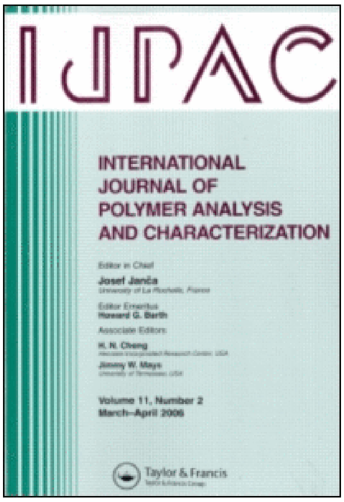

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Coupling of Full Adsorption/Desorption with Size Exclusion Chromatography: Application to Separation and Characterization of Minor Macromolecular Admixtures in Polymer Blends

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Potential of a full adsorption–desorption (FAD)/size exclusion chromatography (SEC) procedure in discrimination, reconcentration and characterization of minor macromolecular admixtures in polymer blends was evaluated. Separation of chemically different macromolecules by means of the FAD method is based on differences in their selective adsorption/desorption onto/from appropriate sorbent. The on-line SEC column allows independent characterization of blend components. Various contingencies were discussed, namely those when either a major or minor blend component is more strongly adsorbed on the FAD column packing. The FAD/SEC approach was tested with several model polymer blends containing up to 99% of a major component: It was shown that if the affinities of blend components toward FAD column packing differ sufficiently, this proposed procedure can provide precise and reliable data on molar masses and molar mass distributions of minor homopolymer admixtures. It is anticipated that the FAD method will allow full analysis and characterization of minor admixtures present in many polymer blends, even at very low concentrations below 1%.

Keywords: Polymer blend; Admixtures; Polymer adsorption; Separation; Size exclusion chromatography

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INTRODUCTION

Mixtures containing two or more chemically different kinds of macromolecules represent technologically very important systems. Various macromolecular admixtures are often added to the basic polymer to modify specific utility properties and/or the price of the resulting blend. Sometimes, a very small amount of polymeric admixture can significantly improve end-use properties of polymeric materials. In contrast with intentionally prepared polymer blends, macromolecular "admixtures" may be spontaneously formed within the "basic" polymer during its synthesis or utilization. For example, parent homopolymers may appear in copolymers as a result of untimely finished and/or undesirably occurring polyreactions. Further, chemically transformed macromolecules can be created within original polymers as a result of their subsequent oxidization, hydrolysis, *etc.*

Independent characterization of polymer blend components in terms of their mean molar mass, chemical structure and molecular architecture, as well as their corresponding distributions usually includes separation steps. Presently, the most useful separation methods for macromolecules are liquid chromatography (LC) and mass spectrometry.

Mutual separation of chemically different polymer blend components is rather straightforward if their mean molar masses and molecular sizes differ enough so that size exclusion chromatography (SEC) is the method of choice. The situation is more complicated if molecular sizes of blend constituents are similar. In this case, separation according to chemical structure or molecular architecture of blend species can be achieved employing an appropriate LC method based on enthalpic interactions between macromolecules, column packing and eluent. A useful tool is the combination of exclusion and interaction-based separation LC mechanisms within one single LC column (coupled procedures) or applying two LC columns packed with different materials and/or the eluent switching approach (two-dimensional procedures).[1–3]

Many polymer blends contain one or several "major" constituent(s) and one or several "minor" macromolecular admixtures, just a few percent and even less. The discrimination and molecular characterization of minor constituents in such blends is very difficult with conventional methods and results obtained are usually not precise enough for monitoring control or deformulation purposes. For example, SEC can be hardly used, even if molar masses of major and minor components differ substantially. This is caused by limited sensitivity of most SEC detectors which cannot monitor precisely enough a minor component of polymer blend. However, as the overall sample concentration is increased, the SEC column may become overloaded and effective separation of blend constituents is not feasible.

