

Workshop "Modeling the Dynamics  
of Liquid Crystal Elastomers"

full material of H. Pleiner

(to be returned, please)

most of the printed pages are available as a pdf file!

# Elasticity of Nematic Side Chain Elastomers

Harald Pleiner, Max Planck Institut für Polymer Research  
Mainz

Mario Liu, Institut für Theoret. Physik  
Universität Tübingen

Helmut R. Brand, Theoret. Physik III  
Universität Bayreuth

<http://www.mpip-mainz.mpg.de/~pleiner/project.html>

experiments: Philippe Martinoty  
Pascal Stein  
Dominique Collin

Université Louis Pasteur, Strasbourg, LDFC

H. Finkelmann, Universität Freiburg

"The concept of "softness", not that of  
"semi-softness" plays a role"

Contents: 1) de Gennes and Warner/Terentjev theories  
soft elasticity

2) Golubovic/Lubensky theory  
spontaneous anisotropy

3) application to nematic side chain elastomers  
experiments

4) summary

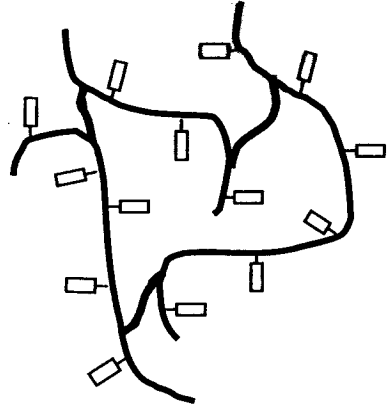
# Liquid Crystallinity

**Liquid crystal elastomers:** New class of materials combining

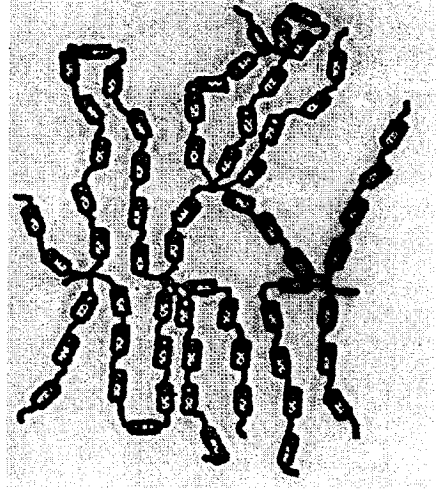
- Elasticity of a rubber
- Orientational order of nematics

**Two main types:**

**Side-chain Liquid Crystal Elastomer**



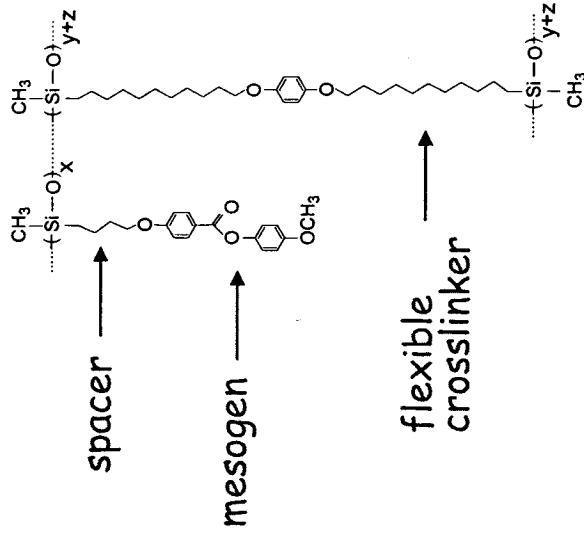
**Main-chain Liquid Crystal Elastomer**



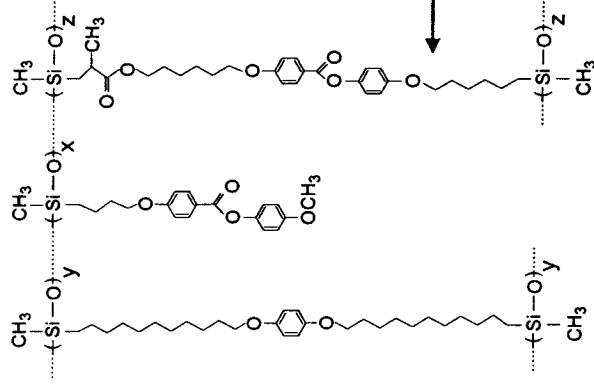
Two Samples

90% mesogens  
10% crosslinkers

a)



b)



x=90% mesogens  
y=6% flexible crosslinker  
z=4% more rigid crosslinker

Both samples only differ by the nature of their crosslinkers

## Why to study them?

### 1- Potential applications

macroscopic contraction-dilatation of the sample at the N-I transition, as a result of order-disorder transition of the mesogens.  $\Rightarrow$  actuators, micro-motors, artificial muscles

### 2- Basic questions

- Are these samples anisotropic rubbers ? (de Gennes, Pleiner, Brand)

or

Physical realization of soft elasticity concept?

"shape change without energy cost" (Lubensky, Olmsted, Warner and Terentjev)

- Is the time-scale of the director different from the time-scale of the network ?

- What is the origin of the viscoelastic modes ?

- Does the time-temperature superposition method work ?

Director  $n$  oriented in the plane of the films

⇒ Two experimental geometries



Coupling between  $n$  and  $v$

*Parallel*

Films thickness:  $300\mu\text{m}$



No coupling between  $n$  and  $v$

*perpendicular*



## 1a) de Gennes theory (linear)

case:  $\hat{n} (\parallel \hat{e}_z)$  perpendicular to shear plane

$$E_g = 2(c_{11} - c_{12}) e_{xy}^2$$

shear deformation

ordinary elasticity

$\rightarrow$  elastic modulus  $G_{\perp}^{\parallel} = 4 \cdot (c_{11} - c_{12})$

## 1b) de Gennes theory

case:  $\hat{n}$  ( $\parallel \hat{e}_z$ ) lies in shear plane

$$E_g = 2c_{44} e_{xz}^2 + \frac{1}{2} D_1 (\Omega_y - \omega_y)^2 + D_2 (\Omega_y - \omega_y) e_{xz}$$

elastic shear  
deformation

relative rotations  
of side-chains  
w.r.t. backbone

bilinear  
coupling term

if the deformations are done slowly enough,  
the director orients such that  $E_g$  is minimized

$$\frac{\partial E_g}{\partial \Omega_y} = 0 \quad \implies \quad D_1 (\Omega_y - \omega_y) + D_2 e_{xz} = 0$$

and

$$E_g = 2 \left( c_{44} - \frac{D_2^2}{4D_1} \right) e_{xz}^2$$

$\tilde{c}_{44}$  renormalized shear elastic modulus

$$G'_{11} = 4 \tilde{c}_{44}$$

# 1c) Warner + Terentjew theory (Olmsted)

based on mesoscopic models

$$\tilde{c}_{44} \equiv 0 \quad \text{"soft elasticity"}$$

or

$$\tilde{c}_{44} \text{ almost zero} \quad \text{"semi-softness"}$$

due to imperfections, is any finite value of  $\tilde{c}_{44}$  a proof for "semi-softness" ???

