Determination of molar mass and radius of gyration by size exclusion chromatography with on-line viscometer and multi-angle laser light scattering. High temperature characterization of polystyrene

Věra Kašpárková and Espen Ommundsen*
Statoil Bamble, Polymer Research and Development Centre, N-3960 Stathelle, Norway

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Size exclusion chromatograph with on-line single capillary viscometer and multi-angle laser light scattering have been used for characterization of narrow polystyrene standards in 1,2,4-trichlorobenzene at 140°C. Mass-average molar mass, intrinsic viscosity and radius of gyration have been determined. From these values Mark–Houwink parameters and radius of gyration dependence on molar mass have been calculated.

(Keywords: polystyrene; 1,2,4-trichlorobenzene; light scattering; size exclusion chromatography; viscometry; radius of gyration)

Introduction

Significant attention has recently been paid to molar-mass-sensitive detectors in the development of size exclusion chromatography (s.e.c.). One of these detectors, multi-angle laser light scattering (MALLS), has greatly increased the information that can be obtained from individual s.e.c. experiments[1,2].

By connecting a MALLS detector to size exclusion chromatograph, or to a chromatograph with an on-line viscometer (s.e.c.–v.), a powerful multidetection system can be obtained, which is a new source for gaining complex information about polymers. In the triple-detector system s.e.c.–v.–MALLS, information about molar mass, molecular size distribution and viscosity properties can be obtained simultaneously[3].

The use of narrow polystyrene (PS) standards for s.e.c. calibration enables easy checking and calibration of on-line light scattering equipment. This procedure has been tested for equipment operating at ambient temperature[4,5], but the situation for high-temperature measurements has not, to the authors' knowledge, been described in the literature. To increase knowledge about the high-temperature operation of s.e.c.–v.–MALLS systems, a test on PS standards dissolved in 1,2,4-trichlorobenzene (TCB) was performed. The results are published in this short communication, because literature dealing with polymer–solvent system PS in TCB at 140°C is insufficient.

For narrow PS standards, mass-average molar mass M_w and z-average radius of gyration $\langle R_g^2 \rangle_z^{1/2}$ from light scattering were evaluated. Values of $\langle R_g^2 \rangle_z^{1/2}$ were compared with radii of gyration (R_g) calculated from s.e.c.–v. by the Flory–Fox and Ptitsyn–Eizner equation. The Mark–Houwink equation and the relation between radius of gyration and molar mass for this polymer–solvent system are given below.

Experimental

Narrow PS standards (Polymer Laboratories, USA) with molar mass range from 3.2×10^3 to 4×10^6 g mol^{-1} were tested. Values of mass-to-number average molar-mass ratio, M_w/M_n, were in the range from 1.03 to 1.06 for these polymers.

A MALLS photometer (Dawn-F, Wyatt Technology Corporation, Santa Barbara, USA), attached to a high-temperature chromatograph with on-line single capillary viscometer (model 150 CV, Waters Chromatography Division, Milford, USA), was used. The set of columns consisted of one TSK-Gel precolumn and three TSK-Gel linear columns, 7.6 × 300 mm (GMHXL-HT, Tosoh, Japan).

Measurements were performed at 140°C in TCB containing 4×10^{-4} g cm^{-3} of 2-tert-butyl-4-methylphenol as an antioxidant. Concentration of injected polymer solutions was in the range from 7.5×10^{-4} to 7.5×10^{-5} g cm^{-3}, in accordance with the molar mass of the PS sample. Flow rate was 0.975 cm^3 min^{-1} and injection volume was 0.5 cm^3.

The MALLS photometer was placed in series after the last s.e.c. column and before the viscometer and the r.i. detector. For the light-scattering measurement the following operating variables were used. The refractive index of pure TCB at 140°C, $n_0 = 1.52$ was calculated by extrapolation from the published data[6]. The optical constant of the equipment was determined[7], using the Rayleigh ratio of TCB, $R_\theta = 3.52 \times 10^{-5}$ cm^{-1}. The refractive index increment of PS in TCB at 140°C, $dn/dc = 0.052$ cm^3 g^{-1}, was measured by the Brice Phoenix Differential Refractometer BP-2000 at wavelength $\lambda_0 = 632.8$ nm.

