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ORIGINAL CONTRIBUTION

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Liquid chromatography of polymer mixtures applying a combination of exclusion and full adsorption mechanisms. 5. Six-component blends of chemically similar polymers

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Abstract The separation of six-component blends of chemically similar homopolymers utilising the full adsorption-desorption (FAD) process is presented. The main advantage of the FAD approach over other methods represents the successive and independent size-exclusion chromatography (SEC) characterisation of all blend components. The method is based on the full adsorption and retention of all *n* or *n*−1 components of the polymer blend from an adsorption promoting liquid (ADSORLI) in a small FAD column. Nonadsorbed macromolecules are forwarded directly into SEC for molecular characterisation. Next, appropriate displacers are successively applied to the FAD column to selectively release preadsorbed blend constituents into the on-line SEC column. Dynamic integral desorption isotherms for single constituents, as well as for polymer blends to be analysed, allow identification of optimal displacer compositions to release just one kind of macromolecule. Model polymer blends containing polystyrene (PS), poly(lauryl methacrylate), poly(butyl methacrylate), poly(ethyl methacrylate), poly(methyl methacrylate) and poly(ethylene oxide) (PEO) or, alternatively, PS, poly(2-ethylhexyl acrylate), poly(butyl acrylate), poly(ethyl acrylate), poly(methyl acrylate) and PEO of similar molar masses can be separated and characterised in one multistep run using nonporous silica FAD packing, toluene as an ADSORLI and its mixtures with a desorption promoting liquid such as ethyl acetate, tetrahydrofuran or dimetylformamide to form displacers with appropriate desorption strength.

Key words Column liquid chromatography · Multicomponent mixtures · Separation · Polymer adsorption/desorption

Introduction

Separation and characterisation of multicomponent polymer blends presents a demanding analytical task. Direct size-exclusion chromatography (SEC) can be used for such purposes only if the blend components have sufficiently different molecular sizes in the SEC eluant [1, 2]. To partially overcome the problem concerning separation of blend constituents with similar molar masses, SEC employing hyphenated detection techniques may be one of the options [3–8]. Besides, several coupled chromatographic techniques have also been used for discrimination of binary polymer blends: liquid chromatography at the critical adsorption point [9–11], temperature gradient interactive chromatography [12], liquid chromatography under limiting conditions of adsorption [13, 14], and liquid chromatography under limiting conditions of solubility [13, 14]. However, the application of these methods is limited as the number of components in the blend increases. Separation of four-component blends containing either poly(methacrylate)s or poly(acrylate)s was successfully performed with help of liquid adsorption chromatography (LAC) [15]: the author used silica column packing and a linear gradient with increasing content of methylethylketone in toluene. In order to obtain the molecular characteristics of the separated components, the fractions from the LAC step must be, however, collected for subsequent off-line SEC measurements.

We have developed and tested a coupled liquid chromatography method based on the combination of full adsorption, stepwise desorption and size exclusion of macromolecules, for analysis of binary [16, 17] and three- and four-component [18, 19] polymer blends. Using a well-chosen adsorption promoting liquid (ADSORLI) as an eluant, one component of a multicomponent polymer blend is not retained while others are fully adsorbed within a small HPLC-like column denoted a full adsorption-desorption (FAD) column. Alternatively, all components of the polymer blend under study can be quantitatively retained within the FAD. An SEC column is connected on-line to the FAD column. In this manner, the polymer component that was not retained within the FAD column can be directly and independently characterised by SEC. As soon as the SEC characterisation of the unretained component of the polymer blend has been completed, the eluant composition is abruptly changed to selectively desorb just one of the blend constituents from FAD into SEC [18, 19]. Using a series of displacers with increasing displacing strength all blend components are successively desorbed and transported from the FAD column into SEC column(s) for characterisation. Displacers are, as a rule, mixtures of an ADSORLI with a desorption promoting liquid (DESORLI). The compositions of such displacers must be carefully optimised by employing dynamic integral desorption isotherms (DIDIs) that are the plots of desorbed polymer amount versus composition of displacer [18]. The FAD approach also turns out to be a useful tool for reconcentration of highly diluted polymer solutions, either for preparative purposes or as an intermediate stage to the multidimensional chromatography of complex polymer systems [20, 21].

