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ORIGINAL CONTRIBUTION

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Adsorption and desorption of macromolecules on solid surfaces studied by on-line size exclusion chromatography 2. Preferential adsorption and exchange processes

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Abstract Preferential and exchange adsorption of polymers differing in molar mass and/or chemical nature under dynamic conditions were investigated using on-line size-exclusion chromatography (SEC). The sample investigated dissolved in an appropriate solvent was injected into a small adsorption–desorption column packed with nonporous silica. A nonadsorbed or desorbed fraction of the polymer was directed into an SEC column for determination of both the amount and the molecular characteristics. This approach is in many aspects superior to other techniques for studies of polymer adsorption onto solid surfaces due to its low sample and time consumption. At a low degree of surface coverage, adsorption and desorption of macromolecules were rapid and were affected by the rate of supply of macromolecules to the adsorbent surface. The exchange between macromolecules at the stage of surface saturation was found to depend on the mean molar masses of preadsorbed and displacing polymer species and possibly also on the chain flexibility of the macromolecules. It was shown that the preferential adsorption driven by the chain-length difference upon saturation of the adsorbent surface was more noticeable if the preadsorbed macromolecules were smaller.

Key words Polymer adsorption and desorption · Fractionation · Preferential adsorption · Exchange

Introduction

The growing interest in adsorption and desorption of macromolecules onto/from solid surfaces is due to their important role in a variety of applications ranging from paints, coatings and lubricants to the stabilization and controlled flocculation of colloidal dispersions [1–7]. Recently, interaction-based liquid chromatography of macromolecules has attracted considerable attention to polymer adsorption in order to understand the separation mechanism(s) and, consequently, to increase separation selectivity and resolution [8–11]. For example, liquid adsorption chromatography has been used for copolymer analysis and characterization in terms of the chemical composition [8].

Technical improvements in instrumentation have led to a number of techniques providing a deeper insight into elementary processes involved in polymer adsorption [2, 3, 5]. Among these techniques, off-line size-exclusion chromatography (SEC) has been employed in static adsorption experiments for the determination of both the adsorbed/nonadsorbed amount and the characteristics of polymer samples [4, 12, 13]. Such studies are usually time- and sample-consuming. They provide information about both preferential adsorption and exchange of polymers with different molar masses. In the former case, larger macromolecules from a polydisperse polymer sample are preferentially attached onto the adsorbent while in the latter case smaller macromolecules, which have been preadsorbed onto the adsorbent,

are displaced (exchanged) by adding the larger ones. The driving force for these exchanges between chemically identical macromolecules differing only in their molar masses is a smaller increase in translational entropy in solution in comparison with the much larger gain in adsorption energy when small chains are displaced from the adsorbent surface into solution by the larger ones [2, 3]. Preadsorbed macromolecules can also be displaced from solid surfaces by adding a low-molar-mass displacer which exhibits a higher adsorption affinity (energy) toward the adsorbent [2, 3].

Recently we developed a new liquid chromatographic method for separation and molecular characterization of polymer blend constituents [14–16]. This method is based on the full adsorption of all n or $n-1$ components of the polymer blend from an appropriate adsorption-promoting liquid (adsorli) onto a suitable adsorbent packed in a high-performance-liquid-chromatography-like minicolumn. The components of the polymer blend retained are then successively desorbed by a stepwise low-molar-mass displacer gradient and forwarded into an on-line SEC column in which their molar masses and molar mass distributions (MMD) are determined independently. The method described is called full adsorption–desorption/SEC coupling (FAD/SEC). It allows rapid separation and characterization of chemically similar polymers using a nonporous silica adsorbent and optimized displacers.

Evidently, the knowledge of the dynamics and other parameters of polymer adsorption, especially of the effects of both the molar mass and the chemical nature of the macromolecules under study is essential for the optimization of FAD and some other adsorption-based liquid chromatographic separation techniques.

We have also applied a dynamic approach similar to FAD for the assessment of dynamic adsorption/desorption of macromolecules at liquid–solid interfaces [17–20]. The adsorbent under study is packed into an appropriate adsorption–desorption column (ADC). The macromolecules investigated are injected into the ADC and the nonadsorbed fraction is directed into the on-line SEC column for molecular characterization. Alternatively, the amount and molecular characteristics of a polymer that was initially retained in the ADC can be readily determined after its displacement from the ADC using a polymeric or monomeric (low-molar-mass) displacer.

