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Separation of polyester oligomers by gradient high-performance liquid chromatography

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Abstract

A highly efficient method for the separation of commercially available polyesters composed of a multitude of individual oligomers by gradient reversed-phase high-performance liquid chromatography (gRP-HPLC) was developed. Oligomers up to a molecular mass of more than 10 000 could be sufficiently resolved on an octadecylsilyl silica (C_{18}) stationary phase using a ternary gradient consisting of acetonitrile, tetrahydrofuran (THF) and aqueous acetic acid. Detection was performed by measurement of signal responses from either UV detection at 230 nm or evaporative light scattering detection (ELSD). Addition of THF to the mobile phase is essential and omission of the co-solvent provided elution of only a few oligomers, the residual amount being trapped on the highly hydrophobic stationary phase. Due to the substantial UV mismatch invoked by THF exhibiting marked absorbance at the chosen wavelength, ELSD, which is not associated with baseline drift phenomena, is much more suited for identification of individual polyester samples on the basis of the chromatographic fingerprint. In one case about sixty sufficiently resolved peaks each attributable to a single oligomer could be observed. A concentration of about 10 mg/ml of sample was required for an unequivocal distinction of the individual polyesters. The use of a C_{18} stationary phase is an ultimate prerequisite for efficient oligomer resolution as impressively evidenced by an almost complete lack of separation into individual oligomers on C_8 or C_{Phenyl} matrices. In the latter cases only few low-molecular-mass oligomers are preceding the broad and unresolved bulk peak envelope of sample constituents.

Keywords: Gradient elution; Polyester oligomers; Polymers

1. Introduction

Polyesters find broad application in different fields of chemistry. The oligomers up to about molecular mass (M_r) 10 000 are preferably used in manufacturing of powder coatings in the lacquer industries, as well as flexibilisers and adhesives. In contrast, the higher-molecular-mass samples are essential constituents for the production of injection moulding parts and toolings. Polyesters are prepared from di-acids and di-alcohols in a typical condensation reaction and, as a consequence, a more or less broad M_r distribution of individual oligomers is to be expected. However, still more complex structural features are encountered when more than one di-acid–di-alcohol pair, or even trifunctional acid and alcohol components, yielding more or less branched products, participate in the esterification reaction. Although, as seen in the case of the much better investigated substance class of polyethers, the product properties strongly depend on either oligomer distribution or chemical composition, only a rela-

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tively small number of highly efficient separation procedures is available in the literature. Krüger et al. [1] reported liquid chromatography of poly(1,6-hexanediol adipates) by gradient reversed-phase high-performance liquid chromatography (gRP-HPLC) on a C_8 matrix with a binary solvent of acetonitrile and water and effected separation of about eighteen individual oligomers. Furthermore, the same authors [2] subjected polyesters prepared from adipic and phthalic acid and different alcohols [e.g., 1,6-hexanediol, 1,4-butanediol, 1,2- propanediol, 1,3-propanediol, 1,2-ethanediol, 2,2-dimethylpropane diol-1,3, di(ethylene glycol), di(propylene glycol), tri-(ethylene glycol)] to the so-called "two-dimensional" separation by normal-phase liquid adsorption chromatography under critical conditions (LACCC) as the first step, followed by size-exclusion chromatography (SEC) in order to evaluate either chemical composition distribution (CCD) or M_r distribution (M_rD) of the polyester samples. Matrix assisted laser desorption ionisation time of flight mass spectroscopy (MALDI–TOF-MS) was used in the first dimension for monitoring of CCD as well as functionality type distribution (FTD). Guarini et al. [3] investigated polyethylene terephthalate oligomers by LC coupled to MS via a thermospray (TSP) interface and Barnes et al. [4] subjected the same substance class to LC using atmospheric pressure chemical-ionisation (APCI) MS. It is furthermore noteworthy, that Milon [5] observed cyclic oligomers of polyethylene terephthalate by LC–plasma spray MS. Klumpermann et al. separated co-polyesters [6] and Philipsen et al. investigated co-polyester resins [7] with a system termed "gradient polymer elution chromatography" (GPEC) providing detailed information on either M_rD or CCD of the samples. In both cases about twenty oligomers could be separated from each other, but unfortunately, baseline separation is only effected for a few low-M_r sample constituents. To our knowledge highly efficient separation methods covering a wide M_r range of polyester oligomers are still lacking, although this will be an ultimate prerequisite for a rapid assignment of different samples to an individual polyester type on the basis of its chromatographic fingerprint, i.e., the so-called "pattern recognition". Results from $^1H/^{13}C$ nuclear magnetic resonance (NMR) spectroscopic measurements in combination with LC–MS investigations will then provide additional information on CCD as well as FTD. For this reason, in order to obtain an unequivocal assignment of a large number of oligomers to defined chemical structures, a high resolution chromatographic separation procedure for polyesters was developed on the basis of gRP-HPLC covering a wide M_r range extending to more than 10 000. As far as we know, resolution of about sixty individual oligomers in polyester samples have not been reported hitherto.

2. Experimental

2.1. Separation media, samples and solvents

Acetonitrile (HPLC-grade) was obtained from Biosolve (Valkenswaard, Netherlands). Tetrahydrofuran (THF) and acetic acid (both HPLC-grade) were from Fluka (Buchs, Switzerland). Water for the use in HPLC was purified with a Milli-Q reagent water system™ from Millipore–Waters (Milford, MA, USA). The polyester samples Alftalat 3258 and Alftalat 3352 were obtained from Hoechst (Frankfurt, Germany), Crylcoat 430 and Crylcoat 801 from UCB (Drogenbos, Belgium). For RP-HPLC the following stationary phases were used: Nucleosil $5C_{18}$ (125×4.6 mm I.D., 5 μm particle size, 100 Å pore diameter), Nucleosil $5C_8$ (125×4.6 mm I.D., 5 μm particle size, 100 Å pore diameter) and Nucleosil 7Phenyl (125×4.6 mm I.D., 7 μm particle size, 100 Å pore diameter) all obtained from Macherey–Nagel (Oensingen, Switzerland). SEC was performed on four PL_{gel} columns operated in series (300×4.6 mm I.D., 5 μm particles) obtained from Ercatech (Bern, Switzerland) consisting of polystyrene cross-linked with divinyl benzene of the following pore diameters: 50 Å, 500 Å, 1000 Å and 10 000 Å, respectively. Narrow range polystyrene standards for molecular mass calibration covering the range from 92 (toluene) to 3 950 000 were obtained from Ercatech.

