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Molar Mass Characterization and Solution Behaviour of Poly(ether amide) Dendrimers

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Summary

Poly(ether amide) dendrimers with different molar masses were investigated using Size Exclusion Chromatography (SEC) with linear standard calibration and Matrix Assisted Laser Desorption/Ionization - Time-of-Flight - Mass Spectroscopy (MALDI-TOF-MS). The SEC behaviour of the dendrimers was investigated in different column systems, in pure and in mixed N,N-dimethylacetamide with water and LiCl. This behaviour was compared to linear poly(styrene) and poly(2-vinyl pyridine) standards. Kuhn-Mark-Houwink-Sakurada relationship yielded evidence about the molecular shapes of the polymers in solution and explained the different solution behaviour of the polymers. The universal calibration method was tested for its application to molar mass determination of poly(ether amide) dendrimers.

Introduction

Ideally, dendrimers are perfectly branched macromolecules with a degree of branching (DB) of 100%. This type of molecules is a result of a number of stepwise chemical reactions [1,2], which allow a high degree of control over the branching growth resulting in nearly monodisperse molar mass distributions. These most important features of dendrimers lead to their globular molecular shape [3,4] with internal cavities and high reactivity due to the large number of end groups. It is these unique properties of dendrimers that renders them interesting for a variety of different applications despite their rather expensive and complicated way of synthesis. Dendrimers were investigated in the last 15 years for application in different fields such as complexing agents [5], photocatalysts [6], MRI (magnetic resonance imaging) contrast agents [7,8] for biomedical [9] and drug delivery applications [10].

In order to deepen the understanding of their application potential and to enhance the control over the specific dendrimer properties many molecular characterization studies were published. In particular, the theoretical modelling and simulations of the solution behaviour of these globular structures [11-15] gave a good indication about the shape of the dendrimers to be more open in the first generations and getting denser at higher generations.

In addition to that, a rather small number of experimental studies have been carried out to verify the theoretical calculations most likely due to the difficult synthesis of high generation dendrimers. One remarkable contribution with regard to this is the work of Mourey et al. [16] who, indeed, showed a strong exponential dependence of the molecular shape on the molar mass of polyether dendrimers, passing through a maximum after the 4th generation, as theoretically predicted. A further demonstration of such behaviour provided Tomalia [17] in his experiments with PAMAM (poly amido amide) dendrimers.

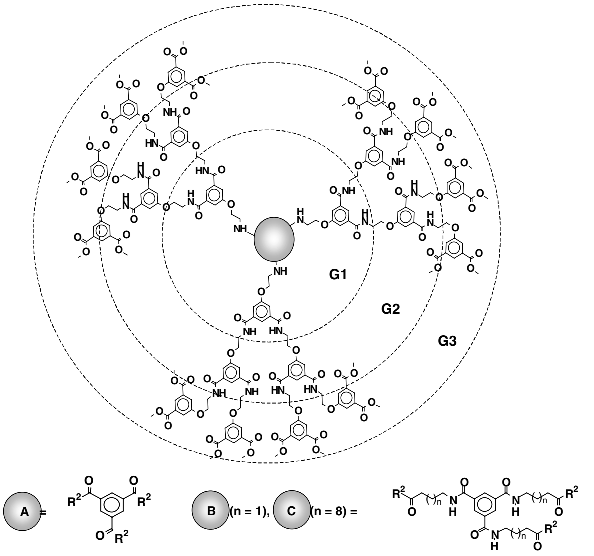
A further challenge on the field of the dendritic polymers is to obtain reliable data about their molar mass especially in the case of the hyperbranched polymers. The traditional size exclusion chromatography (SEC) coupled to a concentration detector in combination with polymer standard calibration is not applicable due to the lack of standards possessing the same branching density as hyperbranched polymers. Coupling SEC with a molar mass sensitive detector such as MALLS (multi angle laser light scattering detector) does not work in the case of low molar masses and MALDI-TOF-MS cannot be applied because of the typically broad molar mass distributions of the hyperbranched molecules. To solve this problem dendrimers could be very useful as model substances with their dendritic topology, very good defined branching density and nearly monodispers molar masses comparable to standard polymers used for calibration in the size exclusion chromatography. Efforts for setting up a calibration curve out of well defined dendritic polymers have been made for dendrimers [16] (with 100% DB) as well as for hyperbranched polymers (approx. 50% DB) [18]. These and other investigations on dendritic polymers [19,20] show that their solution and SEC behaviour, respectively, depends very strongly not only on their degree of branching but also on their chemical character. For this reason comparable investigations on dendritic systems of different chemical structure are necessary to give more clear image of the solution properties of these type of polymers. Therefore, the aim of this work is to investigate this behaviour for a new class of dendrimers - the poly(etheramide) dendrimers, which were for a first time synthesized in our group [21].