The procedure has been tested with nonporous silica ADC packings using polymers and various combinations of adsorli and displacer. It has been revealed that the attachment and detachment of macromolecules in the system studied were very fast. In the framework of experimental errors, the retained/released amount of polymer using the dynamic arrangement described reached 100% for full adsorption as well as full desorption of the polymers. This approach enabled an easy evaluation of the impact of chemical nature, molar mass and MMD of the polymers as well as the temperature on the interaction between the adsorbent on surface and the macromolecules [17, 18].

In this paper, we discuss in detail the on-line SEC study of preferential and exchange adsorption of polymers differing in molar mass and/or chemical nature under dynamic conditions. The advantage of the on-line SEC over other techniques is highlighted. Some implications of our results are discussed in terms of the kinetics of polymer adsorption/desorption under dynamic conditions in the ADC.

Experimental

Equipment

The general experimental set-up used in our study is shown in Fig. 1. The pumps were Waters, model 510 (Milford, Mass., USA). The flow rate was 1 ml/min. Injection (V2) and switching multiport valves (V1, V3 and V4) were from Rheodyne (Cotati, Calif., USA) and Valco (Houston, Tex., USA). ADC of the following sizes were used: 45 × 2, 30 × 3.3 and 150 × 3.3 mm. The SEC linear column was a PL-gel mixed bed, either 600 × 7.5 mm or 300 × 7.5 mm (Polymer Laboratories, Church Stretton, UK). Since changes in temperature may influence adsorption equilibrium the ADC and SEC columns were thermostated in a water bath (Lauda RM6, Königshofen, Germany) or in an air column oven (Knauer, Berlin, Germany) either at 25 °C or as indicated. The possible variation of temperature within the ADC due to viscous heat dissipation was neglected because our preliminary measurements revealed that it was well below 1 °C. The detector was an evaporative light scattering detector, model DDL-21 (Eurosep Instruments, Cergy St. Christophe, France). Polymer amounts were calculated from peak areas employing calibrations for identical experimental conditions.

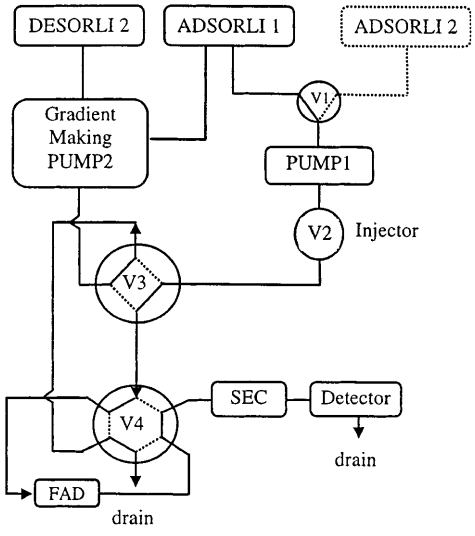

Fig. 1 Schematic adsorption–desorption column (*ADC*)/size-exclusion chromatography (*SEC*) set-up. See text for detailed explanation

Materials

Narrow and broad poly(methyl methacrylate)s (PMMA) of various mean molar masses (MMM) were a gift from W. Wunderlich of Röhm Co. (Darmstadt, Germany). Narrow and broad poly(tetrahydrofuran)s (PTHF) were purchased from Polymer Laboratories. Poly(ethylene oxide)s (PEO) were kindly provided by TOSO Shinnanyo (Tokyo, Japan). Toluene or chloroform were used as adsorlis. THF or N,N-dimethylformamide (DMF) were used as desorption-promoting liquids (desorli). Binary mixtures of adsorlis and desorlis were applied as displacers. Pure desorlis were used for cleaning the ADC prior to each run. All the above solvents were of analytical grade from Merck (Darmstadt, Germany) or from Microchem (Bratislava, Slovakia). THF was distilled immediately before use. Chloroform stabilized with ethanol was used as purchased.

