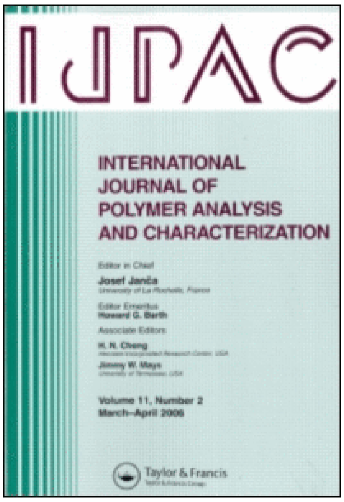


International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Round Robin Test on the Molecular Characterization of Epoxy Resins by Liquid Chromatography

Stepan Podzimek[a]
[a] SYNPO, Pardubice, Czech Republic

To cite this Article Podzimek, Stepan(2004) 'Round Robin Test on the Molecular Characterization of Epoxy Resins by Liquid Chromatography', International Journal of Polymer Analysis and Characterization, 9: 5, 305 — 316

To link to this Article: DOI: 10.1080/10236660490935718

URL: http://dx.doi.org/10.1080/10236660490935718

International Journal of Polymer Anal. Charact., 9: 305–316, 2005

ISSN: 1023-666X print
DOI: 10.1080/10236660490935718

Round Robin Test on the Molecular Characterization of Epoxy Resins by Liquid Chromatography

Stepan Podzimek
SYNPO, Pardubice, Czech Republic

This paper reports results acquired during the IUPAC Project No. 1999-021-1-400 Round Robin Test on the Molecular Characterization of Epoxy Resins by Liquid Chromatography. The results obtained by size exclusion chromatography (SEC) with column calibration are compared with those determined by SEC combined with a light scattering or a viscometric detector and absolute methods of molar mass determination. The influence of SEC experimental conditions on the obtained results is studied.

INTRODUCTION

The great importance of epoxy resins stems from their wide range of applications in many industrial areas. However, only relatively primitive analytical tests are commonly used for routine characterization of epoxy resins. The simple tests are often unable to discriminate among different samples, to find structure versus properties relations, and to evaluate production reproducibility. Molar mass distribution of epoxy resins affects their application properties and can be also used as a sensitive measure of the reproducibility of production. The main objectives of the IUPAC round robin test on the molecular characterization of epoxy resins by liquid chromatography were: (i) to study influence of the

---

The IUPAC support of this project is gratefully acknowledged. Batch MALS and some SEC-MALS measurements of epoxy resins were carried out during the author's stay as visiting scientist with Wyatt Technology Corporation (Santa Barbara, Calif., USA). The author is grateful to Dr. Philip Wyatt, CEO of Wyatt Technology Corporation, for making the stay possible.

Address correspondence to Stepan Podzimek, SYNPO, 53207 Pardubice, Czech Republic.

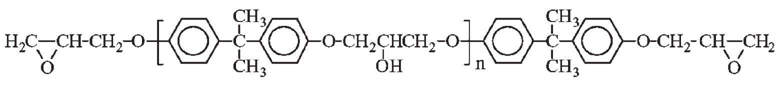
experimental conditions, in particular the type and number of columns and column calibration, on the molar mass averages obtained by size exclusion chromatography (SEC); (ii) to determine attainable reproducibility of SEC results generated in different laboratories, and (iii) to compare SEC molar mass averages with those determined by the absolute methods. Since epoxy resins are typical examples of oligomers, most of the conclusions may be generally applicable to the analysis of other oligomers.

CHARACTERIZATION OF EPOXY RESINS

Two commercially available epoxy resins based on bisphenol A (2,2-bis(4-hydroxyphenyl)propane) (see Scheme 1) of different molar mass distributions were selected for the round robin test. The samples were characterized by vapor pressure osmometry (VPO), method of end groups (EG), multi-angle light scattering (MALS) in batch mode, and matrix-assisted laser desorption ionization mass spectroscopy (MALDI-MS) to allow comparison of chromatographic results with the data from the absolute methods of molar mass determination.

