Chapter 15

Full Adsorption–Desorption/SEC Coupling in Characterization of Complex Polymers

Son Hoai Nguyen and Dušan Berek

Polymer Institute of the Slovak Academy of Sciences, 842 36 Bratislava, Slovakia

A novel liquid chromatographic method is presented that allows molecular characterization of multicomponent polymer systems consisted of chemically different constituents. Polymer sample under analysis is adsorbed onto an appropriate adsorbent. Particular constituents are then successively released from adsorbent by the controlled desorption using e.g. a stepwise eluent gradient. This results in the fractionation of sample, predominantly according to its chemical composition. The fractions are directed into an on-line liquid chromatographic (size exclusion or liquid adsorption chromatographic) system for further separation which provides data on their mean molar masses and molar mass distributions. The above idea was applied to several multicomponent polymer blends and precise values of the molar masses and molar mass distributions of all blend constituents could be assessed. Promising results were obtained also in the case of block and random copolymers.

Tailored polymeric materials often comprise components with different chemical compositions. We speak about complex polymer systems, e.g. blends, copolymers, sequenced and functionalized polymers. The direct molecular characterization of complex polymers by size exclusion chromatography is often not enough precise since the size of macromolecules in solution depends not only on their molar mass and on the thermodynamic quality of solvent but also on polymer chemical and physical structure. Consequently, the retention volumes of copolymers reflect also their chemical composition, lengths of blocks, etc. In the case of polymer blends, their components must be independently detected and the mutual effects of coeluting macromolecules with different nature must be suppressed. Therefore, the combinations of different separation mechanisms are to be applied in liquid chromatography (LC) of complex polymers and we speak about two-dimensional or

216

© 1999 American Chemical Society

coupled LC procedures (1,2). One of these combined methods is called full adsorption - desorption / liquid chromatography (FAD/LC) coupling (3).

FAD/LC consists of a series of independent steps. In the first step, all n or at least n-1 constituents of the complex polymer are fully retained within an appropriate sorbent. Sorbent that exhibits different affinity to macromolecules in dependence on their chemical nature is packed into a (mini)column that is called Full Adsorption - Desorption (FAD) column. Nonadsorbed macromolecules passing FAD column are directly transported into an appropriate on-line LC column for molecular characterization. After the LC analysis has been completed, operational conditions (eluent composition, temperature, pressure) are suddenly changed so that a fraction is released from the FAD column to be evaluated in the LC system. The displacement and LC evaluation steps are repeated until polymer sample is completely characterized.

The described full adsorption - desorption procedure resembles solid phase extraction (SPE) techniques that are often used in the analysis of low molecular analytes. However, the adsorption of macromolecules can be easier controlled provided a well designed system adsorbing liquid - adsorbent is applied. Consequently, recovery and repeatability in the FAD of macromolecules is substantially higher than in the SPE of small molecules. Various liquid chromatographic, spectrometric etc. procedures can be combined with full adsorption - desorption steps, however, size exclusion chromatography (SEC) is the method of choice for high polymers and one speaks about an FAD/SEC coupling.

We have recently shown (3-5) that precise and repeatable mean molar mass and molar mass distribution values can be obtained for constituents of model mixtures of two or three chemically different homopolymers after appropriate optimization of the FAD column packing, and both the polymer adsorption promoting liquid (ADSORLI) and the polymer desorbing liquid (DESORLI). The packing of the FAD column was preferably nonporous bare silica gel to suppress the polymer diffusion effects that may cause excessive broadening and even splitting of the SEC peaks of the retained/desorbed polymer (4). The size of the FAD column had to be just large enough to exhibit appropriate sample capacity, i.e. to retain enough polymer for subsequent size exclusion chromatographic characterization. In turn, the ADSORLI had to be strong enough to ensure the quantitative entrapment of selected sample constituent(s) but not to promote their adsorptive retention within SEC column (4).

In the present study we tested the performance of the FAD/SEC method in discrimination of some selected complex polymer systems and extended its use to copolymers and quaternary polymer blends of chemically similar constituents.