In this paper we have extended the applicability of the FAD/SEC coupling to the separation and on-line molecular characterisation of model six-component blends composed in part of chemically similar homopolymers such as poly(acrylate)s or poly(methacrylate)s having different ester groups. The effects of both desorbing liquid DESORLI and FAD column packing adsorption activity on the separation selectivity are elucidated. Attempts to separate poly(methyl methacrylate) (PMMA) species of different tacticities are also discussed.

Experimental

The chromatographic system (Fig. 1) consisted of two analytical HPLC pumps (Waters, model 510), a V2 injection valve (Knauer, Berlin, Germany) and three multi-port switching valves, V1 (Rheodyne, Cotati, USA), V3 and V4 (Valco, Houston, USA). An evaporative light-scattering detector (ELSD) model DDL-21 (Eurosep Instruments, Cergy St. Christophe, France) was employed. The spheroidal nonporous silica particles of 8 μm mean diameter that were used in previous research [16–21] were packed into a small FAD column (30 × 3.3 mm). A larger FAD column (50 × 4.6 mm) packed with nonporous 5 μm silica Develosil particles (Nomura Chemical Co., Japan) was also employed. The SEC columns (300 × 7.5 mm) (PL-gel mixed B) were purchased from Polymer Laboratories (Shropshire, UK). A variety of broad and narrow polymer samples from different sources were handled as models: poly(styrene) (PS), poly(lauryl methacrylate) (PLMA), poly(n-butyl methacrylate)s (PBMA), poly(ethyl methacrylate)s (PEMA), PMMA, poly(2-ethylhexyl acrylate) (PEHA), poly(butyl acrylate) (PBA), poly(ethyl acrylate) (PEA), poly(methyl acrylate) (PMA), and poly(ethylene oxide) (PEO). Model polymer blends were prepared by dissolving the components (approximately the same weight ratio) in an ADSORLI. Narrow-range PMMA standards were from PSS (Mainz, Germany). Narrow-range PEO standards were obtained from TOSO (Shinnanyo, Japan).

Analytical grade toluene was used as the ADSORLI eluant. Distilled ethylacetate (EAC), tetrahydrofuran (THF) and dimethylformamide (DMF) were used as DESORLI eluants. Displacers for polymer desorption from the FAD column were usually mixtures of toluene or distilled *n*-hexane and one of the above-mentioned DESORLIs with appropriate compositions.

The assessment of DIDIs was previously described in detail [22]. A constant amount of single polymer or polymer blend dissolved in the ADSORLI was injected and retained within the FAD column that was preequilibrated with the same liquid. Next, the displacer of

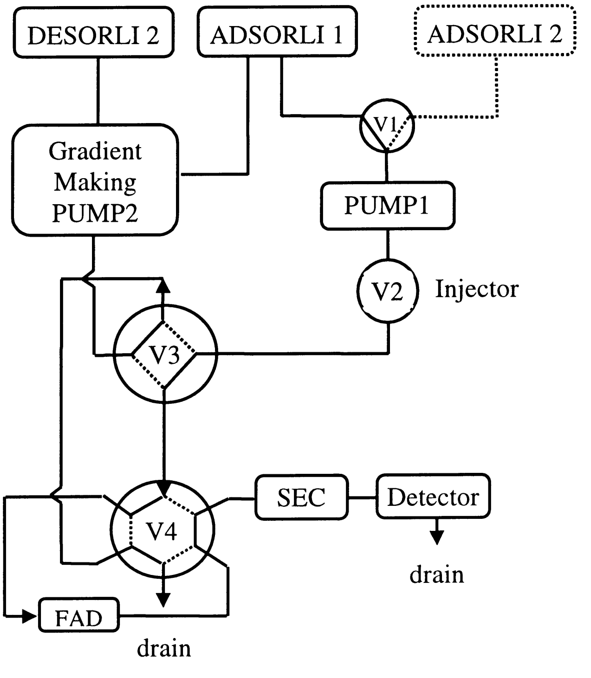

Fig. 1 Schematic representation of full adsorption-desorption (*FAD*) size-exclusion chromatography (SEC) assembly. See text for detailed explanation

