

Determination and Correction of Peak Broadening in Size Exclusion Chromatography of Controlled Rheology Polypropylene

K. LEDERER,* I. BEYTOLLAHI-AMTMANN, and J. BILLIANI

Institut für Chemie der Kunststoffe, Montanuniversität Leoben, A-8700 Leoben, Austria

SYNOPSIS

The peak broadening in size exclusion chromatography of seven commercial polystyrene (PS) standards with narrow molar mass distribution (MMD) and of 6–9 polypropylene (PP) fractions ($\bar{M}_w/\bar{M}_n = 1.34\text{--}2.10$) obtained by direct extraction was determined in four different column sets. The dependence of the Gaussian peak broadening parameter, σ^2 , on the peak elution volume was different for PS and PP. For a commercial grade of controlled rheology PP (CR-PP) (Daplen PT55) with $\bar{M}_w/\bar{M}_n < 3$ it was shown that disregard of the peak broadening effect leads to considerable errors in the MMD at low and high molar mass and in the polydispersity parameter \bar{M}_w/\bar{M}_n . The same lot was studied in an Austrian National Research program for its physical properties in processing and application and in a round-robin test of IUPAC working party IV.2.2. on molecular characterization of commercial polymers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Determination of the molar mass distribution (MMD) of polypropylene (PP) by size exclusion chromatography (SEC) is usually carried out without concern for the peak broadening effect.^{1–8} In the case of grades with narrow MMD, for example, controlled rheology PP (CR-PP) with values of the polydispersity parameter $\bar{M}_w/\bar{M}_n < 3$, this neglect may lead to considerable errors.

To clarify this question, the peak broadening in SEC of PP fractions obtained by the direct extraction procedure of Holtrup⁹ was determined in four different sets of SEC columns by the method developed in the authors' laboratory.^{10,11} Subsequently, the procedure for correction of peak broadening developed by Ishige et al.¹² (method II) was applied to SEC data of the CR-PP grade Daplen PT55.

The same lot of this grade was thoroughly investigated with respect to structure–processing–property relationships in Austria¹³ and with respect to

MMD by IUPAC working party IV.2.2. on molecular characterization of commercial polymers.⁸ The results obtained in this study can therefore be correlated with many different data available in the literature. These results can also be used for direct comparison with further SEC measurements.

EXPERIMENTAL

Materials

Daplen PT55, a low melt index CR-PP, and Daplen KS10, a medium melt index general purpose PP, were obtained from PCD Polymere GmbH (Schwechat and Linz, Austria). The same lots were thoroughly studied with respect to structure–property relationships within the Austrian National Research Program.¹³ Moplen S30S, a medium melt index general purpose PP was obtained from Himont Italia S.r.l. (Ferrara, Italy). The same lots of Daplen PT55 and of Moplen S30S were investigated in a round robin test by IUPAC working party IV.2.2. on molecular characterization of commercial polymers.⁸

PS standards with narrow MMD were obtained from Macherey–Nagel (MN, Düren, Germany),

* To whom correspondence should be addressed.

Table I Molar Mass Data of Polystyrene Standards

Standard No.	Supplier	Data by Supplier (kg/mol)	
		\bar{M}_p	\bar{M}_w/\bar{M}_n
1	MN	0.58	1.14
2	MN	3.25	1.04
3	PSS	10.25	1.06
4	PSS	34.30	1.03
5	PSS	67.00	1.07
6	MN	156.00	1.03
7	MN	500.00	1.06
8	MN	1,130.00	1.04
9	MN	2,950.00	1.11
10	PL	7,700.00	1.14
11	PSS	8,420.00	1.17
12	PSS	12,000.00	1.30

Supplier: MN, Macherey-Nagel; PL, Polymer Laboratories; PSS, Polymer Standard Service. $\bar{M}_p = (\bar{M}_w \cdot \bar{M}_n)^{1/2}$; \bar{M}_w = weight average molar mass, \bar{M}_n = number average molar mass.

Polymer Laboratories Ltd. (PL, Church Stretton, Shropshire, UK), and Polymer Standard Service (PSS, Mainz, Germany). The molar mass data of

these standards, given by the suppliers, are summarized in Table I.

The solvents 1,2,4-trichlorobenzene (TCB), decalin, and diethyleneglycolmonoethylether (DEGME) were each of "pro synthesis" grade and were supplied by Merck (Darmstadt, Germany).

Methods

Preparative Fractionation

The direct extraction procedure developed by Holtrup⁹ was applied. The apparatus used was described in detail by Huber.¹⁴ The solvents contained 0.5 g/L 2,6-di-tert-butyl-4-methylphenol (BHT) to prevent oxidation.

