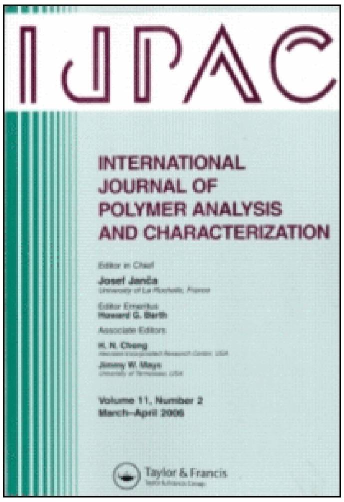

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Separation and Characterization of Polymers Applying Full Adsorption/Desorption Approaches

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The present contribution is a review of the recent progress in combining a full adsorption/desorption procedure with size exclusion chromatography (FAD/SEC) for the separation and characterization of (co)-polymers. FAD includes complete and selective adsorption of the polymer sample to be separated from an adsorption promoting-liquid (adsorli) onto an appropriate adsorbent, which is packed in an especially designed LC-like (micro)column. In the following steps, macromolecules are successively displaced from the adsorbent by different eluents with increasing desorbing strength. Adsorption and desorption of macromolecules are generally governed by their molecular characteristics, primarily by their molar mass (MM) and their chemical nature, that is, by their chemical composition (CC). Therefore, fractionation of polymers according to these parameters can be reached in the course of the FAD process. In this respect, a coupling of an SEC instrument with the FAD column has turned out to be very advantageous. The on-line SEC enables monitoring the amount, molar mass and molar mass distribution of macromolecules leaving the FAD column. In this way, constituents of polymer blends can be discriminated and independently characterized.

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Advantages and problems associated with the applications of FAD approaches are outlined. The assessment of dynamic adsorption/desorption of macromolecules onto/from solid surfaces as part of the optimization procedure is discussed as well.

Keywords: Polymer separation and characterization; Size exclusion chromatography; Polymer blends; Admixtures; Polymer adsorption and desorption

Polymer science and technology is required to meet product and market needs. The effectiveness of R & D should be carried out with a strong regard to product quality, as well as to safety, health and environmental values like waste reduction and energy conservation. Recently, we have witnessed rapid development of high-performance polymeric materials, e.g., polymer blends, copolymers, sequenced and functionalized polymers, i.e., complex polymer systems. Complex polymers exhibit multiple distributions, namely molar mass distribution, chemical composition distribution, distribution of functionalities, distribution of sequence lengths and possibly also physical, structural and topological distributions. These distributions are well known to affect both the processing ability and the end-use properties of polymeric materials. Therefore, the establishment of relationships between structure, processing and properties is of great importance for the development of novel polymeric materials. As a result, measurement of average properties is often inadequate to fully characterize and elucidate the nature of such materials. In other words, methods that do not involve any separation, such as osmometry, light scattering, viscometry, NMR or FT-IR and classical methods for end-group determination, can yield only average values, e.g., molar mass, chemical composition and functionality, but not their distribution(s). A combination of separation and characterization techniques or multidimensional approaches represents one of the options to fulfill the complicated task of analysis and characterization of complex polymers.

During the previous several decades, size exclusion chromatography (SEC) has proved one of the most important techniques for determination of the above-mentioned distribution properties of many polymers. It is, however, well known that single separation mechanism based SEC separates macromolecules according to their size in solution rather than according to molar mass[1,2], and, consequently, this method has limited applicability to complex polymer systems[3]. With respect to the determination of chemical and/or structural heterogeneity of polymers, more powerful separation techniques consist of liquid chromatographic methods based on the interaction between the polymeric solute and stationary phase, which are called interaction chromatography (IC)[4–6]. This group of methods includes gradient polymer elution chromatography (GPEC), liquid adsorption chromatography (LAC), precipitation-redissolution liquid chromatography, liquid chromatography at the point of exclusion-adsorption transition (LC PEAT), etc. In most of these chromatographic methods, adsorption/desorption of the analyzed polymers onto/from column packing must be well controlled to achieve as high as possible separation selectivity and resolution. Therefore, the dynamic of polymer adsorption at solid surfaces and its utilization as a separation mechanism in addition to SEC should be considered for complex polymers as well.

The present review is focused on the applications of the combination of full adsorption/desorption procedure with size exclusion chromatography (FAD/SEC) for the separation and characterization of polymers. It is divided into three sections as follows:

In the first section, an application of the FAD approach to the reconcentration of highly diluted polymer solutions is described. On-line SEC is used to evaluate the reconcentration process. The practical aspects of this approach as an intermediate step in multidimensional liquid chromatography are discussed.

The application of FAD/SEC combination to the separation and characterization of model complex polymer systems, namely multicomponent homopolymer blends, is investigated in the second section. Preliminary results on fractionation of statistical and triblock copolymers are also shown.

The third section is concerned with assessment of adsorption and desorption dynamic of macromolecules onto/from solid surfaces with help of the full adsorption-desorption/SEC coupling. The advantage of this novel approach over other present techniques for studies of polymer adsorption is highlighted.

RECONCENTRATION OF HIGHLY DILUTED POLYMER SOLUTIONS

The reconcentration of highly diluted polymer solutions is very often important when polymer samples are either too diluted by their nature or are being diluted in a particular stage of their processing. An example of the latter is multidimensional liquid chromatography for polymers. To achieve sufficient detectability of analytes, the column effluent that has been diluted during the course of the first separation step must be enriched before being further characterized by other separation mechanism(s).

The reconcentration of diluted polymer solutions based on full adsorption/desorption (FAD) of polymers within an appropriate adsorbent has been proposed and tested[7,8]. As the name implies, this original procedure utilizes the rapid attachment and detachment of macromolecules onto/from the adsorbent surface as far as the surface is undersaturated. The diluted polymer solution in adsorli is first brought into contact with the adsorbent so that the macromolecules are quantitatively retained within an appropriate adsorbent packed in an FAD HPLC-like minicolumn (Figure 1). In the next step, experimental conditions are suddenly changed and macromolecules are detached from the adsorbent within a small volume of displacing liquid. Generally, there are three ways to release macromolecules from the adsorbent surface by a desorbing liquid.

Desorption of Macromolecules by Eluent Switching

The sample solvent (an adsorli) is switched to a desorbing liquid (desorli) and the latter is continuously transported through the FAD

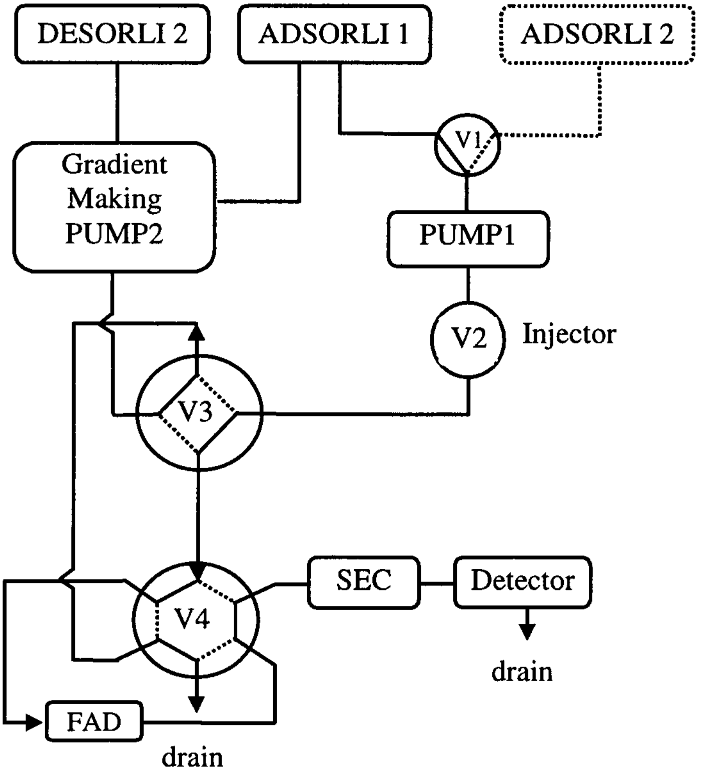

FIGURE 1 Schematic FAD/SEC setup. See Experimental section for detailed explanation.

column. This implies that the adsorli solvent is completely changed to the desorli eluent[7]. In order to control the reconcentration efficiency, the SEC column has been attached to the FAD on-line. In this way, both the amount and molecular characteristics of reconcentrated polymer can be easily monitored.

