

H2. NOVEL FRONTIER BETWEEN LIQUID AND SOLID STATES IN POLYMERS: IDENTIFICATION OF A MACROSCOPIC SOLID-LIKE MODE IN THE MOLTEN STATE.

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Polymers are produced and daily used but their dynamic properties far from being understood, fascinate by their puzzling properties. Indeed, polymers present unexplained large time scale relaxations; reinforced polymers display incredibly high moduli; the polymer dynamic at nanometric [1] and at filmic states [2] reveal solid-like characters incompatible with the conventional macroscopic viscoelastic properties [3]. Various flow behaviours display inexplicable instabilities. One of the most spectacular ones, is the shear induced phase transition observed in the liquid state of liquid-crystal polymer melts [see photograph below and reference 4].

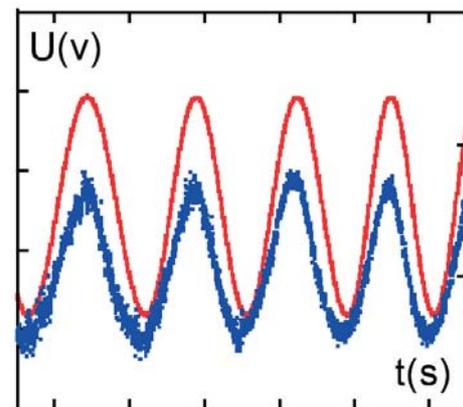
Novel experimental observations carried out at the LLB by controlling the boundary conditions between the polymer and its substrate, give a fresh perspective on their true nature. Indeed, the common and fundamental denominator in flow experiments is the no-slippage interacting condition between the fluid and the substrate(s). The several tens' years of apparent agreement between macroscopic rheological experiments and theoretical models, promoted the no-slippage condition as a postulate, reinforcing the idea that the no-slippage liquid-solid boundary is usually fulfilled.



Above a critical shear rate, the isotropic liquid of liquid crystal polymers (left photo) transforms in a strongly birefringent oriented phase (right photo). Photos are obtained between crossed polarisers in the (velocity, neutral axis) plane.

However, the emergence of new disciplines as microfluidics together with the observation of unexpected macroscopic instabilities as exposed above, shows that the fluid properties are actually strongly dependent on the scale of the observation and also on the nature of the surface interactions, driving numerous studies to reconsider now the static and the dynamic friction states between the fluid and the substrate. Combining the tribology to dynamic relaxation measurements (CEA patent), we propose a new type of dynamic experiment where the interaction of the polymer to the substrate is controlled. Under optimal conditions, we show that the molten state of polymers, far

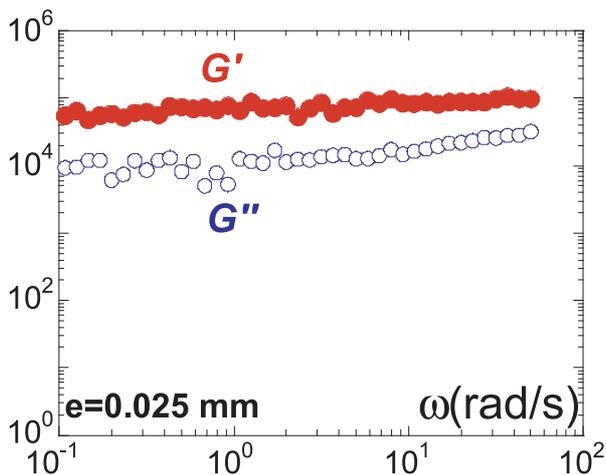
away from any transition, reveals so far unknown long range correlations [5]. The signature of an unpredicted elastic mode, is identified by the invariance of the dynamic response versus frequency and by the in-phase input strain and resulting output stress waves (see figure below).



