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Characterization of low-molar-mass polymers by gradient polymer elution chromatography
I. Practical parameters and applications of the analysis of polyester resins under reversed phase conditions

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Abstract

The application of gradient elution techniques such as gradient polymer elution chromatography (GPEC) for the characterization of low-molar-mass polymers has been known for a long time. Until now, however, practical applications have been lacking. The objective of this study was to find out to what extent GPEC can be useful to provide information on the (micro)structure of these materials. The influence of some practical parameters in GPEC under reversed-phase conditions with tetrahydrofuran and water as the solvent–non-solvent combination, was investigated using a co-polyester resin. A gradient steepness less than 1%/min hardly improves the separation at the cost of a much longer analysis time. Increasing the column length or temperature only significantly improve the separation in the low-molar-mass part of the chromatogram. A sample load of up to 1 mg does not influence the separation. This indicates that separation is probably dominated by sorption (adsorption and/or partitioning) rather than solubility effects. Injection volumes exceeding 10 μl give rise to additional peak broadening due to a sample solvent effect. For different polyesters, an almost linear dependence was found between the reciprocal square root of the molar mass and the percentage of solvent at the point of elution of an oligomer. This dependence was used to calculate average molar masses for one polyester. The M_w thus calculated, agreed well with absolute methods. The oligomer distribution obtained using GPEC was in excellent agreement with the theoretical distribution, thus demonstrating the feasibility of GPEC for providing information on reaction kinetics. By comparison of GPEC results for two co-polyester resins, evidence for differences in chemical composition distribution could be obtained.

Keywords: Gradient elution; Polymers; Adipic acid polyesters; Isophthalic acid polyesters; Bisphenol-A, dipropoxylated, polyesters; Polyesters

1. Introduction

The growing complexity of new polymeric materials which is inherent to the increasing requirements on their properties, has led to a considerable interest in the separation of polymers by non-exclusion liquid chromatographic techniques. The chromatographic behaviour of polymers can be divided into two different modes; exclusion and sorption [1,2], which includes both adsorption and partitioning. Under sorption conditions, retention depends on both chemical composition and molar mass. The applica-

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tion of chromatography under sorption conditions is especially useful for the characterization of copolymers according to their chemical composition distribution [3–10], the separation of polymer blends [11–13] and for the fingerprinting of resins [14–20].

For chromatography under sorption conditions, it is often observed that the chromatographic retention factor, k', increases exponentially with the degree of polymerisation [3,21] (the Martin rule). Consequently, together with the fact that synthetic polymers mostly have polydispersity values far exceeding unity, the application of chromatography under sorption conditions is usually involved with the use of gradient elution techniques. Due to the limited solubility of polymers, the starting eluent in gradient elution often is a non-solvent for at least part of the injected polymer. Thus, retention is governed by three parameters; exclusion, solubility effects and sorption effects. Because existing names such as high-performance precipitation liquid chromatography (HPPLC) [22] or liquid adsorption chromatography (LAC) [6] only refer to a part of the total separation mechanism, we introduced the more generally applicable term, gradient polymer elution chromatography (GPEC) [23,24].

It is well established that gradient elution techniques can be very useful for the detailed characterization of synthetic resins ("fingerprinting") [14–20]. The practical applications however seem to be lacking and due to its wide acceptance, analysis under exclusion conditions (SEC) often remains the method of choice.

Some time ago, we started to study the applicability of GPEC for the characterization of low-molar-mass polymers. The primary goal of our work is to find out to what extent GPEC can be useful to provide information on the (micro)structure and composition of these materials that cannot, or cannot easily, be obtained by other methods such as SEC and nuclear magnetic resonance spectroscopy (NMR). To get a better insight into the working principle of GPEC, we also study the separation mechanism and the contribution of the three mentioned separation parameters. The work presented here, is the first of a series of papers in which the most important results of our studies will be reported.

The potential applicability of gradient elution techniques for polyester resins has been demonstrated by several authors [14–16,18,20]. In most cases, especially for reasons of simplicity, reversed-phase systems were used. This paper has two main objectives. Firstly, we wanted to examine the influence of practical conditions, in order to optimize the separation result for this type of resin on reversed-phase systems. Thus, the effects of some practical parameters such as loadability, injection volume, gradient shape, temperature and (long term) reproducibility were examined. From these experiments, some qualitative information on the retention mechanism was obtained.

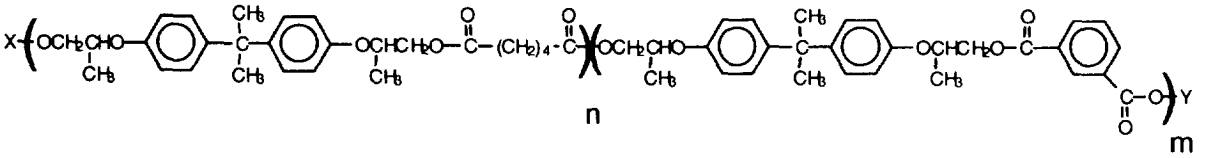
Secondly, we are interested to see to what extent GPEC under reversed-phase conditions can provide insight into the compositional and structural differences of polyester resins. Therefore, for a specific GPEC system, the results of two (co)polyester resins consisting of adipic acid, isophthalic acid and dipropoxylated bisphenol-A, are evaluated. Furthermore, the applicability of GPEC for providing information on molar mass and reaction kinetics is investigated. This will clearly demonstrate the power of GPEC for providing detailed and sometimes unique information on the structure of low-molar-mass polymers, in a relatively fast and easy way.

Future work will focus on separation mechanisms and on the application of GPEC to crystalline polyesters and other types of low-molar-mass polymers.

2. Experimental

2.1. Polymer samples

The polymer samples used were laboratory-made polyester resins. Samples PE1, PE2 and PE3 are co-polyesters consisting of adipic acid (A), isophthalic acid (I) and dipropoxylated bisphenol-A (D). The polymer structure of these resins is given in Scheme 1. Sample PE4 is a homopolyester based on adipic acid and di-propoxylated bisphenol-A and sample PE5 is a homopolyester consisting of maleic acid (M) and di-propoxylated bisphenol-A.



