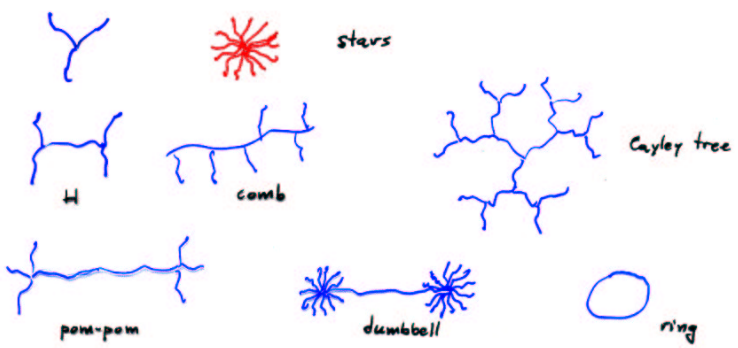
STAR DYNAMICS

DIMITRIS VLASSOPOULOS
FORTH, Heraklion, Crete, GREECE

Some experimental concerns:

1. Fast flows ? Leal-Oberhauser Shridar-Archer-Wagner
2. Is rheometry sufficient tool for probing relaxation mechanisms ? Watanabe
3. The role of macromolecular architecture ?

- Rheometry AND Scattering
- MODEL SYSTEMS



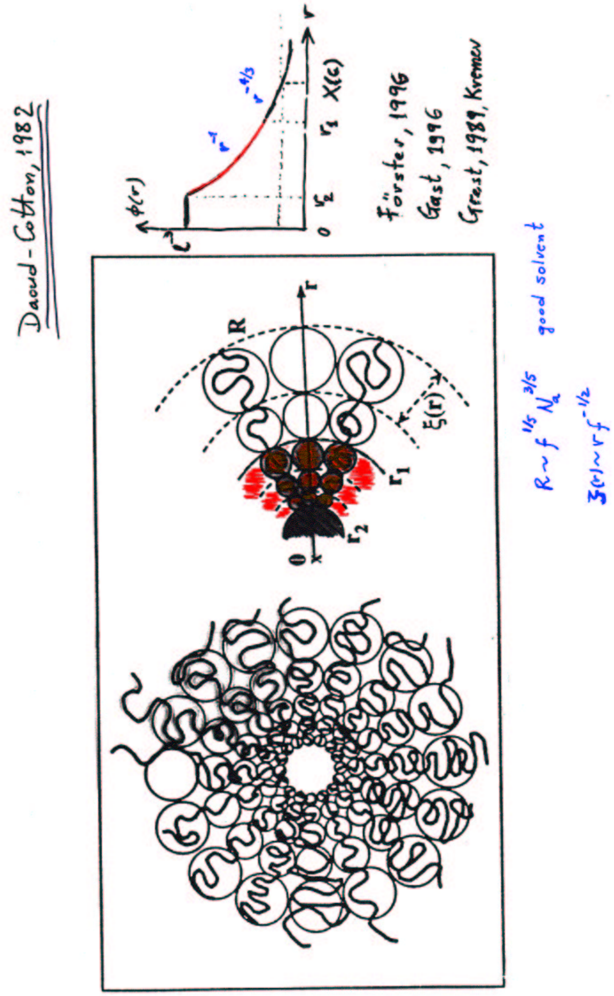
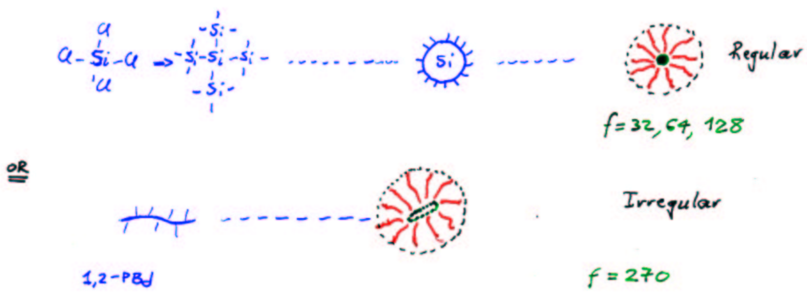


