Macromol. Symp. ***193****, 107–118 (2003)*

Analysis of Polyamides by Size Exclusion Chromatography and Laser Light Scattering

*Jinglu Chen, Wolfgang Radke, Harald Pasch**

Deutsches Kunststoff-Institut (German Institute for Polymers), Schlossgartenstr. 6, 64289 Darmstadt, Germany, E-mail: hpasch@dki.tu-darmstadt.de

SUMMARY: The molar mass analysis of polyamides is complicated due to the fact that only a limited range of solvents can be used and association and aggregation phenomena have to be screened by adding electrolytes to the mobile phase. Optimum SEC behaviour is obtained when hexafluoroisopropanol + 0.05 mol/L potassium trifluoroacetate is used as the mobile phase. The calibration of the SEC system can be conducted in different ways. While a 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 for different types of polyamides are compared with molar masses that are determined by size exclusion chromatography with a light scattering detector and an excellent correlation is obtained.

Introduction

Synthetic polyamides (PA) are amongst the most widely used engineering thermoplastics, owing to their high strength and toughness, stiffness, abrasion resistance and retention of physical and mechanical properties over large temperature ranges. The outstanding material properties are to a large extent due to the semicrystalline morphology and the cooperative intermolecular hydrogen bonding of the amide groups. Although the strength of these dipolar interactions confers an exceptional solvent resistance to PAs, it may lead to serious difficulties in the solution characterization of these polymers, such as the determination of molar mass and its distribution.

Size exclusion chromatography (SEC) of PAs can only be performed in a limited number of solvents. There are currently four approaches for the SEC analysis of PAs described in the literature:

CCC 1022-1360/00/$ 17,50+.50/0

1. High temperature SEC in strong H-bonding solvents such as m-cresol or benzyl alcohol [1-5].
2. Ambient temperature SEC with perfluoroalcohols such as trifluoroethanol (TFE) or hexafluoro isopropanol (HFIP) [6-10].
3. Ambient temperature SEC in mixed solvent systems such as methylene chloride-dichloroacetic acid (80:20, v/v) or HFIP-methylene chloride (5:95, v/v) [7,11].
4. Room temperature SEC in THF after N-trifluoroacetylated derivatization [12-15].

Each of the above systems has characteristic advantages and disadvantages. HFIP appears to be the solvent most convenient to use, although it is expensive and somewhat irritant. There are few studies using HFIP as solvent for the molecular mass characterization of polyamides (SEC and capillary viscosity studies). It has also been shown in previous studies that HFIP is applicable as SEC eluent for the characterization of poly(ethylene terephthalate) (PET), poly(oxymethylene) (POM), polyanilines (PANI), and poly(vinyl butyral) (PVB). Up to now, only few systematic studies have been performed on the characterization of polyamides in HFIP solvent.

The purpose of this work is, using HFIP as the solvent, to determine the molar mass of aliphatic and aromatic polyamide homopolymers and copolymers. In one approach, standard PMMA calibration shall be used. In the second approach, the PMMA calibration shall be corrected with molar mass data from light scattering.

Experimental

SEC: The SEC system consisted of a Waters 510 pump, a six-port injector (sample loop volume: 98 µL), two columns (PSS PFG 100 Å, PSS TFE 1000 Å), a variable-wavelength UV detector (Waters 486), a differential refractive index detector (RI, Waters 410), or Wyatt Dawn EOS multiangle laser light scattering detector. The flow rate was 0.5 ml/min. As polyamides exhibit a salt effect in HFIP, 0.05 M potassium trifluoroacetate were added to the mobile phase as ion pairing agent.

Samples: All samples were technical or research products of BASF AG, Ludwigshafen, Germany.

Results and Discussion

For the optimization of the SEC conditions, sets of polyamides 6 and polyamides 6.6 have been measured in different mobile phases, including trifluoroethanol (TFE) and hexafluoro isopropanol (HFIP). The sample sets consisted of commercial polyamides with differnt molar masses (BASF AG, Ludwigshafen, Germany) and served as reference samples for all investigations. The samples are summarized in Table 1, the average molar masses that are given in the Table have been determined from melt viscosity and, therefore, are only apparent.

