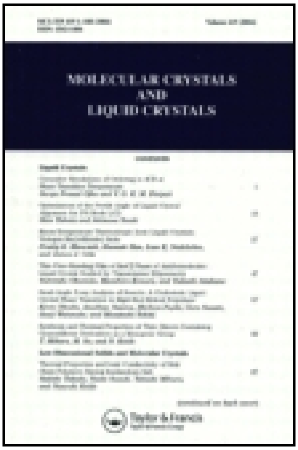

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

The Kinetics of Alignment of a Liquid Crystal Polymer in a D.C. Electric Field

A. Kozak [a] [b], G. P. Simon [a] [c], J. K. Moscicki [c] & G. Williams [a]
[a] University College of Swansea, Department of Chemistry, Singleton Park, Swansea, SA2 8PP, UK
[b] Institute of Physics, Jagiellonian University, 31-059 Krakow, Reymonta 4, Poland
[c] Monash University, Department of Materials Engineering, Clayton, 3669, Adelaide, Australia

To cite this article: A. Kozak, G. P. Simon, J. K. Moscicki & G. Williams (1990): The Kinetics of Alignment of a Liquid Crystal Polymer in a D.C. Electric Field, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 193:1, 155-159

To link to this article: http://dx.doi.org/10.1080/00268949008031819

Mol. Cryst. Liq. Cryst. 1990, Vol. 193, pp. 155–159
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

THE KINETICS OF ALIGNMENT OF A LIQUID CRYSTAL POLYMER IN A D.C. ELECTRIC FIELD.

ANDRZEJ KOZAK*+, GEORGE P. SIMON*×,
JOZEF K. MOSCICKI+ and GRAHAM WILLIAMS*

* University College of Swansea, Department of Chemistry,
Singleton Park, Swansea SA2 8PP, UK.
+ Institute of Physics, Jagiellonian University,
31-059 Krakow, Reymonta 4, Poland.
× Monash University, Department of Materials Engineering,
Clayton 3669, Adelaide, Australia.

(Submitted for publication September 14, 1989)

The realignment of a side-chain liquid crystal polymer in its liquid-crystalline state, induced by a directing d.c. electric field, was studied with the aid of dielectric relaxation spectroscopy. The time dependence of the director order parameter $S(t;V)$ was measured as a function of the applied electric voltage V. Results are discussed in terms of the Martins-Esnault-Volino approach.

INTRODUCTION.

It is known that side-chain liquid crystalline polymers (sc-LCP) may be homeotropically or planarly aligned by an electric field, depending on the frequency and amplitude of the electric field, although this often involves a complicated thermal treatment of a sample [1]. sc-LCP materials having a natural tendency to align in the presence of an electric field in the liquid-crystalline state are of special interest because of their possible application in optical information storage. In this paper we report on our recent investigation by means of dielectric spectroscopy of the alignment kinetics of such a chiral-nematic sc-LCP in response to a d.c. realigning electric field. Dielectric spectroscopy provides a simple and direct method for monitoring the alignment via determination of the apparent director order parameter, S_d [2]. It has been shown by Attard et al. [3] that the order parameter of a liquid crystalline sample can be determined from the known values of the dielectric loss factor:

$$S_d = \frac{3\varepsilon''(f) - [\varepsilon''_{\|}(f) + 2\varepsilon''_{\perp}(f)]}{2[\varepsilon''_{\|}(f) - \varepsilon''_{\perp}(f)]}, \tag{1}$$

where $\varepsilon''(f)_i$, $i = \|, \perp$, are respectively values of the dielectric loss factor measured for the sample aligned parallel and perpendicular to the probing electric field, and $\varepsilon''(f)$ is measured for an investigated state of alignment. f is the frequency of the probing field. Since $\varepsilon''_{\|}$ and $\varepsilon''_{\perp}$ are time independent, by continuously measuring the ε'' of the sample during the course of realignment, one can monitor the kinetics of the process via the transient behavior of S_d.

EXPERIMENTAL RESULTS

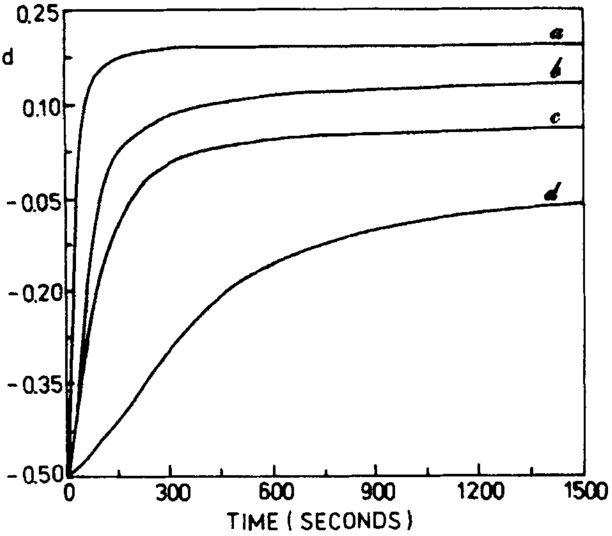

Figure 1. Transient behavior of the director order parameter of malonate I sc-LCP for realigning d.c. voltages of (a) 180, (b) 150, (c) 120, and (d) 90 V, at $T = 278.2K$. The sample was $100\mu m$ thick.