Recently, we have demonstrated the potential of the full adsorption–desorption (FAD) approach to discriminate two- and multicomponent polymer blends.[4–8] The FAD procedure includes immobilization of macromolecules on an appropriate adsorbent from a given adsorption promoting liquid (*adsorli*). The immobilization step is followed by controlled desorption of sample fractions differing in their chemical composition. The adsorption–desorption processes can be quantitatively and semi continuously carried out within an LC-like apparatus by a stepwise adjustment of physico-chemical conditions, such as temperature, eluent composition and possibly also pressure. A very convenient parameter turned out to be the solvent strength of the displacing liquid because desorption of macromolecules attached to the solid surfaces can be easily controlled by adding the appropriate desorption promoting liquid (*desorli*) to the eluent.[6–8]

The adsorption and desorption processes can be continuously monitored by a sensitive LC detector. Further, FAD procedure can be off-line or on-line combined with various analytical methods to characterize desorbed polymer on a molecular level. On-line coupling of FAD with SEC can also be done. This allows direct characterization of polymer fractions released from the FAD column. We have demonstrated[8] that by applying an optimized FAD system, six component polymer blends can be readily separated into single components that were independently characterized with on-line SEC. FAD has been shown to discriminate even chemically similar polymers, such as poly(acrylate)s and poly(methacrylate)s that differed slightly in the nature of their ester groups.[8]

The FAD approach can also be utilized to separate statistical[9] and block copolymers,[10] and to reconcentrate dilute polymer solutions.[11, 12] The latter feature gives FAD the potential to become an important intermediate step of various multidimensional LC procedures.

In this paper, we shall evaluate the applicability of the FAD method to the separation and characterization of minor components of selected model polymer blends. For the sake of simplicity, we shall discuss only blends containing one major constituent (representing more than 90% of the blend) and one minor constituent whose concentration may be less than 10% and often only 1%.

Tentatively, one can recognize several cases in the analytical FAD separation of minor constituents of polymer blends:

(i) *Optimum conditions* *The minor constituent is selectively and fully retained by the FAD column packing while the major constituent is nonadsorbed.* In this case, the FAD column can be flushed with a large amount of solution of a polymer blend in an effective *adsorli*. In general, this selective adsorption of the minor component can be achieved by adding either more effective *adsorli* for the minor constituent or *desorli* for the major constituent to the mainstream eluent depending on the FAD column and the sample solvent nature. After reconcentration, the minor component is desorbed from the FAD column either by eluent switching from *adsorli* to *desorli*[11] or by a pulse of *desorli*.[12] The separation of blend into single constituents is combined with the reconcentration process of the minor constituent.

(ii) *Good conditions* *Both blend constituents are retained within the FAD column, however, the major constituent is less strongly adsorbed than the minor one.* This allows the selective displacement of the major constituent from the FAD column with an appropriate displacer that does not desorb the minor constituent. Next, FAD is reequilibrated with an *adsorli* and a new portion of the sample is retained. The process of full adsorption and selective displacement of major constituent is repeated several times to obtain a sufficient amount of the minor constituent adsorbed within the FAD column. Often, strongly adsorbed macromolecules effectively displace weakly adsorbed polymer species during attachment of the former ones onto the FAD column packing surfaces.[13, 14] In this case, it is not necessary to selectively displace weakly adsorbed major constituent with a low molecular displacer. In other words, the selective reconcentration of the minor component can be carried out in one single adsorption step that is followed by the displacement of the retained polymer by a strong desorli into the SEC column for characterization.

