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Retention Behavior of Linear, Branched, and Hyperbranched Polyesters in Interaction Liquid Chromatography

Michael Al Samman,[†,‡] Wolfgang Radke,*[,‡] Anna Khalyavina,[†,§] and Albena Lederer[§]

[†]*Dutch Polymer Institute (DPI), PO Box 902, 5600 AX Eindhoven, The Netherlands,*
[‡]*Deutsches Kunststoff-Institut (German Institute for Polymers), Schlossgartenstr. 6, 64289 Darmstadt, Germany, and* [§]*Leibniz-Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany*

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ABSTRACT: The retention behavior of aromatic polyesters possessing different degrees of branching was studied in gradient liquid adsorption chromatography (gradient chromatography), liquid adsorption chromatography (LAC), and liquid chromatography at the critical conditions (LCCC). The chromatographic experiments revealed that retention of linear and branched polyesters is influenced by the degree of branching as well as the molar mass of the polymer samples in all enthalpy-dominated chromatographic modes such as LAC, LCCC, and gradient chromatography. At critical conditions of the linear polymer, the corresponding branched structures elute in the adsorption mode, indicating a stronger adsorptive interaction between the stationary phase and the branched polymer molecule. In gradient chromatography, polymer samples with higher degrees of branching are retarded longer on the stationary phase. A clear dependence between the degree of branching and the elution volume was found in both chromatographic modes, which clearly demonstrates a pronounced effect of topology on retention behavior. The results suggest the use of gradient chromatography as a first separation step for a two-dimensional characterization method of branched polymers in order to separate by both degree of branching and molar mass.

Introduction

In recent years, branched polymers have attracted attention from both a scientific and a commercial point of view. The reasons for this development are manifold. Advantages resulting from the use of branched structures include improved rheological and mechanical properties in comparison to their linear counterparts. These can be beneficial especially for controlling processability and the performance of such polymers.[1,2] Despite the importance of branched polymers, their characterization still remains a major challenge in polymer analysis.

A common approach for the characterization of branched polymers is size exclusion chromatography (SEC) coupled with a multiangle laser light scattering detector (MALLS),[3,4] a viscosity detector,[5] or both.[6] These methods allow obtaining molar masses and size information for every SEC fraction. Often it is assumed that SEC yields homogeneous fractions. However, since branched polymers in general possess heterogeneities in both molar mass and topology, coelution of molecules having the same hydrodynamic volume might occur. In theses cases the results obtained for molar mass and size are at least questionable and have to be interpreted as average values.[7−9] Thus, the heterogeneity of the SEC fractions remains a major source of error. One recent approach in order to gain information on the extend of heterogeneity within a SEC slice utilizes the fact that SEC with viscometric detection results in a local number-average molar mass, while light scattering detection yields a local weight-average molar mass. Thus, by applying both detection systems, determination of the local dispersity due to coeleuting polymers differing in molar mass should be possible, in principle.[6,10] However, this approach cannot overcome the principal problem of coelution of different molecular species. Therefore, new non-SEC separation techniques have to be developed for the characterization of branched polymers.

*Corresponding author. E-mail: wradke@dki.tu-darmstadt.de.

Non-SEC separation techniques such as LAC, LCCC, gradient chromatography, and temperature gradient interaction chromatography have been proven to be extremely useful for the characterization of complex polymers.[11,12]

LAC is the method of choice for the separation and quantification of lower molar mass molecules. Retention in LAC is mainly governed by enthalpic interactions between the stationary phase and the repeating units of the analyte molecules. Consequently, retention in LAC mode is expected to be fairly sensitive to molecular weight and less sensitive to topology.

Im et al.[13] demonstrated the use of temperature gradient interaction chromatography for the separation of star-shaped polystyrenes having arms with narrow molar mass distribution. For this system the molar mass increases with the number of branches (arms). Using temperature gradient interaction chromatography, it was possible to resolve polymer species of different number of arms with a far better resolution as compared to SEC.[14,15] However, most synthetic polymers possess broad molar mass distributions, which deteriorate the resolution of the star-shaped polymers with different numbers of branches as the number of branches increases.

