Tailoring of branching for polyesters with fixed molecular parameters

Diese Arbeit beschreibt die Synthese und Charakterisierung eines maßgeschneiderten, aromatisch-aliphatischen Polyesters mit definierten Verzweigungsgraden (hochverzweigt, abgestuft verzweigt und linear). Der neue synthetische Ansatz mit ABB/AB_2-Monomeren führt zu Homopolymeren mit unterschiedlichen Verzweigungsgraden bei identischer chemischer Struktur und gleicher Anzahl an Endgruppen pro Wiederholeinheit. Eingehende Strukturuntersuchungen mittels ^{1}H und ^{13}C NMR Spektroskopie zeigten kontrollierte Verzweigungsgrade mit definierter chemischer Architektur. Mittels SEC konnte nachgewiesen werden, dass vergleichbare Molmassen erhalten wurden, die trotz statistischer Natur der Synthese in Lösung enge Molmassenverteilungen aufweisen. Sowohl die Eigenschaften in verdünnten Lösungen als auch die thermischen Eigenschaften der Polymere sind untersucht worden. Hierbei stellte sich heraus, dass die Polarität der Endgruppen einen größeren Einfluss auf den Glasübergang der Polymere besitzt als auf die Struktureigenschaften in verdünnten Lösungen.*

Die Klärung dieser Eigenschaften ist Voraussetzung für die Entwicklung einer neuen Separationsmethode mittels zweidimensionaler Flüssigchromatographie zur gezielten Auftrennung von unterschiedlich verzweigten Polymeren.

Keywords
hyperbranched polyester
degree of branching
dilute solution properties
SEC

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Introduction

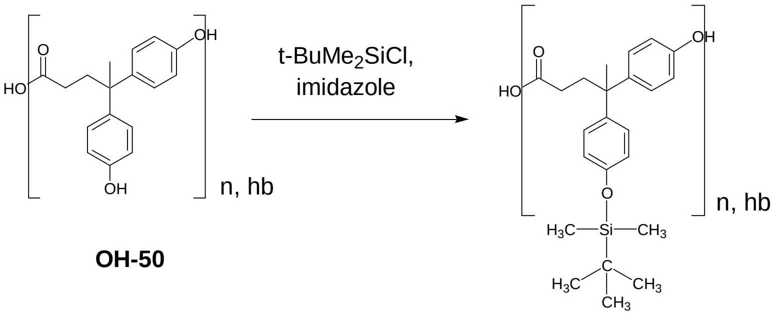
The importance of hyperbranched (hb) polymers in different applications has continuously increased in the last two decades. This can be ascribed to their attractive properties such as globular shape and the large number of terminal groups. Consequently, a large number of hb structures was synthesized and thoroughly characterized. The large interest and the possible wide application domain motivated many researchers to study the structure-property-relationship of hb polymers and to understand them on a molecular level. However, this implies some complications since the conventional techniques of polymer characterization are not directly applicable to characterize hb polymers as these methods are based on assumptions developed for linear polymers [1]. Moreover, hb structures have a special branching topology, globular-like shape and pronounced multifunctionality together with typically broadly distributed molar masses. Therefore, improved methods or even new characterization techniques are required to study their molecular parameters and to correlate them with materials properties. Multidimensional separation techniques are essential for this purpose.

Two dimensional liquid chromatography (2D-LC) helps to obtain simultaneous information on molar mass and on a structural characteristic e.g. topology. Recently, several studies [2-5] on the separation of star and long chain branched polymers from linear analogues were published, revealing the high potential of 2D-LC separations. However, until now the application of 2D-LC has been focused on structures of low branching density. Furthermore, the development of characterization methods for branched polymers faces the lack of hb model compounds and linear polymers of identical chemical structure and the same number of functional groups. So far, the only existing branched model polymer system satisfying the requirements is the combination star polystyrene (PS)/linear PS, obtained by anionic polymerization [2-4]. This system was extensively studied with 2D-LC [2, 3] resulting in the separation of linear and star polymers. However, these experiences cannot be directly extrapolated to hb polymers due to the very densely branched structure and high functionality of that polymer class. Therefore, the need of well defined branched samples of higher branching density is obvious.

In this work we report on the synthesis of well defined hb and gradually branched polymers, which can be used as standards for method development in branched polymer separation. Furthermore, the dilute solution and thermal properties of the obtained samples will be discussed.