In our study we describe the molar mass characterization of the poly(ether amide) dendrimers with different methods and discuss their chromatographic behaviour related to their scaling properties in solution. Investigations of the effect of the branching on the scaling behaviour of dendrimers using 1H PFGNMR (pulsed field-gradient nuclear magnetic resonance) diffusion measurements were carried out. They yielded scaling exponents in the order of magnitude of the Euclidean dimensions for the dendrimers [22].

Despite the use of the convergent synthetic path, which is optimum for obtaining molecules of higher generations, the highest reached generation number of our poly(ether amide) dendrimers was three [21]. In order to extend the portfolio of the investigated molar masses, we used differently sized cores coupled to the different generations of dendrons as shown in Scheme 1.

Experimental

The synthesis of the investigated dendrimers was reported elsewhere [21]. The theoretically calculated molar masses are shown in table 1. The numerical subscript of the samples refers to the dendrimer generation and to the core molecule with different alkyl chain length as shown in scheme 1.



Scheme 1. Presentation of the investigated three different generations dendrimers (G1, G2 and G3) with a core of different size (A, B and C).

Table 1: Theoretically calculated molar masses

Dendrimers	Structure unit between core and dendrons	$M_{theoretical}$ (g/mol)
G1-A	without alkyl spacer	916.86
G1-B	C_3-spacer	1171.2
G1-C	C_{10}-spacer	1465.7
G2-A	without alkyl spacer	2243.0
G2-B	C_3-spacer	2498.0
G2-C	C_{10}-spacer	2793.0
G3-A	without alkyl spacer	4897.7
G3-B	C_3-spacer	5153.0
G3-C	C_{10}-spacer	5447.6

Chromatography:

The SEC measurements were performed at ambient temperature on a modular chromatographic equipment consisting of HPLC pump, refractive index detector and manual injection valve (KNAUER, Germany). Two column/solvent systems were used.

System A: The column set used in this system was ZORBAX PSM 60 (separation range: 500 to 10 000 g/mol) and PSM 300 (sep. range: 3000 to 300 000 g/mol; Rockland Technologies Inc., USA). The eluent was a mixture of N,N-dimethylacetamide (DMAc, Merck, Germany), 2 vol.% water and 3 g/L LiCl (Fluka, Buchs, Switzerland).

System B: The column set used in this system was OligoPore 300/7.8 mm (sep. range: up to 5000 g/mol; Polymer Laboratories, UK). The eluent was pure N,N-dimethylacetamide (DMAc, Merck, Germany).

In all measurements the flow rate was 0,5 ml/min, the injected volume was 20 µL with a solution concentration of 2 g/L. The linear polymer standards used for SEC calibration were poly(styrene) (PS, Polymer Laboratories, UK) and poly(2-vinyl pyridine) (PVP, Polymer Laboratories, UK).

MALDI-TOF-MS:

MALDI-TOF-MS experiments were performed on a HP G2030A MALDI-TOF-MS system (Hewlett-Packard, USA) with delayed extraction option (GSG, Germany). The desorption/ionisation was carried out using a pulsed N_2-laser. Mass spectra were obtained from 28 kV acceleration voltage (positive polarity). The matrices used were 2,5-dihydroxybenzoic acid (DHB/THF, Fluka Germany) or sinapinic acid (SNP/THF, Fluka Germany) with LiCl-modifier. The mixture of the investigated sample and the matrix was dried on a sample holder in a vacuum.

Viscosity:

The solution viscosities were measured in mixed DMAc with 2 vol.% water and 3 g/L LiCl at ambient temperature using an Ubbelohde viscometer. The values of the reduced viscosity ($\eta_{\text{spec.}}$ / c) used instead of intrinsic viscosity for the calculation of the universal calibration and the Kuhn-Mark-Houwink-Sakurada coefficient were obtained by single point measurements (c = 0,15 g/dL). These measurements were chosen because of the small amounts of dendrimer we had at our disposal. According to our experience, the values of the reduced viscosity at that low concentration for linear standards and dendritic, hyperbranched poly(etheramides) are very close to their intrinsic viscosities.

