Characterization of Polyester Resins by Gradient Polymer Elution Chromatography (GPEC) under Reversed Phase Conditions

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ABSTRACT

Gradient Polymer Elution Chromatography (GPEC) can be used for the characterization of complex polymer systems such as co-polymers, polymer blends and resins. In this paper the application of GPEC under reversed phase conditions for the detailed characterization of polyester resins according to molar mass and chemical composition, is described. Resolution in GPEC is shown to be much higher as compared to SEC. Both resolution and selectivity can be modified using ternary and quaternary gradients instead of binary mixtures. From GPEC results, absolute molar masses and oligomer distributions could be calculated. Evidence for differences in both intermolecular and intramolecular microstructure between two co-polyesters having roughly the same average composition, could be obtained. The separation of low molar mass polyesters throughout the whole investigated molar mass range was found to be solely governed by sorption. For a higher molar mass polyester, re-dissolution effects were found to influence the separation, which can give rise to non-reproducible effects in the high molar mass part of the chromatogram. Furthermore, re-dissolution effects were shown to be influenced by time dependent kinetic effects. Crystalline polyesters were found to exhibit non-reproducible chromatographic behaviour in GPEC below a certain temperature which is caused by the formation of a crystalline solid phase after precipitation. This effect can be avoided at higher temperatures, in which case normal elution behaviour, governed by sorption occurs.

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1. INTRODUCTION

The chemical characterization of homo polymers can in general be performed adequately by using Size Exclusion Chromatography (SEC) and a spectroscopic technique such as infrared spectroscopy (IR) or nuclear magnetic resonance spectroscopy (NMR). By SEC, the molar mass and molar mass distribution (MMD) can be obtained and by spectroscopy, the average chemical composition is determined. This characterization is no longer sufficient for more complex polymer systems such as polymer blends, copolymer and telechelic polymers. These products exhibit, next to a MMD, also a distribution in chemical composition (copolymers) or functionality (telechelic polymers) or, in the case of polymer blends, more than 1 MMD. Polymer properties are influenced to a large extent by those additional distributions which implies that relations between synthesis and final properties become more much complex as compared to the case of homo polymers. In order to understand those relations, a more extensive characterization of complex polymer systems is needed. One of the methods that can be used for this purpose is Gradient Polymer Elution Chromatography (GPEC). GPEC can be applied to characterize copolymers with respect to their chemical composition distribution (CCD) [1,2] to separate polymer mixtures [3,4] or the perform a detailed characterization of resins (‘fingerprinting’) [5,6].

In GPEC, a polymer sample is dissolved in a thermodynamically strong solvent and injected into a mobile phase which is a weak displacer. Due to the limited solubility of polymers, this mobile phase is often a non-solvent which causes the polymer to precipitate. Subsequently, a gradient is applied from non-solvent to solvent. The increasing thermodynamic solvent quality causes the polymer to gradually re-dissolve. This re-dissolution process depends on both molar mass and chemical composition. After re-dissolution, the polymer (fraction) will undergo sorption and/or exclusion interactions with the stationary phase and will eventually elute from the column. Therefore, final separation is influenced by precipitation/re-dissolution, sorption and exclusion. The contribution of each of the separation mechanisms depends on the combination of sample and separation system.

This paper describes the application of GPEC under reversed phase conditions (RP-GPEC) on the characterization of (co)polyester resins. Polyesters are formed by the polycondensation of one or more diols with one or more di-acids. Therefore, next to a MMD they also can have a functionality type distribution (FTD). In the case of copolyesters, an additional distribution with respect to composition of the backbone may occur. In this paper we will show that by GPEC detailed information upon composition and composition differences of (co)polyesters can be obtained.
2. EXPERIMENTAL

