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Molar mass analysis of polyamides-11 and -12 by size exclusion chromatography in HFiP

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ABSTRACT

The SEC analysis of polyamide-11 and polyamide-12 can be conducted free of association and aggregation phenomena when hexafluoroisopropanol + 0.05 mol/L potassium trifluoroacetate are used as the mobile phase. The calibration of the SEC system can be conducted in different ways. As stationary phases non-polar polystyrene and polar perfluoro silicagel were tested. The investigations showed that the polystyrene gel exhibits hydrophobic interactions with the polyamides while with the silicagel selective interactions were not found. Investigating different options for SEC calibration it was found that conventional PMMA calibration does not yield correct results. The universal calibration approach based on PMMA calibration did not work either. Correct molar masses were obtained when the PMMA calibration curve was corrected with data from polyamide blends using a simplex algorithm. Alternatively, calibration can be conducted with broadly distributed polyamides that were first fully characterized by SEC–MALLS. The resulting molar mass distributions for different sets of polyamides were compared with molar masses that were determined directly by SEC–MALLS and excellent correlation was obtained.

1. Introduction

Polyamides are thermoplastics that exhibit high strength, abrasion resistance, stiffness and perpetuation of their physical and mechanical properties over a wide range of temperatures. The semicrystalline morphology and the intermolecular hydrogen bonds of the amide groups are responsible for the advantageous properties of the polyamides. On the other hand, morphology and hydrogen bonding influence the dissolution behaviour of polyamides and, hence, the determination of the molar mass and its distribution. Poor solubility in common organic solvents and strong adsorptive interactions are a challenge for the molar mass analysis by size exclusion chromatography. To solve the problems related to SEC analysis, different groups developed a number of strategies. Dudley and others [1–5] used high temperature SEC in *m*-cresol or benzyl alcohol because these are strong hydrogen bonding solvents. Provder and others [6–10] worked at ambient temperature and accomplished SEC with perfluoroalcohols as mobile phases. Also mixed mobile phases like methylene chloride–dichloroacetic acid (80:20, v/v) and HFiP–methylene chloride (5:95, v/v) were used [7,11]. To enhance solubility at ambient temperature different groups proposed a *N*-trifluoroacetylation of the polyamides [12–15].

There are few studies [16,17] using HFiP as solvent for the molecular mass characterization of polyamides, where different salts, temperatures, salt and polymer concentrations were used [16–18]. It has also been shown in previous studies that HFiP is applicable as SEC eluent for the characterization of poly(butylene terephthalate) (PBT) [19], poly(oxymethylene) (POM), poly(vinyl butyral) (PVB) [20], poly(ethylene terephthalate) PET [21] and poly(lactic acid) PLA [22].

Regarding polyamide analysis, most of the studies have been conducted on polyamide-6 and polyamide-6.6. In an extensive study, Mourey et al. reviewed the different SEC approaches using HFiP and proposed to add 0.01 M tetraethylammonium nitrate to HFiP to prevent associate formation and to obtain exact molar masses [23]. Different salts have been used as modifiers for HFiP, e.g. LiBr [24], sodium trifluoroacetate (NaTFAc) [9,18,25–27], potassium trifluoroacetate (KTFAc) [28], but a clear interpretation of the effect of the salt was not given. In addition to the chromatographic conditions, calibration has been addressed. Few authors used conventional or broad PMMA calibration to obtain relative molar masses [18], others used light scattering and viscometry detectors. Moroni and Havard [29] and Nguyen [30] mention that universal calibration behaviour is not observed in HFiP.

In our previous work on polyamides-6 and -6.6 it was shown that optimum SEC behaviour is obtained when HFiP + 0.05 mol/L

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KTFAc are used as the mobile phase [16]. While calibration with narrow disperse polymethyl methacrylate standards does not yield accurate molar mass information, the quantification can be done using an "artificial" calibration curve. This calibration curve is obtained by correcting the PMMA calibration curve with polyamide molar mass data from light scattering. The resulting molar mass distributions were compared with molar masses that were determined by SEC with a light scattering detector and an excellent correlation was obtained.

The purpose of this work is to develop suitable SEC procedures for polyamide-11 and polyamide-12, using HFiP as the solvent. This is an important subject since PA-11 is becoming a fast developing biobased polymer. In addition to optimizing the composition of the mobile phase, polar and non-polar stationary phases shall be tested and compared and different quantification procedures shall be investigated.

2. Experimental

2.1. Samples and mobile phase

HFiP (1,1,1,3,3,3-hexafluoro-2-propanol) was purchased from Fluorochem Ltd., Derbyshire, Great Britain. It was used without any distillation or drying process. KTFAc (potassium trifluoroacetate) had a purity of >99.9% and was obtained from Fluka, Sigma–Aldrich, Buchs, Switzerland.

The PMMA standards with molar masses between 3600 and 965,000 g/mol were products of PSS GmbH, Mainz, Germany. Polyamides 11 and 12 were the products of Arkema, Collombes, France.

