

Molecular Theories of Linear Viscoelasticity

THE ROUSE MODEL (P. 1)

Model polymer dynamics by a system of $N + 1$ beads connected by N springs.

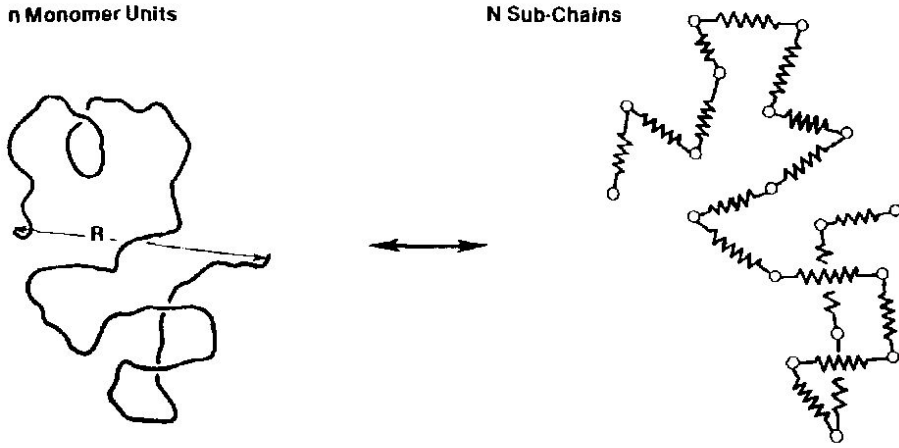


Figure 1: Mapping the Polymer Chain onto a Chain of Beads Connected by Springs.

ROUSE SCALING

Recall that a polymer chain (or part of a chain) acts like a linear spring when stretched.

Spring Length a

Spring Constant $\frac{kT}{a^2}$

Bead Friction ζ

Molecular Theories of Linear Viscoelasticity

ROUSE SCALING (P. 2)

Chain Friction ζN

Einstein Relation:

$$\text{Diffusion Coefficient } D = \frac{kT}{\zeta N} \sim \frac{1}{N}$$

The relaxation time λ is the time the chain takes to diffuse a distance equal to its size R .

$$\lambda \cong \frac{R^2}{D} \sim NR^2 \sim N^2$$

since $R = aN^{1/2}$.

The terminal modulus $G(\lambda)$ is kT per chain

$$G(\lambda) \cong \nu kT = \frac{\rho RT}{M} \sim \frac{1}{N}$$

$\nu = \rho N_0/M$ is the number density of chains

ρ is the density

$R = N_0 k$ is the ideal gas constant

$$\text{Viscosity } \eta \cong \lambda G(\lambda) \sim N$$

Thus the Rouse model correctly predicts the viscosity proportional to chain length for an unentangled polymer.

Molecular Theories of Linear Viscoelasticity

THE ROUSE MODEL (P. 3)

Rouse solved the system of coupled differential equations that describe the chain of springs, and got

$$G(t) = \frac{\rho RT}{M} \sum_{p=1}^N e^{-t/\lambda_p} \quad (2-94)$$

with Rouse relaxation times (eigenvalues)

$$\lambda_p = \frac{a^2 N^2 \zeta}{6\pi^2 p^2 kT} \quad \text{text has typo! } P \equiv N \quad (2-95)$$

Equation (2-94) is in the form of a generalized Maxwell model with N modes of equal weight. From equations (2-94) and (2-95) we can calculate all viscoelastic functions.

$$\text{Viscosity } \eta_0 = \int_0^\infty G(t) dt = \frac{\zeta \rho a^2 M N_0}{36 M_0^2} \quad (2-96)$$