Vapor pressure osmometer Model 233100 (Wescan Instruments) with tetrahydrofuran (THF) as a solvent was calibrated by octaacetyl sucrose. The epoxy equivalent was determined by the titration of resin solutions containing tetraethyl ammonium bromide with perchloric acid according to the ISO 3001 standard. DAWN EOS (Wyatt Technology Corporation) operating at 690 nm was used for the MALS measurements in batch mode. Samples were measured at five different concentrations in THF. The MALS photometer was calibrated by toluene using the Rayleigh ratio of $9.78 \times 10^{-6}\,\text{cm}^{-1}$ and normalized by computing normalization coefficients for each angle using polystyrene with molar mass of 30,000 g/mol. MALDI-MS measurements were performed with a Kompact SEQ (Kratos Analytical, Shimadzu) equipped with a nitrogen laser (337 nm) in a linear mode. The accelerating voltage was 20 kV, and the matrix was 2,5-dihydroxy benzoic acid (DHB)/2-(4-hydroxyphenylazo) benzoic acid (HABA) (sample EP1), HABA (sample EP2).

The number-average (M_n) and weight-average (M_w) molar masses obtained by the particular methods are listed in Table I.



SCHEME 1

TABLE I Characteristics of epoxy resins used for RRT

	M_n (g/mol)			M_w (g/mol)	
Sample	VPO[a]	EG[b]	MALDI-MS	MALS	MALDI-MS
EP 1	1,490	1,500	1,820	3,480	2,320
EP 2	2,780	4,370	2,530	8,330	2,950

[a] Average from two measurements with four-year time distance (specific data: 1470, 1500; 2710, 2850).

[b] Average from two measurements with four-year time distance (specific data: 1530, 1470; 4440, 4300).

SEC EXPERIMENTAL CONDITIONS EMPLOYED BY PARTICIPANTS

The participants in the project are listed in the Appendix. They worked under freely chosen experimental conditions. Some of the participants used more column sets or types of detection. Most of the participants used THF as the mobile phase (participants 6 and 14 with the addition of 1% acetic acid). Flow rate was set to the following values: 0.4 mL/min (participant 5), 0.5 mL/min (13), 0.7 mL/min (14), 0.8 mL/min (11, 12), 0.85 mL/min (9), and 1 mL/min (1–4, 6–8, 10, 15, and 16). The column

TABLE II Molar mass range for the columns used for RRT (manufacturers' data)

Designation	Molar mass range (g/mol)
PLgel 100 Å	Up to 4,000
PLgel 500 Å	500–30,000
PLgel 1000 Å	500–60,000
Styragel HR 2	500–20,000
Styragel HR 3	500–30,000
Styragel HR 4E	50–100,000
Styragel HR 5E	$2{,}000\text{–}4 \times 10^6$
PLgel Mixed-E	Up to 30,000
PLgel Mixed-D	200–400,000
PLgel Mixed-C	$200\text{–}2 \times 10^6$
PLgel Mixed-B	$500\text{–}10^7$
PLgel Mixed-A	2,000–40,000,000
TOSOH TSKgel GMH$_{HR}$-H	Up to 4×10^8

TABLE III Summary of results obtained by conventional SEC with PS calibration

	EP 1		EP 2					
Participant	M_n (g/mol)	M_w (g/mol)	M_n (g/mol)	M_w (g/mol)	Columns	Standards: MM range (g/mol)	Injection	Detection
1	2,180	5,480	4,350	13,220	2 × Styragel HR 5E	16: 1,050–4.34 M	50 µL 0.25%	RI
1	1,940	5,160	4,280	12,690	2 × PLgel Mixed-E	11: 266–34.5 K	20 µL 1%	RI
2	2,050	5,370	4,570	12,840	1 × PLgel Mixed-E	11: 266–19 K	25 µL 1%	RI
2	1,980	5,160	4,440	12,310	2 × PLgel Mixed-E	11: 266–19 K	50 µL 1%	RI
3	1,640	5,260	4,330	12,780	2 × Styragel HR 4E	13: 480–350 K	100 µL 0.15%	RI
4	1,360	3,630	2,810	9,790	2 × TOSOH GMH$_{HR}$-H	14: 500–4.48 M	50 µL 0.13 %	RI
4	1,310	3,580	2,720	9,810	2 × TOSOH GMH$_{HR}$-H	14: 500–4.48 M	50 µL 0.13%	UV 254 nm
5	1,800	4,920	3,890	11,760	2 × PLgel MiniMixed-E	9: 162–22 K	20 µL 1%	RI
6	2,050	5,440	4,500	13,320	3 × PLgel Mixed-C	NR[a]: 162–3 M	150 µL 0.3%	RI
7	1,920	5,250	3,610	11,910	Styragel HR 0.5 + HR 1 + HR 3	9: 162–21 K	50 µL 0.2%	RI
8	1,830	4,940	3,990	12,080	PLgel 100 Å + 500 Å + 1000 Å	5: 1,060–28.5 K	50 µL 1%	RI