Results and Discussion

SEC is based on the principle of the separation of dissolved species as a function of their hydrodynamic volume. Using a standard of known molar mass and the same molecular density, the hydrodynamic volume is to be related to the molar mass of the investigated sample. In general, branched macromolecules are denser than chemically similar linear molecules in solution. For this reason the molar mass determination via SEC does not provide a reliable information using the linear standard calibration method. At the same time, branched polymer standards with the same topology are not available for such calibration. Figure 1 shows SEC separation of the investigated poly(ether amide) dendrimers compared to the mixture of a linear polystyrene standards using SEC system A (see experimental part).

According to this calibration method, the molar masses of the dendrimers should lie between approx. 2000 and 10 000 g/mol. In order to verify these results and to obtain the real molar masses of our samples, we were bound to use an absolute molar mass determination method. Because of the low molar mass region of the samples, MALLS detector for SEC cannot be used for this determination and, therefore, our attention was drawn to MALDI-TOF-MS. This technique can be successfully applied to

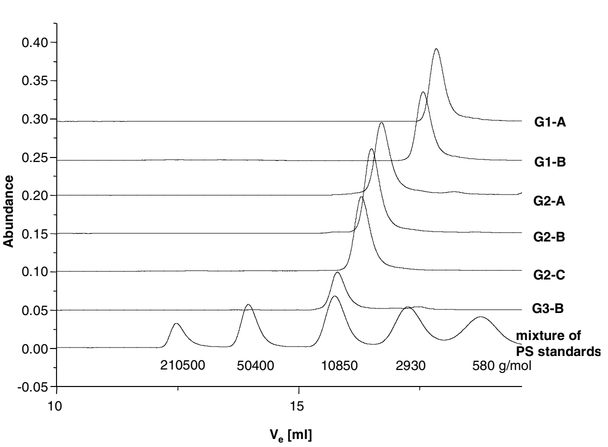


Figure 1. SEC chromatograms of the investigated poly(ether amide) dendrimers and PS standards using system A.

narrowly distributed samples in the lower molar mass region. These two features we suspected in our dendrimers, which as is generally known, are monodispers polymers according to chemical structure as well as to molar mass.

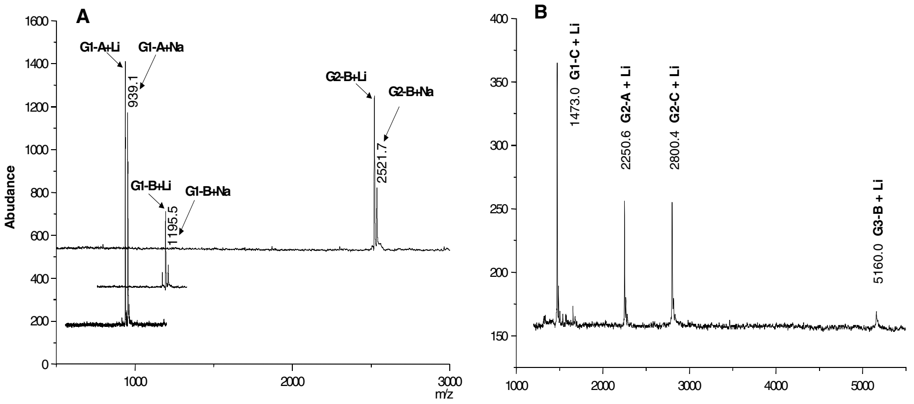


Figure 2. MALDI-TOF spectra: a) molar masses of first and second generation dendrimer – the detected peaks correspond to the Na- and Li-adducts; b) different intensities of detection of dendrimer mixture (the dendrimer samples possess equal concentrations in the solution).

The well defined chemical structure of these samples was already confirmed in previous studies [21]. Their monodispersity according to the molar mass could be followed in figure 2a depicting the spectra of two separately measured dendrimer generations. In table 2 the values of the molar masses of all measured samples using MALDI are listed. The clear spectra and the definite detection of the molar mass (figure 2a) support the assumed narrow molar mass distributions of our samples. Additional measurement of the dendrimer mixture (figure 2b) demonstrates a distinct decrease of the signal quality at higher molar masses, which can be ascribed to the typical for this technique discrimination of species with higher molar masses in samples with broad polydispersities, which we simulated mixing the different dendrimer generations together. The molar masses detected by MALDI are in very good agreement with the theoretically predicted values for the different dendrimer generations with different cores, as listed in table 2.