Five grams of Daplen KS10 pellets were dissolved at 150°C in 208 mL decalin in the extraction vessel. Then 392 mL DEGME was slowly added to precipitate most of the polymer. After 30 min of intensive mixing with a vibrational stirrer at 150°C, the soluble fraction of the polymer was obtained as the filtrate (fraction No. 1, cf. Table II). Then a mixture of 111 mL decalin and 189 mL DEGME preheated at 150°C was pumped into the extraction vessel. After 30 min of intensive stirring at 150°C, fraction

Table II Conditions and Results of Fractionation of Daplen KS10 by Direct Extraction

Fraction No.	Mixture of Solvents		Mass Percentage of Fraction w_i (% w/w)	Molar Mass Data (kg/mol)	
	Volume (mL)	Decalin (% v/v)		$\bar{M}_{w,i}$	\bar{M}_w/\bar{M}_n
A1	600	35.0	25.86	119.0	4.9
A2	300	37.0	9.2	146.0	2.6
A3	300	39.0	7.04	202.0	1.83
A4	300	40.0	12.06	235.0	1.72
A5	300	40.6	16.98	307.0	1.51
A6	300	41.3	11.79	238.0	1.36
A7	300	42.0	9.68	258.0	1.56
A8	300	43.0	2.23	346.0	1.34
A9	300	43.3	0.41	335.0	1.49
A10	300	44.0	0.07	—	—

Molar mass data from SEC by universal calibration via PS standards and after correction for peak broadening by the procedure of Ishige II (σ^2 values from Table VI).

$$\text{Balance: } \sum_{i=1}^{10} w_i (\%) = 95.32\% (= \text{yield of fractionation})$$

$$\bar{M}_w = \sum_{i=1}^{10} w_i \bar{M}_{w,i} = 201.00 \text{ kg/mol}$$

$$\bar{M}_n = \frac{1}{\sum_{i=1}^{10} \frac{w_i}{\bar{M}_{n,i}}} = 62.40 \text{ kg/mol.}$$

Table III Conditions and Results of Fractionation of Moplen S30S by Direct Extraction

Fraction No.	Mixture of Solvents		Mass Percentage of Fraction i w_i (% w/w)	Molar Mass Data (kg/mol)	
	Volume (mL)	Decalin (% v/v)		\bar{M}_w	\bar{M}_w/\bar{M}_n
B1	600	35.0	8.53	64.0	4.03
B2	300	37.0	8.90	115.0	2.07
B3	300	39.0	7.67	181.0	1.78
B4	300	40.0	13.71	292.0	2.08
B5	300	40.6	11.28	312.0	2.08
B6	300	41.3	11.28	223.0	1.82
B7	300	42.0	13.28	262.0	2.05
B8	300	43.0	14.29	312.0	1.79
B9	300	43.3	4.88	232.0	1.55
B10	300	44.0	0.74	396.0	2.04

Molar mass data from SEC by universal calibration via PS standards and after correction for peak broadening by the procedure of Ishige II (σ^2 values from Table VI).

$$\text{Balance: } \sum_{i=1}^{10} w_i (\%) = 99.4\% \text{ (=yield of fractionation)}$$

$$\bar{M}_w = \sum_{i=1}^{10} w_i \bar{M}_{w,i} = 223.0$$

$$\bar{M}_n = \frac{1}{\sum_{i=1}^{10} \frac{w_i}{\bar{M}_{n,i}}} = 79.3$$

Table IV Specification of Column Sets Used in SEC

Set No.	Specification
1 ^a	1 TSK-Gel GMH6-HT (Toso Haas, Montgomeryville, PA), 7.8 mm inner diameter (i.d.), 300 mm length (l), 17 μm particle size (p.s.) 1 Lichrolog PS 40000 (Merck), 7.0 mm i.d., 250 mm l., 10 μm p.s. 1 Lichrolog PS4 (Merck), 7.0 mm i.d., 250 mm l., 5 μm p.s.
2	As set No. 1, but with newly delivered columns
3 ^b	1 Lichrolog PS-Mix 5,000,000 (Merck), 7.0 mm i.d., 250 mm l., 5 μm p.s. 1 Lichrolog PS 4 of Merck (cf. set No. 1)
4	Nearly identical with set No. 2, but separate, new delivery of all three columns; however, Lichrolog PS 4 with 10 μm p.s. instead of 5 μm p.s.

^a This set had already been used in high temperature SEC for more than 6 months prior to usage in this study.

^b The column of type Lichrolog PS-Mix 5,000,000 had been used for 6 months prior to usage in this study; the Lichrolog PS 4 column was newly delivered.

No. 2 was obtained. This procedure was continued until the whole polymer was extracted.

From the extracted solutions, the polymer precipitated after cooling down to room temperature overnight, and was obtained by filtration through a G3 glass frit from Schott (Mainz, Germany). Table II summarizes the conditions and the results of this fractionation, giving also the balance of the fractionation. Calculating the molar mass data for the total of the obtained fraction, a considerable degradation ($\bar{M}_w = 201.00$ kg/mol compared to $\bar{M}_w = 322$ kg/mol of unfractionated Daplen KS10⁷) of the polymer was observed. The calculated \bar{M}_n for the total of the obtained fractions is somewhat larger than the values measured for the original polymer ($\bar{M}_n = 47$ kg/mol $\pm 8\%$ ⁷) that might be caused by loss of material with very low molar mass.