Scheme 1. Polymer structure of the resin.

2.2. Characterization of the polyester samples

Polystyrene equivalent molar masses determined by SEC, average chemical compositions measured by NMR and end group compositions determined by titrimetric analysis are given in Table 1.

The equipment used for SEC measurements consisted of an isocratic pump Model 610, a WISP type 715, a column thermostat, type TCM, which was set at 40°C, and a differential refractometer type 410, all from Waters (Milford, MA, USA), a UV detector type 975 from Jasco (Tokyo, Japan), which was set at 254 nm and a Baseline-815 data system from Waters. A set of four Shodex (Showa Denko, Tokyo, Japan) KF columns (300×8 mm) in series was used (KF804, KF803, KF802.5, KF802 and a guard column type 800P). Tetrahydrofuran (THF) with 1% (v/v) acetic acid was used as the mobile phase at a flow-rate of 1.5 ml/min. The samples (200 μl) consisted of 0.1% solutions in THF. Toluene was added as an internal marker. The columns were calibrated using narrow standard polystyrenes from Waters with molar masses between 418 and 240 000. The reproducibility of the "polystyrene equivalent molar masses" was approximately ±100 (standard deviation).

^{1}H NMR spectra were recorded on a Bruker AC300 (300 MHz) spectrometer. The chemical shifts were determined relative to tetramethylsilane. Spectra were obtained in C^2HCl_3 at a sample concentration of 60 mg/ml and were recorded under quantitative conditions. For the determination of the molar fractions of the different monomeric units, integrals were taken between ^{1}H chemical shift values: δ 7.2–6.5 ppm (D), 8.4–7.9 ppm (I), 2.6–2.0 ppm (A) and 6.3–6.1 ppm (M). The standard deviation was determined to be ±0.01 (absolute). The degree of propoxylation, which is defined as the ratio of the number of propoxy groups over the number of bisphenol-A units, was calculated from the ratio of the integrals between δ 6.0–3.0 ppm and 7.2–6.5 ppm. The standard deviation was ±0.1 (absolute).

The acid number was determined by a potentiometric titration, using a potentiometer, model AT300 from Kyoto Electronic. A 300-mg amount of polyester was dissolved in a mixture consisting of 70 ml of THF and 30 ml of methanol. The solution was titrated with 0.01 *M* potassium hydroxide dissolved

Table 1
Polystyrene equivalent molar masses, end group compositions and average chemical compositions of the investigated polyesters

Sample	SEC			Titrations:	NMR			
	Ps equivalent molar masses			Acid number (mg KOH/g)	Molar fractions			Degree of propoxylation
	M_n	M_w	MMD[a]		A	I	D	
PE1	3 500	7 900	2.3	20	0.12	0.37	0.50	2.4
PE2	3 400	8 200	2.4	24	0.12	0.38	0.50	2.2
PE3	3 300	7 900	2.4	27	0.15	0.35	0.50	2.0
PE4	3 800	8 700	2.3	20	0.51	0	0.49	2.2
PE5	3 900	13 700	3.5	13	0.45	(maleic acid)	0.55	2.0

[a] Molar Mass Distribution.

Table 2
Average molar masses for sample PE1

	absolute[a]	GPEC
M_n	3090±5%[b]	2630±0.4%
M_w	4900±10%	4790±0.6%

[a] Vapour pressure osmometry (M_n) and light scattering (M_w).
[b] Relative standard deviation.

in methanol. The relative standard deviation was approximately ±10% KOH/g.

For sample PE1, the number-average molar mass was also determined by vapour pressure osmometry, using a Mechrolab vapour pressure osmometer (see Table 2). Measurements were performed in chloroform. The absolute weight average molar mass was determined by gel permeation chromatography–low-angle laser light scattering (GPC–LALLS), using a Chromatrix LALLS detector. In this case, 1% (w/w) solutions (80 μl) in chloroform were injected.

2.3. Solvents

The solvents used were water (Lichrosolv quality from Merck, Darmstadt, Germany) and THF (HPLC-grade from Rathburn, Brunschwig Chemie, Amsterdam, Netherlands). To both solvents, 200 μl of acetic acid (Pro Analysi quality from Merck) were added per litre. During the experiments the solvents were constantly sparged with helium (20 ml/min). All solvent mixtures were made by volumetric mixing by the HPLC pump, no premixes were used.

2.4. HPLC column and equipment

The columns used were three NovaPak C_{18} columns (Waters, d_p=4 mm, pore size 60 Å, 75×3.9 mm, 150×3.9 mm and 300×3.9 mm, plate count/m ca. 80 000). All HPLC experiments were performed using a Waters 600E 4 solvent gradient pump and a 717 autosampler from Waters. The detector was a Waters variable wavelength detector, type 484, which was set at 277 nm. The column temperature was controlled using a Mistral type thermostat from Spark-Holland (Emmen, Netherlands), which was set at 35°C unless indicated otherwise. Chromatograms were recorded using the Baseline-815 system from Waters. The eluent flow for all experiments was established at 1.0 ml/min.

2.5. Strategy

Gradient elution was performed as follows. After running each gradient, the system was reset to initial conditions in 1 min, followed by pumping fourteen column volumes of the starting eluent composition to re-equilibrate the column. Prior to the analysis of the samples, two blank gradients were run. All gradients were started at the moment of injection. The gradient performance of the pump (linearity and reproducibility) was checked by running gradients from methanol to methanol+0.1% (v/v) acetone. The system hold-up volume ("dwell volume") was also determined from these experiments and was found to be equal to 4.0 ml. The column dead volume was taken to be equal to the elution volume of the maximum of the system disturbance caused by the injection of 10 μl of THF.

3. Results and discussion

In the reversed-phase chromatography of low-molar-mass species, mostly THF, acetonitrile (ACN) and methanol (MeOH) in combination with water, are used to control selectivity [25]. Due to the different natures of these organic modifiers, which give rise to different types of interaction, almost any desired separation can be obtained by just using these eluents or eluent combinations. The solubility of polymers is mostly restricted to only a few different solvents. Since the high-molar-mass parts of the polyesters used in this study are not soluble in MeOH and ACN, only THF can be used as a strong solvent for GPEC experiments under reversed-phase conditions. Because the eluent strength of MeOH, being the weakest organic modifier in this case, also proved to be too strong to retain the low-molar-mass parts of the polyester resins on a C_{18} column, water has to be used as the non-solvent.