2.1. Polymer samples
The polyester samples used were laboratory-made polyester resins. Samples PE1, PE2 and PE3 are co-polyesters consisting of adipic acid (A), isophthalic acid (I) and di-propoxylated bisphenol-A (D). Polystyrene-equivalent molar masses as determined by SEC and molar fractions determined by NMR are as follows: PE1: \( M_n = 3500, M_w = 7900, A:I:D = 0.12:0.37:0.50 \); PE2: \( M_n = 3400, M_w = 8200, A:I:D = 0.12:0.38:0.50 \); PE3: \( M_n = 3300, M_w = 7900, A:I:D = 0.15:0.35:0.50 \). Sample PE4 is a homo polyester consisting of A and D for which it was determined: \( M_n = 3800, M_w = 8700, A:D = 0.51:0.49 \). PE5 is a homo polyester based on maleic acid (M) and D: \( M_n = 3900, M_w = 13700, M:D = 0.45:0.55 \). PE6 is a co-polyester consisting of adipic acid, terephthalic acid (T) and diethoxylated bisphenol-A (D2) for which it was found: \( M_n = 5600, M_w = 20000, A:T:D = 0.12:0.37:0.51 \). CP1 is a fully hydroxyl-terminated, crystalline homo-polyester based on dodecanedioic acid and butane-diol: \( M_n = 6900, M_w = 16000 \). For more detailed information on the characterization of the polyester samples we refer to [7].

For some experiments, low dispersity fractions (Molar Mass Distribution < 1.1) of sample PE1 were used. For the preparation and the exact characteristics of these fractions the reader is referred to [8].

2.2. Solvents
The solvents used for most HPLC experiments were water, Milli-Q quality from Millipore and tetrahydrofuran (THF), HPLC grade from Rathburn. In some cases also methanol (MeOH) or acetonitrile (ACN) was used. To all solvents, 200 µl acetic acid, Pro Analysis quality from Merck, per litre was added. For HPLC, 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.

2.3. Columns and HPLC equipment
The columns used were a Novapak-C18 column (Waters; \( d_p = 4 \mu m, \) pore size 60 Å, 150 x 3.9 mm) and a 'glass' column (150 x 4.6 mm) which was dry-packed with non-porous glass beads, diameter 40 - 60 µm (Phase Separations, part No. 750138). For all experiments a stainless steel in-line pre-column filter (Waters, part No.084560) was used.

All GPEC experiments were performed, using a Waters 600E 4 solvent gradient pump, and a 715 WISP from Waters. The detector was a variable wavelength detector, Waters, type 484, which was set at 277 nm. The column temperature was controlled using a thermostat type Mistral from Spark-Holland equipped with a peltier element. Chromatograms were recorded using the Baseline-815 system from Waters.

For the equipment and columns used for SEC, the reader is referred to [7].

2.4. Gradient elution experiments
Gradient elution was performed as follows. After running each gradient, the system was reset to initial conditions in one minute, followed by pumping 15 column volumes of the starting eluent composition to re-equilibrate the column. Prior to the analysis of the samples, two blank gradients
were performed. 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 linearity was found to be excellent, thus allowing an easy calculation of the eluting eluent composition at each retention time. The system hold-up volume was also determined from these experiments and was found to be 3.9 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 THF.

3. RESULTS AND DISCUSSION

3.1. Reversed phase GPEC of amorphous polyesters

RP-GPEC was used for the characterization of polyester samples PE1, PE4 and PE5. A Novapak C\textsubscript{18} column was applied with THF-water as Solvent-Non-Solvent (S-NS) system. After some optimization, a separation as is shown in Figure 1, was obtained. In this figure, a comparison is made between SEC analysis and GPEC of the respective samples. As it can be seen, by GPEC the polyesters are separated into a large number of oligomers, and resolution is much higher as compared to SEC. Retention is mainly governed by molar mass/number of diol units, whereas in the low molar mass part a further separation with respect to chemical composition, such as end groups, occurs. Peak assignment has been described in more detail in [7]. RP-GPEC results for the investigated products were found to be highly reproducible so it is possible to use GPEC for fingerprinting purposes in order to determine small differences between samples strongly resembling each other.

From the study to the influence of column length, temperature, injected mass and injection volume, it followed that retention in RP-GPEC over the entire, investigated molar mass range of the samples is dominated by sorption rather than by solubility effects [7], although precipitation/redissolution effects do occur during analysis. Therefore, it was worthwhile checking the influence of the S-NS system, since it is known that in reversed phase chromatography, separation is mainly governed by differences in interactions of the sample with mobile phase. Thus, several iso-elutropic gradients were applied, for which eluent strength, expressed in the Hildebrand solubility parameter at each retention time was equal to that for the binary THF-water gradients as in Figure 1. Results are shown in Figure 2. It is obvious that going from a binary to a ternary or quaternary system causes changes in selectivity, especially in the low molar mass area. Also, resolution in this part of the chromatogram seems to increase and a more detailed separation into various oligomer fractions is obtained, which is in qualitative agreement with results found by other workers [9]. In contrast, resolution in the high molar mass part decreases. Therefore, by using the binary THF-water system, more information upon reaction kinetics can be obtained, since a higher number of respective oligomers can be resolved, whereas ternary or quaternary systems provide more details upon the composition of the low molar part of the resins.

