Polypropylene Characterization by High Temperature Sec Coupled with Lalls

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POLYPROPYLENE CHARACTERIZATION BY HIGH TEMPERATURE SEC COUPLED WITH LALLS

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ABSTRACT

A new and less time consuming procedure for the preparation and the handling of polypropylene solutions has been developed. The precision of direct determination of molar mass from SEC/LALLS is satisfactory in the range near the maximum of the distribution function, but at low molar masses one better relies on a conventional calibration function. Molar mass distributions and averages were evaluated on the basis of a combination of SEC/LALLS and calibration with a broad HDPE standard.

INTRODUCTION

Since 1980 polypropylene consumption in Western Europe increased about 100% (1.3 mio tons/year to 2.4 mio tons/year in 1987 (1), 1987/88 growth of 13% (2)) of which 65% are homopolymers. In view of the fact

that polypropylene homopolymer is of such outstanding
and growing importance, the information in the
literature concerning the molar mass distribution (MMD)
of polypropylenes is rather scarce (3 - 10).
This might be due to the crystalline structure of
isotactic polypropylene, which requires high boiling
solvents in SEC. Therefore preparation of polypropylene
sample solutions requires a delicate compromise between
complete dissolution (tendency to form gels and
aggregates) and oxidative degradation (11). Furthermore
no polypropylene standard samples are available for SEC
calibration and therefore one usually must rely on the
universal calibration. In this study, a new and less
time consuming procedure for the preparation and the
handling of polypropylene solutions has been developed
using the frequency of spikes (gel particles) and the
integral over the LALLS signal (M_w of eluted sample) as
criterion. On the basis of this procedure, the
applicability of universal calibration and the
calibration via polyethylene standards suggested by
Scholte et al. (12) is tested using direct molar mass
detection in the SEC/LALLS system. Finally the
repaetability of SEC and SEC/LALLS measurements
attainable with polypropylene is discussed.

MATERIALS

The samples used were commercial isotactic poly-
propylene homopolymers produced by Petrochemie Danubia
(Vienna, Austria). DAPLEN KS10 (melt flow index
[230 °C/21.19 N] = 8.0 g/10 min) is a injection molding
type polypropylene. DAPLEN PT55 (melt flow index
[230 °C/21.19 N] = 18.0 g/10 min) is a controlled
rheology type polypropylene (CR-PP) with narrower molar

mass distribution than KS10, produced by using a "Visc-
Breaking Process" (13).

Polystyrene calibration standards with narrow
molar mass distribution (M_p = 1260 - $3x10^6$ [g/mole],
$M_w:M_n$ < 1.06; M_p = $7.7x10^6$ [g/mole], $M_w:M_n$ < 1.2) were
obtained from Polymer Laboratories Ltd. (Church
Stretton, Shropshire, UK). A high density polyethylene
standard reference material with broad molar mass
distribution (SRM 1475 HDPE) was supplied by National
Bureau of Standards (Washington, D.C., USA) (14).

METHODS

Size Exclusion Chromatography (SEC)

Molecular mass distribution and molar mass
averages were determined using a high-temperature SEC
system consisting of solvent delivery pump (Model 560,
Waters Associates), sample injector, column oven
(Knauer, Berlin, F.R.G) and two detectors, a low angle
laser light scattering photometer (LALLS) (KMX-6 Milton
Roy, Hasselroth, F.R.G) and an IR detector (DuPont
Company, Wilmington, DE, USA) connected in series. The
commercially available NaCl IR cell was replaced by
infrasil windows and a teflon spacer to increase
mechanical stability and lifetime of the cell. The flow
rate was measured by means of a balance (0.59 ml/min).
At higher flow rates (0.8 - 1.0 ml/min) the LALLS
signal was strongly distorted and could not be used.
Three columns - GMH6-HT, 30 cm (Toyo Soda, Tokyo,
Japan), PS40000 and PS4, 25 cm (Merck, Darmstadt,
F.R.G) - were used with 1,2,4-Trichlorobenzene (TCB) at
T=135 °C as mobile phase. Polymer concentration was
detected by IR using the absorption of the C-H groups

at 3.41 um. The LALLS instrument was operated at an angle of 6-7° and with 0.15 mm fieldstop to minimize the background.

