

Polymer Characterization by AF4-MALS

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Introduction

Asymmetrical flow field-flow fractionation (AF4) provides high-resolution separations for characterizing a wide range of macromolecules and colloidal particles. This method has been called the most generally useful of any of the field-flow fractionation (FFF) family.

Experimental

Instruments

- Isocratic pump – Agilent 1100 Series (Agilent Laboratories).
- Autosampler – Waters 717 Plus (Waters Corporation).
- AF4 separation system – Eclipse 3 (Wyatt Technology Europe).
- MALS detector – DAWN EOS (Wyatt Technology Corporation).
- RI detector – Waters 2410 Differential Refractometer (Waters Corporation).

Separation conditions

- Long channel, 350 μm spacer, 5kDa regenerated cellulose membrane, channel temperature 60°C or 25°C.
- Channel flow – 1 mL/min.
- Cross-flow – gradient from 3 to 0.16 mL/min over 20 or 10 minutes, isocratic at 0.16 mL/min over 10 minutes, cross-flow off over 5 minutes.

Reagents

- Distilled THF stabilized with 2,6-di-tertbutyl-4-methylphenol.

Results

Broad polystyrene standard

This standard represents a group of common polymeric materials with weight average molar mass about 3×10^5 g/mol and polydispersity about 2.4.