LCCC can be used for the characterization of complex polymers as well. Critical conditions for polymers are defined as chromatographic conditions where enthalpic interaction effects are exactly compensated by entropic exclusion effects. Under these conditions linear homopolymers of identical chemical structure elute close to the elution volume of the injection solvent, irrespective of their molar mass. Since the molar mass does not influence the retention volume of homopolymers under critical conditions, the retention volume is controlled by structural differences other than molar mass. LCCC has become particularly valuable for the characterization of polymer blends,[16] block and graft copolymers,[17] endgroup functionality,[18] and stereoregularity.[19]

With respect to branched polymers Pasch et al. applied LCCC to separate star-shaped poly(L-lactide)s according to the number

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of arms.[20] It was shown that the LCCC elution volumes increase linearly with the number of poly(L-lactide)s-OH arms, allowing discrimination of the different branched poly(L-lactide)s in their mixture. However, the separation was not based on topology but utilizes the interaction of adsorptive end groups attached to the ends of the arms.

Besides purely experimental work, theoretical calculations were performed to calculate the partition coefficient of branched polymers and to predict their retention behavior under critical conditions. According to Guttman et al.,[21] the partition coefficient near critical conditions is nearly independent of the chain architecture. That would result in a topology-independent elution under critical conditions for linear and branched polymers. Kosmas et al. derived equations for the elution behavior of star polymers and predicted also identical critical elution behavior of linear and star polymers.[22] However, Wang et al.[23,24] emphasized the importance of the excluded volume interaction which was not taken into account in Guttman's calculations. Wang pointed out that the excluded volume has a nontrivial effect on polymers eluting at critical conditions. Monte Carlo simulations by Wang et al. showed that the star-shaped polymers can elute either before or after the linear molecules, depending on the branch numbers and the size to pore size ratio. Comparison of theoretical predictions and experimental results were described by Radke et al. They were able to explain the experimental results of Pasch on functionalized star-shaped poly(lactide)s.[25]

Despite the slight discrepancies in the theoretical results, it becomes clear that for practical applications chromatography at the critical point of adsorption does not provide sufficient resolution to separate linear and star-shaped polymers. However, this must not be the case for other branched structures.

Therefore, the aim of the work presented in this paper was to investigate the retention behavior of linear, partially branched, and hyperbranched polyesters using LAC, LCCC, and gradient chromatography. In order to obtain clear information about the influence of the topology on the retention behavior, all other molecular parameters, i.e., repeating units, type and number of end groups per monomer unit, and the molar mass, have to be kept constant. According to the authors' knowledge, no theoretical or experimental studies about the retention behavior of linear, partially branched, and hyperbranched polymers in gradient chromatography, LAC, or LCCC have been published yet.

Experimental Part

Equipment. High-performance liquid chromatography (HPLC) measurements were performed using an Agilent 1100 series HPLC system (Agilent Technologies GmbH, Boeblingen, Germany) consisting of a vacuum degasser (G1322A), quaternary pump (G1311A), autosampler (G1313A), column oven (G1316A), and variable wavelength UV-detector (G1314A). In addition, an evaporative light scattering detector (ELS 1000, Polymer Laboratories Inc., Church Stretton, England) was used. The following operating parameters were used: gas flow 1.4 L/min, nebulizer temperature 80 °C, evaporator temperature 120 °C.

For the SEC-multiangle laser light scattering (MALLS) experiments a system composed of a Waters 515 pump (Waters, Milford, MA), a TSP AS100 autosampler, a Waters column oven, a Waters 486 UV detector operated at 254 nm, a Waters 410 RI-detector, and a DAWN DSP light scattering detector (Wyatt Technology, Santa Barbara, CA) was used.

