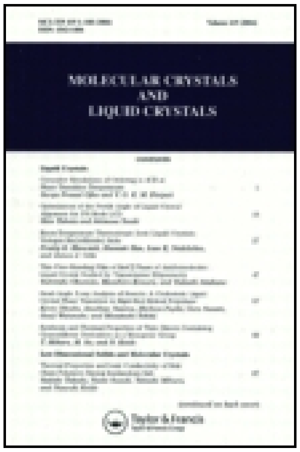

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The Study of Director Alignment in a Nematogenic Side-Chain Siloxane Polymer by Dielectric Relaxation Spectroscopy

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The changes that occur in the amplitudes and shapes of the dielectric loss spectra for a nematogenic side-chain siloxane polymer on going from the nematic to the isotropic phase *via* the biphasic region, and on going from the unaligned to the homeotropically aligned mesophase are described.

Keywords: dielectric relaxation spectroscopy, side chain siloxane polymers, director alignment

INTRODUCTION

Liquid crystalline side chain polymers represent a novel class of hybrid materials with electro- and magneto-optic properties similar to those observed in low molar mass mesogens, and which possess the good film-forming properties characteristic of high molar mass polymers.[1,2] A notable feature of the mesophases formed by the side-chain polymers is that although the induction of director alignment is more difficult than in the mesophases of low molar mass mesogens, once director alignment has been obtained, it appears to be permanent

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following the removal of the aligning perturbation (eg. electric or magnetic fields or shear) even at temperatures > Tg. In view of the implications which this behaviour has for information storage applications, it is important to obtain an understanding of the molecular factors that are responsible for the observed macroscopic properties of these materials.

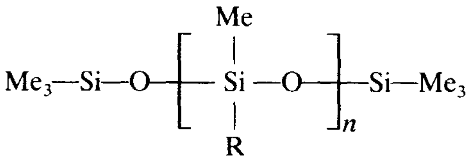
Since most mesogenic side-chain polymers have strong permanent dipoles situated in the head-groups, dielectric relaxation spectroscopy (DRS) provides a convenient method for studying their re-orientational motions, as shown by the studies of acrylate and methacrylate polymers with cyano-biphenyl[3-5] and phenylbenzoate ester head groups,[6,7] and of siloxane polymers with phenylbenzoate ester head groups.[8]

Recently Attard *et al.*[9] found that the dielectric loss spectra of the smectic phase of a siloxane side-chain polymer in its unaligned and homeotropically aligned states exhibited marked differences in both shape and amplitude. On the basis of these differences the conditions that are required to induce homeotropic alignment in the material can be quantified.[9,10]

In the present study we report similar changes for the aligned and unaligned mesophases of a nematogenic side-chain siloxane polymer, and in addition show how the loss spectra change on going from the nematic phase to the isotropic phase *via* the biphasic region.

EXPERIMENTAL

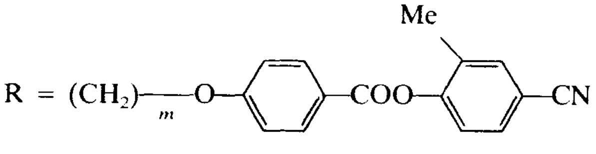
The material investigated was synthesized by Professor G. W. Gray and Dr. D. Lacey of Hull University and has the structure:



$$\mathrm{Me_3{-}Si{-}O}\left[\begin{array}{c}\mathrm{Me}\\ |\\ \mathrm{Si{-}O}\\ |\\ \mathrm{R}\end{array}\right]_n\mathrm{Si{-}Me_3}$$

(I)

where $n \simeq 35$ and



(II)

with $m = 6$.

The transition temperatures of (I) as judged by differential scanning calorimetry were found to be $T_g \simeq 275$ K, $T_N \simeq 314$ K, $T_I \simeq 319$ K; the width of the biphasic $(T_I - T_N)$ region being $\simeq 5$ K.

