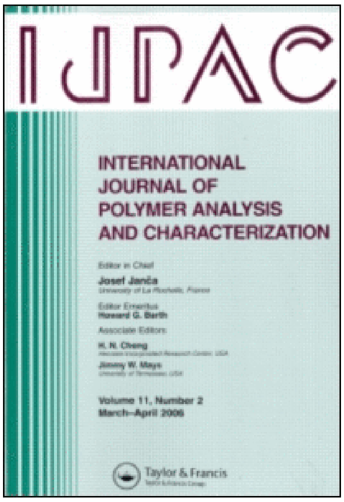

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Static Light Scattering of Polystyrene Reference Materials: Round-RobinTest

Ulrich Just[a]; Barbara Werthmann[a]
[a] Federal Institute for Materials Research and Testing (BAM), Berlin, Germany

To cite this Article Just, Ulrich and Werthmann, Barbara(1999) 'Static Light Scattering of Polystyrene Reference Materials: Round-RobinTest', International Journal of Polymer Analysis and Characterization, 5: 3, 195 — 207

To link to this Article: DOI: 10.1080/10236669908009737

URL: http://dx.doi.org/10.1080/10236669908009737

Int. J. Polym. Anal. Charact.,
1999 Vol. 5, pp. 195–207
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Static Light Scattering of Polystyrene Reference Materials: Round-Robin Test*

ULRICH JUST[†] and BARBARA WERTHMANN

Federal Institute for Materials Research and Testing (BAM),
Unter den Eichen 87, D-12200 Berlin, Germany

(Received 30 September 1998; In final form 21 January 1999)

This paper reports a round-robin test dealing with static light scattering (LS) measurements of three polystyrene standard materials with narrow distributions. Low-angle laser light scattering (LALLS) and multi-angle laser light scattering (MALLS) instruments, as well as other types of goniometers, were used. The results of the two samples with higher molar masses are in good agreement if one and the same Rayleigh ratio value was used for calibrating multi-angle instruments, and refractive indices, and refractive index increments were adjusted. The values of LS measurements for the oligomeric sample exhibited greater deviations in this test.

Keywords: Polymer characterization; Molar mass determination; Light scattering; Polymer reference material

INTRODUCTION

Most macromolecular products are chemically heterogeneous, especially copolymers, as well as nonhomogeneous with regard to their chain lengths. Since the properties of a macromolecular material strongly depend on chemical composition and chain length of the macromolecule, accurate characterization of the generated polymers are indispensable.

---

* Presented at the 11th International Symposium on Polymer Analysis and Characterization, Santa Margherita Ligure, Italy, 25–27 May 1998.

[†] Corresponding author.

The method most frequently used in determining molar mass and simultaneously molar mass distribution is size exclusion chromatography (SEC). SEC is an entropically controlled technique that separates according to the relative size or the hydrodynamic volume of a solvated macromolecule, which is dependent on the mean pore size or pore size distribution of the SEC packing. It is important to realize that SEC is a relative method that needs calibration utilizing polymer standards or reference materials. These standard materials have to be characterized using absolute methods, such as light scattering. In order to obtain more reliable data using this method, an interlaboratory test was organized by the Federal Institute for Materials Research and Testing (BAM), Berlin, Germany. Three polystyrene samples with molecular masses in the oligomeric, the mid-, and high-molecular mass ranges were chosen to determine the limits of light scattering using different instruments.

EXPERIMENTAL

Polystyrene samples A, B, and C were provided by Polymer Laboratories Ltd. (PL) (Church Stretton, Shropshire, UK). The polydispersity M_w/M_n, quoted by PL, was 1.11 for sample A; for sample B, 1.04; and for sample C, 1.05. These values were obtained by SEC measurements. For sample A, cyclohexane was used as the solvent, although participants 5 and 8 used toluene. For samples B and C, toluene was employed. The concentration range for sample A was 0.3–5%; for sample B, 0.08–0.5%; and for sample C, 0.03–0.2%. It was important to stay below the overlapping concentration of polymer coils defined as

$$c = 1/[\eta] \tag{1}$$

where $[\eta] = 0.0075 * M_w^{0.75}$ for polystyrene.[1]