Several gradient profiles using this reversed-phase (RP) C_{18} stationary phase–mobile phase combination were tested. In Fig. 1a an example is given for sample PE1, using a linear gradient with a steepness of 1%/min. Up to twenty oligomers can be resolved

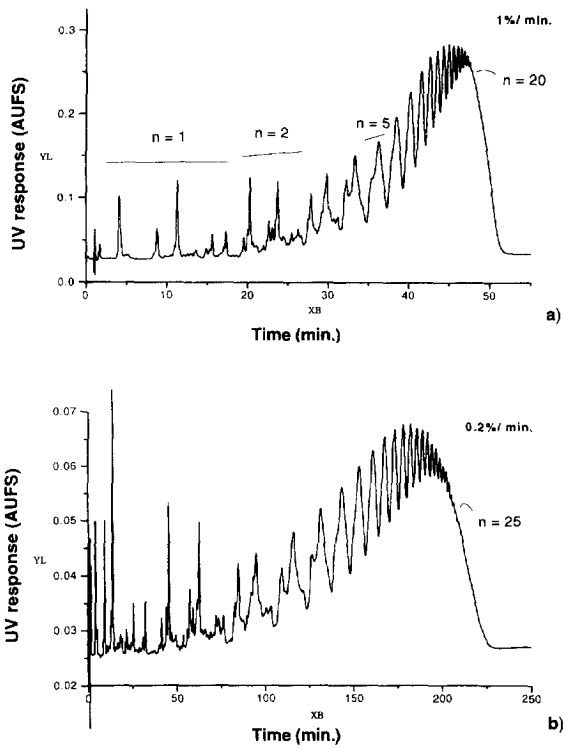


Fig. 1. Effect of gradient speed. (a) 1%-Solvent/min, (b) 0.2%-Solvent/min. Sample: PE1 (40 mg/ml), column. Novapak C_{18} (15 cm), eluent: THF–water (35 : 65) to (85 : 15), flow: 1.0 ml/min, temperature: 35°C, injection: 10 μl, detection: UV at 277 nm. n = oligomer number.

in this way, whereas in the very low-molar-mass part of the chromatogram, an additional separation according to chemical composition within each oligomer is realized. The peak assignment will be discussed later. The use of steeper gradients causes a significant decrease in the total number of oligomers that can be separated. For instance, for a gradient steepness of 3%/min, only twelve oligomers are resolved. When extremely slow gradients are applied, a slight increase in oligomer separation is observed at the cost of much longer analysis times. An example is shown in Fig. 1b, where a steepness of 0.2%/min is used. Therefore, for linear gradients, a steepness of 1%/min proved to be an acceptable compromise between resolution and analysis time. Slightly convex shaped gradients within the same analysis time, consisting of two or three linear segments, developed during further optimization, can provide in some cases additional resolution improvement in the high-molar-mass part of the chromatogram. An example can be seen in Fig. 7. To our experience, the use of continuous convex gradients, instead of these two or three-segment convex gradients, provides no further improvement of resolution, which is in accordance with the findings of other workers [26].

It is interesting to check the influence of column length for this kind of oligomer separation. Since the eluent composition at the start of the GPEC analysis, 35% THF in water, is a non-solvent for the polyester sample, solubility effects, next to sorption, might contribute to the total separation mechanism. Therefore the effect of column length is not obvious [27]. In a case where the solubility could influence the separation by GPEC, a longer column might cause more dispersion effects, thus giving rise to broader peaks and decreasing the resolution. A case where solubility and sorption both influence the separation has also been studied for polystyrene by other workers [28].

In order to keep gradient elution experiments performed on columns that differ in geometry comparable, it is necessary to keep the average retention factors of the components constant. This parameter is given by [25]

$$k_{av} = (t_g F / 1.15\, V_m\, \Delta\varphi S) \quad (1)$$

in which t_g is the gradient time (min), F is flow-rate (ml/min), V_m is the column dead volume, $\Delta\varphi$ is the change in the volume fraction of the strong solvent during the gradient and S is an isocratic parameter determined by the strong solvent and the sample compound. Since S is independent of column geometry and $\Delta\varphi$, which is determined by the starting and end conditions, is not changed, it is obvious that the term $t_g F/V_m$ has to be kept constant. The use of a column with another length therefore means that the gradient time, t_g, has to be changed in accordance, while keeping the flow-rate constant. In Fig. 2, the results for PE1 on a 7.5-cm, 15 cm and a 30-cm column are compared.

It is obvious that an increase in column length in this case causes a significant improvement in the resolution in the low-molar-mass part of the chromatogram. In the high-molar-mass part, the res-

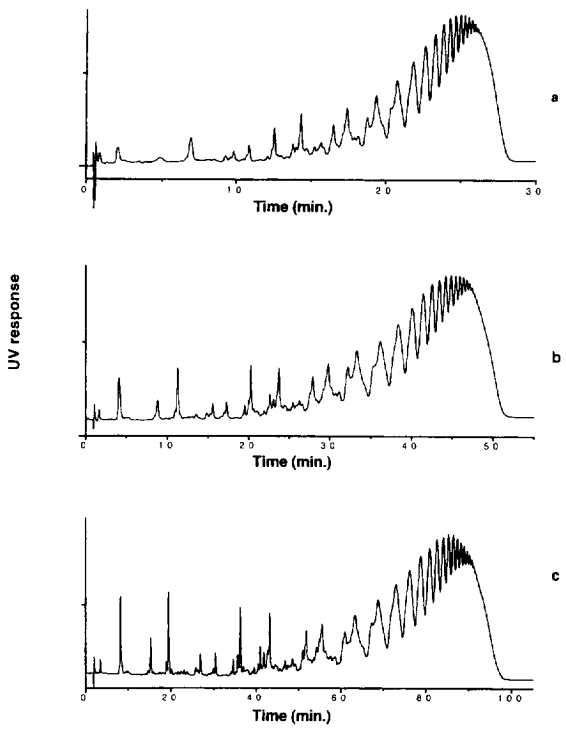


Fig. 2. Effect of column length. (a) 7.5 cm, (b) 15 cm, (c) 30 cm. Sample: PE1 (40 mg/ml), eluent: THF–water (35 : 65) to (85 : 15) (a: 2%/min, b: 1%/min, c: 0.5%/min), flow: 1.0 ml/min, temperature: 35°C, injection: 10 μl, detection: UV at 277 nm.

