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Structure characterization of hyperbranched poly(ether amide)s I. Preparative fractionation

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Abstract

The focus of our investigation lies on the separation of typically broadly distributed hyperbranched poly(ether amide)s into narrow fractions of various molar masses. Their exact molar mass found via size-exclusion chromatography (SEC) with light scattering detection allows us to use these fractions for sample specific calibration in the SEC investigation of other hyperbranched samples. The analysis of the degree of branching, molar mass and viscosity behavior of the fractions gives a first indication about their molecular shape and the contribution of that shape to the overall viscosity. We determined the Mark–Houwink exponent for a hyperbranched sample using a number of narrow fractions which showed that an increase of molar mass leads to an increased molecular density.
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1. Introduction

In contrast to dendrimers, hyperbranched molecules are not perfectly branched but they resemble the flow properties of dendrimers due to a similar dense, branched structure. For this reason, hyperbranched molecules are preferably discussed in applications where a reduction in melt or solution viscosity is advantageous as in coatings or as processing additives for linear polymers. They owe their popularity mainly to the simplicity of their synthesis—a one-step polymerization. This, in turn, results in rather broad molar mass distributions [1–3]. For this reason, the determination of the molar mass dependent structure parameters is difficult and, so far, there was neither a synonymous picture of the structure of such hyperbranched molecules nor is the relation of this structure to the macroscopic properties known. Up to now, these systems were either theoretically modeled or correlated to known structures. There are numerous examples for detailed theoretical calculations about their molar mass distribution [4], their dimensions, and their branching density profile [5,6]. Other simulations were made on their intrinsic viscosity behavior in dependence of the degree of branching [7,8]. Parallels between hyperbranched and cross-linked systems were drawn by Burchard [9]. Viscosity and light scattering experiments, developed for micro gels were also applied to hyperbranched systems [10–13]. However, the determination of the gyration and hydrodynamical radius remained difficult due to the high polydispersity of the polymer samples. Indirect proof of the theoretical studies of the hyperbranched systems was obtained by experiments on biopolymers such as amylopectin [14–17], glycogen and dextrin [18–20] or insulin [21], considering them as model compounds.

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Up to now, models and simulation could not be unambiguously supported by experimental results because the synthesis of hyperbranched polymers with different but controlled composition and molar mass is extremely difficult making an immediate detailed investigation of their structure virtually impossible. In addition to that, the special molecular structure and conformation exert a further difficulty on the determination of the exact molar mass. Routine measurements with size-exclusion chromatography (SEC) failed as they were commonly calibrated with linear standards [22,23] which could not account for the shape of dendritic molecules. One possibility to circumvent this problem might be sample specific calibration.

In our work, we obtained controlled molar masses and compositions simply through preparative fractionation of samples having broad molar mass distributions. For this separation we used method similar to the well-known Baker–Williams fractionation, which employed both temperature and solvent gradient. In our fractionation process we used similarly solvent gradient, but at constant ambient temperature on the way described from Francis et al. [24]. This separation was carried out on hyperbranched poly(ether amide)s, which were described elsewhere [23] (Fig. 1). These hyperbranched systems are of interest especially as blend components, because they can strongly influence the rheological properties of linear polymers [25]. For this reason, these hyperbranched polymers are synthesized in large scales and are fundamentally investigated. At this point, the exact determination of their molar mass and the understanding of their structure–property relationship becomes very important.

