

Molecular Characterization of Statistical Copolymers: 1. Potential and Limitations of Full Adsorption–Desorption Procedure in Separation of Statistical Copolymers

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ABSTRACT: Dynamic integral desorption isotherms for a series of poly(methyl methacrylate) homopolymers and poly(methyl methacrylate)–polystyrene statistical copolymers were measured. Nonporous silica was the full adsorption–desorption (FAD) column packing and various adsorption-promoting and desorption-promoting liquids were used. The aim of this study was to evaluate the applicability of the FAD approach for separation of statistical copolymers. The effects of the adsorbing liquid and desorbing liquid nature were demonstrated on the positions and shapes of desorption isotherms. The desorption isotherms also strongly depended on both (co)polymer molar mass and copolymer chemical composition. This indicates large fractionation potential of the FAD procedure. Simultaneously, the interference of both above parameters prevents the direct use of FAD for fractionation of the copolymers. It is anticipated that the fractionation and/or reconcentration potential of the FAD procedure can be very effectively utilized in combination of FAD with size-exclusion chromatography and/or with gradient elution liquid adsorption chromatography. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 857–864, 2000

Key words: polymer adsorption; separation; characterization; statistical copolymers; liquid chromatography; size-exclusion chromatography

INTRODUCTION

Molecular characterization of synthetic copolymers represents a very difficult task. Usually at least two molecular characteristics must be considered in this case, namely molar mass and chemical composition. For statistical copolymers, length of sequences built of the same kind of monomeric units, the copolymer “blockiness” can be considered an additional parameter. The situ-

ation may complicate further characteristics of molecular architecture such as branching, stereoregularity, head/tail monomer attachment topology, etc. Still, the molar mass and chemical composition remain the most important molecular characteristics of copolymers, and we shall concentrate on them at first. For the sake of simplicity we shall consider only binary statistical copolymers, i.e., macromolecules consisting of only two chemically different monomers.

Both molar mass and chemical composition of copolymers exhibit as rule a certain distribution. We speak about mean molar mass (MMM) and mean chemical composition (MCC), as well as about molar mass distribution (MMD) and chemical composition distribution (CCD). MMM and MCC of copolymers can be determined by numer-

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ous conventional methods dealing with bulk systems, but for assessment of MMD and CCD, copolymer molecules usually have to be separated. Two groups of separation methods presently dominate the field of polymer characterization: mass spectrometry (MS) and liquid chromatography (LC).

The most commonly used LC method for separation of macromolecules including copolymers is size-exclusion chromatography (SEC), called gel permeation chromatography in the case of lipophilic synthetic polymers. As known, SEC separates macromolecules on the basis of differences in their hydrodynamic volumes. The resulting data are transformed into MMM and MMD values. For copolymers, such transformation is feasible only under specific conditions that are fulfilled only exceptionally.

In other words, copolymers can be only rarely quantitatively characterized by means of the single-mechanism-based SEC method.¹⁻³ As a consequence, two or more LC separation mechanisms must be combined to assess different molecular characteristics of copolymers. The intentional combination of different LC separation mechanisms can be done either within one single column or by engaging several different column packings. For sample elution, one can apply isocratic conditions, continuous or stepwise gradient, or eluent switching approach. The methods utilizing two or several different chromatographic systems are often termed two- or multidimensional liquid chromatography. The coupling of two- or more separation mechanisms within one single column or column system can lead either to enhancement of separation selectivity according to one parameter or, more appropriately, to suppression of separation according to one molecular parameter (usually molar mass) while macromolecules remain efficiently separated according to other parameter (chemical composition). The "second dimension" separation may follow in another (preferably on-line) LC system to discriminate macromolecules according to the previously "suppressed" parameter.

Presently, the most powerful tool for liquid chromatographic separation of statistical copolymers represents methods of gradient polymer elution chromatography. They are based either on the local precipitation and successive redissolution of macromolecules¹ or on the local adsorption and successive desorption of macromolecules—eluent gradient liquid adsorption chromatography (LAC).^{1,5,6} In the former case, the redissolu-

tion is governed with a gradually increasing amount of thermodynamically good solvent in eluent, which initially contained an excess of a nonsolvent. In the case of LAC, initial eluent is a liquid that promotes polymer adsorption (an adsorli), and the concentration of liquid is gradually raised in the eluent which promotes polymer desorption (a desorli). In LAC, the experimental conditions can be identified for many copolymers, under which retention of macromolecules depends only on their composition but (practically) does not vary with their molar masses. The explanation of this phenomenon has been attempted recently considering exclusion effects within LAC column.⁸ In any case, the molar mass independent retention of statistical copolymers is a prerequisite for the straightforward two-dimensional coupling of LAC with SEC. The fractions that leave an LAC column and contain macromolecules with narrow composition range but with different molar masses can be further separated according to their molecular size (molar mass) with help of SEC.