Table 1 Apparent average molar masses of the polyamides

Polyamide 6	M_{app} (g/mol)	Polyamide 6.6	M_{app} (g/mol)
Ultramid B6	58.000	Ultramid A5	57.000
Ultramid B5	42.000	Ultramid A4	not determined
Ultramid B4	33.000	Ultramid A3	28.300
Ultramid B35	24.000	Ultramid A25	17.200
Ultramid B3	18.000	Ultramid A15	10.700
Ultramid B25	15.000		
Ultramid B15	10.000		

When the samples were measured in pure TFE or HFIP, non-uniform elution peaks were obtained, indicating that the system did not operate in a clear SEC separation mechanism. This is in agreement with literature data where the addition of salts have been proposed to suppress association and aggregation phenomena. In agreement with the findings of Buijtenhuijs et al. [10] we added potassium trifluoroacetate (KTFA) to the mobile phase. Measuring different concentrations of KTFA in HFIP, optimal SEC behaviour was obtained at a concentration of 0.05 Mol/L KTFA in the mobile phase.

The elution curves of different polyamide samples in Fig. 1 show typical SEC profiles. The order of elution volumes correspond nicely with the order of the apparent molar masses given in Table 2.

The plot log molar mass vs. elution volume in Fig. 2 gives the expected SEC calibration curves. The curves show some differences for polyamide 6 and polyamide 6.6 indicating that their hydrodynamic properties are gradually different.

Table 2 Elution volumes of the polyamides, apparent molar masses from melt viscometry

Polyamid 6	M_{app} (g/mol)	V_e (ml)	Polyamid 66	M_{app} (g/mol)	V_e (ml)
Ultramid B5	42,000	15.68	Ultramid A5	57,000	15.80
Ultramid B4	33,000	15.81	Ultramid A3	28,300	16.22
Ultramid B35	24,000	15.99	Ultramid A25	17,200	16.26
Ultramid B3	18,000	16.18	Ultramid A15	10,700	16.88
Ultramid B25	15,000	16.26			

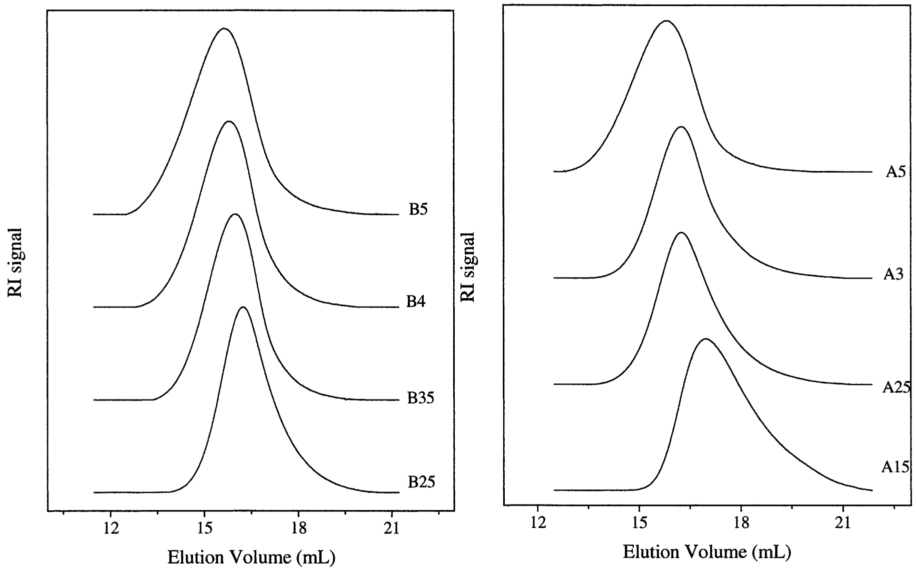


Fig. 1 Elution curves of polyamides, stationary phase: PFG 100 + TFE 1000, mobile phase: HFIP + 0,05 Mol/L KTFA, detector: RI

After the chromatographic conditions have been optimized, the problem of calibration has been dealt with. Typically, a PMMA calibration is used to quantify polyamides. We conducted a 10-point PMMA calibration for our chromatographic system and compared the calculated PMMA-equivalent molar masses with the apparent molar masses measured by melt viscometry, see Table 3.

