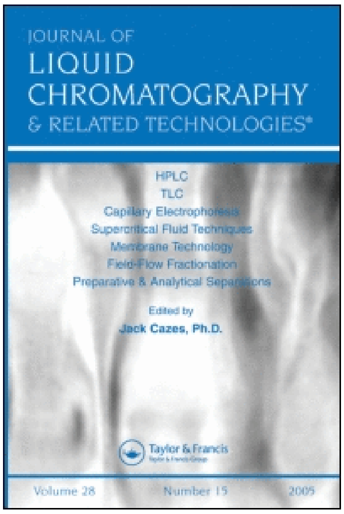

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DETERMINATION OF FUNCTIONALITY AND MOLAR MASS DISTRIBUTION OF ALIPHATIC POLYESTERS BY ORTHOGONAL LIQUID CHROMATOGRAPHY. I.
OFF-LINE INVESTIGATION OF POLY(1,6-HEXANEDIOL ADIPATES)

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ABSTRACT

During polycondensation of polyesters products are formed distributed in molar mass and functionality (end groups). Especially in polyurethane chemistry the knowledge of the distribution of terminal groups is necessary for correlating material properties containing different species in raw materials. The characterization of polyesters by "Liquid Adsorption Chromatography at Critical Conditions" (LACCC) is a new powerful tool for kinetics and modelling. Separation of polyesters according to their terminal groups independently of their molar mass is feasible at the critical conditions determined by the chromatographic system silica/acetone/hexane. Owing to side reactions, the number of combinations of COOH- and OH terminal groups identified was higher than expected. Cyclic species, hexanediol ether structures and alkyl-terminated homologues were identified. Model substances for all structures were synthesized. For orthogonal separation LACCC was combined off-line with SEC. With the help of preparative separation enough material was obtained to identify the species by spectroscopic methods (NMR, MALDI-TOF-MS) and to calibrate both the detector response and SEC. Finally, an algorithm is proposed for the characterization of end-group distributed reactive polymers by orthogonal liquid chromatographic methods.

INTRODUCTION

Polyesters from adipic acid and 1,6-hexanediol with an output of thousands of tons are manufactured for a wide field of applications. Polyester as intermediate product for polyurethanes are distributed in molar mass and are inhomogeneous with regard to end groups. The functionality type distribution (FTD) of these products is important for the properties of the final products, e.g. non-reactive cyclic species are responsible for the "fogging effect" in polyurethane systems. First ENTELIS et al. [1,2] investigated such reactive oligomers by means of liquid chromatography in mixed mobile phases near the "critical conditions of adsorption" of polymers and used this method for the determination of FTD. VAKTINA et al. [3] and TYUTYUNDZHAN et al. [4] separated aliphatic polyesters with OH- and alkyl-terminated groups by means of thin-layer chromatography (TLC) to characterize the thermal degradation. FILATOVA et al. [5] separated diethylene glycol adipic acid polyester with hexane/methyl ethyl ketone on silica gel by gradient elution and found an increasing OH-functionality with increasing elution force. FILATOVA et al. [6] were the first to determine "critical conditions of adsorption" in adipic acid polyesters using ethylene glycol, diethylene glycol, propylene glycol and dipropylene glycol with silica gel as stationary phase and mixed eluents of MEK / chloroform. Information about the existence of cyclic species and ether structures is given in the paper of WICK et al. [7], however, the quantitative separation and determination are not described. The state of the art of gradient HPLC is described by WICK and KRÜGER [8]. Size-exclusion chromatographic separations of aliphatic polyesters are reported in DMF [9], THF [10,11] and toluene [12] with standard polystyrene columns. Indications of the cyclic species are included in [10]. A comparison of SEC with gradient elution was done by GROS et al. [12] and KRÜGER [8].

The investigation of polymers by liquid chromatographic methods has shown that beside SIZE EXCLUSION CHROMATOGRAPHY (SEC) and interaction chromatography (LIQUID ADSORPTION CHROMATOGRAPHY, gradient HPLC), the Liquid Adsorption Chromatography of polymers at Critical Conditions (LACCC) is established and can contribute essentially to increasing the knowledge of the determination of the polymer structure [13]. The review on this liquid chromatographic mode [14] has shown that the critical conditions for the liquid adsorption chromatography of polymers are realized by using solvent mixtures as mobile phase. In SEC the chromatographic process of polymers in a good solvent is caused by a change in entropy, while the separation process of liquid adsorption chromatography is based on the change in enthalpy in a thermodynamically poor solvent. At the critical point, the change in entropy will be compensated by the change in enthalpy. In that case, the basic unit of the polymer chain doesn't contribute to the separation process, the main chain has no chromatographic influence on retention. Under these conditions the retention is independent of the molar mass of the polymers investigated.

The chromatography at critical conditions of polymers can be used to determine the following distributions

→ functionality
→ chemical composition (blend)
→ block length distribution in copolymers
→ distributions according to structural and topological aspects (branching, cycles, tacticities)

The frequent attempts to determine the chemical composition and molar mass distribution of copolymers by orthogonal two-dimensional liquid chromatography (or so-called chromatographic cross fractionation) are incomplete, because the chromatographic mode beside the SEC does not separate independently of the molar mass. A purely orthogonal two-dimensional liquid chromatography is experimentally feasible by using liquid adsorption chromatography at critical conditions in the first dimension and SEC in the second one [15]. Subject of the present paper is the investigation of hexanediol adipate polyesters by two-dimensional liquid chromatography. The determination of functionality distribution by separation in LACCC is the aim in the first dimension. In the second dimension, the molar mass distribution of every functionally different fraction will be determined by SEC. All steps beginning with the determination of critical conditions up to the two-dimensional chromatography are presented. As a result, an algorithm for the systematic investigation by this technique will be proposed.

