

# Polymer Dynamics

# Dynamics of polymers

- Rouse-Bueche theory
- Reptation and chain motion
  - De Gennes Reptation theory
- Fickian and Non-Fickian diffusion
- Experimental methods of determining diffusion coefficients

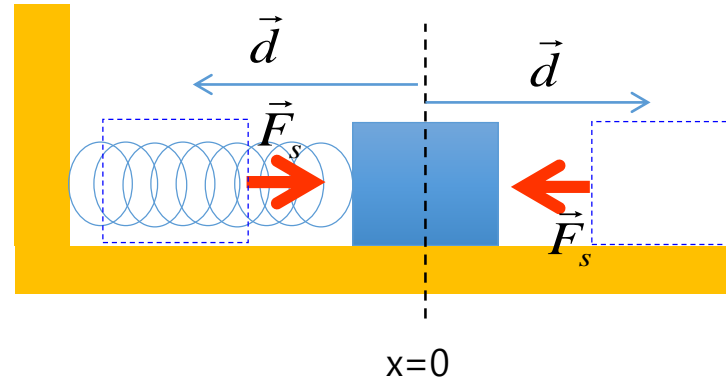
# Macromolecular dynamics

- Polymer motion can take **two forms**:
  - (a) the chain can **change its overall conformation**, as in relaxation after strain
  - (b) it can **move relative to its neighbors**
- Both motions can be considered in terms of **self-diffusion (Brownian motion)**
  - For center-of-mass diffusion:  
the center-of-mass distance diffusion depends on the square root of time
  - For high enough temperatures:  
an **Arrhenius** temperature dependence is found
- Polymer chains find it almost impossible to move “**sideways**” by simple translation, for such motion is exceedingly slow for long, entangled chains.

# The Rouse-Bueche Theory

- The first molecular theories concerned with polymer chain motion were developed by Rouse (a) and Bueche (b), and modified by Peticolas (c).
  - a. P. E. Rouse, *J. Chem. Phys.*, **21**, 1272 (1953).
  - b. F. Bueche, *J. Chem. Phys.*, **22**, 1570 (1954).
  - c. W. L. Peticolas, *Rubber Chem. Tech.*, **36**, 1422 (1963).
- This theory begins with the notion that a polymer chain may be considered as a succession of equal submolecules.
- These submolecules are replaced by a series of beads of mass  $M$  connected by springs with the proper Hooke's force constant.

# Hook's law



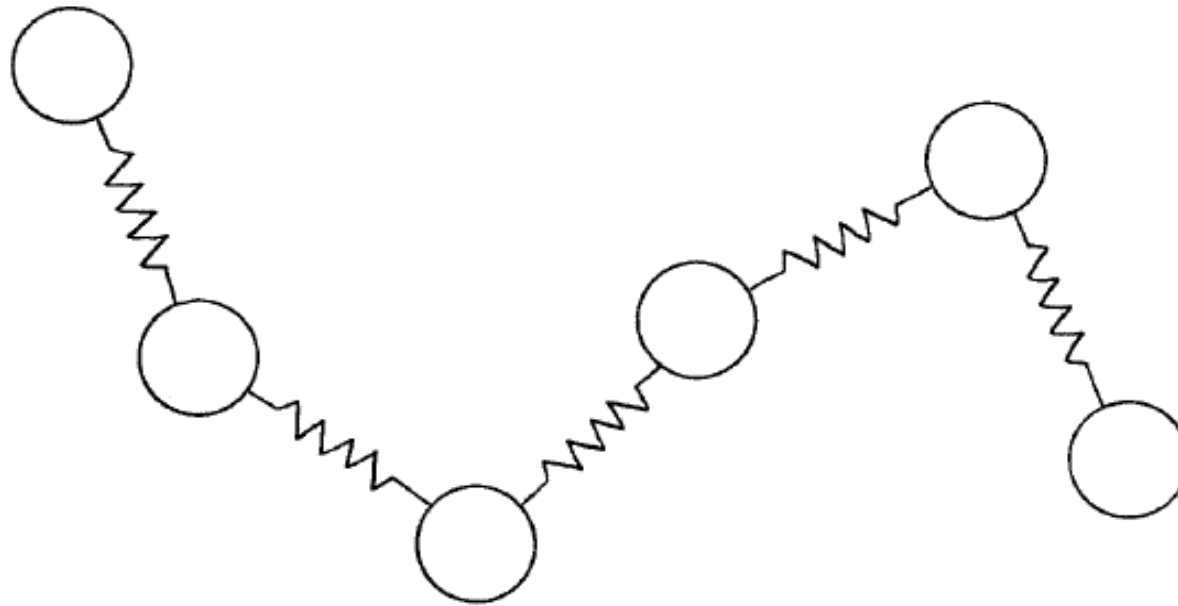
**Hooke's Law:** To a good approximation for many springs, the force from a spring is proportional to the displacement of the free end from its position when the spring is in the relaxed state. The *spring force is given by*