Although in this paper only the application of GPEC under reversed phase conditions is described, it must be mentioned here that polyesters can also be characterized under normal phase conditions. In that case another kind of information is obtained, especially with respect to functionality and functionality differences. Therefore, in our experience NP-GPEC must be considered as a
complimentary technique as compared to RP-GPEC, rather than an alternative technique. Results on NP-GPEC will be published elsewhere.

3.2. Applications of reversed phase GPEC for amorphous polyesters

The application of gradient elution techniques for the characterization of low molar mass polymers is already known for a considerable time. Nevertheless, real practical applications often seem to lack. Probably, one of the reasons for this is the lack of well defined reference samples varying in composition, which hampers a good qualification of observed differences between 'real' samples from practice. Therefore, we synthesized a number of reference (co)polymers differing in adipic acid/isophthalic acid content. Also, a transesterification of homo-polyesters of adipic acid and isophthalic acid with di-propoxylated bisphenol-A was carried out and a number of samples were taken during time. These samples were used to qualify differences in co-polyesters samples.

For samples PE1, PE4 and PE5, a near linear dependence was found between the reciprocal square root of molar mass ($M^{-0.5}$) and %-THF at the point of elution of an oligomer fraction (Figure 3). From this dependence, it was possible to calculate the retention times of the unresolved oligomers in the high molar part of the chromatogram. Subsequently, the chromatogram was divided into slices and $M_n$ and $M_w$ were calculated using their respective definitions. For sample PE1 results from this evaluation were compared with values determined from absolute methods (osmometry and light scattering) and good agreement was found, especially for $M_w$. By light scattering a value of 4900 +/- 10% was obtained, whereas GPEC provided a value of 4790 +/- 0.6%.

For sample PE1, also a comparison was made between the theoretical oligomer distribution which can be calculated from theories on polyesterification kinetics, and the oligomer distribution found by GPEC. As can be concluded from Table 1, both distributions are in good agreement with each other, indicating that the polyesterification of PE1 proceeded in a normal way, without many side reactions. Obviously, GPEC can be used for the determination of absolute molar masses of low molar mass polymers and to obtain information on polymerization kinetics. Results are described in more detail in [7].

In Figure 4, a comparison between two copolyesters, PE2 and PE3, is shown. Both samples were found to have about the same molar mass and molar mass distribution (SEC). Furthermore only small differences in overall chemical composition were found by NMR. Nevertheless, the samples seemed to exhibit somewhat different mechanical properties.

In the low molar mass part of the GPEC chromatograms, chemical differences between both samples are clearly observed. From the different shape of the diol peaks at 4.5 min. it can be seen that the purity of the diol used for both syntheses is different, which was confirmed by NMR analysis of the diol. Furthermore, a large difference can be observed in the peak area ratio of the peaks DA and DI (peak assignment: see Figure 1), due to the reaction products of diol with adipic acid and isophthalic acid, respectively. For sample PE2 a value of 0.29 is found and for sample PE3, a value of 0.62, indicating that PE3 contains much more adipic acid in the low molar mass part. By NMR, the molar ratio of adipic acid to isophthalic acid for the overall sample can be calculated. For samples PE2 and PE3 values of 0.32 and 0.43 were found respectively. Comparison of peak area ratios from GPEC with molar ratios from NMR immediately reveals 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 for PE2. This indicates that the chemical composition distribution and therefore the intermolecular microstructure of both samples is different.

Further evidence for this observation is obtained when peak positions of the oligomers are compared. It can be seen that retention times for oligomers from PE2 elute slightly later than those of PE3. Since we have the availability of copolyesters differing in adipic acid/isophthalic acid ratio, it was possible to study the peak position of oligomers with different degrees of polymerization as a function of chemical composition. An example for oligomer N=6 is shown in Figure 5, from which it can be observed that retention time increases with increasing content of isophthalic acid. It must be mentioned here, that the applied gradient program for these experiments was slightly different from that of Figure 4, which explains the difference in absolute retention times. Peak positions for oligomer N=6 for both PE2 and PE3 have also been plotted in this curve. Again, it can be seen that a large relative composition difference in a small part of the total molar mass distribution can be found. Especially the high fraction isophthalic acid which is found for PE2 is somewhat surprising since the average fraction, determined by NMR, was found to be 0.76. Although studies on this characterization method are still going on, it can be concluded that significant differences in intermolecular microstructure between both polyesters can be found.