EXPERIMENTAL

Equipment

Investigations by gradient elution were performed with the modular equipment HP 1050 of Hewlett & Packard, consisting of a quaternary pump with membrane solvent degasser, an auto sampler and a HP 1040 M series 2 diode array detector. 20 µl samples with a concentration of 5 mg / ml in acetonitrile were separated on a nucleosil column 250 x 4 mm ID with a 5 µm RP 18 phase of the AB type at 303 K. Data handling and computation was done by the HPLC 3D Chem Station with WIN-software.

The measurements for the determination of "critical conditions of adsorption of polymers" were performed on an equipment for isocratic separation mode, comprising a Jasco 880 PU pump, an auto sampler Marathon from Sparc (Netherlands) and an ERC 7511 differential refractometer detector. The chromatographic data were collected by a personal computer with a two-channel high special data acquisition with 24 bit resolution. The interactive processing of chromatographic data by the software NINA of Nuclear Interface (Germany). Stainless steel columns, of Tessek (Czechoslovakia), 250 x 4 mm ID with silica 7 µm with a mean pore diameter of 120 Å were used at 303 ± 1 K.

Preparative separation was carried out on an equipment of Shimadzu consisting of an LC 8 A pump, an SCL 8 A system controller, a 25 ml SIL 8 A autoinjector, a Waters R 401 differential refractometer detector, and an FCV 100 B fraction collector. A Latek Si 60 (20µm) column 500 x 40 mm ID was used with a flow rate of 30 ml min^{-1}. The Shimadzu C-R 4 AX Chromatospac integrator was applied for recording the chromatograms.

The SEC measurements were carried out at ambient temperature. The SEC system consisted of an HPLC pump (model 64 Knauer), a rheodyne injection valve with a 100 µl loop (Knauer), and a refraction index detector (Knauer). Two columns (300 x 8 mm ID), PL-gel, pore sizes of 50 Å and 100 Å, 5 µm particle diameter, separating in the molar mass range up to 10000 g mol^{-1} were used. Acetone was the mobile phase, with a flow rate of 1 ml min^{-1}. Data acquisition and calculation of calibration curves and molar mass distribution was done with the SEC software of Polymer Standard Mainz on an Atari computer.

MATERIALS AND SYNTHESIS

Chemicals and Solvents

The chemicals used in this study, were adipic acid (Merck, Darmstadt, Germany, for synthesis), caproic acid (Merck, for synthesis, distilled), 1,6-

hexanediol (Riedel-de Haën, Seelze, Germany, distilled under reduced pressure), thionyl chloride (Merck, destilled), 1-hexanol (Merck, distilled), 5-hexen-1-ol (Merck, distilled) and 4-toluenesulfonic acid (Merck, Germany). The solvents (methanol, toluene diethyl ether, and N,N-dimethylformamide obtained from Merck, pyridine obtained from Riedel-de Haën) were destilled freshly before application. Acetone, n-hexane and tetrahydrofuran (Baker, Deventer, Netherlands), HPLC grade reagents, were degassed by stitting under vacuum. The acid chlorides (adipic acid chloride, caproic acid chloride) were prepared by treatment of the corresponding carboxylic acid with thionyl chloride in the presence of nitrogen followed by distillation.

Sample Preparation

Definite model polyesters were prepared with favoured end groups to identify the HPLC peaks in the LACCC of industrially manufactured OH-terminated adipic acid / hexanediol polyesters.

For the modification of polyesters, polymer analogous reactions were performed. Polyesters with different end groups (favourably OH/OH, COOH/OH and COOH/COOH) were synthesized from adipic acid and 1,6-hexanediol by variation of stoichiometry in solution in the presence of 4-toluene-sulfonic acid and extra dry grade nitrogen. The water formed was permanently eliminated by toluene (towing agent) . The preparation was performed by precipitation in methanol or diethyl ether followed by sucking, washing and drying at reduced pressure. If adipic acid dichloride was applied, the reaction was carried out with hexanediol in the presence of pyridine by heating. Precipitation was performed in hydrochloric acid / ice water. The resulting product was sucked and washed, dissolved in toluene and precipitated in methanol followed by drying under vacuum. In all cases, white polyester powders were obtained .

The synthesized polyesters containing different end groups were converted once more to produce alkyl end groups. OH end groups were esterified with caproic acid chloride. By variation of stoichiometry (solvent pyridine) and heating polyesters were obtained containing end groups of different nature (Alk/COOH, Alk/OH, Alk/Alk). The purification was done as described above. An acid polyester containing one-sided hexenyl end groups was obtained from α,ω-COOH polyester with 5-hexene-1-ol. Reaction was performed by heating in solution catalyzed by 4-toluenesulfonic acid. Potassium salts were synthesized yielding two excellent polyesters by accurate neutralisation of COOH-groups.

Moreover, oligomer diesters with special end groups were synthesized in order to facilitate the identification of polyester peaks owing to the excellent purity of those substances. These products were the first species of homologous series (six C-atoms in each component). All dihexyl adipates were obtained from adipic acid (or adipic acid dichloride) and excessive 1-hexanol in melt (or pyridine solution). The products were absorbed in diethyl ether and washed thoroughly with an aqueous solution of sodium carbonate. After the evaporation of ether, the substances were fractionated under reduced pressure. The reaction with 5-hexen-1-ol proceeded in the same manner. Analogously, all diesters obtained from 1,6-hexanediol and caproic acid chloride were prepared with a different excess of components (Alk/Alk-, Alk/OH-end groups). The diester with both alkyl and COOH end groups was obtained from adipic acid and 1-hexanol in melt.

In the literature [7] it is mentioned that etherdiol structures in polyesters have been detected too . Therefore, 1,6-hexanediol was treated with 4-toluenesulfonic acid in toluene under the same conditions as for the polyester preparation . The evaporated mixture was distributed between diethyl ether and water before the isolation of the product.