$$\vec{F}_s = -k\vec{d}$$

$$U = -\int F(x)dx = \frac{1}{2}kd^2$$

- The minus sign : the direction of the spring force is always opposite the direction of the displacement of the spring's free end
- $k$  : the **spring constant (or force constant)** , i.e a **measure** of the stiffness of the spring.

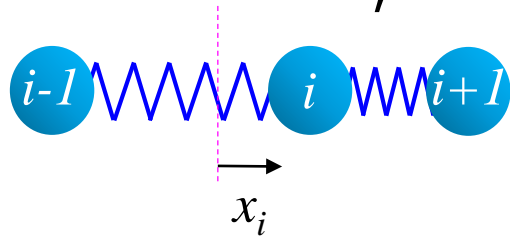
These submolecules are replaced by **a series of beads** of mass  $M$  *connected by springs* with the proper Hooke's force constant.



**Figure 5.6** Rouse-Bueche bead and spring model of a polymer chain.

- If the beads are numbered  $1, 2, 3, \dots, z$ , there are  $z$  springs with  $z+1$  beads

$$f_i = \frac{-3kT}{\bar{r}^2} (-x_{i-1} + 2x_i - x_{i+1}), \quad 1 \leq i \leq z-1$$



$x_i$ : the displacement from its equilibrium position  
 $r$ : end-to-end distance of the segment

$$\Delta x = \underbrace{(x_i - x_{i-1})}_{\text{expansion}} - \underbrace{(x_{i+1} - x_i)}_{\text{contraction}} = -x_{i-1} + 2x_i - x_{i+1}$$

- The segments move through a viscous medium (other polymer chains and segments) in which they are immersed. This viscous medium exerts **a drag force on the system** → **damping out the motions**
- The frictional force is proportional to **the velocity** of the beads
- the bead behaves exactly as if it were a macroscopic bead in a continuous viscous medium

- The viscous force on the  $i$ th bead

$$f_i = \rho \left( \frac{dx_i}{dt} \right) \quad \rho : \text{friction factor}$$

- Zimm's theory
  - concepts of Brownian motion & hydrodynamic shielding (interaction) into the system
  - Drag some of the surrounding solvent
  - friction factor  $\rightarrow$  macroscopic viscosity of the medium  $\rightarrow$  relaxation time

*Time to be equilibrium state,  
the polymer's zero-shear viscosity*

$$\tau_{p,i} = \frac{6\eta_0 M_i^2}{\pi^2 c R T M_w p^2}$$

$\eta_0$ : bulk-melt viscosity

$P$ : running index

$c$ : concentration

Cf. Rouse–Bueche theory is useful especially below 1% concentration  
reasonable for polymer melts, but it is not correct for a polymer in a dilute solution



## The de Gennes Reptation Theory

- While the Rouse–Bueche theory was highly successful in establishing the idea that chain motion was responsible for creep, relaxation, and viscosity, quantitative agreement with experiment was generally unsatisfactory.
- De Gennes model consisted of *a single polymeric chain,  $P$ , trapped inside a three-dimensional network,  $G$* , such as a polymeric gel
  - The gel itself may be reduced to a set of fixed obstacles— $O_1, O_2, \dots, O_n, \dots$ . The chain  $P$  is not allowed to cross any of the obstacles; however, it may move in a snakelike fashion among them.
  - Snakelike motion  $\rightarrow$  reptation
- P. G. de Gennes, J. Chem. Phys., 55, 572 (1971)

- Reptation: thermal motion of very long linear entangled macromolecules (from reptile)
- Repton: a mobile point residing in the cells of a lattice, connected by bonds

