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THE EFFECT OF THE SPACER GROUP ON SIDE-CHAIN LIQUID CRYSTAL POLYMER DIELECTRIC MOBILITY

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Abstract—Dielectric relaxation spectra have been measured for a series of siloxane based side-chain liquid crystal polymers and the effect of the spacer group chemical structure (alkyl and vinylacetic acid) on dielectric motion is presented, as is the effect of spacer length for each polymer with a given spacer type. The effect of increased spacer length is to increase the frequency of motion due to greater mesogen mobility. The materials containing vinylacetic acid spacer units show a biomodal dielectric frequency spectrum due to greater decoupling of the constituent motions of the side chains. The effect of spacer length on the cross-over frequency (which determines the nature of the liquid crystalline alignment by a.c. electric fields of various frequencies) is also discussed.

INTRODUCTION

The polar nature of most mesogens in side-chain liquid crystal polymers (SCLCP) and their ability to be readily aligned in an electric field make these materials ideal candidates for characterisation by dielectric relaxation spectroscopy [1–4].

The motion of the mesogenic unit is influenced by the polymer backbone, the spacer unit and the chemical nature of the mesogenic core. The relaxations that occur can be associated with motions of the mesogenic unit which relate to the perpendicular and parallel dipole moments of the mesogenic groups [2, 3]. The relative contributions of the various relaxation modes are dependent on the alignment of the mesogenic unit. It has been shown that alignment can be obtained in these systems by application of an electric field to SCLCP films whilst cooling very slowly through the biphasic region [4]. In some instances alignment can be achieved by application of a field in the liquid crystalline state [5, 6]. It has been demonstrated that by changing the frequency of the aligning electric field, it is possible to cause homeotropic alignment (mesogens perpendicular to electrode) or planar alignment (mesogens parallel to electrode) [3, 7]. A low frequency electric field results in homeotropic alignment whilst a high frequency field produces planarly aligned samples for materials with side chains of positive dielectric anisotropy.

Most structure–property relationships between chemical structure and dielectric relaxation have been determined for SCLCPs with methacrylate or acrylate backbones and with differing combinations of spacer and mesogenic units [8–10] or have examined the effect of backbone molecular weight variation [11]. Whilst research into the dielectric properties of individual siloxanes has been undertaken [2–4, 12, 13] and well characterized in terms of their fundamental motions and alignment properties, little has been published relating to dielectric mobility and alignment in a systematic study in which the chemical structure of the spacer unit is varied. Some previous comparative dielectric studies of polysiloxanes have varied both spacer and mesogenic unit simultaneously [12] or concentrated on the effect of changing the copolymer content ratio of two mesogenic side-chains attached to a siloxane backbone [14, 15].

In this work we present dielectric data comparing the mobility of smectic siloxane SCLCPs with the same mesogenic unit but with variation in the spacer group type and length. Two types of spacers have been used, a previously reported alkyl chain spacer [2, 3] and a novel vinylacetic acid spacer group synthesised in our laboratory [16, 17]. Thermal analysis of the polymers containing the vinylacetic acid spacers [16, 17] indicates that this flexible spacer results in lower transition temperatures than for alkyl spacers of similar length and this would be expected to have an influence on the dielectric properties of such SCLCPs. It should be noted also that most dielectric studies of similar SCLCPs with alkyl chains reported in the literature have tended to concentrate on mesogenic units which contain laterally attached substituents [2–4] in which the long axis of the mesogenic core is parallel rather than perpendicular to the polymer main chain. Such substituents would be expected to influence mobility since they disrupt the liquid crystalline order. The SCLCP alkyl-spacer systems reported here do not contain such lateral substituents and tend to be smectic. This allows a further degree of comparison between these and the other reported materials.

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Table 1. Thermal properties of the siloxane SCLCPs (1) and (2)

Structure	n	T_g	T_m (°C)	T_{CL} (°C)
1	6	*	50	176
1	11	*	56	189
2	3	−7	†	40
2	6	−4	†	72
2	8	−8	†	96

*Glass transition not observed.
†Melting point not observed.

EXPERIMENTAL

Materials

The polymers synthesized for this study used methods described elsewhere [16, [17].The relevant polymer structural formulae are presented below and their thermal characteristics presented in Table 1. T_g is the glass transition temperature, T_m the melting point and T_{CL} the isotropic temperature between the liquid crystal and isotropic state (also known as the clearing temperature).

