Multi-Angle Light Scattering for the Characterization of Molecular Structure … and some Historical Perspectives

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Outline

- Molecular structure of polymers
- Challenges in the characterization of molecular structure
- Historical remarks
- MALS and SEC
- MALS and AF4
- MALS and online viscometer
- Final remarks

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Molecular Structure of Synthetic and Natural Polymers

- Molar mass and molar mass distribution
- Branching
  - Randomly branched polymers
  - Stars
  - Combs
  - Other (exotic) structures (ladders, centipedes, barbed wire)
- Aggregates
- Conformation of polymer chains is solution
  - Contraction and expansion of polymer chains
    (viscosity modifiers for food additives, motor oils additives)
- Chemical heterogeneity
  - Distribution of chemical composition
  - Chemical composition as a function of molar mass

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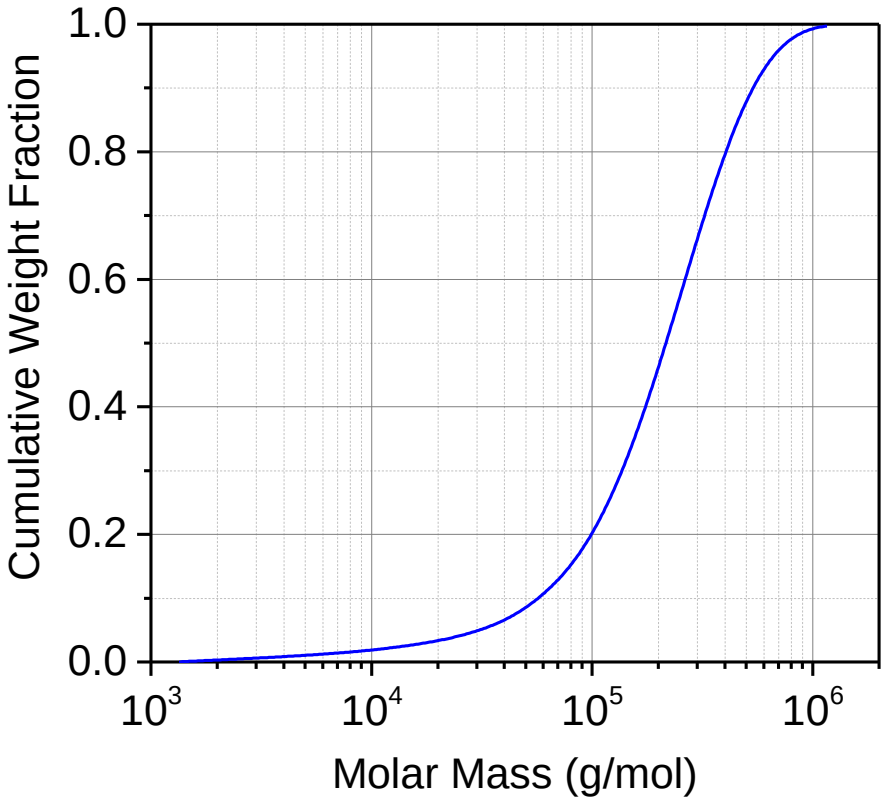
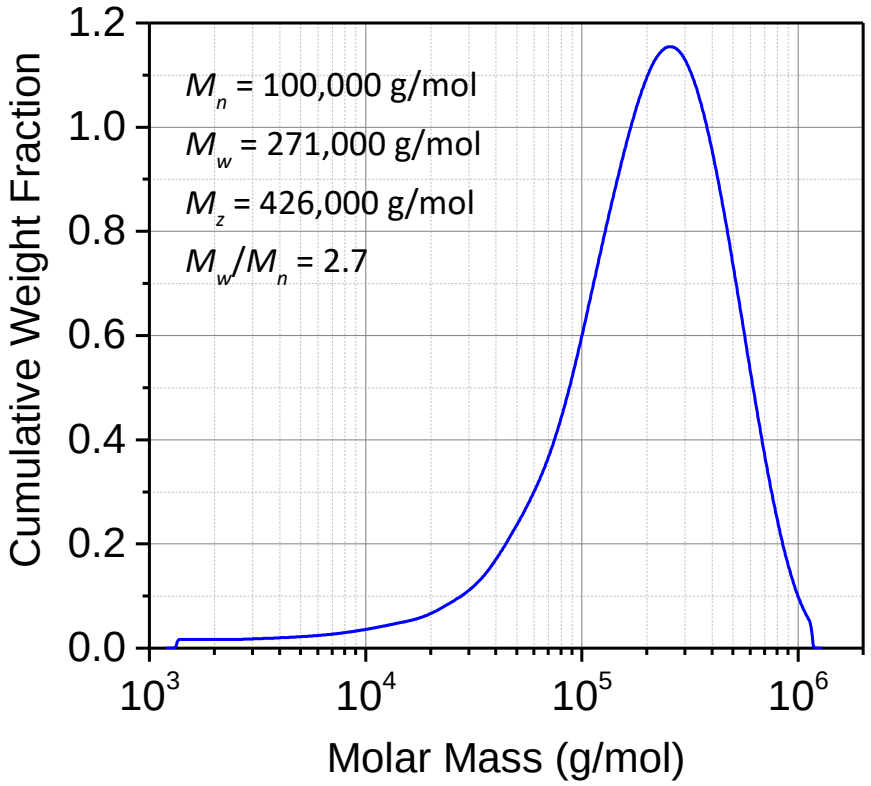
Molecular Structure: Molar Mass Distribution





Cumulative and differential molar mass distributions of polystyrene NIST 706.

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Molecular Structure: Branching

Linear polymer

Branched polymer (Soluble)

Crosslinked polymer (Insoluble, makroscopic gel, micro- or nano-gels)

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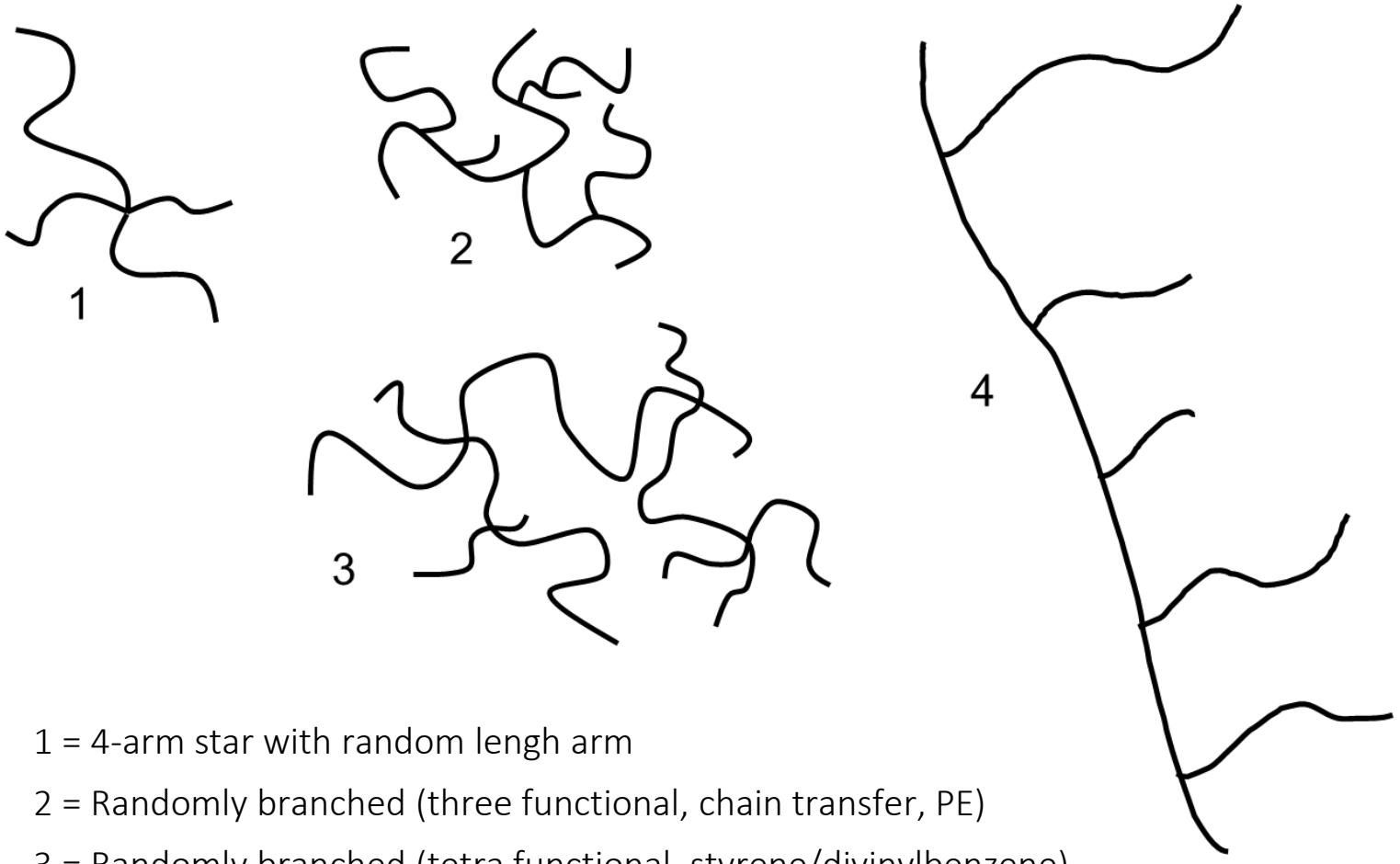
Branching of Polymer Chains



- 1 = 4-arm star with random lengh arm
- 2 = Randomly branched (three functional, chain transfer, PE)
- 3 = Randomly branched (tetra functional, styrene/divinylbenzene)
- 4 = Comb (grafted copolymer)

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Molecular Structure and Polymer Properties

Molar mass distribution

- Properties
  - Mechanical properties
  - Viscoelastiv properties
  - Viscosity of solutions and melts
  - Rheological properties (flow curve)
  - Solubility
  - Second virial coefficient
  - Ability to create films and fibers
  - Processability
  - Degradability
- Information about
  - Polymerization kinetics
  - Manufacturing reproducibility
  - Polymer degradation
  - Polymer batch identity

Branching

- Properties
  - Mechanical properties
  - Viscoelastic properties
  - Viscosity of solutions and melts
  - Rheological properties (flow curve)
  - Solubility
  - Second virial coefficient
  - Ability to crystallize
  - Processability
  - Degradability

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Challenges in Polymer Structure Characterization

- Polymers are complex (often more distributed properties)
  - Molar mass distribution
  - Chemical composition distribution
  - Branching distribution
  - Supermolecular structures (nanogels) versus soluble macromolecules
- Improper separation
  - Band broadening (zone spreading)
  - Interactions with SEC column packing
  - Anchoring of the branched macromolecules in the pores of SEC packing
  - Brownian and steric separation in AF4
- Fluorescence
  - Molar mass overestimation

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Historical Perspectives …

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… From Stepan´s View Point

- SEC/GPC
  - Columns 120 cm × 8 mm, run time hours, chart recorder, mainframe computer, 1982
  - Columns 300 × 8 mm, tens of min, integrator, 1983
  - APC, 150 mm × 4.6 mm, minutes, 2017
- SEC-MALS
  - DAWN F, PC, 1992 (University of Heinrich Heine, Duesseldorf)
  - miniDAWN, 1998
  - DAWN EOS, 1999 (Wyatt Technology, Santa Barbara)
  - QELS, 2001
  - HELEOS, 2011
  - APC-µMALS, 2017 (visit of WTE in Dernbach)
  - HELEOS with infrared laser, 2018
  - APC-µMALS-µVIS, 2018 (Stepan´s samples measured in Santa Barbara)
- AF4
  - Aqueous, 2005; Organic, 2006
- Online viscometry
  - ViscoStar I, 2005; ViscoStar III, 2015

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… From Stepan´s View Point

Waters GPC 200 (SYNPO, seventies); Spectra-Physics HPLC (SYNPO, eighties); and Waters 600 pump, 717 autosampler, 410 RI, 996 PDA, and DAWN F (SYNPO, nineties).

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Characterization of Branching

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Conformation Plot (RMS Radius vs Molar Mass)

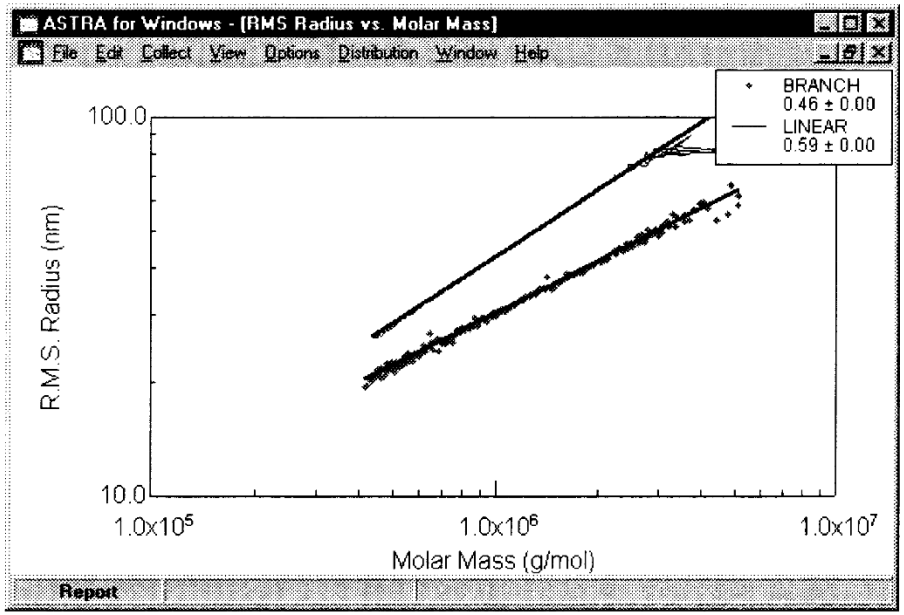

Figure 6-24. RMS Radius vs. MM for branched and linear PMMA.