During its passage along the FAD column, the desorli boundary is spread by diffusion and mixing with adsorli. Therefore, a certain broadening of desorbed polymer zone should be anticipated. It was found, however, that the shape and width of an SEC polymer peak was little affected by the presence of a well-packed FAD minicolumn and, moreover, it remained practically the same for different pore sizes of the FAD column packings (unpublished results).

The eluent switching approach has been tested with a variety of polymers ranging from rather nonpolar polystyrene (PS), to medium polarity poly(methyl methacrylate) (PMMA) and polytetrahydrofuran (PTHF), to highly polar poly(ethylene oxide) (PEO). The efficiency of reconcentration using nonporous silica was found to be very high in the case of medium polar and polar polymers from chloroform or toluene[7]: full recovery of macromolecules was demonstrated by SEC peak sizes and shapes (Table I). 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 both the size and the packing nature of the FAD column were optimized. Very diluted solutions containing 0.1 mg of polymer per liter of solution could be easily treated in this way. On the other hand, it was more

TABLE I Molar mass characteristics of PMMA reconcentrated from diluted solutions using FAD/SEC procedure. The FAD column 45 × 2 mm was packed with 8-μm nonporous silica. The SEC column was PL-gel mixed B (300 × 7.5 mm). A constant amount of PMMA was injected: 0.02 mg. Reprinted from ref. 7 with permission.

Adsorli/ Desorli	Injection volume (μl)	PMMA2.75 K			PMMA461 K		
		$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	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	418	269	1.55
Toluene/ THF	20	3.67	3.22	1.14	429	290	1.48
	100	4.07	3.55	1.15	427	283	1.51
	500	4.26	3.73	1.14	433	267	1.62
	1000	4.01	3.51	1.14	399	251	1.59
	2000	3.75	3.26	1.15	404	253	1.60
	4000	3.89	3.38	1.15	390	261	1.49

TABLE II Molar mass characteristics of PS reconcentrated from diluted solutions in DMF using FAD/SEC procedure. The FAD column 30 × 3.3 mm was packed with 8-μm nonporous silica densely bonded with aliphatic C_{18} groups. The SEC column was the same as in Table I. The injected PS amount was 0.01 mg. Reprinted from ref. 7 with permission.

Adsorli/ Desorli	Injection volume (μl)	PS92K			PS34K*		
		$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	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	29.8	19.6	1.52
DMF/ TO	20	87.0	65.9	1.32	47.7	37.0	1.29
	1000	87.8	67.5	1.30	51.0	40.1	1.30
	2000	85.1	64.5	1.32	48.6	37.1	1.31

*Recovery of PS34K was 30% only.

difficult to effectively reconcentrate polystyrene that was not fully adsorbed on bare silica from most common solvents. (We avoided work with carbon tetrachloride.) Agreement was obtained for molecular characteristics of PS before and after reconcentration from dimethylformamide on C_{18} bonded silica for molar masses above ca. 9×10^4 g/mol (Table II).

It was found that the exchange of adsorli sample matrix can be easily performed during the course of the FAD procedure. This is important if the original sample solvent interferes with further treatment of reconcentrated polymer. Evidently, the new solvent must again be an effective adsorli for a given polymer.

Desorption of Macromolecules by a Narrow Pulse of Desorli

In this case, a small volume of desorli is introduced into the FAD column that is flushed continuously with adsorli. The important question concerning both preparative reconcentration and the intermediate step in multidimensional LC is to obtain the polymer in as small as possible desorli volume. Therefore, one has to determine the minimum volume of desorli needed to fully displace the reconcentrated macromolecules. This value can be estimated from the so-called "dynamic desorption curves" that is, from the plots of desorbed amount vs. volume of desorli injected into the FAD column via injection valve V2 equipped with the loop of variable volume (Figure 1). The shape of desorption curves depended on a number of experimental parameters, such as the nature of both sample solvent and desorli, flow rate of desorli, the nature, molar mass and molar mass distribution of reconcentrated polymer and the FAD size, as

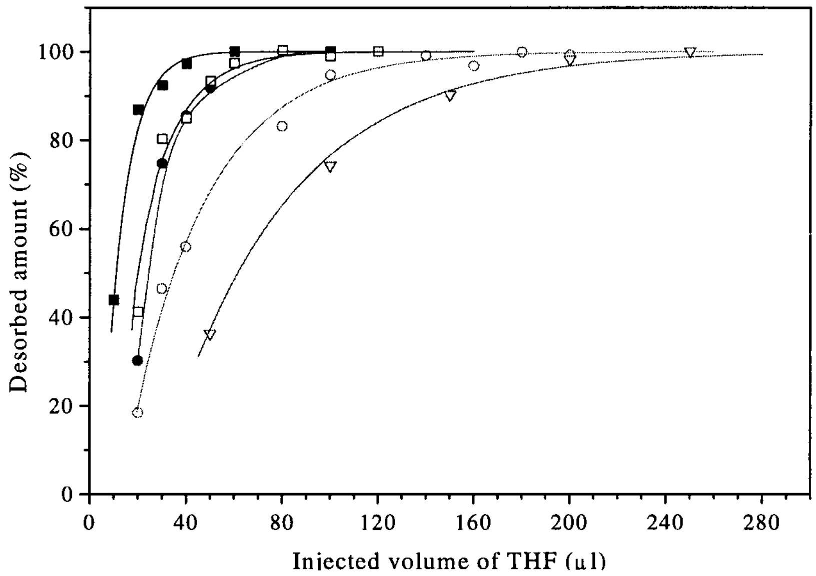

FIGURE 2 Effect of FAD column size on the dynamic desorption curves. Adsorli was toluene and preadsorbed amount of polymer was 0.01 mg. FAD columns were packed with 8-µm nonporous silica. FAD 45 × 2 mm: PMMA31K (■) and PMMA461K (●). FAD 150 × 3.3 mm: PMMA31K (□) and PMMA461K (○), all with pure tetrahydrofuran (THF) desorli. PMMA31K desorbed with its solutions in THF containing the same polymer amount as was preadsorbed within FAD column 150 × 3.3 mm, i.e., 0.01 mg (▽). Reprinted from ref. 8 with permission.

well as on relations between the amount of polymer to be reconcentrated and volume of the desorbing liquid pulse (Figure 2).

The results showed that the minimum volume of a given desorli needed to fully desorb reconcentrated polymer increased with increasing FAD size, polymer mean molar mass and adsorbing strength of adsorli, as well as with decreasing reconcentrated amount of polymer. The preferential desorption of small macromolecules over larger ones was observed when a narrow pulse of displacer was used.

Desorption of Macromolecules by Sudden Change of Temperature

Macromolecules may be detached from the adsorbent surface also by temperature adjustment. However, the controlled change of temperature is rather difficult in the case of FAD columns with increased diameter.

