

be rationalized as follows:  $H_2 + O_2$  recombination reaction occurs on Pt atom sites on the surfaces of Pt particles in Pt/SiO<sub>2</sub> or Pt/Al<sub>2</sub>O<sub>3</sub>. Average size of Pt metal particles is in the range of 4–6 nm. Considering 5 nm Pt particles, the ratio of the total number of Pt atoms to the number of surface Pt atoms is about 6. If all the atoms in the same 5 nm Pt particle are available as the active sites, the rate of  $H_2 + O_2$  reaction should be at least 6 times higher. For the same Pt concentration,  $H_2 + O_2$  reaction rate over Pt/CeO<sub>2</sub> is about 10 times more than Pt/SiO<sub>2</sub>. Therefore, increase in reaction rate from 6 to 10 times seems to originate from the metal–ceria interaction in Pt/CeO<sub>2</sub> catalyst, in addition to all the Pt atoms dispersed in the form of Pt ions. Pt-substituted CeO<sub>2</sub> shows 3 to 5% oxide ion vacancy which increases oxygen storage capacity<sup>18</sup>. Therefore, CeO<sub>2</sub> support plays an additional role on the catalytic activity.

Two salient features of this novel catalyst are that Pt ions are well separated and they are stabilized to  $-Pt^{2+}-O^{2-}-Ce^{4+}-$  kind of linkages in the  $Ce_{1-x}Pt_xO_{2-\delta}$  solid solution. The active sites for the catalytic  $H_2 + O_2$  reaction are Pt ions rather than normally believed Pt metal (Pt<sup>0</sup>). Operationally, Pt/CeO<sub>2</sub> has many advantages over Pt/SiO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub>, such as absence of flashing, hot spot and wetness. The role played by oxygen defects in this catalyst needs further study and is being investigated.

In conclusion, we have shown that Pt ions dispersed over CeO<sub>2</sub> nanocrystallites synthesized by the solution combustion method act as an efficient and cheap catalyst for  $H_2-O_2$  recombination reaction at room temperature. This catalyst has already been successfully employed for  $H_2 + O_2$  reaction in a sealed lead acid battery to prolong its life and efficiency<sup>19</sup>.

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## Intrachain defects in $n-C_{60}H_{122}$ hydrocarbon: A low angle powder XRD study

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**An analysis based on the information obtained from the first reflection (the low-angle reflection) of powder XRD pattern, in case of longer ( $C_{60}H_{122}$ ) and shorter ( $C_{15}H_{31}OH$ ) alkane chains is made. The study is akin to small-angle X-ray scattering (SAXS) studies. Occurrence and increase in the density of intrachain defects in case of long chains and their absence in shorter chains are noticed. The results indicate that the defect formation is a chain length-dependent process, in a sense that longer chain molecules respond to thermal variation and can adopt systematic chain defects, whereas short chains ( $C \leq 15$ ) appear to be immune to such defects in the temperature range investigated.**

THE small angle X-ray scattering (SAXS) studies made by Strobl<sup>1</sup> indicated the formation of intrachain defects in  $n-C_{33}H_{68}$  hydrocarbon with increasing temperature. Kim *et al.*<sup>2</sup> made spectroscopic studies on  $n-C_{60}H_{122}$ ,  $n-C_{50}H_{102}$  and established the occurrence of kink defects. We took up a study on hydrocarbons of different chain lengths, ranging from  $C_{10}H_{22}$  to  $C_{60}H_{122}$ , and certain fatty acids and fatty alcohols. The study covers aspects related to phase transitions, phase strength and inter-chain and intra-chain defects and interface morphology<sup>3–13</sup>. As a part of such programme, we investigated the intrachain defects in case of orthorhombic  $n-C_{60}H_{122}$  hydrocarbon. Linear chain pentadecanol was also investigated to gain information on shorter hydrocarbon chains that are in solid state at room temperature.

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The variable temperature powder XRD data in the low angular range ( $2^\circ < 2\theta < 3^\circ$ ) were employed for such analysis, as they can be treated (in a restricted sense) equivalent to the information that can be obtained through SAXS. The findings are presented in this report.

Fluka (Switzerland)-made high purity (> 98%) linear chain hexacontane ( $n\text{-C}_{60}\text{H}_{122}$ ) and linear chain pentadecanol ( $n\text{-C}_{15}\text{H}_{31}\text{OH}$ ) were employed (in the as-received state) in the present study. These two compounds will briefly be referred to as C60 and C15-ol, in this report. The powder XRD (PXRD) data were recorded on a computer interfaced Rigaku-Rotaflex, model RTP-300RC instrument ( $\lambda = 1.54178 \text{ \AA}$ ) 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 is used for the temperature measurement. The temperature is held constant during any PXRD recording period. Studies on these materials at temperatures that are very close to their melting point  $T_m$  could not be carried out, due to the limitations imposed by the vertical sample holder; the materials would soften and flow down the sample holder, as  $T_m$  is approached.

