Microstructural Characterization of Aromatic Copolyesters Made by Step Reactions, by Gradient Polymer Elution Chromatography

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ABSTRACT: The potentials of Gradient Polymer Elution Chromatography (GPEC) in both the Reversed-Phase (RP) and Normal-Phase (NP) mode, for the characterization of aromatic copolyesters made by step reactions, according to their chemical microstructure, were studied. Hereto, a number of copolyesters, varying in molar mass and chemical composition (CC) were synthesized, which allowed a systematic study on the effects of those parameters in GPEC. By RP-GPEC, highly detailed separations were obtained. Information on chemical composition differences could, however, only be obtained for the lower molar masses. From these results, qualitative evidence for differences in the chemical microstructure of two strongly resembling copolyesters was found that could not be obtained by other methods such as SEC and NMR. Nevertheless, it was found difficult to unambiguously assign observed differences in the high molar mass parts of RP-GPEC chromatograms. Therefore, RP-GPEC must mainly be considered as a versatile, qualitative fingerprinting tool. In contrast, NP-GPEC provides more and quantitative information on microstructural differences. By a combination of SEC and NP-GPEC the Molar-Mass-Functionality-Type-Distribution (MMFTD) of the (co)polyesters, and the Molar-Mass-Chemical-Composition-Distribution (MMCCD) of the fraction containing two alcoholic end groups of the copolyesters could be studied. Significant differences between strongly resembling copolyesters were found which, for the MMCCDs, can only be the cause of the relative importance of reaction kinetics in step reaction copolymers. This makes the assumption that a predictable, theoretical statistically determined CCD is formed in all cases, questionable. J Appl Polym Sci 72: 183–201, 1999

Key words: copolyester; chemical composition distribution; functionality type distribution; chromatography; gradient elution

INTRODUCTION

Due to their structural complexity, the characterization of synthetic polymers still remains a challenge for chemists. These polymers are composed of an enormous number of varying products differing in molar mass and, in the case of copolymers, chemical composition. In relation to the polymer properties, it is of the utmost importance to have the availability of characterization methods by which average values and distributions of both molar mass and chemical composition can be

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determined. The most versatile technique for the determination of the molar mass distribution (MMD) of homopolymers is Size Exclusion Chromatography (SEC). Especially when coupled to modern detection techniques such as differential viscometry and light scattering, additional information on polymer conformation can also be elegantly obtained.[1,2]

For copolymers, the determination of MMD is hampered by the fact that the separation in SEC is based on hydrodynamic volume rather than on molar mass. Because copolymers consist of more than one monomeric unit, a distribution of molecules, having the same hydrodynamic volume but different molar masses, may exist.

Next to an MMD, copolymers also have a chemical composition distribution (CCD), determining their *inter*molecular microstructure and a sequence distribution (SD), the average distribution of the monomers along the polymer chain, determining the *intra*molecular microstructure. The latter characteristic can be determined by the analysis of diad and triad structures by spectroscopic techniques such as NMR[3,4] or, after destructive degradation, by GC or HPLC.[5,6] For the determination of the CCD, especially gradient HPLC has been shown to be a versatile technique. After first being applied by Teramachi[7] the technique has been used by a (still rather limited) number of workers for the structural investigation of statistical copolymers[3,7–25] and, to a lesser extent, of block copolymers[26,27] and graft copolymers.[28–34] A combination of at least two solvents is used, one of which is a chromatographically strong displacer and the amount of which is gradually increased in time. Due to the limited solubility of polymers, the weak solvent often is a nonsolvent, causing precipitation of the polymer after injection. Separation can, therefore, be based on precipitation-redissolution, sorption (adsorption and/or partitioning) and exclusion effects from the porous column packing. The exact separation mechanism has been a matter of debate,[35,36] and depends on the polymer type in combination with the chosen separation system (mobile and stationary phase). In rare cases it is purely based on precipitation-redissolution[10,18] or somewhat more frequently on adsorption,[15,16] but in most cases a mixed separation mechanism is obtained. That is why we prefer the generally applicable term Gradient Polymer Elution Chromatography (GPEC)[37–43] rather than High-Performance Precipitation Liquid Chromatography (HPPLC)[12,18] or Liquid Adsorption Chromatography,[15,16] which refer only to a part of the separation mechanism. It must be emphasized here, that although the combination of SEC with multiple detection such as ultraviolet (UV) and differential refractive index (DRI) detection or with infrared spectroscopy is often used for the detection of polymer inhomogenities,[34,44] this kind of analysis is not capable of providing the CCD. Although useful, such analysis only gives an impression of the average chemical composition as a function of molar mass, saying nothing about the broadness of a CCD and being unable to discriminate between the difference between a polymer blend or a copolymer, which easily leads to misinterpretation.[33,46]

Until now, most work on microstructural characterization of copolymers has focused on polymers, often styrene containing, made by polyaddition reactions. Little attention has been paid to products of relatively low molar mass, synthesized by step reactions, such as copolyesters. Reaction kinetics of these polymers are well described.[47] Due to the occurrence of transesterification reactions next to chain growth, it is often assumed that, in the case of copolyesters, complete randomization will occur. In such a case, a statistical CCD will be obtained that only depends on the initial molar ratios of the monomers. No such phenomenon like a conversion CCD due to reactivity differences of the respective monomers causing composition drift, would occur. In contrast with this, it is sometimes found that, although the average composition of step reaction copolymers is kept constant, the final thermomechanical properties depend on the applied reaction scheme or reaction properties[48] that presumably must be ascribed to differences in microstructure.

In earlier work, we studied the potentials of GPEC in both the reversed phase (RP-GPEC) and normal phase (NP-GPEC) mode for the characterization of amorphous[39,40] and crystalline[41] polyesters. Furthermore, significant attention was paid to the elucidation of retention mechanisms in both separation modes.[42,49,50] From RP-GPEC, qualitative evidence was obtained for the existence of both inter- and intramolecular microstructural differences in strongly resembling copolyesters.[39,43]

In this article we will investigate the potentials of both RP-GPEC and NP-GPEC for the microstructural characterization of amorphous copolyesters, both qualitatively and quantitatively. Hereto, a number of copolyesters, varying in molar mass, average chemical composition, and CCD were synthe-

Table I Polystyrene Equivalent Molar Masses, End-Group Compositions, and Average Chemical Compositions of the Investigated Polyesters

		SEC			Titrations	NMR		
		PS Equivalent Molar Masses				Molar Fractions		
Sample	Reaction Time	M_n	M_w	D[a]	Acid Number (mg KOH/g)	A	I	D
PE2		3400	8200	2.4	24	0.12	0.38	0.50
PE3		3300	7900	2.4	27	0.15	0.35	0.50
DA	4.5 h	3800	8300	2.2	19	0.45	0	0.55
DAI31	8.8	3300	7600	2.3	17	0.37	0.13	0.50
DAI21	10.0	3400	7900	2.3	17	0.33	0.16	0.51
DAI11	12.0	3200	6800	2.1	19	0.26	0.24	0.50
DAI12	14.8	3600	7800	2.2	18	0.16	0.33	0.51
DAI13	18.5	3200	6900	2.2	19	0.12	0.37	0.51
DI	16.8	3000	6600	2.2	25	0	0.49	0.51
DAI13-2	1 h	510						
	2	640						
	3.6	770						
	4.0	780						
	5.0	1180						
	6.0	1300						
	6.5	1320						
	11.3	3200						
	12.3	3640						
	13.3	4180						
	20.5	4100	9170	2.2	14	0.13	0.37	0.50
trans-S2	20 min	3000	6900	2.3				
S3	35	3100	6900	2.2				
S4	50	3200	7100	2.2				
S5	65	3300	7200	2.2				
S6	80	3400	7400	2.2				
S14	204	4900	11,500	2.3				
endpr.	305	6500	16,400	2.5		0.12	0.37	0.51

[a] Polydispersity, M_w/M_n.

sized and used for a systematic study on the effects of those parameters in GPEC. A separation system has been developed that allows a qualitative and quantitative evaluation of CCDs. Relatively large microstructural differences were found between strongly resembling copolyesters. This makes the assumption that a predictable, theoretical statistically determined CCD is formed in all cases, questionable. To our knowledge, this is the first example in which the existence of a CCD in polyesters made by step reactions, is experimentally proven.

EXPERIMENTAL

Polymer Samples, Synthesis, and Characterization

All polymer samples used are copolyesters consisting of adipic acid (A), isophtalic acid (I), and di-propoxylated bisphenol-A (D), and their respective homopolyesters. Two well-characterized samples, PE2 and PE3, which were synthesized on a large scale and which were also used in earlier studies,[39,40] were also used here for comparative characterization. Polystyrene equivalent molar masses as determined by SEC, average chemical composition as measured by ^{1}H-NMR, and end group compositions as determined by titrimetric analysis, are given in Table I. For detailed information on the NMR and titrimetric measurements, the reader is referred to ref. 39.

To study the effect of average chemical composition on the chromatographic behavior, polyesters with varying ratio A : I were synthesized.[51] Equimolar portions of the monomers D and (A + I) (both PA grade from Merck, Darmstadt, Ger-

many) were carefully weighed into a 1-litter glass reactor such that the total amount was about 250 g. As catalyst, 0.25% (m/m) dibutyltinoxide (PA grade, Merck) was added. The mixture was heated up to a temperature of 220°C, which was reached in 20 min, under a nitrogen flow (0.2 L/min) and constant stirring at 150 rpm. During polycondensation, water was constantly removed by the nitrogen flow and was condensed in a Liebig cooler. The progress of the reaction was monitored by SEC and the reaction was stopped at a polystyrene equivalent molar mass of about 7500. Hereto, the hot reaction mixture was poured on a cold metal plate to quench the reaction. See products DA, DI, and DAI31-DAI13 in Table I.

