

# Rheology of polymer systems/ Reologia dos sistemas poliméricos

## 1. Viscosity/Viscosidade

# Polymers

Molecular materials in nature



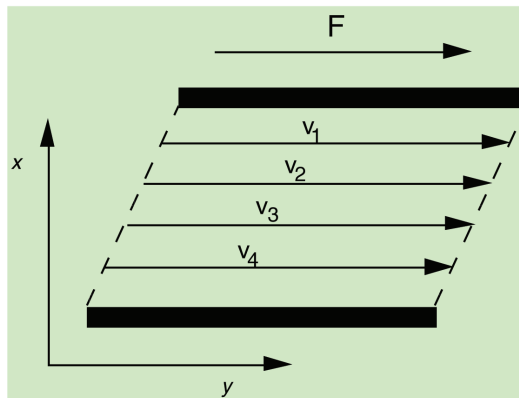
**COMPLEX** behaviour

# ***Viscosity of concentrated solutions and polymer melts***

1. Definition of viscosity ( $\eta$ ).
2. Factors affecting the viscosity of polymer solutions and melts:
  - i. Concentration
  - ii. Molecular weight
  - iii. Pressure
  - iv. Temperature. WLF (Williams, Landel, Ferry) equation .
3. Variation of the viscosity with time and with strain/ deformation rate. Non-newtonian behaviour

# Viscosity

A force per unit area ( $F/A$ ) is required to maintain a constant velocity gradient



$\tau$  Shear stress

$\dot{\gamma}$  rate of shear

$\eta$  shear viscosity

$$\frac{F}{A} = \eta \frac{dv_y}{dx} \quad \tau = \eta \dot{\gamma}$$

“Newton law”-viscosity is independent of stress and shear rate

Dynamic (absolute) viscosity ,  $\eta$  [poise, Pa.s or  $ML^{-1}T^{-1}$ ] and  
kinematic viscosity,  $\nu = \eta/\rho$  [ $L^2T^{-1}$ ]

# Low viscosity liquids

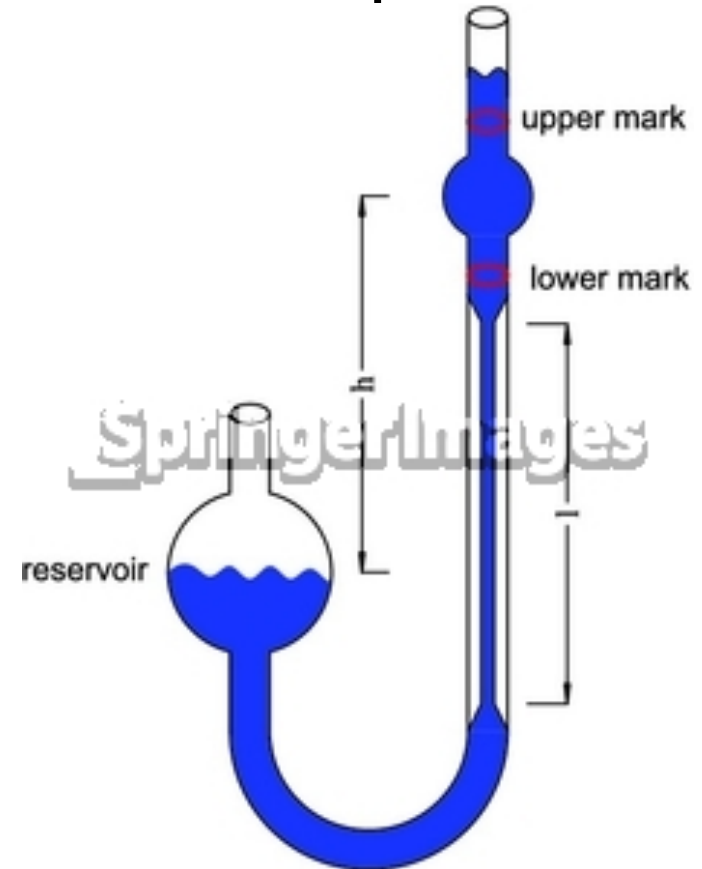
## Capillary viscometer/Viscosímetro de capilar

Kinematic viscosity/Viscosidade cinemática

$$\frac{\eta}{\rho} = At - \frac{B}{t^2}$$

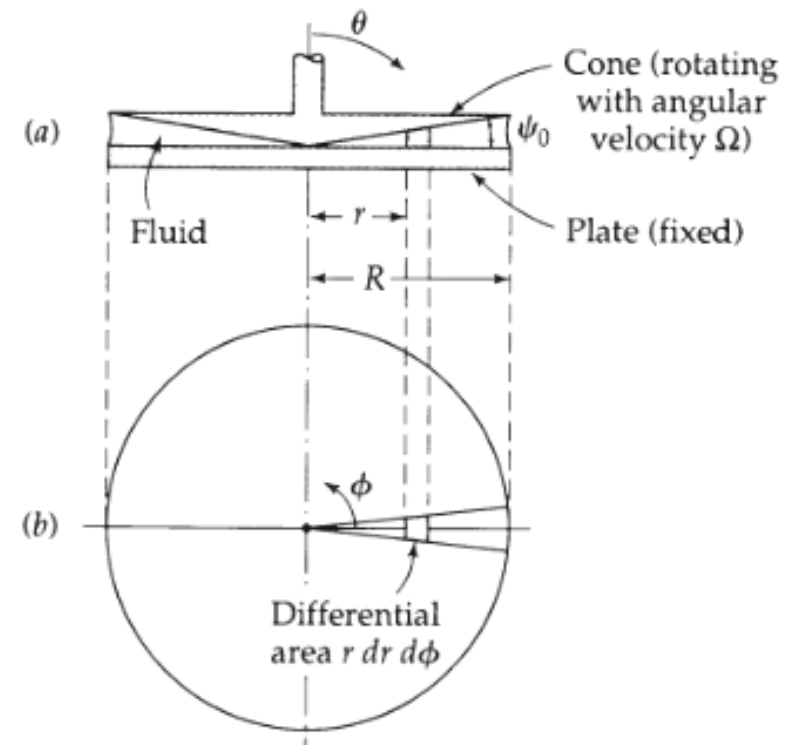
Correction factor

(losses of kinetic energy at the capillary)

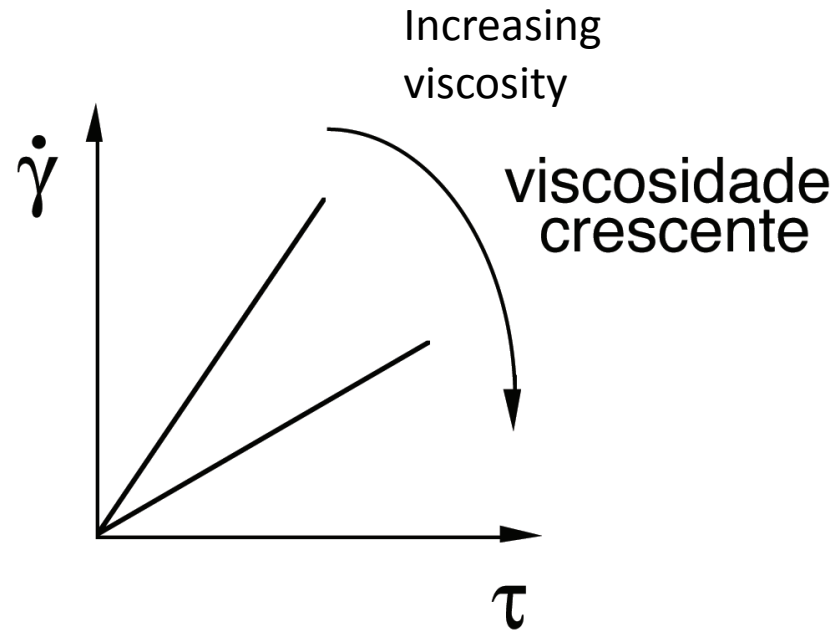


# For flow when viscosity is not constant

Use of externally pressurized capillary and rotational viscometers/Viscosímetros de capilar pressurizados ou rotacionais