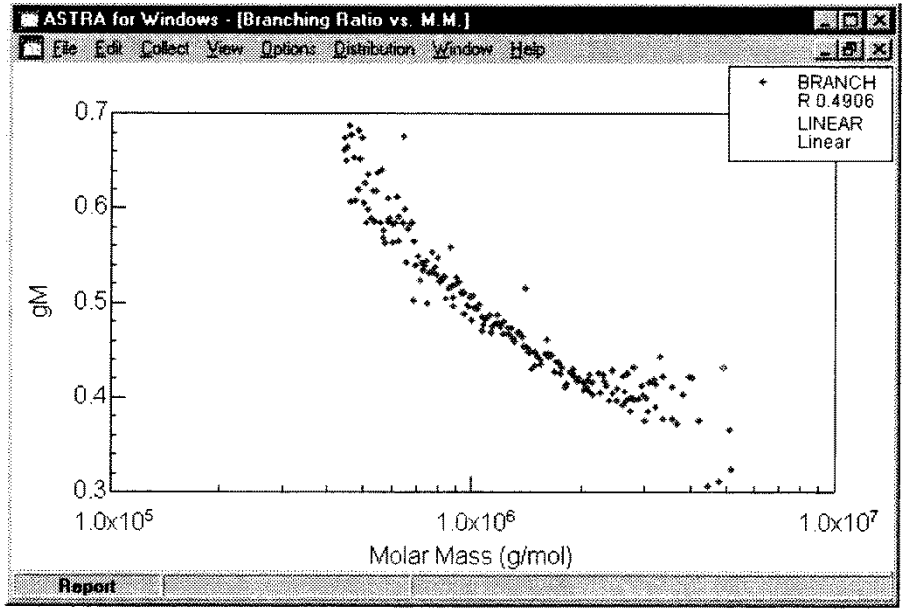

Figure 6-25. Branching Ratio.

Astra USER´s Guide, nineties.

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Branching Studies

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 17, NUMBER 12 DECEMBER, 1949

The Dimensions of Chain Molecules Containing Branches and Rings

BRUNO H. ZIMM
Department of Chemistry, University of California, Berkeley, California

AND

WALTER H. STOCKMAYER
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received May 2, 1949)

Formulas for the mean square radii of various branched and ringed polymer molecules are developed under the usual assumptions regarding the statistics of chain configuration. For branched molecules, the mean square radii vary less rapidly with molecular weight than for strictly linear molecules, while for systems containing only rings and unbranched chains the variation is more rapid than for the linear case. These results show that in principle the quantity of branches or of rings can be determined from light-scattering measurements.

Published before the MALS, SEC, AF4!

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Branching Studies

JOURNAL OF POLYMER SCIENCE VOL. XXXVII, PAGES 19–42 (1959)

Dynamics of Branched Polymer Molecules in Dilute Solution

BRUNO H. ZIMM and RALPH W. KILB, *General Electric Research Laboratory, Schenectady, New York*

I. INTRODUCTION

Out of a great deal of speculation about the properties of branched, high polymer chain molecules, at least one fact has been definitely established experimentally: the intrinsic and bulk viscosities are less than those of linear molecules of the same molecular weight.[1–3] The theory of the bulk viscosity of even linear polymers is still rather uncertain, but the theory of the intrinsic viscosity of linear polymers has developed to the point of quite fair agreement with experiment.[4–7] In this paper we attempt to extend the hydrodynamic theory of the intrinsic viscosity to branched chains.

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Long-Chain Branching

Zimm and Stockmayer: *The Dimensions of Chain Molecules Containing Branches and Rings*, J. Chem. Phys., 17, 1301 (1949).

$$g = \left(\frac{R^2_{branched}}{R^2_{linear}} \right)_M$$

Branching ratio, g

R = root mean square radius (radius of gyration)

Zimm and Kilb: *Dynamics of Branched Polymer Molecules in Dilute Solution*, J. Polym. Sci., 37, 19 (1959).

$$g' = \left(\frac{[\eta]_{branched}}{[\eta]_{linear}} \right)_M = g^e$$

$[\eta]$ = intrinsic viscosity

e = draining parameter ($\approx 0.5 - 1.5$)

Linear polymer: $g = g' = 1$

Branched polymer: $g < 1$, $g' < 1$

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Long-Chain Branching

Zimm and Stockmayer: *The Dimensions of Branched Molecules Containing Branches and Rings*, J. Chem. Phys., 17, 1301 (1949).

$$g_3 = \left[\left(1 + \frac{m}{7} \right)^{\frac{1}{2}} + \frac{4m}{9\pi} \right]^{-\frac{1}{2}}$$

$$g_4 = \left[\left(1 + \frac{m}{6} \right)^{\frac{1}{2}} + \frac{4m}{3\pi} \right]^{-\frac{1}{2}}$$

m number of branch units in randomly branched polymers

3, 4 branch unit functionality (3 in case of chain transfer, e.g. polyethylene; 4 in case of divinyl monomer)

$$g = \frac{6f}{(f+1)(f+2)}$$

f number of arms in random length star

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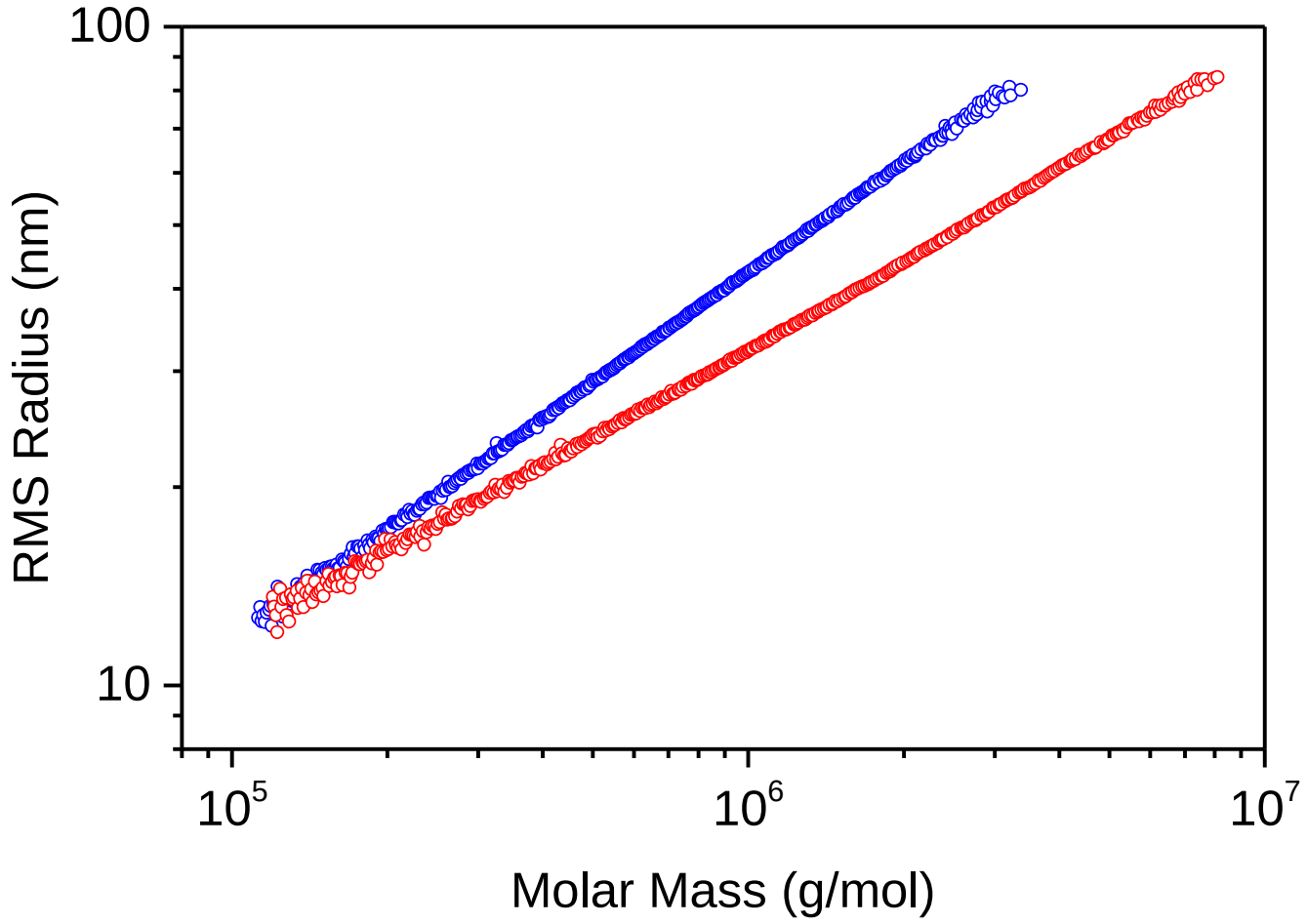
Conformation Plot



Conformation plots of linear and randomly branched polystyrene. Slopes = 0.56; 0.46.
Waters 2 × 300 × 8 mm HR5E columns, miniDAWN, 1999.

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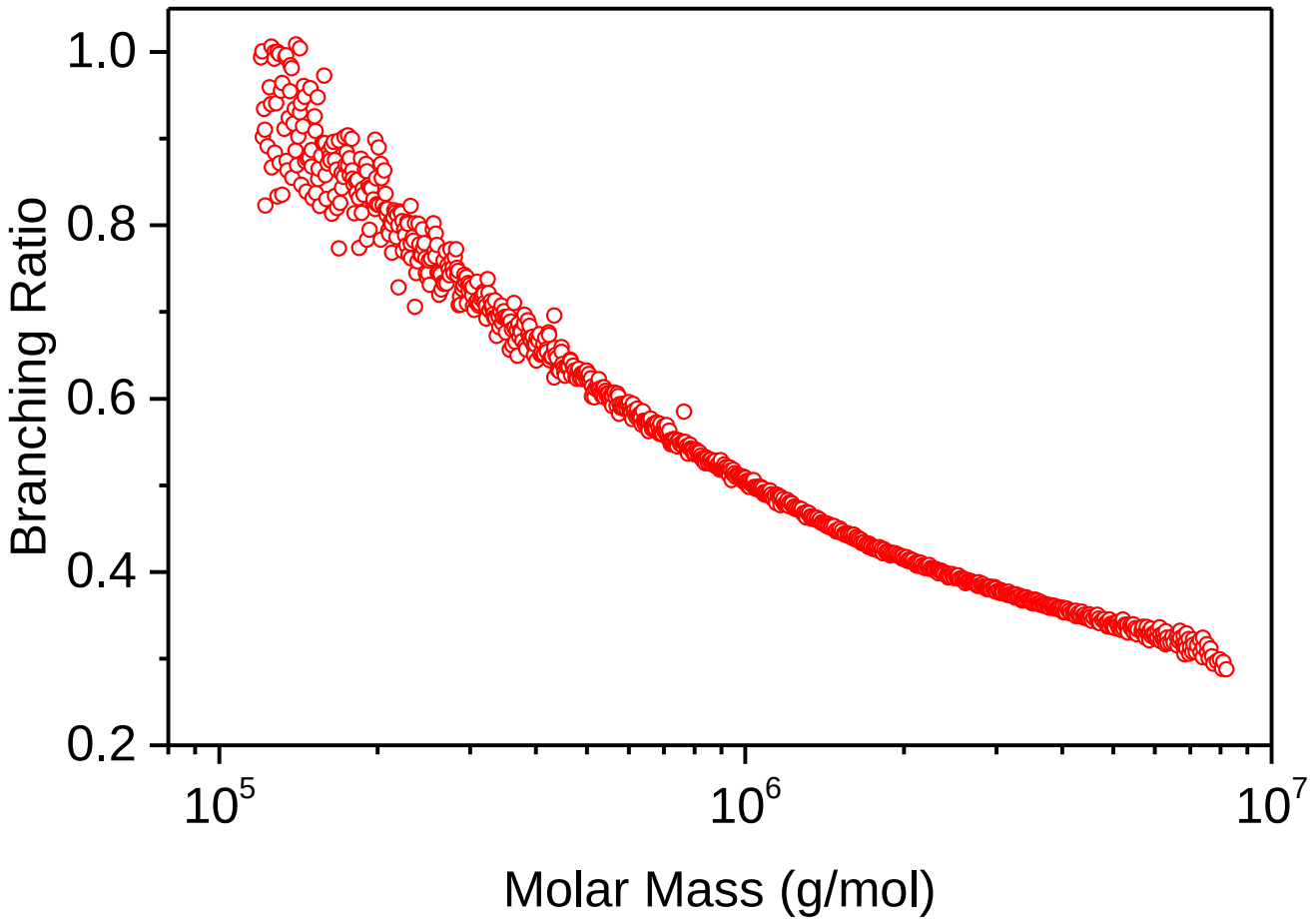
Branching Ratio



Branching ratio of randomly branched polystyrene.
Waters 2 × 300 × 8 mm HR5E columns, miniDAWN, 1999.