N_0 is Avogadro's Number

$M_0 = M/N$ is the molecular weight per spring

Rearranging (2-96)

$$a^2 \zeta = \frac{36 M_0^2 \eta_0}{\rho M N_0}$$

Substitute into (2-95)

$$\lambda_p = \frac{36 M_0^2 \eta_0 N^2}{6\pi^2 p^2 kT \rho M N_0}$$

Canceling terms and using $M = M_0 N$

$$\lambda_p = \frac{6\eta_0 M}{\pi^2 p^2 \rho RT} \quad (2-97)$$

The longest relaxation time ($p = 1$) is

$$\lambda_R = \frac{6\eta_0 M}{\pi^2 \rho RT} = \frac{0.608 \eta_0 M}{\rho RT} \quad (2-98)$$

Molecular Theories of Linear Viscoelasticity

THE ROUSE MODEL (P. 4)

There are N relaxation modes in the Rouse model

$$\lambda_p = \frac{6\eta_0 M}{\pi^2 p^2 \rho R T} \quad (2-97)$$

with $p = 1, 2, 3, \dots, N$

The longest relaxation time is

$$\lambda_R = \frac{6\eta_0 M}{\pi^2 \rho R T} = \frac{0.608\eta_0 M}{\rho R T} \quad (2-98)$$

whereas in our scaling argument we concluded

$$\lambda_R \cong \frac{\eta_0 M}{\rho R T}$$

Scaling always fails to give a prefactor of order unity (in this case $6/\pi^2$).

SIGNIFICANCE OF THE LONGEST RELAXATION TIME

- Relaxation of internal stresses occurs on this time scale
- Determines the diffusion coefficient $D \cong R^2/\lambda_1$
- Determines the viscosity (equation 2-98)

For unentangled polymers,

$$\lambda_R \sim M^2$$

The longest mode involves all N springs

Shorter modes involve smaller numbers of springs, with

$$\lambda_p = \frac{\lambda_R}{p^2}$$

The shortest mode

$$\lambda_N = \frac{\lambda_R}{N^2} = \frac{a^2 \zeta}{6\pi^2 k T}$$

Molecular Theories of Linear Viscoelasticity

THE ROUSE MODEL (P. 5)

$$G(t) = \frac{\rho RT}{M} \sum_{p=1}^N e^{-t/\lambda_p} \quad (2-94)$$

OSCILLATORY SHEAR

Storage Modulus

$$G'(\omega) \equiv \omega \int_0^{\infty} G(s) \sin(\omega s) ds \quad (2-65)$$

$$G'(\omega) = \frac{\rho RT}{M} \sum_{p=1}^N \frac{\omega^2 \lambda_p^2}{1 + \omega^2 \lambda_p^2} \quad (2-99)$$

and Loss Modulus

$$G''(\omega) \equiv \omega \int_0^{\infty} G(s) \cos(\omega s) ds \quad (2-66)$$

$$G''(\omega) = \frac{\rho RT}{M} \sum_{p=1}^N \frac{\omega \lambda_p}{1 + \omega^2 \lambda_p^2} \quad (2-100)$$

Equations (2-94), (2-99) and (2-100) are special cases of the generalized Maxwell model

$$G(t) = \sum_{i=1}^N G_i \exp(-t/\lambda_i) \quad (2-25)$$

$$G'(\omega) = \sum_{p=1}^N \frac{G_i (\omega \lambda_p)^2}{1 + (\omega \lambda_p)^2} \quad (2-67)$$

$$G''(\omega) = \sum_{p=1}^N \frac{G_i \omega \lambda_p}{1 + (\omega \lambda_p)^2} \quad (2-68)$$

$$\text{with all } G_i = \frac{\rho RT}{M}$$

Molecular Theories of Linear Viscoelasticity

THE ROUSE MODEL (P. 6)

Dimensionless Moduli

$$[G']_R \equiv \frac{G' M}{\rho R T} = \sum_{p=1}^N \frac{\omega^2 \lambda_p^2}{1 + \omega^2 \lambda_p^2}$$

$$[G'']_R \equiv \frac{G'' M}{\rho R T} = \sum_{p=1}^N \frac{\omega \lambda_p}{1 + \omega^2 \lambda_p^2}$$

These moduli are UNIVERSAL for the Rouse model in the large N limit.

