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COMMERCIAL POLYMERS*

**MOLECULAR CHARACTERIZATION OF
COMMERCIAL POLYPROPYLENE WITH NARROW
AND BROAD DISTRIBUTION OF MOLAR MASS**

(Technical Report)

Prepared for publication by

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Molecular characterization of commercial polypropylene with narrow and broad distribution of molar mass (Technical Report)

Abstract - The molar mass and the molar mass distribution of two commercial grades of isotactic polypropylene, Moplen S30S of Himont S. r. l. and Daplen PT55 of PCD Polymere GmbH., were investigated by 16 laboratories. For Moplen S30S $M_w = 467$ kg/mole ± 6.0 % (relative standard deviation), $M_n = 83.7$ kg/mole ± 9.8 % and $M_w/M_n = 5.70 \pm 10.1$ % were determined by size exclusion chromatography (31 SEC runs), for Daplen PT55 $M_w = 206$ kg/mole ± 13.6 %, $M_n = 61.4$ kg/mole ± 13.4 % and $M_w/M_n = 3.42 \pm 17.3$ % were found (38 SEC runs). Light scattering measurements gave $M_w = 445$ kg/mole ± 4.1 % for Moplen S30S (4 labs) and $M_w = 212$ kg/mole ± 10 % for Daplen PT55 (3 labs). The intrinsic viscosity in 1,2,4-trichlorobenzene at 140°C of Moplen S30S $[\eta] = 1.87$ dl/g ± 5.4 % and of Daplen PT55 $[\eta] = 1.12$ dl/g ± 6.7 % was measured (9 independent measurements). Samples of the respective lots are available from the authors, Moplen S30S from IM, Daplen PT55 from KL.

INTRODUCTION

Isotactic polypropylene (PP) homopolymer is a type of thermoplastic of very large and fast growing market share. In Western Europe, the total consumption of PP in the year 1991 was of the order of 4 million tonnes, of which about 70 % was homopolymer. The world capacity for PP in 1991 amounted to 17.2 million tonnes (ref. 1).

Due to the great technical importance of PP, there is a frequent need for its molecular characterization. In view of the fact that PP standard samples have hitherto not been available, the IUPAC working party IV.2.2. decided in 1987 to establish two PP standards for the determination of molar mass and molar mass distribution. For this purpose, two PP samples which strongly differ in molar mass distribution were investigated by 16 laboratories; each sample had been taken from a distinct lot of a commercially available grade. Hereby, the main emphasis was on the determination of molar mass distribution by size exclusion chromatography (SEC), supplemented by light scattering measurements and determination of the intrinsic viscosity. In this way, two PP standards are now available with recommendations concerning the procedure of sample preparation and measuring conditions in SEC.

MATERIALS

Two commercial grades of polypropylene with different distribution of molar mass were investigated using samples from the same lot in all laboratories.

Moplen S30S is a medium melt index general purpose grade of Himont S. r. l., Ferrara, Italy, and is recommended for blow moulding of bottles, thermoforming, textile film yarn, ropes, extruded nets and chenille.

Daplen PT55 is a high melt index controlled rheology grade of PCD Polymere GmbH, Linz, Austria, and is recommended for injection moulding of difficult parts with long flow distance, for jet spinning of non-wovens and for filaments.

TABLE 1. Material data according to CAMPUS (ref. 2) of Daplen PT55 and Moplen S30S (b)

Property	Unit	PT55	S30S	Standard	Specimen
Density	g/cm ³	0.901	0.900	ISO 1183	(10x10x4)mm (1,2)
Stress at yield (50 mm/min)	N/mm ²	31	35	ISO 527	ISO3167 4mm thick
Strain at yield (50 mm/min)	%	10	8	" "	" " " "
Strain at break (50 mm/min)	%	-	140	" "	" " " "
Stress at 50 % elong. (50 mm/min)	N/mm ²	16	-	" "	" " " "
Tensile strength (5 mm/min)	N/mm ²	-	26	" "	" " " "
Strain at break (5 mm/min)	%	-	500	" "	" " " "
Young's modulus (secant 1 mm/min)	N/mm ²	1200	1500	" "	" " " "
Impact strength (Izod) +23°C	kJ/m ²	80	108	ISO 180/1C	(80x10x4)mm (1,3)
Impact strength (Izod) -30°C	kJ/m ²	10	11.5	ISO 190/1C	" " " "
Notch.imp.str. (Izod) +23°C	kJ/m ²	2.4	3.8	ISO 180/1A	" " " "
Notch.imp.str. (Izod) -30°C	kJ/m ²	1.2	1.9	ISO 180/1A	" " " "
Notch.tens.imp.strength +23°C	kJ/m ²	52	-	ISO 8256/1B	" " " "
Heat defl.temp./A (1.8 N/mm ²)	°C	42	53	ISO 75	(≥110x10x4)mm (1)
Heat defl.temp./B (0.45 N/mm ²)	°C	-	85	" "	" " " "
Heat defl.templ./C (5.0 N/mm ²)	°C	-	-		" " " "
Vicat A/50 (10 N)	°C	-	155	ISO 306	(10x10x4)mm (1,2)
Vicat B/50 (50 N)	°C	82	96	" "	" " " "
Melt volume index (1 st value)	ml/10min	26	4	ISO 1133	material
at test temperature	°C	230	230		
at test load	kg	2.16	2.16		
Melt volume index (2 nd value)	ml/10min	38	20	ISO 1133	material
at test temperature	°C	190	230		
at test load	kg	5	5		
Isotacticity index (sol. in heptane)	%	4.2	-	ISO 6427 Annex B	material