Data collection and processing for SEC and HPLC were performed using PSS WinGPC version 7 software (Polymer Standards Service, Mainz, Germany). For data acquisition and evaluation of SEC-MALLS experiments Astra version 4.73 (Wyatt Technology, Santa Barbara, CA) was used. The MALLS instrument was calibrated using pure toluene assuming a Rayleigh ratio of 9.78×10^{-6} cm^{-1} at 690 nm. A refractive index increment of 0.16 cm^3/g was assumed for all polyester samples.[26]

Chromatographic Conditions. The injected sample volume for HPLC analysis was 10 μL, sample concentrations were 1−2 g/L, column temperature was 25 °C, and flow rate was 1 mL/min unless mentioned otherwise. The chromatographic experiments were performed on a single Nucleosil C18 column (5 μm, 300 Å, 250 × 4.6 mm i.d., Macherey-Nagel, Düren, Germany).

For the SEC and SEC-MALLS analysis an injection volume of 118 μL, a sample concentrations of 1−2 g/L, a column temperature of 35 °C, and a flow rate of 1 mL/min THF were used unless mentioned otherwise. SEC-MALLS analysis was performed on a high-resolution column set received from Polymer Standards Service GmbH, Mainz, Germany (SDV 5 μm 10^6 Å, SDV 5 μm 10^5 Å, SDV 5 μm 1000 Å). SEC fractionation was performed on a single SEC column (SDV 5 μm 10^5 Å) of the same manufacturer.

Acetone and methanol (VWR, Leuven, Belgium) were of HPLC grade and used as received. Tetrahydrofuran (THF) was refluxed and distilled over calcium hydride (CaH_2).

Polymer Samples. Linear and different branched polyesters possessing different degrees of branching based on 4,4-bis(4′-hydroxyphenyl)valeric acid were prepared by polycondensation in solution at the Leibniz Institute of Polymer Research Dresden according to the ABB*/AB_2 approach. Details of the synthesis are given in the work of Khalyavina et al.[27] A schematic representation of the synthetic route to obtain linear partially branched and hyperbranched polyesters is shown in Figure 1.

Table 1 shows the weight-average molar masses (M_w) from SEC-MALLS experiments. The degree of branching was determined by ^{13}C NMR according to the method described in ref 27.

Results and Discussion

Gradient Liquid Adsorption Chromatography. In order to investigate the influence of the degree of branching on the retention behavior in gradient chromatography, gradient runs were performed on linear, partially branched, and hyperbranched polyesters. In preliminary experiments it was established that a mixture of 75% acetone/25% methanol corresponds to an eluent composition, where the polymer samples were completely adsorbed on the stationary phase, while an eluent composition of 75% acetone/25% THF causes complete desorption. Therefore, a linear gradient running from 75% acetone/25% methanol to 75% acetone/25% THF was applied. Since the polymer samples are soluble in a mixture of 75% acetone and 25% methanol, the separation was based on adsorption/desorption and not on solubility. Figure 2 shows the obtained chromatograms for the different samples under these conditions.

All samples elute as broad peaks within a similar elution range. The presence of small well-resolved peaks (especially for sample DB-0) indicates a separation according to the degree of polymerization within a given sample. The elution volumes for the main peaks at high elution volumes increase with degree of branching, which might be a first indication of an influence of degree of branching on polymer retention.

However, because of the broad peaks obtained in gradient chromatography, it is very difficult to separate clearly the effects of molar mass and degree of branching on the retention volume. In order to distinguish between the influence of molar mass and degree of branching on the retention behavior, all samples were repeatedly fractionated using the same gradient conditions to obtain more homogeneous samples. The first fraction was taken at an elution volume of 2 mL. Subsequent fractions were collected every 0.8 mL. The solvent was removed, and the fractions were redissolved in pure THF for subsequent SEC-MALLS analysis. The results are summarized in Table 2.

