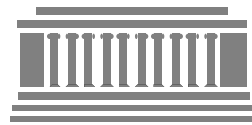


Polymer Characterization: Past, Present and Future

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**Penn-Ohio Border Section
Am. Chem. Soc
February 2001**

A copy of the Lecture Notes may be found at the URL:

<http://www.chem.cmu.edu/Berry>



Photo by Jeff Greenberg

Pittsburgh, Pennsylvania

F. W. Billmeyer Jr. (1976):
J. Polym. Sci.: Symp. (1976) 55: 1-10

"...characterization of polymers is inherently more difficult than that of other materials. Polymers are roughly equivalent in complexity to, if not more complex than, other materials, at every physical level of organization from microscopic to macroscopic..."

"We would wish, ideally, to characterize all aspects of a polymer structure in enough detail to predict its performance from first principles. I seriously doubt that this will ever be possible, and I am sure that even if it were, it would never be economically feasible."

Some Reference Material

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Light Scattering, Classical: Size and Size Distribution Classification

G. C. Berry, In *Encyclopedia of Analytical Chemistry*, R. A. Meyers, ed.; John Wiley & Sons Ltd: Chichester, UK, 2000; 5413-48.

Static and dynamic light scattering

G. C. Berry; P. M. Cotts, In *Experimental methods in polymer characterization*; R. A. Pethrick; R. S. Stein, eds.; John Wiley & Sons Ltd.: Sussex, UK, 1999.

Separation and Analysis of Peptides and Proteins

Andreas F. R. Huehmer; Gabi I. Aced; Melissa D. Perkins; R. Neslihan Guersoy; D. S. Seetharama Jois; Cynthia Larive; Teruna J. Siahaan; Christian Schoeneich, *Anal. Chem.* 69(12), 29R-57R (1997).

Optimization of liquid chromatography-NMR spectroscopy. II-saturation and flow in on-flow liquid chromatography-NMR spectroscopy

Lee Griffiths, *Magn. Reson. Chem.* 35(4), 257-61 (1997).

The development and application of coupled HPLC-NMR spectroscopy

John C. Lindon; Jeremy K. Nicholson; Ian D. Wilson, *Adv. Chromatogr.* 36, 315-82 (1996).

SEC Absolute Molar Mass Detection by Online Membrane Osmometry

U. Lehmann; W. Koehler; W. Albrecht, *Macromolecules* 29(9), 3212-15 (1996).

Analysis of Synthetic Polymers and Rubbers

Charles G. Smith; Patrick B. Smith; Andrew J. Pasztor, Jr.; Marianne L. McKelvy; David M. Meunier; Stephen W. Froelicher, *Anal. Chem.* 67(12), 97-126 (1995).

Chromatographic characterization of polymers: Hyphenated and multidimensional techniques

Theodore Provder; Howard G. Barth; Marek W. Urban, eds. *Advances in Chemistry Series*, ed. R. J. Alaimo et al; Vol. 247, American Chemical Society: Washington, DC, 1995.

Polymer Analysis and Characterization

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Modern analytical ultracentrifugation: Acquisition and interpretation of data for biological and synthetic polymer systems

Todd M. Schuster; Thomas M. Laue, eds., ed. Birkhauser: Boston, 1994.

Hyphenated and multidimensional techniques

T. Provder; M. W. Urban; H. G. Barth, eds. *ACS Symposium series*, ed. R. J. A. e. al; Vol. 581, American Chemical Society: Washington, DC, 1994.

Hyphenated techniques in polymer characterization: Thermal-spectroscopic and other methods

Theodore Provder; Marek W. Urban; Howard G. Barth, eds. *ACS Symposium Series*, ed. Vol. 581, American Chemical Society: Washington, DC, 1994.

Polymer analysis and characterization

A. Abe et al, ed. *Adv. Polym. Sci.*, ed. Vol. 114, Springer-Verlag: New York, 1994, 233-90.

Modern methods of polymer characterization

Howard G. Barth; Jimmy W. Mays, eds. *Chemical analysis*, ed. Vol. 113, J. Wiley: New York, 1991.

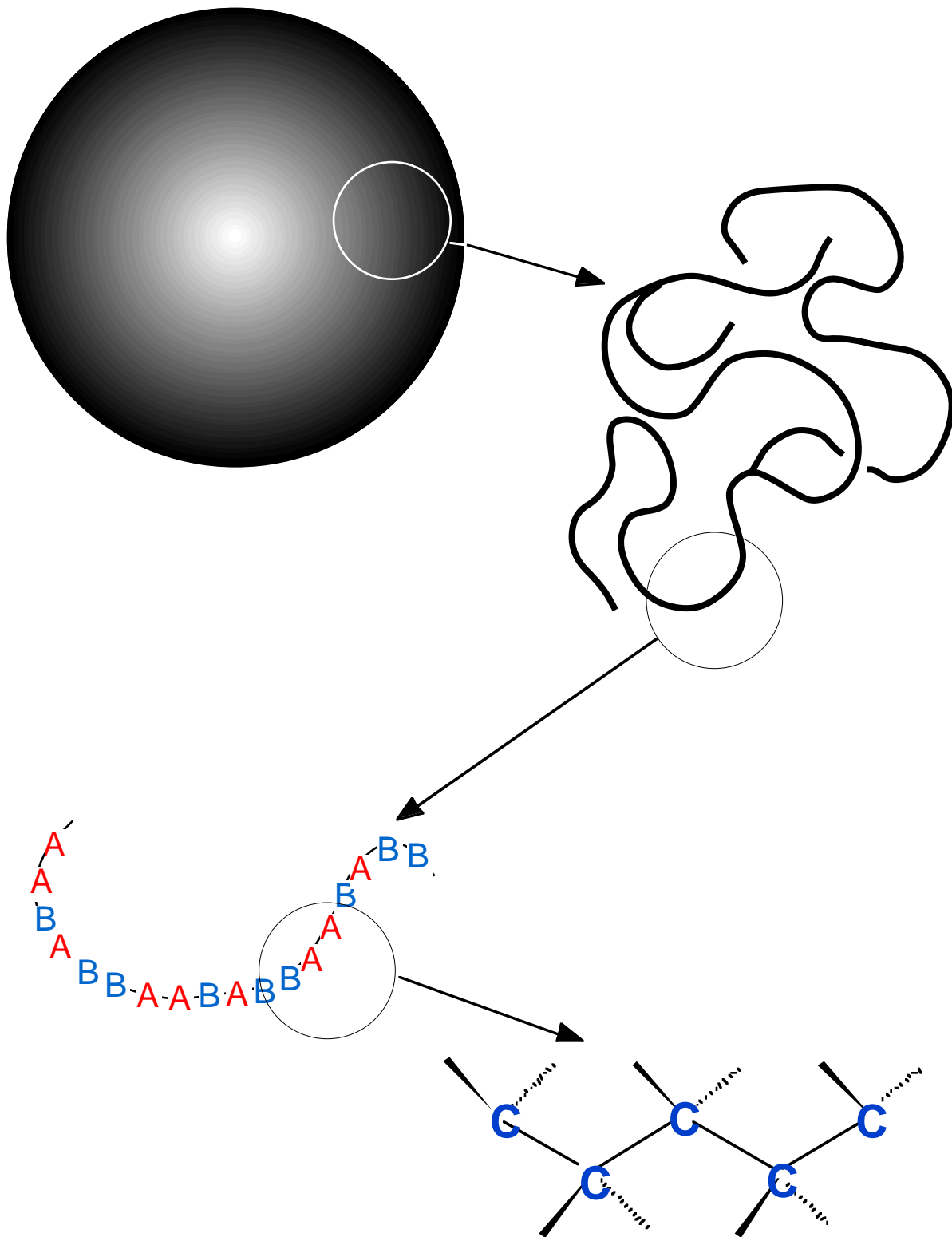
Polymer characterization by liquid chromatography

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G. C. Berry, *Encycl. Polym. Sci. Eng.* 8, 721-94 (1987).

Microscopic Characterization Needed at Many Resolutions:



Characterization Needed for a Variety of Macroscopic Structures:

- ◇ The Amorphous State (including glasses, fluids and gels) over a wide range of length scales
- ◇ The (Partially) Crystalline State (including fibers, biaxially oriented films and bulk samples)
- ◇ The Liquid Crystalline State (including main-chain and side-chain mesogenic polymers)
- ◇ Polymers in Confined Environments
- ◇ Copolymers, including the morphology of micro-phase separated systems

A Stipulation:

Given the very large span of topics encompassed in Characterization, this short presentation will be purposely limited to a narrow range of topics:

A subset of the characterization methods applicable to techniques involving dilute solutions, recognizing that this neglects a Workshop full of important topics.

The presentation will be structured around three major sections:

- ◇ A Reminder of Times Past--
The principal methods for characterizing the distribution of certain molecular properties available circa 1950-70
- ◇ A Survey of the Present--
Some of the principal methods in current use to characterize molecular properties, including molecular weight and composition distribution, etc.
- ◇ Some Thoughts on the Future

A Reminder of Times Past

- ◇ Liquid-Liquid Separations
 - ⇒ Separation by molecular weight for linear homopolymers
 - ⇒ Complex separation for branched homopolymers
 - ⇒ Complex separation for linear or branched copolymers
 - ⇒ Often problems with crystallizable polymers
 - ⇒ Slow and labor intensive; large volumes of solvent
 - ⇒ Not amenable to column separations

- ◇ Liquid-Solid Separations
 - ⇒ Most useful for crystallizable polymers and sometimes for copolymers
 - ⇒ Separations often complex

- ◇ Miscellaneous Methods
 - ⇒ Refractive index, Infra-red and UV spectroscopies, specific volume, end-group analysis

◇ Ultracentrifugation

- ⇒ M_w , M_z , M_{z+1} , ... by equilibrium methods
- ⇒ Distribution of hydrodynamic radii R_H by sedimentation velocity (e.g., MWD for linear homopolymers)
- ⇒ Sometimes requires complex analysis
- ⇒ Complicated by branching and copolymer distributions
- ⇒ Requires an expert analyst and complex equipment

◇ Osmotic Pressure

- ⇒ Determination of M_n and $A_{2,\Pi}$
- ⇒ M_n independent of branching, copolymer composition, etc.
- ⇒ Requires a suitable membrane; limited to solute neither too high nor too low in molecular weight components

◇ Vapor Phase Osmometry

- ⇒ A reasonable approximation to M_n for very low molecular weight polymers (not a thermodynamic method)
- ⇒ Subject to errors difficult to control and assess

- ◇ Light Scattering (Static)
 - ⇒ Determination of M_{LS} , $R_{G,LS}$ and $A_{2,LS}$
 - ⇒ $M_{LS} = M_W$ for homopolymer (independent of branching)
 - ⇒ M_{LS} , $R_{G,LS}$ and $A_{2,LS}$ complicated for copolymers
 - ⇒ Method requires a tedious, and sometimes difficult, optical clarification of the solution
 - ⇒ The values of M_{LS} and $R_{G,LS}$ may be severely biased by a minor component of aggregated species
 - ⇒ Requires an expert analyst and specialized equipment

- ◇ Viscometry
 - ⇒ Determination of $[\eta]$ and k'
 - ⇒ The relation $M[\eta] = \Phi'R_G^3$ provides analysis procedure ($[\eta] = KM_v^a$ for most linear homopolymers, with $M_n < M_v < M_w$ for flexible chains)
 - ⇒ Analysis complicated for branched chain and copolymers
 - ⇒ Measurements possible with minimal experience and simple equipment

- ◇ Chromatographic Separations
 - ⇒ Size exclusion chromatography using a detector for eluent concentration
 - ⇒ Column separations based on solubility-- usually for crystalline polymers



An Example: The characterization of long-chain branching in a homopolymer.

