

Micro- and Macroconformation of Macromolecules

9. Cyclotetracosane Solid and Molten State Phase Transitions by DSC, Brillouin Scattering, Dielectric and ^{13}C -NMR High Resolution Measurements

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S U M M A R Y

Cyclotetracosane exhibits complex phase behaviour in the solid state as well as in the melt as evidenced by complementary methods, DSC, BRILLOUIN scattering, dielectric constant and PE-MAS ^{13}C -NMR. Three solid phases have been verified, one of them - within the range from 299.5 to 312 K - exhibits extremely high molecular mobility. Between the start of melting, 312 K, and the first order transition at ~ 321 K a mesomorphic type region develops. Two additional transitions have been detected in the melt. That occurring at 361 K (DSC), 356 K (BRILLOUIN data) resembles the T_u as observed in n-alkanes.

I N T R O D U C T I O N

In the foregoing paper ¹⁾ n-alkanes and cyclotetracosane have been investigated as low molecular weight models for the crystalline and for the amorphous phase of polyethylene, respectively. The proton enhanced magic angle ^{13}C -NMR spectrum has indicated a highly mobile pseudorotating phase at room temperature for cyclotetracosane, since all carbons within the ring showed up identical average conformational surrounding at the NMR time scale. The conformational balance of anti and gauche conformers has been calculated from the chemical shift. On the basis of these data and of the chemical shifts of the n-alkane carbons as well as of the conformational shift of the gauche conformer derived from slow exchange solution spectra of meso-4,5-dimethyloctane PE-MAS solid state ^{13}C -NMR spectra of polyethylene have been interpreted in terms of the anti-gauche ratio within the amorphous folds.

In the following differential scanning calorimetry, BRILLOUIN scattering and dielectric measurements, in the solid state and in the melt, are reported, which substantiate the findings derived from nuclear magnetic resonance and which expand the insight into the complex phase behaviour of cyclotetracosane.

M E T H O D S A N D R E S U L T S

DIFFERENTIAL SCANNING CALORIMETRY

The DSC measurements have been performed with the PERKIN-ELMER DSC-2, at a heating rate 10 K min^{-1} , DSC range 20 mcal sec^{-1} , 7.18 mg sample weight. As shown in Figures 1 and 2 six thermal anomalies have been resolved within the 100 to 370 K range.

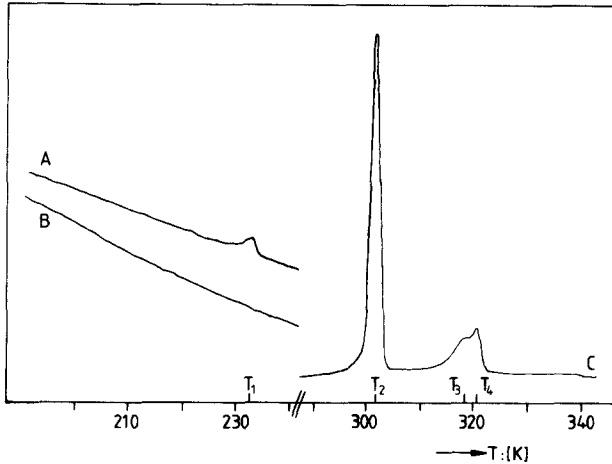


Figure 1: DSC on cyclotetracosane, heating rate 10 K min^{-1} , DSC range 20 mcal sec^{-1} . A sample run, B base line. $T_1 - T_4$ transition temperatures

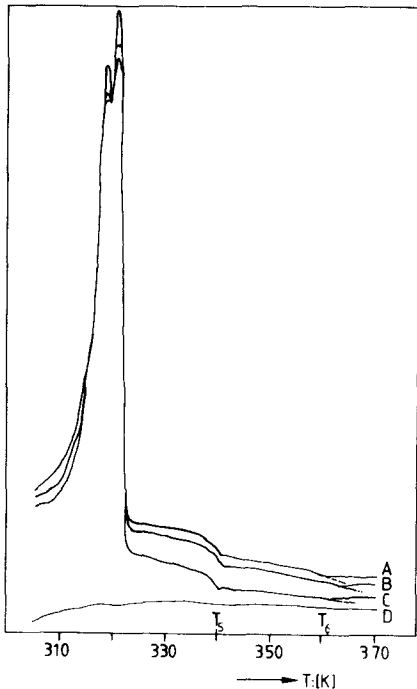


Figure 2: DSC on cyclotetracosane, heating rate 10 K min^{-1} , A,B,C different runs, D base line

A weak transition is found at $T'_1 = 228 \text{ K}$ (' indicating the flank), T_1 (peak maximum) = 233 K . The transition heat is 52 mcal only . A strong first order transition is observed at $T'_2 = 299.5 \text{ K}$, with a latent heat of 23.5 cal g^{-1} . At about 320 K two specific peaks overlap indicating a complex character of the melting process. Figure 2 shows that two additional thermal anomalies occur at 340 and 361 K , respectively. In order to judge the reproducibility three different DSC runs (A,B,C) are given in Figure 2, with D the baseline.