To study the effect of both differing SD and CCD on the chromatographic behavior, a copolymerization by transesterification was carried out. Hereto, portions of the two homopolyesters, DA and DI (Table I) were carefully weighed in a 250-mL glass reactor such that the molar ratio A : I was 1 : 3 (comparable to samples PE2 and PE3) and the total amount was about 60 g. The reaction mixture was heated up to 204°C. Other conditions were the same as described above. During reaction, samples of about 500 mg were taken (samples *trans* in Table I) and the reaction was stopped after 5 h.

Chromatography Experiments

The HPLC equipment used for GPEC consisted of a Waters (Milford, MA, USA) 600E 4 solvent gradient pump, and a Waters 717 autosampler. The detector was a variable wavelength detector, Jasco (Tokyo, Japan) type 975, set at 277 nm. The column temperature was controlled using a thermostat type Mistral from Spark-Holland (Emmen, The Netherlands). Chromatograms were recorded using the Baseline-815 system from Waters.

For RP-GPEC, the column was a Novapak-C_{18} (C_{18}) column (d_p = 4 μm, pore size 60 Å, 150 × 3.9 mm) from Waters, and the solvents were water (Lichrosolv quality from Merck) and THF to both of which 200 μL acetic acid per litter was added.

End group analysis by NP-GPEC was based on a former study.[40] For this purpose, a Jordi Gel DVB Polyamine column (d_p = 5 μm, pore size 500 Å, 250 × 4.6 mm) from Jordi (Bellingham, MA) was used at a temperature of 35°C and a flow rate of 1.32 mL/min. The applied gradient was heptane (HEP) : dichloromethane (DCM) : THF : methanol (MeOH) (70 : 30 : 0 : 0) (v/v) to (0 : 100 : 0 : 0) (0 to 23.3 min), (0 : 100 : 0 : 0) to (0 : 0 : 100 : 0 (23.3 to 56.6 min), (0 : 0 : 100 : 0) to (0 : 0 : 0 : 100) (56.6 to 80 min), followed by an equilibration procedure as described in ref. 40 (HEP, DCM, and MeOH, all Lichrosolv quality from Merck).

For the determination of CCDs by NP-GPEC, a Nucleosil-100-5-NH_2 ('NH_2') column (d_p = 5 μm, pore size 100 Å, 200 × 4.0 mm) from Machery Nagel (Düren, Germany) was used. Prior to use, the solvents, DCM and THF, were dried overnight on molecular sieve, 0.3 nm (Merck). 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. Unless indicated otherwise, for RP-GPEC, samples were dissolved in THF and for NP-GPEC in DCM to a concentration of 10 mg/mL of which 10 μL was injected. For gradient strategy, the reader is referred to refs. 39 and 40.

SEC analysis was the same as described in ref. 39, except that a set of four Shodex (Showa Denko, Tokyo, Japan) KF columns (300 × 8 mm) consisting of KF805, KF804, KF803, KF802, and a guard column, 800P, was used. Unstabilized tetrahydrofuran (THF, HPLC grade from Rathburn, Brunschwig Chemie, Amsterdam, The Netherlands) with 1% (v/v) acetic acid was used as the mobile phase. This SEC system was also used for fractionation experiments to obtain low polydispersity fractions.

For the isolation of eluting fractions from SEC or GPEC, a fraction collector, type FC-205 from Gilson (Villiers-le-Bel, France) was used.

RESULTS AND DISCUSSION

Characterization of Copolyesters by RP-GPEC

The separation of aromatic (co)polyesters by RP-GPEC has been extensively studied and results with respect to resolution optimization and the influence of practical parameters as well as a discussion about the retention mechanism have been described in detail elsewhere.[39,42] The RP-GPEC separation of the two homopolyesters, DA and DI, and the copolyester PE2, are compared in Figure 1. Highly detailed chromatograms with respect to oligomers and end groups, containing much more structural information compared to SEC,[39] are obtained. Peak assignment is as indicated in the chromatograms and has been discussed in ref. 39. It is easily recognized that in the

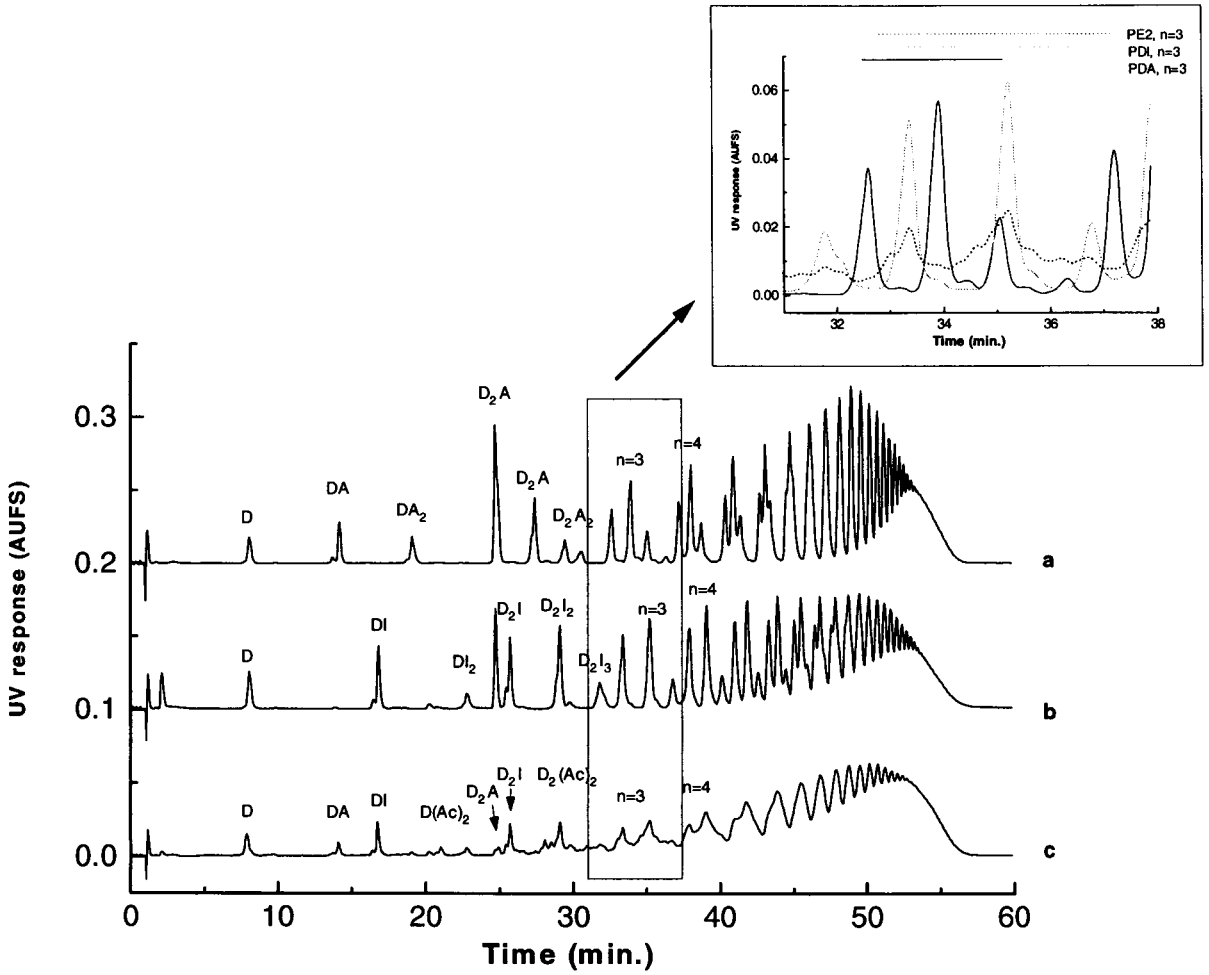

Figure 1 RP-GPEC chromatograms for homo polyesters PDA (a) and PDI (b) and copolyester PE2 (c). Column: Novapak-C_{18} (150 × 3.9 mm), temperature: 35°C, eluent: water-THF (+200 μL acetic acid per litre) (70 : 10) to (10 : 90) (0 to 60 min), flow: 1.0 mL/min, injection: 10 μL, concentration: 10 mg/m, detection: UV at 277 nm. D = diol, A = adipic acid, I = isophtalic acid, Ac = acid.

chromatogram of PE2 extra peaks and shoulders compared to the homopolyesters are present, which must be due to copolymer products. This indicates that RP-GPEC can be used to detect the formation of certain products during and after the copolymerization.