2. Experimental

2.1. Preparative fractionation

The fractionation was carried out by extracting a 2 g sample of poly(ether amide) with a solvent mixture of tetrahydrofuran (THF, Acros Organics, NJ, USA)

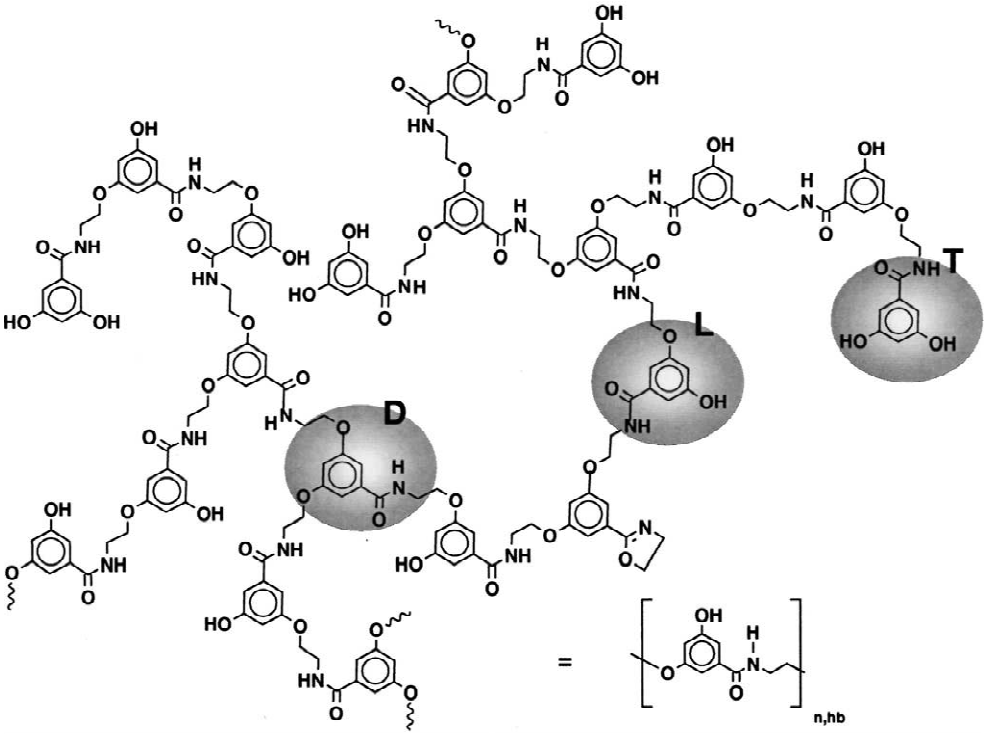


Fig. 1. Hyperbranched poly(ether amide) with indicated terminal, dendritic and linear units, synthesized as described in Ref. [23].

and *N*,*N*-dimethylformamide (*N*,*N*-DMF, Merck, Darmstadt, Germany) with increasing *N*,*N*-DMF content during the procedure. For this purpose, we used a glass column filled with Ballotini (glass beads of 0.1–0.2 mm diameter) coated with hyperbranched polymer. The coating of the surface of the glass beads was carried out by exposing the glass material (400 ml) to 0.02 g/ml polymer solution in *N*,*N*-DMF (100 ml) followed by vacuum evaporation (10 mbar) of the organic solvent at 80 °C. For the extraction of fractions having different molar masses we utilized the different solubility of the polymer in THF (bad solvent) and *N*,*N*-DMF (good solvent). The composition of the mixed solvent was varied between 0 and 76% (v/v) *N*,*N*-DMF in THF. For subsequent investigations, the solvent of the extracts was evaporated and the isolated solid polymer was dried for 48 h at 50 °C in vacuo.

2.2. SEC, light scattering and viscosity measurements

2.2.1. Choice of the solvent

In addition to *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide (*N*,*N*-DMA, Merck) is another good solvent for poly(ether amide)s. Using both pure solvents for the SEC measurements of the hyperbranched samples, we observed bimodal elution curves. Most likely, this effect can be explained by the formation of aggregates due to intermolecular interactions between the polymer molecules caused by specific solvation effects [26] or by enthalpic effects with the stationary phase of the chromatographic column. In order to avoid such interactions we chose a mixed solvent of *N*,*N*-DMA with 3 g/l LiCl (Fluka, Buchs, Switzerland) and 2% (v/v) water (DMA–LiCl–water) for our SEC investigations, as used in previous work for similar purposes [23]. Additionally, we compared the viscosity behavior of our samples in the two preferred solvents—DMA–LiCl–water and pure DMF. The calculated values for the Schulz–Blaschke and Huggins constants of more than 1.0 in DMF and below 0.5 in DMA–LiCl–water proved again the better solubility in the mixed DMA–LiCl–water.

