

# Molecular Structure Effects

## MOLECULAR RELAXATION PROCESSES

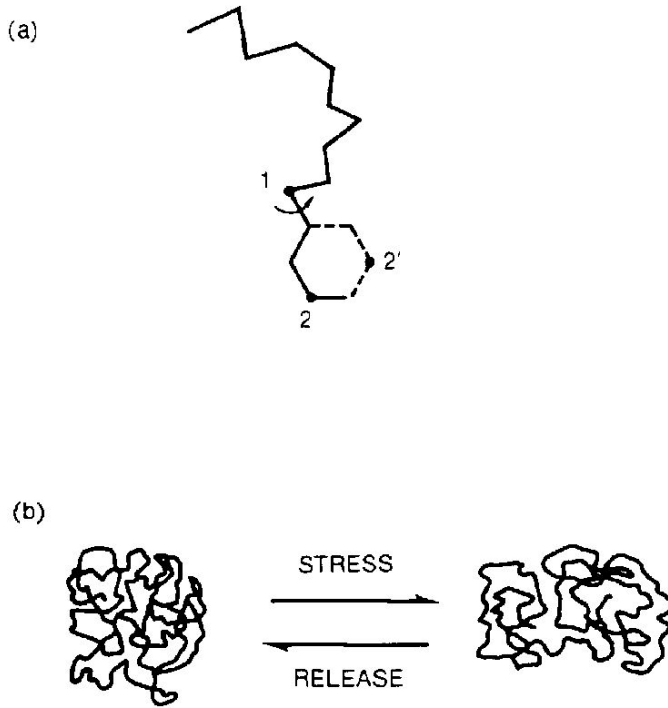


Figure 1: Molecular Relaxation: (a) The shortest mode is an elementary bond flip (conformation change). (b) Many bond flips allow the entire chain to return to a random configuration and hence relax stress.

The equilibrium state of the chain is a random walk, with mean square end-to-end distance  $\langle R^2 \rangle$ .

$$\langle R^2 \rangle = Nl^2 \quad (10-1)$$

$N$  is the number of monomers.

$l$  is the monomer size.

# Molecular Structure Effects MOLECULAR RELAXATION PROCESSES MONODISPERSE LINEAR CHAINS

If **unentangled**, the chains relax to their random walk statistics by free Rouse Motion.

$$\lambda \sim M^2$$

$$G(\lambda) \sim \frac{1}{M}$$

$$\eta_0 \cong \lambda G(\lambda) \sim M$$

$$J_e^0 \sim \frac{1}{G(\lambda)} \sim M$$

If **entangled**, the chains relax more slowly to their random walk statistics because the Rouse motion is confined to occur inside the tube of surrounding chains.

$$\lambda \sim M^{3.4}$$

$$G(\lambda) \cong G_N^0 \quad (\text{independent of } M)$$

$$\eta_0 \cong \lambda G(\lambda) \sim M^{3.4}$$

$$J_e^0 \sim \frac{1}{G_N^0} \quad (\text{independent of } M)$$

# Molecular Structure Effects

## MOLECULAR WEIGHT DISTRIBUTION

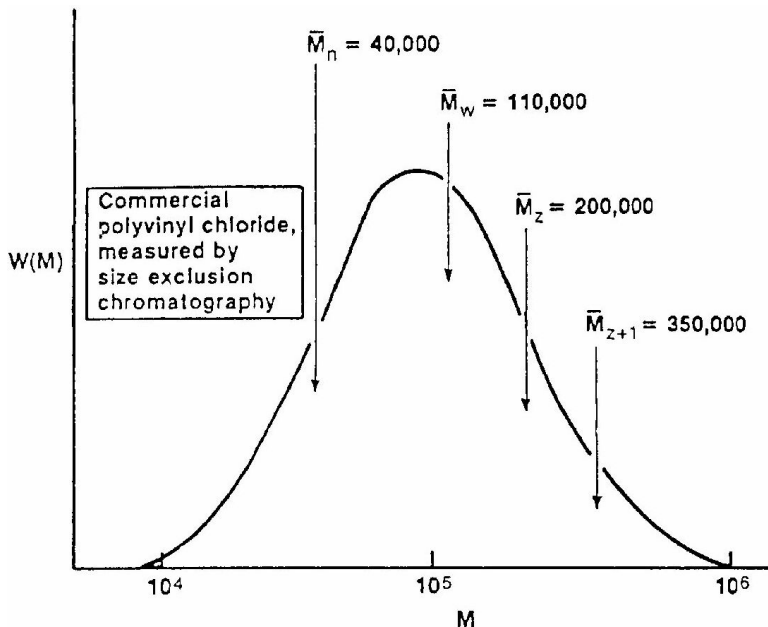


Figure 2: Molecular Weight Distribution with Relevant Averages.

