



The Importance of Online Viscometer in the Age of Multi-Angle Light Scattering

Stepan Podzimek^{1,2,3}

¹Wyatt Technology Europe GmbH

²SYNPO, Pardubice, Czech Republic

³University of Pardubice, Republic



Outline

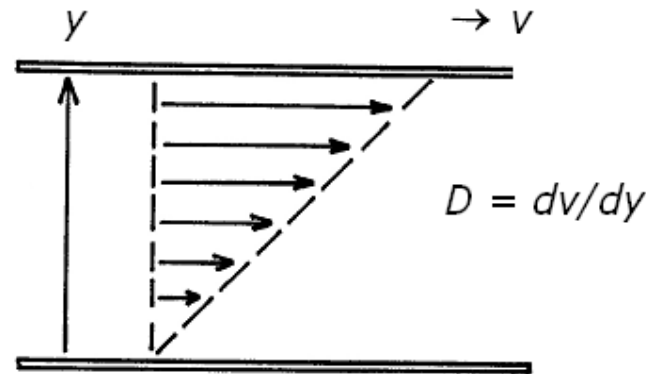
- What is (and what is not) the intrinsic viscosity
- Applications of online viscometer
 - Universal calibration
 - Mark-Houwink equation
 - Mark-Houwink plot
 - Flory-Fox equation
 - Hydrodynamic radius
- Online viscometer for the structural studies
- Online viscometer for fluorescent polymers
- Final remarks

Intrinsic Viscosity

- Intrinsic viscosity is not viscosity!!!
- Viscosity is the proportionality constant in the Newton's law for fluids
- Newton's law for fluids

$$\tau = \eta \frac{dv}{dy}$$

- τ = shear stress (N/m²)
- η = viscosity (Pa.s)
- dv/dy = velocity gradient (s⁻¹)



Velocity profile in liquid placed between moving and stationary plate.

Temperature Dependence of Viscosity

$$\eta \approx e^{\frac{E}{RT}}$$

η viscosity
 E activation energy of flow
 T temperature
 R universal gas constant

Temperature Dependence of Intrinsic Viscosity

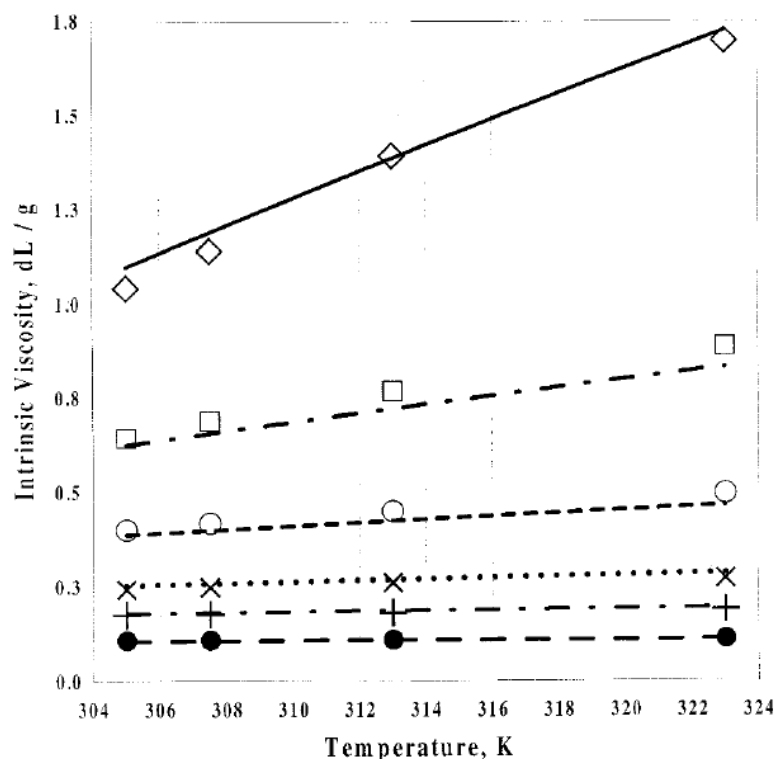


Figure 2 Solution intrinsic viscosities of polystyrene in cyclohexane. (Solid curve and diamonds) $1.8 \cdot 10^{-6}$ g/mol molecular weight polymer; (dashed-dot curve and squares) 600,000 g/mol; (dashed curve and open circles) 233,000 g/mol; (dotted curve and x's) 100,000 g/mol; (solid curve and pluses) 50,000 g/mol; (dashed curve and solid circles) 17,500 g/mol.

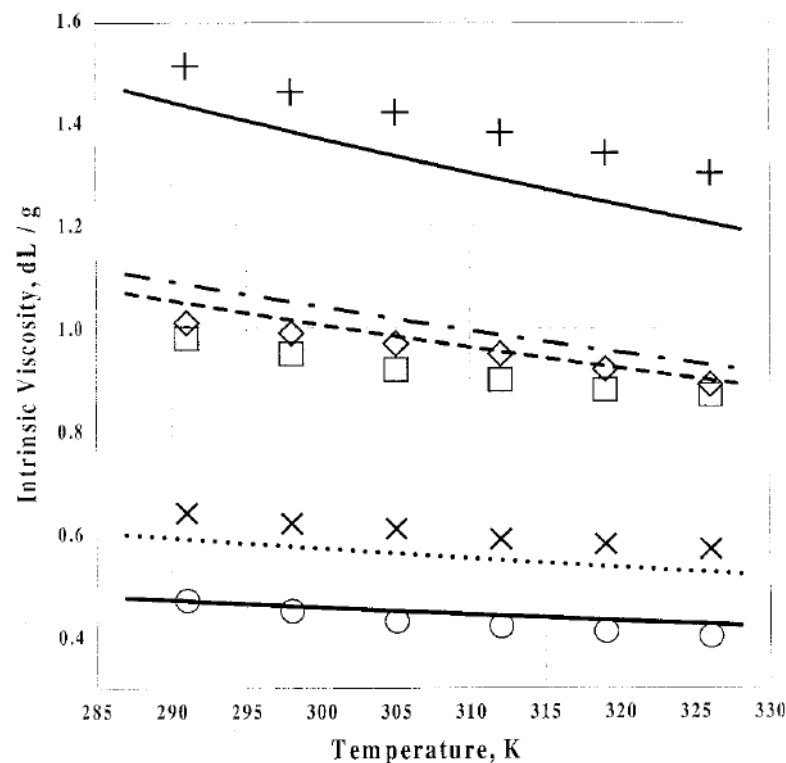
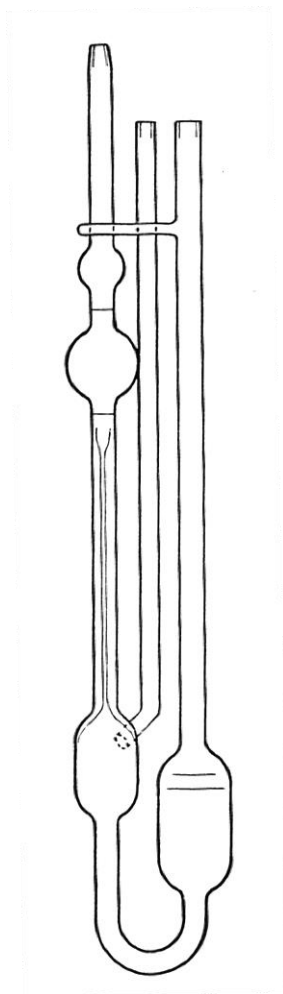


Figure 3 Solution intrinsic viscosities of poly(vinyl acetate) in chloroform. (Solid curve and pluses) 217,000 g/mol molecular weight polymer; (dashed-dot curve and diamonds) 148,000 g/mol; (dashed curve and squares) 141,000 g/mol; (dotted curve and x's) 61,000 g/mol; (solid curve and circles) 43,000 g/mol.

From T. S. Rushing and R. D. Hester, *J. Appl. Polym. Sci.*, 89, 2831 (2003).

Intrinsic Viscosity



- Intrinsic Viscosity

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \quad \eta_{sp} = 2.5\phi$$

- Fundamental property characterizing polymer chain conformation and thermodynamic quality of the solvent

ϕ = volume fraction of polymer in solution

c = concentration in mg/mL

- Specific viscosity

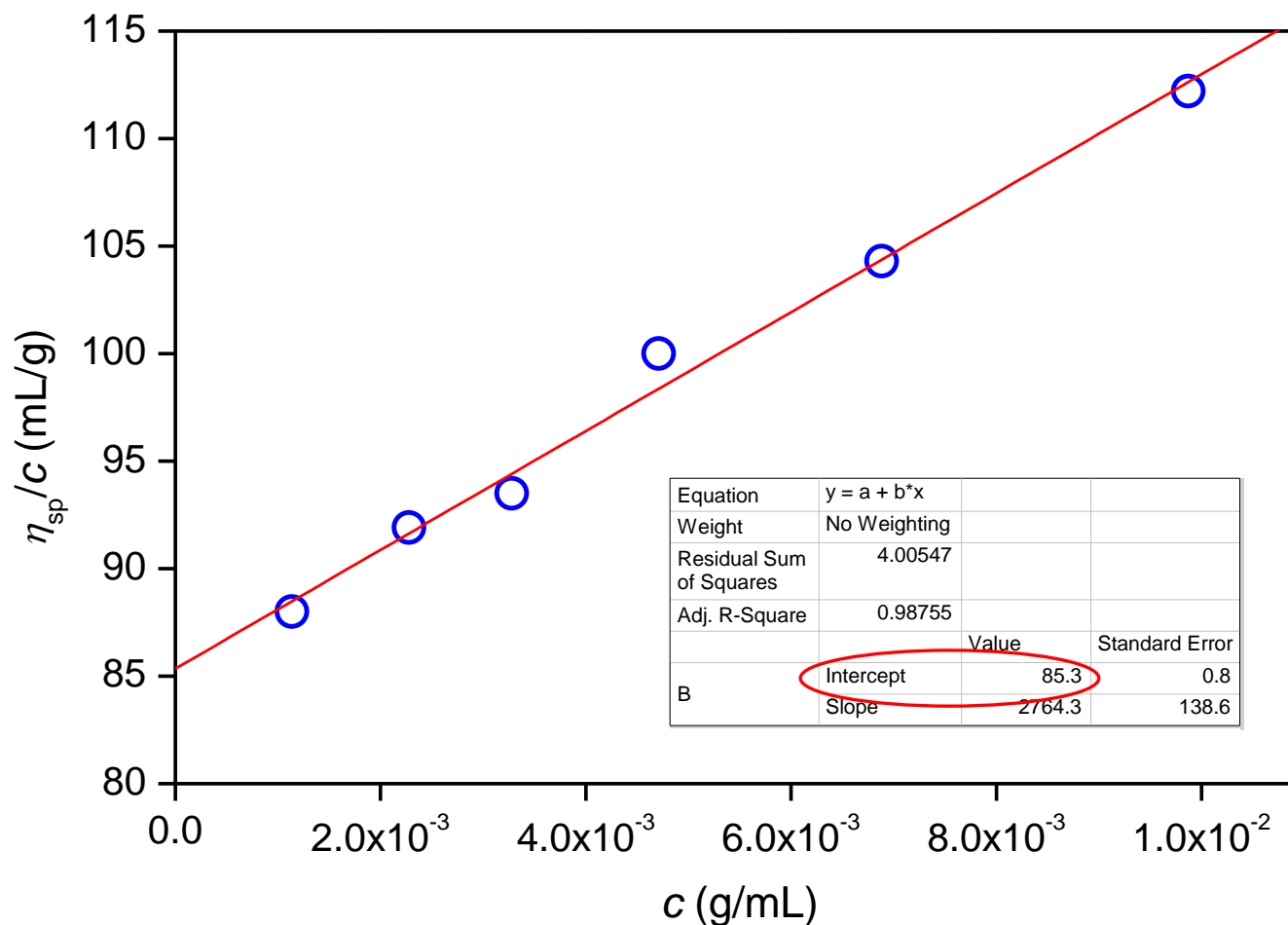
$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta_{relative} - 1$$

η = viscosity of polymer solution

η_0 = viscosity of pure solvent

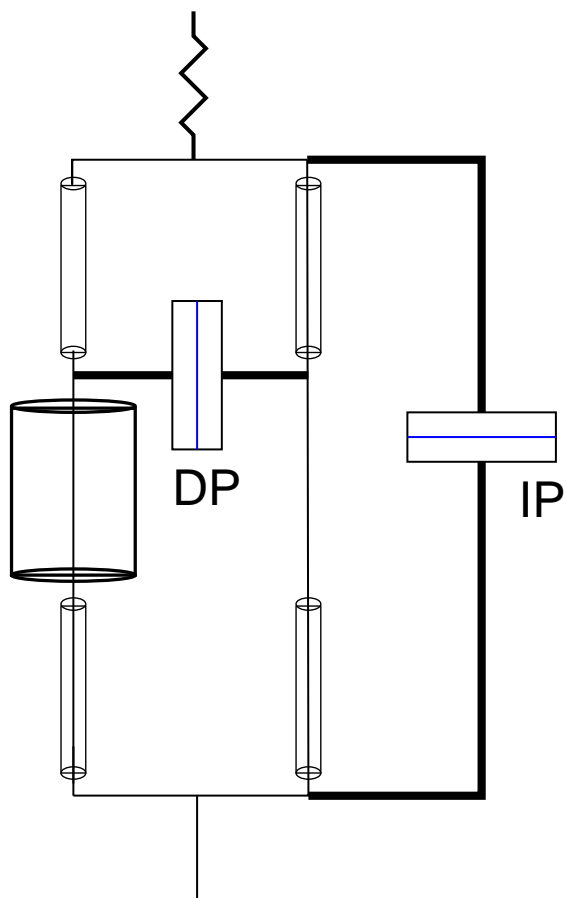
t = time needed for solution or solvent to flow from one mark to the other

Classical Determination of Intrinsic Viscosity



- Determination of intrinsic viscosity of polystyrene NIST 706 in THF, 25 °C.
- Data obtained by Ubbelohde capillary viscometer.