## Newtonian flow

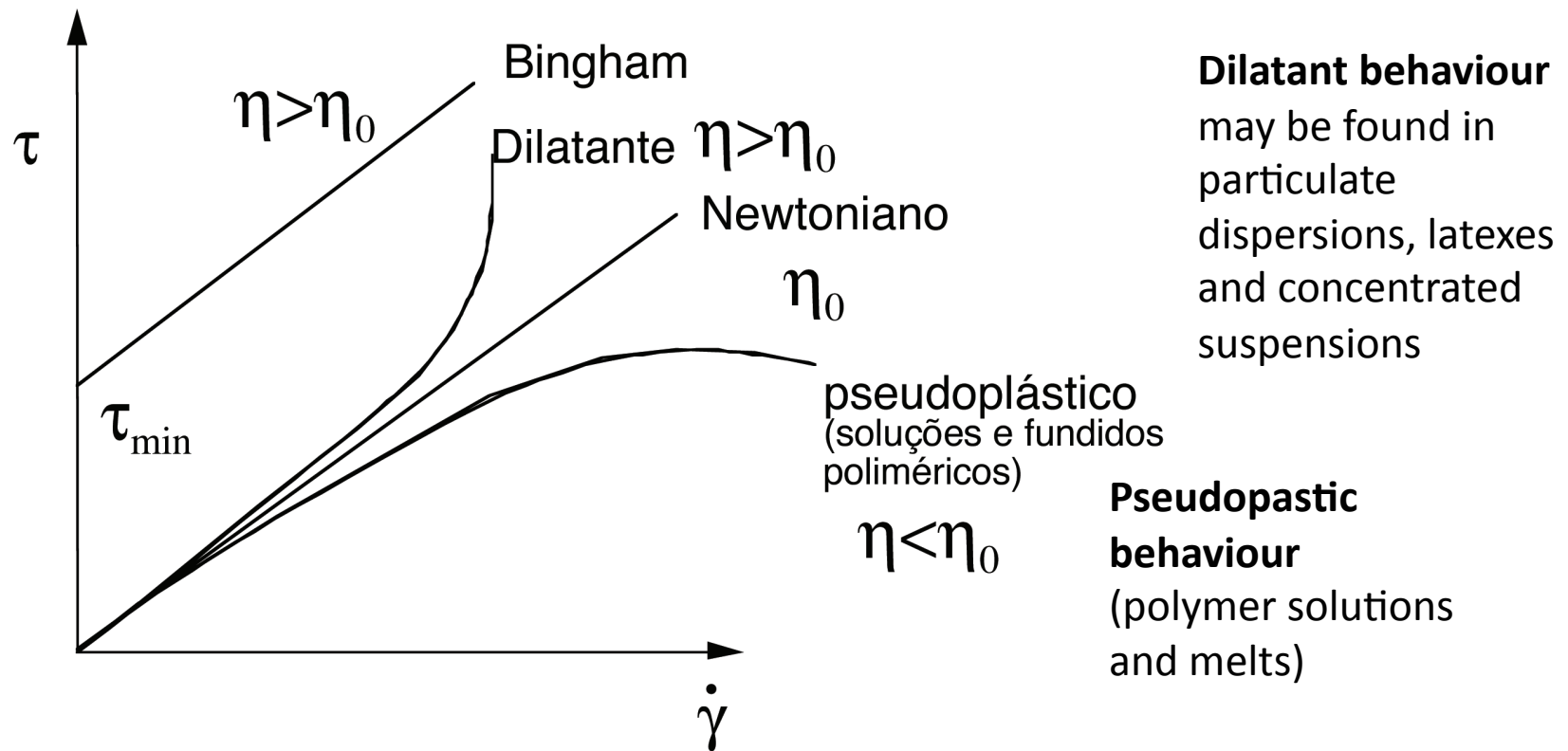


## Non-newtonian flow

$$\eta = f(\dot{\gamma}, t)$$

# Non-newtonian flow

## *i) Effect of shear rate/ velocidade de deformação*



Upon increase of the molecular weight (expected for  $M > 1-2 \times 10^6$ ), the non-newtonian behaviour occurs at lower shear rate.



# Non-newtonian flow

## *i) Effect of shear rate/ velocidade de deformação*

- In simple liquids viscosity is constant but in polymers it may depend on shear rate