By the same procedure, 5 g of a sample of Moplen S30S was fractionated (cf. Table III). In this case, the yield of the fractionation was very high (99.4%). The calculated molar mass data for the total of the obtained fractions ($\bar{M}_w = 223.0$ kg/mol and $\bar{M}_n = 79.3$ kg/mol) also deviated considerable from the data of the unfractionated sample of Moplen S30S⁸ ($\bar{M}_w = 467$ kg/mol $\pm 6.0\%$ (1σ), $\bar{M}_n = 83.7$ kg/mol

$\pm 9.8\%$) with respect to \bar{M}_w ; whereas the agreement in \bar{M}_n was rather good.

SEC Experimental Conditions

SEC was carried out in a self assembled apparatus with the following components.

HPLC Pump. Waters Model 510, Millipore-Waters, (Milford, MA) set to a flow rate of about 1 mL/min.

Column Oven. Supplied by Knauer (Berlin, Germany) held at 135°C.

Sample Injector. Six way valve (Knauer), sample loop volume 305 μ L, held at 135°C.

Concentration Detector. IR detector of Du Pont Instruments, (Wilmington, DE) with modified detector cell⁷ set to $\lambda = 3.41 \mu\text{m}$.

Molar Mass Detector. LALLS photometer KMX-6, Chromatix Inc., (Sunnyvale, CA) operated at an angle of 6–7° with 0.15 mm fieldstop.

Columns. Four different column sets, each on the basis of PS-divinylbenzene, were used in four independent series of measurement (cf. Table IV).

The sample solutions were prepared by dissolving between 2.5 and 25 mg of polymer in 25 mL TCB at 170°C with 1 h dissolving time for PP samples and 20 min for the PS standards. In the experiments with column set No. 4, dissolution was carried out with careful exclusion of oxygen by flushing with nitrogen.

The molar mass calibration of SEC was carried out by universal calibration¹⁵ using the following values for the coefficients of the Staudinger–Mark–Houwink equation $K = 1.75 \cdot 10^{-2} \text{ mL/g}$ and $a = 0.67$ for PS,¹⁶ and $K = 1.90 \cdot 10^{-2} \text{ mL/g}$ and $a = 0.725$ for PP,¹⁷ both for TCB at 135°C.

For each of the columns sets, a linear calibration function $\log M(v)$ was observed, as is shown for column set No. 4 in Figure 1.

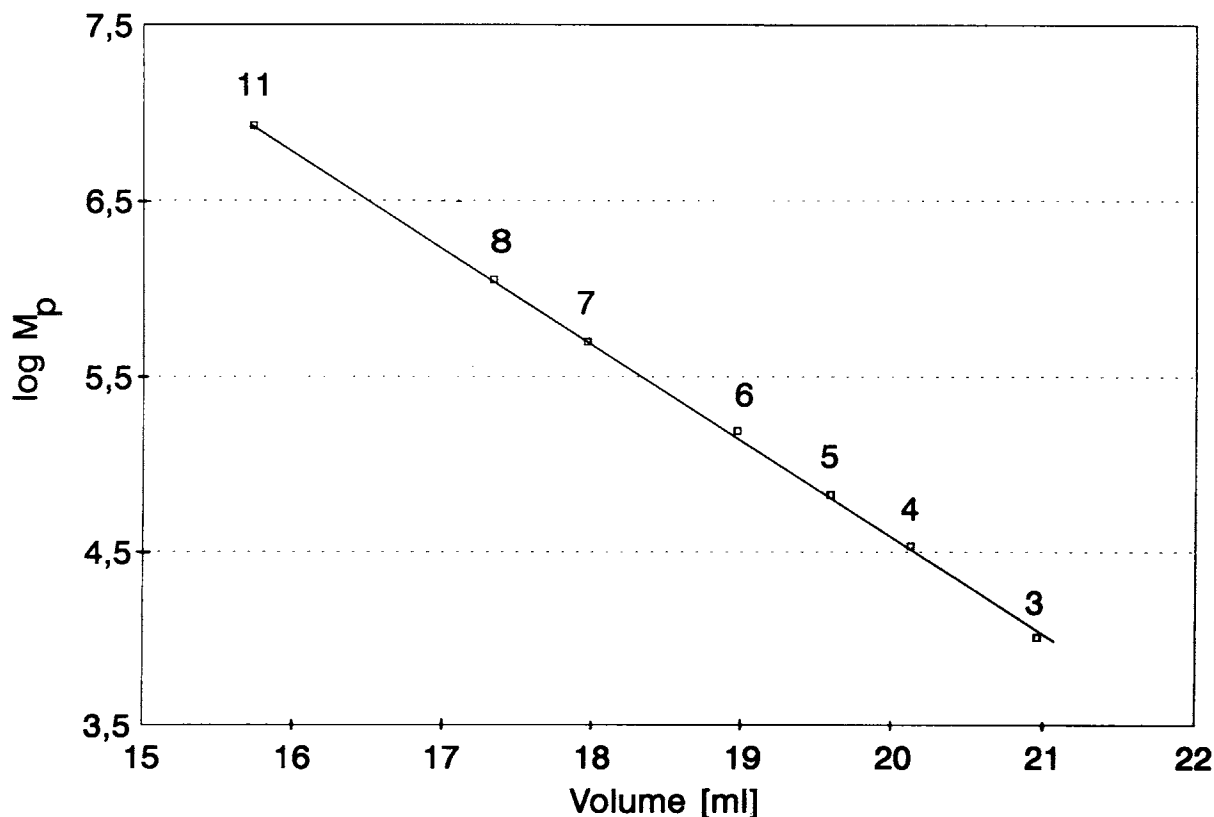


Figure 1 Calibration of column set No. 4 with PS standards Nos. 3, 4, 5, 6, 7, 8, and 11 (cf. Table I) in the plot $\log M_p$ (data of supplier) vs. peak elution volume (mL).