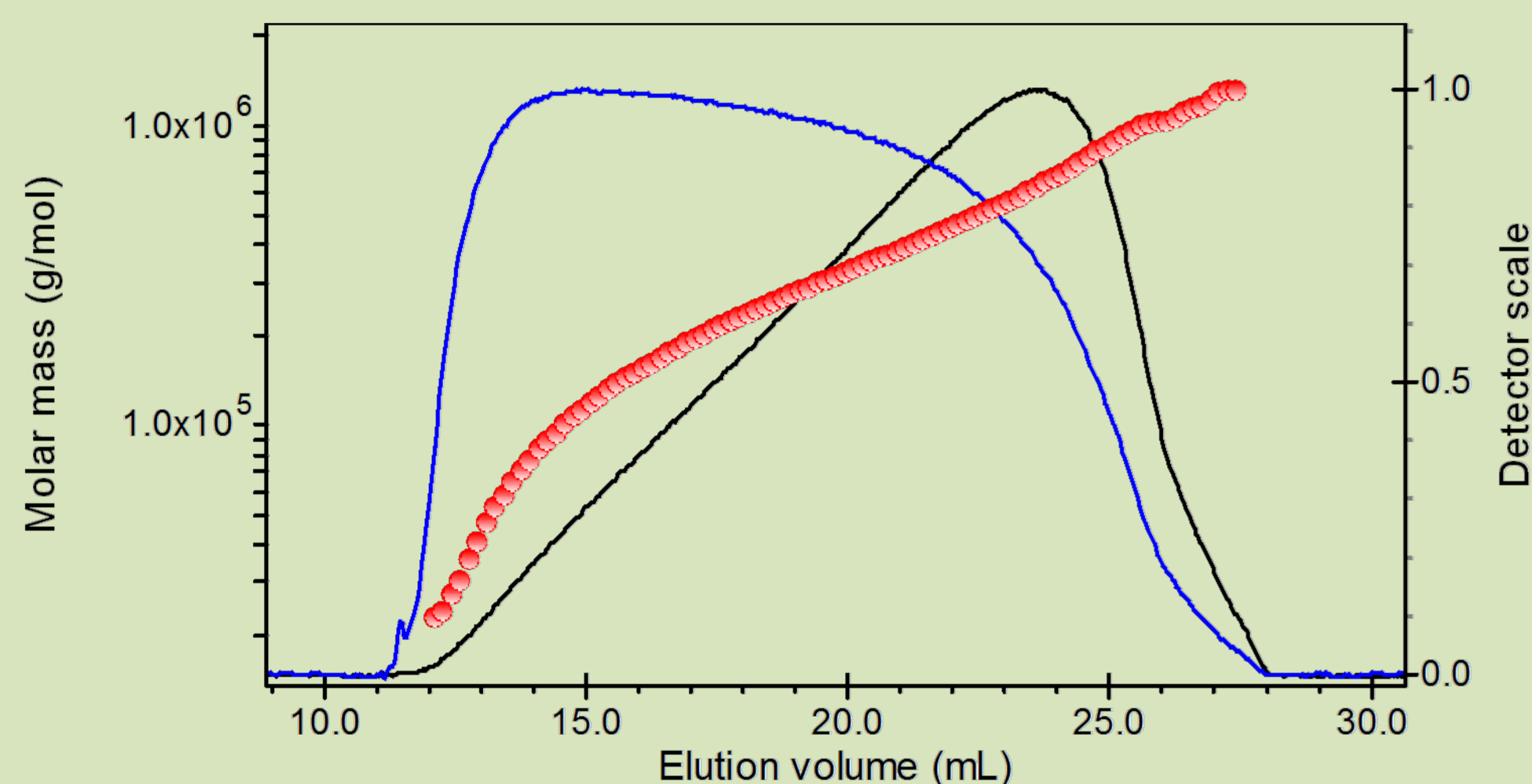


Figure 1 - RI, MALS fractograms and molar mass versus elution volume plot for broad polystyrene standard measured at 60 °C.

Table 1 – Comparison of molar mass averages of broad polystyrene determined by AF4-MALS and SEC-MALS.

Method	M_n [g/mol]	M_w [g/mol]	M_z [g/mol]	R_w [nm]
SEC-MALS	135×10^3	323×10^3	639×10^3	25
AF4-MALS	136×10^3	315×10^3	614×10^3	24

Polyisobutylene

Polyisobutylene in Figure 2 is an example of polymeric material containing very small amount of ultra-high molar mass fraction. Figure 2 shows almost baseline separation of lower molar mass and ultra-high molar mass fractions.