2.2.2. Chromatographic measurements

SEC analysis was carried out in DMA–LiCl–water as the eluent on three chromatographic systems:

System A: HP Series 1100 chromatographic system (Hewlett-Packard, Waldbronn, Germany) with two columns Zorbax PSM Trimodal-S, 250 mm×6.2 mm (Rockland Technologies, Newport, DE, USA) and a flow-rate of 0.5 ml/min using refractive index (RI) and UV (280 nm) detection. The molar mass and molar mass distributions were calculated using a calibration relationship determined with the linear polymer standards poly(styrene), poly(2-vinyl pyridine), poly(ethylene oxide).

System B: PL-GPC 220 (Polymer Labs., Shropshire, UK) in combination with RI and multi-angle light scattering (MALLS) detection (DAWN-EOS, Wyatt Technologies, Santa Barbara, CA, USA) with PL Gel HTS-D column, 150 mm×7.5 mm (Polymer Labs.) at a flow-rate of 1 ml/min.

System C: Modular builded SEC (Knauer, Berlin, Germany) in combination with RI and low-angle light scattering (LALLS, 5°) detection (PL-LALS, Polymer Labs.) using a PL Gel Mixed B-LS column, 300 mm×7.5 mm (Polymer Labs.) at a flow-rate of 1 ml/min.

The chromatographic measurements were carried out at ambient temperature.

2.2.3. Viscosity

The solution viscosities were measured in DMA–LiCl–water at 25 °C using an Ubbelohde viscometer or an RI–viscometer detector (Knauer) in batch mode. The values ($\eta_{spec.}/c$) for the calculation of the universal calibration and the Mark–Houwink coefficient were obtained by single point measurement (c=0.2 g/dl). Concentration dependent viscosity measurements were carried out for selected samples in order to determine Schulz–Blaschke and Huggins constants (see Section 2.2.1)

2.3. Nuclear magnetic resonance (NMR)

^{1}H-NMR data were recorded on a Bruker DRX 500 NMR spectrometer (Brucker Analytik, Rheinstetten, Germany) and was used to calculate the degree of branching. The spectra were measured in [$^{2}H_{6}$]dimethyl sulfoxide (DMSO-d_6; Merck) with tetramethylsilane (Sigma–Aldrich, Steinheim, Ger-

many) as internal standard. The interpretation of the spectra was performed as described elsewhere [23].

3. Results and discussion

For the investigation on the structure properties of the hyperbranched molecules a series of samples were available, shown in Table 1. As described in a previous paper on the synthesis and analysis of similar molecules [23], we met obstacles in the determination of the molar mass. Table 1 shows the results of the SEC measurements as determined by SEC, system A. The investigated poly(ether amide)s do not show an unusual behavior—the observed elution curves were monomodal (not shown). The molar masses (M_w) of the substances were calculated using linear poly(styrene) calibration and were found to be between $1.43 \cdot 10^4$ and $2.22 \cdot 10^4$ g/mol. In comparison to the SEC results, independent static light scattering measurements of sample PEA4 gives about 10 times higher values ($1.8 \cdot 10^5$ g/mol). This observation leads to the assumption that strong differences between the solvation behavior of the used poly(styrene) standard and our hyperbranched polymer exist.

The correct calibration of the SEC seems to play an important role in the characterization of this class of polymers. There are two possibilities to obtain more reliable molar mass data for polymers having unusual geometry by the SEC method: the universal calibration method using the common calibration standards and viscosity measurements [27], and the sample specific calibration using similar standards or fractions of the samples with known molar mass and narrow molar mass distribution, respectively.