a particular composition was transported into the FAD column. The desorbed portion of polymer was forwarded either directly or through the SEC column into the ELSD. In this way, the amount of desorbed single polymer and, if necessary, also its molecular characteristics could be determined. Next, the non-desorbed polymer fraction that remained within the FAD was completely washed out by use of the pure DESORLI (DMF in the case of blends containing PEO; THF for all other polymers). Eventually, the FAD was reequilibrated with the ADSORLI to be used for a new polymer loading and subsequent desorption. The procedure was repeated using different DESORLI concentrations in displacers till complete desorption of preadsorbed polymer(s) was achieved, i.e. the full desorption point was reached.

The data were collected on-line by use of a Waters PC-based data acquisition system. The nonadsorbed/desorbed amounts of single polymers were calculated from detector peak areas employing appropriate calibration for the experimental conditions used. However, precise desorbed amounts of polymers in the case of blends could not be obtained in this way because the ELSD response depended on various parameters, for example, the chemical nature of the polymer and the eluant [23]. Consequently, the DIDIs for polymer blends were constructed by plotting the area of the desorbed peak versus the composition of displacer rather than plots of desorbed amount of polymer versus the displacer composition constructed in our previous papers [22].

Results and discussion

It has been shown [18, 19] that the efficient FAD discrimination of a given multicomponent polymer blend requires optimisation step(s). The courses of DIDI for single constituents of polymer blends could be used to predict the selectivity of the FAD processes. However, our detailed studies of parameters influencing the courses of DIDIs indicated that the latter were affected by several experimental factors such as preadsorbed polymer amount, FAD size, polymer molar mass and molar mass distribution, temperature, as well as ADSORLI and DESORLI nature [18]. In other words, the optimum conditions for the successive and selective release of preadsorbed blend constituents from the FAD column should be identified by means of the DIDI measured with the polymer blends to be analysed rather than with the single blend constituents.

We found that PS was not adsorbed on bare silica from many ADSORLIs including toluene while PEO was strongly attached on FAD silica-based column packing even from pure THF which otherwise desorbed most other polymers from the silica surface. A four-component blend consisting of PS, PBMA, PMMA and a very polar PEO was recently separated and the constituents were characterised using FAD/SEC coupling with dichloroethane as an ADSORLI, while THF and DMF were used as DESORLI components of displacers [18]. In that system the DIDIs for PMMA and PBMA were very close to each other. As a result, no further poly(methacrylate)s such as PEMA could be separated from PBMA and PMMA. In this present study, our objective is to test possibilities to raise the selectivity of the FAD procedure by optimisation of adsorbent - ADSORLI - displacer systems. In practice we sought the appropriate conditions for the discrimination of as many poly(acrylate)s or poly(methacrylate)s as possible in the multicomponent polymer blends.

Figure 2 depicts the DIDIs for a series of broad poly(acrylate)s and poly(methacrylate)s that were preadsorbed within the FAD column (30 × 3.3 mm) from toluene, which is an effective ADSORLI for these polymers. Generally, desorption of a preadsorbed polymer starts when the desorbing strength of the displacer is sufficiently high. The displacer composition which is needed to initiate polymer desorption is called the desorption threshold. If the displacer composition reaches the so-called full desorption point, all preadsorbed macromolecules are completely released from the adsorbent surface. Evidently, the full desorption points for PEMA and PEA are rather close to the desorption thresholds for PBMA and PBA, respectively. The same conclusion can be made for other PMMA/PMA and PEMA/PEA pairs. This means that the methyl group on the main chain does not strongly influence the overall adsorption behaviour of macromolecules. Consequently, poly(acrylate) and poly(methacrylate) with the same ester group cannot be separated from each other using the experimental conditions shown in Fig. 2. As mentioned earlier, the course of DIDI reflects to a certain extent the mean molar mass and molar mass distribution of polymer. It is anticipated that the lower mean molar mass and the broader molar mass distribution of the PMA sample (Table 1) might be responsible for its desorption behaviour in this system represented by a rather flat course of DIDI.