The  $d_{001}$  values of C60 in monoclinic ( $\beta_m$ ) and orthorhombic ( $\beta_o$ ) forms are 69.25 Å and 78.04 Å, respectively. The  $d$ -value of the first peak of the PXRD pattern recorded at ambient temperature is 37.7927 Å. This peak is recognized as due to (002) reflection; the projected  $d_{(001)}$ -value is 75.5854 Å, which is close to the  $d_{001}$  value of  $\beta_o$  form. Therefore the peak is recognized as that of the  $\beta_o$  phase. The  $d$ -value of this first peak of all the PXRD patterns, recorded at different temperatures and projected as  $d_{001}$  is shown in Figure 1a. The  $d$ -value continuously decreased with increase in temperature up to 95°C. On cooling from 95°C to 30°C, the  $d$ -value did not change. At 95°C, the  $d$ -value was 69.1082 Å. The change in the  $d$ -value ( $\Delta d_{001}$ ) was 6.4772 Å when the increase in the temperature ( $\Delta T$ ) was 71°C. The absolute intensity (Figure 1b) increased up to 65°C and then decreased and touched a minimum value at 95°C; it did not regain its value when the material was cooled back to ambient temperature. The peak width (Figure 1c) also touched a minimum at 95°C. But the value increased on cooling to 30°C; the frozen-in defects being responsible for it. The diffraction patterns of C60 recorded at various temperatures are shown in Figure 2. In case of C15-ol, the  $d$ -values showed insignificant variations in the temperature range studied (Figure 3a). The peak intensity almost continuously decreased with increase in temperature (Figure 3b). The peak width (Figure 3c) after an initial increase (in the range 24–30°C), remained constant during the rest of the heating.

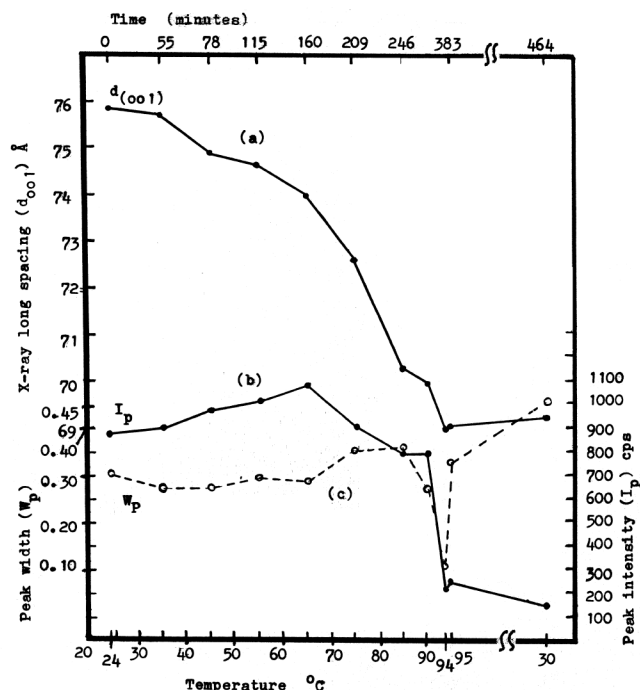


Figure 1.  $n$ -hexacontane – (a) Gradual decrease in chain length; (b) Changes in peak intensity; (c) Changes in peak width.

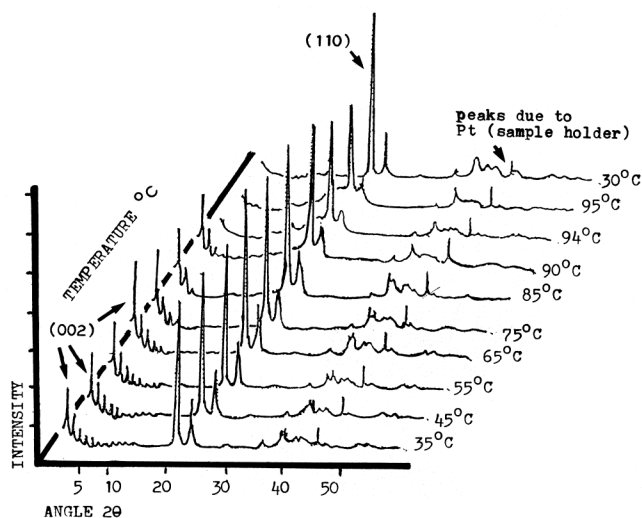


Figure 2. PXRD patterns of  $\text{C}_{60}\text{H}_{122}$  hydrocarbon obtained at different temperatures.