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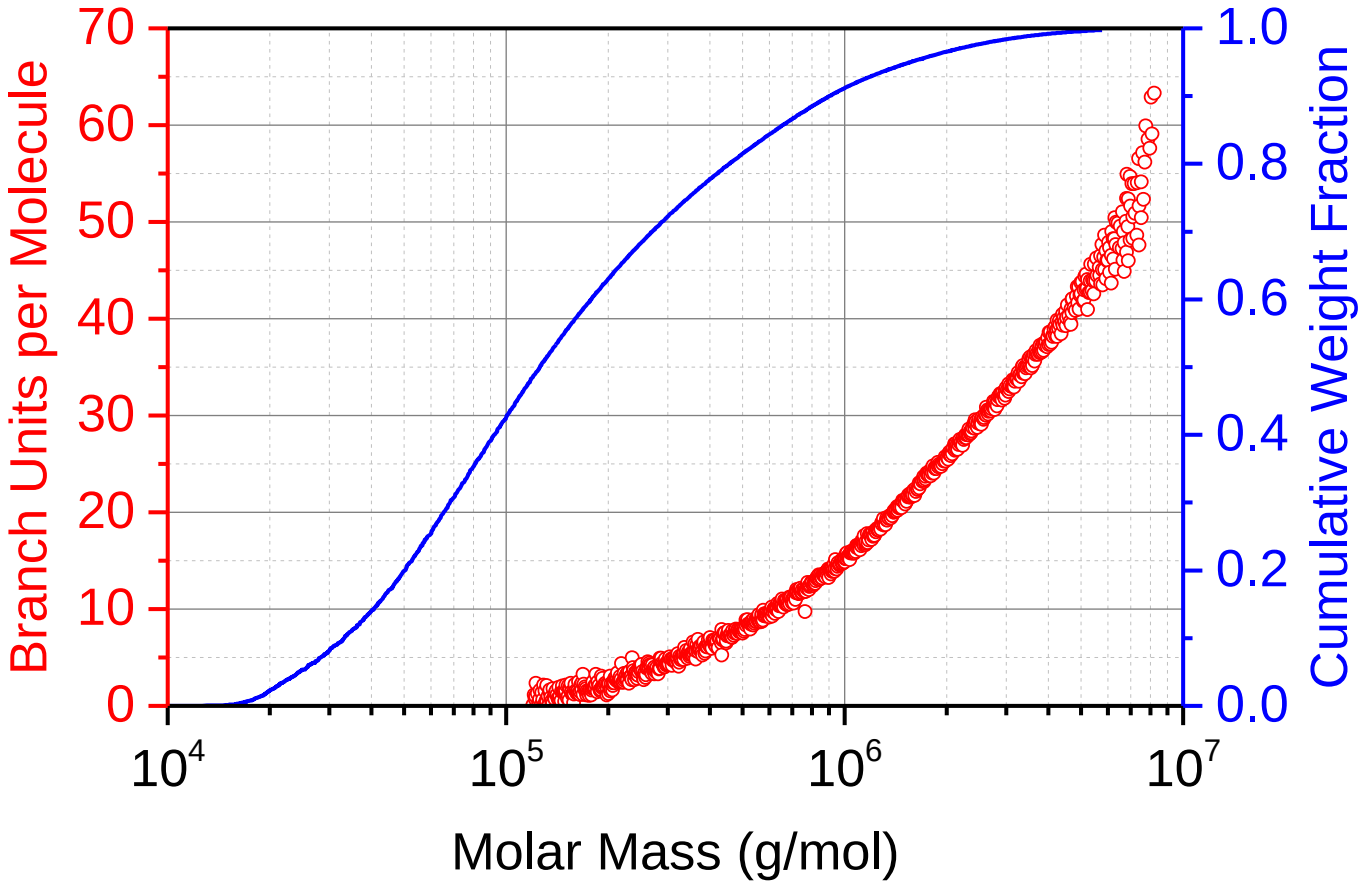
Number of Branch Units per Molecule



Number of branch units per molecules for randomly branched polystyrene overlaid on cumulative molar mass distribution.

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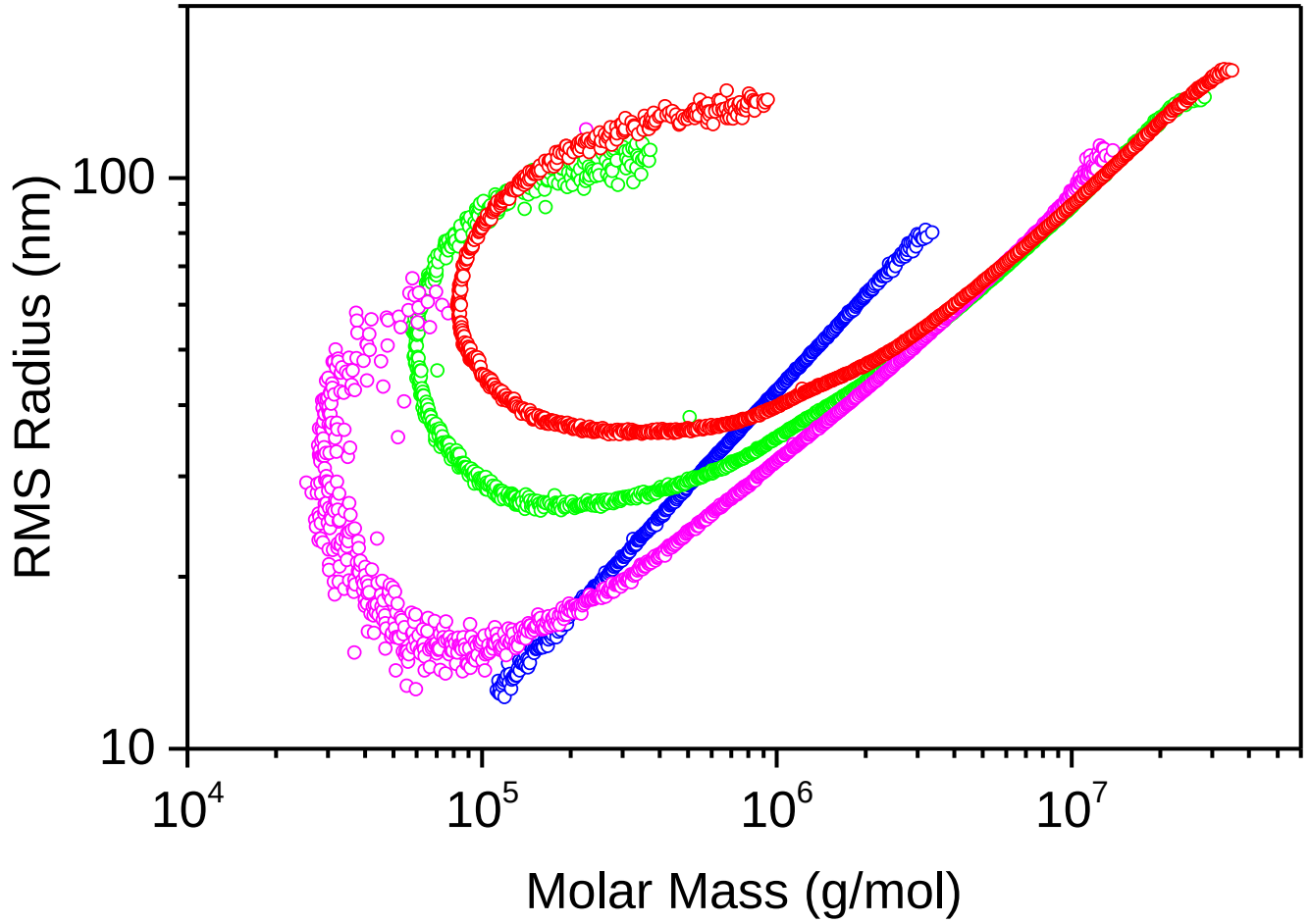
Abnormal Conformation Plots



Conformation plots of linear and randomly branched polystyrene with increasing degree of branching in the order of magenta, green, and red; miniDAWN 1999.

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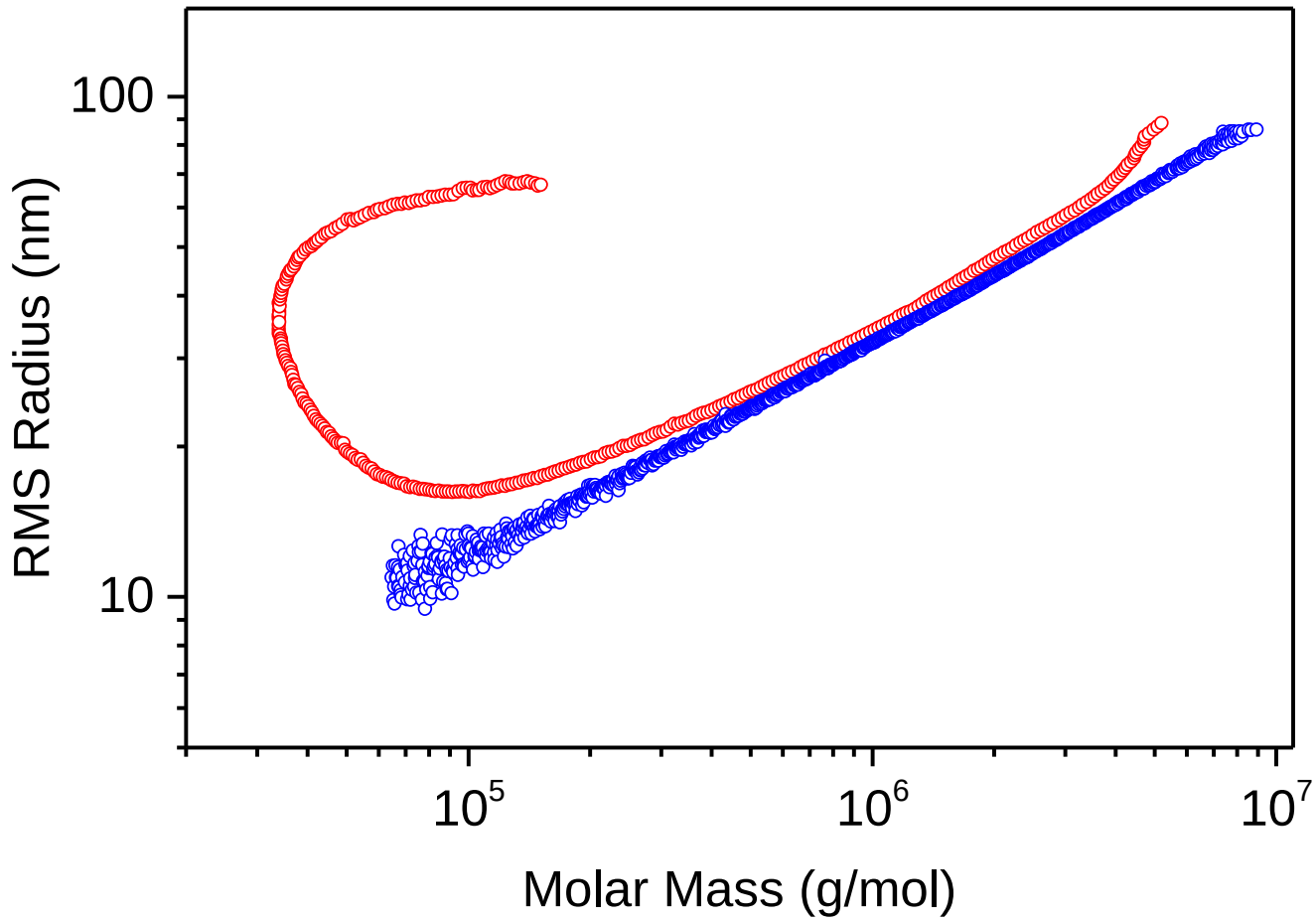
Abnormal Conformation Plots



Randomly branched polystyrene displaying and not displaying abnormal conformation plot separated on 2 × 300 × 8 mm columns Styragel HR5E (measured 1999) and Plgel Mixed-C.