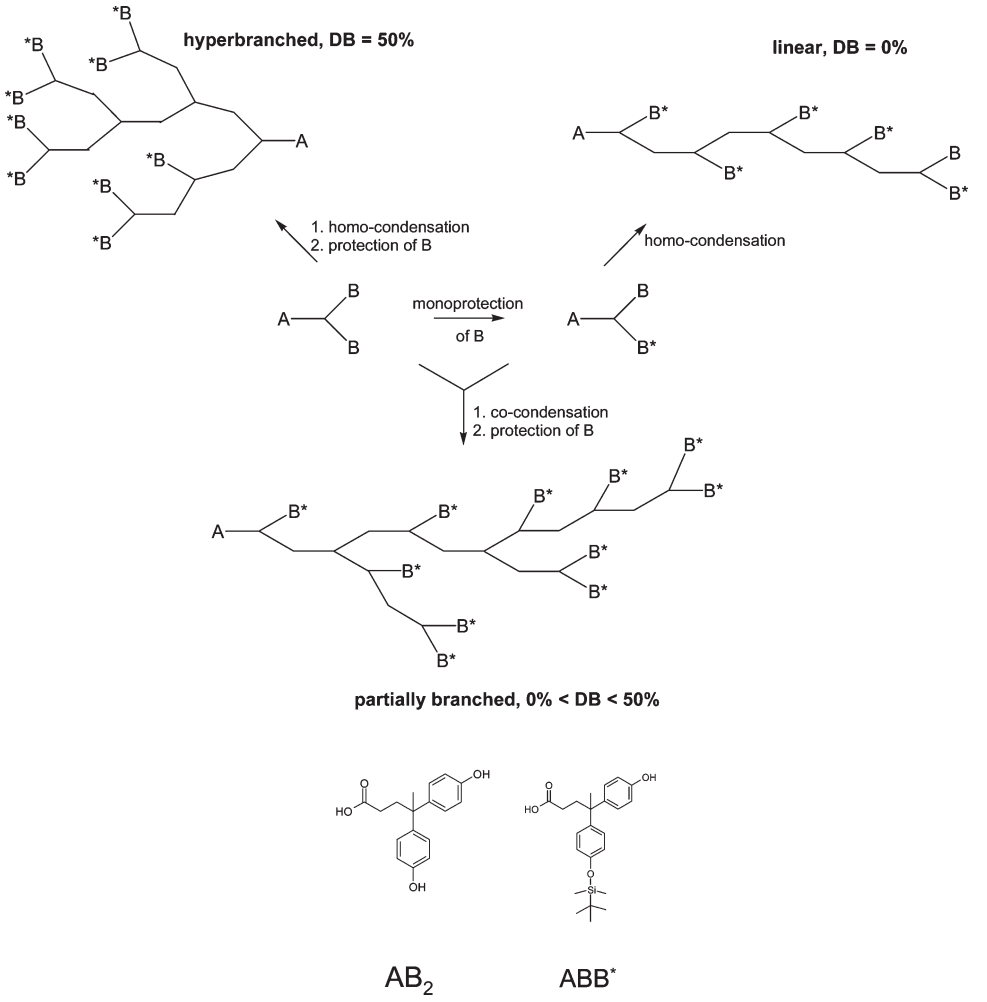

Figure 1. Schematic representation of the synthetic routes for polyesters with different degrees of branching. The monomer AB_2 corresponds to 4,4-bis(4′-hydroxyphenyl)pentanoic acid, and the protection group B* corresponds to *tert*-butyldimethylsilyl chloride.

Table 1. Characterization Details of the Linear and Different Branched Polyesters[a]

sample code	degree of branching[b] [%]	M_w determined by SEC-MALLS [g/mol]
DB-0	0	29 300
DB-18	18	46 440
DB-38	38	48 460
DB-50	50	39 810

[a] A degree of branching of 0% corresponds to the linear samples, while a hyperbranched sample possesses a degree of branching of 50%. [b] The determination of the degree of branching by ^{13}C NMR spectroscopy is described in ref 27.

