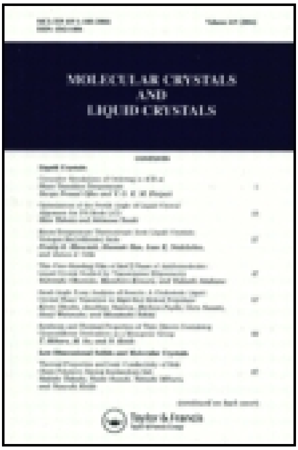

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Dielectric Spectroscopy of Side Chain Siloxane Liquid Crystal Copolymers

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DIELECTRIC SPECTROSCOPY OF SIDE CHAIN SILOXANE LIQUID CRYSTAL COPOLYMERS

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Abstract Side chain siloxane liquid crystal polymers (LCPs) are being investigated as potential optical storage media. Dielectric relaxation spectroscopy has been used to examine the real and imaginary components of permittivity as a function of frequency and temperature. The spectra obtained are discussed from the standpoint of both their molecular significance and their device implications. Spectra of liquid crystal homopolymers and a particular class of copolymers have been found to exhibit different features due to the larger free volume available to the mesogenic moieties in the copolymers. The relaxation behaviour of five LC copolymers is discussed and then two equivalent pairs of homopolymer and copolymer LCPs are considered in more detail. One pair shows anomalous relaxation behaviour and extra relaxation processes are attributed to internal reorientations.

INTRODUCTION

Recently there has been considerable interest in developing an optical storage device using liquid crystal side-chain polymers [LCPs][1,2]. These materials combine the mechanical properties of polymers with the electrical and optical properties of liquid crystals. The physical properties of several side chain siloxane LCPs synthesised by G.W. Gray's group at Hull University have been studied to provide operational parameters for device applications and information about molecular dynamics.

The real and imaginary components of permittivity have been measured as a function of frequency and temperature. Dipolar relaxations are seen as peaks in the frequency spectra of the imaginary component and their relative spacing and temperature response elucidate the molecular dynamics. In this paper the relaxation behaviour of several LC copolymers is discussed and compared with the response of comparable homopolymers. Knowledge of the DC conductivity is a monitor of material quality, while the frequencies of dielectric relaxation must be known if an AC field is to be applied across the sample without power loss. The dielectric spectrum is also indicative of the feasibility of dielectric heating or two-frequency switching of LC polymer devices.

EXPERIMENTAL

A microcomputer controlled HP4192A impedance analyser was used to measure the capacitance and conductivity of each sample as a function of frequency. The temperature was regulated to within 0.1°C using a Linkam TH600 hot stage and controller. The LCPs were retained in 25 μm thick glass sandwich cells with a simple overlap electrode pattern etched into low resistivity (5 Ω/□) ITO. Permittivity measurements on standard liquids (e.g. 1,2-dichloromethane, gold label, Aldrich) agreed with the literature to between 1 and 5% depending on the quality of the cell.

The loss spectra of the LCPs were fitted interactively using a conductivity curve and two overlapping Fuoss Kirkwood curves. The fitting programme was supplied by staff at the University College of Wales and the criteria for adequacy of fit are described elsewhere[3].

RESULTS AND DISCUSSION

The structures and transition temperatures of the materials studied are shown in Table 1.

TABLE I Structures and transition data of the LCPs.

The general structure of the copolymers is:
$(CH_3)_3\ SiO\ [SiO(CH_3)X)]_a\ [SiO(CH_3)_2]_b\ Si\ (CH_3)_3$
where a:b = 21:19

CODE	X	TRANSITION DATA	
GN3/14	$-(CH_2)_6.O.C_6H_4.CO_2.C_6H_4.CN$	$T_g = -12°C$	$T_{S_A}-I = 100°C$
GN3/3	$-(CH_2)_5.O.C_6H_4.CO_2.C_6H_4.CN$	$T_g = -9°C$	$T_{S_A}-I = 119°C$
GN3/19	$-(CH_2)_5.O.C_6H_4.C_6H_4.CN$	$T_g = -14°C$	$T_{S_A}-I = 107°C$
GN3/16	$-(CH_2)_8.O.C_6H_4.CO_2.(o-CH_3.C_6H_3).CN$	$T_g = -15°C$	$T_{S_A}-I = 65°C$
GN3/22	$-(CH_2)_6.O.C_6H_4.CO_2.C_6H_4.OCH_3$	$T_g = -15°C$	$T_N-I = 57°C$
GN3/18	$-(CH_2)_6.O.C_6H_4.CO_2.C_6H_4.CO_2CH_2C^*H(CH_3)(C_2H_5)$	$T_g = -25°C$	$T_{S_A}-I = 30°C$
GN3/17$^+$	$-(CH_2)_6.O.C_6H_4.CO_2.C_6H_4.CO_2CH_2C^*H(CH_3)(C_2H_5)$	$T_g = -9°C$	$T_{S_C}-I = 76°C$

+GN3/17 is a homopolymer, i.e. X is attached to all backbone sites,
giving $(CH_3)_3SiO[SiO(CH_3)X]_nSi(CH_3)_3$ where n ≃ 40.