The low-angle laser light scattering detector (LALLS) used was a KMX-6 (Thermo Separation Products (TSP), Darmstadt, Germany). The following multi-angle laser light scattering (MALLS) were employed: ALV-1800 and ALV-5000 (ALV-Laser, Langen, Germany); DAWN DSP (Wyatt Technology, Woldert, Germany); PL-LSD (Polymer Laboratories, Church Stretton, UK); Fica (ARL France, Le Mesnil-Saint Denis-Yveslines, France) with alterations made by SLS-Systemtechnik (Hausen i.W., Germany); Sofica (ARL France, Le Mesnil-Saint Denis-Yveslines, France). The goniometers used were ALV-SP86 and ALV-SP125 (ALV-Laser, Langen, Germany).

Round-robin participants in this study were Akzo Nobel, Obernburg; BASF AG, Ludwigshafen; Federal Institute for Materials Research and Testing (BAM), Berlin; Hoechst AG, Frankfurt; Martin-Luther-Universität (MLU), Halle-Wittenberg; Polymer Laboratories Ltd (PL), Church Stretton, Shropshire, UK; Polymer Standards Service GmbH (PSS), Mainz; Röhm GmbH Chemische Fabrik, Darmstadt; Schering AG, Berlin; Universität Essen, Essen; Johannes-Gutenberg-Universität, Mainz; Wyatt Technology Deutschland GmbH, Woldert.

RESULTS

Using light scattering, molar mass M_w and simultaneously the second virial coefficient A_2 can be determined via the basic equation

$$K * c/R_\theta = 1/M_w + 2A_2 * c \tag{2}$$

where K is the optical constant of the light scattering instrument, c the concentration of the polymer solution, and R_θ the difference of Rayleigh ratios of the polymer solution and the solvent. The physical constant K is given by

$$K = 4\pi^2(\mathrm{d}n/\mathrm{d}c)^2 n^2/(N_a\lambda^4) \tag{3}$$

where n is the refractive index of the solvent, N_a is Avogadro's number, λ the wavelength of the incident light in vacuum, and $\mathrm{d}n/\mathrm{d}c$ is the refractive index increment of the solution. With MALLS instruments, the mean-square-radius of gyration R_g^2 can be calculated also. The results are summarized in Tables I–VI.

Table I shows the results of light scattering measurements of polystyrene sample A in cyclohexane. Only participants 5 and 8 used toluene as the solvent. The mean value of molar mass M_w was 1,210 (std. dev. 9%). The mean value of molar mass M_w for sample B was 293,000 (std. dev. 6.1%), and for sample C, the mean value of M_w was 3,060,000 (std. dev. 8.5%) (Tables III and V).

TABLE I Light scattering results of polystyrene sample A (Solvent: cyclohexane, participants 5 and 8 used toluene.)

Participant	*Instrument*	*Wavelength* (nm)	*RI* (*n*)	d*n*/dc (ml/g)	*Rayleigh-ratio* *R* (E–6)	M_w (g/mol)	A_2 (mol * ml/g^2)
1	PL-LSD	633	1.4260	0.1521	14.02	1080	0.000118
2	DAWN DSP	633	1.4260	0.1521	14.06	1180	−0.0153
3	DAWN DSP	633	1.4260	0.1521	14.06	1320	0.00044
4	Sofica	633	1.4260	0.1521	13.00	1290	0.00276
5	KMX-6	633	1.4898 (Tol.)	0.1100 (Tol.)	11.40	1100	0.019
7	DAWN DSP	488	1.4288	0.1612	39.75	1230	0.000798
8	DAWN DSP	488	1.5053 (Tol.)	0.0890 (Tol.)	39.75	1130	0.0016
9	KMX-6	633	1.4260	0.1521	5.25 (c-hex.)	1180	0.0039
10	KMX-6	633	1.4260	0.1521	4.30 (c-hex.)	1150	0.0158
11	KMX-6	633	1.4260	0.1521	5.30 (c-hex.)	1470	0.002
12	ALV-SP86	647	1.4260	0.1521	12.70	1190	0.000164
12	ALV-SP 125	514	1.4260	0.1521	31.90	1200	−0.00005
12	ALV-1800	514	1.4260	0.1521	31.90	1250	0.00000012
Mean						**1210**	
Std. dev.						**104 (9%)**	

TABLE II Recalculated light scattering results of polystyrene sample A (Solvent: cyclohexane, participants 5 and 8 used toluene.)