In order to probe the causes for decrease in the long spacing (the  $d_{001}$  value) with increasing temperature, a basic question may be asked on the possibility of occurrence of decrease in long spacing, without causing any change in the chain length. It may be noted that hydrocarbon chains are stacked as parallel arrays, such that a lamella is formed. Several such lamellae, when placed one above the other in a systematic manner generate a 3D crystal. If the hydrocarbon chains are perpendicular to the lamellar surface (the 001 plane), then an ortho-

rhombic cell can be defined, in which length of the chain is parallel to  $c$ -axis of the cell. Between the lamellae, there is a certain free space. The width of such interlamellar space and the length of the chain together give the value of the  $c$ -parameter of the orthorhombic unit cell. Estimation of interlamellar spacing is made from published  $d_{001}$  values and variations in the spacing are noticed (Figure 4). However, the range of such variations is 1.75 Å only. It is this spacing that mini-

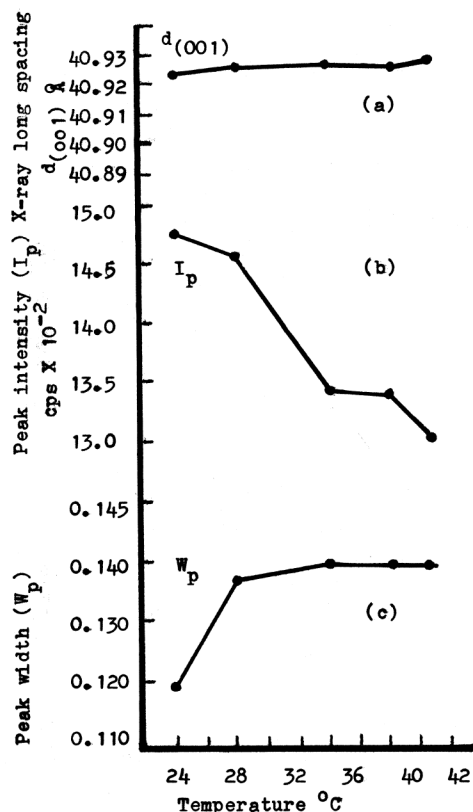


Figure 3. Case of  $n$ -pentadecanol – (a) Negligible variation in chain length; (b) Changes in peak intensity; (c) Changes in peak width.

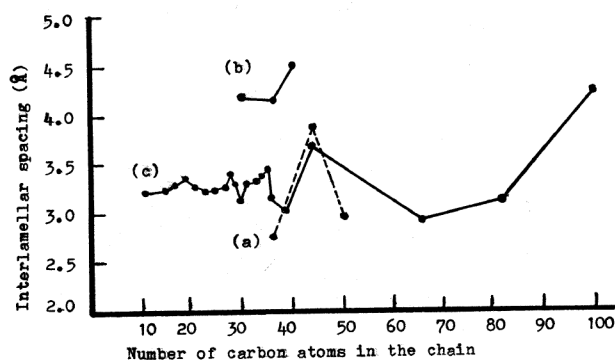


Figure 4. Interlamellar spacing values of different hydrocarbons. Values are estimated from data published in ref. 14 (curve (a)), ref. 19 (curve (b)) and ref. 20 (curve (c)).

mizes the repulsions and maximizes the van der Waal interaction between the end methyl groups. As such, there is no way of decreasing the interlamellar spacing indefinitely. (On the other hand, an NMR study<sup>14</sup> indicates that the value of the spacing may actually increase due to defective packing of layers.) Therefore, in view of the fact that  $d_{001}$  is not only the interplanar spacing, but is defined by the thickness of the lamellae, which in turn is defined by the chain length of the molecule itself, it may be stated that the  $d_{001}$  value essentially and necessarily depends on the chain length and there is no way of decreasing it (as long as the hydrocarbon continues to stay in a given phase), without modifying the chain length. A phase transition from orthorhombic to monoclinic phase can lead to decrease in the value of  $d_{001}$  through the formation of lamellae. In the monoclinic phase the molecules are inclined with respect to the (001) plane. However such a phase transition occurs only when a high-temperature (orthorhombic) phase is cooled to a low-temperature (monoclinic) phase and does not take place during increasing temperature.