Details of sample preparation and conventional s.e.c.–v. and/or MALLS treatment have already been given[8,9].

Data collection and processing were performed simultaneously by the Multidetection s.e.c. software written by Professor Lesec in s.e.c.–v. and by the Astra™ program from Wyatt Technology for s.e.c.–MALLS.

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* To whom correspondence should be addressed

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Results and discussion

The mass-average molar mass M_w and z-average radius of gyration $\langle R_g^2 \rangle_z^{1/2}$ from light scattering were calculated for each elution slice from the dependence of R_θ/Kc *versus* $\sin^2(\theta/2)$ (Debye plot) from the intercept and slope of this plot for $\theta = 0°$ (where K is optical constant, R_θ is excess Rayleigh ratio for angle θ, θ is scattering angle and c is concentration of polymer solution). The second virial coefficient was taken as being equal to zero for all samples. M_w and $\langle R_g^2 \rangle_z^{1/2}$ for the whole polymer were obtained by summation of the data from each elution slice. These values and peak values of the above-mentioned magnitudes are given in *Table 1*.

In the s.e.c.–v. analysis using universal calibration, the molar mass and the intrinsic viscosity $[\eta]$ are determined for each elution slice. Besides the principal molecular characteristics (M_w, M_n, $[\eta]$), radius of gyration can in this case be calculated by the Flory–Fox and Ptitsyn–Eizner equation[10,11]:

$$R_g = (1/\sqrt{6})([\eta]M/\Phi_0/(1 - 2.63\varepsilon - 2.86\varepsilon^2))^{1/3} \qquad (1)$$

where $\Phi_0 = 2.86 \times 10^{23}$ is the Flory parameter, $[\eta]$ is the intrinsic viscosity, $\varepsilon = (2a - 1)/3$ and a is the exponent in the Mark–Houwink equation. For PS in TCB at 140°C, parameter $a = 0.7$ was used (see below). Values of radii of gyration are given in *Table 1* together with intrinsic viscosity $[\eta]$ from the s.e.c.–v. measurement.

Good agreement between the mass-average molar mass evaluated by MALLS and the molar mass of PS declared by the supplier indicate that both calibration procedure and refractive index increment value were correctly chosen. In the span of molar masses from 9.2×10^3 to 4×10^6 g mol^{-1} the MALLS method yields correct values of M_w.

Intrinsic viscosity $[\eta]$ (s.e.c.–v.) and mass-average molar mass M_w (MALLS) were employed for calculation of K and a Mark–Houwink parameters (*Figure 1*). The following equation was obtained:

$$[\eta] = 1.34 \times 10^{-2} M_w^{0.7} \qquad (2)$$

Parameters of this equation are in good agreement with published values: $K = 1.21 \times 10^{-2}$ and $a = 0.707$, and $K = 1.36 \times 10^{-2}$ and $a = 0.697$, from refs 12 and 13, respectively.

The relationship between radius of gyration and molar mass can be expressed by the equation:

$$R_g \sim M^{\alpha} \qquad (3)$$

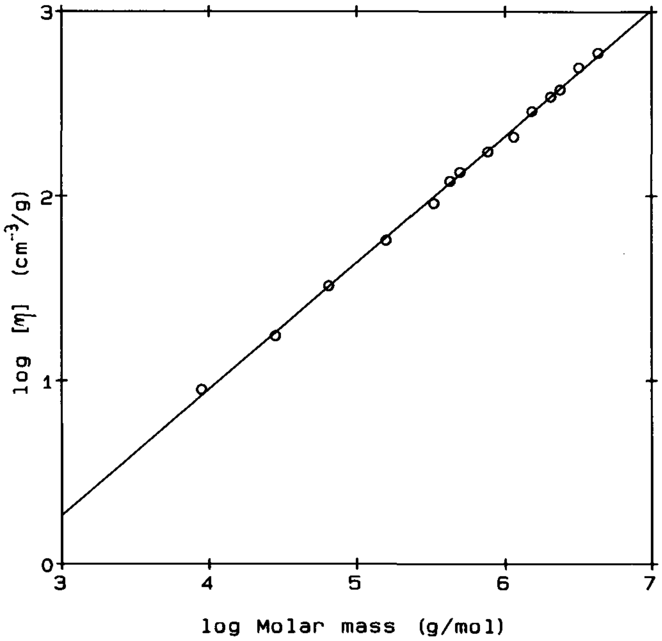

Figure 1 Mark–Houwink equation of polystyrene in TCB at 140°C

Table 1 Mass-average molar mass, intrinsic viscosity and radius of gyration of polystyrene standards determined by s.e.c.–v.–MALLS in TCB at 140°C