(iii) *Feasible conditions The minor blend constituent is less strongly adsorbed within the FAD column than the major constituent but the difference in the adsorption strength of both polymers is sufficiently large*. In this case, a large FAD column should be used to retain enough minor constituent together with the major constituent within one single step. Next, the minor constituent is displaced selectively and the effluent is collected for SEC characterization. This preseparation step can be repeated in order to obtain the polymer amount needed for SEC analysis. In this case, one has to keep in mind the possible decreased desorption selectivity of both polymer components as a result of a leftward shift of the desorption isotherm of the major component.[6-8] Moreover, increased size of the FAD column brings about several experimental problems.[4-8] For example, the volume of the initial *adsorli* released from the FAD column will increase proportionally to column size. This liquid would accompany the desorbed polymer and may interfere with the separation in the next step. A more feasible approach seems to be the selective retaining of the major component. The diluted solution of the minor constituent released from or passed through the FAD column 1 may be reconcentrated within the FAD column 2 packed with a more active adsorbent than that in the FAD column 1. Alternatively, the same adsorbent could be used in both FAD columns 1 and 2, but either an effective *adsorli* can be added to the effluent mainstream leaving the FAD column 1 or the temperature of the FAD column 2 is adjusted. It is important to note that the amount of the major component in the sample solution being injected into the system must not exceed the loadability of the FAD column 1. Subsequently, the FAD column 1 has to be cleaned separately with a *desorli* and again reequilibrated with the *adsorli*. The required number of repetitions of entire procedure obviously depends on the difference in adsorption capacities of both FAD column packings, as well as on the nature of sample constituents and on their relative concentration in the sample.

(iv) *Difficult and impossible conditions The adsorption strength of the major and minor blend constituents is similar or almost identical.* In this case, FAD column packing must be changed and *adsorli* nature has to be optimized. Still, it may be very difficult to identify the appropriate experimental conditions for quantitative separation of constituents. One example, is the separation of poly(acrylates) from poly(methacrylates) with the same ester group, and also poly(methyl methacrylate) from poly(tetrahydrofuran) using the FAD procedure.

EXPERIMENTAL

The general experimental setup described previously[6–8] was used either directly or after slight modification for particular samples containing less polar polymers as the minor component (Fig. 1).

Common LC components were analytical HPLC pumps Waters Model 510, gradient maker (Knauer, Berlin, Germany), an injection valve V2, multiport switching valves V1, V3, V4 and T-valve

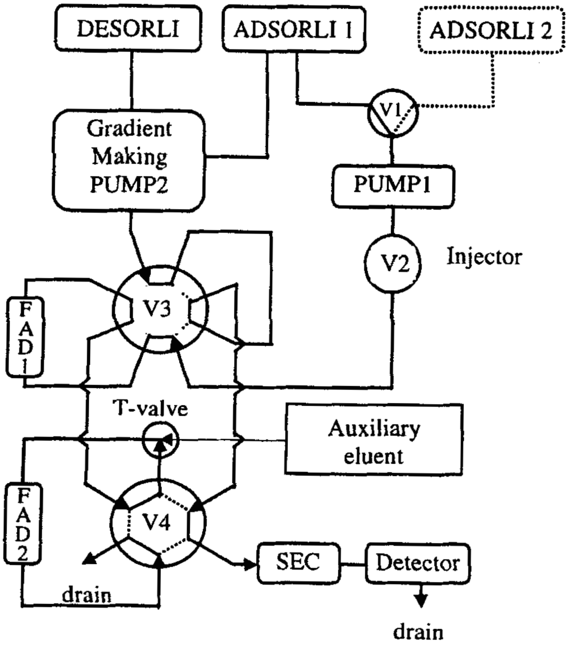

FIGURE 1 General FAD/SEC assembly. In most experiments with one FAD column, either the previous setup[7] was used or FAD column 1 was replaced with a by-pass capillary.

(Rheodyne, Cotati, CA, USA and Valco, Houston, TX, USA). Evaporative light scattering detector (ELSD) model DDL-21 (Eurosep Instruments, Cergy St. Christophe, France) was employed for effluent monitoring. Two FAD columns (30 x 3.3 mm) were used in this study. One of them (column 1) was used in our previous experiments.[4-8] It was packed with spheroidal nonporous silica particles of mean diameter 8 μm that have been prepared by firing an ultrapure narrow pore silica gel. FAD column 2 was packed with 3 μm-nonporous silica particles (MICRA Scientific, Inc., IL, USA). The SEC column 600 x 7.5 mm (PL-gel mixed B) was purchased from Polymer Laboratories (Church Stretton, UK).