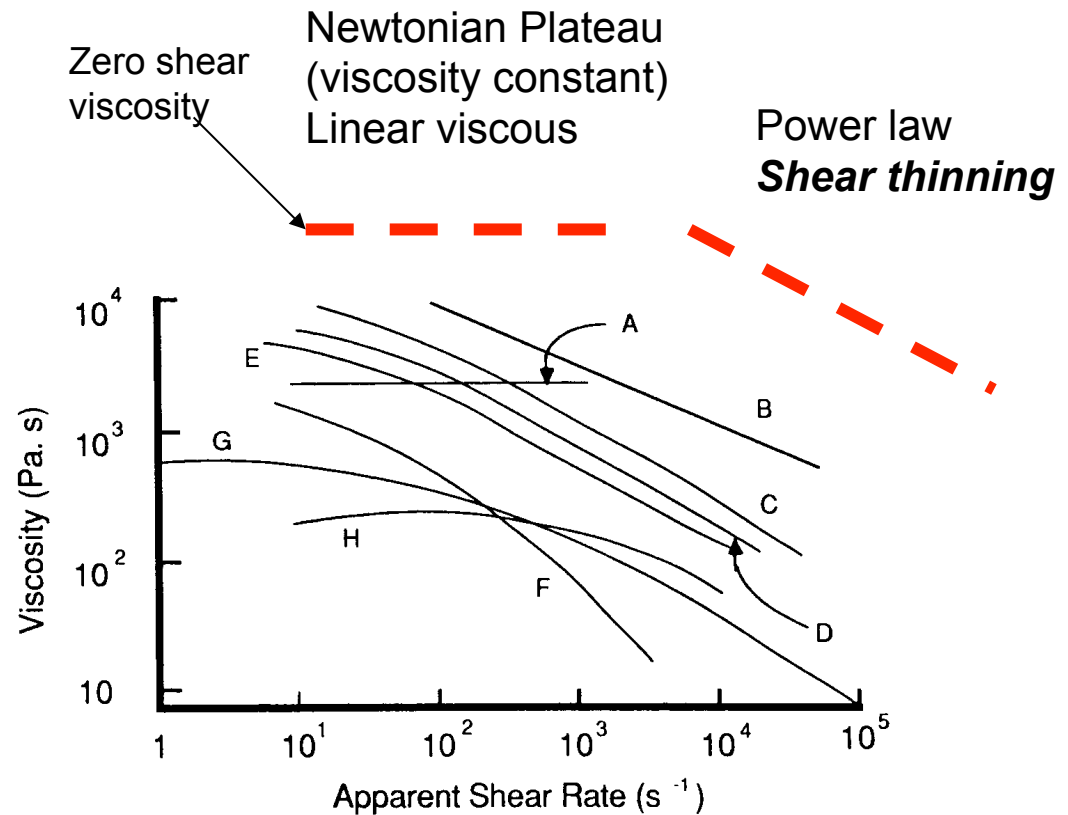
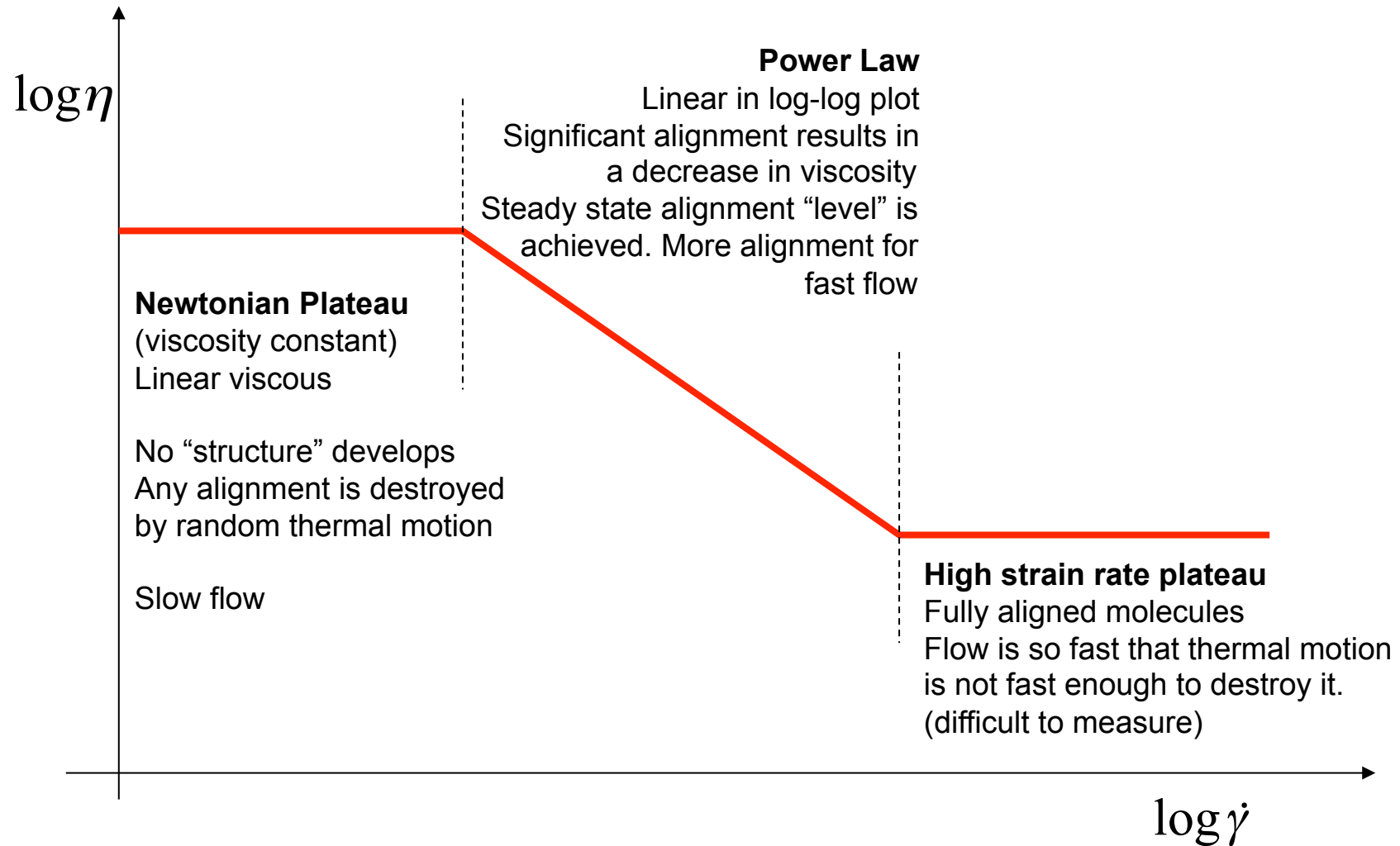


Figure 4.11. Shear Rate-Dependent Viscosities for Several Commercial Polymers at Typical Processing Temperatures (11). Curve A: Polycarbonate (PC) (288°C). B: General Purpose PS (230°C). C: PMMA (200°C). D: HDPE (232°C). E: LDPE (235°C). F: PP (230°C). G: PMMA (250°C). H: Nylon 6 (PA-6) (288°C).

## Different types of Viscosity

- Shear-thickening liquids-low viscosity when stirred slowly, but viscosity increases when mixed quickly
- Shear thinning liquids-high viscosity when mixed slowly, easier to mix quickly
- Bingham liquids-at low stress behaves like a solid, high stress behaves like a liquid
- Granular materials-like Bingham, but do not have a well-defined viscosity

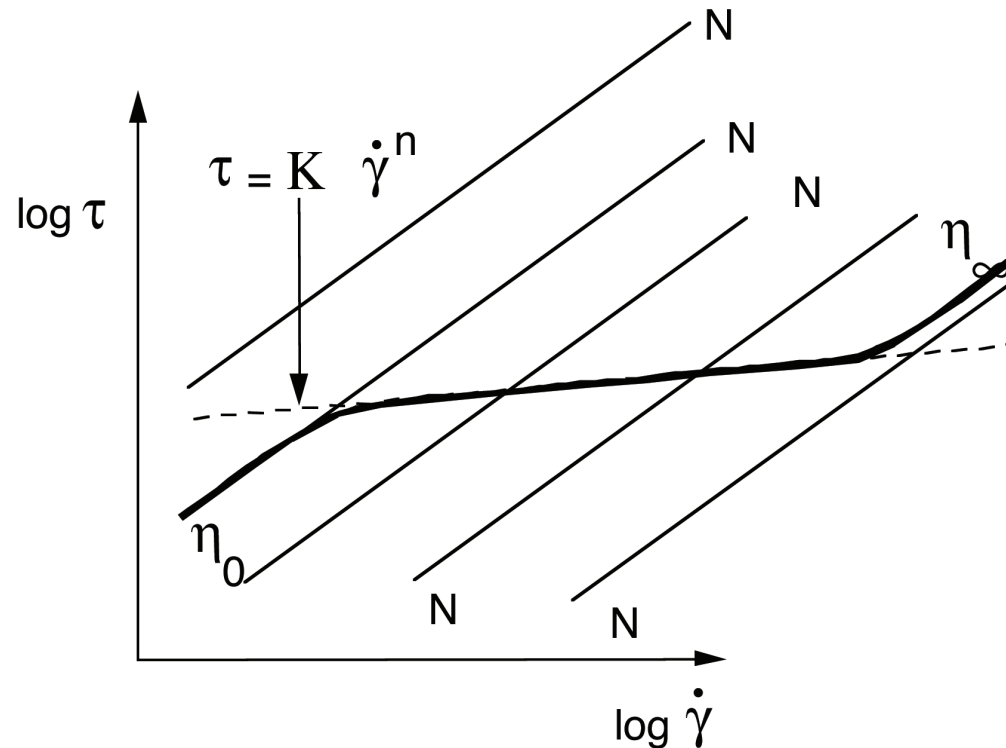
# The role of molecular orientation in viscosity vs. shear rate relation



# Non-newtonian flow

## Models

### i) Power-law



- *Valid for melts over few decades of shear rate, but fails when approaching the newtonian behaviour*
- *Also: at zero shear rate -> infinite viscosity  
at infinite shear rate -> zero viscosity*