Apparently such two-dimensional separations were done so far, mainly in an off-line arrangement,^{6,7} which is very intensive as to labor, time, and material. There are at least three reasons for this situation: (a) sample capacity of LAC columns is rather limited, and therefore, the corresponding fractions contain only a small amount of the polymer. Often, the LAC elution must be repeated several times to obtain the necessary sample size for the second dimension separation.⁷ Moreover, the LAC fractions are as a rule very diluted; (b) as known from gradient HPLC of small molecules, the repeatability of the gradient generation is often imperfect with many instruments currently available, and it may be difficult to precisely control retention volumes of analytes. The local variations in composition of eluent are usually rather pronounced with essentially all LC gradient making devices; (c) following to (b), but also from a purely pragmatic experimental point of view, it is difficult to precisely set the elution start within the second dimension column. Two-way eight-port valves are sometimes used for this purpose. They are equipped with two sample loops⁹: one loop is filled with the column #1 effluent, while another loop is just emptied—injected into the column #2, and vice versa; and (d) solvent injected into column #2 together with the polymer sample exhibits a changing composition, and this may complicate the second dimension separation process.

The recently developed method called full adsorption–desorption (FAD)^{10–14} can mitigate at least some of above problems. As the name indicates, FAD is based on the temporary immobilization of the complex polymer sample within a specially designed (micro)column from which macromolecules are successively released in a controlled way by means of a series of desorbing liquids with increasing displacement strength. The FAD procedure can be hyphenated with different methods of polymer analysis. Very advantageous are the combinations of FAD with other separation methods—e.g., with mass spectrometry and liquid chromatography. We have thoroughly studied the coupling of FAD with SEC.^{10–12} This two-dimensional procedure allowed determination of molar mass characteristics of constituents in numerous mixtures of polymers. Up to six component polymer blends were effectively discriminated, including systems that contained very similar polymers, for example, poly(acrylate)s or poly(methacrylate)s slightly differing in the length of their ester groups.¹⁴ FAD also proved efficient in separation of minor macromolecular admixtures (less than 1%) in polymeric materials.¹⁵ Size-exclusion chromatographic column attached to the FAD system, also enabled evaluation of the processes of adsorption and desorption of macromolecules onto/from solid surfaces.^{16,17}

The release of macromolecules from the FAD column under optimum conditions has been found fast and quantitative.¹⁷ Therefore, the transport of polymer species from a FAD column into the second dimension LC column can be easily controlled, and the start of elution in this latter column is well defined.

Another important advantage of the FAD approach is its ability to reconcentrate very diluted polymer solutions,^{18,19} as well as to serve for the storage and transfer of polymer samples. This allows for also applying the FAD procedure as an intermediate step in the course of multidimensional LC separations for collecting identical fractions from repeated prefractionation and for their quasi-on-line transfer into the next LC step.

The successful separation of multicomponent polymer blends also indicates potential of the FAD method for discrimination of copolymers according to their composition. On the other hand, separation of copolymer species with continuous chemical composition distribution is much more complicated than that of the polymer blends. For example, the difference is very small in adsorp-

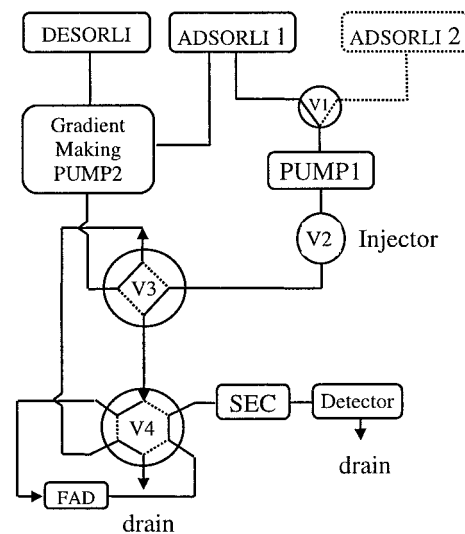


Figure 1 General scheme of the ADC/SEC setup. See text for detailed explanation.

tivity of macromolecules differing only slightly in their composition. Further, macromolecules adsorbed on the surface of the FAD column packing mutually affect their desorption behavior. This influence may increase with the increasing relative amount of polymer adsorbed that is with adsorbent surface coverage, and probably also with increasing difference in chemical composition of coadsorbed macromolecules.