Table 2: Comparison of the molar masses obtained by MALDI-TOF and by specific sample calibration (SSC)

Dendrimers	$M_{theoretical}$ (g/mol)	M_{MALDI} m/z	M_{SSC}^{*} (g/mol)
G1-A	916.86	917.5	900
G1-B	1171.2	1172.5	1100
G1-C	1465.7	1466.8	1500
G2-A	2243.0	2244.2	2200
G2-C	2793.0	2793.0	3300
G3-A	4897.7	4898.0	4300
G3-B	5153.0	5154.6	4800

*Molar mass of peak maxima

Using these results as the real molar masses of our dendrimers we were able to establish a calibration relationship for the SEC experiments. We call this Specific Sample Calibration (SSC). The SEC separations of the dendrimers using system B in comparison to a dendrimer mixture used as calibration standard are plotted in figure 3. The differences in the separation of the dendrimers between system A and B can be explained by the different molar mass separation ranges of the used SEC columns (fig. 1 and 3). In both cases the separation is controlled rather by the SEC mechanism than by chemical interactions with the column material.

Additionally, we proved the quality of the solvent for the separations (fig. 1 and 3). The use of different solvents, pure and mixed N,N-dimethylacedamide with water and salt, does not influence significantly the separation process of the poly(ether amide) dendrimers. This can be derived from the obviously appropriate separation with both systems according to hydrodynamic volume and molar mass, respectively (table 3). The molar masses obtained by calibrating with PVP are well comparable with the results from the SSC at the same chromatographic system. This means that the densities of the dissolved PVP-molecules in pure DMAc are similar to these of the dendrimers. Anyhow, a mixed solvent was preferred in most of the measurements in order to be able to compare it to the polystyrene solution behaviour, which is strongly dependent on the water content at contents below 2% as we observed (see text below).

For a better understanding of the SEC behaviour of the dendrimers we compared their calibration relationship (SSC) to the calibration curves of linear polymers. Linear standards possessing the same chemical structure are not available and thus we chose two linear standards, poly(styrene) and poly(2-vinyl pyridine), which have to be rinsed by the solvent in a different way, according to their chemical character. The different SEC behaviour of the polymer standards is reflected by the molar mass results in table 3 after calibration with PS and PVP as standards.

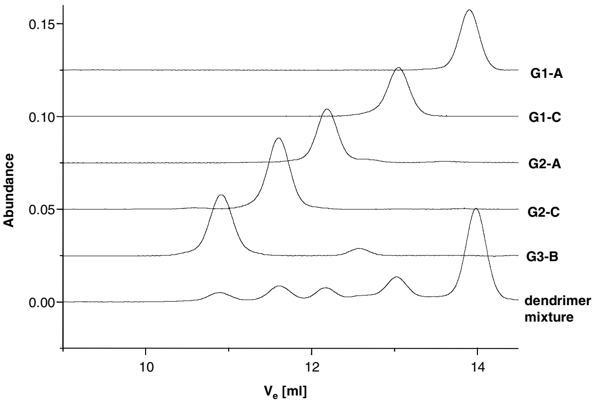


Figure 3. SEC separation curves of the investigated poly(ether amide) dendrimers and a dendrimer mixture using system B. The different peak intensities are due to non-equal proportions of the dendrimer samples in the mixture.

Table 3: Comparison of the number averaged molar masses based on the different SEC systems. Due to the fact that the dendrimers are monodispers samples (see MALDI-TOF results), the measured polydispersities up to 1.1 are result of the peak broadening during the chromatographic process.