Preparation of Sample Solutions

Polystyrene sample preparation for calibration involved room temperature dissolution over night in TCB and heating to 135 °C in nitrogen atmosphere prior to injection. Polyethylene solutions were prepared as suggested by Grinshpun et al. (15). Dissolution of polypropylene pellets can be very difficult and the limited stability of polyolefines in solution at high temperatures is known. For preparation of polypropylene solutions samples are usually heated for 24 to 48 hours at 145 °C in TCB (8,11).

To speed up dissolution time, the temperature was raised to 170 °C. The effect of dissolution time on the molar mass distribution was investigated. Figure 1 shows the effect of dissolution time on the chromatograms of polypropylene solutions (KS10) at 170 °C. At a dissolution time of 120 min after thorough swelling of the pellets, degradation becomes clearly observable (curve 2 in Fig. 1) and after 1300 min (curve 5 in Fig. 1) the weight average molar mass was down to 27% of the original value. From this data a maximum duration of 90 min for dissolving polypropylene at 170 °C without significant degradation was estimated. Gentle stirring by means of a magnetic stirrer improved dissolution speed. Dissolution times less then 60 min showed significant increase of spikes at the LALLS signal as well as a perceptible pressure rise in the system, indicating incomplete dissolution
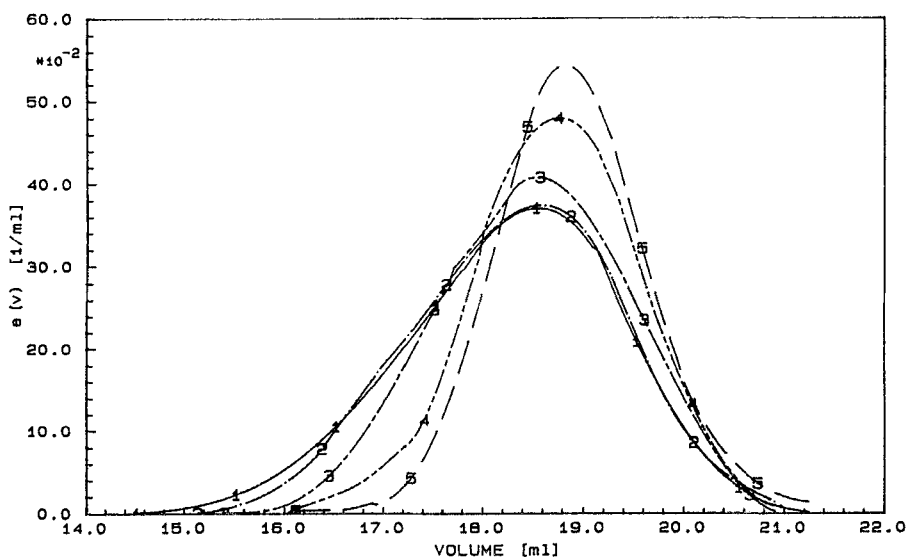
FIGURE 1. Normalized chromatograms e(v) of sample KS10
after dissolution times of 90 min. (1),
120 min. (2), 135 min. (3), 155 min. (4) and
1300 min. (5).

(eg. supermolecular aggregates, gels) and partial
clogging of the inlet frits. After a series of
experiments the following procedure for preparing
solutions from polypropylene pellets was established
and applied for all further investigations.

Polypropylene solutions are heated under nitrogen
at 170 °C for 90 min after thorough swelling (after
about 15 min. for a 30 mg pellet). The solution is
stirred gently for about five minutes before injection.
0.5 mg/ml of stabilizer Irganox 1010 or 2,6-di-tert.
butyl-4-methylphenol (BHT) is added to all samples
before dissolution to prevent oxidation. The second one

is usually preferred since it elutes later than the
first one and interferes less with the low molar mass
tail of the chromatogram. The stabilizer peak is used
as internal standard for flow rate monitoring. Sample
concentrations were in the range 0.1 mg/ml - 1.0 mg/ml.
The sample solutions were injected without prior
filtration, using 0.305 ml loop volume.

Calibration and Data Evaluation

The system was calibrated with a series of narrow
polystyrene standards in the range of peak molecular
weight M_p = 1260 to 7.7×10^7 and a broad high density
polyethylene standard SRM 1475 using the integral
calibration method (16) and the conversion procedure
proposed recently (11). Polystyrene calibration data
were converted to polypropylene by universal calibra-
tion using the following Staudinger-Mark-Houwink
constants, K = 1.75E-2 ml/g, 1.9E-2 ml/g, and a =
0.670, 0.725 for polystyrene (17) and polypropylene
(12), respectively. These calibration data were fit to
a fourth order polynominal by a least squares method.