2.2. SEC

A chromatography system Agilent Series 1100 (Agilent Technologies, Santa Clara, USA) with an isocratic pump (G1314A), an autosampler (G1313A) and a column heater was used. The operating temperature was 35 °C. The light scattering measurements and the measurements for the specific calibration were performed with an injection volume of 100 μL, a flow rate of 1 mL/min and a sample concentration of 2 mg/mL. The viscometric measurements were performed with an injection volume of 50 μL, a flow rate of 0.6 mL/min and a sample concentration of 3.5 mg/mL.

The following columns were used: PSS PFG 100 Å, PSS PFG 300 Å, PSS PFG 1000 Å, two columns PSS PFG linear (all 8 × 300 mm, 7 μm average particle size, PSS GmbH, Mainz, Germany), two PL HFiP Gel columns (7.5 × 300 mm, Polymer Laboratories, Shropshire, UK).

2.3. Detectors

The RI (G1362A) detector was a product of Agilent Technologies (Santa Clara, USA), the multiangle light scattering detector Dawn Eos (wavelength of 690 nm) was produced by Wyatt Technologies (Santa Barbara, USA) and the viscosity detector ETA-2010 was purchased from PSS GmbH (Mainz, Germany).

The light scattering measurements were performed by using Astra 4.90.08 software (Wyatt Technologies, Santa Barbara, USA), the SEC separation and the measurements of viscosity were performed by the software WinGPC7 (PSS GmbH).

3. Results and discussion

For suitable SEC conditions, the composition of the mobile phase and the type of stationary phase must be optimized. In agreement with previous findings of Buijtenhuijs et al. [10] and our own work on polyamides-6 and -6.6 we used HFiP as the mobile phase and added potassium trifluoroacetate in order to prevent aggregate formation. Using different concentrations of KTFAc in HFiP we found that a concentration of 0.05–0.1 mol/L KTFAc in the mobile phase is sufficient to obtain solutions where the polyamides are molecularly dissolved. The elution curves of a polyamide-11 (PA-11) in Fig. 1 show typical SEC profiles. When no salt is added to the mobile phase, early elution is observed that could indicate some aggregate formation. Salt addition increases the elution volume of the sample and at salt concentrations of 0.1 and 0.2 mol/L, identical elution behaviour is observed. Further increase of the salt concentration does not change the elution behaviour. This behaviour is observed for both PSS PFG and PL HFiP Gel columns.

The early elution of the polyamides in HFiP without salt can be caused by aggregate formation, polelectrolyte effects or repulsive interactions with the stationary phase. A detailed study of the different effects has not been conducted within the scope of the present investigation. The addition of salt suppresses these effects and at salt concentrations above 0.05 mol/L stable conditions are obtained. Multiple measurements showed that a minimum salt concentration of 0.05 mol/L is required. For stable operating conditions a salt concentration of 0.1 mol/L is used throughout this study.

For the optimization of the stationary phase two different types of materials were tested, (A) non-polar crosslinked styrene–divinylbenzene copolymer of PL/Varian, and (B) polar functionalized perfluoro silicagel of PSS GmbH. In order to evaluate resolution and the linearity of the calibration function, different column sets were tested with PMMA calibration standards. The calibration curves for two typical column sets using a mobile phase of HFiP + 0.1 Mol/L KTFAc are presented in Fig. 2. They indicate that proper separation is obtained over more than three decades of molar masses (10^3–10^6 g/mol) being fully sufficient for the polyamides under investigation.

3.1. Molar mass analysis by SEC–light scattering

One of the major problems of molar mass analysis of polyamides by SEC is the lack of proper calibration standards. Narrow disperse polyamides are not commercially available and the suitability of a calibration with PMMA or polyethylene oxide (PEO) is under question. A suitable alternative is the molar mass analysis by SEC coupled to a multiangle light scattering detector. For monitoring the concentration as a function of elution volume, a refractive index (RI) detector is coupled to the SEC–MALLS system. The molar mass is calculated from the Rayleigh ratio $R(\theta)$ according to the following equation:

$$\frac{K^* c}{R(\theta, c)} = \frac{1}{M_w P(\theta)} + 2A_2 c$$

where θ is the scattering angle, $K^* = 4\pi^2 n_0^2 (\mathrm{d}n/\mathrm{d}c)^2 \lambda_0^{-4} N_a^{-1}$ is the optical constant, c is the concentration of the solute (obtained from the RI detector signal), n_0 is the refractive index of the solvent at the laser wavelength λ_0, N_a is Avogadro's number, and A_2 is the second virial coefficient. The form factor $P(\theta)$ at low angles is $1 - q^2 R_g^2/3$, where R_g is the radius of gyration and $q = 4\pi n \sin(\theta/2)/\lambda_0$ is the scattering vector. The specific refractive index increments $\mathrm{d}n/\mathrm{d}c$ for the polyamides were measured in HFiP + 0.1 mol/L KTFAc, i.e. in the SEC mobile phase, using the refractive index detector signals. No action was undertaken to correct the $\mathrm{d}n/\mathrm{d}c$-values for the polychromatic character of the light source of the refractive index detector.

