# Adsorption and Desorption of Macromolecules on the Solid Surfaces Studied by On-Line SEC. 1. The Principle of Method

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ABSTRACT: Size exclusion chromatography is shown to produce valuable information on the adsorption−desorption processes of macromolecules onto/from solid surfaces from/into a solvent under dynamic conditions. The adsorbent under study is packed into an appropriate adsorption−desorption column (ADC). The investigated macromolecules are injected into the ADC and the nonadsorbed fraction is directed into an on-line SEC column for molecular characterization. Alternatively, the amount and molecular characteristics of a polymer fully retained by the adsorption−desorption column can easily be determined after its desorption from the ADC by an appropriate displacing liquid. The exchanges within the adsorbed layer of macromolecules among species differing in their molar masses or/and chemical compositions can be readily studied in this way, as well.

## Introduction

The adsorption and desorption processes of macromolecules from dilute solutions on various solid surfaces have enormous practical impact. Let us just mention popular adsorption-based separation methods aimed at analysis, characterization, and purification of polymers, as well as numerous modification procedures of various surfaces by polymers to control adhesion, compatibility, flocculation, and catalysis.[1−3]

The characteristics of polymer adsorption and desorption are in most cases assessed by means of the slow, tedious, and both sample and labor intensive static measurements.[1−8] Sorbent is brought into contact with polymer solution and after equilibrium has been reached the supernatant solution is analyzed by different methods including size exclusion chromatography (SEC) to determine concentration and molecular characteristics of the nonadsorbed polymer. Alternatively, the adsorbent bearing adsorbed macromolecules is processed, e.g., polymer is desorbed and off-line characterized by different methods including SEC.[2,5,6]

An important progress in the study of polymer desorption was introduced by Cohen Stuart et al.[9−12] Their method has evolved from experimental studies of Inagaki et al.[13,14] In the above cases, thin-layer chromatography (TLC) was applied to determine displacer strengths that are necessary either to start or to complete desorption of macromolecules. From these data and solvent strength data available in the literature, sequential adsorption energies of polymers are calculated.[11,14] Using TLC for desorption assessment the sample consumption was substantially reduced and measurements became faster. On the other hand, the amount and molar mass of macromolecules partially retained on the TLC plate could not be determined. Moreover, the TLC method is still rather labor-intensive and cannot produce large quantities of desorbed polymer sufficiently for further evaluation.

Furusawa et al.[15−17] proposed an alternative approach to study the desorption processes in a dynamic arrangement. The particles of sorbent on which macromolecules were deposited under static conditions were packed into a column and, subsequently, the preadsorbed polymer was dynamically displaced by an appropriate desorption promoting liquid at a low flow rate. The macromolecules released from adsorbent were directed into a flow-through liquid chromatographic (LC) detector. In this way the amount of desorbed polymer and the shape of liquid zone containing macromolecules could be determined. Again, Furusawa's method is labor-intensive and does not produce information on the molecular characteristics of the nonadsorbed/desorbed polymer.

We have developed a method for molecular characterization of binary polymer blends based on the combination of dynamic adsorption−desorption processes with the size exclusion chromatography:[18,19] One constituent of polymer blend is selectively and quantitatively adsorbed from appropriate adsorption-promoting liquid on an appropriate adsorbent that is packed in the full adsorption−desorption (FAD) column. The system must be chosen so that the second constituent of polymer mixture is not retained by adsorbent and passes into an on-line SEC system for characterization. After the SEC separation of the nonadsorbed blend constituent has been completed, the SEC column is equilibrated with a desorption-promoting liquid. Subsequently, this desorbing liquid is directed into the FAD column to release macromolecules and to carry them into the SEC system, as well. In this stage, the desorbing liquid serves as the SEC eluent. The important prerequisite of a successful polymer blend analysis by the full adsorption−desorption/SEC coupling (FAD/SEC) is the identification of appropriate system of adsorbent−adsorption-promoting liquid−desorbing liquid system and the optimization of the FAD column. We have found that the nonporous silica FAD packing gives better results than the porous silica gel.[18] The latter produces broadened and split SEC chromatograms—probably due to an excessive mixing and slow diffusion of macromolecules within the FAD column, due to the complicated desorption patterns of macromolecules from porous particles,[17] the competitive adsorption processes, and the possible desorbing liquid (dis-