It should be noted that the SCLCPs with an alkyl spacer group (**1**; $n = 6$ and 11) have the same number of atoms between the mesogen and the siloxane backbone as those with the vinylacetic acid spacer **2**; $n = 3, 8$.

All materials showed smectic—a textures in transmission optical microscope experiments with crossed-polars above T_g or T_m.

Dielectric measurement

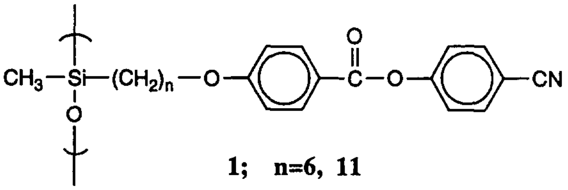
Variable frequency dielectric spectroscopy was performed using equipment (Gen Rad 1689 Digibridge) and techniques described elsewhere [2–4]. The data presented involves G/ω where G is the sample conductance and ω is the angular frequency of measurement ($\omega = 2\pi f$ where f is between 10 and 10^5 Hz). G/ω is a dielectric parameter related to the imaginary component of the dielectric constant, $\epsilon'' = G/\omega \times C_0$. C_0 is the empty capacitance of the sample and hence determination of ϵ'' requires knowledge of the sample thickness. Samples were all of similar thickness (about 0.2 mm). Since we are interested only in peak position and shape in this work G/ω vs $\log f$ is presented as is done elsewhere [2–4, 6, 7]. In the same way the dielectric permittivity, ϵ', is represented by the capacitance of the samples, C_p where $\epsilon' = C_p/C_0$ and can also be displayed as a function of $\log f$. The temperature was varied by sealing the cells and immersing them in a water bath. This allowed dielectric measurements of up to 80°C.

Electrical alignment procedure

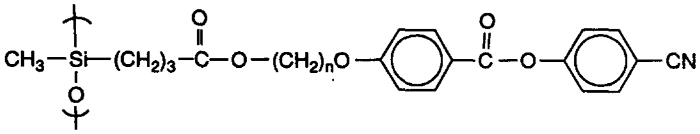
Samples were aligned in the cells described above using a LD501 Aim Oscillator amplified to produce a voltage output of up to 200 V (RMS) between 10 and 30 kHz. In this work all samples were aligned at 190 V (RMS) by cooling slowly through the isotropic region at 0.1°C/min with the voltage applied.

RESULTS AND DISCUSSION

The unaligned loss spectra (G/ω) for all SCLCP materials are presented in Figs 1–5. The spectra of unaligned SCLCPs **1**; $n = 6$ and 11 are shown in Figs 1 and 2. In both cases the increasing loss tails at low frequencies indicate some residual impurity in the samples which lead to conductivity. In both spectra the dielectric loss maxima first becomes visible at temperatures of about 50°C and above—similar to the melting points of samples 1 and 2 (Table 1). The loss spectra seen here are attributed to a combination of motions of the mesogenic unit since the siloxane backbone is relatively non-polar. The results indicate that the degree of crystallinity in sample 1 is quite high and that melting of the crystals is required for the side-chains to have sufficient mobility to result in relaxations in the 10–15^5 Hz range. Clearly, since the material is semi-crystalline, those units not involved in crystallites will be in the mobile, liquid crystalline state above the glass transition whilst the others will be in the frozen liquid crystal state. Above the melting point, all mesogenic units will be involved in liquid crystalline behaviour. This high degree of crystallinity is reflected in our inability to observe the glass transition by DSC measurement (Table 1). This is due either to there being an insufficient amorphous phase in which to observe T_g or to the high degrees of crystallinity acting as thermoreversible "cross links" and restricting the molecular mobility of the polymer chains of the amorphous phase. The inability to experimentally determine T_g has been observed in many semi-crystalline siloxane SCLCP studies [18, 19]. However, most dielectric studies on siloxane SCLCPs have been performed on SCLCP materials which are wholly amorphous due either to short spacer groups or to the presence of laterally attached substituents on the terminal aromatic ring [1]. In those studies it was found necessary to exceed the glass transition temperature to observe the strong dielectric motions in the 10–10^5 Hz frequency range [20]. Our results demonstrate that similar conditions apply to semi-crystalline SCLCPs and that, for large scale motion of the mesogens to be observed, the sample must be entirely in the liquid crystalline state.



