Absolute molar masses for phenol formaldehyde resins with GPC/SEC-ESI-MS

Application Note Chemical Manufacturing

Author
Dr. Daniela Held, Friedhelm Gores
contact: info@polymer.de

Hyphenation of an electrospray ionization-mass spectrometer (ESI-MS) with a GPC/SEC system allows the determination of absolute molar masses for low molar mass samples or samples with an unknown dn/dc. This technique combines the separation ability of GPC/SEC with the sensitivity and specificity of MS detection. GPC/SEC-MS is therefore a perfect alternative, when GPC/SEC-light scattering can not be applied.

Introduction
Phenol formaldehyde resins are formed by a step-growth polymerization. GPC/SEC with RI and UV detection is often used to characterize resins and to quantify the amount of different oligomeric species. Additional information is available if an ESI-MS-spectrometer is on-line attached to the GPC/SEC system. This allows to identify oligomeric species and to learn about the degree of CH_2-OH substitution.

System Requirements

	Conditions
Pump	PSS SECcurity GPC1260 isocratic pump • flow rate [mL/min]: 0.3 • mobile phase: THF
Injection system	PSS SECcurity GPC1260 Autosampler • injection volume variable
Columns	• PSS SDV precolumn (8*50mm) • PSS SDV 5µ 5µm 50 Å, 100 Å, 1 000 (8*300mm each)
Loading	• 1.5 mg/mL, 100 µL injection volume
Detectors	• PSS SECcurity UV detector at 254 nm • Refractive index PSS SECcurity 1260 RI • Thermo Fisher LXQ ESI spectrometer
Software	PSS WinGPC UniChrom with mass spectrometry module Thermo Fisher Excalibur 2.07

Procedure, Results & Discussion
A suitable design of on-line GPC/SEC-ESI-MS hyphenation is shown in Figure1.
A parallel array of concentration-sensitive detectors (UV, RI) and mass spectrometry, allows to operate all detectors under optimized flow rates. The bulk of the eluent (270 mL/min) is passed after the separation to the UV-Vis and RI detector to minimize band broadening processes by mixing volumes of the detector cells, which are particularly significant at low flow rates. One-tenth of the eluent (30µL/min) is passed to the mass spectrometer. For this split ratio of 9:1, ideal tubing dimensions are shown in Figure 1.[1,2]
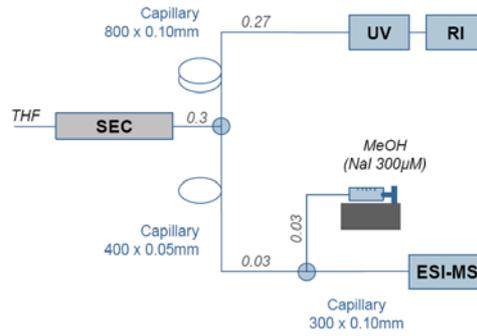
Fig. 1: Scheme for an online GPC/SEC-ESI-MS setup
(with permission of Dr. Till Gründling)

Figure 2 shows the elugram of an oligomeric phenol formaldehyde resign, separated into three different peaks with 1, 2 and 3 repetition units. The mass spectra are then measured online for each species.
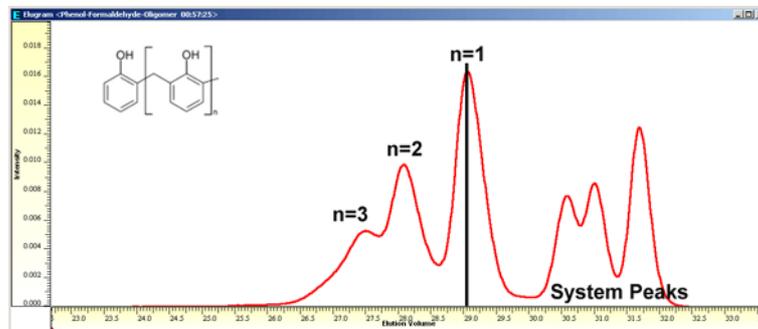

Fig. 2: RI trace oligomeric phenol formaldehyde resin, degree of polymerization identified from corresponding mass spectrum

Figure 3 shows as example the mass spectrum of Peak n=1, while Table 1 summarizes the masses possible in theory and identified (green) or not detected (grey). This combined approach can be used for molar masses up to approx. 2 000 Da, higher degrees of polymerization have also been investigated.
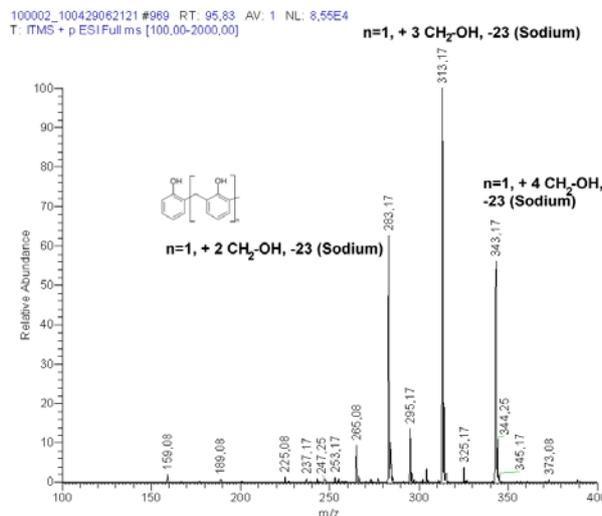

Fig. 3: Mass spectrum for n=1 showing the 3 different species (CH_2-OH substitution)

Table 1: Expected molar masses for different degrees of polymerization (n) and for CH_2OH units at the aromatic ring.
Color code: grey: possible in theory but not found, green: identified in MS spectrum

n	0 CH_2OH	1 CH_2OH	2 CH_2OH	3 CH_2OH	4 CH_2OH	5 CH_2OH
1	200	230	260	290	320	-
2	306	336	366	396	426	456
3	412	442	472	502	532	562

GPC/SEC-ESI-MS therefore allows to detect that different species elute within 1 peak, e.g. within the peak for n=1 molecules with 2, 3, and 4 CH_2OH substitutions elute. This information is not available when GPC/SEC only is used. On the other hand a fractionation by GPC/SEC before measuring the mass spectra results in easier to analyze spectra. In addition it is possible to go to higher molar masses than in ESI-MS alone. Another advantage of the combined approach is that the molar masses obtained from the MS detector can be used to construct a GPC/SEC calibration curve, that allows to measure true molar mass averages and molar mass distributions.

Literature
[1] T. Gruendling, M. Guilhaus, C. Barner-Kowollik, Anal. Chem. 2008, 80, 6915.
[2] T. Gruendling, M. Guilhaus, C. Barner-Kowollik, Macromolecules 2009, 42, 6366