9	2,040	5,240	4,280	12,760	PLgel Mixed-E + 10^3 Å + 500 Å + 100 Å	10: 92–37 K	50 µL 1%	RI
9	1,910	4,980	3,950	12,420	PLgel Mixed-E + 10^3 Å + 500 Å + 100 Å	10: 92–37 K	50 µL 1%	UV 260 nm
10	1,750	5,230	4,260	14,190	3 × PLgel Mixed-D	7: 162–30.3 K	100 µL 1%	UV 254 nm
11	1,640	5,090	4,010	12,710	Styragel HR 2 + HR 3	10: 600–63 K	200 µL 0.7%/0.5%	RI
11	1,530	5,020	3,770	12,810	Styragel HR 2 + HR 3	10: 600–63 K	200 µL 0.7%/0.5%	UV 262 nm
12	1,620	4,760	3,530	12,300	PLgel Mixed-C + Mixed-D + Mixed-E	8: 266–113 K	100 µL 0.1%	RI
13	2,380	5,590	4,710	13,560	2 × PLgel Mixed-B	8: 7,530–2.7 M	100 µL 0.43 % / 0.28 %	RI
14	1,610	4,800	3,830	12,100	2 × PLgel Mixed-D	NR[a]: 580–629.5 K	50 µL 0.8%	RI
15	1,570	4,600	3,300	11,970	PSS SDV 500 Å + 10^3 Å + 10^4 Å	20: 1,620–2.57 M	100 µL 0.5%	RI
16	1,240	5,460	3,980	13,900	2 × PLgel Mixed-C + Chrompack 100 Å	12: 410–1.987 M	20 µL 0.64%/0.45%	RI

[a] = not reported.

temperature ranged from ambient to 50°C; five participants measured it at 40°C. The participants employed various SEC columns of different separation ranges. In order to facilitate the evaluation and comparison of results obtained using different SEC columns, Table II lists molar mass separation ranges as stated by the column manufacturers. The columns were calibrated by polystyrene (PS) standards (their number and molar mass range are reported in Table III). A participant not reported in Table III used N-methyl-2-pyrrolidone (NMP) as a solvent at a flow rate of 0.5 mL/min and calibration by either PS or polysaccharide standards.

RESULTS AND DISCUSSION

The discrepancies of some results obtained by EG and MALDI-MS (see Table I) can be explained by chain end defects in the case of EG and high-mass discrimination in the case of MALDI-MS. Based on the limitations of particular methods the VPO and MALS data can be considered as the true molar mass averages determined by absolute methods.

The results obtained by conventional SEC using calibration by PS standards are summarized in Table III together with relevant experimental conditions. The results obtained by SEC coupled either to a light scattering photometer or a viscometer are reported in Table IV. Table IV also lists the values of specific refractive index increment (*dn*/*dc*) that is needed for the calculation of molar mass from SEC-MALS data. The *dn*/*dc* values used by the participants are consistent and close to the previously reported values[1]. Tables V and VI show the results statistics. The results obtained with NMP (Table VII) illustrate great dependence of SEC results on mobile phase and type of standards used for column calibration.

The number and type of SEC columns have relatively little effect on the obtained results. The data reported by participant 1 can serve as an example. No significant difference was obtained in this case even though the Styragel HR 5E columns might be expected to be of poor resolution in the oligomeric region (see Table II). However, the experimental calibration curve for this column proved that separation was adequate down to molar mass of a few hundreds. Anyway, the use of TOSOH GMH$_{HR}$-H ultrahigh molar mass columns (Table III, participant 4) most likely resulted in the perceptibly lower molar mass averages compared with the values obtained by the most of the participants.