1; n=6, 11



2; n=3, 6, 8

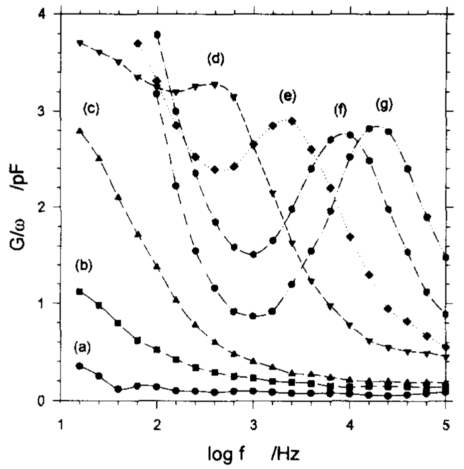


Fig. 1. G/ω (pF) against $\log f$ (Hz) for unaligned **1**; $n = 6$ (see Table 1) at different temperatures: (a), 22°C; (b), 33°C; (c), 42°C; (d), 52°C; (e), 62°C; (f), 72°C and (g), 80°C.

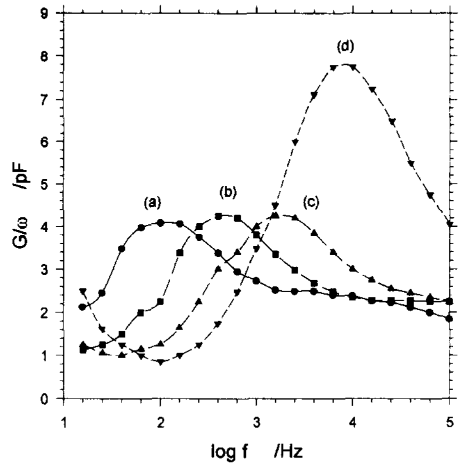


Fig. 3. G/ω (pF) against $\log f$ (Hz) for unaligned **2**; $n = 3$ at different temperatures: (a), 22°C; (b), 30°C; (c), 38°C and (d), 42°C.

In contrast, the dielectric spectra of polymers of **2**; $n = 3, 6, 8$ (Figs 3–5) show dielectric peak maxima at all measured super-ambient sample temperatures. All three of these materials are non-crystalline (Table 1) and the glass transition is well below the temperatures of measurement, illustrating the previous point about the need to investigate mesogenic mobility by dielectric spectroscopy in the liquid crystal state.

The shapes of SCLCP dielectric curves have been well-described in the literature [21, 22] and assigned to various motions of the polar mesogenic unit in the liquid crystal state. Two basic relaxations are observed for mesogens with a longitudinal dipole moment (terminal cyano group) and a lateral dipole (ester group). These are labelled δ and α in increasing order of frequency. The δ peak is related to motion of the longitudinal dipole around the mesogens short axis whilst the α relaxation is largely due to motion of the mesogens transverse dipole around the long axis of the mesogen. This latter motion (which does not require a large scale molecular rearrangement as in the δ process) occurs at a higher frequency (a faster motion). The correctness of these assignments can be demonstrated if the samples are aligned homeotropically or planarly [1–4, 22, 23]. Because the δ peak is entirely due to motion of the longitudinal dipole it increases in magnitude with homeotropic alignment whilst the α peak becomes more prominent with planar alignment.

The unaligned dielectric spectra, Figs 1–5 show different behaviour dependent both on the chemical structure of the spacer unit (1) or (2) and the length of the spacer (value of n). Figures 1 and 2, for example, show slightly different relaxational behaviour due to the difference in alkyl spacer chain length. To meaningfully compare the effects of spacer length on parameters such as maximum frequency of the dielectric relaxation, it is necessary to compare different spectra at the same reduced temperature, T_{red} [12], where $T_{\text{red}} = T_{\text{exp}}/T_{\text{CL}}$ and all temperatures are in absolute Kelvin. This scaling recognises that the clearing point, T_{CL}, of SCLCPs with different

