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Identification of finite shear-elasticity at low thickness in the liquid state of molecular (OTP) and polymeric glass formers (PBuA)

L. Noirez[1], H. Mendil-Jakani[2], P. Baroni[1]

[1]*Laboratoire Léon Brillouin (CEA-CNRS), CE-Saclay, 91191 Gif-sur-Yvette Cédex, France*
[2]*Current address : Structure et Propriétés d'Architectures Moléculaires, UMR 5819 SPrAM (CEA-CNRS-UJF), CEA-Grenoble, 17, avenue des Martyrs, 38054 Grenoble, cedex 9, France.*

*Correspondance to: Laurence Noirez
E-mail: laurence.noirez@cea.fr

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Finite shear elasticity has been identified in the liquid state. The study is expanded to a van der Waals molecular glass former, the o-Terphenyl and to an ordinary polymer melt, the polybutylacrylate as a function of its molecular weight. These fluids exhibit elasticity at the sub-millimeter scale and far above any phase transition. This macroscopic property challenges the conventional terminal relaxation modes (α-process or reptation times) in terms of individual molecular process.

Keywords: glass formers, liquid state, elastic properties.

1. Introduction

To define three states of matter such as solid, liquid or glass and the transitions between them, the shear and bulk moduli are certainly of the most useful and relevant characteristic features[1]. The shear modulus presents a substantial advantage over the bulk modulus because a specific instrumentation has been elaborated to routinely measure the dynamic properties of viscoelastic materials (materials displaying dynamic behaviours intermediate between liquid and solid). These apparatus are dynamic mechanical analysers, rheometers, shear resonators, surface force apparatus… Based on the same principle, these devices measure the stress or the motion transmitted by simple contact between the sample and the surface submitted to small mechanical oscillatory solicitations. This mechanical technique is currently the only one able to probe long time scales.

The boundary conditions between the surface and the sample play a major role in this measurement since the efficiency of the transmission of the motion, and thus in the quality of the measurement are completely dependent on the interaction between the surface and the material. Up-to-date progresses in the sensitivity of the instrumentation and in the techniques allow the access to the measurement of the shear modulus with a high precision and over 6 decades of magnitude. These improvements have considerably widened the frequency window and the modulus range, and therefore enable the detection of subtle properties that would not been considered before. Recent developments have shown that it is also possible to improve significantly the measurement by controlling the boundary conditions between the material and the substrate whereby the stress and the measurement are transmitted[2]. Using this method, a protocol has been established to measure elastic properties at the sub-millimetre scale in the liquid state of various materials as glass formers (Glycerol, PPG,

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presently o-Terphenyl) but also polymer melts so far considered as viscous liquids far away from any phase transition[3,4]. These results showing that the shear modulus in liquids is not zero, contrast with the conventional macroscopic description. The solid-like property is usually not considered since this delicate signal mostly observable at low thickness geometry is hidden in conventional mechanical measurements. However, new studies and results emerging from different disciplines as microrheology[5], dielectric relaxation[6], NMR [7], X-ray photon correlation spectroscopy[8], voltage effects[9] evidence relaxation modes much slower than those described in conventional theoretical models. It points out that a pure viscous approach of the liquid state as adopted for example to interpret the phenomenology of the supercooling formation and of the glass transition cannot be satisfying. The consideration of this non-negligible macroscopic component is of first importance to redefine the relevant parameters for a better understanding of glass and glass former properties and more generally, of the fluid properties.