Dendrimer	$M_{theoretical}$	System A, [g/mol]		System B, [g/mol]	
	[g/mol]	M_{PS}	M_{SSC}^*	M_{PVP}	M_{SSC}^*
G1-A	916.86	1900	900	1000	900
G1-B	1171.2	2400	1100	1400	1300
G1-C	1465.7	2900	1500	1500	1400
G2-A	2243.0	4900	2200	2400	2200
G2-B	2498.0	5100	2900	2900	2700
G2-C	2793.0	6400	3300	3500	3100
G3-B	5153.0	9500	4800	5000	4500

* Molar mass of peak maxima

The calibration plots of the three polymer systems are shown in figure 4. For the establishment of this plot the measurements were performed on system A with a DMAc as a solvent mixed with water and LiCl. The different polymer systems show calibration relationships according to the following equations:

$$\log M_{dendrimers} = -0{,}346 V_e + 9{,}196 \qquad (\mathbf{1})$$

$$\log M_{PS} = -0{,}401 V_e + 10{,}562 \qquad (\mathbf{2})$$

$$\log M_{PVP} = -0{,}355 V_e + 9{,}946 \qquad (\mathbf{3})$$

The different separation of the molar masses of the three polymers visible in figure 4 is on the one hand a result of the different molecular densities of the linear and the dendritic molecules, as mentioned above. On the other hand, the chemical structure of the polymers plays an important role for their molecular shape in solution. The shape of the macromolecules and the degree of penetration of the solvent into the polymer coil could be proven using the well known Kuhn-Mark-Houwink-Sakurada (KMHS) relationship, based on the equation (4):

$$[\eta] = KM^{a}, \qquad \textbf{(4)}$$

where the value of the exponent a is to be related to the molecular shape. Values from 1 to 0,6 are typical for an expanded, well-dissolved random coil, a=0,5 corresponds to a random coil in θ–conditions and decreasing to a=0 the solved molecules are hard spheres.

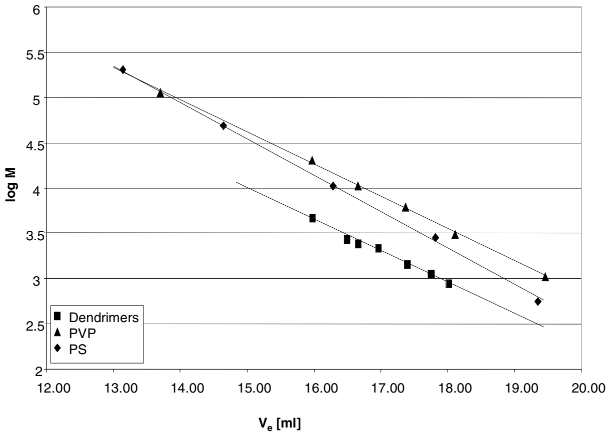


Figure 4. Calibration curves of linear poly(styrene)(◆), poly(2-vinyl pyridine) (▲) standards and dendrimers (■,specific sample calibration) using system A.

In order to obtain information about the exponent a of our polymers, we plotted the reduced viscosity (see experimental part) as a function of the molar mass of the polymers in a double logarithmic plot (figure 5). For this we used the absolute molar masses of the PS and PVP standards and the molar masses of the dendrimers determined by MALDI-TOF. The results extracted from the measurements in DMAc with water and LiCl lead to a=0,867 for the dendrimers, a=0,344 for the poly(styrene) standard and a=0,528 for the poly(2-vinyl pyridine) standard. These three different values correspond to the three different solution states of the molecules described above: the dendrimers behave as well dissolved random coils, poly(styrene) is a molecule collapsed to a nearly hard sphere and the poly(2-vinyl pyridine) behaves like an undisturbed random coil in a θ–solvent. Compared to the linear polymers the dendrimers did not, as we originally expected, show lower a-values. In our interpretation this means firstly, that in addition to the branching topology, the chemical character is an important factor impacting the interaction between the solvent and the dendrimer. Secondly, this behaviour is due to the low generation number of our dendrimers. Theoretical calculations [13,15] and computational simulations [12] showed that dendrimers do not behave monotonically in a Kuhn-Mark-Houwink-Sakurada plot. The intrinsic viscosity of the dendrimers increases in the first three generations and after the 4th generation it decreases. Mourey et al. [16]

supported this hypothesis by experiments on poly(ether) dendrimers and showed again a maximum in the viscosity depending on the molar mass. In our work we were not able to analyse higher generation dendrimers because sterical hindrances and H-bonding interactions did not allow for their synthesis [21].