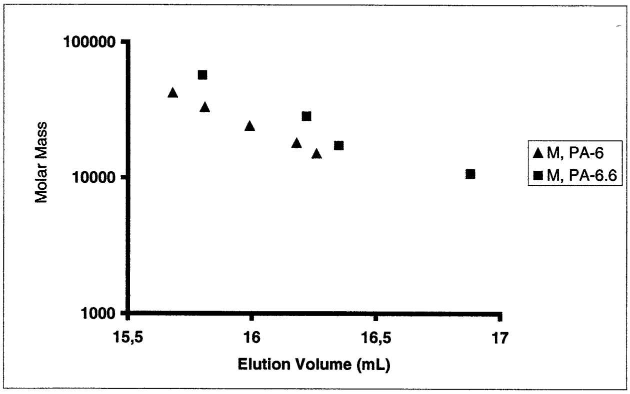


Fig. 2 Calibration curves log molar mass vs. elution volume for polyamide 6 and polyamide 6.6, chromatographic conditions see Fig. 1

Table 3 Comparison of polyamide molar masses determined by SEC with PMMA calibration and apparent molar masses from melt viscometry

Polyamide	M_{app} (g/mol)	M_w (g/mol)	M_n (g/mol)	M_w/M_n
Ultramid B5	42,000	168,000	68,400	2.46
Ultramid B4	33,000	131,000	62,300	2.10
Ultramid B35	24,000	104,000	54,100	1.93
Ultramid B3	18,000	74,500	33,400	2.23
Ultramid B25	15,000	62,600	29,400	2.13
Ultramid A5	57,000	140,000	57,900	2.42
Ultramid A3	28,300	72,000	29,900	2.41
Ultramid A25	17,200	63,400	24,700	2.57
Ultramid A15	10,700	29,800	11,700	2.54
Polyamid 12	6,000 (M_w)	15,900	5,430	2.94

Even considering that there must be differences between the apparent molar masses and the PMMA equivalents, these differences are by far too large. It must, therefore, be assumed that a PMMA calibration is not suitable for the determination of correct molar masses and such procedure can only be used to obtain relative data for comparison of different polyamides with each other.

For a proper calibration of the SEC system another procedure can be used. This procedure is based on a calculated "artificial" polyamide calibration curve which is produced by recalculating the PMMA calibration curve. To produce the artificial PA calibration curve, a broadly distributed polyamide 6 sample is analyzed with the PMMA calibration curve. The same sample is also analyzed by SEC-light scattering. By comparison of the true molar mass and the molar mass from the PMMA calibration, the deviations in molar mass for each elution volume can be determined and plotted against the elution volume. As a result, a correction function for the PMMA calibration is obtained, see Fig. 3, that enables the recalculation of the PMMA calibration curve into the artificial polyamide 6 calibration curve that can be used to quantify polyamide samples.

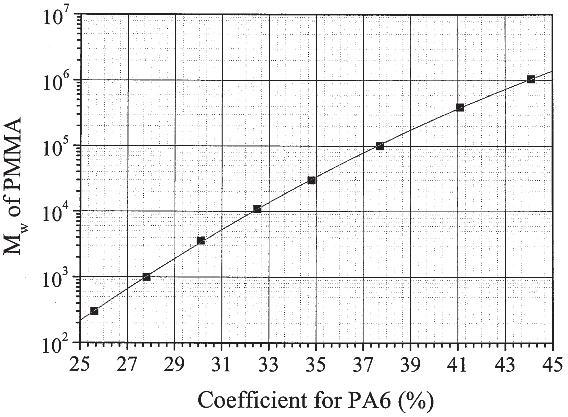


Fig. 3 Relation between the PMMA equivalent of the molar mass and the percentage deviation from the "true" polyamide 6 molar mass, data obtained from Ref. [16]

The present relation is, of course, a function of the mobile phase due to the fact that the hydrodynamic volumes of PMMA and polyamide behave differently in different solvents. However, taking HFIP + 0.05 Mol/L KTFA as the mobile phase, any PMMA calibration curve can be recalculated into a polyamide 6 calibration curve. This is shown for the present chromatographic system in Fig. 4.

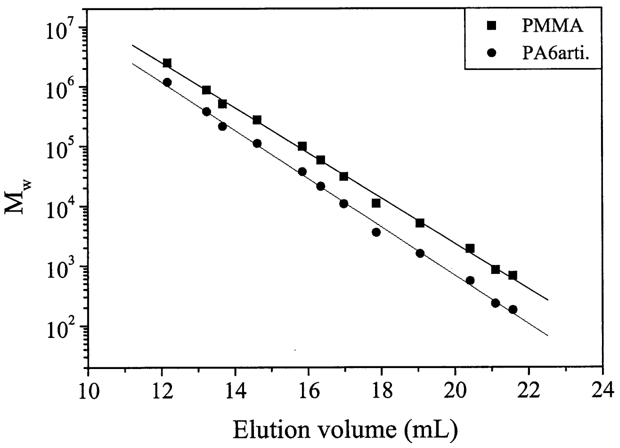


Fig. 4 Artificial calibration curve for polyamide 6 calculated from PMMA calibration by the correction given in Fig. 3