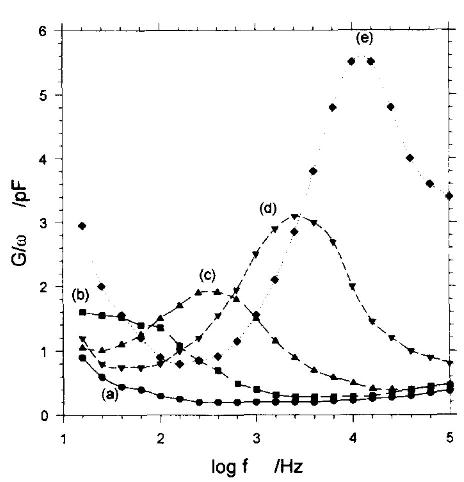


Fig. 2. g/ω (pF) against $\log f$ (Hz) for unaligned **1**; $n = 11$ at different temperatures: (a), 30°C; (b), 40°C; (c), 50°C; (d), 60°C and (e), 70°C.

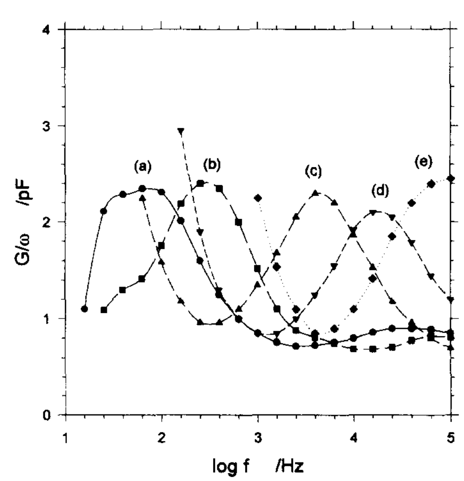


Fig. 4. G/ω (pF) against $\log f$ (Hz) for unaligned **2**; $n = 6$ at different temperatures: (a), 22°C; (b), 30°C; (c), 50°C; (d), 63°C and (e), 73°C.

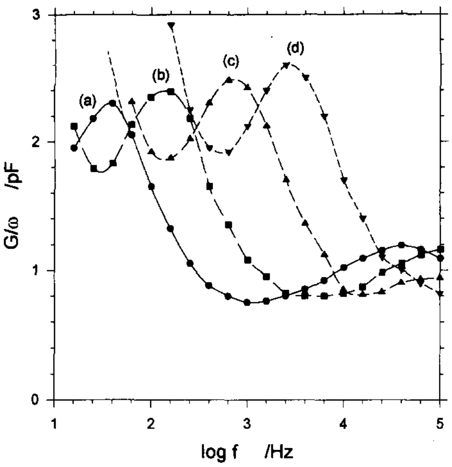


Fig. 5. G/ω (pF) against $\log f$ (Hz) for unaligned **2**; $n = 8$ at different temperatures: (a), 22°C; (b), 30°C; (c), 40°C and (d), 50°C.

spacer units differs, and that comparing frequency maxima at a constant experimental temperature, T_{exp} may be misleading.

Comparison of the maxima of the peak positions of **1**; $n = 6$ at 52°C (Fig. 1) and with **1**; $n = 11$ at 60°C (Fig. 2) where both have the same reduced temperature, $T_{red} = 0.72$, shows that the maxima of the sample with the longer spacer length **1**; $n = 11$ is significantly higher by $\log f = 0.7$. Although the dielectric loss curves consist of a superposition of δ and α peaks, the peak maximum is essentially that of the δ relaxation (motion of the longitudinal dipole moment) and it appears a longer spacer unit such as in **1**; $n = 11$ results in a faster δ motion.

In addition, the spectrum of the SCLCP with the longer spacer unit (**1**; $n = 11$) is significantly broader than that of its homologue **1**; $n = 6$. This seems to reflect a greater prominence of the α relaxation for the polymers with the longer spacer unit. The reason for this is not totally clear since little work has been previously published on the dielectric relaxations of SCLCPs with very long spacer lengths (such as **1**; $n = 11$ for sample 1). It appears as though the long spacer unit may allow increased motion of the transverse dipole moment around the long axis of the mesogen (α motion) due to greater side chain flexibility. The δ relaxation on the other hand, requiring motion of the entire side chain (mesogen and spacer) around the siloxane backbone, is not as readily enhanced in strength although it does occur at a higher frequency. In addition, the difference in spacer chain length may influence the nature of the spontaneous alignment attained due to surface interactions between the SCLCP polymer and the stainless steel electrodes.