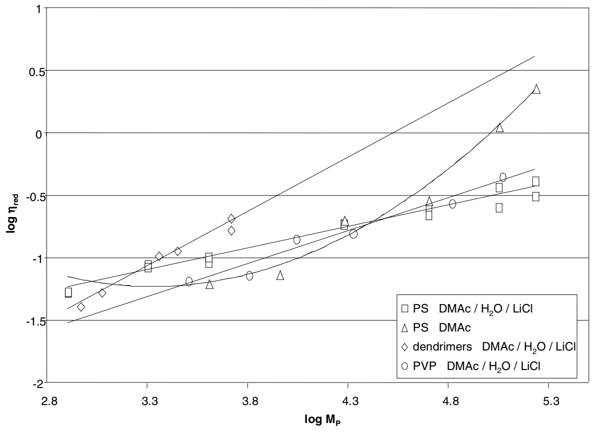


Figure 5. Kuhn-Mark-Houwink-Sakurada plot from [η]-Mp-results for dendrimers (◇), poly(2-vinyl pyridine) (○) and poly(styrene) in mixed DMAc with 2vol% water and LiCl (□) and poly(styrene) in pure DMAc (△).

The relatively high value of the KMHS-exponent *a* of 0,87 is not typical for dendritic polymers. Typically dendrimers in the first generations [16,17] and hyperbranched polymers [19,23] behave as globular structures with KMHS-exponents below 0,5. These values correspond to the fractal dimensions of hard sphere (0) or a randomly branched chain (0,5) in a good solvent. And indeed, former investigations on a series of the same poly(ether amide) dendrimers using their self-diffusion rates for calculating the relationship between hydrodynamic radius and molar mass [22] arrive at the conclusion that these species behave like hard spheres. The difference between these results and the results of our work arise from the different solvent used in the both cases. Eucledian dimensions were found for our dendrimers in dimethylsulfoxide (DMSO), a solvent most commonly used in NMR experiments. Obviously, DMSO cannot penetrate into the dendrimer molecules as thoroughly as DMAc. The different behaviour of the poly(ether amide) dendrimers in the both solvents leads to the assumption that the molecules are flexible, which allows the collapse of their structure in DMSO. Previous investigations on dendritic molecules of chemically similar character – fractionated hyperbranched poly(ether amide)s – showed that these structures are flexible: the shape of the molecules varied from randomly branched coil to a hard sphere depending in this case on their molar mass [19].

The data plotted in figure 5 comprise the KMHS-relation for PS in mixed solvent with 2% water, as well as values from the viscosity measurements of the PS standards in a pure solvent. Both relationships differ very strongly, which shows again the role of the solvent for the molecular shape of the dissolved polymers. Additional measurements of the solvation of the linear poly(styrene) depending on the water content in DMAc were carried out to follow systematically this behaviour. Figure 6 shows the calibration curves in DMAc with 0%, 1%, 2% an 3% water content.

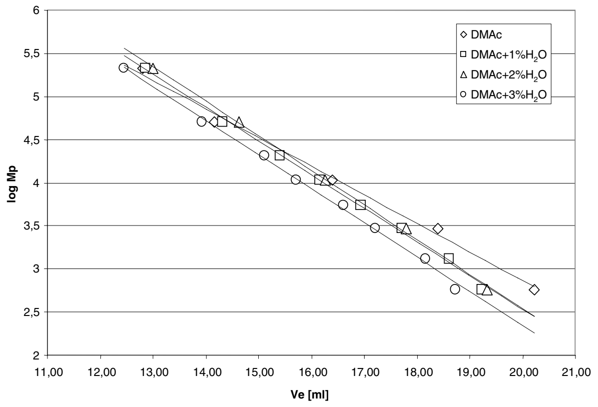


Figure 6. Dependence of the SEC behaviour of poly(styrene) on the water content of the DMAc- solvent: calibration curves of PS in pure DMAc (◇) and DMAc with 1 vol.% (□), 2 vol.% (△) and 3 vol% (○) water content measured on System A.

In this graph strong differences in the relationships depending on the water content can be observed, whereas at contents above 2% water a kind of saturation in the dissolved state of the PS molecules occurs and the slopes of the curves remain nearly constant. For this reason this water content was chosen to compare between the dendrimers and the linear polymer standards. Additional investigations on the influence of the water content on the separation mechanism including the interplay between enthalpic and entropic effects were not intended in this work. Nevertheless, a kind of combined separation-process between SEC and liquid absorption chromatography (LAC) could not be completely excluded keeping in mind previous investigations on PS in polar solvents, where interactions of the PS with cross-linked poly(styrene) with divinylbenzene column material were observed [24,25]. We tried to minimize possible LAC interactions using columns with porous silica microspheres as a packing material, which should remain indifferent to our polymers in the given mobile phase (see System A).