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placer) zone deformations. To obtain reliable SEC results, the size of the FAD column and the strength of adsorption-promoting liquid must be optimized, as well.[19] Too large an FAD column strongly contributes to the SEC peak broadening and, evidently, too small an FAD column does not retain the entire polymer sample. The zone of adsorption-promoting liquid that is displaced from the FAD column by desorbing liquid together with macromolecules may affect the SEC data: This zone must not be too broad nor its adsorption strength too high.[19] We have shown that multicomponent polymer mixtures can be easily separated and characterized by the FAD/SEC procedure provided appropriate desorbing liquids can be identified to achieve a controlled stepwise and selective polymer desorption.[20,21] The full polymer recovery is achieved in the optimized system of adsorbent−adsorption-promoting liquid−desorbing liquid. Consequently, the mean molar mass and molar mass distribution data determined by means of the FAD/SEC method agree very well with those obtained for the same polymers by direct SEC analysis that is without adsorption and desorption steps: the differences in data hardly exceeded the data variation observed during repeated direct SEC measurements which was generally ±5%. These results show that both the adsorption and desorption of macromolecules can be considered quantitative in the framework of experimental errors. So far the following medium polarity homopolymers were investigated by the FAD/SEC method: polyacrylates, polymethacrylates, polytetrahydrofurans, polyvinyl acetates, and poly(ethylene oxide)s with molar masses ranging from a few thousands up to several hundred thousands grams per mole. In most cases, the adsorbent was nonporous silica and a variety of adsorption-promoting liquids and desorbing liquids were applied.[18−21] On the other hand, polystyrenes with molar masses higher than 90 000 g/mol were quantitatively retained from dimethylformamide by nonporous silica bonded with dimethyl octadecyl groups.[22] In this case, the desorbing liquid was toluene or tetrahydrofuran. Lower molar masses of polystyrene were not retained quantitatively from so far tested adsorption-promoting solvents.

The FAD/SEC procedure is rather promising also in the copolymer analysis.[21] Random copolymers of styrene and methyl methacrylate and block copolymers of methyl methacrylate and glycidyl methacrylate were effectively separated by the FAD method according to their chemical composition, though the results were influenced also by the molar mass of copolymer species.

The full adsorption−desorption approach was also applied to reconcentration of diluted polymer solutions[22,23] and the process efficiency was evaluated by SEC. We have shown that polymer can be rapidly and quantitatively trapped even from highly diluted solutions in its adsorption-promoting liquid (concentration $10^{-4}$ mg/mL) on an appropriate adsorbent and subsequently be desorbed into a small volume of a desorbing liquid.[23] The adsorption-promoting sample solvent can be exchanged and the FAD column flushed by another adsorption-promoting liquid without desorbing the attached macromolecules. The selective reconcentration of multicomponent diluted polymer solutions can be achieved in a similar way, as well.[22]

In the present paper, we shall demonstrate, using some selected examples, that an on-line SEC system can also easily and rapidly produce reliable data on various aspects of the adsorption−desorption-exchange proper. In this case, we are not committed exclusively to the full adsorption or full desorption of macromolecules and the on-line SEC can be applied also to the evaluation of partial or selective adsorption and desorption of macromolecules. Therefore we shall adopt the term adsorption−desorption column rather than full adsorption−desorption column in the present study.