# Non-newtonian flow

## *Models*

### *ii) Ellis Model*

$$\frac{\eta_0}{\eta} - 1 = k\tau^a$$

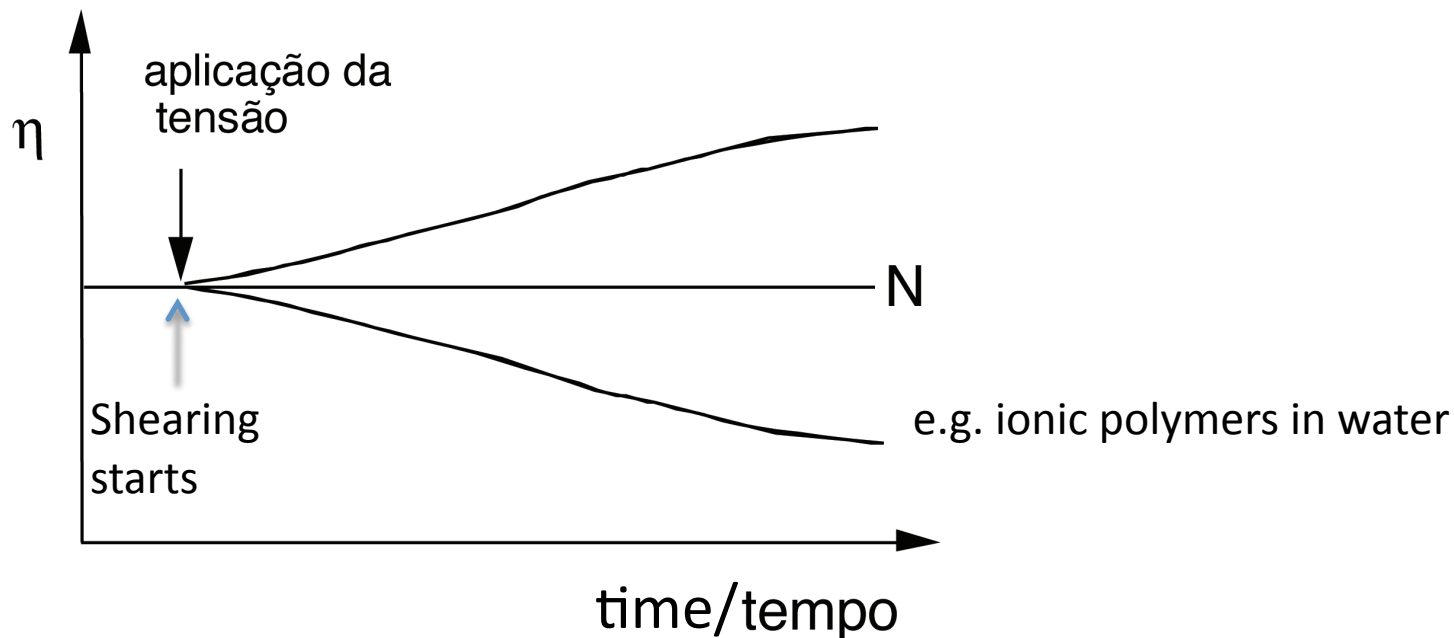
Se  $\dot{\gamma} \rightarrow 0; \eta \rightarrow \eta_0$   
Se  $\dot{\gamma} \rightarrow \infty; \eta \rightarrow 0$

- Combines newtonian behaviour at low shear stress ( $\tau$ ) and power law at high  $\tau$

# Non-newtonian flow

## *ii) Effect of time*

Upon shearing at a steady state, the viscosity may increase or decrease with time



Expected when viscosity is partially due to intermolecular structures that take some time to be formed or destroyed

# **Viscosity of polymers (solutions and melts)**

# Viscosimetric terms/Designações

Name	Symbol	Units
Solvent viscosity/Visc. do solvente	$\eta_s$	Poise= =g.cm <sup>-1</sup> .s <sup>-1</sup>
Solution viscosity/Visc. da solução	$\eta$	Poise
Relative viscosity/Viscosidade relativa	$\eta_{rel} = \eta/\eta_s$	Adimens.
Specific viscosity/Visc. específica	$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s}$ $= \eta_{rel} - 1$	Adimens.
Reduced viscosity/Visc. reduzida	$\eta_{red} = \frac{\eta_{sp}}{C}$	dL/g
Inherent viscosity/Visc. inerente	$\eta_{inh} = \frac{\ln \eta_{rel}}{C}$	dL/g
Intrinsic viscosity/Visc. intrínseca	$[\eta] = \lim_{C \rightarrow 0} \frac{\eta_{sp}}{C}$	dL/g



# Factors affecting the viscosity of polymer solutions and melts:

## **1. “Intrinsic” factors**

- Intermolecular interactions
- Side groups
- Molecular weight

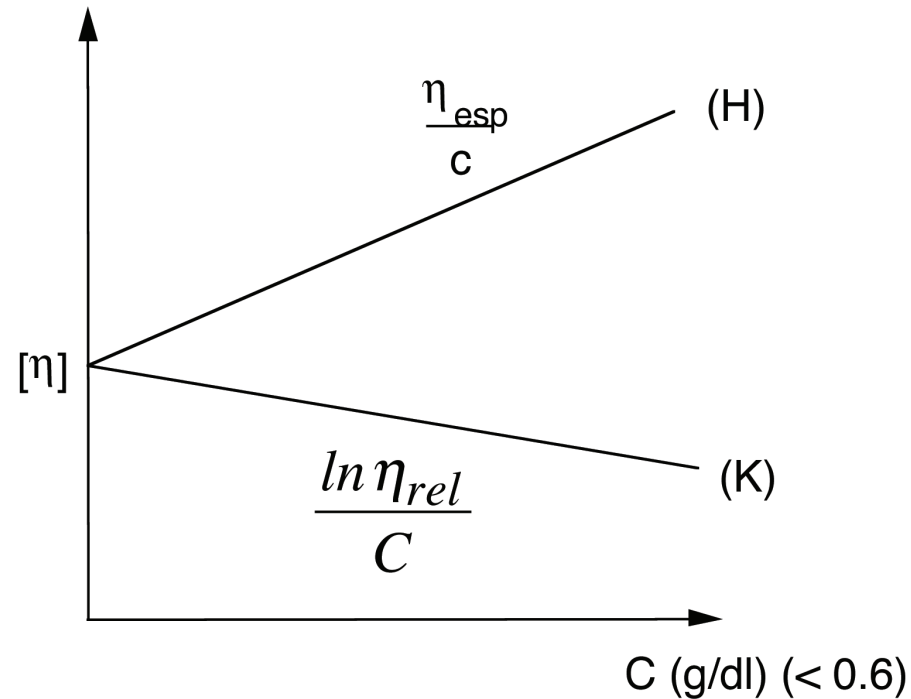
## **2. “Extrinsic” factors**

- Solution concentration
- *Pressure*
- *Temperature*
- Shear rate/*Velocidade de escoamento*
- Shearing time/*Tempo de escoamento*

## 2.1 Effect of concentration on $\eta$

- ***Dilute solutions*** – *molecules act independently from each others.*
- ***Concentrated solutions*** – *limitations to movement; existence of some “cooperation” during flow*