Finally, a distinct difference in peak heights of oligomers 10-20 is observed between PE2 and PE3, whereas peak areas are almost the same [7]. It was considered that this can possibly be explained by the fact that the chemical composition distribution under each oligomer peak is somewhat narrower for PE3, thus giving rise to sharper peaks. Evidence for this assumption was obtained from the results of a transesterification reaction of both homo-polymers. GPEC chromatograms of various samples taken during this reaction, are shown in Figure 6. It can be seen that during transesterification, peak heights decrease and peak widths increase. This can be explained from the increasing number of different products that is being formed, each having slightly different retention times thus giving rise to peak broadening. The observed differences due to transesterification are qualitative the same as the differences found between PE2 and PE3. Therefore, it is likely that PE3 is less randomized and contains more ‘blocky’ fractions as compared to PE2. Due to a lower number of different oligomers in such a case, peak widths of the oligomer fractions in GPEC are smaller. Thus, by GPEC next to intermolecular microstructure, also information upon differences in intramolecular microstructure can be obtained. In a future publication these results will be discussed in more detail.

3.3 Influence of solubility effects in reversed phase GPEC of amorphous polyesters
Although it was shown that separation of the investigated polyester resins is likely dominated by sorption effects [7], precipitation/re-dissolution effects also occur in the investigated system. Studies to the influence of precipitation effects in polymer chromatography are mostly concerned with the comparison of eluent compositions at the point of elution with cloud points, determined by turbidimetric titrations [10,11]. This approach cannot be used for low molar mass polymers, since at low molar masses cloud points depend to a large extent on concentration and molar mass [12]. Therefore, to study the influence of solubility effects in RP-GPEC, sample PE1 was separated into several low polydispersity fractions by SEC. The elution behaviour of these fractions was studied
on a C<sub>18</sub> column and on a column packed with non-porous glass beads which was shown to be inert under the conditions chosen [8].

In Figure 7, %-Solvent at the peak-ends (ϕ<sub>e</sub>) for the respective fractions on both columns are compared. A lower fraction number indicates a higher molar mass. For instance, fraction 1 represents a polystyrene equivalent M<sub>w</sub> of 38000 and the M<sub>w</sub> of fraction 10 is 800. It can be seen that for almost all fractions, ϕ<sub>e</sub> for C<sub>18</sub> is higher than for glass, which indicates that elution on C<sub>18</sub> over the entire molar mass distribution is governed by sorption. It is also obvious, however, that retention difference for a separation which is controlled by solubility effects as compared to a separation based on sorption, decreases for increasing molar mass. This is explained in more detail in [8].

To further study the influence of re-dissolution effects, a comparison was made between measurements of maximum solubility of three different polyester fractions in varying S-NS compositions and the concentrations profiles of the eluting fractions during gradient elution on the inert glass column. Results are shown in Figure 8. It can be seen that concentration profiles obtained from chromatographic measurements do no coincide with the curves of maximum solubility. This is trivial for the high %-Solvent part of the distribution, since the available mass gets exhausted. For the low %-Solvent part, however, this is remarkable since in this part of the analysis, enough mass is available to obtain saturated solutions. This indicates that during eluting, no thermodynamic equilibrium is reached, which is due kinetic effects. Further experiments indeed proved the existence of time dependent re-dissolution effects in the RP-GPEC analysis of polyesters [8].

Although these effects did not influence the final separation result of the polyesters investigated so far, in contrast for PE6, a higher molar mass polyester, indications were found that re-dissolution effects can affect separation. From an analysis in duplicate, which is shown in Figure 9, it can be seen that the high molar mass part of the RP-GPEC chromatogram of this polyester contains non-reproducible peaks. These effects were found especially at high values of injected mass. Therefore, a comparison was made between elution of the entire, unfractionated polyesters PE1 and PE6 on both C<sub>18</sub> and glass. From the results in Figure 10 it can be observed that elution curves on both columns coincide in the high molar mass part of sample PE6. This indicates that for this sample, unlike for sample PE1, elution in the high molar mass part is governed by re-dissolution effects rather than by sorption. The fact that elution on glass is somewhat later than on C<sub>18</sub> can probably be explained from the difference in exclusion effects between the porous silica based C<sub>18</sub> and the non-porous glass particles. A retention mechanism which is governed by re-dissolution effects obviously can give rise to non-reproducible elution behaviour, the cause of which is not completely clear at this moment.