A representative elugram and the corresponding calibration curve generated from the laser light scattering measurement are shown in Fig. 3. For molar masses determined by SEC–MALLS one has to bear in mind that the relative sensitivity of the light scattering detector at low molar masses is rather low. Measurements at

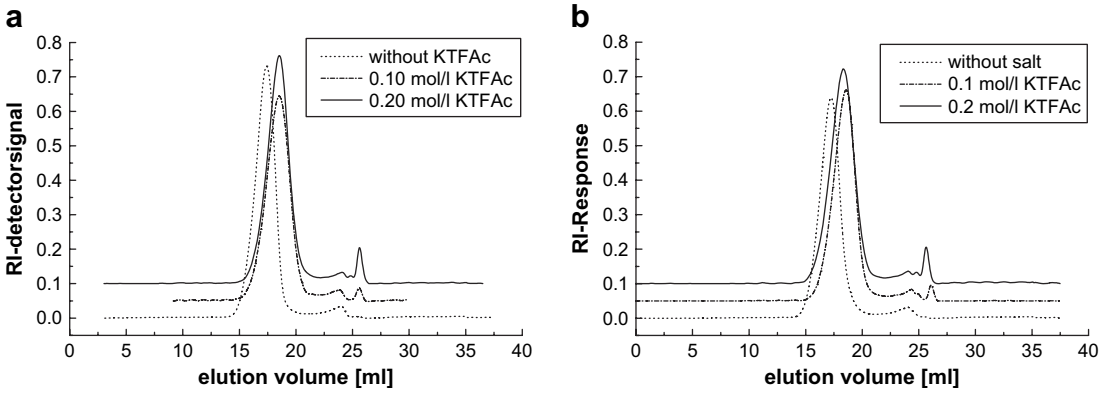

Fig. 1. Elugrams of (a) PA-11 (sample B1) and (b) PA-12 (sample A1) at different mobile phase compositions; stationary phase: PSS PFG 100 Å and PSS PFG 1000 Å; mobile phase: HFiP + KTFAc.

the high molar mass end of the elution curve are much more precise. Therefore, very frequently the calculated M_n values are gradually too high.

The proper operation of the system was checked with a number of PMMA calibration standards, see Table 1. The determined molar masses and refractive index increments were in agreement with the molar masses given by the manufacturer and the dn/dc value given in literature, being 0.190 mL/g [20]. dn/dc was calculated from the injected sample mass and the area under the RI detector signal.

In a similar way, the molar masses of sets of PA-11 and PA-12 were determined. These molar masses were assumed to be close to the true molar masses and were used as reference values for the forthcoming investigations.

3.2. Molar mass analysis by SEC–viscometry

As has been pointed out, suitable calibration standards for polyamides are not available commercially. It was shown several times that a calibration with PMMA may not be suitable and may result in incorrect molar mass values. A second option in addition to SEC–MALLS is the coupling of SEC with an on-line viscometer. In this case, the principle of universal calibration is applied for molar mass analysis.

The universal calibration concept is based on the assumption that SEC separates macromolecules by size and that different polymers may be placed on the same curve if a measure of molecular volume is used rather than molar mass [31]. For Gaussian coil polymers, the molecular volume controlling the size exclusion separation can be expressed in terms of the polymer intrinsic viscosity [η] times the molar mass of the polymer.

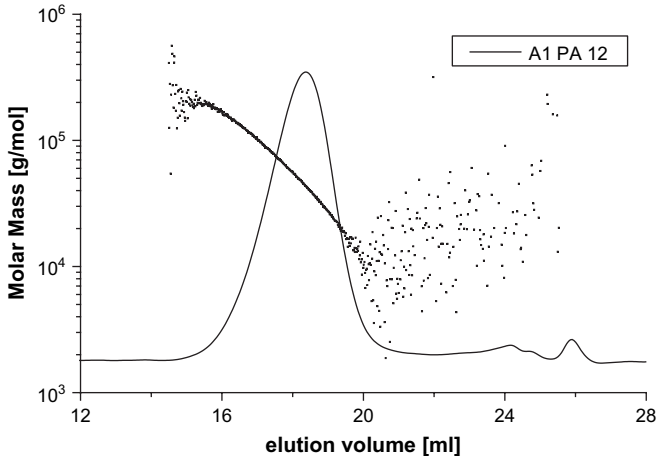

Fig. 3. SEC–MALLS analysis of PA-12 (sample A1); stationary phase: 2 × PL HFiP Gel, mobile phase: HFiP + 0.1 mol/L KTFAc.