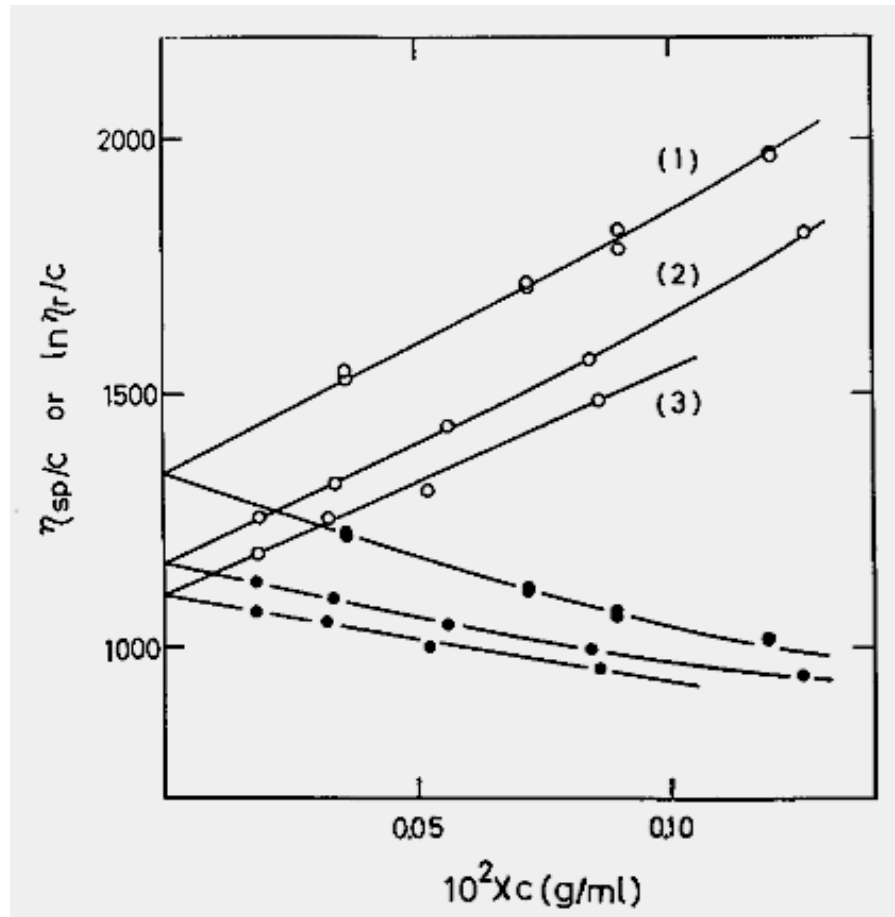
## i) Dilute solutions ( $c \leq 0.5$ g/dl)



**Huggins:** 
$$\eta_{red} = \frac{\eta_{esp}}{C} = [\eta] + k'[\eta]^2 c$$

**Kraemer:** 
$$\frac{\ln \eta_{rel}}{C} = [\eta] - k''[\eta]^2 c$$
 Válidas se  $\eta_{rel} < 2$

## i) Dilute solutions ( $c \leq 0.5$ g/dl)



Relative viscosity :

$$\eta_r = \frac{\eta_{\text{solution}}}{\eta_{\text{solvent}}} = 1 + [\eta]c + k'[\eta]^2c^2 + \dots$$

Specific viscosity :

$$\eta_{\text{sp}} = \frac{\eta_{\text{solution}} - \eta_{\text{solvent}}}{\eta_{\text{solvent}}} = \eta_r - 1$$

Intrinsic viscosity :

$$[\eta] = \left( \frac{\eta_{\text{sp}}}{c} \right)_{c \rightarrow 0}$$

An example of viscosity versus concentration plots for polystyrene ( $M_w = 7.14 \times 10^6$  g/mol) in benzene at 30 °C. White circles: plot of  $\eta_{\text{sp}} / c$  vs.  $c$ ; black circles: plot of  $(\ln \eta_r) / c$  vs.  $c$ .

T. Kotaka et al., J. Chem. Phys. **45**, 2770-2773 (1966).

## ii) Concentrated solutions and polymer melts

Increase of concentration leads to the formation of *entanglements/emaranhados*

The molecules must disentangle first – effect of shear rate/flow on the viscosity – **non-newtonian behaviour**:

- ***Low shear rate /baixas velocidades de escoamento(fluxo)*** – thermal movement that tends to bring the molecules back to the entangled configuration (equilibrium configuration) prevails and the viscosity approaches that of the solution at rest.
- ***High shear rate/elevadas velocidades de escoamento*** – the orientation of the molecules prevails over the increase of their interaction with the solvent, so the viscosity decreases

## ii) Concentrated solutions and melts

- ***To determine the intrinsic viscosity:***

i)  $C \longrightarrow 0$

ii) def. rate  $\longrightarrow 0$

- ***When approaching the melt situation ( $c > 50$  g/dl):***

$$\eta_{\text{solution}} = \eta_{\text{pol.}} \cdot v_2$$

$v_2$  = volume fraction of polymer

## 2.2 Effect of molecular weight on $\eta$

***Dilute solutions - (Mark-Houwink-Sakurada)***

$$[\eta] = K M^a$$

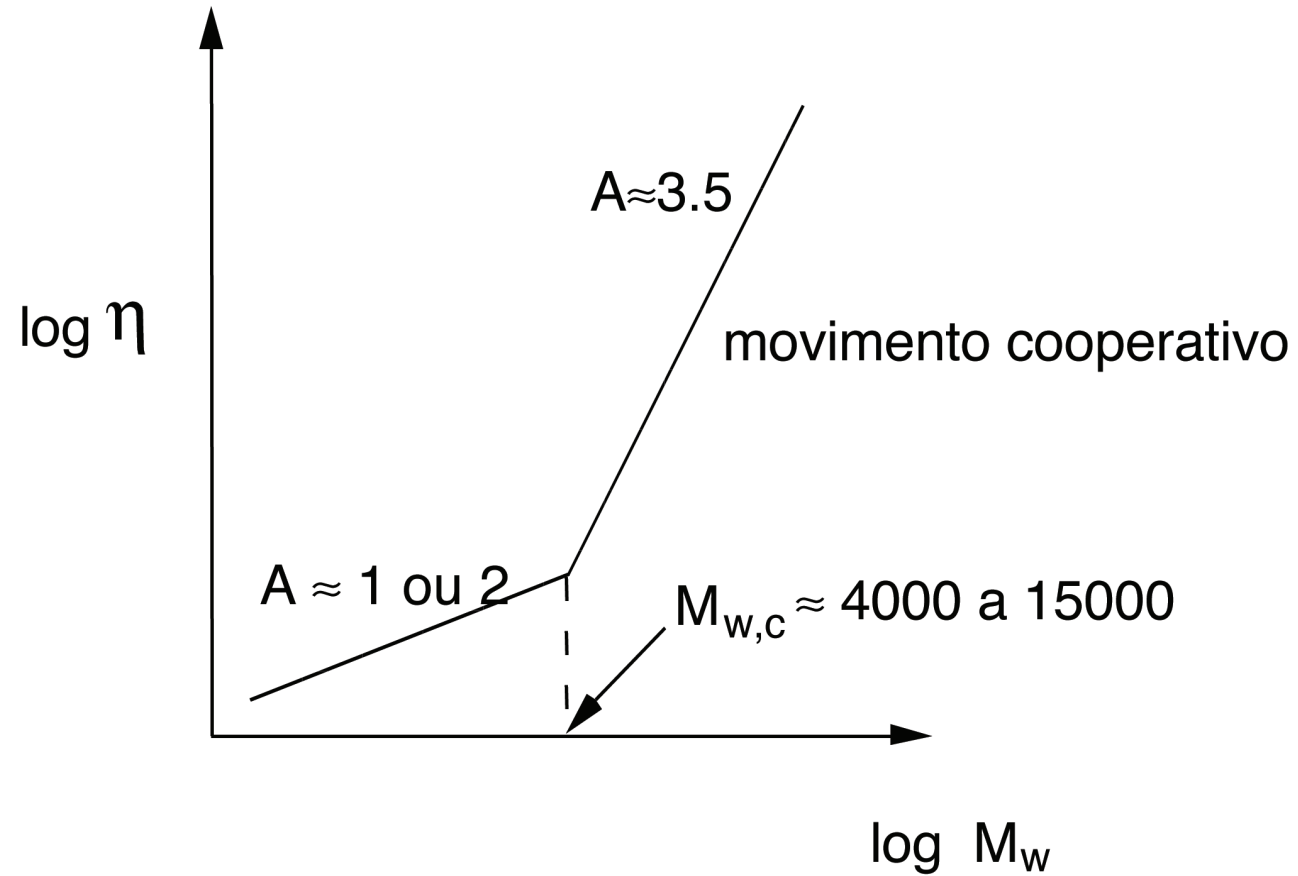
$$a=0.5-1; K=0.05-0.5 \text{ mL/g}$$

***Polymer melts:***

- *Presence of side groups or branched chains makes the molecules flow more difficult/difículta o deslizamento das cadeias;*
- The molecular weight has a significant effect on the viscosity because the molecules have to disentangle in order to flow.

