Identification of Gel-Like Behaviour in Side-Chain Liquid Crystal Polymer Melts

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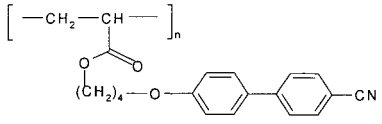
Summary: We show through extensive rheological studies that Side-Chain Liquid Crystalline Polymer melts reveal an unexpected and surprising strong elasticity instead of a classical flow behaviour. Neutron Scattering experiments demonstrate that this elastic plateau cannot be correlated to the long range order of the nematic phase.

Keywords: birefringence; gel behaviour; liquid-crystalline polymer; neutron scattering; non-linear viscoelasticity; shear induced transitions

Introduction

Thermotropic Liquid Crystal Polymers (LCPs) are attractive materials both to academic research and to industrial applications [1]. The present letter is focused on side-chain LCPs. In such a case, the liquid crystal molecules are grafted, for example as an ester group, on the side of an ordinary polymer chain.

Here we report on a comparative analysis of the mesophase structure carried out by neutron scattering with an extensive non-linear rheological investigation. The polymer chosen is a low polydisperse liquid crystalline polyacrylate (PACN) of chemical formula:



Mw =91 000 g.mol^{-1}, Ip=1.1

It displays the following mesophase sequence: *I(isotropic) - 119°C – N(nematic) - 30°C - Glassy state* (temperatures determined by Differential Scanning Calorimetry).

These rheological studies reveal a spectacular and unexpected cohesion within the melt. This striking behaviour demonstrates that LCP melt behaves as a gel. The shear induced nematic-isotropic phase transition identified in 2001[2] on Side-Chain-LCP melts can be explained as a consequence of the deformation of an elastic structure. Neutron Scattering measurements demonstrate that the gel behaviour cannot be due to the long range order of the mesophases.

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Rheology

Viscoelastic measurements were carried out with an ARES rheometer equipped with an air-pulsed oven and used in dynamic frequency sweep mode. This thermal environment ensures temperature control within 0.1°C. The samples were placed between a cone-plate fixture (20mm diameter and angle 2.25°) and thermalised during several hours before starting the measurements.

Figure 1 displays the typical frequency dependence of the elastic modulus $G'(\omega)$ and $G''(\omega)$ at strain amplitudes from γ=1 up to 100%. The rheological spectrum reveals a completely new behaviour: the LCP exhibits a pseudo-solid-state behaviour instead of a classical flow regime.

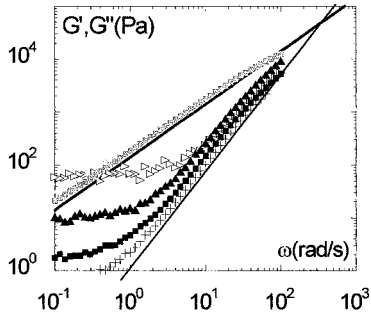

Figure 1. Frequency dependence of the viscoelastic moduli ($G'(\omega)$ and $G''(\omega)$) at $T-T_{NI}=\Delta T=+1°C$ (cone-plate geometry (20mm diameter and angle 2.25°)) at different strain amplitude γ :(▷)1% (▲)5% (■)50% (+)100%. The straight lines display the extrapolation to ω and ω^2 scaling.

At low strain (γ=1%) the magnitude of the elastic plateau G_p' reaches 10^2Pa. The larger the strain amplitude, the lower is G_p'. It defines a non-linear frequency regime. In such conditions, the time-temperature superposition fails. The extrapolation of $G'_p(\gamma)$ to zero strain rate gives an estimation of the non-disturbed structure; $G'_0(\gamma=0)$ is about $10^{5\pm1}$Pa. This elasticity persists below (-14°C), through and far above (at least +15°C) the Isotropic-Nematic transition temperature T_{NI}. The high magnitude of the elastic plateau, its persistence through and far from the transition indicate that this gel behaviour should not be coupled with pretransitional dynamics [3].

Except true rubbers, systems known to display low-frequency elastic plateaus are heterogeneous. This is the case of gelation processes, for instance in associative polymer systems or in copolymer solutions (G_p'#10^4Pa) [4]; viscoelastic emulsions (G_p'#10^2-10^3Pa) [5]. In these examples, the low frequency elastic plateau comes out from an heterogeneous structure or a transition ordering. Such arrangement is starting at local scale and propagating to the whole sample. Our system is fundamentally different since it is chemically homogeneous. We observe a novel type of cohesion not due to chemical heterogeneities or a cross-linking. We checked of course that the molar weight unchanges before and after the rheological investigations.

At high frequency and high strain, the classical polymer melt behaviour is recovered: $G''(\omega)$ and $G'(\omega)$ fit with ω and ω^2 scaling respectively. The non-linearity shows that the gel-like behaviour becomes viscoelastic under increasing strain; we propose to describe the elastic modulus behaviour by two terms: $G'(\omega,\gamma) = G'_p(\gamma) + \eta.\tau_{term}.\omega^2/(1 + \omega^2.\tau^2)$ where τ_{term} is the viscoelastic terminal time. The first term accounts for the non-linear elasticity, whereas the second contains the conventional viscoelastic contribution. τ_{term} is deduced from the intersection of the two straight lines; $\tau_{term}(\Delta T=+1°C) \cong 4.10^{-3}$s where ΔT is the temperature interval $T-T_{NI}$. The insensitivity of $G''(\omega)$ down to 10rad/s indicates that the material keeps a viscous component coherent with a gel behaviour.

This observation leads to the conclusion that this cohesion is apparently not reminiscent from the mesophases. Is it connected to a supramolecular structure unrevealed till yet? Neutron scattering measurements are carried out to characterize the structural organization within the liquid crystal melt over a wide range of temperature below and above the Isotropic-Nematic transition.