Viscosity measurements can be used for molar mass analysis through SEC coupled to on-line viscometry, where the specific viscosity and mass concentration at each volume fraction are determined. At the very low concentrations used in SEC the intrinsic viscosity equals $[\eta] \approx \eta_{spec}/c$. From [η] at each volume fraction and the universal calibration curve $\log([\eta]M) = f(V_e)$ of a known polymer, the molar mass M at each volume fraction can be

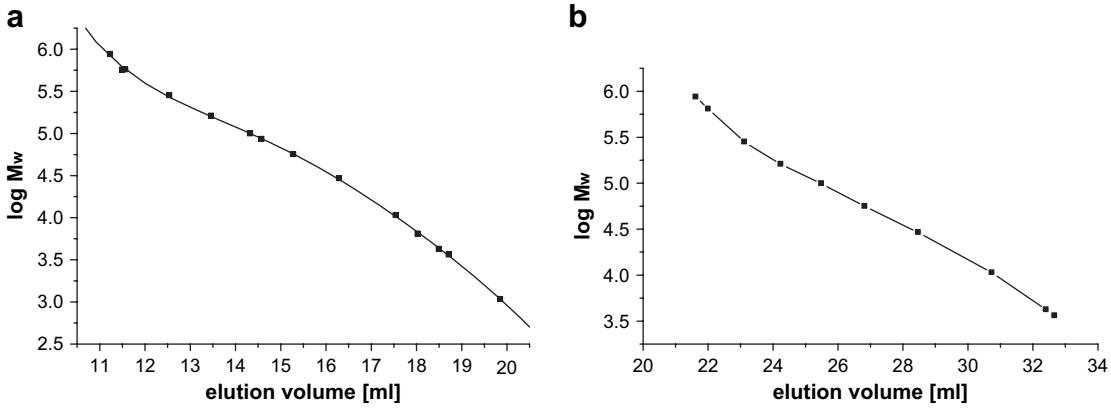

Fig. 2. PMMA calibration curves for different stationary phases, stationary phase: (a) 2 × PL HFiP Gel, (b) PSS PFG 100 Å + 300 Å + 1000 Å; mobile phase: HFiP + 0.1 mol/L KTFAc.

Table 1
PMMA molar masses and d*n*/d*c* determined by SEC–MALLS

Sample	M_w (manufacturer) [g/mol]	d*n*/d*c* [mL/g]	M_w [g/mol]
PMMA1	10,600	0.184	10,000
PMMA2	55,900	0.188	52,000
PMMA3	160,000	0.189	162,500
PMMA4	570,000	0.187	576,000

calculated. The summation across the entire elution curve yields the average molar mass and the polydispersity.

Using this approach, the present SEC system was coupled to a dual RI–viscometer detector ETA-2010. The increasing [η] values obtained by SEC–viscometry correlate with the increasing molar masses determined by SEC–MALLS.

The intrinsic viscosities determined by SEC–viscometry and the corresponding molar masses M_w determined by SEC–MALLS can now be used to investigate if the universal calibration approach is valid for polyamides. According to the concept of universal calibration, each elution volume in SEC corresponds strictly to one hydrodynamic volume irrespective of the type of macromolecules. If the hydrodynamic volume which is a direct function of $[\eta]M$ is plotted against the elution volume, then a universal calibration curve shall be obtained that is supposed to be valid for all types of polymers.

Strictly speaking the universal calibration approach is only valid for polymer samples with low polydispersities. For larger polydispersities the viscosity–average molar mass (the value that correlates directly with [η]) deviates increasingly from the M_n or M_w values that are measured by colligative methods or light scattering, respectively. Viscosity–average molar masses, however, are difficult to access due to the fact that reliable Mark–Houwink parameters are not readily available from literature. The absolute molar mass that is closest to the viscosity average is the weight average M_w that can be determined quite precisely by light scattering. It has been shown for polydisperse polymers that a Mark–Houwink relation that is derived from M_w is much more accurate than one derived from M_n [34,35]. Therefore, all further considerations are based on the M_w values given in Table 2.

The "universal" calibration curves $\log[\eta]M_w$ vs. V_e are shown in Fig. 4. The viscosity data were taken from the SEC–viscometry measurements. The molar masses M_w were taken from Table 2. The universal calibration approach is based on the assumption that the polymer to be analysed and a known calibration polymer give the same universal calibration curve. As has been discussed before, PMMA was frequently used for calibration of polyamide separations. A clear picture on the universal calibration behaviour of PMMA as compared to polyamides, however, has not been given.

Fig. 4 shows the "universal" calibration curve of PMMA that was determined on two PL HFiP Gel columns. As can be seen here, PMMA, PA-11 and PA-12 do not give a common "universal" calibration curve. This is somehow in contrast to previous findings were at least PA-6 and PA-6.6 exhibited a common universal

Table 2
Polyamide molar masses and d*n*/d*c* determined by SEC–MALLS

Sample	M_w [g/mol]	d*n*/d*c* [mL/g]
A1 PA12	63,500	0.210
A2 PA12	60,250	0.205
A3 PA12	39,500	0.210
A4 PA12	36,750	0.215
A5 PA12	27,750	0.215
B1 PA11	49,750	0.224
B2 PA11	43,000	0.220
B3 PA11	30,750	0.215
B4 PA11	27,250	0.217