The peculiarities of the dynamic adsorption and desorption processes of macromolecules must be known in detail to optimize the reconcentration procedure. It is necessary to elucidate the dynamics of attachment and detachment processes, the role of adsorli-desorli microgradients formed during eluent switching and the desorli pulse progression, as well as the effects of macroscopic parameters of the systems. The concentration profiles of desorbing liquid pulse can be monitored, for example, with a density detector[8].

It can be concluded that the experimentally feasible procedure based on the full adsorption-full desorption processes of macromolecules can be used for efficient reconcentration of highly diluted polymer solutions. Reconcentration factors of at least several hundreds can be readily obtained applying the appropriate adsorbent and desorbing liquid for a given polymer and its solvent (adsorbing liquid), provided the experimental conditions (amount of adsorbent, volume of desorbing liquid, temperature, etc.) are carefully optimized. If the FAD column capacity is higher than the amount of polymer to be reconcentrated in a given system, no problems are anticipated even with more diluted systems. The polymer recovery and its molecular characteristics can be easily evaluated by an on-line size exclusion chromatograph. Further, the FAD procedure allows changing sample solvent. It can also be used to selectively reconcentrate particular constituent(s) of polymer blends from their dilute solutions. These results, in turn, indicate indirectly that both adsorption and desorption of macromolecules under optimized dynamic conditions are quantitative and very fast processes.

An important practical disadvantage of the adsorption-desorption based reconcentrations lies in limited availability of tailored adsorbents that are needed for efficient reconcentration of particular polymers. These adsorbents must exhibit controlled adsorption-desorption strength, high sample capacity and good mechanical properties.

SEPARATION AND CHARACTERIZATION OF MULTICOMPONENT POLYMER SYSTEMS

The principle of the FAD/SEC coupling has already been briefly described in the Introduction. In general, the optimization of this method includes the assessment of dynamic integral desorption isotherms (DIDI) for a polymer blend to be separated[9–13]. Typical DIDI for various homopolymers are depicted in Figure 3. They provide a reasonable estimation of appropriate displacer compositions that can be chosen for successive and selective desorption of blend constituents.

The precondition for successful separation and characterization of polymer blends is the appearance of distinct steps on the corresponding DIDI in an optimized system: adsorli, desorli, FAD column packing

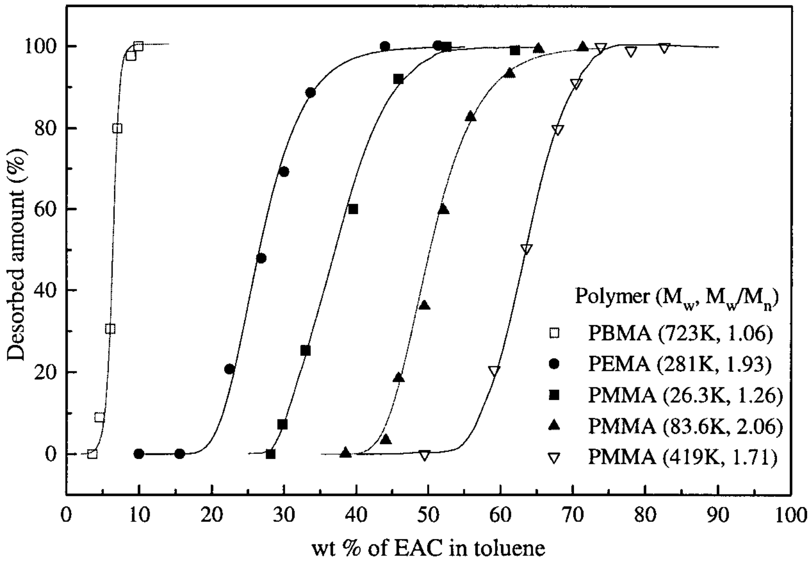

FIGURE 3 Dynamic integral desorption isotherms for various poly(methacrylates). FAD column 30 × 3.3 mm was packed with nonporous silica. Preadsorbed amount of polymer from toluene was 0.01 mg and desorli was ethylacetate (EAC).

(Figure 4). In other words, the positions of DIDI for single components of polymer blend must be mutually sufficiently shifted, otherwise, high selectivity of separation is not attained. It has been shown that the appropriate selection of adsorli/desorli pairs for a given polymer/adsorbent system could help achieve high selectivity. For example, a combination of the weak desorli (EAC) with the strong adsorli (toluene) increased the difference in desorption behavior among various poly(acrylates) or poly(methacrylates).

Another important parameter is the FAD column packing activity. Nonporous silica produced in our laboratory by sintering ultra-pure silica gels seemed to have low adsorption activity. This is due to a low silanol concentration on the surface of this material. Higher alkyl esters of poly(acrylates) or poly(methacrylates) such as poly(ethylhexyl acrylate) (PEHA) or poly(lauryl methacrylate) (PLMA) were not fully adsorbed in the FAD columns packed with this material. In order to increase the number of components in poly(acrylate) or poly(methacrylate) blends that can be discriminated using one single FAD column, we were forced to use commercial nonporous silica Develosil that was also able to retain less polar PLMA or PEHA.

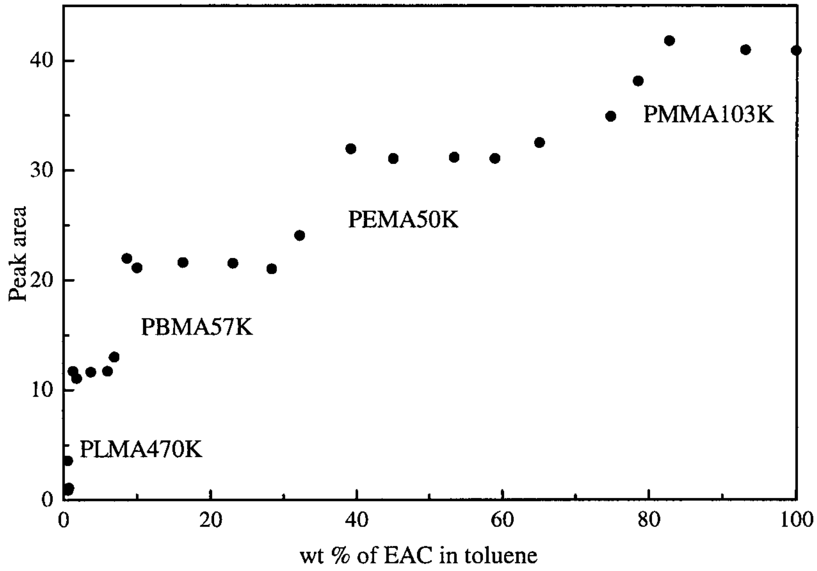

FIGURE 4 Dynamic integral desorption isotherm for the polymer blend containing PS92K + PLMA470K + PBMA57K + PEMA50K + PMMA103K + PEO45K. FAD column was Develosil 50 × 4.6 mm, preadsorbed amount was 0.01 mg per each polymer, adsorli was toluene and desorli was ethylacetate (EAC). Polystyrene was not retained on bare silica from toluene. PEO was not desorbed with pure EAC and could be released by adding dimethylformamide. Reprinted from ref. 12 with permission.

The FAD/SEC method has been successfully applied to the separation and characterization of numerous model multicomponent blends containing up to six homopolymers of similar chemical nature such as polystyrene (PS), PLMA, poly(butyl methacrylate) (PBMA), poly(ethyl methacrylate) (PEMA), poly(methyl methacrylate) (PMMA) and poly(ethylene oxide) (PEO) or PS, PEHA, poly(butyl acrylate) (PBA), poly(ethyl acrylate) (PEA), poly(methyl acrylate) (PMA) and PEO (Figure 4).