In this series of articles, we shall evaluate various methods of statistical copolymer characterization. We shall start with the FAD approach to separation of statistical copolymers. The copolymers of styrene and methyl methacrylate (PS-*stat*-PMMA) were chosen as models in the present work.

EXPERIMENTAL

The experimental setup in Figure 1 consisted of common HPLC components. Analytical pumps were from Waters, Model 510 (Milford, MA) and Knauer, model 64 (Berlin, Germany). Injection and multiport switching valves from Rheodyne (Cotati, CA) and Valco (Houston, TX), respectively, were used. The FAD columns of different sizes were packed with homemade nonporous silica.¹⁰ The SEC linear column was PL-gel mixed bed either 600 × 7.5 mm or 300 × 7.5 mm (Polymer Laboratories, Church Stretton, UK). A flow rate of the mobile phase was 1 mL/min. Three types of detectors were employed to obtain the

Table I Styrene Content and Effective Molar Mass Characteristics of PS-*stat*-PMMA Samples (Calculated Directly from SEC Column Calibration with PS Standards)

Sample	Styrene (mol %)	$M_w \cdot 10^{-3}$	$M_n \cdot 10^{-3}$	M_w/M_n
A	85.5	174	89.8	1.94
B	57.4	115	57.0	2.02
C	48.7	118	60.8	1.94
D	42.1	117	52.3	2.12
E	26.5	148	65.9	2.24
F	15.2	173	58.1	2.97
C-1	48.4	233	179	1.30
C-2	48.4	192	89.3	2.15
C-3	48.4	38.3	19.2	1.99

amount and/or chemical composition of the (co)polymers. A variable wavelength UV detector (Knauer) was operated at 233 nm. An evaporative light-scattering detector (ELSD) model DDL-21 (Eurosep Instruments, Cergy-St. Christophe, France) was used in most experiments, designed to construct desorption isotherms. In some cases, the chemical composition of copolymers was determined with the help of an HPLC-FTIR interface (100 LC-Transform, Lab Connections Inc., Marlborough, MA). The principle of this interface has been described previously.²⁰ The FTIR scanning was carried out on Perkin-Elmer FTIR 1710 (Norwalk, CT) using Spectra Calc Collect Arithmetic software (Galatic Industries Corp., Salem, NH). FTIR spectra at an 8-cm⁻¹ resolution were collected by averaging 20 scans.

Analytical-grade solvents purchased from Merck (Darmstadt, Germany) and Slavus (Bratislava, Slovakia) were purified prior to use.

The assessment of desorption isotherms was performed applying the same procedures as given in our previous articles.^{16,17}

Statistical copolymers of styrene and methyl methacrylate with different chemical composition were employed as model samples. Both the preparation and properties of samples A, B, C, D, E, and F were described in detail elsewhere.²¹ Their basic data are collected in Table I.

The sample C-1 was obtained by the preparative SEC fractionation of the PS-*stat*-PMMA produced by radical copolymerization using α, α' -azoisobutyronitrile (AIBN) as an initiator.²² The sample C-2 was prepared by the same procedure as sample C-1 at an AIBN concentration of 6.1×10^{-2} mol/L. Reaction time was 5 h at 50°C. The

conversion of monomers was fairly below 10 wt %. The polymerization was finished by quenching the ampoule in ice water. The copolymer was isolated from toluene solution by precipitation in an excess of methanol. A trace amount of hydroquinone was added to methanol to prevent polymerization within the precipitated polymer. The copolymer flakes were decanted five times by methanol and dried in vacuum to a constant weight.

To obtain PS-*stat*-PMMA with a decreased molar mass (C-3), an AIBN concentration of 4.2×10^{-2} mol/L and the transfer agent dodecanethiol at a concentration of 0.15 mol/L have been applied. The polymerization proceeded 14.5 h at 60°C. The monomer conversion was roughly estimated to be about 50 wt %.

