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Phase Transformations in n-Hexadecan-1-ol

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The $\beta \rightarrow \alpha$ and $\gamma \rightarrow \alpha$ phase transformations in crystalline *n*-hexadecan-1-ol have been studied by the resonant bar technique using an alcohol + graphite composite. Although the $\gamma \rightarrow \alpha$ transformation can be eliminated by quenching, the $\beta \rightarrow \alpha$ transformation persists despite annealing. It is suggested that the oscillatory shear inherent in the technique produces the β-phase from the γ-phase.

INTRODUCTION

It is well established that there exist three crystallographic modifications of *n*-hexadecan-1-ol within 8°C range below the melting point, T_m. These phases, α, β and γ have been individually characterised to varying extents by X-ray diffraction,[1,2,3] dielectric properties,[4,5] infra-red absorption,[3] pmr,[6] and specific heat measurements[7] such that there is now little doubt about their regions of stability and the main features of their structures. However, hysteresis effects and the evident co-existence of the β and γ phases in certain experiments have to some extent obscured the relationship between these two phases.

The α-phase is the supposedly hexagonal rotator or waxy phase in which spinning hydrocarbon skeletons are aligned perpendicular to the basal plane.[2] This phase exists between T_m ($\sim$ 48.6°C) and the γ - α transition at 46°C and/or the β - α transition point at 42°C, according to experimental conditions. The β-phase is supposedly orthorhombic with the hydrocarbon skeletons perpendicular to the *ab*-plane, whereas the γ-phase, which is the phase stable at room temperature, is monoclinic. The relationships between these structures are

shown schematically in Fig. 1. Note that the α and β structures have on occasion been indexed as monoclinic, with the angle $\beta \sim 91\text{-}96°$, but that the β-structure, when regarded as orthorhombic, is the limiting case of a highly twinned γ-structure.

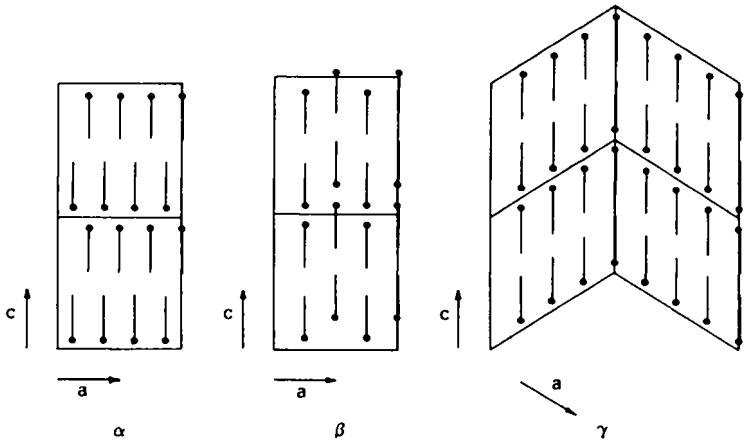

FIGURE 1. The crystal structures in schematic form of the α, β and γ phases of n-hexadecan-1-ol viewed along the *b*-axis. For the γ-phase, a twin boundary with composition plane (100) is illustrated. The crystal parameters are: α-phase, hexagonal, $a = 4.81$ A, $c = 43.83$ A; β-phase, orthorhombic, $a = 7.38$ A, $b = 5.04$ A, $c = 44.90$ A; γ-phase, monoclinic, $a = 7.34$ A, $b = 4.93$ A, $\frac{1}{2}c = 44.05$ A, $\beta = 122°$.

The γ-phase is best formed by slow cooling from the melt.[1,2] It readily forms twins,[8] but annealed samples at room temperature consist predominantly of this phase. In contrast, it is clear from X-ray results[2] and specific heat measurements[7] that rapid cooling from T_m gives the β-phase at room temperature.

In this note, we describe an application of shear modulus measurements to this problem. The technique is distinguished from others which have been used in that the alcohol is continuously subjected to oscillatory shearing forces.

EXPERIMENTAL

The resonant bar technique was used throughout. The specimen bar was Morganite graphite EY9A, 15 cm x 0.6 cm x 0.4 cm, vacuum impregnated with about 250 mg of *n*-hexadecan-1-ol (Specially pure grade, BDH). We report the compliance $J(\omega)$

$$J(\omega) = J_u + \frac{J_r - J_u}{(\omega^2 - \omega_0{}^2) + \eta^2/4 + i\eta\omega}$$

in terms of the peak frequency $\omega_p = (\omega_0^2 - \eta^2/4)^{1/2}$ for amplitude resonance and of the viscous damping coefficient η, as a function of temperature. J_r and J_u are respectively the relaxed and unrelaxed compliances of the impregnated bar, ω_0 is the resonant frequency in the fundamental normal mode in the limit $\eta \to 0$ and ω is the applied frequency. For small damping, the peak frequency is thus directly linked to the shear modulus of the impregnant and η to the loss modulus in shear.