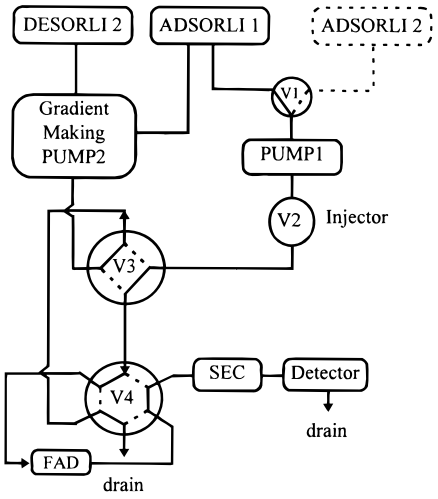


**Figure 1.** Schematic assembly of ADC/SEC. See text for detailed explanation.

## Experimental Section

Various arrangements can be applied to the dynamic polymer adsorption−desorption-exchange studies by means of the on-line SEC. Basically, one needs a complete SEC apparatus equipped with the additional switching valves and with an appropriate adsorption−desorption column (ADC).[18−21] Depending on the studied system and process the volume of analytical ADC ranges from a few microliters up to several milliliters. For preparative purposes, large ADC can be applied, diverting only a part of the desorbed solution into the analytical SEC system. The ADC is packed by the adsorbent under study. The mean diameter of adsorbent particles ranges from about 1 $\mu$m to a few millimeters. The lower limit of particle sizes is determined by the present standards of the HPLC technology, mainly by the narrow pore filters in the column end pieces that must keep microparticles within ADC columns but must not cause extensional shearing degradation of macromolecules, as well as by the availability of the high-pressure pumping systems. The upper limit of particle sizes is given by the sensitivity of the SEC detectors since the maximum adsorbed amount of polymer that is the sample capacity dramatically drops with increasing particle size of the adsorbent. For general purposes preferably nonporous, 2−10-$\mu$m spherical sorbent particles are packed into ADC by using the HPLC procedures to keep the desorbed zone as narrow as possible. Soft adsorbent particles can be used as well, but in this case an additional *low-pressure storing system* must be added to protect the ADC from the elevated pressure applied in the SEC system. Both the ADC and SEC column should withstand sudden changes of eluents with different polarities. The adsorptive properties of the SEC column should be as low as possible.

For the purpose of demonstration of the adsorption−desorption/SEC coupling we have used the experimental setup schematically shown in Figure 1. The ADC/SEC assembly consisted of two analytical (model 64) pumps, a six-port three-way injection valve V2 (both from Knauer, Berlin, Germany), and three multiport switching valves V1, V3, and V4 (Rheodyne, Cotati, CA, and Valco Instruments, Co. Inc., Houston, TX). The detector was either a variable wavelength UV detector from Knauer or an evaporative light scattering

detector model DDL-21 (Eurosep Instruments, Cergy St. Christophe, France). The ADC columns were packed with spherical nonporous silica particles of mean diameter 8 $\mu$m. The nonporous silica was prepared by sintering ultrapure, porous silica gel in this laboratory. The sizes of the ADC columns were 45 × 2 mm, 30 × 3.3 mm, and 150 × 3.3 mm, respectively. The SEC columns were purchased from Polymer Laboratories (Church Stretton, UK) and their sizes were either 300 × 7.5 mm or 600 × 7.5 mm. Poly(methyl methacrylate)s (PMMA), poly(glycidyl methacrylate) (PGMA), and poly(ethylene oxide) (PEO) of various molar masses and polydispersities were used. Narrow molar mass distribution PMMA's were a gift of Dr. W. Wunderlich (Röhm Co., Darmstadt, Germany). Narrow PGMA was prepared by anionic polymerization by Dr. G. Hild in Institute Sadron, CNRS, Strasbourg, France. Narrow PEO's were obtained from TOSO Co., Shinnanyo, Japan.

Analytical grade toluene, dichloroethane (DCE), and chloroform ($CHCl_3$) were used as adsorption-promoting eluents. DCE and $CHCl_3$ were stabilized by ca. 1 wt % of ethanol. Distilled tetrahydrofuran (THF) or its mixtures with above adsorption-promoting eluents were employed as displacers.

The measurements of polymer desorption by monomeric displacers were carried out in the following way: A constant amount of polymer (0.015 mg) was deposited onto the ADC packing surface from its solution in an adsorption-promoting liquid. Subsequently, eluent was switched to a mixture of adsorption-promoting liquid and displacer. The amount as well as the molar mass and molar mass distribution of desorbed polymer was determined by means of SEC. In the next step, the nondesorbed polymer was fully washed out of the ADC column by pure THF. ADC was reequilibrated with adsorption-promoting liquid to be used for the next polymer preadsorption. The desorption steps were repeated with displacers of various desorbing strengths applying the same starting conditions. Most experiments were performed at the flow rate of 1 mL/min and at temperature 25 °C by using a Knauer thermostated column oven.

The data were on-line collected by using a Waters maxima/baseline PC based data acquisition system. The amounts of adsorbed and desorbed polymers were calculated from detector peak areas by using appropriate calibration for given experimental conditions.