2.2. Analytical equipment

The whole HPLC system consisted of a P 4000 quaternary HPLC pump, an AS 3000 autosampler with an intergrated column oven and equipped with a

10 μl sample loop, a type UV 2000 UV detector and a PC 1000 data acquisition unit, all obtained from Thermo Separation Products (San Jose, CA, USA). For evaporative light scattering detection (ELSD) a type Sedex 45 apparatus from Sedere (Vitry sur Seine, France) equipped with a 20 W iodine lamp was applied. For SEC a system consisting of a P 4000 quaternary HPLC pump, an AS 1000 autosampler equipped with a 100 μl sample loop and a type UV 1000 UV as well as a Shodex RI 71 refractive index (RI) detector, all obtained from Thermo Separation Products, was chosen. Determination of number average M_r (M_n) and weight-average M_r (M_w) values was done on the basis of calibration with narrow range polystyrene standards with the PSS evaluation software from Polymer Standard Services (Mainz, Germany).

2.3. Sample preparation and chromatographic separation

For gRP-HPLC solutions of the individual polyester samples were prepared in THF (5%, w/v), whereas for SEC concentrations of 0.5% (w/v) in THF were used. Chromatography was carried out at a flow-rate of 1.5 ml/min with a ternary mobile phase consisting of acetonitrile, THF and water containing a final concentration of 0.5% (w/v) acetic acid for separation on the C_{18} column and a binary system of acetonitrile and water containing a final concentration of 0.5% (w/v) acetic acid for separation on the C_8 and C_{Phenyl} stationary phases. The individual gradient profiles are depicted in Tables 1–3. The column temperature was adjusted to 40°C for separations on the C_{18} matrix, whereas the C_8 and C_{Phenyl} phases were operated at ambient temperature. The column effluent was measured simultaneously by either evaporative light scattering detection or UV at 230 nm. In ELSD the nebulisation chamber was heated to 40°C and the nitrogen flow adjusted to 4.5 l/min corresponding to an inlet pressure of 200 kPa. SEC was performed isocratically with THF as the mobile phase at a flow-rate of 1 ml/min and measurement of either UV (254 nm) and refractive index responses. The column temperature was adjusted to 29°C. Injection volumes for RP-HPLC and SEC were 10 μl and 100 μl, respectively.

Table 1
Gradient system I

Time	%Acetonitrile	%THF	%Water	%Acetic acid (50%, w/v)
0	10	0	89	1
25	75	0	24	1
35	94	5	0	1
60	79	20	0	1
75	79	20	0	1
76	10	0	89	1
90	10	0	89	1

Table 2
Gradient system II

Time	%Acetonitrile	%THF	%Water	%Acetic acid (50%, w/v)
0	80	5	14	1
30	94	5	0	1
50	89	10	0	1
75	79	20	0	1
90	79	20	0	1
91	80	5	14	1
110	80	5	14	1

3. Results

The results of the molecular mass determinations of four selected polyester samples by SEC based on calibration with narrow range polystyrene standards are depicted in Table 4. All four samples show comparable values for the M_n and M_w data as well as the polydispersity index (M_w/M_n). No separation of the four polyesters into their individual oligomers was seen even in the elution region of the low-molecular-mass (M_r) sample constituents (results not shown). In contrast, the gRP-HPLC technique effected excellent resolution of a multitude of oligomers

Table 3
Gradient system III

Time	%Acetonitrile	%Water	%Acetic acid (50%, w/v)
0	20	79	1
40	99	0	1
55	99	0	1
56	20	79	1
70	20	79	1

Table 4
M_n, M_w and M_w/M_n values of the investigated polyesters

Sample	M_n	M_w	M_w/M_n
Alftalat 3258	2173	10 610	4.88
Alftalat 3352	2950	10 790	3.66
Crylcoat 430	2705	11 260	4.16
Crylcoat 801	2513	13 110	5.22

on a C_{18} stationary phase as shown in Figs. 1–4. In the case of Alftalat 3352 about sixty different oligomers are recognisable in both the HPLC–ELSD and HPLC–UV traces, whereas separation of high-M_r oligomers was less pronounced in Alftalat 3258 and substantially reduced in Crylcoat 430 as well as Crylcoat 801. In the latter samples high-M_r oligomers elute as a broad "peak envelope" dropping rapidly to the chromatographic baseline as seen in the HPLC–ELSD trace. Unlike polyethers [8–12], where sensitivity of detection was approximately one to two orders of magnitudes better by use of UV monitoring after derivatisation with 3,5-dinitrobenzoyl chloride, ELSD provides substantial advantages over UV detection primarily due to the so-called "UV mismatch" at the chosen wavelength of 230 nm. The reason for this lies in the continuously increasing concentration of THF, which is added as the co-solvent up to a final concentration of 20% in order to increase sample solubility (see Fig. 1b, 2b, 3b and 4b). As the consequence, the baseline exhibits a rather strong drift, which markedly impairs an individual assignment of the polyester samples to a distinct type of polyester on the basis of the chromatographic fingerprint. In contrast, ELSD still allows a clear distinction of the individual polyester samples.

Unfortunately, despite the impressive separation characteristics obtained by use of elution system I (see Figs. 1–4), baseline separation of the individual oligomers has not been achieved. For this reason, the gradient profile was modified in order to improve separation of a multitude of oligomers. Indeed, as impressively shown in Fig. 5a (HPLC–ELSD trace), about thirty oligomers could be baseline resolved. As expected, resolution was identical with UV detection as depicted in Fig. 5b, but as already demonstrated in Figs. 1b, 2b, 3b and 4b, a significant UV mismatch is observed due to gradually admixed THF.

For this reason, only the ELSD fingerprints were chosen for recognition of individual polyesters. A concentration of about 10 mg/ml is required for sufficient discrimination of the different polyester batches used in this study.

