Short and long range correlations in liquid crystals composed of non-rod-like molecules

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Dielectric data of a polymer siloxane derivative have been analysed. The deviation from the Debye behaviour has been interpreted using the many body, cooperative model. Comparison with the results for liquid crystals composed of elongated molecules has been made from the point of view of short and long range correlations.

1. Introduction

A growing number of dielectric relaxation data show that simple Debye behaviour is hardly ever observed experimentally in imperfectly structured materials [1]. It has been found [2] that the asymptotic frequency dependence of the electric susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ is universal for various materials. The behaviour given by

$$\chi''(\omega) \sim \chi'(\omega) \sim (\omega/\omega_{max})^{n-1}, \qquad \text{for} \quad \omega > \omega_{max}, \qquad (1)$$

$$\chi''(\omega) \sim (\chi'(0) - \chi'(\omega)) \sim (\omega/\omega_{max})^m \quad \text{for} \quad \omega < \omega_{max}, \qquad (2)$$

is observed over many decades of frequency with $0 < n, m < 1$ where ω is the angular frequency and $\omega_{max}(\equiv 2\pi \nu_{max})$ is a characteristic relaxation rate. The parameters n and m (illustrating the shape of the dielectric response) together with $\chi'(0)$ and ω_{max} can give a complete description of the relaxing system. In the cluster model [3] admitting that the reorientation of each molecule goes via cooperative rearrangement of its neighbours the parameters n and m give information about the extent of the correlation of intra-cluster and inter-cluster motions. They can be understood as a measure of the structural ordering in the relaxing system on the local and long range level. The case with $n \to 0$ and $m \to 1$ corresponds to systems which consist of independently relaxing molecules and recovers the Debye limit. The opposite case with $n \to 1$ and $m \to 0$ corresponds to a fully cooperative response, typical of crystals with a perfect structural lattice. The behaviour of the relaxation process occurring in imperfectly ordered materials is intermediate between those two limits. The equation of motion for dielectric response function $\phi(t)$

$$d^2\phi/dt^2 + t^{-1}(2 + n + \omega_{max}t)d\phi/dt + t^{-2}(n + \omega_{max}t(1 + m))\phi = 0, \qquad (3)$$

has been proposed [4] to describe the time evolution of various systems during the relaxation phenomenon. The conservative nature of this second order equation is weakened progressively in time, due to the time dependence of the force constant $\sim (n + \omega_{max}t(1 + m))t^{-2}$ and damping factor $\sim (2 + n + \omega_{max}t)t^{-1}$. The

solution of equation (3) can be obtained analytically giving $\chi(\omega)$ as [3, 4]

$$\chi(\omega) = \chi'(0) * (1 + i\omega/\omega_{max})^{1-n} *_2F_1(1 - n, 1 - m; 2 - n; (1 + i\omega/\omega_{max})^{-1}),$$

(4)

where $_2F_1$ is the hypergeometric Gauss function. The high and low frequency limits of this expression have already been given in equations (1) and (2), respectively.

We have applied this non-Debye approach to the interpretation of the kHz relaxation data [6] observed for a side chain polymer with a liquid-crystalline phase.

2. Experimental details

To investigate the dielectric properties of the side chain siloxane polymer the complex capacity $C = C' - iC''$, (C' is the real part, C'' is $(2\pi\nu R)^{-1}$ where R is the resistivity) has been chosen [6] instead of the permittivity. The measurements were performed on a modified Sawyer–Tower bridge using a voltage of about 5 V. The sample was placed in a microcapacitor $0.5\,cm^2$ in area and with a $0.025\,mm$ separation between the electrodes. No orienting magnetic field was applied. The capacity has been studied for several temperatures during slow cooling of the sample from 342 K to 295 K in the frequency range from 2 Hz to 10 kHz. Due to ionic transport [6], part of the C'' data at low frequencies, deviates from the $\log C''(\log \nu)$ linear behaviour and so was excluded from further consideration.
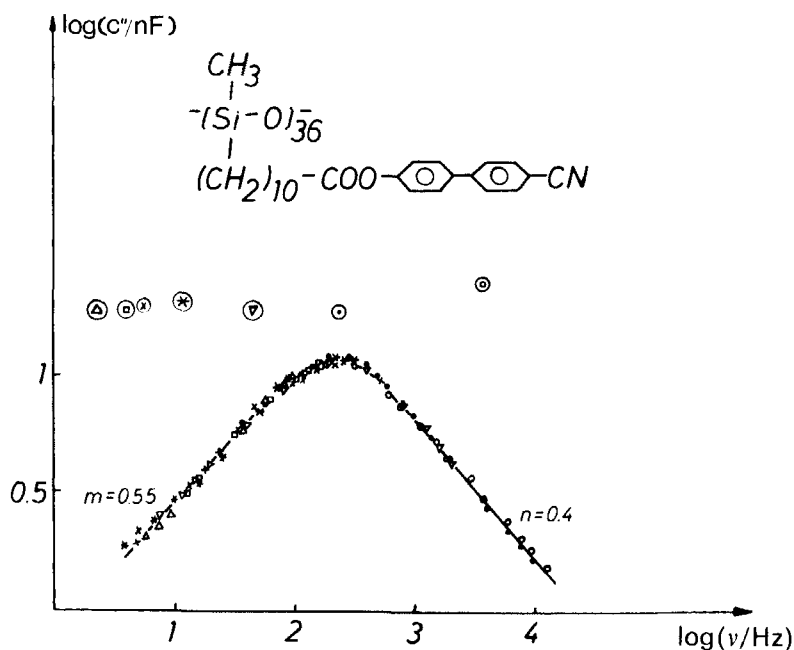