$$M_n = \frac{\sum M_i n_i}{\sum n_i} = \frac{\int M n(M) dM}{\int n(M) dM}$$

$$M_w = \frac{\sum M_i^2 n_i}{\sum M_i n_i} = \frac{\int M^2 n(M) dM}{\int M n(M) dM}$$

$$M_z = \frac{\sum M_i^3 n_i}{\sum M_i^2 n_i} = \frac{\int M^3 n(M) dM}{\int M^2 n(M) dM}$$

$$M_{z+1} = \frac{\sum M_i^4 n_i}{\sum M_i^3 n_i} = \frac{\int M^4 n(M) dM}{\int M^3 n(M) dM}$$

# Molecular Structure Effects ZERO SHEAR VISCOSITY

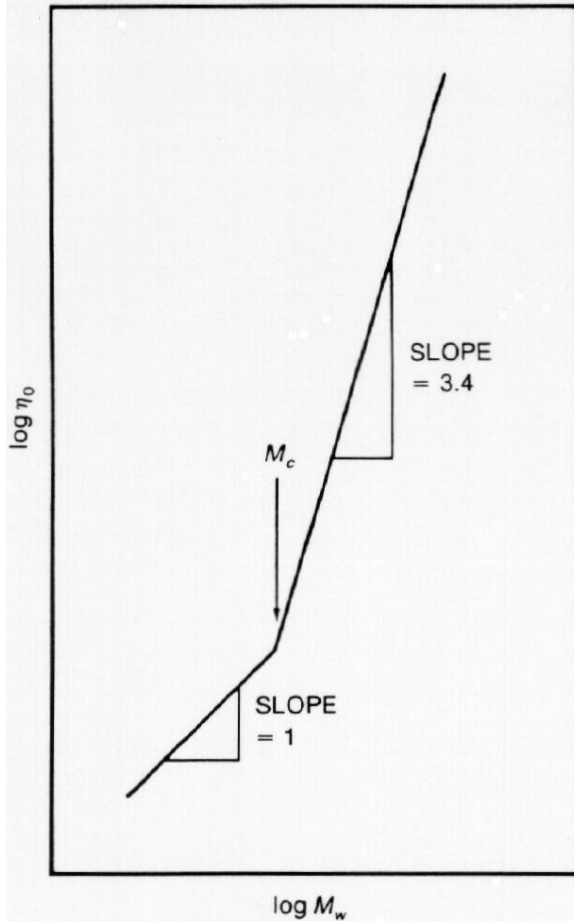


Figure 3: Viscosity-Molecular Weight Relation.

Zero shear viscosity is simply a function of weight-average molecular weight.

$$\eta_0 = K_1 M_w \quad \text{for } M_w < M_c \text{ (unentangled)} \quad (10-2a)$$

$$\eta_0 = K_2 M_w^{3.4} \quad \text{for } M_w > M_c \text{ (entangled)} \quad (10-2b)$$

