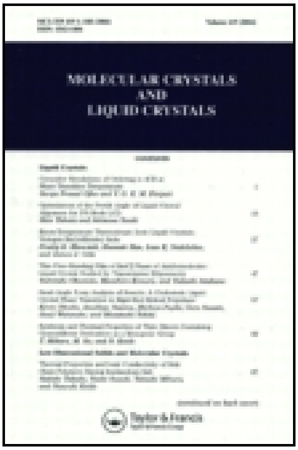

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Dielectric Relaxation in Crystalline n-Hexadecan-1-ol

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Dielectric Relaxation in Crystalline n-Hexadecan-1-ol

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Time-domain reflectometry has been applied to a study of the dielectric permittivity and relaxation in crystalline n-hexadecan-1-ol (cetyl alcohol). The quantity ($\epsilon_S - \epsilon_\infty$) rises monotonically from zero at about 40°C through the $\gamma \rightarrow \alpha$ phase transition at about 46°C to reach a maximum just below the melting point at 49.0°C, whereas the corresponding relaxation time, about 2.5×10^{-10} s, reaches a maximum at the $\gamma \rightarrow \alpha$ transition point. The results can be interpreted in terms of molecular rotations characteristic of the α-phase. ϵ_∞ exceeds n_D^2 and thus incorporates the effect of -OH group relaxation in the absence of more general molecular motions.

INTRODUCTION

By studying the resonance and damping characteristics of a porous graphite bar impregnated with n-hexadecan-1-ol, it has been shown[1] that maxima occur in the (viscous damping coefficient, T) plots just at the $\beta \rightarrow \alpha$ and $\gamma \rightarrow \alpha$ transitions of the alcohol.[2, 3] These phases are thought to interconvert by deformation twinning or homogeneous shear parallel to the hydrocarbon chain backbone (c-axis). Specifically, the hexagonal α-phase, termed the *rotator phase* because the hydrocarbon backbones spin about their own long axes, exerts very little damping, whereas the orthorhombic β-phase which, with respect to $-$OH group packing is intermediate in structure between the γ- and α-phases, damps mechanical motion more effectively. Damping by the monoclinic γ-phase is generally small. This mechanical relaxation technique is simple, but does require a relatively large specimen, which thus reduces the resolution of temperature scans. Furthermore, there is some interaction between the alcohol and the measuring technique, in that the oscillatory shear stress intrinsic to the method seemingly can induce the $\gamma \rightarrow \beta$ transition to occur.

Thin disc time-domain reflectometry, applied to dielectric permittivity and relaxation, lacks these disadvantages.[4] This technique suffers from poor accuracy at the highest frequencies, but proves to be reasonably well adapted to the study of the α-phase. We first give the principles of the method with some formulae, and then describe an application to n-hexadecan-1-ol.

THIN DISC TIME-DOMAIN REFLECTOMETRY

For a detailed discussion, reference should be made to Fellner-Feldegg[4] or to a review by Suggett.[5] Here we outline the method as it concerns the present experiment.[4, 6]

A cylindrical, co-axial transmission line of characteristic impedance Z_0 (Fig. 1a) contains a cylinder of non-conducting dielectric of length ℓ with relative complex magnetic permeability μ_r^* and dielectric permittivity ϵ_r^*. A sharp, transversely polarized wavefront propagated at velocity c along the line induces a displacement current in the dielectric which, representing a transient short circuit, effectively reduces the local impedance of the line to Z, whereby, for such period as it flows, part of the incident wavefront is reflected. The reflectivity is given by

$$\Gamma = \frac{Z - Z_0}{Z + Z_0} \tag{2.1}$$

where $Z = (\mu_r^*/\epsilon_r^*)^{\frac{1}{2}} Z_0$. However, for finite l one must consider conditions at face B. which requires the transmission coefficient z of the signal through the slab

$$z = \exp[-j(\omega \ell / c)(\mu_r^* \epsilon_r^*)^{\frac{1}{2}}]. \tag{2.2}$$

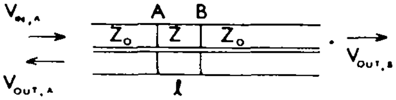

FIGURE 1a Schematic diagram of the sample of length ℓ installed in the transmission line.