Preliminary ^{13}C NMR investigations (results not shown[1]) revealed unequivocally that the Alftalat 3258 is a copolymer composed of benzene-1,4-dicarboxylic acid (terephthalic acid), benzene-1,3-dicarboxylic (isophthalic acid), acid 2,2-dimethylpropane diol (neopentylglycol) and two other hitherto unidentified alcohol components as the monomeric constituents, whereas Alftalat 3358 is composed of terephthalic acid, isophthalic acid, neopentylglycol and one other hitherto unidentified alcohol component as the monomeric units. Crylcoat 430 is composed of terephthalic acid, isophthalic acid, neopentylglycol, ethylene glycol and two additional hitherto unidentified alcohols, whereas Crylcoat 801 is composed of terephthalic acid, isophthalic acid, neopentylglycol, 1,1,1-tris(hydroxymethyl)propane (trimethylolpropane) and one additional hitherto unidentified alcohol component as the monomeric units. It was found that neopentylglycol was the preponderantly used di-alcohol in all four samples.

Furthermore, LC coupled to atmospheric pressure chemical-ionisation MS (LC–APCI-MS) was applied in order to obtain additional information with respect to either M_r or chemical composition of the individual oligomers (results not shown). Unfortunately, this aim was only achievable with a few low-M_r members, because the M_r determination range of the used APCI apparatus is restricted to about 2500 Da. Nevertheless, it was possible to roughly estimate the M_r data of the high-M_r oligomers in particular in the case of the two Alftalat samples by extrapolating the mass differences between the measurable low-M_r members to later eluting but still sufficiently resolved oligomers, representing sample constituents of high-M_r. In both Alftalat samples the oligomers attributable to the terephthalic acid neopentylglycol ester repeating unit (M_r=234) were easily recognisable. In this respect M_r values >12 000 Da were estimated, which, for this reason, are in a similar range as those

[1]The NMR investigations of polyesters will be the subject of a separate publication.

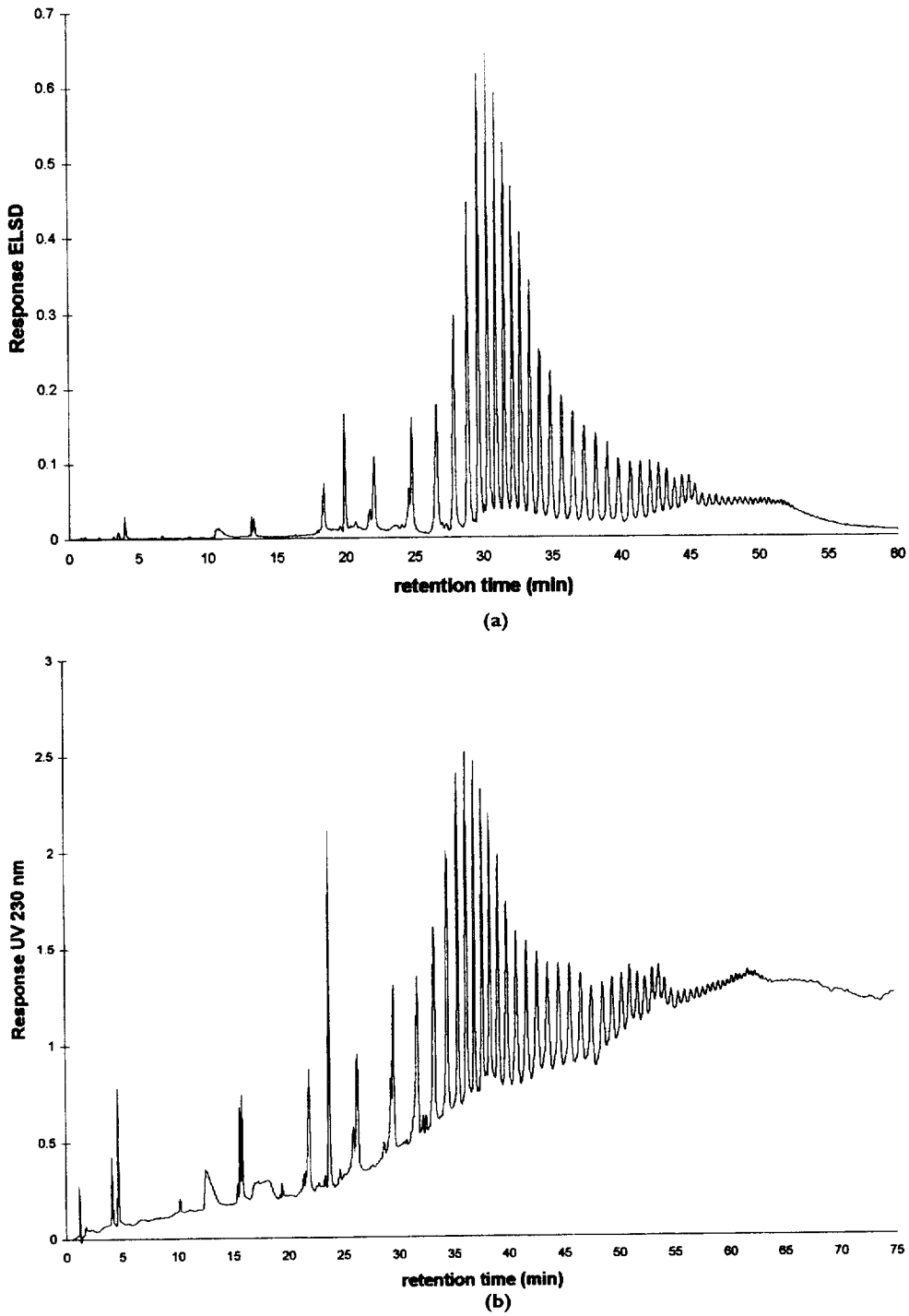

Fig. 1. Chromatograms of Alftalat 3258 by gRP-HPLC on a C_{18} stationary phase (125×4.6 mm I.D., 5 μm particles) at 40°C using gradient system I. (a) ELSD, (b) UV detection at 230 nm; for details see Section 2.