The data were acquired over the frequency range $12 - 10^5$ Hz at different temperatures in the nematic, biphasic, and isotropic regions by means of a computer controlled Gen Rad 1689 Precision RLC Digibridge. The sample was prepared as a disc $\simeq 1.1$ cm diameter and $\simeq 0.1$ mm thickness, sandwiched between two metal electrodes in a three terminal cell. The inter-electrode separation was kept fixed by means of a PTFE spacer. The temperature stability at the sample was estimated to be of the order of ± 0.02 K. The aligning a.c. voltage was obtained by stepping up the output of an AIM low distortion oscillator. The homeotropically aligned nematic phase was prepared by cooling the isotropic phase with 360 V r.ms at 1 kHz applied, at a rate < 0.02 K min^{-1}.

RESULTS AND DISCUSSION

The experimental data is in the form of the equivalent parallel conductance (G/ω), which is related to the dielectric loss factor, ϵ'', by

$$(G/\omega) = \epsilon'' C_a, \tag{1}$$

where C_a is a geometric capacitance of the interelectrode space occupied by the sample and $\omega = (2\pi\nu)$. Representative loss spectra for the nematic (N) and isotropic (I) phases, and for the biphasic region ($N + I$) are shown in Figure 1. The data for the unaligned mesophase are denoted by empty squares and the data for the aligned mesophase are denoted by solid squares.

(1) In the unaligned nematic phase the loss curves are broad and asymmetric indicating the presence of two overlapping processes, labelled δ and α in ascending order of frequency.

(2) The spectra of the aligned material are more symmetric and of increased amplitude compared with the spectra of the unaligned phase. The curve appears to be predominantly due to the δ process.

(3) At a given temperature in the nematic phase the position of maximum loss for the aligned material appears to be slightly shifted to lower frequencies in comparison with the unaligned material.

(4) A continuous change in the shapes and amplitudes of the nematic curves (aligned and unaligned samples) is observed on going through the biphasic region.

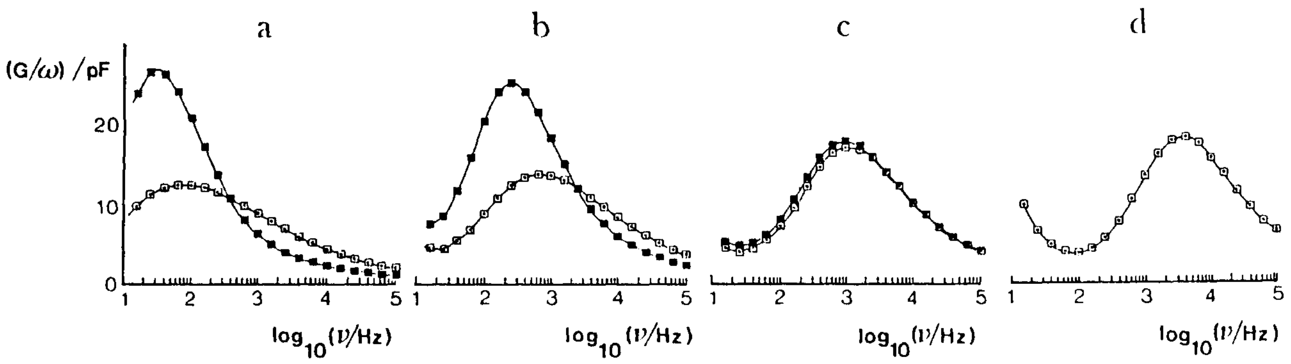


FIGURE 1 Representative examples of dielectric loss spectra. (■) aligned nematic; (□) isotropic and unaligned nematic, (◤) overlapping ■ and □.
a) T = 305.2 K, b) T = 314.2 K, c) T = 316.2 K, d) T = 323.2 K.