Figure 1. Master absorption curve for the siloxane side chain polymer in a double logarithmic scale. The curve has been obtained by the appropriate shift of the $\log C''(\log \nu)$ curves for each temperature along both coordinate axes. The magnitude of each translation is given by the vector connecting the reference point, i.e. the dot in the circle, whose position was chosen arbitrarily, and the encircled point being the trace of the reference point after shifting the data. The absolute values of ν_{max} can be obtained after symmetrical reflection of each encircled point with respect to the dot in the circle. $\bigcirc = 295.3\,K$, $\bullet = 306.8\,K$, $\nabla = 316.3\,K$, $* = 325.3\,K$, $\times = 330.8\,K$, $\square = 336.3\,K$, $\triangle = 341.3\,K$.

3. Results and discussion

The complex capacity data for the polymer siloxane derivative analysed in [6] using the Cole–Cole representation has demonstrated, in kHz frequency range, only one complex relaxation process ($\alpha \approx 0.16$) related to reorientation of the side chain around the silicon chain. The temperature dependence of the estimated relaxation rate has indicated a typical glassy behaviour with T_0 of 243.7 K.

In figure 1 the dielectric absorption is illustrated by the frequency dependence of the capacity of the sample in the double logarithmic scale in the compact form. The $\log C''(\log v)$ response curves have been shifted at each temperature along both coordinate axes to obtain the single master absorption curve. Superimposition of a number of experimental curves enlarges the effective frequency range of dielectric loss and reduces the experimental inaccuracies. The scaling procedure (described earlier [2, 3, 7]) is possible due to the form of the frequency dependence of the susceptibility (and capacity) proposed by equation (4). In figure 1 the scaling has been done with respect to v_{max} at the temperature chosen of 306 K; the reference point is marked by the dot in the circle. The experimental points for this temperature, represented by dots, are the only ones on the absolute scale. The encircled points represent the traces of the reference point after shifting the respective absorption curves.
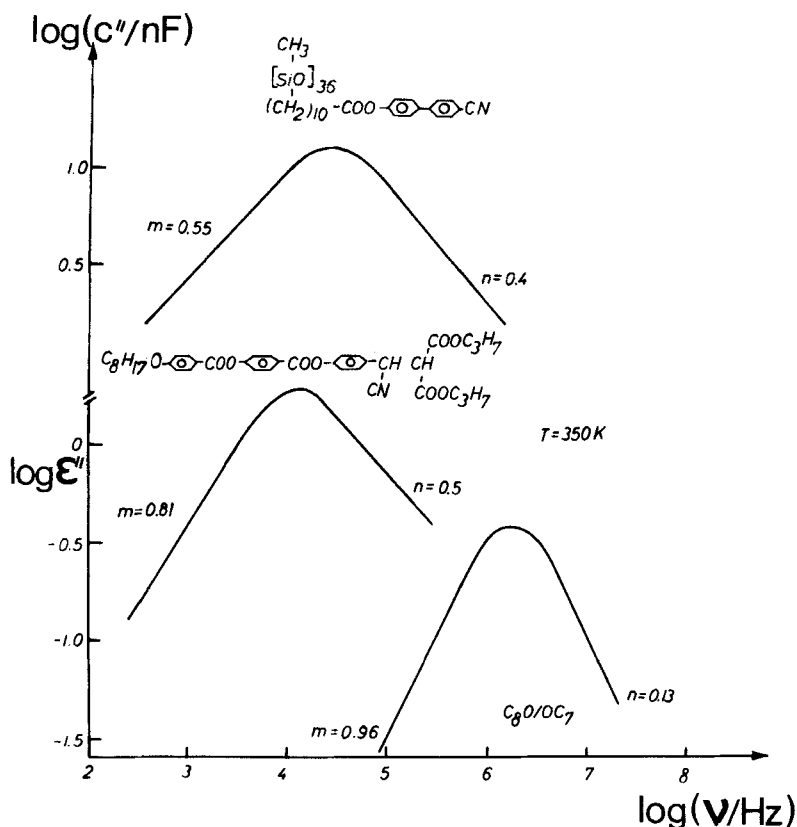

Figure 2. The dielectric response of the polymer siloxane derivative, swallow-tail compound (the substituted benzylidene malonate with a cyano-side group [5]) and 4-*n*-octyloxyphenyl-4′-*n*-heptyloxybenzoate. For each substance the master absorption curve has been scaled with respect to the peak loss at the temperature close to 350 K.

