

Marrucci talkBasic CCR (1996)

Steady shear:

$$S_{xy}(\dot{\gamma}) = \int_0^{\infty} \frac{dt}{\tau} e^{-t/\tau} Q_{xy}(\dot{\gamma}t) \quad \underline{Q} = \text{D-E tensor}$$

$$\frac{1}{\tau} = \frac{1}{\tau_d} + \beta \dot{\gamma} S_{xy} \quad \underline{\underline{\tau}} = \underline{\underline{\tau}} \quad \underline{\underline{S}} = \langle \underline{\underline{u}} \underline{\underline{u}} \rangle - \frac{1}{3} \underline{\underline{1}}$$

$$\text{if } \beta = 0 \quad (\text{no CCR}) \quad S_{xy} \rightarrow 0 \quad \text{as } \dot{\gamma} \rightarrow \infty$$

$$\text{for any } \beta > 0 \quad S_{xy} = S_{xy}^{\infty} > 0 \quad \text{as } \dot{\gamma} \rightarrow \infty$$

$$\dot{\gamma} \rightarrow \infty \quad T_{xy} \rightarrow \alpha G_{\text{plateau}} \quad \alpha = \text{numerical f.} < 1$$

$$\eta \rightarrow \frac{\alpha G_{\text{plateau}}}{\dot{\gamma}} \quad (\text{independent of } M)$$

$$\eta = G \tau = G / \dot{\gamma} \quad \dot{\gamma} \text{ large}$$

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PLATEAU AND TERMINAL ZONES, UNCROSS-LINKED CH. 13

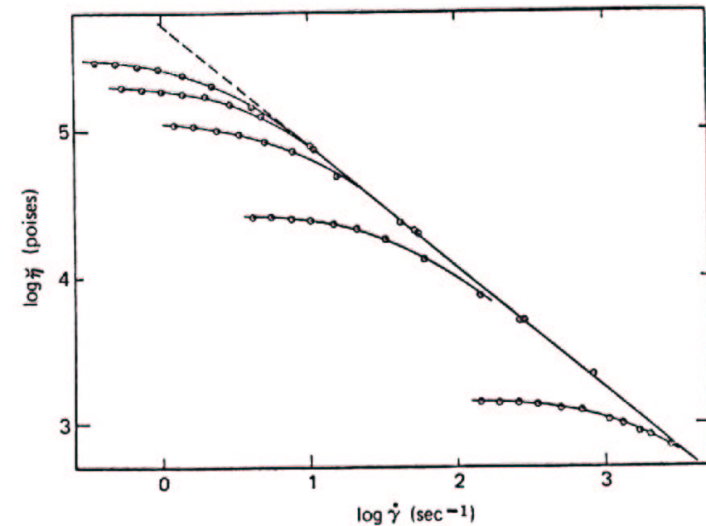


FIG. 13-9. Non-Newtonian viscosity  $\eta$  plotted against shear rate, for narrow-distribution polystyrenes.<sup>45</sup> Molecular weights from top to bottom,  $\times 10^{-4}$ : 24.2, 21.7, 17.9, 11.7, 4.85.