The concentration signal S(v) was normalized with
respect to the area $e(v) = S(v) / \int S(v) \, dv$. The LALLS
signal E(v) was normalized so, that $E(v)/e(v) = M_w(v)$ and
$\int E(v) \, dv = M_w$, where $M_w(v)$ is the weight average molar
mass within the detector cell content. For the system
polypropylene/1,2,4-trichlorobenzene at 135 °C the
specific refractive index increment has been measured
(dn/dc = -0.095 ± 0.003 ml/g). During the sample run
the analog data from the IR and LALLS detectors were
collected and digitized by means of a personal computer
equipped with a commercially available analog/digital
converter device (DASCON, Keithley, USA). Computer

programs for data acquisition and interactive pro-
cessing of the SEC data including graphical selection
of baseline, integration limits and calculation of the
normalized signals e(v) and E(v) were developed and are
to be published. No resolution correction was applied
to the chromatograms.

RESULTS AND DISCUSSION

        System performance was checked by repeated runs of
different sample solutions. Using a balance as flow-
meter and the stabilizer peak as internal reference,
the precision of the flow rate was determined to be
better than 0.2%. Variations in the area of the stabi-
lizer peak were less than 1%. The ratio of peak area
over injected mass of polymer gives a good indication
for erroneous runs. The precision of this ratio was
better than ±3%. In the concentration range of 0.1 –
1.0 mg/ml no significant change in the MMD of both
polypropylene samples was observed. Averages and stand-
ard deviations of the normalized chromatograms were
calculated for each data interval. Averaged chromato-
grams and relative error (ratio of signal/standard
deviation) for each data interval are given in
Figure 2. The averaged effective calibration $M_w(v)$ of
KS10 and the corresponding error band is shown in
Figure 3. Within the center region of the chromatogram
the standard deviations of the molar masses calculated
from SEC/LALLS are in the range of about 6%. In that
region the signal-to-noise ratio of both the detectors
is better than 20. In the peripheral regions of the
distribution, particularly in the range of low molar
masses, the errors increase rapidly since a ratio of
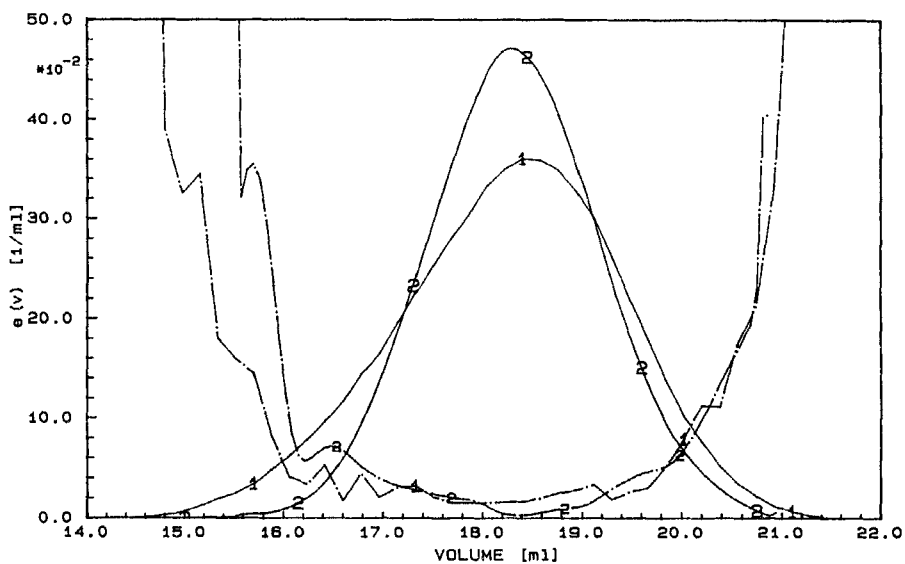signals with low signal-to-noise ratio must be