Nonporous silica adsorbent particles were used in all experiments to minimize possible problems with transport of both macromolecules and displacer to/from the adsorbent surface [13, 14]. Particles of 8-μm nonporous silica were prepared by sintering ultrapure spheroidal silica gel at 1200 °C for 2 h.

ADC conditioning

The ADC was flushed with desorli THF for about 5 min prior to each adsorption experiment with the medium polarity polymers in order to remove residuals from previous measurements. Because PEO was not desorbed by THF, DMF was used to clean the ADC. Subsequently, the ADC was equilibrated with the particular adsorli for about 5 min.

Results and discussion

Effect of polymer molar mass

The preferential adsorption experiments were carried out for PMMA and PTHF of various MMM and MMD. Polymer samples were dissolved at a concentration of 1 g/l in the same adsorli which was used as the SEC eluent. A constant amount of 0.05 mg of polymer was injected into the ADC/SEC system. At first few injections of the polymer solution were fully retained within the ADC. No polymer desorption was observed even after flushing the ADC containing adsorbed macromolecules with the pure adsorli for 1 h. At a certain number of injections we arrived at the so-called adsorption threshold [17]. Starting from this point, only the larger macromolecules from the injected solution preferentially attached onto the ADC adsorbent and at the same time displacement of smaller macromolecules from the surface was observed. The total amount of injected polymer retained became larger with an increasing number of injections. Eventually, the full saturation of the ADC packing surface was achieved and the entire newly injected polymer sample was monitored by the detector. The typical SEC traces and their corresponding MMM and polydispersity values for PMMA samples are shown in Figs. 2–4. As is evident, the MMM values of unretained polymer fractions increased with the number of injections while the polydispersity values remained almost unchanged. Beyond the full saturation point the MMM and MMD of the unretained polymer was equal to that of the original polymer within experimental error. The highest ratio of MMM of the original polymer to that of the first nonadsorbed fraction was obtained for the PMMA sample with the lowest starting MMM (PMMA19k) and this ratio decreased slightly with increasing MMM of the original polymer. In other words, we observed some "fractionation of the PMMA sample during the preferential adsorption but, surprisingly, the fractions exhibited a broad MMD similar to the original polymer, especially for initial polymers with higher molar masses.

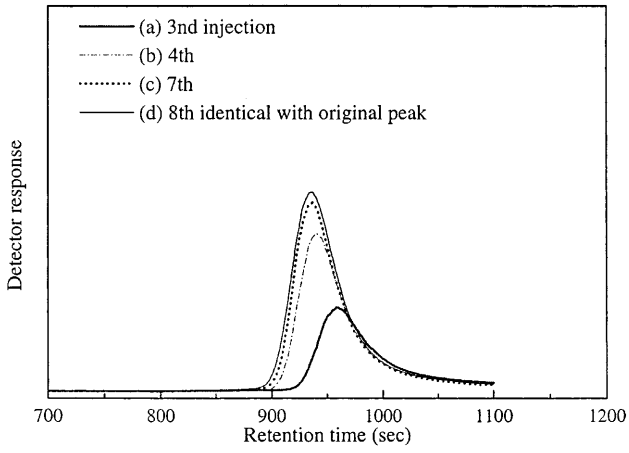

Fig. 2 SEC traces of nonretained fractions of poly(methyl methacrylate) (*PMMA*)19k. The amount of polymer in each injection was 0.05 mg; adsorli: chloroform, ADC (150 × 3.3 mm), SEC (600 × 7.5 mm). M_w (g/mol) and polydispersity values calculated using PMMA calibration are (*a*) 11,600, 1.11; (*b*) 17,200, 1.08; (*c*) 19,000, 1.12; (*d*) 19,500, 1.11