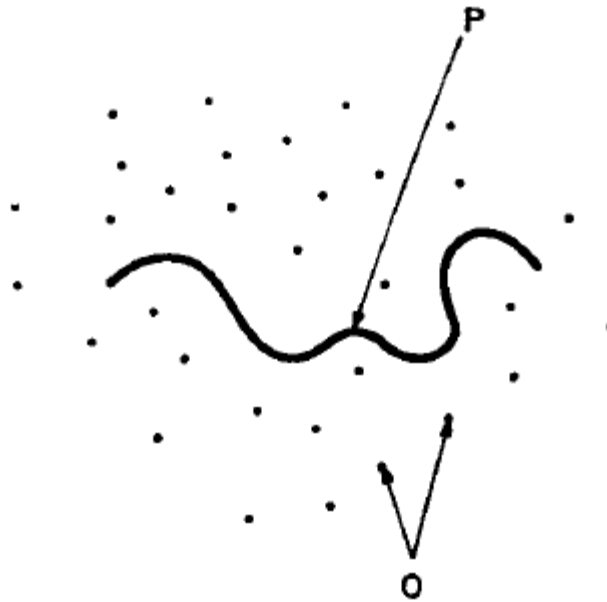
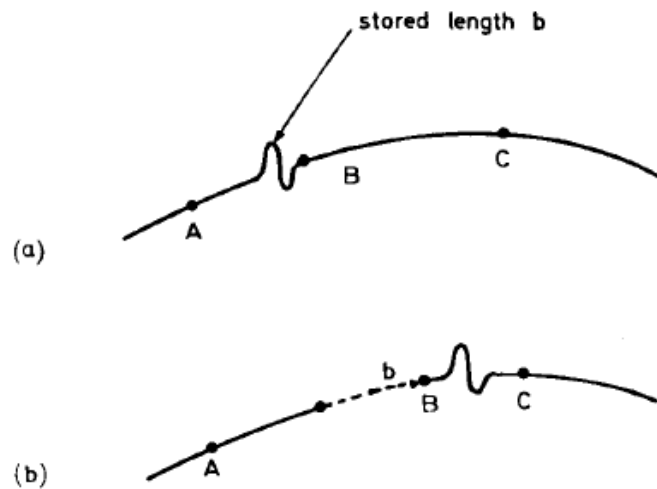


Figure 5.7 A model for reptation. The chain *P* moves among the fixed obstacles, *O*, but cannot cross any of them.

- Chain has “defects”, each with stored length  $b$
- Defects migrate along the chain in a type of defect current
- When the defects move, the chain progresses
- The tubes are made up of the surrounding chains
- The velocity of the  $n$ th mer is related to the defect current  $J_n$

$$\frac{d\vec{r}_n}{dt} = bJ_n$$



- The reptation motion yields forward motion when a defect leaves the chain at the extremity
- Assumption: The direction decided by the head is random

**Figure 5.8** Reptation as a motion of defects. (a) The stored length  $b$  moves from A toward C along the chain. (b) When the defect crosses mer B, it is displaced by an amount  $b$