olution enhancement is only minor. When using a 30-cm column instead of a 7.5 cm, nineteen instead of twenty one oligomers can be resolved. This is in accordance with the findings of other workers [27,29], but the cause is not absolutely clear. Since K_{av} was kept constant by the increase of t_g in our experiments, the counterbalance of the increase in plate number by a decrease in K_{av}, as mentioned in [29], provides no explanation. The S value of Eq. (1), however, is known to increase with molar mass [30], thus giving rise to very high values for high-molar-mass substances. According to Eq. (1), this also leads to very low values of K_{av}, which means that during migration the distribution into the stationary phase is minor. This might explain the rather limited influence of column length in the high-molar-mass part. Furthermore, from a comparison with the low-molar-mass part of the chromatogram, it is obvious that the high-molar-mass peaks are composite peaks, consisting of several different components (see also discussion on peak assignment). In such a case, the apparent band width will be the result of two effects; the width of each band for a single species and the width of the composite band, as determined by differences in retention for each species. To a first approximation, the apparent width for a high-molar-mass peak can be given by:

$$W^2 = W_c^2 + W_o \tag{2}$$

in which W_c represents the width of an individual species and W_o is the width, determined by the retention time difference between the first and last component eluting in this band. An increase in column length results in a decrease of W_c, which can be observed in the low-molar-mass part of the chromatogram. For high-molar-mass bands, however, W_c becomes so small that W will be mainly determined by W_o, thus causing no further improvement in resolution. This effect has also been recognized by other workers [27] and provides another possible explanation for the limited influence of column length. The results, however, indicate that sorption effects are probably dominant in the total separation mechanism.

As already reported by Rissler and Fuchslueger [19], this also implies that the investigation of the effect of the nature of the organic modifier on resolution would be highly recommendable. Although MeOH or ACN cannot be used as "strong" solvents for the polyester investigated here, they can be used as intermediate eluents to modify the separation. In that case at least ternary systems, consisting of water, an intermediate and THF, will have to be used. The use of such systems and further investigations of the role of solubility effects in the separation of polyester resins will be the subject of future publications.

The influence of temperature can be observed from Fig. 3. An increase in temperature causes the oligomer distribution to shift to lower retention times. Presumably this may be due to a decrease in sorption. Furthermore, at higher temperatures, resolution increases, especially in the first part of the chromatogram. This is probably due to the increase in diffusion coefficients, giving rise to faster mass transfer and therefore a decrease in peak broadening. The rather limited resolution enhancement in the

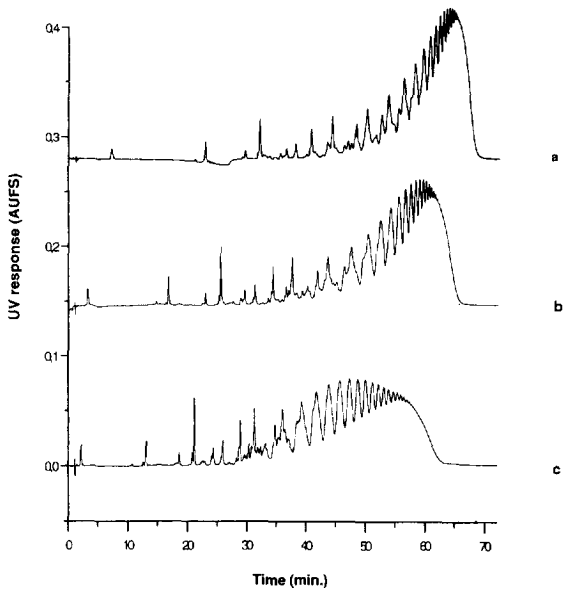


Fig. 3. Effect of temperature. (a) 10°C, (b) 40°C, (c) 70°C. Sample: PE1 (40 mg/ml), column: Novapak C_{18} (15 cm), eluent: THF–water (25 : 75) to (90 : 10) (0 to 65 min), flow: 1.0 ml/min, injection: 10 μl, detection: UV at 277 nm.

high-molar-mass part can, as is the case for column length, presumably be ascribed to W_0 (Eq. (2)) which dominates the resolution for the later-eluting bands. The calculation of the number of theoretical plates makes no sense in the case of gradient elution. Peak widths, however, are known to be roughly constant during gradient elution. Therefore, peak widths for the peak caused by the product "DI" (see Fig. 5) were calculated. The values obtained were 0.24 min, 0.17 min and 0.10 min at 10°C, 40°C and 70°C, respectively, thus further illustrating the influence of temperature on peak broadening processes.

The observed increase in resolution is much less than the effects earlier reported for aliphatic polyether-type oligomers on conventional porous supports [31] and for a water-soluble resin on nonporous supports [32]. The cause of this difference is rather unclear and may be effected by various things. The separation mechanism may be different in the respective cases. Furthermore, conformational changes caused by temperature variation which might sometimes influence the separation [33,34], can be different for different types of polymers. Finally, it is not sure whether experimental conditions, e.g. the method of temperature control, are completely comparable for all cases. Therefore, further study of different polymer types under comparable conditions is needed to get further insight into the effect of temperature on oligomer separations.

The influence of sample load was studied by injecting different concentrations of sample PE1, while keeping the injection volume constant. These experiments showed that no effect could be observed up to an injected mass of 1000 μg (data not shown). This observation further supports the idea that sorption effects are dominant in the chromatographic process. If the separation was mainly determined by solubility effects, a clear increase of retention with increasing sample load should have been observed [3,28]. The high loadability can be contributed to the relatively low-molar-mass of the investigated polymer. This reduces the possibility of problems due to high viscosity, such as "viscous fingering", occurring. Furthermore, due to the elution of the polyester over a wide retention range, the momentary sample load will also be lowered to a great extent, thus contributing to a high allowable sample load.

