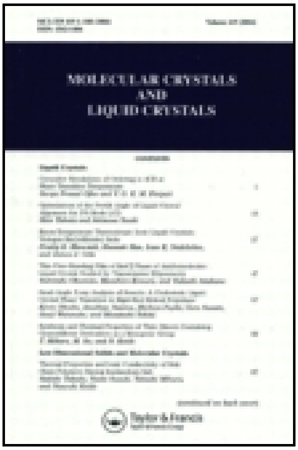

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Dielectric Spectroscopy of a Side Chain Liquid Crystal Polymer

A. Kozak [a] [b] , G. P. Simon [a] [c] , J. K. Moscicki [b] & 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

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DIELECTRIC SPECTROSCOPY OF A SIDE CHAIN LIQUID CRYSTAL POLYMER

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.

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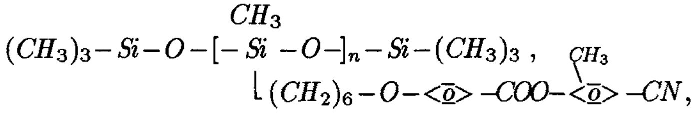
The dielectric properties of a new high purity siloxane side-chain liquid crystalline polymer are investigated using low and radio frequency techniques. Side-chain mesogenic units are aligned homeotropically or planarly by cooling from the isotropic melt in the presence of the electric field. Results of dielectric measurements are interpreted in terms of the Araki, Attard, Kozak, and Williams theory. The two-frequency addressing principle important for practical applications is also examined.

INTRODUCTION.

The side mesogenic groups of side-chain liquid crystal polymers (sc-LCP) are easily aligned by either electric or magnetic fields and the polymer backbone allows the alignment to remain after the aligning field is removed, even at temperatures above the glass transition [1,2]. Since polar groups are frequently incorporated in the mesogenic units and in the main-chain, the dielectric relaxation (DR) spectroscopy is an effective method for studying molecular dynamics and the alignment of the sample [3,4,5].

In this paper a summary of our recent DR studies of the siloxane back bone sc-LCP:



$$\begin{array}{l} \qquad\qquad\qquad\qquad CH_3 \\ (CH_3)_3-Si-O-[-Si-O-]_n-Si-(CH_3)_3\,, \qquad CH_3 \\ \qquad\qquad\qquad\qquad \llcorner (CH_2)_6-O-<\overline{\underline{o}}>-COO-<\overline{\underline{o}}>-CN\,, \end{array}$$

is presented. A less pure sample of this polymer has already been studied [4], however, the significant change in properties of purer sample [different phase transition temperatures: $T_{IS} = 325K$ (the biphasic range of $\Delta T = 1K$) and $T_g = 290.3K$, and the smectic phase as the first LC phase occuring during cooling] makes it worth investigation.

EXPERIMENTAL

The dielectric data were collected on the Gen Rad 1689 Precision Bridge, capable of doing measurements between 10 to 10^5 Hz. A three-terminal cell was used as described previously [2]. The main variables determined were the conductance of the sample, G and its capacitance C, which are related to the complex dielectric permittivity, $\hat{\varepsilon}(w) = \varepsilon'(w) - i\varepsilon''(w)$, where $w = 2\pi f$ is the angular frequency, in the following manner

$$C_p = \varepsilon' C_a \quad \text{and} \quad G/w = \varepsilon'' C_a \,, \tag{1}$$

where C_a is the geometric capacitance of the cell. Therefore, the complex dielectric permittivity is known to within the proportionality factor C_a.

Measurements were carried out for unaligned, homeotopically and planarly aligned samples. Sample were aligned by heating into the isotropic phase and cooling slowly through the biphasic region with voltage applied at the required frequency. On cooling down in the presence of the aligning field, the amount of the aligned LC-phase increases at the expence of the isotropic fraction. Using this procedure it is possible to align the sample homeotropically or planarly depending on the frequency of the aligning field (*two-frequency principle*)[6,7].

RESULTS

Typical G/w vs. $\log f$ curves for unaligned, homeotropic and planar samples are shown in Fig.1. In each case the dielectric relaxation spectrum can be resolved into two peaks associated with the basic modes predicted by Attard et al.[4,8]. The theory predicts the presence of four basic modes active in DR spectroscopy, independent of the nature of stochastic motions involved. For the probing electric field in the direction of the nematic director, the theory predicts the DR-spectrum of the type:

$$\varepsilon(w)_{\|} - \varepsilon_{\|}^{\infty} = \frac{\mathcal{G}_{\|}}{3kT}[(1+2S)\mu_l^2 F_{00}(w) + (1-S)\mu_t^2 F_{01}(w)] \,, \tag{2}$$

while for the direction perpendicular to the director

$$\varepsilon(w)_\perp - \varepsilon_\perp^\infty = \frac{\mathcal{G}_\perp}{3kT}[(1-S)\mu_l^2 F_{10}(w) + (1+S/2)\mu_t^2 F_{11}(w)]\,, \qquad (3)$$

where subscripts $||$ and $\perp$ denote directions of the probing field with respect to the director of LC phase, while the superscript ∞ denotes the permittivity at optical frequencies. $\mathcal{G}$ is the local field factor, μ_l and μ_t are the longitudinal and transverse components of the permament molecular dipole moment, S is the nematic order parameter and F the Fourier transform of an appropriate correlation function. Subscripts *00*, *01*, *10*, and *11* denote the basic modes of relaxation; *00* mode is associted with the end-over-end reorientation of the mesogenic unit, *01* with reorientation about its long axis, *10* with so-called stochastic precession and *11* is a combination of the precession and reorientation about the long axis.