- remarks:
- elastic shear is completely (or almost) compensated for by director rotations
  - elastic shear does not cost any energy
  - there is no restoring force for shear deformations
  - liquid-like
  - this notion of "softness" is not contained in de Gennes' theory

$$E_g = 2c_{44} \left( e_{xz} + \frac{D_2}{4c_{44}} [\Omega_y - \omega_y] \right)^2 + \frac{1}{2} D_1 \frac{\tilde{c}_{44}}{c_{44}} (\Omega_y - \omega_y)^2$$

can be compensated, but  
in order to get  $E_g = 0$

still  $\tilde{c}_{44} = 0$  needed

2) How can it be that the shear modulus vanishes in a solid?

Golubovic + Lubensky theory

If an isotropic solid undergoes a spontaneous shape change (anisotropic state) at  $T_c$ , then the phase below  $T_c$  must not have a finite shear modulus!

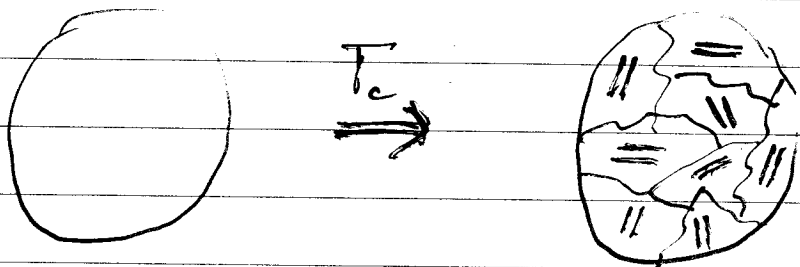
independent on how the transition isotropic - anisotropic is obtained

3) Is this concept applicable to nematic side chain elastomers?

answer: experiments  $\Rightarrow$  ~~by Ph. Martinoty~~ by Ph. Martinoty

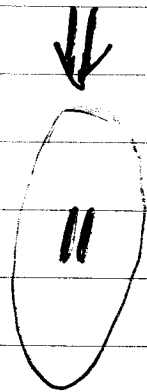
a) spontaneous shape change?

in reality:



polydomains!

$\Downarrow$   
external mechanical field



anisotropic monodomain

$E_{\hat{n}\text{-texture}} < E_{\text{deformation}}$

better explanation:

a) if crosslinked in the nematic state, anisotropy is fixed

⇒ isotropic state still contains a residual anisotropy ("paranematic")

⇒ GL argument not applicable [de Gennes / Olumuxa]

β) even if crosslinked in the isotropic state, there is a small residual anisotropy:

why?

Due to the viscoelastic nature of the (isotropic) polymeric state, strain/stress fluctuations relax slowly, in particular close to the glass transition.

Nematic order fluctuations also relax slowly, since they are coupled bilinearly to strain/stress fluctuations.

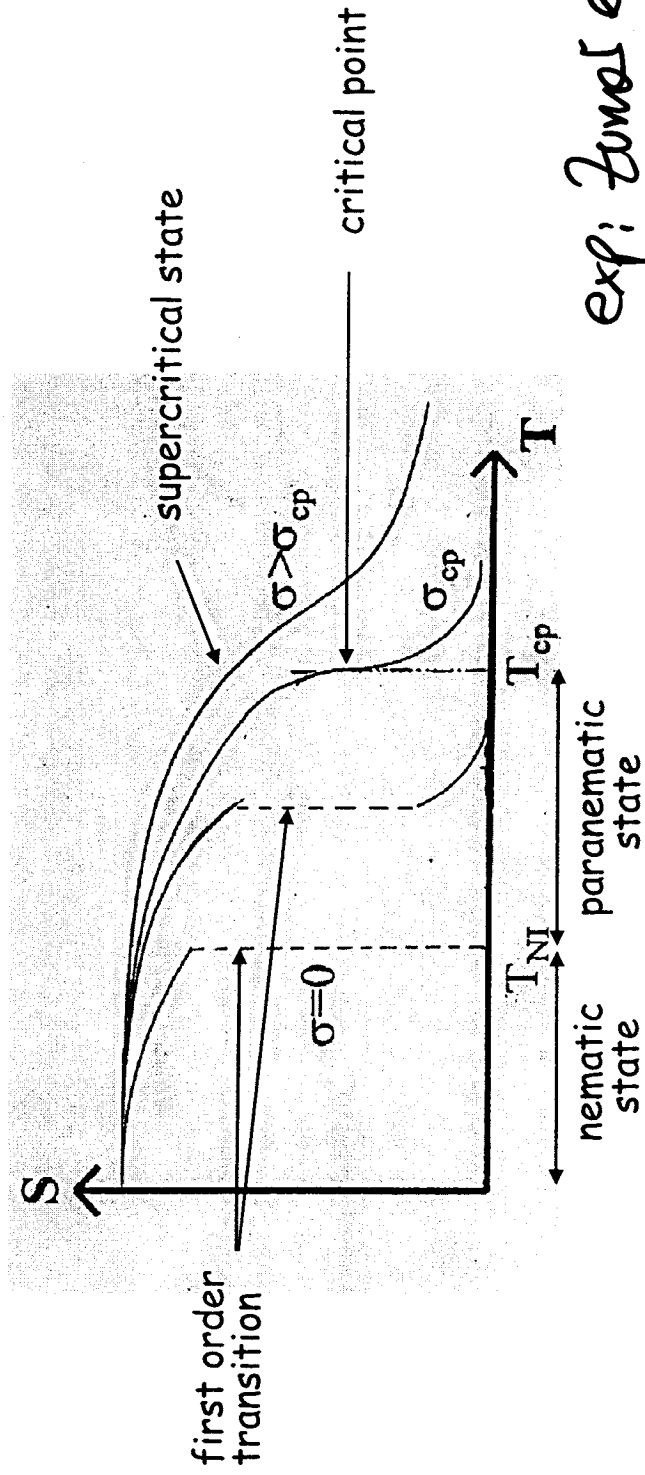
Upon crosslinking these nematic fluctuations are frozen in [Kawasaki + Brand] and lead to the polydomain director structure below  $T_c$ .

this argument applies also to singly crosslinked samples;

Synthesis of a monodomain sample: Finkelmann's procedure.

- Two steps crosslinking process
- Mechanical stress is applied before the second crosslink step  
load attached to the sample.

The critical mechanical point (de Gennes)