Results

Synthesis of hb polyester SY-50



OH-50

SY- 50

Scheme 1:
Synthesis of hb polyester SY-50

The synthesis of hb hydroxyl terminated polyester OH-50, was performed according to the work of Schallausky et al. [6]. Its modification with t-butyldimethylsilylchloride (TBDMS-Cl) and imidazole in DMF for 48 hours gave the silylated sample SY-50 in 55 % yield. The modification of more than 99 % of hydroxyl groups was confirmed by ^{13}C NMR. The molar mass values for both OH-50 and SY-50 are listed in Table 1.

The number average molar mass, detected by SEC-MALLS, should be interpreted carefully since lower molar masses could remain undetected by the light scattering detector. Nevertheless, the high refractive index increment value (dn/dc) of 0.155 mL/g for SY-terminated samples in THF at room temperature allows good detection even in the oligomer molar mass region. For this reason, a good overlapping of the RI and LS signals was observed that leads to a reliable calculation of the molar mass values in the high as well as in the low molar mass regions.

Synthesis of gradually branched polymers

The synthetic approach used in this work is the so called ABB*/AB$_2$ approach. It utilizes the copolymerization of the AB$_2$ with an ABB* monomer, whereas the ABB* monomer is obtained by protection of one of the phenolic groups of the AB$_2$ monomer prior to polymerization (B*). Therefore, only the A and one B functions are mutually reactive. The synthesis of gradually branched polymers employs the copolymerization of the ABB* and AB$_2$ monomers in different ratios. The resulting polymer possesses one functional group per repeating unit, which is an essential difference to the AB/AB$_2$ approach, where one obtains different numbers of functional groups per monomer units and, therefore, different thermal and dilute solution properties were observed [7]. The dependence of the degree of branching DB_{theor} in AB_2/AB copolymers on the linear comonomer molar fraction X_{AB} was theoretically treated by Frey et al. at full conversion and at equal reactivity of the comonomers [8]. The adaptation of these considerations for our AB_2/ABB* system gives Eqs. 1 and 2. Thus, one is able to control the DB of the branched copolymers in the range of 0-50 % via the molar contents AB_2 and *ABB** of the copolymers.

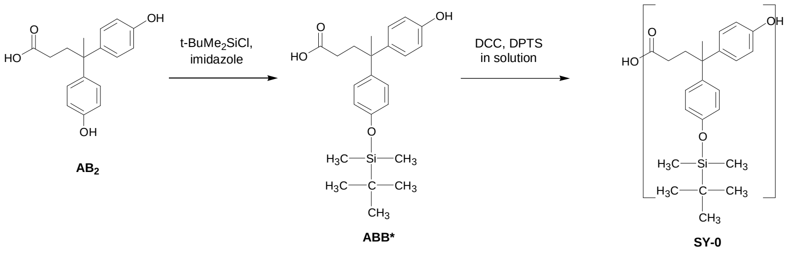
$$X_{ABB*} = \frac{ABB*}{AB_2 + ABB*} \tag{1}$$

$$DB_{theor} = 2\frac{1 - X_{ABB*}}{(2 - X_{ABB*})^2} \tag{2}$$

The theoretically expected DB and the used linear comonomer molar fractions X_{ABB*} are listed in Table 1. As a result, the synthesized gradually branched SY-terminated polyesters reflected a very good correlation between theoretically expected and experimentally found DB and, additionally, comparable molar masses. In contrast to that, the OH-terminated samples have different molar masses due to the applied deprotection procedure.

Synthesis of the linear polyester SY-0

Homopolymerization of the protected monomer ABB* results in linear polymer structure with one functional group per repeating unit (Scheme 2).



Scheme 2: Synthesis of the linear polyester SY-0

First, the ABB* monomer was prepared according to the work of Wooley [9] by silylation of the AB_2 monomer, which was obtained in 40 % yield after flash chromatography separation. The polycondensation of ABB* with DPTS/DCC [10] gives a linear polymer SY-0 in 70 % yield. The molar masses of the resulting linear sample are listed in Table 1. The linearity is confirmed by ^{13}C NMR spectroscopy.