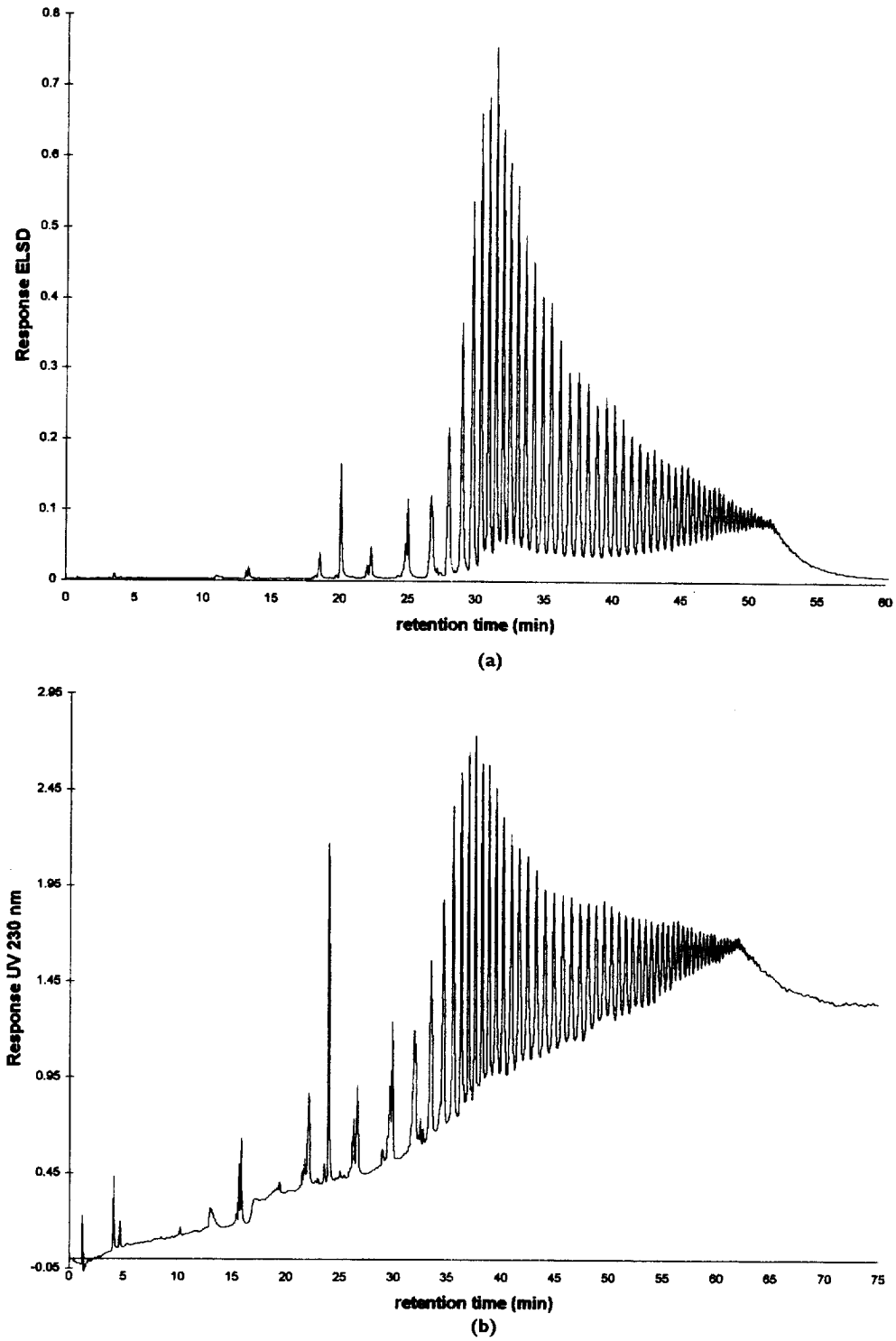

Fig. 2. Chromatograms of Alftalat 3352. Conditions and panels as in Fig. 1.