Further, we used a weaker DESORLI, namely EAC, instead of THF for displacing poly(methacrylate)s from the same 30 × 3.3 mm FAD column. In this system the

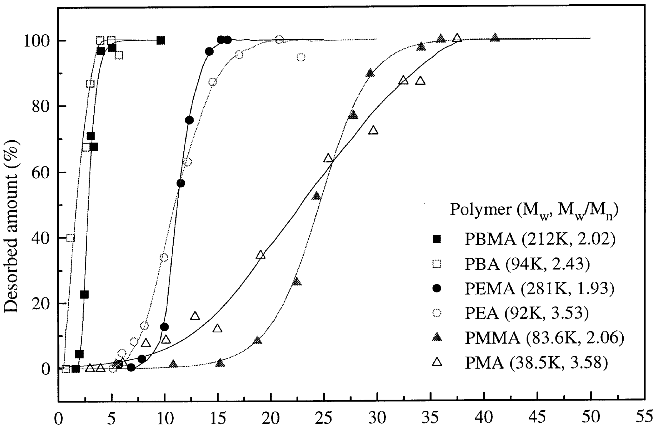

Fig. 2 Typical dynamic integral desorption isotherms (*DIDI*) for various broad poly(acrylate)s and poly(methacrylate)s. The FAD column (30 × 3.3 mm) was packed with nonporous silica; the preadsorbed amount of polymer from toluene was 0.01 mg

Table 1 Molar mass characteristics of single polymers and polymers in blends. Polystyrene (*PS*) and poly(ethyleneoxide) (*PEO*) standards were used for the calculation of the mean molar mass (*MMM*) of PS92K and PEO45K, respectively. Otherwise, effective MMM values of poly(acrylate)s and poly(methacrylate)s were obtained employing (*PMMA*) standards in the same size-exclusion chromatography (*SEC*) eluants as were used as displacers in the full adsorption - desorption SEC studies

Polymer	Eluant/displacer	$M_w \times 10^{-3}$ (g/mol)	$M_n \times 10^{-3}$ (g/mol)	M_w/M_n	Note
PS92K	Toluene	97.5	73.3	1.33	Single polymers
PEHA95K	3.5 wt % EAC in toluene	95.2	38.9	2.45	
PBA94K	25 wt % EAC in toluene	94.5	28.8	3.28	
PEA110K	60 wt % EAC in toluene	111	31.4	3.53	
PMA700K	75 wt % THF in toluene	697	259	2.69	
PLMA470K	3.5 wt % EAC in toluene	445	185	2.41	
PBMA57K	25 wt % EAC in toluene	55.9	48.6	1.15	
PEMA50K	60 wt % EAC in toluene	49.9	36.4	1.37	
PMMA103K	75 wt % THF in toluene	89.4	71.0	1.26	
PEO45K	20 wt % DMF in toluene	43.0	35.5	1.21	
PS92K	Toluene	89.9	69.7	1.29	Blend 1
PEHA95K	3.5 wt % EAC in toluene	101	40.2	2.51	
PBA94K	25 wt % EAC in toluene	94.7	28.6	3.31	
PEA110K	60 wt % EAC in toluene	107	30.7	3.49	
PMA700K	75 wt % THF in toluene	681	258	2.64	
PEO45K	20 wt % DMF in toluene	43.6	35.7	1.22	
PS92K	Toluene	93.6	71.5	1.31	Blend 2
PLMA470K	3.5 wt % EAC in toluene	451	189	2.39	
PBMA57K	25 wt % EAC in toluene	58.3	49.4	1.18	
PEMA50K	60 wt % EAC in toluene	55.6	41.2	1.35	
PMMA103K	75 wt % THF in toluene	85.6	68.5	1.25	
PEO45K	20 wt % DMF in toluene	41.0	33.1	1.24	

selectivity of polymer blend separation for poly(methacrylate)s with similar mean molar masses is slightly enhanced (DIDIs not shown). However, higher alkyl ester poly(methacrylate)s and poly(acrylate)s which are less polar than PBMA or PBA, respectively, were not fully retained within this FAD column from toluene ADSORLI. On the other hand, more polar poly(methacrylate)s such as poly(glycidyl methacrylate) could not be used as models in our study since they are poorly soluble in toluene.