## Results and Discussion

**1. Polymer Attachment−Detachment Kinetics.** It is generally accepted that both adsorption and desorption of macromolecules are slow processes. The adsorption and desorption of macromolecules should be considered a complex series of elementary steps including polymer attachment (trapping) on and detachment (releasing) from the adsorbent surface, conformation changes of attached macromolecules, partial and total mutual exchanges of adsorbed macromolecules, etc. Several above processes are affected by the transport rate of macromolecules that may eventually control the number of contacts between polymer segments and adsorbent surface.[3] Our previous experiments indicate that the attachment and detachment of macromolecules may be very fast—at least for the systems we have so far studied. This is indirectly proved by the very high total recovery of macromolecules in the course of their adsorption and desorption as well as by the agreement of the SEC data obtained with and without adsorption−desorption steps as discussed in the Introduction. Further proof of this surprising fact is represented in Figure 2. Here the amount of nonadsorbed polymer expressed directly by the peak area (Figure 2a) or as a fraction of nonadsorbed sample in percents (Figure 2b) is plotted as function of number of injections that is the total polymer amount in contact with the adsorbent.

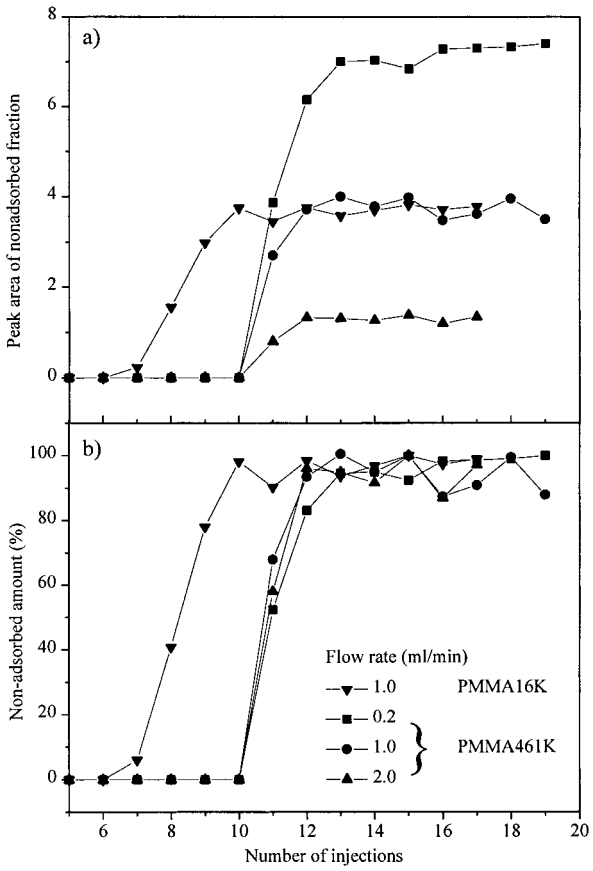


**Figure 2.** Flow rate (in)dependence of PMMA461K adsorption on silica from toluene. The adsorption curve for PMMA16K is depicted to show the molar mass effect. ADC 45 × 2 mm; injected polymer amount 0.005 mg.

Various flow rates of adsorption-promoting liquid were considered. The physical meaning of this dependence is discussed more in detail in the next paragraph. For the present reasoning we have just to point out that the peak area of the nonadsorbed polymer fraction changes with the adsorption-promoting liquid flow rate (a); however, the actual amount of nonadsorbed macromolecules seems to be fairly independent of the adsorption-promoting liquid flow rate (b). The entire residence time of polymer solution in the ADC column varied from only 3 to 30 s in the experiments at a flow rate of 1 mL/min. The contact time of macromolecules with the thin slice of adsorbent within the ADC column in which they are eventually retained is even substantially shorter. We can conclude that the attachment of macromolecules onto the solid surface is an extremely rapid process. A similar conclusion can be drawn also from our desorption−displacement experiments:[22−24] The detachment processes are very fast, as well, provided the system is rapidly macroscopically homogenized by an efficient mixing as is the case in the liquid chromatographic columns, and nonporous adsorbent particles are applied—so that transport phenomena do not play an important role. Future detailed experiments should show the role of rearrangements of adsorbed macromolecules on the adsorbent surface.