- ◇ No method was available to effect a separation according to long-chain content or molecular weight; Liquid-liquid separation gives a complex mixture according to these attributes
- ◇ Sedimentation velocity ultracentrifugation provided a weighted distribution of $R_H = h(R_H)_{lin}$ for the sample or fractions thereof, where $h \leq 1$ depends on the long-chain branch content (expected to vary with M in some samples)
- ◇ Equilibrium ultracentrifugation provided M_w , M_z , M_{z+1} , ... for the sample or fractions thereof
- ◇ Static light scattering provided M_w and $R_{G,LS}$ for the sample or fractions thereof; $R_G = g^{1/2}(R_G)_{lin}$, where $g^{1/2} \approx h \leq 1$ depends on the long-chain branch content (expected to vary with M in some samples)

- ◇ Osmometry provided M_n for the sample or fractions thereof (unless M_n is too large)
- ◇ Viscometry provided $[\eta]$ for the sample or fractions thereof, where $[\eta] = g'[\eta]_{lin}$, with $g' \approx gh \approx g^{3/2} \leq 1$ for some types of branching
- ◇ Analysis required assumption of some model for h , g and g' , along with approximations of the effects on the measured $R_{G,LS}$ and $[\eta]$ of the (*a priori* unknown) distributions in branch content and M that characterized any real sample (unless a model compound)
- ◇ Uncertainties in the analysis generally made definitive determination of branching impossible for a given sample, even with the determination of a number of parameters

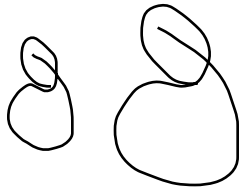
A Survey of the Present

- ◇ Size Exclusion Chromatography
 - ⇒ Separation according to molecular size and shape
 - ⇒ Separation essentially according to molecular weight for linear homopolymers, including crystallizable chains
 - ⇒ Amenable to the use of multiple detectors to analyze the eluent and computer-aided data collection and analysis
 - ⇒ Complex separation for branched homopolymers
 - ⇒ Complex separation for linear or branched copolymers
 - ⇒ May be automated for enhanced efficiency

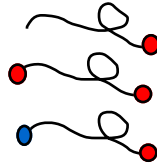
- ◇ Chromatography Based on Composition
 - ⇒ Separation by preferential adsorption
 - ⇒ Separation by melting
 - ⇒ Separation by preferential solubility
 - ⇒ Often complementary to SEC separation, and may be followed or preceded by a separation via SEC

A problem in the characterization of mixtures of polymeric compounds

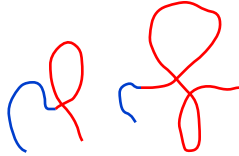
Chain Length



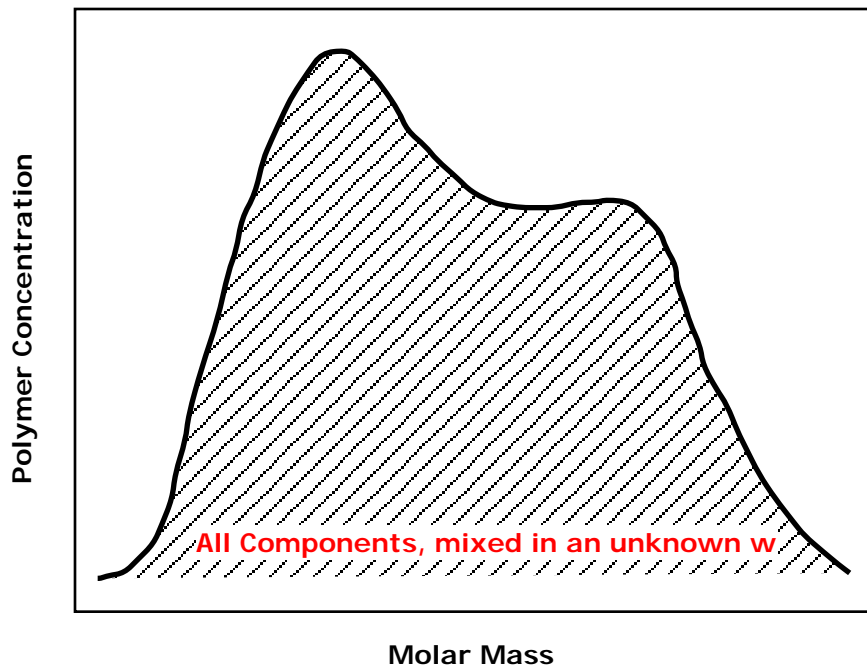
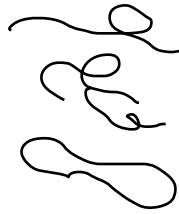
End Groups