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Abnormal Conformation Plots

Characterization of Branched Polymers by Size Exclusion Chromatography Coupled with Multiangle Light Scattering Detector. I. Size Exclusion Chromatography Elution Behavior of Branched Polymers

S. PODZIMEK,[1] T. VLCEK,[2] C. JOHANN[3]

[1] Wyatt Technology Corporation, Santa Barbara, California 93117

[2] University of Pardubice, Institute of Polymer Materials, 532 10 Pardubice, Czech Republic

[3] Wyatt Technology Deutschland, 57614 Woldert, Germany

ABSTRACT: The elution behavior of branched macromolecules during their separation by size exclusion chromatography (SEC) was studied. The elution behavior of branched polymers was investigated using samples of randomly branched polystyrene and star branched poly(benzyl methacrylate) of different levels of branching by means of a SEC chromatograph coupled with a multiangle light scattering detector. Abnormal SEC elution behavior was found to be typical for highly branched polymers. After a normal elution at small elution volumes the molar mass and root mean square radius of the eluting molecules increased with increasing elution volume. Several SEC experiments were carried out to find explanation for this effect and SEC separation was compared with the separation by thermal field flow fractionation. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1588–1594, 2001

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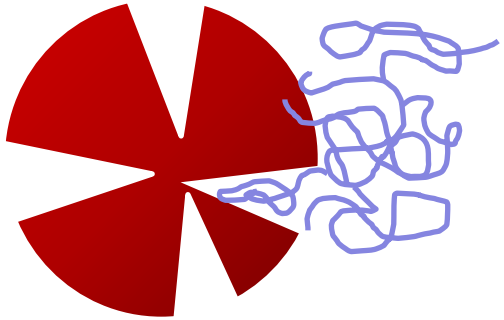
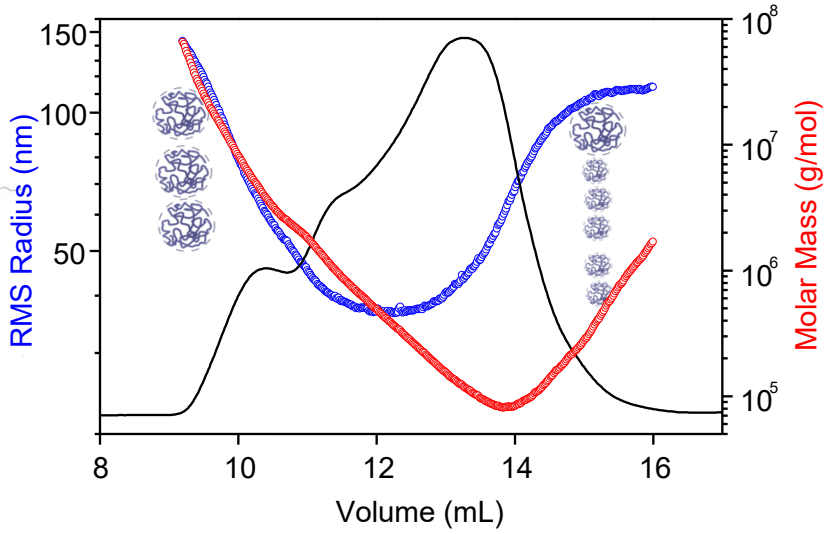
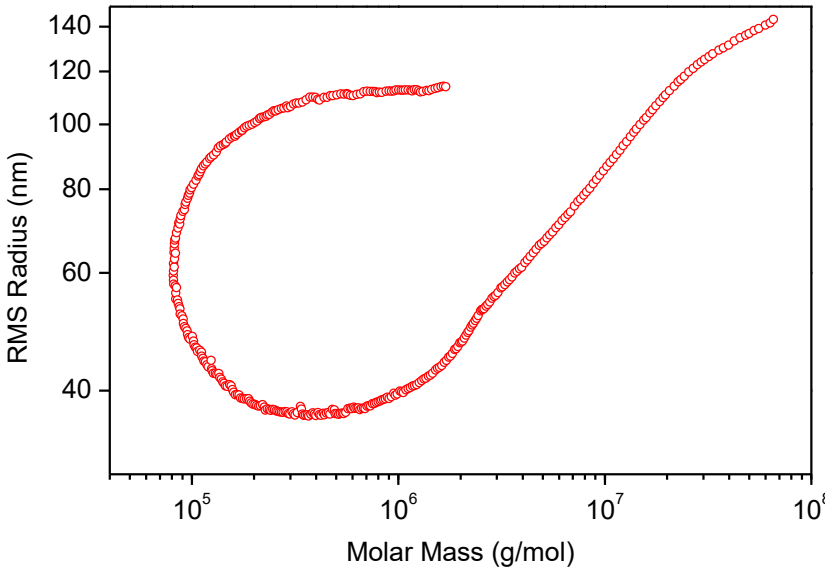
Explanation of Abnormal Conformation Plots







- For polydisperse slices MALS measures M_w and R_z
- Conformation plot R_z versus M_w

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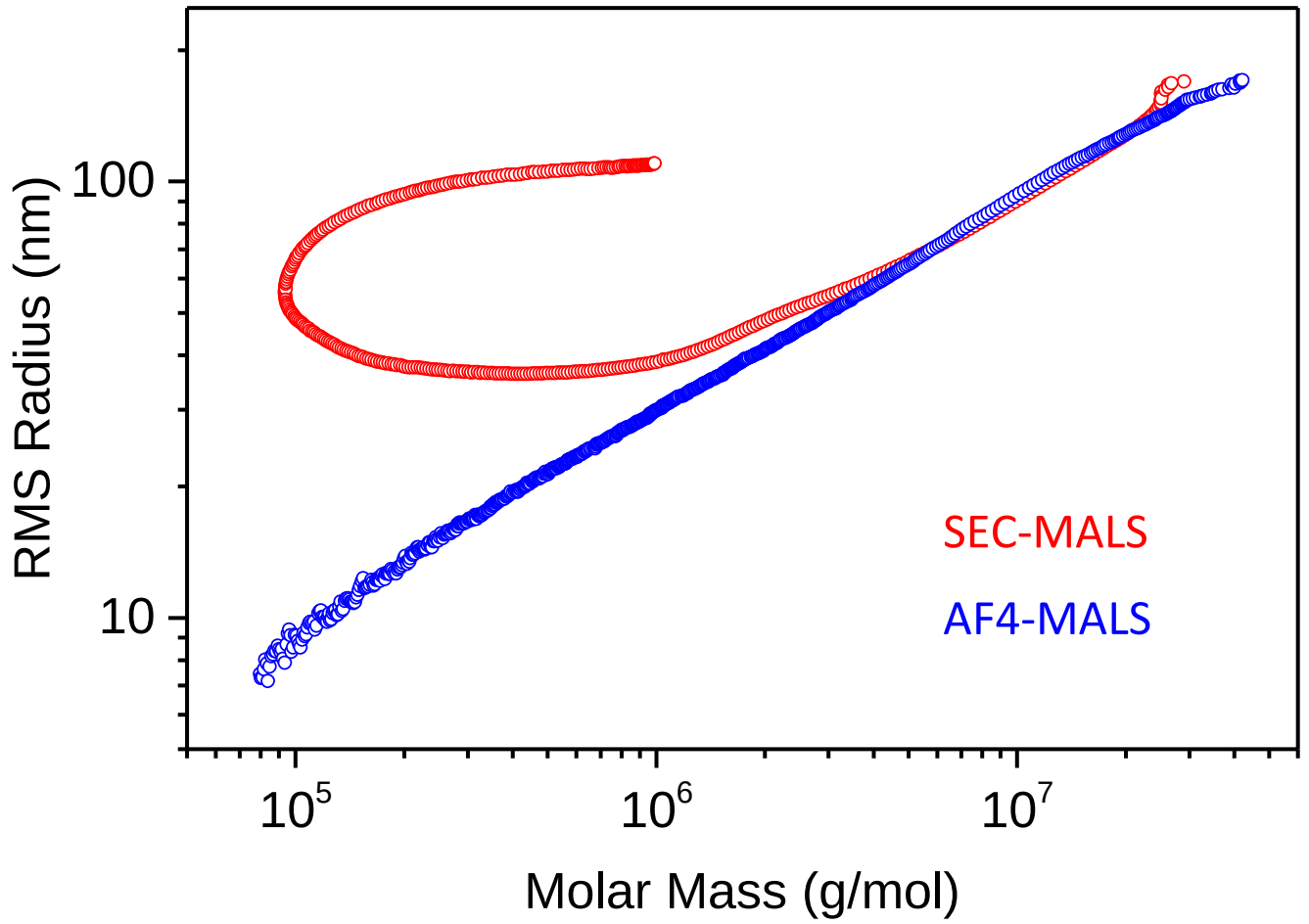
Asymmetric Flow Field Flow Fractionation (AF4) for Branching



Conformation plots of highly branched polystyrene.

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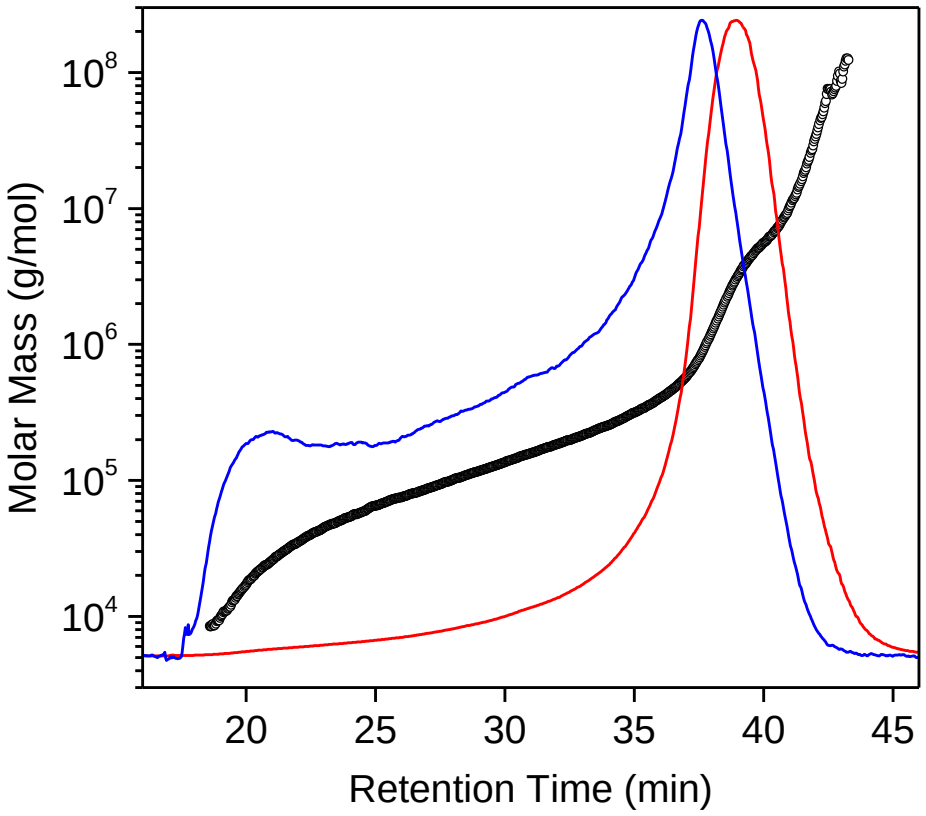
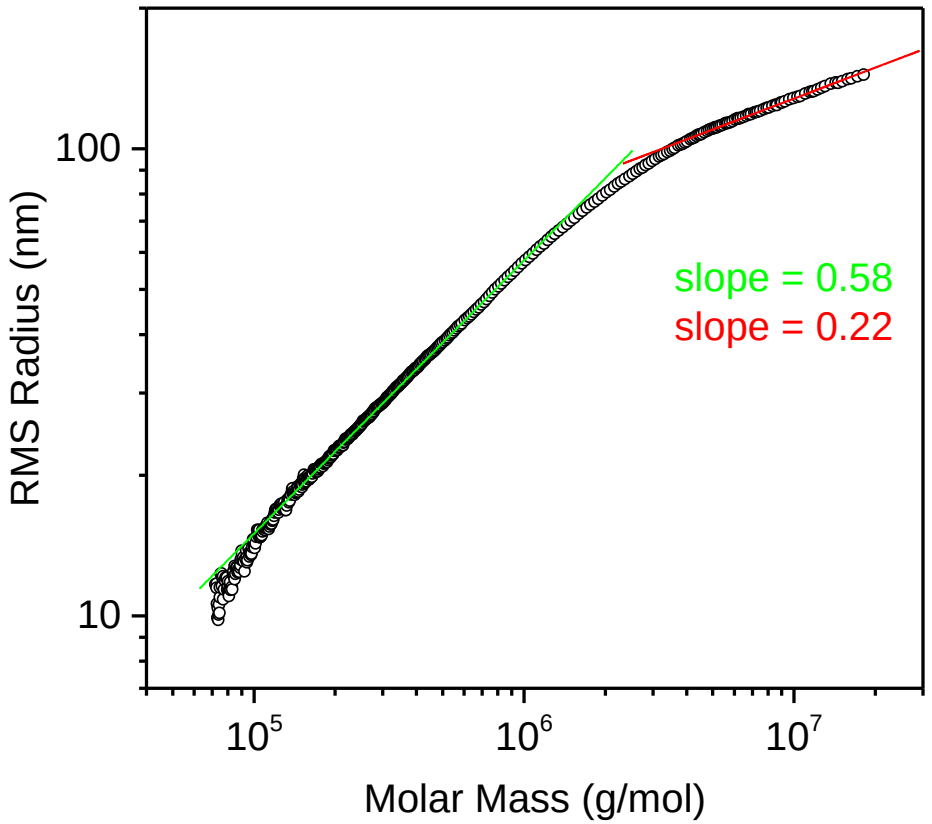
AF4 for Branching Studies and High Molar Mass Polymers





Molar mass vs time and conformation plots of ultra-high molar mass polybutadiene.