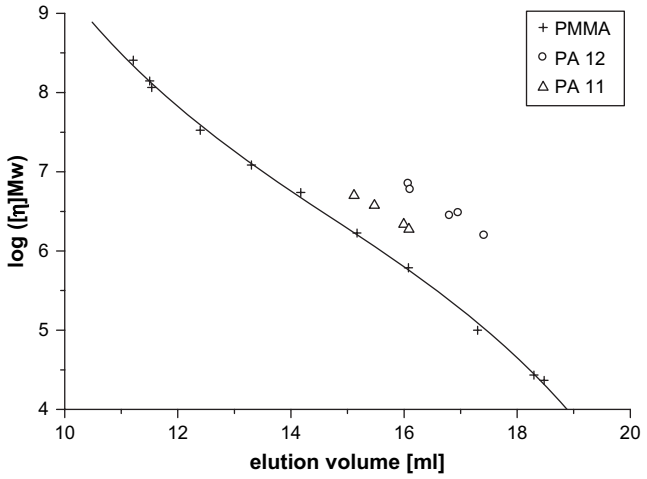

Fig. 4. Universal calibration curves for PMMA, PA-11, and PA-12; stationary phase: 2 × PL HFiP Gel, mobile phase: HFiP + 0.1 mol/L KTFAc.

calibration curve, which did not fit the PMMA calibration curve. Therefore, in the present case one also would expect to get a common calibration curve for PA-11 and PA-12.

In order to verify that PA-11 and PA-12 show a linear dependence of log[η] and log M_w, the Mark–Houwink–Sakurada (MHS) diagrams of the two polymers were obtained, see Fig. 5. As expected, PA-11 and PA-12 exhibit parallel curves indicating very similar solution behaviour. The Mark–Houwink–Sakurada exponents are 0.684 (PMMA), 0.747 (PA-11) and 0.766 (PA-12). The Mark–Houwink–Sakurada exponents for the present polyamides are very close to those for PA-6 (0.6 [32]) and PA-6.6 (0.7 [33]).

A further interpretation of the results given in Fig. 4 could be selective interactions of the polyamides with the stationary phase. The stationary phase used in Fig. 4 was a non-polar crosslinked styrene–divinylbenzene copolymer. For comparison, the samples were measured on a polar functionalized perfluoro silicagel. The universal calibration curves for PMMA and different polyamides on this column set are presented in Fig. 6.

A comparison of the "universal" PMMA calibration curve with the behaviour of the polyamides shows that they are not identical. Thus, PMMA cannot be used for universal calibration on the polar stationary phase similar to the non-polar stationary phase. Further, PA-6 and PA-6.6 show behaviours that are different from PA-11 and PA-12. This indicates that universal

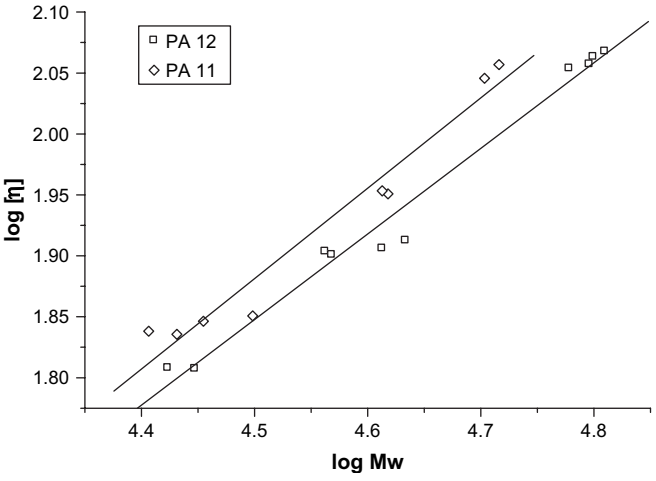

Fig. 5. Mark–Houwink–Sakurada diagrams for PA-11 and PA-12; solvent: HFiP + 0.1 mol/L KTFAc.

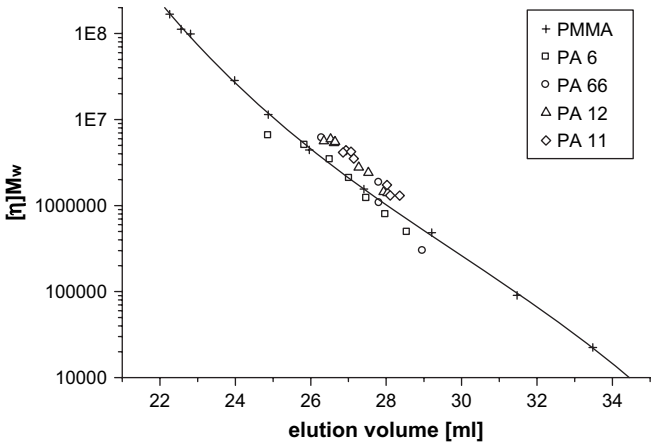

Fig. 6. Universal calibration curves for PMMA, PA-6, PA-6.6, PA-11, and PA-12; stationary phase: PSS PFG 100 Å + 300 Å + 1000 Å, mobile phase: HFiP + 0.1 mol/L KTFAc.

calibration cannot be used for all polyamides irrespective of chemical composition.

