

Abnormal Viscoelastic Behavior of Side-Chain Liquid-Crystal Polymers

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We show that, contrary to what is commonly believed, the isotropic phase of side-chain liquid-crystal polymers has viscoelastic properties which are totally different from those of ordinary flexible melt polymers. The results can be explained by the existence of a transient network created by the dynamic association of mesogenic groups belonging to different chains. The extremely high sensitivity of the compound to the state of the surfaces with which it is in contact offers us an unexpected method of studying surface states.

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Side-chain liquid-crystal polymers (SCLCP) are composed of a polymer chain onto the sides of which mesogenic molecules have been grafted using a flexible chain called a spacer [1]. This physical link between the mesogenic groups and the polymer chain should in theory make the "polymer" characteristics (viscosity, elasticity) anisotropic, and modify the order of magnitude of the purely "liquid-crystal" characteristics (torsional viscosity γ_1 , curvature elastic constants). The Fredericks transition experiments [2] and the transient electrical birefringence experiments [3,4] performed in the nematic and isotropic phases show that the static properties of these mesophases are close to those of conventional liquid crystals (no substantial modification of either the birefringence or the curvature elastic constants), while their dynamic properties are essentially governed by the chains themselves (increase of viscosities and relaxation times). A certain number of rheology experiments have also been carried out [5], and these confirm that the presence of the liquid-crystal order has no significant role to play in the dynamics of the nematic and isotropic phases, which consequently have viscoelastic properties which are qualitatively similar to those of ordinary flexible polymers. However, these experiments have not revealed the rubbery plateau which is characteristic of entanglement effects, and which is replaced by an extended distribution of relaxation times the origin of which is unknown. The polymer's polydispersity or/and a relaxation of the mesogenic groups have been invoked to explain this distribution [5].

In this Letter, we present new experiments realized

with a rheometer, which enabled us to study orientated samples with very low shear strains. The results obtained reveal a viscoelastic behavior which is quite different from that of conventional polymers, and this suggests the existence in the melt of elastic clusters of varying sizes up to 100 μm . We will also show that the rheological behavior observed is extremely sensitive to the state of the surfaces in contact with the sample.

The experimental setup was inspired by that previously developed by Cagnon and Durand in their study of the plastic behavior of certain lamellar liquid crystals [6]. The sample, of thickness e between 13 and 120 μm , is placed between two glass or silica slides, adjusted for parallelism to within $\pm 5 \times 10^{-4}$ rad. The sample can be observed *de visu* through an aperture. A sine wave displacement with an amplitude between 1 and 500 \AA is applied to one surface of the sample using a piezoelectric ceramic. The amplitude and dephasing of the transmitted stress are measured on the other surface by an identical ceramic. The stress-over-strain ratio gives the complex rigidity modulus $G^* = G' + iG''$. The cell is thermostatically controlled to within 0.02 $^\circ\text{C}$, and placed on a vibration-free table. For all the experiments, we checked that the compound gave a linear response as a function of the distortions applied, up to a maximum of 3×10^{-3} . The setup was tested on a silicone elastomer of known rigidity modulus.

The polymer studied is the one used in transient electrical birefringence experiments [4]. The polymer chain is a polysiloxane, and the mesogenic groups have the formula $(\text{CH}_2)_6\text{-O-}\varnothing\text{-CO}_2\text{-}\varnothing\text{-O-CH}_3$. The phase diagram of the compound is as follows:

glass-3 $^\circ\text{C}$ \rightarrow smectic C (SmC)-46 $^\circ\text{C}$ \rightarrow nematic (N)-108 $^\circ\text{C}$ \rightarrow isotopic (I).

The molecular weight of the compound is $M_w = 31\,000$, its polydispersity $M_w/M_n = 1.1$, and its polymerization degree $N = 80$.

Two types of experiments were carried out: experiments as a function of the state of the surface of the sample-bearing slides, and experiments as a function of sample thickness.

The influence of the state of the surface of the sample-bearing slides on the compound's response was tested by using silica slides polished with felt (standard quality), or pitch (to $\lambda/4$), floating glass slides, and glass slides scratched in a given direction with diamond-based paste. For the thickness experiments, the minimum thickness of $13\ \mu\text{m}$ was used first. The cell gap was then increased using calibrated spacing shims, without touching the surface of the sample-bearing slides so as not to alter the wall anchoring. In order to keep the sample in permanent contact with the same part of the slides, extra product was injected for each new thickness.

Although measurements were taken in all phases, most of the results given below only concern the isotropic phase. This is in order to facilitate discussion, since in this phase measurements are not affected by any problem arising from the influence of orientation quality.