**2. Adsorbed Amount of Polymer and Its Characteristics.** When a small portion of polymer solution in the adsorption-promoting liquid is injected into the ADC which is equilibrated with the same solvent, detector does not show any response since all macromolecules are trapped by the adsorbent. The adsorbed

macromolecules are not released even when a large volume of adsorption-promoting liquid flows through the FAD column.[15,18,22] When, however, the polymer solution is injected repeatedly, we arrive at the *saturation threshold* where the adsorbent surface starts to be occupied with macromolecules. Some polymer is no longer retained and reaches the SEC column and LC detector. Further injections cause increasing amounts of polymer to flow into the SEC column and LC detector. Eventually, we arrive at the *full saturation point* at which polymer can no longer be trapped by the ADC; i.e., the entire amount of injected polymer will be detected. Both the saturation threshold and the full saturation point are important characteristics of the adsorbent chemical nature and physical structure represented by its surface area. Saturation threshold and full saturation point positions depend also on the nature of both adsorption-promoting liquid and displacer and on temperature as well as on the polymer nature.[20,21]

Typical examples of dependences amount of nonretained polymer vs number of injections are shown in Figure 2. The first few portions of PMMA probe are fully retained within ADC packed with nonporous silica. Starting from a certain amount of injected polymer, macromolecules partially pass through the ADC. The saturation threshold can be easily identified in this way. Further portions of macromolecules are less and less retained and, eventually, the full saturation point is reached where entire polymer passes through the ADC into the detector. From Figure 2, it is evident that the total amount of retained polymer rises with increasing molar mass. The oscillations are observed in the vicinity of the full saturation point in many systems (Figure 2b). These oscillations exceed the experimental errors of the nonadsorbed polymer amount determination (±5%). So far, we do not have any reliable explanation for this phenomenon. Apparently, the kinetics of macromolecular exchanges is controlled by the complicated conformation adjustment of adsorbed macromolecules. The conformation adjustments could account for the oscillations shown in Figure 2, and together with the exchange processes and hindered transport of macromolecules, they may be responsible for very slow establishment of adsorption equilibrium reported in the static systems, especially for porous adsorbents.[3,8]

Despite the above oscillations, the repeatability of the saturation threshold and full saturation point determinations is better than ±7.5% in all so far investigated systems.

It is known that the adsorption strength of macromolecules increases with their molar mass ($M$). This means that the extent of polymer adsorption depends on $M$ and that larger macromolecules are preferentially attached to the adsorbent surface. Consequently, longer chains that are present in the newly injected solution will displace the shorter ones in the region between the saturation threshold and the full saturation point. Above full saturation point the adsorbent surface will be occupied solely by the largest macromolecules present in the polymer sample. These exchanges can be easily evidenced and quantitatively studied by the ADC/SEC coupling. The SEC chromatograms of nonadsorbed/displaced polymer fractions and their corresponding mean molar masses and molar mass distributions are shown in Figure 3. It is evident that the fractions with smallest molar masses leave the ADC when the amount

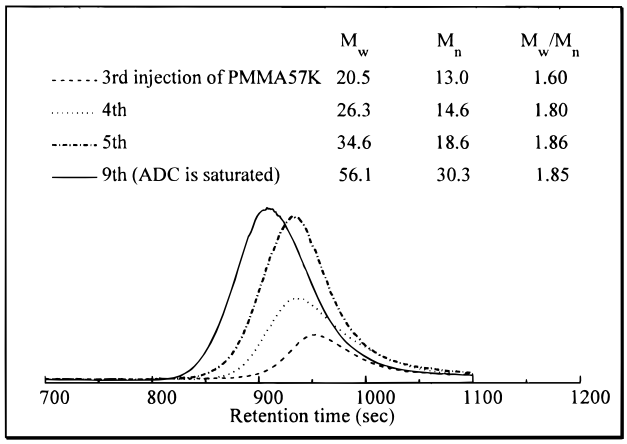


**Figure 3.** Preferential adsorption of PMMA with higher molar masses on the nonporous silica evidenced by SEC. Column set: ADC (150 × 3.3 mm) and SEC column 600 × 3.3 mm. Adsorption-promoting liquid, chloroform; injected polymer amount 0.05 mg. The mean molar masses ($\times 10^3$ g/mol) and polydispersity values are indicated.

of polymer in contact with the adsorbent just exceeds saturation threshold. Successively, larger macromolecules pass through/are released from the ADC when the amount of retained polymer increases. Eventually, the entire amount of injected polymer passes through the ADC in the very moment this is fully saturated with the largest macromolecules and no further polymer exchange is possible. This result indicates a possibility to preparatively fractionate macromolecules according to their molar masses utilizing the exchange/displacement processes.