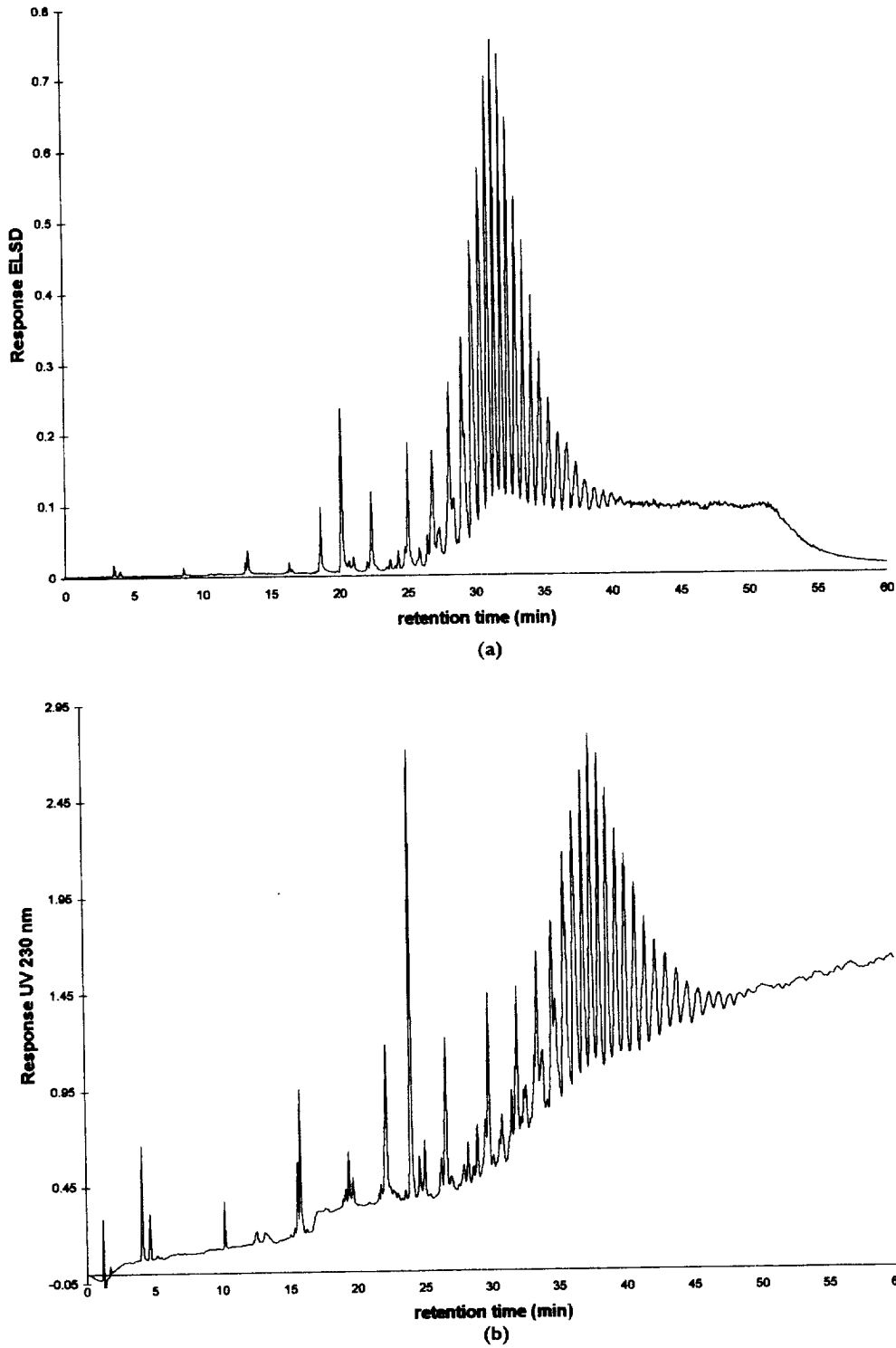

Fig. 3. Chromatograms of Crylcoat 430. Conditions and panels as in Fig. 1.

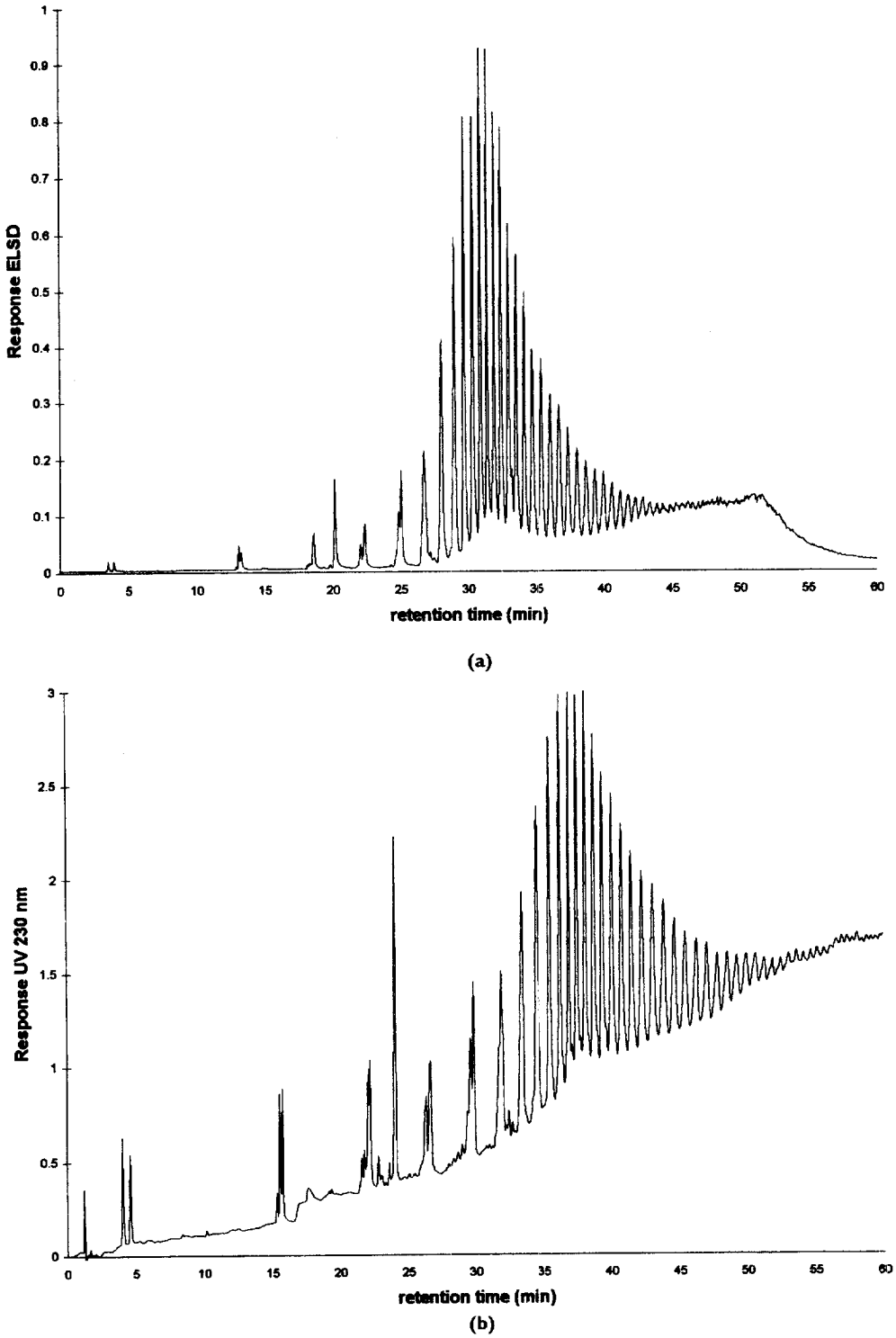

Fig. 4. Chromatograms of Crylcoat 801. Conditions and panels as in Fig. 1.