In this paper, a new series of experimental results is presented illustrating the measurement of a finite shear modulus in the liquid state of two Van der Waals glass formers. The first one, the o-Terphenyl (OTP) is a molecular glass former. It displays a melting point at 56°C and a glass transition temperature at about -30°C[10]. Classified as a fragile glass former (the viscosity is not obeying to Arrhenius temperature dependence in the supercooled state), the o-Terphenyl crystallises from the supercooled state at around 35°C when it is slowly cooled down. The crystallisation can be prevented by a rapid cooling of the melt, giving rise to an amorphous glass below the glass transition temperature. The non or delayed crystallisation properties are due to the no-planarity of the molecule because of the short distances between non-bonded carbon atoms[11]. The other studied material, the polybutylacrylate (PBuA), is a polymeric Van der Waals glass former. The polybutylacrylate is an amorphous material characterised only by a glass transition temperature (Tg=-64°C) and therefore does not display any supercooled state. Its molecular weight is a variable parameter and its influence on the shear modulus will be examined. Finally, the concept of terminal relaxation time of polymers (reptation time for entangled polymers and Rouse time for unentangled chains) deduced from conventional viscoelastic measurements will be discussed. Similarly, the *alpha* process, the slowest relaxation mode in molecular liquids as the OTP, corresponding roughly to molecular rotation[12] will be examined. This mode is usually not accessible via mechanical measurements. This dynamics is typically characterised by dielectric spectroscopy[13], dynamic light scattering [14], NMR [15], quasi-elastic neutron scattering [16] (the cited references are related to the OTP).

2. Experimental

o-Terphenyl was purchased from Aldrich (99% purity). It presents a glass transition at about -30°C ± 1°C and a melting point at 56°C (see Table 1). The working temperatures are ranging from 54.6°C up to 100°C, thus mainly above the melting point and some slightly below it. The polymer is an ordinary polybutylacrylate of well-defined molecular weight. The series of different molecular weight monodisperse PolyButylacrylate was purchased from Polymer Source (Table 1). Its glass transition temperature is -64°C. The working temperature is the room temperature. Before the experiment, the samples were observed by optical microscopy (to ensure the absence of air bubbles) and maintained under vacuum before the experiment. The sample is deposited between two disk-like alumina surfaces freshly cleaned by thermal treatment (400°C). The two surfaces are approached until the full contact with the liquid is achieved.

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The experiments are carried out using a dynamic mechanical analyser (ARESII, TA-Instruments) following the protocol described in [2-4] to improve the dynamic response and determine the non-vanishing low frequency shear modulus. The room is equipped with an air conditioning and the temperature on the sample is ensured with an air pulsed oven ensuring a thermal stability of less than ±0.1°C. The zero gap is set by contact; the error is positive and less than 0.005mm. The measurement consists in applying a constant shear strain of amplitude (γ) to the sample by imposing a small oscillation of variable frequency (ω) on one disk (strain imposed mode). The second disk is immobile and coupled with a transducer on its central axis. It measures the torque (σ) transmitted by the material under solicitation. The moduli are classically extracted from the difference between the input and the output signals; the component in phase with the strain determines the elastic (or storage) modulus (G'), whereas the out of phase component defines the viscous (or loss) modulus (G'') following the relationship: $\sigma(\omega) = \gamma_0.(G'(\omega).\cos(\omega.t) + G''(\omega).\sin(\omega.t))$. The representation of $G'(\omega)$ and $G''(\omega)$ versus frequency provides the dynamic signature of the material and points out its eigen modes. A typical relaxation mode (reptation time) in polymeric liquids (melt and solutions) is given by the interception of G' and G'' that signs the slowest relaxation time before entering in the low frequency flow regime.

3. Results

The validity of a dynamic relaxation experiment is entirely depending on the efficiency of the transmission of the motion by contact between the sample and the surfaces (fixtures). Because of symmetry reasons, surface properties differ from the 3D properties. The ideal boundary conditions should exhibit an energy at the frontier between these two homogeneous media as low as possible; in other words, the surface energy has to be as high as possible. A good criterion is the observation of a total wetting of the fluid onto the substrate[17]. This is achieved for example by employing zero porosity alumina substrates[2]. The use of total wetting substrate reinforces the liquid/substrate interaction, and prevents the slippage[18]. Using the total wetting boundary conditions, we have already shown that it is possible to improve the dynamic response and to reveal a non-vanishing low frequency shear modulus far above the glass transition in various viscous liquids[3,4]. This measurement protocol is here applied to the liquid state of a glass former, the o-Terphenyl and to an amorphous polymer, the polybutylacrylate in the molten state at temperatures far away from the glass transition.