Participant	*Instrument*	*Wavelength* (nm)	*RI* (*n*)	d*n*/d*c* (ml/g)	*Rayleigh-ratio* *R* (E−6)	M_w (g/mol)	A_2 (mol * ml/g^2)
1	PL-LSD	633	1.4260	0.1521	14.06	1080	0.000118
2	DAWN DSP	633	1.4260	0.1521	14.06	1180	−0.0153
3	DAWN DSP	633	1.4260	0.1521	14.06	1320	0.00044
4	Sofica	633	1.4260	0.1521	**14.06**	**1390**	0.00276
5	KMX-6	633	1.4898 (Tol.)	**0.0920** (Tol.)	11.40	**1570**	0.019
7	DAWN DSP	488	1.4288	0.1612	**42.91**	**1330**	0.000798
8	DAWN DSP	488	1.5053 (Tol.)	**0.0940** (Tol.)	**42.91**	**1090**	0.0016
9	KMX-6	633	1.4260	0.1521	5.25 (c-hex.)	1180	0.0039
10	KMX-6	633	1.4260	0.1521	4.30 (c-hex.)	1150	0.0158
11	KMX-6	633	1.4260	0.1521	5.30 (c-hex.)	1470	0.002
12	ALV-SP86	647	1.4260	**0.1515**	**12.88**	**1220**	0.000164
12	ALV-SP 125	514	**1.4280**	**0.1590**	**32.35**	**1110**	−0.00005
12	ALV-1800	514	**1.4280**	**0.1590**	**32.35**	**1160**	0.00000012
Mean						**1250**	
Std. dev.						**154** (12%)	

TABLE III Light scattering results of polystyrene sample B (Solvent: tolune.)

Participant	*Instrument*	*Wavelength* (nm)	*RI* (*n*)	d*n*/dc (ml/g)	*Rayleigh-ratio* *R* (E−6)	M_w (g/mol)	$A_2 * 10^4$ (mol * ml/g^2)	R_g (nm)
1	PL-LSD	633	1.4898	0.1096	14.02	311,000	3.58	21
2	DAWN DSP	633	1.4898	0.1096	14.06	300,000	5.73	20
3	DAWN DSP	633	1.4898	0.1096	14.06	318,000	4.41	25
4	Sofica	633	1.4898	0.1096	13.00	282,000	7.66	18
4	KMX-6	633	1.4898	0.1096	12.97	280,000	—	—
5	Fica	633	1.4898	0.1096	13.00	266,000	5.40	14
5	KMX-6	633	1.4898	0.1100	15.80	294,000	4.41	—
6	ALV-5000	532	1.4960	0.1100	27.16	279,000	5.13	22
7	DAWN DSP	488	1.5053	0.1120	39.75	265,000	5.18	21
8	DAWN DSP	488	1.5053	0.1040	39.75	307,000	4.22	25
9	KMX-6	633	1.4898	0.1096	14.60	310,000	3.58	—
10	KMX-6	633	1.4898	0.1096	9.70	263,000	6.80	—
11	KMX-6	633	1.4898	0.1096	14.40	304,000	4.90	—
12	ALV-SP86	647	1.4960	0.1096	12.70	307,000	4.30	19
12	ALV-SP125	514	1.4960	0.1096	31.90	297,000	4.50	22
12	ALV-1800	514	1.4960	0.1096	31.90	299,000	4.70	21
Mean						**293,000**	**4.97 E−4**	**21**
Std. dev.						**18,000 (6.1%)**	**1 E−4**	**3**

TABLE IV Recalculated light scattering results of polystyrene sample B (Solvent: toluene.)