The effect of injection volume was checked by injecting approximately constant amounts of 100 μg in different volumes. As can be seen from Fig. 4, up to an injection volume of 20 μl, no additional peak broadening can be observed, whereas for an injection volume of 50 μl, the lowest molar mass peaks are seriously distorted. This so-called sample–solvent effect is well known in chromatography and can be explained by the difference in solvent strength between polymer solvent and eluent [25]. Increasing injection volumes also causes the peak at 1.0 min to increase significantly. Comparison with injections of THF revealed that this peak is solely caused by the solvent. Despite the large injection volumes, no breakthrough occurred, an effect that is frequently observed in the chromatography of polymers [35,36]. It causes part of the sample to elute unretained, due to insufficient mixing of the injection plug with the eluent.

To suppress peak broadening, injection volumes should be as low as possible and, in this case, should not exceed 10 μl, which is approximately 1% of the total column volume.

The obtained separation results by GPEC can be

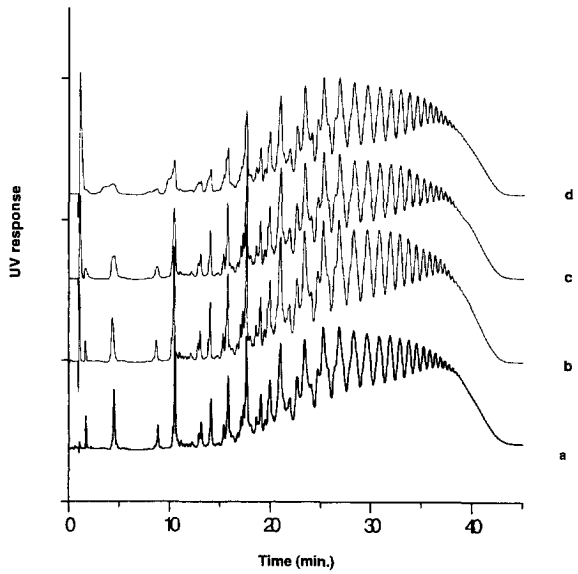


Fig. 4. Effect of injection volume. (a) 1 μl, (b) 10 μl, (c) 20 μl, (d) 50 μl. Sample: PE1, injection solvent: THF, injected amount: 100 μg, eluent: THF–water (35 : 65) to (60 : 40) (0 to 14 min), (60 : 40) to (68 : 32) (14 to 20 min), (68 : 32) to (85 : 15) (20 to 43 min), flow: 1.0 ml/min, temperature: 35°C, detection: UV at 277 nm.

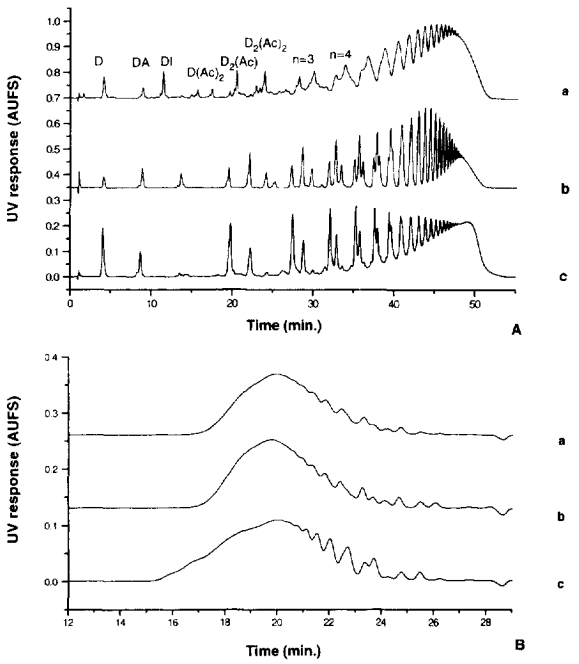


Fig. 5. Comparison between GPEC (A) and SEC (B). a: PE1, b: PE4, c: PE5. GPEC: sample concentration: 40 mg/ml, column: NovaPak C_{18} (15 cm), eluent: THF–water (35 : 85) to (85 : 15) (0 to 50 min), flow: 1.0 ml/min, temperature: 35°C, injection: 10 μl, detection: UV at 277 nm. D = diol, A = adipic acid, I = isophthalic acid, Ac = acid. SEC: concentration: 1.5 mg/ml, columns: Shodex KF804 (10^4 Å) KF803 (10^3 Å), KF802.5 (500 Å), KF802 [100 Å (in series)], flow 1.5 ml/min, injection 200 μl, detection: UV at 254 nm.

used for fingerprinting purposes. GPEC and SEC chromatograms for samples PE1, PE4 and PE5 are shown in Fig. 5a and Fig. 5b, respectively. Although the columns used for SEC were especially suited for relatively low-molar-mass polymers, it is obvious that GPEC can provide much more detailed information on the composition of these resins. A larger number of peaks can be observed in the GPEC chromatogram for sample PE1 compared to those of PE4 and PE5. This is caused by the fact that PE1 is a copolyester containing two different di-acids. Consequently, the number of different products that are formed during synthesis is larger.

Peak assignment for samples PE4 and PE5 is rather straightforward. In the low-molar-mass part of the chromatograms, repeating patterns consisting of three peaks, can be recognized. From reversed-phase chromatography it is known that retention factors will increase with increasing molecular surface area [34]. For the polyesters used in this study, molecular surface area will be mainly determined by the number of diol units, since the molar mass of a diol monomer far exceeds that for both di-acids. It is therefore very probable that the observed repeating patterns is caused by oligomers with a certain number of repeating units, having respectively none, one and two acid end groups. Proof of this assumption was obtained by injection of the diol monomer and a product having mainly diol end groups.