RESULTS AND DISCUSSION

For a complete description of the heterogeneity of polyesters the information of SEC and LACCC separation must be combined. Because the analysis of such a complex sample as a polyester containing small amounts of undesired structures (below three percent) is more difficult, the above-mentioned model polyesters were used for identification. For this purpose, the following experimental step must be solved.

Diagnosis of functionality distribution

Chemical heterogeneity can be recognize by comparing of chromatograms of samples with different end groups in SEC or in HPLC with gradient elution.

Therefore polyesters of adipic acid and 1,6-hexanediol with different structures were synthesized. The content of the expected terminal group combinations HO—OH, HO—COOH and HOOC—COOH depends on the molar ratio of dicarboxylic acid to diol in synthesis. The data of characterizing at the obtained model polyesters by classical mean values from chemical end-group analysis (OH- and COOH-value) and vapour pressure analysis are presented in Tab. 1. It reveals that no product has a mean functionality of whole numbers. In Tab. 2 the dates of other in this paper used AA-HD-polyesters are shown.

To indicate the influence of terminal groups on the elution behaviour of polyesters with preferred COOH end groups or OH end groups [Fig.1] they were separated with acetone as above for SEC defined conditions. The high-resolution separation system can distinguish between the low-molecular range of both the homologous series [Fig.1] and the raw materials. It must be checked if the reason for the differences in the elution volume is caused by adsorption or solvation. The calibration function should be controlled for the homogeneous series.

The gradient elution chromatogram [Fig.2] shows the separation of a sample PE2, preferred terminal OH-groups and a small carboxylic content. The shape of the eluted species clearly shows all homologues with two OH end groups, since the retention increases with molar mass. Between the main peaks there are some small peaks which are caused by other terminal groups. These species can't be separated at higher polycondensation degrees, because of the small difference of interaction. A quantitative determination of all existing homologous series by adding up the peaks in the adsorption or gradient mode of LC is not possible. Only in the LACCC separation mode all species with the same end groups will be eluated in one peak and can be determined quantitatively.

Selection of the phase system

Polyesters with typical terminal groups resulting from polycondensation and polyesters with other end groups caused by side reactions (cyclization, dehydration and thermal ester cracking) differ in a wide range of polarity. Silica gel and reversed phases were tested to separate HO—OH, HO—COOH and HOOC—COOH

TABLE 1: Selection of Synthesized Model Polyesters

Main structure of synthesized polyesters	Acid number (mgKOH/g)	Hydroxyl number (mgKOH/g)	Molar mass M_n (g mol^{-1})	Functionality
HOOC–PE–OH	9.2	7.0	6800	1.96
HO–PE–OH	1.2	86.2	1270	1.98
HOOC–PE–COOH	123.6	5.8	810	1.87
Alk–PE–Alk	0	0	2100	0
Alk–PE–OH	3.1	17.6	2520	0.93
Alk–PE–COOH	115.7	4.0	450	0.96
HOOC-PE-Alk(unsatur.)	19.6	0	2600	0.91
HO–O–OH	0	361	310	1.99

TABLE 2: Characterization of Polyester Samples

Polyester samples	Acid number (mgKOH/g)	Hydroxyl number (mgKOH/g)	Molar mass M_n (g mol^{-1})	Functionality
PE 1	0.16	110.3	930	1.83
PE 2	2.36	74.3	1300	1.78
PE 3	0.63	56.7	1650	1.69
PE 4	0.76	36.9	2400	1.61
PE 5	5.43	103.3	1020	1.98
PE 6	7.09	67.4	1400	1.86
PE 7	6.13	51.7	1810	1.86
PE 8	8.45	35.1	2220	1.73
PE 9	6.6	8.9	5940	1.64

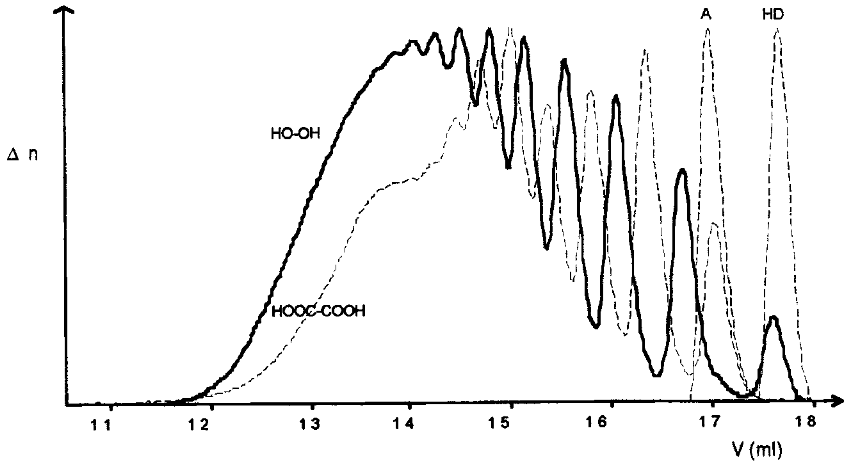

FIGURE 1: Separation of AA-HD polyester with preferred OH/OH- and COOH/COOH functionalities in SEC mode (see equipment)