Notes

- (1) poss. taken out of tension test specimen
- (2) poss. taken out of 80x10x4-test specimen
- (3) poss. cut to 63.5 mm length

The melting point determined according to ASTM D 3417-83 by DSC is 163.0 ± 2.2 °C for Moplen S30S and 162.2 ± 2 °C for Daplen PT55; these values are the arithmetic mean and the standard deviation from 9 and 11 determinations, respectively, by this working party.

Both grades contain neither fillers nor reinforcing additives. Their material data catalogue according to CAMPUS (ref. 2) are summarized in Table 1. Samples from the lots investigated in this study are available from the authors: Moplen S30S from I. Mingozzi, Daplen PT55 from K. Lederer.

Only methods routinely applied in industrial laboratories were used. For this reason, the applied procedures could not be standardized thoroughly.

DISSOLUTION OF SAMPLES

As described in the literature (ref. 3 - 5), polypropylene shows a tendency to thermooxidative degradation. Therefore in most experiments antioxidants were added in small concentrations (about 0.1×10^{-2} g/cm³). In the course of this work, the following conditions were recommended and agreed upon by the members of this working party: solvent 1,2,4-trichlorobenzene (TCB), polymer concentration 0.1 - 1.0 g/l, addition of antioxidant (0.5 g/l), dissolution time 4 h at a temperature of 150°C under nitrogen with occasional stirring. These conditions were however not closely followed by most of the laboratories (cf. Table 2 and Table 4), due to internal guidelines and automatic handling of samples.

SIZE EXCLUSION CHROMATOGRAPHY (SEC)

SEC was performed predominantly with Waters Model 150 C, Millipore-Waters Corp., Milford, Mass., USA, and partially with Waters Model 200, e. g. in run 14 - 21 in Table 2 and in run 14 in Table 4. Furthermore, a self assembled multicomponent system with an IR-Detector ($\lambda = 3.41 \mu\text{m}$) of Du Pont-Instruments Corp., Wilmington, Del., USA, was used e. g. in run 22 - 24 in Table 2 and in run 15 - 19 in Table 4.

Generally, a flow-rate of about 1 ml/min and a concentration of sample solutions of 0.1 - 0.3 g/l were chosen. Working with polystyrene-divinylbenzene columns, 1,2,3-trichlorobenzene (TCB) was preferably used as eluent; in the case of silica-gel columns, o-dichlorobenzene (ODCB) was used.

Further details of experimental conditions are presented in Table 2 for the sample Moplen S30S and in Table 4 for the sample Daplen PT55.

Basically, three different methods of calibration were used (cf. Table 2 and 4):

Method (a) used high density polyethylene samples with known and broad molar mass distribution (MMD), e. g. the NBS standard SRM 1475 (ref. 6), the integral calibration method (ref. 7) and the conversion procedure by Scholte et al. (ref. 8). In some cases two different high density polyethylene samples with broad MMD were used (method a'). Method (b) uses the universal calibration procedure established by Grubisic et al. (ref. 9) applied to polystyrene standards with narrow MMD using the following Staudinger-Mark-Houwink constants for TCB at 135°C:

$$K = 1.75 \times 10^{-4} \text{ dl/g}, a = 0.670 \text{ for polystyrene (ref. 10),}$$

and $K = 1.90 \times 10^{-4} \text{ dl/g}, a = 0.725$ for polypropylene (ref. 8)

Method (c) uses a polypropylene sample with broad MMD; this MMD was established by the respective users (laboratories III, IX, XV) independent of each other.

Often, a combination of methods (a) and (b) was used (calibration a + b), preferably with method (a) in the range of low molar mass, and method (b) at high molar mass. In some cases, two different calibration methods were applied independently, e. g. method (c) and method (a) (cf. Table 2 and 4, lab No IX and XV), calibration c/a.

Table 3 and Table 5 give the arithmetic mean and the standard deviation of the values of molar mass for Moplen S30S and Daplen PT55, respectively.