Fig.1a displays the response of the o-Terphenyl above the melting point, at +7.7°C above Tm and 45µm gap thickness. The upper points of the figure indicates a solid-like response; the shear modulus G' is independent of the frequency within this observation window (which is the conventional frequency range). These results have been obtained at low strain amplitude using total wetting surfaces. These surfaces made of alumina with zero porosity are characterised by a low roughness number [2] and wide flat zones at the atomic scale as shown in the upper photograph (Fig.1b). The bottom photograph illustrates the geometry of the experiment, the dimensions and the quality of the parallelism between surfaces spaced by a 45µm gap thickness. The transmission of the light through the sample guaranties the absence of any contact that could explain the solid-like behaviour above Tm and points out the macroscopic character of the probed property. This protocol reveals long range elastic cohesive correlations in a glass former so far considered as purely viscous in the liquid state.

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The data symbolized by opened circles in Fig.1a are obtained at very high strain amplitude (γ =1000%). Only the viscous modulus is presented, the shear modulus being below the limit of resolution of the device. This behaviour was already observed and illustrated in [3,4] for Glycerol and ordinary polymer melts. It shows the fragility of the solid-like response with respect to the strain parameter and also the experimental difficulty to access to this primary elastic regime. At high strain amplitude, the viscous modulus follows the conventional ω-scale behaviour the slope of which indicating the dynamic viscosity ($G'' = \eta.\omega$). The estimated value (η = 0.011Pa.s at 64°C and 45µm) is in agreement with the usual tabulated values [19].

On Fig.1c, we detail the strain induced transition from solid-like to viscous behaviour, showing separately its effect on the shear and on the viscous moduli. The right inset gathers the results at 10rad/s. These measurements have been carried out at the same temperature as the data of Fig.1a, but at a lower thickness (25µm). The moduli in the linear regime are higher in agreement with the gap evolution presented in Fig.1d. The increase of the strain amplitude produces a lowering of the terminal elasticity which is progressively replaced by the "conventional" behaviour. At high strain and in the high frequency zone (typically above 5 rad/s), the viscous modulus does not evolve anymore with the strain amplitude (see Fig.1a and Fig.1c) exhibiting the onset of the conventional viscous curve scaling as ω.

Fig.1d displays the evolution of the shear modulus of the o-Terphenyl as a function of the gap thickness. As already observed on other materials, the low frequency elasticity is accessible at small gaps only, dependent on the gap thickness and typically measurable for sample thicknesses lower than 50-100µm. At higher gap thickness, the conventional behaviour is recovered exhibiting the usual viscous law, similarly to what is observed at very high strain amplitudes.

The second series of measurements with the o-Terphenyl starts from the supercooled state. Fig.1e displays data obtained at T = Tm – 1.4°C; the predominant elastic character is also established in the supercooled phase. The solid-like response seems to be reinforced compared to values obtained above Tm. The thermal evolution of the elasticity is displayed in the inset of Fig.1e. The low temperature range is hardly accessible since the instrument can be damaged if a crystallisation occurs after long equilibration times or is induced by applying weak strain stresses. At high temperature, the measurement is limited by the balance between the acquisition time and the evaporation time.

The same experimental protocol is applied to polymer melts. Fig.2a illustrates the dynamic behaviour at 90°C above Tg, of a polybutylacrylate of molecular weight (Mw = 47500). This value indicates that the melt is in its entanglement regime (Me = 22000). The study of unentangled polymers has been already considered in [20]. A particular change of dynamic behaviour is observed as the chain length increases. This change is attributed to the occurrence of an entanglement regime above a critical molecular weight $M^* = 2.Me$, where Me is the molecular weight between entanglements. Below M^*, the viscosity varies almost linearly with the chain length and no viscoelastic plateau is observed in the dynamic response. Over M^*, the viscosity obeys to scaling laws with the molecular weight, and the dynamic relaxation response displays a high frequency elastic plateau called "entanglement plateau" or "rubbery plateau"[21, 22, 23]. At low frequency (terminal regime), both (entangled and unentangled) melts of polymer display a flow behaviour characterised by a continuous decrease of both elastic and viscous moduli ($G' \propto \omega^2$, $G'' \propto \omega$). Using the total wetting protocol, Fig.2a shows that a terminal elasticity is observable at low gap thickness. This measurement has been carried out at 25µm but the elasticity remains observable at larger gaps as illustrated in Fig.2b. In all cases, the length scales probed correspond to macroscopic

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dimensions that are several orders higher than the molecular dimensions and thus, the elasticity has to be considered as the result of long range intermolecular interactions.