Evaluation of Data from SEC/LALLS

For the determination of peak broadening, the method developed by Lederer et al. was used.¹⁰ Hereby, a Gaussian peak broadening function defined by its variance σ^2 is assumed. From the concentration signal, $e(v)$, which is normalized so that

$$\int e(v) dv = 1$$

and the light scattering signal, $E(v)$, which is normalized so that

$$\int E(v) dv = \bar{M}_{w,ep},$$

where $\bar{M}_{w,ep}$ = weight average molar mass of the total eluted polymer (ep), the variance σ^2 can be calculated. In the case of a linear calibration function $\ln M(v)$

$$\ln M(v) = A - Bv,$$

and with known parameters A and B , the following equations are solved for the unknown σ^2 by a non-linear regression method¹¹:

$$E(v) = e(v - B\sigma^2) \exp(B^2\sigma^2/2) \\ \times \exp(A - Bv)$$

$$e(v) = E(v + B\sigma^2) \frac{\exp(B^2\sigma^2)}{\exp(A - B \cdot v)}$$

Table V Values of Instrumental and Sample Related Parameters in LALLS Detection of Polypropylene and Polystyrene

Refractive index of TCB at 135°C	1.52
Detector lag between LALLS and IR-detector	50.0 μ L
Scattering angle	4.27°
Wavelength of laser	632.8 nm
Geometric constant in LALLS ($1/\sigma^2$)	723.8
Refractive index increment	
Polypropylene	-0.095 mL/g
Polystyrene	-0.050 mL/g
Second virial coefficient of osmotic pressure, A_2	
Polypropylene	1.10^{-4} mL mol g^{-2}
Polystyrene	1.10^{-4} mL mol g^{-2}

Table VI Peak Broadening Parameter σ^2 Determined with Different Column Sets

Column Set No.	Polystyrene Standards			Polypropylene Fractions			
	No.	c (g/L)	σ^2 (mL ²)	No.	c (g/L)	σ^2 (mL ²)	
1	3	3.99	0.068	A2	1.42	0.25	
	4	2.74	0.053	A3	1.12	0.18	
	5	2.06	0.063	A4	1.04	0.19	
	6	1.77	0.063	A5	1.49	0.24	
	7	1.43	0.084	A6	1.32	0.24	
	8	0.98	0.084	A7	0.99	0.16	
	9	0.87	0.078	A8	0.97	0.19	
	10	0.43	0.032	A9	0.99	0.24	
	2	3	3.36	0.060	A2	1.96	0.11
		4	2.71	0.040	A3	1.30	0.29
5		2.72	0.070	A4	1.74	0.16	
6		2.27	0.070	A5	1.81	0.16	
7		1.81	0.054	A7	1.88	0.23	
8		1.88	0.084	A8	1.23	0.24	
9		1.84	0.074				
3		4	1.27	0.027	A2	0.785	0.042
		5	1.16	0.044	A3	0.842	0.052
	6	1.21	0.036	A4	0.501	0.042	
	7	1.17	0.048	A5	0.631	0.055	
	8	0.79	0.050	A6	0.558	0.055	
	9	0.40	0.014	A7	0.502	0.053	
				A8	0.423	0.063	
	4	3	5.63	0.012	B2	1.31	0.024
		4	4.22	0.017	B3	0.95	0.022
5		2.88	0.039	B4	0.92	0.020	
6		2.01	0.045	B5	1.45	0.016	
7		0.91	0.061	B6	1.14	0.013	
8		0.96	0.117	B7	1.50	0.025	
11		1.05	0.373	B8	1.51	0.026	
				B9	2.00	0.036	
				B10	1.39	0.048	

Compare Table IV in SEC/LALLS measurements on solutions of various polystyrene standards (cf. Table I) and fractions of polypropylene (cf. Tables II and III). c, concentration of injected sample solutions.

For the numerical calculation a software package developed by Rois¹⁸ was used (available from authors' institute).

For the calculation of the function $E(v)$ from the recorded light scattering signal the values of instrumental and of sample related parameters given in Table V were used.