Transformation of the acid end groups of PE1 into sodium salts, followed by extraction with water and injection of the water extract, proved that peaks at 9 and 11 min can be assigned to oligomers having one acid end group. Peaks between 13 and 18 min were shown to represent oligomers having two acid end groups. By comparing chromatograms of PE1 and PE4 it becomes clear that the peak at 9 min is due to the product diol-adipic acid, so the peak at 11 min is assigned to the oligomer, diol-isophthalic acid.

Due to the fact that no peaks (except for the unretained peak) are observed in the blank chromato-

gram, all peaks are known to result from the polyester itself. The use of "aged" THF sometimes resulted in the occurrence of small peaks, interfering with the low-molar-mass polyester peaks. Therefore, only fresh THF was used, thus avoiding this problem.

It can therefore be concluded that by GPEC under reversed-phase conditions, polyesters are mainly separated according to molar mass, whereas in the low-molar-mass part, a further separation with respect to chemical composition, such as end groups, occurs.

Since GPEC is frequently used for fingerprinting purposes, it is necessary that separation results are highly reproducible. For sample PE1, over a period of more than three years, we observed no significant differences in the low-molar-mass part of the chromatogram, although small retention shifts due to the use of new columns, necessitates injection of a reference sample in each analysis sequence. In the high-molar-mass part, however, sometimes small disturbances in the chromatograms occur, the cause of which has not been clarified yet. Duplication of the results for each sample therefore remains highly recommendable.

In order to understand the separation mechanism, it is useful to study the dependence between oligomer number (or molar mass) and retention time. Glöckner [37] has proven that the volume fraction of the non-solvent, ϕ_{NS}, at the cloudpoint of a polymer is related to the molar mass by the empirical equation:

$$100\phi_{NS} = C_1 + C_2 M^{-0.5} \quad (3)$$

in which C_1 and C_2 are constants, dependent on the solvent–non-solvent system and the temperature. Glöckner has also shown that for HPLC separations of polymers that are mainly based on solubility differences, molar mass effects can also be evaluated according to this equation. For relatively high-molar-mass polystyrenes it was proven that plots of the percentage solvent ($=100-100\varphi_{NS}$) at the point of elution of a certain molar mass and $M^{-0.5}$ were approximately linear [38]. To our knowledge, this equation has never been evaluated in the molar mass range of oligomers. It is therefore interesting to check whether it also holds for the separation of polyester oligomers, although sorption effects are probably dominant in the retention process.

The results of this evaluation for samples PE1, PE4 and PE5 are shown in Fig. 6. The gradient used for these experiments was started at a lower percentage solvent, to ensure that all products eluted in the gradient part of the chromatogram. Starting with

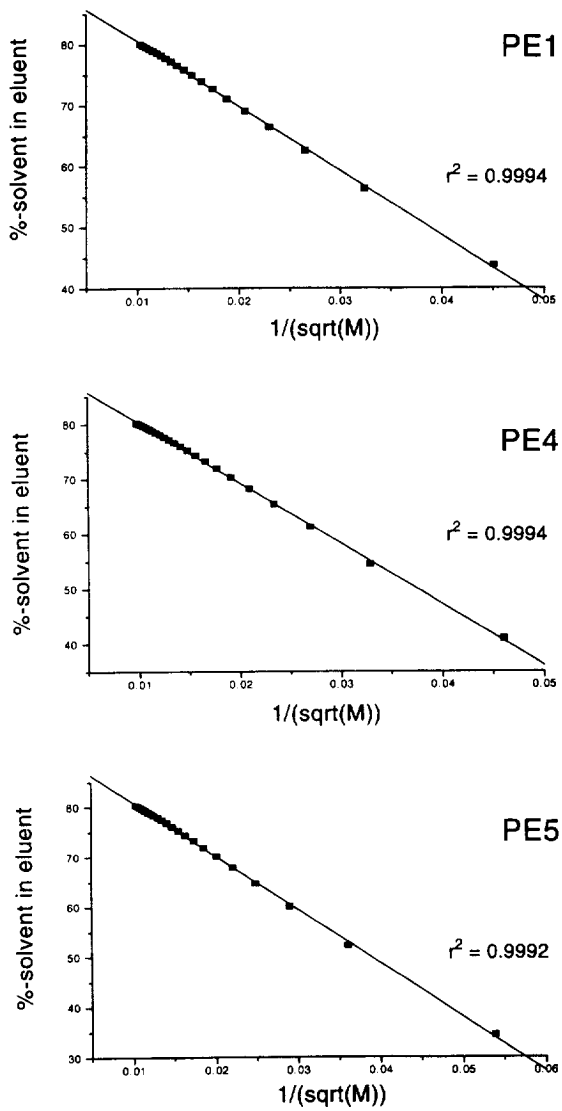


Fig. 6. Plots of % solvent versus $1/\sqrt{M}$ for three polyesters. Conditions: sample concentrations: 40 mg/ml, column: NovaPak C_{18} (15 cm), eluent: THF–water (25 : 75) to (90 : 10) (0 to 65 min), flow: 1.0 ml/min, temperature: 25°C, injection: 10 μl, detection: UV at 277 nm. r^2 = coefficient of regression.

oligomer number $n=6$, the molar mass of the peak was taken to be equal to the molar mass of the product having (n) diol units and (n) diacid units for samples PE1 and PE4 and to the molar mass of the product having (n) diol units and ($n-1$) diacid units for sample PE5. For the lower-molar-mass oligomers for which a distinct separation with respect to end groups can be observed, for PE1 and PE4 only the products having (n) diol units and (n) diacid units and for PE5 only the products having (n) diol units and ($n-1$) diacid units, were taken into account. For the molar mass of a di-acid unit in sample PE1, the weighted average was taken of the molar masses of adipic acid and isophthalic acid, based on their molar ratio.

It is easily recognized that for all three polyesters an almost linear dependence is found starting at an oligomer number of $n=1$, although the curves tend to be slightly sigmoidally shaped. For lower molar masses, a small but obvious deviation from this line occurs, whereas in the high-molar-mass area a slight curvature can be observed. The occurrence of a linear dependence can obviously also be found for the case where sorption effects dominate retention. It is therefore no evidence for a retention process governed by solubility. Further research into the extent to which the exact shape of plots such as those shown in Fig. 6 can give additional information on retention processes will be subject of future publications.