A variety of commercial, broad and narrow polymer samples (Tab. I) from different sources served as model polymers: polystyrene (PS), poly(lauryl methacrylate) (PLMA), poly(iso-butyl methacrylate) (PiBMA), poly(methyl methacrylate) (PMMA) and poly(butyl acrylate) (PBA). Model polymer blends were prepared by dissolving the components in an *adsorli* at total concentration of 1 g/L (Tab. II). Narrow PS and PMMA standards were from Pressure Chemical Co. (Pittsburgh, PA, USA) and PSS (Mainz, Germany), respectively.

TABLE I Nominal values of molar mass and polydispersity of polymer samples. Except for PS, data were calculated directly from a calibration curve constructed with PMMA narrow molar mass distribution standards

Sample	$M_w \times 10^{-3}$ *(g/mol)*	$M_n \times 10^{-3}$ *(g/mol)*	M_w/M_n
PS	336	179	1.88
PBA	94.5	28.8	3.28
PLMA	445	185	2.41
PiBMA	244	110	2.21
PMMA	9.60	8.00	1.20

TABLE II Model polymer blends containing 99 wt% major component and 1 wt% minor component

		Component	
Model	*Case*	*Major*	*Minor*
A	(i)	PS	PBA
B	(ii) → (i)	PLMA	PMMA
C	(ii) → (i)	PiBMA	PMMA
D	(iii)	PMMA	PiBMA

Analytical grade toluene and cyclohexane (CYC) were used as *adsorli.* Distilled tetrahydrofuran (THF) was used as the *desorli.*

RESULTS AND DISCUSSIONS

The blend PS+PBA (wt ratio 99/1) was chosen as blend model A (Tab. II) representing the above-mentioned case (i). A solution of such a blend (polymer concentration 1g/L) represents a very diluted system with respect to the minor component PBA. Our preliminary adsorption experiments revealed that PS did not adsorb onto FAD column 1 from either pure toluene or a mixture of toluene/cyclohexane (90/10). However, PBA was partially retained within FAD column 1 from pure toluene. This indicated that there is some affinity among PBA and silica gel. One of the possibilities of increasing adsorption affinity of PBA in toluene was to use a more adsorption-active column FAD column 2. The Micra nonporous silica was able to fully retain a sufficient amount of PBA and to selectively reconcentrate this polymer from its mixture with PS. Increased activity of nonporous silica from Micra can be understood when considering differences in the preparation of FAD columns 1 and 2 packings. Agglutination of silica gel at 1200°C to close its pores removed silanol groups on the adsorbent surface. The material was not intentionally rehydroxylated. Only a small amount of silanol groups could be created by hydrolysis of the silica surface, *e.g.*, with moisture from eluents. However, the nonporous HPLC silica from MICRA supposedly was prepared by controlled hydrolysis of tetraethoxysilane and thus would contain increased concentration of free silanols on its surface.

Full and selective adsorption of PBA from blend A in less adsorption-active FAD column 1 could be attained by increasing the adsorbing strength of the eluent, for example, by adding 10 wt% of cyclohexane to toluene. Under these conditions, PBA was quantitatively trapped in the FAD column. The nonadsorbed PS was readily and directly characterized by the online SEC column attached to the FAD column. An appropriate volume of the sample solution leaving the FAD column was introduced directly into the chromatographic system. For collecting sufficient amount of PBA for further SEC characterization, 1500 μL of diluted solution of sample A (total concentration 1 g/L) was transported through FAD the column. In Table III are the molecular characteristics of PS and PBA with different FAD columns/*adsorli* systems of minor PBA in blend A.

