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Dielectric relaxation in the planarly-aligned nematic phase of a siloxane side-chain polymer Comparison of theory with experiment

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PRELIMINARY COMMUNICATION

Dielectric relaxation in the planarly-aligned nematic phase of a siloxane side-chain polymer

Comparison of theory with experiment

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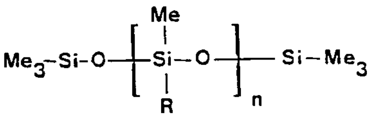
We show that the dielectric loss spectra of the planarly-aligned nematic phase of a liquid-crystalline siloxane side-chain polymer consist of a single broad curve, as predicted by theory.

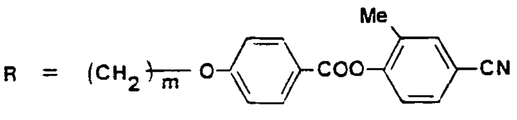
The study of dielectric relaxation in the mesophases of liquid-crystalline side-chain polymers with 4-cyanophenylbenzoate head groups has revealed that the loss spectra of these materials are broad, asymmetric, and with poorly resolved features [1–5]. Recently Attard [6] proposed that these loss spectra can be resolved into at least two component curves (δ and α) of different intensities by fitting the experimental spectra with a sum of suitable lineshape functions. The intensities, A_δ and A_α, of the two curves could then be related to $\bar{P}_2$, the order parameter of the mesogenic head-groups with respect to the director, and to $\langle P_2 \rangle$, the order parameter of the director with respect to a laboratory axis, via a molecular theory of dielectric relaxation in mesophases having an arbitrary degree of director alignment [6]. The theory makes definite predictions about the relative magnitudes of A_δ and A_α for given values of $\langle P_2 \rangle$, and in particular, it is predicted that when $\langle P_2 \rangle$ is $-0{\cdot}5$ (i.e. in planarly-aligned mesophases) A_δ should vanish for all values of $\bar{P}_2$. Consequently, the dielectric loss spectrum of a planarly aligned mesophase would be expected to be composed of a single curve, namely the α curve. In this communication we report experimental loss data for a planarly-aligned nematic phase which confirm the predictions made by the theory.

The material studied was synthesized by Professor G. W. Gray, Dr. D. Lacey and Mr. G. Nestor of Hull University, and has the structure



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

where n is approximately 35 and



(II)

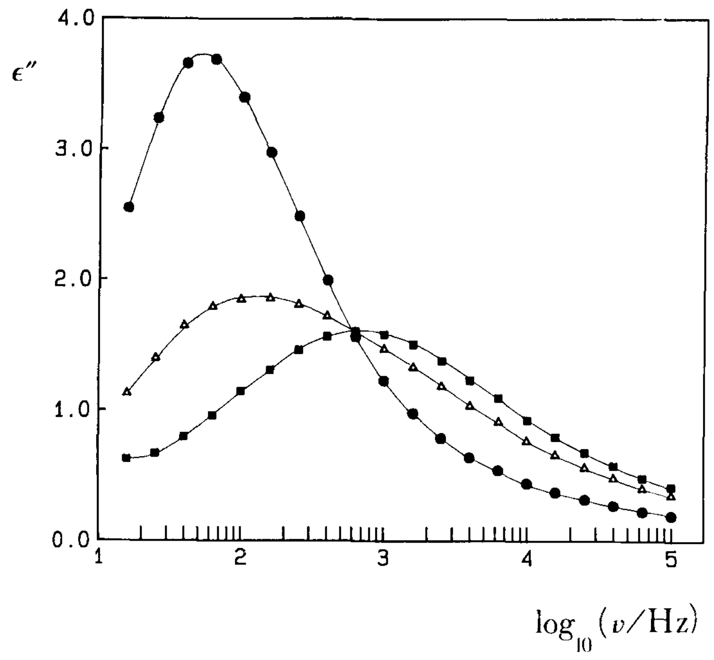
where m is 6. The transition temperatures of (I) as determined by D.S.C. are: $T_g \simeq 275\,K$, $T_N \simeq 314\,K$, $T_I \simeq 319\,K$; the width of the biphasic region being about 5 K. The sample was prepared as a thin film of approximately 1·1 cm diameter sandwiched between two metal electrodes whose surfaces were not pre-treated in any way. Constant sample dimensions were maintained by means of a PTFE ring spacer of about 100 μm thickness. The dielectric loss and capacitance data were acquired over the frequency range 12–10^5 Hz with a computer controlled Gen Rad 1689 Precision RLC Digibridge. Aligned specimens were prepared by cooling the sample from the isotropic phase at a rate of approximately 0·02 K min^{-1} in the presence of an a.c. electric field. The required voltage (100 V rms) was obtained by increasing the output of an AIM Low Distortion Oscillator. Our dielectric studies show that for an aligning frequency of 10 kHz the nematic phase was formed with planar director alignment, while for an aligning field of 600 Hz the nematic phase was formed with homeotropic director alignment. The sample studied has the property that once director alignment is established it does not appear to decay appreciably for several days following the removal of the aligning field. This is true even at temperatures in the nematic phase which are much higher than T_g, the apparent glass transition temperature. This property is very convenient as it enables us to make dielectric measurements on the mesophase without the need to maintain the external field to sustain director alignment.

