Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 20 Apr 2011.

To cite this article: Sun Zheng-min & M. Kléman (1984): Measurement of the Three Elastic Constants and the Shear Viscosity γ_1 in a Main-Chain Nematic Polymer, Molecular Crystals and Liquid Crystals, 111:3-4, 321-328

To link to this article: http://dx.doi.org/10.1080/00268948408072441

Mol. Cryst. Liq. Cryst., 1984, Vol. 111, pp. 321–328
0026-8941/84/1114–0321/$15.00/0

Printed in the United States of America

Measurement of the Three Elastic Constants and the Shear Viscosity γ_1 in a Main-Chain Nematic Polymer

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(*Received March 26, 1984*)

K_1, K_2, K_3 and γ_1 have been measured for the first time in a typical main-chain polymer belonging to a polyester series. K_1 is very large compared to conventional nematics, while K_2 and K_3 have more conventional values. K_1 have been measured by two methods, one of them consisting in the measurement of the characteristic rise time of regular striped domains.

INTRODUCTION

In the last several years chemists have successfully synthetized a number of liquid crystalline polymers (LCP) whose physical properties differ in many respects from those of conventional thermotropic liquid crystals. This is examplified in a number of studies concerning mostly nematic phases, like DSC measurements, miscibility studies in isotropic solvants and conventional nematics, X-Ray diagrams, dielectric properties, measurement of the order parameter, etc . . . Clearly, the molecular weight, the length of the flexible parts in the polymeric chain, the conformation of the chain itself (main-chain polymers and side-chain polymers behave differently) . . . , play a role. The reader might consult ref [1] and [2] for details. However this important experimental knowledge has hardly opened yet to structural models,

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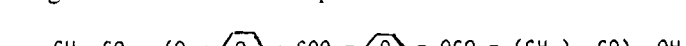
and is sometimes subject to criticism, since factors like high viscosities, polydispersity, chemical degradation, might cast some doubt in some cases on the reality of the equilibrium state which is studied. This makes all the more wanting a better knowledge of the structural properties.

In this respect, studies of defects, textures, and measurements of viscoelastic constants constitute an essential methodological approach, to which this paper aims to contribute at a modest level. Let us remind that, in what concerns nematic phases, the few existing structural models agree on the prediction of a large splay constant K_1 in main-chain polymers, proportional to the length L of the chain[3], or to[4] L^2, according to whether entropic contributions[3] or elastic ones[4] are stressed. On the other hand, K_2 and K_3 should not differ markedly from their values in conventional nematics. Friction coefficients are expected to scale like[4] L^2.

This paper reports on the measurement of K_1, K_2, K_3 and γ_1 in a main chain nematic polymer belonging to a isomorphic series of polyesters synthetized by Strzelecki and Liébert[5] and whose textures and defects have been studied by Kléman et al.[6] From this study it was inferred that K_1 is very large, while K_2 and K_3 are smaller, with $K_3 > K_2$. The present results will partly corroborate these conclusions, especially in what concerns K_1.

The general formula of our produce is:



with $n = 5$ and $x \sim 24$.

Our method of measurement uses the static and dynamic Freederickx transition under a magnetic field; specifically, we follow the method described in [7] for K_3, and the method described in [8] for K_2 and γ_1. In what concerns K_1, we have not used the conventional technique where K_1 and γ_1 are obtained simultaneously from the measurement of the relaxation time τ when the sample is suddenly brought from a field $H > H_c$ to $H_f < H_c$, with

$$\tau^{-1} = \frac{2\chi_a}{\gamma_i}\left(H_c^2 - H_f^2\right)$$

because we have not been able to observe regular oscillations of the transmitted intensity. In fact, we have used two methods of measurement of K_1, which give similar results. In the first one, we observe the change of the transmitted intensity when the molecules begin to tilt, at $H = H_c$, approaching H_c from below. Since the relaxation time is

presumably infinite at $H = H_c$, this method provides us with a excess value of H_c, hence of K_1. In the second method, we measure the relaxation time of the sample brought from $H = 0$ to $H > H_c$, for decreasing values of H. The extrapolation to $\tau^{-1} = 0$ gives a value of H_c of the same order than the first one. We return to this question below.

All our measurements have been performed at the temperature of 180°C.