Neutron Scattering

Small Angle Neutron Scattering (SANS) was performed on the PAXY spectrometer of the Laboratoire Léon Brillouin. A wavelength of 4Å and a sample-multidetector distance of 1,5m were chosen. A magnetic field of 1.4T was used to ensure the alignment of the sample.

The identification of structural arrangements and of their temperature dependence can be characterized by diffraction. We will show that the evolution of the structure of the mesophases is independent of the non-linear elasticity exhibited by the sample.

Figure 2 displays the 2D-SANS pattern obtained at ΔT=-20°C.

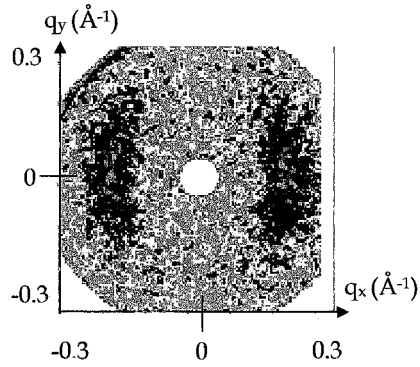

Figure 2. 2-D neutron scattering pattern (sample-detector distance: 1.5m, wavelength: 4Å covering a scattering range from 0.03Å^{-1} up to 0.3Å^{-1} displayed at ΔT=-20°C (nematic phase) by a monodomain sample oriented with the director parallel to the Ox axis (PAXY spectrometer at the LLB).

In the reciprocal space, we observe a diffracted intensity at a distance d=2π/q=28.6Å. It is due to S_{Ad} smectic fluctuations within the nematic phase. Since the molecular length of the mesogen is about 17Å, it corresponds to a partial overlap.

On Figure 3, the amplitude and the scattering vector of the S_{Ad} smectic fluctuation intensity are reported as a function of the temperature. As already reported [6] in systems displaying monolayer smectic phase (S_{A1}), the scattering vector amplitude slightly increases with the temperature. It has been interpreted in terms of restriction of the motion of the side-chain. The intensity of the smectic fluctuations decreases as the temperature increases: the local mesogen arrangement leading to a local smectic order weakens. At the Isotropic-Nematic temperature transition, this intensity drops close to zero and the associated scattering vector diverges as expected.

The scattering pattern above the I-N transition looks similar to every ordinary isotropic phase of liquid crystals and does not contain any information on structural arrangement within this scattering observation window. In contrary, as previously discussed, the elastic plateau is insensitive to the I-N transition. Both antagonist behaviours demonstrate that the elastic plateau cannot be correlated to the long range nematic order or other supra molecular arrangement.

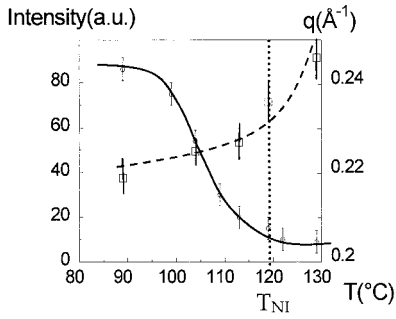

Figure 3. Diffracted intensity and scattering vector of the S_{Ad} smectic fluctuations as a function of the temperature. One can notice the abrupt decrease of the intensity and increase of q at the Isotropic-Nematic temperature transition. The straight, dotted and dashed lines are guides for the eyes.

Conclusions

Instead of a conventional flow behaviour, we have observed a strong cohesion within the liquid crystal polymer melt. These observations imply that extra long length and time scales exist. The confrontation with the structural study by neutron diffraction shows that this huge elasticity does not originate from mesomorphic properties. This is a melt property which should be observable in other viscoelastic materials [7] .

This study extends at a macroscopic scale and in the non-linear regime, the very interesting pioneering work evidencing a gel-like behaviour in polymers on low thickness samples [8]. Far above phase and glass transitions, these long range interactions may explain spectacular non-linear phenomena as the shear induced Nematic-Isotropic phase transition in LCPs [2]. This transition is revealed by the abrupt emergence of birefringence above a critical shear rate $\dot{\gamma} > \dot{\gamma}^*$ (Fig.4). Figure 4 illustrates the evolution of the birefringence at ΔT=+1°C in steady shear conditions. To explain such a phenomenon, a direct coupling with the life time of the pretransitional fluctuations is not relevant [3,9]. A coupling with the viscoelastic terminal time τ_{term}, is also not satisfying since $1/\dot{\gamma}^*$ is significantly larger than $\tau_{term}(\Delta T=+1°C) \cong 4.10^{-3}$s. A classical approach is not sufficient to elucidate neither the huge melt cohesion nor the spectacular shear induced transition. Any theoretical attempt should indeed account for the following time scale cartography: $1/\dot{\gamma}^* >> \tau_{term} > \tau_{fluc}$. Although the liquid crystal polymer melt does not correspond to the definition of an entangled melt (low degree of polymerisation and absence of rubbery

plateau at high frequency), theories developed for elastomers [10] and for branched polymers [11] could be very challenging approaches for the understanding of these non-conventional behaviours.

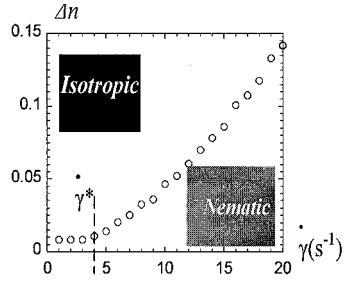

Figure 4. At $T=T_{NI}$ +1°C and $\dot{\gamma} > \dot{\gamma}^*$, emergence of the shear induced nematic phase within the isotropic phase (observation between cross-polarisers, plane: velocity, neutral axis, gap thickness e=100μm).

Acknowledgements

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