If the line is terminated in its characteristic impedance Z_0, so there is no reflection from that source, we then require $V_{out,A}(t)/V_{in,A}(t)$ obtained from the S-matrix of the network, specifically the element S_{AA} known as the scattering coefficient for reflection. Such a network is represented by the signal flow chart in Fig. 1b, where the v_i are Laplace transforms into the complex frequency domain of the time dependent voltages V(t) appearing at the nodes in the network, and the t_{ij} are the transfer functions.[7] We then require $S_{AA} = v_4/v_1$ for reflection, noting that S_{BA} gives the, for us, unwanted transmission signal.

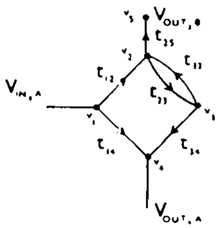

FIGURE 1b Signal flow diagram. The v_i are the Laplace transforms into the complex frequency domain of the V(t) appearing in the real system and the t_{ij} are the transfer functions.

After a little manipulation, this network gives

$$S_{AA} = \frac{(1 - z^2)\,\Gamma}{1 - z^2\,\Gamma^2} \tag{2.3}$$

On substituting (2.2) into (2.3) and linearising the exponential terms, one obtains an approximate formula appropriate to thin disc conditions

$$\begin{aligned} S_{AA} &= \frac{2j\omega\ell}{c}\,(\mu_r^* \epsilon_r^*)^{\frac{1}{2}}\,\frac{\Gamma}{1 - \Gamma^2} \\ &= \frac{j\omega\ell}{2c}\,(\mu_r^* - \epsilon_r^*). \end{aligned} \tag{2.4}$$

Should the incident signal be a true single-step pulse, we obtain the step response in the frequency domain simply by dividing by its Laplace transform $j\omega$, viz

$$(S_{AA})^{\omega}_{\text{step}} = \frac{\ell}{2c}\,(\mu_r^* - \epsilon_r^*) \tag{2.5}$$

when, for a non-magnetic sample, transformation into the time-domain gives

$$(S_{AA})^{t}_{\text{step}} = \frac{\ell}{2c}\,(1 - \mathcal{L}\,(\epsilon_r^*)). \tag{2.6}$$

For a Debye response,

$$\epsilon_r^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau} \tag{2.7}$$

when

$$(S_{AA})^{t}_{\text{step}} = \frac{\ell}{2c}\,(1 - \epsilon_\infty)\,\delta(t) - \frac{\ell}{2c\tau}\,(\epsilon_s - \epsilon_\infty)\,e^{-t/\tau} \tag{2.8}$$

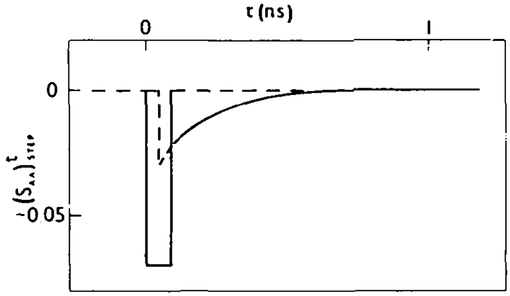

FIGURE 2 The ideal reflected signal. Axes are dimensioned to correspond approximately to the practical case considered in this paper.

in which case the response may schematically be pictured as the sum of two terms, shown in Fig. 2. ϵ_∞ is obtained from the area of the delta function, with τ and ϵ_S obtained from logarithmic plots of the relaxation.

This is the form of response which applies to n-hexadecan-1-ol, for it is non-magnetic and its proton conductivity is far too low to be detected by this technique. Practical difficulties[5] concern the risetime of the incident signal, in our case about 22 ps, and multiple reflections which introduce structure into the curves.[4] Fortunately, such structure is extremely stable and can be subtracted out by careful attention to phase. The finite risetime is dealt with by reference to a sample of known characteristics, but plainly sets limits on the determination of ϵ_∞.

Expressed in terms of dipole correlation functions,[8] this experiment gives the macroscopic response function, which is connected to the true dipole, time-dependent correlation function by the inclusion of a local field term of order unity. The risetime of the tunnel diode excludes short time, non-exponential, inertial relaxation, so one expects a simple exponential decay, even though terms of the form $<\mu_i (0). \mu_i (t)>$ and $<\mu_i (0). \mu_j (t)>$ will contribute.