It is important to note that poly(acrylate)s and poly(methacrylate)s containing the same alkyl ester group apparently cannot be separated from each other using the FAD approach with nonmodified silica gel. Similarly, neither can PMMAs of different tacticities and similar molar masses be separated applying this adsorbent since their DIDIs (Figure 5) exhibit almost the same shapes. This observation reveals a lower selectivity of the chromatography-like, on-and-off FAD approach in comparison with true chromatographic procedures that employ con-

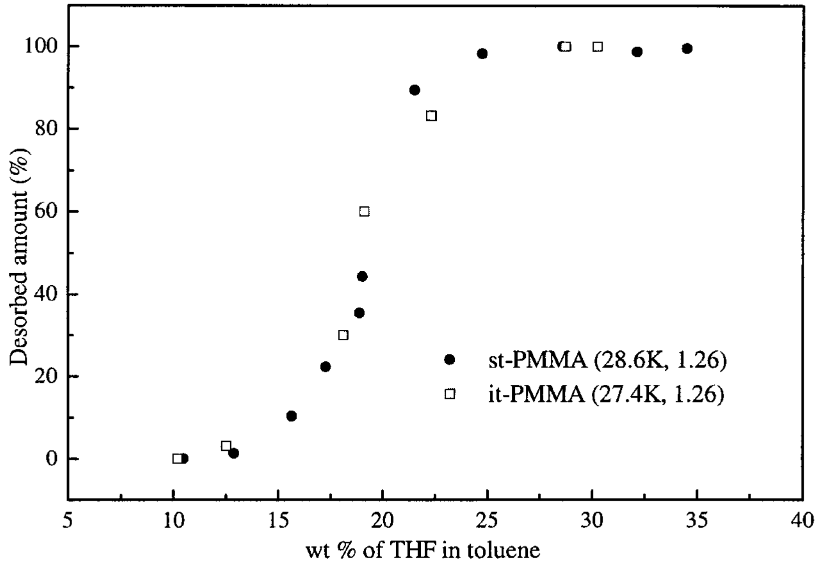

FIGURE 5 Dynamic integral desorption isotherms for iso- and syndiotactic PMMAs with molar mass as indicated. FAD column 30 × 3.3 mm was packed with nonporous silica. Preadsorbed amount of polymer from toluene was 0.01 mg and desorli was tetrahydrofuran.

tinuous eluent macro or microgradient where the attachment and detachment of macromolecules is many times repeated in the course of the separation.

The primary advantage of the FAD approach over the true chromatographic techniques is the possibility not only of separation but also of simultaneous independent SEC characterization of all constituents of the polymer system. Both time and sample consumption are comparable with the conventional chromatographic techniques such as LAC or GPEC. However, the latter procedures are more difficult to couple on-line with SEC. In contrast to other two-dimensional couplings such as GPEC/SEC[4] or LC PEAT/SEC[6,14], the precise calibration(s) of the FAD/SEC system can be obtained. Additionally, the use of stepwise eluent gradient for a selective release of blend components from the FAD into the SEC column can allow the use of an absolute detector for MMM and MMD determination. In some cases, single component displacers (desorlis) can also be applied.

Statistical P(S-MMA)[15] and tri-block PGMA-PMMA-PGMA[16] copolymers have also been used to test the selectivity of the FAD approach in terms of chemical composition separation. Our preliminary results indicate that this procedure can be used to fractionate copolymers according to chemical composition (Figures 6 and 7). However, the problem concerning selectivity of copolymer fractionation deserves more attention since molar mass effects are always incorporated upon (co)-polymer desorption (Figure 8).

Current efforts are to be focused on optimization of the system adsorli/desorli/FAD packing in order to suppress the above-mentioned influence of molar mass. Alternatively, coupling of the type SEC/FAD/SEC could be one of the solutions to this problem. With this approach, copolymer sample is fractionated in the "first dimension" SEC from which copolymer fractions are reconcentrated and separated in a series of FAD columns (see previous section). Next, fractionated copolymer having a narrow size distribution in each FAD column is subjected to a selective desorption into an SEC column for molecular characterization. Generally, copolymers with low adsorption affinity might need highly active adsorbent for their quantitative entrapment.

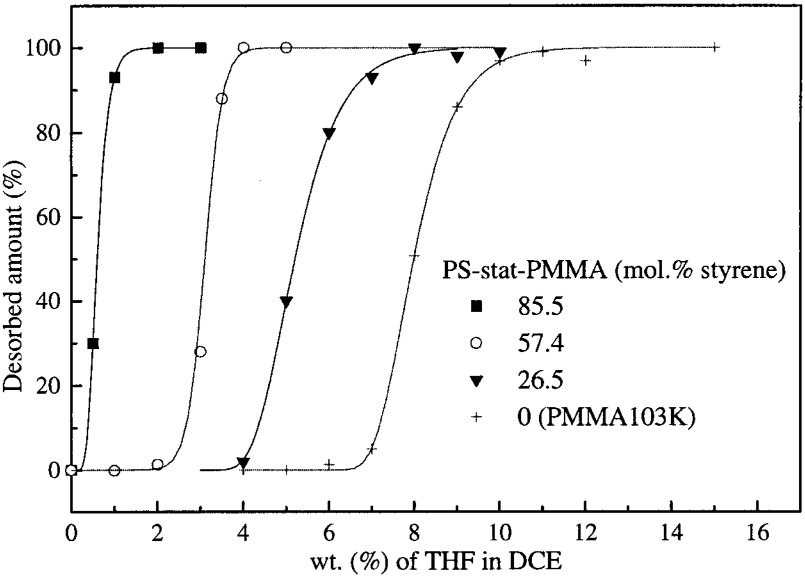

FIGURE 6 Dynamic integral desorption isotherms for PS-stat-PMMA samples. Adsorli: dichloroethane (DCE), desorli: THF. FAD column 150 × 3.3 mm size was packed with nonporous silica. Preadsorbed amount of polymer was 0.015 mg. Reprinted from ref. 15 with permission.

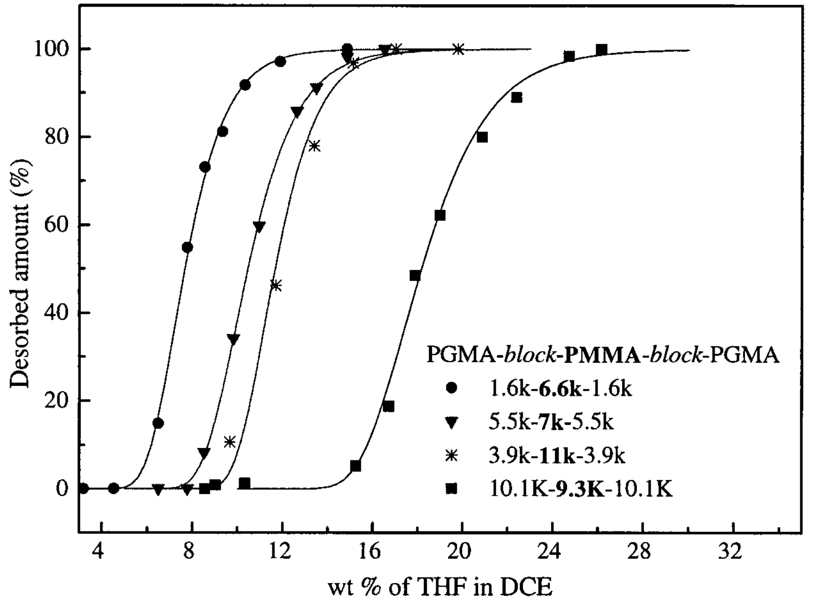

FIGURE 7 Dynamic integral desorption isotherms for block copolymers of PMMA and PGMA with similar sizes of central blocks. Adsorli: dichloroethane (DCE), desorli: THF. FAD column (30 × 3.3 mm) was packed with nonporous silica. Preadsorbed amount of polymer was 0.015 mg. Reprinted from ref. 16 with permission.