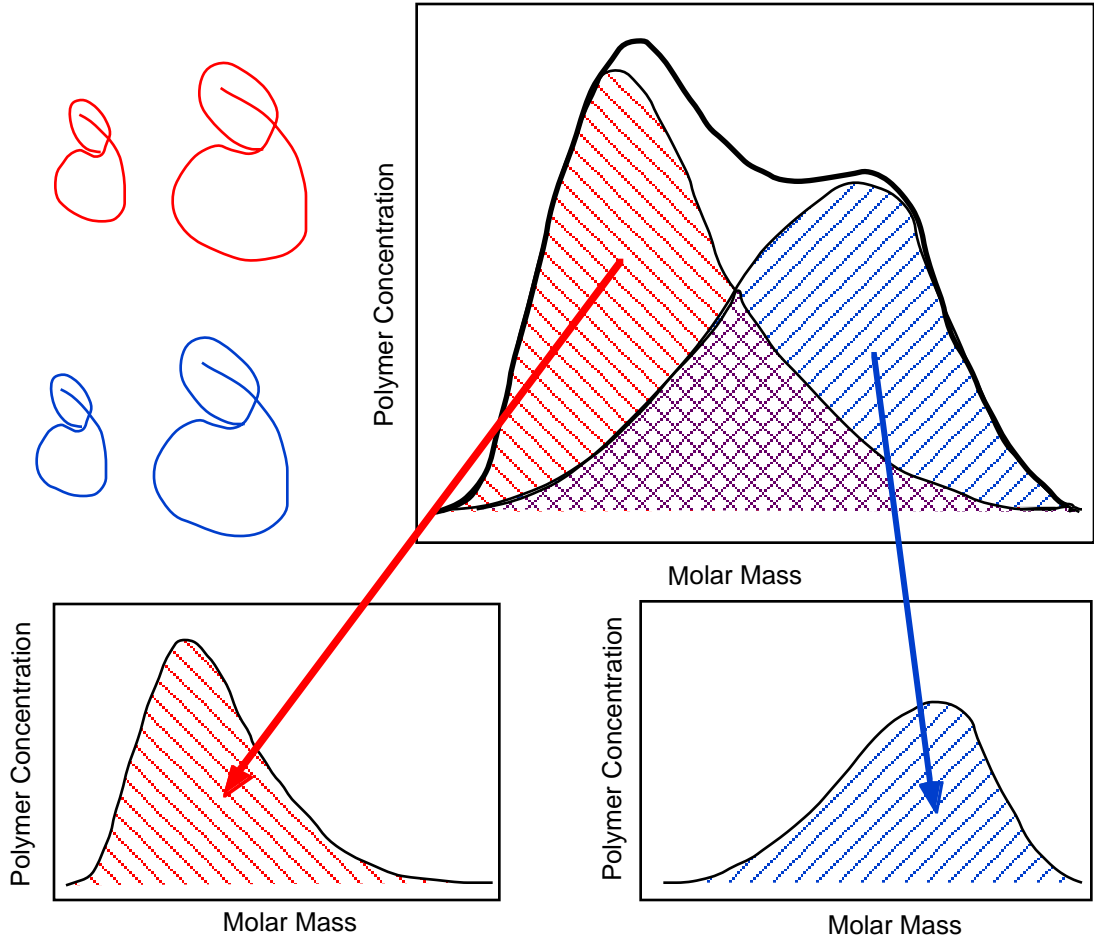


Composition/Block Length

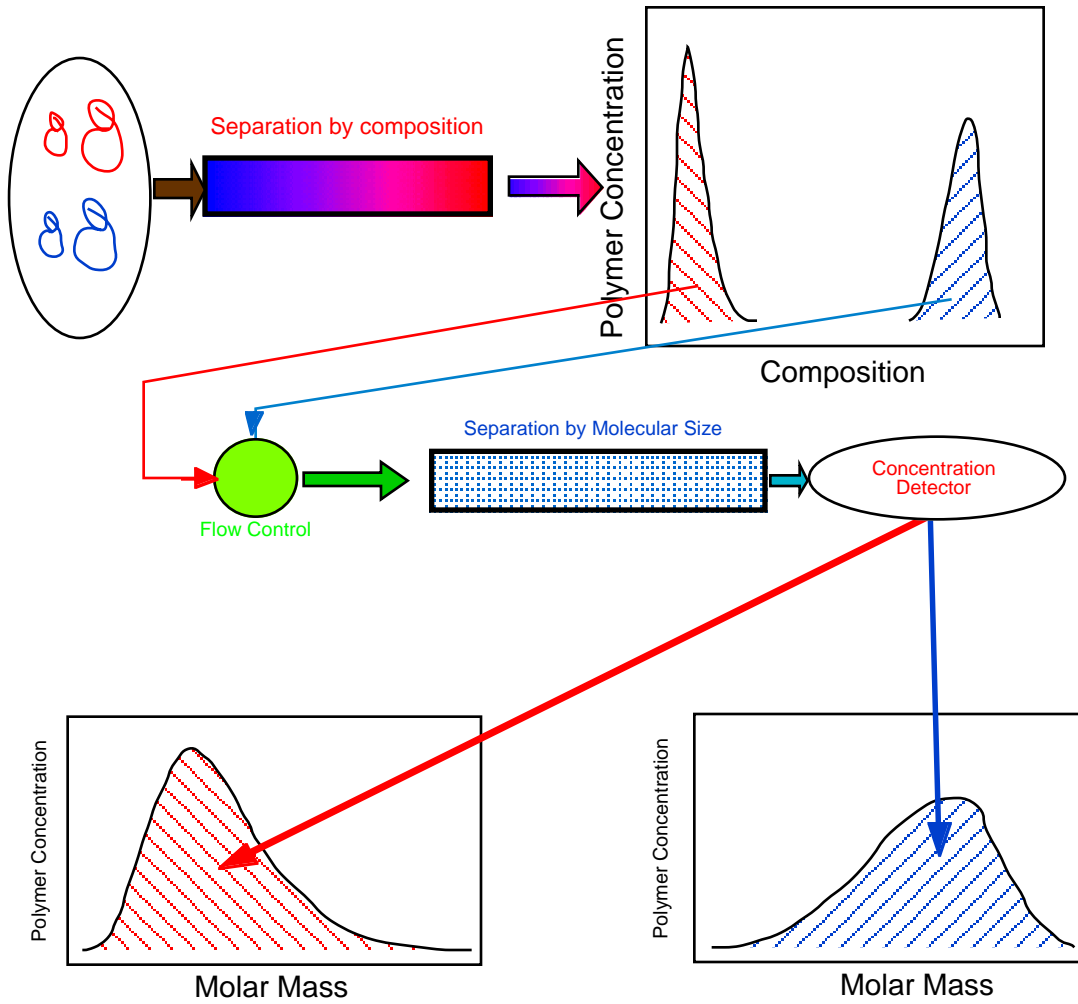


Architecture

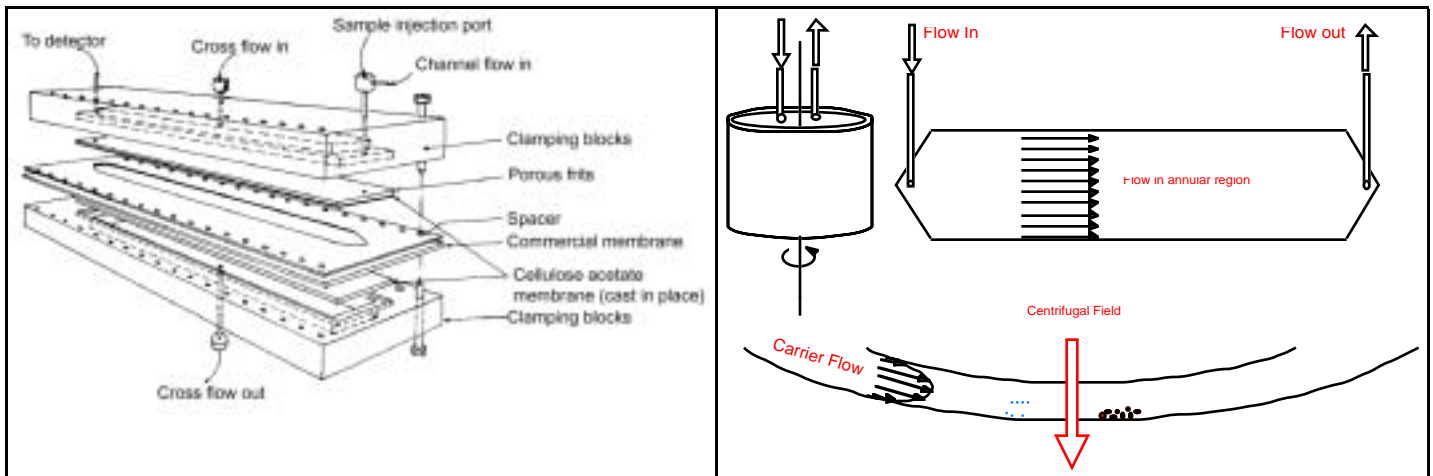




"Two-dimensional chromatographic separation"



- ◇ Other Chromatographic Methods
 - ⇒ Field Flow Fractionation methods (flow under the influencing of an external field orthogonal to the flow, e.g., centrifugal field, cross-flow, temperature gradient, etc.)
 - ⇒ Hydrodynamic chromatography (separation via the velocity gradient in capillary flow)



- ◇ Ultracentrifugation
 - ⇒ Only modest changes from prior art
 - ⇒ Not widely used with synthetic polymers--more often used with biological macromolecules. Cannot be used as an on-line SEC detector

- ◇ Osmotic Pressure
 - ⇒ Only modest changes from prior art
 - ⇒ Not widely used; some attempts to develop an on-line detector

- ◇ Vapor Phase Osmometry
 - ⇒ No change from prior art
 - ⇒ Rarely used; cannot be used as an on-line SEC detector

◇ Light Scattering (Static)

- ⇒ Principles of data analysis only modestly advanced in recent years
- ⇒ Instrumentation advance by the use of lasers for incident light (smaller scattering volumes possible), and the use of computer-aided data analysis
- ⇒ Used as an on-line detector with SEC; optical clarification of the solution automatic in this case (provided the column does not shed debris)
- ⇒ Instrumentation for on-line use with SEC is often more primitive than desirable (e.g., some commercial models neglect or approximate the angular dependence)

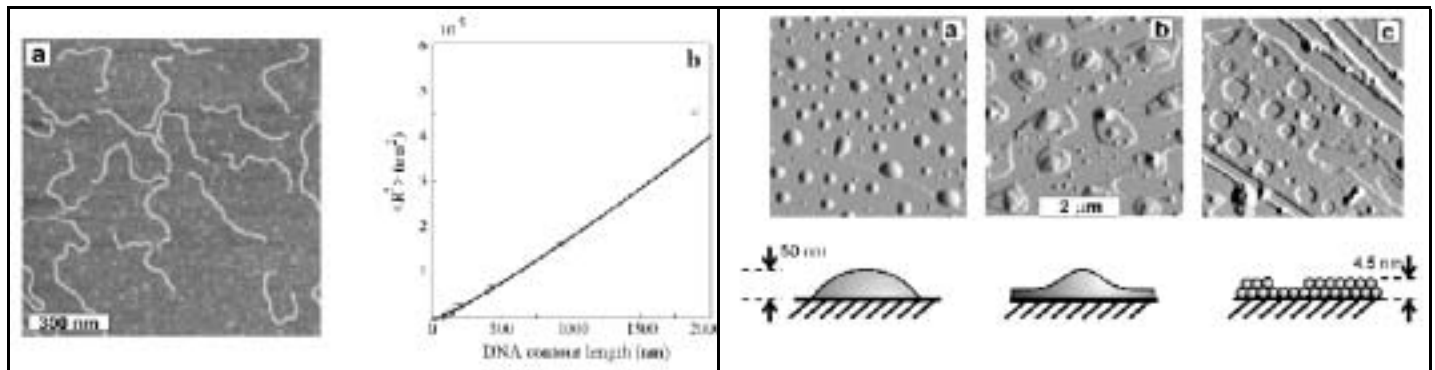
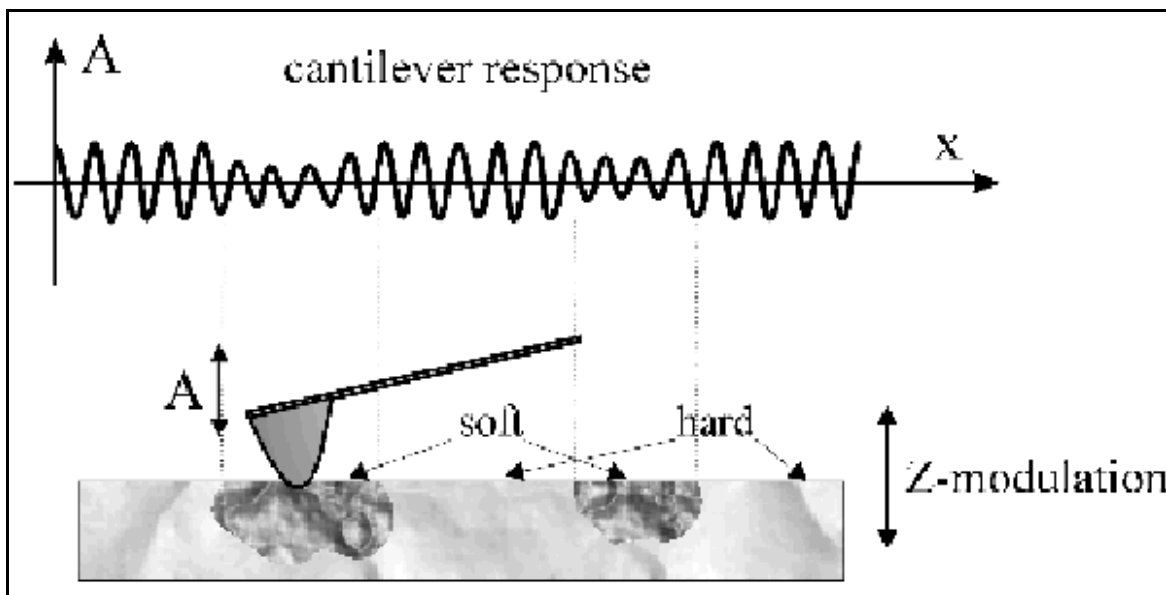
- ◇ Light Scattering (Dynamic)
 - ⇒ Determination of $R_{H,LS}$ and a weighted distribution of R_H
 - ⇒ The distribution of R_H coupled with the angular dependence of the static scattering is often useful in characterizing supramolecular association
 - ⇒ Usually not suitable for on-line SEC detector (owing to sampling time requirements)
 - ⇒ Method requires a tedious, and sometimes difficult, optical clarification of the solution
 - ⇒ Requires an expert analyst and specialized equipment

- ◇ Viscometry
 - ⇒ Only minor changes from prior art except for development of on-line instruments
 - ⇒ Used as an on-line detector for SEC
 - ⇒ Analysis in terms of molecular weight distribution requires a molecular model