Most importantly, however, PA-11 and PA-12 show identical behaviour indicating that they can be analysed using a common calibration curve.

3.3. Selective interactions between polyamides-11 and -12 and the non-polar stationary phase

As indicated in Fig. 7, PA-11 and PA-12 of similar molar masses exhibit different elution behaviours on non-polar crosslinked polystyrene. In contrast, on polar silicagel both polyamides elute similarly.

In order to investigate the origin of these differences, PA-11 and PA-12 were separated at different mobile phase compositions on the non-polar stationary phase. The elution behaviour at salt concentrations of 0.0, 0.1 and 0.2 mol/L KTFAc is presented in Fig. 8. This figure clearly indicates that the elution behaviour of PA-12 is significantly affected by the salt concentration while for PA-11 only a minor effect is seen.

A further interesting result was obtained by analysing polyamides with different endgroups. In this case standard PA-11 and PA-12 were compared with samples that are rich in polar amino endgroups. As can be seen in Fig. 9, there is no effect of these polar endgroups on the elution behaviour. Different PA-11 elute together irrespective of the endgroups but different from PA-12.

To summarize, the investigations show that the elution behaviour of PA-11 and PA-12 is not affected by polar endgroups. On the other hand, for PA-12 the elution behaviour is strongly affected by the salt concentration in the mobile phase. The comparison of the elution volumes of samples with similar molar masses shows later elution of PA-12 as compared to PA-11. Accordingly, the interactions with the stationary phase must be stronger for PA-12. A possible explanation for this observation would be strong hydrophobic interactions of the CH_2-groups of the polyamide backbone with the non-polar stationary phase. Apparently, the difference of one CH_2-group between PA-11 and PA-12 is sufficient to cause the different elution behaviours. With the polar (silicagel) stationary phase such interactions cannot occur and, therefore, PA-11 and PA-12 behave similarly. Thus it appears that the column set of PSS PFG 100 Å + 300 Å + 1000 Å is superior for the SEC analysis of PA-11 and PA-12.

3.4. Molar mass analysis through adjustment of a PMMA calibration curve

Polyamide calibration curves over a broader range of molar masses can be produced when well characterized polyamide blends are used. Still, these calibration curves do not cover a very wide range of molar masses due to the fact that commercial polyamides are only available in very limited molar mass ranges. To increase the molar mass range of the calibration, a conventional PMMA calibration curve was adjusted based on the SEC–MALLS data obtained for PA-11 and PA-12 blends. Table 3 shows artificial blends where two polyamides with different molar masses are mixed to produce samples with higher polydispersities. These polymer blends were measured by SEC–MALLS to determine their molar mass averages and distributions. At the same time the column system was calibrated with narrow PMMA standards, see Fig. 10. In the next step, the PMMA curve was adjusted to produce the expected molar masses and polydispersities for the PA blends that were known from SEC–MALLS. This adjustment was done using a multistep iterative process (simplex algorithm) that was available from the SEC software. The iteration was conducted until the new "artificial PA calibration curves" produced the correct molar mass distributions. These calibration curves for PA-11 and PA-12 are shown in Fig. 10.

Using the artificial PA calibration curves, a MALLS detector is not required anymore. The molar masses of different polyamides determined by the simplex procedure as compared to the molar masses determined by SEC–MALLS are summarized in

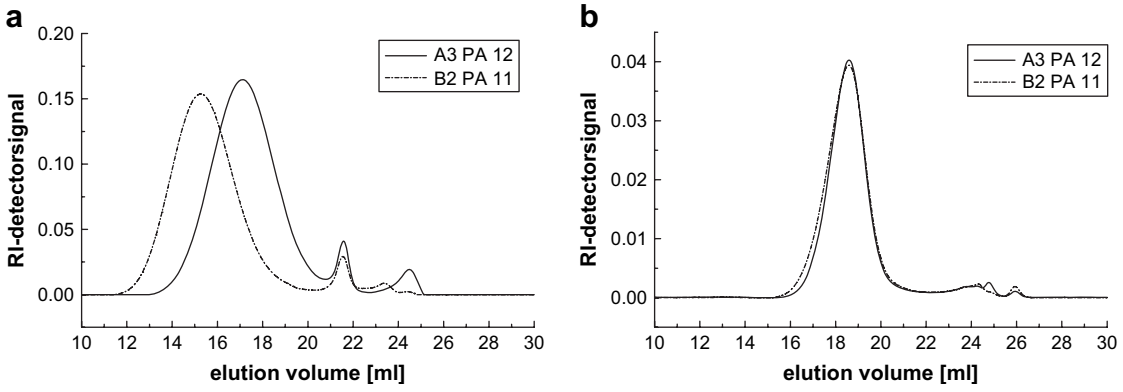

Fig. 7. SEC elution behaviour of PA-11 and PA-12 on polar and non-polar stationary phases; stationary phase: (a) 2 × PL HFiP Gel, (b) PSS PFG 100 Å + 300 Å + 1000 Å; mobile phase: HFiP + 0.1 mol/L KTFAc.