The evolution of the shear modulus is displayed from 0.025mm up to 0.500mm on Fig.2b. The terminal elastic mode is visible for all these sample thicknesses. It is reinforced by decreasing the gap thickness and disappearing by increasing the gap below the device resolution. At high thickness (above 0.5mm – 1mm for polymer melts), the conventional viscoelastic spectrum is restored displaying the typical flow behaviour. The low frequency elasticity measured in the polymer melt is several decades higher and extended to larger thicknesses compared to the o-Terphenyl. The reinforcement of the elasticity in polymers indicates strongly that its origin is linked to long range intermolecular interactions.

The dependence with the thickness is not trivial and cannot be strictly restricted to a surface effect since the length scales are largely above several molecular lengths. The increase of the volume of the sample is concomitant with the increase of voids, of freedom degrees. Since the transducer measurement is obtained by transmission over the sample thickness (it is a transmission measurement), increasing dissipative contributions (self-diffusion, voids, mobility...) may explain the lowering of the elasticity. Analogies with scaling mechanical properties can be found with cements and foams[24, 25].

Since at low gap, unentangled melts [4] and molecular glass formers display a terminal elasticity, entanglements are thus not at the origin of the rubbery plateau. How to relate this terminal elasticity to the rubbery plateau? Fig.2c displays the evolution of the shear elasticity as a function of the molecular weight.

Unentangled polymers ($Mw < M^*$) display an elasticity that increases rapidly with the molecular weight up to M^*(Fig.2c, yellow part). Beyond ($Mw > M^*$), the elastic modulus does not increase significantly and saturates at a rather constant value of about $G' \approx 8.10^4$Pa. This value merges with the ordinary rubbery plateau $G' = G_N^0$ [20]. Moreover, the transition between these two regimes seems to coincide with the occurrence of the entanglement regime; i.e. $M^* = 2.Me$ ($2.Me$= 44000 for the PBuA [20]). In the frame of these results pointing out that the notion of flow behaviour becomes elusive at low thickness because replaced by a terminal elasticity, it is emphasized that the notion of entanglement and of "entanglement plateau" is also relative and cannot be simply interpreted in molecular terms. Clearly the terminal elasticity, identified in both simple liquid glass formers and from low to high molecular weight polymer melts is a condensed matter property.

4. Conclusions - Discussions

This study of the o-Terphenyl and of entangled polymers confirms the generic character of elastic properties present at a macroscopic scale in the liquid state (length scales up to 0.500mm have been probed with polymers). The measurement of finite shear elasticity at low frequency indicate very long solid-like correlations and implies for the low molecular weight glass former that the α-process cannot be the slowest relaxation process in the liquid state. Similarly, the reptation time of polymers defined in conventional viscoelasticity by the interception at low frequency of the ω and ω^2 scaling of the elastic and viscous moduli, is not the longest time for the melt state of polymers since the flow regime is replaced at low thickness by an elastic plateau.