## 2.2 Effect of molecular weight on $\eta$

**Melts:**



$$\log \eta = A \log M_w + B$$

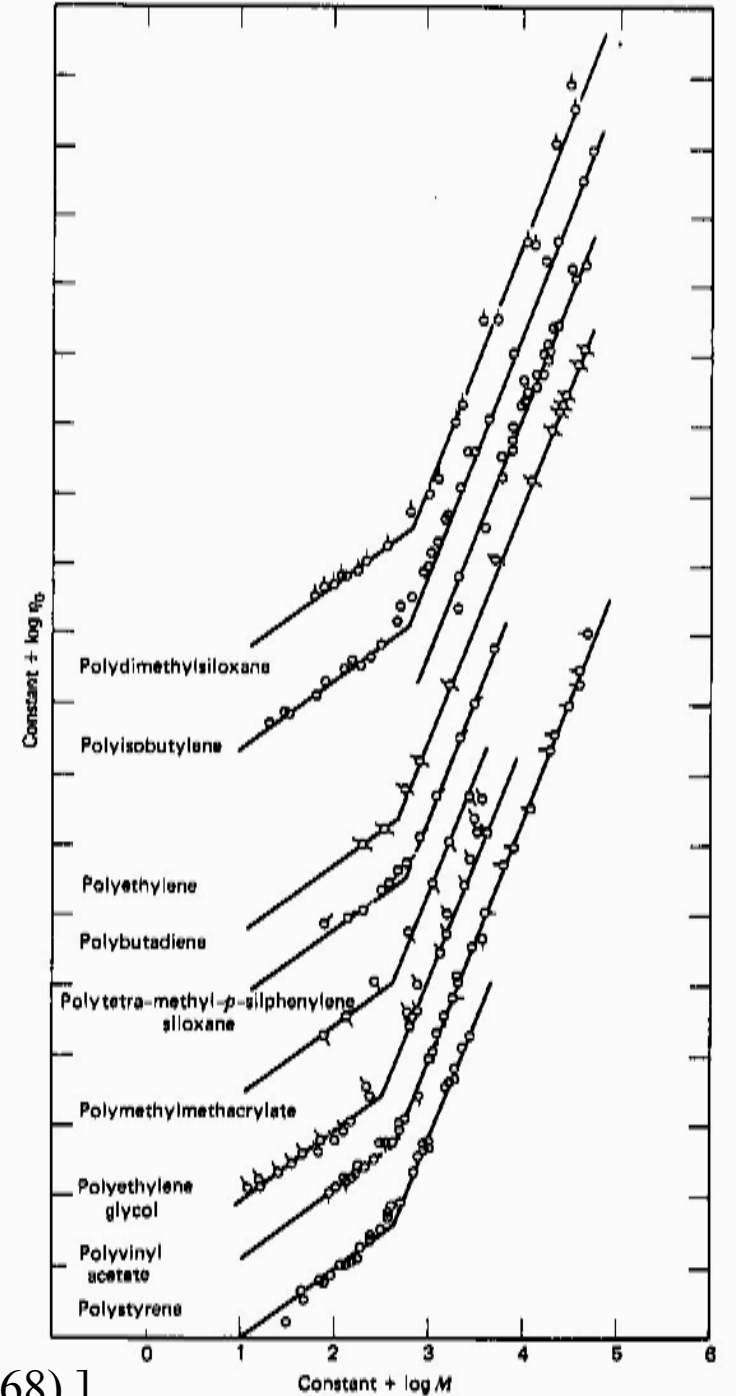


# 2.2 Effect of molecular weight

## *Linear polymer melts:*

:

Molecular weight, $M_w$	Zero-shear viscosity, $\eta_0$	Relaxation time, $\tau$
$< M_c$	$\sim M_w$	$\sim M_w^2$
$> M_c$	$\sim M_w^{3.4}$	$\sim M_w^3$



[G. C. Berry and T. G. Fox, Adv. Polym. Sci. 5, 261-357 (1968).]

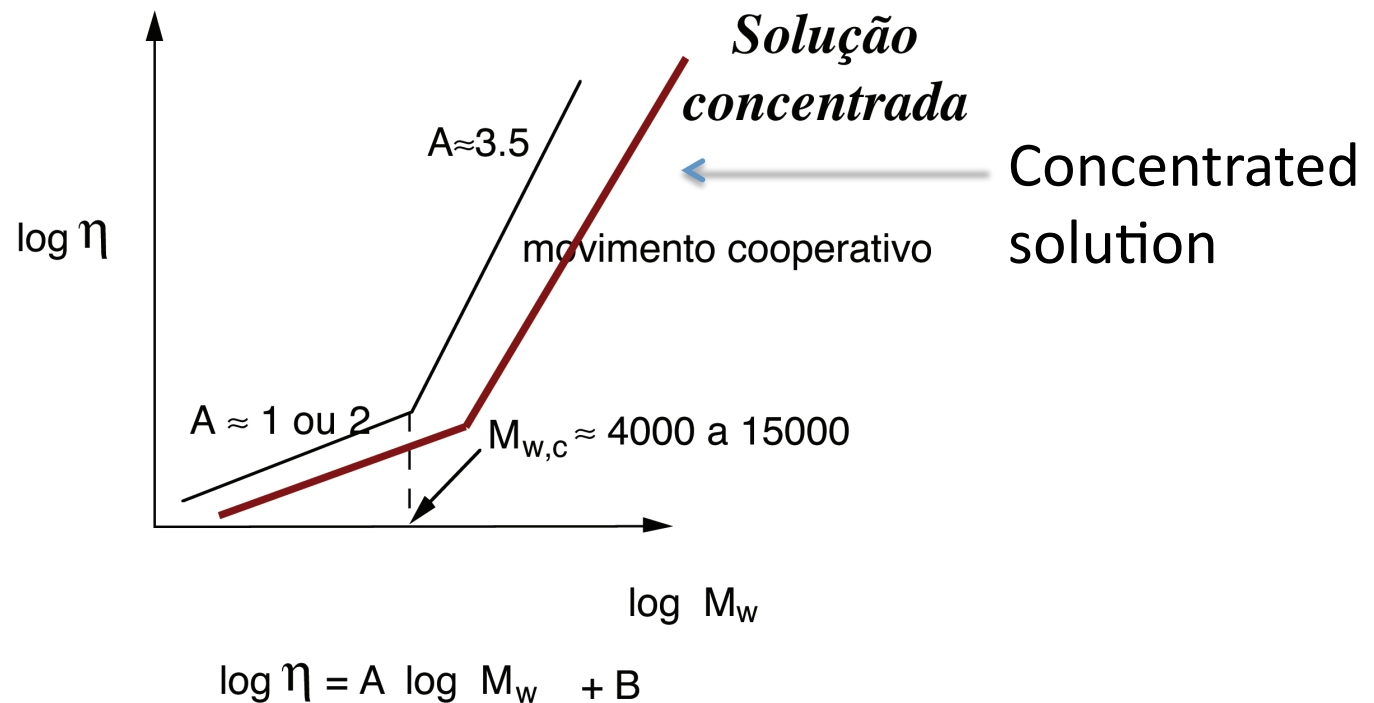
## 2.2 Effect of molecular weight on $\eta$