FIGURE 2. Averaged normalized chromatograms e(v) (———)
          and ratio of signal/standard deviation (–•–)
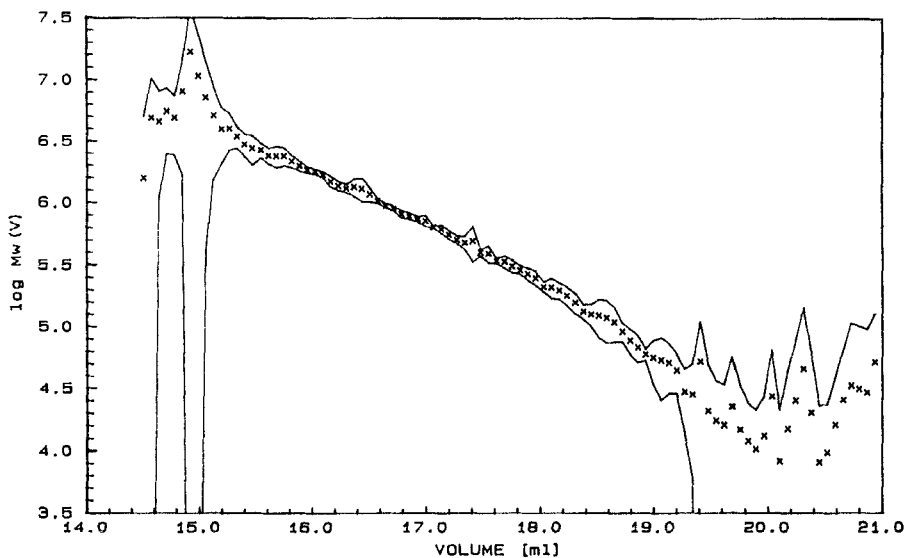   of KS10 (1) and PT55 (2).

FIGURE 3. Averaged effective calibration line $M_w(v)$ of
          KS10 (x) and corresponding standard
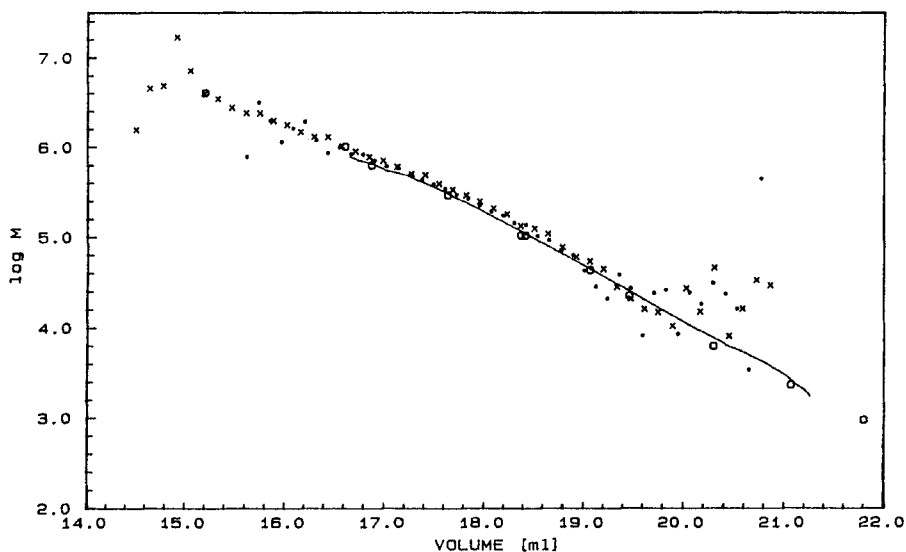   deviations (———) calculated from 6 runs.

FIGURE 4. Calibration curves for SEC of polypropylenes;
narrow polystyrene standards + universal
calibration (o), broad polyethylene SRM 1475
+ integral calibration + shift to
polypropylene (———), $M_w(v)$ of KS10 (x) and
PT55 (•)

calculated. A similar pattern of SEC/LALLS precision
has recently been proposed by a theoretical model of
the errors in SEC/LALLS (18).

Figure 4 shows calibration curves obtained from
narrow polystyrene standards by universal calibration,
from NBS 1475 HDPE utilizing the integral calibration
method and conversion to polypropylene (by factor
1.55), and the averaged effective calibration lines
$M_w(v)$ from SEC/LALLS online of KS10 and PT55. Calibra-
tion data from PS and HDPE agree quite well between

TABLE 1

Molar Mass Averages, Standard Deviations and
Polydispersities of the Polypropylene Samples KS10 and
PT55 Resulting from the Calibration Curves and from
SEC/LALLS Online