As an example, the formation of dimers consisting of two diol units and one di-acid unit, D_2A and D_2I, respectively (see also Fig. 1), was followed during the synthesis of DAI13-2. In Figure 2, the logarithm of the peak-area-ratio D_2A : D_2I is plotted vs. the reaction time. It can be seen that during the first stage of the polycondensation the product D_2A was mainly formed, in spite of the fact that the initial amount of the monomer A was much less than the amount of monomer I. During the reaction, the peak-area ratio D_2A:D_2I gradually changes in favor of the latter product. These observations indicate large reactivity differences between both di-acids. This is in accordance with theory from which it would be expected that due to sterical hindrance, the reactivity of I would be considerably smaller than that of A.[52] Even after a reaction time of 19 h, when a weight average molar mass of 8000 was reached (Table II), the peak-area-ratio has not reached a stable value, indicating that the chemical composition in this part of the molar mass distribution is still changing. Qualitatively, the same results were obtained for peak ratios for oligomers with a higher degree of polymerization (p).[51] This indicates that the expectation of the formation of a purely statisti-

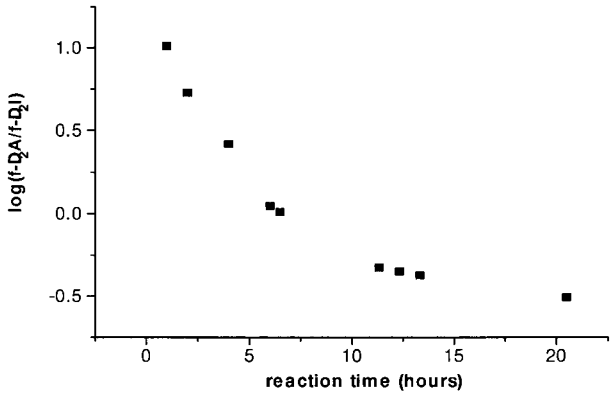

Figure 2 Logarithm of the peak area ratio of peaks $D_2A : D_2I$ of product DAI13-2 measured by RP-GPEC as function of reaction time. RP-GPEC conditions, see Figure 1.

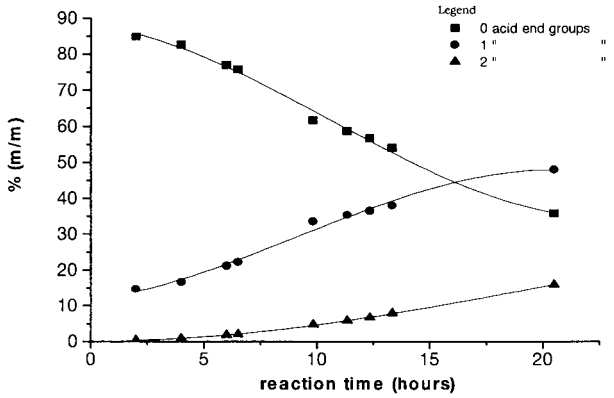

Figure 3 Relative amounts [% (w/w)] of oligomers with p = 2, having different end groups, as function of reaction time, measured by RP-GPEC. RP-GPEC conditions, see Figure 1.

cally determined CCD, based on the assumption of a thermodynamic equilibrium, is not justified in this case.

The formation of oligomers having 0, 1, or 2 acidic end groups can also be followed from RP-GPEC. An example for the oligomer p = 2 of sample DAI13-2 is shown in Figure 3, but qualitatively the same observations were made for other oligomers and other copolyesters with a different average chemical composition. During the first stage of the reaction, preferentially oligomers with two alcoholic end groups are formed, whereas the formation of oligomers containing one or two acidic end groups increases when the reaction proceeds. Nevertheless, even after 19 h no statistical distribution of 1 : 2 : 1 for oligomers containing 0, 1, and 2 acidic end groups, which would be expected from the molar ratios of the monomers, is reached. This also indicates that the formation of end groups does not follow directly from statistics.

Table II Peak Area Percentages from NP-GPEC for the End Group Fractions of Various (Co)polyesters

Sample	2 Alcoholic End Groups (%)	1 or 2 Acidic End Groups (%)
PE2	0.30 ± 0.01	0.70 ± 0.01
PE3	0.40	0.60
DA	0.33	0.67
DAI31	0.36	0.64
DAI21	0.40	0.60
DAI11	0.39	0.61
DAI12	0.38	0.62
DAI13	0.41	0.59
DI	0.39	0.61

The highly detailed RP-GPEC separations with respect to degree of polymerization can also be used for the determination of an oligomer distribution. In a former study, results for samples PE2 and PE3 were found to be in excellent agreement with the theoretical distribution.[39] Thus, polyesterification proceeded in a normal way, without the occurrence of many side reactions caused by, for example, anhydride formation. Furthermore, RP-GPEC was used for the calculation of average molar masses of these samples.[39]

In Figure 4, the two large scale copolyesters, PE2 and PE3, which are similar in overall chemical composition, as was confirmed by SEC and NMR (Table I), are compared by RP-GPEC. Both samples appear to exhibit somewhat different mechanical properties. Several chemical differences between both products can be indicated from the low molar mass part of the chromatograms. At first, from the different peak shape of the diol peaks, it can be concluded that the purity of this monomer is different in both cases, which was confirmed by NMR analysis. Furthermore, a large difference between the peak area ratio DA : DI (Fig. 4) is found: 0.29 ± 0.01 for PE2 vs. 0.62 ± 0.01 for PE3. Although this indicates that PE3 contains more adipic acid, these differences are much larger than the differences in molar ratios A : I found by NMR: 0.32 ± 0.02 for PE2 and 0.43 ± 0.02 for PE3. Because NMR provides information on the bulk composition and GPEC, in this

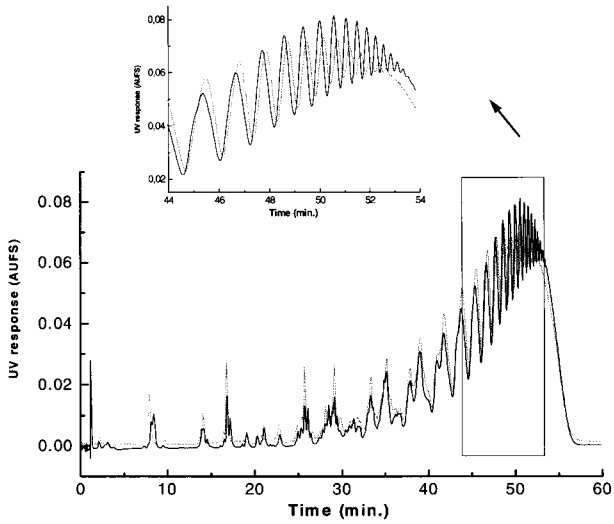

Figure 4 Comparison of PE2 (gray line) and PE3 (black line) by RP-GPEC. RP-GPEC conditions, see Figure 1.

case, on the composition of a low molar mass part, it is obvious that for PE3 the ratio of adipic acid in the low molar mass part of the sample compared to the average is much higher than for PE2. This suggests that the distribution of A and I over the molar mass distribution, at least in the low molar mass part, is not completely homogeneous and clearly different for PE2 and PE3. The existence of such intermolecular microstructural differences cannot be detected by a conventional method such as NMR alone.

Effect of Chemical Composition on Elution Characteristics in RP-GPEC

From Figure 4, several other differences between the elution patterns of PE2 and PE3 can be observed. Retention times of the higher molar mass oligomers are somewhat higher for PE2 than for PE3. Furthermore, peak heights of oligomers 10–20 are significantly larger for PE3 than for PE2. All differences were found to be highly reproducible and must, therefore, be the result of chemical differences between both copolyesters. Therefore, the effect of several parameters, for example, average chemical composition, CCD, and end group composition, on the peak retention times and peak widths was further investigated. It was hoped that this would provide more insight in the nature of the observed differences between both copolyesters.

For the investigation of the influence of average chemical composition on oligomer retention, retention times for all oligomers of the polyesters DA, DI, and DAI31-DAI13 were determined. A characteristic example is shown in Figure 5, from which it can be seen that for oligomer p = 12 retention time decreases with increasing amount of A. Qualitatively, the same trends were found for all other oligomers. Subsequently, for all oligomers with varying p, retention times were fitted vs. chemical composition. Finally, for the two copolyesters of interest, PE2 and PE3, the chemical composition for each oligomer was determined from the respective calibration curves of retention time versus chemical composition (as indicated in Fig. 5). In all cases, for PE2 lower values of f-A compared to PE3 were found, which is in qualitative agreement with NMR (Table I). However, especially for PE2, the observed values were significantly less than zero, thus having no physical relevance, of course. Obviously, peak position is also influenced by other parameters than average chemical composition.

Therefore, as a next step, the effect of end group composition on the oligomer peak position was investigated. For the higher molar mass oligomers, peaks are, in fact, composite peaks, consisting of fractions containing 0, 1, and 2 acidic end groups. As was demonstrated before,[39] retention time within an oligomer fraction with a certain degree of polymerization, p, increases with increasing number of acidic end groups. Therefore, the average end group composition of the various copolyesters was determined by NP-GPEC (see Experimental section), to elucidate whether differing peak positions could possibly be explained from differing end group compositions. Results are shown in Table II.

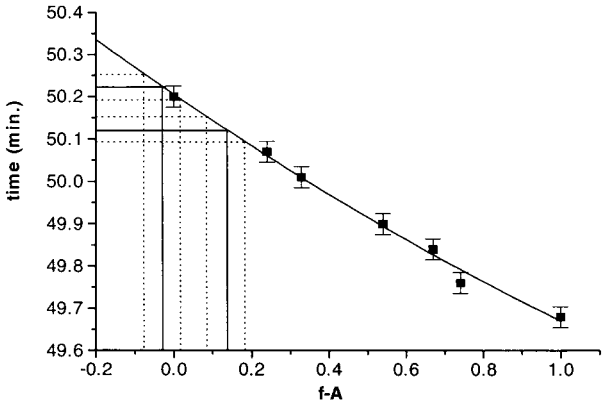

Figure 5 Retention time of oligomer p = 12 as a function of the average chemical composition of the copolyesters. RP-GPEC conditions, see Figure 1.