The apparent molar masses of all copolymers were determined by SEC in tetrahydrofuran using the polystyrene calibration curve.

The monomers were purified according to the standard methods. Stabilizers were removed from monomers by washing with alkaline water solution. Subsequently, monomers were dried and distilled under reduced pressure of nitrogen. The composition of samples C-2 and C-3 (Table I) was estimated using data presented by T. Fukuda et al.²³ and Kaim et al.²⁴

Poly(methyl methacrylate) homopolymers PMMA31K and PMMA461K with a medium broad molar mass distribution were generously provided by Dr. W. Wunderlich of Röhm Co. (Darmstadt, Germany). Their characteristics are described elsewhere.²⁶ Polystyrene standards were bought from Pressure Chemicals (Pittsburgh, PA).

RESULTS AND DISCUSSION

The most important step for a successful FAD separation represents selection of an appropriate adsorbent-adsorli-desorli system for a given polymer sample at a given temperature. In the case of copolymers, the difference in adsorptivity of both comonomers must be as large as possible to attain high selectivity of the adsorption-desorption-based separations. Unfortunately, the choice of adsorbents for the FAD columns is rather limited. In our present work, we have chosen nonporous silica as the FAD packing to suppress possible problems with transport of macromolecules that appeared with porous adsorbents.¹⁰ Consequently, the active surface area for

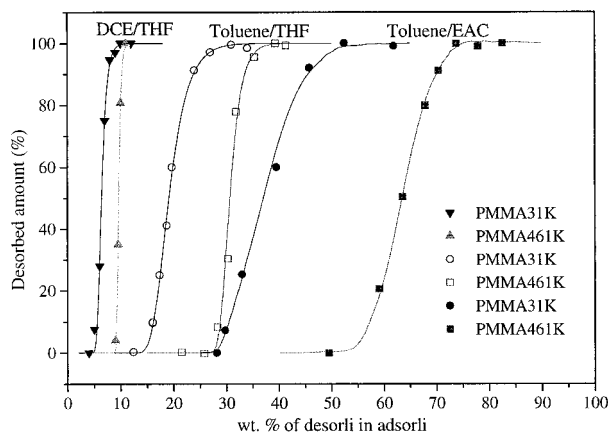


Figure 2 Dynamic integral desorption isotherms for different adsorli/desorli systems as indicated. Polymer samples were PMMA31K and PMMA461K. The ADC size was 45×2 mm, and the preadsorbed amount of the polymer was 0.015 mg.

polymer immobilization was dramatically decreased for large, nonporous, ($8 \mu\text{m}$) particles, and thus, the sample capacity of our FAD columns was sacrificed. The FAD column sample capacity was not very important for separation of two- and even multicomponent polymer blends with a nearly equal relative concentration of constituents.¹² On the other hand, the limited FAD column sample capacity could represent an important problem in the case of copolymer fractionation where an increased number of fractions must be produced.

The course of polymer desorption can be easily assessed applying a pilot FAD approach to simultaneously evaluate and optimize the experimental system. For this purpose, we have monitored the dynamic integral desorption isotherms^{12–17} of model PMMAs and copolymers. Samples with different MMMs, medium broad MMDs, and rather narrow CCDs were selected.

Typical examples of desorption isotherms for PMMA homopolymers of different molar masses and molar mass distributions are depicted in Figure 2. They were generated using toluene and dichloroethane (DCE) adsorli and tetrahydrofuran (THF), as well as ethylacetate (EAC) desorli. The course of desorption isotherms depended on the polymer MMM. The desorption isotherms are steeper for higher molar masses. Recently, we have shown that desorption isotherms also reflect polymer MMD: the narrower the MMD, the steeper the desorption isotherms.^{13,17} These results reveal a high potential of the FAD separa-

tion of macromolecules according to their molar mass but, simultaneously, they also indicate one of the limits for FAD separation of copolymers: besides their chemical composition the copolymer molar mass also affects the course of desorption. Irrespectively of their molar masses, polystyrene homopolymers were not retained within nonporous silica FAD column packing from toluene adsorli. This corroborates a large difference in the adsorptivity of PMMA and PS on nonporous silica surface so that good FAD separation selectivity for styrene–methyl methacrylate statistical copolymers according to chemical composition can be anticipated. On the other hand, copolymers containing high concentration of styrene units may remain nonadsorbed on the silica, and their separation would be impossible. From Figure 2 it also follows that DCE is a less efficient adsorli than toluene, and EAC is a less powerful desorli than THF for the PMMA/silica system.