As evident from Tables I and III, the agreement of M_w and polydispersity values for PS with and without the presence of FAD columns is reasonable. This indicates that a small FAD column with a volume of 256 µL does not substantially influence the SEC results, otherwise, appropriate corrections should be introduced. Similarly, M_w and polydispersity values for the PBA sample determined directly and after reconcentration from its mixture with an excess of PS agree well in the framework of the experimental errors typical for the present SEC system. The *adsorli* (toluene or toluene/hexane) zone leaving the FAD column does not affect retention of PBA, though the PS/DVB linear column from PL may exhibit high interactivity toward slightly polar polymers.[15] Eventually, both the less active FAD column 1 and

TABLE III Molecular characteristics of major and minor components determined using the FAD/SEC procedure

Polymer	$M_w \times 10^{-3}$ *(g/mol)*	$M_n \times 10^{-3}$ *(g/mol)*	$M_w \times M_n$	*Note*
		Model A		
PS	326	175	1.86	FAD column 1
PBA	99.6	29.6	3.36	
PS	349	195	1.79	FAD column 2
PBA	100	30.9	3.24	
		Model B		
PLMA	451	181	2.49	FAD column 1
PMMA	9.23	7.57	1.22	
PLMA	445	187	2.38	FAD column 2
PMMA	9.00	7.31	1.23	
		Model C		
PiBMA	240	106	2.26	direct reconcn.
PMMA	9.90	8.21	1.21	
PiBMA	229	100	2.29	THF added
PMMA	9.83	7.86	1.25	
		Model D		
PiBMA	248	109	2.27	off-line
PMMA	9.47	7.64	1.24	
PiBMA	251	109	2.31	on-line
PMMA	10.3	8.37	1.23	

the more interactive FAD column 2 have produced comparable data. We can conclude that the proposed FAD/SEC procedure can readily assess the molecular characteristics of homopolymer minor admixtures, if the FAD column packing/*adsorli* system is available that selectively retains only minor component (case (i)).

The studied system (model A) is by far not the simplest one. A situation when the minor admixture is more polar than PBA and more strongly adsorbed on bare silica is even more appropriate for its effective separation from the major component, reconcentration and subsequent characterization. For blend B (case (ii), Tab. II) containing two adsorbing polymers PMMA and PLMA, we could in fact use an approach similar to that for blend A. In this case, the polarity of the minor component PMMA differed substantially from the polarity of the major component PLMA. This allowed the transformation of to (ii) system into an (i) system just by adjusting the strength of the sample solvent. For example, the polymer sample was dissolved in a mixture of toluene with THF (wt ratio 97.5/2.5), in which PMMA was reconcentrated within the FAD column 1 while PLMA passed nonadsorbed (Tab. III). Alternatively, the polymer sample was dissolved in toluene and injected into the FAD/SEC system in which the sample solvent, before entering the FAD column 1, switched on-line to the mixture of toluene with THF (wt. ratio 97.5/2.5) by pumping THF at an appropriate flow rate into the FAD column 1 *via* a T-valve (Fig. 1).

Our independent adsorption/exchange experiments showed that PMMA could effectively displace the entire preadsorbed PLMA from FAD column 2 in pure toluene due to the sufficiently larger affinity of PMMA than PLMA toward nonporous silica. Consequently, the selective attachment of PMMA in blend B dissolved in toluene onto FAD column 2 packing surface was achieved. In this way, the displacement of PLMA by PMMA changed blend B into blend A and we could again arrive at case (i) (Fig. 2).