The malonate liquid crystal polymer **I** [4] was used for the kinetic study. The sample preparation and the technique of mesurements were described previously [5]. Measurements of ε'' were made at fixed freuquency of $10kHz$. Each sample was initially planarly oriented and $\varepsilon''_{\perp}$ was measured. The d.c. voltage V, was next applied across the sample and $\varepsilon'' = \varepsilon''(t)$ was monitored at regular time intervals until the new alignment equilibrium (homeotropic) was reached (i.e. $\varepsilon'' = \varepsilon''_{\|}$). Measurements were repeated for different values of V. $S_d(t;\mathrm{V})$ transients were calculated with the aid of Eq.(1).

Typical results are presented in the Fig 1. Two steps in the alignment prosess are clearly visible. Nearly immediately after the d.c. voltage is applied, there is an abrupt change of alignment manifested by a sharp increase of S, followed by a slow approach to a plateau value. This plateau value is sensitive to the strength of the electric field used, i.e., it increases on increasing V.

NUMERICAL SIMULATION

To simulate the realignment kinetics of the sample, we benefitted from results of a work of Martins et al.[6], originally developed to describe the realignment of a sample in a magnetic field. In particular, we adopted for our needs their equation for bend-splay deformation in the presence of an external magnetic field, by replacing the term accounting for interaction with the magnetic field with the term accounting for interaction with the electric field [5,6,7]:

$$[\gamma_1 - j^2(\vartheta)/g(\vartheta)]\frac{\partial\vartheta}{\partial t} - \frac{\Delta\varepsilon}{8\pi}E^2\sin 2\vartheta - K(\vartheta) = 0 \qquad (2)$$

where

$$\begin{aligned} K(\vartheta) &= f(\vartheta)\frac{\partial^2\vartheta}{\partial z^2} + \frac{1}{2}\frac{\partial f(\vartheta)}{\partial\vartheta}\left(\frac{\partial\vartheta}{\partial x}\right)^2 && (3) \\ f(\vartheta) &= k_{11} - (k_{11} - k_{33})\cos^2\vartheta && (4) \\ j(\vartheta) &= \alpha_2 - \gamma_2\sin^2\vartheta && (5) \\ g(\vartheta) &= (\alpha_1\cos^2\vartheta + \gamma_2)\sin^2\vartheta + \eta_c && (6) \end{aligned}$$

where ϑ is the angle between the nematic director and the realigning electric field, and α_i, $i = 1, 2$, are the Leslie viscosities, η_c is the third Miesowicz viscosity, and γ_i, $i = 1, 2$, are the rotational viscosities [8]. The k_{ii}, $i = 1, 3$, are respectively the bend and splay elastic constants [8]. E is the strength of the electric field, and $\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp}$ is the anisotropy of the dielectric constant. Eq. (2) can be solved using the fourth-order Runge-Kutta method [5].

In order to make a qualitative comparison with experimental results, Eq.(2) was first solved for different values of E (i.e. V) while the rest of the parameters were kept constant. Additional simulations were performed for different values of the γ_1 and η_c viscosities, and of the k_{11} elastic constant. Typical results of such simulations are presented in Fig. 2.

DISCUSSION

Numerical results show essentially the same transient behavior of S_d as observed experimentally. This is clear evidence that the realignment