For all the experiments, the compound was introduced into the cell which had been heated to 150°C , and the first measurements taken at 129°C , i.e., about 21°C above the NI transitions temperature, after being annealed for 12 h at this temperature.

We shall first of all present the results obtained by varying the state of the surface of the sample-bearing slides, the cell having a gap of $13\ \mu\text{m}$.

With sample-bearing slides made of ordinary felt-polished silica (standard manufacturer's polishing), the isotropic phase reveals a low-frequency elastic response characterized by the existence of a static rigidity modulus G_s of the order of $10^4\ \text{N/m}^2$, and a loss angle δ close to 0° . This behavior is totally unexpected, since the isotropic phase has always been described as a fluid phase with the characteristic low-frequency response of viscoelastic fluids ($G' \propto \omega^2$ and $G'' \propto \omega$ when $\omega \rightarrow 0$). This abnormal behavior is our fundamental result, and the remainder of the article is devoted to determining and discussing its origin.

In order to determine whether it is the microgrooves from the felt polishing which induce the low-frequency elastic behavior, we used particularly smooth slides, made of floating glass of silica polished to $\lambda/4$. In this case, modulus G_s drops sharply to values as low as some $10^2\ \text{N/m}^2$, which are at the limits of measurability with our experimental setup.

Having thus established the influence of grooves, we intentionally scratched the surface of the floating glass slides in a given direction, using a diamond-based paste ($0.25\ \mu\text{m}$). The results obtained show that the response of the compound depends on the orientation of the scratches in relation to the shear direction. This is shown by Fig. 1, also obtained with a $13\ \mu\text{m}$ sample, which shows that the low-frequency response of the compound is either elastic or viscous, depending on whether the scratches are perpendicular or parallel to the shear direction. The same figure also shows that the value of the rigidity modulus has increased by 2 orders of magnitude in comparison with the case corresponding to the ordinary

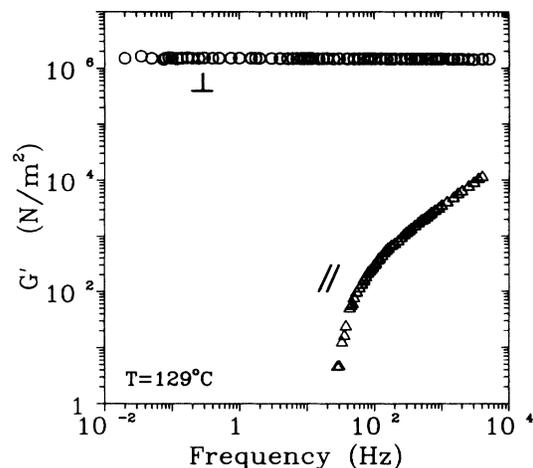


FIG. 1. Frequency behavior of the real part of the complex rigidity modulus, showing the existence of an elastic or viscous behavior, according to whether the sample-bearing slides have grooves which are perpendicular to the shear (upper curve) or parallel to the shear (lower curve).

silica slides. All measurements were taken at 129°C . Those taken at lower temperatures show that the rigidity modulus slightly increases as temperature decreases, which indicates that it is only weakly coupled to the local orientational order, which strongly increases as $T \rightarrow T_{NI}$. Further measurements are necessary to determine whether this slight variation with temperature is a critical effect. The measurements taken in the N phase (oriented by the influence of the scratches) on the same $13\ \mu\text{m}$ cell reveal, as in the isotropic phase, the existence of a low-frequency rigidity modulus when the scratches are perpendicular to the shear. The very slight variation of this modulus with temperature indicates that this latter is not very sensitive to the orientational order of the nematic phase.

We shall now present the experiments conducted as a function of sample thickness. The results obtained on the cells using sample-bearing slides with grooves perpendicular to the shear show that the value of the static rigidity modulus G_s decreases gradually as sample thickness e increases, as indicated in Fig. 2, and that it cannot be measured at the $120\ \mu\text{m}$ thickness. This gradual fall of the elastic rigidity modulus as sample thickness e increases indicates that the compound is neither a viscoelastic solid, nor a yield-stress liquid of the Bingham type. Figure 2 also shows that the low-frequency elastic behavior disappears gradually as a frequency increases, to be replaced by a viscoelastic behavior. This change in behavior occurs at a frequency which is all the lower as sample thickness increases, and ceases to be observable for the $120\ \mu\text{m}$ sample which is characterized by a $\omega^{0.8}$ law. The experiments on slides with grooves parallel to the shear show that G' also follows a $\omega^{0.8}$ -type power law when the sample thickness is greater than $20\ \mu\text{m}$. This peculiar be-