TABLE 2. Results of size exclusion chromatography with Moplen S30S

M_w = mass-average molar mass, M_n = number-average molar mass, u = undisclosed

Lab No	Run No	M_w kg/mole	M_n kg/mole	M_w/M_n	Calibration(1)	Dissolution conditions	SEC conditions
I	1	352*	82*	4.29*	a	24 h at 140°C stirring every 2 h	Shodex A806/S, A80M/S, A804 S/, TCB (200 ppm antioxidant) at 140°C
	2	386*	67*	5.76*	a	4 h at 180°C + 10 min at 200°C + 30 min at 135°C	5 Waters Styragel columns $10^7 - 10^3 \text{ \AA}$ TCB at 130°C
II	3	520	75	6.93	a	1 h at 145°C	

(1) a = HDPE, * cf. Table 3 (31 runs)

TABLE 2, continued

Lab No	Run No	M_w kg/mole	M_n kg/mole	M_w/M_n	Cali- bration(1)	Dissolution conditions	SEC conditions
III	4	232*	54*	4.30*	c	u	Shodex 50301 and 50926, eluent: u
IV	5	363*	74*	4.91	a+b	8 h at 150°C	Polymer Laboratories-Gel 10 μ m mixed bed; TCB (200 ppm BHT) at 140°C
V	6	390	81	4.81	a+b	2 h at 150°C, N ₂	2x TSK GMH6-HT (PS-DVB); TCB (Irgafos 168 and Topanol CA) at 135°C
VII	7	386*	79*	4.89*	b	u	Waters Ultrastyrigel 500, 10 ⁴ , 10 ⁶ Å; TCB at 145°C
VIII	8	280*	74*	3.78*	a	u	Waters Ultrastyrigel 500, Mix, 10 ⁴ , 10 ⁶ Å; TCB at 135°C
	9	462/418	90/73	5.12/5.69			3 x TSK GMHXL-HT (30 cm);
	10	464/411	88/78	5.22/5.26		ODCB	ODCB (0.5 g/l BHT)
	11	445/412	89/72	5.01/5.73	c/a	1 h at 135°C	at 135°C
	12	446/403	90/73	4.98/5.52			
	13	467/423	89/73	5.24/5.83			
IX	14	474	78	6.10			
	15	470	77	6.14			Spherosil 10 ³ - 10 ⁷ Å
	16	466	74	6.30		ODCB	particle size 37 - 75 μ m
	17	470	77	6.09	c	1 h at 145°C	4 columns, 4 feet x 3/8"; ODCB at 135°C
	18	481	79	6.07			
	19	478	80	5.98			
	20	446	69	6.46			
	21	469	73	6.42			
	22	419	87	4.82	a+b	1 h at 175°C, N ₂	2x TSK GMHXL-HT (30 cm); TCB (0.5 g/l BHT) at 135°C
X	23	487	85	5.73	a+b	1 h at 175°C, N ₂	TSK GMH6-HT (30 cm) + Lich- rogel PS 40000 (25 cm) +
	24	469	75.5	6.21	b	1 h at 175°C, N ₂	Lichrogel PS4 (25 cm); TCB (0.5 g/l) Irganox 1010) at 135°C
XII	25	336*	55*	6.11*	a	u	Polymer Laboratories-Gel 10 μ m (10 ³ - 10 ⁶ Å); ODCB at 135°C
XIII	26	316*	62*	5.10*	a	2 h at 180°C	u
	27	304*	68*	4.47*			
	28	224*	54*	4.15*	a'	4 h at 170°C	3 x TSK GMHXL-HT;
	29	326*	55.8*	5.84*	a'	1 h at 140°C	TCB (not stabilized) at 140°C
XIV	30	436	81	5.28	a'	2 h at 150°C (slow stirring)	
	31	438	83	5.28		+ 1 h at 140°C, N ₂	

(1) a = HDPE, a' = HDPE (SRM 1475 + broad MMD PE sample), b = universal calibration (PS standards),
c = broad MMD-PP-sample

* cf. Table 3 (31 runs)

TABLE 2, continued

Lab No	Run No	M_w kg/mole	M_n kg/mole	M_w/M_n	Cali- bration(1)	Dissolution conditions	SEC conditions
	32	510	99.2	5.14		N 6 homogenized by	3xTSK GMHXL-HT:
	33	504	90.2	5.59		7 precipitation from solution;	TCB (0.5 g/l N-phenyl-2- naphthylamine) at 135°C
	34	512	96.7	5.29	c	10 2 - 3 h at 140°C	
	35	486	93.4	5.20		11 (gentle shaking)	
XV	36	495/492	80.1/78.3	6.18/6.28		8 +1 h at 135°C (spinned)	
	37	502/496	91.6/85.9	5.48/5.77	c/a	9 +N hours at 135°C	
	38	476	90.8	5.24		6 Solution made from	
	39	460	85.7	5.37		7 pellets. Dissolution	
	40	468	75.1	6.23	c	6 as with runs 32 - 37	
	41	450	72.6	6.20		7	
XVI	42	330*	47*	7.02*	a	2 h at 160°C	4 x Silica 10^3 - 10^7 Å; ODCB
	43	432	67	6.45		(ODCB)	3 x Waters μ -Styragel HT linear ODCB (BHT) at 140°C

(1) a = HDPE, c = broad MMD-PP-sample

* cf. Table 3 (31 runs)

TABLE 3. Arithmetic mean, \bar{x} , standard deviation, σ , and relative standard deviation, σ (%), of results by SEC with Moplen S30S as given in Table 2; for runs 9 - 13, 26 and 37, only values obtained by calibration method c were considered.