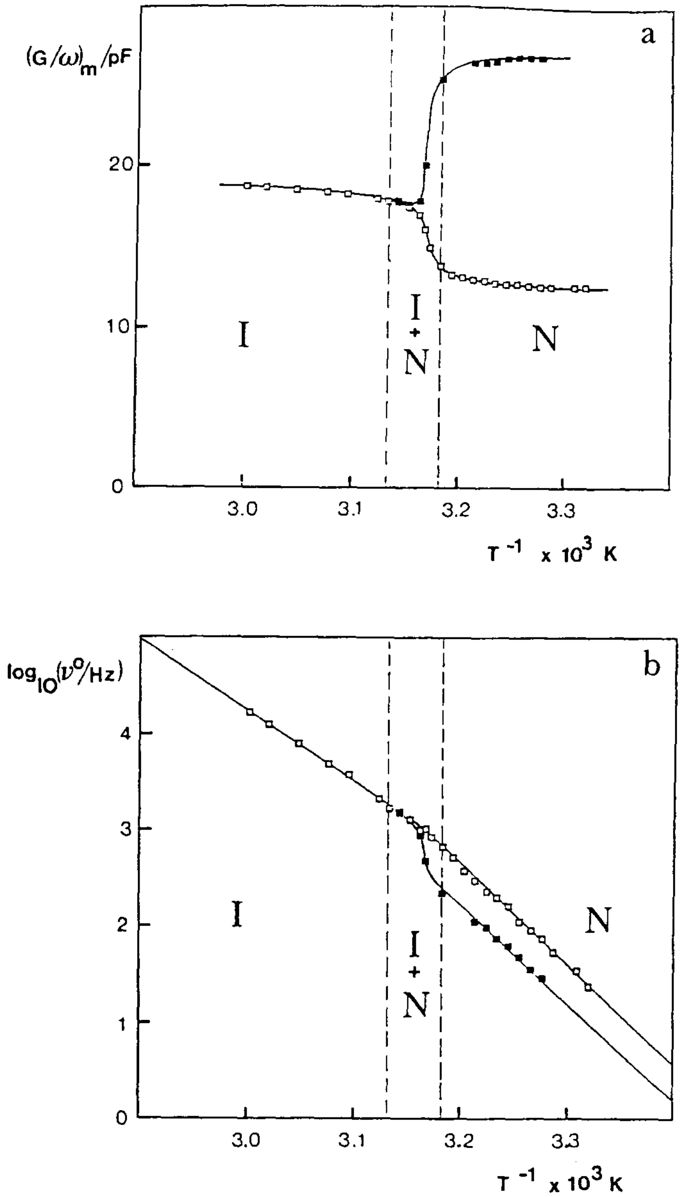


FIGURE 2 a) Amplitude of maximum loss, $(G/\omega)_m$ and b) $\log_{10}$ (frequency of maximum loss); shown as functions of T^{-1}.

(5) The loss spectra in the isotropic phase are fairly symmetric and intermediate in amplitude between those of the unaligned and those of the aligned nematic phase.

(6) To within experimental error, the areas of the loss curves of the aligned, unaligned, and isotropic material appear to have a $(T)^{-1}$ dependence indicating that a constant mean square dipole moment is being relaxed throughout the temperature range studied.

The variations of the amplitude of maximum loss and of the frequency of maximum loss with temperature are illustrated in Figures 2a and 2b. The activation energies obtained from the data shown in Figure 2b are $\simeq$ 139 kJ mol^{-1} in the isotropic phase and $\simeq$ 195 kJ mol^{-1} in both the aligned and unaligned mesophases. These values compare well with those obtained for the $m = 5$ homologue of (I).[8]

Although the ratio $(G/\omega)^{al}_{m}/(G/\omega)^{un}_{m}$, for a given temperature, is a useful empirical measure of the degree of director alignment, it is not well defined with respect to the amplitudes of the α and δ curves that constitute the experimental spectra, since as has been shown by Attard,[11] resolution of the experimental spectra for the unaligned mesophase shows that the δ is the smaller of the two processes, whereas resolution of the spectra for the aligned mesophase shows that the α-process virtually disappears and the δ process is enhanced.[12] These changes in the relative intensities of the underlying loss curves on alignment account for the apparent shift in the frequency of maximum loss that can be seen in Figure 2b. A more fundamental measure of the degree of director alignment is given by $\langle P_2 \rangle$ the second rank orientational order parameter for the director. The magnitude of $\langle P_2 \rangle$ together with the magnitude of $\overline{P}_2$, the molecular order parameter, may be obtained from the loss curves shown in Figure 1 by the method proposed by Attard.[11] The analysis of our data to yield these fundamental parameters $\langle P_2 \rangle$ and $\overline{P}_2$ will be presented elsewhere.

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