EXPERIMENTAL

Commercial equipment supplied by Hewlett-Packard was used throughout. The system comprised a sampling oscilloscope 183A, TDR units 1815A and 1817A, and a tunnel diode of risetime 22 ps with suitable demountable co-axial airlines and matching terminations. Outputs were taken to an XY-recorder. Equipment was not available for transformation into the frequency domain, so there are no Cole-Cole plots. All analysis is in the time domain.

The sample was about 0.4 cm thick in order to meet the thin disc condition [equation (25) of reference (4)]. It was supported on a thin Teflon disc. Calibration was effected using a 0.25 cm thick Teflon disc, taking $\epsilon_\infty=2.00$ for this material.†

The n-hexadecan-1-ol (m. pt. 49.0°C) was BDH Specially Pure grade. Runs were conducted at heating rates of about 1°C/h. Scans through the response were signal-averaged and took 1 min. The delta function and the relaxation process were separated by first analysing the relaxation for $t \geqslant 0.2$ ns beyond the delta function, extrapolation to the centre of the delta function, subtraction and re-analysis. Oscillatory structure arising from multiple reflections was eliminated by subtracting runs in which there was no relaxation process, in practice for $T < 40°C$, from the runs at higher temperature. Using this analysis, only one relaxation time was found at each temperature, justifying use of the simple Debye Model equation (2.7).

RESULTS AND DISCUSSION

A short sequence of representative runs is illustrated in Fig. 3. There is no detectable change in response for $12°C < T < 40°C$ for $t \geqslant 0.2$ ns beyond the delta function, and the calculated value of ϵ_∞ throughout this range is 2.51. This is distinctly higher than the true (optical) $\epsilon_\infty \equiv n_D^2$, which we estimate to be $(1.452)^2 = 2.11$, in general agreement with the C_3 to C_{12} n-alkan-1-ols studied by Garg and Smyth.[9] Since the temperature dependence of ϵ_∞ is too small to be measured by the present technique, we concentrate attention on $\epsilon_s - \epsilon_\infty$, the form in which the permittivity ϵ_s is originally obtained in this experiment. For convenience in comparisons with the work of Garg and Smyth, we rename our $\epsilon_\infty = 2.51$ as $\epsilon_\infty \equiv \epsilon_{03}$ and our ϵ_s as ϵ_{02}, when the relaxation time is denoted τ_2 and the true $\epsilon_\infty \equiv n_D^2$ is termed $\epsilon_{\infty 3}$. Given this nomenclature, plots of $\epsilon_{02} - \epsilon_{\infty 2}$ and of τ_2 against temperature are presented in Fig. 4. These data are for polycrystalline material annealed just below the $\gamma \rightarrow \alpha$ transition temperature. Reproducibility of ϵ- and τ- data is better than 2%. Relative values are thus highly reliable. Absolute values have only qualitative significance, say ± 10%.

As with the mechanical relaxation experiments,[1] the permittivity, which corresponds to the compliance in those experiments, gives little indication of the transition point itself, though melting is clearly marked. Similarly, the relaxation time, corresponding to viscous damping in the earlier work, gives well structured data which confirm that the system responds most sluggishly at the transition point. There is no question of obedience to expressions of the form $\tau^{-1} = A\exp(-Q/kT)$ in any part of the temperature range under study, though it is true that τ_2 does fall towards a constant value as the temperature of the α-phase is raised.

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† e.g., van Krevelen, D. W., Properties of Polymers (Elsevier, Amsterdam, 1972).