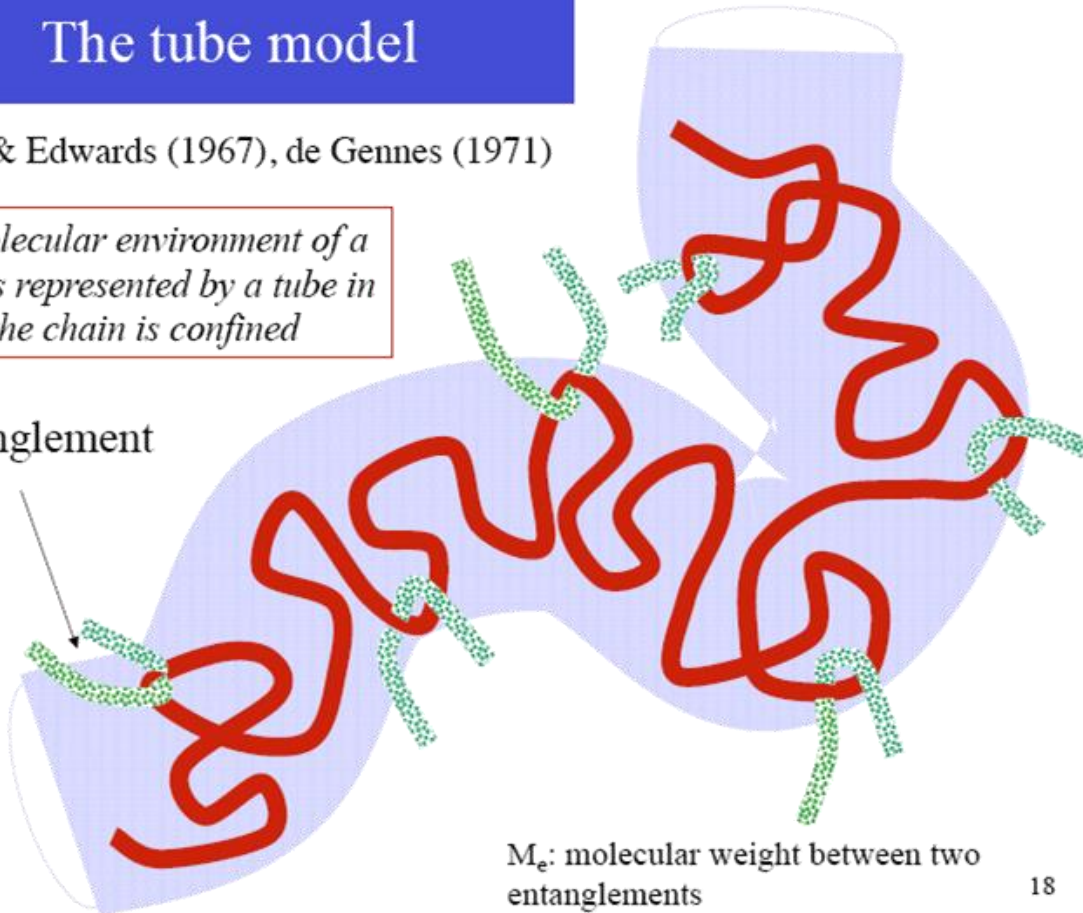
# Linear chain in a tube (de Gennes model)

## The tube model

Doi & Edwards (1967), de Gennes (1971)

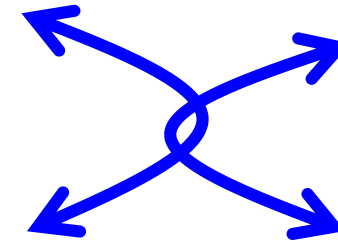
*The molecular environment of a chain is represented by a tube in which the chain is confined*

entanglement



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Entanglement: topographical restriction of molecular motion by other chains



Two chains cannot pass through one another creates topological interactions known as entanglements that raise the network modulus.