The dynamic integral desorption isotherms for a series of PS-*co*-PMMA samples and for a homopolymer of PMMA, all with similar MMM using toluene adsorli are shown in Figure 3. As expected, macromolecules containing more than 95 mol % of styrene would hardly be trapped from toluene within a small FAD column packed with nonporous silica. Instead, they would create one single fraction together with the polystyrene homopolymer. Copolymers containing less than 95 mol % of styrene were firmly attached to the silica packing from toluene adsorli. The positions of desorption isotherms strongly depended on the com-

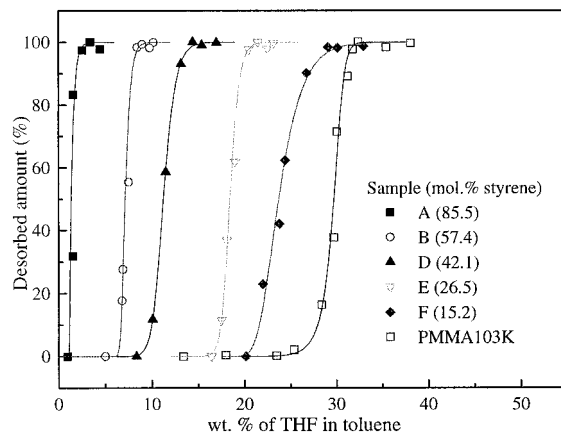


Figure 3 Dynamic integral desorption isotherms for PS-*stat*-PMMA copolymers and the PMMA103K homopolymer. Adsorli was toluene, and desorli was THF; the FAD column was 150×3.3 mm, and the preadsorbed amount of the polymer was 0.01 mg.

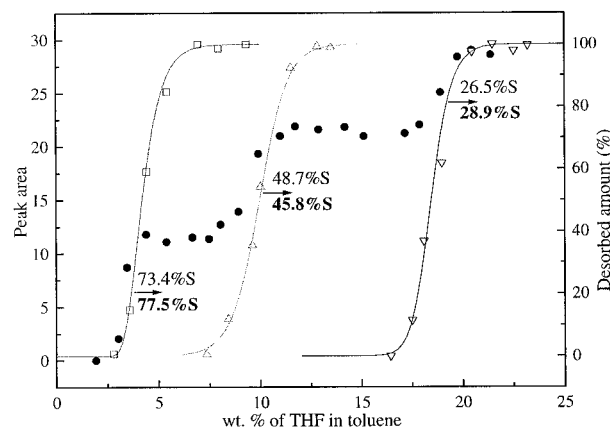


Figure 4 Dynamic integral desorption isotherm for a mixture of three PS-*stat*-PMMA samples (●). For comparison, the isotherms for single copolymers are depicted as well. The nominal styrene contents are indicated vs. those in the desorbed fractions from the FAD column obtained by FTIR (in bold).

position of copolymers. The qualitative inspection of the desorption isotherm courses suggested that all present five copolymers and the PMMA homopolymer of similar mean molar masses could be effectively separated with the help of the FAD system applied.

The mutual affects of adsorbed copolymer molecules with different compositions were found not critical for a three-component blend of copolymers (Fig. 4). The average compositions of desorbed copolymers at the plateau positions monitored by FTIR interface reasonably agreed with the compositions of individual copolymers measured independently. Still, the relative scatter of data increases due to both the limited sample capacity of the FAD column and sensitivity of the FTIR spectrometer. This will certainly be one of the complicating factors in the direct FAD separation of statistical copolymers possessing broad CCD.