We can conclude that the on-line SEC can rather easily afford reliable data on the adsorbed amount of polymer and produce evidence on the preferential adsorption of high molar mass fractions onto the surface. Temperature (and pressure) effects on the adsorption of various polymers on various adsorbents can be readily assessed in a similar way including the role of the adsorbent porous structure.[24]

**3. Desorption-Displacement Processes.** Detachment of macromolecules from the adsorbent surface can also be studied by on-line SEC. One deposits a certain amount of polymer on the adsorbent surface from the appropriate adsorption-promoting liquid. Subsequently, temperature, pressure, flow rate, etc. are stepwise varied to induce polymer desorption. Alternatively, an appropriate desorbing liquid is added into the adsorption-promoting liquid to adjust the desorbing strength of the displacer or a completely different desorbing liquid is introduced into ADC so that macromolecules are detached. The amount and/or the molecular characteristics of released macromolecules are determined with help of an LC detector without or with the SEC separation. The desorption-displacement can be performed also by means of a small zone of low molecular displacer, and the eluent remains the initial adsorption-promoting liquid.[23] In this case, the displacer zone is separated from the polymer peak within the SEC column due to exclusion of macromolecules. Therefore the retentive properties of the SEC column packing must be substantially lower than that of the ADC packing, otherwise the resulting SEC data are influenced by the polymer adsorption within the SEC column.

The simplest desorption-displacement measurements include the assessment of the dynamic integral desorp-

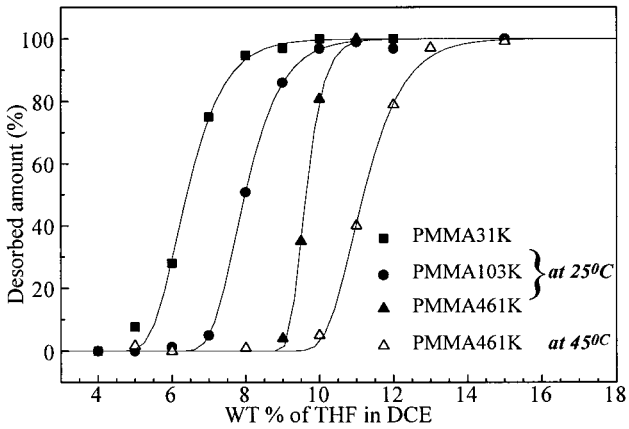


**Figure 4.** Desorption isotherms of PMMA's: The effect of polymer molar mass and temperature. ADC (45 × 2 mm); adsorption-promoting liquid DCE; desorbing liquid THF; preadsorbed amount of polymer 0.015 mg; UV detector at 233 nm.

tion isotherms, which are the dependences of the desorbed amount of polymer on displacing eluent composition or on temperature. An example of the former type of desorption isotherms monitored at different temperatures is shown in Figure 4.

It is evident from Figure 4 that the adsorption strength of PMMA on the nonporous silica in dichloroethane/tetrahydrofuran system rises with increasing both polymer molar mass and temperature. This means that a higher amount of the THF desorbing liquid is needed to desorb larger macromolecules at higher temperature. At the same time, also the shapes of adsorption isotherms change in dependence on temperature as well as on the mean molar mass and molar mass distribution of adsorbed macromolecules. This indicates the possibility of using also the stepwise desorption procedure for polymer fractionation. The desorption threshold, which is the displacer composition at which the polymer detachment just starts, seems to depend on temperature more pronouncedly than the full desorption point, which is the displacer composition at which polymer is entirely released from the adsorbent. Consequently, the desorption isotherms measured at increased temperature exhibit a less steep course (Figure 4). The shapes of dynamic integral desorption isotherms under otherwise identical experimental conditions strongly depend also on the polymer chemical nature, preadsorbed polymer amount, and ADC sizes.[20,24]

The molar mass distributions of displaced polymer fractions are qualitatively shown in Figure 5. As expected, smallest macromolecules are desorbed first. This again brings evidence of the possibility of fractionating macromolecules according to their molar masses by stepwise desorption.