# Molecular Structure Effects

## STEADY STATE COMPLIANCE

### MONODISPERSE CASE

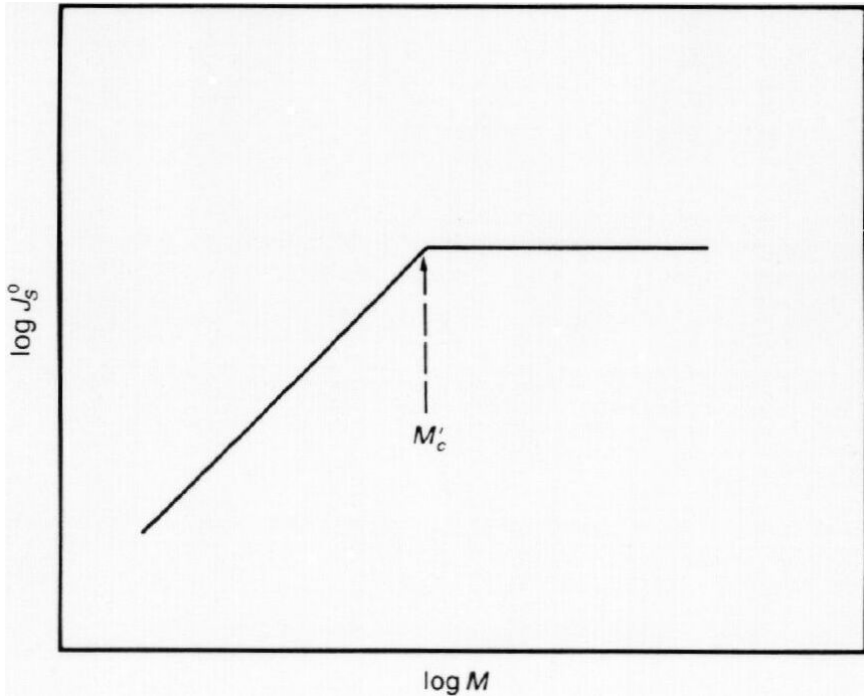


Figure 4: Steady State Compliance of Monodisperse Polymers.

$$J_s^0 = \frac{0.4M}{\rho RT} \quad \text{for } M_w < M'_c \text{ (unentangled)} \quad (2-101)$$

$$J_s^0 = \frac{0.4M'_c}{\rho RT} \quad \text{for } M_w > M'_c \text{ (entangled)} \quad (10-3)$$

# Molecular Structure Effects

## STEADY STATE COMPLIANCE

### POLYDISPERSE CASE

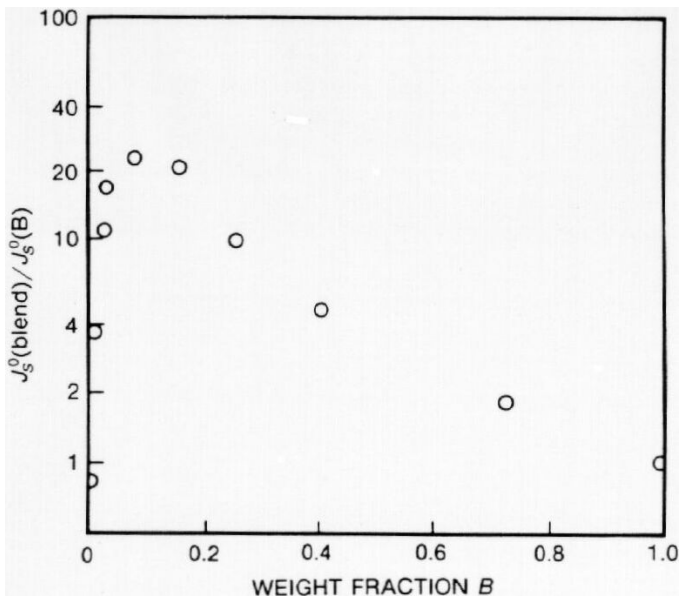


Figure 5: Steady State Compliance of Binary Blends of Polydisperse Commercial Polydimethylsiloxanes.  $(M_w)_A = 58500$  and  $(M_w)_B = 596000$ .

Steady state compliance is a strong function of polydispersity.

$$J_s^0 = \frac{0.4M'_c}{\rho RT} f(MWD) \quad (10-4)$$

$$\text{Rouse Model} \quad f = \frac{M_z M_{z+1}}{M_w^2} \quad (10-5)$$

$$\text{Reptation Model} \quad f = \frac{M_{z+4} M_{z+3} M_{z+2}}{M_{z+1} M_z M_w}$$

$$\text{Empirical} \quad f = \left( \frac{M_z}{M_w} \right)^a \quad \text{with } 2 < a < 3.7 \quad (10-6)$$

# Molecular Structure Effects STEADY SHEAR VISCOSITY and DIE SWELL

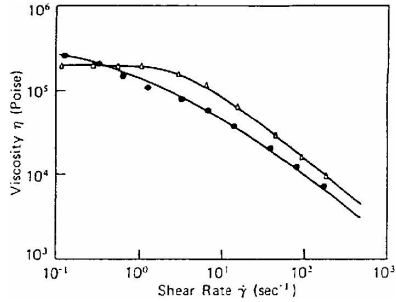


Figure 6: Apparent Viscosity in Steady Shear for Polystyrene. Filled symbols have  $M_w = 260000$  with  $M_w/M_n = 2.4$ . Open symbols have  $M_w = 160000$  with  $M_w/M_n < 1.1$ .