Online Determination of Intrinsic Viscosity

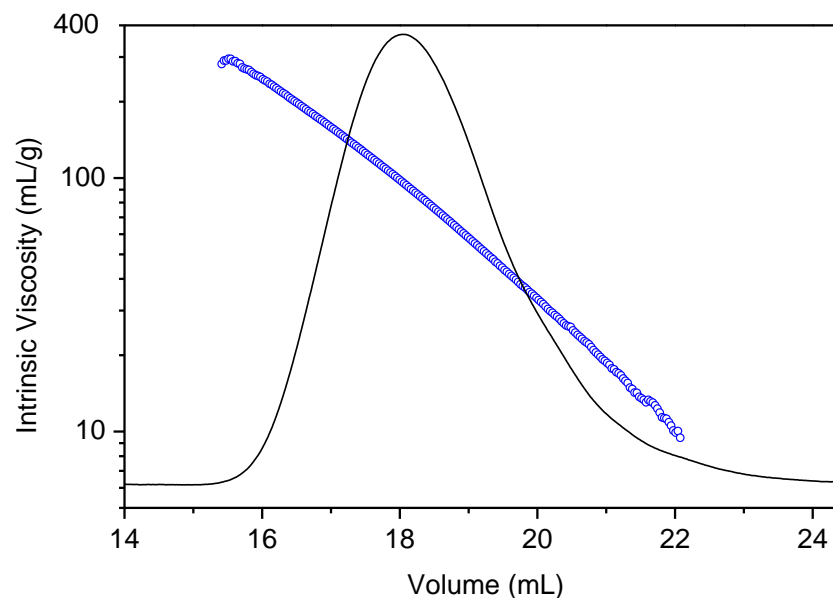


$$\eta_{sp} = \frac{4\Delta P}{IP - 2\Delta P} \quad [\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c}$$

ΔP imbalance pressure across the bridge

IP pressure drop from inlet to outlet

η_{sp} specific viscosity





Applications of Intrinsic Viscosity in Polymer Science

- Molar mass from Mark-Houwink equation
- Hydrodynamic radius from $[\eta]$ and molar mass
- Root mean square (RMS) radius (radius of gyration) from $[\eta]$ and molar mass
- SEC with universal calibration for the determination of molar mass distribution
- Polymer structure from Mark-Houwink plot: $\log [\eta]$ vs. $\log M$



Mark-Houwink Equation

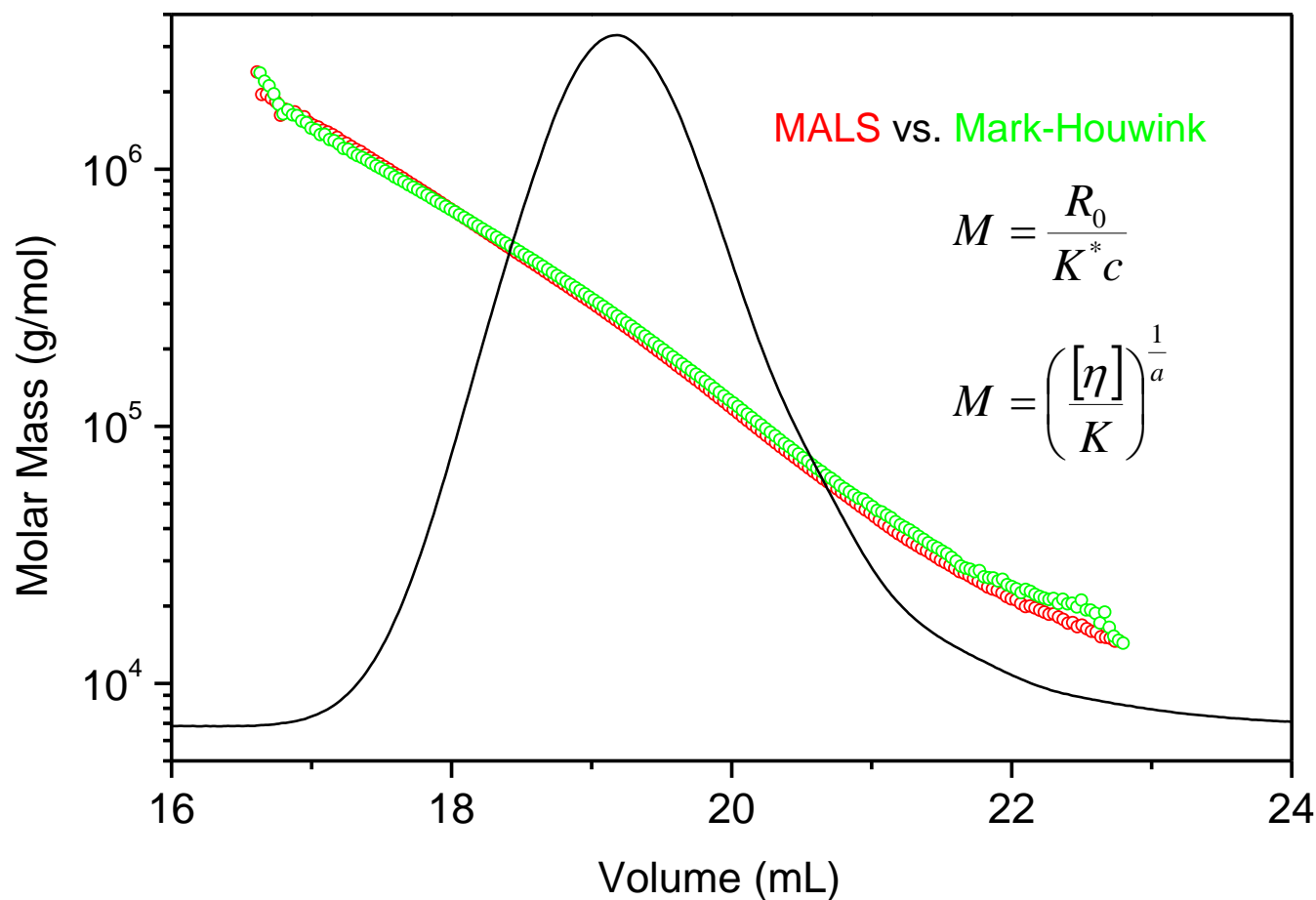
Traditional way of molar mass determination

Mark-Houwink Equation

$$[\eta] = KM^a$$

- K, a = constants of Mark-Houwink equation for given polymer, solvent and temperature; M = molar mass
- Traditional method of the determination of molar mass
- Viscosity average (M_v) close to weight-average (M_w)
 - NIST 706, $[\eta] = 85.3 \text{ mL/g}$; $M_v = 244,000 \text{ g/mol}$; $M_w \approx 270,000 \text{ g/mol}$
 - $K = 0.0117 \text{ mL/g}$, $a = 0.717$ (THF, 25 °C, M. Kolinsky and J. Janca, *J. Polym. Sci., Polym. Chem. Ed.*, 12, 1181 (1974)).

Molar Mass from Mark-Houwink Equation



Molar mass versus elution volume plots of linear polystyrene by **MALS** and calculated from **Mark-Houwink equation**.

Hydrodynamic Radius

Hydrodynamic Radius

$$V_{sphere} = \frac{4}{3} \pi R^3$$

$$V_h = \frac{[\eta]M}{2.5N_A}$$

$$R_h = \left(\frac{3[\eta]M}{4\pi \cdot 2.5N_A} \right)^{\frac{1}{3}}$$

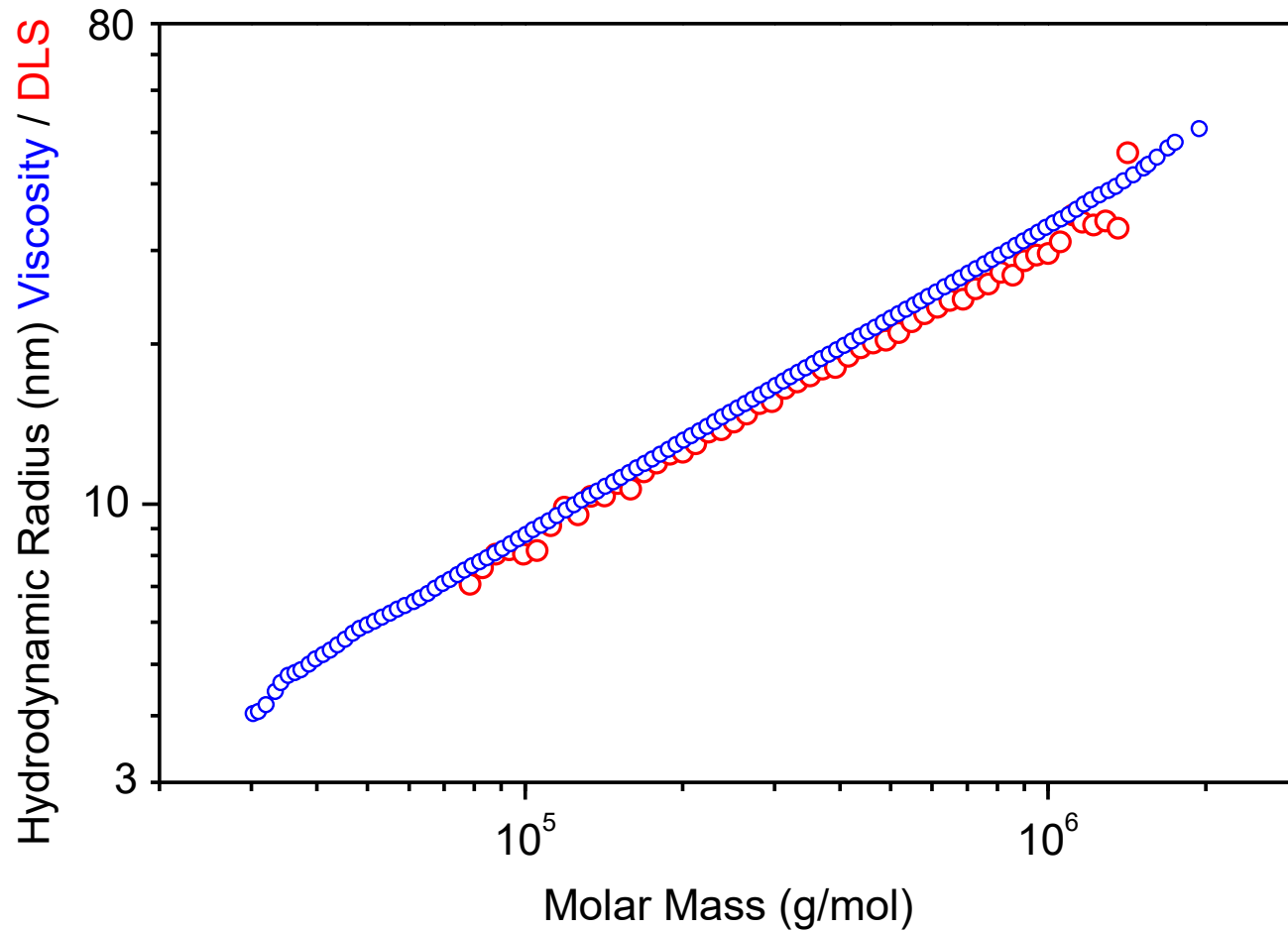
V_h = hydrodynamic volume

M = molar mass

N_A = Avogadro's number

- Hydrodynamic radius (R_h)
 - R_h is radius of hydrodynamically equivalent sphere, i.e., a hypothetical sphere having the product of intrinsic viscosity and molar mass the same as the polymer molecule.
 - It can be used as an alternative size parameter to RMS radius.
 - Viscometry is often more sensitive than a golden standard dynamic light scattering.

Hydrodynamic Radius: DLS versus Viscometry



Conformation plots of polystyrene based on hydrodynamic radius determined by [online viscometer](#) and [dynamic light scattering](#).