Number of runs	statistical parameter	M_w kg/mole	M_n kg/mole	M_w/M_n
all 43 runs	\bar{x}	426	77.4	5.53
given in Table 2	σ	76	12	0.74
	σ (%)	17.8	15.5	13.4
31 runs	\bar{x}	467	83.7	5.70
values in Table 2 marked with * not included	σ	28	8.2	0.58
	σ (%)	6.0	9.8	10.1

TABLE 4. Results of size exclusion chromatography for Daplen PT55. M_w = mass-average molar mass, M_n = number-average molar mass, u = undisclosed

Lab No	Run No	M_w kg/mole	M_n kg/mole	M_w/M_n	Cali- bration(1)	Dissolution and SEC conditions
I	1	198*	74.5*	2.66*	a	24 h at 140°C, stirring every 2 h; SEC as in Table 2
II	2	210*	66*	3.18*	a	4 h at 180°C + 10 min at 200°C + 30 min at 135°C; SEC as in Tab. 2
	3	203	53	3.83	a	4 h at 150°C; SEC as in Table 2

(1) a = HDPE

* cf. Table 5 (30 runs)

TABLE 4, continued

Lab No	Run No	M_w kg/mole	M_n kg/mole	M_w/M_n	Cali- bration(1)	Dissolution and SEC conditions
III	4	128*	48*	2.67*	u	dissolution undisclosed; SEC as in Table 2
IV	5	192*	62*	3.10*	a + b	8 h at 150°C; SEC as in Table 2
V	6	190	57	3.33	a + b	2h at 150°C, N ₂ ; SEC as in Table 2
VII	7	173*	68*	2.54*	b	u
IX	8	268/243	51/46	5.22/5.29	c/b	1 h at 135°C (ODCB); SEC as in Table 2, run 8 - 13 with TSK GMHXL-HT, run 14 with Spherosil
	9	257/225	66/61	3.88/3.66		
	10	260/234	62/52	4.10/4.53		
	11	261/232	64.5/54	4.01/4.26		
	12	255/229	74/62	4.53/3.68		
	13	251/222	67/54.5	3.73/4.07		
	14	216	61	3.54		
	15	217	66	3.29	a + b	45 min at 165°C + 5 min stirring, N ₂ ; SEC as in Table 2, run 22
X	16	205	54	3.80	a + b	1 h at 170°C occasional gentle stirring, N ₂ SEC as in Table 2, run 24
	17	207	59	3.51	b	
	18	220	68	3.23	b	
	19	210	77.4	2.72	b	
XII	20	168*	41*	4.10*	a	dissolution undisclosed; SEC as in Table 2
XIII	21	163*	57*	2.86*	a	u
XIV	22	221.5	51.8	4.08	c	2 h at 150°C + 1h at 140°C, N ₂ ; SEC as in Table 2
	23	208.0	51.3	4.06	c	
XV	24	216	71	3.04	c	N 6 solution from pellets, 7 2-3 h at 140°C (gentle 8 shaking) + 1 h at 135°C 9 (spinned) + N hours at 135°C; 10 SEC as in Table 2 11 12 13 14
	25	192	66.5	2.89		
	26	212	69.7	3.04		
	27	197	64.3	3.06		
	28	192	71.0	2.70		
	29	190	67	2.84		
	30	194	68.6	2.83		
	31	198	55.9	3.54		
	32	208/198	60.6/57.6	3.43/3.44		
	33	202/201	54.4/52.3	3.71/3.84		
	34	189/186	58.3/57.3	3.24/3.25		
XV	35	188/200	61.5/64.6	3.05/3.10	c/a	6 6 7
	36	187/199	60.8/63.8	3.07/3.12		

(1) a = HDPE, b = universal calibration (PS standards), c = broad MMD-PP-sample
* cf. Table 5 (30 runs)

TABLE 4, continued

Lab No	Run No	M_w kg/mole	M_n kg/mole	M_w/M_n	Cali- bration(1)	Dissolution and SEC conditions
XVI	37	188*	51*	3.69*	a	2 h at 160°C, air; SEC as in Table 2 at run 42 for run 37 and at run 43 for run 38
	38	199	52	3.83		

(1) a = HDPE

* cf. Table 5 (30 runs)

TABLE 5. Arithmetic mean, \bar{x} , standard deviation, σ , and relative standard deviation, σ (%), of results by SEC with Daplen PT55 as given in Table 4; for runs 8 - 14 and 32 - 36, only values obtained by calibration method c were considered.