When results of cloud point titrations are compared with the percentage solvent at which the last part of the polyester elutes, φ_e, approximately the same values are found. For sample PE1 for instance, a value of 80% THF is found for the cloud point of a 40 mg/ml sample at 35°C, whereas φ_e is 81%. Obviously, a correspondence between cloud point and φ_e does not necessarily mean a retention process that is governed by solubility effects, which is accordance with the findings of other workers [28]. It must be kept in mind, however, that for relatively low-molar-mass polymers, the cloud point is strongly dependent on the initial concentration. Since the actual concentration at the end of the column will be significantly lower (due to chromatographic dissolution) compared to the initially injected concentration, a direct comparison between cloud point and chromatographic value is difficult.

For very low-molar-mass polymers that can be completely separated into oligomers, it is easy to calculate absolute molar masses, provided that the detector response factors of the individual oligomers are known or that these are approximately the same. Molar masses of the resins used in this study, however, are too high to obtain complete resolution of all oligomers. For sample PE1, we tried to determine whether the observed dependence of φ_e vs. $M^{-0.5}$ could be useful in this case. This sample was chosen since the absolute average molar masses were known from absolute methods.

Here, φ_e vs. $M^{-0.5}$ was described by a new first order polynomial, starting at oligomer number 3, to cancel out the observed deviation in the low-molar-mass part. From this fit, retention times of the oligomers in the high-molar-mass range of the chromatogram, up to $n=50$, were calculated. Using these retention times, the chromatogram was divided into slices, where each slice represents the weight fraction of the corresponding (known) molar mass. Finally, M_n and M_w values could be calculated using their respective definitions. Results are shown in Table 2, together with the molar masses from absolute methods. M_n and M_w from GPEC are average values from nine determinations. Relative standard deviations were approximately 0.4% for M_n and 0.6% for M_w.

It is obvious that the M_w calculated from GPEC is in excellent agreement with the absolute value, whereas the deviation in M_n is somewhat larger. This is probably caused by the fact that in the lower molar mass area, detector response will not be independent of molar mass, which mainly influences M_n. In the high-molar-mass part, this dependence will be much smaller, since products slightly differing in chemical structure, such as end groups are taken together into one "oligomer number", having roughly the same average chemical composition. Furthermore, the detection wavelength, 277 nm, was chosen at the absorption maximum of the diol used. The UV absorption is therefore mainly caused by the diol parts of the oligomers, thus reducing the influence of the diacid type.

The high reproducibility of the molar mass determinations can easily be explained by the fact that, unlike in SEC measurements, no external calibration with narrow standard polymers is needed. Inac-

curacies due to temperature or flow variations from run to run do not influence the results.

Therefore, the method presented here can be considered as an attractive new alternative for the determination of molar masses of relatively low-molar-mass polymers. Beside polyesters, this method has also been applied to other types of resins, the results of which will be presented elsewhere. A condition for successful application of this method is of course a certain knowledge about the chemical composition which is required for the proper assignment of the oligomer peaks.

The detailed oligomeric separations for polyesters obtained by GPEC can also be of help for kinetic studies. Kinetics of polyesterification reactions have been extensively studied [39]. Expressions for molar mass distributions were derived from kinetic as well as statistical considerations. It has been shown that the number and weight average molar mass can be expressed according to [39]

$$M_n = [1/(1-p)]m \quad (4)$$

$$M_w = [(1+p)/(1-p)]m \quad (5)$$

in which p represents the extent of reaction and m equals the molar mass of the repeating unit. Furthermore, it can be found that the weight fraction w_x of molecules with a of degree of polymerization, x, is given by

$$w_x = x(1-p)^2 p^{(x-1)} \quad (6)$$

Since M_w and M_n were already determined by GPEC, p could be calculated from either Eq. (4) or Eq. (5). In both cases, a value of 0.821 is found. Knowing p, the theoretical oligomer distribution could be determined from Eq. (6).

Since the response of a concentration-sensitive detector, such as a UV detector, is directly related to the weight fraction, the oligomer distribution can also be determined from the GPEC chromatogram. In this case, peaks having $(x-1)$, x and $(x+1)$ diacid units were taken together. The results for the theoretical and practically determined oligomer distribution of sample PE1 are shown in Table 3.

It is obvious that the theoretical distribution is in excellent agreement with the results found from GPEC. For sample PE1 it can therefore be concluded that the polyesterification proceeded in a normal way, without the occurrence of many side reactions caused by e.g., anhydride formation. This also corresponds to the fact that the oligomer patterns found in GPEC are very regularly shaped. No unusual peak patterns due to side products can be observed.

Table 3
Oligomer distributions for PE1, PE2 and PE3

Oligomer number	Percentage by weight			
	PE1 (GPEC)	PE1 (theoretical)	PE2 (GPEC)	PE3 (GPEC)
1	3.2±0.1[a]	3.2	3.2±0.1	3.2±0.1
2	5.4	5.3	5.0	4.9
3	6.4	6.5	6.4	6.1
4	7.2	7.1	6.7	6.5
5	7.2	7.3	6.8	6.6
6	7.1	7.2	7.0	6.6
7	6.7	6.9	6.6	6.3
8	6.1	6.4	5.9	6.0
9	5.7	6.0	5.5	5.6
10	5.1	5.4	5.0	5.1
11	4.7	4.9	4.6	4.7
12	4.2	4.4	4.1	4.2
13	3.8	3.9	3.7	4.2
14	3.4	3.4	3.4	3.5
15	3.0	3.0	3.0	3.1
16	2.6	2.7	2.7	2.7
17	2.3	2.3	2.3	2.5
18	2.1	2.0	2.1	2.2
19	1.8	1.7	1.9	1.9

[a] Standard deviation.

It is interesting to note that at the detection wavelength used, the monomeric diol concentration can be determined directly from the relative peak area without calibration. By this method, the same result is obtained as by a method using external standards. Furthermore, GPEC eliminates the need for laborious extraction procedures for the determination of monomers.