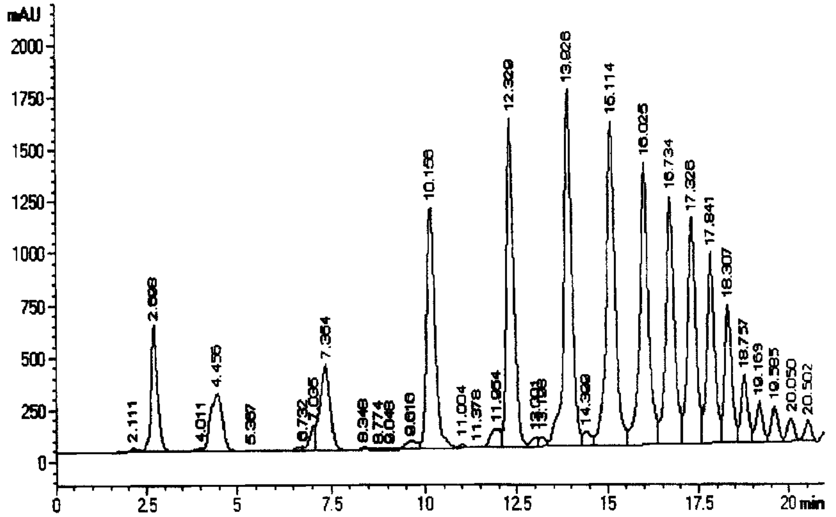

FIGURE 2: Gradient elution chromatogram of PE 2 with RP 18, 5μm column at 40°C, flow 1ml/min, solvent A: water, solvent B: ACN; gradient 65%B at the start, 1 min at 65%, in 15 min to 100%B, 5 min at 100%, detector wave length 210 nm

homologues. The reversed phase system was unsuitable because of unsufficient selectivity. The precipitation point was near the critical conditions, that means parts of polyester were precipitated on the column.

A mixture of acetone and hexane as mobile phase and silica gel as stationary phase was preferred because of the good solubility of polyesters, the possibility of evaporation after preparative separation, and low toxicity. The influence of small amounts of water (below 200ppm) could be neglected in the selectivity and retention of the peaks. At last, the mean pore diameter of the separation phase has to be optimized. Therefore were compared silica gels of different pore size of the same producer. It is necessary that all dissolved polymer molecules are able to contact the polar SiOH groups on the silica gel surface and that exclusion effects do not occur. The retention decreases with the mean pore size diameter of the phases. The phase ratio is proportional to the surface area. Nucleosil 50 Å, 100 Å, 300 Å and 500 Å were tested (Fig.3). Optimal resolution and peak shape were found with phase material of 100 Å mean pore diameter. For Nucleosil 50 Å not all pores of the phase were available for the polymer molecules, the transport of macromolecules was hindered. In that case the mean fraction was eluated as a broad peak. Retention and selectivity of Nucleosil 500 Å, however, exclude the separation of all species. For the measurements were used columns of Tessek, 120 Å, as written in "Equipment", with the same resolution. For the first orientation regarding the pore size selection of the stationary phase it is necessary that there are no exclusion peaks under conditions of SEC separation. Exactly the separation range must be checked by inversed liquid chromatography.

Determination of critical conditions of adsorption for AA-HD polyesters

For the determination of critical conditions it is necessary to separate samples with different molar masses. In that case the samples were in the molar mass range from 1000 to 6000 g mol^{-1} (see Tab.2) with preferably two OH groups in isocratic mode on the above-described chromatographic equipment. The mobile phase near the critical condition had to be premixed by weighing, the water content had to be controlled (<0.02%). The concentration of the samples in the mobile phase were about 1wt-%. It is favourable to begin the variation of the mobile phase with a thermodynamically good solvent in SEC mode thus avoiding precipitation or

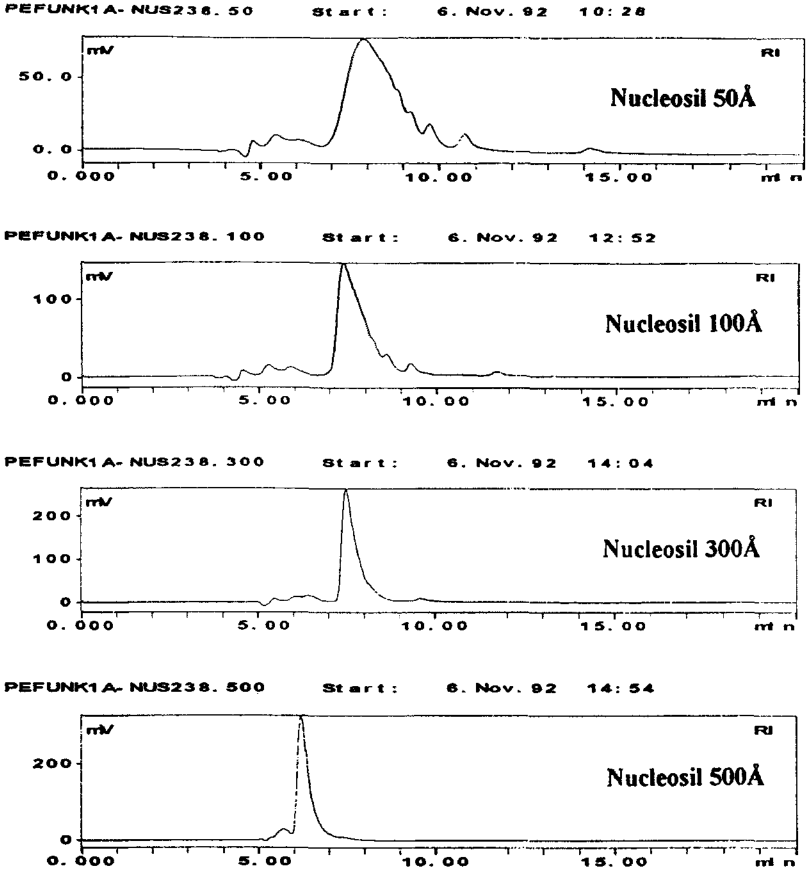

FIGURE 3: Separation of AA-HD polyester PE1 at critical conditions (49 Vol% hexane / 51 Vol% acetone) on Nucleosil 50 Å, 100 Å, 300 Å and 500 Å

irreversible adsorption on the stationary phase. In the size exclusion mode samples with higher molecular masses at lower elution volume were eluted in acetone (left series of peaks in Fig.4). By the addition of hexane, the difference in the elution volume of the used samples decreases. Near the critical conditions, at 47 vol-% hexane (Fig.4), the difference is very small. At critical conditions of adsorption, all standard samples elute at the same retention volume independent of their molar mass. The variation of the retention volume of the used standards should be smaller than the measured standard deviation of the dead volume peak. In the right curve at 53 vol-% hexane the standards were eluted in adsorption mode (Fig. 4). The elution is reversed to the SEC mode. The peaks (Fig.5) are asymmetric near the critical point of eluent in the LAC mode and with higher molar masses they become very broad. The elution volume for a molar mass range can be tuned by the eluent mixture. The high-molecular part of the sample is adsorbed strongly, as for instance PE 9 in the right group of peaks in Fig. 5. For a complete elution in the adsorption mode the column must be washed by acetone between the separations.