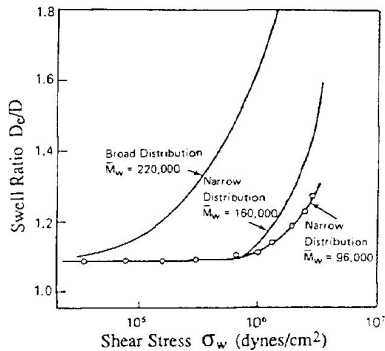


Figure 7: Effect of Molecular Weight and Distribution on the Die Swell of Polystyrene.

Polydispersity greatly increases the longest relaxation time and thus increases the stored elastic energy in flow.

$$MWD \uparrow \implies \lambda \uparrow \implies J_s^0 = \frac{\lambda}{\eta_0} \uparrow \implies \text{More Die Swell}$$

# Molecular Structure Effects

## LONG-CHAIN BRANCHING

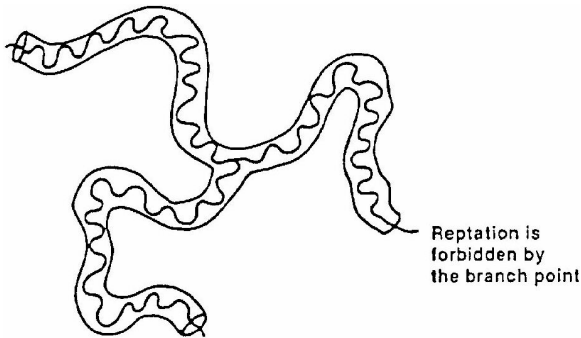


Figure 8: Simplest Branched Polymer is a Star.

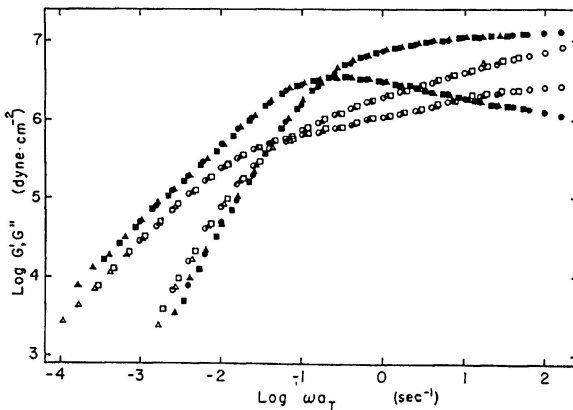


Figure 9: Oscillatory Shear for Linear (filled symbols,  $M_w = 435000$ ) and 3-Arm Star (open symbols,  $M_w = 127000$ ) Polybutadienes at 25°C.

Branched polymers relax by **arm-retraction** because reptation is not allowed by the branch point.



# Molecular Structure Effects LONG-CHAIN BRANCHING

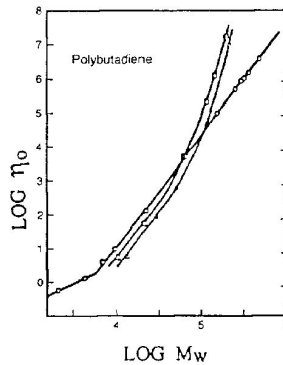


Figure 10: Viscosity of Linear (circles), 3-Arm Star (squares) and 4-Arm Star (triangles) Polybutadienes at 107°C.

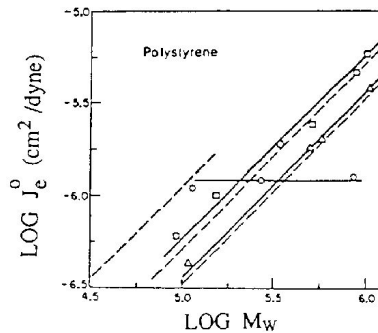


Figure 11: Steady State Compliance of Entangled Linear (circles), 4-Arm Star (squares) and 6-Arm Star (triangles) Polystyrenes.

$$\eta_0 \sim \exp\left(\frac{\nu M_b}{M_e}\right) \quad J_s^0 = \frac{0.6M_b}{cRT}$$

$M_b$  is the molecular weight of the star arm.