It is also instructive to calculate the activation energies of motion in the liquid crystal state by plotting $\log f_{max}$ vs $1/T$ (where f_{max} is the frequency position of the peak maximum) at each temperature and assume an Arrhenius relationship. The activation energy for the relaxations in Figs 1 and 2 are 138 and 165 kJ/mol, respectively. Since the peak maxima of the unaligned samples are similar to those of the δ relaxation, the activation energies are essentially those of the motion of the longitudinal dipole moment. The greater activation energy of the longer side chain indicates a greater potential energy barrier to motion of the longer side chain around the siloxane backbone. This aspect will be discussed later in this paper when the activation energies of samples **2**; $n = 3, 6, 8$ are presented and discussed.

It is informative to compare the dielectric properties of one of our samples **1**; $n = 6$ with the dielectric spectra the SCLCP reported in [25]. This latter SCLCP is similar to **1**; $n = 6$ reported here having the same chemical structure, length of spacer unit and degree of polymerisation of the siloxane backbone but with an additional methyl group attached to the end aromatic ring in the position meta to the cyano group [25]. This SCLCP with the methyl group has a dramatically lower clearing point (41°C) [25] than that of **1**; $n = 6$ (176°). In addition it demonstrates a lower order nematic phase due to the disruptive effect of the methyl group. Comparison of the spectra of both materials indicates that the broadness of the unaligned spectra is much greater in the case of the methyl substituted SCLCP [25] than in **1**; $n = 6$. This is indicative of a merging of the δ and α relaxations. In addition, whilst **1**; $n = 6$ reported here has an activation energy of 138 kJ/mol, a value of 195 kJ/mol was found for the comparable methyl-substituted material [25]. These results are consistent with the difference in the phases, smectic and nematic, respectively, and reflect restriction of motion of the side chain due to the methyl group.

The unaligned spectra of **2**; $n = 3, 6, 8$ are shown in Figs 3–5. The use of a vinylacetic acid spacer can be seen to dramatically reduce the clearing temperatures compared to those with alkyl spacers (Table 1). In addition, the unaligned dielectric spectra of samples **2**; $n = 3, 6, 8$ show distinct, well separated δ and α loss peaks in contrast to those for **1**; $n = 6, 11$ (Figs 1 and 2). This is the first time (to our knowledge) that a wide distinct frequency separation between the δ and α relaxation has been reported in dielectric spectra of SCLCPs. In previous work, the α peak position has usually been determined by deconvolution (assuming, for example, a Fuoss–Kirkwood empirical relaxation function [22, 23] of the broad, overlapping δ–α peaks). However, in the dielectric spectra of polymers of **2**; $n = 3, 6, 8$ reported here two separate peaks can be seen. It appears that the flexibility of the SCLCP with vinylacetic acid spacer groups results both in low clearing point temperatures and more strongly decoupled δ and α motions than reported previously.

Comparison of Figs 3–5 allows the effect of vinylacetic acid spacer length on the position of the dielectric relaxation peaks to be compared. It can be seen that the longer the vinylacetic acid spacer units, the greater is the distinction between the δ and α peak and it is most distinct for **2**; $n = 8$ seen in Fig. 5.

It is possible to compare the frequency position of some of these similar materials at the same reduced temperature. In the range of temperatures in which dielectric measurement could be carried out, comparable reduced temperatures can be obtained for **2**; $n = 6, 8$. For example, **2**; $n = 6$ (22°C, $T_{red} = 0.85$) can be compared with **2**; $n = 8$ (40°C, $T_{red} = 0.86$). The frequency of motion of the δ relaxation the longer chain material sample is $\log f_{max} = 2.9$ compared to

$\log f_{max} = 1.9$ for the shorter spacer. As in the case of the SCLCPs with the methylene spacer, increased length results in increased frequency of motion. However, in contrast to SCLCP samples with methylene spacer **1**; $n = 6, 11$ we can now also directly examine the position of the decoupled higher frequency α motion in **2**; $n = 6, 8$. Examination of Figs 4 and 5 indicate that, at the same $T_{red} = 0.86$, the distinct α peak increases from $\log f_{max} = 4.5$ for **2**; $n = 6$ to a value greater than $\log f = 5$ for **2**; $n = 8$ (above the maximum frequency measurable on our equipment). That is, the α relaxation (like the δ relaxation) also increases in frequency with spacer length.

