REACH Polymer Status determined with GPC/SEC

Application Note Chemical Manufacturing

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Introduction

REACH (short for **R**egistration, **E**valuation, **A**uthorisation and restriction of **Ch**emicals) came into force on June 1st 2007 and applies in all EU member states.
Polymers are “special substances” in terms of REACH. However, companies have to prove that their products/educts are polymers.

A polymer molecule in the sense of REACH is a molecule that contains a sequence of at least 3 monomer units M, covalently bound to at least one other monomer unit or reactant (initiator). This definition is the so called (3M+1) – rule.
Additional requirements are:
a) Over 50 percent of the weight for that substance consists of polymer molecules (> 3M+1).
b) The amount of polymer molecules with the same chain length must be less than 50 weight percent of the substance.

The preferred method to identify whether a substance falls under the definition of a polymer is Gel Permeation Chromatography (GPC), also known as Size Exclusion Chromatography (SEC). GPC/SEC separates substances by chain length enabling percent weight per chain length to be determined. One result of a GPC/SEC experiment is a table with molar mass/number of monomer units and peak area. Table 1, with 2 examples for substances which are not polymers and one substance which is a polymer, illustrates the REACH criteria.

Table 1: REACH criteria discussed with 3 different examples

Monomer units	***Sample A***	***Sample B***	***Sample C***
M=1	***0***	***35%***	***0%***
M=2	***5%***	***20%***	***10%***
M=3	***55%***	***10%***	***20%***
M=4	***20%***	***10%***	***30%***
M=5	***10%***	***10%***	***20%***
M=6	***5%***	***10%***	***10%***
M=7	***5%***	***5%***	***5%***
M=8	***0%***	***0%***	***5%***
Polymer definition	***failed (b)***	***failed (only 45% > 3M+1)***	***passed***

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System Requirements

	Conditions
Pump	PSS SECcurity GPC1260 isocratic pump • flow rate [mL/min]: 1 • mobile phase: THF (other solvents possible)
Injection system	PSS SECcurity GPC1260 Autosampler • injection volume 100µL
Columns	• PSS SDV precolumn (8*50mm) • PSS SDV 3µ 1 000 Å (8*300mm) • PSS SDV 3µ 1 000Å (8*300mm) • PSS SDV 3µ 1 000Å (8*300mm)
Calibration	PSS Polystyrene ReadyCal Low
Loading	5 mg/mL, 20µL injection volume
Detectors	Refractive index PSS SECcurity 1260 RI
Software	PSS WinGPC UniChrom

Procedure, Results & Discussion

Polyols are alcohols with multiple hydroxyl groups. They are used for very different applications, such as sugar substitutes in Feed & Food or as reactants to produce high quality products in polymer chemistry. In order to determine if the above stated REACH polymer requirements for a polyol are true, a GPC/SEC experiment using high resolution SDV columns was performed.

Figure 1 shows the graphical results for a Polyol showing the size-based separation into individual R-$(M)_x$ peaks.

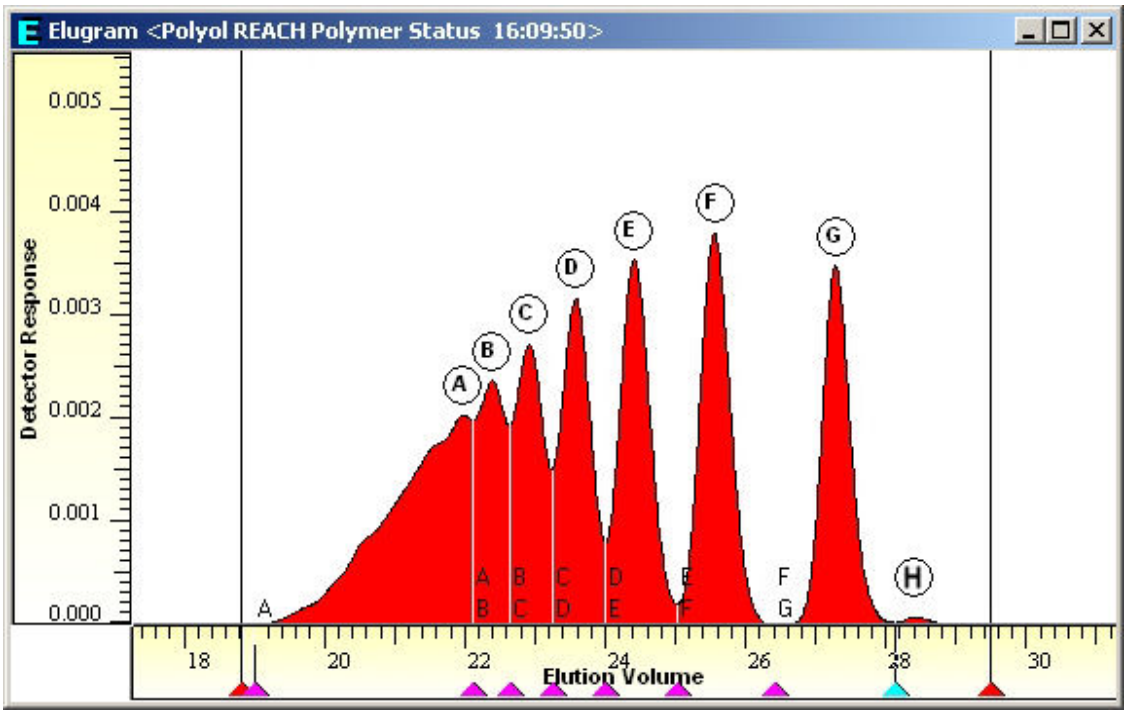

Figure 1: GPC/SEC separation of a polyol into the individual oligomer chains.

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The REACH criteria are then applied to all identified individual chains of the Polyol. Table 2 lists peak area (obtained from the detector signal) and the molar mass (obtained using a previously established calibration curve) and comments this with respect to the REACH requirements.

Table 2: Content and molar mass for a Polyol and comments to the REACH requirements.

	Content [%]	Relative Molar Mass M_n [Da]*	Comment	Polymer
R-M, Peak H	0.20	350	Less than 50% below (3M+1)	Yes
R-M-M Peak G	13.4	650		
R-M-M-M Peak F	15.7	960	distribution, (3M+1)-Rule no individual chain > 50%	Yes Yes
Peak E	14.8	1 270		
Peak D	13.3	1 580		
Peak C	11.0	1 890		
Peak B	9.30	2 200		
Peak A	22.3	2 550		

* Polystyrene equivalents

As a

- molar mass distribution with higher molar masses than 3M+1 was measured
- where no individual chain contributes to more than 50%
- and as the combined content of Peak G and H is below 50%

it can be concluded that this Polyol is a polymer according to the definition by REACH.

While it is easy to assign the peaks in the example above, there are also examples where it is more difficult to identify M of the repetition units. In these cases GPC/SEC hyphenated with mass spectrometry, MS, can be a good tool to determine the molar mass of M to ensure a correct REACH data analysis.