No evident effect of the concentration and volume of injected solutions suggests that these parameters have markedly lower effect in the oligomeric region compared with the higher molar mass polymers. Within the reported range the column temperature and flow rate are insignificant. There is no significant difference among the molar mass

TABLE IV Results obtained by SEC with molar mass sensitive detectors

	EP 1		EP 2					
Participant	M_n (g/mol)	M_w (g/mol)	M_n (g/mol)	M_w (g/mol)	Columns	Injection	Detection	dn/dc (mL/g) EP1/EP2
1[a]	1,470	3,370	3,250	8,140	2 × PLgel Mixed-C	100 µL 2%/1%	MALS 3-angle	0.178/0.183
1[b]	1,570	3,370	3,400	8,090	MZ 100 Å, 10^4 Å	100 µL 3%/2.5%	MALS 18-angle	0.178/0.183
4	1,810	3,370	3,270	8,060	2 × TOSOH GMH$_{HR}$-H	90 µL 2.5%	MALS 18-angle	0.181/0.185[c]
9	2,510	3,980	4,700	8,420	PLgel 10^5, 10^3, 100 Å	100 µL 0.8%	MALS 18-angle	0.175/0.184
9	2,410	4,030	4,360	8,420	PLgel Mixed-E, 10^3, 500, 100 Å	100 µL 4.6%	MALS 18-angle	0.175/0.184
11	1,120	3,820	2,300	8,840	Styragel HR 2 + HR 3	200 µL 0.7%/0.5%	Viscometer	—
13	2,770	4,090	3,930	9,120	2 × PLgel Mixed-B	100 µL 0.43%/0.28%	MALS 18-angle	0.186 ± 0.005[d]
13	2,030	3,640	4,080	8,060	2 × PLgel Mixed-B	100 µL 0.43%/0.28%	Viscometer	—
14	1,500	2,900	3,000	7,400	2 × PLgel Mixed-D	50 µL 0.8%	RALS[e]	0.177/0.183[e]
14	1,150	3,100	2,530	7,700	2 × PLgel Mixed-D	50 µL 0.8%	Viscometer	—

[a] Averages from three measurements, EP 1: $M_n = 1460$, 1460, 1490 g/mol; $M_w = 3370$, 3370, 3380 g/mol; EP 2: $M_n = 3310$, 3230, 3220 g/mol; $M_w = 8120$, 8140, 8150 g/mol.

[b] Averages from two or three measurements, EP 1: $M_n = 1560$, 1570 g/mol; $M_w = 3370$, 3370 g/mol; EP 2: $M_n = 3330$, 3440, 3440 g/mol; $M_w = 8100$, 8060, 8110 g/mol.

[c] Determined in SEC mode assuming 100% mass recovery.

[d] Measured using Brice Phoenix Precision Instrument Co. refractometer, Model BP-2000-V at 633 nm, three solutions, calibration by six solutions of NaCl in water.

[e] Right-angle light scattering.

[f] RI detector calibrated by PS using dn/dc 0.183 mL/g.

TABLE V Statistics of results obtained by conventional SEC (THF, calibration by PS standards)

	EP 1		EP 2	
	M_n (g/mol)	M_w (g/mol)	M_n (g/mol)	M_w (g/mol)
Mean	1,780	5,000	3,960	12,440
Standard deviation	290	530	530	1090
Relative std. dev. (%)	16	11	13	9
Minimum	1,240	3,580	2,720	9,790
Maximum	2,380	5,590	4,710	14,190
Participants #	16	16	16	16
Measurements #	21	21	21	21

averages calculated from the signals of refractive index (RI) and UV detectors.

The results obtained by means of conventional SEC with PS calibration are significantly above those determined by VPO and MALS. The application of universal calibration using the constants of the Mark-Houwink equation for PS $a = 0.717$, $K = 0.0117\,\mathrm{mL/g}$ and epoxy resins $a = 0.765$, $K = 0.0148\,\mathrm{mL/g}$ (THF, 25°C)[2,3] provided results close to those obtained by VPO and MALS (Table VIII). However, only one participant attempted to apply the universal calibration concept in addition to PS calibration. The application of PS calibration by all participants is in accordance with a common approach to apply PS calibration for all polymers even if parameters for universal calibration are available.