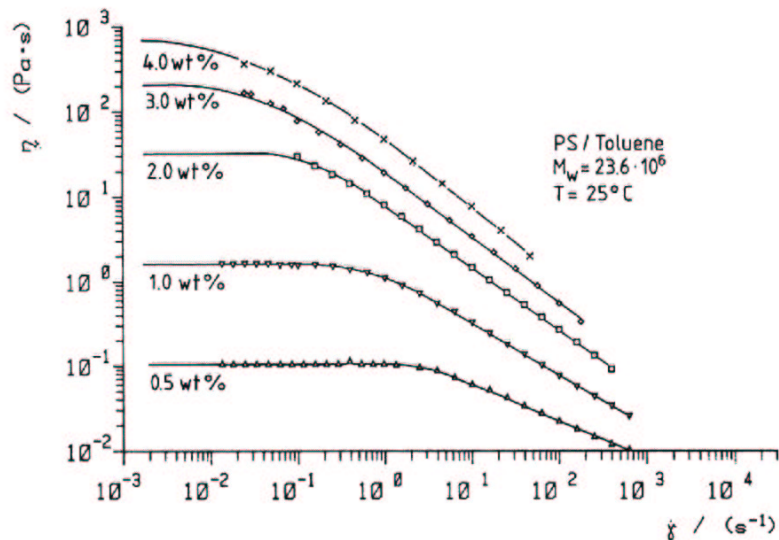


Fig. 1. Viscosity versus shear rate for polystyrene  $23.6 \cdot 10^6$  in toluene for various concentrations at  $25^\circ\text{C}$ .

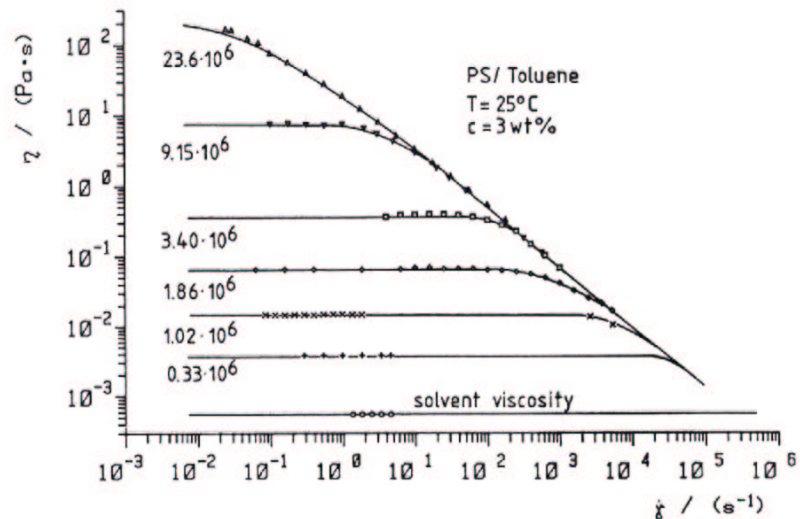
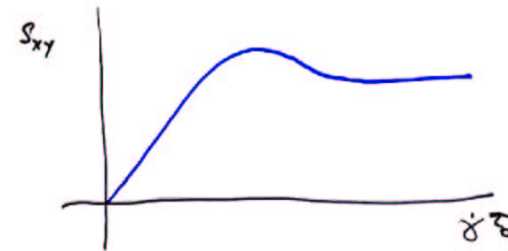


Fig. 2. Viscosity versus shear rate for polystyrene samples of various molar masses in toluene at  $25^\circ\text{C}$ .

What was certainly wrong with basic theory

$$S_{xy}(\dot{\gamma}) = \int_0^\infty \frac{dt}{\tau} e^{-t/\tau} Q_{xy}(\dot{\gamma}t)$$

$$\frac{1}{\tau} = \frac{1}{\tau_d} + \beta \dot{\gamma} S_{xy}$$



Maximum for all  $\beta < 3$

Mead, Larson, Doi (1998)

Include stretch  
fluctuation

$\beta = 1$  binary interaction model.

Additional physics (CCR2)

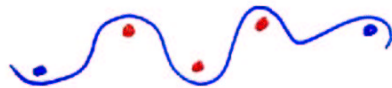
Paper: G.I. and G.M., JNNFM, 95, 363 (2000)

CCACCR2

We know that convection increases average distance between existing entanglements



CCR2 postulates that (without stretch) the extended primitive chain "wanders" laterally



and gets caught in new entanglements, partly renewing orientation

CCR2 adds to CCR

A quantitative theory

1st part: forget CCR temporarily  
only consider CCR2

Assumption: Elongated primitive chains only keep their affine orientation for a length "a".  
The rest goes random.