Flory-Fox Equation

Flory-Fox: RMS Radius by Viscometry ... or $[\eta]$ by MALS

$$R = \frac{1}{\sqrt{6}} \left(\frac{[\eta]M}{\Phi} \right)^{\frac{1}{3}}$$

$$\Phi = 2.86 \times 10^{21} (1 - 2.63\varepsilon + 2.86\varepsilon^2)$$

$$\varepsilon = \frac{2a-1}{3}$$

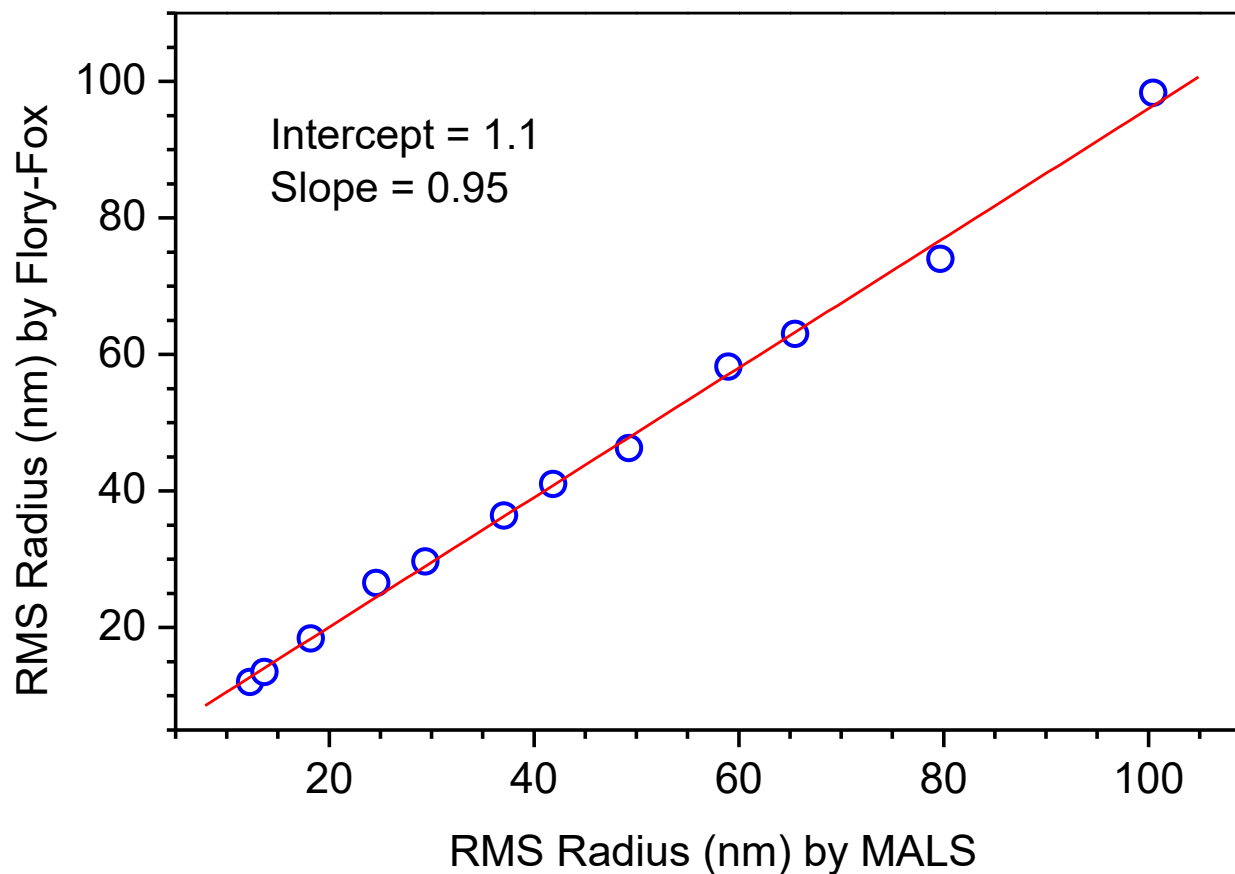
Φ = Flory-Fox constant

a = exponent of Mark-Houwink equation

$[\eta]$ in dL/g, R in cm

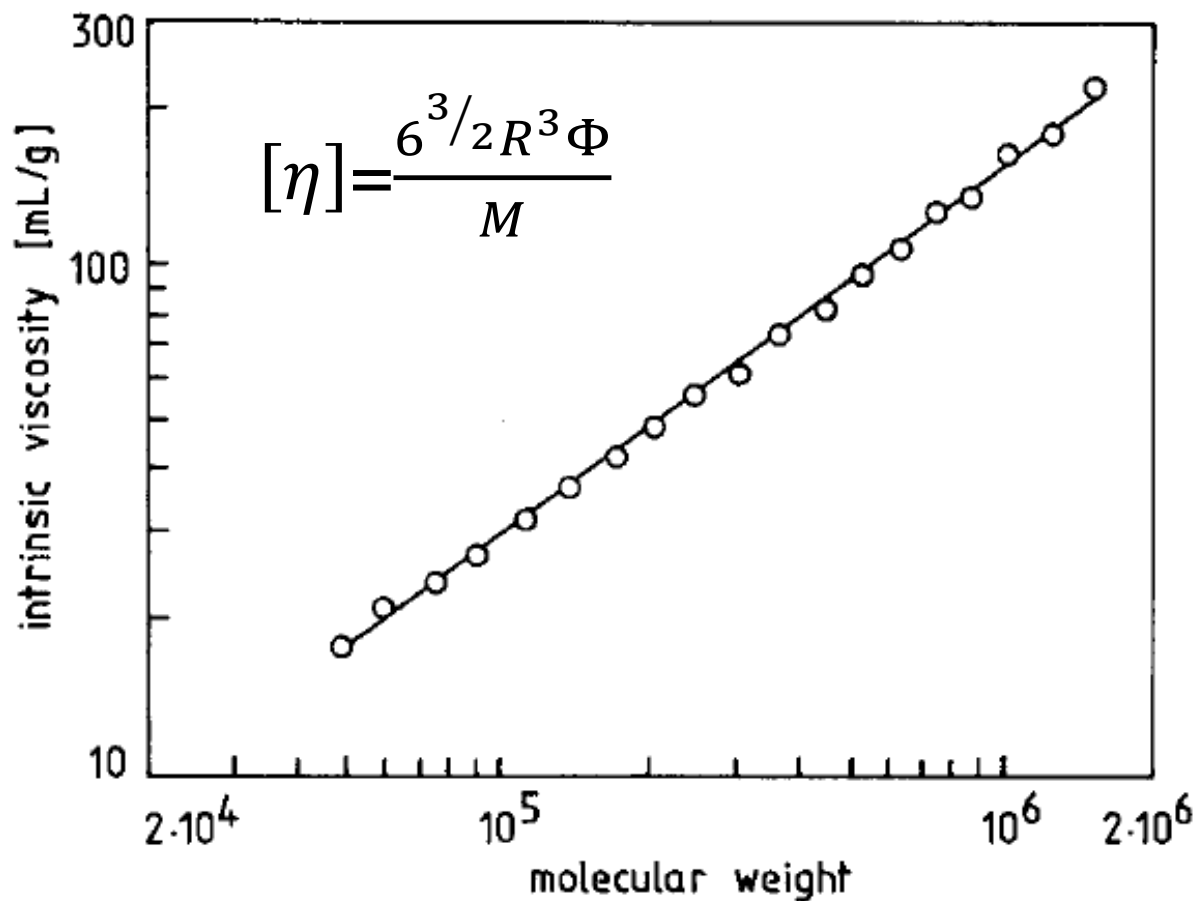
- T. G. Fox and P. J. Flory, *J. Am. Chem. Soc.*, **73**, 1904 (1951)
- O. B. Ptitsyn and Yu. E. Eizner, *Sov. Phys. Tech. Phys.*, **4**, 1020 (1960)

RMS Radius by MALS vs. Viscometry



Correlation of RMS radius by Flory-Fox with MALS (Polystyrene, THF, 25 °C).

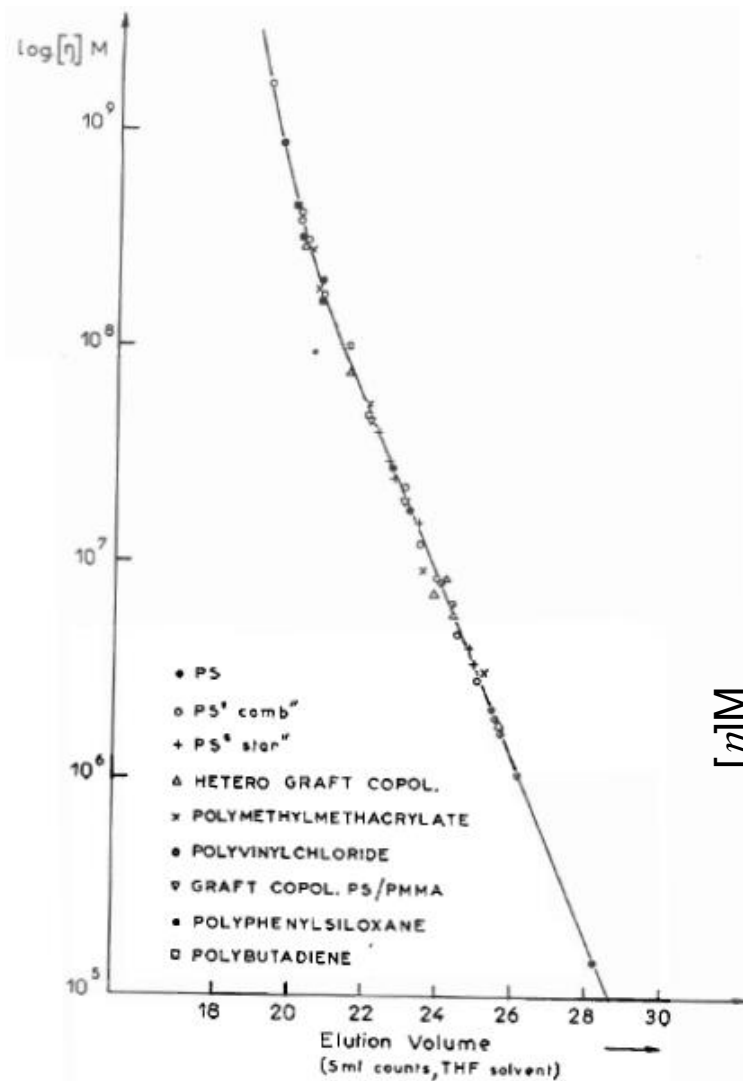
Intrinsic Viscosity by MALS



From S. Podzimek, *J. Appl. Polym. Sci.*, 54, 91 (1994). PMMA, THF, 25 °C, $a = 0.72$.