exp: Zumer et al  
PRR last week

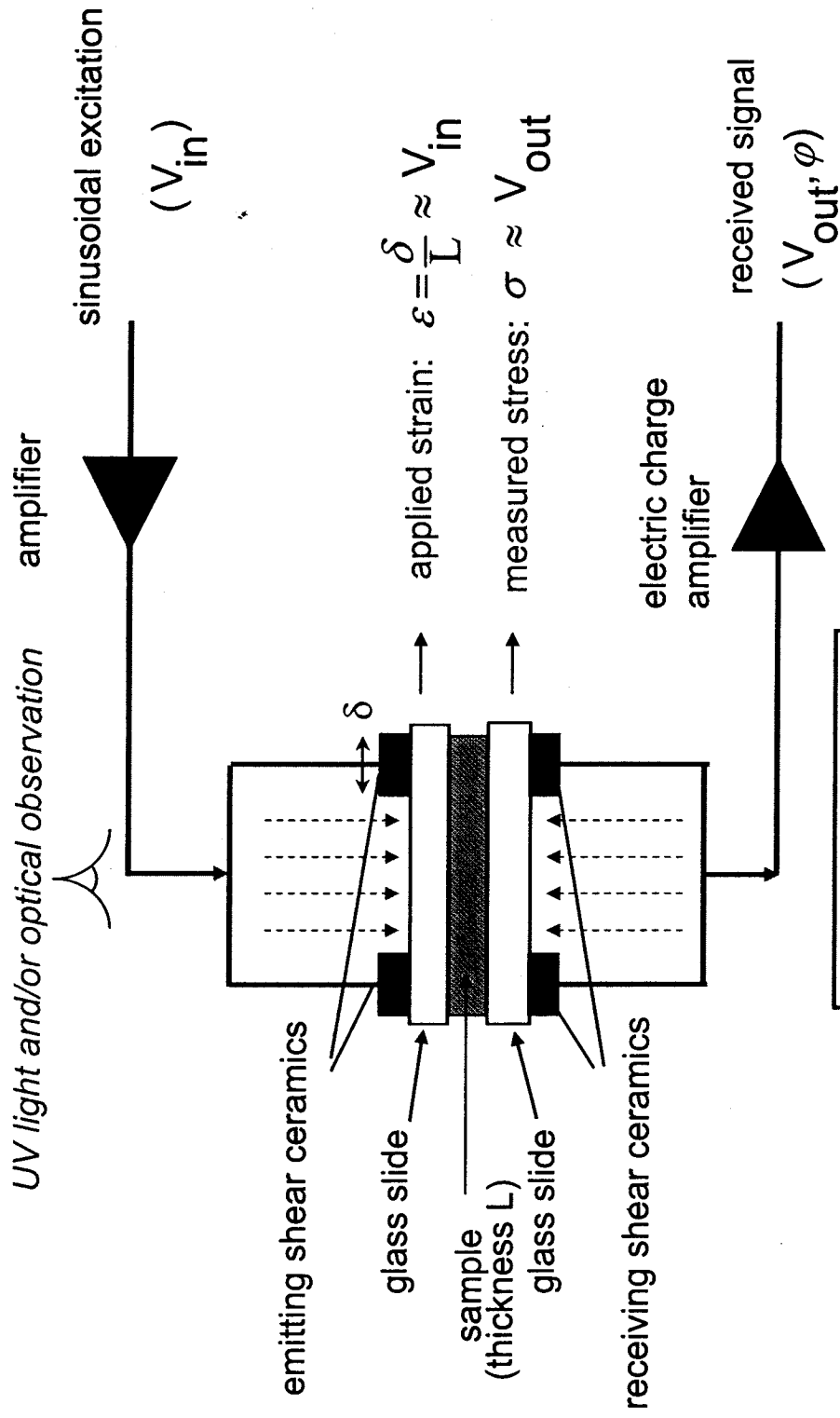
Semi-soft: If the finite value of  $\tilde{c}_{44}$  goes down ( $\rightarrow 0$ ) when the imperfections in the isotropic state are reduced  
 $\Rightarrow$  semi-soft

if not (or even goes up)  $\tilde{c}_{44} = \text{finite}$   
has nothing to do with soft-elasticity  
concept.



# Experimental setup

## Piezo-rheometer



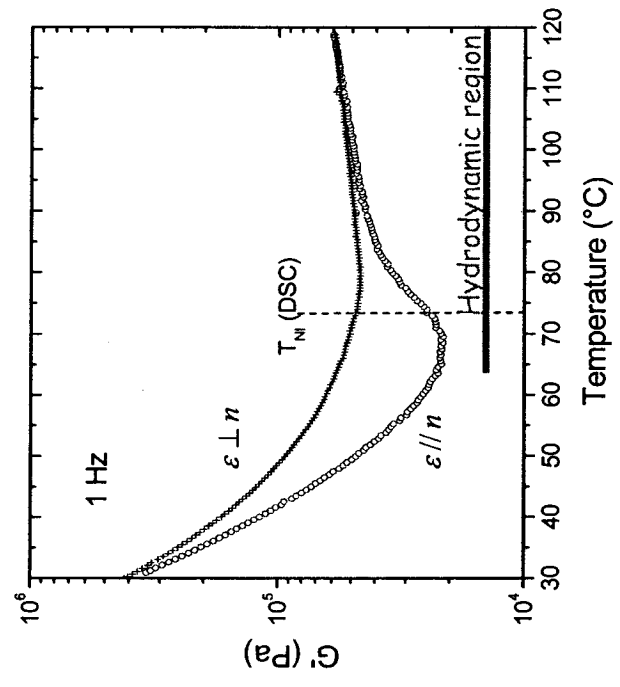
$$\frac{\sigma}{\epsilon} = G^* = G' + iG''$$

## **Interesting features for the present study**

- Large frequency range available ( $10^{-2}$  Hz to  $10^4$  Hz).
- Very small strain applied to the samples ( $10^{-6}$  to  $10^{-3}$ ).  
Linear response regime.

The mechanical anisotropy in the hydrodynamic regime and the question of softening of elasticity concept

Sample with flexible crosslinkers



- $G'_{\perp}$  no anomaly around  $T_{NI}$
- $G'_{\parallel}$  softening around  $T_{NI}$  due to the n-v coupling
- Anisotropy above  $T_{NI}$  } Paraneumatic state or Supercritical state ?
- Anisotropy ratio:  $\frac{G'_{\perp}}{G'_{\parallel}} \sim 3$

Two options:

The sample is supercritical → no semi-soft elasticity (no N-I transition)  
 Anisotropy ratio is that of a conventional uniaxial nematic elastomer

The sample is in the paranematic state: memory of soft elasticity could survive.

Check: modify the width of the paranematic state

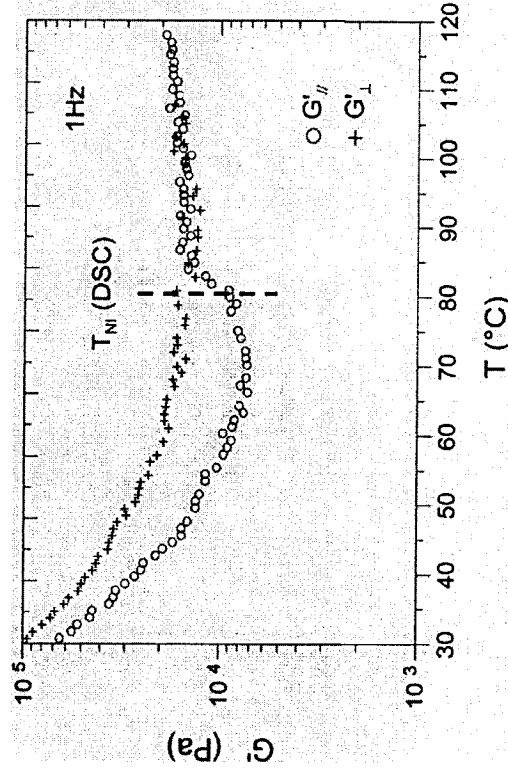
Study a sample prepared with the same chemical composition but with a different crosslinking process.

A decrease in the anisotropy of the isotropic phase should be accompanied by an increase of the anisotropy in the nematic phase.