Sample	M_z	M_w	M_n	M_w/M_n
		(1000 g/mol)		
Universal calibration using PS standards				
KS 10	1360 ±14%	322 ± 3%	47 ± 8%	6.8
PT 55	522 ± 4%	205 ± 5%	59 ± 8%	3.5
SEC/LALLS online				
KS 10	1380 ± 6%	336 ± 6%	79 ±13%	4.3
PT 55	613 ±15%	221 ± 3%	78 ±13%	2.8
SEC/LALLS online combined with HDPE calibration				
KS 10	1311 ±14%	330 ± 3%	52 ± 8%	6.3
PT 55	525 ± 4%	210 ± 5%	66 ± 8%	3.2

17.5 and 19.0 ml, but in the range of 19.5 - 21.0 ml
significant deviation is found. In the central region
of the sample distribution, the $M_w(v)$-functions trom
KS10 (x in Fig.4) and PT55 (• in Fig.4) are very close
to the other calibration curves. Especially, in the low
molar mass region (v < 19 ml), molar masses from
SEC/LALLS are overestimated. Since HDPE and PP are much
more related chemically than PS and PP, the calibration
line based on HDPE was assumed to be true and finally a
modified calibration function was synthesized and fit
to a polynomial, putting the calibration data from HDPE
for the low molar mass region and parts of the $M_w(v)$-
functions (range v = 17.5-16.5 ml of KS10, v = 17-15.5
ml of PT55). A comparison of average molar masses of
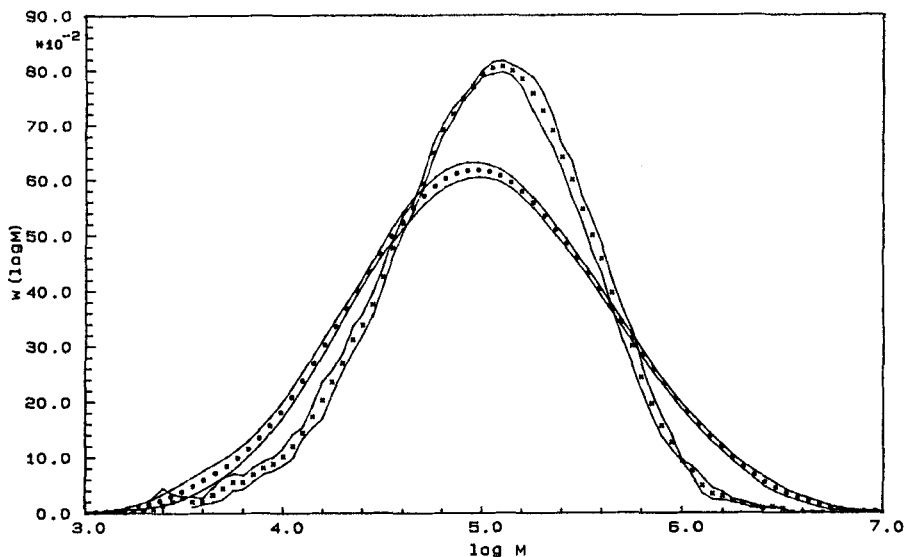the polypropylene samples calculated from SEC/LALLS

FIGURE 5. Differential molar mass distribution of KS10
(o) and PT55 (x) and the standard deviations
(——) calculated from 6 runs.

online, from universal calibration (based on poly-
styrene standards) and from the merged calibration is
summarized in Table 1. Whereas M_z and M_w coincide quite
well beween the different calibration methods, the
number average comes highest from SEC/LALLS and lowest
from polystyrene calibration. The smaller polydis-
persity from SEC/LALLS has been reported earlier and
was contributed to axial dispersion effects (19) and
this assumption was confirmed by model calculations
recently (20). The differential molar mass distri-
butions and the error bands calculated from calibration
via SEC/LALLS online combined with data from the broad
HDPE standard sample are given in Figure 5.

CONCLUSIONS

It has been shown, that polypropylene solutions can be prepared at 170 °C in nitrogen athmosphere within about 90 min. The precision of determination of the effective calibration line $M_w(v)$ from SEC with a LALLS detector online is satisfactory in the range near the maximum of the distribution function ($M = 10^5$-10^6), but in the peripheral regions of the MMD and particularly at low molar masses one better relies on a conventional calibration function. Unfortunately there is some disagreement between universal calibration based on narrow PS standards and integral calibration using a broad HDPE standard in the lower molar mass region. Therefore the determination of the molar mass distribution of polypropylene on an absolute scale requires further investigations of calibration relations and it would be desirable to develop well characterized broad polypropylene standards similar to SRM 1475 for PE.

ACKNOWLEDGEMENT

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