- ◇ High Resolution NMR
 - ⇒ Provides analysis of the statistics of stereoregular and copolymer placements (both averaged over the sample studied)
 - ⇒ Difficult to apply as an on-line SEC detector owing to sensitivity, but prototypes are under development

- ◇ Mass Spectroscopy
 - ⇒ Determination of a weighted (ideally, a number) distribution of molecular weights; very low to moderately high M
 - ⇒ Matrix-Assisted Laser-Desorption Ionization--Time of Flight MS (MALDI-TOF);
Useful for a variety of polymers, up to moderately high molecular weight (polymer degradation sometimes occurs);
Difficult to use as an on-line SEC detector, but prototypes have been tested
 - ⇒ Electrospray Ionization-MS is suitable for lower molecular weight solute; use as an on-line SEC detector has been demonstrated

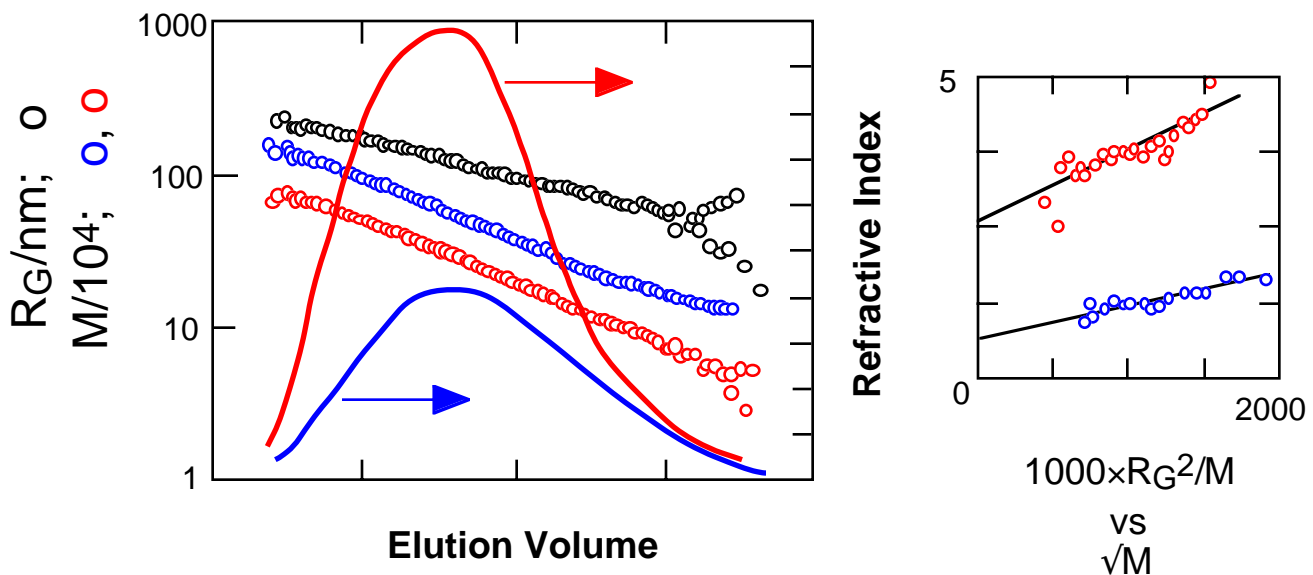
- ◇ Atomic Force Microscopy & Related Methods
 - ⇒ A new and rapidly developing method to explore surface features and molecules at surfaces
 - ⇒ A new and rapidly developing method, that is presently most effectively used by a specialist



S.S. Sheiko, Adv. Polym. Sci. (2000) 151:61-174

Example 1: Comparison of the conformational properties of homopolymers

- ◇ SEC permits separation of the sample into an eluent with approximately common R_G or common $M[\eta]$ at any given elution time
- ◇ On-line multiple angle static light scattering and refractive index detectors permit measurement of $M_w \approx M$, $R_{G,LS} \approx R_G$ and solute concentration as functions of the elution time.



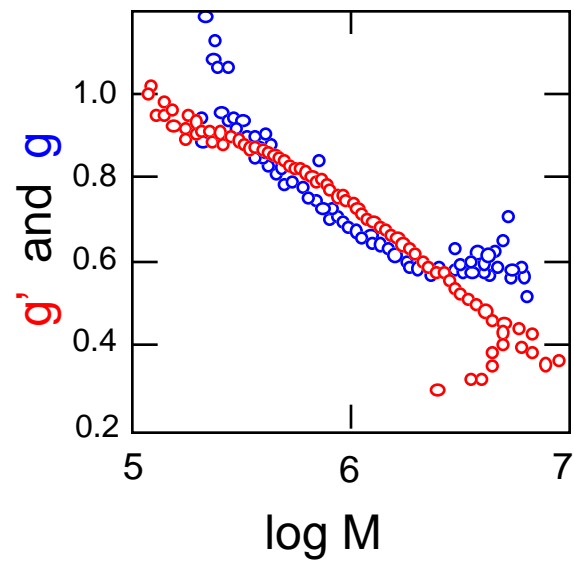
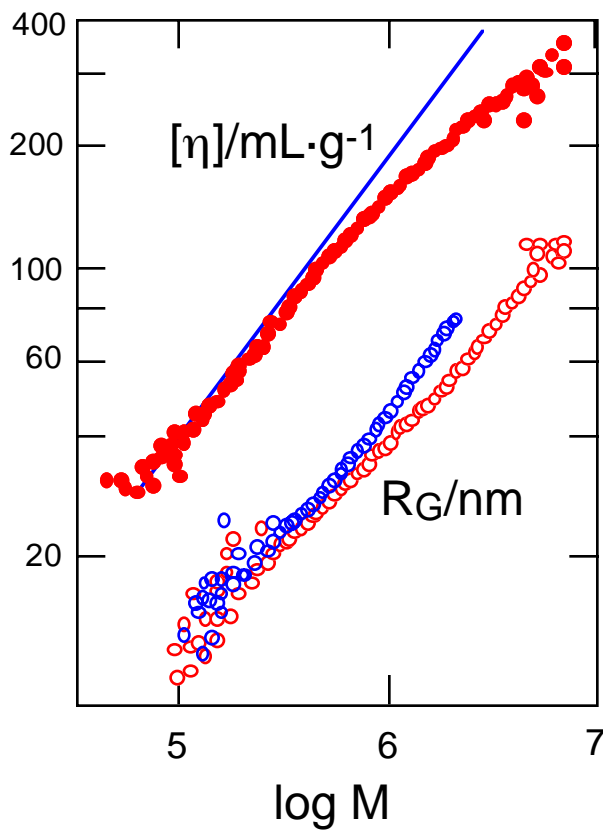
poly(di-n-hexylsilane) & poly(phenyl-n-hexylsilane)
P. M. Cotts *J. Poly. Sci.: Pt. B: Polym. Phys.* (1994) 32:771-8.

Example 2: The characterization of long-chain random branching.

- ◇ SEC permits separation of the sample into eluents with approximately common $R_G = g^{1/2}(R_G)_{lin}$ or common $M[\eta] = Mg'[\eta]_{lin}$ at any given elution time
- ◇ On-line multiple angle static light scattering and refractive index detectors permit measurement of M_w , $R_{G,LS}$ and solute concentration as functions of the elution time. Information on $R_{G,lin}$ as a function of M , and the assumption that $R_{G,LS} \approx R_G$ then permits an estimate of g for each M , and a measure of the long-chain branching given a model for g .
- ◇ On-line small angle static light scattering and refractive index detectors permit measurement of M_w and solute concentration as functions of the elution time. Off-line measurement of $R_{H,LS} \approx R_H = hR_{H,lin}$ for samples of known elution time then permits an estimate of h given information on $R_{H,lin}$ as a function of M , and a measure of the long-chain branching given a model for $h \approx g^{1/2}$

- ◇ On-line viscosity and refractive index detectors permit measurement of $[\eta]$ and solute concentration as functions of the elution time. The assumption that elution takes place with respect to $M[\eta]$ (the "universal calibration") and information on $[\eta]_{lin}$ as a function of M then permits an estimate of g' for each M , and a measure of the long-chain branching given a model for g' .

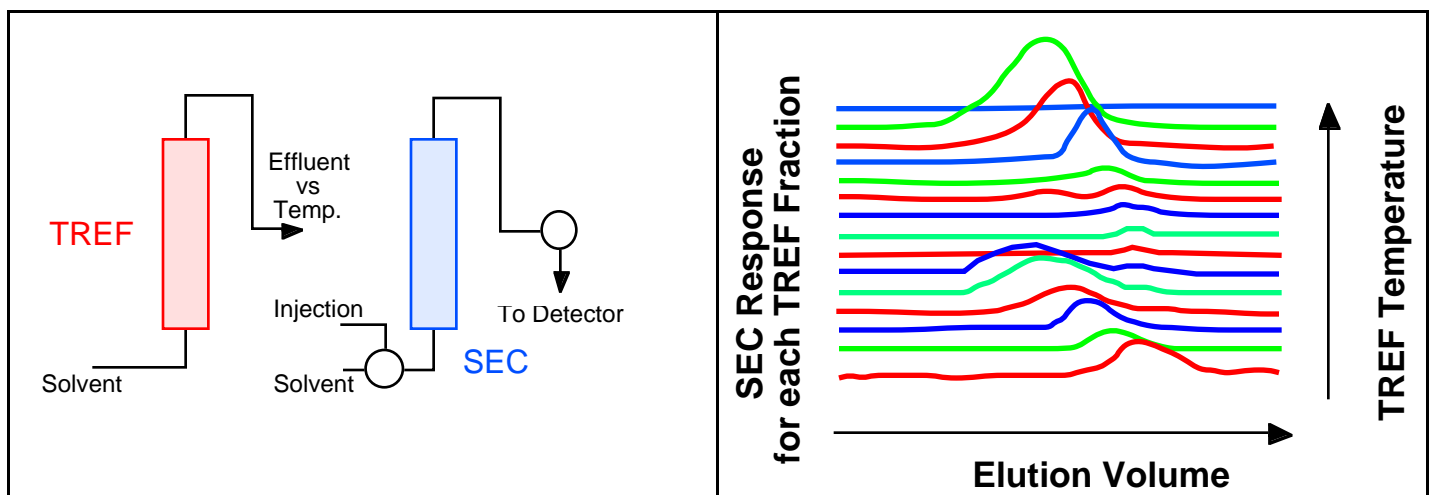
Branched & Linear SEC Eluent



Randomly Branched PMMA
C. Jackson, Y.-J. Chen, J. W. Mays,
J. Appl. Polym. Sci. (1996) 59: 179

Example 3: The characterization of composition and MWD.