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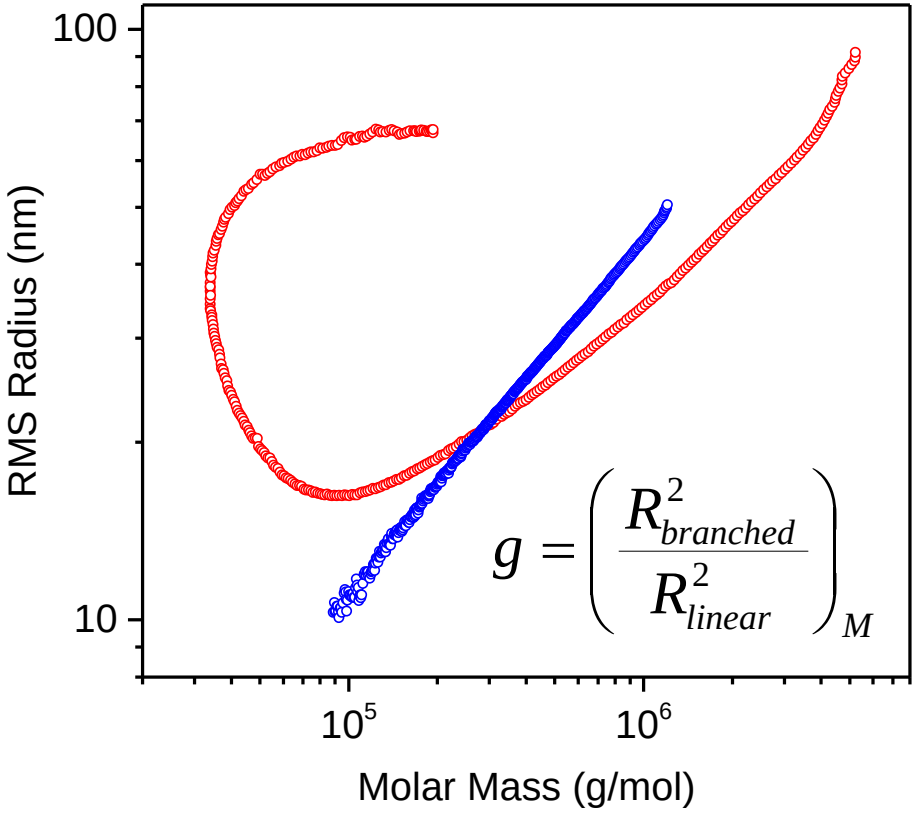
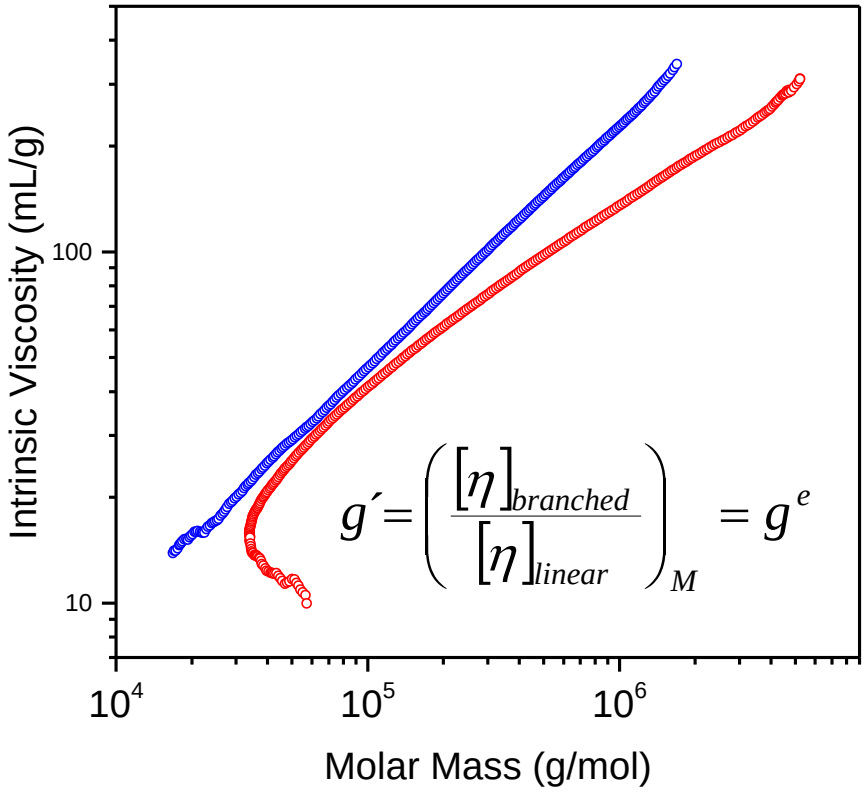
Conformation Plot versus Mark-Houwink Plot





Conformation and Mark-Houwink plots of linear and randomly branched polystyrene.

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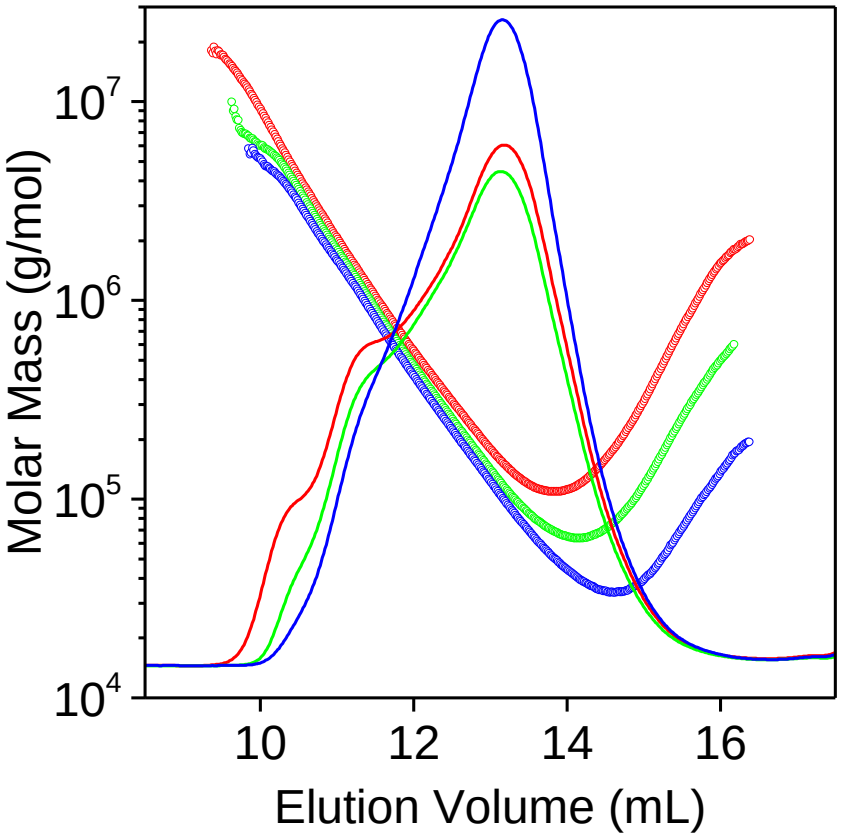
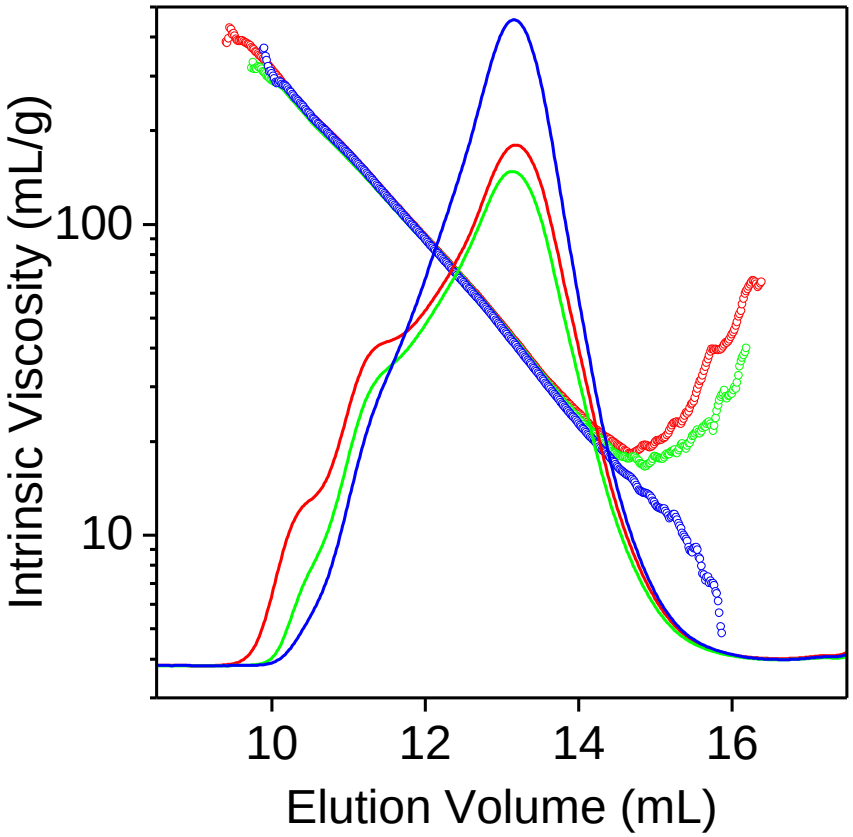
Molar Mass versus Intrinsic Viscosity Plots





$$[\eta]_w = w_{lin}[\eta]_{lin} + w_{br}[\eta]_{br} \approx w_{lin}M_{lin}^{a} + w_{br}M_{br}^{\alpha}$$

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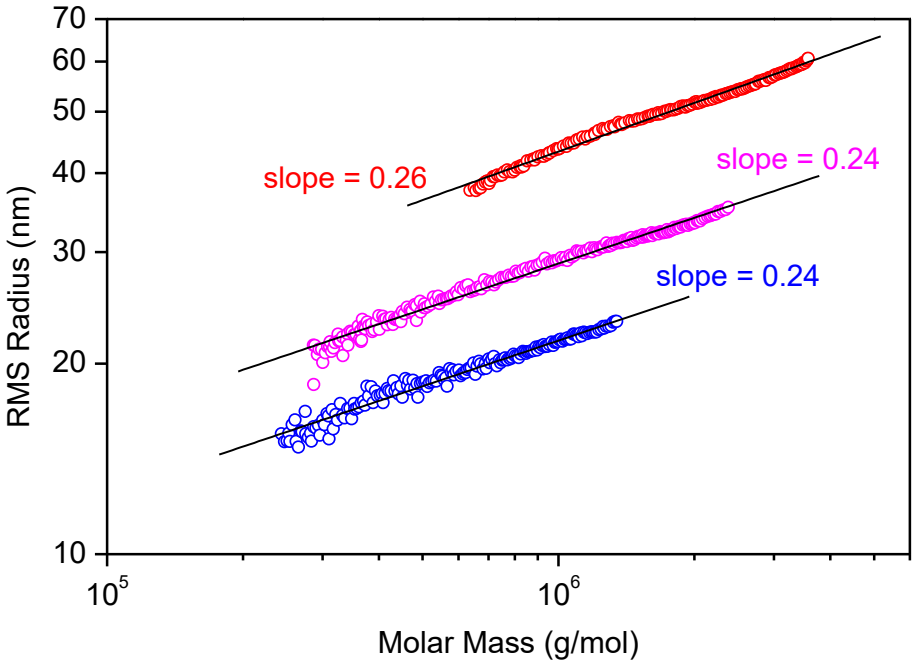
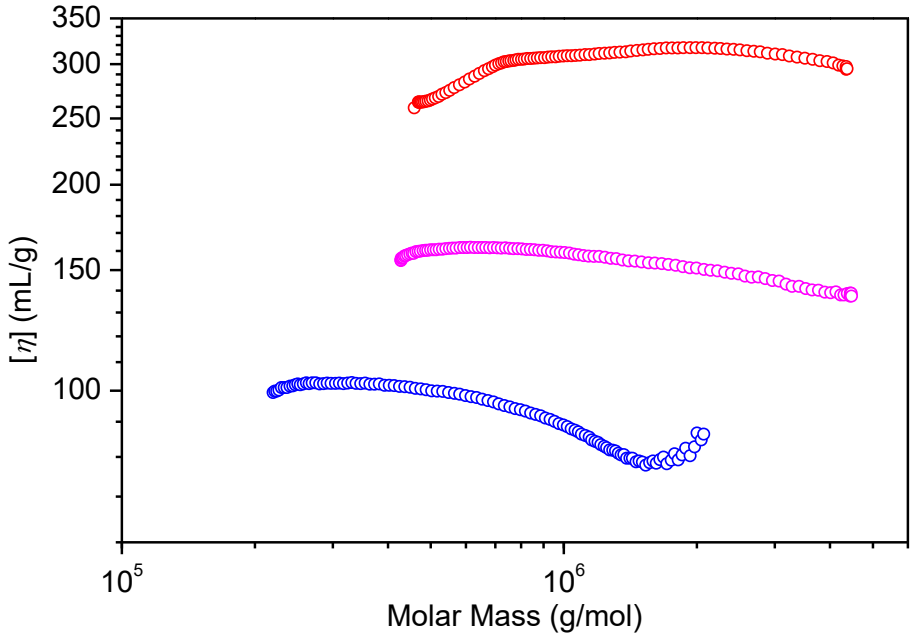
Molecular Structure by AF4-MALS and SEC-MALS-VIS





- Highly compact sphere-like polymers
- Different compactness as seen from the mutual shift of the plots
- Negative slope of MH plot ≈ polymer growing faster in density than in radial growth

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Fluorescent Polymers

Lignin

Humic acids

Bitumen

Polymers modified with fluorescent species

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Fluorescence

- Compounds with conjugated pi-electrons are suspicious of fluorescence
- Symptoms of fluorescence
  - Absorption of laser light (forward MALS monitor)
  - Suspiciously high molar mass increasing with elution volume
  - Different signals between bare photodiodes and photodiodes covered with interference filters