In the polymer case, the elastic effects are sufficiently strong to provide a solid-like response measurable up to 0.5mm gap thickness and that merges with the high frequency rubbery elasticity at low thickness (0.025mm). The study of several melts ranging from small to high molecular lengths shows that the narrow gap elasticity coincides, via its modulus value ($G' = G_N^0$) to the ordinary rubbery plateau; the elastic and the entanglement forces are

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undistinguishable. The existence of a terminal elasticity in the melt of entangled polymers and of unentangled polymers proves that the notion of entanglements remains vague and that it cannot be considered as a unique origin of the elasticity. This claim is supported by other observations confirming the undefined physical meaning of entanglements[26]. In this frame, a special attention should be paid to theoretical approaches[27] taking into account intermolecular interactions, and not only intrachain statistics (Rouse, reptation). NMR measurements[28] have shown that dominant contributions may be due to interchain forces. More generally, theoretical approaches describing the liquid state [1,29,30] as a condensed matter state predict a finite shear modulus. In this frame, an advanced theoretical development called NEVET [30] is even able to foresee dimensional effects as those observed in the present results. Interestingly, this model explains the supercooled state as an extraordinary expanded crystal-melt phase transition[30].

Solid-state properties in liquids have been already reported mainly due to the pioneering Surface Forces Apparatus measurements[31,32,33] and piezorheometry[34]. Related to surface induced effects or to intrinsic properties, they reveal scale-dependent interactions at molecular scale or at a multiple of that. At a micron scale, the first claim of identification of non-vanishing shear elasticity interpreted as a condensed matter property is due to Derjaguin using the atomic vibration of a piezomembrane to impose the strain. At higher frequencies (10MHz) and using similar techniques, Bund et al report on also on elastic properties in low and medium viscosity liquids[35]. Later, a gel-like behaviour is reported in untangled polymer melts up to 50μm gap thicknesses, but it was interpreted by dynamic heterogeneities (clusters) associated to the glass transition[36]. The present results show that the liquid state of the o-Terphenyl displays a non-negligible and macroscopic *solid-like* character observable at temperatures significantly over the melting point. These observations carried out significantly over the glass transition and the melting point, exclude effect of glass transition clustering[14,36], dusts, of confinement-induced solidification, shear-induced crystallisation near the supercooled state. Very recently, stress-imposed experiments[37] have revealed in the supercooled state a delicate elastic response in the supercooled state of the o-Terphenyl. X-ray photon correlation spectroscopy shows that the analysis of capillary waves of supercooled PPG requires an elastic term in addition to the viscous contribution[8] Other recent developments in dielectric relaxation may indicate a slow relaxation mode so far unidentified[6]. These are converging results; they show that against the common wisdom, the α-relaxation and the reptation time cannot be considered as the terminal relaxation time, i.e. the longest time scale in the sample. The intermolecular interactions and the elastic properties related to these ones contribute to the energy of the condensed matter state. The necessity of applying considerable negative pressures for a solid-vapour transition shows that this energy is not negligible[38]. The finite shear elasticity might be one aspect of this property.

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Figure captions:

Figure1a: Dynamic relaxation response in the liquid phase of the o-Terphenyl displayed at 63.7°C (Tm=56°C) and 45µm (alumina surfaces, plate-plate geometry): - the upper data are measured in the linear regime at 1% strain amplitude (shear modulus *G'(•)*, loss modulus *G"(■)*), - the low value data are measured at high strain amplitudes (500%: *G''(Δ)*, 1000%: *G''(○))*, *G'* is not represented being below the device resolution). The conventional viscous law ($G'' = \eta.\omega$) symbolised by the blue straight line is fulfilled at large strain amplitude.

Figure1b: Upper Photograph: AFM picture of a flat zone of the alumina substrate. The grained relief is produced by the alumina crystallites.
Bottom photograph: alumina fixture setup (20mm diameter) – the gap (filled with liquid OTP) is 45µm.

Figure 1d: Influence of the gap thickness on the shear modulus dynamic response *G'(■)*, in the liquid phase of the o-Terphenyl (OTP) displayed at 66°C (Tm=56°C) (alumina surfaces, plate-plate geometry, strain amplitude γ=1%). The dotted line is an eye guide.

Figure 1c: Strain dependence (non-linear regime) of the shear modulus *G'* (red curves) and viscous modulus *G''* (blue curves) as a function of the strain amplitude (%) measured in the liquid phase of the OTP (T=64°C). The strain amplitude is indicated on the left extremity of each curve. The dotted line symbolises the ω-scaling dependence. The gap is 25µm. The right inset points out the opposite strain-induced evolution of the elastic modulus *G'(•)* and of the viscous modulus *G'(•)* at 10rad/s.