The double peak around 320 K exhibits a latent heat of 7.0 cal g^{-1} , $\sim 30 \%$ only of that at 299.5 K .

DIELECTRIC INVESTIGATION

The dielectric investigations were performed with a completely automated dielectric measurement set up, including a WAYNE KERR automatic precision bridge B 905 2). The measurements were carried out at $1, 3$ and 10 kHz , with increasing temperature. The quantities measured are the capacitance C and the conductance G , as a function of temperature and frequency. From these quantities the complex dielectric constant, ϵ^* , can be determined

$$\epsilon^* = \epsilon' - j\epsilon''$$

$$\text{with } \epsilon' = C \cdot d / \epsilon_0 \cdot A$$

$$\text{and } \epsilon'' = \epsilon' \cdot G / \omega \cdot C$$

[$\epsilon_0 = 8.8542 \text{ pF m}^{-1}$, d = thickness of the sample, A = area of the sample electrodes, $\omega = 2\pi \cdot \text{frequency}$]

Appropriate lozenge samples were pressed from the $\text{C}_{24}\text{H}_{48}$ powder at room temperature, 5 mm diameter and $.5 \text{ mm}$ thickness. The samples

were plated than with gold leaf. In Figure 3 $\epsilon'(T)$ is shown for the frequencies 1 kHz (■) and 10 kHz (●). In addition $\epsilon''(T)$ is plotted for 10 kHz (▲).

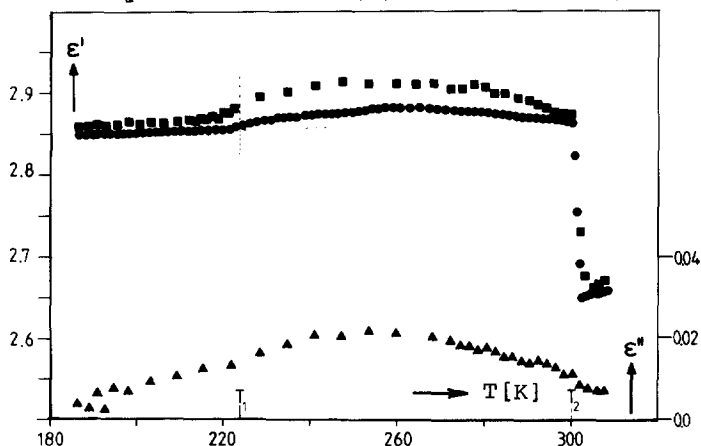


Figure 3: Dielectric measurements on cyclotetrasiloxane, $\epsilon'(T)$ at 1 kHz (■) and 10 kHz (●), $\epsilon''(T)$ at 10 kHz (▲).

Between about 180 K and T_1 , 224 K, ϵ' varies linearly with temperature. Between T_1 and T_2 , 300 K, it passes through a maximum, which is more pronounced at 1 kHz than at 10 kHz. The data at 3 kHz are not shown. They are situated between the 1 and 10 kHz $\epsilon'(T)$ curves. At T_2 $\epsilon'(T)$ drops discontinuously $\sim 13\%$ indicating a phase transition of the first order. The dielectric behaviour between T_1 and T_2 seems to indicate a slight dielectric dispersion at low frequencies, with the relaxation time below 1 kHz. The transition temperatures T_1 and T_2 as found from dielectric measurements are in fairly good agreement with those determined by DSC.

BRILLOUIN SPECTROSCOPY

BRILLOUIN spectroscopy has been performed on the melt and the polycrystalline cyclotetrasiloxane. The spectrometer has been described elsewhere using the 90A scattering geometry ³⁾. Thus -

for the UV scattering arrangement - the phonon wavelength Λ remains a constant

$$\Lambda = \lambda / 2n_0 \cdot \sin \phi_0 / 2$$

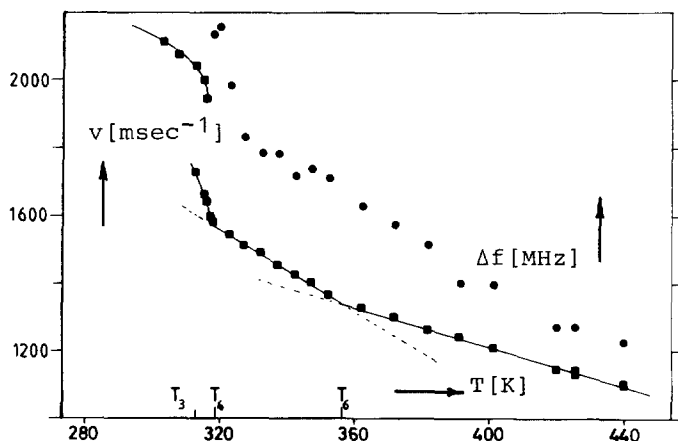


Figure 4: BRILLOUIN scattering on cyclotetrasiloxane, 90 A scattering geometry. Hypersonic velocity (■) and hypersonic attenuation (●)

with $n_o \cdot \sin \phi_o / 2 = n_i^{(i,s)} \cdot \sin \phi_i / 2$ (SNELLSIUS law) .