In case of C60, continuous shrinkage of the chain length with increase in the temperature has to be understood in terms of increasing concentration of intrachain defects. The length of shortest possible intrachain defect (kink)  $2g1$ , is equal to the C–C bond length<sup>15,16</sup>. It can be seen from Figure 1a that at temperature 64°C ( $\Delta T = 40^\circ\text{C}$ ),  $\Delta d_{001} = 1.544$  Å. It may therefore be stated that the first kink is formed at 64°C. Due to the increased flexibility offered by the thermal motion, it is possible that re-orientation of the diffracting domains takes place in the temperature range of 65°C, contributing to increase in intensity at 65°C to a maximum value. The fall in the peak intensity and peak width in the temperature range of 65–75°C up to 95°C may be indicative of the increased level of pre-melting<sup>17</sup>. If the overall situation is taken into consideration, it can then be seen that the ratio between 6.4772 Å (which is the  $\Delta d_{001}$  for  $\Delta T = 71^\circ\text{C}$ ) and 1.544 Å is 4.1 ( $\approx 4$ ). It can therefore be stated that average kink concentration per chain at 95°C is 4. It may be recalled that each kink is formed by two gauche bonds ( $g$  and  $-g$ ), the additional volume  $V$  required by each kink is  $V = 2.6V_0$ , where  $V_0$  is the volume occupied by one  $\text{CH}_2$  group<sup>18</sup>. Still larger free space (additional volume) is required, if the higher-order kinks<sup>15</sup> such as  $2g3$  or  $4g4$  are considered.

In view of the fact that hydrocarbons and polyethylene exhibit large anisotropy in lateral thermal expansion<sup>1</sup>, more free space may be available. Thus there is a possibility for the occurrence of higher-order kinks in the hydrocarbon chain of sufficient length (such as C60), when the material happens to be close to  $T_m$ . In fact, at temperatures that are away from  $T_m$ , the thermal energy for formation of higher-order kinks<sup>15</sup> is not available to the chains. In case of C15-ol, since the range of temperature ( $\Delta T = 16.5^\circ\text{C}$ ) does not cover the

range where first kink (of the type 2 g1) is formed, it fails to show any shrinkage of the chain. However, C15-ol chain exhibits a small expansion along the C-axis. Such a change is masked by the other effects (such as discussed in case of C60) in case of long chain molecules.

In case of C60, Kim *et al.*<sup>2</sup> noticed that almost constant gauche bonds per chain exist up to 70°C and the concentration of gauche bonds increase from 70 to 95°. They also suggested that the disordering process in the shorter and longer chain hydrocarbons was similar.

Our present results establish that at no temperature the concentration of intrachain defects remains constant (Figure 1 a) once their formation is triggered. It may be stated from the continuous fall in the peak intensity and constant peak width (Figure 3 b and c) noticed in case of C15-ol that the disordering processes in shorter and longer hydrocarbon chains may not be similar. While kinks and jogs promote the disorder in longer chains ( $C \geq 60$ ), probably it is the thermally-triggered chain vibrations and flip-flap rotational jumps that are the chief contributors to disorder in case of shorter chains ( $C \leq 15$ ).

SAXS or low angle PXRD investigations on the behaviour of C60 and C15-ol in the temperature range of 95°C –  $T_m$  and 40.5°C –  $T_m$ , employing a horizontal sample holder, should be able to throw more light on the behaviour of the molecular chains.

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## Heterocarpous flowers resulting from a recessive mutation in periwinkle *Catharanthus roseus*

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**Wild-type *Catharanthus roseus* flower possesses a bicarpellary gynoecium. An induced mutant has been isolated in which a higher number of floral meristems were formed to develop into flowers. Some of the flowers possessed tricarpellary gynoecium. The mutant phenotype appeared to be related to the higher level of floral meristematic activity. It is concluded that wild type *hcf* gene has limiting effect on number and size of fruits, ovary compartmentation and seed number.**

IN angiospermic plants, the seeds are contained in an ovary which is a part of the gynoecium. The ovary may be simple or compound. The simple ovary may contain one or more seeds/ovules. The compound ovary has several sections, each containing one or more ovule(s). In a typical gynoecium, the ovary extends into a style which terminates into a stigma. In the process of pollination, the pollen-grains that arrive on the stigma germinate and produce pollen tubes which travel through the style and enter into the ovules to enable double-fertilization. There is large variation among angiosperms in the structure of the gynoecium. In some species, the gynoecium has a single carpel possessing its

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