# Molecular Structure Effects LONG-CHAIN BRANCHING STEADY SHEAR VISCOSITY

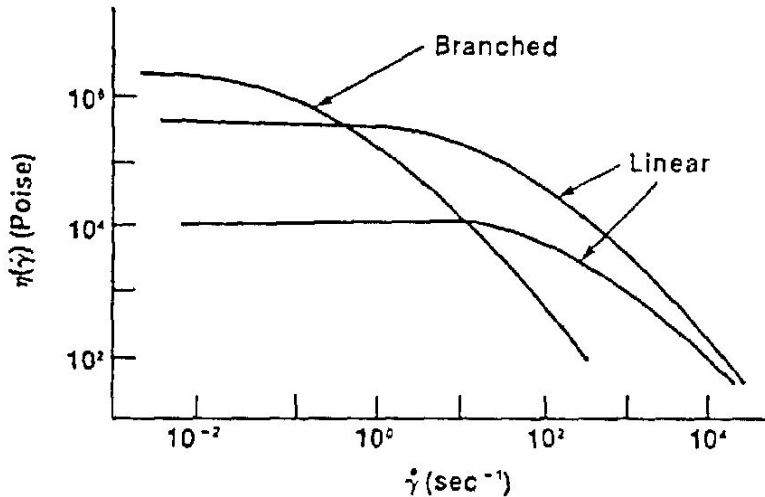


Figure 12: Apparent Viscosity of Randomly Branched Polymers Compared to Linear Polymers.

Branching makes for **more chain ends** per unit volume. Thus branched chains have more arm retraction relaxations induced by a strong flow, and exhibit stronger shear thinning than linear polymers.

Branching provides a means to tailor the rheology to certain needs.

EXAMPLE: Blow Molding

# Molecular Structure Effects CHARACTERIZATION OF LONG-CHAIN BRANCHING

Since branching has such a profound effect on rheology, it is crucial to characterize the extent of branching in the polymer.

## DILUTE SOLUTION CHARACTERIZATION

The hydrodynamic volume of a branched polymer is somewhat smaller than a linear polymer of the same molecular weight.

Intrinsic viscosity  $[\eta]$  is the initial slope of viscosity vs. concentration:

$$\eta = \eta_s (1 + [\eta]c + K_H ([\eta]c)^2 \dots)$$

$K_H$  is the Huggins coefficient.

$$\text{Intrinsic Viscosity} \quad \left( \frac{[\eta]_{star}}{[\eta]_{lin}} \right)_M = \frac{\sqrt{3f-2}}{f} < 1$$

$f$  is the number of arms in the star.

Thus branching can be determined by a combination of light scattering (determines  $M_w$ ) and intrinsic viscosity. This is usually done with light scattering and viscosity detectors coupled with size exclusion chromatography.

Note that the effect of branching on dilute solution viscosity is **subtle**. Conversely, the effect of branching on melt rheology is **striking**. Since melt rheology directly influences processing, one is far better off measuring branching effects with melt rheology.

# Molecular Structure Effects RANDOMLY BRANCHED POLYMERS

Random branching always makes an extremely broad molecular weight distribution.

The Rouse model of randomly branched polymers predicts a weak dependence of viscosity on molecular weight.

$$\eta_0 \sim M_w^{0.75}$$

The steady state compliance is a somewhat stronger function due to polydispersity effects.

$$J_s^0 \sim M_w^{1.5}$$

In general the molecular weight dependence of viscosity depends on the number of monomers between branch points  $N$ .

$$\eta_0 \sim M_w^{s/\gamma}$$

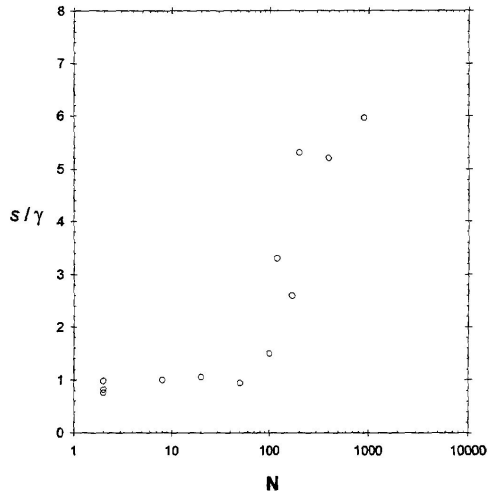


Figure 13: Dependence of the Exponent Describing the Viscosity - Molecular Weight Relation for Randomly Branched Polymers on the Chain Length between Branch Points.