Universal Calibration

Universal Calibration

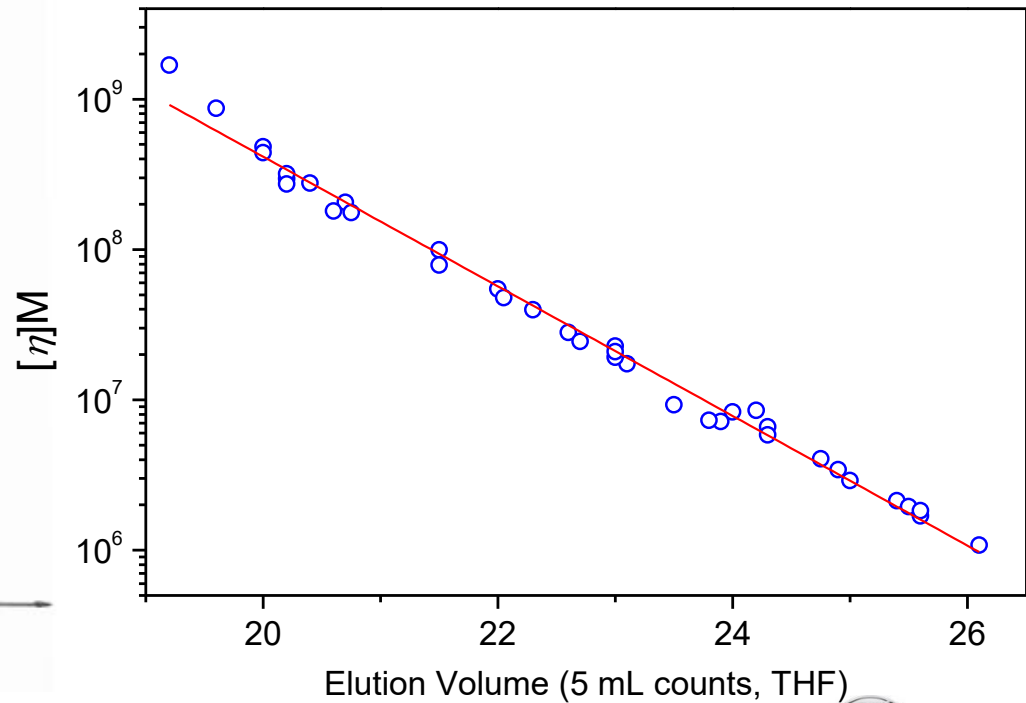


Z. Grubisic, P. Rempp, H. Benoit, *Polymer Letters*, 5, 753 (1967)

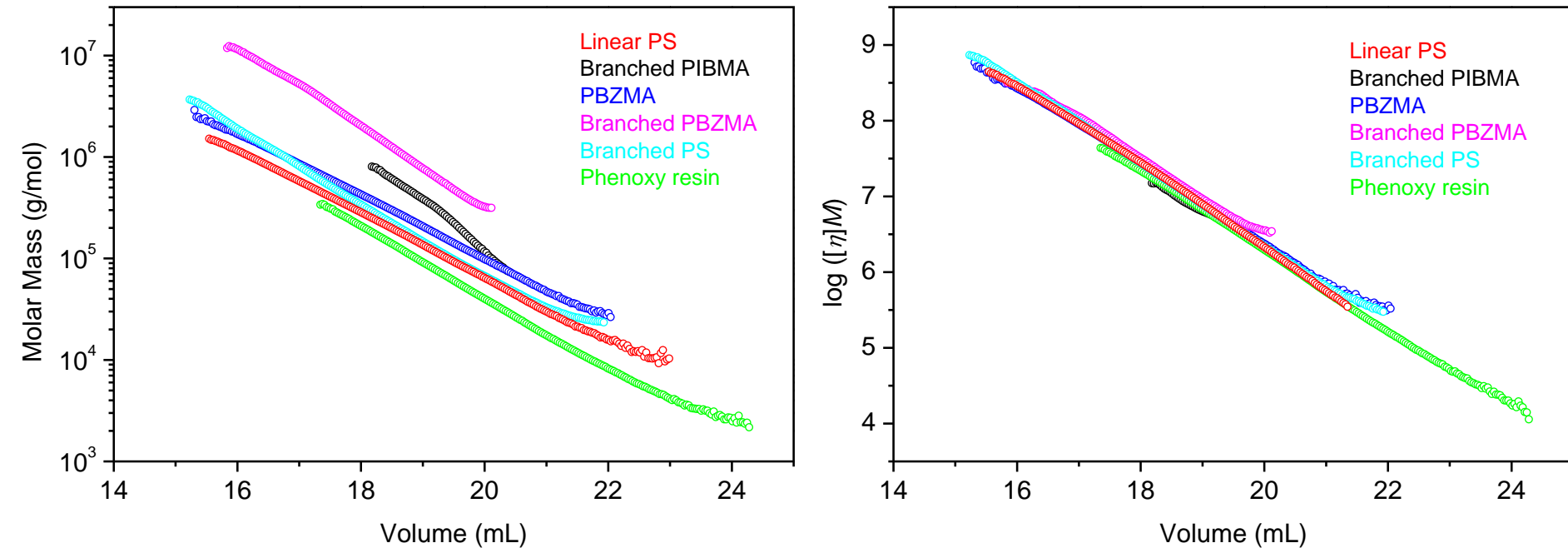
$$\log([\eta]M) = a + bV + \dots$$

$[\eta]$ intrinsic viscosity

M molar mass

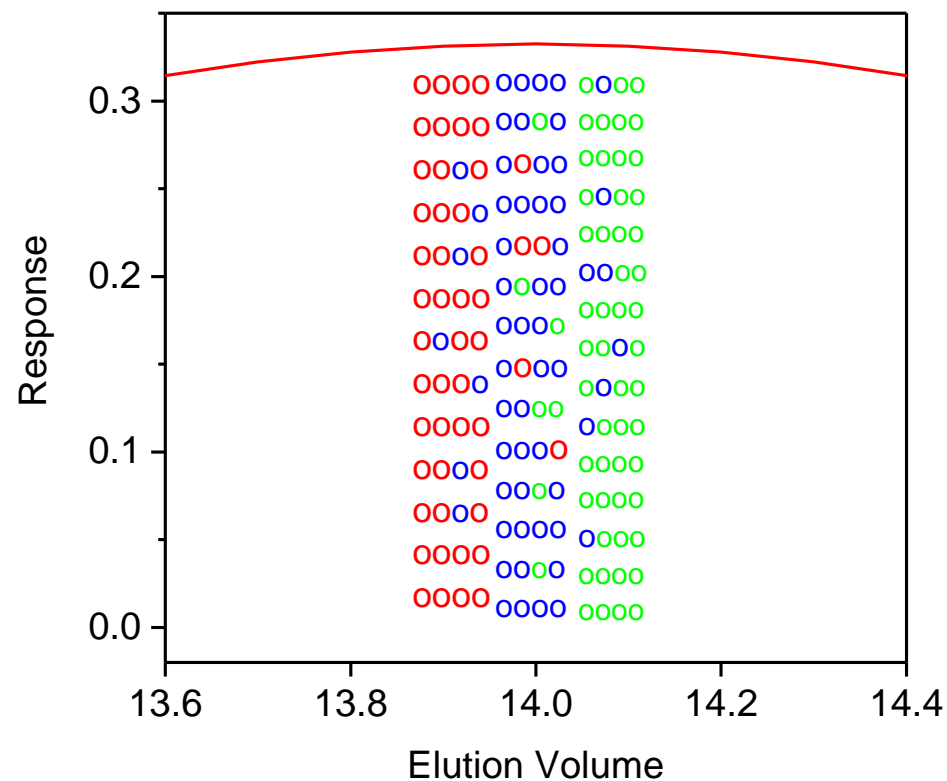
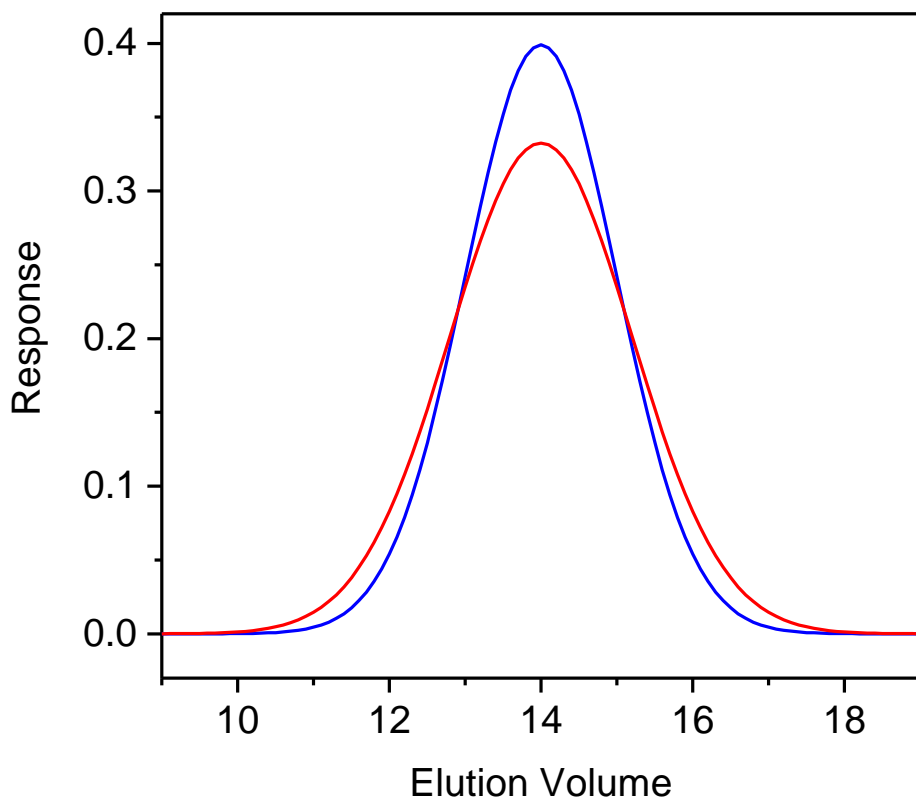


Universal Calibration



- Conventional calibration (left) versus universal calibration (right).
- Once the universal calibration is established typically by narrow standards, the molar mass of polymer is calculated from the intrinsic viscosity determined by viscometer and universal calibration curve.

Universal Calibration vs. MALS: Band Broadening in SEC



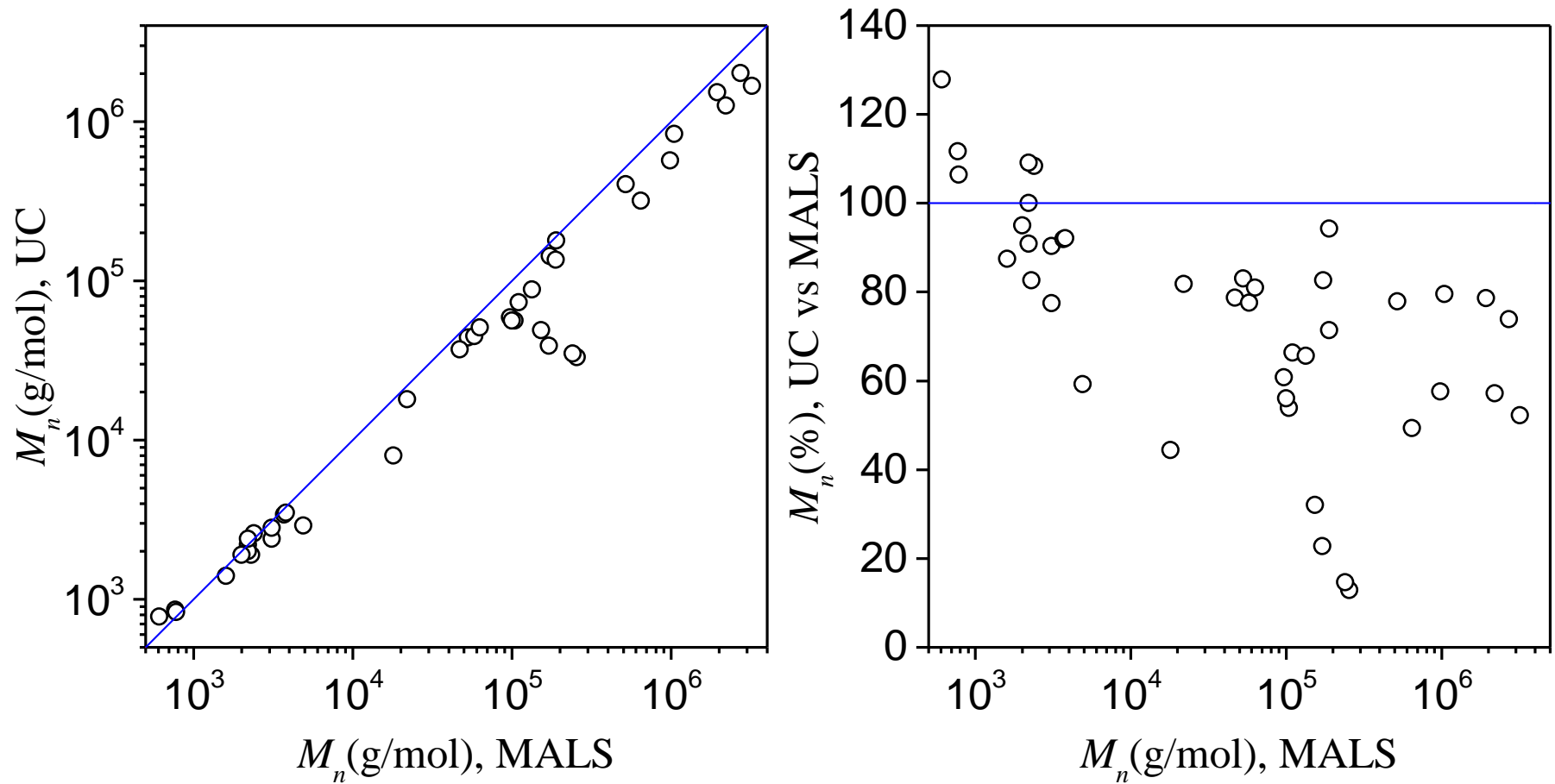
Ideal and experimental broadened chromatogram and polydispersity within elution volume slice.