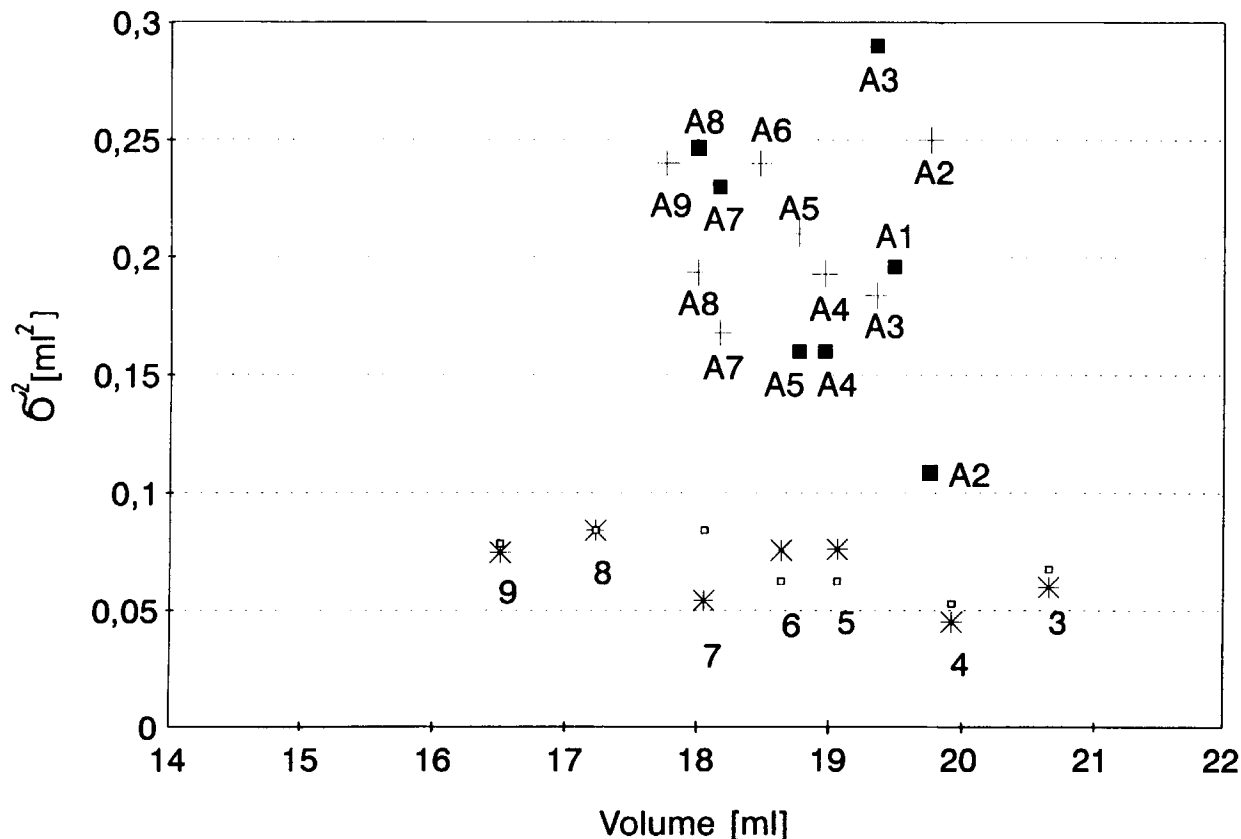


Figure 2 Dependence of the peak broadening parameter (variance of the respective Gaussian), σ^2 (mL^2), as a function of the peak elution volume (mL) in SEC with column set No. 1: (\square) PS standards, (+) PP fractions; and with column set No. 2: (*) PS standards, (\blacksquare) PP fractions. Samples and σ^2 values as summarized in Table VI.

RESULTS AND DISCUSSION

The values of σ^2 found in the experiments by use of the PS standards described in Table I and of the PP fractions presented in Tables II and III, respectively, are summarized in Table VI.

Figure 2 shows the dependence of the peak broadening parameter (variance of the respective Gaussian), σ^2 , as a function of the peak elution volume of the PS standards and the PP fractions, respectively, in SEC with column sets Nos. 1 and 2 (cf. Table VI); Figure 3 gives the respective dependence for the column sets Nos. 3 and 4.

From Figure 2 it is evident that the PS standards show a distinctly different dependence of σ^2 on the peak elution volume, v , than the PP fractions. In the case of the PS standards, the functions $\sigma^2(v)$ determined with column sets Nos. 1 and 2 agree fairly well and show the expected decay with increasing elution volume.¹⁹ In the case of PP fractions, considerably higher values of σ^2 than with PS

standards are observed, and the values of σ^2 vary unsystematically for the column sets Nos. 1 and 2 and for different values of the elution volume.

In the experiments with column sets Nos. 3 and 4, a better agreement of $\sigma^2(v)$ for PS standards and PP fractions was observed (cf. Fig. 3).

These findings demonstrate that the concept of a universal function $\sigma^2(v)$ for different linear homopolymers under identical experimental conditions is not generally valid.²⁰ Therefore, the function $\sigma^2(v)$ should always be determined with samples with narrow molar mass distribution of the respective polymer.