Fig. 5 presents the dependence of elution volumes of polyesters with different molar masses (Tab. 2) on the composition of the mobile phase.

Identification of peaks at critical conditions of adsorption

Fig. 6 shows chromatograms of AA-HD polyesters with different molar masses of 930, 1300, 1650 and 2400 g mol^{-1}. The peaks representing different end-group combinations can be found in all four chromatograms independent of the molar mass. The relative amount of undesired structures in the products increases with higher molar masses.

The main peak 7 at 13 min. is caused by homologues with two OH-groups. The peak 10 eluated at 21 min. is related to 1,6-hexanediol as raw material. The rest of the peaks has to be identified by means of model polyesters. Polyesters with defined structures (see Tab.1) are separated at critical conditions for identification (Fig. 7) by retention data. The structures of the peaks 1 - 5 in the chromatogram (Fig.7) correspond with the models. After preparative separation, the NMR-spectra and MALDI-TOF-MS-spectra of the fractions agree with the proposed structures. Peak 8 and 9 could not be identified in such a way.

The possibility to synthesize ether structures from 1,6-hexanediol in acid medium under dehydration conditions was studied (substance with ether structures, Tab.1). In Fig. 8a the chromatogram of the polyester PE 3 is shown. The part which was saponified after preparative fractionation is marked. The separation of isolated diols after alkaline saponification and purification is shown in the chromatogram 8c. The retention of the dimer and trimer structures is identical with the synthesized

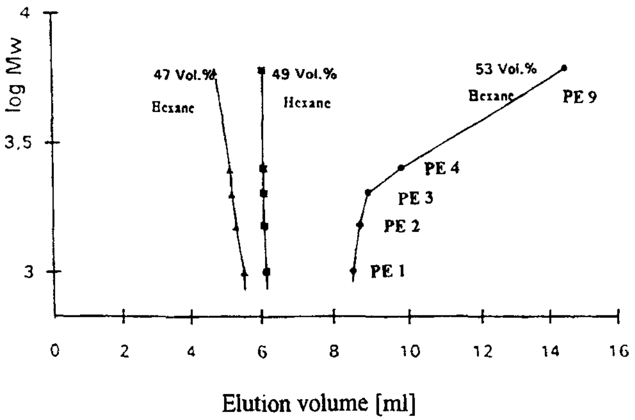

FIGURE 4: Dependence of the elution volume on molar mass (PE1,PE2,PE3,PE4,PE9) in eluents of 47% hexane / 53% acetone ▲, 49% hexane / 51% acetone ■ and 53% hexane / 47% acetone ●; silica gel column: Tessek 250x4 mm ID, 7μm, 120 Å

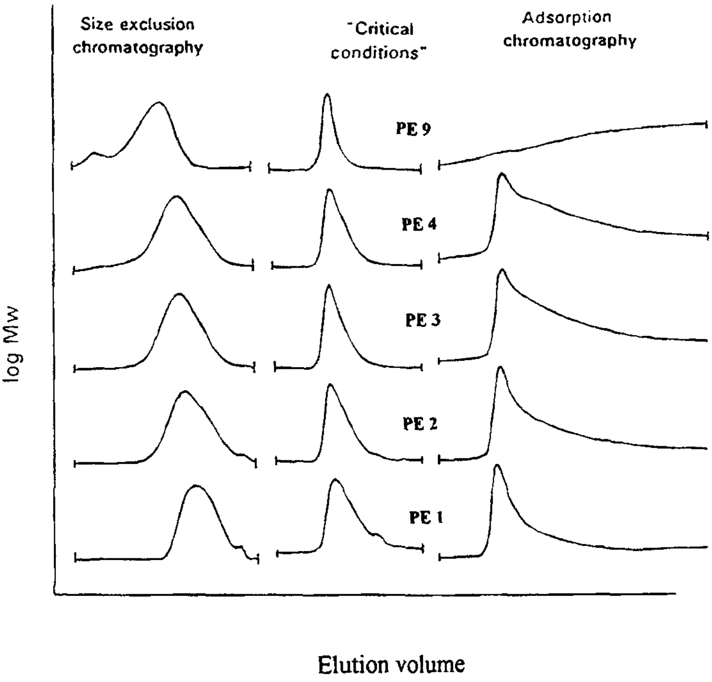

FIGURE 5: Peak shape of samples with different molar masses in dependence on the hexane / acetone ratio (left 47/53, middle 49/51, right 53/47)