M^a ($\times 10^{-3}$)	$M_w{}^b$ ($\times 10^{-3}$)	$M_{w,p}{}^c$ ($\times 10^{-3}$)	$[\eta]^d$ (cm^{-3} g^{-1})	$\langle R_g \rangle_z{}^b$ (nm)	$\langle R_g \rangle_{z,p}{}^c$ (nm)	$R_g{}^e$ (nm)
3.2	–	–	4.6	–	–	1.70
9.2	9.3	8.9	8.9	–	–	2.96
28.5	26.7	28.0	17.2	–	–	5.50
66.0	66.3	65.0	32.3	–	10.0	9.00
156.0	160.0	159.0	57.9	–	19.5	14.5
330.0	333.4	334.0	90.9	26.8	28.0	21.8
435.0	444.5	429.8	119.6	31.3	31.0	26.0
514.0	519.5	504.0	135.8	32.1	31.5	28.8
770.0	779.0	771.0	172.5	38.1	37.0	35.7
1030.0	1032.0	1148.0	208.9	43.0	41.6	41.9
1570.0	1560.0	1540.0	290.8	56.3	56.6	53.9
1960.0	1970.0	2070.0	348.5	63.1	63.2	61.5
2310.0	2360.0	2410.0	382.1	70.3	69.4	67.0
3040.0	3184.0	3240.0	506.7	85.7	83.5	80.7
4000.0	4131.0	4350.0	599.1	96.9	96.5	93.6

[a] Molar mass of PS standards as given by supplier
[b] Mass-average molar mass or z-average radius of gyration evaluated by MALLS for whole polymer
[c] Peak values of mass-average molar mass or z-average radius of gyration evaluated by MALLS
[d] Intrinsic viscosity evaluated by s.e.c.–v.
[e] Radius of gyration calculated from s.e.c.–v. measurements by Flory–Fox and Ptitsyn–Eizner equation

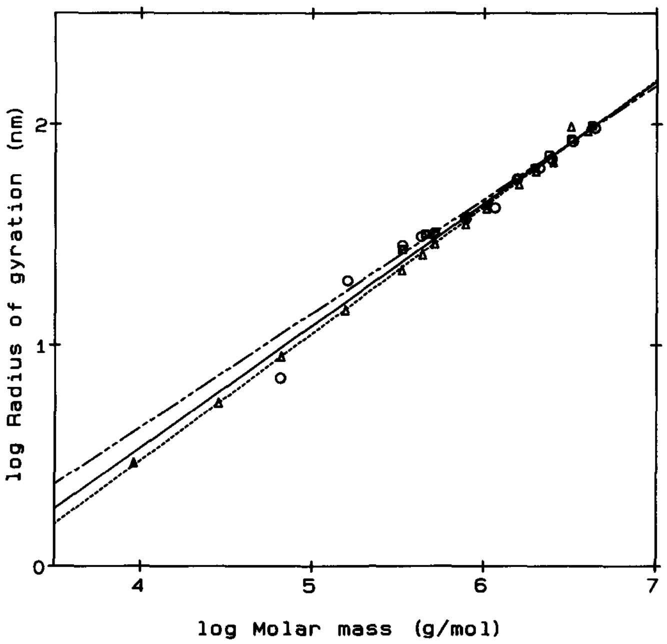

Figure 2 Dependence of radius of gyration R_g *versus* molar mass M for polystyrene in TCB at 140°C. △----, Radius of gyration calculated from s.e.c.–v. data *versus* molar mass from supplier of the samples; ○———, peak values of $\langle R_g^2\rangle_z^{1/2}$ and M_w from MALLS; □-·-·-·—, $\langle R_g^2\rangle_z^{1/2}$ and M_w from MALLS for whole polymer