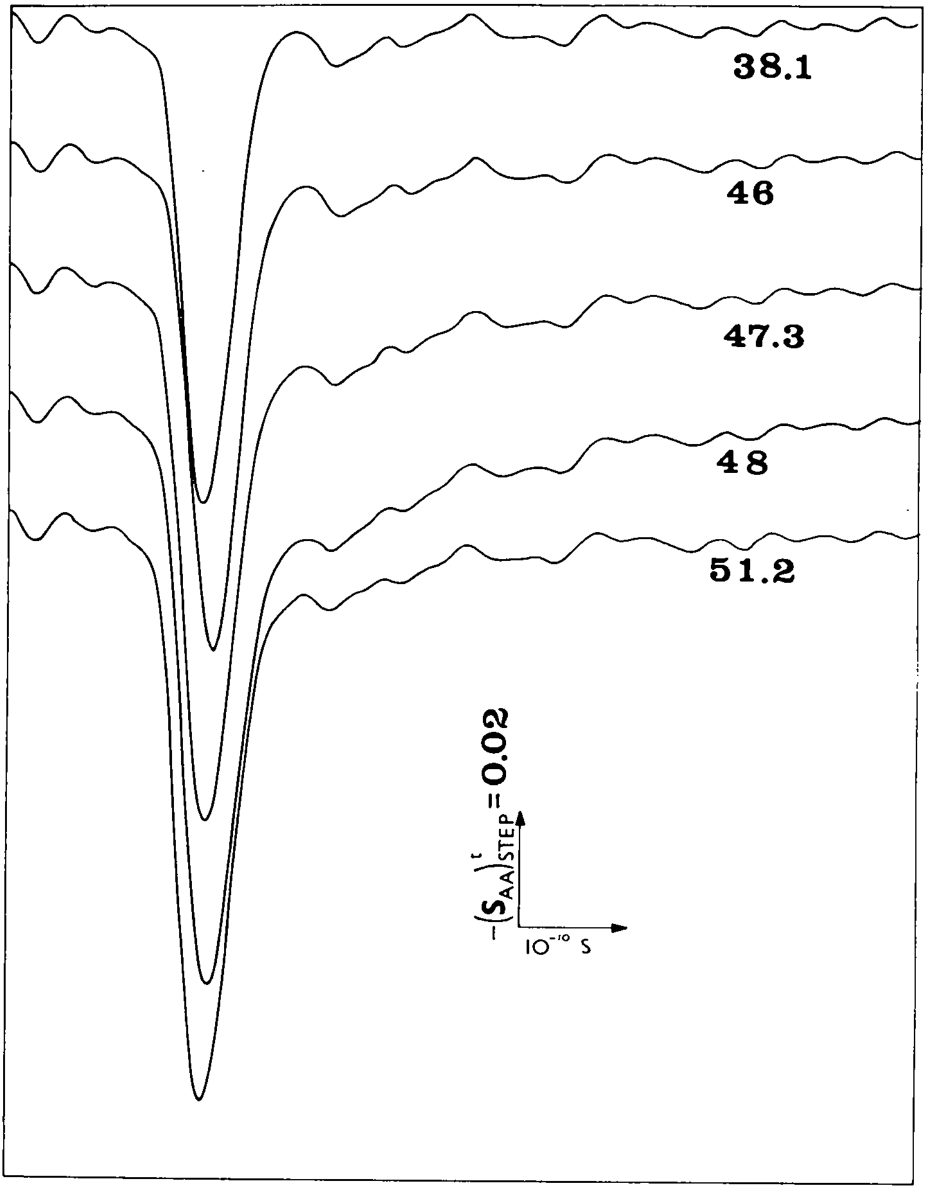

FIGURE 3 Representative plots of reflected signals obtained at the temperatures indicated on each curve.

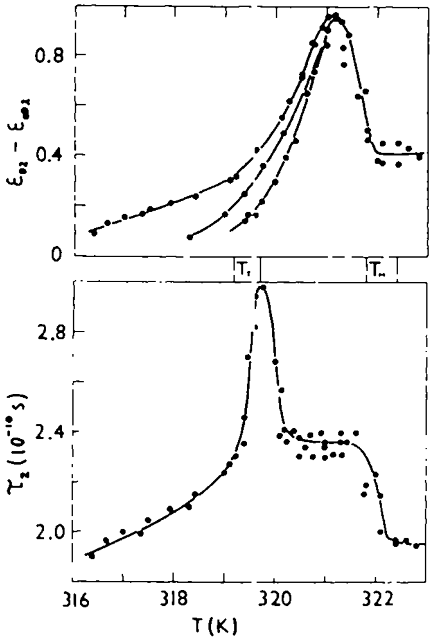

FIGURE 4a Plot of ($\epsilon_{02} - \epsilon_{\infty 2}$) against T/K for three samples. Divergences at low temperature are thought to arise from orientation and crystal size effects.