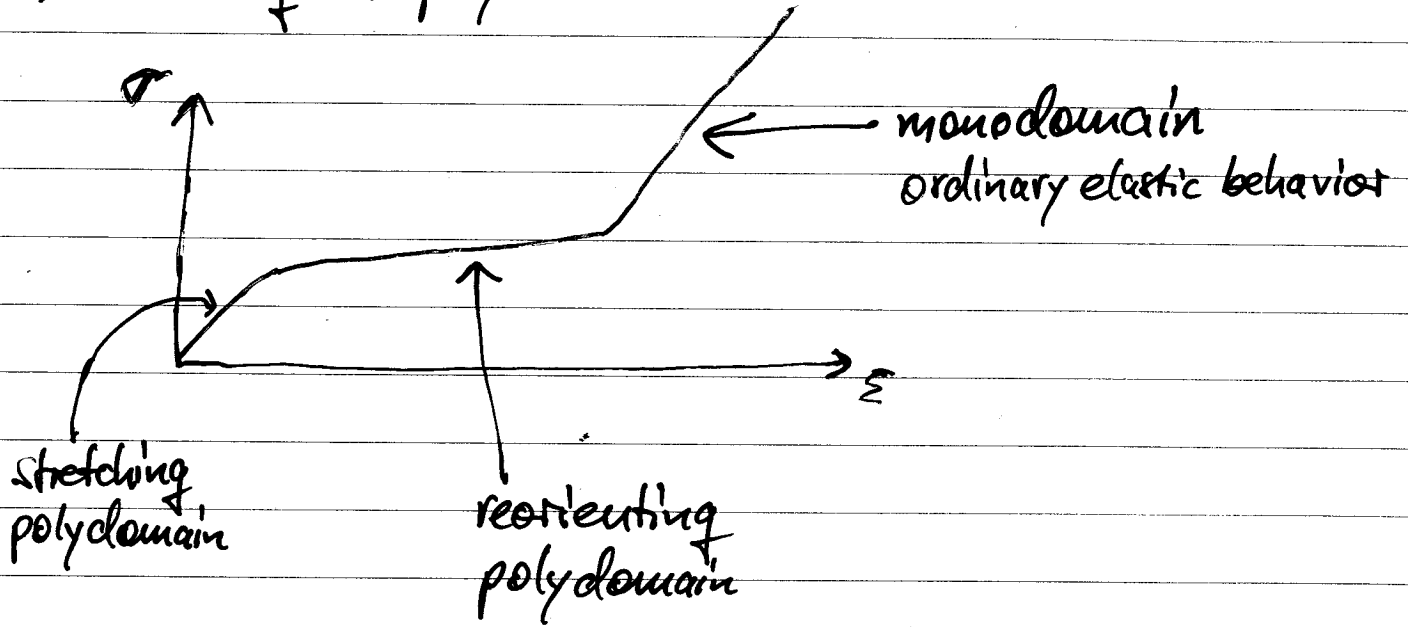
Opposite behavior observed.



Contrary to semi-soft elasticity concept

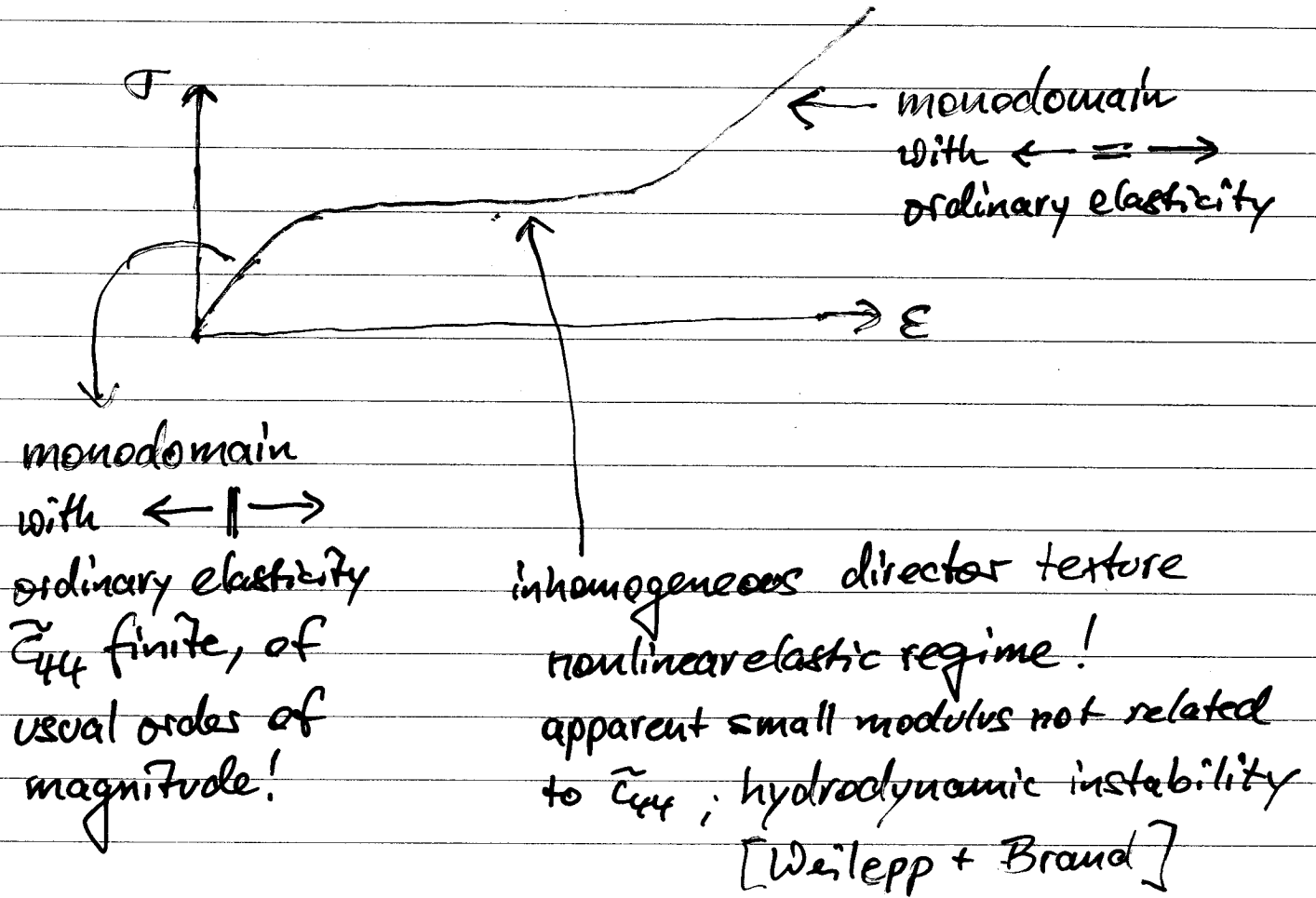


### 3b) stretching of polydomains

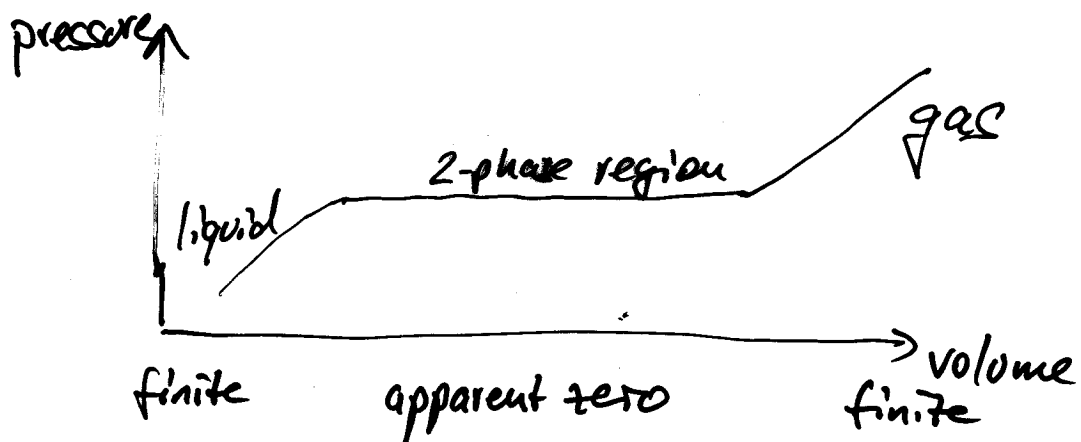


↓  
apparent small modulus not related  
to soft elasticity ( $\tilde{C}_{44} \approx 0$ ), but rather  
to reorientation of domains - not described  
by de Gennes' energy [Uchiyama]  
not by Waite / Terentjev