Universal Calibration vs. MALS

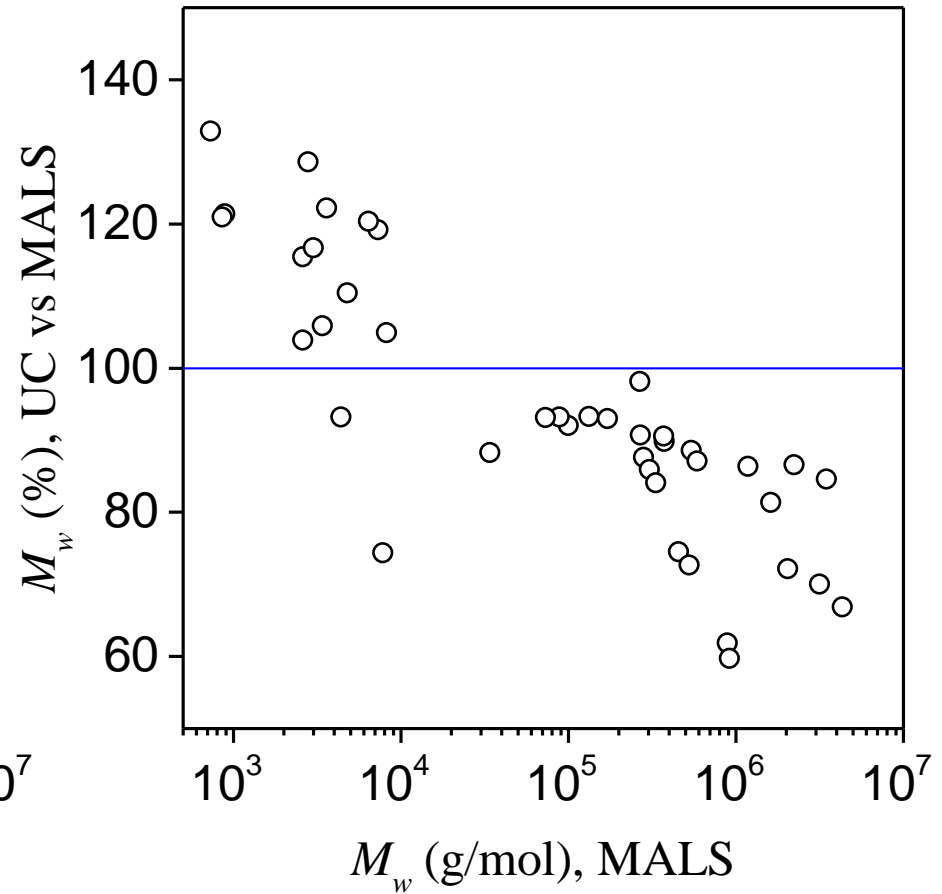
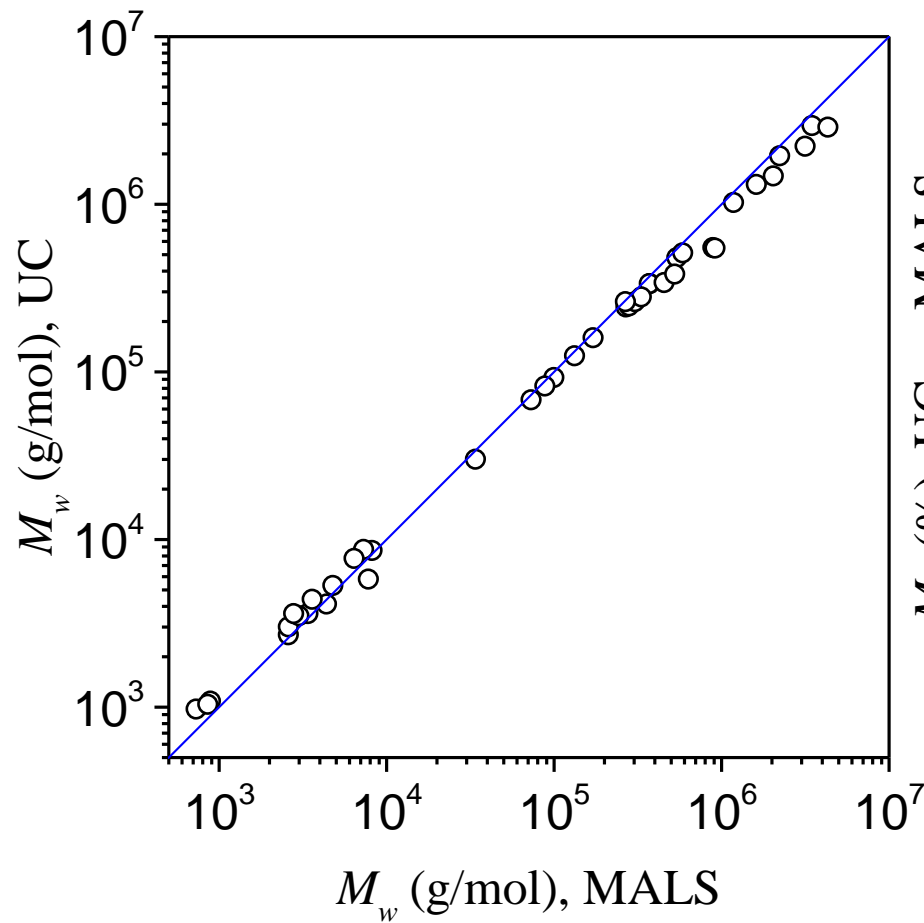
Polydisperse slice

- Slice polydispersity is always larger in case of branched polymers compared to linear polymers
- Molar masses are not M_i
- MALS measures weight-average $M_{w,i}$
- SEC-VIS-UC measures number-average $M_{n,i}$ (Balke, S. T., Mourey, T. H., and Harrison, C. A. *J. Appl. Polym. Sci.* **1994**, 51, 2087)
- Molar mass versus elution volume plots from MALS and UC should be parallel and the difference should indicate the slice polydispersity

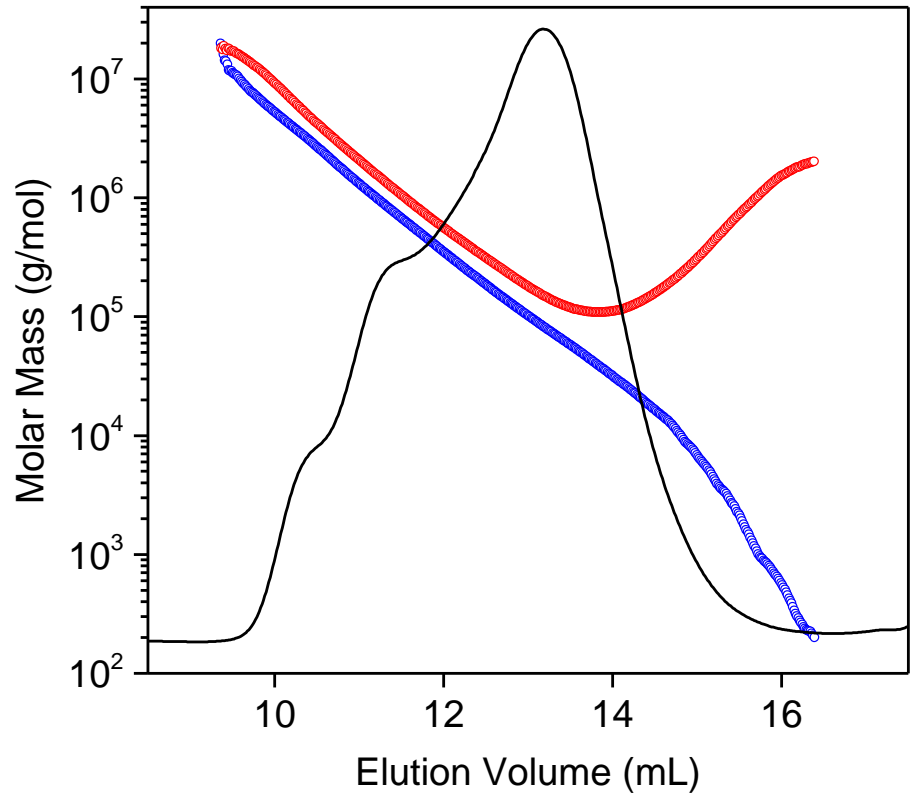
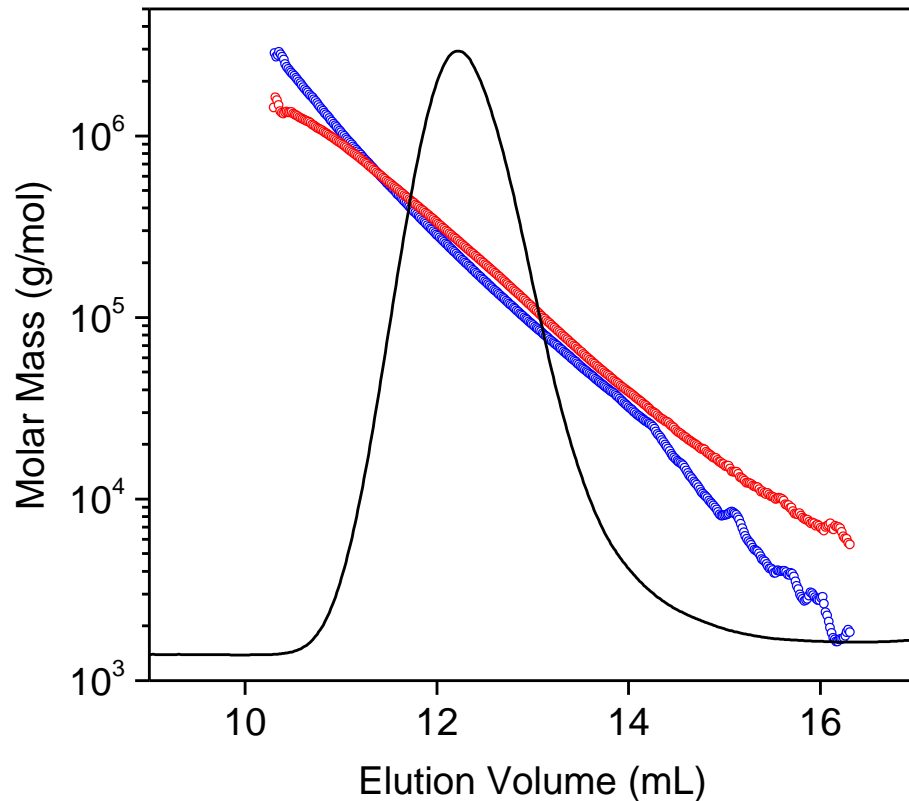
Universal Calibration vs. MALS: Number-Average M_n



Universal Calibration vs. MALS: Weight-Average M_w

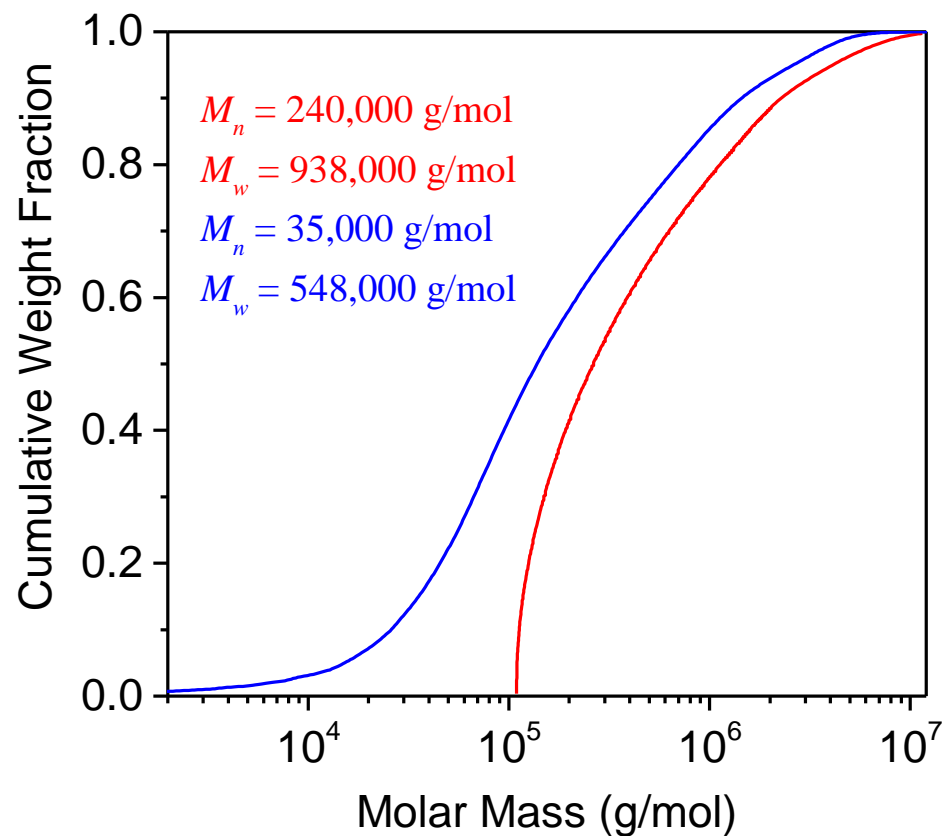
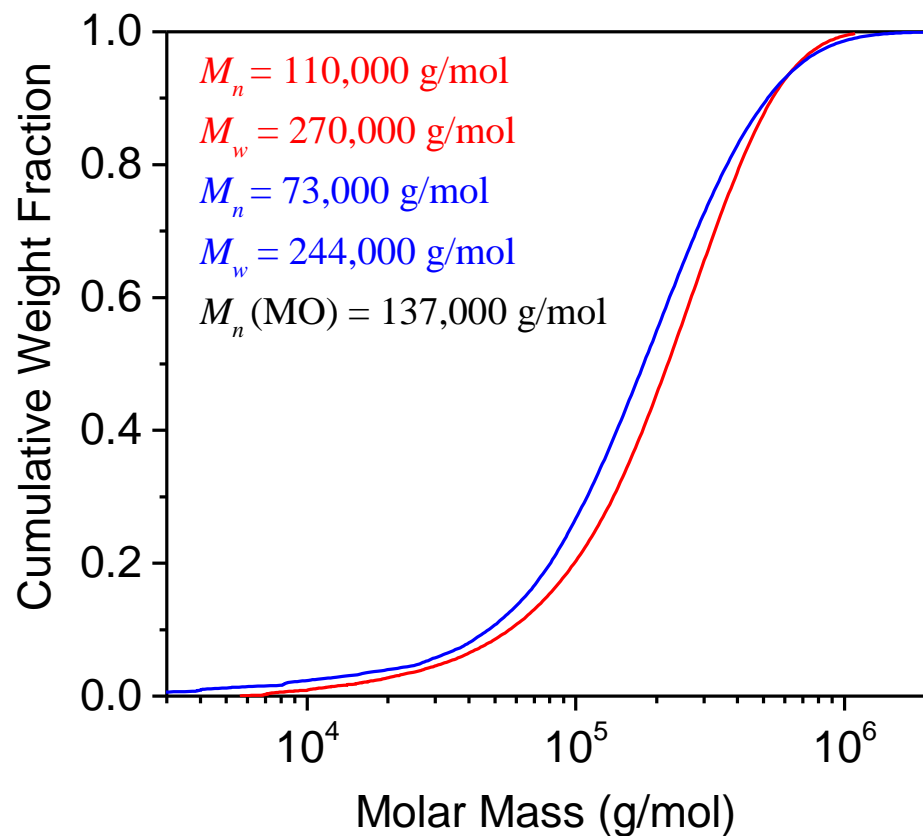


