

# Measuring the molecular mass distribution of a polymer

## Introduction

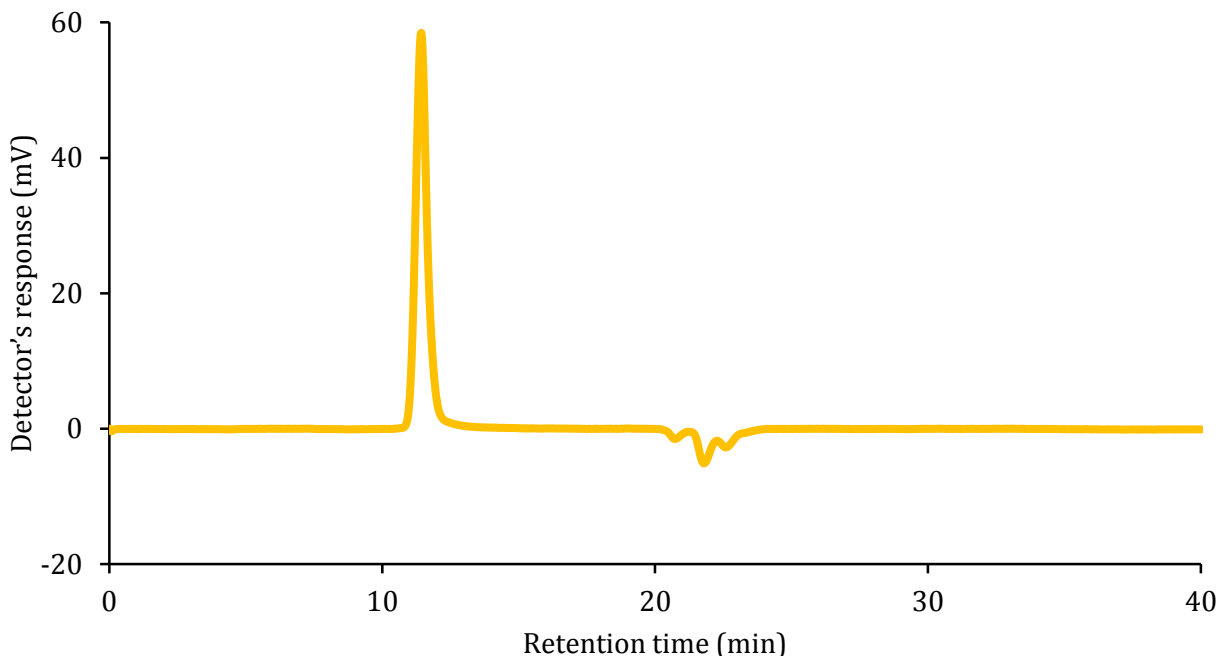
A polymer is made of molecular chains of various sizes and masses. **Their distribution in mass or size is a key parameter for many physical properties such as mechanical strength or thermal stability; therefore it is crucial to predict the behaviour of the polymer in use and its processability.**

In size exclusion chromatography (SEC), polymer chains are separated according to

their size in solution. As they flow in the mobile phase through the porous stationary phase, they are retained for a specific time depending on their size: the smaller the chains the longer they are retained. Each polymer chain size is hence associated with a retention time, which is then transformed into a molecular mass using a calibration curve.

## Experimental details

- Method: ISO 16014 determination of molecular mass distribution of polymers using size-exclusion chromatography [1, 2]
- Instrument: *Agilent 1260 GPC/SEC MDS*
- Mobile phase: GPC-grade tetrahydrofuran (THF) flowing at 1 mL/min
- Stationary phase: two columns PLgel 5  $\mu\text{m}$  MIXED-D 300  $\times$  7.5 mm by *Agilent*
- Sample: polystyrene standard diluted in THF at 1.5 mg/mL
- Injection volume: 100  $\mu\text{L}$
- Detector: differential refractometer (DRI)

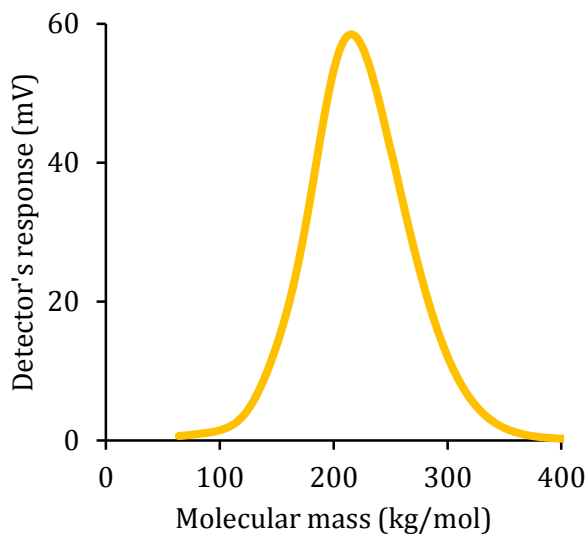


*Evolution of the differential refractometer's response with respect to the retention time in the stationary phase. One single peak appears at 11 min, meaning that there is one single population of polymer chains. The negative multiple peak after 20 min is characteristic of the stabiliser contained in the mobile phase.*

## Results

The retention time has to be converted into a molecular mass. This is done by the means of a calibration curve using polystyrene samples of known, narrow molecular mass distributions, here in the range of 0.2 to 460 kg/mol. The curve on the right is then obtained, with the peak maximum around 200 kg/mol.

As the refractometer's response is equivalent to the number of chains detected at a given mass, the curve on the right is interpreted as the distribution of chain masses. From it different parameters can be calculated, whose values are in the table on the right: the peak maximum  $M_p$ , the number-average  $M_n$ , which separates the distribution into two groups of identical number of chains, and the mass-average  $M_w$ , which separates the distribution into two groups of identical mass [1]. The narrowness of the distribution is commonly estimated by the polydispersity index: it is the ratio of  $M_w$  over  $M_n$ , here 1.06.



Molecular mass average	Value (kg/mol)
$M_p$	207
$M_n$	201
$M_w$	213

## Conclusion

- The molecular mass distribution and molecular mass averages can be calculated using size exclusion chromatography.
- A calibration curve must be created to convert retention time into molecular mass; the standard samples should be the same polymer as the specimen to analyse.
- If adequate standard samples are not available it is better to use more detectors (viscometer, light scattering) and calculate the molecular mass distribution from more complicated equations and calibration curves: universal calibration, etc.

[1] Plastics — Determination of average molecular mass and molecular mass distribution of polymers using size-exclusion chromatography — Part 1: General principles, ISO 16014-1:2012(E)

[2] Plastics — Determination of average molecular mass and molecular mass distribution of polymers using size-exclusion chromatography — Part 3: Low-temperature method, ISO 16014-3:2012(E)