Table 1. Molecular characteristics of of the 1,4-polybutadiene stars

Code	f	$M_w \times 10^6$ (g mol)$^{-1}$	ε[a]	N_a[b]	T_g (°C)	R_g (nm)[c]
PB165	2	0.165	—	1528	−96	18
4S40	4	0.159	0	736	−96	16
4S120	4	0.375	0	1732	−96	26
1518	18	0.311	0	320	−92	12.4
2518	19	0.541	0.056	555	−92	17.4
3718	18	0.762	0	782	−92	19.9
3210	31	0.301	0.031	174	−92	10
3216	32	0.558	0	322	−92	13.4
3220	33	0.644	0.031	372	−92	14.5
3237	35	1.33	0.094	768	−92	22.4
3280	34	3.01	0.063	1738	−92	37.6
6407	62	0.395	0.031	117	−92	9.8
6415	60	0.725	0.062	224	−92	12.7
6430	56	1.34	0.125	443	−92	18.5
6460	61	2.89	0.047	880	−92	28
12 807	124	0.84	0.031	126	−92	10.5
12 814	125	1.62	0.023	241	−92	15.8
12 828	114	2.98	0.078	483	−92	21.6
12 856	127	5.95	0.008	870	−92	34.5
12 880	122	8.8	0.047	1333	−92	42.4

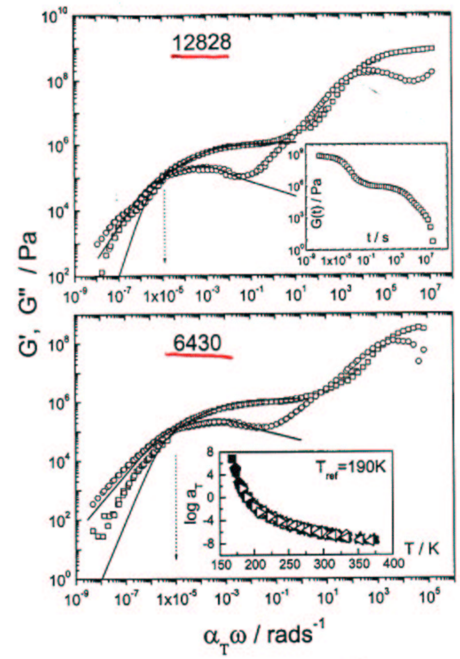
[a] Functionality polydispersity, estimated as $\varepsilon = |f_n - f|/f$ where f_n is the nominal functionality and f the tabulated measured one.
[b] Number of monomers per star arm.
[c] From light scattering measurement in dilute cyclohexane (good solvent) solution.



Roovers et al, Macromolecules 1993
1989

Confirm by SANS (Loppinet et al, Macromolecules 2001)

3



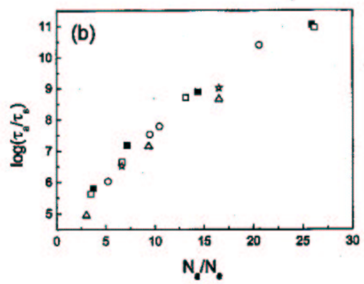
At $T_{ref} = 190K$

$M_e = 1815$ g/mol $\tau_e = 0.35$ s $G_N^0 = \frac{2}{\pi}\int_{-\infty}^{+\infty}(G''(\omega) - G''_s(\omega))\, d\ln\omega$

MM theory fits
f-independent arm relaxation

Kapnistos et al, JCP 1999

4



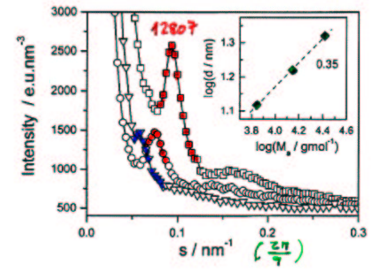
Fast mode:

Isofrictional arm relaxation (τ_a/τ_s) for all stars

$f = 4 \ldots 128$

$M_a = 7{,}000 \ldots 80{,}000$ g/mol

PBd and PI



$d = a \frac{2\pi}{q_{peak}}$ $a \simeq 1.23$

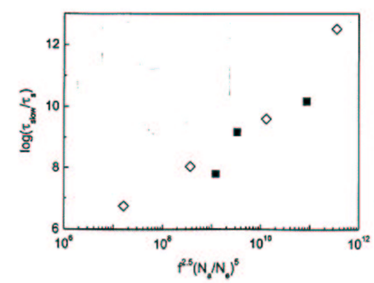
12807
12814
12828 ↑

Slow mode: STRUCTURAL (soft colloids)

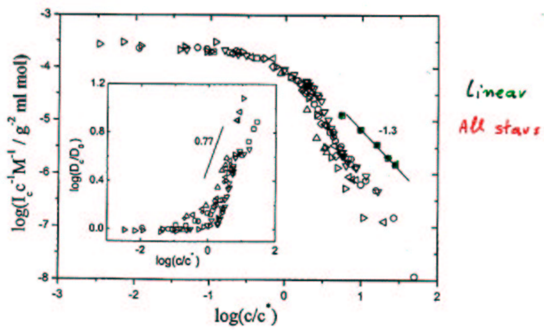
$$\frac{\tau_{slow}}{\tau_0} \sim f^{11/9} N_a^{26/9} N_e^{-1} \exp\left[X_1 \frac{f^{5/3}}{N_a^{1/3}} + X_2 \frac{N_a^{11/3}}{N_e^{3} f^{4/3}} \right]$$

Semenov, 1999

Controlled by corona deformation



Isofrictional structural time



Fast mode: Cooperative Diffusion

$$F = F_{\text{ideal gas}} + F_{\text{interaction}}$$

↓ excluded volume stretching

Semenov, 1999

$$\frac{I_c}{\phi M} \sim \phi^{-1.3}\left[1+0.21(1+\delta)\left(\frac{\phi}{\phi^*}\right)^{-1.3}\right]$$

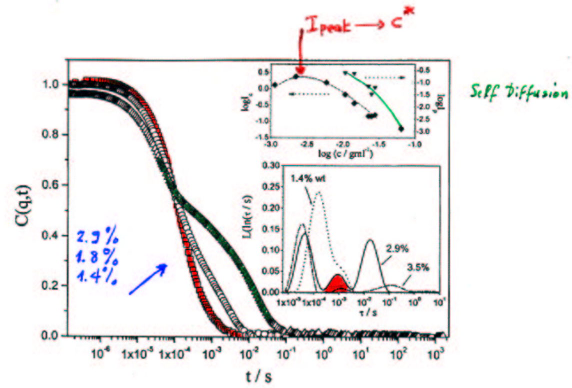
$$D_c \sim D_0\,\phi^{0.77}\left[1-0.21\,\delta\left(\frac{\phi}{\phi^*}\right)^{-1.3}\right]$$

$\delta \sim$ corona stretching

12856 STAR

$q = 0.035\ \text{nm}^{-1}$

2.9 %
1.8 %
1.4 %



$$C(q,t) = \int_{-\infty}^{+\infty} L(\ln\tau)\exp(-t/\tau)\,d\ln\tau \qquad \text{(CONTIN)}$$