Universal Calibration vs. MALS: Molar Mass Plots



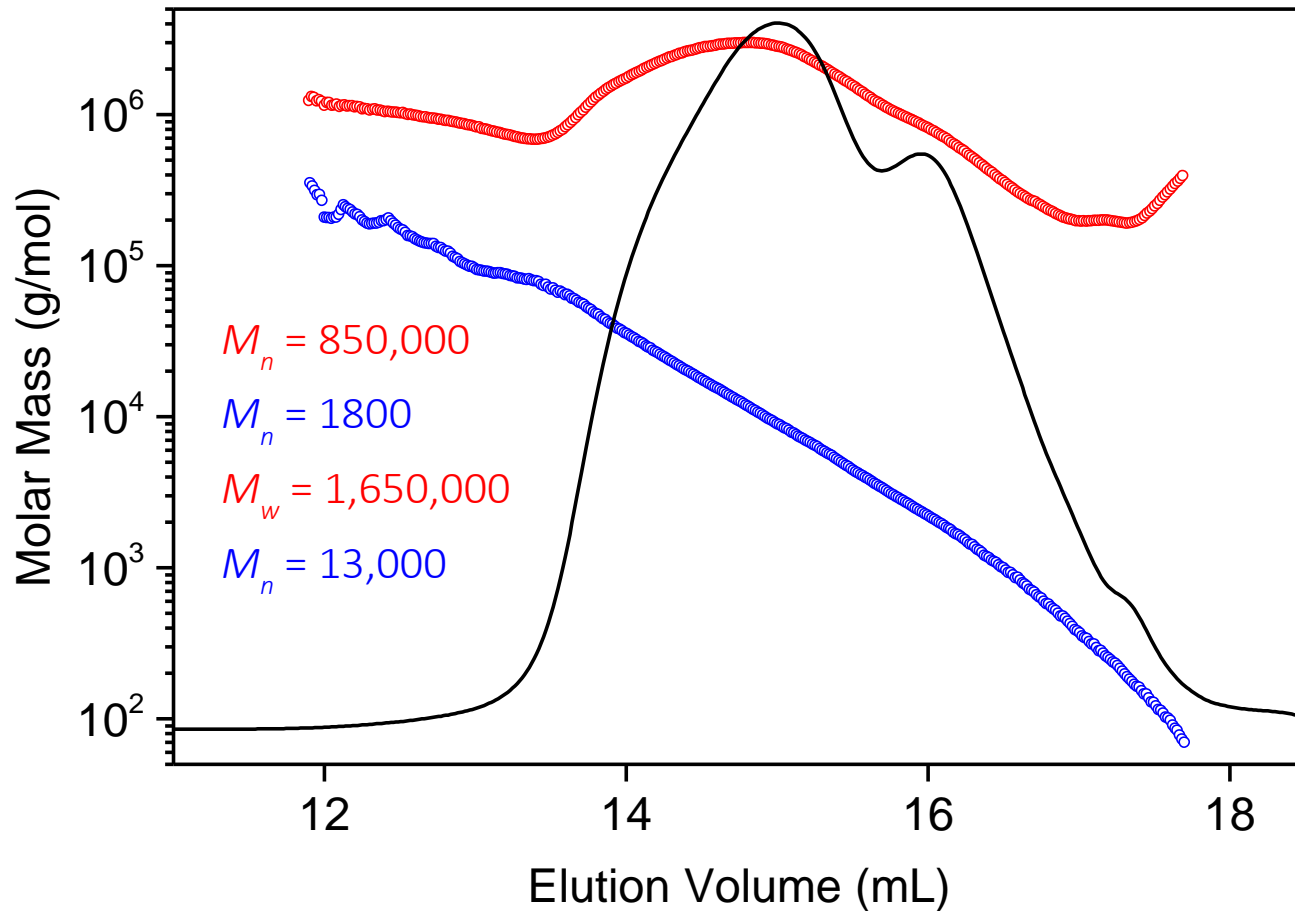
Molar mass versus elution volume plots from **MALS** and **universal calibration** for linear polystyrene (left) and branched polystyrene (right).

Universal Calibration vs. MALS: Molar Mass Distribution



Cumulative molar mass distributions from **MALS** and **universal calibration** for linear polystyrene (left) and branched polystyrene (right).

Universal Calibration vs. MALS: Molar Mass Plots



Molar mass versus elution volume plots from **MALS** and **universal calibration** for fluorescent polymer (lignin). RI chromatogram is shown here.



Mark-Houwink Plot

Characterization of Polymer Structure

$\log\text{--}\log [\eta]$ versus molar mass

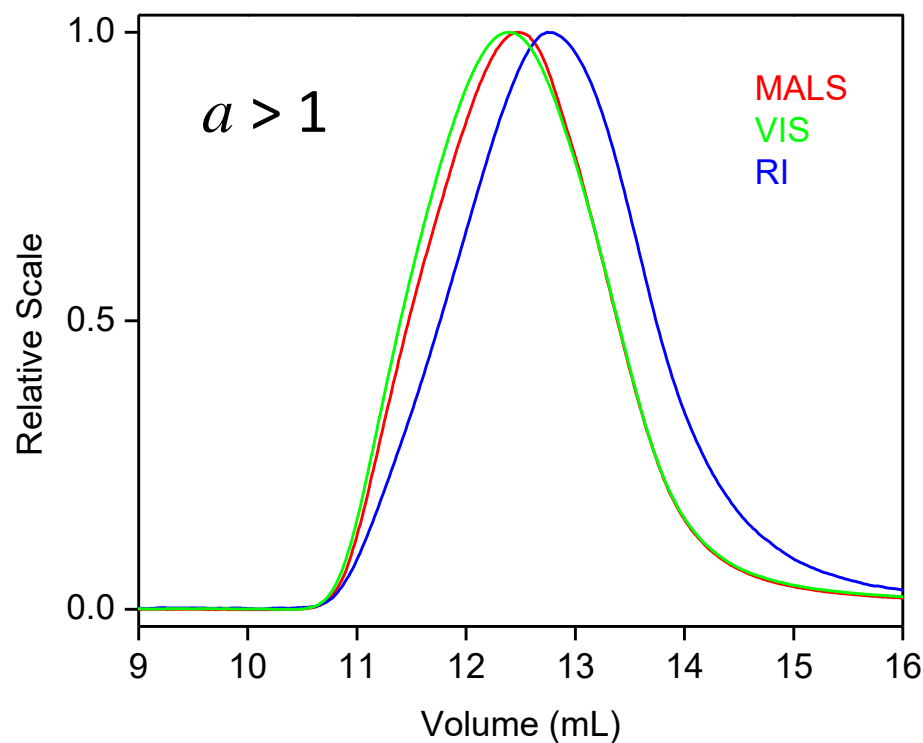
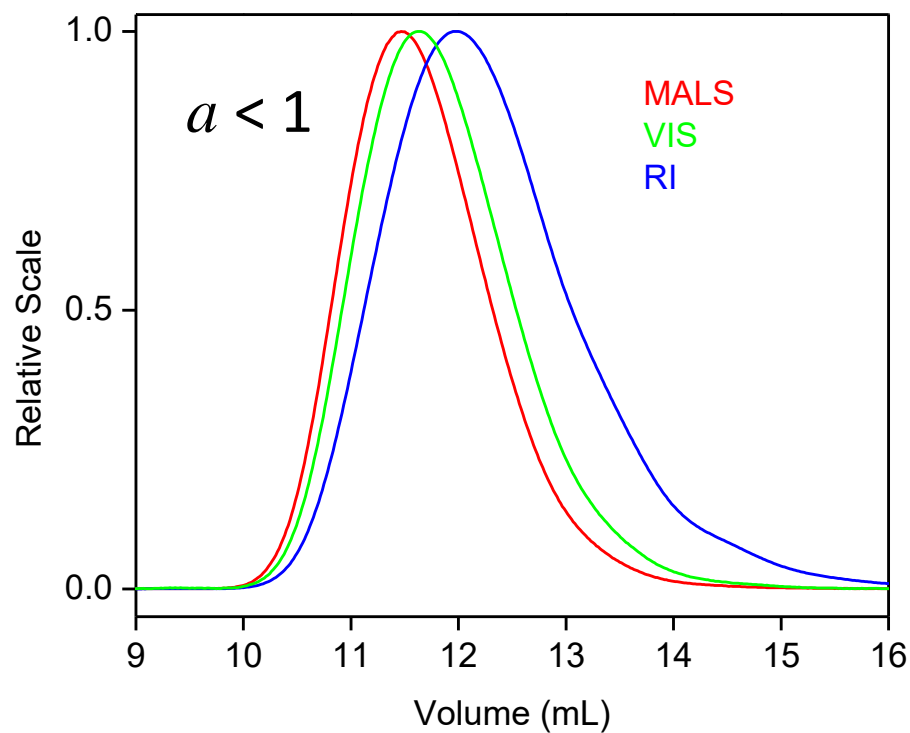


Molecular Structure from Mark-Houwink Plot

Exponent of Mark-Houwink equation

- Linear macromolecules in thermodynamically good solvents: $a \approx 0.7$
- Linear macromolecules in thermodynamically poor solvents: $a \approx 0.5$
- Oligomers: $a \approx 0.5$
- Hard spheres: $a \approx 0$
- Extended chains: $a \approx 0.8$ to ≈ 1.5
- Linear polymers have linear MH plots
- Curved plots indicates branching

Chain Stiffness from VIS/MALS Chromatograms



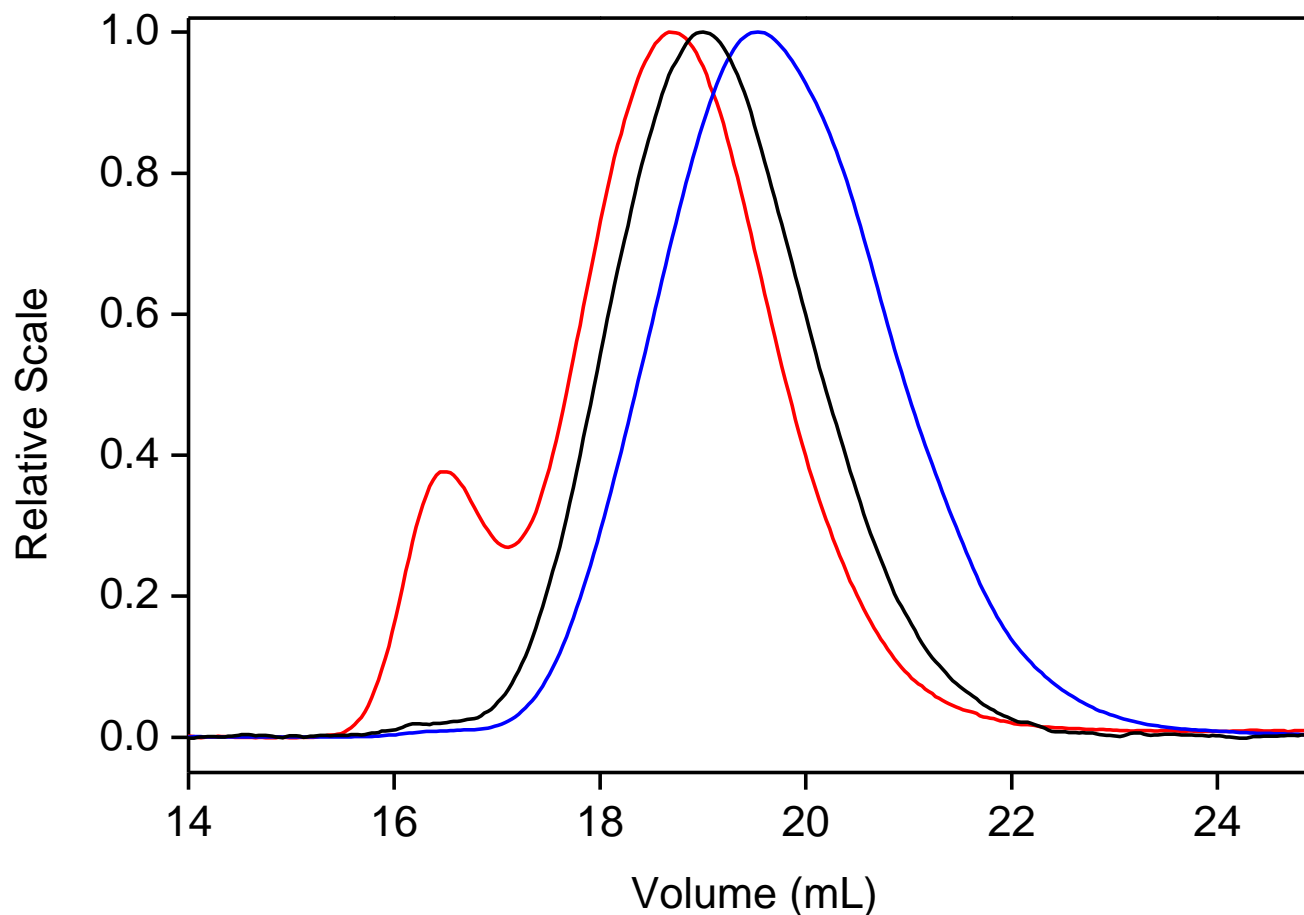
SEC- MALS-VIS-RI chromatograms of PS (left) and cellulose tricarbanilate (right) in THF.