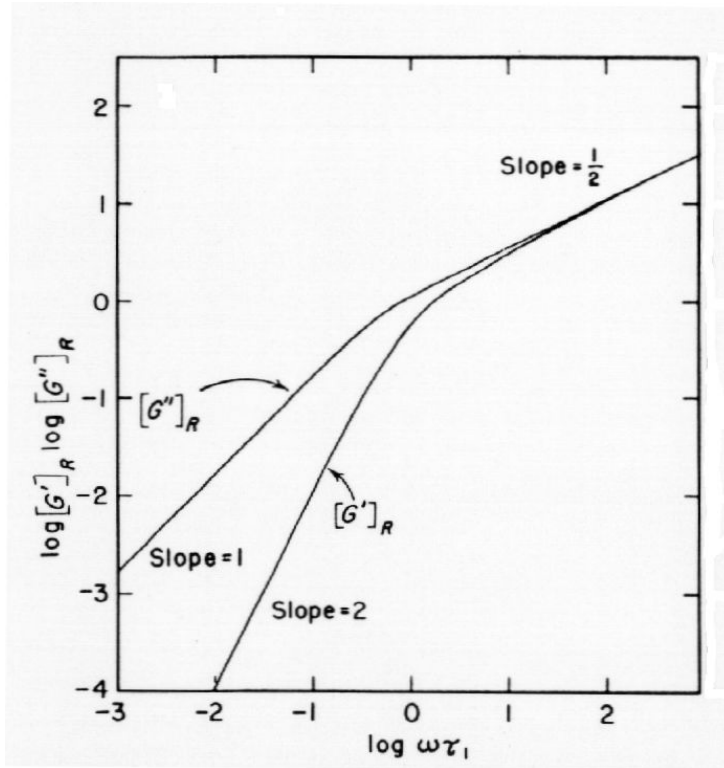


Figure 2: Rouse Model Predictions of Storage and Loss Moduli. Note that $\tau_1 \equiv \lambda_1$.

Molecular Theories of Linear Viscoelasticity

THE ROUSE MODEL TERMINAL RESPONSE

$$G' = \left[\frac{1.08\rho RT}{M} \right] \omega^2 \lambda_R^2 = \frac{0.4M\eta_0^2\omega^2}{\rho RT} \quad (2-102)$$

$$G'' = \frac{1.645\rho RT\omega\lambda_R}{M} = \omega\eta_0 \quad (2-103)$$

Recall the steady state compliance

$$J_S^0 = \lim_{\omega \rightarrow 0} \left(\frac{G'}{(G'')^2} \right)$$

$$J_S^0 = \frac{0.4M}{\rho RT} \quad (2-101)$$

HIGH FREQUENCY (SHORT TIME) RESPONSE

Rouse model is a POWER LAW at short times

$$G(t) = Ct^{-1/2} \quad (2-104a)$$

$$C = \sqrt{\frac{3\rho RT\eta_0}{2\pi M}} \quad (2-104b)$$

$$G'(\omega) = G''(\omega) = \sqrt{\frac{\pi}{2}} C\omega^{1/2} \quad (2-106)$$

$$\tan(\delta) = \frac{G''}{G'} = 1$$

Whenever $G(t)$ is a power law

$$G(t) = ct^{-m} \quad (2-26)$$

The storage and loss moduli are parallel power laws

$$G'(\omega) \sim G''(\omega) \sim \omega^m$$

$$\delta = \frac{m\pi}{2}$$

Molecular Theories of Linear Viscoelasticity

APPLICATIONS OF THE ROUSE MODEL

1) UNENTANGLED MELTS

The Rouse Model correctly describes the full viscoelastic character of short polymers. However, there is another complication at low molecular weights because the monomeric friction coefficient depends on chain length. This is reflected in the glass transition temperature.