Figure 4 shows the effect of correction for peak broadening applying an average value of $\sigma^2 = 0.2025 \text{ mL}^2$ for the SEC data obtained with column set No. 1. In Figure 5, the MMD obtained after correction for peak broadening with column set No. 1 ($\sigma^2 = 0.2025 \text{ mL}^2$) and with column set No. 3 are compared. In the case of column set No. 3, the peak broadening correction was carried out with a step-

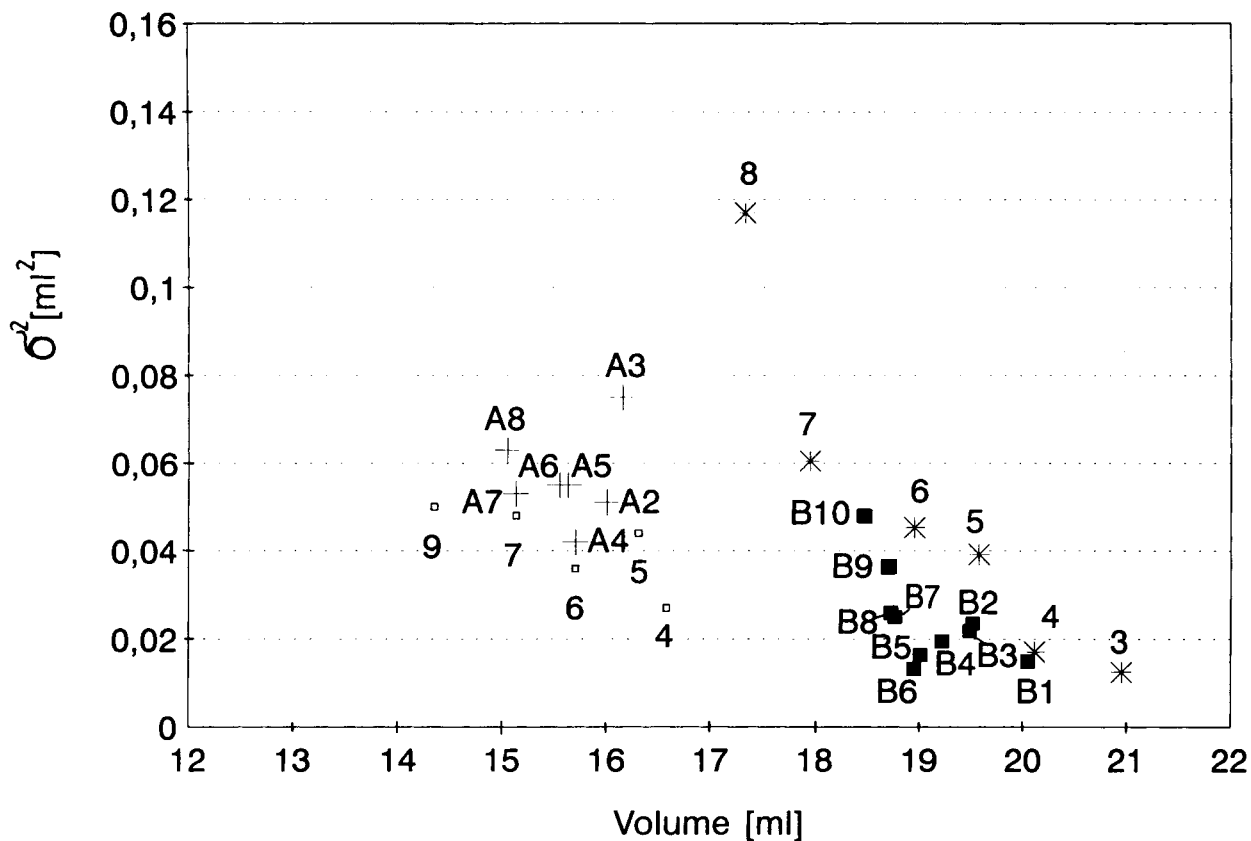


Figure 3 Dependence of the peak broadening parameter, σ^2 (mL^2), as a function of the peak elution volume (mL) in SEC with column set No. 3: (\square) PS standards, (+) PP fractions; and with column set No. 4: (*) PS standards, (\blacksquare) PP fractions. Samples and σ^2 values as summarized in Table VI.

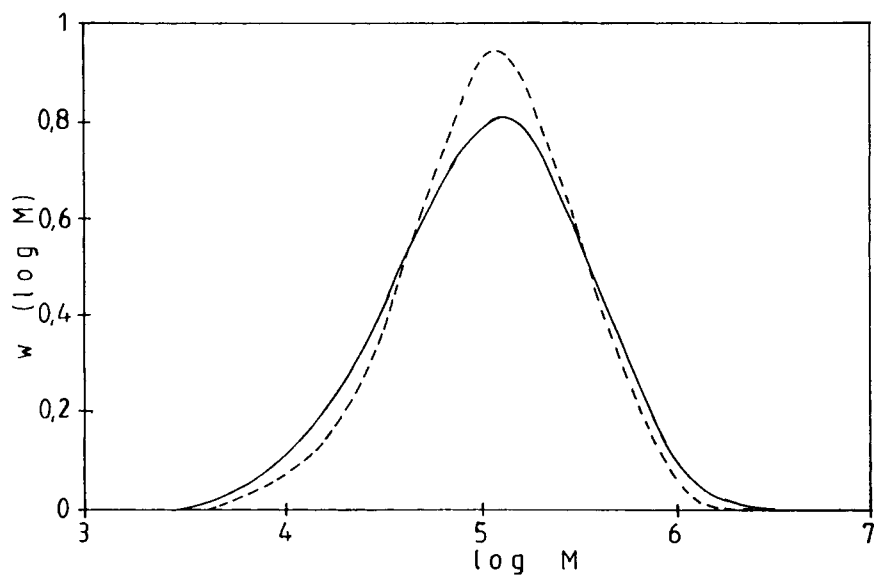


Figure 4 Mass distribution of molar mass, $w(\log M)$, of Daplen PT55 measured with column set No. 1: (—) not corrected for peak broadening and (---) corrected for peak broadening.