Table 1
Molar masses of poly(ether amide)s detected by SEC (system A)

Sample	Molar mass[a]	
	M_w	PD[b]
PEA 1	17 700	1.74
PEA 2	20 700	1.91
PEA 3	14 300	1.69
PEA 4	17 150	1.69
PEA 5	22 200	2.33
PEA 6	16 750	2.39

[a] Polystyrene as a linear standard.
[b] Polydispersity M_w/M_n.

We considered it necessary for both approaches to fractionate a regular sample with a broad molar mass distribution of our hyperbranched poly(ether amide)s into fractions having a more narrow distribution and clear differences in the M_p (peak maximum molar mass), since the knowledge of the true molar masses of such fractions will support the determination of the structure parameters of the hyperbranched molecules in solution. This becomes feasible using a combination of concentration detection and molar mass specific detection. In order to utilize this option, we used RI detection along with MALLS and LALLS detection in our SEC experiments to determine the absolute mass of the fractions.

For the necessary fractionation, we chose PEA5 taking into account its higher molar mass and polydispersity (PD). PEA5 was fractionated as described in Section 2.1. The first successful fractionation we carried out on small amounts (50 mg) of the sample. The isolated fractions were characterized by SEC, system A and the results are presented in Fig. 2a. However, for detailed investigation we needed larger amounts of the polymer fractions. We therefore scaled up the fractionation to 2 g PEA5. We obtained 17 fractions (Fig. 2b) having a narrow molecular mass distribution and satisfactory polymer amounts and fraction mass distribution (Fig. 3).

The determination of the relative molar mass of hyperbranched substances using sample specific calibration standards is, as mentioned above, not facile because there are no adapted standards known. We intended to find the optimum linear standard for the analysis of our systems. Therefore, in addition to polystyrene (PS), we used poly(ethylene oxide) (PEO) and poly(2-vinyl pyridine) (PVP) in order to find a standard having a hydrodynamical shape comparable to our hyperbranched molecules in the used solvent. We focused on these three systems because of their good solubility in our solvent and since it can be assumed that these polymers have a coil form in *N*,*N*-DMA. In order to support this assumption, we carried out viscosity measurements on these linear polymers and determined their Mark–Houwink exponent, *a*, from the Mark–Houwink equation:

$$[\eta] = KM^a \quad (1)$$

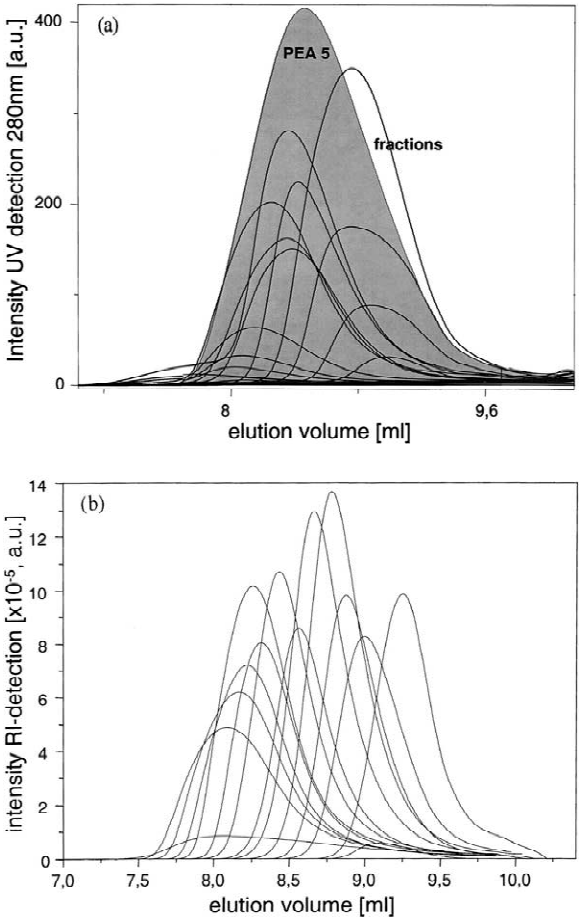


Fig. 2. SEC analysis (system A): (a) of the hyperbranched polymer PEA5 and its fractions, obtained in the fractionation experiment on 50 mg PEA5 (number of fractions 15); (b) of the fractions, obtained in the fractionation scaled up to 2 g PEA5 (number of fractions 17).