Figure 1e: Dynamic response obtained in the supercooled phase of the OTP at 54.6°C (T = Tm – 1.4°C) and 45µm gap thickness (alumina surfaces, plate-plate geometry). Data measured at 1% strain amplitude (shear modulus *G'(•)*, loss modulus *G"(■)*) are superposed to those determined at 3% (shear modulus *G'(◊)*, loss modulus *G"(○)*). The inset in the figure displays the evolution of the shear modulus as a function of the temperature.

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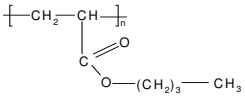
Figure 2b: Solid-like dynamic response observed at low frequency in the melt state of an entangled Polybutylacrylate sample *(PBuA Mw=47500)* at 25°C and at 25µm.

Figure 2c: Influence of the gap thickness *e*, on the shear modulus *G'* of the Polybutylacrylate sample *(PBuA Mw=47500)* at 25°C and at 25µm. The dotted line is an eye guide.

Table 1:

o-Terphenyl (OTP)	**Polybutylacrylate (PBuA)**					
Tg= -30± 1°C, *Tm*=56°C	 *Me*=22000; Tg=-64°C					
Molecular weight: 230	Molecular weight: Polydispersity:	13500 1.10	20000 1.10	25700 1.08	47500 1.08	91000 1.18

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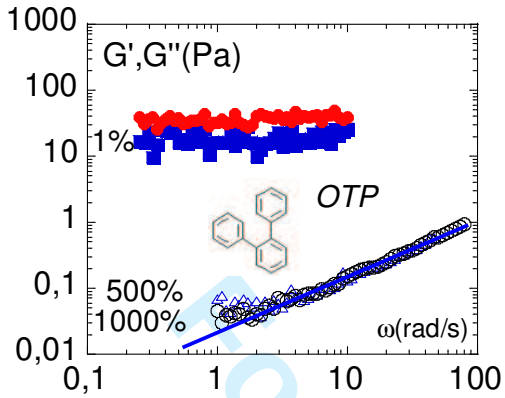