From the results of Table 2, the dependencies of gradient elution volume on molar mass were established for all polymer samples. These are shown in Figure 3.

From Table 2 and Figure 3 it becomes clear that an increase in molar mass results in higher elution volumes at a given degree of branching. However, with increasing molar mass the variation in elution volume becomes less pronounced, indicating that the molar mass dependence will vanish for high molar mass samples. Such behavior is commonly observed in gradient chromatography of polymers.[29,30] Additionally, it is obvious that the different branched polyester samples follow different calibration curves, indicating that the elution behavior is influenced by the degree of branching as well. Upon comparing the different molar mass dependencies, it becomes clear that at

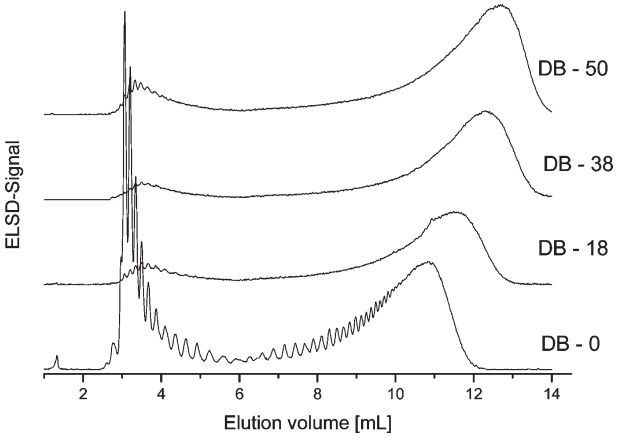

Figure 2. Chromatograms of linear, partially branched, and hyperbranched polyesters in gradient chromatography. Eluent (THF/acetone/MeOH): 0−2 mL (0/75/25), 12 mL (25/75/0), 12.01−13 mL (100/0/0), and 13.01−20 mL (0/75/25).

a given molar mass samples of higher degree of branching elute later than those of lower degree of branching.

Since linear, partially branched, and hyperbranched polymers of a given molar mass consist of the same numbers and types of structural units (phenyl groups, silyl groups, ester linking, etc.), the reason for the dependence of degree of branching on elution volume cannot result from differences

Table 2. SEC-MALLS Data of the Gradient Chromatography Fractions of Linear, Partially Branched, and Hyperbranched Polyesters

fraction number	collected elution volume in gradient chromatography [mL]	M_w of DB-0	M_w of DB-18	M_w of DB-38	M_w of DB-50
1	2.8 −3.6	3 113	3 995	2 795	4 037
2	3.6−4.4	5 713	5 165	4 700	4 221
3	4.4−5.2	7 604	6 254	6 038	6 339
4	5.2−6.0	10 220	9 146	7 619	6 830
5	6.0−6.8	12 020	9 557	11 140	8 676
6	6.8−7.6	14 750	12 140	10 200	9 600
7	7.6−8.4	17 890	14 590	13 700	12 090
8	8.4−9.2	22 000	17 470	16 420	13 100
9	9.2−10. 0	28 460	21 100	20 290	16 000
10	10.0−10.8	37 750	26 650	25 130	19 020
11	10.8−11.6	45 170	37 380	32 160	23 930
12	11.6−12.4	n.a.	54 630	43 750	31 940
13	12.4−13.2	n.a.	n.a.	66 080	41 610
14	13.2−14.0	n.a.	n.a.	n.a.	51 030