with $[\eta]$ as intrinsic viscosity, K – Mark–Houwink constant, and M as molar mass.

The found low values for the Mark–Houwink exponents, $a=0.34$ for PS, $a=0.53$ for PVP and $a=0.19$ for PEO, verify a rather dense shape, as observed for collapsed coils. From this one should conclude that these polymers are suitable standards for the SEC analysis of hyperbranched polymers which also exhibit a dense structure and a low hydrodynamic volume. We carried out the calculation of the molar masses of the fractions using the calibration curves described by Eq. (2) for PS, Eq. (3) for PVP and Eq. (4) for PEO:

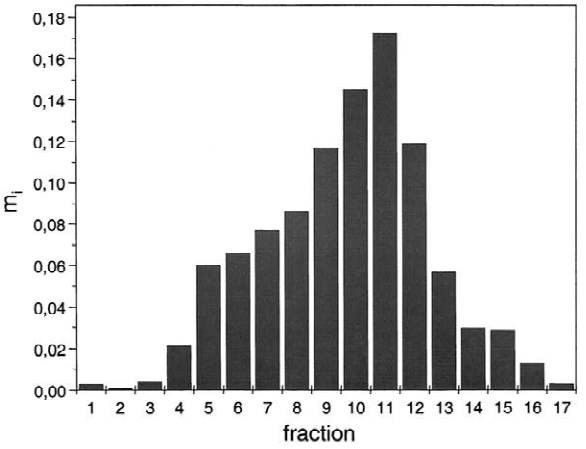


Fig. 3. Mass distribution of the fractions from fractionation of 2 g PEA5.

$$\log M_{PS} = -0.4892V_e + 12.87 \quad (2)$$

$$\log M_{PVP} = -0.481V_e + 12.54 \quad (3)$$

$$\log M_{PEO} = -0.533V_e + 13.27 \quad (4)$$

where M_{PS}, M_{PVP} and M_{PEO} are the M_w's of the linear standards and V_e is the elution volume.

In Table 2 some representative results of molar masses and polydispersities for selected fractions are given calculated from the above calibration curves. In this table a comparison can be drawn to the results of light scattering detection (systems B and C), which leads to absolute mass average molar mass values. There are clearly strong differences between the calibration using the MALLS and any of the linear standard calibrations.

In previous investigations of perfectly branched poly(ether amide)s [28] the best fit in comparison to theoretically calculated values and the values determined by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) of the SEC data was obtained by PVP calibration. This does not hold for our samples since also the PVP calibration differs strongly from the MALLS results. One has to aware that in contrast to our hyperbranched fractions, these dendrimers are monodispersed substances with molar masses lower than 5500 g/mol, which can explain these differences.

Table 2
Molar masses of selected fractions of PEA5 (total 17 fractions), calculated by the use of relative (SEC, system A) and absolute determination methods (SEC, systems B and C)

Fraction	$[\eta]$ (dl/g)	Linear standard calibration						Universal calibration, M_p	Light scattering detection	
		PS		PVP		PEO				
		M_w	PD	M_w	PD	M_w	PD		M_w	PD
F6	0.06	9100	1.28	7100	1.31	4300	1.48	20 109	62 991	1.08
F9	0.09	16 900	1.33	14 000	1.44	9900	1.46	36 510	73 458	1.09
F11	0.13	28 700	1.46	24 300	1.57	17 600	1.44	48 671	128 870	1.04
F13	0.17	41 500	1.72	35 200	1.78	27 000	2.08	51 878	428 800	–
F15	0.18	54 800	1.96	46 000	2.00	36 900	1.83	79 915	724 300	–