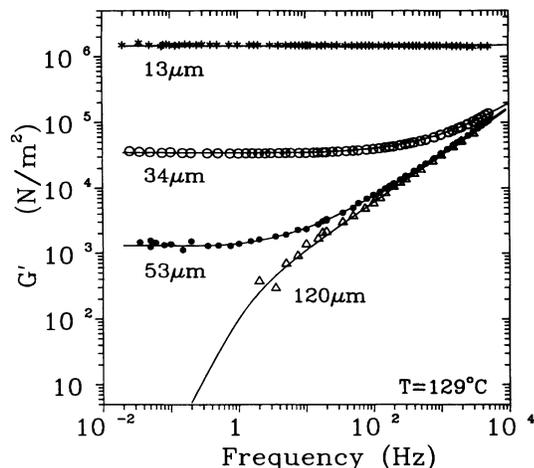


FIG. 2. Behavior of the real part of the rigidity modulus, for various sample thicknesses, when the sample-bearing slides have grooves which are perpendicular to the shear. The solid curves show the fit by Eq. (1).

havior of G' , which appears to be intrinsic to the compound, cannot be associated with either a polydispersity effect, which is weak for our compound, or a relaxation of the mesogenic groups, since the characteristic time determined by transient electrical birefringence corresponds to frequencies higher than 10 kHz [4]. It can be compared to that observed by Colby *et al.* [5] in conventional rheology experiments on a polyacrylate ($N=90$) and a polymethacrylate ($N=328$). These experiments show that, between the low-frequency terminal region and the high-frequency elastic response, there exists a wide range of relaxation times, characterized by $G' \propto \omega^{0.75}$ ($N=90$) and $G' \propto \omega^{0.67}$ ($N=328$).

Our results pose three questions: What is the origin of the low-frequency elastic modulus for thin samples? What mechanism is responsible for the $\omega^{0.8}$ -type viscoelastic behavior? Why does the compound's response depend on the orientation of the grooves in relation to the shear direction? We propose a model capable of answering these three questions, which is based on the hypothesis that the compound consists of elastic clusters of various sizes, separated by viscous regions. In such conditions, the response of the compound is elastic as long as sample thickness remains less than the size of the largest clusters. If this is not the case, the response is that of a viscoelastic liquid with a distribution of relaxation times whose width is a reflection of the number of clusters relaxing. This model requires the existence of two antagonistic mechanisms, one allowing a network to form, the other limiting the spatial extension of such a network (via defects, for example). This network is unlikely to be associated to the presence of entanglements, because of the low mass of polymer studied, and the absence of any rubbery plateau in the response of the compound when

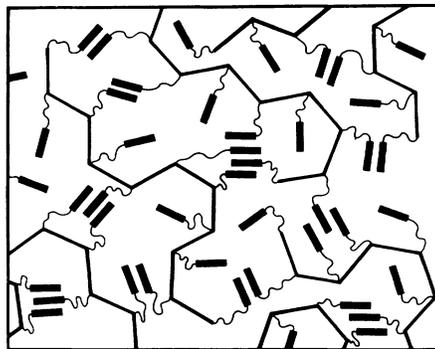


FIG. 3. Schematic representation of a network structure created by the temporary association of mesogenic groups belonging to different chains.

the slides have grooves which are parallel to the shear. On the other hand, an effect of dynamic association of the mesogenic groups, similar to that shown in Fig. 3, would allow a network to form without it being necessary for the polymer coils to become entangled [7]. Only a strong dynamic anchoring to the surface, which would result in elastic coupling between the slides and the compound, could reveal the elastic behavior. This anchoring occurs when the slides have grooves which are perpendicular to the shear. The molecules are then trapped by the grooves, and obliged to follow any movement of the sidewall. If the dynamic anchoring is only weak (smooth surfaces, or slides with grooves parallel to the shear), then sliding takes place at the sidewalls, and the compound has a response of the viscoelastic liquid type with an apparent rigidity modulus which is given by $G'_{app} = G'_{slid} + G'_{comp}$. In the case of thin samples ($e < 20 \mu\text{m}$) the measured rigidity modulus is essentially G'_{slid} . With thicker samples, the viscous effects associated with the sliding become negligible, and the measured rigidity modulus can be identified with the intrinsic rigidity modulus G'_{comp} which scales as $\omega^{0.8}$.