ADC/SEC coupling enables also studies of polymer displacement by polymeric displacers. In this case, the solution of the displacing macromolecules in an adsorption-promoting liquid is repeatedly injected into the ADC. The polymeric displacer may possess either higher molar mass than the displaced macromolecules (Figure 6) or a chemical composition that differs from that of the preadsorbed polymer (Figure 7). Figure 6 quantitatively demonstrates the extent of displacement of smaller PMMA macromolecules by larger ones. Thus the ADC/SEC method not only brings evidence of the dependence of the affinity of macromolecules toward adsorbent on their molar mass but also easily affords

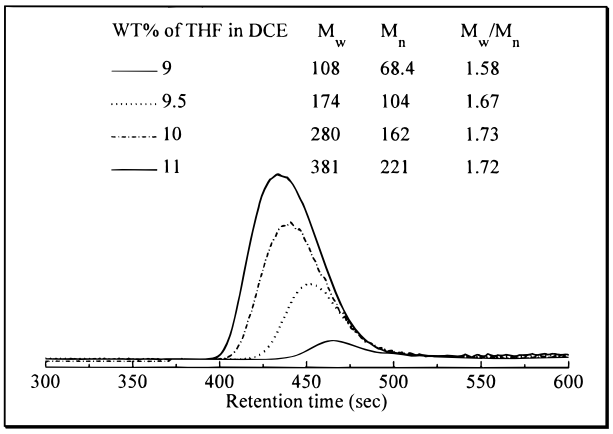


**Figure 5.** Preferential desorption of PMMA's with lower molar masses evidenced by SEC. The same conditions as in Figure 4 except for SEC column 300 × 7.5 mm and ELS detector. The mean molar masses ($\times 10^3$g/mol) and polydispersity values were calculated by using PMMA standards in pure THF.

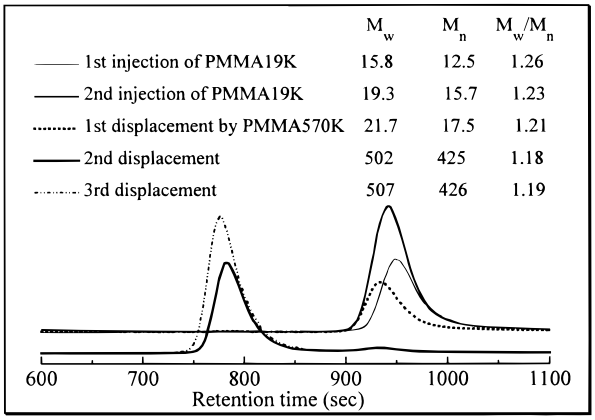


**Figure 6.** Displacement of PMMA19K from the silica surface by the PMMA570K sample as evidenced by SEC. ADC 30 × 3.3 mm; SEC column 600 × 7.5 mm; injected polymer amount 0.05 mg; adsorption-promoting liquid chloroform. The mean molar masses ($\times 10^3$ g/mol) and polydispersity values are also indicated.

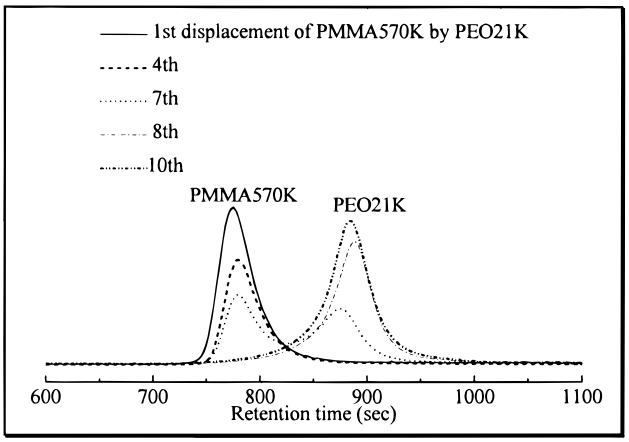


**Figure 7.** Displacement of PMMA570K from the silica surface by the PEO21K sample. ADC 150 × 3.3 mm was fully saturated with PMMA570K solution in chloroform. SEC column 600 × 7.5 mm; injected PEO21K amount 0.05 mg.

quantitative data. Similarly also the affinity of macromolecules of different chemical structure toward adsorbent can be compared (Figure 7). The effect of the chemical structure of macromolecules can exceed the