II. SAMPLE PREPARATION

The samples for measuring K_1 and K_3 are in a planar texture between two glass plates, rubbed in a fixed direction with diamond paste. We used samples oriented this way with thickness varying between 60 and 200 μm. The samples for measuring K_3 are in a homeotropic texture and more difficult to prepare: they are aged at 180°C during 2 days under a magnetic field of about 10 kG, perpendicular to the plates. We can prepare good homeotropic samples with thickness varying between 20 and 40 μm. We cannot exclude the fact during this long period of aging there is some chemical degradation (see parag. III).

Cladis' method for measuring K_2 and γ_1 requires to observe the rotation of an interference figure in conoscopic illumination. As soon as the magnetic field is set up, walls parallel to the field appear between domains of opposite desorientation (fig. 1); they totally blur the conoscopic figure. However these walls can be easily removed by positioning the sample at some angle ($\sim$20°) of its working position, in a high field ($H/H_c \sim 10$). After one hour or more, most of walls disappear and there are only a few closed walls remaining; then the sample is set back to the normal position and the interference figure (the hyperbolas) can be observed clearly.

III. RESULTS AND DISCUSSION

Table I summarizes our results. The margin of error on each value is of the order of 25%, taking into account the inaccuracy on the sample thickness. χ_a[9] is of the order of $1.0\ 10^{-7}$ cgs. Our measurement of γ_1 (on the K_2 geometry) leads to:

$$\gamma_1 \sim 80 \text{ poises}$$

i.e. two orders of magnitude larger than in MBBA. K_1 is one order of

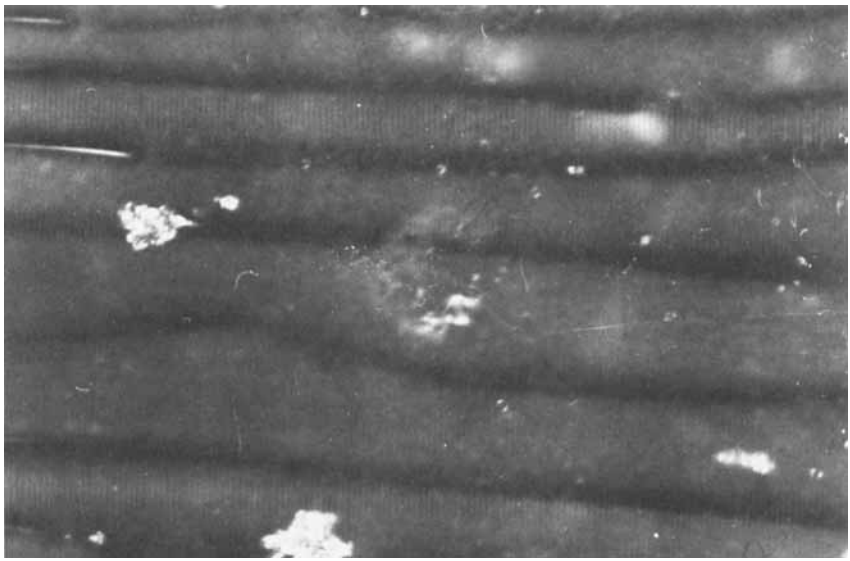


FIGURE 1 Walls parallel to the field and perpendicular to the unperturbed director in a planar sample (K_2 set-up); thickness: 110 μm; $H = 4700$ G; crossed polars.

magnitude larger, K_2 and K_3 of the same order of magnitude than in conventional nematics.

But at this stage, we should not consider only the standard causes of error in the measurements, but also the particular nature of our system. We have here non-standard nematics; on one hand they are endowed with an elasticity which involves not only torque elasticity, but also stress elasticity in an extent which depends on the molecular weight and the end-to-end interactions (we can disregard the effect of entanglements, since we are considering phenomena with rather long characteristic times); on the other hand, our samples are far from perfect; they are polydisperse and chemically labile. All our results, although quite reproducible, should therefore not be considered on the same footing than results of the same nature obtained in conventional nematics.

1. We have aged 26 hours planar samples at a temperature of 180°C in an atmosphere of argon, submitted to a vertical magnetic field; contrarily to their already indicated evolution in air, they do not become homeotropic. This experiment, which was suggested to us by Dr. C. Noël, shows that the molecules suffer chemical degradation in

TABLE I

Measurements of elastic constants K_{11}, K_{22} and K_{33}.