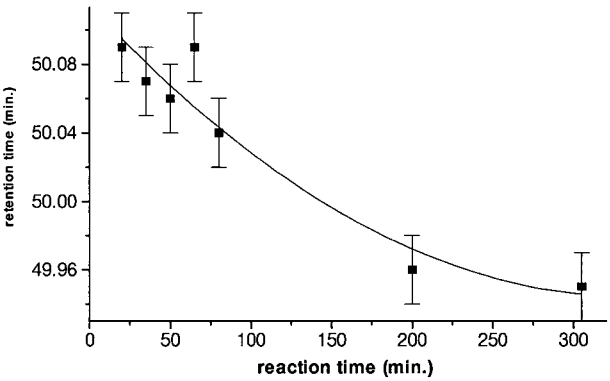

Figure 6 Retention time of oligomer p = 12 of the copolyester made by transesterification as function of transesterification time. RP-GPEC conditions, see Figure 1.

Clearly, PE2 contains more acidic end groups than PE3 and the other, "model" copolyesters. This will result in somewhat longer retention times of the respective oligomers. It is, furthermore, worthwhile noting that the end group composition of PE3 is roughly the same as that of most model copolyesters, whereas for PE2 a significant difference is found. Thus, end groups differences may (partly) account for the observed retention time differences between oligomers from PE2 and PE3. Nevertheless, when looking at Figure 4, it is our feeling that this explanation cannot completely account for the differences in the oligomer patterns, because retention time shifts for especially the higher molar mass oligomers are relatively large compared to the total peak width.

Another possible explanation for retention time differences is a difference in blockiness between the copolyesters. From comparative studies on block and random copolymers[26] it is known that retention time differences between both types of polymers will occur, due to the fact that block copolymers behave more like homopolymers of one kind. To check whether such intramolecular structural differences also influence retention behavior of copolyesters, the elution behavior of samples *trans* that were taken during the transesterification reaction was studied. In these products, the blockiness will decrease during time, resulting in a more randomized product. In Figure 6, only the retention time of oligomer p = 12 is plotted as a function of the transesterification time, but exactly the same trends were found for the other oligomers. Clearly, retention decreases with increasing reaction time. This is not caused by a changing end group composition during transesterification, because NP-GPEC measurements revealed no significant differences between the respective products. Therefore, observed retention differences may be attributed to the fact that in the beginning of the reaction, products will behave more like a homopolymer with isophtalic acid. Later on, more randomized copolymers are formed, thus giving rise to a decrease in retention. This, however, is somewhat speculative, because opposite trends, for example, increasing oligomer retention times, were found for products taken during another transesterification, where the molar ratio of A : I was 1 : 1.[51] In any case, oligomer retention is clearly influenced by its intramolecular microstructure.

Next to differences in oligomer retention times, also differences in resolution for the higher molar mass oligomers between PE2 and PE3 are found (Fig. 4). Peak widths of the various oligomers are certainly related to the broadness of the distributions according to chemical composition, oligomer sequence, and end groups. This is evidenced from the comparison of the chromatographic behavior of products *trans*-S2–*trans*-S6 (Fig. 7). Due to the transesterification, a broadening of SD and CCD occurs that obviously results in an increasing peak width for the respective oligomers. The increasing peak widths cannot be ascribed to end groups, because, from NP-GPEC, the end group composition was found to remain constant during transesterification (result not shown).

Thus, indeed differences in SD and/or CCD *might* be the cause of the difference in oligomer resolution between PE2 and PE3. Nevertheless,

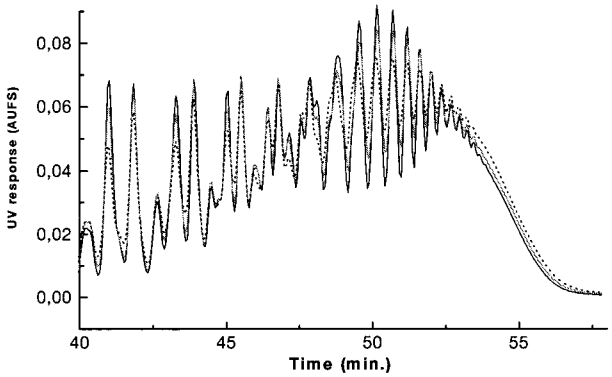

Figure 7 Influence of transesterification time on the peak width in the high molar mass part of the RP-GPEC chromatograms. Black line: *trans*-S2 (20 min), gray line: *trans*-S4 (50 min), dotted line: *trans*-S6 (80 min). RP-GPEC conditions, see Figure 1.

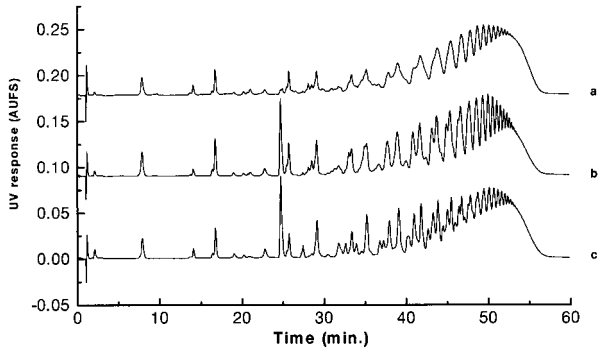

Figure 8 Comparison of PE2 (a, copolyester made at large scale), DAI13 (b, copolyester made at laboratory scale), and *trans*-S6 (c, copolyester from transesterification) by RP-GPEC. RP-GPEC conditions, see Figure 1.

they may also be caused by the observed differences in end group composition (Table II), or FTD. From RP-GPEC alone, it is not possible to discriminate between the various phenomena.

During the transesterification reaction in which products *trans* were formed, the molar mass changed only to a minor extent (Table I) during the first 80 min, and no differences at all could be observed from NMR[51] in contrast to RP-GPEC (Fig. 7). After this time, molar mass started to increase, which could be observed from both SEC and RP-GPEC. These results suggest that in the beginning mainly transesterification reactions occur, and after a certain time, chain growth becomes more important. Thus, RP-GPEC provides more information on the proceeding of copolymerization by transesterification than conventional methods do. Nevertheless, due to the relatively low resolution especially within the higher molar mass oligomers, it cannot unambiguously be seen, whether the transesterification after 80 min has led to a completely random product.

In conclusion, it has been shown that both peak retention and resolution of oligomer peaks of copolyesters with nearly equal molar mass in RP-GPEC are influenced by various parameters. RP-GPEC seems to be very sensitive to microstructural differences between copolyesters. This is again demonstrated in Figure 8, where three copolyesters, made by polymerization at a large scale, polymerization at laboratory scale, and polymerization by transesterification respectively, are compared. Although SEC and NMR measurements suggested the products to closely resemble each other (Table I), clear differences are observed from RP-GPEC. Nevertheless, from RP-GPEC alone it is difficult to assign those variations, especially for the higher molar mass oligomers, to either end group, chemical composition, or sequence differences. This is mainly due to the fact that separation is dominated by molar mass, and resolution with respect to chemical composition differences is relatively low. Therefore, RP-GPEC for low molar mass copolyesters must be considered mainly as a qualitative fingerprinting tool, rather than a method by which structural differences can be quantitatively detected.

Determination of the MMFTD of Copolyesters by a Combination of NP-GPEC and SEC

In an earlier study, it was shown that in NP-GPEC separation of (co)polyesters is dominated by their chemical composition, especially the end group composition, whereas molar mass plays a less important role compared to RP-GPEC.[40] Two examples of NP-GPEC separations are given in Figure 9.

In Figure 9(A), the separation of the two homopolyesters, PDA and PDI, and copolyester PE2 on a polyamine (PA) column is shown. It can be seen that a distinct separation according to functionality, for example, fractions containing respectively 0, 1, or 2 acidic end groups and a fraction containing cyclic products, is obtained. The identity of those fractions was confirmed by preparative fractionation, followed by RP-GPEC[40] and NMR and by LC-MS. From these chromatograms, the amounts of the various end group fractions can be determined. For the two copolyesters, the weight fraction containing two alcoholic end groups was found to be 0.30 ± 0.01 for PE2 and 0.40 for PE3. This significant difference in average end group composition was not reflected in the acid numbers from titration analysis, which revealed $24 \pm 10\%$ mg KOH/g for PE2 and 27 for PE3 (Table I). Obviously, results from NP-GPEC are much more sensitive for deviations in end group composition than titration analysis. It must be mentioned here that quantitative analysis of the chromatograms is possible, because the detection wavelength, 277 nm, was chosen at the absorption maximum of the diol. The UV absorption is, therefore, caused mainly by the diol parts of the oligomers, thus strongly reducing the influence of the diacid type, as was already shown in previous work.[39]

Next, it is interesting to determine the molar mass distributions (MMD) of the respective end