### ***Concentrated solutions:***

Mechanism is similar to that of the melts

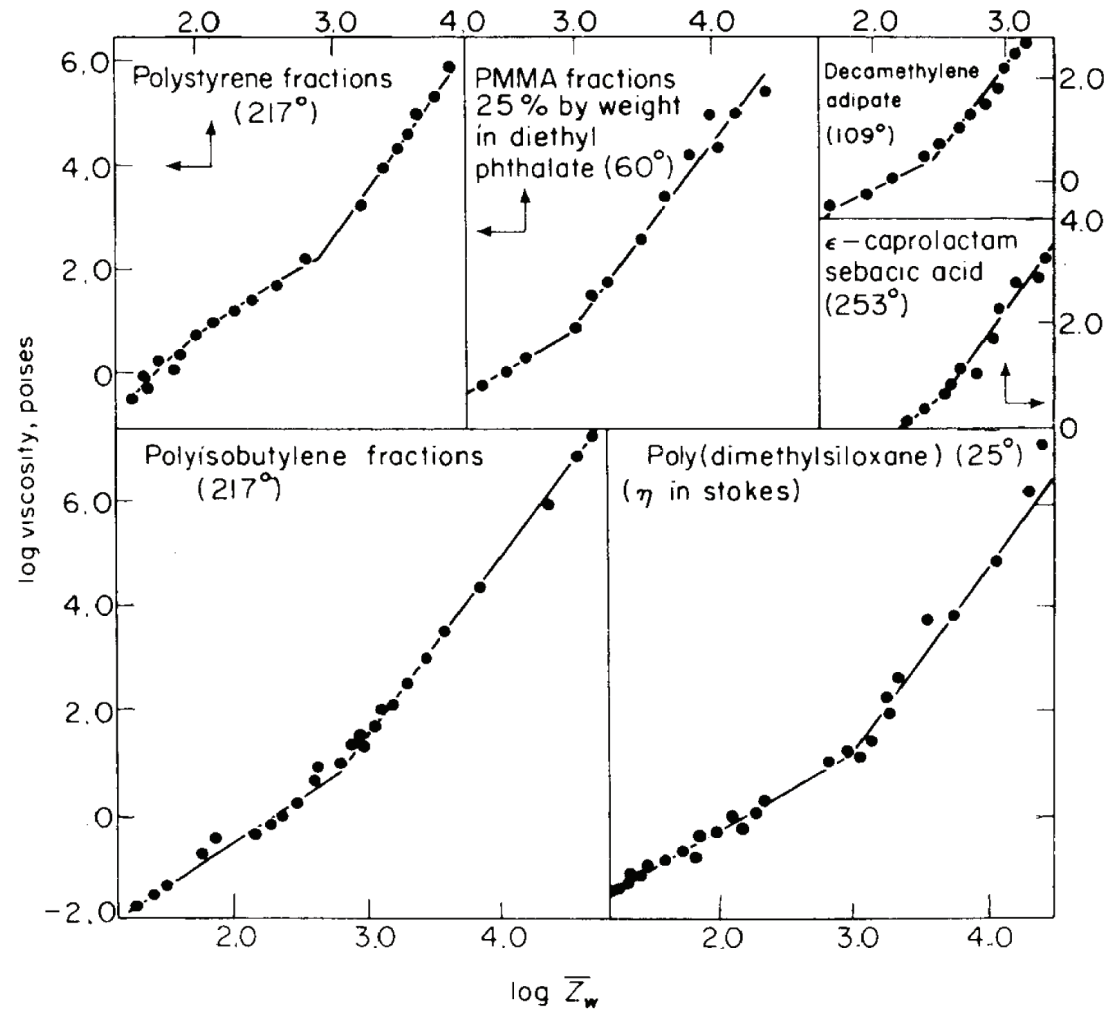
$$M_{w,crit,sol} = \frac{M_{w,crit,fund}}{v_2}$$

$v_2$  - fracção, em volume, de polímero na solução



## 2.2 Effect of molecular weight on $\eta$

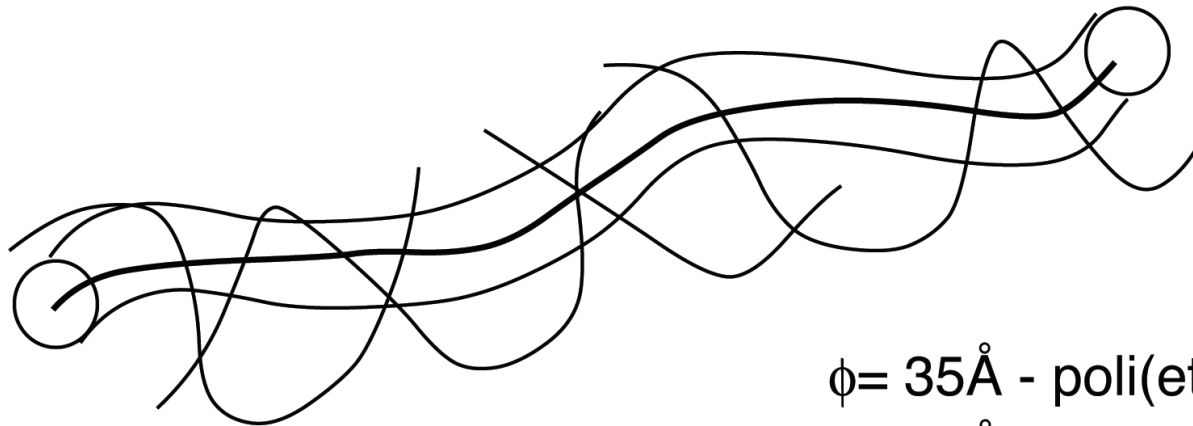
**Concentrated solutions**



**Figure 4.6** The dependence of melt viscosity on weight-average number of chain atoms  $Z_w$  for several polymers. (Reprinted from F. Rodriguez, *Principles of Polymer Systems*, 2nd ed. Copyright © 1982, McGraw-Hill, New York.)

## 2.2 Effect of molecular weight on $\eta$

- ***Entanglement theory or reptation theory/  
teoria dos emaranhados ou teoria da  
reptação***



$\phi = 35\text{\AA}$  - poli(etileno)

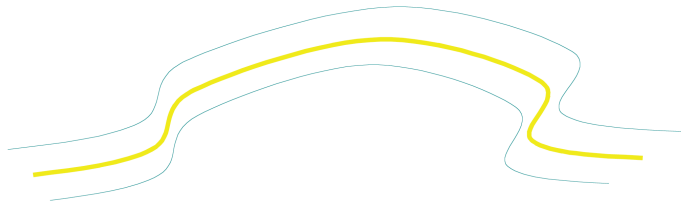
$\phi = 80\text{\AA}$  - poli(estireno)

movimento apenas difusivo

# Reptation theory/teoria da reptação

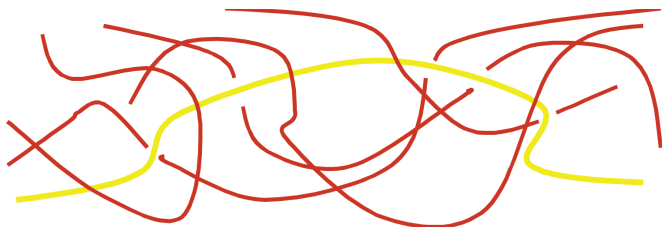
Polymer chain is pictured as being confined into a tube by the entanglements of its neighbours. The chains escapes its tube by a reptile type movement\_diffusion (brownian motion)