The relaxation behaviour of GN3/17 and GN3/18 will be considered separately later. Two overlapping loss peaks are seen in the spectra of the other LCPs. From studies of aligned samples they may be assigned to the δ and α relaxation mechanisms described in the literature for similar LCPs[4]. A typical fitted curve is shown in Figure 1.

The δ loss peak arises from the longitudinal component of the mesogen's dipole whereas the α peak also includes contributions from the transverse component. The relative peak amplitudes may be related to the degree of alignment of the director[5]. The variation of δ peak amplitude with temperature for the copolymers is shown in Figure 2. This change of alignment suggests that the thermal stability of information written onto films of these materials using either negative or positive contrast modes, may vary according to the properties of the LCP being used.

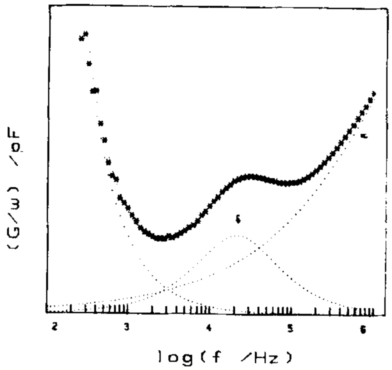

Figure 1
GN3/14 at 56°C fitted with a conductivity curve and two Fuoss Kirkwood curves

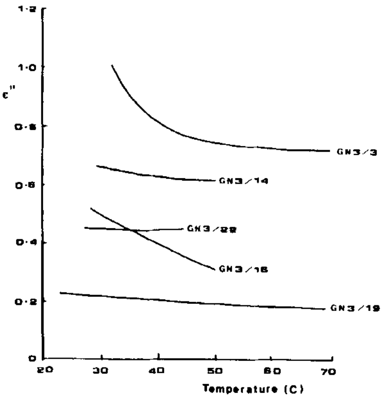

Figure 2
Variations of δ peak amplitude for unaligned samples of the copolymers. [The curve for GN3/22 was produced using the α peak of a homogeneously aligned sample].

The δ and α peak behaviour of the copolymers is summarised in Table 2. Also shown is the behaviour of LCP "A" which is the homopolymer equivalent of GN3/16 and has been extensively studied by Attard[6].

TABLE 2 δ and α relaxation peak parameters

	GN3/14	GN3/3	GN3/19	GN/22	GN3/16	A
$T^{\neq}$ (°C)	56.4	67.4	65	26	30.6	60
δ Peak position at T ($\log_{10}$ Hz)	4.33	4.66	4.76	2.94	3.3	3.57
α Peak position at T($\log_{10}$ Hz)	6.94	6.92	6.95	6.66	4.92	4.82
δ Peak Activation Energy (kJ/mol)	92.5	96.5	80	124	98	120*
α peak Activation Energy (kJ/mol)	89	87	68	48	72	130*
Core overlap (from X-ray data[7] (Å))	19.2	17.7	10.7	15.4	8.4	-

≠ $T/T_c = 0.92$ where T_c is the clearing temperature.

* Shown to be very temperature dependent

The features of the spectra of each material are discussed below and interpreted in terms of molecular hindering.

GN3/14

The relatively high α-peak activation energy with respect to the other LC copolymers and the small shift in alignment with temperature (see Figure 2) suggests a restriction of the transverse dipole component motion and a fairly stable director configuration. This is due to steric hindrance arising from the odd alkoxy spacer length[8].

GN3/3

In contrast to GN3/14, this exhibits a large shift in alignment with temperature and this, together with the fairly high frequency of the δ-peak position, suggests a relatively unhindered structure. Since the only difference is the even spacer length the explanation may be that this aligns the mesogen approximately orthogonal to the backbone, reducing the steric hindrance.

GN3/19

The loss peaks of this LCP are at high frequencies and have low activation energies. There is also a small peak height shift with temperature. The stable director configuration and relatively unrestricted dipole motion may be associated with the specific local fluid structure. From Table 2 the core overlap distance is virtually identical to that observed in the corresponding monomeric cyanobiphenyl. In the polymers such local structure will induce intra- or inter-chain correlations which may stabilise the director configuration.

GN3/22

The δ peak is at a low frequency and has a high activation energy while the α peak is well separated and has a very low activation energy. The weak longitudinal dipole component is restricted by steric hindrance, while the free transverse motion may result from the relatively unrestricted methoxy terminating species or from cooperative effects between adjacent ester groups.