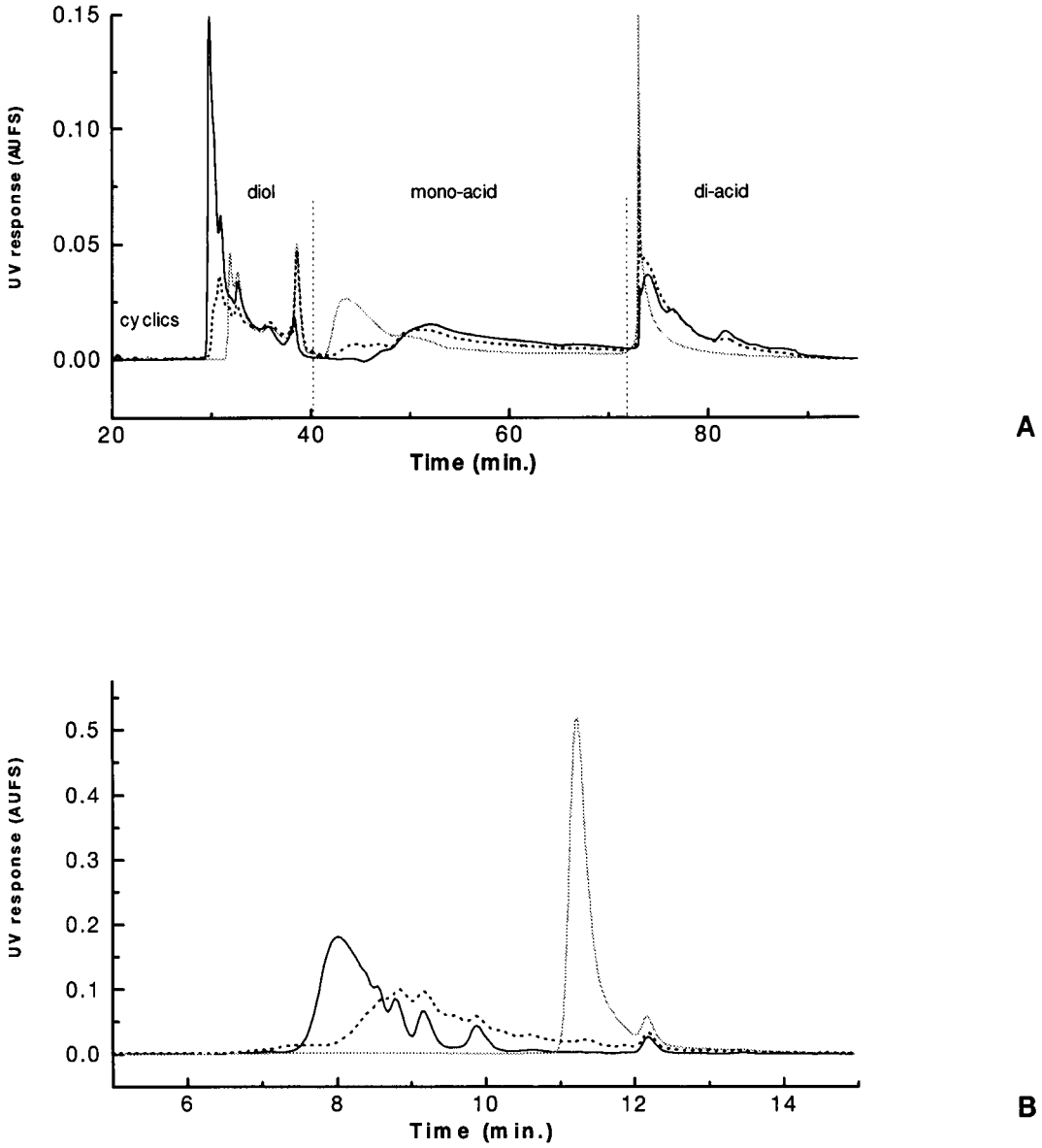

Figure 9 Separation of homo polyesters PDI and PDA and copolyester PE2 on a polyamine column (A) and an NH_2 column (B). In (B) only the elution of the diol fractions is shown. Sample concentrations: 10 mg/mL (in DCM). Black line: PDI, gray line: PDA, dotted line: PE2. (A) Eluent: HEP-DCM-THF-MeOH (100 : 0 : 0 : 0) to (0 : 100 : 0 : 0) (0 to 33.3 min), (0 : 100 : 0 : 0) to (0 : 0 : 100 : 0) (33.3 to 66.6 min), (0 : 0 : 100 : 0) to (0 : 0 : 0 : 100) (66.6 to 100 min), flow: 1.32 mL/min, injection: 10 μL, detection: UV at 277 nm. (B) Eluent: DCM-THF (100 : 0) to (94 : 6) (0 to 15 min), temperature: 45°C, flow: 1.5 mL/min, injection: 10 μL, detection: UV at 277 nm.

group fractions, to obtain information about the distribution of the end groups over the MMD. Hereto, samples PE2, PE3, and PE7 were separated into three fractions on the PA column, for example, cyclics, diol, and mono-acid + di-acid. The latter two fractions were taken together, because no baseline separation could be achieved in NP-GPEC.[40] The thus obtained fractions were characterized by SEC, together with an unfractionated polyester sample. The resulting chromatograms for PE2 and PE7 are shown in Figure 10, and the corresponding polystyrene equivalent weight average molar masses in Table III. It can be seen that the MMDs of the respective end

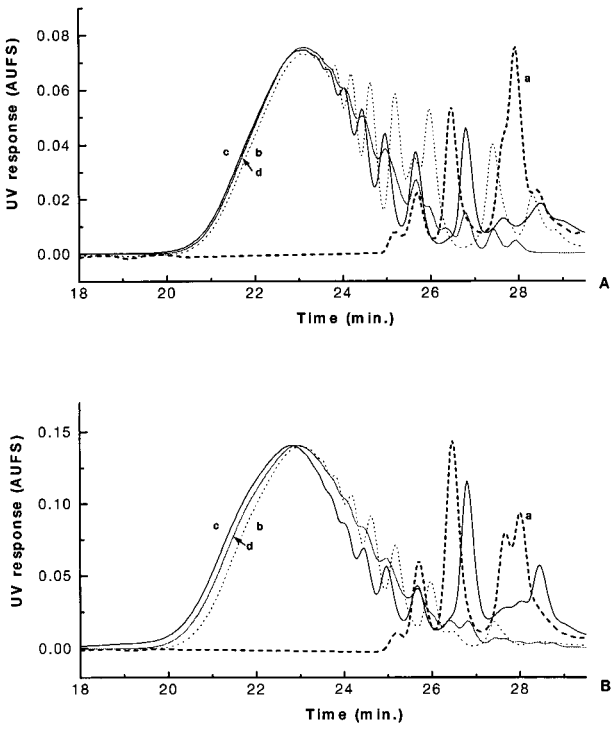

Figure 10 SEC chromatograms of NP-GPEC fractions of PE7 (A) and PE2 (B). a (dash): cyclics, b (dot): diol, c (black): mono + di-acid, d (gray): unfractionated polyester. NP-GPEC conditions, see text. SEC conditions: columns: Shodex KF805, KF804, KF803, KF802, KF800p (guard columns) (in series), temperature: 40°C, eluent: THF + 1% (v/v) acetic acid, flow: 1.5 mL/min, injection: 200 μL, detection: UV at 254 nm.

group fractions are not identical to the MMDs of the unfractionated polyesters. The molar masses of the cyclic products are very low, as is expected from theory.[47] Molar masses of all diol fractions are shifted towards lower molar mass compared to the unfractionated polyesters, whereas a shift towards higher molar masses is found for the mono-acid + di-acid fractions. Shifts are comparable for both PE2 and PE3 (not shown), but significantly lower for PE7. These results are in qualitative agreement with results from other workers.[32,53] Shifts in molar masses most probably cannot be attributed to differences in hydrodynamic volume due to differing end groups, because it was shown for other polyester types that above a molar mass of about 700, such differences do not affect hydrodynamic volumes any more.[53]

To further confirm these results, the reversed analysis was carried out. For this purpose all three polyesters were separated into 14 fractions on SEC, which were subsequently injected on a PA column. End group compositions were determined for each SEC fraction, the results of which are shown in Figure 11. They qualitatively confirm the NP-GPEC/ SEC results. For PE7, only slight changes of end group compositions as function of molar mass are observed, whereas changes for both PE2 and PE3 are much more pronounced. In contrast to the analysis described above, differences between PE2 and PE3 are also found. This is presumably due to the higher number of fractions taken from SEC in this analysis compared to the NP-GPEC fractionation described above, thus providing more detailed information. Obviously, by combining SEC and NP-GPEC, differences in FTMMD between closely resembling polyesters can be determined. The explanation for the nonhomogenous distribution of end groups over the MMD is not known at this moment, and does not follow straightforwardly from theories on kinetics of polyesterification.

Determination of the MMCCD of Copolyesters by SEC/ NP-GPEC

Next to a separation according to end groups, a further separation to the chemical composition of the backbone is obtained by NP-GPEC. This can be observed from a comparison between the elution patterns of the diol fraction (no acidic end groups) of both homopolyesters in Figure 9(A). The diol fraction of PDI elutes somewhat earlier than that of PDA, whereas the elution maximum of PE2 lies in between both homopolyesters. On an NH_2 column, resolution between the respective end group fractions is much larger, and the di-acid fraction cannot be eluted at all.[40] On the other hand, separation to the chemical composition of the polyester backbone within one end group fraction is much more pronounced and there are no interferences with other end group fractions due to relatively low selectivity. This is demonstrated in Figure 9(B), where the chro-

Table III Weight-Average Molar Masses (M_w) of the End Group Fractions Obtained by NP-GPEC

	M_w			
Sample	Unfractionated	Cyclics	Diol	Mono + di-acid
PE2	8200	1200	7600	9500
PE3	7900	1200	7500	8800
PE7	6800	1200	6300	6900