The activation energies of the δ peak (from the positions of the spectra maximum) have been determined for each sample with different vinylacetic spacer lengths (**2**; $n = 3, 6, 8$). Unfortunately a similar determination could not be made with the α peaks since they rapidly increase above the frequency field of measurement with increasing temperature and there are insufficient points for a meaningful Arrhenius plot. However, the activation energies found for **2**; $n = 3, 6, 8$ are 184, 109 and 122 kJ/mol, respectively.

This shows a general downward trend with increasing spacer group length although $n = 8$ has a slightly greater value than $n = 6$. This is despite a monotonic increase in frequency of motion of the δ peak for all samples with structure (2). A general decrease in activation energy was found by Simon *et al.* [12] and Parneix *et al.* [9] for increasing alkyl spacer chain lengths in polysiloxane and polyacrylate-backbone SCLCPs, respectively. Simon *et al.* [12] also found oscillating values of activation energy with chain length and ascribed it to the "odd–even" effect often seen in SCLCPs. It should be noted, however, that in this work activation energies increased for both polymers with the longest spacer groups (i.e. **1**; $n = 11$ and **2**; $n = 8$) and it may be that if the chain is sufficiently long there is an increased energy barrier to overcome.

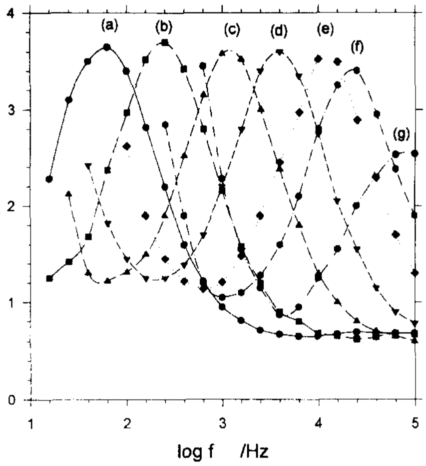


Fig. 7. G/ω (pF) against $\log f$ (Hz) for homeotropically aligned **2**; $n = 6$ at different temperatures: (a), 20°C; (b), 30°C; (c), 41°C; (d), 50°C; (e), 60°C; (f), 65°C and (g), 73°C.

The assignment of the δ relaxation can be confirmed by the determination of dielectric spectra of homeotropically aligned materials, measured over a range of temperatures. In homeotropic alignment the long axis of the side-chain which contains the strong, longitudinal dipole moment becomes aligned perpendicular to the electrodes, resulting in a loss spectrum of greater magnitude as described earlier. Homeotropic alignment would be expected to reduce the magnitude of the α relaxation and indeed, in most other SCLCP systems [23], homeotropic alignment results in the retention of only the δ relaxation.

Figures 6–8 are dielectric spectra of homeotropically aligned samples **2**; $n = 3, 6, 8$. They can be seen to be homeotropically aligned because the magnitude of the low frequency portion of the peak of the G/ω curve is greater than that of the unaligned sample (Figs 3–5). It can be seen that despite homeotropic alignment, and a stronger δ relaxation, the high frequency α relaxation is still visible and in the sample with the longest spacer **2**; $n = 8$ (Fig. 8) the α relaxation remains as a totally separate peak.

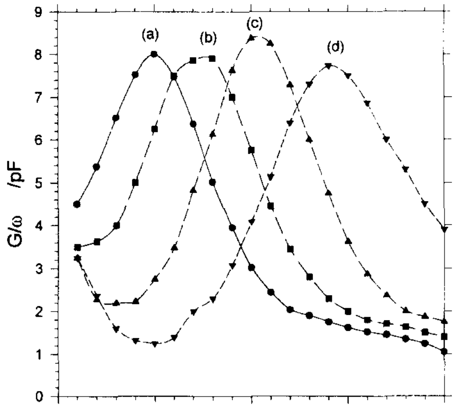


Fig. 6. G/ω (pF) against $\log f$ (Hz) for homeotropically aligned **2**; $n = 3$ at different temperatures: (a), 22°C; (b), 30°C; (c), 36°C and (d), 42°C.