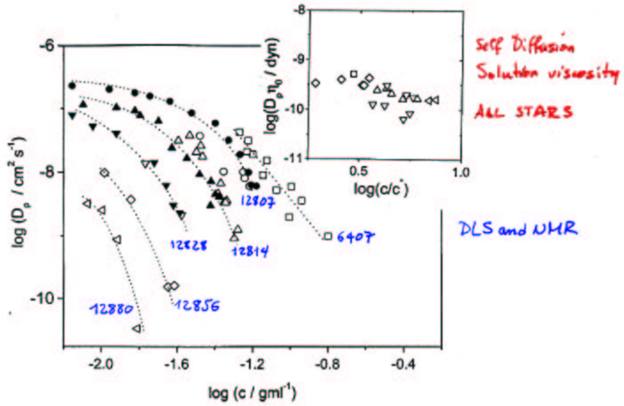
Relaxation rate Γ

Diffusion $\Gamma \sim q^2$ **Relaxation** $\Gamma \sim q^0$ (usually)

Intensity $I \sim q^0$ $I \sim q^x$ structure (order – clusters)

$$S(q,t) = S(q)\exp(-Dq^2 t)$$

Semenov et al, Langmuir 1999



Slow mode: Self Diffusion

Semenov, 1999

Polydispersity $\varepsilon^2 \sim M_w/M_n - 1$

$$\begin{cases} f_1 = f(1-\varepsilon) & \phi_1 \\ f_2 = f(1+\varepsilon) & \phi_2 \end{cases}$$

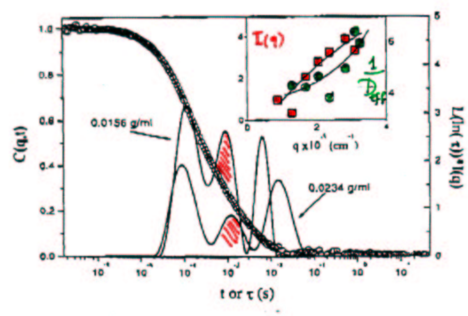
$\varepsilon << 1 \Rightarrow$ homogeneous binary mixture

$$I_P \sim \frac{f^2 \varepsilon^2}{N_a} \phi^{-1.6}$$

$\Gamma_P \simeq D_P q^2$

Verify with PFG-NMR (Fleischer, 1999)
Also zero-shear viscosity

12880 STAR
2%, 3%



Intermediate mode: Structural Relaxation

- high concentrations
  $I \nearrow$ with q : Structure

$$S(q) \simeq \frac{\Lambda(q)}{D(q)}$$

- better observed in larger star-like micelles

Sigel et al, PRL 1999

High concentrations: Gelation - non-ergodicity

MULTIARM STARS

Statics: G. GREST, L. FETTERS, J. HUANG, D. RICHTER
Adv. Chem. Phys. 1996 94 65

Dynamics: DV, G. FYTAS, T. PAKULA, J. ROOVERS
J. Phys: Condens. Matter 2001 13 R855

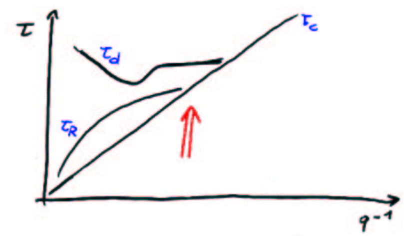
Why interesting?

- model ultrasoft colloids (polymer-colloid features)
  - glass-like gelation
  - shear banding
  - effective depletion interactions
  - crystallization?
- molecular control

VISCOELASTIC MODES

Coupling of concentration fluctuations to viscoelasticity

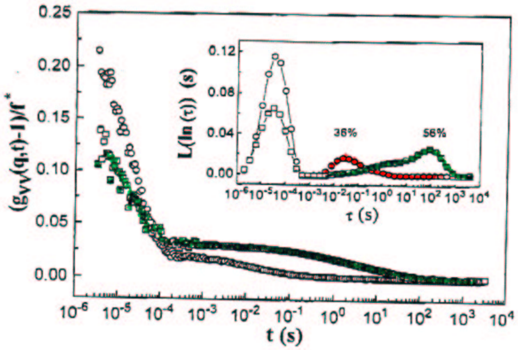
Brochard-de Gennes, Macromolecules 1977 TWO-FLUID MODEL
Semenov 1990
Doi-Onuki 1992 VISCOELASTIC LENGTH
Milner 1993