The results depicted in Table 2 and Fig. 2b clearly show that the fractionation process is controlled by the molar mass. However, the molar masses calculated directly by using the PEO, PVP and PS standards are extremely low in comparison to the light scattering values. This is brought about by different density of the polymer tangle of a linear molecule in comparison to that of the hyperbranched molecule. In order to exclude the influence of the polymer structure on the calculations of the molar mass, we applied the universal calibration method [27]. This method works independently of the molecular shape according to [27] and will therefore be used to relate the elution volume to $M_p[\eta]$, where $M_p[\eta]$ is proportional to the hydrodynamic volume for a wide area of polymers. This method has already been successfully applied to the description of hyperbranched structures in the works of Mourey et al. [29] for small dendrimer generations, in Patton et al. [10] for randomly branched poly(ester)s and in Geladé et al. [30] for hyperbranched poly(ester amide)s with molar masses below 10 000 g/mol. Mourey suggested deviations of the real molar mass at higher dendrimer generations of up to 20%. Our results using the universal calibration of the PS and PVP standards are presented in Fig. 4. The obtained molar mass values are slightly higher than those obtained from the classical standard calibration (Table 2).

Determining the molar mass of the hyperbranched molecules is also possible without using a standard. We performed this investigation with a light scattering detector connected to the SEC system (systems B and C) and obtained values much higher than the molar mass calculated by the use of standards. Table 2 shows the LALLS and MALLS determined molar masses and polydispersities of our samples. These values show that we succeeded in separating our poly(ether amide) into fractions having a very narrow molecular mass distribution. The polydispersity appears to be low enough to determine scaling parameters using light scattering experiments.

The large differences in the values of the molar mass determined by light scattering and by standard calibration speak in favor of a phenomenally strong dependence of the molecular density on the molar mass. This is due to the fact, that the molecules are separated in the chromatographic column according to their volume. The volume of hyperbranched molecules with a molar mass of about 60 000 g/mol corresponds to that of the PS or PVP with a molar

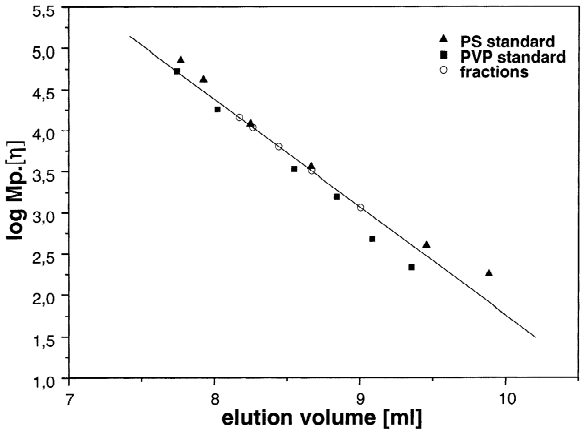


Fig. 4. Universal calibration calculated via linear standards PS (triangle) and PVP (square) of the SEC (system A) analysis of the fractions (circle).

mass of ca. 20 000 g/mol. This result shows that the universal calibration does not work for our case, even if it is adapted to different molecular shapes and despite the inclusion of the viscosity into the calculation. The hyperbranched molecules we investigated show a significantly high increase of the density with increasing molar mass. This does not go along with a constant increase of the viscosity. Hence, a correct interpretation using universal calibration is not possible. Fig. 5 shows the Mark–Houwink plot of the molar mass versus the viscosity according to Eq. (1). The shape of the curve is well known from theoretical calculations and corresponds to the conversion of the molecular shape from a statistical coil to a hard sphere. This is reflected in the change of the curve slope a from 1.5 to 0.1. Such a behavior of hyperbranched molecules is to be expected according to the theoretical calculations of Widmann and Davies [7] and Aerts [8]. The authors found a similar Mark–Houwink behavior of hyperbranched molecules and dendrimers, actually with a maximum in the curve. In our case, molar masses are in the range of 60 000 to 700 000 g/mol, and we do not reach an maximum in the curve. Different results were obtained by Turner et al. [31] for hyperbranched polyesters who observed a Mark–Houwink behavior with concave curve shape and low exponent values ($a<0.4$).