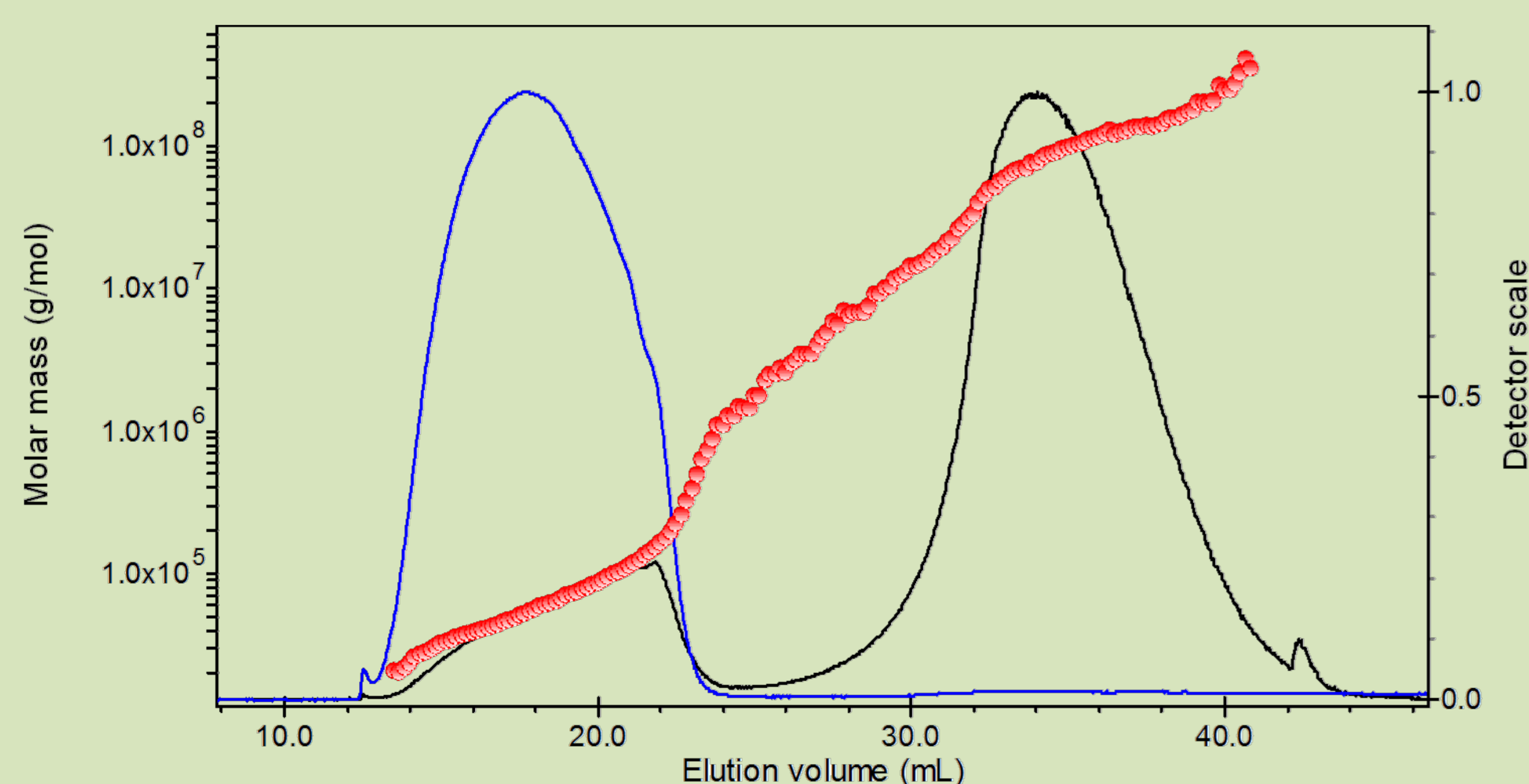


Figure 2 - RI, MALS fractograms and molar mass versus elution volume plot for polyisobutylene measured at 25°C.

Table 2 – Average molar masses and RMS radius of polyisobutylene.

M_n [g/mol]	M_w [g/mol]	M_z [g/mol]	R_z [nm]
54×10^3	1.73×10^6	1.25×10^8	279

Acrylic copolymer prepared by emulsion polymerization

This sample represents group of polymeric materials mostly used for water based organic coatings. Sample was prepared from 63% methyl methacrylate, 36% butyl acrylate and 1% acrylic acid. Figure 3 shows efficient separation of the sample across the entire fractogram up to ultra-high molar mass fraction of 10^8 g/mol.