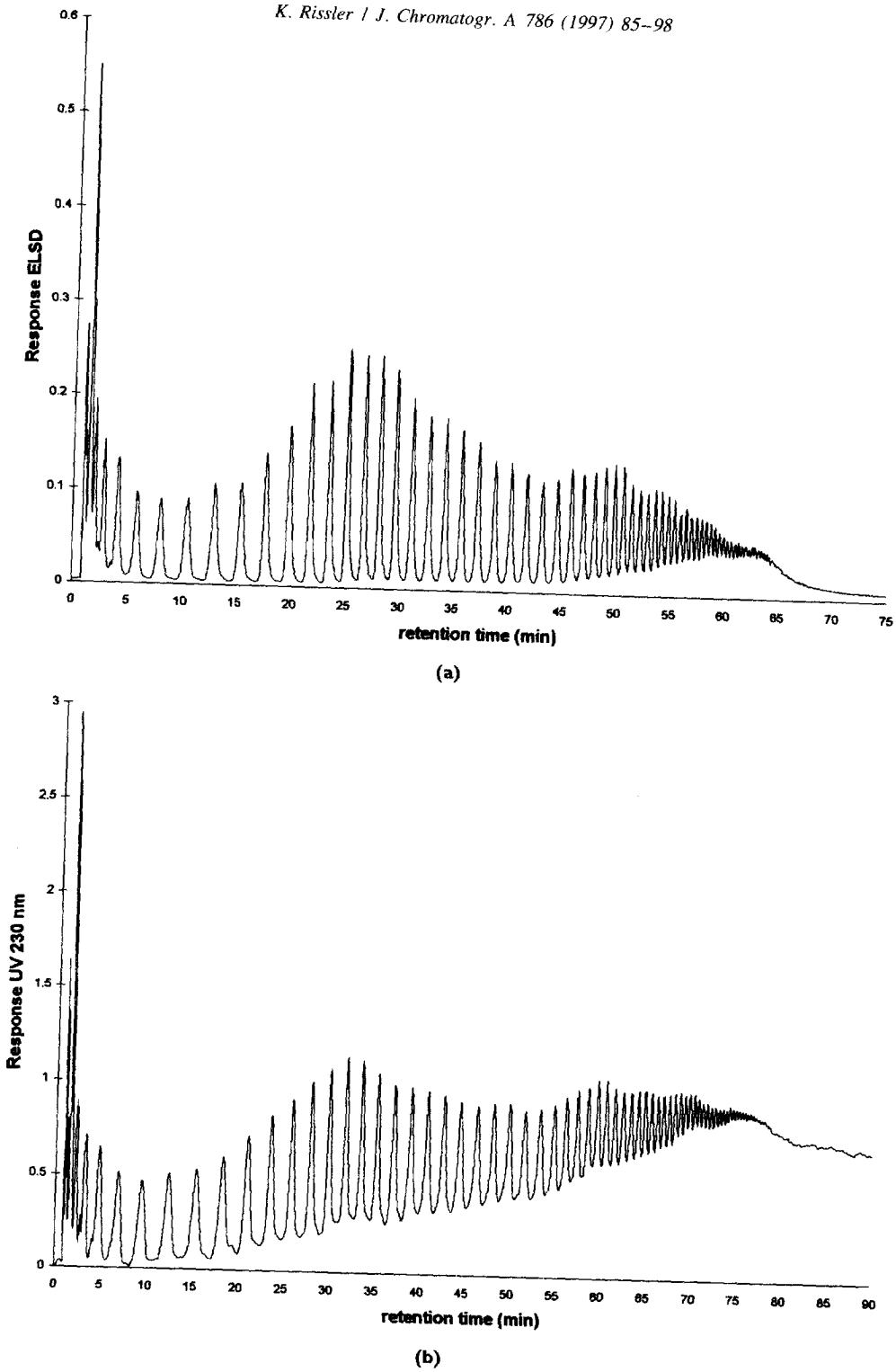

Fig. 5. Chromatogram of Alftalat 3352 by gRP-HPLC on a C_{18} stationary phase (125×4.6 mm I.D., 5 μm particles) at 40°C using gradient system II. (a) ELSD, (b) UV detection at 230 nm; for details see Section 2.

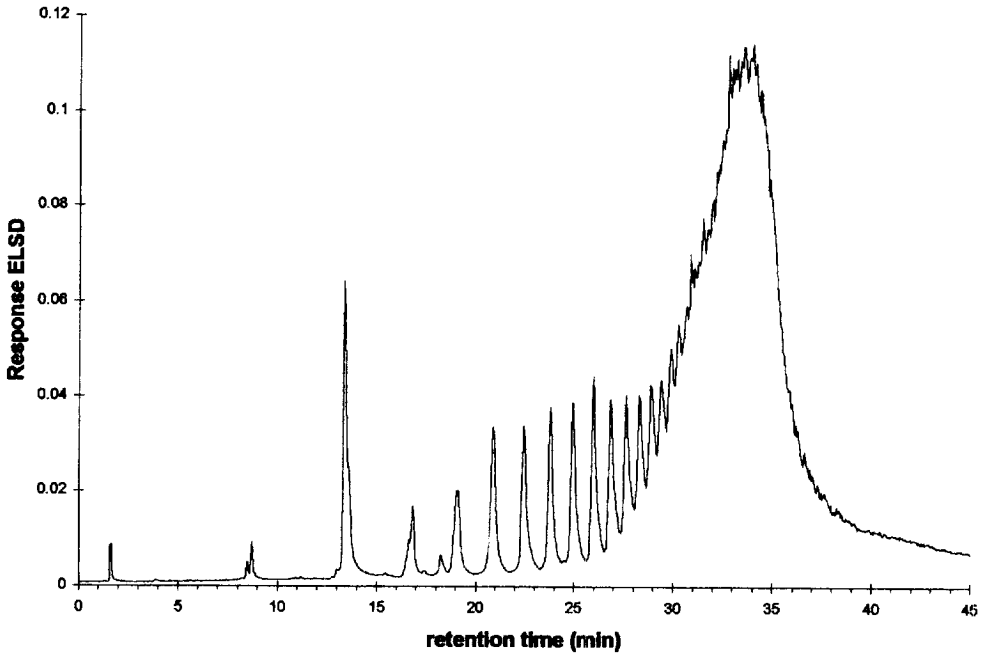

Fig. 6. Chromatogram of Alftalat 3352 by gradient RP-HPLC on a C_8 matrix (125×4.6 mm I.D., 5 μm particles) at ambient temperature using gradient system III; signal monitoring by ELSD.

measured by SEC based on polystyrene calibration. In addition cyclic oligomeric structures formed between terephthalic acid and neopentylglycol were observed, which in most cases do not occur as individual signals but coincide with those from the linear homologues[2].