Table 4 Molar masses of the polyamides as determined through the artificial PA calibration curve

Polyamide	M_{app} (g/mol)	V_e (ml) (1)	M_w (g/mol)	M_n (g/mol)	M_w/M_n
Ultramid B5	42,000	15.685	68,700	23,400	2.93
Ultramid B4	33,000	15.808	51,400	22,100	2.33
Ultramid B35	24,000	15.993	40,700	18,900	2.15
Ultramid B3	18,000	16.185	28,000	11,200	2.50
Ultramid B25	15,000	16.256	23,800	9,700	2.45
Ultramid A5	57,000	15.797	55,300	20,100	2.75
Ultramid A3	28,300	16.220	27,100	9,900	2.74
Ultramid A25	17,200	16.261	23,700	8,100	2.94
Ultramid A15	10,700	16.881	10,600	3,700	2.90
Polyamid 12	6,000 (M_w)	17.607	5,450	1,610	3.38
PA6/66		16.450	19,000	7,900	2.42
PA6/THF		16.278	27,600	10,300	2.68
PA6/6I		16.501	16,200	5,600	2.89

Using the artificial PA calibration curve, the molar mass distributions of the present reference samples have been determined. Additionally, a few copolymers have been investigated that have been prepared by transamidation in melt, including polyamide 6/66, polyamide 6/PTHF and a copolymer with isophthalic acid (polyamide 6I). A polyamide 12 has been obtained from Ems Chemie, Switzerland. The molar mass distributions of the samples are summarized in Table 4.

As compared to the molar masses in Table 3, the present numbers are much closer to the M_v (BASF) values that have been determined by melt viscometry. This at least gives a first indication for a correct procedure.

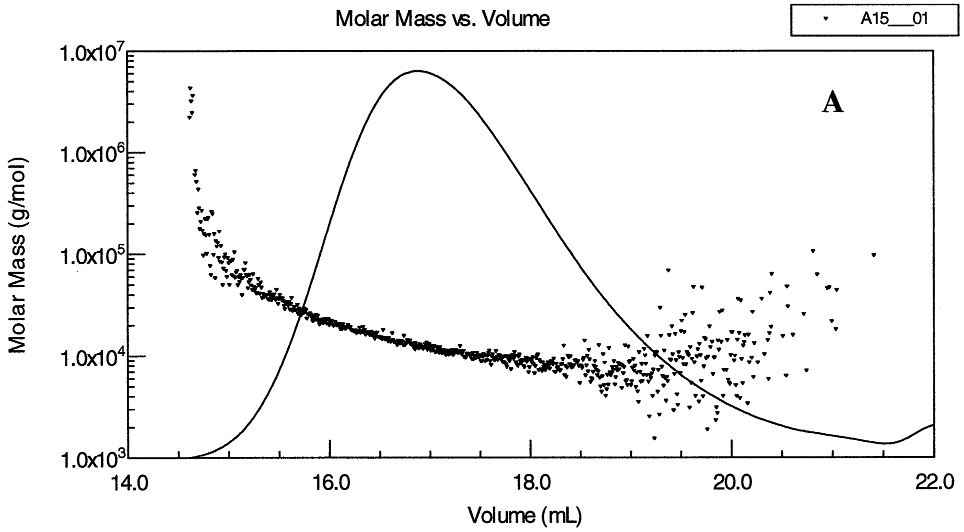
In order to verify the present results, in a next set of experiments the samples have been investigated by SEC laser light scattering detection. The molar mass is calculated from the Rayleigh ratio $R(\theta)$ according to equation 1:

$$R(\theta)/\,Kc \sim MP(\theta) \qquad (1)$$

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, n_0 is the refractive index of the solvent at the laser wavelength λ_0, N_a is Avogadros number, and A_2 is the second virial coefficient. The form factor $P(\theta)$ at low angles is $1 - q^2R_g^2/3$, 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 d*n*/d*c* for the polyamides have been measured in HFIP + 0.05 Mol/L KTFA, i.e. in the SEC mobile phase, using an Optilab 903 refractometer of Wyatt Technology. The d*n*/d*c* values for polyamide 6 and polyamide 6.6 were 0.240 mL/g and 0.242 mL/g, respectively.

Some representative elugrams and the corresponding calibration curves generated from the laser light scattering measurements are shown in Figs. 5 and 6. The molar mass distributions calculated from the SEC-light scattering data are summarized in Table 5. When comparing the molar masses one has to bear in mind that the relative sensitivity of the light scattering detector at low molar masses is rather low. Measurements at 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.