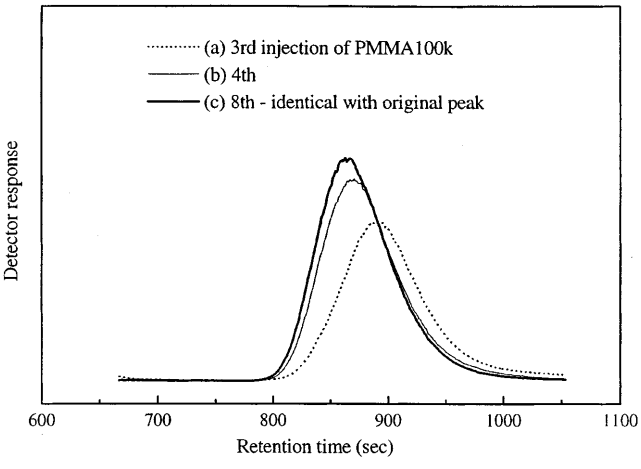

Fig. 3 SEC traces of nonretained fractions of PMMA100k. Other conditions were the same as in Fig. 2. M_w (g/mol) and polydispersity values calculated using PMMA calibration are (*a*) 65,100, 2.03; (*b*) 91,500, 2.04; (*c*) 101,000, 2.02

In contrast to PMMA, more noticeable preferential adsorption was observed within the PTHF70k sample (Fig. 5). Here both the MMM and polydispersity values changed with the number of injections: fractions with lower molar mass were preferentially displaced from the ADC. In order to verify the adsorption preference of larger macromolecules over smaller ones, PTHF macromolecules retained within the ADC after its saturation were also desorbed with pure THF into the on-line SEC for molecular evaluation (Fig. 5). Much higher MMM and narrower MMD of the retained PTHF fraction than that of the original PTHF70k indicated distinct adsorption fractionation.

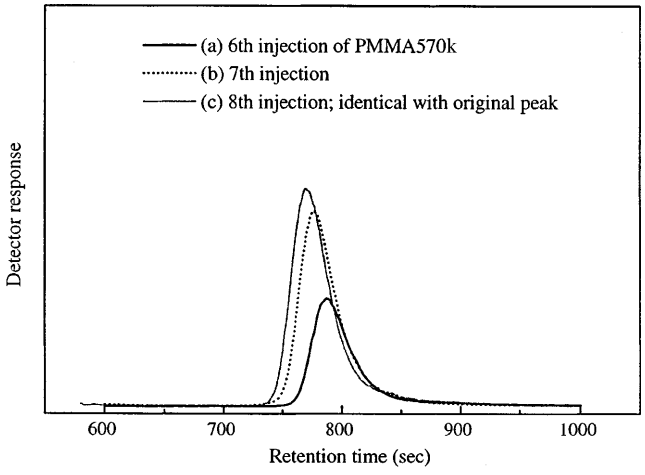

Fig. 4 SEC traces of nonretained fractions of PMMA570k. Other conditions were as in Fig. 2. M_w (g/mol) and polydispersity values calculated using PMMA calibration are (*a*) 389,000, 1.11; (*b*) 497,000, 1.15; (*c*) 575,000, 1.15

Effect of polymer chemical nature

In an experiment similar to that shown in Fig. 5, we used a solution of PEO21k as a displacer instead of pure THF. First, the ADC was oversaturated with five injections of PTHF70k solution in chloroform adsorli. Next, constant amounts of 0.05 mg PEO21k dissolved in the same solvent were successively injected into the ADC/SEC system. The SEC chromatograms as well as MMM and polydispersity data for displaced fractions of PTHF are shown in Fig. 6. The SEC peak of PEO21k appeared as soon as the SEC peak of PTHF had faded out (results not shown). After the third injection of PEO21k, PTHF was fully desorbed from the ADC. This tendency is similar to the previous experiments (Fig. 5) when PTHF macromolecules were desorbed with pure THF.

The remaining question is what is responsible for the pronounced narrowing of the MMD of the retained macromolecules of PTHF70k in Figs. 5 and 6 in comparison with the results for PMMAs where the fractionation effect was not evident (Figs. 2–4). The adsorption characteristics of PTHF on silica were found to be similar to those of PMMA [21]. Moreover, both the MMM and the polydispersity values of original PTHF70k were only slightly lower than those of original PMMA100k (Fig. 3). It seems that the higher flexibility of PTHF chains in comparison with that of PMMA