Since the theory is general and does not predict the particular shape of each peak (which, in turn, has to be related to the particular mechanisms of the stochastic motions involved), we have used the phenomenological Fuoss-Kirkwood equation[2] to separate different domains, see Fig.1.

According to Attard [9], the low frequency peak of the unaligned sample is associated with the *00* mode while the high frequency combines the *01*,

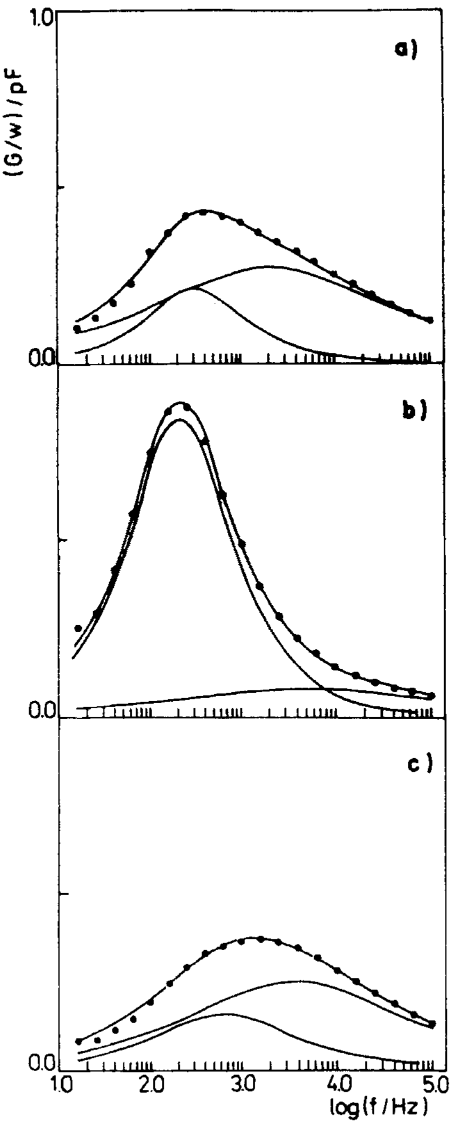


Figure 1. Siloxane sc-LCP. G/ω as a function of frequency at $323K$ for (a) unaligned, (b) homeotropic and (c) planar samples.

10 and *11* modes, cf, Fig.1*a*. For aligned samples the theory directly links peaks for the homeotropic sample with the *00* and *01* modes while for the planar one are linked with the *01* and *11* modes.

We also studied the degree of polymer orientation under the electric field. The crucial parameter responsible for the aligment achieved is the frequency of the aligning field. At low frequencies the dielectric anisotropy $\Delta\varepsilon(w) = \varepsilon'_{\|}(w) - \varepsilon'_{\perp}(w)$, is positive whereas at radio frequencies it becomes negative, which results in homeotropic or planar aligment. According to Attard [9], the height of the dielectric peak should be directly associated with the degree of alignment. Therefore, the maximum of the dielectric loss spectrum R, has been monitored as the function of voltage and frequency during cooling through the biphasic region. Results of measurements of the degree of aligment as a function of frequency and electric field strength are presented in Fig.2.

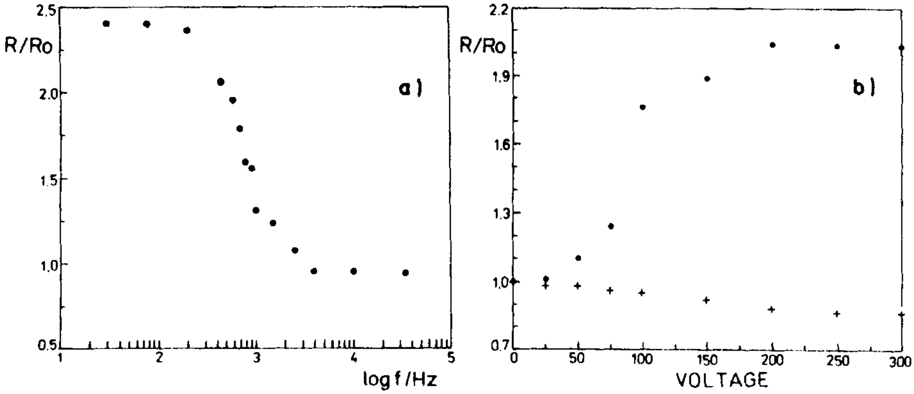


Figure 2. Siloxane sc-LCP. Normalized maximum of the dielectric loss as a function of (a) frequency (for V= $200V$), and of (b) voltage [at $f = 100Hz$ (•) and $f = 10kHz$ (+)] at $323K$. The sample was prepared by cooling ($0.02K/min$) from $330K$.

CONCLUSIONS

Our results confirm the presence of four basic modes active in DR-spectroscopy of sc-LCP and we were able to estimate characteristic frequencies for these modes. The use of the Fuoss-Kirkwood equation to describe the single relaxation domain reflects a distribution of relaxation times. Such a distribution is probably due to an influence of backbone flexibility [10] and/or steric hinderances [11]. A more detailed discussion of results in terms of the molecular dynamics as well as of the nature of the alignment process, will be presented elsewhere [10].

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