### 3c) director reorientation by stretching:



analogue to gas-liquid 2-phase region



compressibility

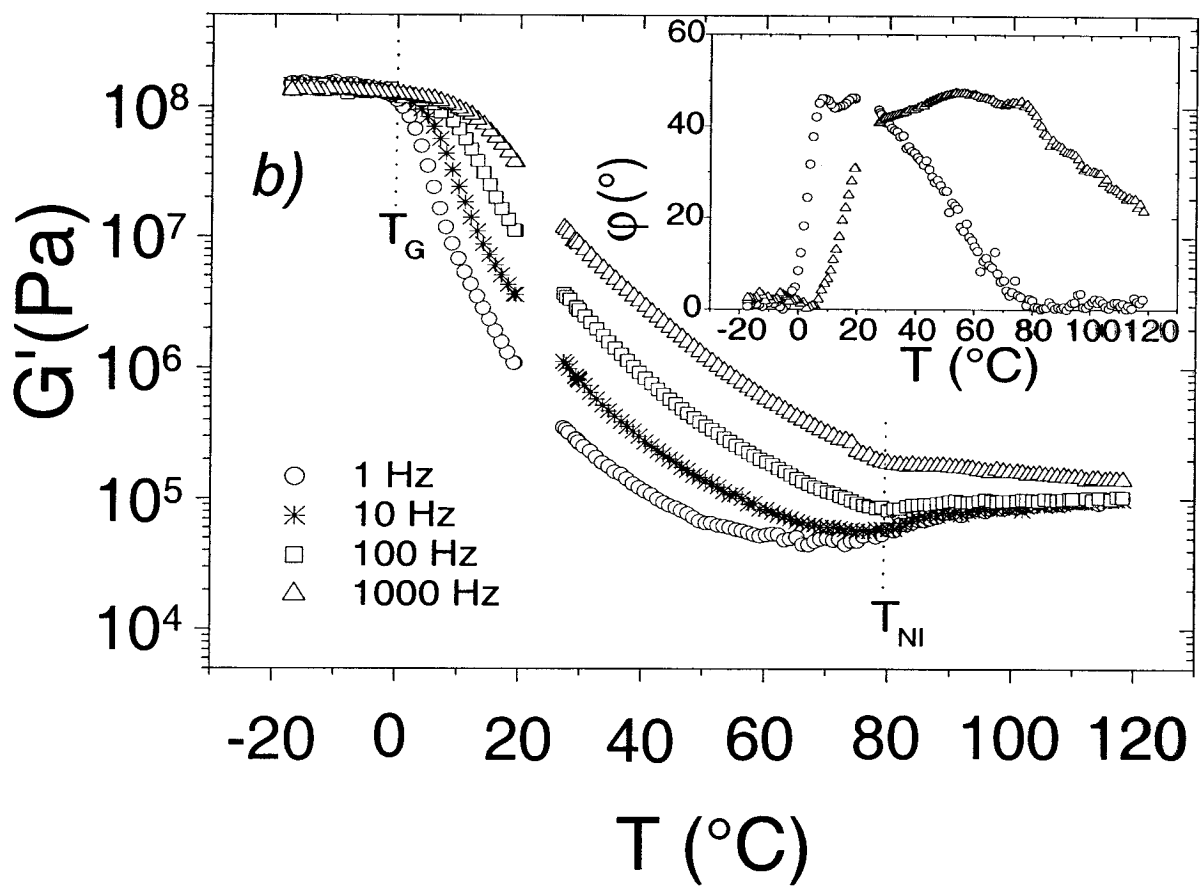
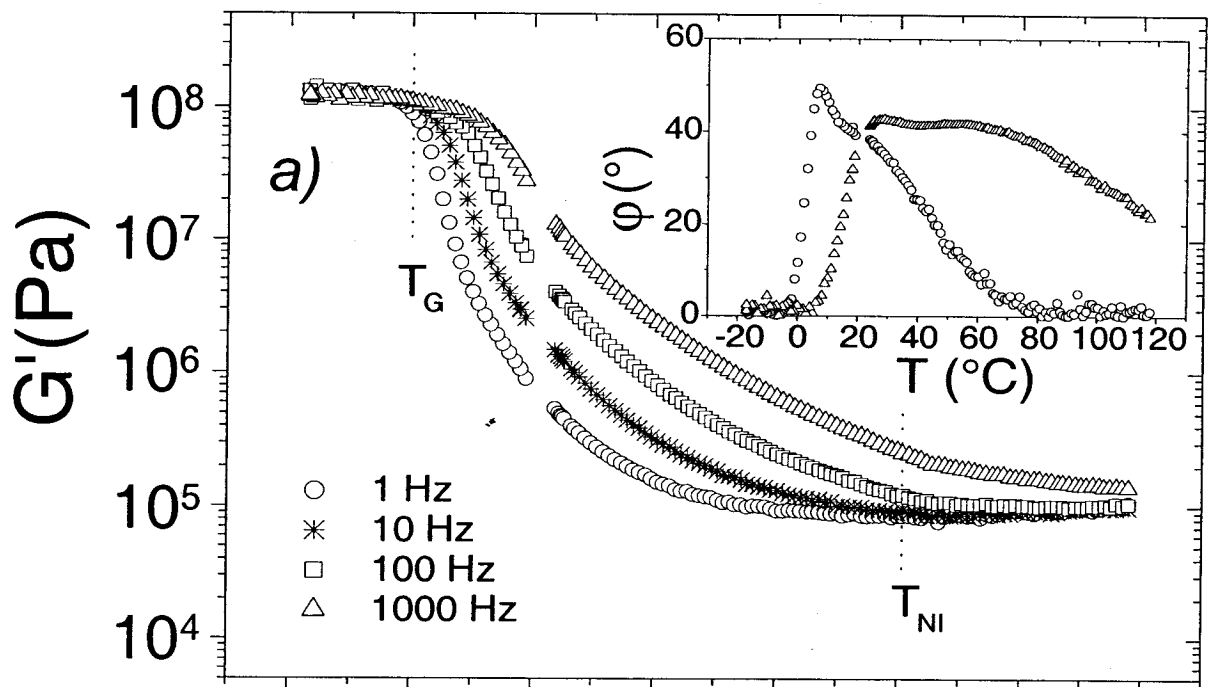