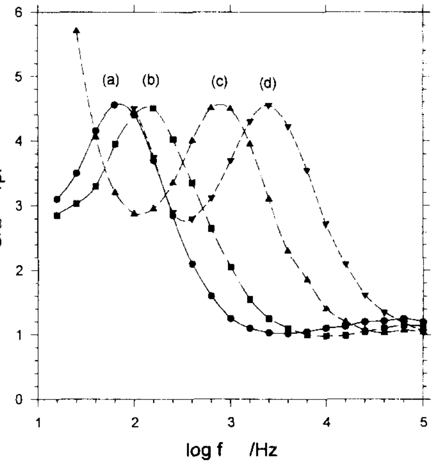


Fig. 8. G/ω (pF) against $\log f$ (Hz) for homeotropically aligned **2**; $n = 8$ at different temperatures: (a), 25°C; (b), 30°C; (c), 41°C and (d), 49°C. The data is the same dielectric sample as that shown in Fig. 5 and can be directly compared to it.

Since the α peak is least prominent in the sample of structure 2 for the $n = 3$ material it was of interest to planarly align this material and confirm that this would lead to an increase in magnitude of the α relaxation. This was done by cooling the sample through the isotropic temperature at 0.1°C/min with a voltage of 190 V (RMS) and a high frequency of 3 kHz. As expected, the magnitude of the δ relaxation decreased and that of the α relaxation increased. This is best shown by comparison at one temperature (22°C) of the homeotropic, unaligned and planarly aligned **2**; $n = 3$ in Fig. 9. Figure 9 clearly exhibits an isobestic point (a common point of intersection of the three loss curves at about $\log f = 3.2$). This phenomena is readily observed in most SCLCP dielectric studies (for example [26]) and it is found that for a given SCLCP and temperature the intersection point is unique for all alignments from full homeotropic to fully planar. It is also found that the dielectric permitivity ϵ' (or capacitance C_p) demonstrates an isobestic point at a different frequency than that of the dielectric loss curves. This latter point is particularly important when using SCLCPs as two frequency addressable materials [26]. The isobestic point of the permitivity curves is that at which anisotropy of the dielectric permitivity changes from positive to negative and is denoted the "cross-over frequency", $\omega_c = 2\pi f_c$. The crossover frequencies are isobestic points and are predicted by the equation of Attard *et al.* [3] who derived the relationship

$$\epsilon'(\omega) = \tfrac{1}{3}(1 + 2S_d)\cdot\epsilon'_{\parallel}(\omega) + \tfrac{2}{3}(1 - S_d)\cdot\epsilon'_{\perp}(\omega) \qquad (1)$$

which predicts the dielectric constant $\epsilon'(\omega)$ at a given frequency as a function of the domain order parameter, S_d and the dielectric constant parallel, $\epsilon'_{\parallel}(\omega)$ and perpendicular, $\epsilon'_{\perp}(\omega)$ to the mesogen. From this equation, it can be seen that if $\epsilon'_{\parallel}(\omega_c) = \epsilon'_{\perp}(\omega_c)$ then the dielectric constant at that frequency is independent of degree of order. If the sample is aligned at frequencies less than the cross-over frequency, the alignment is homeotropic. If the material is aligned at frequencies greater than the cross-over frequency, planar alignment occurs. Such behaviour is seen in low molar mass liquid crystal systems but at much higher frequencies [27]. Most reports on this phenomena represent studies on only one material [26, 28, 29] and show that increasing temperature increases the magnitude of the cross-over frequency. In this work we are able to compare the effect of spacer length on the cross-over frequency.

The unaligned and homeotropically aligned spectra for **2**; $n = 6$, and **2**; $n = 8$ at the same reduced temperature, $T_{red} = 0.85$ are shown in Fig. 10(a) and (b). The cross-over frequencies are $\log f = 3.08$ and 4.3, respectively. It can be seen that by changing the flexibility (increasing the length) of the spacer unit by increasing n from 6 to 8 there is a concomitant increase in the cross-over frequency by an order of magnitude. The effect of increasing spacer length is the same as that of increasing temperature [26, 28, 29]. That is, increased side chain mobility (due to higher temperatures or longer spacer lengths) leads to higher cross-over frequencies. This demonstrates that judicious molecular design of the spacer unit in SCLCPs can readily lead to manipulation of the position of the cross-over point. This may be important in the design of two-frequency addressable optoelectronic materials.