Table 1:
Characterization data of OH–terminated and SY-protected linear and gradually branched polyesters, synthesized in solution using various linear comonomer molar fractions X_{ABB^*} for the co-condensation of ABB and AB_2.*
a) DB_{theor} - DB, calculated according to Eq.2
b) DB_{exp} – DB, determined by ^{13}C NMR according to Eq.3
c) determined by SEC-MALLS in THF
d) linear homopolymer
e) hyperbranched homopolymer

Sample	X_{ABB^*}	$DB_{theor}{}^{a}$, %	$DB_{exp}{}^{b}$, %	$M_{w,SEC\text{-}MALLS}{}^{c}$ g/mol	$M_{n,SEC\text{-}MALLS}{}^{c}$ g/mol	α	T_g, ºC
SY-terminated samples							
SY-0	1^{d}	0	0	64 000	25 600	0.59	124
SY-8	0.956	8	7	41 600	17 700	0.49	114
SY-13	0.925	13	13	59 800	26 500	0.44	119
SY-18	0.889	17	18	45 400	22 800	0.43	118
SY-22	0.856	21	22	60 300	22 300	0.41	119
SY-38	0.658	38	37	47 000	23 700	0.43	113
SY-50	0^{e}	50	50	41 900	22 000	0.35	108
OH-terminated samples							
OH-8	1^{d}	0	8	23 800	14 500	0.58	155
OH-18	0.889	17	18	10 800	4 800	0.43	140
OH-38	0.658	38	37	21 000	8 900	0.42	137
OH-50	0^{e}	50	50	33 900	16 800	0.36	152

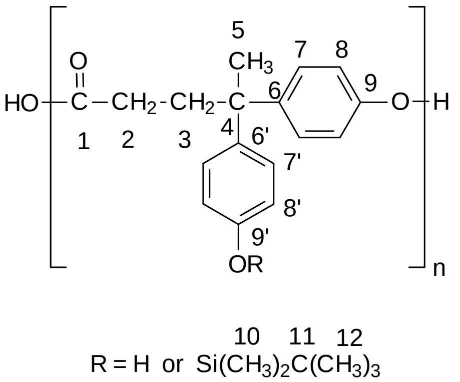
Deprotection of the linear polyester SY-0 into OH-0

The deprotection of the TBDMS group was performed by using 3 eq of trifluoroacetic acid (TFA) in DMF [11], where cleavage of more than 97 % of TBDMS groups was reached. Since the TFA deprotection method involves the acidic hydrolysis, both the transesterification and the ester-bonds hydrolysis took place. As a result sample OH-8 with degree of branching of 8 % and molar mass of 23 800 $g \cdot mol^{-1}$ was obtained. For samples OH-18 and OH-38 lower molar masses were determined at nearly complete deprotection (Table 1).

NMR structural characterization

Previous investigations on hyperbranched polymers obtained from 4,4-bis-(4'-hydroxyphenyl) pentanoic acid by melt [12] and solution [6] polycondensation showed that at high conversion the DB value approaches 50 %, which corresponds to a statistical type of branching as theoretically described by Flory [13]. Based on a detailed ^{1}H and ^{13}C NMR signal assignment [12] it was found that several ^{13}C NMR signals, e. g. those of C_4, $C_6/C_{6'}$ and $C_9/C_{9'}$ (Scheme 3), show a signal splitting caused by the three different subunits and, thus, their intensities from quantitative ^{13}C NMR spectra can be used to calculate DB. The silylation of the phenolic groups of L and T units results in characteristic ^{1}H and ^{13}C chemical shift effects and, fortunately, a signal splitting due to the subunit remains. This is illustrated in Fig. 1, which depicts regions from the ^{13}C NMR spectra of the linear sample SY-0 containing only L units and of two branched samples with different DB. The lowered content of T and D units of the gradually branched sample SY-22 compared with the hyperbranched sample SY-50 is obvious. The experimental degree of branching (DB_{exp}) was determined according to Frey [14] (Eq. 3) based on the intensities of C_4, $C_6/C_{6'}$ and $C_9/C_{9'}$ signals characteristic for terminal (T), linear (L) and dendritic (D) units (Fig. 1). The mean value is given in Table 1 and compared with the theoretical value calculated from the AB_2/ABB* feed ratio according to Eq. 2.