$$S_{MALS} \approx c \times M$$

$$S_{VIS} \approx c \times M^a$$

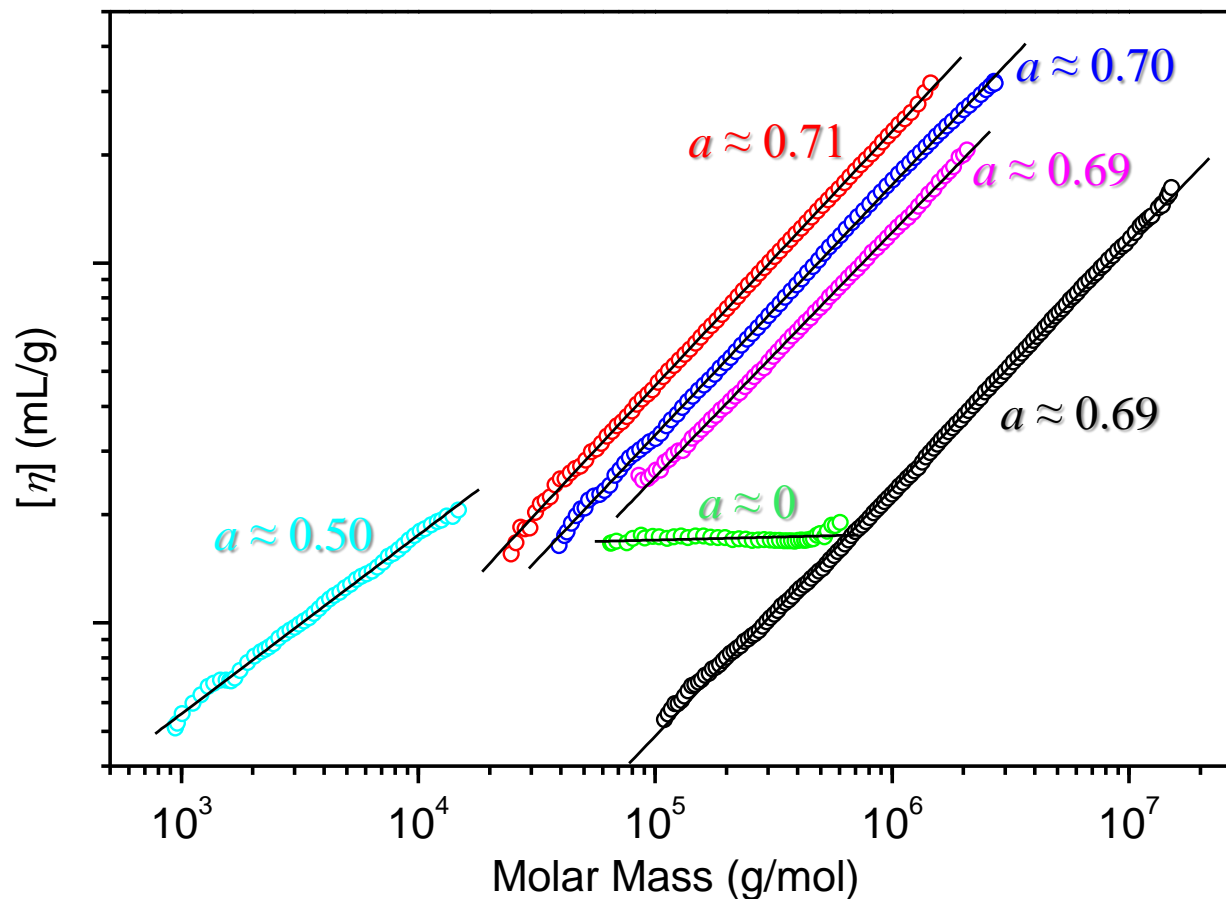
$$S_{RI} \approx c$$

High-Molar-Mass Highly Branched Fractions



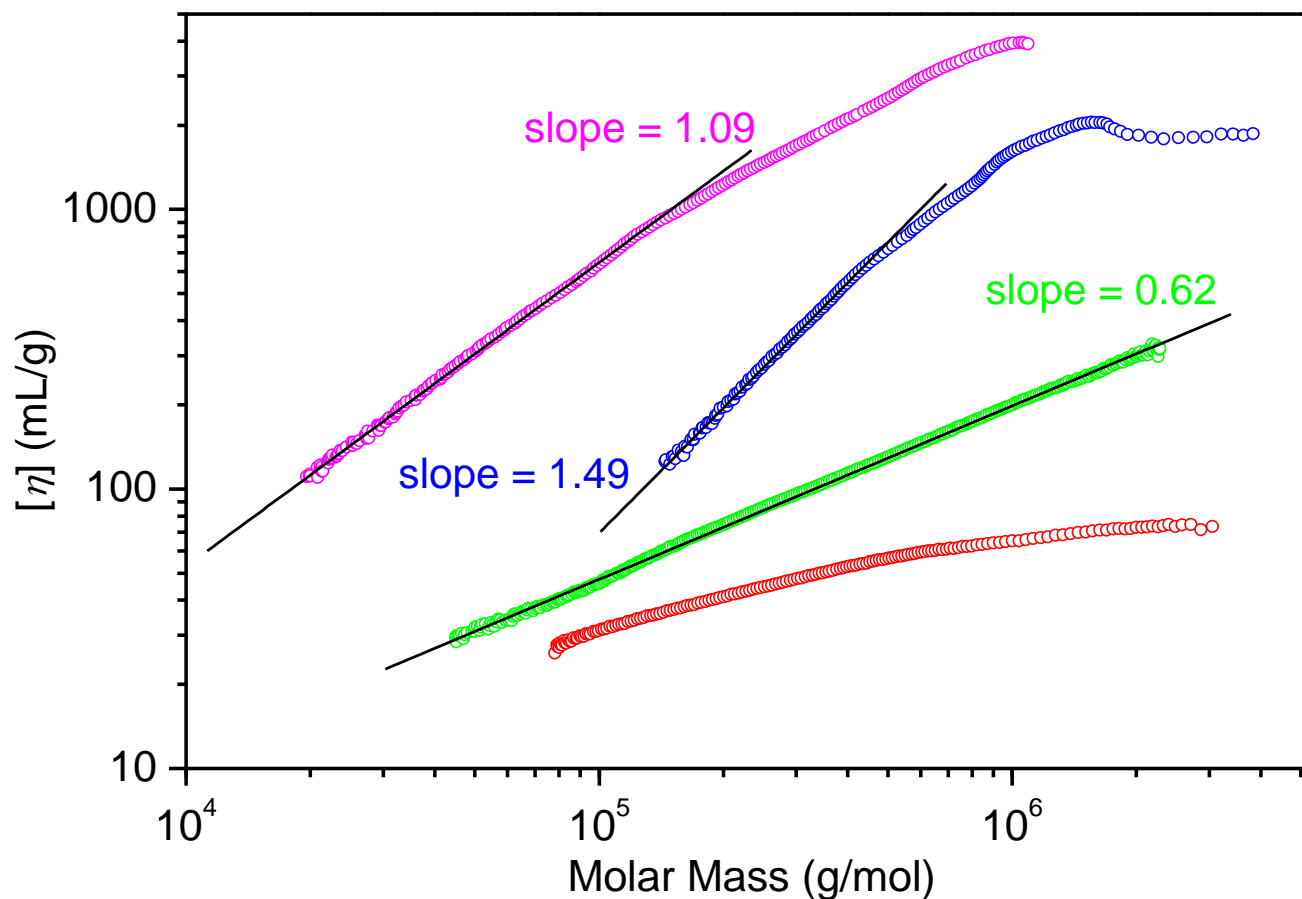
- Chromatograms from **MALS**, viscometer and **infrared detector** for NIST 1476 branched PE.
- Mark-Houwink exponent $a \rightarrow 0$ makes response of viscometer proportional to concentration.

Molecular Structure from Mark-Houwink Plot



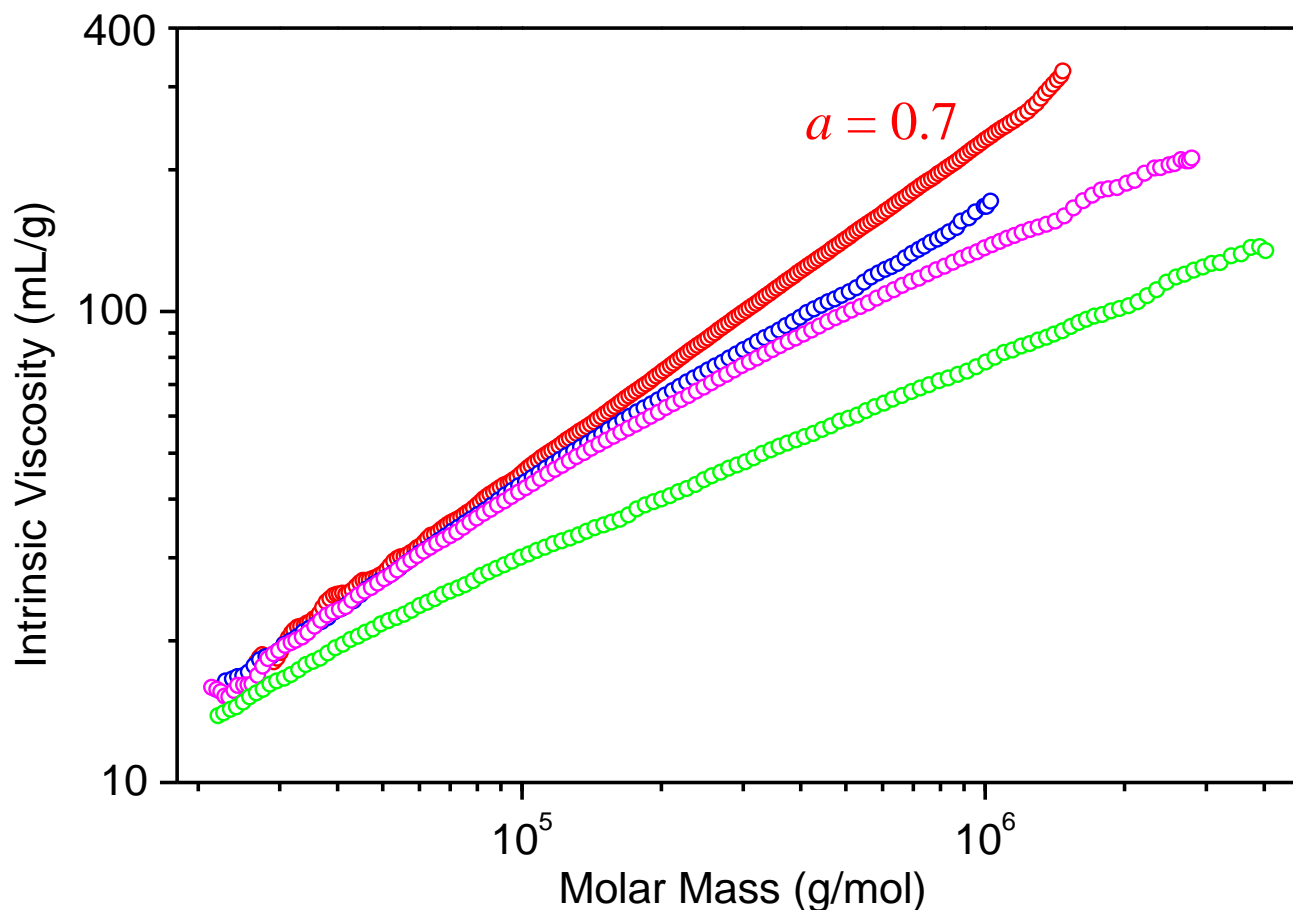
- Mark-Houwink plots of epoxy resin, linear polystyrene, linear poly(methyl methacrylate), linear poly(benzyl methacrylate), linear poly(iBuPOSSMA) and star-branched poly(isobutyl methacrylate).