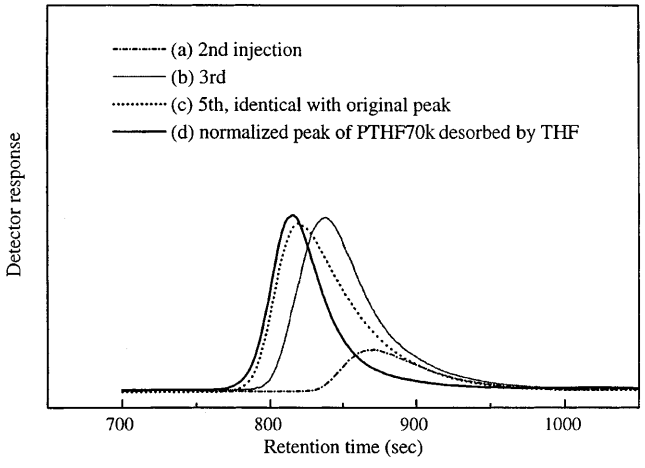

Fig. 5 Normalized SEC chromatograms of nonretained fractions of poly(tetrahydrofuran) (*PTHF*)70k. The amount of polymer in each injection was 0.05 mg; adsorli: chloroform, ADC (30 × 3.3 mm), SEC (600 × 7.5 mm). M_w (g/mol) and polydispersity values calculated using PTHF calibration nonadsorbed fractions (*a*) 28,500, 1.48; (*b*) 59,300, 1.54; (*c*) 78,000, 1.72 and retained fraction desorbed with pure THF (*d*) 99,800, 1.40

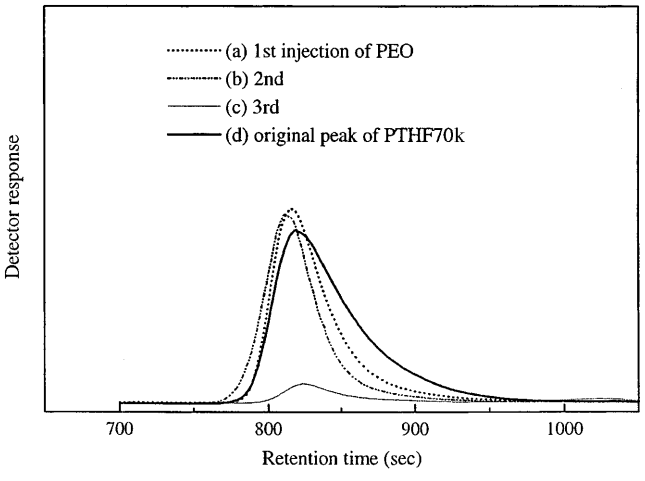

Fig. 6 SEC chromatograms of retained fractions of PTHF70k which were desorbed by poly(ethylene oxide) 21k after saturation of the ADC (30 × 3.3 mm) with five injections of PTHF70k. Other conditions were the same as in Fig. 5. M_w (g/mol) and polydispersity values calculated using PTHF calibration are (*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

chains gave rise to more effective exchange between large and small PTHF chains within the oversaturated ADC under the dynamic conditions of the present experiments.

Preferential adsorption

It is well known that preferential adsorption takes place within the broad MMD samples if the length ratio of the larger macromolecules to the smaller ones is high enough. On the basis of Scheujens–Fleer theory, complete preferential adsorption occurs if the chains differ in length by a ratio of about 2 or more [22]. However, our SEC results (Figs. 2–4) show that not only the molar mass (length) ratio is significant but also the absolute molar mass values of the initial polymer sample play an important role in preferential adsorption. In other words, for about the same polydispersity values of the injected polymers, more pronounced preferential adsorption will occur in the polymer sample having a lower MMM value. Our results indicate the presence of kinetic barriers in connection with the long protruding tails and loops which might prevent later-arriving macromolecules from attaching onto the adsorbent surface that has been already saturated.