$$T_g = T_{g\infty} - \frac{K}{M_n} \quad (\text{D-2})$$

This is understood as a chain end effect — chain ends have more free volume v_f than segments in the middle of the chain.

$$v_f = v_{f\infty} + \frac{C}{M_n}$$

The free volume theory of the glass transition relies on a constant amount of free volume at T_g , so an increase in free volume lowers T_g . It also lowers the monomeric friction coefficient and hence the viscosity via the Doolittle equation.

$$\ln \eta = \ln A + \frac{B(v - v_f)}{v_f} \quad (\text{10-11})$$

2) ENTANGLED MELTS

- The Rouse model describes the short time (or high frequency) relaxation of high molecular weight polymers.
- The molecular theory for terminal relaxation of high molecular weight polymers, REPTATION, is simply Rouse motion of a chain confined in a tube.

Chain End Effects THE GLASS TRANSITION

$$\text{Chain Ends} \sim \frac{1}{M_n}$$

$$T_g = T_{g\infty} - \frac{K}{M_n} \quad (\text{D-2})$$

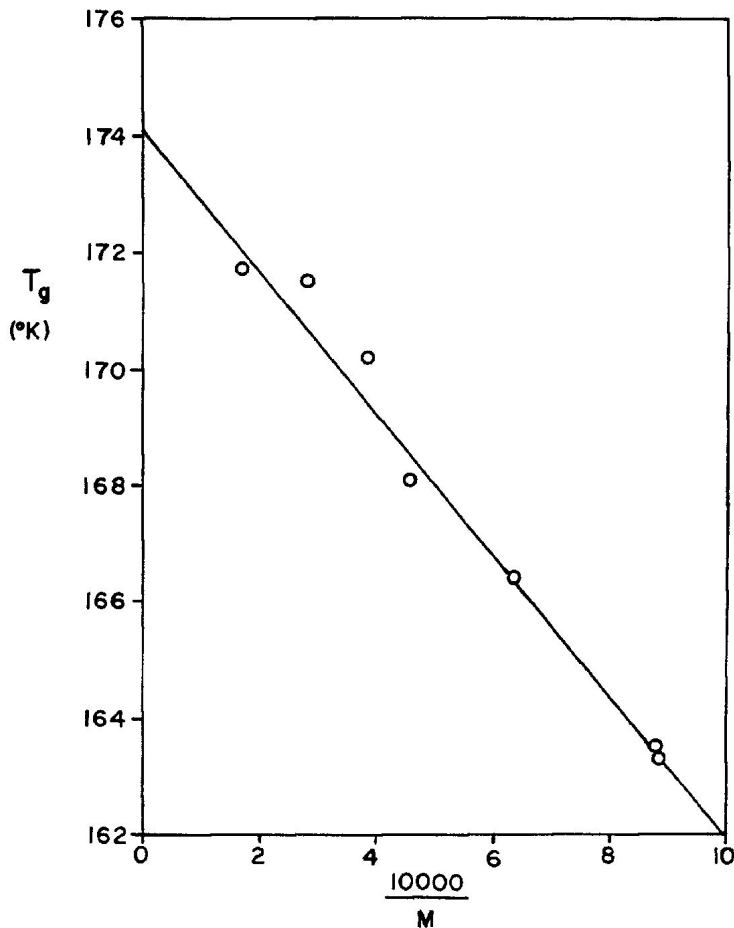


Figure 3: Glass Transition Temperature of Low Molecular Weight Polybutadiene.