Table 1. The shape parameters for molecules in liquid-crystalline or plastic phases.

No	Substance	Phase diagram	Shape parameters	
			m	n
1	C_8O/OC_7†	C 335 K S_C 343 K S_A 361 K I	0·96	0·13
2	polymeric	C 317 K S_A 443 K I	0·55	0·4
3	cyclohexanol	Phase II 267 K phase I 298 K I	0·61	0·41
4	swallow-tailed (racemic mixture)	C 333 K S_A 373 K N 404 K I	0·81	0·5

†No large difference between the dynamical properties of the S_A and S_C phases has been found [7].

In figure 2 we show master absorption curves for the liquid-crystalline phases of 4-n-heptyloxyphenyl 4'-n-octyloxybenzoate [7], and of the swallow-tail compound [5], in both cases for the parallel component of the permittivity, and of the polymer siloxane derivative scaled to the temperature close to 350 K. (Due to very different values of clearing temperature (see the table) it was impossible to present the data at the same reduced temperature, i.e. ($T_{LC-I} - T$) for each material.) As the ν_{max} values are on an absolute scale we can compare the characteristic rates of the cyano-biphenyl reorientation around the main chain and of reorientations around the short axes of two other types of molecule. In the table the n and m parameters determined from the linear wings of the master absorption curves are collected together with typical results for plastic crystals [2]. In all cases the n values are not zero, unlike the Debye model. However, for the example of rod-like molecules n is rather small, which corresponds to weak coupling of their reorientations around the short axes. In other cases the n values are much larger. In the smectic A phase of the swallow-tail compound it is due to the antiparallel pairing of the molecules which has been observed experimentally [5].

For the siloxane side chain polymer the deviation of the observed relaxation from the Debye limit is significant. The increase in the short range order can be explained by both the interaction of the neighbouring CN dipoles and the relatively fixed positions of the side groups with respect to the main chain. The relatively high long range order (in comparison with the other two examples of liquid crystals) may be connected with the coupling of the cyano biphenyl motion with the main chain movement via the spacer group. The reorientation of the side group as a whole are rare and occur via large rearrangement of the non-polar spacer groups and non-polar back-bones in the environment; this causes a considerable reorientation of other dipoles and/or molecular units. Studies of the influence of the chemical structure of the main chain on the mobility of the side groups and on the glass transition temperature [6] provide experimental evidence to justify such an interpretation. Moreover it seems that the size of the local and long range correlations in the liquid-crystalline polymer is similar to that in plastic crystals [2]. In their structural organisation the role of the crystal lattice transmitting energy/information through the whole sample is replaced by the long back bone polymer groups.

4. Conclusions

The kHz-frequency relaxation observed for the smectic A phase of the polymer siloxane derivative has turned out to have the power law behaviour differing significantly from the nearly Debye form in compounds with rod-like molecules. In the side

chain polymer a cooperative motion of polar side groups is predicted in which the spacer and the main chain take place.

References

[1] JONSCHER, A. K., 1977, *Nature, Lond.*, **267**, 673.
[2] DISSADO, L. A., and HILL, R. M., 1983, *Proc. R. Soc.* A, **390**, 131. SHABLÁKH, M., DISSADO, L. A., and HILL, R. M., 1983, *J. chem. Soc. Faraday Trans. I*, **79**, 369.
[3] HILL, R. M., and JONSCHER, A. K., 1983, *Contemp. Phys.*, **24**, 75.
[4] DISSADO, L. A., and HILL, R. M., 1987, *Chem. Phys.*, **111**, 193. DISSADO, L. A., NIGMATULLIN, R., and HILL, R. M., 1985, *Dynamical Processes in Condensed Matter* (Advances in Chemical Physics, Vol. 63, edited by M. R. Evans) (Wiley), chap. 3.
[5] KRESSE, H., RABENSTEIN, P., STETTIN, H., DIELE, S., DEMUS, D., and WEISSFLOG, W., 1988, *Res. Cryst. Technol.*, **23**, 135; MASSALSKA-ARODŹ, M., STETTIN, H., and KRESSE, H., *Molec. Crystals. liq. Crystals* (to be published).
[6] KRESSE, H., WIEGELEBEN, A., and KRUCKE, B., 1988, *Acta pol.*, **39**, 583.
[7] MASSALSKA-ARODŹ, M., 1988, *Acta phys. pol.* A, **74**, 773.