Finally, two closely resembling polyester samples, PE2 and PE3, are compared by GPEC. The polyesters seem to exhibit somewhat different mechanical properties. By SEC, only small differences in molar mass distribution can be observed, whereas NMR analysis revealed that PE3 has a slightly higher ratio of adipic acid to isophthalic acid (see Table 1). Furthermore, it appeared that the degree of propox-

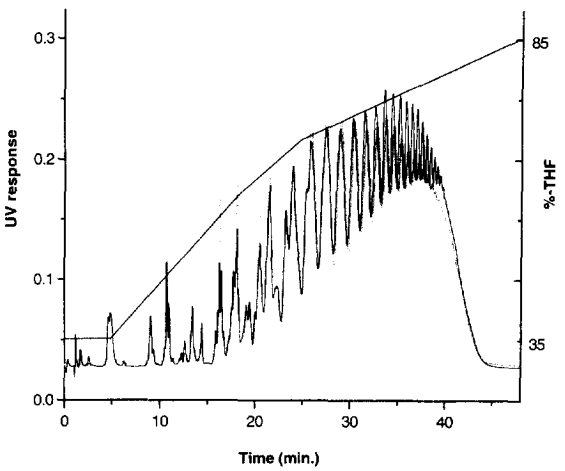


Fig. 7. Comparison of PE2 (grey line) and PE3 (black line) by GPEC. Concentrations: 40 mg/ml, column: NovaPak C_{18} (15 cm), eluent: THF–water (35 : 65) (v/v) to (60 : 40) (0 to 14 min) (60 : 40) to (68 : 32) (14 to 20 min), (68 : 32) to (85 : 15) (20 to 43 min), flow: 1.0 ml/min, temperature: 35°C, injection: 10 μl, detection: UV at 277 nm.

ylation of the monomeric diol used for synthesis was somewhat lower in the case of PE3.

In Fig. 7, the GPEC chromatograms are shown. A comparison of both chromatograms immediately confirms the observation from SEC that molar masses are roughly the same. The distributions end at approximately the same percentage solvent and the quantitative oligomer distributions are highly comparable (see Table 3).

Chemical differences are clearly observed in the low-molar-mass part. The peak shape of the diol peak is different, indicating differences in purity, which is confirmed by the NMR analysis of the diol monomers. Furthermore, for the peak-area ratio of the peaks DA– DI (see Fig. 5), due to the reaction products of diol with adipic acid and isophthalic acid, respectively, a value of 0.29±0.01 (standard deviation) is found for PE2 versus 0.62±0.01 for PE3. This clearly indicates that PE3 contains more adipic acid. It must be mentioned that these values are not equivalent to the ratio of the weight fractions, since the response factors of both low-molar-mass products will certainly be different.

It is also interesting, however, to compare these ratio values with the molar ratios of adipic acid to isophthalic acid obtained by NMR. NMR provides information on the bulk composition of the sample whereas the values generated by GPEC yield information on the composition in the low-molar-mass part of the sample. By NMR, a value of 0.32±0.02 is found for PE2 versus 0.43±0.02 for PE3. Comparison of the peak ratio value from GPEC and the molar ratio from NMR immediately shows that for PE3 the ratio of adipic acid in the low-molar-mass part of the sample compared to the bulk is much higher than that obtained for PE2. This is a clear indication that the chemical composition distributions of both samples are different.

Furthermore, peaks heights of oligomers 10–20 are much larger for PE3 compared with PE2, whereas peak areas expressed in weight fractions in Table 3 are almost the same. This can possibly be explained by the fact that for PE3 the chemical composition distribution under each oligomer peak is somewhat narrower, thus giving rise to sharper peaks. This further confirms the results described above.

Summarizing, it can be concluded that by GPEC, information on molar mass and chemical composition differences can be obtained in a rather simple way, for which at least two other techniques, e.g. SEC and NMR, would have to be used otherwise. Furthermore, GPEC can provide information on differences in chemical composition distribution, information at present not revealed by any other technique.

4. Conclusions

GPEC has been shown to be capable of providing detailed information on molar mass and chemical composition of polyester resins. The obtained separation result can be adjusted by several practical parameters. A gradient steepness of 1%/min was shown to be a good compromise between resolution and analysis time. Column length only influences the separation in the low-molar-mass part of the chromatogram, whereas the total number of oligomers that can be resolved is hardly influenced. An increase in temperature also mainly influences the separation in the low-molar-mass region, due to a decrease in peak broadening. Temperature effects appears to be

much less pronounced compared to the results obtained by other workers for other types of polymers. The cause of this difference is still unclear. It might be caused by differences in either the retention mechanism, conformational changes or experimental conditions. Further research is needed to get more insight into the effect of temperature changes. No effects on the separation could be observed up to a sample load of 1000 μg. This indicates that separation is probably dominated by sorption (adsorption and/or partitioning) rather than solubility effects. Injection volumes exceeding 10 μl gave rise to additional peak broadening for the low-molar-mass products, due to the sample–solvent effects. However, no breakthrough could be observed under these conditions.

It was shown that by GPEC under reversed-phase conditions, polyesters are mainly separated according to molar mass, whereas in the low-molar-mass part, a further separation based on chemical composition occurs. An almost linear dependence was found between the reciprocal square root of the molar mass and the percentage solvent at the point of elution of oligomers, although the curves tend to be slightly sigmoidally shaped. This dependence was used to calculate molar masses of a polyester sample. The M_w found was to be in good agreement with the value determined by absolute methods, whereas the M_n showed some deviation. This is probably caused by the varying detector response in the low-molar-mass part. The applied method for the evaluation of molar masses was shown to be highly reproducible. GPEC can also be of help for kinetic studies. The oligomer distribution, which could be calculated from the GPEC chromatogram, is in very good agreement with the theoretical distribution, indicating that polyesterification proceeded in a "normal" way. Finally, from a comparison of peak ratios obtained from GPEC and NMR results on bulk composition, indications for chemical composition distribution differences between two co-polyester samples could be obtained. This observation was further supported by differences in the oligomer patterns in the high-molar-mass part of the GPEC chromatograms. This information can not be obtained by any other technique at present, underlining the great importance of GPEC in the area of microstructural characterization of polymers and resins.

Acknowledgments

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