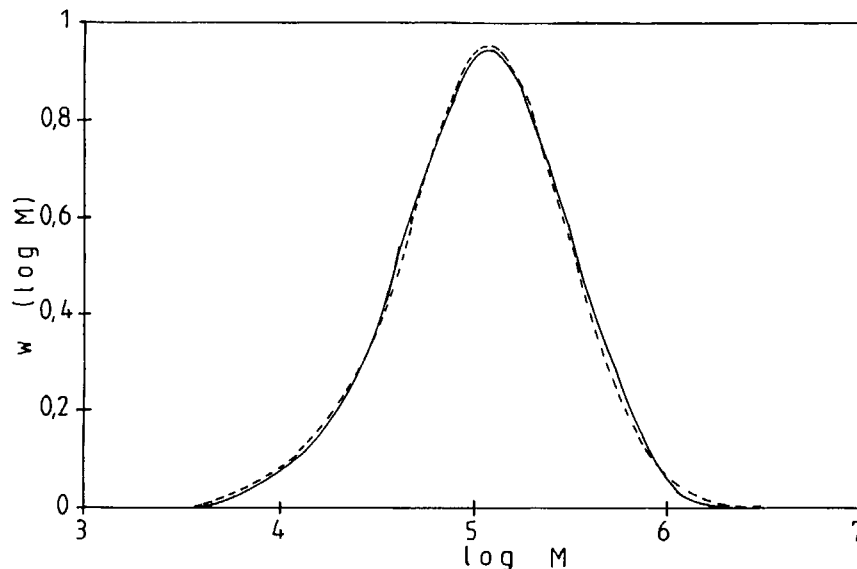


Figure 5 Mass distribution of molar mass, $w(\log M)$, of Daplen PT55 determined (—) in column set No. 1 and (---) in column set No. 3 (with correction for peak broadening).

wise change of σ^2 : $\sigma^2 = 0.15 \text{ mL}^2$ for $v < 13.75 \text{ mL}$; $\sigma^2 = 0.12 \text{ mL}^2$ for $v = 13.75\text{--}13.83 \text{ mL}$; $\sigma^2 = 0.10 \text{ mL}^2$ for $v = 13.83\text{--}14.00 \text{ mL}$; $\sigma^2 = 0.078 \text{ mL}^2$ for $v = 14.00\text{--}14.10 \text{ mL}$; $\sigma^2 = 0.061$ for $v = 14.10\text{--}14.20 \text{ mL}$; $\sigma^2 = 0.057$ for $v = 14.20\text{--}14.52 \text{ mL}$; and $\sigma^2 = 0.050$ for $v > 14.52 \text{ mL}$. As can be seen from Figure 5, the corrected functions $w(\log M)$ agree very well for both column sets.

Table VII summarizes the average molar mass values of Daplen PT55 determined by SEC with column sets Nos. 1, 3, and 4. These values lie in the same range as those determined in the round robin test by IUPAC working party IV.2.2. without correction of peak broadening⁸; however, the value of $(\bar{M}_w/\bar{M}_n)_{\text{corr}}$ is significantly smaller than the average value \bar{M}_w/\bar{M}_n (without correction for peak broadening) reported by this working party (\bar{M}_w/\bar{M}_n

$= 3.51 \pm 0.58$). This finding strongly suggests that the effect of peak broadening in SEC of CR-PP should, in general, not be neglected.

The significantly higher value of $M_{w,\text{corr}}$ determined with column set 4 (cf. Table VII) is probably due to the careful exclusion of oxygen during the preparation of sample solutions.

Even in the case of the very low value of σ^2 observed with column set No. 4 (cf. Table VI), the effect of the peak broadening correction carried out with an average value of $\sigma^2 = 0.0286 \text{ mL}^2$ on the $w(\log M)$ function cannot be neglected, especially in the range of very high and very low molar mass as is shown in Figure 6. This clearly demonstrates the necessity of correction for peak broadening for a precise determination of the MMD of CR-PP even in the case of high performance SEC columns.

Table VII Results of SEC Measurements on Daplen PT55

Column Set No.	\bar{M}_w (kg/mol)	$\bar{M}_{w,\text{corr}}$ (kg/mol)	\bar{M}_n (kg/mol)	$\bar{M}_{n,\text{corr}}$ (kg/mol)	\bar{M}_w/\bar{M}_n	$(\bar{M}_w/\bar{M}_n)_{\text{corr}}$
1	207	183	58.8	69.4	3.52	2.64
3	206	189	72.3	74.7	2.85	2.53
4	210	200	77.4	77.9	2.71	2.57

\bar{M}_w and \bar{M}_n = weight and number average molar mass without correction for peak broadening; $\bar{M}_{w,\text{corr}}$ and $\bar{M}_{n,\text{corr}}$ = average molar mass corrected for peak broadening.