There are two ways to explain these differences assuming that the molecules have the same solubility

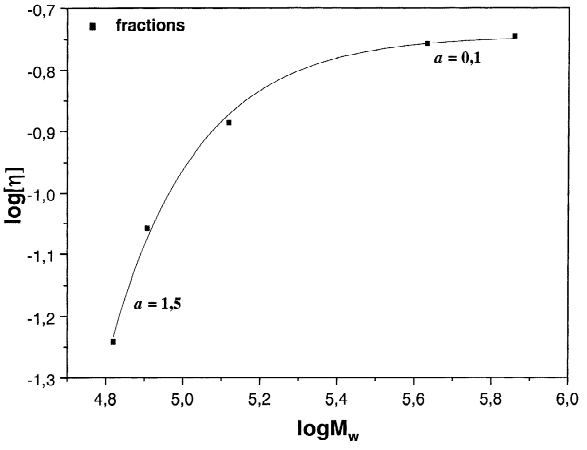


Fig. 5. Mark–Houwink behavior of the fractions using their MALLS detected (SEC, system B) molar mass (see Table 2).

in the applied solvents. Firstly, a different stiffness of the molecules as discussed by Aerts [8] who investigated aliphatic polyesters. He compared them to polyester described by Turner et al. [31] which contained stiffer monomer units. In the case of Turner et al. the molecules are compact having a low a. They do not have aliphatic chains which could have freedom to fold back leading to a variable molecular shape. We investigated molecules that contain less stiff monomer units. According to Aerts, this fact should accomplish the Mark–Houwink behavior of our molecules with an increased compactness of the molecule with the molar mass. The second reason may be the difficulty in using dual viscometric–concentration detection in the chromatographic measurements as utilized in [31]. In such chromatographic systems the interdetector peak broadening leads to a false Mark–Houwink exponent [32]. Commercial software allows to work around this error only for a limited number of materials [32].

A detailed study of the molecular shape by the use of the Mark–Houwink exponent, as well as the deduction of structure parameters of the hyperbranched molecules, will be investigated in future work.

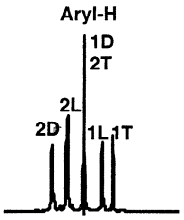
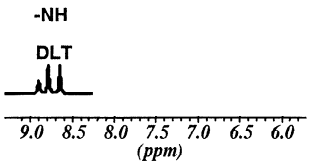
In order to prove that the different shapes of our molecules are not due to the different degrees of branching (DBs) in the fractions, we performed ^{1}H-NMR measurements and determined DB. The spectra were interpreted, as shown in [23], by the methods of Hawker et al. [33] and Hölter et al. [34]:

$$\mathrm{DB}_{\mathrm{Fréchet}} = \frac{T + D}{T + D + L} \tag{5}$$

$$\mathrm{DB}_{\mathrm{Frey}} = \frac{2D}{2D + L} \tag{6}$$

where T, D and L are the terminal, dendritic and linear units, respectively, as depicted in Fig. 1 and Table 3. Table 3 summarizes the calculated values, which are evidence of a high DB, approximately 50%. As Table 2 shows our fractions have broad molar mass spectrum. For this reason, we assume that Hölter et al.'s method is relevant to our case, because it also covers molecules with a lower polymerization degree. As expected, we observed a slight increase of the DB with the molar mass. Nevertheless, this increase should not exert an influence on the solution behavior of the hyperbranched molecules.