When either C_8 or C_{Phenyl} matrices are applied for separation of the four polyesters, no THF is required for complete elution of the whole amount of oligomers from the column, but unfortunately, the excellent separation seen on C_{18} phases almost completely disappeared as shown for Alftalat 3352. As can be deduced from Figs. 6 and 7 (ELSD traces), only a few oligomers were resolved, whereas more than 90% of the sample eluted as a broad and unresolved peak similar to the patterns usually obtained by SEC.

4. Discussion

As can be concluded from the SEC data (Table 4), a more or less broad oligomer distribution has to be taken into account, which makes high demands on separation into individual oligomers for the distinction of different polyester samples on the base of their chromatographic fingerprints. Due to the participation of terephthalic and isophthalic acid moieties, signal monitoring can be done by UV detection. Nevertheless, the marked UV mismatch, i.e., the gradual increase of the baseline with increasing amounts of THF in the mobile phase causes a strong impairment of "pattern recognition" using the chromatographic fingerprint, in particular in the higher-M_r range. For this reason, ELSD was used as a suitable alternative detection method, which was already successfully applied to underivatised polyether samples [8–12]. Although the investigated samples possess relatively polar ester groups, the overall hydrophobicity of the aromatic as well as aliphatic structural moieties exerts a dominating influence on solute–stationary phase interactions. As a consequence, mobile phases with strong eluotropic properties are required for complete elution of all sample constituents, in particular from highly hydrophobic materials, such as, e.g., C_{18} matrices.

[2] The results from the LC–MS investigations will be published separately.

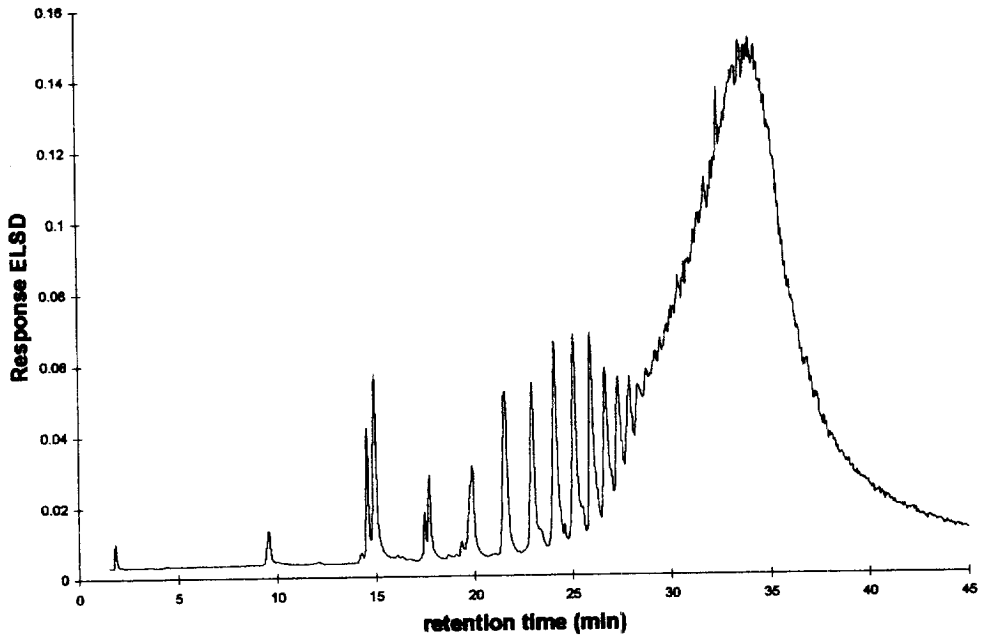

Fig. 7. Chromatogram of Alftalat 3352 by gradient RP-HPLC on a C_{Phenyl} matrix (125×4.6 mm I.D., 7 μm particles) at ambient temperature using gradient system III; signal monitoring by ELSD.

As shown with unpolar poly(butylene glycol) (PBG) samples, acetonitrile, although in most cases being a stronger eluent than methanol, only effected elution of low-M_r sample constituents from C_{18} stationary phases, whereas in contrast, the protic solvent affords elution of more than twice the number of oligomers [8]. This beneficial effect on sample elution, which is still much more marked with ethanol and 2-propanol, was ascribed to a more pronounced solvation of the ether oxygens by formation of hydrogen bonds [9]. Therefore, the strong solute–matrix interactions were much more efficiently counterbalanced by the protic solvents compared with acetonitrile as the organic modifier. In contrast to alcohols, possessing both "donor" and "acceptor" properties, the aprotic acetonitrile has only "acceptor" properties and thus is unable to interact with ether groups by hydrogen bonding. For this reason, the same behaviour has to be taken into account when acetonitrile is used as the only organic modifier for RP-HPLC of polyesters. Unfortunately, methanol, ethanol and 2-propanol, all capable of hydrogen bond formation, cannot be used due to either low solubility of the used polyesters in methanol and ethanol or the relatively high column backpressure of 2-propanol. As seen with hydrophobic PBG, the low-M_r oligomers are more efficiently separated from each other than the corresponding strongly polar poly(ethylene glycol) (PEG) oligomers [8], which is ascribed to more pronounced hydrophobic interactions of the tetramethylene bridges with unpolar stationary phases compared with the dimethylene units in PEG. These interactions are so strong that only solvents capable of hydrogen bond formation, such as alcohols, effect complete elution of the whole amount of oligomers from the column matrix. However in contrast to the good separation of low-M_r PBGs, signals of high-M_r oligomers merge into a broad and unresolved peak envelope when protic eluents are used [9] and thus raising the question if a more or less marked participation of a SEC mechanism may be involved.