Fig. 3



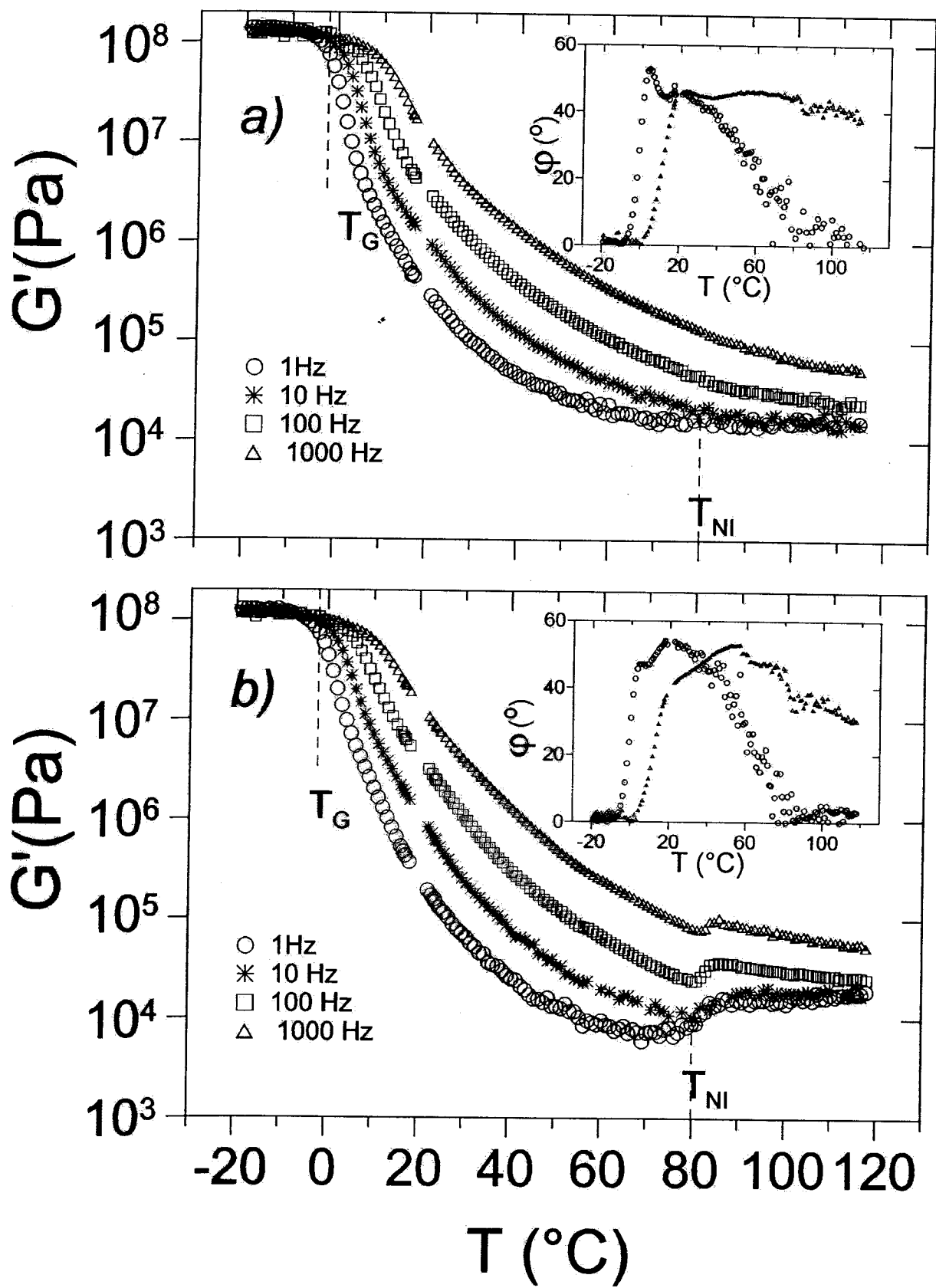


Fig. 2

isotropic

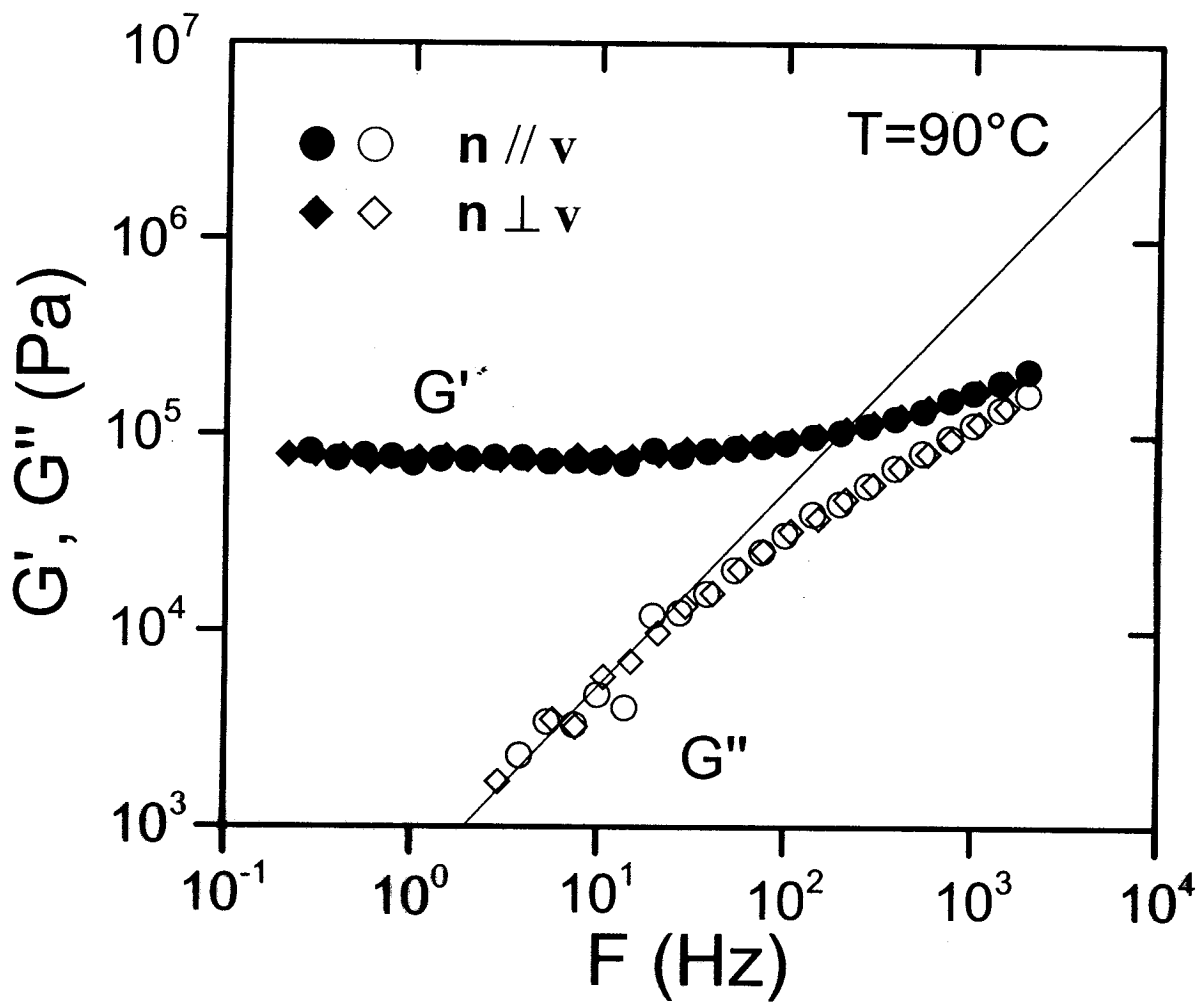


Fig. 8