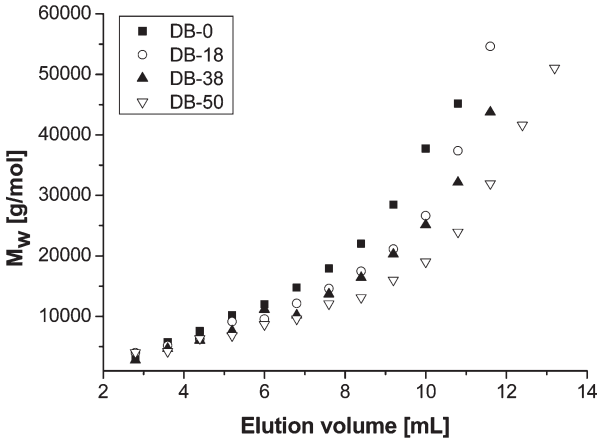

Figure 3. Dependencies of elution volume on molar mass for polyesters with difference degree of branching in gradient chromatography.

in the chemical structure but must be related to topological effects.

A possible explanation might be the more compact structure of branched polymers as compared to their linear analogues of the same molar mass.[28] The topological difference causes a higher density of segments at the periphery of the polymer coil enabling more repeating units to interact with the stationary phase. This effect enhances the total enthalpic interactions of the polymer with the stationary phase. Therefore, highly branched polymers are expected to adsorb stronger on the stationary phase for a given molar mass than less branched ones.

At the early stage of a gradient run (low eluent strength) adsorption of all polymer molecules onto the stationary phase takes place due to enthalpic interactions between the stationary phase and the repeating units. With increasing content of the stronger eluent (increasing eluent strength), the polymer molecules desorb and start moving. For high molar mass polymers, desorption from the stationary phase occurs only in a narrow region of eluent composition close to the critical one. Therefore, high molar mass samples elute at an eluent composition which is very close to the critical one.[29,30] The experiments showed that in the high molar mass limit the elution time increases with increasing degree of branching. This is a first indication of a dependence of the critical eluent composition on degree of branching. Hence, the more densely branched hyperbranched molecules, which possess stronger affinity to the column

Table 3. SEC-MALLS Data of the Fractions of Linear, Partially Branched, and Hyperbranched Polyesters Obtained from SEC Fractionation

fraction number	M_w of DB-0	M_w of DB-18	M_w of DB-38	M_w of DB-50
1	45 177	59 430	55 710	78 210
2	34 780	48 400	43 500	60 330
3	31 050	35 610	33 070	43 300
4	24 446	28 020	25 090	33 170
5	20 067	21 090	20 320	22 240
6	14 280	18 750	17 090	16 150
7	10 390	15 260	14 480	10 170

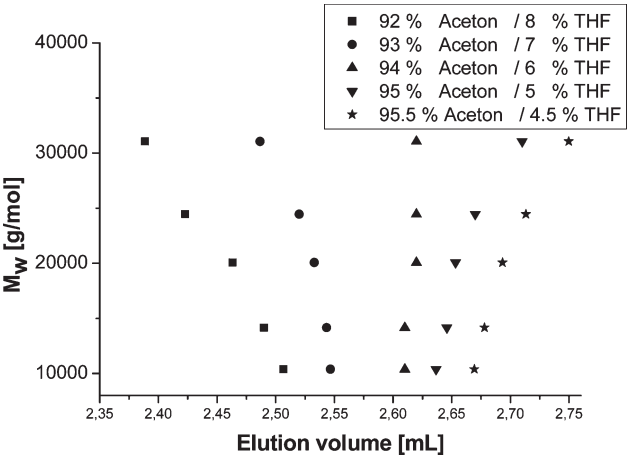

Figure 4. Dependence of molar mass on elution volume for fractions of linear polyester (DB-0) at various eluent compositions.

material, require a stronger eluent compositions to desorb than those with lower degrees of branching. That is the reason why in the gradient experiments the linear polymer molecules elute first, followed by the partially branched polymer molecules and ending with the hyperbranched polymer samples.

These findings are in contrast to the experimental results found on star-shaped polymers by Gerber et al.[31,32] They observed a negligible variation of gradient elution volume on the number of arms and thus on the molar mass. However, the sorbent−solvent system as well as the chemical and topological structure of branched polymers in their experimental studies differ strongly from those used in the present investigation.