CONCLUSION

In this paper we have presented results of a study of the dielectric relaxations of siloxane backbone SCLCP materials in the liquid crystal state. These relaxations consist of motions of both the longitudinal (δ motion) and transverse (α motion) dipole

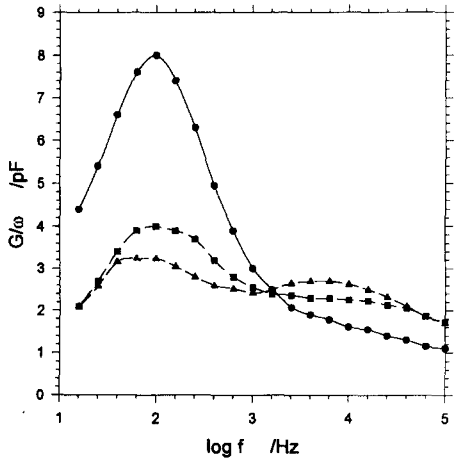


Fig. 9. G/ω (pF) against $\log f$ (Hz) for (a), homeotropically aligned; (b), unaligned and (c), planarly aligned, **2**; $n = 3$ measured at 22°C.

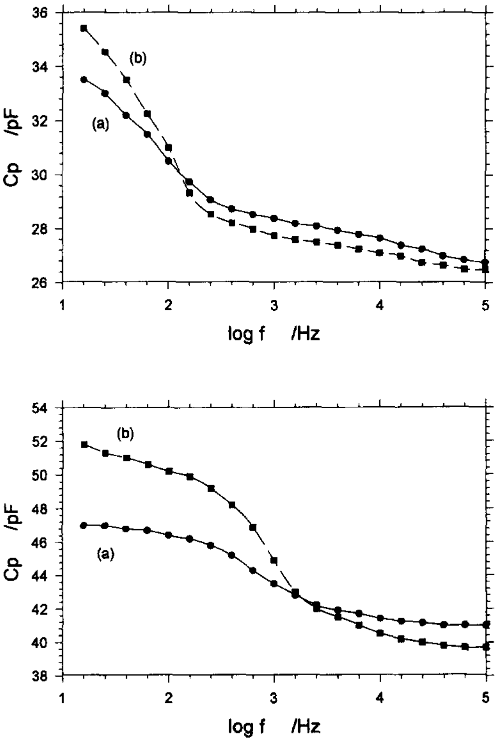


Fig. 10. (i) Cp (pF) against $\log f$ (Hz) for (a), unaligned and (b), homeotropically aligned, **2**; $n = 6$ at 22°C, $T_{red} = 0.85$; (ii) Cp (pF) against $\log f$ (Hz) for (a), unaligned and (b), homeotropically aligned, **2**; $n = 8$ at 40°C, $T_{red} = 0.85$.

moments of the mesogen. We have looked independently at the effect of systematically varying the type of spacer and the length of spacer whilst the mesogen remains the same.

Two different spacer units, an alkyl and a vinylacetic acid spacer were used. Increasing the length of the alkyl spacer resulted in a greater frequency of motion for a given reduced temperature, presumably due to greater side chain flexibility and mobility. However, in the same system, an increase in the length of the spacer group resulted in a greater activation energy of the δ motion and a broader relaxation peak—indicating a greater contribution of the α relaxation due to rotation around the long axis of the mesogen. It appears that even though the frequency of the δ motion is greater, an extremely long spacer group increases the activation energy of the δ motion.

It was found that the use of vinylacetic acid spacers results in samples with much lower clearing points than seen in alkyl spacer SCLCPs. In addition, unlike alkyl spacer materials, the dielectric spectra of vinylacetic acid spacer SCLCPs show two distinct δ and α relaxations, for all spacer lengths and this has not been reported previously in the literature for other SCLCPs. This is due to the decoupling of δ and α motion by the flexible vinylacetic acid spacer. Increasing the length of the spacer results in higher frequency motion of the δ and α peaks (as also seen in alkyl spacer material). Homeotropic and planar alignment of some of the vinylacetic acid samples confirm the assignments of α and δ relaxations by changing their relative magnitude, depending on the method of alignment.

We have demonstrated that the "cross-over frequency" (the frequency at which the dielectric anisotropy of the longitudinal and transverse dipole moment of the mesogen changes from positive to negative at a given temperature) of two vinylacetic acid spacer SCLCP materials increases with increased spacer length (flexibility). This means that, in addition to temperature, the chemical structure of the spacer unit may be an important variable in tuning the electrical switching of these materials for use in electroptical devices.

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