$$DB_{Frey} = \frac{2D}{2D + L} \tag{3}$$



Scheme 3:
Numbering of atom positions for the assignment of NMR signals

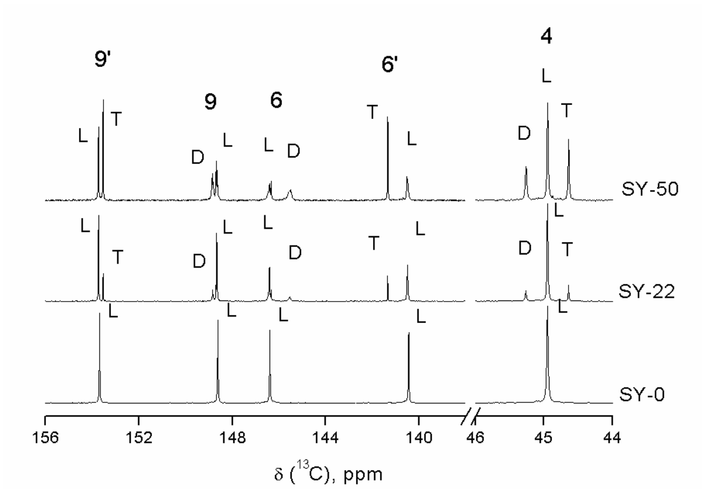


Fig. 1:
^{13}C NMR spectra (regions) of the silylated polymers SY-0, SY-22 and SY-50 (solvent: $CDCl_3$)

By both ^{1}H and ^{13}C NMR the successful purification from DCC-urea as well as high degree of modification/deprotection of all the samples was confirmed. Whereas the completeness of deprotection can easily be proved by disappearance of the H_{10} and H_{12} signals in the ^{1}H NMR spectrum, the proof of complete protection of the phenolic groups requires ^{13}C NMR. Protection is accompanied with insolubility in DMSO-d_6 and, thus, $CDCl_3$ was used as solvent. Residual phenolic protons which can be well detected for samples soluble in DMSO-d_6 result in broad signals in $CDCl_3$ which are not appropriate for quantification. However, the signals of $C_{8'}$ in phenolic units at about 115 ppm which are shifted to about 119.5 ppm after silylation (Fig. 2) are well distinguishable even in traces by their signals in a ^{1}H-^{13}C correlated spectrum.

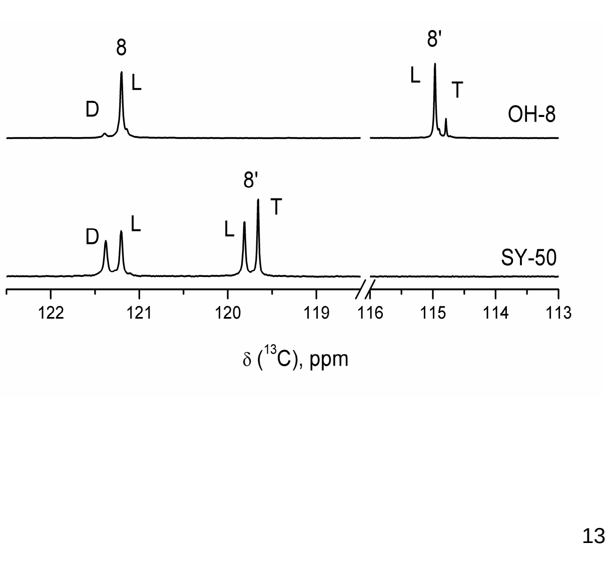


Fig. 2:
^{13}C NMR spectra (region of C_8/$C_{8'}$ signals) of OH-8 (top) and SY-50 (bottom) (solvent: top- DMSO-d_6, bottom- $CDCl_3$)

Dilute solution properties

The intrinsic viscosity of the prepared OH- and SY-terminated polyesters was measured by SEC-MALLS coupled to viscosity detector. The Kuhn-Mark-Houwink-Sakurada (KMHS) exponents *α* are listed in Table 1. Fig. 3 shows the dependence of α on the DB.
In a series of prepared samples a clear trend was observed for the dependence of KMHS exponents on DB. The α values are decreasing with DB from 0.59 to 0.35 for the non-polar polymers and from 0.58 to 0.36 for the OH-terminated polymers, which indicates a more compact shape of the macromolecule at higher DB. Interestingly, there is no difference between the OH- and SY-terminated hb samples having KMHS exponents of 0.36 and 0.35, respectively.
This fact was unexpected since one supposes a denser macromolecule structure of the SY-terminated sample due to its quite voluminous protective groups. On the other hand, this change in polarity leads to an increased affinity to the solvent, which enables the polymer coil to be better rinsed and opened up by the solvent. However, this influence seems to disappear at lower DB and the deviation of the KMHS exponents at the same DB becomes more pronounced.