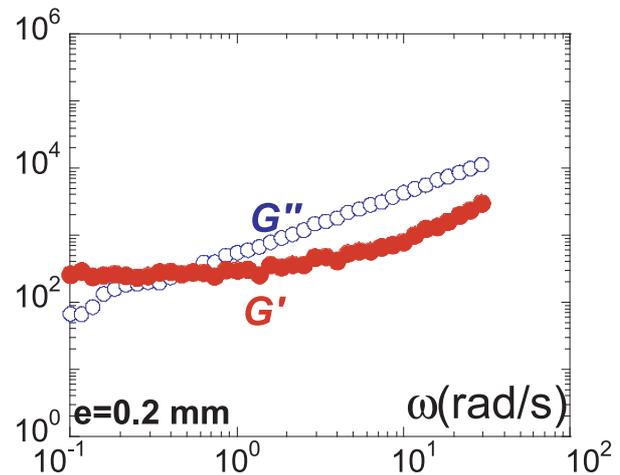
In phase entrance strain wave (red points) and resulting output wave (resulting torque - blue points) plotted versus time, evidencing a solid-like response for an ordinary polybutylacrylate at 100°C above the glass transition temperature ($M_w = 40000$, $I = 1.1$, $\omega = 0.1 \text{rd/s}$).

This elastic property is a dimensional parameter; it progressively vanishes by increasing the sample thickness, as shown in the following figures (from a to c). The solid-like response observed at low thickness (here 0.025mm) is no more measurable at large thickness (typically 1mm) and is progressively dominated by the conventional polymer viscoelastic response (figure c). The sample is an ordinary polymer measured about 100°C far away from the glass transition temperature.

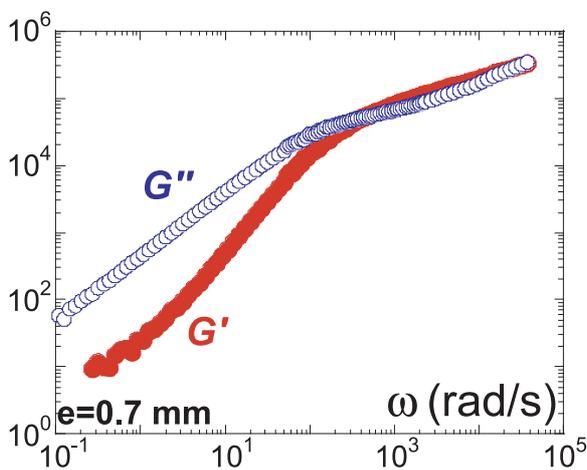
The identification of this size-dependent elasticity is of fundamental importance. It implies that the system contains unexpected giant time & length correlations at scales much larger than those described of the usual viscoelastic description (Rouse, reptation). Indeed, the low thickness solid-like response (typically measured at 0.020-0.040mm) corresponds to a gigantic scale with respect to the individual molecular scale (which is about 50-100Å). The definition of the conventional elementary polymer relaxation time described as the intercept of the ω and ω^2 scaling of the viscous and the elastic responses respectively, should be revisited since it does not reflect a terminal relaxation time.



a)



b)



c)

This experimental observation, carried out on various polymer types (LC-polymers, Polybutadiene, Polymethacrylates, Polybuty-lacrylates...) should shed light on various disagreements between experimental observations, theoretical developments and applications and open new routes for the understanding of polymer science and complex fluid dynamics, including the up to date active debate on the discontinuous dynamic behaviour from nanometric to macroscopic scale dynamics.

Dynamic relaxation spectra showing the linear response of the viscous (G'' (●)) and the elastic (G' (●)) moduli versus frequency, at different sheared thicknesses ($e=0.025\text{mm}$, 0.2mm , 0.7mm). The sample is a monodisperse polybutylacrylate ($M_w=47000$) measured at $T=T_g + 90^\circ\text{C}$.

1. H.Wu, S. Granic, *Science* **258** (1992) 1339.
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3. "Viscoelastic Properties of Polymers", J.D. Ferry, . Wiley & Sons Editor (1980).
4. C. Pujolle-Robic, L. Noirez, *Nature* **409** (2001) 167
5. H. Mendil, P. Baroni, L. Noirez, *Eur. Phys. J. E (Focus Point)* **19** (2006) 77-113, *ibidem*, *Eur. Phys. E* **19** (2006) 20, H. Mendil, I. Grillo, P. Baroni, L. Noirez, *Phys. Rev. Lett.* **96** (2006) 077801.