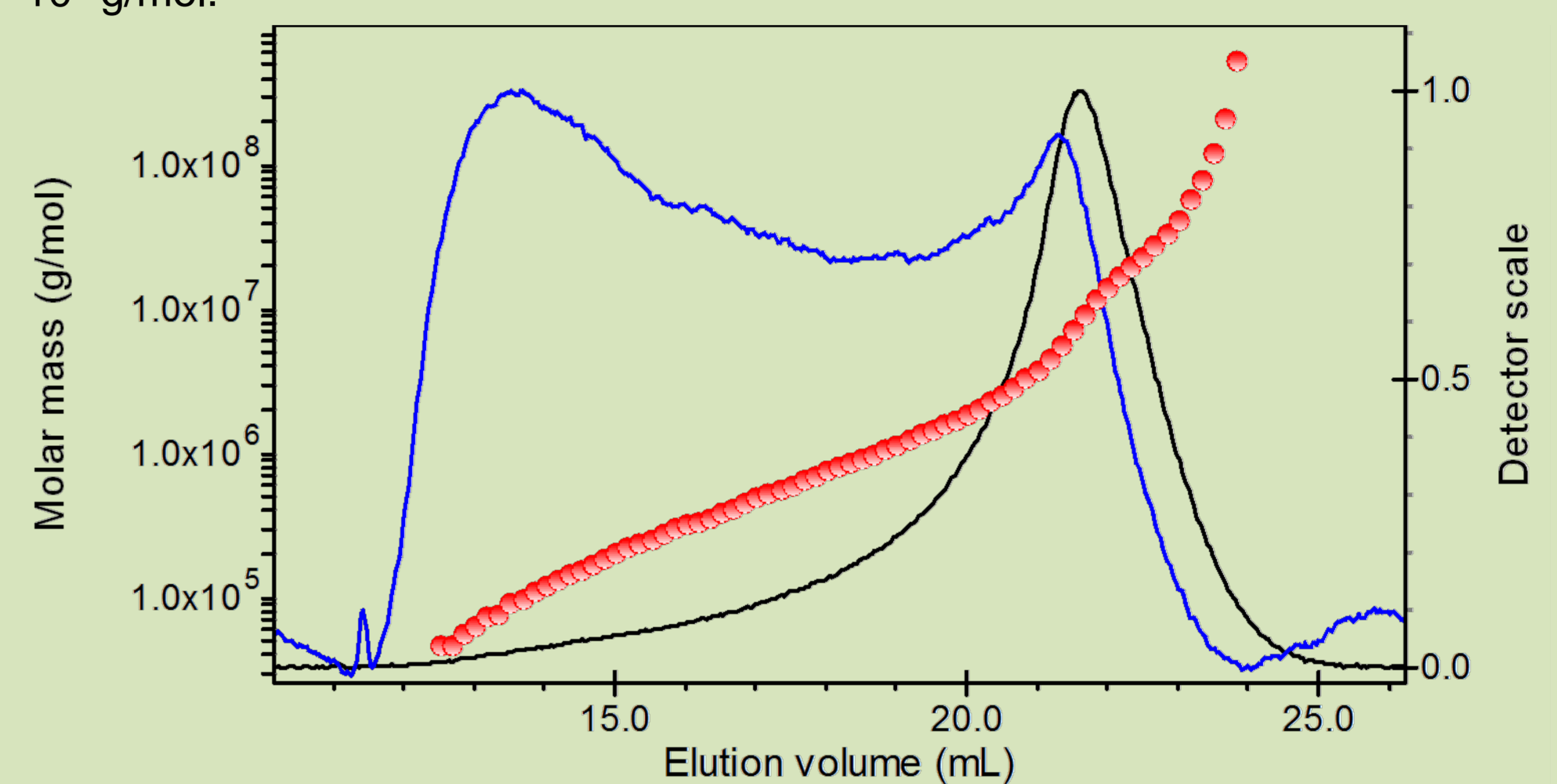


Figure 3 - RI, MALS fractograms and molar mass versus elution volume plot for acrylic copolymer dissolved in THF and measured at 60 °C.

Table 3 – Molar mass averages and RMS radius of acrylic copolymer.

M_n [g/mol]	M_w [g/mol]	M_z [g/mol]	R_z [nm]
168×10^3	2.078×10^6	1.441×10^7	207

Synthetic rubber

Styrene-butadiene copolymer is very important polymeric material for its possibility of substitution of natural rubber. Figure 4 shows separation of the macromolecules. Figure 5 depicts the conformation plot of the sample which describes branching of macromolecules.