Figure 1a

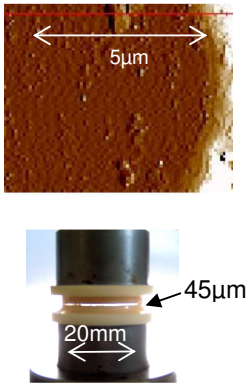

Figure 1b

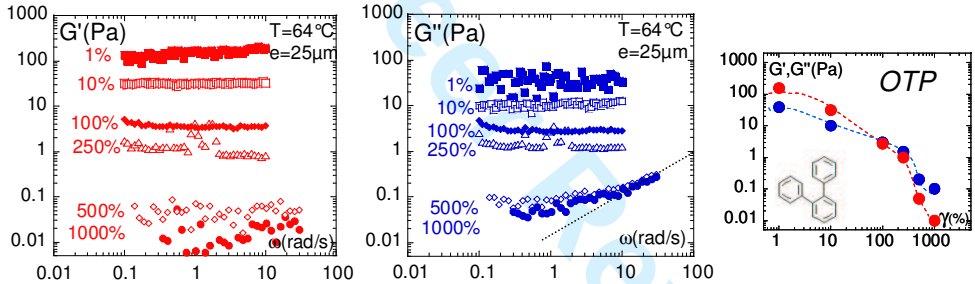

Figure 1c

Influence of the thickness gap

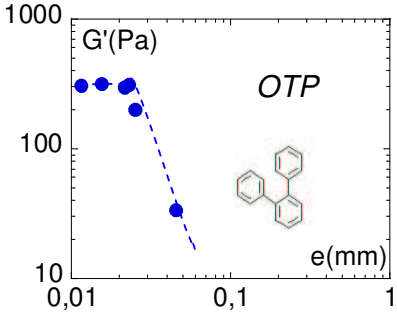

Figure 1d

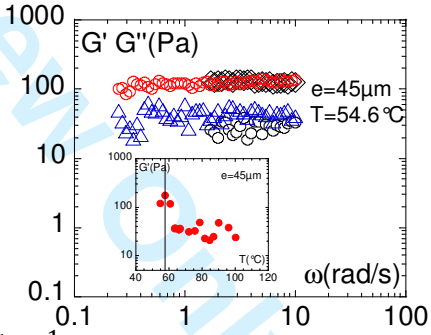

Figure 1e

Influence of the thickness gap

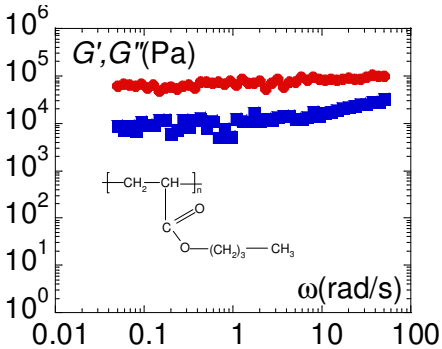

Figure 2a

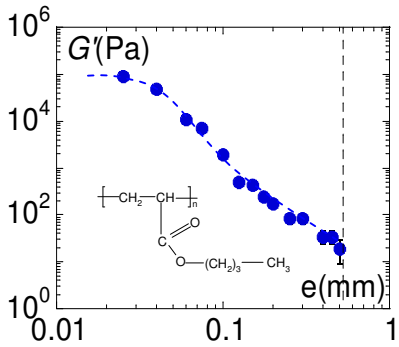

Figure 2b

Influence of the molecular weight

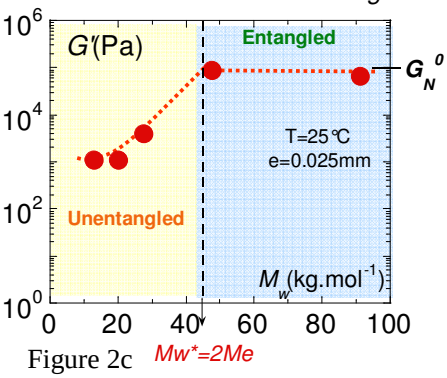

Figure 2c

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Short biographical notes:
Laurence Noirez is CNRS Research Director.
Hakima Mendil-Jakani is CEA senior scientist.
Patrick Baroni is CNRS Engineer.

References:

[1] Granato A.V., J. de Physique IV, C8 6 (1996) p.1.

[2] Baroni, P., Mendil, H., Noirez, L., Fr. Pat., 05 10988, (2005), P. Baroni, H. Mendil-Jakani, L. Noirez, *Techniques de l'Ingénieur*, TI Editions, 1 (2010) RE145.

[3] L. Noirez, P. Baroni, J. of Molecular Structure, 972 (2010) p.16.

[4] H. Mendil, P. Baroni, L. Noirez, *Eur. Phys. J. E* 2006, 19, p.77.

[5] J. Goyon, A. Colin, G. Ovarlez, A. Ajdari, L. Bocquet, Nature, 454 (2008) p.84, J. Goyon, A. Colin and L. Bocquet, DOI: 10.1039/c001930e.

[6] H. Jansson, R. Bergman, J. Swensson, Phys. Rev. Lett. 104 (2010) p.17802.

[7] U. Tracht, M. Wilhelm, A. Heuer, H. Feng, K. Schmidt-Rohr, H.W. Spiess, Phys. Rev. Lett. 81 (1998) p.2727.

[8] Y. Chushkin, C. Caronna, A. Madsen, A., EPL, 2008, 83, p.36001.

[9] E.C. Fuchs, P. Baroni, B. Bitschnau, L. Noirez, J. of Physics D, 43 (2010) p.105502.

[10] S.S. Chang, A.B. Bestul, J. Chem. Phys. 56 (1972) p.503.

[11] I. Lugoski, Karle, L.O. Brockway, JACS, 66 (1944) p.1974.