Dielectric loss and capacitance data were recorded for compound (I) (*a*) in the homeotropically-aligned nematic phase, (*b*) in the planarly-aligned nematic phase, (*c*) in the non-aligned nematic phase, and (*d*) in the isotropic phase. The static permittivities of the nematic phases aligned in these different ways were estimated from the data obtained at 307·2 K, and are shown in the table. Note that the value quoted for the isotropic phase was obtained by extrapolating to 307·2 K the value of ε_0 at 328·2 K, assuming a T^{-1} dependence. The average static permittivity, $\bar{\varepsilon}$, is calculated to be about 12·7. Since $\bar{\varepsilon}$ is greater than the value of ε_0 for the non-aligned mesophase it appears that the non-aligned nematic has some degree of planar alignment. A similar observation was made for the homologue of (I) with m equal to 5 [6].

Static permittivities of polymer (I) estimated at 307·2 K

Phase	ε_0
Homeotropic nematic	16·2
Non-aligned nematic	12·2
Planar nematic	11·0
Isotropic	13·8

In the figure we show representative loss data obtained for the homeotropically-aligned, the planarly-aligned, and the non-aligned nematic phase of (I). The loss spectra for the non-aligned and homeotropically-aligned mesophase are similar in shape and relative amplitudes to the loss spectra reported for the $m = 5$ and 8 homologues of polymer (I) [4, 5]. The loss curve of the planarly-aligned mesophase is broad and symmetric. The frequency of maximum loss appears to be shifted to higher values relative to the frequency of maximum loss of the curve for the homeotropically aligned material.



Dielectric loss spectra for polymer (I) in its homeotropically-aligned nematic phase (●), planarly-aligned nematic phase (■), and non-aligned nematic phase (△), at 307·2 K.

According to the model proposed by Attard [6], the intensities of the δ and α relaxation curves for a mesophase with an arbitrary degree of director alignment are related to $\bar{P}_2$ and $\langle P_2\rangle$ by

$$A_\delta = (c\mu_l^2/9kT)(1 + 2\langle P_2\rangle + 2\bar{P}_2 + 4\langle P_2\rangle\bar{P}_2), \qquad (1a)$$

$$A_\alpha = (c\mu_l^2/9kT)(2 - 2\langle P_2\rangle - 2\bar{P}_2 + 2\langle P_2\rangle\bar{P}_2 + 3R_\mu[1 - \langle P_2\rangle\bar{P}_2]), \qquad (1b)$$

where $R_\mu = (\mu_t/\mu_l)^2$, in which μ_t and μ_l are respectively the transverse and longitudinal components of the molecular dipole moment. Note that the intensities defined by equations (1 *a*) and (1 *b*) are those for processes observed with the measuring field parallel to the aligning field. For homeotropic alignment $\langle P_2\rangle$ is 1, and equations (1 *a*) and (1 *b*) reduce to

$$A_\delta|_{\langle P_2\rangle=1} = (c\mu_l^2/3kT)(1 + 2\bar{P}_2), \qquad (2a)$$

$$A_\alpha|_{\langle P_2\rangle=1} = (c\mu_t^2/3kT)(1 - \bar{P}_2). \qquad (2b)$$

According to these equations the loss spectrum for a homeotropically-aligned specimen should consist of two curves. Provided that $\mu_l > \mu_t$, the low frequency component (i.e. the δ curve) would be expected to have the larger intensity. For a planarly-aligned mesophase $\langle P_2\rangle$ is $-0{\cdot}5$, and equations (1 *a*) and (1 *b*) reduce to

$$A_\delta|_{\langle P_2\rangle=-0\cdot5} = 0, \qquad (3a)$$

$$A_\alpha|_{\langle P_2\rangle=-0\cdot5} = (c\mu_l^2/3kT)[(R_\mu + 1) + (\tfrac{1}{2}R_\mu - 1)\bar{P}_2], \qquad (3b)$$

and so the loss spectrum would be expected to consist only of the high frequency component (i.e. the α curve). Thus in the limits of homeotropic and planar alignment equations (1 *a*) and (1 *b*) reduce to functional forms which are consistent with those obtained from the pre-exponential factors which occur in the Nordio–Rigatti–Segre theory [7].

It is clear that the predictions made by the theory are confirmed by the data presented in the figure. Further evidence supporting our identification of the curve for the planarly-aligned material with the α curve can be obtained from its half-height width, which is found to be about 2·5 units of $\log_{10}\nu$. This value is in good agreement with the values obtained by Attard [6] from fitting the data of the non-aligned nematic phase of the homologue of (I) with m equal to 5.

Since at a given temperature the frequencies of maximum loss of the component curves do not appear to change for different degrees of director alignment [8], then the separation of the peak maxima in the spectra of the homeotropically- and planarly-aligned material should provide a reasonable estimate of the peak separation in the non-aligned material. For the data shown in the figure the separation is found to be about 1·2 units of $\log_{10}\nu$. This value falls in the range of separations estimated for the $m = 5$ and 8 homologues of polymer (I) [6, 8].

From equations (2 *a*) and (3 *b*)

$$\bar{P}_2 = (1 + R_\mu - R_{\alpha\delta})/(1 - \tfrac{1}{2}R_\mu + 2R_{\alpha\delta}), \tag{4}$$

where

$$R_{\alpha\delta} = [A_\delta|_{\langle P_2\rangle=-0\cdot5}][A_\alpha|_{\langle P_2\rangle=1}]^{-1}. \tag{5}$$

If we assume that the curve for the homeotropically-aligned material has no α component, then from the figure $R_{\alpha\delta}$ is found to be approximately 0·67. By using the value of R_μ ($\sim 0{\cdot}7$) which was obtained for the $m = 5$ homologue of (I) we find that at 307·2 K $\bar{P}_2$ is 0·5, which is in reasonable agreement with the values obtained previously [6].

A detailed analysis of our complete set of loss data for mesophases with varying degrees of planar and homeotropic alignment has been undertaken and will be presented at a later date.

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