The surprising observation that the hydrophobic PBGs are more efficiently separated on a less polar C_4 stationary phase with the aprotic solvent acetonitrile as the organic modifier still yielding sufficient solute–matrix interactions for excellent oligomer separation [11], prompted us to use stationary phases

of medium-to-low polarity, such as C_8 and C_{Phenyl} columns, respectively, for our initial trials to separate polyesters into a great number of oligomers. Additionally, we speculated on possible $\pi-\pi$ interactions between the aromatic moieties in the solute molecules and those of the C_{Phenyl} column matrix, which might also be exploited for oligomer resolution. Unfortunately, the desired beneficial effect of the two less polar C_8 and C_{Phenyl} matrices was not observed and resolution of only a few low-M_r oligomers was effected on both columns, the bulk amount of polyester molecules being eluted as a broad and unresolved signal envelope (see ELSD traces in Figs. 6 and 7). For this reason, it is assumed that in the region of bulk polyester elution, solute matrix interactions are very low and oligomers will be more or less eluted according to their M_r. At first sight, it may be a reasonable assumption to postulate a SEC-like separation mechanism in this elution region. This explanation is comparable to the observation of Noguchi et al. [13] who provided evidence for a SEC mechanism for separation of PEG on a vinyl alcohol coplymer even with water as the mobile phase. However, it should be taken into account that for sufficient separation, the high-M_r sample amounts would eventually require a much higher pore diameter than 100 Å as used throughout the whole study. For this reason, a precipitation-based mechanism cannot be completely ruled out under the used experimental conditions. This argument is supported by the observation that elution of the high-M_r sample constituents takes place in a volume of about 15 ml, which is markedly lower compared with the total pore volume of the column.

The observation that only a small fraction of polyester oligomers are eluted from the C_{18} stationary phase using gradient system III lacking THF as the co-solvent (results not shown) is similar to the chromatographic behaviour of the hydrophobic PBGs and the total amount of polyester sample constituents is only "released" from the stationary phase when matrices with substantially lower hydrophobicity, such as C_8 and C_{Phenyl}, were used. The fact that gradual admixture of the "good" solvent THF up to a final concentration of 20% effected either complete elution or excellent separation of oligomers on a C_{18} column is in accordance with a marked effect of solubility on the retention properties. Nevertheless, a precipitation–redissolution mechanism, preferably observed for high-M_r samples far above >10 000 Da and termed as "high-performance precipitation liquid chromatography" (HPPLC) by Glöckner and coworkers [14–21,24] as well as by Schultz and coworkers [22,23] cannot be excluded. Separation primarily based on HPPLC is characterised by a shift of solute peaks to higher retention times with increasing sample size. However, such an effect will only be easily recognisable when a polymer sample preferably elutes in a single band, whereas in contrast, it may be markedly more difficult in the case of well-resolved oligomers, in which the sample splits into a multitude of individual components. It is noteworthy that the recently introduced GPEC technique [6,7] also exploits precipitation of oligomers and subsequent separation according to solubility and M_r by increasing the amount of "good" solvent.

However, despite the poor solubility of the samples at the starting conditions of gradient separation, which for this reason, meets to some extent conditions similar to "sudden transient gradients", as described by Glöckner et al. [25–28], the "good" solvent THF is expected to prevent sudden precipitation of the sample at the column head, although this may not hold true for high-M_r samples much greater than 10 000 Da.

A possible explanation of an almost complete "trapping" of the samples has to consider the fact that the unpolar polyester oligomers are interacting with the C_{18} column matrix in such a strong way, that they undergo "dissolution" within the network of the highly hydrophobic octadecylsilyl chains. Unfortunately, acetonitrile, although exhibiting excellent eluotropic properties, is unable to counterbalance these strong interactions when it is used as organic modifier without a "solubility-enhancing" co-solvent, such as THF. Due to the general observation that THF, although possessing only "acceptor" properties, proved as a very strong solvent for a wide variety of polymer samples largely differing in either polarity or molecular mass, it was used as a co-solvent in combination with acetonitrile. Admixture of THF as well as to change its concentration during the chromatographic run is of fundamental importance, because only a few low-M_r oligomers are eluted from the C_{18} column, when it is omitted from the mobile phase (results not shown).

Furthermore, due to the fact that the polyester samples still contain carboxyl endgroups, addition of

a final concentration of 0.5% acetic acid to the mobile phase is required. This measure effects protonation of residual silanols and thus efficiently contributes to either minimization of silanophilic interactions with the column matrix or improvement of peak shape. In addition, the "solubility-enhancing" effect at elevated temperature leading to "release" of a markedly higher number of PBG oligomers by use of the aprotic acetonitrile, as reported by Rissler et al. [8], was also exploited and chromatography was performed at 40°C. However, despite these modifications, the sample constituents with highest M_r are not further separated into individual oligomers. The observation that they elute in a broad and unresolved signal envelope from the column matrix can be explained by strongly weakened solute–stationary phase interactions. These could at first sight be ascribed to a more or less marked size exclusion separation mechanism. Nevertheless, as stated above for separation on C_8 and C_{Phenyl} matrices, precipitation of those sample constituents cannot be neglected.

The observed excellent separation of a large number of oligomers offers great perspectives for the use in combination with on-line MS techniques for individual characterisation according to either CCD or FTD. As mentioned in Section 3, the APCI technique has a limited application range of only about M_r 2500 and thus cannot be exploited for high-M_r samples. As an alternative technique MALDI–TOF-MS should provide more detailed data up to M_r values of about 10 000 [6], but as seen in recent investigations with resins based on bisphenol-A-diglycidylether, structural information strongly decreases even at M_r values of ca. 8000 Da [29]. Nevertheless, it is expected that liquid chromatography on-line coupled to the (ESI–TOF-MS) technique as used by Prokai and Simonsick [30] and Nielen [31] in SEC of terephthalic acid-neopentylglycol polyesters, will offer a powerful tool for future applications in the field of oligomer as well as polymer characterisation.

5. Conclusions

Excellent separation of polyester samples all having M_w values exceeding 10 000 Da was accomplished on a C_{18} stationary phase using gradient elution with a ternary mobile phase of acetonitrile, water, THF and aqueous acetic acid and detection by measurement of either UV and ELSD responses. In one case about sixty individual oligomer signals were recognisable. In contrast, less polar column matrices, such as C_8 and C_{Phenyl} materials, did not effect separation into a multitude of individual oligomers, as seen on the substantially more hydrophobic C_{18} matrix. Therefore, it is postulated that the strong interactions between the unpolar polyester sample constituents and the hydrophobic stationary phase favours solubility of the oligomers within the network of octadecylsilyl substituents, which are only releasible from the column when THF, which proved to be a good solvent for polymer samples, was gradually admixed to the mobile phase up to a final concentration of 20%. To our knowledge this is the first report describing separation of polyesters into a large number of individual oligomers, which can be exploited for further characterisation with respect to CCD and FTD by means of mass spectrometry on-line coupled to liquid chromatography.

Acknowledgments

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