Variable temperature powder XRD study on C\textsubscript{32}H\textsubscript{66} hydrocarbon

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A powder X-ray diffraction study was made on dotriacontane, a saturated linear chain hydrocarbon, at different temperatures, that ranged from ambient to (close to) melting point. Strength of the phases was estimated. Possibility of the existence of intermediate phase during the onset of phase transition, from monoclinic to orthorhombic state, was examined. Inferences were made on the formation and nature of chain defects.

The concept of phase strength was used in case of certain mixtures of hydrocarbons\textsuperscript{1,2}. The concept was also applied to the case of pure hexatriacontane\textsuperscript{3}, which was subjected to slow heating on the stage of powder X-ray diffractometer. The results indicated that phase strengths of monoclinic and orthorhombic phases varied in a non-linear way. The studies\textsuperscript{3} also indicated the formation of intermediate phase and role of defects. Kim et al.\textsuperscript{4} studied pentacontane and hexacontane hydrocarbons and noticed the occurrence of premelting conformational disorder. The study was based on Raman and IR spectroscopic methods. Electron diffraction measurements made by Dorset et al.\textsuperscript{5} on epitaxially crystallized n-hexatriacontane showed chain-defect mechanism for linear chain melting. The chain defects play an important role in the present knowledge on the dynamics of long chain molecules. The aim of the present study is to apply the concept of phase strength in case of dotriacontane and to study the behaviour of phases during phase transition (including the role of chain defects). Variable temperature powder XRD investigations were made to achieve this object.

The concept of strength of phases in a material which is a mixture of different crystallographic phases is not new. However, a new approach was adopted by the present authors\textsuperscript{1,2} and it is specific to long chain molecular compounds. Based on this approach, let a hydrocarbon be a mixture of two crystallographic phases A and B. If \( PS(A) \) and \( PS(B) \) are the strength of phases A and B respectively, then:

\[
PS(A) = \frac{NP(A) \times 100}{NP(A+B)}, \quad \text{and} \quad PS(B) = \frac{NP(B) \times 100}{NP(A+B)}
\]

where \( NP(A) \) and \( NP(B) \) are the number of peaks belonging to phases A and B, respectively. The utility of this approach was demonstrated earlier\textsuperscript{6} from these laboratories.

Experimental

Aldrich (Switzerland) made dotriacontane (n-C\textsubscript{32}H\textsubscript{62}) hydrocarbon (briefly C32) (purity >99\%) was employed in the present studies. The crystallographic state of C32 was investigated by employing computer interfaced Rigaku-Rotaflex, Model RTP-300RC powder X-ray diffractometer (\( \lambda = 1.54178\)Å), in the variable temperature mode, using a vertical platinum sample holder at normal pressure. A Pt-Rh thermocouple (incorporated into the sample holder), in combination with a nanovoltmeter, were used to measure the temperature. The sample was heated from ambient temperature and powder X-ray diffractograms were recorded at 24°, 35°, 45°, 55°, 60°, 65° and 68°C. The temperature was held constant during any recording period.

Results

The peaks were indexed in the usual method\textsuperscript{1}. The X-ray long spacings of the lamellae at different index values and at gradually increasing temperature were examined. The data related to a few peaks are shown in Figs 1(a)-(b) as difference \( (D_\omega) \) between observed and calculated \( d \)-values.

It can be noticed in case of monoclinic phase [Fig. 1(a)] that the difference \( D_\omega \) initially increases up to 35°C and then decreases. However, the difference \( D_\omega \) does not become zero. It may be
understood that (initial) increase and decrease in the X-ray long spacing may be due to usual thermal expansion and chain defects\(^5\), respectively. It is interesting to note that such changes are noticed mainly in the case of (001) planes, and the values of (120), (110) and (200) planes remain fairly constant [Fig. 1(a) and Table 1]. It may be established from such behaviour that: (i) the variations noticed in the \(d/\theta_{001}\) values may not be due to error in the measurements, and (ii) variations in the length of the long molecules may primarily be responsible for the difference value \(D_{\infty}\), and (iii) the non-involvement of the length of the chain (in the form of lattice parameter \(c\)) may be the primary aspect that is responsible for the near constancy of the values of \(d/\theta_{hk0}\).

The situation related to the orthorhombic phase is shown in Fig. 1(b). It is interesting to note that the value of \(D_{\infty}\) in orthorhombic phase at 55°C is relatively large. This aspect shall be discussed in the next section. Fig. 2(a) shows the powder XRD pattern of C32 at 55°C where the existence of monoclinic and orthorhombic phase the onset of orthorhombic phase may be noted. Fig. 2(b) illustrates the modifications in the powder XRD patterns at different temperatures. Strength of phases was estimated as described earlier\(^5\) and the results are shown in Fig. 3.