To confirm the above fact, two series of experiments were performed. The small ADC (30 × 3.3 mm) was saturated with various volumes of PMMA solution in chloroform (1 g/l). The two PMMA samples studied had about the same polydispersity values but their MMM values differed more than tenfold. The SEC chromatograms for both retained polymer fractions and the original polymers are depicted in Figs. 7 and 8. The higher molar mass fractions of PMMA57k, which were retained within the partially saturated ADC, exhibited much narrower MMD than the corresponding original polymer. Furthermore, the MMM of the retained polymer increased slightly with increasing volume of the polymer solutions injected to saturate the ADC (Fig. 7). In contrast, insignificant fractionation took place within the PMMA654k sample even when the ADC was oversaturated with 5 ml PMMA654k solution (Fig. 8). Obviously, a larger volume of polymer solution used for the ADC saturation represents a larger supply of the larger macromolecules to the surface. The same slight increase in MMM and almost no change in the polydispersity value of the retained polymer fraction after saturation of the ADC were observed with another PMMA sample (M_w = 830,000; M_w/M_n = 1.79) in experiments similar to those in Fig. 8 (results not shown). It can be concluded that the exchange between preadsorbed smaller macromolecules and arriving larger ones is kinetically limited upon the saturation of the surface. It seems that the kinetics of the exchange process at the saturation stage depends strongly on the length of the tails and loops formed by early adsorbed macromolecules and, consequently, on the length of the original macromolecules. The length of the tails and loops is, in turn, a function of a number of factors, for example, the adsorli and adsorbent nature, polymer concentration in the supernatant, etc. [2].

Both adsorption and desorption within the ADC are inherently dynamic processes and differ from static adsorption studies [17, 18, 20]. Static adsorption experiments indicate that equilibrium adsorption and, in

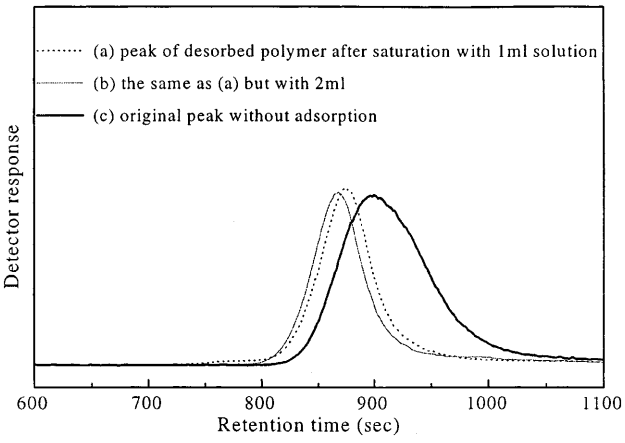

Fig. 7 Normalized SEC traces of retained polymer fractions desorbed by pure THF after the (over)saturation of the ADC with various volumes of PMMA57k solution in toluene (1 g/l). The ADC and SEC columns were 30 × 3.3 mm and 600 × 7.5 mm, respectively. The M_w (g/mol) and polydispersity values calculated using PMMA calibration are (*a*) 103,000, 1.30; (*b*) 116,000, 1.30. For comparison the original PMMA57k peak is depicted (*c*) 57,100, 1.81

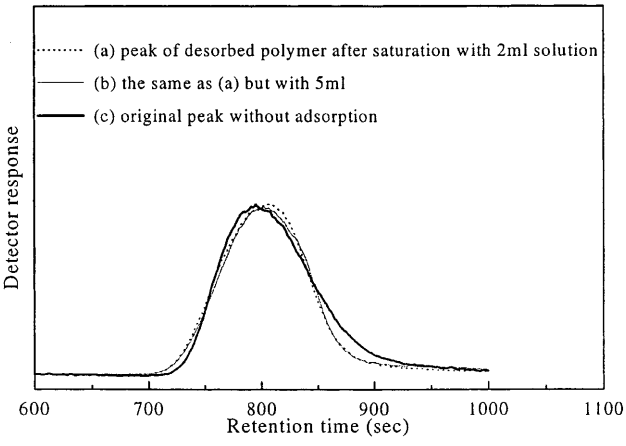

Fig. 8 Normalized SEC traces of retained polymer fractions desorbed by pure THF after the (over)saturation of the ADC with various volumes of PMMA654k solution in toluene (1 g/l). The ADC and SEC columns were 30 × 3.3 mm and 600 × 7.5 mm, respectively. The M_w (g/mol) and polydispersity values calculated using PMMA calibration are (*a*) 720,000, 1.90; (*b*) 722,000, 1.88. For comparison the original PMMA57k peak is depicted (*c*) 654,000, 2.13