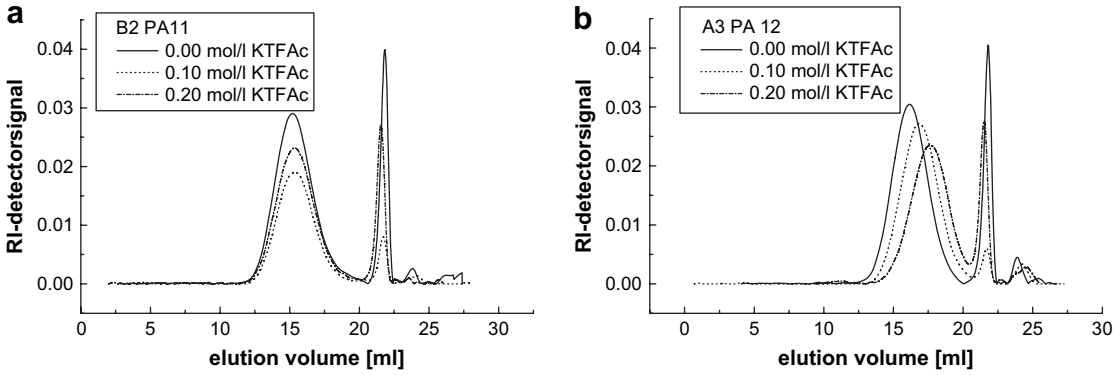

Fig. 8. SEC elution behaviour of PA-11 and PA-12 at different salt concentrations in the mobile phase; stationary phase: 2 × PL HFiP Gel, mobile phase: HFiP + KTFAc.

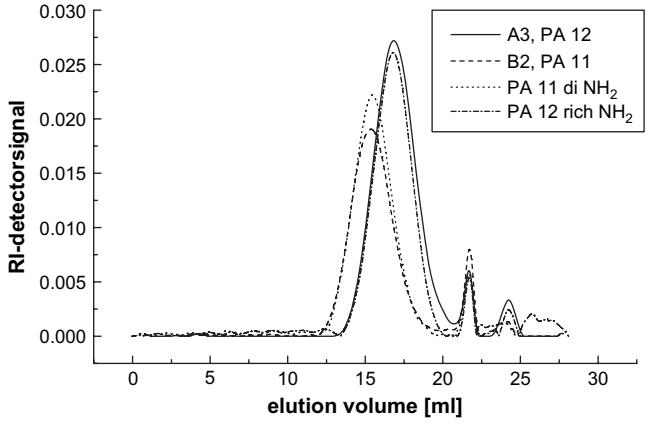

Fig. 9. SEC elution behaviour of PA-11 and PA-12 with different endgroups; stationary phase: 2 × PL HFiP Gel, mobile phase: HFiP + 0.1 mol/L KTFAc.

Table 3
Composition and molar masses of polyamide blends

Blend	A1 [%]	A5 [%]	M_w [g/mol]	Blend	B1 [%]	B4 [%]	M_w [g/mol]
AI	30	70	37,400	BI	30	70	38,500
AII	70	30	53,100	BII	50	50	41,250
AIII	50	50	48,900				

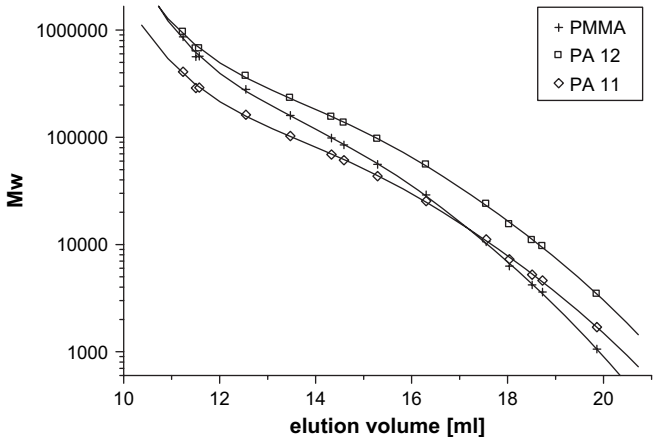

Fig. 10. Conventional calibration curves for PMMA, PA-11 and PA-12 from SEC–MALLS; stationary phase: 2 × PL HFiP Gel, mobile phase: HFiP + 0.1 mol/L KTFAc.

Table 4
Molar masses through PMMA calibration and the simplex procedure

Sample	M_w (LS) [g/mol]	M_w (simplex) [g/mol]	Δ [%]
A1 PA12	63,500	68,750	8.3
A2 PA12	60,250	62,500	3.7
A3 PA12	39,500	39,750	0.6
A4 PA12	36,750	37,250	1.4
A5 PA12	27,750	21,500	−22.5
PA12natural	63,000	68,250	8.3
REF2PA12	64,300	64,500	0.3
REF3PA12	28,750	25,500	−11.3
B1 PA11	49,750	52,750	6.0
B2 PA11	43,000	46,250	7.6
B3 PA11	30,750	31,750	3.3
B4 PA11	27,250	31,000	13.8
PA11natural	51,750	50,750	−1.9
REF4PA11	24,250	27,000	11.3
REF5PA11	56,500	51,750	−8.4

Table 4. The molar mass comparison indicates that the simplex procedure can be used for sufficiently high molar masses. For the lowest molar masses, deviations (Δ) of up to 22% are obtained.