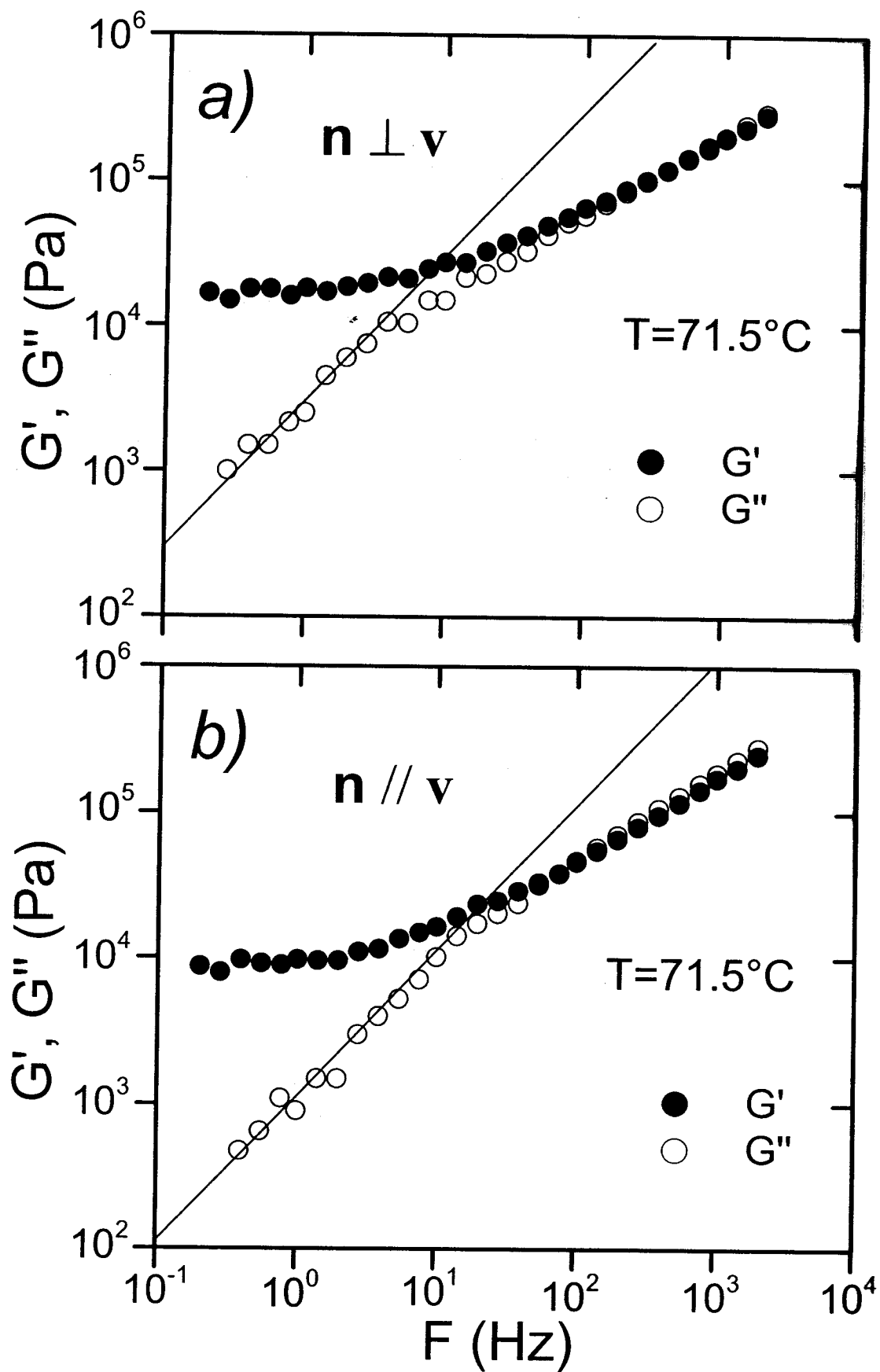


Fig. 9

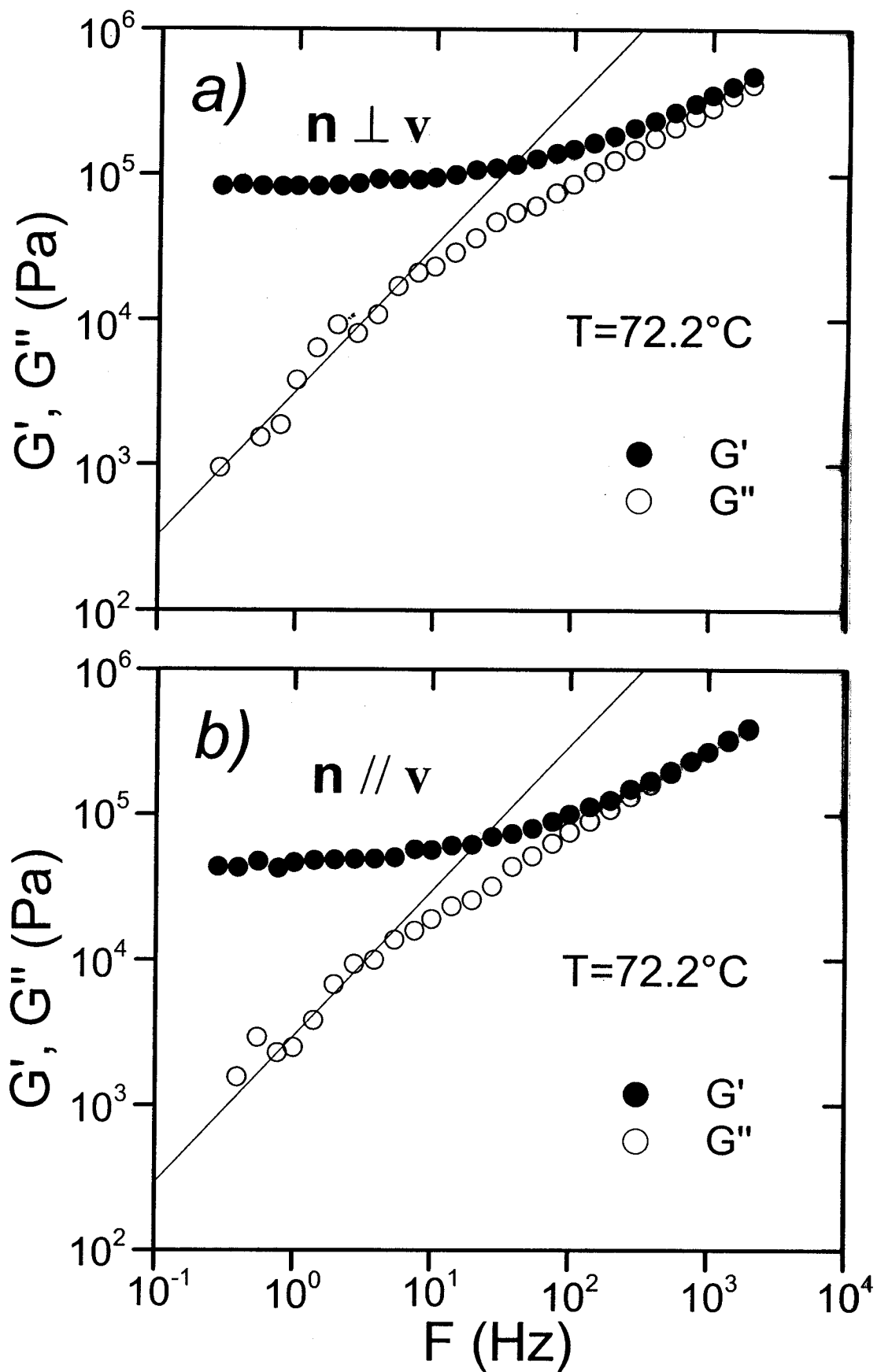


Fig. 10

Dynamic soft elasticity theory (Terentjev, Warner)