Participant	*Instrument*	*Wavelength* (nm)	*RI* (*n*)	d*n*/dc (ml/g)	*Rayleigh-ratio* *R* (E−6)	M_w (g/mol)	$A_2 * 10^4$ (mol * ml/g^2)	R_g (nm)
1	PL-LSD	633	1.4898	0.1096	**14.06**	**312,000**	3.58	21
2	DAWN DSP	633	1.4898	0.1096	14.06	300,000	5.73	20
3	DAWN DSP	633	1.4898	0.1096	14.06	318,000	4.41	25
4	Sofica	633	1.4898	0.1096	**14.06**	**305,000**	7.66	18
5	Fica	633	1.4898	0.1096	**14.06**	**288,000**	5.40	14
5	KMX-6	633	1.4898	0.1096	**42.91**	**292,000**	4.22	—
6	ALV-5000	532	**1.5010**	**0.1103**	15.80	**296,000**	4.41	22
7	DAWN DSP	488	1.5053	**0.1107**	28.18	**293,000**	5.13	21
8	DAWN DSP	488	1.5053	0.1107	**42.91**	**293,000**	5.18	25
9	KMX-6	633	1.4898	0.1096	14.60	310,000	3.58	—
11	KMX-6	633	1.4898	0.1096	14.40	304,000	4.90	—
12	ALV-SP86	647	**1.4880**	**0.1095**	**12.88**	**314,000**	4.30	19
12	ALV-SP125	514	**1.5030**	**0.1105**	**32.35**	**295,000**	4.50	22
12	ALV-1800	514	**1.5030**	**0.1105**	**32.35**	**294,000**	4.70	21
Mean						**301,000**	**4.8 E−4**	**21**
Std. dev.						**9,500 (3.2%)**	**1 E−4**	**3**

TABLE V Light scattering results of polystyrene sample C (Solvent: toluene.)

Participant	*Instrument*	*Wavelength* (nm)	*RI* (*n*)	d*n*/d*c* (ml/g)	*Rayleigh-ratio* *R* (E-6)	M_w (g/mol)	$A_2 * 10^4$ (mol * ml/g^2)	R_g (nm)
1	PL-LSD	633	1.4898	0.1065	14.02	3,420,000	2.08	89
2	DAWN DSP	633	1.4898	0.1065	14.06	3,280,000	2.43	97
3	DAWN DSP	633	1.4898	0.1065	14.06	3,404,000	2.53	102
4	KMX-6	633	1.4898	0.1065	12.60	2,860,000	3.70	—
5	KMX-6	633	1.4898	0.1100	16.20	3,063,000	2.18	—
5	Fica	633	1.4898	0.1100	13.00	3,020,000	2.51	105
6	ALV-5000	532	1.4960	0.1080	27.16	2,405,000	2.01	69
7	DAWN DSP	488	1.5053	0.1120	39.75	2,810,000	2.97	97
8	DAWN DSP	488	1.5053	0.1040	39.75	3,168,000	1.71	75
9	KMX-6	633	1.4898	0.1065	14.60	3,181,000	2.45	—
10	KMX-6	633	1.4898	0.1065	9.20	2,950,000	2.70	—
11	KMX-6	633	1.4898	0.1065	14.10	3,323,000	1.98	—
12	ALV-SP86	647	1.4960	0.1096	12.70	3,080,000	2.00	81
12	ALV-SP125	514	1.4960	0.1096	31.90	3,050,000	2.10	81
12	ALV-1800	514	1.4960	0.1096	31.90	2,910,000	2.20	79
Mean						**3,060,000**	**2.37 E−4**	**88**
Std. dev.						**260,000 (8.5%)**	**0.49 E−4**	**12**

TABLE VI Recalculated light scattering results of polystyrene sample C (Solvent: toluene.)

Participant	*Instrument*	*Wavelength* (nm)	*RI* (*n*)	d*n*/dc (ml/g)	*Rayleigh-ratio* *R* (E−6)	M_w (g/mol)	$A_2 * 10^4$ (mol * ml/g^2)	R_g (nm)
1	PL-LSD	633	1.4898	0.1065	**14.06**	**3,430,000**	2.08	89
2	DAWN DSP	633	1.4898	0.1065	14.06	3,280,000	2.43	97
3	DAWN DSP	633	1.4898	0.1065	14.06	3,400,000	2.53	102
5	KMX-6	633	1.4898	**0.1065**	16.20	**3,270,000**	2.18	—
5	Fica	633	1.4898	**0.1065**	**14.06**	**3,480,000**	2.51	105
7	DAWN DSP	488	1.5053	**0.1075**	**42.91**	**3,290,000**	2.97	97
8	DAWN DSP	488	1.5053	**0.1075**	**42.91**	**3,200,000**	1.71	75
9	KMX-6	633	1.4898	0.1065	14.60	3,180,000	2.45	—
11	KMX-6	633	1.4898	0.1065	14.10	3,320,000	1.98	—
12	ALV-SP86	647	**1.4880**	**0.1063**	**12.88**	**3,360,000**	2.00	81
12	ALV-SP125	514	**1.5030**	**0.1073**	**32.35**	**3,050,000**	2.10	81
12	ALV-1800	514	**1.5030**	**0.1073**	**32.35**	**3,200,000**	2.20	79
Mean						**3,290,000**	**2.30 E−4**	**90**
Std. dev.						**120,000 (3.6%)**	**0.37 E−4**	**11**