Molecular Structure from Mark-Houwink Plot



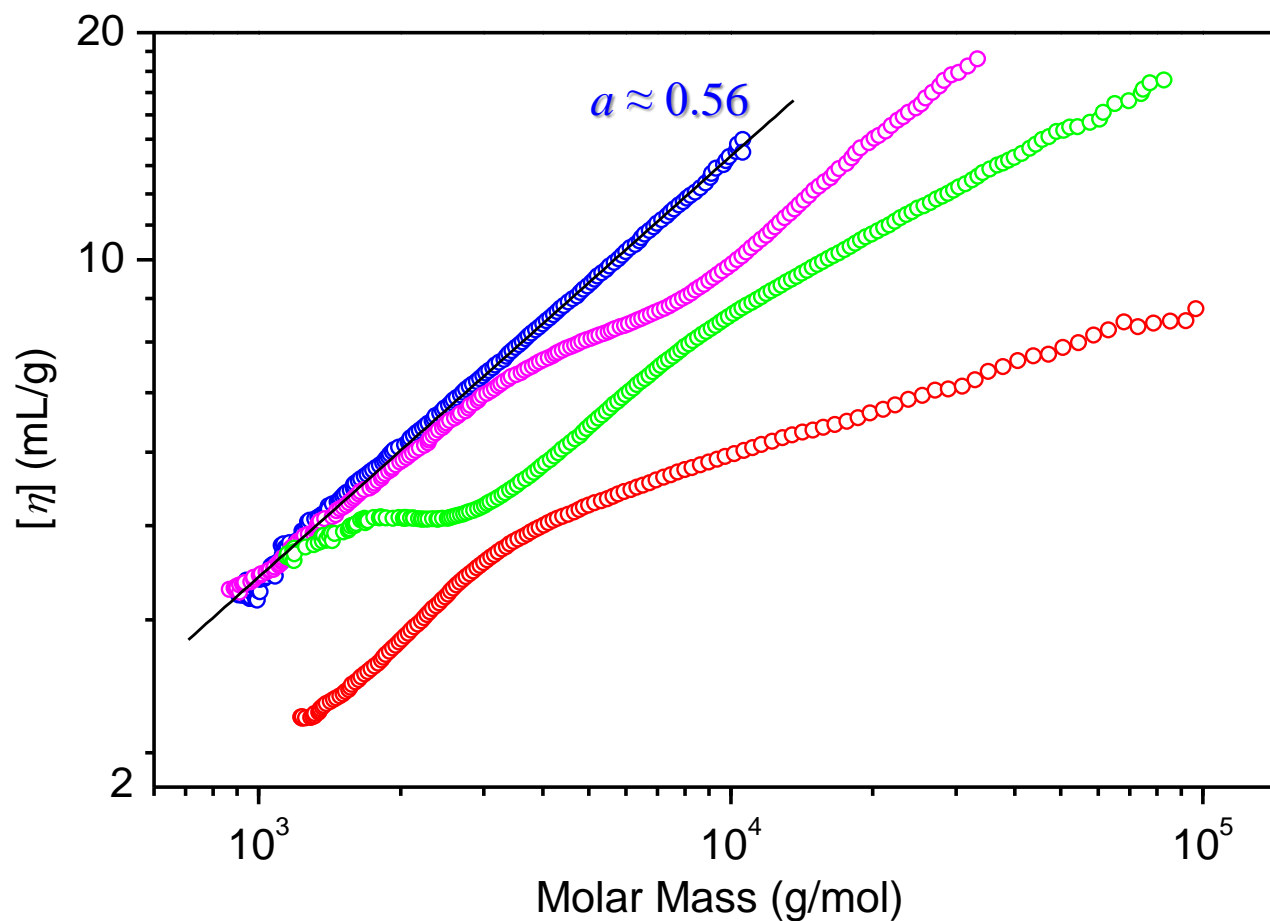
Mark-Houwink plots of **alginate**, **xanthan**, **pullulan**, and **dextran** in aqueous NaNO_3 .

Branching from Mark-Houwink Plot



Mark-Houwink plots of **linear polystyrene** and **branched** polystyrene prepared by copolymerization of styrene with various amounts of divinylbenzene. The degree of branching grows in the order of **blue**, **magenta** and **green**.

Branching from Mark-Houwink Plot



Mark-Houwink plots of linear PLGA 50/50 and branched PLGA containing 0.5 %; 3 % and 5 % dipentaerythritol.



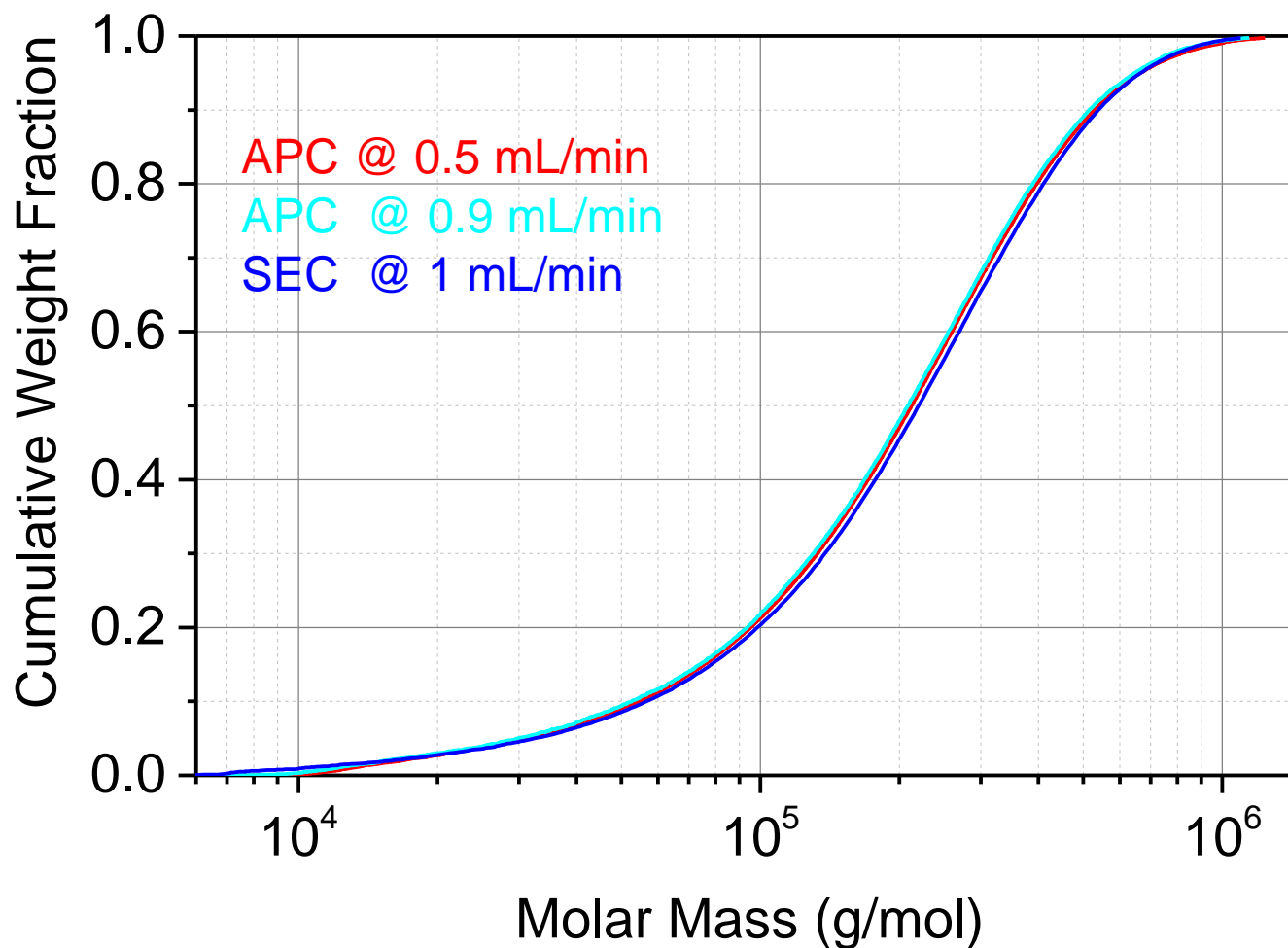
Micro-Viscometer

Advanced Polymer Chromatography, APC

μ -SEC

μ -DAWN, UT-rEX, μ -ViscoStar

SEC-MALS versus APC- μ MALS: Molar Mass Distribution



Cumulative molar mass distribution of NIST 706 polystyrene.

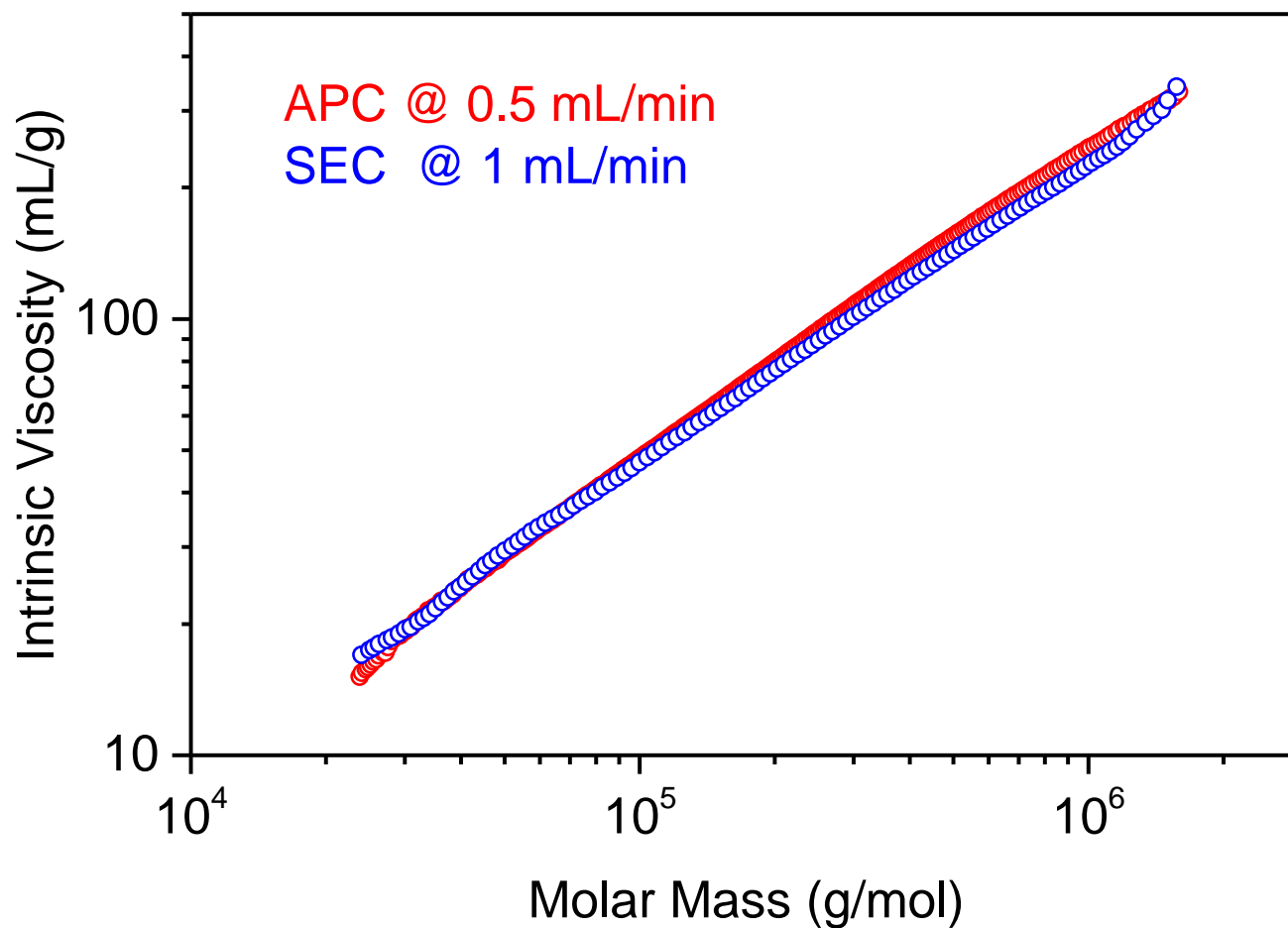
APC-μMALS- μVIS: Molar Mass and Intrinsic Viscosity Averages

Set-up	M_n (10 ³ g/mol)	M_w (10 ³ g/mol)	M_z (10 ³ g/mol)	$[\eta]$ (mL/g)
SEC-MALS-VIS* 1 mL/min	110 ± 1	269 ± 1	424 ± 4	87.8 ± 0.1
SEC-μMALS-μVIS** 0.9 mL/min	127 ± 7	259 ± 3	410 ± 3	89.4 ± 0.5
SEC-μMALS-μVIS** 0.5 mL/min	116 ± 4	263 ± 1	426 ± 2	91.1 ± 0.3

*Agilent 1100 HPLC; PLgel Mixed-C 300 × 7.5 mm 5 μm columns; HELEOS, T-rEX, ViscoStar III

**Waters Acquity APC; 900 Å, 4.6 × 150 mm, 2.5 μm; 450 Å, 4.6 × 75 mm, 2.5 μm; 125 Å, 4.6 × 150 mm, 2.5 μm; and 45 Å, 4.6 × 150 mm, 1.7 μm; μDAWN, UT-rEX, μViscoStar

SEC-MALS versus APC- μ MALS: Mark-Houwink Plot





Summary

- Universal calibration is valid, but less accurate and robust than MALS.
- UC for highly branched polymers (M_n) and fluorescent polymers.
- The major application of online viscometer is in the area of structural studies.
- Mark-Houwink plot provides information about polymer chain conformation and branching.
- Intrinsic viscosity allows calculation of hydrodynamic radius with higher sensitivity than DLS.
- Wyatt Technology ViscoStar® III is a successor of the previous two generations of the instrument with several advanced features.
 - Bridge balance autotune
 - Faster pressure sensors (less peak broadening)
- Wyatt Technology μ -ViscoStar is compatible with APC