The desorption isotherms for the same copolymer samples applying DCE adsorli are depicted in Figure 5. As expected, the adsorption of PS-*stat*-PMMA copolymers on SiO₂ adsorbent was generally weaker from DCE than from toluene, and the desorption isotherms were shifted toward lower concentration of THF in displacer. Still, the mutual distance of the desorption isotherms for copolymers with a high content of styrene applying DCE adsorli exceeded that observed with toluene adsorli, and so also would the separation selectivity of the corresponding copolymer species. The situation was reversed for copolymers containing an excess of methyl methacrylate for

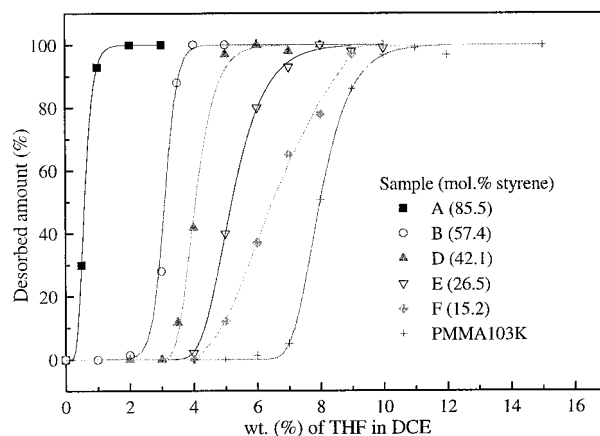


Figure 5 Dynamic integral desorption isotherms for PS-*stat*-PMMA samples. Adsorli: DCE, desorli: THF. The FAD column was 150 × 3.3 mm in size, and was packed with nonporous silica. The preadsorbed amount of the polymer was 0.015 mg.

which the separation selectivity would be much higher using the toluene/THF system.

The role of both the initial adsorli and displacer nature in the copolymer desorption is evidenced in Figure 6. Initial adsorli only slightly influenced the position of desorption isotherms if the same displacers were applied (highly effective toluene vs. less effective DCE adsorli in combination with EAC/DCE displacers). By contrast, the desorli nature in the displacer strongly affected the position and also the shape of desorption isotherms (toluene initial adsorli in combination with either THF/toluene or EAC/toluene displacers). The latter displacer composed of a less effective desorli and highly effective adsorli gave rise to a very flat

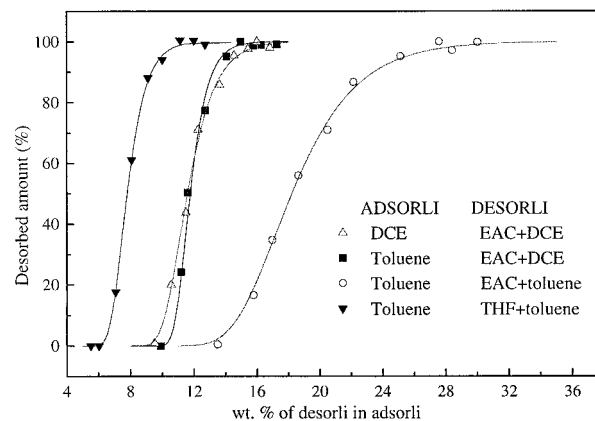


Figure 6 Effect of adsorli and desorli on the desorption course of PS-*stat*-PMMA samples.

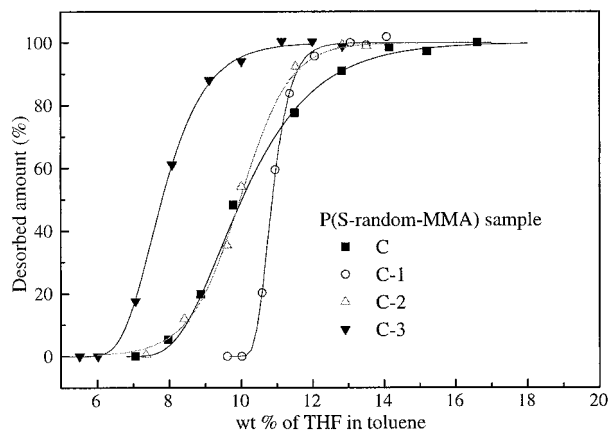


Figure 7 Effect of copolymer mean molar mass and molar mass distribution on the courses of dynamic integral desorption isotherms. The copolymer composition was nearly equal for all samples (about 48 mol % of styrene). The FAD size was 30×3.3 mm. The preadsorbed polymer amount was 0.01 mg and adsorli was toluene.

desorption isotherm. In this system, a very selective separation of copolymers would be achieved.

It can be concluded that the course of polymer desorption and, consequently, the selectivity of the FAD separation, can be effectively adjusted by the choice of experimental conditions that should be optimized for each particular system.