- ◇ Cross (or 2D or Orthogonal) method with SEC analysis of each of several fractions prepared by Temperature Rising Elution Chromatography (TREF)
- ◇ TREF separation is based on the dependence of the melting temperature on the polymer composition
- ◇ The method has been used, for example, to elucidate the composition and MWD in copolymers of ethylene and propylene:

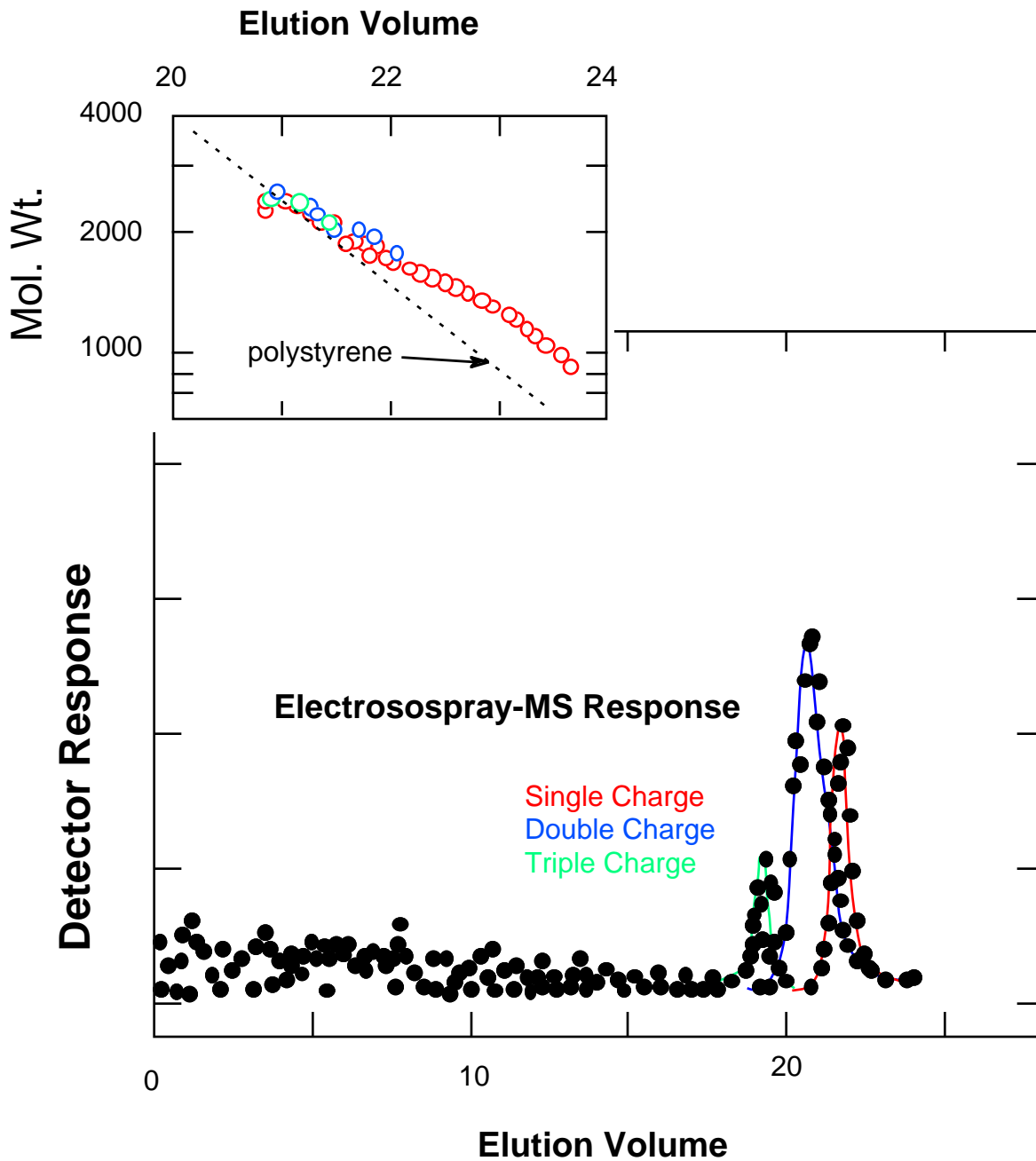


Analysis of poly(ethylene-co-propylene)

T. Usami et al. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* (1993)
52: 145 (ISPAC-5)

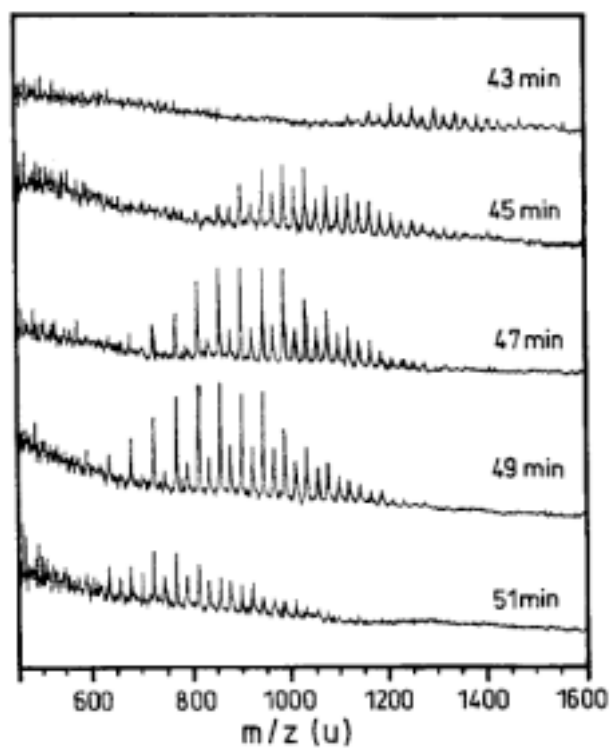
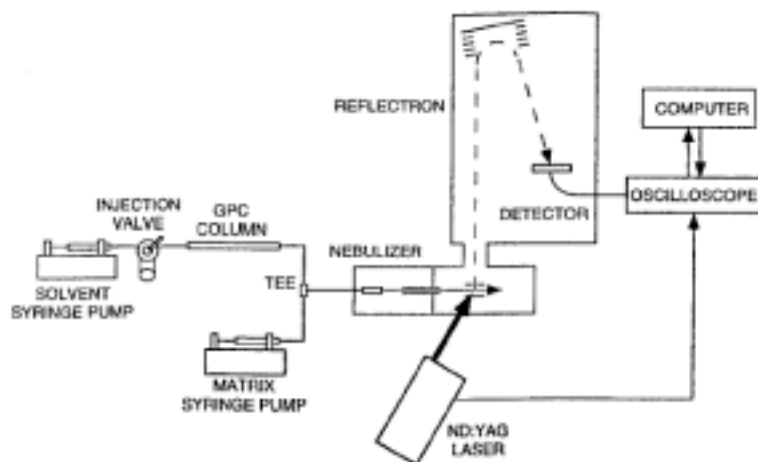
Example 4: The use of mass spectrometry to study the MWD of low M polymers

- ◇ UV and Electrospray Ionization-MS Detection on eluent of a low molecular weight oligomeric solute (doped with a sodium salt to provide charge)
- ◇ The ESI-MS method used includes responses from singly, doubly and triply charged oligomers
- ◇ An analysis was made on a mixture of oligomers with the



W. J. Simonsick Jr. and L. Prokai, in *Chromatographic Characterization of Polymers*, T. Provider, H. G. Barth and M. W. Urban, Eds. *Adv. Chem. Series* 247, (1995), p. 41

A Matrix Assisted Method



X. Fei and K. K. Murray (1996) Anal. Chem. 68:3560

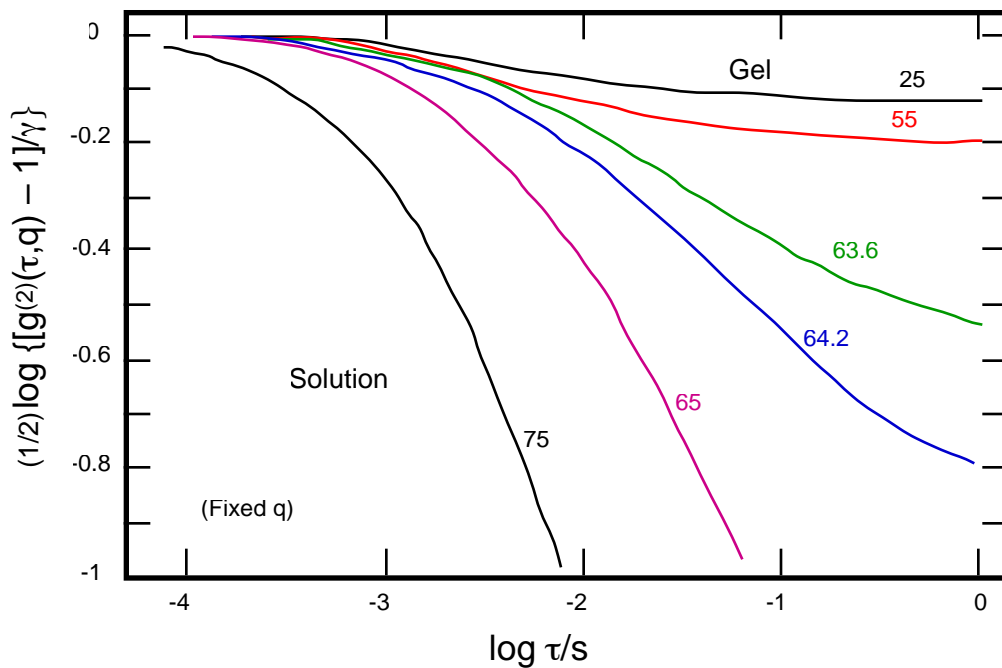
Example 5: Dynamic light scattering on gels

Time averaged scattering photon count auto-correlation function:

Correlation function for an ergodic system with no heterodyne source:

$$g^{(2)}(\tau, q) = \frac{\langle n_q(t + \tau)n_q(t) \rangle_t}{\langle n_q(t) \rangle_t} = \frac{\langle n_q(t + \tau)n_q(t) \rangle_E}{\langle n_q(t) \rangle_E} = 1 + \gamma |g^{(1)}(\tau, q)|^2$$

For a system undergoing a sol-gel transition $g^{(2)}(\tau, q)$ is similar to that for the rheological function $G'(\omega)$:



G. Merkle and W. Burchard *Macromolecules* 29: 3574-8 (1996)

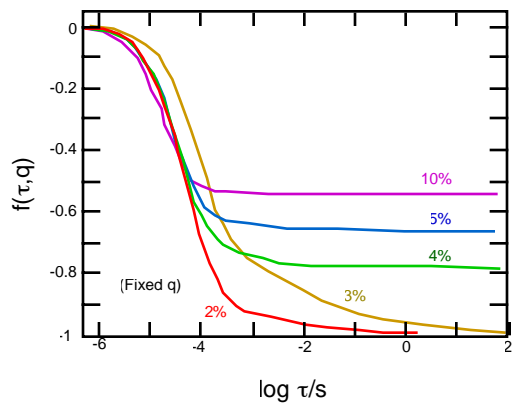
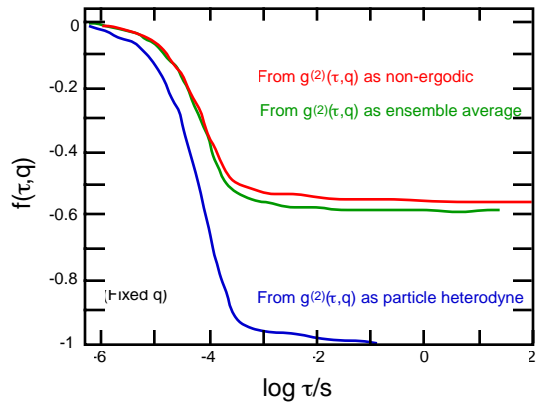
$$\{g^{(2)}(\tau, q) - 1\} / \gamma = 2X(1 - X)\{f(\tau, q) - f(\infty, q)\} + X^2\{f^2(\tau, q) - f^2(\infty, q)\}$$

Heterodyne with static scattering n_{static} :

$$X = n_{\text{static}} / \langle n_q(t) \rangle_t; \quad f(\infty, q) = 0$$

Non-ergodic medium with ensemble average scattering $\langle n_q(t) \rangle_E$:

$$X = \langle n_q(t) \rangle_{E,t} / \langle n_q(t) \rangle_t; \quad 1 \geq f(\infty, q) \geq 0; \quad f(\infty, q) = \exp(-q^2 \langle \delta \rangle^2)$$



J. G. H. Joosten, J. L. McCarty and P. N. Pusey *Macromolecules* 24: 6690-9 (1991)

Example 6: Branched Chain Polymers (Concentrated or undiluted)

$$\eta(M, c, T) \approx \eta_{\text{LOC}}(T) F(M, c, T)$$

$$\eta_{\text{LOC}}(T) \approx [\eta_{\text{LOC}}(T)]_{\text{LIN}}; \text{ Rare exceptions to this known}$$

$$F(M, c, T) \approx 1 + [\eta]^{(c)}c$$

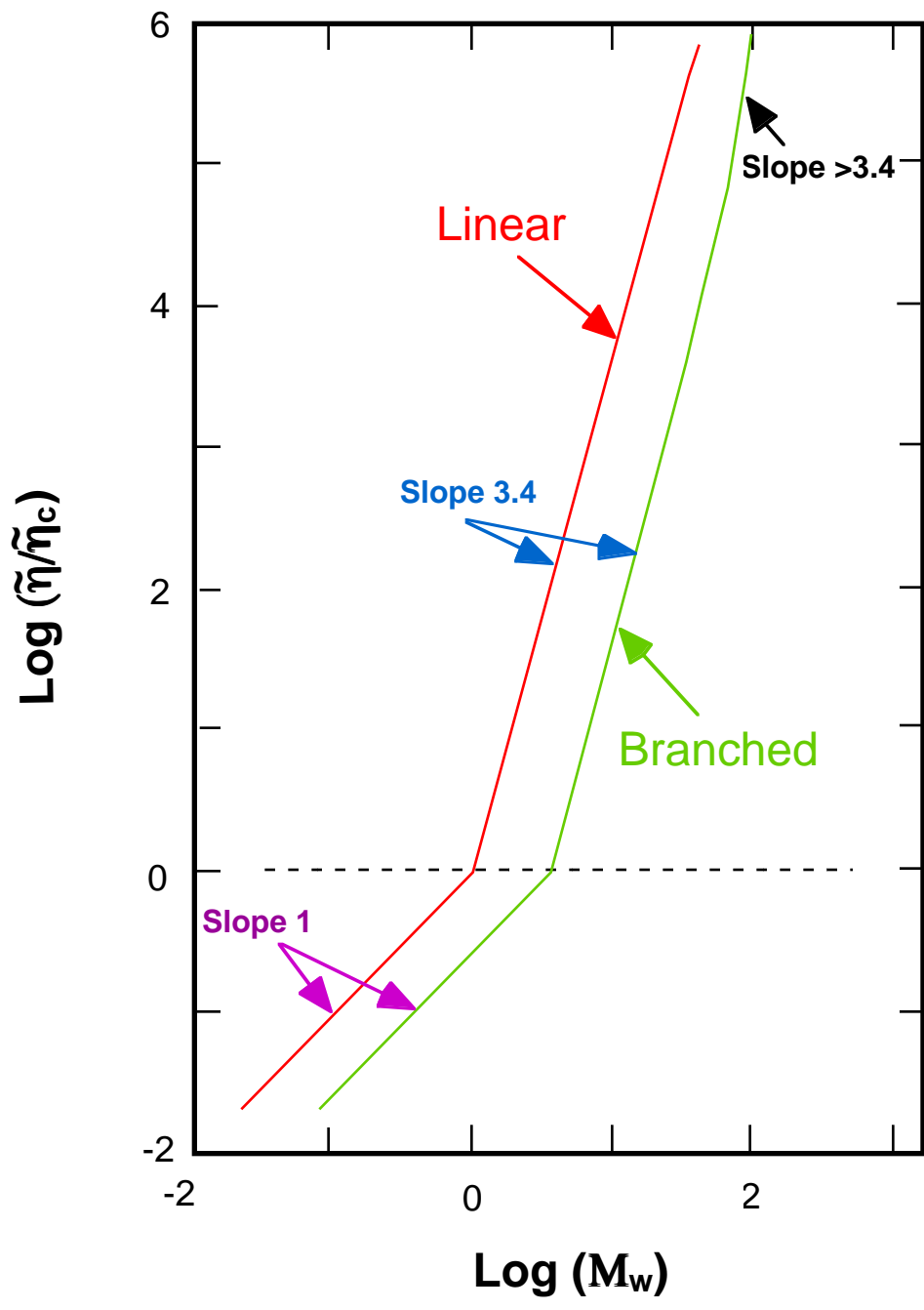
$$[\eta]^{(c)} = \pi N_A (\hat{a}/3) gM$$

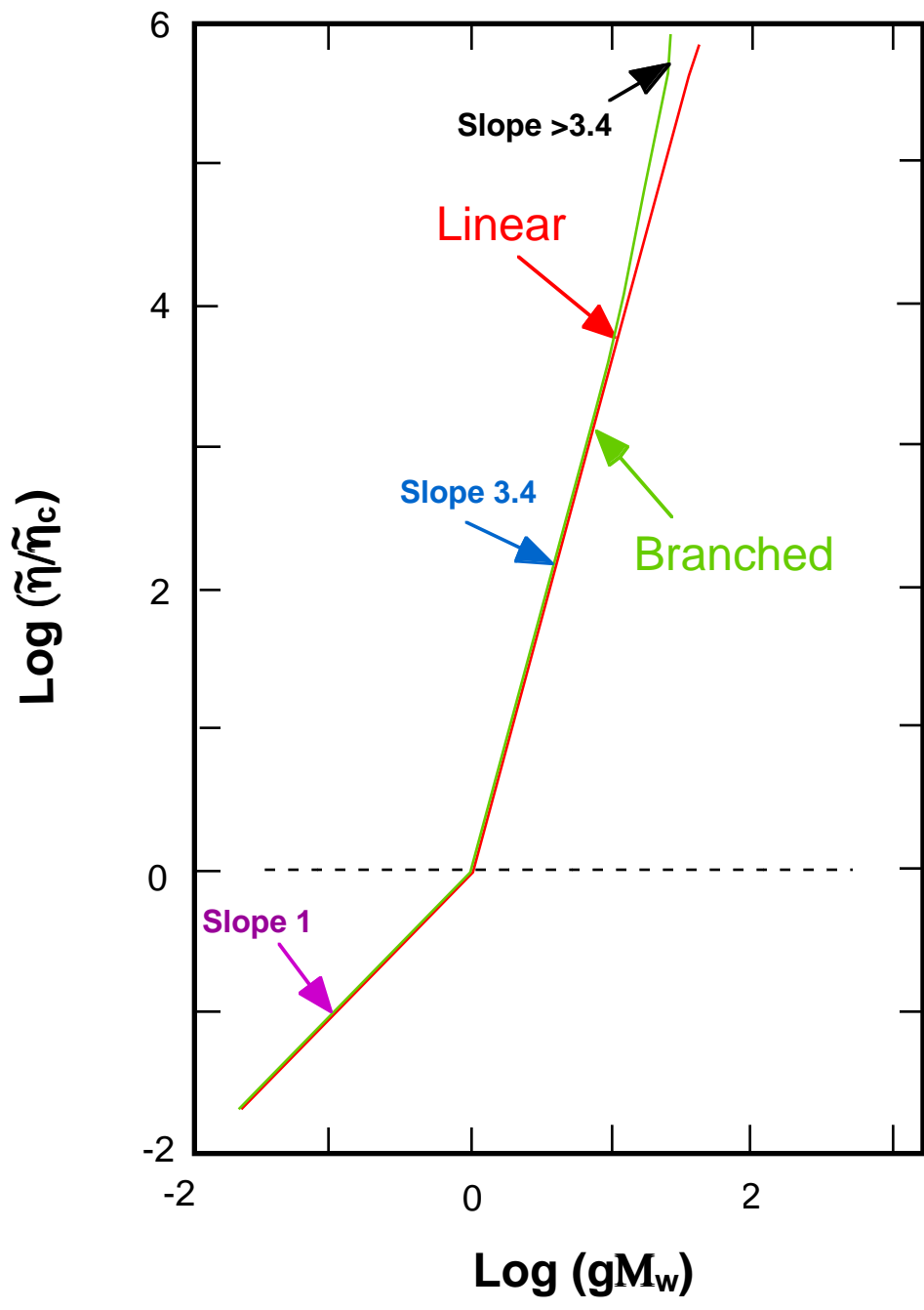
$$F(M, c, T) \approx 1 + \tilde{X}E(\tilde{X}/\tilde{X}_c); \quad \tilde{X} = [\eta]^{(c)}c$$