DYNAMIC ADSORPTION/DESORPTION OF MACROMOLECULES ONTO/FROM SOLID SURFACES STUDIED BY ON-LINE SEC

It has been shown in previous sections that the study of polymer adsorption and desorption is part of the optimization stage involved in the reconcentration procedure of dilute polymer solutions as well in the FAD/SEC coupling. Evidently, the FAD approach is based on the selective adsorption/desorption of macromolecules at the liquid-solid interfaces. However, a simple assembly such as shown in Figure 1 can be utilized also for the study of polymer adsorption. The most important advantages of this novel approach over classical static techniques for the study of static polymer adsorption, i.e., its low time and sample consumption, high repeatability and reasonable accuracy, are demonstrated in this section[17,18].

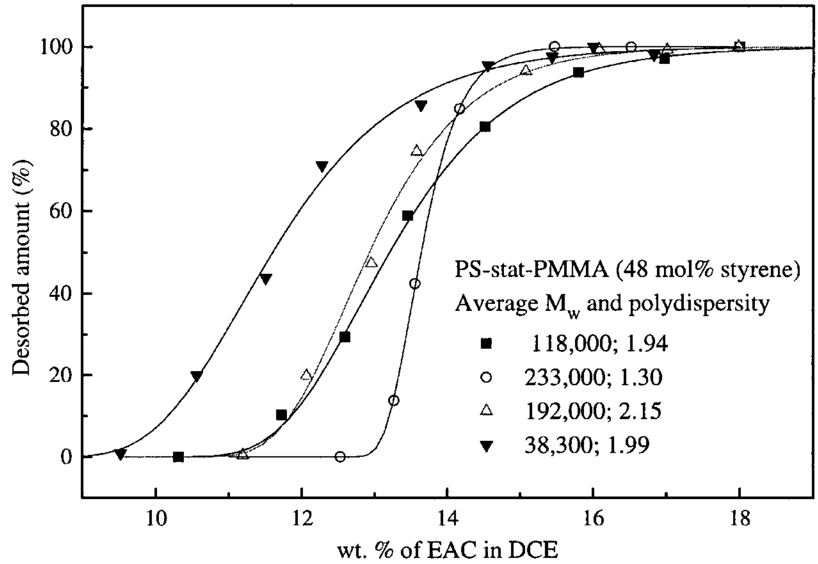

FIGURE 8 Effect of copolymer mean molar mass and molar mass distribution on the courses of dynamic integral desorption isotherms. FAD size was 30 × 3.3 mm. Preadsorbed polymer amount was 0.01 mg. Adsorli and desorli was DCE and EAC, respectively.

Preferential and Exchange Adsorption of Macromolecules at Liquid–Solid Interfaces

The approach has been applied to the study of preferential and exchange adsorption induced by differences in molar masses and/or chemical structure[17,18]. The attached on-line SEC allows evaluation of the adsorbed amount as well as mean molar mass and molar mass distribution of fractions of nonadsorbed/desorbed polymers.

In the case of preferential adsorption, the polymer sample was successively introduced into the full adsorption-desorption column (pulse-wise introduction). The lapse of time between injections was set sufficiently long for the SEC characterization of nonadsorbed polymer fraction. Complete retention of the first injections in the FAD column indicated that, as far as the FAD is undersaturated, the attachment of macromolecules onto the adsorbent surface is fast and quantitative (Figure 9). Consequently, the amount and molecular characteristics of adsorbed polymer that was released from the FAD into the SEC agreed well with that of the initial polymer. At a certain amount of

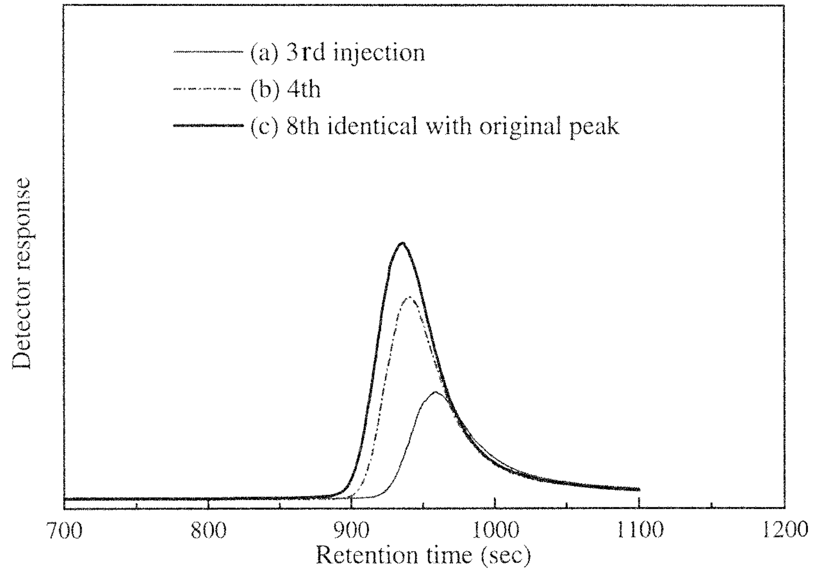

FIGURE 9 SEC tracings of nonretained fractions of PMMA19K. Polymer amount of each injection was 0.05 mg; adsorli: chloroform, FAD (150 × 3.3 mm), SEC column 600 × 7.5 mm was PL-gel mixed B. M_w (g/mol) and polydispersity values calculated using PMMA calibration are: (a) 11,600; 1.11; (b) 17,200; 1.08; (c) 19,500; 1.11. Reprinted from ref. 18 with permission.

injected polymer, macromolecules were only partially retained within the FAD and a fraction of injected polymer reached the detector. The adsorption (saturation) threshold had been reached. From this point, preferential adsorption occurred: the largest macromolecules from the injected sample displaced smaller ones already adsorbed on the surface from previous injections. When sample injections continued, we arrived at the full saturation point where the amount and molar mass characteristics of nonadsorbed polymer fraction were identical with those of the starting polymer. In other words, the entire injected polymer reached the detector and no further adsorption/exchange took place.

In principle, polymer solutions could be continuously introduced into the FAD column instead of the above-described pulsed approach. Polymer solutions of a certain concentration were delivered by means of an HPLC pump. The effluent leaving the FAD was directed into an evaporative light scattering detector. The breakthrough curves for PMMA57k and PMMA654k samples at different flow rates are depicted in Figure 10. The adsorbed amounts calculated from inflection points of the breakthrough curves were found to be virtually independent of flow rate. Furthermore, the adsorbed amounts obtained by means of pulsed[17,18] and continuous introduction of the same polymer solutions agreed well.

However, the continuous approach is rather sample-consuming and unreliable at both high concentrations of polymer solutions and flow rates where small variations in flow rate can lead to a large error in the calculated adsorbed polymer amount. The reliability of pumps strongly decreases with the viscosity of the transported liquid. Additionally, the continuous approach does not enable evaluation of molecular characteristics of nonretained polymer fractions. Therefore, the pulsed approach was further used to study the effects of flow rate and polymer concentration on the maximum adsorbed amount of polymer. The results are shown in Figure 11. Evidently, the amount of polymer adsorbed did not depend on either flow rate or concentration of polymer solution in a well-detectable range of polymer concentration from 0.01 mg/mL to 2 mg/mL.