Another possibility to increase the number of separated components in blends of poly(methacrylate)s or poly(acrylate)s appears to be the use of a more active FAD column. In the next series of experiments we tested the commercial Develosil FAD column packing. As mentioned in the Experimental section, our nonporous silica was prepared by sintering silica gel at 1200 °C. At such high temperature all surface silanols were removed and probably only some of them were reintroduced during column packing and other manipulations. In contrast, most commercial nonporous silicas are prepared by controlled hydrolysis of tetraethoxysilane in an ethanol/water/ammonia mixture [24]. Accordingly, the resulting materials exhibit high concentration of surface silanols and this was also anticipated in case of Develosil. As a matter of fact, using an FAD column packed with Develosil, less polar PLMA or PEHA were found to be fully adsorbed within the FAD column from toluene while PS was not retained at all under these conditions. The DIDIs for blends containing either a series of poly(acrylate)s or poly(methacrylate)s with PS and PEO are presented in Figs. 4 and 5. Polymer constituents in each model blend were chosen to have as similar a molar mass range as possible. PMA700K used in blend 1 (Fig. 3) seemed to be partially adsorbed with pure EAC while PMMA103K in blend 2 (Fig. 4) was completely desorbed under these conditions. Furthermore, independent desorption experiments

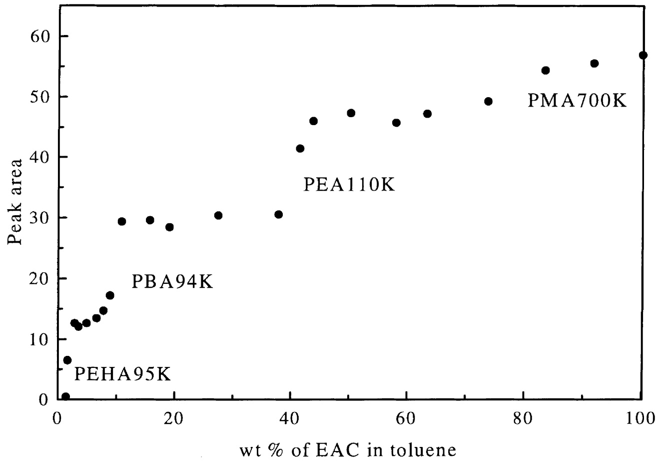

Fig. 3 DIDI for the polymer blend containing PS92K + PEHA95K + PBA94K + PEA110K + PMA700K + PEO45K. The FAD column was Develosil (50 × 4.6 mm); the preadsorbed amount was 0.01 mg for each polymer; ADSORLI toluene. See text for explanations

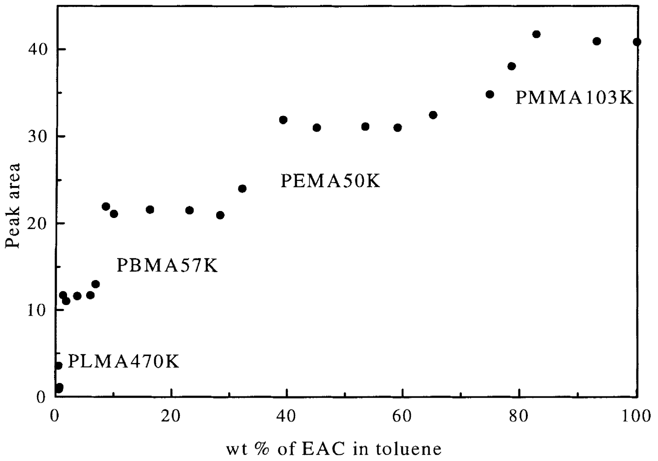

Fig. 4 DIDI for the polymer blend containing PS92K + PLMA470K + PBMA57K + PEMA50K + PMMA103K + PEO45K. Other conditions are as in Fig. 3. See text for explanations