However, this latter approach could not be applied to blend C because PMMA could not fully displace preadsorbed PiBMA. Evidently, PiBMA exhibited higher adsorption affinity toward silica surface than PLMA.[8] The smallest macromolecules of PMMA did not quantitatively displace the largest species of PiBMA. As a result, the reconcentrated polymer fraction in the FAD column 2 contained

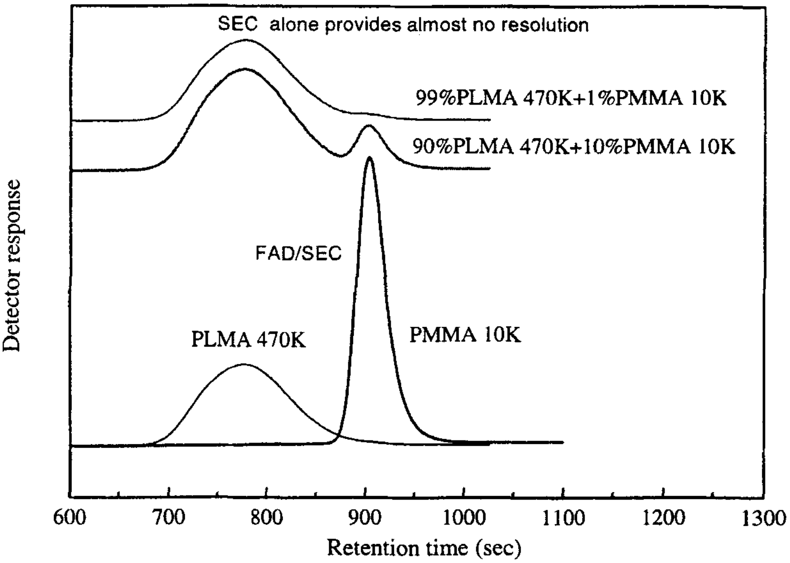

FIGURE 2 Upper SEC tracings are for the PLMA 470 K/PMMA 10 K blends with weight ratios 99/1 and 90/10. Lower SEC tracings are for single polymers separated by the FAD procedure (all with an ELS detector): 20 µL solution (1 g/L) of the 99/1 blend in toluene was introduced into the FAD column packed with nonporous SiO_2. PLMA was not retained and was directed into the SEC for characterization. Subsequently, PMMA reconcentrated within the FAD column from 1.5 mL of the sample solution was displaced from the FAD column with THF and eluted through an on-line SEC column equilibrated with the same eluent THF.

part of a high molar mass PiBMA that was observed as a large shoulder in the SEC peak after its desorption onto the SEC column (result not showed). In contrast, good agreement of molar mass values for separated PiBMA and PMMA in blend C (Tab. III) with their nominal values (Tab. I) was obtained by selective reconcentration of the minor PMMA from the mixture toluene/THF (wt ratio 95/5) in the FAD column 1. Again, THF was continuously added to pure toluene if the polymer sample were dissolved in the latter solvent.

For the above three blends A, B and C, the separation of components could be performed by full adsorption of both major and minor components which would be followed by the selective displacement of the major (less adsorbing) component with an appropriate low molecular displacer. Obviously, one should repeat this procedure several times depending on the sensitivity of the SEC detector and on the concentration of the minor component in the sample. According to our experience with numerous *adsorli/desorli/* polymer systems, no experimental problems are anticipated in the course of such process, however, it is rather time and material consuming. For example, using the small FAD column 2, one would have to repeat the above cycle about 15 times. Therefore, we did not try to apply this approach to the samples containing as low as 1 wt% of the minor polymer. It can be concluded that the direct selective reconcentration of a minor component by on-line adjusting the eluent composition is preferred.