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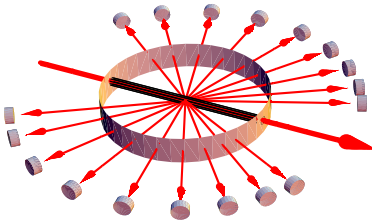
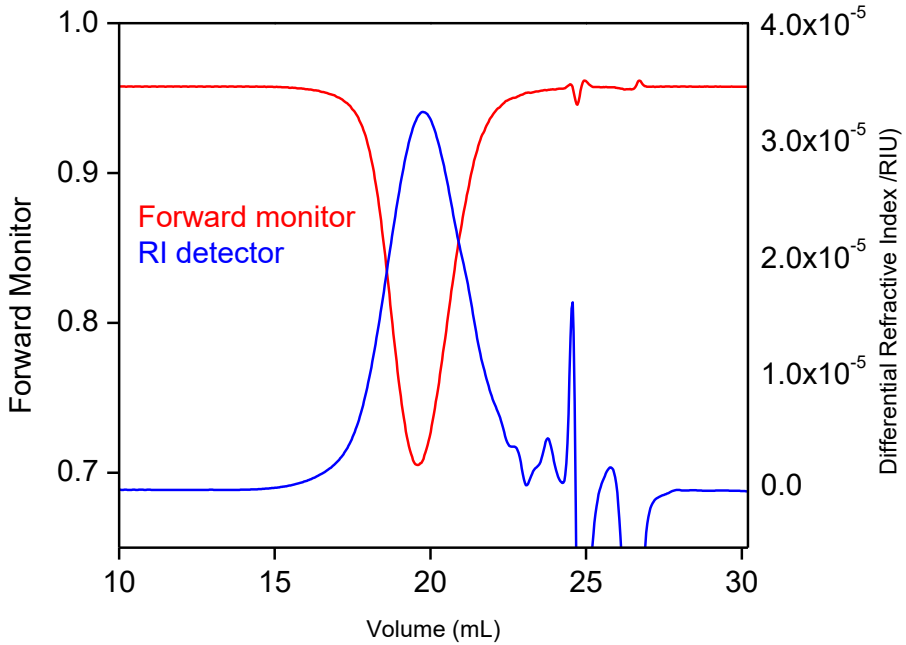
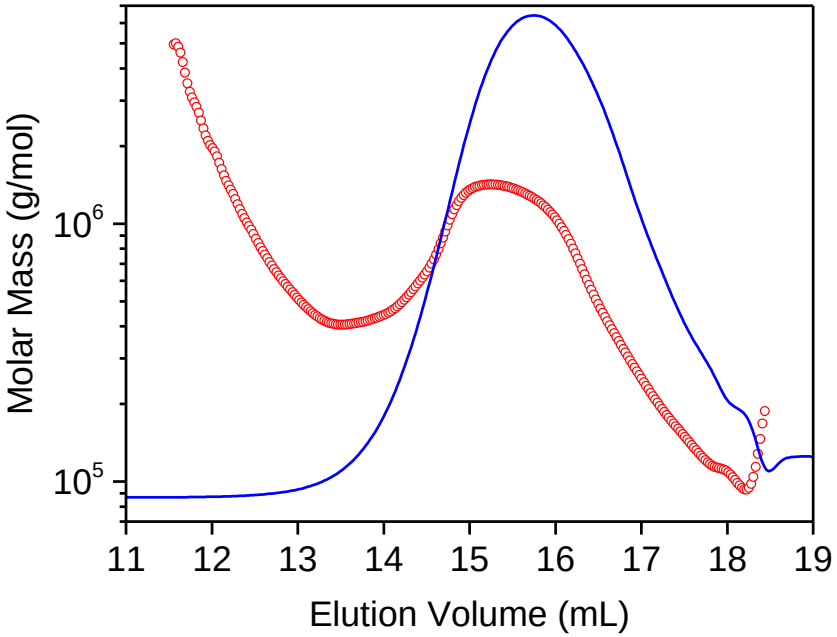
Symptoms of Fluorescence: Forward Monitor and High MM



Forward monitor





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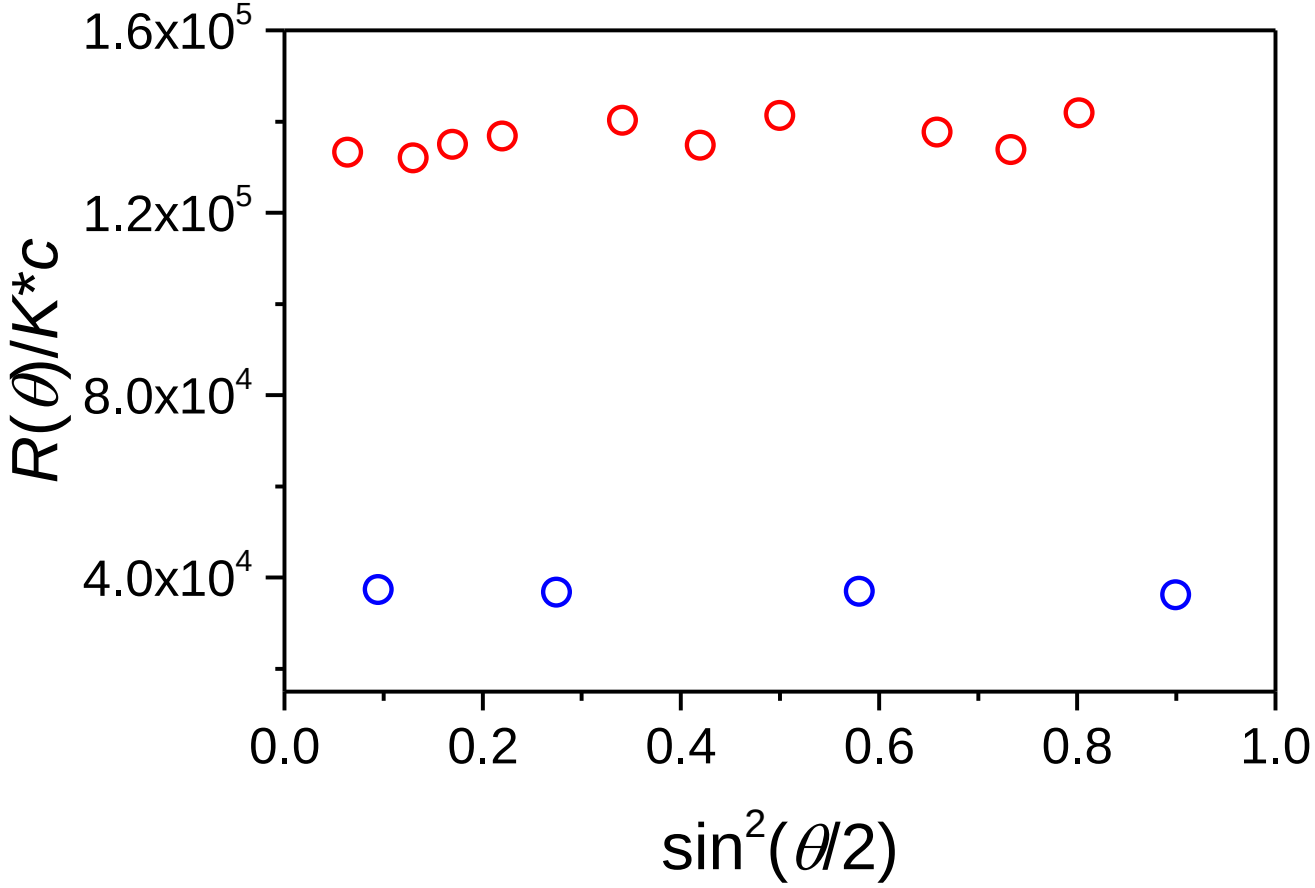
Symptoms of Fluorescence: Different Signals with and w/o Filters



Signals of photodiodes covered with interference filters and without filters.

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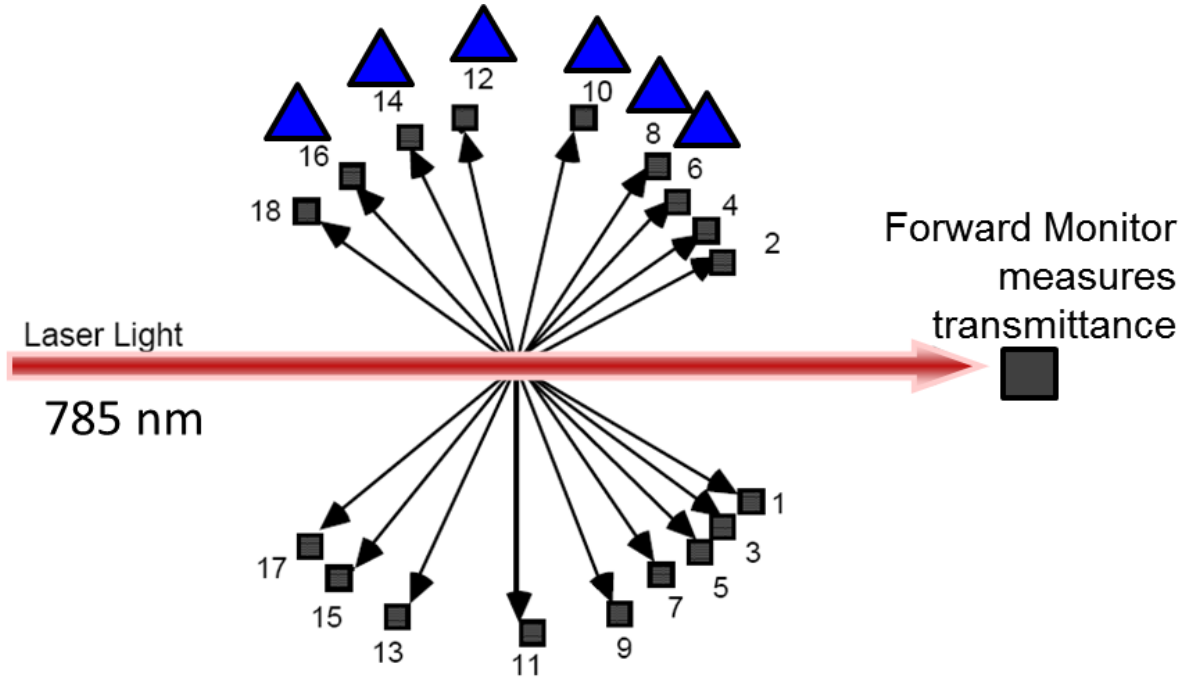
Compensation for Fluorescence

- Interference filters (bandwith 20 nm)
- Infrared laser (785 nm) instead of regular laser (≈ 660 nm, ≈ 630 nm)
- Infrared laser + interference filters



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Compensation for Fluorescence

HELEOS	Filters	M_n (10^3 g/mol)	M_w (10^3 g/mol)	M_z (10^3 g/mol)
Regular	No	555	669	743
Regular	Yes	52	100	148
IR	No	70	138	208
IR	Yes	30	71	136
UC	-	2	13	38

Molar mass averages for strongly fluorescent acetylated lignin measured by various MALS detectors and calculated using universal calibration and viscometer.

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IR MALS of Non-Fluorescent Polymers

Sample	M_w (660 nm) (10^3 g/mol)	M_w (785 nm) (10^3 g/mol)	785 vs 660 (%)
Polyester*	0.86	0.97	113
Epoxy 1	3.38	3.68	109
Epoxy 2	8.16	8.84	108
PMMA (J)	84	97	115
PS (NIST 706)**	≈ 271	291	107
PMMA (Y)	516	598	116

**dn/dc* = 0.078 ml/g; **certified M_w = 258,000 g/mol (LS); 288,000 g/mol (UC);
M_w (recertified) = 285,000 ± 23,000 g/mol

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Chemical Heterogeneity

Composition versus molar mass

Styrene-acrylate and styrene-butadiene copolymers

Protein conjugates with polysaccharides or PEG

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Chemical Heterogeneity

- SEC and AF4 cannot separate according to chemical composition
- Separation according to hydrodynamic volume
- Molar mass and average composition for a given molar mass
- Chemical composition versus molar mass
- RI and UV detectors, styrene-containing copolymers
  - Wyatt ASTRA Copolymer composition module
  - $dn/dc_{polyacrylate} \approx 0.07$ mL/g
  - $dn/dc_{polystyrene} = 0.185$ mL/g
  - $dn/dc_{polybutadiene} = 0.130$ mL/g
  - $\varepsilon_{254\ nm} = 1.595$ mL/(mg cm)