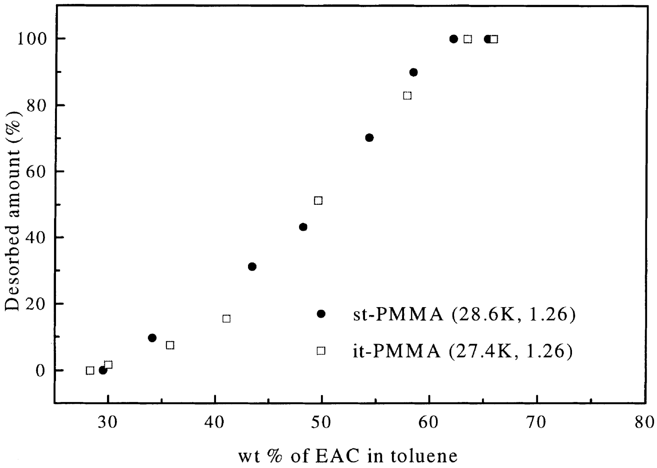

Fig. 5 DIDI for iso-(*it*) and syndiotactic (*st*) poly(methyl methacrylate)s (*PMMAs*) with molar mass and polydispersity as indicated. Other conditions were the same as in Fig. 2 except ethyl acetate (*EAC*) was used instead of tetrahydrofuran (*THF*)

showed that PMA could be fully released from the FAD column packed with Develosil using a mixture of 75 wt % THF and 25 wt % toluene, which is still a strong ADSORLI for PEO. We also found that the mixture DMF/toluene (20/80 wt/wt) was able to fully desorb PEO45K from Develosil adsorbent under otherwise identical conditions. According to the courses of the DIDIs for the two model blends, we used a series of displacers for separation and independent molecular characterisation of all blend 1 and 2 constituents as given in Table 1. Polymer blends were dissolved in toluene and injected into the FAD/SEC system. Non-adsorbed PS was directly characterised by SEC with toluene eluant. Next, the SEC column was flushed with a new eluant containing 3.5 wt % EAC in toluene. With this displacer, either PEHA or PLMA were selectively desorbed from FAD into SEC for molar mass determination. Similar steps were carried out with displacers containing 25 wt % EAC in toluene, 60 wt % EAC in toluene, 75 wt % THF in toluene and 50 wt % DMF in toluene for PBA (PBMA), PEA (PEMA), PMA (PMMA) and PEO, respectively. For comparison, single polymers were also fully adsorbed and consequently desorbed into an SEC column applying the same displacers as for blend separation. For example, PMMA was first fully adsorbed from the mixture EAC/toluene (60/40 wt/wt) and desorbed with the mixture THF/toluene (75/25 wt/wt), etc. In these comparative experiments, both the adsorption and the desorption extent of particular polymer were carefully checked with the ELSD. The molecular characteristics obtained for single polymers and blend constituents are comparable within the SEC error (Table 1).

Evidently, the prerequisite for highly selective separation of blend constituents by means of the FAD procedure is the appearance of distinct steps on the DIDI for each constituent of an analysed polymer blend (Figs. 4, 5). In general, the course of DIDI also reflects to a certain extent the sample heterogeneity with respect to its molar mass and/or chemical structure. In the case of an unknown blend containing polymers with broad molar mass distributions, the SEC/FAD/SEC coupling could be, therefore, applied to avoid the problem regarding low selectivity due to the above-mentioned molar mass effect involved upon selective desorption of blend constituents from the FAD column. In other words, the polymer sample to be analysed should be prefractionated in the "first" SEC step. SEC fractions would be separated and simultaneously reconcentrated in a series of appropriate FAD columns. Next, the selective desorption and SEC characterisation of all FAD fractions could be performed to obtain detailed information on all blend constituents.