Experimental

The measuring assembly is schematically shown in Figure 1. Sample solutions were injected into the FAD column by means of valve V1. The adsorptive constituents of the analysed sample were retained within the FAD column packing while the non-adsorptive constituent passed through FAD column unretained and it was directed into the SEC column for characterization. Next, SEC column was equilibrated with

a new eluent introduced via valve V2 and possessing increased desorbing power. Subsequently, valve V3 was switched so that this new displacing eluent (e.g. single DESORLI or an appropriate solvent mixture) was directed into FAD column to release a selected constituent of polymer blend or a copolymer fraction and to transport it into the SEC column. The chosen displacer or displacer set was prepared in extra containers or, alternatively, it was produced with help of the Knauer (Berlin, Germany) gradient making device. The latter approach was very convenient for separation of multicomponent polymer systems. The resulting displacer composition had to be, however, smoothed in latter case to avoid the local variations in the displacer composition. Otherwise, polymer recovery could not be effectively controlled. The SEC column equilibration and the FAD column desorption steps were several times repeated with different displacers until whole sample has been processed. Instead of stepwise gradient, also continuous gradient of eluent composition or, alternatively, temperature variations can be used for successive desorption of macromolecules from the FAD column. It is important that the SEC column withstands repeated switching of eluents with different polarities and that the adsorptive properties of the SEC column are as low as possible.
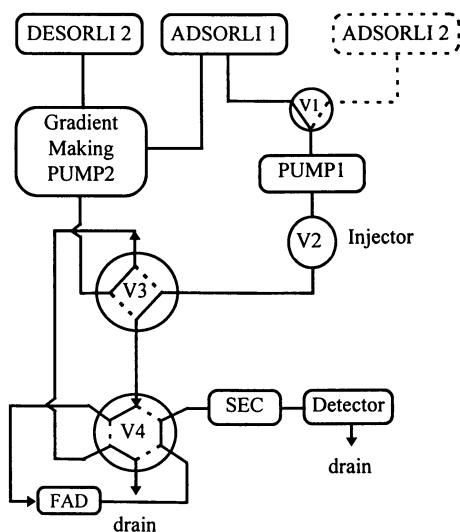

Figure 1. Schematic representation of FAD/SEC assembly. See text for detailed explanation

To optimize experimental conditions for polymer displacement, desorbing properties of various ADSORLI-DESORLI displacers must be assessed. This can be done by a series of independent measurements using the same experimental assembly (Figure 1). If necessary, FAD columns of different sizes and packed with different adsorbents can be utilized. In present work, the two-component displacers

of various compositions and displacing strengths were introduced into the FAD column containing known preadsorbed amount of a single polymer under study. Both amount and molar mass characteristics of desorbed macromolecules were measured by means of the SEC column and detector. After the desorption experiment had been completed the FAD column was flushed with the pure DESORLI to remove the rests of polymer. DESORLI was then displaced by the pure ADSORLI, the initial amount of polymer was again applied onto FAD column and the desorption procedure was repeated with another displacer mixture. In this way, the plots of desorbed polymer amount vs. displacer composition were constructed. Such dependences are called the dynamic integral desorption isotherms.

The common HPLC pumps and valves were used. The detectors were either an evaporative light scattering detector ELSD Model DDL-21 (Eurosep, Cergy St. Christophe, France) or UV variable wavelength photometers (Knauer) operating at wavelength 233 nm for mixed eluents dichloroethane / tetrahydrofuran. Since UV detector response at 233 nm was found to be the same for both PS and PMMA, it is linearly related to P(S-MMA) copolymer amount. In any case, the desorbed amounts of (co)polymers were calculated from detector response employing appropriate calibration for the same experimental conditions.

A series of model homopolymers and their mixtures was investigated: PS, PMMA, poly(n-butylmethacrylate)s (PBMA) and poly(ethylene oxide)s (PEO) with different molar masses. They were obtained from Pressure Chemicals (Pittsburgh, PA, USA), Polymer Laboratories Co. (Church Stretton, UK), Polymer Standards Service Co. (Mainz, Germany) and TOSO Co. (Shinnanyo, Japan).