[12] M.D. Ediger, C.A. Angell, S. R. Nagel, J. Phys. Chem. 100 (1996) p.13200.

[13] G.P. Johari M. Goldstein, J. Chem. Phys. 53 (1970) p.2373.

[14] W. Steffens, A. Patkowski, G. Meier, E.W. Fischer, J. Chem. Phys. 96 (1992) 4171, E.W. Fischer, Physica A 201 (1993) p.183.

[15] F. Fujara, B. Geil, H. Sillescu, G. Fleischer, Z. Phys. B 88 (1992) p.195.

[16] W. Petry, E. Bartsch, F. Fujara, M. Kiebel, H. Sillescu, B. Farago, Z. Phys. B 83 (1991) p.175.

[17] T. Young, *An essay of the cohesion of fluids*, Philos. Trans. Soc., London, 95 (1805) p.65; P.G. de Gennes, F. Brochard-Wyart, D. Quéré, "*Gouttes, bulles, perles et ondes*", Belin Ed. 2005.

[18] D. Tolstoï, Molecular Theory for slippage of liquids over solid surface, Doklady Akad. Nauk. SSSR 85 (1952) p.1089.

For Peer Review Only

[19] W. H. Hedley, M. V. Milnes, W. H. Yanko, *J. Chem. Eng. Data*, 15 (1) (1970) p.122.

[20] H. Lakrout, C. Creton, D. Ahn, K.R. Shull, *Macromol*. 34 (2001) p.7448.

[21] J.D. Ferry, Viscoelastic properties of polymers, Wiley 1971; W. Graessley, Adv. Poly. Sci. 16 (1974) p.1; Graessley, Polymer 21 (1980) p.258.

[22] J. Rault, J. Non-Newtonian Fluid Mechanics 23 (1987) p.229.

[23] M.D. Ediger, C.A., Angell, Nagle S.R., J. Phys. Chem. 100 (1996) p.13200.

[24] Z.P. Bazant, *Scaling of Structural Strengths*, Hermes Penton Science, London, 2002.

[25] J.P. Heller and M.S. Kuntamukkula, Ind. Eng. Chem. Res. 26 (1986) .318.

[26] J.A. Martins, Macromol. Theory Simul. 19 (2010) p.360.

[27] J.P. Ibar, *J.M.S. –Rev. Macromol. Chem. Phys*., C37 (1997) p.389.

[28] P. Sotta, B. Deloche, J. Herz, A. Lapp, D. Durand, J.-C. Rabadeux, *Macromol.*, 20 (1987) p.2769.

[29] A.V. Granato., Materials Science and Engineering A 521 (2009) p.6.

[30] F. Volino, Annales de Physique, 22 n°1 & 2 Chapter VI (1997).

[31] Hu H.-W.,Carson, Granick S. *Phys.Rev.Lett*., 1991, 66, 2758; Zhu Y., Granick S. *Phys. Rev. Lett.*, 93 (2004) p.0961011; J.N. Israelachvili, P.M. Mcguiggan, A.M. Homola, *Science* 240 (1988) p.189.

[32] J.N. Israelachvili, R. Pashley, *Nature* 300 (1982) p.341.

[33] A. Maali., T. Cohen-Bouhacina, G. Couturier, J.P. Aimé, *Phys. Rev. Lett.*, 96 (2006) p.861051.

[34] B.B. Badmaev., U.B. Bazaron, B.V. Derjaguin, O.R. Budaev, Physica B 122 (1983) p.241, B.V. Derjaguin, U.B. Bazaron, K.T. Zandanova, O.R. Budaev *Polymer*, 30 (1989) p.97.

[35] A. Bund, G. Schwitzgebel, Anal. Chem. 70 (1998) p.2584.

[36] D. Collin, P. Martinoty, *Physica* A, 320 (2002) p.235.

[37] R. Zondervan, T. Xia, H. van der Meer, C. Srorm, F. Kulzer, W. van Saarloos, M. Orrit. PNAS, 105 (2008) p.4993.

[38] A.R. Imre, Phys. Stat. Sol. 244 (2007) p.893.

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