K_{11}

d (μm)	H_c (Gauss)	K_{11}/χ_a (c.g.s)
70	2420	29.1
145	1310	37.6
195	880	29.2

K_{22}

d (μm)	H_c (Gauss)	K_{22}/χ_a (c.g.s)
95	510	2.37
140	360	2.56
185	300	3.13

K_{33}

d (μm)	H_c (Gauss)	K_{33}/χ_a (c.g.s)
20	2330	2.7
25	2420	3.7
35	1590	3.0

air, possibly leading to the formation of smaller molecules which reorient homeotropically more easily, maybe because of some new chemical character of the ends. This suggests also that when the long molecules are not degraded, they can be considered from a structural stand-point as quasi-infinite with perhaps reasonably strong end-to-end bondings, favoured by the small terminal dipole moments (see also [3]). Therefore stress elasticity should not be a negligible effect . . .

2. Planar samples prepared for K_1 measurements and set in a perpendicular magnetic field $H \gtrsim 1.5H_c$ display a regular texture of striped domains (fig. 2) at an angle of approximately 80° to the nematic alignment when $H \sim 2H_c$. We have measured the characteristic rise time of these domains (see fig. 3) in function of H/H_c and of the thickness of the sample (fig. 4). This is the second method to measure K_1 we alluded to in para. I. There is a striking similarity between these results and those obtained by Guyon et al.[10]; as in their model, which is dynamical in essence (the stripes are rolls with backflow, akin to Williams domains), the relaxation frequency increases roughly linearly with H and with the square of the thickness; as in their model also, we have $q_x = 0$ below some value of H. A difference arises with the alignment of the stripes, which in their case is perpendicular to the unperturbed nematic alignment. In our case,

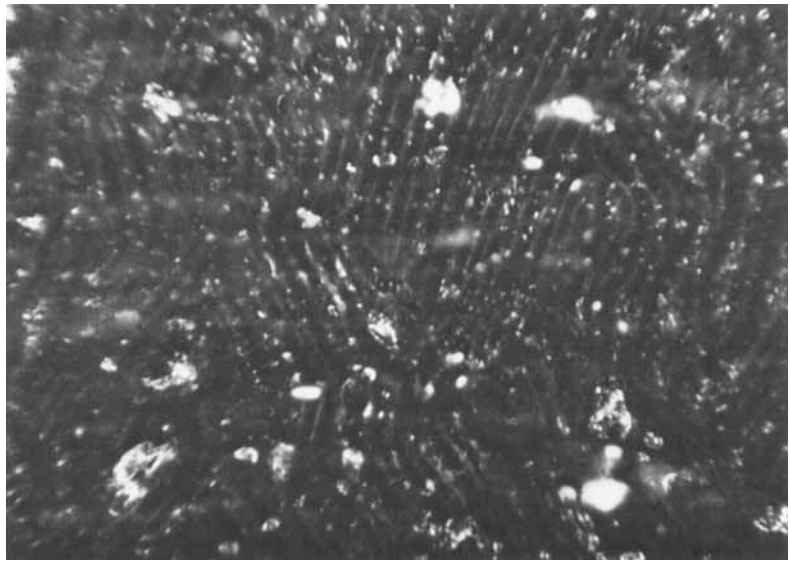


FIGURE 2 Striped domains observed in a 140 μm thick planar sample immediately after 15 mn in a field $H = 2800$ G ($\sim 2\ H_c$). The field was perpendicular to the sample; the unperturbed director is horizontal (K_1 set-up). Thickness: 140 μm; $H = 2800$ G for 15 mn; approximate periodicity 70 μm.

as revealed by the observation in the polarizing microscope, the molecular alignment rotates towards the perpendicular to the stripes, which we explain by a mechanical effect unknown in [10], a response of the very long molecules to the hydrodynamical stresses σ due to the backflow which has no equivalent in ordinary nematics. The final angle of 80° indicates a balance between stress and curvature elasticities. Another possibility could be some relaxation of splay-induced

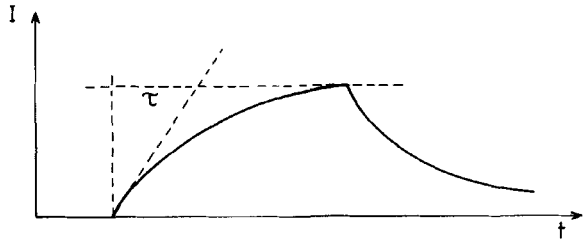


FIGURE 3 Schematic variation of light intensity in the K_1 set-up when applying a magnetic field perpendicular to the sample and removing it; τ is the characteristic time plotted in fig. 4.