The above established variations of the dependence of molar mass on retention time for samples differing in degree of branching seem to indicate different critical conditions for linear, partially branched, and hyperbranched polyesters. To verify this hypothesis, the influence of the degree of branching under critical conditions was investigated.

Liquid Chromatography at Critical Conditions (LCCC). In order to establish the critical eluent composition, linear, partially branched, and hyperbranched polymers were fractionated by SEC. The fractions were dried, characterized by SEC-MALLS, and afterward used to investigate the dependence of elution volume on molar mass for different eluent compositions. A summary of the characterization details is given in Table 3.

The molar masses of the fractions of the linear polyesters are plotted against the elution volumes in Figure 4 for various isocratic eluent compositions.

As can be seen in Figure 4, an eluent composition containing more than 6% THF results in an increase of the elution volume with decreasing molar mass, indicating an SEC-like

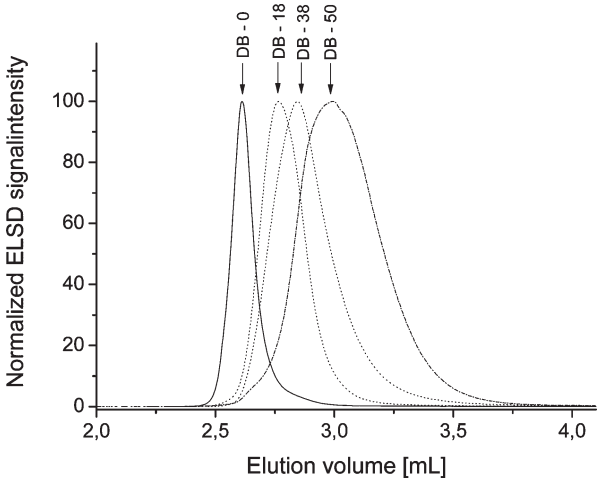

Figure 5. Overlay of chromatograms of linear, partially branched, and hyperbranched polyesters of similar molar masses (fraction no. 5) for isocratic runs at an eluent composition of 94% acetone and 6% THF. This eluent composition corresponds to the critical eluent composition of the linear polymer.

elution order. In contrast, a THF content of less than 6% results in the typical LAC-like increase of the elution volume with molar mass. A nearly molar mass independent isocratic elution can be observed at an eluent composition of 94% acetone and 6% THF. Hence, this eluent composition can be defined as the critical one.

According to theoretical predictions by various authors, the critical composition at a given temperature is characteristic of a particular polymer−stationary phase−mobile phase system and independent of topology for linear and star-shaped polymers. However, our results let us suspect that this assumption is not valid for polymers differing in degree of branching. If critical conditions would be independent of topology, all samples should elute in rather narrow peaks at the same elution volume, irrespective of molar mass and degree of branching.

In order to test this assumption, the identical isocratic experiments were performed on all fractions of partially branched and hyperbranched polyesters at an eluent composition of 94% acetone and 6% THF, which corresponds to the critical conditions of the linear polyester. An overlay of LCCC chromatograms for linear, partially branched, and hyperbranched fractions of lower molar mass (fraction no. 5) is depicted in Figure 5.

As can be seen from Figure 5, the linear and the various branched polymers elute at different elution volumes. The linear sample elutes as a narrow peak close to the void volume of the column, as expected for elution in LCCC. The elution volumes of the branched samples, however, increase with increasing degree of branching.