Number of runs	Statistical parameter	M_w kg/mole	M_n kg/mole	M_w/M_n
all 38 runs given in Table 4	\bar{x}	206	61.4	3.42
	σ	28	8.2	0.59
	σ (%)	13.6	13.4	17.3
30 runs values in Table 4 marked with * not included	\bar{x}	213	62.2	3.51
	σ	25	7.3	0.58
	σ (%)	11.7	11.7	16.5

LIGHT SCATTERING

Light Scattering was performed both coupled to SEC and off-line ("static").

SEC coupled with light scattering was carried out with the low-angle laser light scattering (LALLS) instrument KMX-6 of Chromatrix, Inc., Mountain View, Cal., USA, which operates with a He-Ne-laser of wave-length $\lambda = 632.8$ nm. The refractive index increment dn/dc of polypropylene in TCB at 135 and 145 °C, respectively, for $\lambda = 632.8$ nm was taken from the literature (ref. 3 and ref. 11) and from measurements carried out with Moplen S30S and Daplen PT55 (ref. 12 and 13); these authors used either the Brice-Phoenix Model BP-2000-V of Phoenix Precision Instrument Comp., Philadelphia, Penn., USA, or the Chromatrix KMX-16 differential refractometer.

Table 6 summarizes the values of the weight-average molar mass determined by SEC coupled with LALLS using different values of refractive increment and values corrected to the same value of refractive increment ($dn/dc = -0.0935$ ml/g). The various values of the refractive index increment of polypropylene in TCB found in the literature or communicated to the one of us (KL) by cooperating laboratories are given in Table 7.

In static light scattering, the instrument FICA 50, Sofica, St. Denis, France, was used, applying unpolarized light of wave length $\lambda = 546.1$ nm. As solvent, 1-chloronaphthalin (1-CN) was preferred due to its high refractive index increment for polypropylene. For further experimental details see Table 8.

TABLE 6. Mass-average molar mass, M_w , of Moplen S30S and Daplen PT55 determined with SEC coupled to LALLS by use of different values of the refractive index increment, dn/dc , and M_w corrected to $dn/dc = -0.0935$ ml/g, $M_w, corr.$

Sample	Lab No	M_w kg/mole	dn/dc ml/g	$M_w, corr.$ kg/mole
Moplen S30S	II	388	-0.108	518
	V	402	-0.104	460
	X	463	-0.095	478
		570	-0.095	588
		507	-0.095	523
		487	-0.095	503
		Statistical parameters (cf. Table 3)	x	512
σ (%)	44	8.7		
Daplen PT55	II	207	-0.108	276
	V	190	-0.104	217
		192	-0.104	220
		208	-0.104	238
		202	-0.095	209
	X	207	-0.095	214
		217	-0.095	224
		199	-0.095	205
		184	-0.095	189
		Statistical parameters (cf. Table 5)	x	221
	σ (%)	25	11.1	

TABLE 7. Refractive index increment, dn/dc , of polypropylene in 1,2,4-trichlorobenzene (wave-length = 632.8 nm)

Sample	Temperature °C	dn/dc (cm ³ /g)	Apparatus	ref.
Daplen PT55	135	-0.093	KMX-16	13
Moplen S30S	135	-0.096	KMX-16	13
Daplen PT55	135	-0.095±0.003	Brice-Phoenix	12
commercial grade (MFI = 3)	145	-0.092	KMX-16	3
commercial grade (MFI = 12)	145	-0.094	KMX-16	3
commercial grade	145	-0.091	KMX-16	*
commercial grade	135	-0.102	Brice-Phoenix	11

* Chromatix, KMX-16 Application Note LS 7

TABLE 8. Results and experimental conditions of static light scattering with Moplen S30S and Daplen PT55. M_w = mass-average molar mass, A_2 = second osmotic virial coefficient, $[s^2]$ = mean-square of the radius of gyration, dn/dc = refractive index increment at wave-length 546.1 nm used in data evaluation, 1-CN = 1-chloronaphthalin, DPM = diphenylmethane

Lab No	M_w (kg/mole)	$10^4 \times A_2$ (mole ml g ⁻²)	$[s^2]^{1/2}$ (nm)	Solvent	Temp. (°C)	dn/dc (ml/g)	Angular range (degree)	Dissolution conditions
V	423	3.5	55	1-CN	140	-0.189	30-150	4 h at 150 °C
IX	468	2.18	47.5	1-CN	140	-0.191	30-150	3 h at 145 °C
IX	444	3.62	47.6	1CN	150	-0.191	30-150	2 h at 150 °C
XI	444±22	2.0	54	DPM	142	-0.126	30-150	9 h at 150 °C
Statistical parameters	x 445	2.83	51.0					
cf. Table 3	σ 18.4	0.85	4.0					
	σ(%) 4.1	30	7.9					