In the exchange experiments, the FAD column was first saturated with a given polymer A. Next, polymer B, possessing higher adsorption affinity toward the adsorbent surface (higher molar mass or higher interaction energy), was introduced into the FAD. The displaced fraction of polymer A was monitored by the on-line SEC. The displacement of preadsorbed poly(methyl methacrylate) (PMMA) and polytetrahydrofuran (PTHF) by polymeric displacer poly(ethylene oxide) (PEO) was as fast and quantitative as with the monomeric displacer THF. Smaller but strongly adsorbed PEO macromolecules easily exchanged large PMMA or PTHF macromolecules on the silica surface. In both cases, the kinetic effects induced by long tails and loops of preadsorbed macromolecules on the exchange processes were not observed in our systems (Figure 12).

The conclusions from preferential and exchange adsorption experiments for PMMA species of different mean molar masses (MMM) were that the dynamic exchange of small macromolecules by the large ones was governed by the chain length ratio between preadsorbed and displacing macromolecules, by the MMM of initially preadsorbed polymer and possibly also by the chain flexibility. The exchange at the saturation stage of the surface became less effective as the mean molar mass of the preadsorbed macromolecules increased. In other words, large preadsorbed macromolecules were expected to exhibit long protruding tails and loops that might prevent attachment of later arriving macromolecules on the adsorbent surface. Dynamic preferential adsorption in a given system was more noticeable with a polydisperse polymer having broader molar mass distribution and lower MMM.

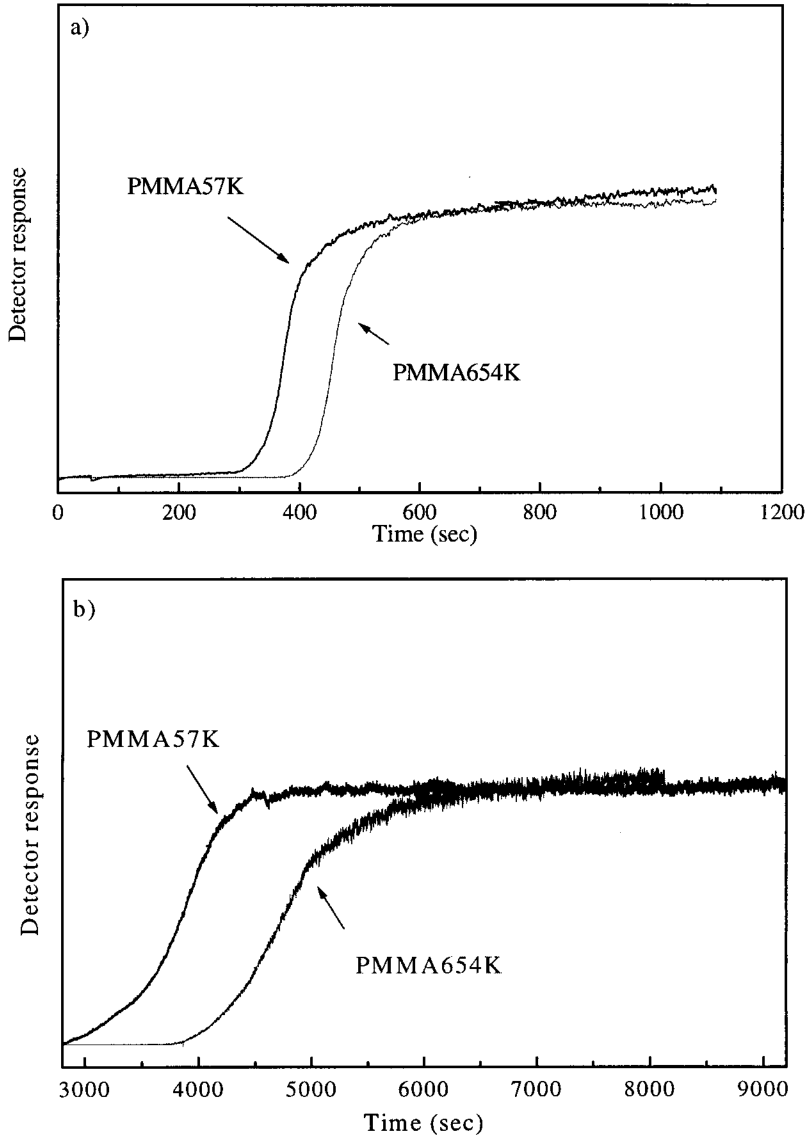

FIGURE 10 The breakthrough curves monitored with an ELSD. Polymer solutions (concentration 0.01 mg/mL) were continuously introduced into the FAD (30 × 3.3 mm) at two different flow rates: a) 1 mL/min; b) 0.1 mL/min.

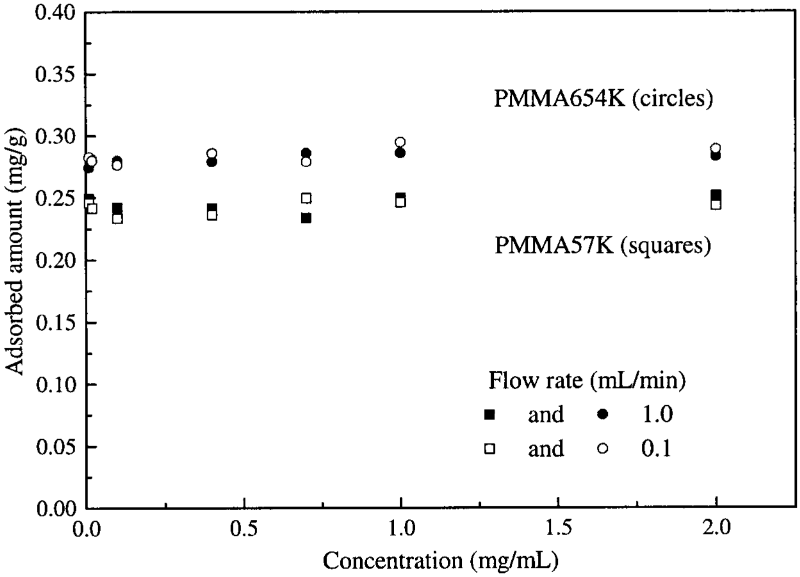

FIGURE 11 The adsorption isotherms: adsorbed amount vs. concentration of PMMA with different molar masses in toluene at flow rate 0.1 and 1.0 mL/min as indicated above. Adsorbent was nonporous silica.

Dynamic Desorption of Macromolecules from Solid Surfaces by Low Molar Mass Displacers

As mentioned above, the appropriate displacers for selective desorption of a particular component of a polymer complex system can be identified from the course of the dynamic integral desorption isotherms (DIDIs), that is, from the plots of desorbed polymer amount vs. composition of displacing liquid (displacer)[19]. Therefore, a detailed study has been focused on the dependence of the course of DIDI on various factors such as flow rate of displacing liquid; adsorli, desorli and polymer nature; polymer molar mass and molar mass distribution; preadsorbed amount of polymer; FAD column geometry; and temperature.