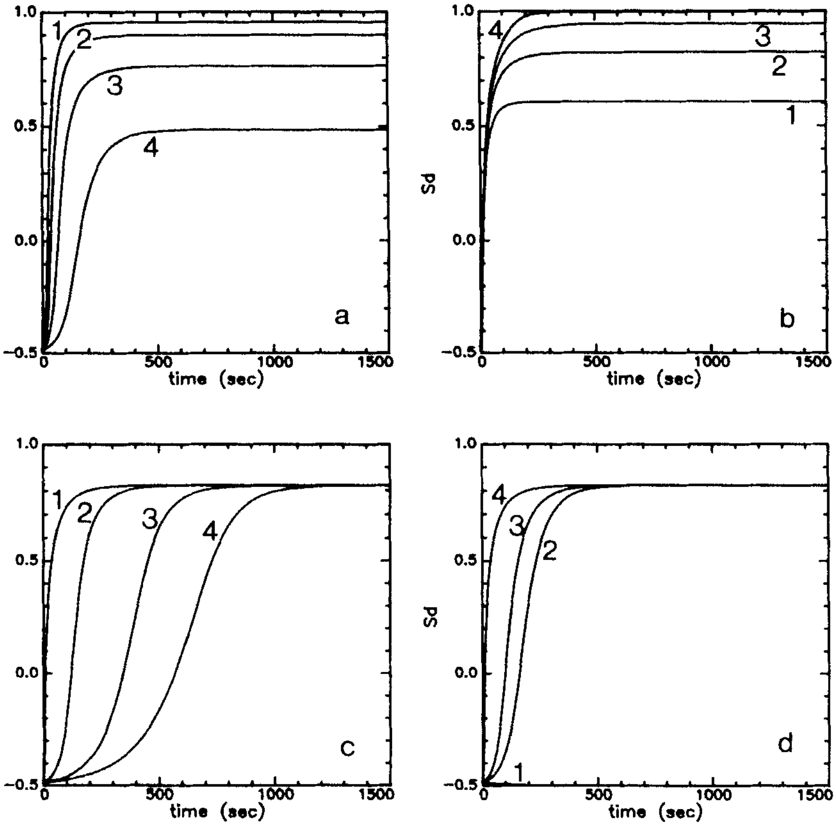

Figure 2. Simulated transient behavior of the director order parameter as a function of (a) aligning field strength, (b) the k_{11} elastic constant, (c) the γ_1 viscosity, and (d) the η_c viscosity. Calculations were performed for (a): $E =$ (1) 30, (2) 24, (3) 18, and (4) 12 [cgsm u.], and $\gamma_1 = 15, \alpha_1 = -15, \alpha_2 = -18$, and $\eta_c = 22$ [kPoise], $k_{11} = 50$ and $k_{33} = 1$ [dyne/cm^2], and $\Delta\varepsilon = 5$; (b): $k_{11} =$ (1)100, (2)50, (3)25, and (4) 5, and $E = 20$; all units and other parameters as in (a); (c): $\gamma_1 =$ (1)15, (2)20, (3)30, and (4)40, and $E = 20$; all units and other parameters as in (a); (d): $\eta_c =$ (1)40, (2)30, (3)22, and (4) 10, and $E = 20$; all units and other parameters as in (a).

process begins as a pure *bend* deformation, then gradually transforms to the *splay* deformation which next relaxes to homeotropic alignment. This result complements the results of Martins et al.[6] obtained for the realignment following the magnetic field.

From Figs. 1 and 2A, one can note that the value of S_d at the plateau is directly related to the strength of the electric field (applied d.c. voltage).

Therefore, the degree of the final alignment can be controlled by varying the d.c. voltage. Additionally, the higher the applied voltage, the faster is the "switching" time from the planar to homeotropic alignment.

The observed dependence of the plateau level and of "switching" time on the applied d.c. electric field is of great importance for future search for sc-LCP materials appropriate for electro-optical applications, since the response of the material to the electric field and to temperature changes are the key factors in such applications. Therefore, we also studied the response of the alignment kinetics to changes in values of the k_{11} elastic constant and of γ_1 and η_c viscosities, cf. Figs 2B, 2C and 2D. It has to be noted that the plateau level is very sensitive to the value of k_{11}; the smaller k_{11}, the higher is the plateau level. On the other hand, the transient behavior of S_d is very sensitive to variations in viscosities. In general, at higher viscosities, longer "switching" times should be expected.

In-depth discussion of numerical and experimental results will be presented elsewhere [7].

We want to emphasize a very important implication of the present results for a potential application of the dielectric spectroscopy in studying viscosities of sc-LCP. Sensitivity of the solution of Eq.(2) to variations in $\gamma_1, \alpha_1, \alpha_2$ and η_c enables evaluation of these viscosities from fitting the solution to experimental data. The applicability of this technique to determine the whole set of the anisotropic viscosities of a thermotropic polymer has been first demonstrated by Martins et al. in NMR studies [6]. We plan to carry out similar investigations in the near future by means of the dielectric method.

ACKNOWLEDGEMENTS

This work was supported by the S.E.R.C.(U.K.) under its Electroactive Polymers Initiative. One of us (A.K.) acknowledges partial support of his visit to University College of Wales by the Polish Academy of Sciences under Project CPBP 01.12.

REFERENCES.

[1] N.A. Plate and C.P. Shibaev *'Comb-shaped Polymers and Liquid Crystals'*, Plenum Press, New York, 1987.
[2] G.S. Attard, *Mol.Phys.*,**58**, 1087 (1986).
[3] G.S. Attard, K. Araki and G. Williams, *Brit. Polym.J.*, **19**, 119 (1987).
[4] A.C. Griffin, A.M. Bhatti, and R.L. Hung, *Mol.Cryst.Liq.Cryst.*, **155**, 129 (1988).
[5] A. Kozak, G. Simon and G. Williams, *Polymer Comm.*, **30**, 102 (1989).
[6] A.F. Martins, P. Esnault and F. Volino, *Phys.Rev.Lett.*, **57**, 1745 (1986).
[7] A. Kozak, G. Simon, J.K. Moscicki and G.Williams, *to be published.*
[8] P.G. de Gennes *'The Physics of Liquid Crystals'*, Clarendon Press, Oxford, (1974).