Another way to obtain information about the molecular weight of branched molecules using polymer standards is the universal calibration method [26]. Empiric evidences showed that this method works independently of the molecular shape and chemical character of the investigated sample. This is possible because the viscosity, which is responsible for the correction of the molecular shape, is included in the calculation of the real molar mass:

$$[\eta]M = \phi R^3 g^{x-3/2}, \qquad (5)$$

where R is the radius of gyration, ϕ is the universal constant, g is the parameter presented by Zimm and Stockmayer [27] and x is an exponent which ranges between 0,5 and 1,5 depending on the branching character. In separation methods utilizing the hydrodynamic dimensions of the molecules, i.e. SEC, this relation should work for molecules with the same retention volume independently on their structure.

If this method works for our branched molecules, the linear standard polymers and dendrimers should lie on the same line in the $[\eta]M$ vs. V_e plot. To exclude possible misinterpretations on the basis of combined LAC-SEC separations, which could influence the retention volume of the PS, we made this calculations for both the PS

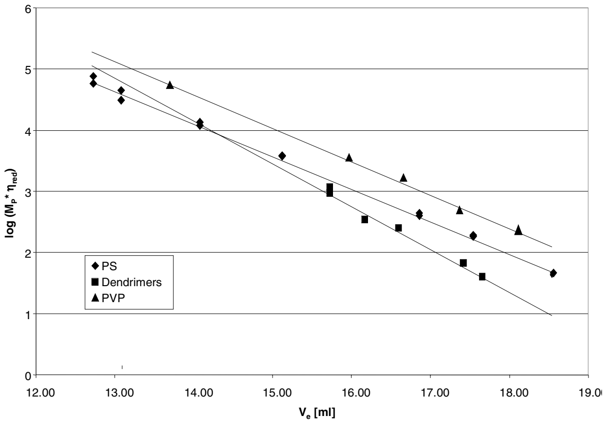


Figure 7. Universal calibration plot of poly(styrene) standard (◆), poly(2-vinylpyridine) standard (▲) and dendrimers (■) based on system A.

and the PVP standards. Figure 7 shows that the linear fit of the dendrimers deviate from that of the linear polymers standards. Similar results were already observed in previous investigations on hyperbranched poly(ether amide)s, which posses only 50% degree of branching, but the same dendritic branching [19]. On the other hand this observation do not fit the results of Mourey [16] on poly(ether) dendrimers, which match very well the universal calibration, and futrthermore his assumption, that universal calibration would fit very well dendritic molecules with a molar mass less than 10 000 g/mol. The deviation of our poly(ether amide) dendrimers from the universal rule cannot lie on their molar mass, which is less than 5000 g/mol. The unique branching topology of the dendrimers is obviously not the only reason for that behaviour. Another important feature which influences it is the chemical character, which combined with the big number of branches multiplies this effect. Our further investigations are focused on this interplay between branching and chemical structure on the solution behaviour of the polymers. However, from these results could be concluded that the theoretical calculations, on which universal calibration is based, obviously cannot be generally used to describe the behaviour of the dendritic polymers and need optimisation for these macromolecules.

Conclusions

Molar mass determination of different generation poly(ether amide) dendrimers with cores of different size was successfully carried out by MALDI-TOF-MS. SEC experiments showed, that the dendrimers can be separated according to their molar mass and that their real molar masses could be better fitted by using poly(2-vinyl pyridine) as a standard compared to poly(styrene). The molar masses and the intrinsic viscosities were used to establish KMHS relationships, which showed that the investigated dendrimers behave as open structures in DMAc mixed with water and LiCl with a=0,87 (extremely good solvent conditions). The core dimension does not influence strongly the solution behaviour of the dendrimers.

In contrast to the dendrimers, linear poly(styrene) standards have a very compact structure with a=0,34 (bad solvent conditions) and poly(2-vinyl pyridin) standards have a structure of a random coil with a=0,53 (θ–conditions) in the same solvent. These results explain the differences in the SEC-values obtained from the different standard calibrations.

Applying the universal calibration method we arrived to the conclusion, that this method cannot be used directly for our poly(ether amide) dendrimers.

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