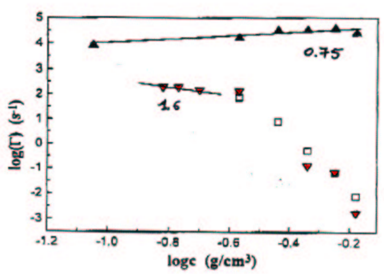
Semenov 1990

$$C(q,t) = A_c C_c(q,t) + A_R C_R(q,t) + A_d C_d(q,t)$$

$$\sum_i A_i = 1$$



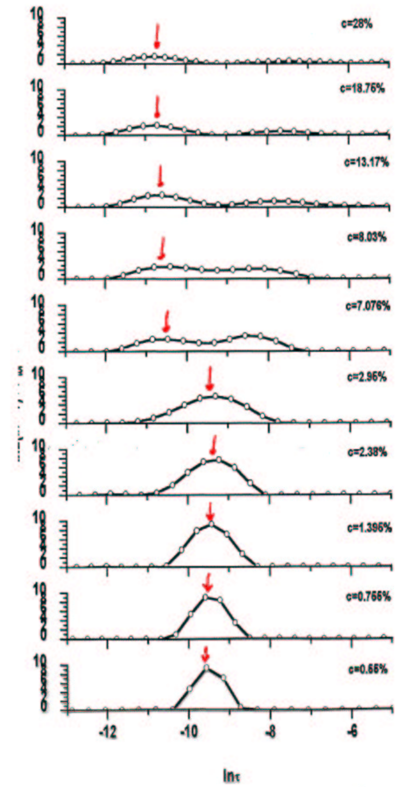
Linear polymers : Polybutylacrylate in dioxane
M ~ 100 000 g/mol
c ≳ 27% entangled
Jian et al, Colloid Polym Sci. 1996 274 4033



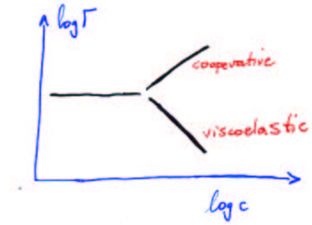
cooperative (90°)

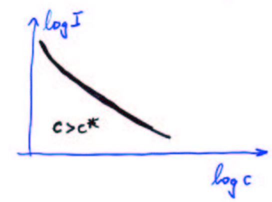
- Also θ-solvents , Nicolai - Brown 1993 Macromolecules
- Also wormlike micelles , Candau (TCBM book 1997)
  Nemoto , Macromolecules 1997-99

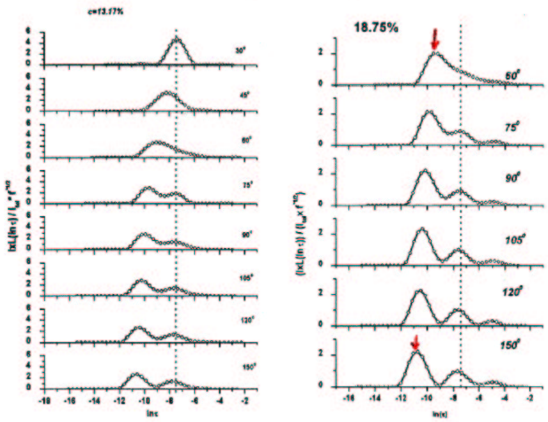
Star polymers : 1,4 polybutadiene / decane
$f = 4$
$M_a \simeq 100\,000$ g/mol
(work in progress !)



c_e







Fast mode: $\Gamma \sim q^2$ $I \sim q^0$ ∴ cooperative diffusion

Slow mode(s): $\Gamma \sim q^0$ $I \sim q^0$ Relaxation : viscoelasticity ?

- Star modes ?