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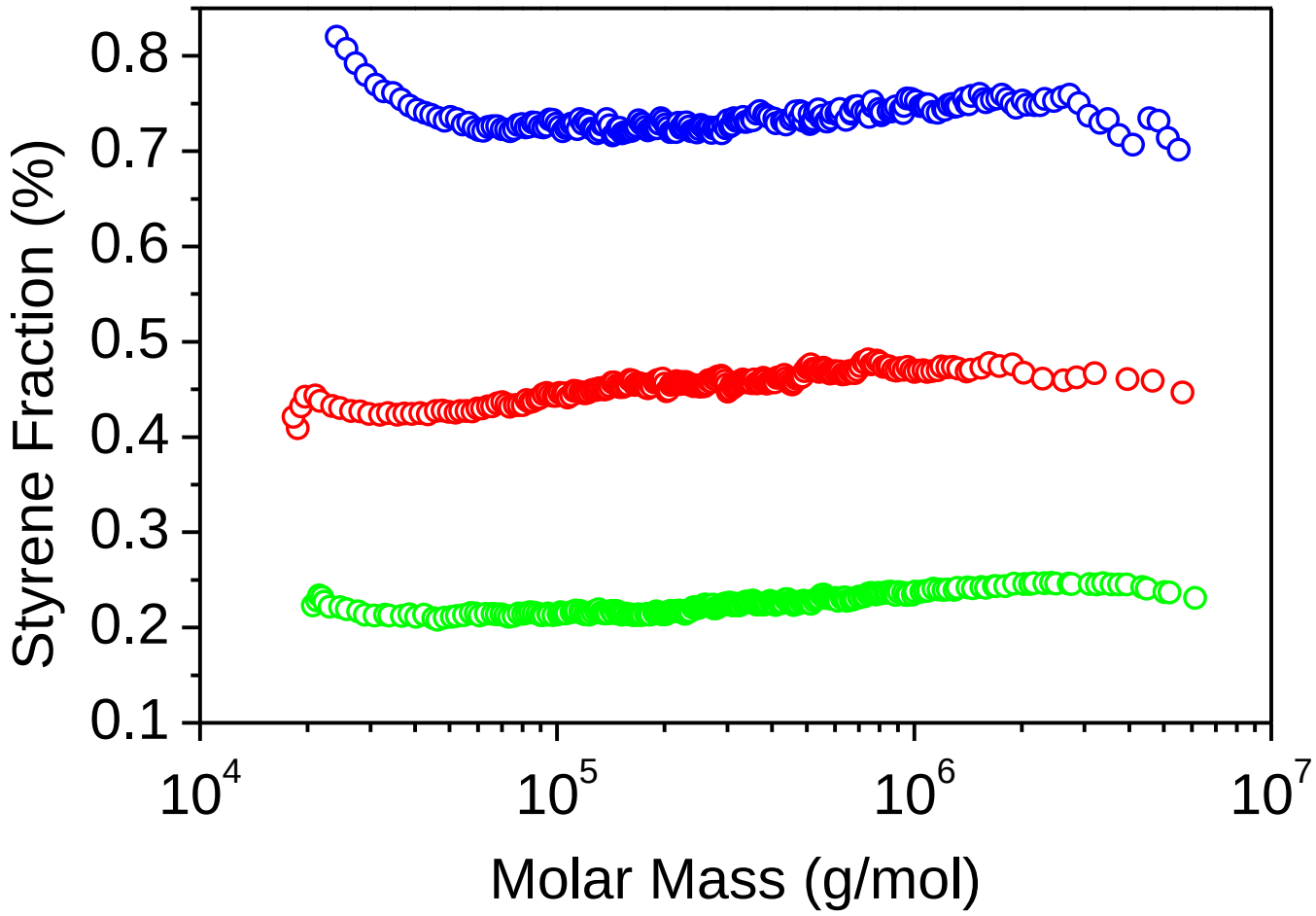
Chemical Heterogeneity



Fraction of styrene as a function of molar mass for copolymers of styrene and ethyl acrylate containing 23 %, 48 %, and 73 % styrene.

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Dynamic Light Scattering (DLS)

Hydrodynamic radius (R_h)

$\rho = R/R_h$

Burchard et al., *Macromolecules*, 13, 1265, (1980)

$\rho \approx 1.78$ linear random coil

$\rho \approx 0.78$ hard sphere

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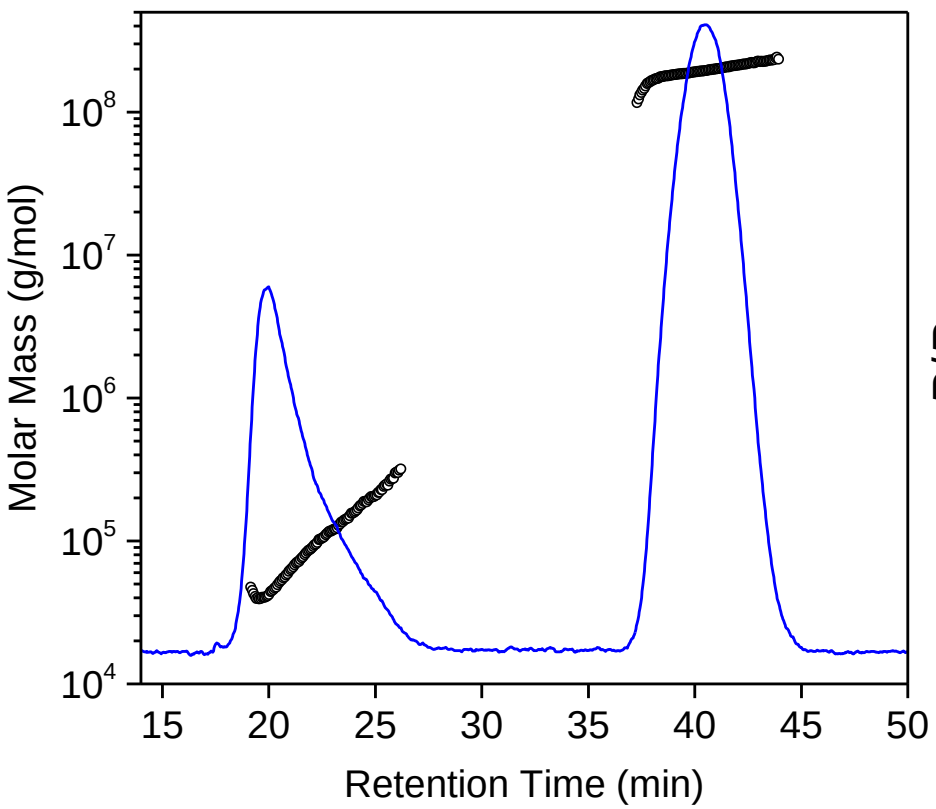
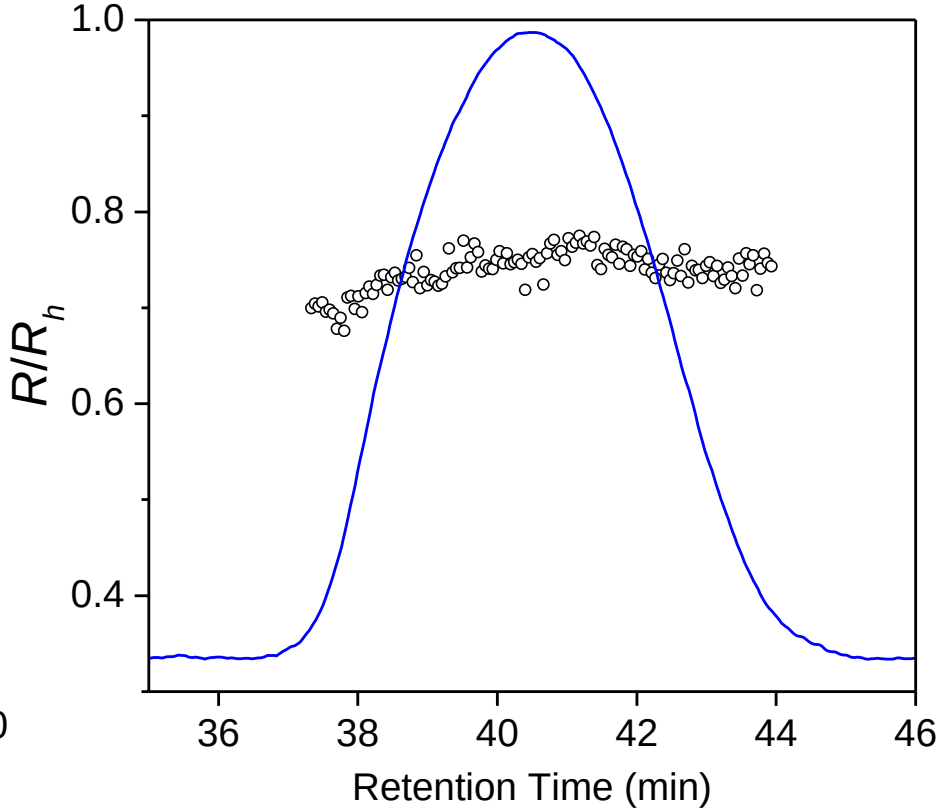
Molecular Compactness





Molar mass versus retention time and ratio ρ of core-shell acrylic latex copolymer overlaid on RI fractogram.

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Online Viscometry

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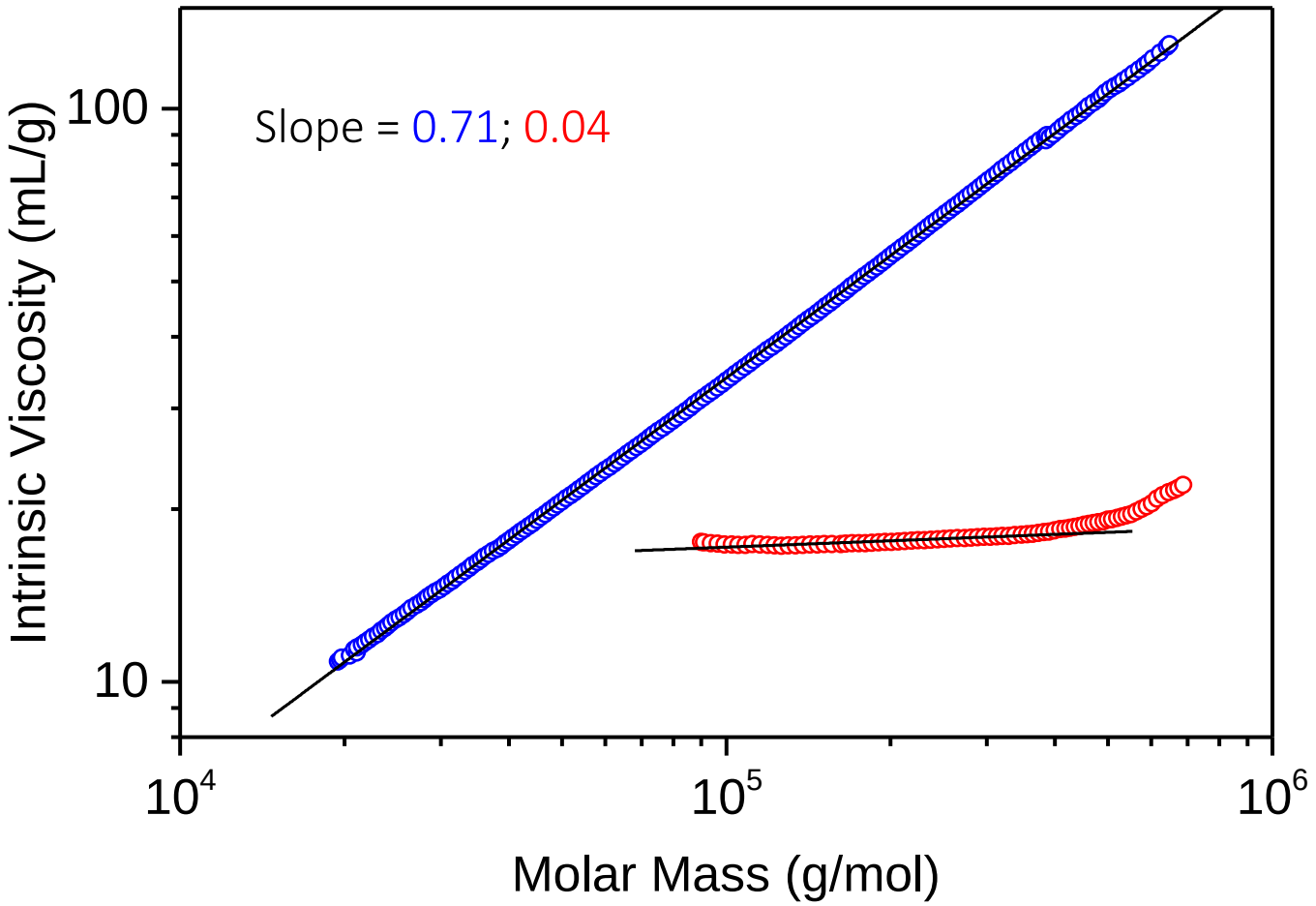
Mark-Houwink Plot



Mark-Houwink plots of linear and star-branched poly(isobutyl methacrylate).

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Advanced Polymer Chromatography

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Inception of GPC

JOURNAL OF POLYMER SCIENCE: PART A VOL. 2, PP. 835–843 (1964)

Gel Permeation Chromatography. I. A New Method for Molecular Weight Distribution of High Polymers

J. C. MOORE, *Texas Basic Research Department, The Dow Chemical Company, Freeport, Texas*

Synopsis

Polystyrene gels crosslinked in the presence of diluents have been made in fine-mesh bead form suitable for packing into chromatographic columns. A series of narrow molecular weight range polymer fractions was eluted through such columns with aromatic and chlorinated solvents. Effluent concentrations were detected and recorded by a continuous differential refractometer. The fractions were shown to be efficiently separated. Columns capable of separating adjacent polymeric samples of high molecular weight were prepared from gels crosslinked in the presence of large amounts of diluents having little or no solvent action on polystyrene. Smaller proportions of diluents and those with more solvent action yielded columns with lower molecular weight permeability limits. Such studies provided a unique quantitative view of the topology of the gels. They also demonstrated that rapid repetitive molecular weight distribution data can be obtained in this way on polymers for which solvents compatible with the gels are available.