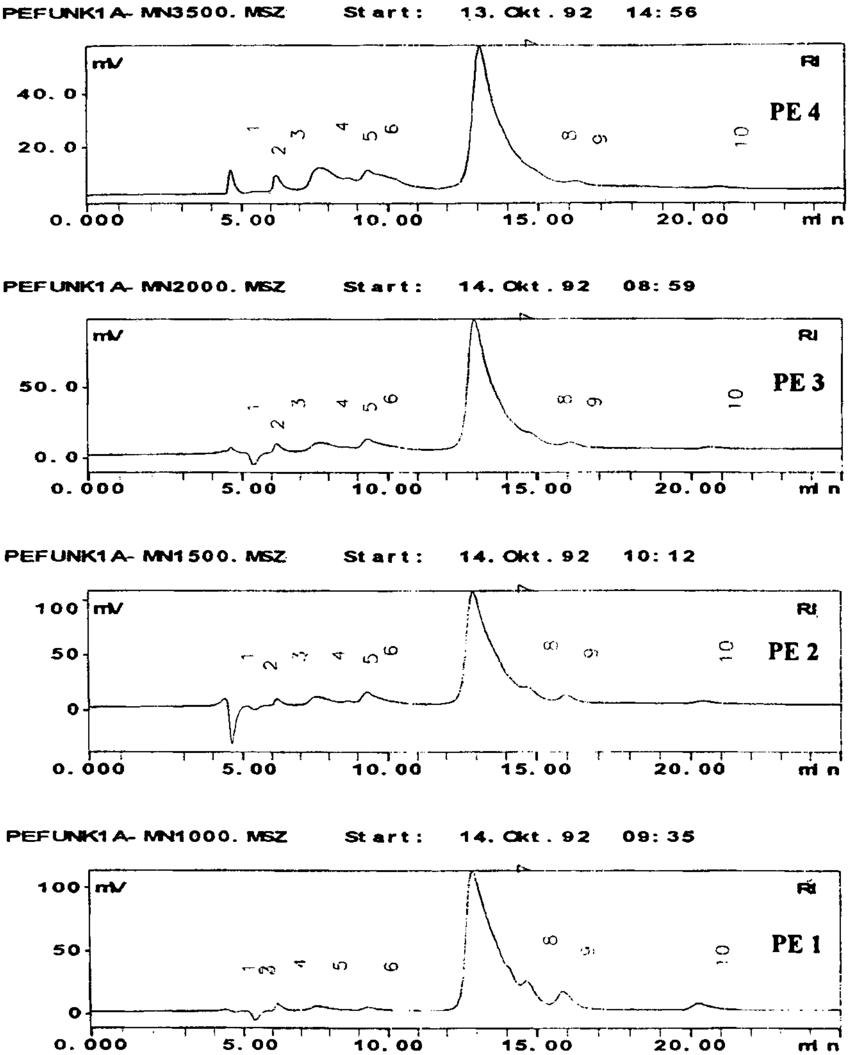

FIGURE 6: Chromatograms of AA-HD polyesters of different molar masses at critical conditions: 1: Alk-PE-Alk; 2: cycles; 3: Alk-PE-COOH; 4: Alk-PE-OH; 5: HOOC-PE-COOH, 6: HOOC-PE-OH, 7: HO-PE-OH; 8,9: HO-O-OH; 10: 1,6-hexanediol

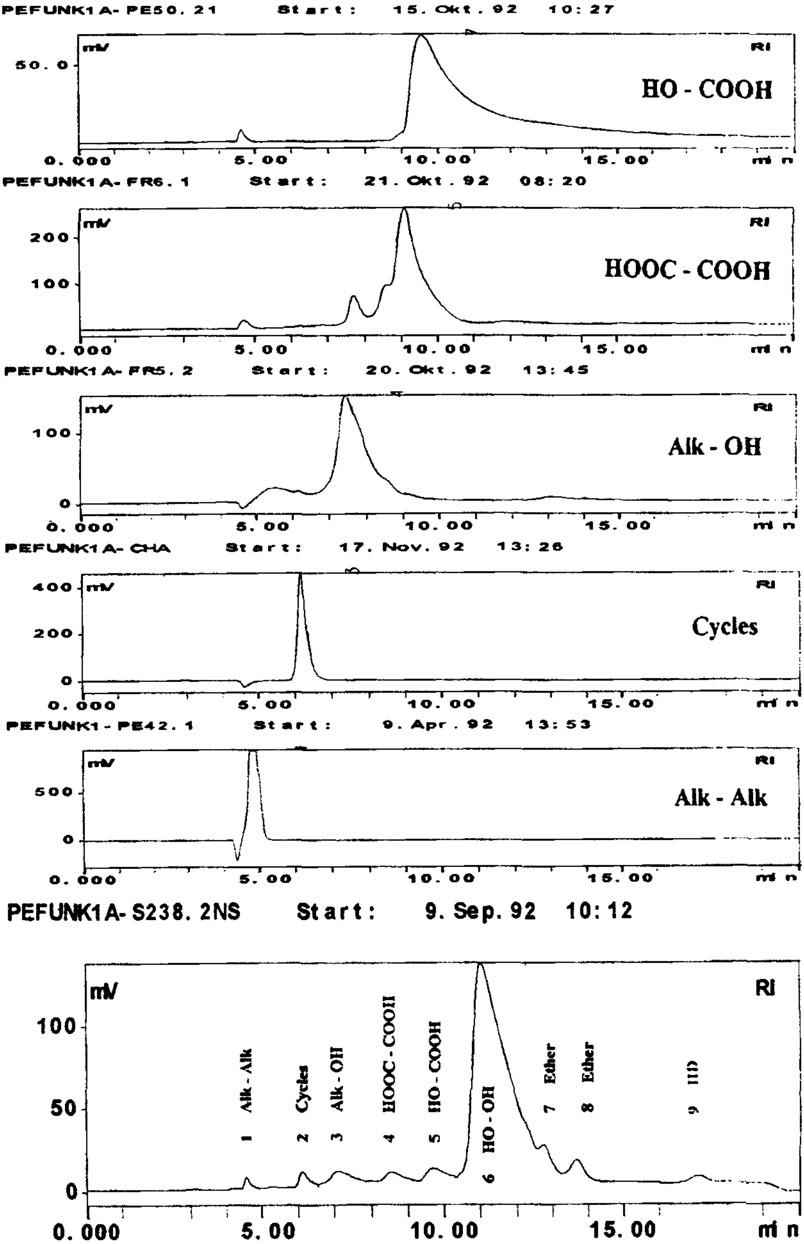

FIGURE 7: Chromatograms of AA-HD polyesters with defined structures of end groups