[$\lambda = 514.5$ nm optical wave length, $n_o = 1$ outer refractive index, $n_i^{(i)} = n_i^{(s)}$ refractive index for the incident (i) and scattered light (s), $\phi_o = 90^\circ$ outer scattering angle, $\phi_i =$ inner scattering angle.]

From the measured hypersonic frequency, f , the hypersonic velocity, v , can be determined: $v = f \cdot \Lambda$. Therefore the sound velocity data presented in Figure 4 do not contain the usual uncertainty of the refractive index. They all are measured for the same acoustic wave length $\Lambda = 363.8$ nm. The absolute accuracy of the sound velocity data presented ranges about 1 %. The hypersonic attenuation, Δf , is reported in Figure 4 too. The linewidth is accurate within ~ 10 %.

From the hypersonic behaviour above 300 K three transitions are indicated, T_3 at 313 K, T_4 at 318 K and T_6 at 356 K. T_5 , which is clearly detected by DSC, shows no feature in the hypersonic velocity. The hypersonic attenuation increases strongly below T_4 . This is probably due to acoustic RAYLEIGH scattering on mesomorphic domains because in the same temperature range - between T_3 and T_4 - the sample is slightly opaque. This is indicative for optical heterogeneities of the size of the optical wavelength which is comparable to the acoustic one.

PROTON ENHANCED MAGIC ANGLE ^{13}C -NMR SPECTROSCOPY

As reported in the preceding paper cyclotetracosane exists in a highly mobile phase at 303 K, near T_2 . All carbons within the ring show up identical chemical shift.

DISCUSSION

On the basis of the complementary methods applied the complex phase behaviour of cyclotetracosane may be interpreted as follows:

The weak low temperature transition, T_1 , has been verified by DSC and by dielectric measurements, at 233 and 224 K, respectively. Between T_1 and T_2 real as well as imaginary part of the dielectric constant go through a maximum. A slight dielectric dispersion at low frequencies with the relaxation time below 1 kHz is concluded.

At $T_2 = 301,5$ K by DSC and 300 K by the drop in the dielectric constant ϵ' - a strong first order transition occurs. Proton enhanced ^{13}C -NMR under magic angle spinning condition evidences an extreme molecular mobility. Within the enduring crystalline state more degrees of freedom are generated than at the melting point phase transition. This extreme mobility within this cyclotetracosane crystalline state from ~ 300 K up to T_3' (DSC), 312 K, is compatible with empirical and theoretical results on the pseudorotation in smaller rings 4) 5). This type of phase may be analogous to the high temperature phase of polyethylene. It contrasts, however, with the rotator phase of n-alkanes and of C_{36} and greater rings 6), which occurs $6^\circ - 8^\circ$ below the melting point. The latent heat of those rotator transitions ranges far below that of the melting transition, thus indicating that

the structural changes at this transition are much less dramatic than those effected at T_2 of the cyclotetracosane. In consequence it seems to be feasible to denominate this highly mobile phase as a pseudorotating one.

The melting process of $C_{24}H_{48}$ is a complex one. One may argue consistently that T_3 is the melt transition of the highly mobile pseudorotating phase, whereas between T_3 and T_4 mesomorphic domains exist as discussed above from the BRILLOUIN spectroscopy. The double peak in the DSC diagram supports the existence of two neighboured phase transitions around 320 K.

The first transition within the clear melt could be verified by differential scanning calorimetry only ($T_5 = 340$ K).

The T_6 transition in the melt has been detected by DSC (361 K) as well as by BRILLOUIN spectroscopy (356 K). At T_6 the hypersonic velocity in molten cyclotetracosane behaves like observed in n-alkanes at T_u ³⁾⁷⁾⁸⁾. The sound velocity gradient changes discontinuously at T_6 from $\delta_{T>T_6} = 8.1 \cdot 10^{-3} K^{-1}$ to $\delta_{T<T_6} = 16.2 \cdot 10^{-3} K^{-1}$. These gradients are, however, much larger as in n-alkanes ³⁾⁸⁾. The question remains open, which type of intra- or intermolecular ordering affects both the elastic and the thermal behaviour of cyclotetracosane at T_6 .

In conclusion the complex phase behaviour of cyclotetracosane could be elucidated with the aid of complementary methods of investigation in the solid state as well as in the melt. Some of the findings may be relevant for judging the phase behaviour of polyethylene in the semicrystalline state and in the melt as well as in its high temperature phase.

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