MOPLEN S30S

Lab No	M_w (kg/mole)	$10^4 \times A_2$ (mole ml g ⁻²)	$[s^2]^{1/2}$ (nm)	Solvent	Temp. (°C)	dn/dc (ml/g)	Angular range (degree)	Dissolution conditions
V	206	4.9	34	1-CN	140	-0.189	30-150	4 h at 150 °C
IX	236	3.15	33.7	1-CN	140	-0.191	30-150	3 h at 145 °C
XI	195±2	2.45	47	DPM	142	-0.126	30-150	5 h at 150 °C
Statistical parameters	x 212	3.50	38.2					
cf. Table 5	σ 21.2	1.26	7.5					
	σ(%) 10	36	20					

DAPLEN PT55

LIMITING VISCOSITY NUMBER

Limiting viscosity number was measured in TCB at 140°C with conventional Ubbelohde viscometers available from Schott Comp., Mainz, Germany, and with the differential viscometer Model 100 of Viscotek Corp., Poster, Tex., USA. The dissolution conditions were similar to those given in Table 2 and Table 4 for the corresponding laboratories.

The values of the limiting viscosity number measured by four different laboratories in 9 independent experiments are given in Table 9.

DISCUSSION

Table 2 and Table 4 give the values of the mass- and number-average molar mass, M_w and M_n , and the polydispersity parameter M_w/M_n of 43 and 38 SEC runs, carried out in 14 and 13 laboratories, respectively. The values marked with an asterisk (*) are considered to be influenced by thermooxidative degradation due to severe conditions of dissolution (longer dissolution time, higher dissolution temperature); neglecting these values leads to better agreement of these molar mass data as shown in Table 3 and Table 5. There is good agreement of SEC-data especially for M_w measured for Moplen S30S in 31 selected runs.

Figure 1a and Figure 1b show the mass distribution of the molar mass, $w(\log M)$, which is normalized so that

$$\int_0^\infty w(\log M) d \log M = 1$$

The agreement among these distribution curves is however not fully satisfactory.

TABLE 9. Limiting viscosity number, $[\eta]$, of Moplen S30S and Daplen PT55 in 1,2,4-trichlorobenzene at 140°C

Lab No	$[\eta]$ (dl/g)		
	S30S	PT55	
I	1.80	1.00	
	1.84	1.10	
IV	1.74	1.21	
XIV	1.96	1.04	
	1.98	1.10	
	2.01	1.17	
	1.94	1.19	
	1.85	1.20	
	1.75	1.09	
Statistical parameters	\bar{x}	1.87	1.12
	σ	0.10	0.075
cf. Table 3	$\sigma(\%)$	5.4	6.7

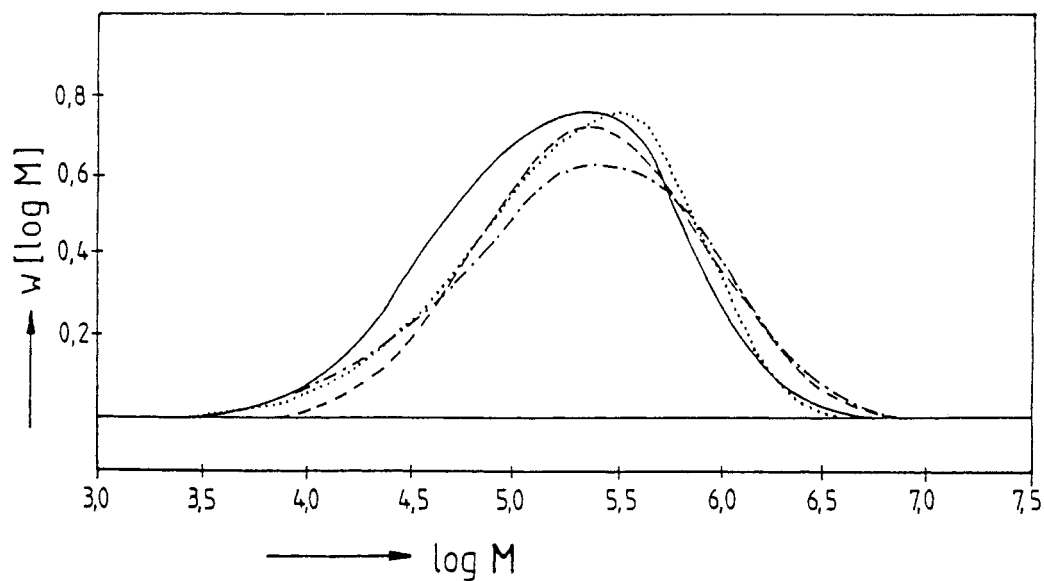


Fig. 1a. Molar mass distribution of Moplen S30S measured by SEC (cf. Table 2): (.....) run 1, (—) run 7, (-.-.-) run 9 and (----) run 24. Molar mass in g/mole.