The general procedure was to measure $J(\omega)$ or $J''(\omega)$ as a function of temperature during heating to about 50°C from between 20-36°C. Three classes of run are distinguished: (i) heating at about 4°C/h of specimens which had been annealed at 20°C for 17 days or at 36 °C for 2 h, (ii) heating at about 4 °C/h after quenching (10 min) from 50 °C and (iii) heating at less than 2 °C/h of specimens which had been annealed at 35 °C for 2 days, followed by slow cooling to 20 °C. All runs reported in this paper were carried out on the same bar.

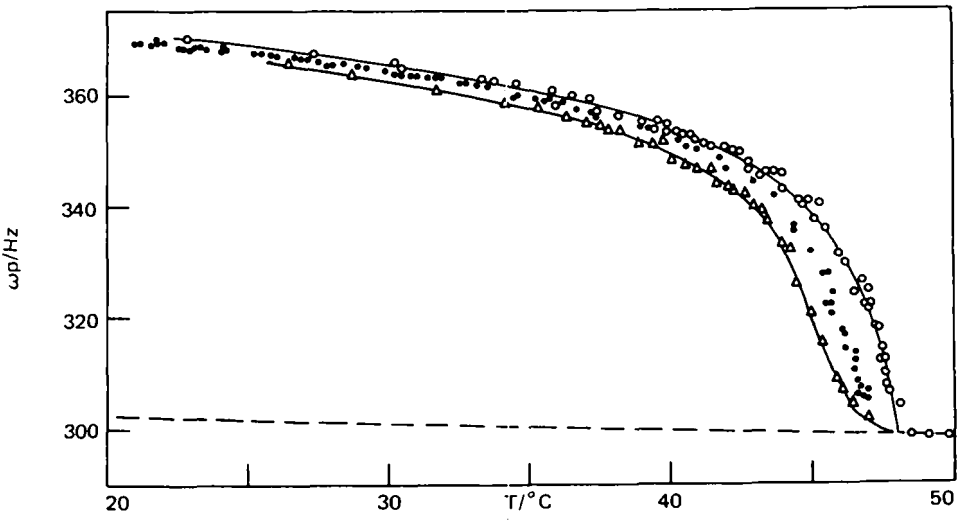

FIGURE 2. Peak frequency ω_p plotted against temperature for three classes of heating cycle: (i) Intermediate heating and cooling rates. (•); (ii) Quenched, moderate heating rate. (Δ); (iii) Carefully annealed, slow heating. (○).

RESULTS

In Fig. 2 is illustrated a collection of (ω_ρ, T) data. These curves have essentally the same shape as the (shear modulus, T) curves found with crystalline polymers. Important features are that in all runs the excess shear modulus due to impregnant falls to zero by T_m, but that for well annealed material (○) the data establish the high frequency boundary to the range of observed values, whereas specimens which have been quenched (Δ) resonate at a lower frequency-delineating the lower bound of the observed range of values. In particular, the excess modules in quenched specimens falls to low values some 2-3 °C below the melting point. All other data (●) correspond to conditions between the extremes of (ii) and (iii) and fall within the observed range of values. Apart from the break at T_m, there is no structure in these curves which enables one to locate and identify transformations.

The (η, T) curves illustrated in Fig. 3 are more useful in this respect. Thus the quenched specimen (Δ) has generally the highest viscous damping, which in-

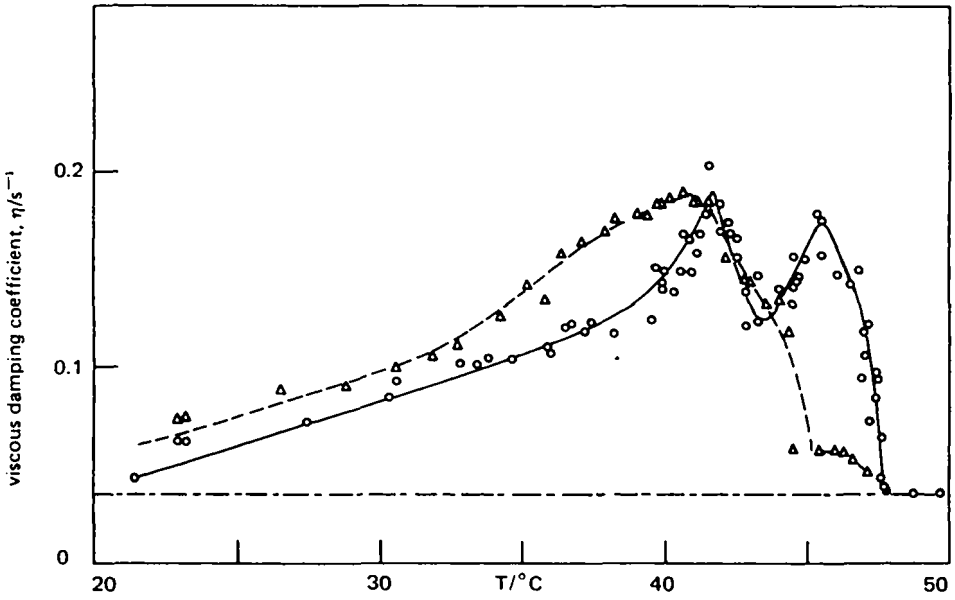

FIGURE 3. Viscous damping coefficient η plotted against temperature. Symbols as for Fig. 2. In both Fig. 2 and 3, the near-horizontal dashed line represents the behaviour of the pristine graphite, normalized to the loaded mass of the bar.