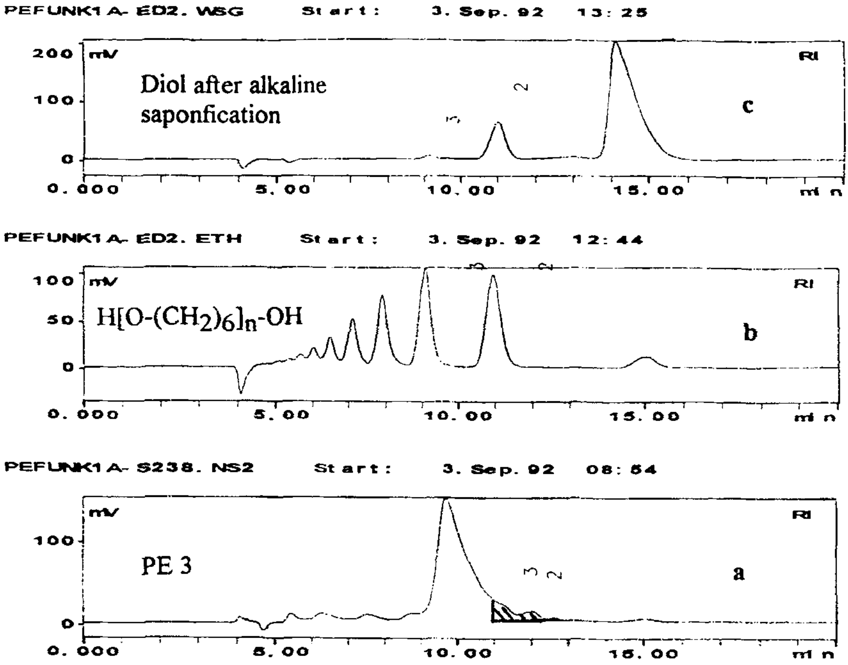

FIGURE 8: Chromatograms for the identification of ether structures in AA-HD polyester at critical conditions

oligomers of the chromatogram 8b. These ether structures are incorporated in all polyesters (Fig. 6). The content of these structures decreases in polyesters with higher molecular masses. It is well known that this ether structure is responsible for autoxidation processes.

Preparative fractionation

The preparative separation of manufactured products of AA-HD polyesters was performed on the equipment described above. About 5 g of sample were separated to isolate enough substance for the differentiation of alkyl / alkylene end groups by NMR. 10 ml of sample solution with about 800 mg of polyester were separated in one run. In the chromatogram (Fig. 9) typical overload effects by concentration or

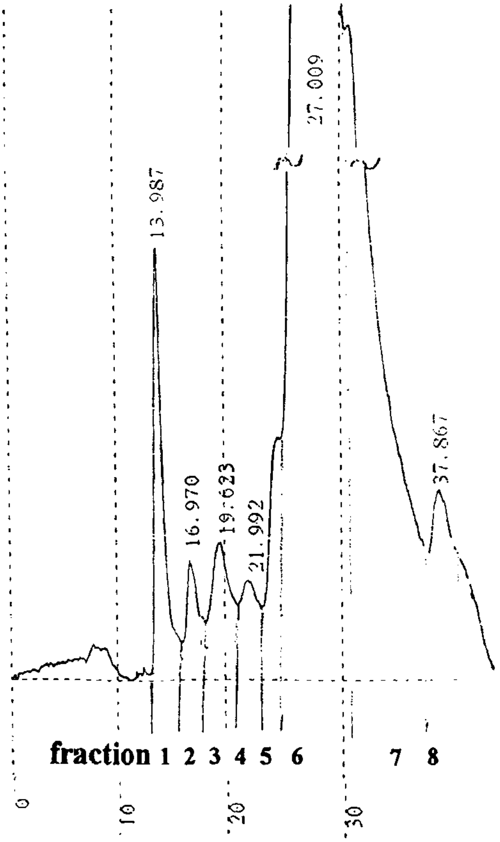

FIGURE 9: Preparative chromatogram with marked fractions

volume do not occur. The isolation of polymer fractions from the mobile phase was performed in a vacuum rotary evaporator. Degradation by saponification was not observed in the mobile phase used During a rechromatography of fractions the impurity peaks observed were ascribed to the mobile phase, they could not be observed using an evaporative light scattering detector (ELSD). After controlling by LACCC the fractions could be applied as calibration substances for the differential refractometer and ELSD. Finally, the fractions were measured by SEC to get the molar mass distribution in the second dimension of two-dimensional chromatography.

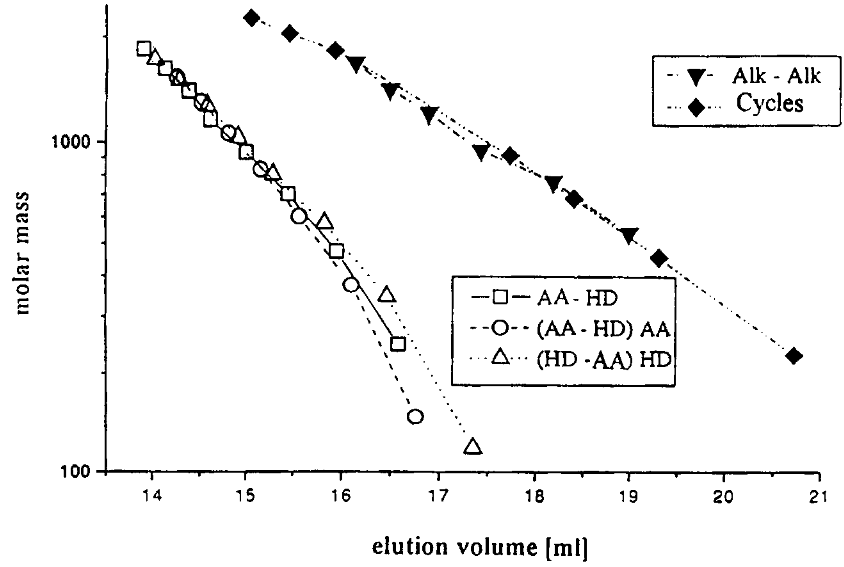

FIGURE 10: SEC calibration curves for AA-HD polyesters with different functionality