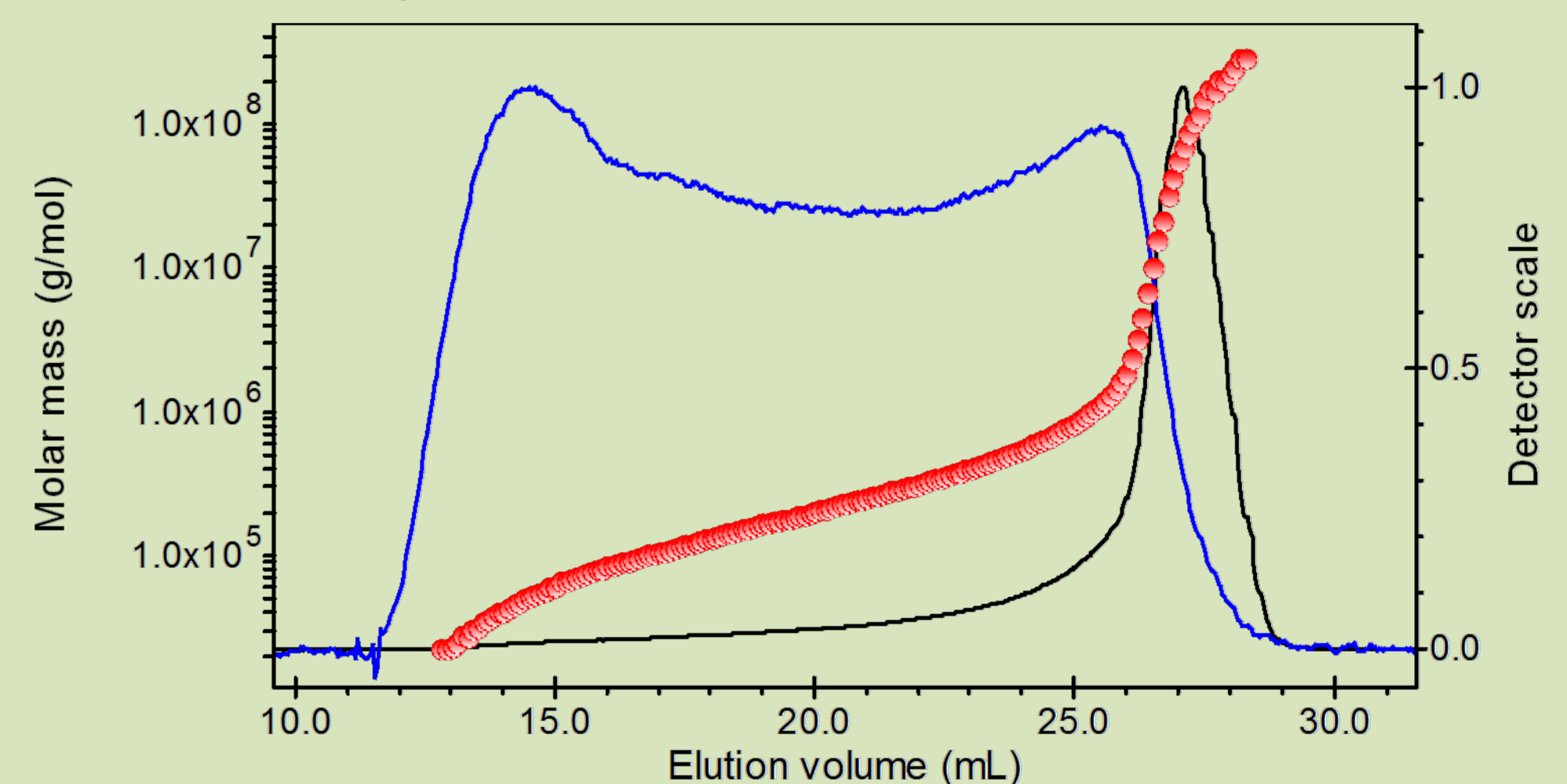


Figure 4 - RI, MALS fractograms and molar mass versus elution volume plot for synthetic rubber measured at 60 °C.

Table 4 – Average molar masses and RMS radius of synthetic rubber.