The desorption of preadsorbed macromolecules from the adsorbent surface by low molar mass (monomeric) displacer was independent of the displacer flow rate. This observation indirectly indicated that in our dynamic systems the supply rate of monomeric displacer to the liquid–solid interface was high enough not to affect the detachment process of macromolecules. This finding is very important for the successive desorption of preadsorbed constituents of multicomponent polymer

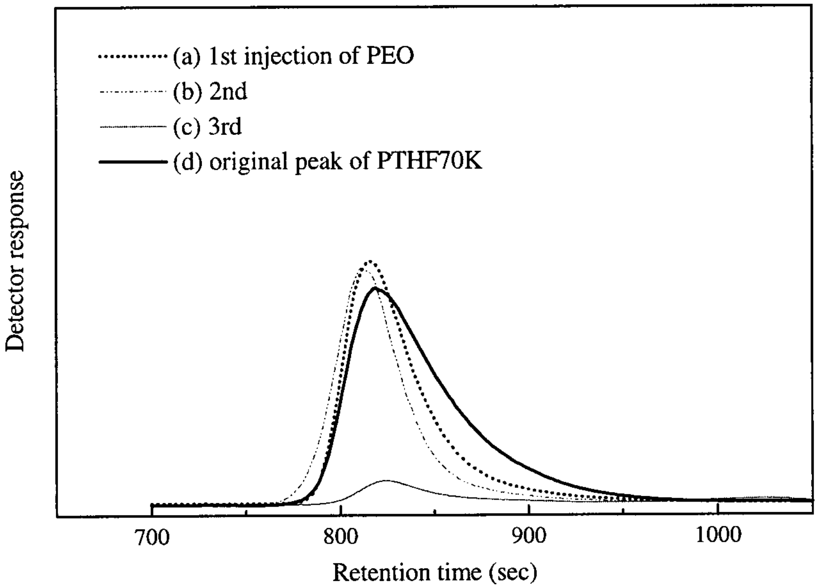

FIGURE 12 SEC chromatograms of retained fractions of polytetrahydrofuran PTHF70K that were desorbed by PEO21K after the saturation of the FAD (30 × 3.3 mm) with 5 injections of PTHF70K. Adsorli was chloroform and SEC column was of dimension 600 × 7.5 mm. M_w (g/mol) and polydispersity values calculated using PTHF calibration are: (a) 91,600; 1.49; (b) 110,000; 1.37; (c) 76,900; 1.36. The original PTHF70K peak is also shown for comparison: (d) 78,000; 1.72.

blends when applying monomeric displacers with different desorbing strengths.

Both adsorption and desorption within the adsorption-desorption column represent dynamic processes. The desorption processes occurring within the adsorption-desorption column depend to a large extent on the free surface of adsorbent still available for further (re)adsorption after the preadsorption step. Our results showed conclusively that the chemical heterogeneity of the FAD packing as well as of the polymer sample significantly affected the desorption characteristics of polymer[19]. The desorption of preadsorbed macromolecules also includes readsorption processes. This may explain the differences between the results of some static and dynamic adsorption studies. As a result, macromolecules are more difficult to detach from the adsorbent surface if larger FAD or a smaller preadsorbed amount of polymer was employed. A similar tendency was observed when increasing temperature with the adsorli/desorli pairs: toluene/THF (Figure 13) and dichloroethane/THF. In contrast to some literature sources, it was shown that the full desorption point depended on both molar mass and molar mass distribution of polymer (Figure 3).

Another important result of our dynamic measurements indicated that macromolecules were more difficult to release from the adsorbent surface in the systems where the maximum attainable adsorbed amount of polymer was higher. In general, the overall desorption strength of a two-component displacer increased with decreasing adsorbing power of adsorli constituent or increasing desorbing power of desorli constituent. This is consistent with the published conclusions made on the basis of the static adsorption studies. An important question still remains unanswered, namely, if one could use the values of full desorption points obtained from our dynamic approach for determination of interaction parameter χ_s. In any case, the dynamic desorption studies may help in understanding interactions between constituents of systems.

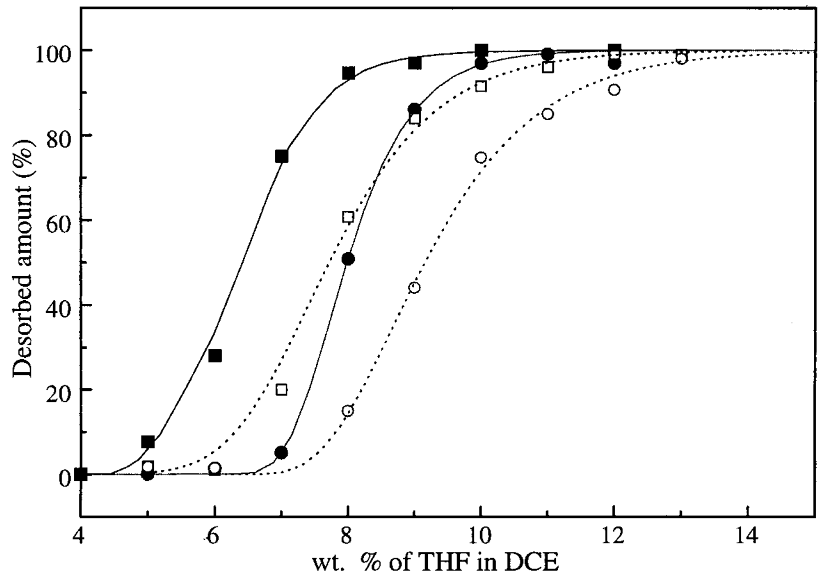

FIGURE 13 Temperature effect on the course of the dynamic integral desorption isotherms. Preadsorbed amount of PMMA was 0.015 mg; FAD column 45 × 2 mm was packed with nonporous silica. Adsorli: dichloroethane (DCE), desorli: THF: (■) PMMA31K and (●) PMMA103K at 25°C; (□) PMMA31K and (○) PMMA103K at 45°C. Reprinted from Ref. 17 with permission.

EXPERIMENTAL

Equipment

Pumps

Waters Model 510 (Milford, Massachusetts); Knauer Model 64 (Berlin, Germany); flow rate was 1 mL/min, unless indicated otherwise.

Valves

Injection valve was either a six-port three-way valve or a six-port two-way valve (Knauer), Rheodyne 7125, 7725i (Cotati, California) or Waters Model U6K universal injector.

Switching valves were ten- and six-port Valco valves (Houston, Texas), Rheodyne Model 7010, 7030 and 7060.

Columns

FAD columns 45 × 2, 30 × 3.3 and 150 × 3.3 mm were packed with nonporous silica (8 μm in diameter), either bare or C18 bonded. The former was prepared by sintering ultrapure silica gels (Kavalier Votice, Czech Republic) at 1200°C for 2 h in this laboratory. These particles exhibited a somewhat rough surface likely due to crystallization of SiO_2 during sintering. After rehydroxylation, this material was bonded with dimethyl octadecyl groups to a high degree of coverage forming the "polymeric phase" by Prof. B. Buszewski (Copernicus University, Torun, Poland). In some cases, FAD column 50 × 4.6 mm packed with nonporous silica particles (5 μm) from Nomura Chemical Co., Ltd. (Kyoto, Japan) was used.

SEC linear columns (PL-gel mixed B) purchased from Polymer Laboratories (Church Stretton, U.K.) had dimensions of either 300 × 7.5 mm or 600 × 7.5 mm.

Column Temperature Control

Column Air Oven (Knauer) or water bath thermostat Lauda Model RM6 (Königshofen, Germany).

Detectors

Refractometric detectors ERC-7515A (ERC Inc., Tokyo, Japan), Knauer model 198, or Waters Model 410. UV variable-wavelength detector and UV photometer (both Knauer Model 198). Density Detection System DDS 70 (Chromtech, Graz, Austria). Evaporative light scattering detectors (ELSD): DDL-21 (Eurosep Instruments, Cergy-St. Christophe, France), SEDEX Model 45 and 55 (Sedere, Paris, France) and PL-EMD 960 (Polymer Laboratories, Church Stretton, U.K.).