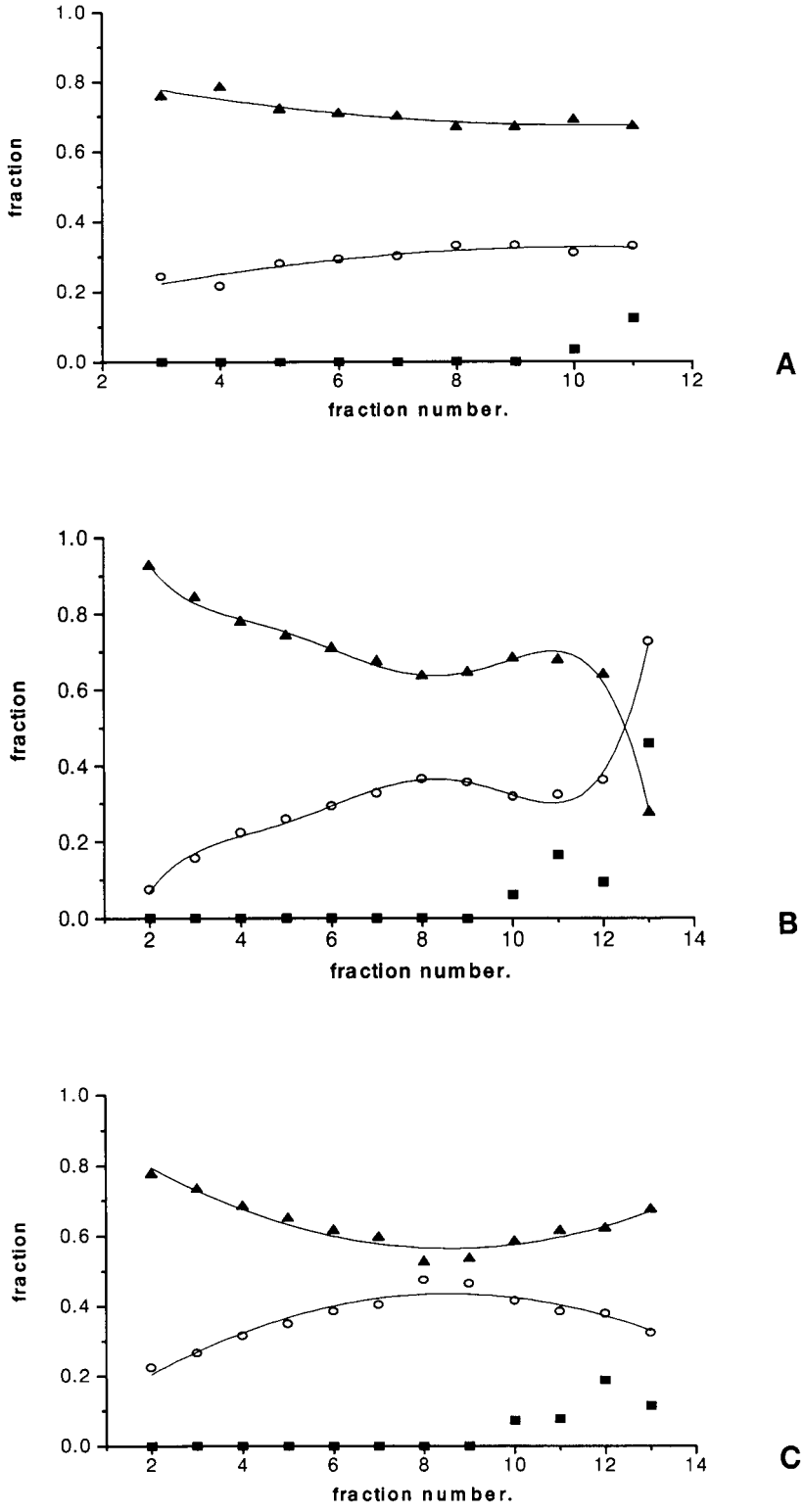

Figure 11 Amounts of the respective end group fractions versus SEC-fraction number. (A) PE7, (B) PE2, (C) PE3. Square: cyclics, circle: diol terminated chains, triangle: mono- and di-acid terminated chains. SEC conditions, see text. NP-GPEC conditions, see Figure 10(B).

matograms of the diol fractions of the homopolyesters and copolyester PE2 are compared. A distinct separation between both homopolymers is obtained, whereas the copolyester elutes in between the homopolyesters. Therefore, this separation can possibly be used to study the CCD of copolyesters without interference of the end group composition. It must be mentioned that this, for the kind of copolyesters in this study, can only be done for the diol fractions. In the monoacid and di-acid fractions, end groups can be either isophtalic acid or adipic acid. Because this will also influence the separation, for these fractions no method that is independent of end group composition can be is obtained.

To use NP-GPEC for the determination of CCDs, at first the separation was optimized. It was found that a gradient steepness of 0.4% (v/v) THF/min. is a good compromise between resolution and analysis time[54] and that, at a temperature of 45°C, molar mass resolution is minimized. Figure 9(B) shows the optimal separation result.

Because molar mass influences cannot be completely suppressed in NP-GPEC, an additional step is necessary to obtain a separation that is only governed by the chemical composition of the polyester backbone. Therefore, as a first step, (co)polyesters were fractionated by SEC. Thus, for each (co)polyester, low dispersity fractions with equal hydrodynamic volume and, therefore, approximately equal molar masses, were obtained. Polystyrene equivalent molar masses and polydispersity values, obtained by reinjection of the fractions on SEC, are given in Table IV. For the subsequent analysis by NP-GPEC, SEC fractions were redissolved up to a concentration of 2.0 mg/mL in DCM. Care was taken that the final concentrations of 2.0 mg/mL were made accurately, because concentration variations were

Table IV Polystyrene Equivalent Molar Masses of Low Polydispersity Fractions of (Co)polyesters Obtained by SEC

Fraction Number	M_n	M_w	MMD[a]
3	25,500	27,600	1.08
4	16,800	18,200	1.07
5	11,600	12,400	1.05
6	8000	8600	1.08
7	5400	5700	1.06
9	2400	2500	1.07

[a] Molar Mass Distribution (M_w/M_n).

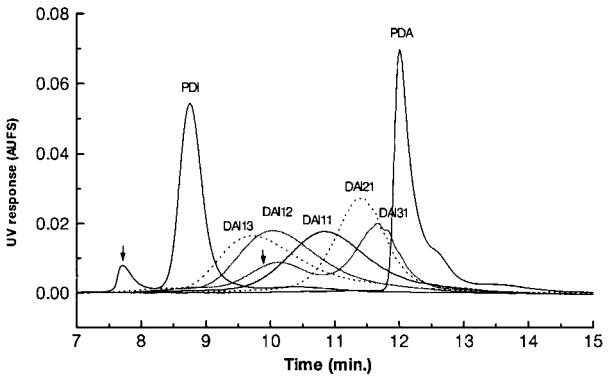

Figure 12 NP-GPEC chromatograms of SEC fraction 5 of homo polyesters PDA and PDI and copolyesters DAI31-DAI13. Contaminations indicated with arrows (DAI31 is probably contaminated with DAI12). NP-GPEC conditions, see Figure 10(B).

found to influence retention time.[54] This, of course, is unfavorable here, because retention is used for the estimation of chemical composition. Thus, by combined SEC/NP-GPEC, in fact, a three-dimensional separation, for example, subsequent separation on molar mass, end groups, and chemical composition of the polyester backbone, is obtained, in which the latter two separation steps are brought about in one chromatographic step.

In Figure 12, NP-GPEC chromatograms of SEC fractions 5 of the homopolyesters and copolyesters DAI31-DAI13 are shown. For both homopolyesters, relatively narrow peaks are obtained. The retention of the copolyesters steadily increases with increasing f-A, which is in accordance with expectations based on the chromatographic behavior of the homopolyesters. It is interesting to note that the observed retention time dependence is opposite to what was found in RP-GPEC (Fig. 5), which would also be anticipated from polarity rules. The peak width for the copolyesters is significantly larger than that for the homopolyesters. This must be due to the fact that the chemical composition of the former polymers is less homogeneous, thus proving that copolyesters indeed have a CCD. To our knowledge, this is the first example of an experimental verification of the occurrence of a CCD in a copolyester made by step reaction.

To further confirm the separation as shown in Figure 12, SEC fraction 3 of sample PE2 was further separated into fractions by NP-GPEC. For this purpose, fractions were taken every 0.7 min between 6.5 and 13.5 min. The obtained NP-

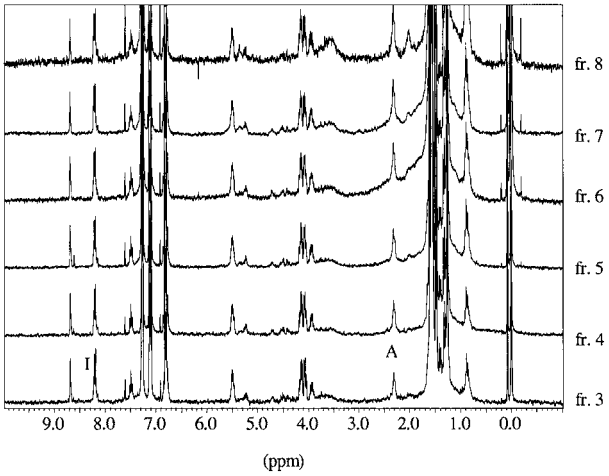

Figure 13 ^{1}H-NMR spectra of NP-GPEC fractions of SEC fraction 3 of PE2. NP-GPEC fractions as indicated. NP-GPEC fractionation conditions, see text. NMR conditions: 2.5 mm micro capillary probe, solvent: $CDCl_3$.

GPEC fractions 3–8 were measured by ^{1}H-NMR, using a 2.5-mm microcapillary probe. NMR spectra are shown in Figure 13. The different signal-to-noise ratio for the respective spectra is due to a differing number of pulses, as is indicated in the figure. Signals at 8.2 and 8.6 ppm are due to isophtalic acid, and the signal at 2.3 ppm is due to adipic acid. It is easily recognized that the relative intensity of the signal at 2.3 ppm increases with increasing fraction number, indicating an increasing amount of adipic acid. This confirms earlier observations that the NP-GPEC separation is indeed based on the chemical composition of the polyester backbone.