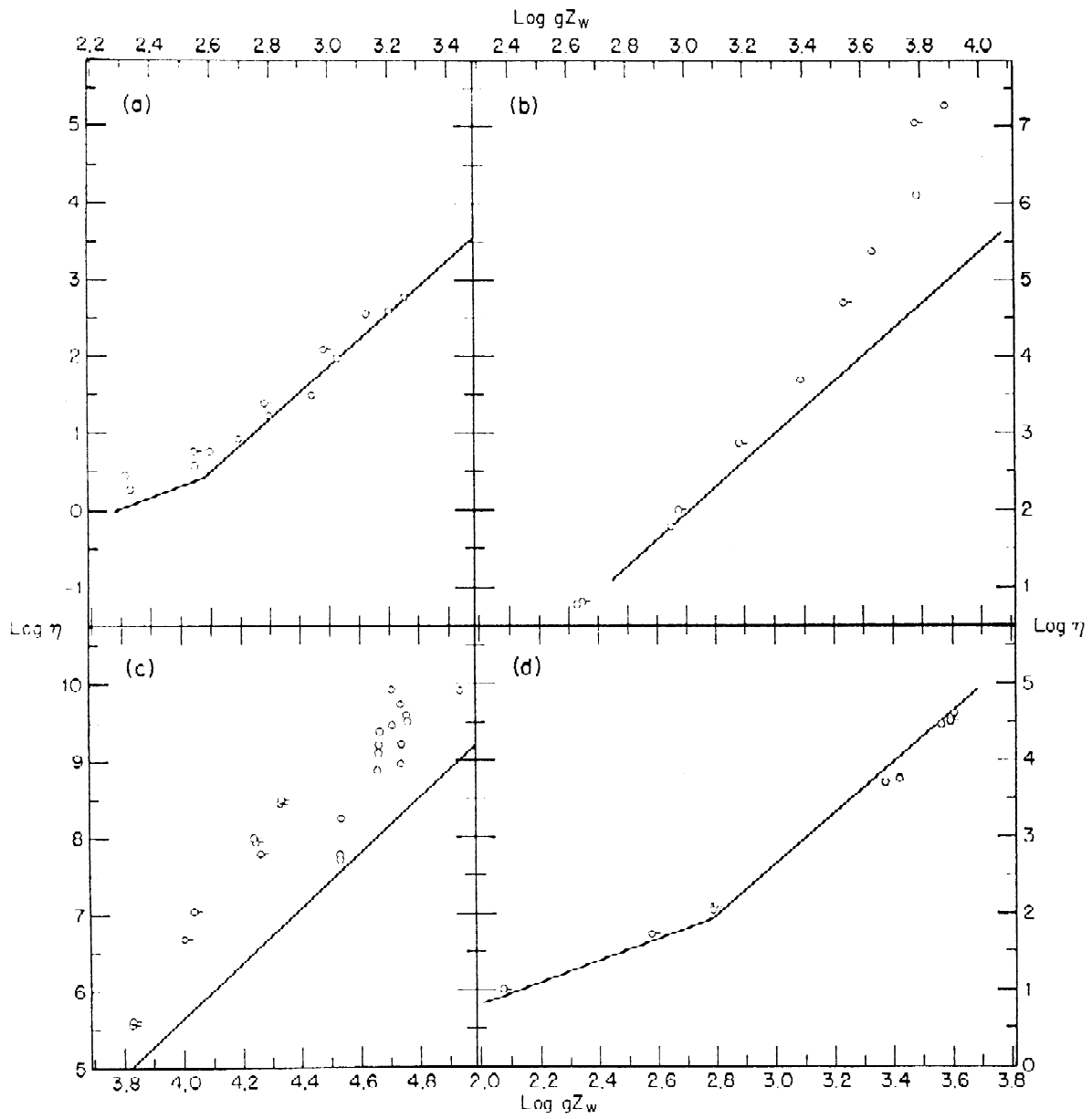
$$E(\tilde{X}/\tilde{X}_c) = \{1 + B(g, M_{\text{BR}}/M_c)(\tilde{X}/\tilde{X}_c)^{4.8}\}^{1/2}$$

$$B(g, M_{\text{BR}}/M_c) \approx 1 \text{ unless the branch molecular } M_{\text{BR}} > M_c$$

$$\tilde{X}_c = \pi N_A (\hat{a}/3) \rho M_c \approx 100 \text{ for many polymers}$$







Approximate Representation of Enhancement Effect

$$\tilde{\eta} = \eta / \eta_{\text{LOC}}^{(c)} \approx \tilde{X} E(\tilde{X} / \tilde{X}_c) F(\sigma \tilde{X} / \tilde{X}_c)$$

The function $F(\sigma \tilde{X} / \tilde{X}_c) \geq 1$ is intended to account for the enhancement effect, with σ the ratio of the molecular weight of a branch to the total molecular weight, e.g., for a comb branch molecule with n branches, $\sigma = (1 - \lambda) / n$.

An empirical relation suggested for $F(\sigma \tilde{X} / \tilde{X}_c)$:

$$F(\sigma \tilde{X} / \tilde{X}_c) \approx \exp\{b[(\sigma \tilde{X} / \tilde{X}_c) - 1]\}$$

$$(\sigma \tilde{X} / \tilde{X}_c) \geq 1; \quad b \approx [2.16 + 0.848\lambda](1 - g)$$

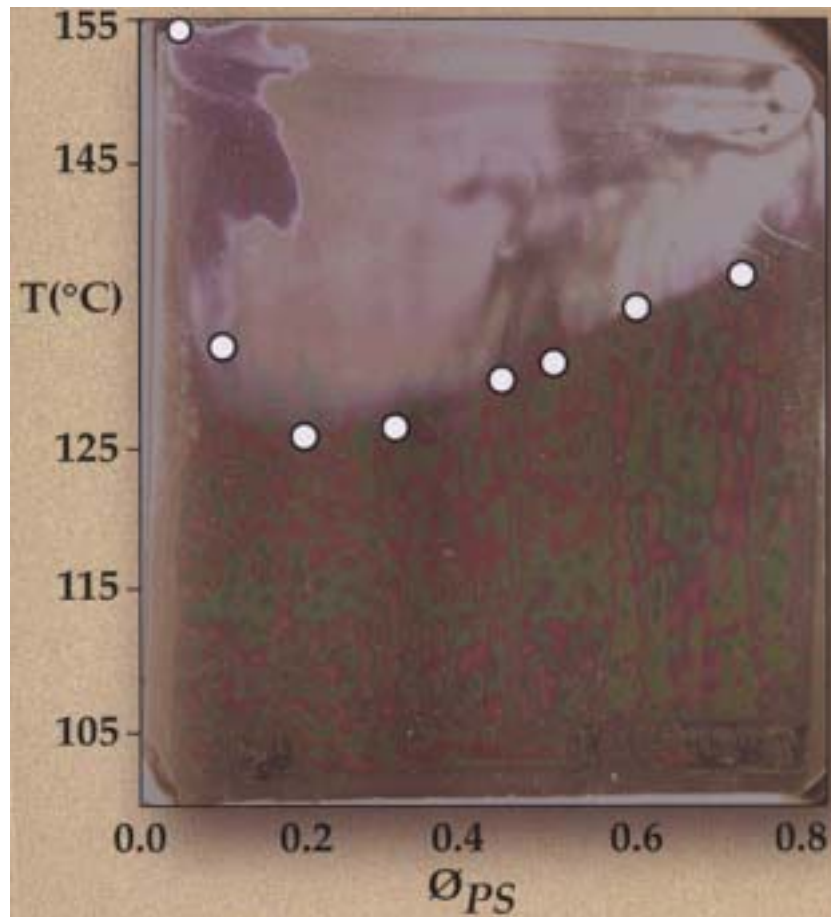
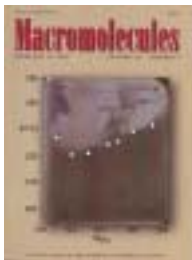
$$(\sigma \tilde{X} / \tilde{X}_c) < 1; \quad b \approx 0$$

Reptation models provide a qualitative description for the behavior, but not as yet a quantitative one.

Some Thoughts on the Future

- ◇ Some easy predictions
 - ⇒ Methods will become increasingly computer intensive, both in the control of the experiment and in the analysis of the results
 - ⇒ Chromatographic methods will become increasingly complex, with multiple detectors, and with combinations of chromatographic separations in a "single" analysis
 - ⇒ Methods will become faster, with more information issuing from the experiment; information "overload" will become more of a problem

- ⇒ Methods will become increasingly prone to misinterpretation, with the analyst becoming further removed from the "raw data" of the experiment
- ⇒ There will be a drive to increase the throughput of experimental data, perhaps using methods adapted from the "Genome Project"





Some Critical Needs



Methods to characterize the distribution of properties within a single SEC elution fraction, e.g., branch nature, copolymer composition distribution



Methods to characterize the sequence distribution in copolymers; existing methods are specialized and usually not amenable to SEC on-line use



Methods (chemical or enzymatic) to systematically disassemble complex macromolecules



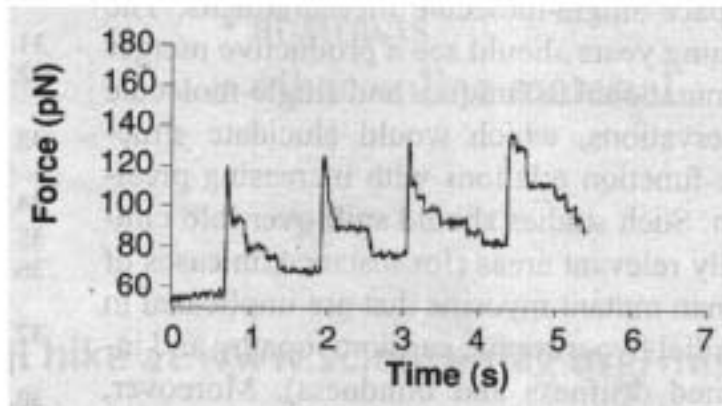
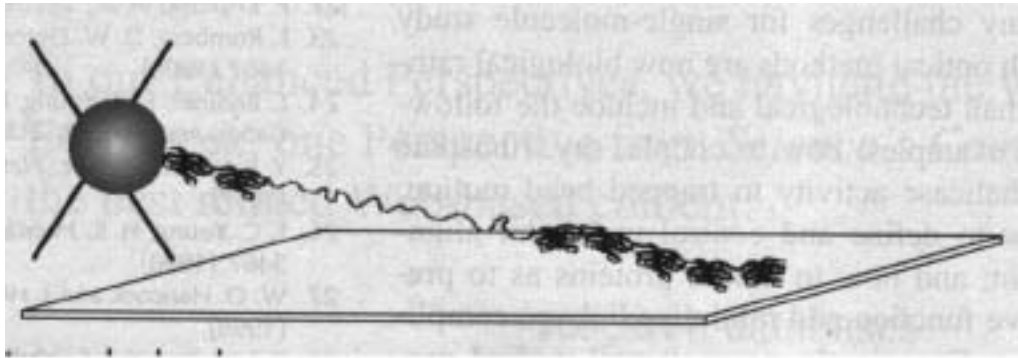
Robust instrumentation and methods applicable to process control applications