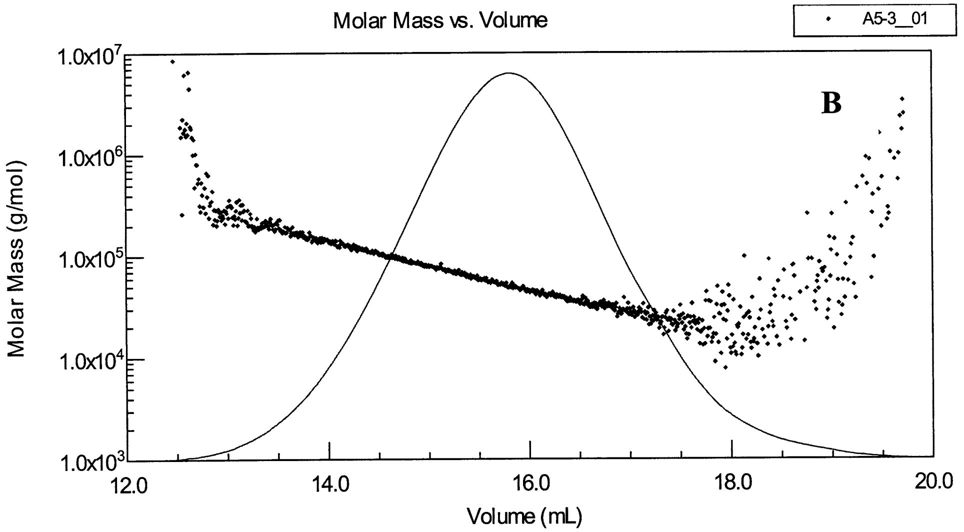


Fig. 5 SEC-light scattering measurements of polyamides 6.6, sample A15 (A), sample A5 (B), chromatographic conditions see Fig. 1