In Figures 7 and 8, the effect of mean molar mass and molar mass distribution of statistical copolymers on the courses of desorption isotherms is demonstrated. Similarly, as in the case of homopolymers of methyl methacrylate (cf. Fig. 2), the courses of desorption isotherms depended rather strongly on both polymers MMM and MMD. Thus, FAD separation of copolymers would simultaneously reflect both the chemical composition and molar mass of copolymer species. In other words, the full adsorption-desorption method would hardly discriminate styrene-methyl methacrylate statistical copolymers solely according to their composition. The careful optimization of the FAD system viz. adsorbent-adsorli and desorli used for a given copolymer may help suppress the molar mass effects; however, the universal applicability of FAD separation cannot be guaranteed. As mentioned, the situation is further complicated by the limited amount of the original sample that can be treated with the present FAD columns. A decrease of particle size of the FAD column packing would substantially rise its sample capacity. However, the pressure drop within the microparticulate FAD packing

bed increases dramatically, and the pressure strokes resulting from the eluent switching may impair the adjacent SEC column. On the other hand, the application of large FAD columns for trapping a bigger original sample of the copolymer brings about new problems. The larger the FAD column, the larger also the volume of adsorli zone leaving the FAD system, together with the displaced macromolecules. This adsorli zone may adversely affect SEC behavior of the displaced polymer sample.¹⁰

The molar mass effects accompanying the FAD separation of statistical copolymers apparently contradict retention of copolymers when applying a continuous eluent gradient in LAC. As already mentioned, in the latter case, molar mass-independent retention was many times observed in LAC,⁵⁻⁷ probably as a result of a presence of exclusion as the secondary mechanism within an LAC column.⁸ The best molar mass-independent retention of copolymers in LAC was observed with the narrow pore packings.^{5,6} On the contrary, exclusion of macromolecules is negligible from the nonporous packing of our FAD microcolumns, and therefore, it cannot cause any molar mass-independent retention.

Despite our conclusion concerning simultaneous effects of MM and CC of statistical copolymers on their elution from the full adsorption-desorption column, FAD may represent a very valuable intermediate step in statistical copolymer characterization. For example, FAD could be applied for the separation of statistical copolymers prefractionated by SEC. The semiprepara-

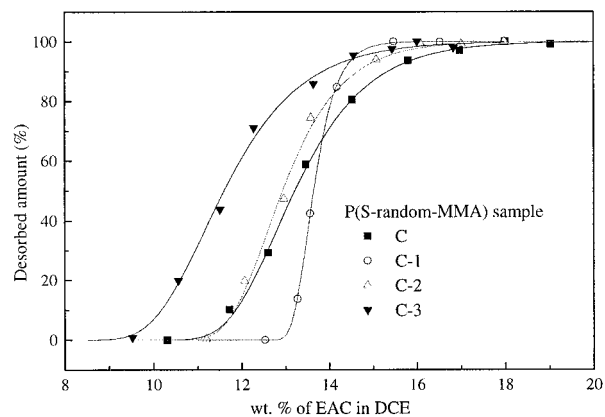


Figure 8 Effect of copolymer mean molar mass and molar mass distribution on the courses of dynamic integral desorption isotherms. Adsorli and desorli was DCE and EAC, respectively. Other conditions were the same as in Figure 7.

tive SEC would produce copolymer fractions with narrow MMD, which would be subject to FAD separation almost exclusively according to copolymer chemical composition. Alternatively, corresponding fractions from repeated analytical-scale SEC can be trapped within a FAD system. In the third step, copolymer fractions released from the FAD column would be further separated and characterized with an analytical SEC instrument. Eventually, we have an SEC/FAD/SEC three-step, two-dimensional separation. A series of similar FAD columns can be applied via appropriate switching valves to avoid overload problems that could be encountered using one single FAD column.

Another three-step separation approach is the LAC/FAD/SEC combination. Repeated LAC separations would produce copolymer fractions of different compositions, each containing different molar masses but about the same chemical composition. A set of the FAD columns can be used to reconcentrate, collect, and store the corresponding LAC fractions before their reinjection into a SEC column. In this way, sufficient amounts of samples needed for the SEC analysis can be easily created, and the SEC elution start can be precisely identified. These combinations are now under study in this laboratory.

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