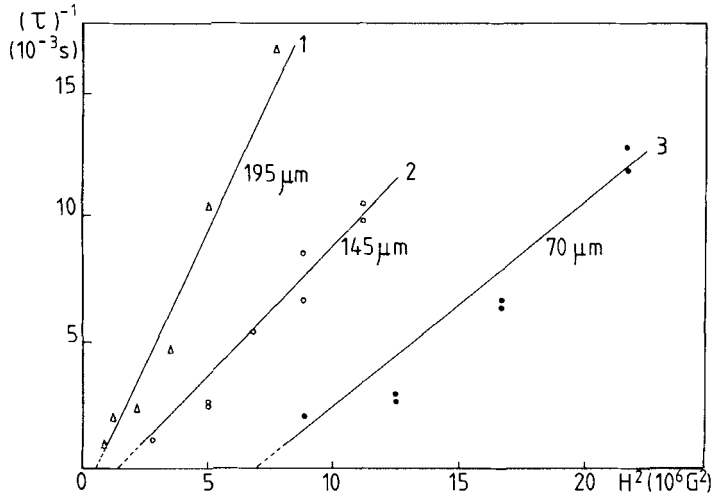


FIGURE 4 Characteristic inverse time τ^{-1} defined in fig. 3 as a function of H^2 in the K_1 set-up, when the sample displays striped domains.

deformation by bend or twist deformation. But more is needed to understand in details this effect, which is currently under study.

3. In the conoscopic measurement for K_2 and γ_1, the conoscopic figures are far from sharp; we attribute this widening to the fact that the angular direction of the molecules is defined but to some random deviation $\Delta\theta$ whose quadratic mean value $\langle\Delta\theta\rangle^2$ is of the order of[4]

$$\langle\Delta\theta^2\rangle \sim \frac{k_B T}{K_i} l d^{-2}$$

where K_i is a Frank constant (here $i = 2$), l some persistence length along the chains, and d the mean distance between chains. This quantity is not negligible compared to the angular deviation due to the field, which is of order

$$\theta^2 \sim \frac{2K_2}{K}\left(\left(\frac{H}{H_c}\right)^2 - 1\right),$$

where K is some mean between K_1 and K_3.

Clearly, the same effect exists in the measurements of K_1 and K_3.

4. Since the preparation of the homeotropic samples for K_3 requires some degradation of the molecules, there is suspicion that the values obtained for K_3 are smaller than the true values. In fact, because of

our observations of defects and textures made in [5], we expected much larger values of K_3.

5. We have observed walls of a roughly elliptic shape separating domains of opposite angular deviations in the K_3 geometry. Such types of walls have been observed and discussed in conventional nematics;[11,12] the ratio of the major to the minor axes has been shown to be of the order of K_1/K_2. In our case this ratio is of the order of 10, in complete agreement with our measurements of K_1 and K_2. However, this agreement should be considered with care, since our samples are chemically degraded; but this is perhaps the indication that the degradation affects only the molecules which are near the surfaces, not in the bulk, or that molecules degraded in the bulk move towards the surfaces.

In conclusion, we have presented in this paper the first systematic measurements of Frank constants and γ_1 in a main chain polymer, at only one temperature at the time being. These measurements and some observations coupled to them confirm that K_1 and γ_1 have non-conventional large values, but also stress some important features of the physics of polymer liquid crystals, like chemical instability (in this case) and the importance of stress elasticity.

Acknowledgements

We acknowledge helpful advices of P. Piéranski and P. E. Cladis for the experimental set-up, fruitful discussions with L. Léger, C. Casagrande and M. Veyssié, and are especially grateful to L. Strzelecki for the provision of samples. This work benefited of a C.N.R.S. (ATP) contract.

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