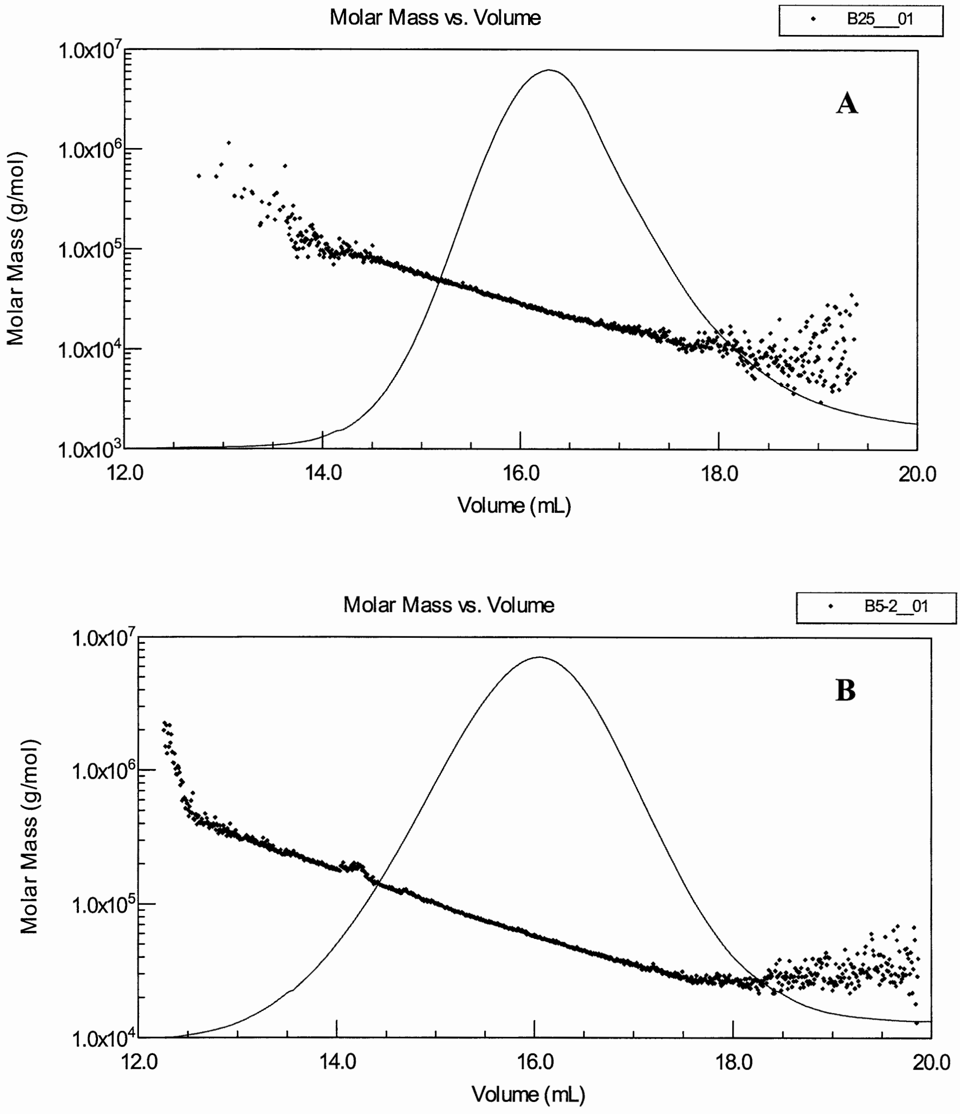


Fig. 6 SEC-light scattering measurements of polyamides 6, sample B25 (A), sample B5 (B), chromatographic conditions see Fig. 1

Table 5 Molar masses of polyamides as determined by the artificial polyamide calibration curve (1) and by SEC-light scattering (2)

Polyamide	M_{app} (g/mol)	M_w (g/mol) (1)	M_w (g/mol) (2)
Ultramid B5	42.000	68.700	74.200
Ultramid B4	33.000	51.400	54.500
Ultramid B35	24.000	40.700	43.200
Ultramid B3	18.000	28.000	
Ultramid B25	15.000	23.800	28.800
Ultramid A5	57.000	55.300	56.000
Ultramid A3	28.300	27.100	31.500
Ultramid A25	17.200	23.700	27.800
Ultramid A15	10.700	10.600	11.500
Polyamid 12	6.000 (M_w)	5.450	
PA6/66		19.000	
PA6/THF		27.600	
PA6/6I		16.200	

The table clearly shows a very good agreement between the two approaches. For polyamide 6 as well as for polyamide 6.6 with both methods data are obtained that deviate only marginally from each other. Accordingly, the calculation of the molar masses through the artificial calibration curves can be used for the daily routine or in places where a light scattering detector is not available.

Acknowledgement

The authors wish to thank Bundesminister für Wirtschaft through Arbeitsgemeinschaft industrieller Forschungsvereinigungen e.V. (AiF) for financial support of this work (AiF-research project Nr. 12725, 18/0-90).

1. M.A. Dudley, *J. Appl. Polym. Sci.*, **1972**, *16*, 493
2. Z. Tuzar, P. Kratochvil, *Adv. Polym. Sci.*, **1979**, *30*, 117
3. W.W. Yau, J.J. Kirkland, D.D. Bly, *Modern Size Exclusion Chromatography*

Wiley Interscience, New York, **1979**

4. G. Pastuska, U. Just, *Angew. Makromol. Chem.,* **1979**, *81*, 11
5. G. Marot, J. Lesec, *Proc. Int. GPC Symposium*, Itasca, IL, USA, **1987**
6. T. Provder, J.C. Woodbrey, J.H. Clark, *Sep. Sci.* **1971**, *6*, 101
7. J. Cazes, X. Delaware (Hrsg.) *Liquid Chromatography of Polymers and Related Materials*, Marcel Dekker, New York, **1977**, *Vol. 8*, p. 41
8. C.A. Veith, R.E. Cohen, *Polymer*, **1989**, *30*, 942
9. C. Jackson, H.G. Barth, M.C. Han, *Polym. Mater. Sci. Eng.,* **1993**, *69*, 270
10. F.A. Buijtenhuijs, H.J.F.M. van den Ven, A.M.C. van de Riet, *Proc. 1st European GPC/Viscometry/Light Scattering Symposium*, Frankfurt, **1993**, #8
11. T.H. Mourey, T.G. Bryan, *J. Chromatogr.,* **1994**, *679*, 201
12. E. Jacobi, H. Schuttenberg, R.C. Schulz, *Makromol. Chem., Rapid Commun.,* **1980**, *1*, 397
13. K. Weisskopf, G. Meyerhoff, *Polymer* , **1983**, *24*, 72
14. K. Weisskopf, *Polymer,* **1985**, *26*, 1187
15. E. Biagini, E. Gattiglia, E. Pedemonte, S. Russo, *Makromol. Chem.,* **1983**, *184*, 1213
16. private communication Polymer Standards Service GmbH, Mainz, Germany