TABLE VI Statistics of results obtained by SEC with molar mass sensitive detectors (seven light scattering photometers, three viscometers)

	EP 1		EP 2	
	M_n (g/mol)	M_w (g/mol)	M_n (g/mol)	M_w (g/mol)
Mean	1,830	3,570	3,480	8,230
Standard deviation	580	410	780	500
Relative std. dev. (%)	32	11	22	6
Minimum	1,120	2,900	2,300	7,400
Maximum	2,770	4,090	4,700	9,120
Participants #	6	6	6	6
Measurements #	10	10	10	10

TABLE VII Results obtained by SEC in NMP with PS and polysaccharide calibration

		M_n (g/mol)		M_w (g/mol)	
Sample	Column	PS	Polysaccharide	PS	Polysaccharide
EP 1	PLgel Mixed-D	6,920	3,250	12,340	5,200
	PLgel Mixed-A	5,780	4,580	9,770	5,290
EP 2	PLgel Mixed-D	14,210	6,280	26,330	10,780
	PLgel Mixed-A	12,840	6,900	27,000	8,590

Detection: UV at 280 nm in Mixed-D and evaporative light scattering in Mixed-A system.

The reproducibility of M_n obtained by means of SEC with molar mass sensitive detectors is markedly worse compared to conventional SEC. A possible explanation is scattering of data points at the low molar mass region in consequence of low signal between adjacent oligomers. In this case improvement of resolution of particular oligomers may increase the uncertainty of the M_n determination. The reproducibility of M_w is significantly better and the obtained results are close to the true values. An example of SEC-MALS results is shown in Figure 1, which depicts a 90° light scattering chromatogram and molar mass versus elution volume plot obtained for sample EP 1. The scattering of data points at the region of low signal is addressed by the extrapolation from the region where the data are reliable. Very good repeatability and results close to those from absolute methods reported by participant 1 indicate that SEC-MALS is a powerful tool for the characterization of epoxy resins.

The original intention of the project was to characterize the samples by gradient liquid chromatography (HPLC) as well. Unfortunately, only two participants applied the HPLC method, which does not

TABLE VIII Molar mass averages determined by SEC with PS and universal calibration

	M_n (g/mol)		M_w (g/mol)	
Sample	PS calibration	Universal calib.	PS calibration	Universal calib.
EP 1	2,180	1,570	5,480	3,760
EP 2	4,350	3,090	13,220	8,840

Columns: 2 × Styragel HR 5E.

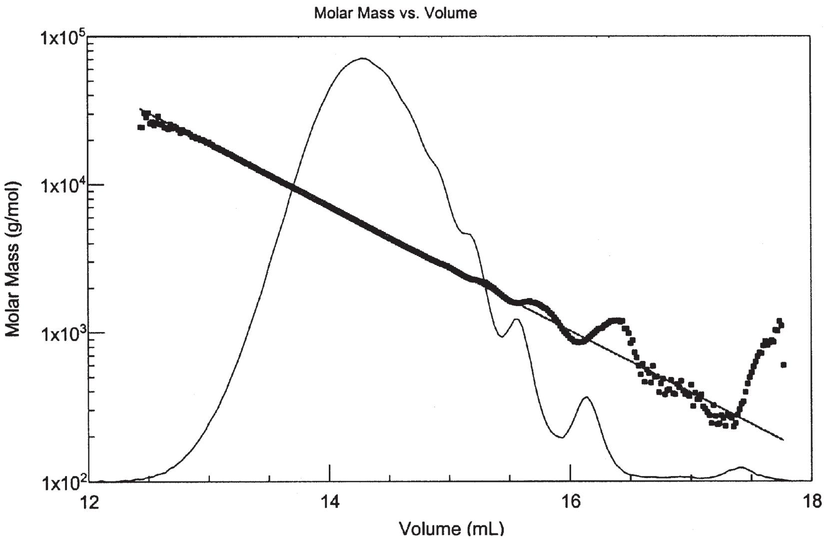


FIGURE 1 Molar mass versus elution volume plot for sample EP 1 determined by SEC-MALS (participant 1). A 90° light-scattering chromatogram is superimposed in the plot together with results extrapolation.

allow drawing any serious conclusions. The HPLC chromatograms of both samples, together with experimental conditions, can be found in Podzimek[4] in Figures 2 and 3.