particular, desorption of macromolecules are slow. This is at least partially explained by slow transport processes in static systems, especially if porous adsorbents are applied. Consequently, the time needed for a polymer to reach a true equilibrium state on the surface may be longer than the timescale of most experiments, probably in the time range of several days or weeks [2, 6, 7]. Under dynamic conditions such as in the ADC, the contact time of the polymer solution with the adsorbent surface is significantly shorter since the residence time of macromolecules within the ADC is only a few seconds. This short residence time may be responsible for lower maximum adsorbed amounts of the polymer under dynamic conditions [18]. In addition, it was found that the adsorption rate depends on the degree of surface saturation [7, 23]. The adsorption rate (adsorbed amount/time) is constant up to about 90% of surface saturation amount of polymer and then it rapidly decreases.

We were interested in a distribution of the macromolecules along the ADC: at the inlet, in the middle and at the outlet. Instead of one ADC we used three ADC (each 45×2 mm) connected in series. We found that polymer amounts of 0.2 mg (PMMA57k) or 0.25 mg (PMMA654k) dissolved in toluene (1 g/l) were fully adsorbed in the three-column set, i.e. the systems were still below the adsorption thresholds. After the introduction of different volumes of polymer solutions with concentrations of 1 g/l into the ADC set, the polymer fractions retained in each ADC were independently desorbed into the SEC. The molecular characteristics of the macromolecules retained in each ADC for various injected volumes of PMMA solution, i.e. for various degrees of (over)saturation, are given in Table 1.

Table 1 Molecular characteristics of the retained polymer fractions after the saturation of the adsorption–desorption column (ADC) with poly(methyl methacrylate) (*PMMA*) solution in toluene (1 g/l). The ADC was a set of three 45×2-mm columns connected in series. For comparison, the mean molar masses and the molar mass distributions of the initial polymers are given

Column	Injected volume (μl)	$M_w \times 10^{-3}$ (g/mol)	$M_n \times 10^{-3}$ (g/mol)	M_w/M_n
Initial PMMA57k		57.1	31.6	1.81
ADC1	200	72.3	45.5	1.59
	300	71.1	45.6	1.56
ADC2	200	49.8	28.8	1.73
	300	69.1	42.3	1.56
ADC3	200	36.7	21.1	1.74
	300	72.2	47.8	1.51
Initial PMMA654k		654	307	2.13
ADC1	250	702	334	2.10
	400	703	333	2.11
ADC2	250	631	295	2.14
	400	698	354	1.97
ADC3	250	615	290	2.12
	400	702	360	1.95

Evidently, when 200 μl of PMMA57k solution or 250 μl PMMA654k solution was introduced into the ADC set, the largest macromolecules were preferentially retained in the first ADC and the smallest ones in the third ADC. For the low-molar-mass sample (PMMA57k), the polydispersity value in each column was lower than that of the original polymer while it remained nearly unchanged for the high-molar-mass PMMA654k. When 300 μl PMMA57k solution or 400 μl PMMA654k solution was used for the oversaturation of the ADC column set, i.e. a fraction of injected macromolecules passed the ADC set, the fractionation occurred similarly to that observed in Figs. 7 and 8: the MMM and polydispersity values of retained macromolecules in ADC2 and ADC3 became equal to those in ADC1, in which almost no fractionation took place because of oversaturation. The exchange of macromolecules retained early in ADC1, i.e. the largest macromolecules from the first 200 μl or 250 μl injected polymer solution, with those arriving later from later-injected solutions (i.e. from the rest of the total 300 μl or 400 μl injected solution, respectively) was insignificant because of small differences in their molar masses. On the other hand, smaller macromolecules preadsorbed in ADC2 and ADC3 from the first injected portion were readily exchanged with the largest ones from the next injected portion because of much larger differences in molar mass between preadsorbed and displacing macromolecules. This leads to a more pronounced exchange of smaller macromolecules for larger ones in both ADC2 and ADC3 than in ADC1 after oversaturation of the ADC set. These data again support our previous conclusion: the most significant preferential adsorption occurs within the polymer sample with the broadest MMD and the lowest MMM.