GN3/16 and A

The loss behaviour of this equivalent pair of homopolymer and copolymer LCPs may be compared. The loss peaks of the copolymer are narrower (i.e. they are more Debye-like), they have lower activation energies and a wider separation. The copolymer structure presents less hindrance to the motion of the mesogenic dipole components.

GN3/17 and GN3/18

These are an equivalent pair of homopolymer and copolymer LCPs which produce anomalous loss spectra. Examples at 0.95 Tc and 1.06 Tc are given in Figures 3 to 6 and the peak positions are summarised in Table 3.

TABLE 3 Peak Positions of GN3/17 and GN3/18

LCP	Temperature	Peak 1 Position ($\log_{10}$ Hz)	Peak 2 Position ($\log_{10}$ Hz)
GN3/17	0.95 Tc (55°C)	4.5	6.8
	1.06 Tc (95°)	5.34	6.14
GN3/18	0.95 Tc (15°C)	3.7	5.8
	1.06 Tc (50°C)	4.61	5.22

The relaxation behaviour of the copolymer and homopolymer are similar due to the large core overlap in each case. X-ray studies of these LCPs showed interdigitation of the mesogenic groups with almost complete overlap for the copolymer. In figures 3 and 4 the lower frequency peak is interpreted as a superposition of δ and α relaxations. The relatively high microviscosity of this copolymer (due to the interdigitation) causes the relaxation peaks to be at lower freqencies than than those of the homopolymer.

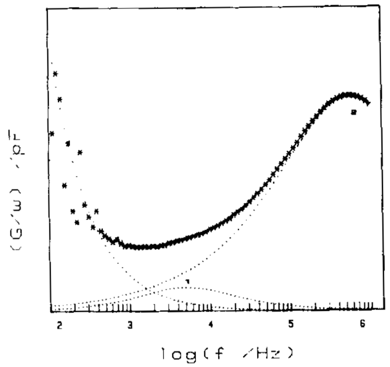

Fig 3: GN3/18 at 0.95 T_c
(15°C)

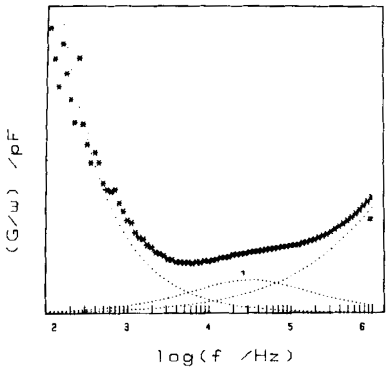

Fig 4: GN3/17 at 0.95 T_c
(55°C)

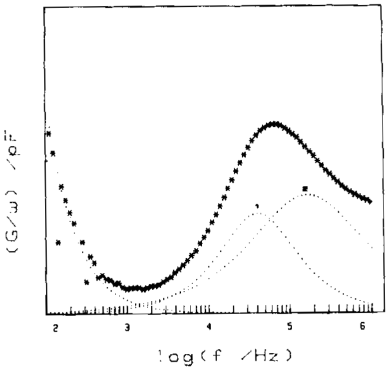

Fig 5: GN3/18 at 1.06 T_c
(50°C)

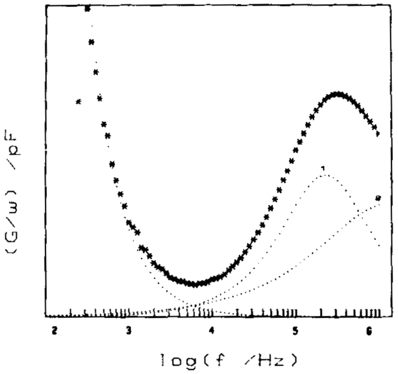

Fig 6: GN3/17 at 1.06 T_c
(95°)

The large peak occurring at high frequency in the spectra of Figures 3 and 4 may be fitted with two overlapping peaks at lower temperatures. It is proposed that these peaks arise from internal reorientation of the ester groups and are analogous to the β relaxations seen by Zentel[4]. The splitting of the peak may result from the presence of two ester groups in this mesogen, although the particularly wide splitting for GN3/17 and the greatly differing amplitudes of the components suggest that the higher component may be due to some other unidentified internal reorientation, the lower peak being an unresolved peak due to the ester reorientations.

Figures 5 and 6 show the isotropic spectra. The experimental peak can be clearly resolved into two components reminiscent of those seen in a study of dialkyl phenyl benzoate esters[9]. In that case the splitting was attributed to a large anisotropy of the rotational diffusion tensor in the isotropic phase. The same interpretation gives values for $D_{\parallel}$ rot./$D_{\perp}$ rot. of about 7.5 for GN3/18 and 12 for GN3/17. This suggests a degree of local ordering remains in the isotropic phase.

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