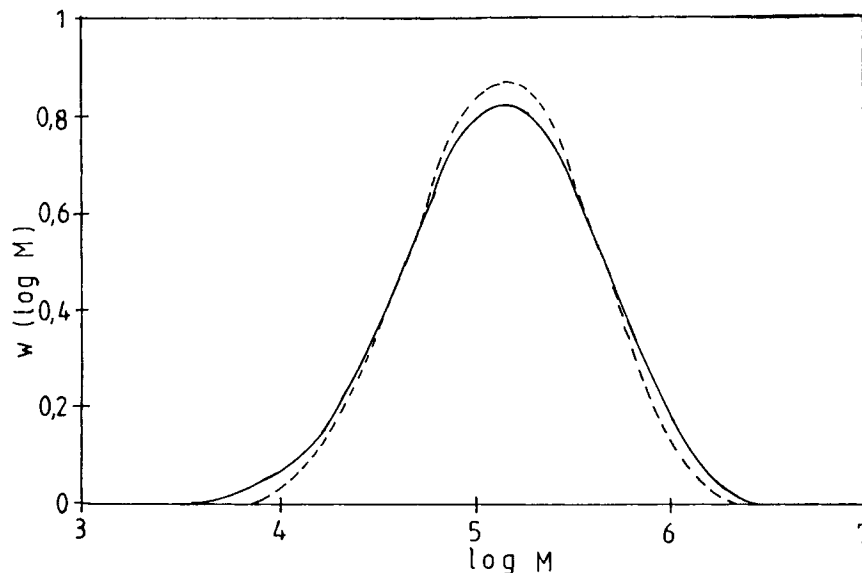


Figure 6 Mass distribution of molar mass, $w(\log M)$, of Daplen PT55 measured with column set No. 4: (—) not corrected for peak broadening and (---) corrected for peak broadening.

The generous support of this study by the Fonds zur Förderung der wissenschaftlichen Forschung within the Austrian National Research Program "Forschungsschwerpunkt Kunststoff-Formteile" is gratefully acknowledged. Part of the instrumentation was financed through the Jubiläumsfonds of the Österreichische Nationalbank (Project No. 1193).

REFERENCES

1. T. B. MacRury and M. L. McDonnel, *J. Appl. Polym. Sci.*, **24**, 651 (1979).
2. J. L. Vidal, P. Crouzet, and A. Martens, *J. Chromatog. Sci.*, **20**, 252 (1982).
3. V. Grinsphun and A. Rudin, *J. Appl. Polym. Sci.*, **30**, 2413 (1985).
4. Y. Quicong, X. Ping, L. Yong, and Q. Renyuan, *J. Liq. Chromatog.*, **9**, 1233 (1986).
5. R. Lew, D. Suwanda, and S. T. Balke, *J. Appl. Polym. Sci.*, **35**, 1049 (1988).
6. R. Lew, P. Cheung, D. Suwanda, and S. T. Balke, *J. Appl. Polym. Sci.*, **35**, 1065 (1988).
7. J. Billiani and K. Lederer, *J. Liq. Chromatog.*, **13**, 3013 (1990).
8. K. Lederer and I. Mingozzi, to appear.
9. W. Holtrup, *Makromol. Chem.*, **178**, 2335 (1977).
10. K. Lederer, G. Imrich-Schwarz, and M. Dunky, *J. Appl. Polym. Sci.*, **32**, 4751 (1986).
11. J. Billiani, G. Rois, and K. Lederer, *Chromatographia*, **26**, 372 (1988).
12. T. Ishige, S.-I. Lee, and A. E. Hamielec, *J. Appl. Polym. Sci.*, **15**, 1607 (1971).
13. H. Janeschitz-Kriegl, Ed., Final Report of the Austrian National Research Program "Forschungsschwerpunkt Kunststoff-Formteile," University of Linz, Austria, March 1991.
14. B. Huber, Diplomarbeit, Montanuniversität Leoben, Leoben, Austria, 1987.
15. Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci., Polym. Lett. Ed.*, **5**, 753 (1967).
16. A. Rudin, V. Grinsphun, and K. F. O'Driscoll, *J. Liq. Chromatog.*, **7**, 1809 (1984).
17. Th. G. Scholte, N. L. Meijerincx, H. M. Schoffeleers, and A. M. G. Brands, *J. Appl. Polym. Sci.*, **30**, 3763 (1984).
18. G. Rois, Diplomarbeit, Montanuniversität Leoben, Leoben, Austria, 1987.
19. R.-S. Cheng, Z.-L. Wang, and Y. Zhao, *ACS Symp. Series*, **352**, 281 (1987).
20. J. Billiani, I. Amtmann, T. Mayr, and K. Lederer, *J. Liq. Chromatogr.*, **13**, 2973 (1990).

Received September 29, 1993

Accepted March 6, 1994