We calculated the amount of polymer adsorbed per unit of adsorbent weight in each column of the ADC set. The results obtained confirm our hypothesis [18, 20]: as long as the ADC is able to retain all injected macromolecules, different amounts of injected polymer occupy different areas of the adsorbent surface but the amount adsorbed per adsorbent surface area unit decreases only slightly from the column inlet to the column outlet.

Conclusions

The molar mass and the chemical nature of the macromolecules are two main factors influencing the adsorption/desorption behavior at liquid–solid interfaces. Our results show that the dynamic exchange of small macromolecules by large ones is governed by their length ratio, by the MMM of preadsorbed macromolecules and possibly also by the chain flexibility. Preferential adsorption is more pronounced within polymer samples exhibiting broader MMD and

lower MMM. The exchange characteristics of macromolecules possessing different chemical structures depend mainly on the differences in their affinities toward the adsorbent surface. Small, but strongly adsorbed PEO macromolecules, easily displace large PTHF macromolecules from the silica surface and the exchange of preadsorbed PTHF by PEO is as effective as in the case of the low-molar-mass displacer THF. In both cases, the kinetic effects caused by long tails and loops of preadsorbed macromolecules on the exchange processes are almost negligible, at least in our dynamic arrangement.

It can be concluded that on-line SEC is a powerful method to study dynamic preferential adsorption/desorption from the point of view of the molecular characteristics of both retained and unretained macromolecules. The use of selective detector(s) is anticipated to simplify studies of these phenomena, especially the exchange processes between macromolecules of different chemical nature.

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References

1. Napper DH (1983) Polymeric stabilization of colloidal dispersions. Academic Press, New York
2. Fleer GJ, Cohen Stuart MA, Scheutjens JMHM, Cosgrove T, Vincent B (1993) Polymers at interfaces; Chapman and Hall, London
3. Cohen Stuart MA, Cosgrove T, Vincent B (1986) Adv Colloid Interface Sci 24:143
4. Kawaguchi M (1990) Adv Colloid Interface Sci 32:1
5. Kawaguchi M, Takahashi A (1992) Adv Colloid Interface Sci 37:219
6. Chakraborty AK, Tirrell M (1996) MRS Bull 21:28
7. Cohen Stuart MA, Fleer GJ (1996) Annu Rev Mater Sci 26:463
8. Glöckner G (1991) Gradient HPLC of copolymers and chromatographic cross-fractionation. Springer, Berlin Heidelberg New York
9. Pasch H, Trathnigg B (1997) HPLC of polymers. Springer, Berlin Heidelberg New York
10. Berek D Proceedings of the 5th Latin American Polymer Symposium. Mar del Plata, December 1996, p 37
11. Berek D Macromol Symp, Kusatsu Symposium 1997 (submitted)
12. Felter RE, Moyer ES, Ray LN (1969) J Polym Sci Part B Polym Phys 7:529
13. Anada S, Kawaguchi M (1992) Macromolecules 25:6824
14. Jančo M, Berek D, Prudskova T (1995) Polymer 36:3295
15. Jančo M, Prudskova T, Berek D (1997) Int J Polym Anal Charact 3:319
16. Nguyen SH, Berek D (1998) Chromatographia 48:65
17. Nguyen SH, Berek D (1999) In: Provder T (ed) Chromatography of polymers: hyphenated and multidimensional techniques. ACS Symposium Series 731. American Chemical Society. Washington, D.C., pp 216
18. Berek D, Nguyen SH (1998) Macromolecules 31:8243
19. Nguyen SH, Berek D Colloids Surf A in press
20. Nguyen SH, Berek D, Chiantore O (1998) Polymer 39:5127
21. Nguyen SH, Berek D (1999) J Polym Sci Part A Polym Chem 37:267
22. Nguyen SH, Berek D, Mendichi R (1997) IPCG Newsletter 28:4
23. Scheutjens JMHM, Fleer GJ (1981) In: Tadros TF (ed) The effects of polymers on dispersion properties. Academic Press, London, pp 145
24. Dijt JC, Cohen Stuart MA, Fleer GJ (1992) Macromolecules 25:5416