M_n [g/mol]	M_w [g/mol]	M_z [g/mol]	R_z [nm]
130×10^3	3.161×10^6	1.173×10^8	162

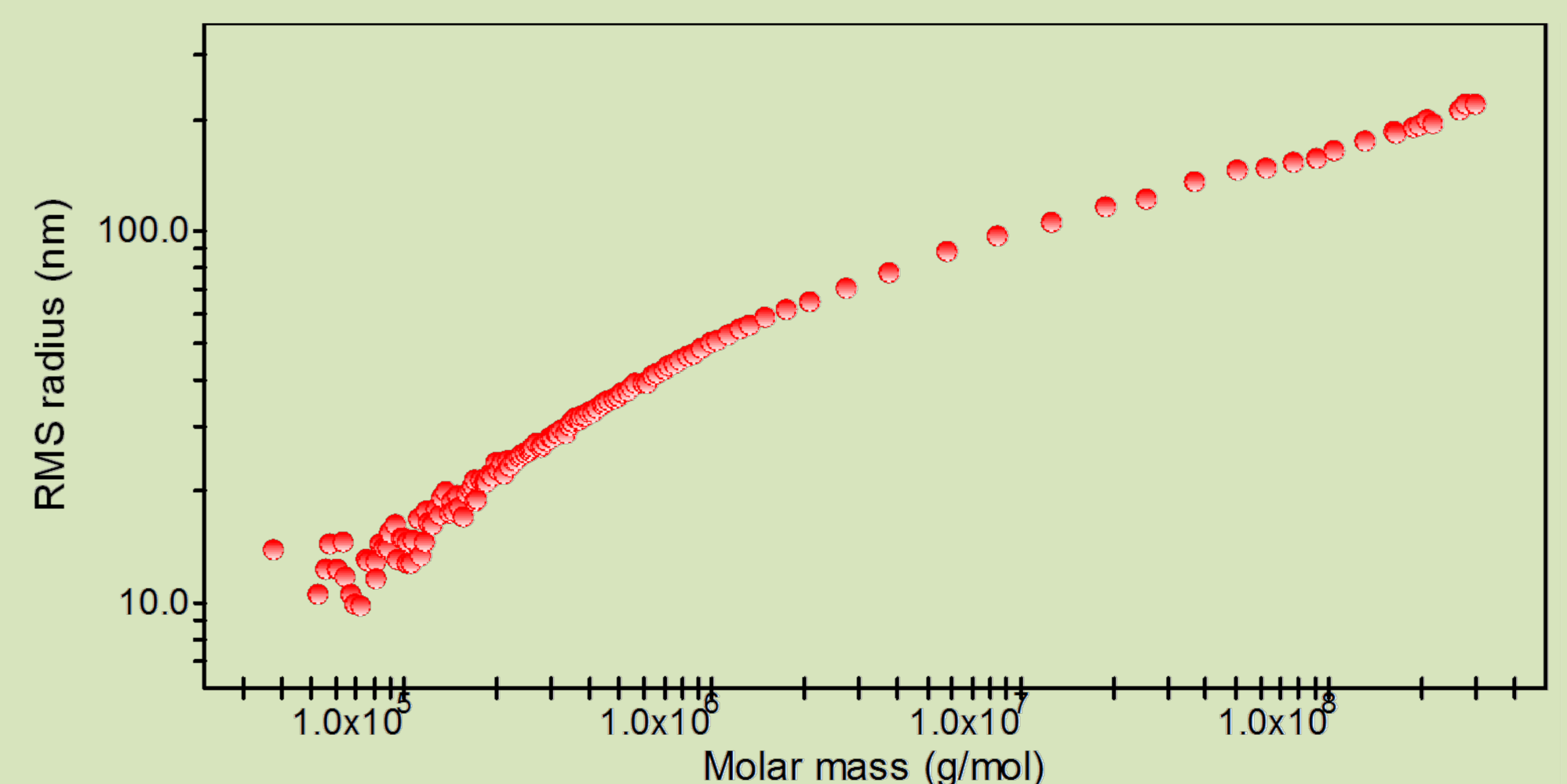


Figure 5 – Conformation plot of synthetic rubber. Bending of the RMS radius vs. molar mass dependence indicates branching of the macromolecules.

Conclusion

AF4 provides very efficient separation for many kinds of polymeric materials such as linear or branched polymers, polymers containing ultra-high molar mass fractions, natural polymers or polymers prepared by emulsion polymerization.