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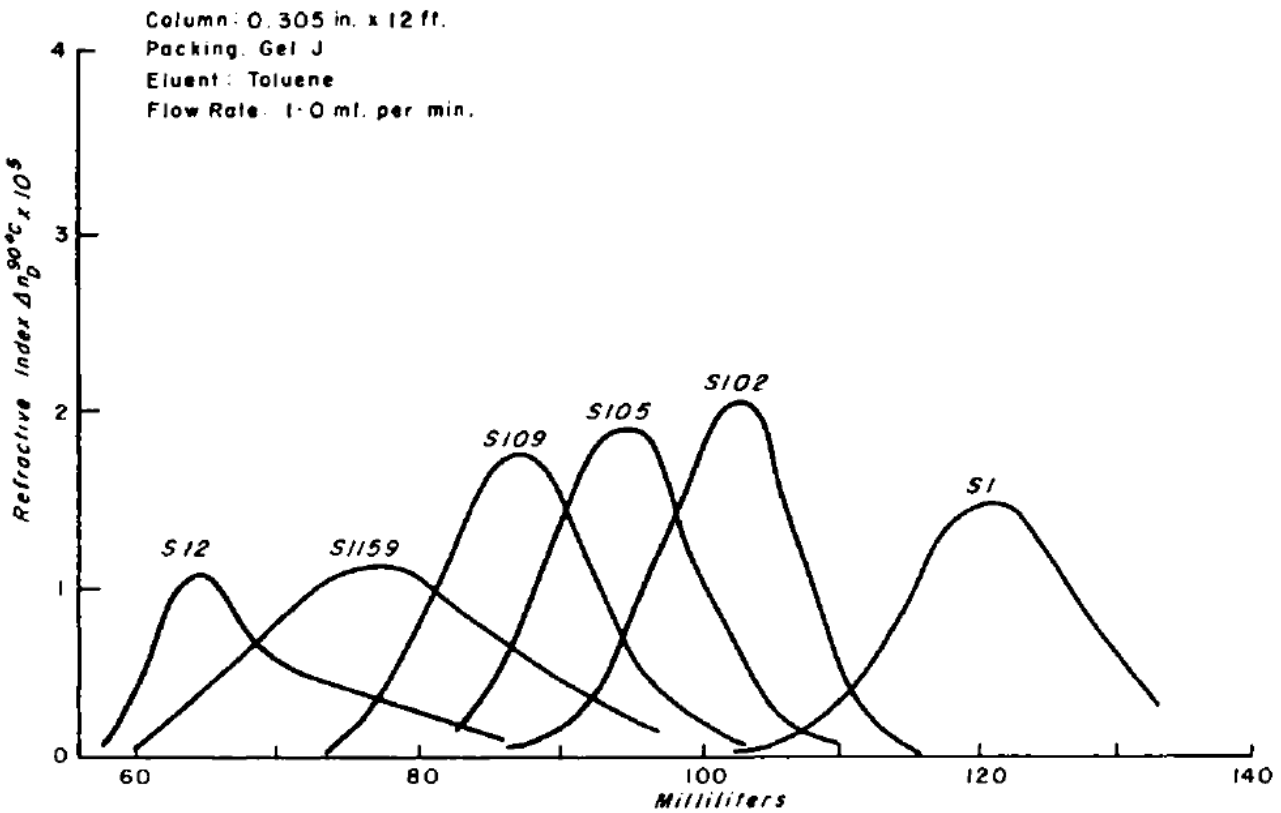

Fig. 3. Superimposed traces of elution peaks for polystyrene samples (Table I) obtained with gel J.

From J. C. Moore, *J. Polym. Sci.: Part A*, 2, 835 (1964).

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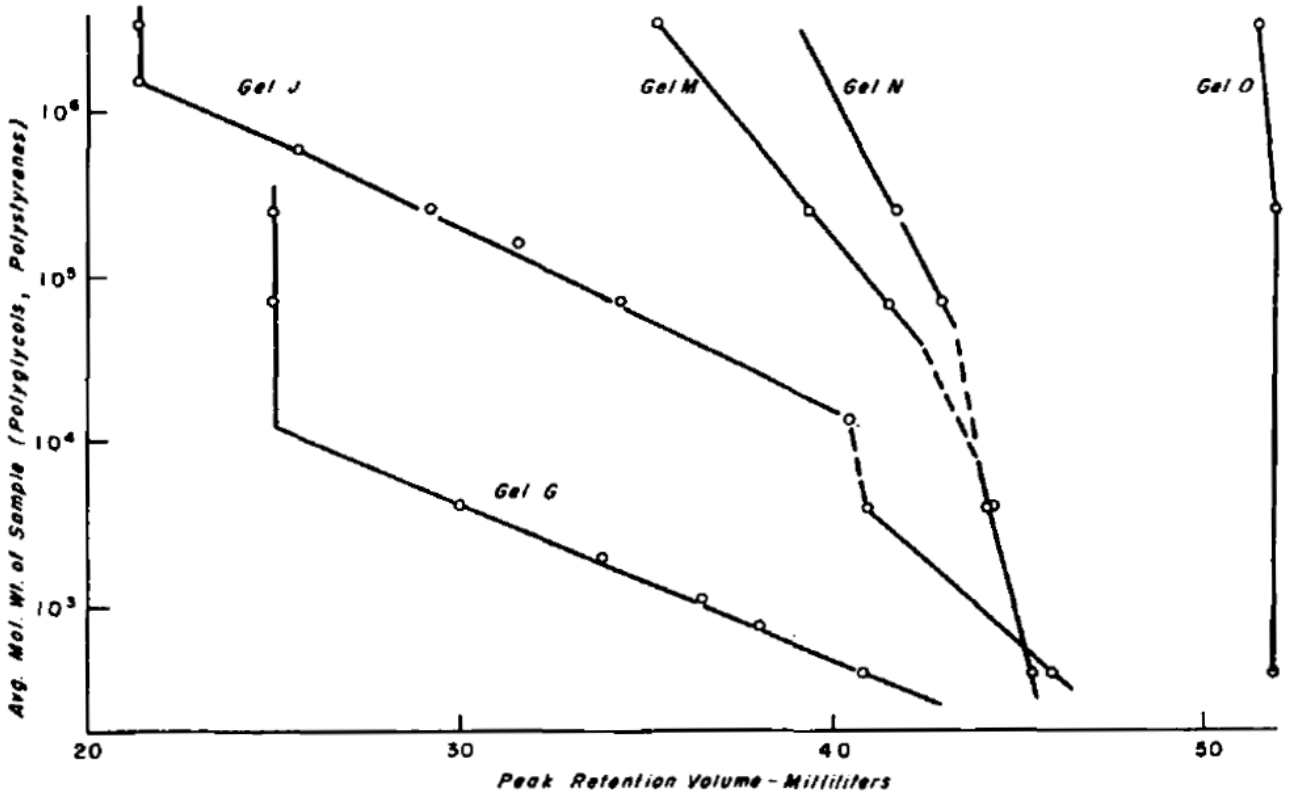

Fig. 4. Representative permeability curves for gels from Table III.

From J. C. Moore, *J. Polym. Sci.: Part A*, 2, 835 (1964).

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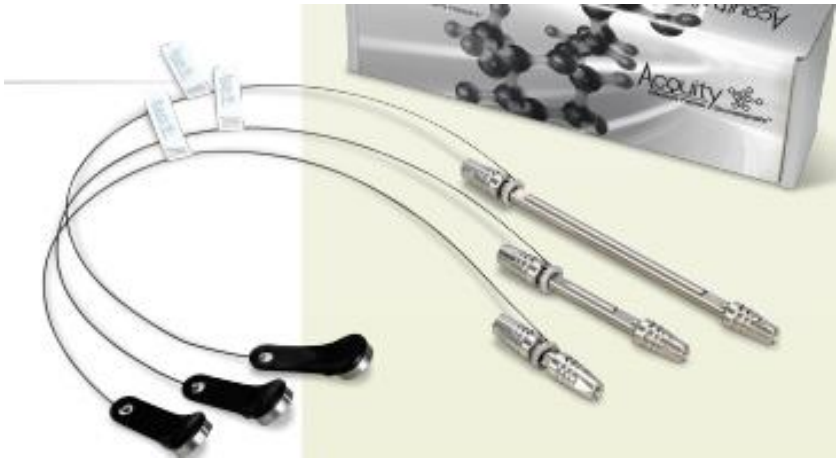
GPC/SEC Column Development

Waters Styragel old column of 120 cm length, 8 mm inner diameter (≈ 60 µm particle size) vs. PLgel Mixed-C 30 cm (5 µm particle size). Student´s height = 165 cm.



- Sub 3µm particles
  BEH (Ethylene Bridged Hybrid) technology
- Rapid solvent switching
  One column bank for any solvent
- Short analysis time
- Low solvent consumption, solvent costs (HFIP) and waste disposal cost
- Molar mass up to ≈ 2,000,000 g/mol; then possibility of shearing degradation

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Waters-Wyatt APC-µMALS Instrumental Set-up

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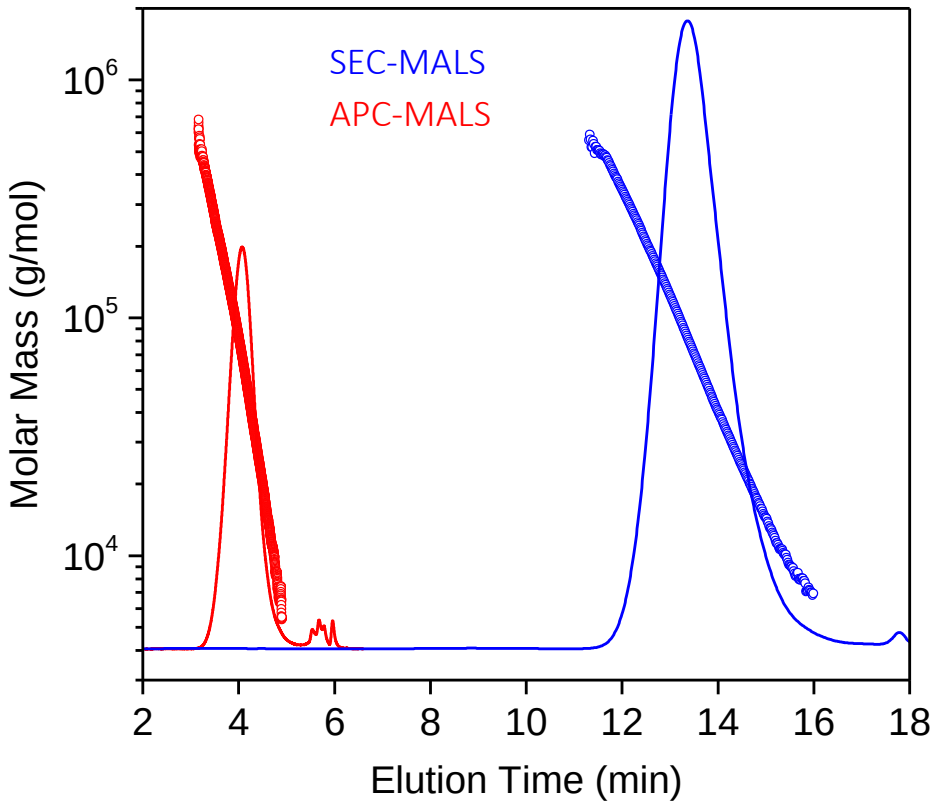
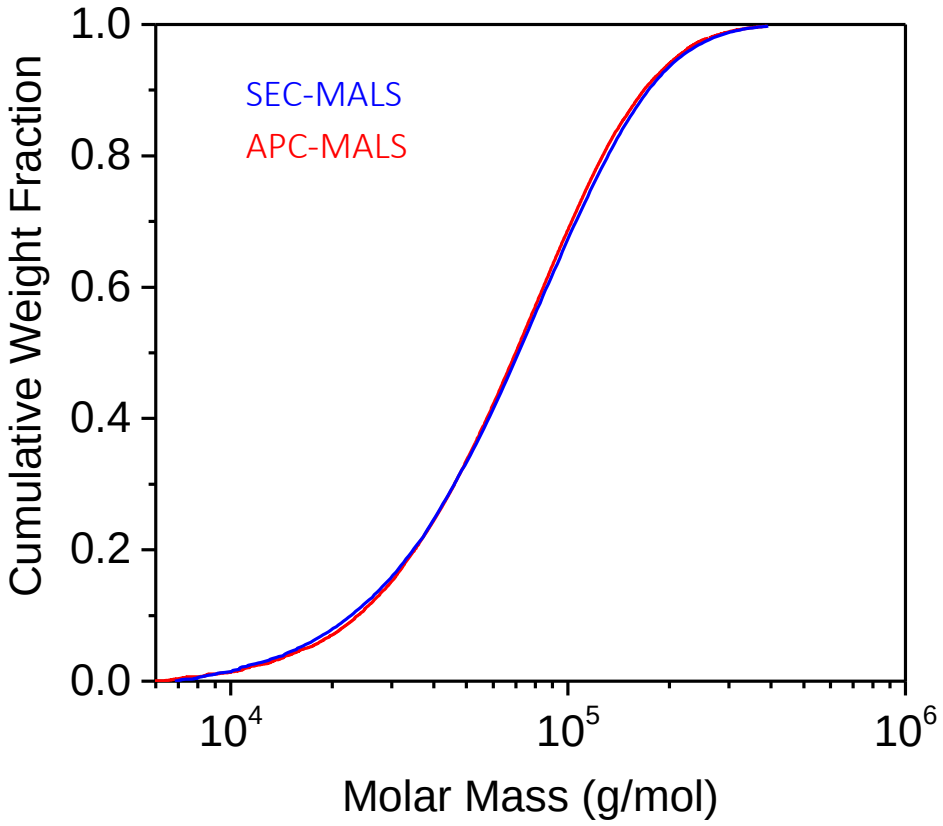
APC versus SEC





PMMA measured on 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 and 2 × Agilent PLgel Mixed-C 300 × 7.5 mm.

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Final Remarks

- Polymer characterization by light scattering
  - Molar mass distribution and molar mass averages
  - Branching
  - Polymer chain conformation
  - Chemical composition versus molar mass
- Various combinations of MALS
  - Regular MALS and infrared MALS
  - MALS and DLS/QELS
  - MALS and viscometry
- Two separation methods
  - SEC/GPC; APC
  - Asymmetric flow field flow fractionation (AF4)

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