The selected random P(S-MMA) (from Prof. S. Mori, Mie University, Tsu, Japan) (Table I) and block P(MMA-b-GMA) copolymers (from Dr. G. Hild, Institute Sadron, Strasbourg, France) were also subject to preliminary investigations. They were prepared by radical (6) or anionic (7,8) copolymerization, respectively.

Table I. Styrene content (6) and molar mass characteristics of P(S-co-MMA) random copolymers (using PS standards calibration)

Sample	Styrene (mol%)	$Mw.10^{-3}$	$Mn.10^{-3}$	Mw/Mn
I	85.5	174	89.8	1.94
IV	57.4	115	57	2.02
VIII	26.5	148	65.9	2.24

ADSORLI solvents were toluene and dichloroethane (DCE) for polar polymers and dimethylformamide (DMF) for PS. Tetrahydrofuran (THF) was used as a typical DESORLI. All solvents of analytical grade were distilled prior to use. DCE was stabilized with 50 ppm amylene.

The packings of the FAD columns were nonporous silicas (8 μm in diameter) either bare or C18 bonded. Nonporous silica was prepared in this laboratory by agglutination of a highly pure spheroidal mesoporous silica gel Silpearl (Kavalier

Votice, Czech Republic) for 2 hours at 1200°C. After rehydroxylation, this material was bonded with dimethyl octadecyl groups by Prof. B. Buszewski (Corpernicus University, Torun, Poland) (9).

Results and discussion

The dynamic integral desorption isotherms for selected homopolymers in system ADSORLI (toluene) and DESORLI (THF) are shown in Figure 2. The effect of polymer chemical nature on the course of dynamic desorption isotherms is evidenced. It is clearly seen that PBMA can be easily separated from PMMA in the present system of adsorbent-ADSORLI-DESORLI. On the other hand, PEO remained fully adsorbed within FAD column in pure THF. To release PEO from the bare silica sorbent, DMF can be used. Typical examples showing the performance of the FAD/SEC coupling in the separation and molecular characterization of various polymer blends are given in Table II. The molar mass data obtained by direct SEC analysis of single polymers without and with FAD step agree well. It is to be concluded that FAD procedure can readily discriminate medium polar and polar polymers, even if they are chemically rather similar. The separation of nonpolar polymers, e.g. polystyrenes was found to be more complicated. The adsorptive properties of nonpolar macromolecules are not well pronounced using bare silica FAD column packing. On the other hand, polystyrenes could be quantitatively retained on the silica C_{18} particles in dimethylformamide as an ADSORLI if their molar mass exceeded 90,000 g/mol. In this system, polar polymers were not retained and could be directly forwarded into SEC column. The optimization of this „reverse FAD system" is subject to our further study.
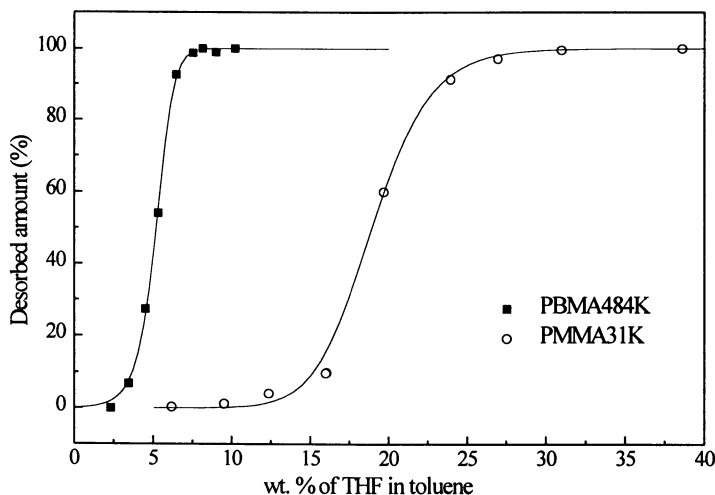

Figure 2. Dynamic integral desorption isotherms for homopolymers with M_W values as indicated. System nonporous silica / toluene / THF. FAD column (45x2mm); preadsorbed polymer amount 0.01mg. ELS detector.