Chain End Effects SPECIFIC VOLUME

$$\frac{1}{\rho} = \frac{1}{\rho_{\infty}} + \frac{C}{M_n}$$

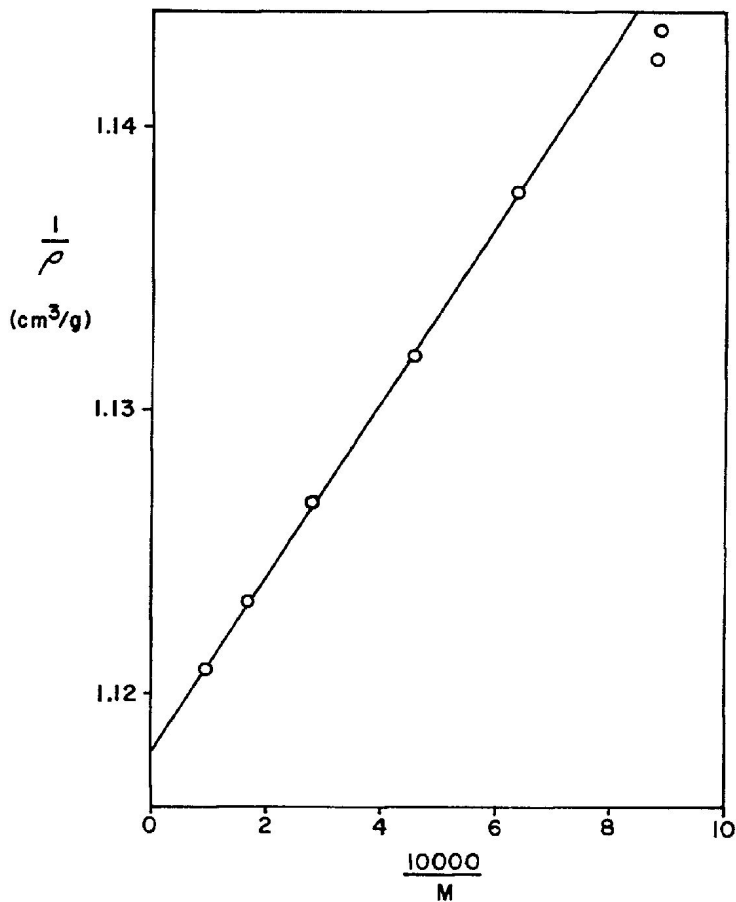


Figure 4: Density of Low Molecular Weight Polybutadiene.

Chain End Effects KINEMATIC VISCOSITY

$$\nu \equiv \frac{\eta}{\rho} \quad \text{units } \textit{Stokes} = \frac{\textit{cm}^2}{\textit{s}}$$