creases to a maximum near the $\beta \rightarrow \alpha$ transformation temperature, thereafter falling sharply to very low values. There is little evidence in this curve of any $\gamma \rightarrow \alpha$ transition. On the other hand, in the curves for annealed samples (○), the damping at low temperatures is lower, rising first to a peak near the $\beta \rightarrow \alpha$ transformation before dipping and rising again at the $\gamma \rightarrow \alpha$ transformation. In specially well annealed samples, the intensity of the $\gamma \rightarrow \alpha$ peak is somewhat enhanced, but an outstanding feature is the persistence of the $\beta \rightarrow \alpha$ peak in all cases. It has not proved possible so to anneal the specimens that the $\beta \rightarrow \alpha$ peak does not appear *in these experiments*, though Tanaka *et al.*[2] in their specific heat measurements clearly observed a $\gamma \rightarrow \alpha$ peak in the absence of a $\beta \rightarrow \alpha$ peak.

DISCUSSION

The structure of the (η, T) curve for the quenched specimen (Δ) confirms that rapid cooling gives predominantly the β-phase, which thus is associated with a low shear modulus and high damping. The proposed crystal structure indicates 3 orthogonal slip planes. Though the favoured slip systems are not identified, limited homogeneous shear parallel to the *c*-axis, which leaves unchanged the nearest neighbour OH-OH distances, is an obvious possibility. In the α-phase, not only will such shear become easier when the molecules are rotating, the smearing of the interchain field being here almost complete, slip perpendicular to the *c*-axis will also be facilitated. Such slip is held to be responsible for the loss of damping above 43 °C in quenched specimens. Furthermore, while it is possible that intergranular sliding might be responsible for some of the viscous damping and associated loss of shear modulus in quenched material at lower temperatures, this can not be the only cause, for reasons given later.

From results on well annealed samples, on the other hand, it is plain that one must associate a high shear modulus and low damping with the γ-phase. Even though these samples are prepared by methods which give predominantly γ-phase, one still obtains a strong $\beta \rightarrow \alpha$ peak in the (η, T) plot, which can not be removed by careful annealing. The problem is not so much the high shear modulus and low damping, for even a low density of γ-twins with a (100) composition plane as illustrated in Fig. 1 will ensure this by suppressing slip parallel to the *ab* plane, but is rather whether the shear which is an intrinsic part of the present experiment can induce the $\gamma \rightarrow \beta$ transformation to occur and thus inhibit the elimination by annealing of the β-phase.

This problem has been approached in two ways. First we noted the effect of stress amplitude on $J(\omega)$ under the assumption that the strain in the alcohol component accomodates to the strain in the graphite. A 5-fold increase of stress amplitude leads to a reduction in ω_p and increase in η. Representative figures for 30.5 °C, in the stable γ-region, are

stress amplitude	ω_p/Hz	η/s^{-1}
1	366.1 ± 0.1	0.0925
5	365.2 ± 0.1	0.1017.

Whilst this result is consistent with a shear induced transformation of $\gamma \rightarrow \beta$, the observed increase in η could merely be the effect of a general non-linear response, as described by Nowick and Berry.[9] Accordingly, we examined whether pre-exposure to high stress amplitudes at the resonant frequency could affect the ω_p and η values measured subsequently at normal stress amplitudes. At 30.5 °C, no such aftereffect was observed beyond the limits of normal experimental scatter (± 0.1 Hz). However, at 23.2 °C, reproducible results of aftereffect were obtained. Pre-exposure to stress amplitudes some 20 times above normal measurement levels for periods of 1 min to 1 h led to subsequent increases in η and reductions in ω_p, which quantities reverted to normal during periods of 1 h or so at measurement temperature. The effect was reversible and could be repeated reproducibly provided normal stress amplitudes were maintained during recovery, and $J(\omega)$ was measured within 5 min of the cessation of exposure to high stress amplitudes. Representative results for 23.2 °C are

	ω_p/Hz	η/s^{-1}
pristine	370.2 ± 0.1	0.0626
after exposure	369.6 ± 0.1	0.0743.

Evidently, pre-stressing leads to a long lived change in structure at low temperatures, though this anneals out rapidly above 30 °C. In the light of these results we suppose that the instantaneous ($J(\omega)$, stress amplitude) dependence arises from the same effect. Since it is argued that twinning inhibits slip on the *ab* plane in the γ-phase, the slip associated with pre-stressing, and *ipso facto* with the normal experiment, must be parallel to the *c*-axis. The crystallographic relationship between the β and γ phases then leads us to propose that the stress induced aftereffect is in fact that homogeneous shear which creates twin boundaries with composition plane (100) and, in the limit, transforms $\gamma \rightarrow \beta$.

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