To be able to calculate CCDs of copolyesters, the NP-GPEC system had to calibrated. This was done by fitting the retention times of the distribution maxims of SEC fractions 3–7 vs. chemical composition (f-A). Thus, for each SEC fraction, i.e., molar mass, a calibration curve was obtained. Although, like for RP-GPEC, again several curve types providing a reasonable fit of the data points were obtained, for further calculations only one curve type showing a monotonously increasing function, was taken into account.[54] Because the peak maximum does not necessarily represent the average composition, the method used here must mainly be considered as a rough, first approximation for the quantitative calculations of polyester CCDs. Improvements could be made by using an iterative procedure as was proposed by Teramachi et al.[28] to calculate the retention time corresponding to the average chemical composition. SEC fractions 1 and 2 were not taken into account due to the low amounts of sample available. This was also the case for fractions 8 and higher, because separations into oligomers were obtained, thus hindering unambiguous chemical composition calibration.

In Figure 14, the calculated CCDs of fractions 3–6 of both PE2 and PE3 are shown. Distinct differences between both copolyesters are found. For SEC fractions 4–6, it is easily recognized that the average f-A of PE2 is lower than that of PE3. This is in qualitative accordance with results from NMR (Table I), although the found differences by NP-GPEC seem to be relatively large compared to differences found by NMR. In contrast, for fraction 3, f-A for PE3 is slightly lower than that for PE2, which indicates differences in the distribution of both di-acids over the molar mass distribution. The relatively high f-A for PE3 in the low molar mass fractions qualitatively confirms RP-GPEC results where peak ratios were compared with NMR results (see before).

Because the ratio A : I for PE3 deviates somewhat less from unity than that for PE2, it might be expected that the CCDs for the former copolyester are somewhat broader. This is indeed the case for fractions 5–7. Nevertheless, the differences in broadness for fractions 5 and 6 seem to be larger than what might be expected from the small difference in average composition. This is confirmed by a comparison of the chromatograms of those fractions with the chromatograms of corresponding fractions of copolyesters DAI13 and DAI12 (see Fig. 15). Although f-A for PE3 lies in between that of DAI13 and DAI12 (Table I), the distribution for PE3 is significantly broader. In contrast, the broadness of the distribution of PE2 is comparable to that of DAI13 and DAI12. It seems that in terms of CCD, PE2 much more resembles the model copolyesters than PE3 does, whereas with respect to the end group composition the opposite was found (Table II). Furthermore, the somewhat broader CCD of PE2 compared to PE3 for fraction 3 is also unexpected.

For statistical reasons, the broadness of the CCD is expected to decrease with increasing molar mass, because the probability of the formation of long chains with a chemical composition largely differing from the average composition is lower than that of the formation of short chains. Especially for PE2, the opposite trend is observed, which indicates that the CCDs of the respective molar mass fractions cannot be purely described

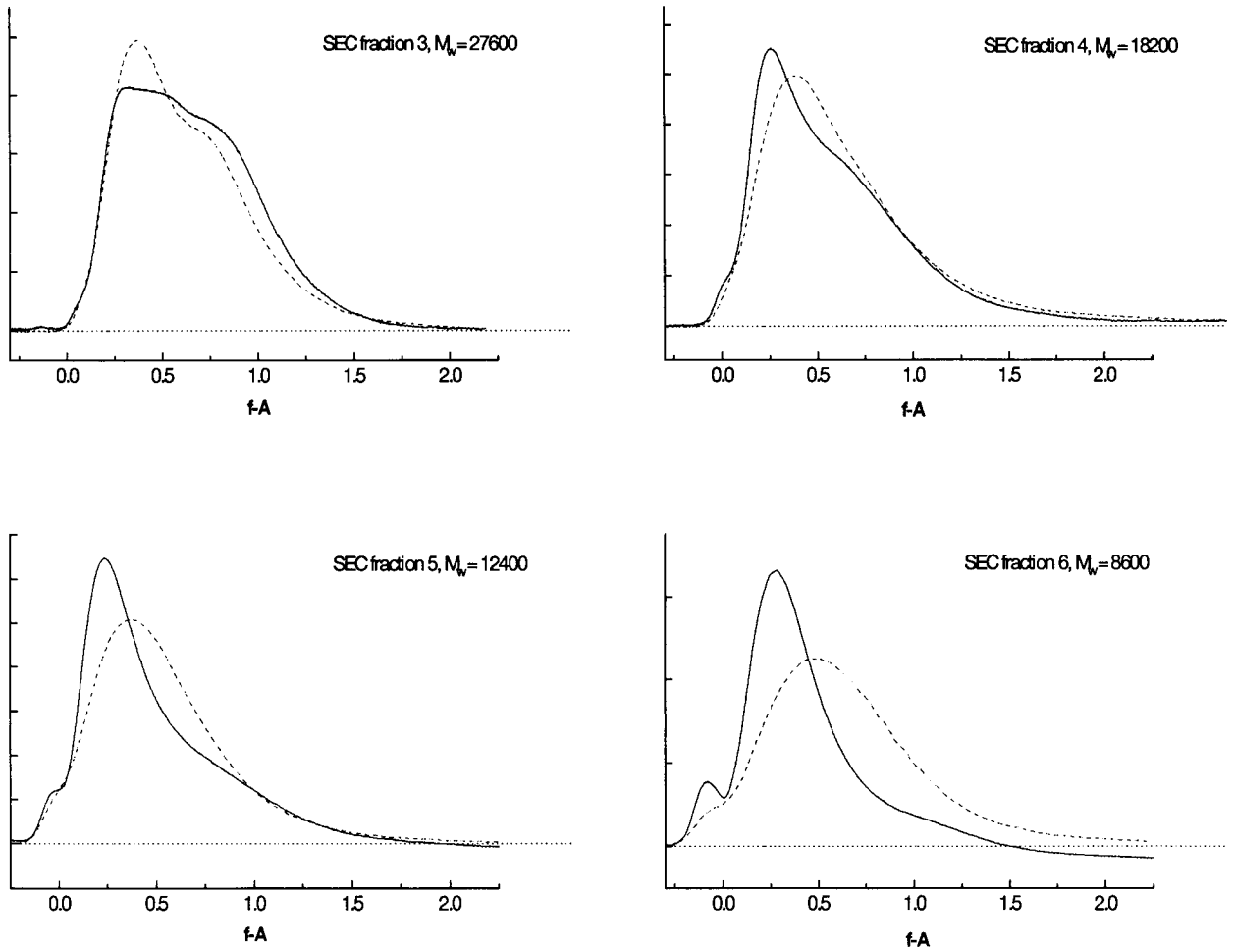

Figure 14 Comparison of calculated CCDs of SEC fractions 4–6 of PE2 (straight line) and PE3 (dashed line).

from statistics based on the assumption of thermodynamic equilibrium conditions. It must be mentioned here that a part of the increasing broadening with molar mass may be attributed to increasing chromatographic band dispersion due to lower diffusion coefficients for the higher molar mass fractions. However, these effects cannot explain the different behavior for PE2 as compared to PE3. Obviously, microstructural differences found between both copolyesters can qualitatively only be explained from the different reaction kinetic behavior, determining the rates of transesterification vs. chain growth reactions and, thus, the final microstructure also.

It must be kept in mind that the calculated CCDs in Figure 14 are not corrected for chromatographic broadening, which explains f-A values exceeding unity. This effect influences the total peak width to a significant extent as can be concluded from a comparison of the homopolyesters and the copolyesters in Figure 12. Therefore, the differences between the two copolyesters are certainly masked by the chromatographic broadening, indicating that the relative differences due to chemical composition variations are even larger than would be concluded from Figure 14. Unfortunately, a model for the chromatographic broadening correction for polymers in adsorption chromatography under nonequilibrium, gradient elution conditions is not available at this moment.

A final comparison between PE2 and PE3 is made in Figure 16, where the MMCCD plots (which, for reasons mentioned earlier, cover only a part of the total molar mass distribution) for the diol fractions are given. From this figure and from the discussions above, it is clear that the chemical microstructure of both products is different,