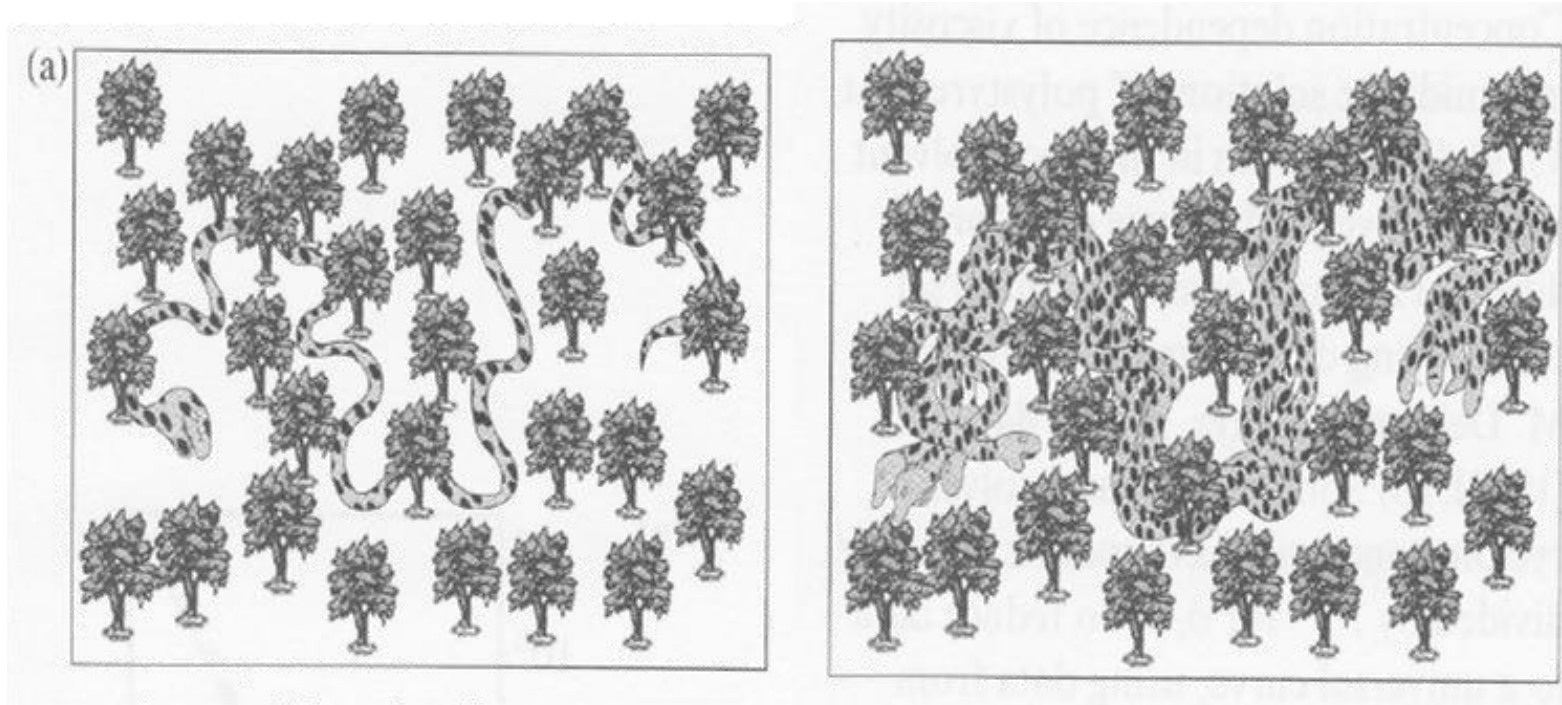


Edwards (1967)



De Gennes (1971)

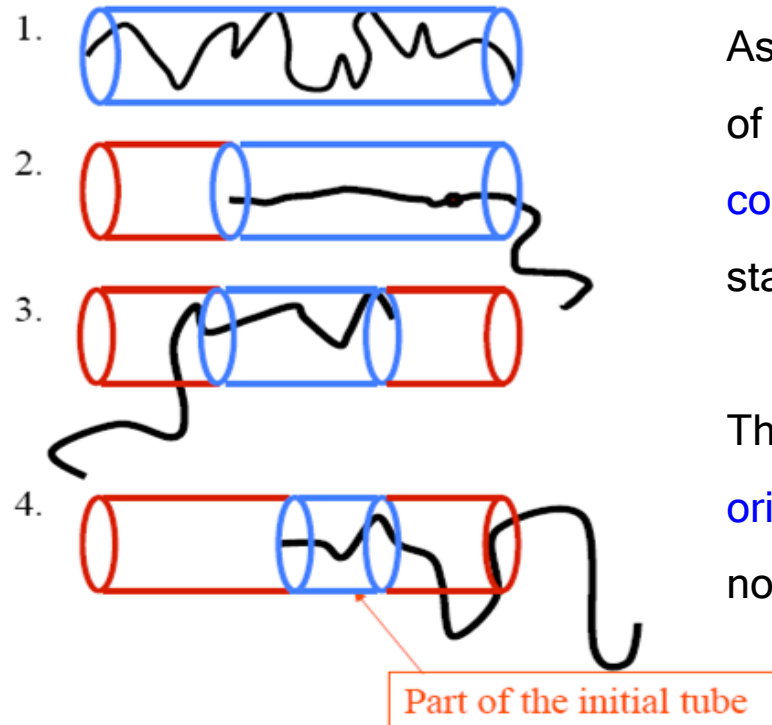
# Tube model and entanglements



A long-exposure photograph of the giant snake in the forest clearly defines its confining tube.

# Reptation

## 1D curvilinear diffusion



As the primitive chain diffuses out of the tube, a new tube is continuously being formed, starting from the ends.

This new tube portion is randomly oriented even if the starting tube is not.

