcentration by FAD/SEC | THF | PMMA613K | — | 564 | 312 | 1.81 |
|  |  | > mixture | 2000 |  |  |  |
|  | DMF | PEO45K | — | 43.0 | 33.5 | 1.28 |
|  | THF | PMMA31K | — | 30.2 | 22.9 | 1.32 |
|  |  | > mixture | 2000 |  |  |  |
|  | DMF | PEO45K |  | 44.3 | 34.2 | 1.30 |

Column set FAD2/SEC. The diluted mixture of PMMA plus PEO in $CHCl_3$ was in the first step adsorbed within the FAD column. In the next step, PMMA was desorbed by THF and finally PEO was released into the SEC column by DMF. The injected amount was 0.01 mg for each polymer

and divinylbenzene-based SEC column packing[6]. This means that toluene which is displaced by the DESORLI eluent from the FAD column together with PMMA causes some adsorption of the polymer sample within common SEC columns. Consequently, the SEC data obtained are incorrect unless the size of the FAD column is minimized[6] or the sample solvent altered. After sample adsorption was complete, the FAD column was flushed with auxiliary solvent $CHCl_3$ which was also an ADSORLI eluent for PMMA with silica sorbent, however, it was a DESORLI for PMMA with polystyrene SEC column packing. Subsequently, the PMMA sample was released from the FAD column by THF. The molar mass values obtained in this way were again in good agreement with the initial data (*Table 4*).

Results of the simultaneous FAD reconcentration and discrimination of binary polymer blend constituents are shown in *Table 5*. The diluted solutions containing equal amounts of polyethyleneoxide and poly(methylmethacrylate) in trichloromethane have been adsorbed within column FAD2. Subsequently, PMMA has been desorbed by THF and transported into the SEC column for measurement of $M$. Finally, PEO was flushed from the FAD column into the SEC column by dimethylformamide. The agreement is good between $M_w$ and $M_n$ values obtained without and with the reconcentration and discrimination step. This fact manifests again the potential of the FAD procedure in the analysis and characterization of complex polymer systems such as polymer blends[5,6], provided the affinity of particular blend constituents towards FAD column packing in given ADSORLI/DESORLI eluents differs sufficiently.

Evidently, the prerequisite of a successful reconcentration FAD procedure is the quantitative polymer adsorption within the FAD column used. Too small an FAD column would release the sample fractions with the lowest molar masses[6,9]. At the same time, too large an FAD column may cause an extensive broadening or even splitting of the desorbed solution zone[5,10] thus decreasing the reconcentration efficiency. As discussed previously, large FAD columns may also bring about severe problems in subsequent separation processes, if the sample solvent acts as an ADSORLI also for the SEC column packing[6]. Therefore, the size of the FAD column must be optimized for a given reconcentration system. Our experiments[8,9] have shown that the optimum FAD columns had the capacity to retain the three times the amount of polymer necessary for SEC determination.

The polymer breakthrough curves can be easily measured by attaching an appropriate LC detector to the free ('waste') port of the V3 valve. On the other hand, the polymer recovery can be easily controlled by comparing areas of the SEC peaks without and with the FAD step. In the framework of experimental errors, the recoveries have reached 100% in our experiments when applying optimized FAD columns. This is further proof of the quantitative nature of the adsorption and desorption processes.

Another important parameter of the FAD procedure is the rate of the basic processes. Static measurements often indicate that adsorption of macromolecules might be a slow process[2–4]. However, our latest dynamic experiments show the opposite to be the case[11]. It seems that the process of adsorption on a molecular level i.e. the attachment proper of macromolecules onto the sorbent surface may be very fast. Consequently, the effects observed by static measurements reflect the diffusion rate of polymer solutes and the exchange, displacement phenomena rather than the rate of the attachment and detachment of macromolecules on the sorbent surface. This is especially pronounced with porous adsorbents. The residence times of polymers in our FAD columns ranged approximately from 6 to 8 s only, depending on the size of the FAD column used. Still, even this short time was enough for the full retention of macromolecules. In the case of very dilute solutions where the driving force for diffusion is extremely low, the intensive mixing processes within the FAD column ensure the effective contact of practically all solute molecules with the sorbent surface.