- ◇ Instrumental Developments
 - ⇒ Development of robust, "TURN KEY" instruments will continue for multiple detector SEC chromatography, including instruments suitable for process control applications
 - ⇒ The escalating cost of sophisticated instrumentation will present a barrier to its "every-day" use; increased reliance on computer-aided methods may help control this trend
 - ⇒ The implementation of serial multiple separation methods will expand, but will likely remain a tool for the research laboratory and the specialist to be applied for critical problems

◇ People issues

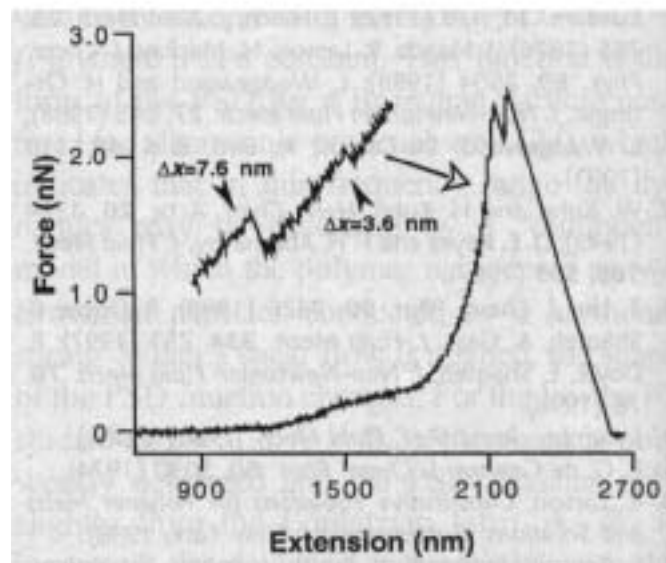
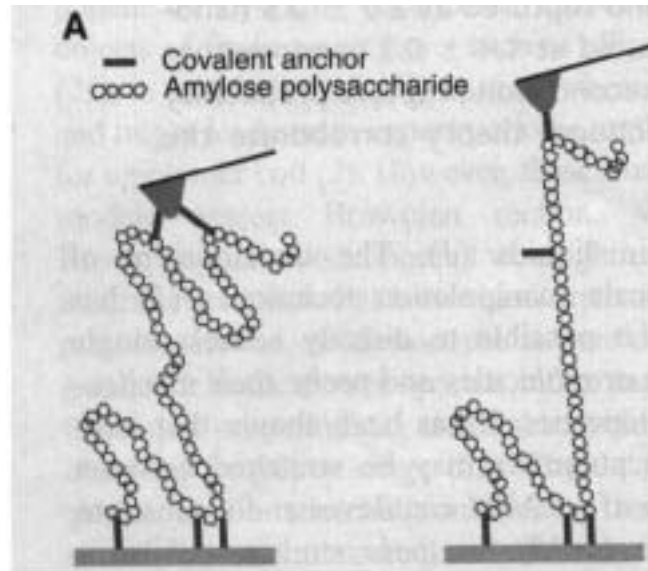
- ⇒ Analysts will be required to continually upgrade their skills in instrumentation, separation methods, and the application of computer-aided methods
- ⇒ The challenges and opportunities of materials characterization must be transmitted to the student population at all levels

Stretching a molecule using a bead manipulated in a calibrated optical trap



Science 283: 1689 (1999)

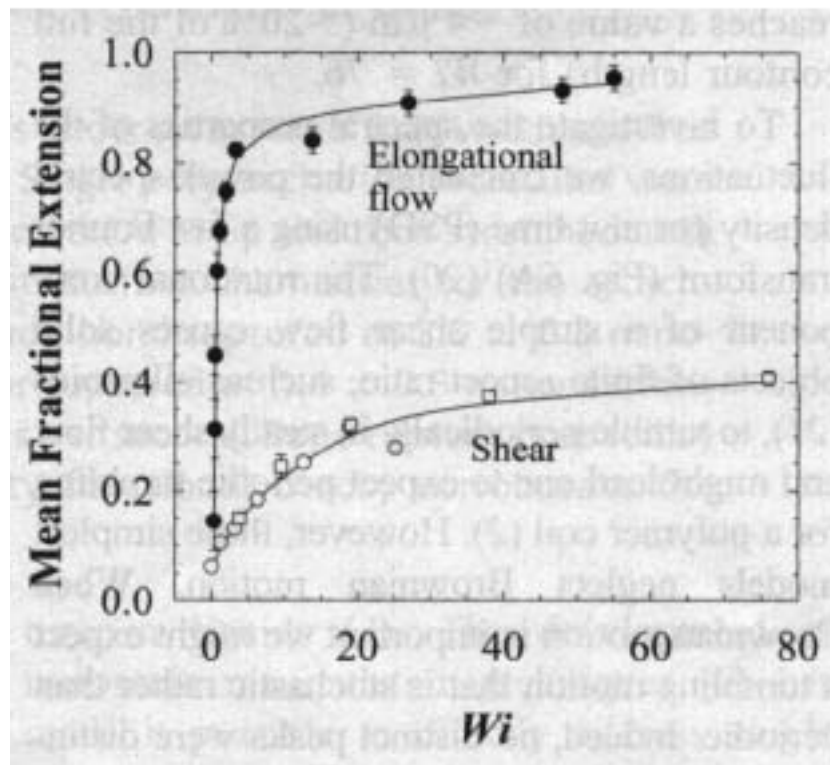
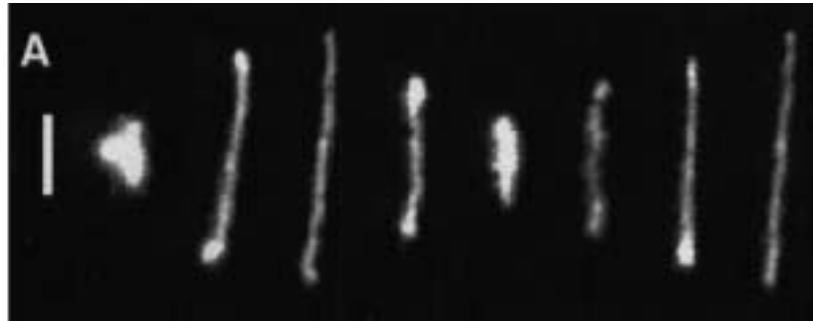
Stretching a molecule using a calibrated cantilever beam



Science 283: 1727 (1999)

Stretching a molecule in a flow field

Fluorescent labeled DNA

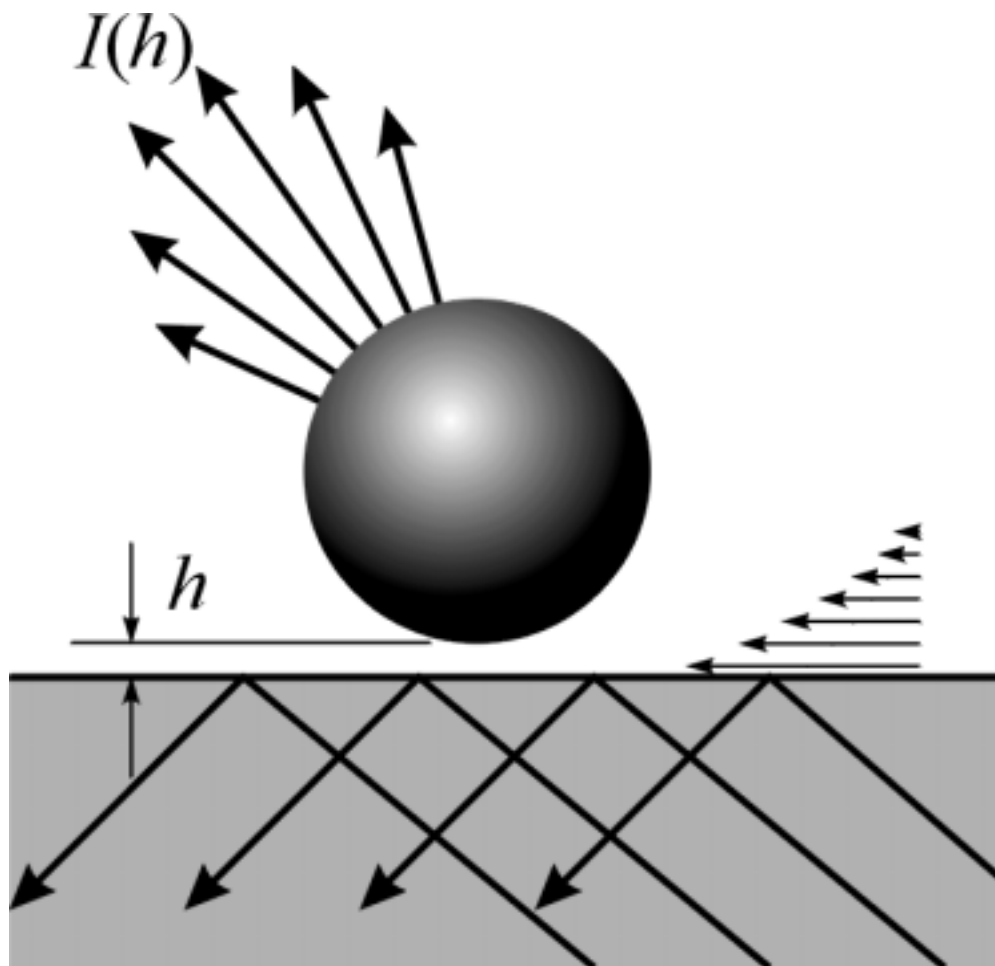


Science 283: 1724 (1999)

Total Internal Reflectance Microscopy

The vertical movement of the bead provides information on the mean potential of the bead and the surface

Adsorbed polymers
Electrostatic interactions



D. C. Prieve, Adv. Colloid Interface Sci. 1999.