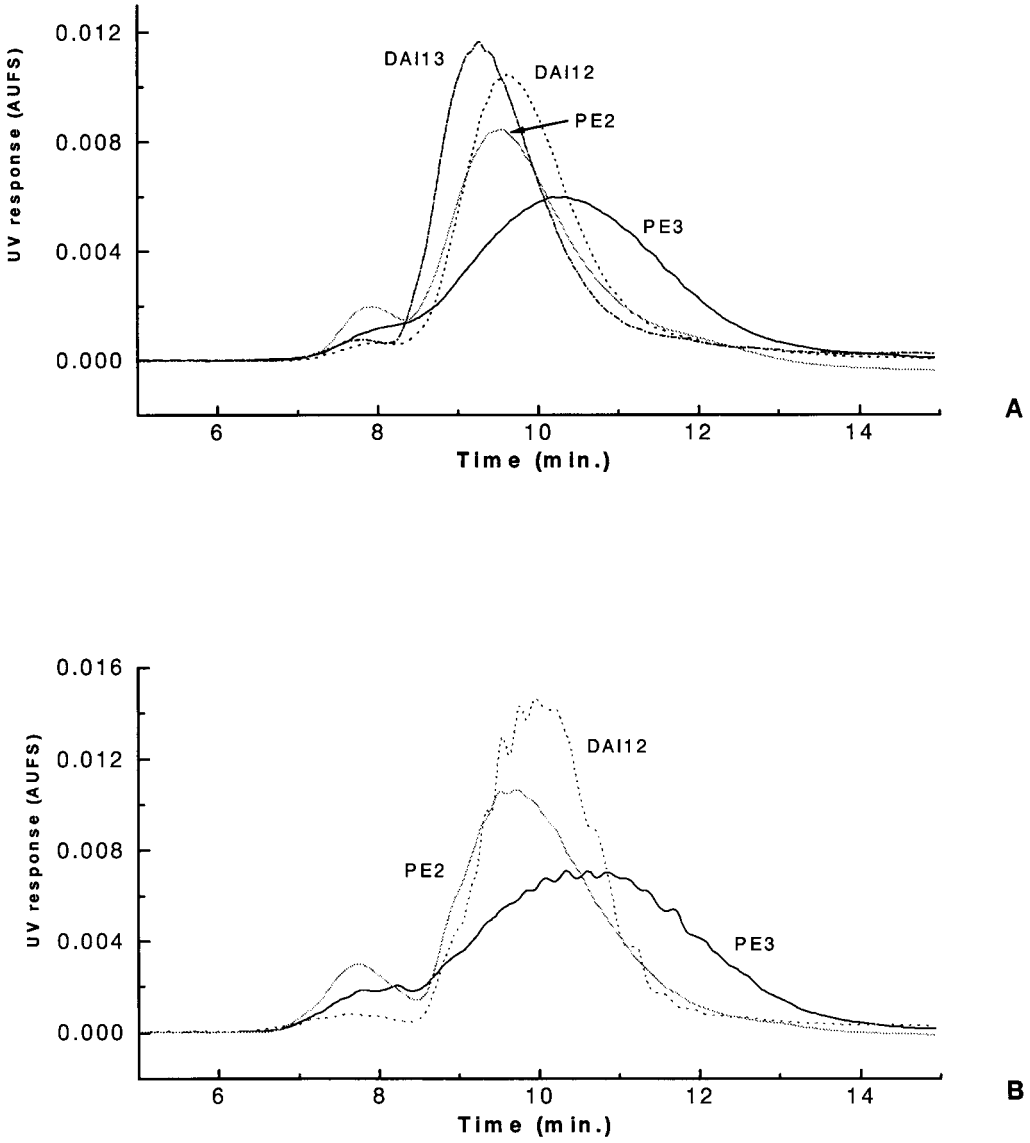

Figure 15 Comparison of peak broadness in NP-GPEC of SEC fraction 6 (A) and 7 (B) of PE2, PE3, DAI12, and DAI13. NP-GPEC conditions, see Figure 10(B).

which is not revealed from the slightly different average composition.

In Figure 17, a comparison is made between chromatograms of SEC fraction 5 of both homopolyesters and products *trans*-S3 and *trans*-S6 taken during the transesterification reaction. It is observed that in the copolyesters relatively large fractions of the homopolyesters are present and that the CCDs are far from a statistical distribution. This indicates that the transesterification reaction after 80 min (*trans*-S6) has not led to a product with a degree of randomization that is comparable to the other copolyesters in this study. This conclusion could not unambiguously be drawn from RP-GPEC, where the observations on oligomer peak width in the high molar mass part even might suggest that randomization of this product is complete.

It is obvious that NP-GPEC provides more insight in the chemical microstructure of copolyesters than RP-GPEC. Where RP-GPEC is mainly a fingerprinting tool that can be used as a relatively simple and versatile method to detect differences between samples, by NP-GPEC it is possible to determine, both qualitatively and quantitatively, the origin of these differences, for example, either end group distribution or the CCD of the backbone. In the future, the coupling of NP-GPEC

results with practical behavior of polyesters will provide more insight into relations between chemical microstructure and properties of copolyesters.

CONCLUSIONS

RP-GPEC was shown to provide highly detailed separations for aromatic copolyesters. Especially for the low molar masses, information upon chemical composition (CC) differences was obtained. It was found that even after a polyesterification time of 19 h, the chemical microstructure of the investigated copolyesters still changed. This makes the assumption that a predictable, statistically determined CCD is formed in all cases, questionable. Indeed, from a comparison between the chemical composition in the low molar mass parts of two strongly resembling copolyesters, by RP-GPEC and their corresponding average compositions, qualitative evidence for differences in their respective microstructures was found. It was found difficult to unambiguously assign differences in the high molar mass parts of RP-GPEC chromatograms, which is due to the fact that separation is dominated by molar mass, and resolution with respect to CC differences is relatively low. Peak position of the oligomers was shown to depend on the average CC of the copolyester, the end group composition and the SD and/or CCD of each oligomer fraction. The width of the oligomer peaks is also influenced by SD and/or CCD and can, furthermore, be expected to depend on the FTD. Therefore, although RP-GPEC provides more information on structural differences than conventional methods such as SEC and NMR do, the technique must mainly be considered as a versatile, qualitative fingerprinting tool, rather than a method by which these differences can be quantitatively verified.

In contrast, NP-GPEC provides more and quantitative information on microstructural differences. This is due to the fact that the separation in NP-GPEC is more strongly based on CC. Dependent on the separation system, primarily a separation according to end groups was found. Orthogonal experiments, for example, GPEC/SEC and SEC/GPEC for two closely resembling copolyesters and a homopolyester revealed that low mo-

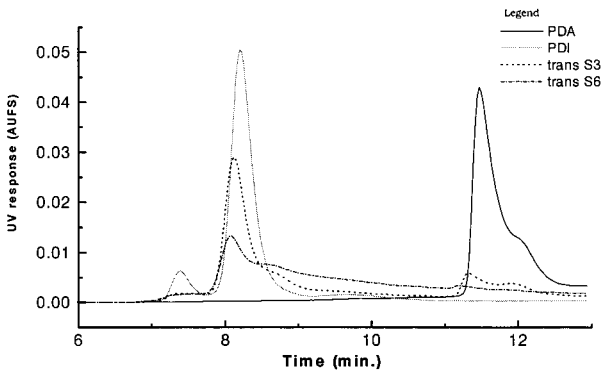

Figure 17 NP-GPEC chromatograms of SEC fraction 5 of homo polyesters PDA (black) and PDI (gray) and transesterification products *trans*-S3 (dotted) and *trans*-S6 (dashed). NP-GPEC conditions, see Figure 10(B).

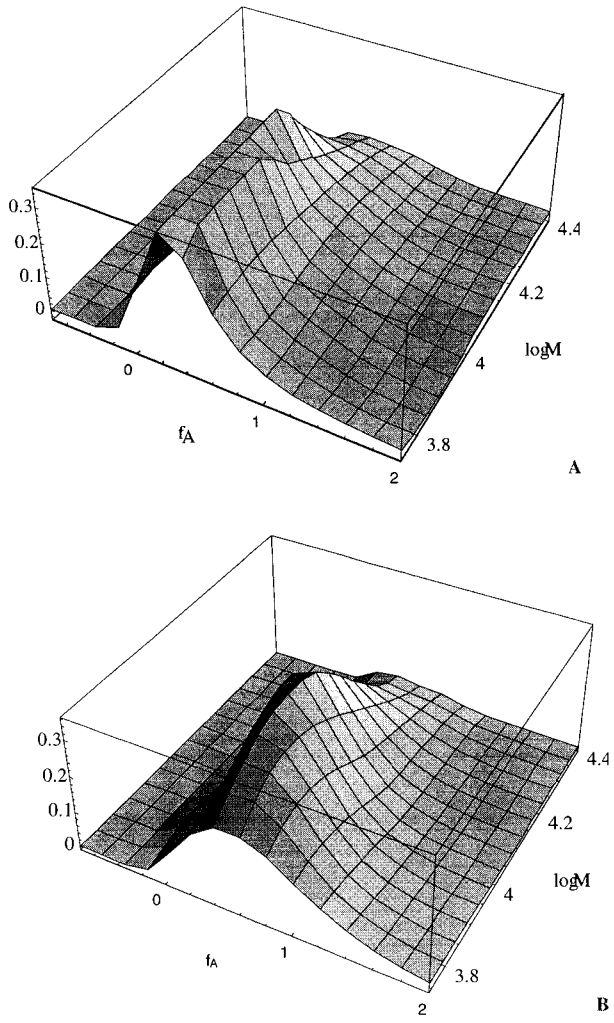

Figure 16 Comparison of (a part of) the MMCCDs of the diol fractions of PE2 (A) and PE3 (B). SEC conditions, see text. NP-GPEC conditions, see Figure 10(B) (on the vertical axis, relative amounts, e.g., weight fractions, are plotted).

lar mass fractions are enriched in diol-terminated chains, whereas the high molar mass fractions contain somewhat more acidic end groups. Furthermore, significant differences in FT-MMD between the two copolyesters were found. Within a specific end group fraction, a further separation according to the composition of the polyester backbone was obtained. By a combination of SEC and NP-GPEC on an NH_2 column the MMCCD of the diol fraction of copolyesters was studied. From these results, an experimental verification of the existence of a CCD in copolyesters made by step reactions, was obtained. The developed separation could be used to follow the proceeding of a transesterification reaction. Furthermore, significant differences between the MMCCDs of the two strongly resembling copolyesters were found. In contrast to RP-GPEC, information on CCDs could be quantified and could also be studied for the high molar masses. The observed differences can only be explained by the relative importance of reaction kinetics in step reaction copolymers, which obviously has been underestimated until now.

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