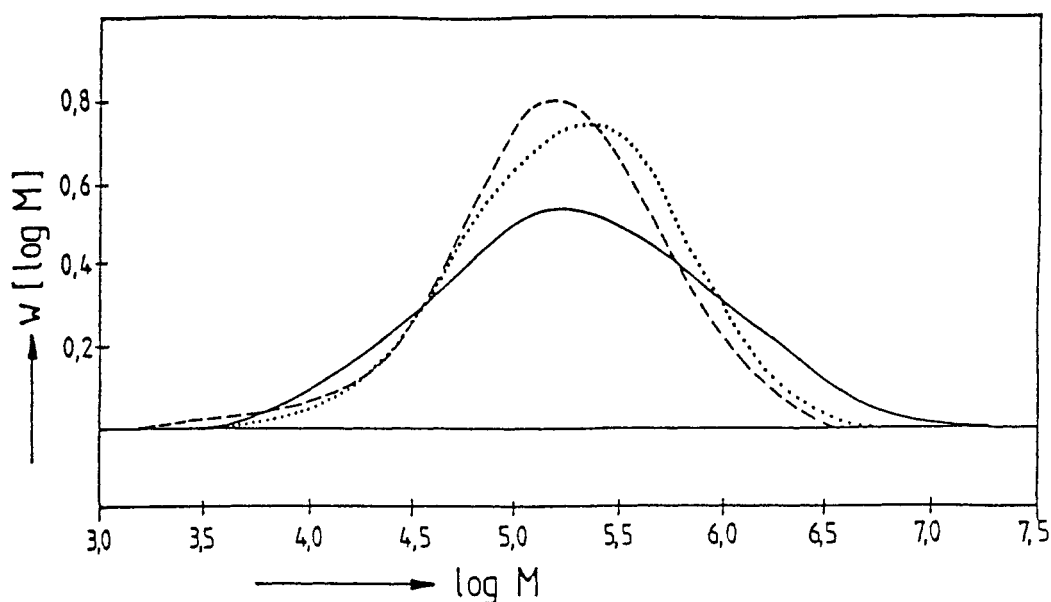


Fig. 1b. Molar mass distribution of Moplen S30S measured by SEC (cf. Table 2): (---) run 26, (—) run 40 and (····) run 43. Molar mass in g/mole.

In the case of Daplen PT55, the selection of 30 runs out of 38 runs hardly improves the standard deviation of the M_w values (cf. Table 5). Obviously, thermooxidative degradation does not have such large influence as in the case of Moplen S30S. The molar mass distributions, $w(\log M)$, in Fig. 2a and Fig. 2b agree quite well in the range of medium molar mass, but show considerable deviations in the range of very low and very high molar mass. This leads to a high uncertainty of the polydispersity parameter M_w/M_n (cf. Table 5) which is probably caused by the influence of the peak broadening effect.

In the case of Moplen S30S, the arithmetic mean of $M_{w,corr}$ in Table 6 (6 SEC/LALLS runs) is 9.6 % larger than the corresponding value in Table 3 (31 SEC runs). $M_{w,corr}$ is calculated by correcting to the same value of refractive index increment, $dn/dc = -0.0935$ ml/g, which is the arithmetic mean of the values given in Table 7, when neglecting the value $dn/dc = -0.102$ ml/g (ref. 11). The standard deviation of the $M_{w,corr}$ -values from SEC/LALLS is however slightly greater than with conventional SEC.

In the case of Daplen PT55, the arithmetic mean of $M_{w,corr}$ in Table 6 (also corrected to $dn/dc = -0.0935$ ml/g) from 9 SEC/LALLS runs is only 3.7 % larger than the corresponding value in Table 5 (30 SEC runs).

These findings show that the agreement between SEC/LALLS and SEC results is strongly improved by correction to a value of refractive index increment of $dn/dc = -0.0935$ ml/g.

Comparison of the mean values for M_w in Table 3 and Table 5 with M_w measured by static light scattering in Table 8 shows good agreement.

The values of the limiting viscosity number by four laboratories show good agreement. These data may be used to calculate the Staudinger-Mark-Houwink constants for polypropylene in TCB at 140°C on the basis of the molar mass distributions given in Fig. 1 and Fig. 2 (ref. 14).