- Chain surrounded by “frozen” chains

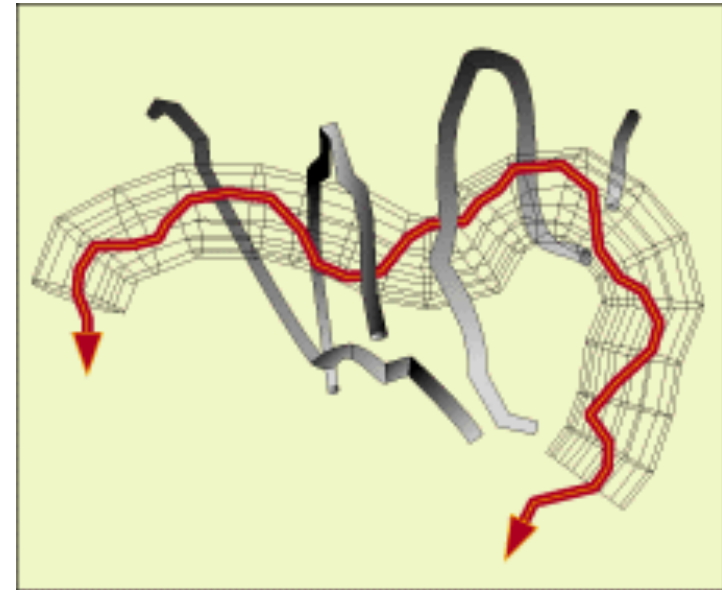


Movement by diffusion only

- Chain surrounded by “unfrozen” chains



diffusion is faster than disentanglement relaxation/relaxação dos constrangimentos



## 2.3 Effect of temperature on $\eta$

*Viscous flow- jumps of molecules or molecule segments to holes (free space) (specific **free volume,  $V_f$** ).*

**Doolittle- melts:**  $\log \eta = A + B \frac{V_0}{V_f}$

*with  $V_f = V - V_0$*

*Upon increase of pressure ,  $V_f$  decreases, increasing the viscosity of melts*

## 2.4 Effect of temperature on $\eta$

The increase of temperature facilitates the creation of free volume where a molecule or a molecule segment can jump to (jumps from a position in a lattice to a vacant hole)

i) At high temperatures:

$$\eta = \eta_{\infty} e^{\frac{E_{\eta}}{RT}}$$

ii) For melts of glassy polymers between  $T_g$  and  $T_g+100$ ,

**WLF (Williams, Landel and Ferry) empirical relation\_melts:**

$$\log \frac{\eta(T)}{\eta(T_0)} = \frac{a_1(T - T_0)}{a_2 + (T - T_0)}$$

## 2.4 Effect of temperature on $\eta$

WLF temperature shift parameters

	PS	PDMS	PIB	PMMA	1,4PBd	1,4-PI
$T_g$ (K)	373	150	205	381	205	200
$T_0$ (K)	373	303	298	381	263	248
$T_\infty$ (K)	323	81	101	301	149	146
$c_1^0$ (K)	12.7	1.90	8.61	34.0	5.97	8.86
$c_2^0$ (K)	50	222	200.4	80	123.2	101.6

WLF (Williams - Landel - Ferry) equation :

$$\log a_T = \frac{-c_1^0(T - T_0)}{c_2^0 + T - T_0} = \frac{-c_1^0(T - T_0)}{T - T_\infty}$$

J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed., Wiley: New York (1980).



## 2.4 Effect of temperature on $\eta$

$$\text{WLF: } \log \frac{\eta(T)}{\eta(T_0)} = \frac{a_1(T - T_0)}{a_2 + (T - T_0)}$$

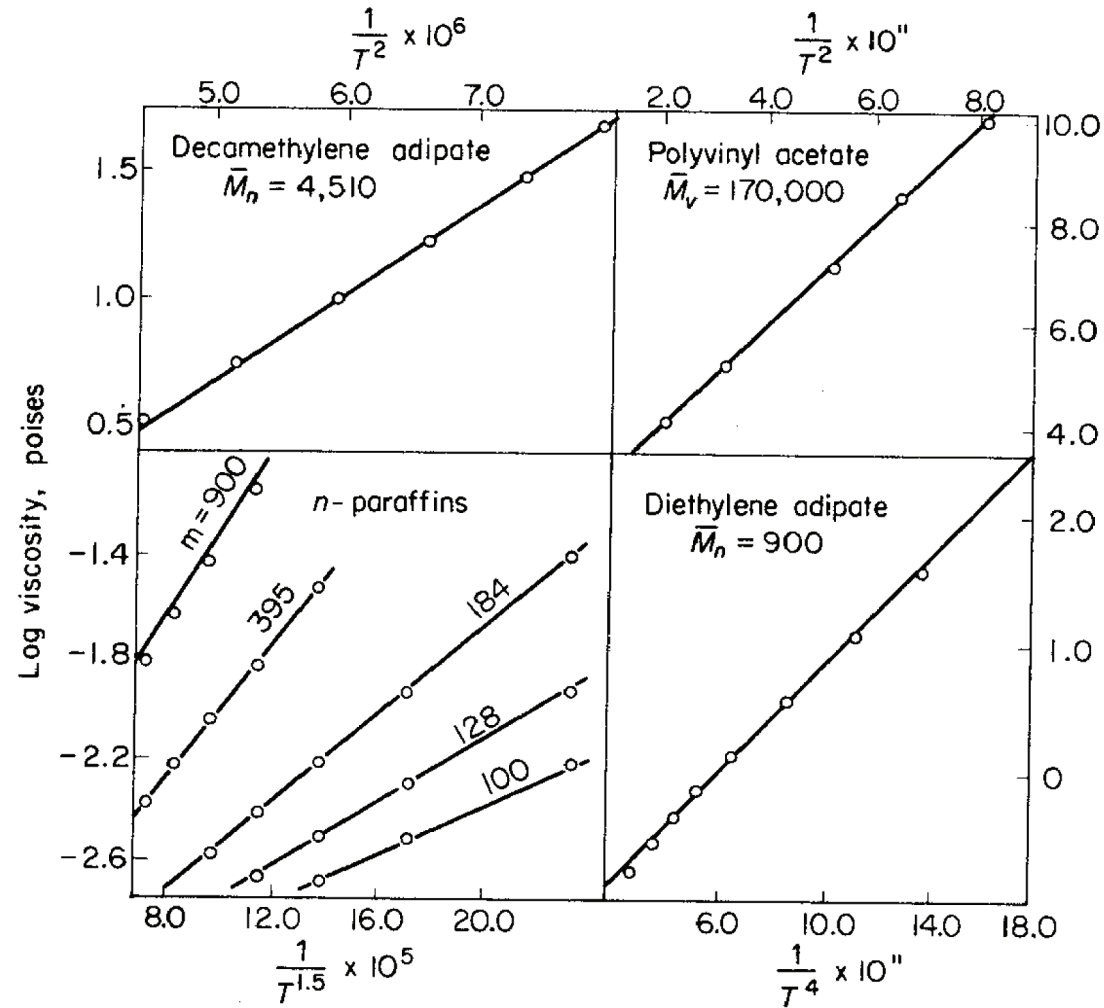
$$\text{If } T_0 = T_g, a_1 = -17.44; a_2 = 51.6$$

When  $T - T_g > 100$  °C, the behaviour is better described by the more general equation

$$\log \frac{\eta(T)}{\eta(T_R)} = B' \left( \frac{1}{T^a} - \frac{1}{T_R^a} \right) \exp\left(-\frac{\beta}{M}\right)$$

$B'$  and  $\beta$  are fitted constants,  $M$ -molecular weight

## 2.4 Effect of temperature on $\eta$



**FIGURE 7-8**  
Viscosity-temperature curves according to Eq. (7-30) [20].

# References

- “Principles of Polymer Systems”, 2<sup>nd</sup>ed., F. Rodriguez, McGraw-Hill-Int. Student Ed., 1983: § 7.1 - 7.6
- “Introduction to Macromolecular Science”, P. Munk, John Wiley & Sons, 1989: § 4.1.4
- “Giant Molecules-Here, There and Everywhere ...”, A. Yu. Grosberg, A.R. Khokhlov, Academic Press, 1997.