SEC

The resulting SEC calibration curves were obtained from the oligomer peaks of the homologous series of structurally different samples (Fig. 10). Therefore, the model substances described above and the synthesized first species of homologous series were used. In the case of cycles, substances were applied obtained from the former manufacturer of polyesters (Synthesewerk Schwarzheide).

Comparing the elution volumes of oligomer peaks of different end groups it could be observed that the calibration curves are different. The influence of the end group is remarkable in the first members of the homologous series. The elution volumes of polyesters with alkyl end groups and of cycles are significantly higher than of OH- or COOH- terminated polyesters. That means that in the case of comparable molar masses the hydrodynamic volumes are much smaller. The solvation of the end groups (OH or COOH) with molecules of the mobile phase could be the reason for that behaviour.

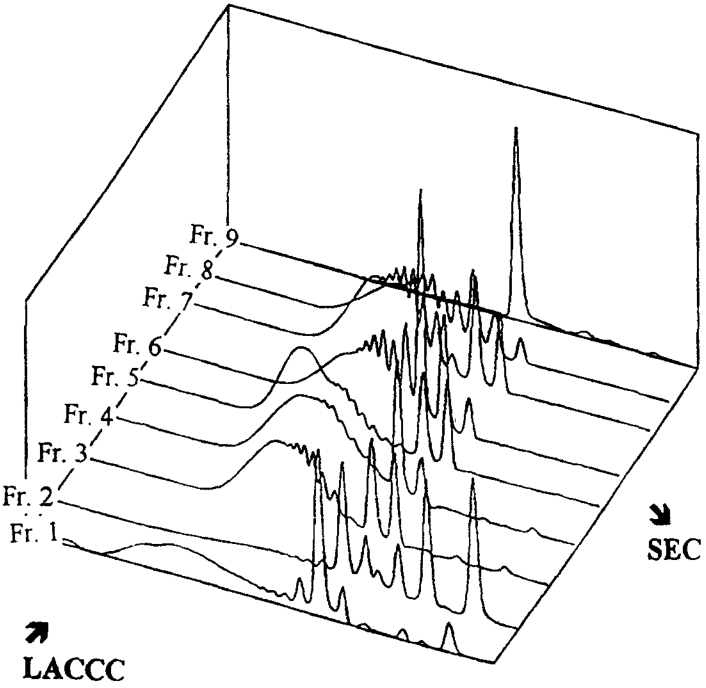

FIGURE 11: SEC chromatograms from LACCC preparative fractions of AA-HD polyester PE1

TABLE 3: Results of Off-Line Coupling LACCC / SEC (AA-HD Polyester PE1)

Structure	Fraction	M_n (SEC)	M_w (SEC)	Content from LACCC (%)
Alk—Alk	1	806	1740	0.2
Cycles	2	496	1165	0.5
Alk—OH	3	945	1190	1.1
HOOC—COOH	4	938	2071	1.2
HOOC—OH	5	1194	2863	1.3
HO—OH	6	986	1720	76.8
HO—O—OH	7	1400	2074	16.3
HO—O—OH	8	760	1760	
HD	9	112	118	2.6

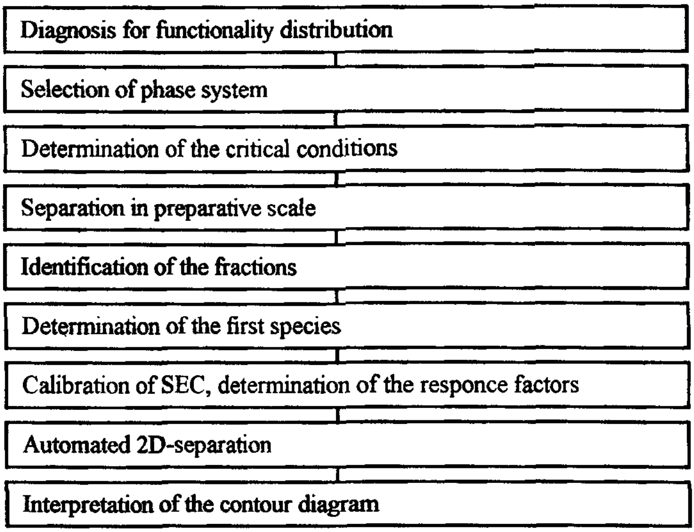

FIGURE 12: Algorithm of characterization molar mass distribution and chemical heterogeneity by two-dimensional liquid chromatography

In Fig. 11 the SEC curves of preparatively separated fractions are presented.

The molar masses, calculated from the corresponding calibration curves and the content of different species, measured in the LACCC mode by using the ELSD are presented in Tab. 3. The results differ strongly in M_n- and M_w-values of the species. Further investigations are necessary to cover and to interprete the data by kinetics and the technological process of polycondensation.

With the results of Tab. 3 a complete description of the polyester structure with regard to molar mass and functionality is given .

On the basis of the presented experiences it is possible to characterize other end-group distributed reactive polymers including macromers and telechelics. The following scheme for an algorithm is proposed (Fig. 12).

The last two operations in the algorithm will be discussed in part II, where the on-line coupling of the two chromatographic modes and their relations to synthesis will be presented.

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