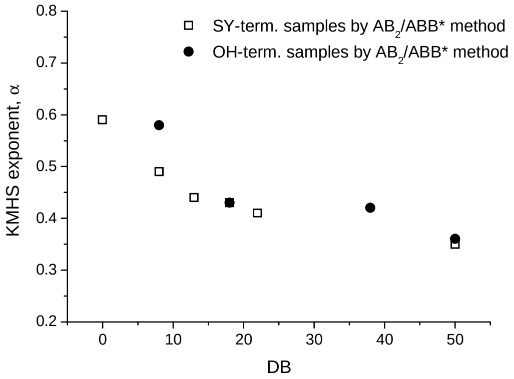


Fig. 3:
The KMHS exponent dependence on the DB in the series of branched aromatic-aliphatic polyesters

Therefore, we conclude that the behaviour of the KMHS exponents is in a good agreement with the theoretical expectations providing a clear comparison of the polymers solely depending on the branching architecture.

Thermal behavior

It is well known that branching could affect the thermal behavior of polymers, e.g. crystallinity and glass transition temperature. Our calorimetric results, listed in Table 1 and presented in Fig. 4 indicate a gradual decrease of T_g with the branching for SY-terminated polyesters. Due to their identical chemical structure, comparable molar masses and total absence of crystallinity, the pure effect of the branching on T_g can be extracted. For SY-terminated polyesters a shift of 16 K was observed between hyperbranched (DB = 50 %) and linear sample (DB = 0 %).

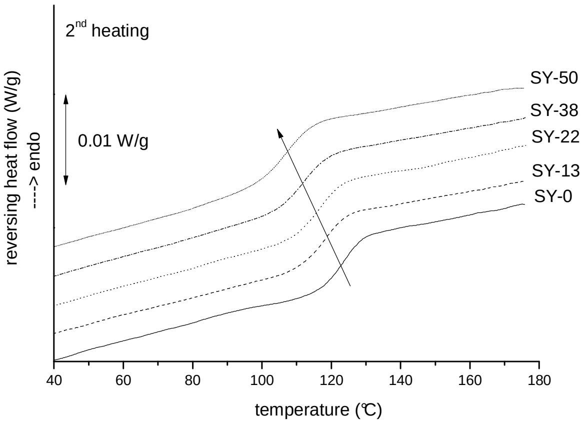


Fig. 4:
T_g dependence on the degree of branching for SY-terminated polyesters. SY-8 was not taken into account due to deviating M_n (see Table 1)

A deviating behavior was observed for OH-terminated samples. The T_g value of OH-50 is 152 ºC, which is much higher in comparison to SY-50 (108 ºC) as a consequence of multiple hydrogen bonds. In a similar manner, the decrease of T_g with introduction of protective group was observed in the work of Mikhaylova [15], where the T_g values (227 ºC) of OH-terminated hb aromatic polyesters drops down to 158 ºC when hydroxyl groups were end-capped.

No systematic variation of T_g with DB was observed for OH-terminated samples due to the strongly deviating molar masses. The only meaningful comparison can be carried out between OH-8 (155 ºC) and OH-50 (152 ºC), which interestingly possess similar T_g values. This observation leads to the conclusion that hydrogen bonds have a stronger influence on the glass transition temperature than branching. This fact is supported by the results of Wooley et al. [9], where similar T_g values were obtained for fully aromatic OH-terminated linear (204 ºC) polyester, hyperbranched (197 ºC) and dendritic (201 ºC) polyesters with comparable amount of phenolic groups. Additionally, Schallausky et al. [6] observed that the branching effect could be completely overlapped by the H-bonding effect.