Table 3
Degree of branching of selected fractions of PEA5, determined by ^{1}H-NMR

^{1}H-NMR signals	Fraction	$DB_{Fréchet}$	DB_{Frey}
	F6	0.54	0.45
	F9	0.54	0.47
	F11	0.55	0.51
	F13	0.56	0.52
	F15	0.56	0.52
	F6	0.56	0.48
	F9	0.57	0.50
	F11	0.57	0.53
	F13	0.56	0.53
	F15	0.56	0.54

Finally, we used the molar mass of the described fractions for the correct calibration of the SEC measurements of the samples shown in Table 1. For this purpose, we took the LALLS determined characteristics of the fractions (SEC, system C). The values of the original hyperbranched polymers determined by the calibration with the fractions are shown in Table 4. Fig. 6 illustrates the calibration curve of the hyperbranched fractions compared to the linear standards. As expected, their molar masses lie generally higher than those of the linear standards. There is a very strong increase of the molar mass with decreasing elution volume above approx. 150 000 g/mol, which has to be ascribed to the dependence of the molar mass on the compactness of the hyperbranched molecules, as discussed above. Our results clearly show the necessity of sample specific calibration for the determination of the molar mass of hyperbranched systems by SEC, not coupled to an absolute molar mass detector.

Table 4
Molar masses of poly(ether amide)s detected by SEC (system C, RI detection) after sample specific calibration with the fractions of PEA5 in comparison to the SEC values from Table 1

Sample	Molar mass			
	SEC[a]		SEC[b]	
	M_w	PD	M_w	PD
PEA 1	17 700	1.74	–	–
PEA 2	20 700	1.91	101 750	1.24
PEA 3	14 300	1.69	–	–
PEA 4	17 150	1.69	91 200	1.22
PEA 5	22 200	2.33	94 400	1.21
PEA 6	16 750	2.39	84 000	1.20

[a] Polystyrene as a linear standard.
[b] PEA5 fractions as sample specific standard.

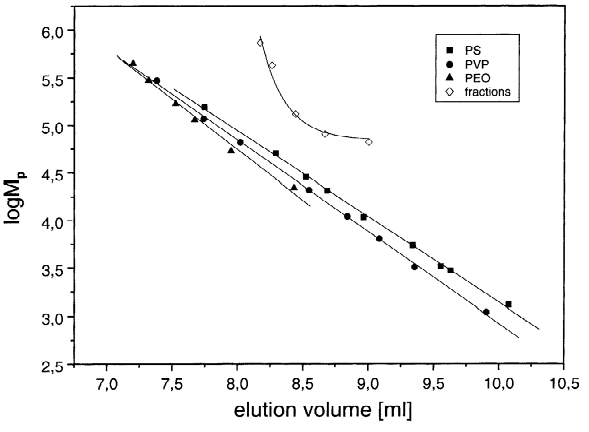


Fig. 6. Calibration curves of the fractions (diamonds) in comparison to the linear standards PS (square), PVP (circle) and PEO (triangle) for the SEC analysis (system A).

4. Conclusions

Using extraction fractionation, we succeeded in separating a hyperbranched poly(ether amide) synthesized in broad molar mass distribution. The fractions possessed a degree of branching of approximately 50%. The obtained amounts and the narrow molar mass distributions of the fractions enabled us to perform a detailed investigation on the molar shape of the molecules within these fractions using light scattering and viscosity measurements.

The determination of the exact molar mass of the fractions allowed a comparison to conventional calibration methods of SEC measurements of hyperbranched samples. We showed that the use of linear standards can mislead the interpretation of such measurements even applying universal calibration. This was proven by light scattering detection of the molar mass and by using the Mark–Houwink relation which indicated a strong increase of the density of the molecules with their molar mass. This led us to the conclusion that the calibration of chromatographic system for characterization of hyperbranched molecules shall be performed only through sample specific standards, preferably through sample specific calibration.

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