Materials

Polymer Standards

PS standards set (Pressure Chemical Co., Pennsylvania); PnBMA and PMMA standards sets (PSS, Mainz, Germany); PTHF standards (Polymer Laboratories); PEO standards (Toso Co., Tokyo, Japan).

Homopolymers

A variety of commercial polymers with broad molar mass distributions were used as models: polystyrenes (PS), poly (lauryl methacrylate) (PLMA), poly (butyl methacrylate) (PBMA), poly (ethyl methacrylate) (PEMA), poly (methyl methacrylate) (PMMA), poly (2-ethylhexyl acrylate), poly (butyl acrylate) (PBA), poly (ethyl acrylate) (PEA), polytetrahydrofurans (PTHF), poly (vinyl acetate) (PVAc), poly (ethylene oxide) (PEO).

Statistical Copolymers

Statistical copolymers of styrene and methyl methacrylate of various compositions and molar masses were prepared by radical copolymerization. The conversion was kept well below 10%.

Block Copolymers

Anionic copolymerization of MMA and GMA was employed to obtain well-defined triblock-copolymers P(GMA-b-MMA-GMA). Bifunctional initiator was 1,1,4,4-tetraphenyl-1,4-dilithiobutane.

The aforementioned commercial polyacrylates and polymethacrylates were kindly provided by Prof. O. Chiantore (Turin, Italy), Dr. Y. Brun (Waters Co., Milford, Massachusetts) and Dr. W. Wunderlich (Röhm Co., Darmstadt, Germany). Other samples were prepared by Dr. J. Pavlinec (Bratislava, Slovakia), Profs. K. Hatada and T. Kitayama (Osaka, Japan), Dr. G. Hild (Strasbourg, France), Prof. S. Teramachi (Tokyo) and Prof. S. Mori (Nagoya, Japan).

Solvents

Tetrahydrofuran (THF), dichloroethane (DCE), toluene, dimethyl formamide (DMF), ethyl acetate (EAC) and *n*-hexane (*n*-HEX) of analytical grade were purchased from Merck (Darmstadt, Germany) and Microchem (Bratislava, Slovakia). Most of them were distilled and/or stabilized prior to use. Chlorinated solvents such as DCE and chloroform were additionally stabilized with 50 ppm of amylene. In some experiments, chloroform stabilized with ethanol was used as purchased. Solvents were dried with calcium chloride. In some cases, on-line multiple solvent degasser ERC-3215 was used to remove dissolved gas from eluents.

Procedures

FAD Conditioning

Generally, the FAD was flushed with THF for about 5 min prior to each preadsorption experiment with medium polar polymers in order to remove remnants of adsorbed polymers from preceding experiments. It is important to note that THF was unable to quantitatively desorb highly polar polymers such as poly(ethyleneoxide)s from bare silica. In this case, DMF was used instead of THF to clean the FAD column. Cleaning the FAD column from medium polar polymers with DMF or THF led to essentially identical adsorption and desorption characteristics in terms of both the adsorbed amounts of polymers and the courses of dynamic integral desorption isotherms.

Dynamic Adsorption Experiments

A constant volume of the polymer solution in the adsorli (concentration 1 mg/mL) were repeatedly injected into the FAD, which was continuously flushed with adsorli. The attachment of macromolecules onto the adsorbent surface was very fast, and adsorbed macromolecules were not released when flushing adsorption-desorption columns with pure adsorli. Still, we allowed a relatively long and constant time for the FAD adsorption equilibration after each injection: 3 min for the small FAD, 45 × 2 and 30 × 3.3 mm, and 5 min for the large one, 150 × 3.3 mm. Fractions of polymer that had not been retained within the FAD have been forwarded either directly or through the SEC column into the evaporative light scattering detector (ELSD). It is known that the ELSD response depends on several operating parameters, such as solvent, and polymer nature, nebulizer gas flow rate and temperature. Therefore, careful calibrations preceded determination of the nonadsorbed amount of polymer. The introduction of new portions of polymer into the system was finished when the nonadsorbed amount of polymer detected by the ELSD corresponded with the total injected amount of sample, that is, when the FAD column was fully saturated.

A continuous introduction of polymer solution into the FAD column was also performed for comparison with the pulsed approach.

Assessments of Dynamic Integral Desorption Isotherms

A constant volume of polymer solution in adsorli (concentration 1 mg/mL) has been introduced into the FAD column through the valves V2, V3 and V4 (Figure 1). Next, valves V3 and V4 have been switched to the positions allowing displacer produced by the gradient making pump 2 to be transported into the FAD. Alternatively, a series of displacers of different compositions were successively pumped by pump 2 into the FAD. A constant time of 5 min was allowed for desorption. This time was found to be sufficient to attain a stable detector baseline. Again, desorbed amounts of polymer were calculated using the calibrations for otherwise identical experimental conditions.

REFERENCES

[1] Yau, W. W., Kirkland, J. J. and Bly, D. D. (1979). *Modern Size Exclusion Chromatography*, Wiley Interscience, New York.

[2] Berek, D., Kubín, M. and Marcinka, K. (1983). *Gélová Chromatografia*, Veda, Bratislava, Slovak Republic (in Slovak).

[3] Rudin, A. (1995). In *Handbook of Size Exclusion Chromatography*, ed. C. S. Wu, Marcel Dekker, New York, 147.

[4] Glöckner, G. (1991). *Gradient HPLC of Copolymers and Chromatographic Cross-Fractionation*, Springer-Verlag, Berlin.

[5] Pasch, H. and Trathnigg, B. (1997). *HPLC of Polymers*, Springer, Berlin.

[6] Berek, D. (1999). In *Chromatography of Polymers: Hyphenated and Multidimensional Techniques*, ed. T. Provder, ACS Symposium Series, American Chemical Society, Washington, D.C., vol. 731, 178.

[7] Nguyen, S. H., Berek, D. and Chiantore, O. (1998). *Polymer*, **39**, 5127.

[8] Nguyen, S. H. and Berek, D. (1999). *J. Polym. Sci. A, Polym. Chem.*, **37**, 267.

[9] Jančo, M., Berek, D. and Prudskova, T. (1995). *Polymer*, **36**, 3295.

[10] Jančo, M., Prudskova, T. and Berek, D. (1997). *Int. J. Polym. Anal. Charact.*, **3**, 319.

[11] Nguyen, S. H. and Berek, D. (1998). *Chromatographia*, **48**, 65.

[12] Nguyen, S. H. and Berek, D. (1999). *Colloid Polym. Sci.*, **277**, 318.

[13] Nguyen, S. H. and Berek, D. (1999). In *Chromatography of Polymers: Hyphenated and Multidimensional Techniques*, ed. T. Provder, ACS Symposium Series, American Chemical Society, Washington, D.C., vol. 731, 216.

[14] Trathnigg, B. (1995). *Prog. Polym. Sci.*, **20**, 615.

[15] Berek, D., Nguyen, S. H. and Pavlinec, J. (2000). *J. Appl. Polym. Sci.*, **75**, 857.

[16] Berek, D., Nguyen, S. H. and Hild, G. (2000). *Eur. Polym. J.*, **36**, 1101.

[17] Berek, D. and Nguyen, S. H. (1998). *Macromolecules*, **31**, 8243.

[18] Nguyen, S. H. and Berek, D. (1999). *Colloid Polym. Sci.*, **277**, 1179.

[19] Nguyen, S. H. and Berek, D. (2000). *Colloids Surfaces A: Physicochem. Eng. Aspects*, **162**, 75.