The more complicated case (iii) was represented by blend D that was composed of the same components as blend C, but the minor component was the less adsorbing PiBMA. Evidently, the procedures described before could not be utilized for this blend. As a consequence, the off-line FAD/SEC approach was used here though it was rather inconvenient. The polymer blend was dissolved in the toluene/THF (wt ratio 95/5) mixture and was introduced into the FAD column 1 in small portions (0.05 mg) in order not to exceed the adsorption capacity of the column FAD column 1. FAD effluent, which contained solely PiBA was collected. This process was repeated 30 times. The diluted solution of PiBA was evaporated, redissolved in THF and reinjected into the SEC column for characterization. As already mentioned in the Introduction, we tried to use a second more active column (FAD 2) for on-line reconcentration of the minor PiBMA leaving the first column (FAD 1) nonadsorbed (Fig. 1). The problem was to find the appropriate composition of the *adsorli* to quantitatively retain PiBMA within FAD column 2. It was attempted by continuously adding pure toluene to the initial mixed eluent toluene/THF 95/5 that was used for trapping PMMA within FAD column 1. Independent reconcentration experiments for PiBMA dissolved in the toluene/THF (wt ratio 95/5) mixture and applying different ratios of flow rates for mixed eluent *vs.* pure toluene showed that PiBMA could be fully adsorbed within the FAD column 2 provided that this ratio was less than 2:3. Evidently, the lower this ratio, that is the larger amount of toluene that is added, the longer the time is needed for analysis of each sample. This approach may become experimentally unfeasible if the difference in adsorption behavior of blend components is so small that too low flow rate has to be used to deliver the sample into the FAD column 1 because a large volume of strong *adsorli* has to be added to the FAD column 1 effluent. Further, this approach requires multiple injections of small portions of the polymer sample, followed by cleaning the FAD column 1 from PMMA and its reequilibration with the initial eluent. Although the results obtained with both approaches are quite reasonable (Tab. III), further optimization concerns enhanced adsorption capacity and selectivity of FAD columns to substantially reduce the number of repeated sample injections as well FAD column regenerations. It is clear that even after optimization, the above on-line and off-line FAD/SEC approaches are experimentally impractical for system (iii) which should be better transformed into (ii) or even (i). To do so, one would certainly need to adjust FAD column packing nature.

The FAD procedure is based on typical on-and-off processes. To provide their efficient control and maintain high sample recovery and precision of analysis, the adsorptivity of blend components must differ substantially. Therefore, the FAD column/*adsorli*/*desorli* system must be chosen very carefully. In this situation, the major concern of a successful application of the FAD procedure represents a limited choice of appropriate adsorbents with controlled adsorption properties, particle sizes and mechanical strength. The FAD column packing must withstand multiple changes of eluents with different polarities. Still, even highly efficient, tailor-made FAD packings may fail to separate similar blend components. Under these circumstances, the simple on-and-off process must be substituted with multiple, chromatographic processes, for example with eluent or temperature gradient elution liquid chromatography. In this case, the FAD procedure will assume only the second part of its role described in this work, *viz.* the reconcentration of already separated species for subsequent analysis.

CONCLUSIONS

We have proposed the separation of minor macromolecular admixtures from major components of polymer blends by applying a full adsorption–desorption (FAD) procedure. In the same step, the admixture is reconcentrated and subsequently its mean molar mass and molar mass distribution can be determined with an on-line SEC chromatograph. Alternatively, spectroscopic (IR, NMR, MS) and other appropriate techniques can be combined with the FAD procedure to determine the chemical nature, molar mass, amount/concentration and molecular architecture of an admixture.

The FAD/SEC procedure was tested with model blends of homopolymers. It was shown that under optimum conditions the quantitative separation and characterization of blend components was feasible. The important prerequisite for a successful FAD separation is the identification of an appropriate FAD column packing/*adsorli*/*desorli* system in which the affinities of blend components toward the FAD column packing differ substantially. The most advantageous systems allow full, quantitative adsorption of minor admixture within the FAD column, while major blend component(s) remain(s) nonadsorbed. In this respect, the most important weakness of this proposed approach relates to the limited choice of appropriate FAD column packings. It is anticipated that the FAD procedure will enable simple, fast and reliable separation, concentration, analysis and molecular characterization of many macromolecular minor admixtures, even at concentrations below 1%.

Acknowledgments

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