3.5. Calibration with broadly distributed polyamides

The most feasible way to accurate molar masses of PA-11 and PA-12 is to use well characterized broadly distributed polyamides. The measurements of these polyamides by SEC–MALLS produce calibration curves that can be used in simple SEC–RI experimental setups. The SEC–MALLS calibration curves for PA-11 and PA-12 produced from samples "B1 PA11" and "A2 PA12" are presented in Fig. 11.

The calibration curves for PA-11 and PA-12 in Fig. 11 are absolutely identical and prove similar chromatographic behaviour of the two polyamides. They show that the accuracy of LS measurements at high molar masses (low elution volume of the peak) is very good. At low molar masses (high elution volumes) the accuracy is rather low due to the strong scattering of the LS signal. This is due to low absolute LS signal intensity at low molar masses.

The molar mass data obtained by SEC–RI using the calibration curves presented in Fig. 11 are summarized in Tables 5 and 6, where M_w 1 indicates the first measurement and M_w 2 the repetition. A comparison to molar masses obtained by SEC–MALLS is given.

The data show clearly that both the PA-11 and the PA-12 calibration curves are equally suitable for molar mass analysis. The agreement with the SEC–MALLS data is very good in all cases and an excellent repeatability is obtained.

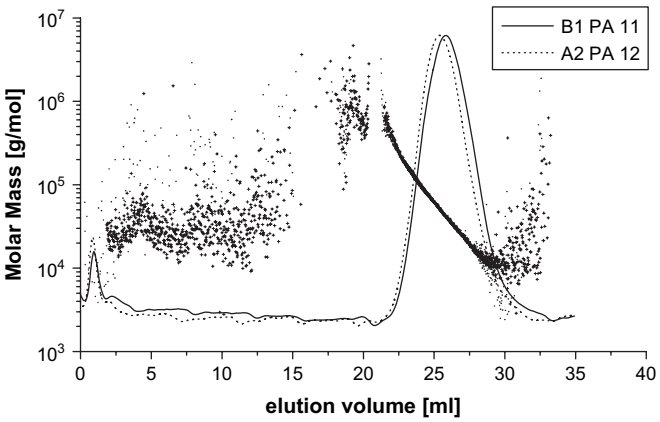

Fig. 11. Elution profiles and calibration curves from SEC–MALLS; stationary phase: PSS PFG 100 Å + 300 Å + 1000 Å, mobile phase: HFiP + 0.1 mol/L KTFAc.

Table 5
Polyamide molar masses calculated using the PA-11 calibration curve

Sample	M_w (LS) [g/mol]	M_w 1 [g/mol]	M_w 2 [g/mol]
A1 PA12	63,500	60,200	58,600
A2 PA12	60,250	59,900	59,000
A3 PA12	39,500	39,200	38,700
A4 PA12	36,750	37,500	37,400
A5 PA12	27,750	28,300	27,300
B1 PA11	49,750	51,100	50,400
B2 PA11	43,000	46,000	46,000
B3 PA11	30,750	31,600	30,900
B4 PA11	27,250	28,400	28,000

Table 6
Polyamide molar masses calculated using the PA-12 calibration curve

Sample	M_w (LS) [g/mol]	M_w 1 [g/mol]	M_w 2 [g/mol]
A1 PA12	63,500	62,600	60,000
A2 PA12	60,250	61,300	60,300
A3 PA12	39,500	39,700	39,100
A4 PA12	36,750	37,900	37,800
A5 PA12	27,750	28,500	27,400
B1 PA11	49,750	52,100	51,500
B2 PA11	43,000	46,800	46,700
B3 PA11	30,750	31,100	31,900
B4 PA11	27,250	28,200	28,500

4. Conclusions

Using HFiP with 0.1 mol/L KTFAc on a stationary phase PSS PFG 100 Å + 300 Å + 1000 Å polyamides show stable SEC behaviour. As was suggested the calibration with narrow PMMAs does not result in the right molar masses that can be obtained by multiangle laser light scattering measurements. A non-polar polystyrene-based stationary phase was found not to be suitable for SEC analyses due to hydrophobic interactions with the polyamide backbone. Proper SEC behaviour was obtained on a polar functionalized perfluoro silicagel. In the case that a MALLS detector for direct molar mass analysis is not available, there are different options for calibration. To determine the molar masses of PA-11 and PA-12 one can use a simplex algorithm to adjust a PMMA calibration curve to polyamides or one can calibrate the SEC with broadly distributed PA. For PA-11 and PA-12 similar MALLS-derived calibration curves were obtained indicating that both polyamides are suitable for molar mass determination.

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