A further look on the peak width reveals that higher values of the degree of branching result in broader peaks. This phenomenon is probably due to two reasons. On the one hand, one can assume that the enthalpic interactions between the functional groups of the polymer sample and the stationary phase are more pronounced for highly branched polymers as compared to linear polymers. Thus, at a given molar mass, the exclusion effect is overcompensated by the enthalpic contribution, resulting in a molar mass dependent elution for branched polymers at the critical conditions of the linear one. This molar mass dependence causes a broader peak for branched polymers as compared to linear polymers. In addition, partially branched and hyperbranched polymer samples consist of many different topological isomers

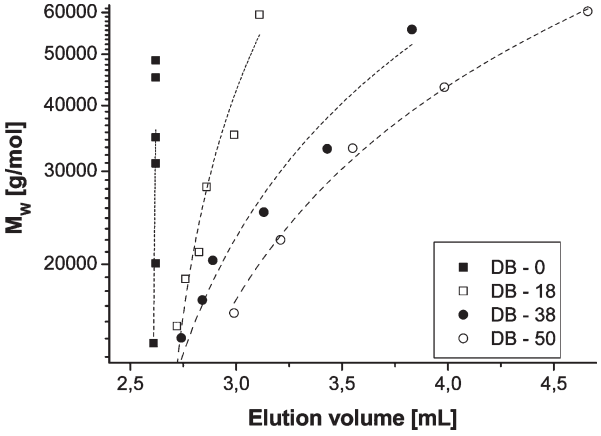

Figure 6. Plot of log M_w versus peak elution volume for linear and branched polymers at critical conditions of the linear polyester 94% acetone and 6% THF. Molar masses were determined by SEC-MALLS. The lines serve as a guide for the eye.

coeluting in SEC. Each of these topological isomers varies in both topology and molar mass and will therefore elute at a different elution volume at the critical conditions for the linear polymer. This adds to the peak widths of the branched samples.

To evaluate the retention behavior of all fractions, a plot of the elution volumes against the molar mass of the fraction was constructed and is shown in Figure 6.

Figure 6 illustrates that linear, partially branched, and hyperbranched polymer samples of a given molar mass exhibit different retention volumes. While the linear polymer sample elutes independent of molar mass, an increasing retention volume with increasing molar mass is observed for the branched polymers. This can again be explained by the higher density of functional groups on the surface for branched polymers. For very high molar masses, the enthalpic interactions between the stationary phase and the branched polymer molecules become so strong that the branched sample is not eluting at all from the stationary phase. In order to ensure complete elution of the injected sample from the stationary phase, the eluent composition was suddenly changed after 5 min to 100% THF, which corresponds to an eluent composition, where all polymer samples desorbs from the stationary phase (SEC conditions). Significant amounts of THF-desorbed polymer were observed only for fractions of DB-50 above 40 000 g/mol.

At this point it becomes clear that the critical conditions of the polymers are governed not only by the chemical composition but are strongly dependent on their topology even for homopolymers, as we have shown for the partially branched and hyperbranched polyesters.

Conclusion

The dependence of retention volume on molar mass and degree of branching was studied for linear and partially branched and hyperbranched polyesters. It was found that the retention behavior of linear and branched polymers at the critical point of adsorption of the linear polymer and in gradient chromatography are functions of degree of branching and molar mass.

In gradient chromatography, the retention volume clearly increases with increasing degree of branching for a given molar mass. This is in contrast to studies on star-shaped polymers where the effect of topology on elution volume was found to be negligible. At lower molar masses the elution volume depends on both molar mass and degree of branching, while for higher

molar masses the elution volume is governed exclusively by the degree of branching.

At the critical conditions of the linear polyester the branched polyesters get stronger adsorbed on the stationary phase than the linear ones. The affinity to the stationary phase increases with increasing degree of branching. For a given degree of branching the retention volume increases with increasing molar mass. The stronger adsorptions of hyperbranched polymers in gradient chromatography and at the critical conditions are assumed to be a consequence of the higher segment density in the periphery of the polymer coil.

The different dependencies for linear, partially branched, and hyperbranched polyesters in gradient chromatography and at critical conditions would enable separations of linear and branched polymers of high molar mass either in gradient chromatography or at critical conditions. However, for samples containing fractions of lower molar mass, two-dimensional separations have to be applied.

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