Table II. Examples of molar mass characteristics of single polymers and polymers in blends separated and characterized by FAD/SEC coupling. Injected amount was 0.005mg for each polymer.

| Procedure	Polymer	Single or mixed displacer	$M_w \cdot 10^{-3}$ (g/mol)	$M_n \cdot 10^{-3}$ (g/mol)	M_w/M_n
SEC for single polymers	PS350K	toluene	336	179	1.88
	PBMA484K	THF	499	406	1.23
	PMMA31K	THF	30.6	22.3	1.37
	PMMA461K	THF	446	249	1.79
	PEO45K	DMF	43.4	35.9	1.21
FAD/SEC for blend components	PS350K	Toluene	329	179	1.85
	PBMA484K	8 wt.% THF in toluene	507	409	1.24
	PMMA31K	THF	29.4	22.3	1.32
	PBMA484K	8 wt.% THF in toluene	493	391	1.26
	PMMA461K	THF	429	313	1.37
	PEO45K	DMF	44.0	35.5	1.24
	PS350K	Toluene	356	188	1.89
	PBMA484K	8 wt.% THF in toluene	502	415	1.21
	PMMA31K	THF	28.6	21.0	1.36
	PEO45K	DMF	42.6	34.9	1.22
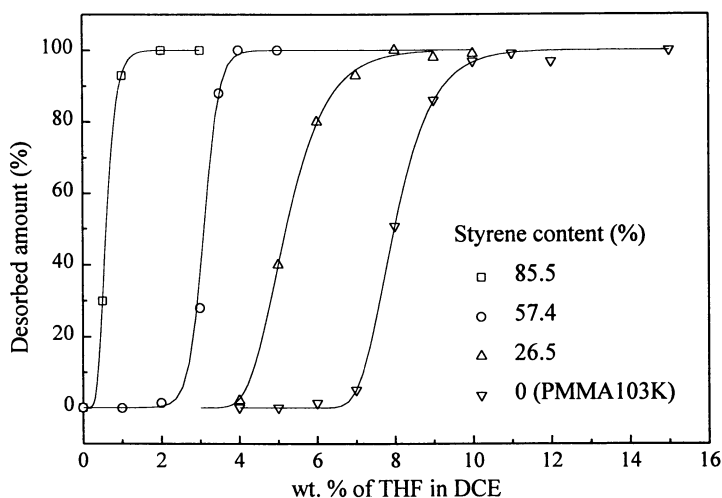
Figure 3. Dynamic integral desorption isotherms for random copolymers P(S-co-MMA) (Table I) and for PMMA103K for comparison in the system nonporous silica / DCE / THF. FAD column (150x3.3mm); preadsorbed polymer amount 0.015mg. UV detectors at 233 and 264nm.

The dynamic desorption isotherms for selected P(S-co-MMA) random copolymers and for some PGMA-b-PMMA-b-PGMA triblock copolymers are shown in Figures 3 and 4, respectively. Positions of the dynamic desorption isotherms strongly depended on the copolymer chemical structure. In the case of random copolymers, differences in their composition necessitated remarkable changes in the strength of displacer that was needed to desorb macromolecules (Figure 3). In the case of triblock copolymers, the end blocks seemed to play more important role in the adsorption-desorption processes than did the central blocks (Figure 4). The preliminary results indicate potential of the full adsorption-desorption procedure to discriminate copolymers according to their composition. The subsequent SEC separation step can produce at least semi-quantitative information on the molar mass distribution of each fraction.
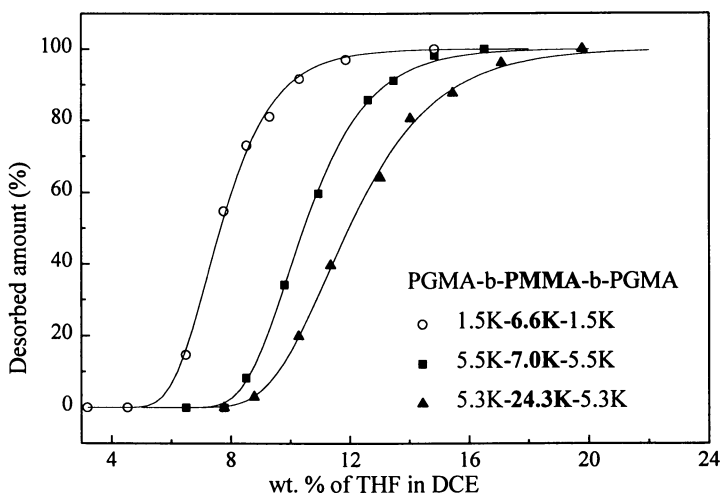