CONCLUSIONS

1. The project confirmed the general trend of SEC to process data using PS calibration regardless of the actual chemical composition of the polymer under analysis.
2. The molar mass averages of oligomers determined in different laboratories can differ by several tens of percents.
3. The molar mass averages of bisphenol A based epoxy resins obtained by PS calibration systematically deviate from the VPO and MALS values. The universal calibration provides good agreement.
4. The uncertainty of M_n values is higher compared with the values of M_w.
5. The molar mass averages calculated from the signals of refractive index and UV detectors are almost identical.

6. The number and type of SEC columns have minor effect on the results.
7. There is no evident effect of injected volume or concentration, column temperature, or flow rate within the reported values.

APPENDIX: PARTICIPANTS

In alphabetical order (17 reported SEC results; the results are reported anonymously, i.e., the first participant in the alphabetical list does not correspond to participant number 1): D. Berek (Polymer Institute of the Slovak Academy of Sciences, 842 36 Bratislava, Slovak Republic).

T. Chang (Pohang University of Science and Technology, Pohang, Kyungbuk, 790–784 Korea)

J. Chmelik (Institute of Analytical Chemistry, 611 42 Brno, Czech Republic)

Z. Dobkowski (Industry Chemistry Research Institute, 01–793 Warszaw, Poland)

H. Geerts (DSM Resins, Zwolle, The Netherlands)

D. Held (Polymer Standards Service, 55120 Mainz, Germany)

A. Herod (Department of Chemical Engineering and Chemical Technology, Imperial College, London SW7 2BY, UK)

M. Kaska (SYNPO, 532 07 Parubice, Czech Republic)

A. Kastanek (SYNPO, 532 07 Parubice, Czech Republic), S. Matsuyama (National Institute of Materials and Chemical Research, Tsukuba, Ibaraki, 305–8565 Japan)

J. Minnee (Uniqema Int, 2802 BE Gouda, The Netherlands)

M. Netopilik (Institute of Macromolecular Chemistry, Academy of the Sciences of the Czech Republic, 162 06 Prague, Czech Republic)

T. Q. Nguyen (Federal Institute of Technology, CH-1015 Lausanne, Switzerland)

H. J. A. Philipsen (Oce Technologies, NL-5900 MA Venlo, The Netherlands)

S. Podzimek (SYNPO, 532 07 Pardubice, Czech Republic; for 2000–2001, Wyatt Technology Corporation, Santa Barbara, Calif., USA)

J. Pulda (Kaucuk, 278 52 Kralupy nad Vltavou, Czech Republic)

S. Rumbelow (Uniqema Technical Innovation Center, New Castle, DE 19720, USA)

G. Saunders (Polymer Laboratories, Church Stretton, Shropshire, SY6 6AX, UK)

G. Verreyt (Nitto Europe, 3600 Genk, Belgium)

M. Zigon (National Institute of Chemistry, SI-1000 Ljubljana, Slovenia)

REFERENCES

[1] Podzimek, S. and A. Kastanek. (1999). Characterization of bisphenol A-based epoxy resins by HPLC, GPC, GPC-MALLS, VPO, viscometry and end group analysis: On the identification of 2,3-dihydroxypropyl-containing compounds, determination of molar mass distribution, and branching. *J. Appl. Polym. Sci.* **74**, 2432–2438.

[2] Kolinsky, M. and J. Janca. (1974). Some applications of gel-permeation chromatography in investigations of structure and solution properties of radical-initiated poly(vinyl chloride). *J. Polym. Sci. Polym. Chem. Ed.* **12**, 1181–1191.

[3] Myers, G. E. and J. R. Dagon. (1964). Distribution of molecular weight and of branching in high molecular weight polymers from bisphenol A and epichlorohydrin. *J. Polym. Sci. Part A* **2**, 2631–2645.

[4] Podzimek, S. (2001). A review of the application of liquid chromatography to the characterization of epoxy resins. *Int. J. Polym. Anal. Charact.* **6**, 533–546.