The experimental proofs of the above conclusions, namely the presented SEC results, are, however, only indirect. We do not show any data on the size and shape of the desorbed reconcentrated polymer solution zones without the SEC column. Our SEC results, however, indicate that these zones should be rather narrow and their quantitative evaluation is a subject for further studies. Recently, Chen and Furusawa[10] have shown that the zones of dynamically desorbed polymers from controlled porous glass flushed directly into a photometric LD detector had rather sharp boundaries but often exhibited several concentration maxima. The authors explain the presence of such multiple peaked zones by the differences in the adsorption strength of given macromolecules which depends on the adsorbent pore size. In our opinion, the presence of different active groups on the sorbent surface and, especially, the shape of the DESORLI zone and the competitive interactions between the adsorbent surface, ADSORLI, DESORLI and macromolecules should also be considered.

The knowledge of rules according to which the zones of desorbed macromolecules are formed will allow us to quantitatively express the reconcentration factors obtainable for particular systems sorbent–polymer–ADSORLI–DESORLI. Consequently, the reconcentration efficiency can be optimized and the processes of adsorption and desorption of macromolecules on solid surfaces from diluted solutions can be better understood.

## CONCLUSIONS

Diluted polymer solutions can be efficiently reconcentrated by applying controlled full adsorption–desorption (FAD) processes. The nonporous adsorbents may allow quantitative adsorption and desorption of macromolecules in the dynamic, intensively mixed systems, although the contact time between the macromolecules and the sorbent surface is very short. This indicates that the attachment/detachment processes are very fast for macromolecules onto/from the solid surfaces.

An important disadvantage of the FAD reconcentration method is the limited choice of appropriate column packing, especially for totally nonpolar and for highly polar polymers. On the other hand, the FAD procedure allows both changing sample solvent and discriminating constituents of polymer blends: these can also be reconcentrated selectively.

## ACKNOWLEDGEMENTS

The authors acknowledge support from the Slovak Grant Agency VEGA, project No. 2/4012/97 and from the USA–Slovak Scientific Technical Cooperation Program, project 007-95.The gifts of PMMA samples from Rohm Co, of PS samples from Institute Sadron, of PEO samples from Toso Co., as well as a DVB column from Jordi Assoc. are also acknowledged. We are indebted to Professor B. Buszewski for bonding nonporous silica with $C_{18}$ groups.

## REFERENCES

1. Moret, S., Grob, K. and Conte, L. S., *J. High Resol. Chromatogr.*, 1996, **19**, 434.
2. Fleer, G. J., Cohen Stuart, M. A., Scheutjens, J. M. H. M., Cosgrove, T. and Vincent, B., Polymers at Interfaces. Chapman and Hall, London, 1993.
3. Kawaguchi, M. and Takahashi, A., *Adv. Colloid Interface Sci.*, 1992, **37**, 219.
4. Van de Van, T. G. M., *Adv. Interface Sci.*, 1994, **48**, 121.
5. Janĉo, M., Prudskova, T. and Berek, D., *Polymer*, 1995, **36**, 3295.
6. Jancŏ, M., Prudskova, T. and Berek, D., *Int. J. Polym. Anal. Charact.*, 1997, **3**, 319.
7. Poppe, H., Kraak, J. C., Huber, J. F. K. and van den Berg, J. H. M., *Chromatographia*, 1981, **14**, 515.
8. Nondek, L., Buszewski, B. and Berek, D., *J. Chromatogr.*, 1986, **367**, 171.
9. Nguyen, S. H. and Berek, D., Chromatographia, in press.
10. Chen, M.-H. and Furusawa, K., *Colloids Surf. A: Phys. Chem. Eng. Asp.*, 1996, **109**, 175.
11. Berek, D. and Nguyen, S. H., Macromolecules, submitted.