FIGURE 4b Plot of τ_2 against T/K for the same three runs. Note that the discrepancies at low temperature which are apparent in Fig. 4a do not occur with τ_2. The probable locations of T_m and the $\gamma \to \alpha$ transition temperature T_t are indicated.

On the other hand, plots of $\ln T(\epsilon_{02} - \epsilon_{\infty 2})$ against T^{-1} are linear, all samples having common intercepts at T_m. However, the energy term involved here is 10.4 eV, so all one can fairly say is that the number of relaxing entities does increase smoothly as the temperature is raised through $T_{\gamma \to \alpha}$ to T_m.[‡]
This increase in disorder can also be represented in terms of the Pople-Karasz two-site model. Accordingly, it is incorrect to suppose that the α-phase is characterised by free rotation over barriers of order kT, with a sharp onset of rotation at $T_{\gamma \to \alpha}$. Rotation increases steadily throughout the range of stability of the phase and may indeed be measurable in the γ-phase. These questions are perhaps

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[‡] A similar high energy, for proton conduction of order 10^{-11} to 10^{-8} (ohm cm)$^{-1}$, has been reported for this temperature range by Thomas *et al.*[15] A Grotthus chain mechanism requiring molecular rotation such as described here for the α-phase is believed to be involved. Note that such a mechanism does not imply a highly correlated dipole response such as observed with ferroelectrics, so the low value of ϵ_S in this work does not conflict with Thomas' suggestion.

best resolved by pmr second moment measurements.[10,11]

To facilitate comparison with earlier work,[1] one sample which had been annealed below the $\beta \rightarrow \alpha$ transition at 42°C was examined. These results are not illustrated, but they do show the $\beta \rightarrow \alpha$ transition in the (τ_2, T) plot, that τ_2 in the β-phase is almost twice τ_2 in the γ-phase at the same temperature and they confirm the weak temperature dependence of τ_2 in the α-phase. The $(\ln T(\epsilon_{02}-\epsilon_{\infty 2}), T^{-1})$ plot converges onto the common point at T_m for the other samples, confirming a smooth increase in the number of relaxing entities.

In attempts to identify the relaxation mechanisms, one notes from the work of Hoffmann,[12] Chapman and Whittington,[13] Meakins[14] and of Garg and Smyth,[9] for example, that there are two main relaxation mechanisms in the solid and three in the liquid. Thus, reorientation of the -OH group without motion of the backbone is termed process 3 and has $\tau_3 \approx 4 \times 10^{-12}$s, say, with $\epsilon_{\infty 3} = 2.11$ and $\epsilon_{03} = \epsilon_{\infty 2} = 2.51$. Because of the long risetime, this process cannot be separated from true high frequency polarisation such as occurs at optical frequencies, or analysed as inertially controlled relaxation. Process 2, reorientation of the -OH group as a consequence of rotation of the hydrocarbon backbone about its long axis, involves a frequency of $\sim 10^9$ s^{-1}.[12,13] This is consistent with our value of $\tau_2 \approx 2.5 \times 10^{-10}$ s, even allowing for a local field correction. Furthermore, our value of $\epsilon_{02}(T_m) = 2.92$ agrees well with values extrapolated from the data of Garg and Smyth, 2.91. Process 1 is not observed in these experiments. According to Garg and Smyth and others, it involves the dissociation of alcohol plurimers and subsequent relaxation of the -OH group so freed. Such association is not possible below T_m, given the crystalline periodicity of the α-phase, but it could account for the sharp drop in ϵ_{02} on melting.

CONCLUSION

We conclude that chain rotation, process 2, increases smoothly through the $\gamma \rightarrow \alpha$ transition to the melting point, but that the relaxation time passes through a maximum at or about the $\gamma \rightarrow \alpha$ transition. There is no evidence of a relaxation time distribution at this peak. Accordingly, we note the high value of τ_2 in the β-phase and follow the argument of Chohan *et al.* to suggest that during the shear transformation from $\gamma \rightarrow \alpha$ the β-phase forms transiently, coincident with the deformation twin density in the γ-phase attaining its limiting value.

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