- formation of a loop at the tail of the snake and elimination of the tail segment of the confining tube
- Propagation of the loop along the contour of the tube
- Release of the loop at the head of the snake and formation of a new section of the confining tube

- In de Gennes model: The self-diffusion coefficient  $D$  of a chain depends on the molecular weight  $M$

$$D \propto M^{-2}$$

- $D$ :  $10^{-12} \sim 10^{-6} \text{ cm}^2/\text{s}$
- Polyethylene of  $1 \times 10^4 \text{ g/mol}$  at  $176^\circ \rightarrow D$  is  $1 \times 10^{-8} \text{ cm}^2/\text{sec}$
- Polyethylene of  $1 \times 10^6 \text{ g/mol}$  at  $175^\circ \rightarrow D$  is  $1 \times 10^{-12} \text{ c}$

- The reptation time  $T_r$

$$T_r \propto M^3$$

# Mechanical properties

- Doi and Edwards developed the relationship of the dynamics of reptating chains to mechanical properties

$G_N^0 \propto M^0$  : rubbery plateau shear modulus

$J_N^0 \propto M^0$  : steady - state reversible compliance

$\eta_N^0 \propto M^3$  : steady - state viscosity

*Experimentally, the viscosity is found to depend on the molecular weight to the 3.4 power (Chapter 10), higher than predicted*

*the modulus and the compliance are independent of the molecular weight (above about  $8 M_c$ ) is that the number of entanglements are large for each chain and occur at roughly constant intervals.*



# Polymer Dynamics

- Unentangled polymer dynamics
  - Diffusion of a small colloidal particle
  - Diffusion of an unentangled polymer chain
- Entangled polymer dynamics
  - Tube models
  - Equilibrium state: in a polymer melt or in a concentrated solution
  - Relaxation processes in linear chains

# Fickian and Non-Fickian Diffusion

## ▪ Fickian diffusion

- No-entanglement
- The three-dimensional self diffusion coefficient,  $D$ , of a polymer chain in a melt

$$X = (6Dt)^{1/2}$$

$$\left\langle [\vec{r}(t) - \vec{r}(0)]^2 \right\rangle = 6Dt$$

- $X$ : displacement of the colloidal particle during  $t$
- $t$ : time
- 6: from 3D  $\rightarrow$  2 in 1D

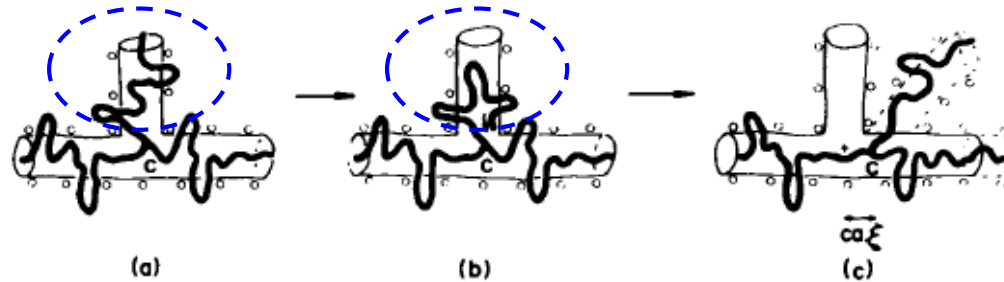
## Non-Fickian diffusion

Entanglement

Reptation model of de Gennes

## Nonlinear chains

- How do branched, star, and cyclic polymers diffuse?
- retracting a branch → retraces its path along the confining tube to the position of the center mer → extend outward again → adopting a new conformation at random



The basic diffusion steps for a branched polymer. Note motion of mer C, which requires a fully retracted branch before it can take a step into a new topological environment

- the probability  $P_1$  of an arm of  $n$ -mers folding back on itself

$$P_1 = \exp\left(\frac{-\alpha n}{n_c}\right)$$

- ✓  $n_c$ : the critical number of mers between physical entanglements
- ✓  $\alpha$ : constant

$$n_c \uparrow \rightarrow P_1 \downarrow$$

The result is that diffusion in branched-chain polymers is much slower than in linear chains.