3.4. Reversed phase GPEC of crystalline polyesters

Crystalline polyester were found to exhibit highly non-reproducible chromatographic behaviour in GPEC under certain conditions, as compared to amorphous polyesters. An example for sample CP1 is shown in Figure 11. The bimodality of the distribution cannot be explained from

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polyesterification kinetics and the position and the ratio of both peaks were found to vary with experimental conditions. It was found that this anomalous chromatographic behaviour of crystalline polyesters can be explained from the formation of a solid, crystalline phase at the top of the column after precipitation, leading to a dominance of precipitation/re-dissolution effects in the total retention mechanism [13]. The formation of a solid phase does not occur for amorphous products since glass transition temperature ($T_g$) is much more affected by the presence of solvent than a melting temperature ($T_m$). Due to a large $T_g$ depression due to the solvent, a swollen polymer rich phase is formed in the case of amorphous polyesters rather than a real solid phase. It is likely that the re-dissolution behaviour of a crystalline solid phase is different from that of a swollen polymer rich phase, which explains the dependence on experimental conditions in the case of crystalline products.

A further study to the influence of experimental parameters provided more information on the total retention mechanism of crystalline polyesters [13]. It was found that separation was influenced by both kinetic and thermodynamic effects. Especially from minor effects of increasing sample load and gradient steepness, however, it was concluded that separation is mainly governed by thermodynamics by which it is determined at what % Solvent during the gradient, the melting point drops below the environmental temperature. Therefore, separation can at best be influenced in a thermodynamic way. Indeed, raising the system temperature above a certain value finally led to highly reproducible, normal elution behaviour, which is shown in Figure 12. This is due to the fact that above a certain temperature, the depressed melting temperature of the crystalline polyester is exceeded. This prevents the formation of a crystalline, solid phase which leads to the occurrence of normal elution behaviour governed by sorption rather than by precipitation/re-dissolution. Therefore, to ensure normal elution behaviour of crystalline polyesters in GPEC, system temperature has to be higher than the depressed melting temperature at the initial conditions of the gradient.

4. CONCLUSIONS

By GPEC under reversed phase conditions, detailed information on molar mass and chemical composition of polyester resins can be obtained. The resolution was found to be much higher as compared to SEC. By using ternary or quaternary gradients instead of binary mixtures, resolution and selectivity can be modified, especially in the low molar mass part of the chromatogram. A linear dependence was found between the elution time of an oligomer and the reciprocal square root of its molar mass. From this dependence, molar masses of a polyester could be calculated which were in good agreement with the values found from absolute methods. From a comparison between peak ratios from GPEC and NMR results on bulk composition, indications for differences in intermolecular microstructure between two co-polyester samples could be obtained. This observation was further supported by differences in peak positions of the oligomers. Furthermore, from a qualitative comparison of peak heights for the higher molar mass oligomers of the two polyesters with the results obtained from products taken during a transesterification reaction, evidence for differences in randomness, e.g. intramolecular microstructure, was obtained.
For relatively low molar mass polyesters, it was found that separation throughout the whole investigated molar mass range is solely determined by sorption effects. For higher molar mass polyesters, re-dissolution effects can govern separation especially in the high molar mass part of the chromatogram which can give rise to non-reproducible elution behaviour. A comparison of chromatographic results of three low dispersity polyester fractions on an inert glass column with measurements of maximum solubility under static equilibrium conditions in various S-NS combinations, revealed that re-dissolution behaviour in chromatography is influenced by time dependent kinetic effects.

In contrast to amorphous polyesters, crystalline polyesters were found to exhibit non-reproducible chromatographic behaviour in GPEC below a certain temperature which was shown to be due to the formation of a crystalline, solid phase after precipitation. This effect can be avoided by raising the temperature above the depressed melting temperature at the initial conditions of the gradient. In that case, highly reproducible, normal elution behaviour governed by sorption, is found.

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6. REFERENCES

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*: standard deviation