The mean values for the second virial coefficient A_2 were not calculated in the case of sample A because of the broad scattering of values. For sample B, the mean A_2 value was about $5.0 * 10^{-4}$ mol * ml/g^2 (Table III), and the value for sample C was $2.4 * 10^{-4}$ mol * ml/g^2 (Table V). The mean A_2 values of these measurements were in good agreement with those calculated using the equation for PS in toluene:[2]

$$A_2 = 1.25 * 10^{-2} * M_w^{0.272}. \tag{4}$$

A_2 calculated for sample B was $4.1 * 10^{-4}$, and for sample C, $2.2 * 10^{-4}$ mol * ml/g^2. Using the recalculated M_w values, as will be explained below, the corrected A_2 values of samples B and C were $4.0 * 10^{-4}$ and $2.1 * 10^{-4}$ mol * ml/g^2, respectively (Tables IV and VI).

The radii of gyration R_g could only be measured with MALLS instruments and the goniometers. For sample B the mean R_g value was 21 nm (Table III), and for sample C, it was 88 nm (Table V). The second recalculation of sample B gave 90 nm (Table VI). These values were nearly identical with values calculated for PS in toluene using[2]

$$R_g = 1.37 * 10^{-2} * M_w^{0.586}. \tag{5}$$

Using Equation (5), we obtain $R_g = 21$ nm for sample B, and 88 nm for sample C, and $R_g = 22$ and 90 nm for sample B and C, respectively, with the recalculated M_w values.

A second evaluation or recalculation of molar mass M_w was done with each sample taking into account corrections of some values. The refractive index and refractive index increment values measured at 633 nm and 25°C for sample A in cyclohexane ($n = 1.426$, $dn/dc = 0.1521$), for sample B in toluene ($n = 1.4898$, $dn/dc = 0.1096$), and for sample C in toluene ($n = 1.4898$, $dn/dc = 0.1065$) had been given to all participants. Some participants, however, used these values with their light scattering photometers equipped with lasers emitting light at other wavelengths. Furthermore, different Rayleigh ratio values were used for calibrating the MALLS instruments and goniometers with toluene. Therefore, the values of n, dn/dc and R were made consistent, and the results were recalculated using the new values of these parameters.

In Tables II, IV, and VI, the values of n, dn/dc, and R used for recalculation of molar mass M_w for the three polystyrenes are shown. All corrections and changes are printed in bold type. Some explanations how the corrections were done are made as follows. For example, the refractive index measurement of cyclohexane had been made at 633 nm and 25 °C with the result of $n = 1.426$ as mentioned above and also at 488 nm with $n = 1.4288$. Therefore, the refractive index value at 514 nm (participant 12) was interpolated and changed from $n = 1.426$ (the value that was given to all participants, valid for the laser light wavelength of 633 nm) to $n = 1.428$.

In a similar way, corrections were done with some values of the refractive index increments used in Table I. For example, with sample A the corrected dn/dc values at 647 and 514 nm (with participant 12) were obtained by means of a plot of dn/dc values (measured at 633 and 488 nm in cyclohexane) versus $1/\lambda^2$. Furthermore, the dn/dc value of 0.11 ml/g (participant 5), which is valid for sample B, was changed into 0.092 ml/g, measured in toluene at 633 nm and 25°C. With participant 8, the dn/dc value was changed to 0.094 ml/g. Likewise, corrections were made for the refractive index values of toluene and the dn/dc values for sample B and C as shown in Tables III and VI.