Then:

$$S_2(s, t) = \int_{-\infty}^t dt' \frac{\partial f(s, t, t')}{\partial t'} \underline{\underline{Q}}[\underline{\underline{E}}(t, t')]$$

where  $\underline{\underline{Q}}$  is D-E IAA tensor, and  $f$  is fractional number of entanglements existing at  $t'$  survived up to  $t$  in the  $s$ -location along chain  $(-\frac{L}{2} \leq s \leq \frac{L}{2})$

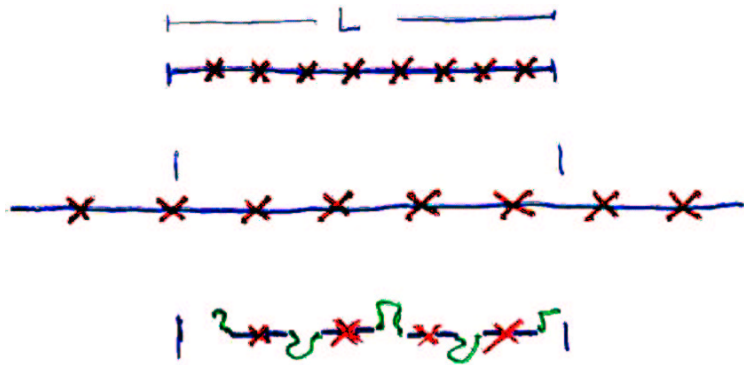
$f$  obeys:

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial s^2} - \frac{\partial}{\partial s}(vf)$$

$$\text{i.e. } t=t' \quad f=1$$

$$\text{B.e. } s=\pm L/2 \quad f=0$$

$$v(s, t) = \underline{\underline{V}}(t) : \int_0^1 \underline{\underline{S}}(s', t) ds'$$



So far no CCR (only CCR2)

2nd part : To include CCR we write :

$$\bar{S}(s, t) = \int_{-\infty}^t dt' \frac{\partial P(s, t, t')}{\partial t'} Q[\bar{E}(t, t')]$$

where :

$$P(s, t, t') = f(s, t, t') \bar{f}(t, t')$$

$$\bar{f}(t, t') = \frac{1}{L} \int_{-L/2}^{L/2} ds f(s, t, t')$$

Assumption of binary contacts ( $\beta=1$ ) and of independence

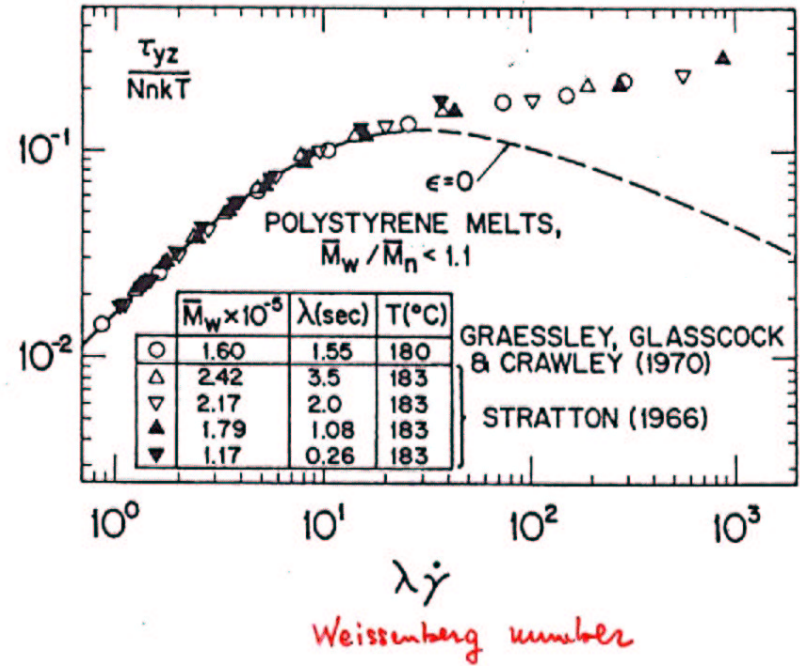
Notice :

$$\bar{S}(t) = \int_{-\infty}^t dt' \frac{\partial}{\partial t'} [\bar{f}^2(t, t')] Q[\bar{E}(t, t')]$$

similarly to double reptation.

Hence DCR model.





Saak, Bird, Curkiss      J. Chem. Phys. 1982