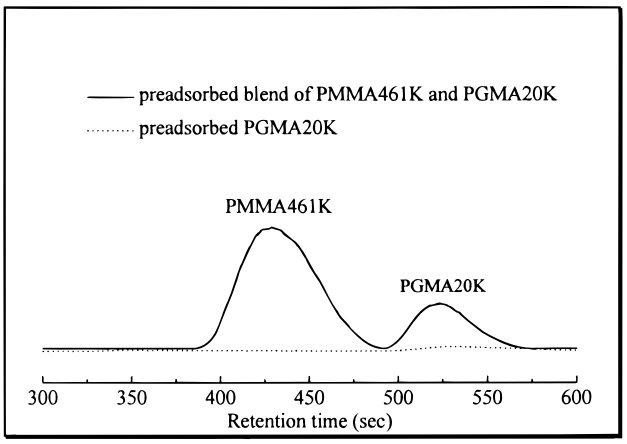


**Figure 8.** SEC chromatograms of desorbed PGMA20K and PMMA461K that were adsorbed as a blend. Desorbing liquid was a mixture of 10 wt % THF in DCE. The same mixture does not desorb PGMA20K preadsorbed in the absence of PMMA461K. The preadsorbed amount of PGMA20K was the same in both cases, viz., 0.01 mg; ADC 30 × 3.3 mm.

effect of their molar mass. For example, poly(ethylene oxide) exhibits much higher affinity toward a silica surface than poly(methyl methacrylate) in chloroform. Consequently, smaller macromolecules of PEO21K easily displace much larger macromolecules of PMMA570K (Figure 7). Notice that at the seventh displacement both kinds of macromolecules, that is, the displaced and displacing species, appear in the column effluent.

It is known that the desorption of a given polymer depends to some extent on the structure of the adsorbed layer and on the history of preadsorbed macromolecules.[7,8] This is often considered a result of conformation adjustment/relaxation processes occurring within the adsorbed layer. So far, these processes were followed by using ATR-FTIR, nuclear spin relaxation, NMR techniques, etc. These measurements are limited in their universality and they need demanding instrumentation.[3] Simple ADC/SEC experiments are able to provide essential information on the effect of a second polymer on adsorption−desorption properties of macromolecules under study. One such example is shown in Figure 8. PGMA20K was deposited onto adsorbent either individually or together with PMMA461K that was added to the solution of PGMA20K. In both cases, the adsorbed amount of PGMA20K was the same and the total amount of preadsorbed polymer(s) was fairly below the saturation threshold. Our results show that the presence of PMMA segments in the adsorbed layer of PGMA decreases the bound fraction of PGMA so that its chains are more loosely attached to the adsorbent surface. In other words, individually adsorbed PGMA macromolecules are more strongly adsorbed than the same macromolecules adsorbed in the presence of PMMA species. The individually adsorbed PGMA is not released at all by a mixture of 10 wt % THF in DCE that desorbs PGMA attached in blend with the PMMA chains. The influence of preadsorbed amount and polymer−polymer incompatibility on adsorption−desorption characteristics is a subject of our further study.[24]

## Conclusions

We have demonstrated high potential of size exclusion chromatography in the direct assessing of the interaction of macromolecules with the solid surfaces. Polymer is dynamically adsorbed onto/desorbed from the adsorbent situated in the high performance liquid chromatographic-like column, and the course of the sorption processes is readily monitored by an on-line size exclusion apparatus. Both the attachment and detachment of macromolecules in the system studied are very fast. As a result, the data on polymer adsorption obtained by using the dynamic arrangement are fairly independent of the flow rate in the case of nonporous silica-based adsorbents. The ADC/SEC coupling enables determination of saturation threshold, full saturation point, and desorption/displacement isotherms. Effects of temperature, polymer molar mass, and molar mass distribution as well as its chemical structure and supposedly also of further parameters of the system on the interactions between the sorbent surface and macromolecules can be readily evaluated, too. It is anticipated that, due to its experimental feasibility, high speed, and precision, as well as due to its low material consumption, the ADC/SEC coupling can also be applied to assess valuable characteristics of the adsorbent surface. In this case, the adsorption−desorption data of well-defined polymer probes are to be compared for a series of adsorbents under study.

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