Radius of gyration *versus* molar mass relationships for PS samples are plotted in *Figure 2*. Results from both MALLS and s.e.c.–v. were employed and compared as follows: (1) radius of gyration calculated from s.e.c.–v. and molar mass of PS from supplier are related giving the dependence ($R_g \sim M^{0.58}$); (2) peak values of $\langle R_g^2\rangle_z^{1/2}$ and M_w from light scattering measurements are plotted ($\langle R_g^2\rangle_z^{1/2} \sim M_w^{0.56}$); and (3) values of $\langle R_g^2\rangle_z^{1/2}$ and M_w from light scattering for whole polymers are employed ($\langle R_g^2\rangle_z^{1/2} \sim M_w^{0.52}$).

From *Figure 1* and *Table 1* it can be concluded that radii of gyration calculated from s.e.c.–v. data are consistent in the whole range of molar masses, and that equation (1) makes it possible to calculate R_g values lower than 10 nm. This value has been given as the lower size limit in the MALLS measurement of PS in ref. 1.

Radii of gyration evaluated by MALLS are higher than those calculated from s.e.c.–v., both for peak values and for the whole polymer. This is more significant for the samples with molar mass up to 5×10^5 g mol^{-1}. Better agreement for the remaining values is reached in the high-molar-mass region where all three values do not differ by more than 3.5 nm.

In the low-molar-mass region, reproducible values of $\langle R_g^2\rangle_z^{1/2}$ can be obtained from molar mass 3×10^5 g mol^{-1} for the whole polymer and 6.6×10^4 g mol^{-1} for peak values of $\langle R_g^2\rangle_{z,p}^{1/2}$. The limitations of the light scattering method in the low-molar-mass region and a partial explanation of differences between calculated R_g and measured $\langle R_g^2\rangle_z^{1/2}$ are given in ref. 2 and are not the subject of this paper.

Conclusions

The relationship between radius of gyration and molar mass has been evaluated for R_g calculated from the s.e.c.–v. and for $\langle R_g^2\rangle_z^{1/2}$ values measured by MALLS. Absolute values of M_w and $[\eta]$ were employed for calculation of the Mark–Houwink equation of narrow PS standards in TCB at 140°C. Despite the fact that the high-temperature multidetection system s.e.c.–v.–MALLS is more sophisticated and sensitive to parameters which are not critical in individual methods, preliminary results are promising. Further investigation of the multidetection system and its practical exploitation and application to polyolefins is in progress.

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References

1 Barth, H. W. and Yau, W. W. International SEC Symposium, 1989, Newton, Massachusetts
2 Yau, W. W. *Chemtracts-Macromol. Chem.* 1990, **1**, 1
3 Jackson, C., Smith, G. A., Barth, H. G. and Yau, W. W. International SEC Symposium, 1991, San Francisco, California
4 Jackson, C., Nilson, L. M. and Wyatt, P. J. *J. Appl. Polym. Sci., Appl. Polym. Symp.* 1990, **45**, 191
5 Jackson, C., Nilson, L. M. and Wyatt, P. J. *J. Appl. Polym. Sci., Appl. Polym. Symp.* 1989, **43**, 99
6 'Beilsteins Handbuch der Organischen Chemie', Berlin, 1990, Vol. 5, p. 204
7 MacRury, T. B. and McConnell, M. L. *J. Appl. Polym. Sci.* 1979, **24**, 651
8 Yau, W. W., Kirkland, J. J. and Bly, D. D. 'Modern Size-Exclusion Liquid Chromatography', Wiley, New York, 1979
9 Wyatt, P. J., Jackson, C. and Wyatt, G. K. *Am. Lab.* 1988, (June), 108
10 Fox, T. G. and Flory, P. J. *J. Am. Chem. Soc.* 1951, **73**, 1904
11 Ptitsyn, O. B. and Eizner, Yu. E. *Sov. Phys. Tech. Phys.* 1960, **4**, 1920
12 Coll, H. and Gilding, D. K. *J. Polym. Sci., A-2* 1970, **8**, 89
13 Moldovan, D. G. and Polemanakos, S. C. International SEC Symposium, 1987, Milford, Massachusetts