Increase in the background areas of the powder XRD patterns was noticed and the values of such areas were due to diffuse scattering of X-rays\(^2\). It can be seen from Fig. 4 that the curve representing the diffuse scattering increases steeply from 60°C onwards. It is also fascinating to note that the values of areas at 24°, 35° and 45°C fit in to a smooth curve and the values of areas at 60°, 65° and 68°C fit into a straight line. However, there was a certain mismatch between the values at 55° and 60°C. Precisely, this was the range of temperature at which orthorhombic phase appeared and (low temperature) monoclinic phase disappeared (Fig. 3). It, therefore, can be believed that the deviations in the values of the areas in Fig. 4 are not due to any causal reasons.

<table>
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<th>S. No</th>
<th>Plane</th>
<th>25°C</th>
<th>35°C</th>
<th>45°C</th>
<th>55°C</th>
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<td>1</td>
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<td>-0.0365</td>
<td>-0.0363</td>
<td>-0.0378</td>
</tr>
<tr>
<td>2</td>
<td>(110)</td>
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<td>+0.0026</td>
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<tr>
<td>3</td>
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<td>-0.0081</td>
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<tr>
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<tr>
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Fig. 2(a)—Powder XRD pattern recorded at 55°C showing onset of β₁ phase (Pt peaks due to platinum)

Fig. 2(b)—A qualitative illustration of modifications in the powder XRD patterns at various temperatures

Discussion

The fascinating aspect related to the onset of phase transitions was that the excitation of molecules in monoclinic (β₂ₚ₁) phase was triggered between 45° and 55°C (Fig. 3). Such temperature range was much below the suggested value. The relatively large value \(D_{\text{ac}}\) in the orthorhombic (β₂) phase at 55°C needs consideration. Since the chain length of C32 molecule is 39.37 Å units, the expected X-ray long spacing for (001) plane is 42.7 Å in β₂ state. However, according to the method of Nyberg and Potworowski, when a sample is slightly impure, two hydrocarbon molecules chains are present in a unit cell along the c-axis. In that case the c-parameter of C32 is 84.973 Å. Our calculations show that the planes of C32 in β₂ phase can be better indexed when 84.973 Å is taken as c. It means that molecules forming monomolecular thick layers (in β₂ₚ₁ phase) have to undergo a complex manoeuvre such that almost a bi-molecular thick layer shall be generated for transition into β₃ phase. Based on the \(D_{\text{ac}}\) values of planes in β₂ phase (at 55°C), it is to be supposed that the molecules from the monomolecular thick layers first acquire an upright position [exhibiting increase in the over all (001) value] and then fuse into Nyburg-Potworowski type combination generating β₃ phase.

Therefore, the β₃ phase noticed between 45-55 °C has to be a sort of intermediate phase, between β₂ₚ₁ and β₃ phases. We believe that it may be better to denote it as a distinct phase β₃. The strength of β₃ was noticed to be 15% (Fig. 3).
In order to index the (hkl) planes of (i) $\beta$, at 55°C and $\beta$, at 60°C and 65°C and (ii) at 68°C, it was necessary to assume expansion of lattice in the $a$-direction, to an extent of (i) 10% and (ii) 25%, respectively. Large anisotropy in the thermal expansion coefficients of hydrocarbons and polymeric hydrocarbons is known; the expansion of $a$-axis is more than 50 times that of the $b$-axis. As such, the situation of phase transition once again becomes important at 68°C. The $D_{\infty}$ acquires relatively large negative value [Fig. 1(b)] and lattice becomes loose to a considerable extent (due to large lattice expansion).

If the shrinkage [Fig. 1(b)] in the chain length (due to the formation of chain defects) is coupled with the large increase in the $a$-parameter, then it appears that the true crystallographic state may not be anymore orthorhombic. We believe that this state once again can be treated as an intermediate state between (true) orthorhombic and rotator crystalline or melt state.

Further, the small difference between the values of $D_{\infty}$ at 65°C and 68°C indicates a reversal of shrinkage beyond 65°C suggesting increase in $d$-values. This is possible when molecules (in considerable number) prop-up from their parent layers. This should result in a highly defective layer stacking, including depairing of the molecules (from the Nyburg-Potworowski type combination) present in single unit cell (probably leading, at least partially to the formation of highly defective mono-molecular thick layers). The enhanced diffuse scattering of X-rays at this temperature range (Fig. 4) supports this view. In fact, it can also be stated from the diffuse scattering profile noticed in the temperature range 55°C-65°C (Fig. 4), that a great deal of change must have taken place in the state of the molecules, in terms of order and disorder.

The extent of chain length dependence of the phase behaviour and the formation and concentration of chain defects shall become evident from the rest of the work that we have undertaken, involving shorter and longer chain hydrocarbons.

**Conclusions**

The present studies establish, at least in principle, the formation of intermediate phase between the low and high temperature phases and it may be considered as a necessary requirement in phase transitions in long chain hydrocarbons. Even during the increasing temperature and consequent thermal vibrations, the hydrocarbon molecules surprisingly prefer to adopt Nyburg-Potworowski type combination, while they transit into high temperature phase.

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**References**