We shall now determine the apparent rigidity modulus G'_{app} of the compound. We shall call S the total area of the sample and s the area of elastic regions (with a rigidity modulus G_0) in simultaneous contact with the two slides; $S-s$ then represents the sidewall area of the viscoelastic regions. We shall assume that these regions can be modeled with a Cole-Davidson type law usually used to describe liquids which are characterized by a distribution of relaxation times [8]. Parallel association of the elastic and viscoelastic regions gives the following equation for the apparent rigidity modulus:

$$G'_{app} = \chi G_0 + (1 - \chi) \frac{\omega \eta \sin \beta \theta}{(1 + \omega^2 \tau^2)^{\beta/2}}, \quad (1)$$

where $\chi = s/S$, η is the viscosity of the viscous parts, τ a relaxation time, and β an exponent comprised between 0 (infinite relaxation time) and 1 (a single relaxation time).

θ is defined by $\theta = \arctan(\omega\tau)$. The static rigidity modulus G_s is given by $G_s = \chi G_0$. We have assumed that χ varies with thickness e according to the law $\chi(e) = \exp(-e/k)$, which verifies the boundary conditions $\chi(0) = 1$ and $\chi(\infty) = 0$. k is a positive number.

Analysis of the variation of G_s with thickness e enables G_0 and k to be determined: $G_0 = 1.4 \times 10^7$ N/m² and $k = 5.7$ μ m.

Equation (1) enables the variation of G' to be analyzed as a function of frequency. Since G_s is known from the previous analysis, there are only three adjustable parameters: η , τ , and β . These have been determined using data for the 53 μ m thickness, chosen since it represents solid and viscoelastic liquid behaviors in comparable proportions. The values obtained, $\eta = 86$ Pas, $\tau = 0.15$ s, and $\beta = 0.29$, were used to plot G' at other thicknesses, represented as solid lines in Fig. 2. The good fit [9] to the experimental plot, obtained without adjustable parameters, indicates that the proposed model gives a satisfactory account of our observations. More especially, the 120 μ m plot shows that, in the case of greater thicknesses, conventional flow behavior $G' \propto \omega^2$ reappears at low frequencies ($\omega\tau \ll 1$).

In summary, this article shows that the dynamic properties of side-chain liquid-crystal polymers are completely original, and resemble neither those liquid crystals of low molecular weight, nor those of conventional flexible polymers. The results bring up new questions, the most acute being that of the solid-type behavior observed at low frequencies. This would appear to be a general behavior, at least for low-mass polymers, having also been observed on a polymethacrylate with a polymerization degree of 56. We hope that these results will encourage elaboration of a theory which would allow us to understand why the transient network is spatially limited. Our results also show that SCLCPs are extremely sensitive to the state of the surfaces in contact with the sample, since the presence or absence of a strong dynamic anchoring with the sidewall involves a radical change in the behavior observed: viscoelastic in the case of sliding, elastic solid in

the other case. SCLCP can therefore serve as an unexpected means of studying surface effects. Finally, it should be pointed out that the slight distortions undergone by the samples make our setup appropriate for studying systems with a fragile organization.

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- [1] See, for example, *Side-Chain Liquid Crystal Polymers*, edited by C. B. McArdle (Blackie, Glasgow, 1989).
 - [2] P. Fabre, C. Casagrande, M. Veyssie, and H. Finkelmann, *Phys. Rev. Lett.* **53**, 993 (1984).
 - [3] V. Reys, Y. Dormoy, J. L. Gallani, P. Martinoty, P. Le Barny, and J. C. Dubois, *Phys. Rev. Lett.* **61**, 2340 (1988).
 - [4] V. Reys, Y. Dormoy, D. Collin, P. Keller, and P. Martinoty, *J. Phys. II (France)* **2**, 209 (1992).
 - [5] See, for example, R. H. Colby *et al.*, *Liquid Crystals* **13**, 2 (1993); and **13**, 233 (1993), and references therein.
 - [6] M. Cagnon and G. Durand, *Phys. Rev. Lett.* **45**, 1418 (1980).
 - [7] The fact that G_s varies slightly with temperature could be explained by assuming that the rise in the local orientational order has the effect of increasing the number of molecules which constitute a "bridge," without significantly modifying the number of bridges (cf. Fig. 3).
 - [8] See, for example, A. J. Matheson, *Molecular Acoustics* (Wiley-Interscience, London, 1971).
 - [9] We have used the values of e deduced from the analysis of the variation of G_s with thickness. The difference between these values and those measured is systematically within experimental limits ($\pm 3\%$).