# Experimental methods of determining diffusion coefficient *D*

- a. by measuring the broadening of concentration gradients as a function of time
- b. by measuring the translation of molecules directly using local probes such as NMR

*D* to 150,000 g/mol and 135°C

Polystyrene	$1.2 \times 10^{-15} \text{ cm}^2/\text{s}$	<i>SANS</i>
Poly(methyl methacrylate)	$6.9 \times 10^{-17} \text{ cm}^2/\text{s}$	<i>H2, D2</i>
Poly( <i>n</i> -butyl methacrylate)	$8.0 \times 10^{-11} \text{ cm}^2/\text{s}$	<i>Layered structure</i>

Table 5.9 Diffusion coefficients of hydrogenated polybutadienes<sup>†</sup>

Method	Shape	<i>T</i> , °C	<i>M<sub>w</sub></i> , g/mol	<i>D</i> , cm <sup>2</sup> /s	Reference
SANS	Linear	125	$7.3 \times 10^4$	$4.8 \times 10^{-11}$	(a)
Forward recoil spectrometry	3-arm	125	$7.5 \times 10^4$	$2.4 \times 10^{-14}$	(b)
SANS	3-arm	165	$7.5 \times 10^4$	$1.4 \times 10^{-13}$	(c)

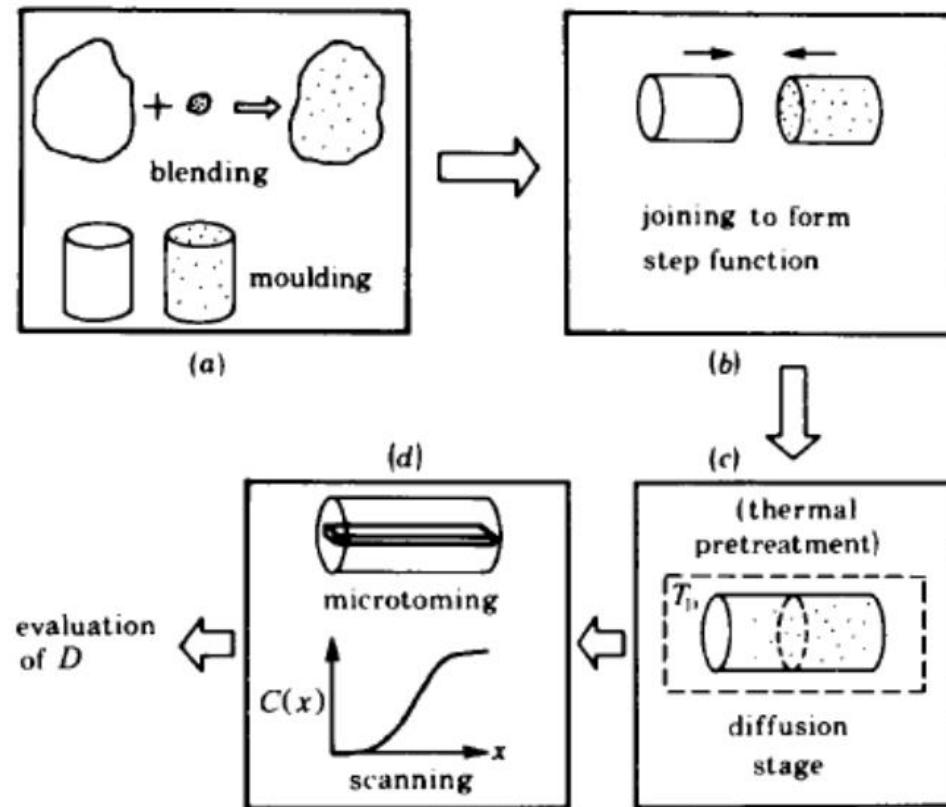
References: (a) C. R. Bartels, B. Crist, and W. W. Graessley, *Macromolecules*, **17**, 2702 (1984).  
(b) B. Crist, P. F. Green, R. A. L. Jones, and E. J. Kramer, *Macromolecules*, **22**, 2857 (1989).  
(c) C. R. Bartels, B. Crist Jr., L. J. Fetters, and W. W. Graessley, *Macromolecules*, **19**, 785 (1986).

<sup>†</sup>Hydrogenated polybutadiene makes polyethylene. In this case, a narrow polydispersity polymer not available otherwise.

## The measurement of the interdiffusion

### ■ Direct nonradiative energy transfer, DET

- fluorescence technique
- the chains contain a “donor” group, while in the other, an “acceptor” group is attached
- When the two groups are close to one another, the excitation energy of the donor molecules may be transferred by the resonance dipole–dipole interaction mechanism → DET



**Figure 5.11** Schematic flowchart showing the stages involved in an interdiffusion experiment (68). The slices are scanned in an IR microdensitometer to obtain the broadened concentration profile, from which  $D$  is evaluated.