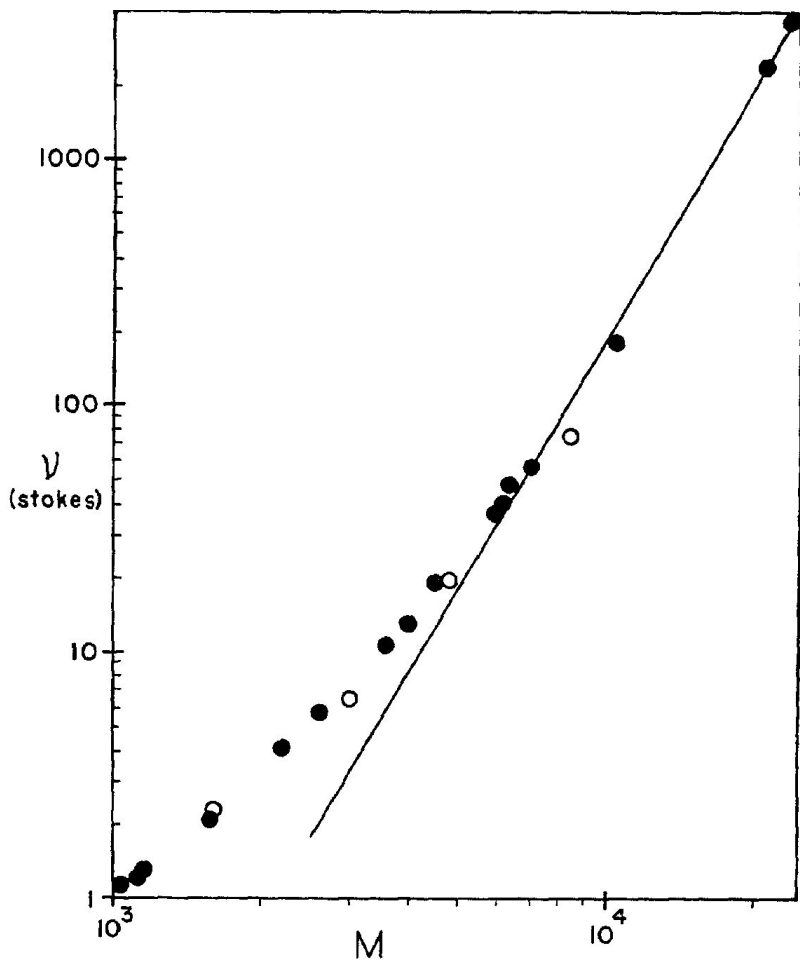


Figure 5: Isothermal Kinematic Viscosity of Low Molecular Weight Polybutadiene.

Chain End Effects CORRECTED KINEMATIC VISCOSITY

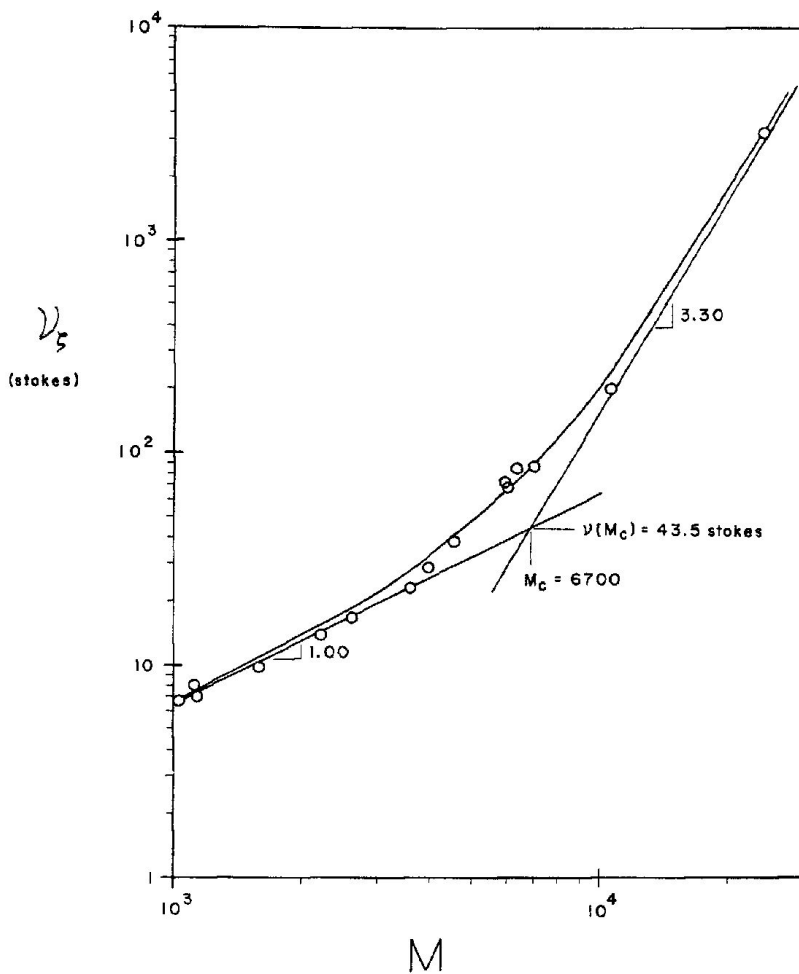


Figure 6: Kinematic Viscosity at Constant Friction Coefficient for Low Molecular Weight Polybutadiene.