The next step was adjusting the values of Rayleigh ratios R. The R values with participants 9–11 in Table I had been determined in cyclohexane and had only been measured with LALLS, all other values correspond to toluene as the solvent. Some participants used $13.0 * 10^{-6}$ 1/cm as the Rayleigh ratio value used for calibrating MALLS instruments with toluene at 633 nm, others applied $13.1 * 10^{-6}$, $13.47 * 10^{-6}$ or $13.865 * 10^{-6}$ 1/cm. Since molar mass is directly proportional to the Rayleigh ratio, a unified value was used to recalculate the molar mass results of the round-robin test. At 633 nm the Rayleigh ratio value of $R = 14.06 * 10^{-6}$ 1/cm for toluene was chosen because this value is most frequently used in the literature.[3]

To calculate R for different wavelengths of laser light, the following equation was used:

$$R_i/R_j \approx (\lambda_j/\lambda_i)^4, \qquad (6)$$

and the corresponding values $R = 12.88 * 10^{-6}$ 1/cm at 647 nm, $32.35 * 10^{-6}$ 1/cm at 514 nm, and $42.91 * 10^{-6}$ 1/cm at 488 nm were obtained.

Usually Zimm plots were made by the participants with the exception of participant 12 who utilized a Berry extrapolation for sample C. Participant 7 used Zimm and Berry; the molar mass results by means of the Zimm evaluation were 3% higher than by Berry extrapolation in the case of sample B and 5% higher with sample C. The tables show the higher values from the Zimm plots for participant 7.

As can be seen in Table III, sample B was recalculated without the result of participant 10 because of a too low Rayleigh ratio value ($R = 9.7 * 10^{-6}$ 1/cm). Sample C was recalculated without the values of participants 4 and 10 for the same reason, and also without the value of participant 6 because it deviates strongly from the other results of molar mass M_w (Table V). The recalculated mean values of molar mass for samples B and C ($M_w = 301{,}000$ and 3,290,000 g/mol) showed 3% and 7% higher values compared to the mean of the uncorrected results reported by the participants. The recalculated standard deviations of the mean molar mass values decreased from 6% to 3% for sample B and from 9% to 4% for sample C. Thus, using consistent n and dn/dc values and especially unified Rayleigh ratio values the accuracy of light scattering measurements is increased. The values of molar masses of the oligomeric sample A (Table I) showed greater deviations in this round-robin test. For this low-molar mass sample, other methods beside light scattering should be considered, for example, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS), vapor pressure osmometry (VPO), or supercritical fluid chromatography (SFC).

CONCLUSION

Accurate characterization of polymer reference materials must be performed since SEC is a relative method and needs to be calibrated using well-characterized standard materials. SEC results cannot be better than its calibration standards. Light scattering is a valuable technique for absolute determinations of molar masses of polymer reference materials, which is well known.

The M_w values of the three polystyrenes used in this round-robin test did not show any significant dependencies on instruments, cell geometries, or wavelengths of laser light; however, refractive index increment values (dn/dc) must be determined carefully. With LALLS instruments, better agreement of results were obtained if the Rayleigh ratio R for toluene at 633 nm was determined using $14 * 10^{-6}$ 1/cm, as expected with these instruments. If the R results differ significantly, the instrument (e.g., optical alignment) and the solvent (solvent grade, filtration) must be checked.

Solvents should be filtered with a fine filter, especially for calibrating MALLS instruments. With MALLS equipment and goniometers, molar mass values can only be compared if the same Rayleigh ratio R at the same wavelength of laser light is used. The most widely reported value for toluene at 633 nm and 25°C is $14.06 * 10^{-6}$ 1/cm. It would be desirable if the suppliers of polymer standards would use identical Rayleigh ratios in dependence of different wavelengths of laser light for calibrating their MALLS instruments. In any case, the value of the Rayleigh ratio used in light scattering measurements of polymer standard materials should be mentioned in the certificates. SEC results would depend on absolute measurements and unequivocal declarations of measurements of polymer reference materials.

References

[1] J. Brandrup and E.H. Immergut (Eds.) (1989). *Polymer Handbook*, 3rd edn., VII/15 (John Wiley & Sons, New York).
[2] W. Yunan, X. Zhongde, J. Li, W.M. Rosenblum and J.M. Mays (1993). *J. Appl. Polym. Sci.*, **49**, 967.
[3] W. Kaye and J.B. McDaniel (1974). *Appl. Opt.*, **13**, 1934.