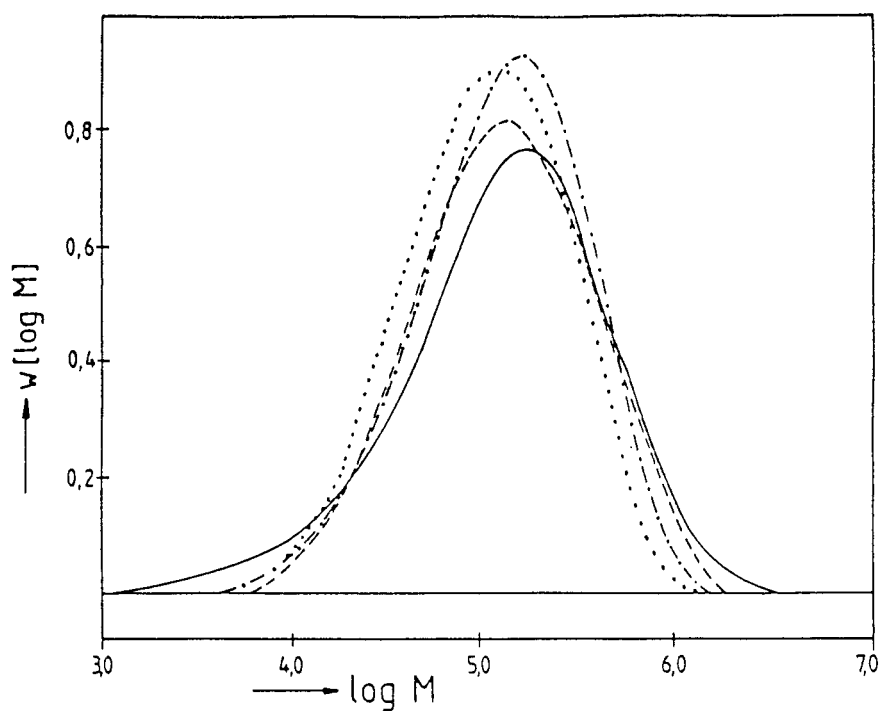


Fig. 2a. Molar mass distribution of Daplen PT55 measured by SEC (cf. Table 4): (---) run 1, (....) run 7, (—) run 9 and (-.-) run 19. Molar mass in g/mole.

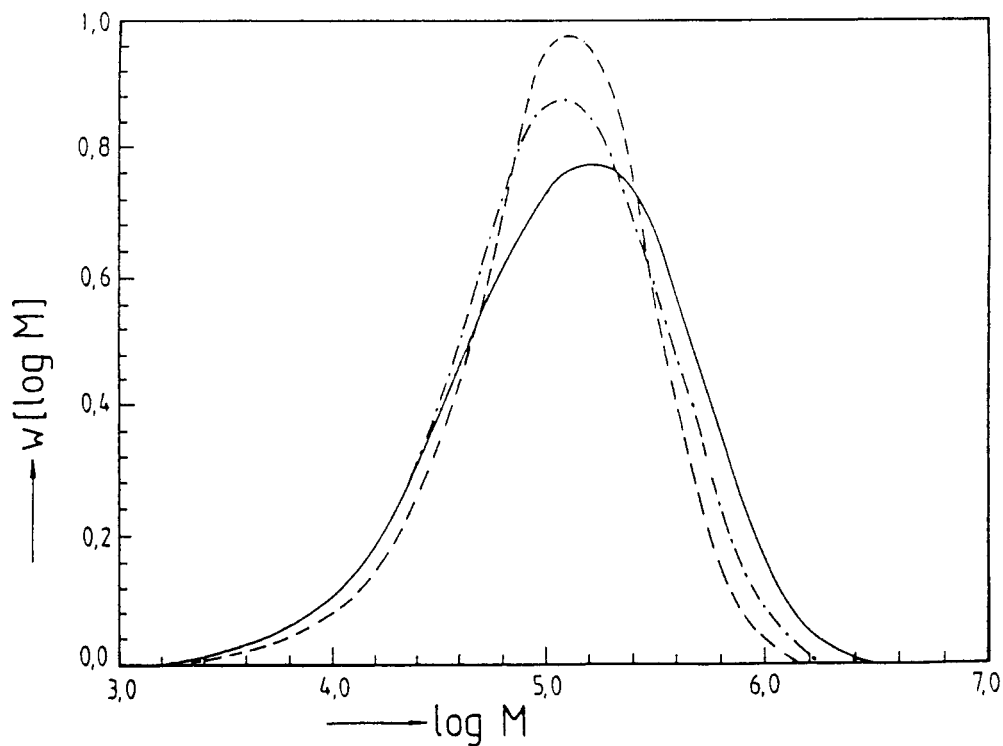


Fig. 2b. Molar mass distribution of Daplen PT55 measured by SEC (cf. Table 4): (---) run 21, (-.-) run 36 and (—) run 38. Molar mass in g/mole.

CONCLUSIONS

The inter-laboratory agreement of SEC measurements for two PP samples is not fully satisfactory. The observed discrepancies may be caused by thermooxidative degradation during the preparation of sample solutions, by in column shear degradation, by aging of the column packing, by different calibration procedures and by the peak broadening effect. To improve inter-laboratory agreement, closer matching of the applied procedures in high-temperature SEC would probably be helpful.

SEC/LALLS-coupling does not enhance the inter-laboratory agreement. SEC/LALLS does appear to have its merits mainly for the detection of molecular degradation (ref. 15), for more precise measurement in the range of high molar mass (ref. 16) and for calibration and correction of peak broadening (ref. 17 and 18).

The inter-laboratory agreement of light scattering and of limiting viscosity number is satisfactory in view of the slightly different procedures used for the preparation of sample solutions and the influence of thermooxidative degradation.

The availability of samples from the lots characterized in this study of both Moplen S30S and of Daplen PT55 will make it possible to continue this work with improved methods. The authors believe that the results so far should greatly enhance the scientific interest in the molecular characterization of polypropylene.

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