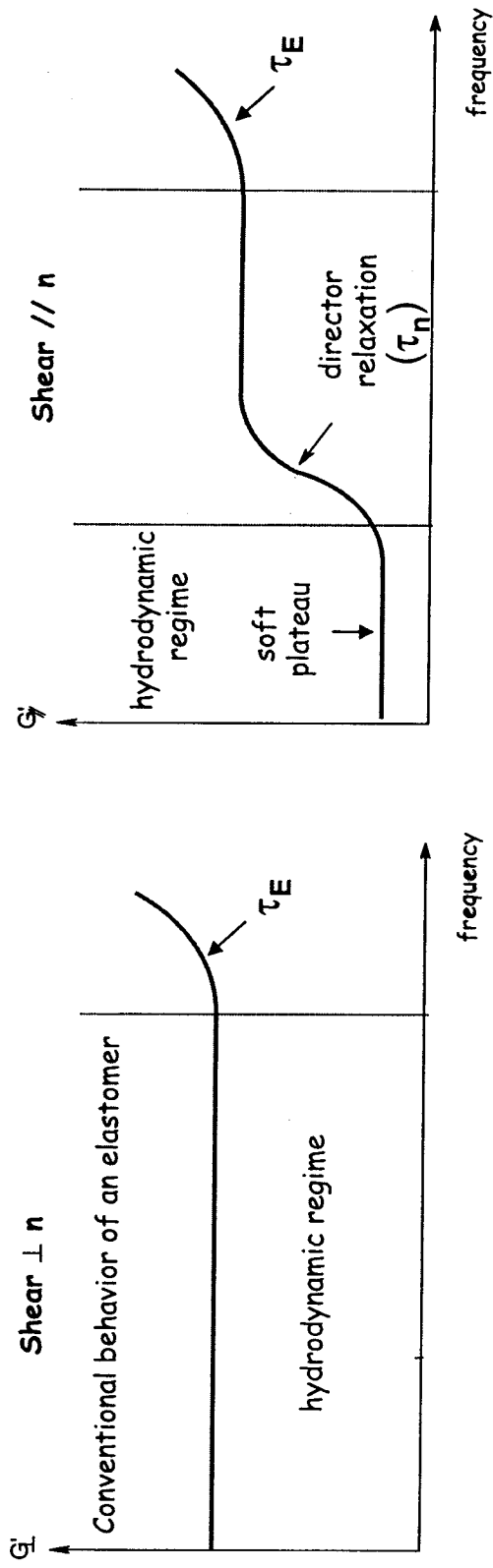
linear theory:

- Hydrodynamic behavior of an elastic network + independent relaxation of the director

Separation of time scales: essential part of the description

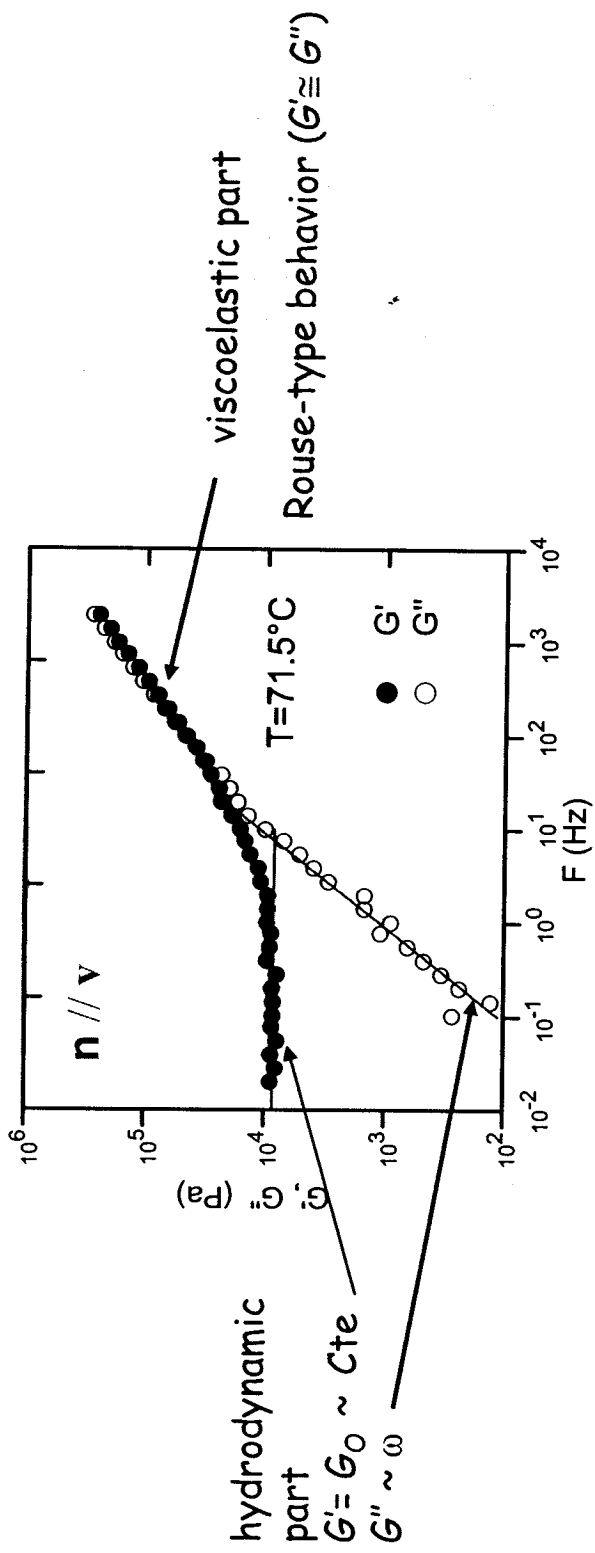
$$\tau_n \text{ (director)} \gg \tau_E \text{ (network)}$$

$$10^{-1} - 10^{-2} \text{ s} \quad 10^{-6} \text{ s}$$



Measurement of  $G''$  as a function of frequency: direct test of soft elasticity and separation of time scales

**The question of separation of time scales**



**-relaxation time of the network:** (intersection of the  $G'$  and  $G''$  curves associated with the hydrodynamic regime)

$\tau_E \sim 10^{-2} \text{ s}$  ( $\tau \sim 10^{-5} - 10^{-6} \text{ s}$  for a classical system)

**relaxation time of the director:**

$\tau_n \sim 10^{-2} \text{ s}$  (light scattering- Schönstein, Stille, Strobl)

$\Rightarrow \tau_n \sim \tau_E \Rightarrow$  no separation of time-scales

Mode-coupling: director relaxation not visible independently in the frequency response.

Summary: Side Chain nematic elastomers show a very complicated elastic behavior, in particular in the nonlinear elastic domain or in an elastically or orientationally inhomogeneous state, but

show ordinary anisotropic elastic behavior in the linear domain, in particular no soft elasticity ( $\bar{c}_{44} \approx 0$ ).

## Conclusion

- Monodomain SCLCE do not represent the physical realization of soft or semi-soft elasticity concept.

They do not correspond to the idealized case where they form spontaneously from the isotropic phase. They are "above" the mechanical critical point.

- They are uniaxial networks with a small anisotropy in the hydrodynamic regime, and a Rouse-like frequency dependence in the viscoelastic region.
- Specific model including nematic interactions is needed to explain the small and temperature-dependent deviations from the Rouse behavior.