We also tried to apply the FAD/SEC procedure to the separation of PMMAs possessing different stereoregularity. Highly isotactic and syndiotactic PMMA samples with similar mean molar masses [25] were employed as model polymers. Their DIDIs obtained in various ADSORLI/DESORLI systems are depicted in Figs. 5 and 6. It is clear that in the system toluene/EAC, which was used for poly(methacrylate)s, there is only a negligible difference in the desorption characteristics of narrow molar mass distribution isotactic and syndiotactic PMMA of similar mean molar mass (Fig. 5). A much larger difference in the DIDI courses was observed when polymers preadsorbed from toluene were desorbed with mixtures of *n*-hexane and THF (Fig. 6). The syndiotactic PMMA was evidently more strongly attached onto bare nonporous silica than the isotactic one; however, no full separation of syndiotactic and isotactic PMMA could be expected even in the latter system. It is

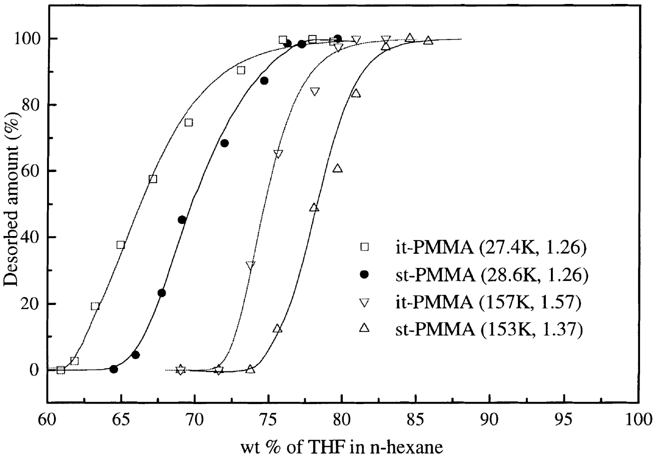

Fig. 6 DIDI for it and st PMMAs with molar mass and polydispersity as indicated. Other conditions were the same as in Fig. 2 except the displacers were mixtures of *n*-hexane and THF

interesting to mention here that a mixture of the same liquids has been found to be the "critical" eluant in liquid chromatography at the critical adsorption point, namely 83.2 wt % THF and 16.8 wt % *n*-hexane [11]. Under these conditions, highly syndiotactic PMMAs with different mean molar masses were eluted at the same retention volume (critical adsorption point) while highly isotactic PMMAs were eluted in the SEC mode and could be conventionally characterised without interference from syndiotactic PMMA macromolecules. This indicates a substantial difference in behaviour of macromolecules under conditions of weak (critical) and strong adsorption in dynamic systems.

Conclusions

Many multicomponent polymer blends can be readily separated using the FAD procedure. The discriminated components can be further characterised by applying an on-line SEC system or other analytical techniques. The FAD experimental conditions must be carefully optimised to attain highly selective, successive polymer desorption from the FAD column that initially retained all *n* or *n*−1 constituents of the polymer blend. The highly selective release of macromolecules from the FAD column is necessary for quantitative multicomponent polymer blend separation. In this work, the displacer nature and FAD column packing activity were used as parameters for discrimination of model polymer blends consisting mainly of poly(acrylate)s and poly(methacrylate)s. The adjustment of the FAD column packing adsorption capacity seems to be an additional tool to control FAD separation selectivity. A combination of ADSORLI, DESORLI and FAD column packing of matched adsorptivity enables quantitative separation of up to six polymers having similar molar mass and chemical structure. It is supposed that multidimensional FAD procedures applying multi-step adsorption-desorption with a series of ADSORLIs, DESORLIs and a cascade of FAD column packings can discriminate even more complex polymer systems. This may make the FAD procedure a potential tool for studies of copolymers and multicomponent blend of macromolecules formed, for example, during chemical modifications and transformations including polymer oxidation. The product deformulations represent another potential FAD/SEC application area.

Our result relating to the effects of ester groups on the FAD of poly(acrylate)s and poly(methacrylate)s is similar to that observed by Mourey [15], Van der Beek et al. [26] and Inagaki [27]. Typically, methyl, ethyl, butyl and higher alkyl esters of these polymers can be selectively separated by applying appropriate systems. At the same time, however, methyl groups on the main chain did not play an important role in the adsorption-desorption processes. As a result, poly(acrylate)s could not be effectively separated from poly(methacrylate)s containing the same alkyl ester group. Similarly, the effect of the stereoregularity of PMMA was found to be hardly large enough to allow discrimination of PMMAs according to their tacticity. Probably the behaviour of strongly adsorbed and fully retained macromolecules on the solid surface differs from that of weakly adsorbed macromolecules, which continue eluting from the liquid chromatographic column.

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