Figure 4. Dynamic integral desorption isotherms for triblock copolymers P(GMA-MMA-GMA) with block lengths (M_n) as indicated (7,8). System nonporous silica / DCE / THF. FAD column (30x3.3mm); preadsorbed amount 0.015mg. ELS detector.

Conclusions

Full adsorption-desorption / SEC (FAD/SEC) coupling allows discrimination and molecular characterization of various complex polymers. In the case of polymer blends, also chemically rather similar constituents can be readily separated. In contrast to other LC techniques suitable to discrimination of two- and multi-component polymer blends (1,2,12), such as liquid chromatography at the critical adsorption point, gradient polymer elution chromatography or liquid adsorption chromatography, FAD/SEC combination enables also precise and repeatable determination of molar masses and other molecular characteristics of separated

blend constituents. The utilization of the FAD/SEC method for molecular characterization of copolymers is limited to the systems in which constituents exhibit rather different adsorptive properties, e.g. due to different polarities. The course of polymer adsorption/desorption often depends not only on the chemical nature but also on the molar mass of macromolecules, as well as on their load on the adsorbent and on the presence of further analytes (5). Therefore, appropriate adsorbent-ADSORLI-DESORLI systems must be identified to take provision for the above effects. Other separation methods can be combined with the full adsorption-desorption procedure, as well. For example, the FAD fractions can be characterized by liquid adsorption chromatography or by mass spectrometry. In this way, the FAD technique represents an important step in the multidimensional liquid chromatographic and spectrometric characterization of complex polymer systems. Full adsorption-desorption procedure can be used also for reconcentration of highly diluted polymer solutions (10,11). Further developments include preparation of tailored FAD column packings and identification of highly selective displacers. It is anticipated that desorption of macromolecules from an adsorbent can be controlled not only by changing composition of displacers but also by temperature and possibly also by pressure variations, both stepwise or in the continuous gradient mode.

Acknowledgement

Literature Cited

1. Glöckner, G. *Gradient HPLC of Copolymers and Chromatographic Cross-Fractionation*, Springer-Verlag , Berlin 1991.
2. Berek, D. *Molecular Characterization of Complex Polymers by Coupled Chromatographic Procedures*, This book, T. Provder, Ed., ACS Press, Washington, D.C. 1998.
3. Jančo, M., Prudskova, T., Berek, D. *Polymer*, **1995**, *36*, 3295.
4. Jančo, M., Prudskova, T., Berek, D. *Int. J. Polym. Anal. Charact.* **1997**, *3*, 319.
5. Nguyen, S.H., Berek, D. *Chromatographia*, in press.
6. Mori, S., Uno, Y. and Suzuki, M. *Anal. Chem.* **1986**, *58*, 303.
7. Hild, G., Lamps, J-P., Rempp, P. *Polymer* **1993**, *34*, 2875.
8. Hild. G., Lamps, J-P. *Polymer* **1995**, *36*, 4841.
9. Nondek, L., Buszewski, B. and Berek, D. *J. Chromatogr.* **1986**, *367*, 171.
10. Nguyen, S.H., Berek, D., Chiantore, O. *Polymer*, in press.
11. Nguyen, S.H., Berek, D. *J. Polym. Sci., Part A: Polym. Chem.*, accepted.
12. Kilz, P., Krüger, R.P., Much, H., Schulz, G., In *Chromatography of Polymers: Characterization by SEC and FFF*; Provder, T., Ed., ACS Symp. Series 247; ACS Books: Washington DC, 1995, p. 223.