TGA measurements on the SY-terminated samples showed a high thermal stability up to 350 ºC with the 10 % weight loss occurring at 385 ºC, with the maximum of decomposition temperature between 415 and 430 ºC. OH-terminated samples except OH-50 are thermally stable up to 300 ºC with the maximum of decomposition temperature around 410 ºC. The lower thermal stability (up to 250 ºC) of the sample OH-50 is the subject of further investigation.

2D Chromatography development

The method development in 2D chromatography is performed in cooperation with Dr. W. Radke and Michael Al Samman (DKI Darmstadt) within DPI project #601 BranChar.

Since hb polymers have broad distribution in both branching and molecular weight, there is a need in a combination of techniques, whereas the first separation approach must be sensitive towards molecular weight and the second towards branching. The separation according to branching is based on the different affinity of linear and branched polymers to the column material. This affinity cannot be controlled by chemical character, since the polymers of different DB possess the same type and number of repeating units. The reason should be searched in topological difference, which causes higher density of active 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. Hence, at a given molar mass, highly branched polymers are expected to adsorb on the stationary phase stronger than the less branched [16].

Therefore, for the first dimension size exclusion chromatography (SEC) was used, while for the second dimension the gradient liquid adsorption chromatography was chosen as separation technique. One of the first results is the separation of linear and hb samples. Figure 5 shows the 2D-chromatograme of hb sample SY-50. The elution volume of this sample is used as a reference for further experiments. In Figure 5 the 2D-chromatograme of the mixture of hb and linear samples SY-50 and SY-0 is presented. A clear shift of 3 mL in the gradient elution volume for the high molar mass linear polymer is noticeable, while in the region of lower molar mass (elution volume 18-20 mL) no separation can be observed.

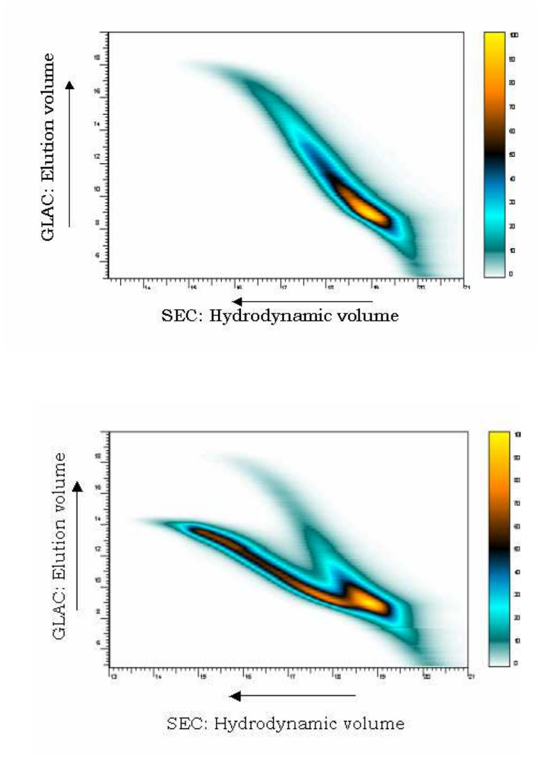


Fig. 5:
2D-chromatographic separation of the mixture 1:1 hb to linear polyesters SY-50 and SY-0 achieved within the project DPI #601

Conclusions

Within this work a set of model compounds (with polar and non-polar end groups) of the same chemical origin and with tailored degree of branching and glass transition temperatures was obtained employing an ABB*/AB_2 approach. The structure of these compounds was proved by ^{1}H and ^{13}C NMR spectroscopy. The theoretically predicted decrease of KMHS exponents of the samples was observed. The performed modification of the OH-terminated samples with the voluminous t–butyldimethylsilyl groups causes an increase in the packing density of the macromolecules and therefore, slightly lower values of KMHS exponent for SY-terminated samples in comparison to OH-terminated analogues have been obtained. Different dependence of the thermal properties on branching was found for OH- and SY-terminated samples. While the maximum difference in the T_g values between linear and hb structures was found to be 16 K for SY-terminated samples, nearly identical values have been obtained for OH-terminated linear and hb polyesters due to the strong effect of hydrogen bond formation. Therefore, we assume that the hydrogen bonding influences the glass transition stronger than branching. The first results on the method development on 2D chromatography show that at lower molecular weight hb and linear polymers co-elute, while in the region of higher molar mass hb and linear samples can be clearly resolved.

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