

On the Molecular Arrangement of Some Organic Films

By

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Abstract

Thin films of paraffin waxes were prepared on metal foils and plates, and their structural changes with temperature were examined by electron diffraction method. It was found that the crystalline state in the basal part of the film was maintained up to a certain definite temperature above its melting point. This temperature increased linearly with increase of the number of carbon atoms in paraffin molecule, but was different from "transition temperature" named by K. Tanaka, at which the regularity of molecular arrangement in the surface layer of the film was completely destroyed. It was also found that molecules in the surface layer of the film were maintained in quasi-crystalline state up to the temperature mentioned above (transition temperature of the second kind). It was inferred that this phenomenon occurred even in the surface layer of the molten paraffin wax in bulk from its cooling curve. Extremely thin film of paraffin wax and films of some other similar compounds were also examined.

Introduction

It was reported by K. Tanaka¹ that the regular molecular arrangement in the surface layer of thin film of a long-chain compound formed on metal surface was maintained up to a definite temperature above its melting point and this phenomenon was reversible with temperature for paraffin, alcohol and others. This temperature was called "transition temperature" of the film by him. There exists a linear relationship between that temperature and the number of methylene groups contained in the molecule for each homologous series. The writer took interests in the internal structure of these films and intended to examine them by transmission method of electron diffraction.

Experiment

Specimens used were five Merck's paraffin waxes whose melting points ranged from 44° C to 74° C. Films of these waxes were prepared on

1. K. Tanaka: This Memoirs, 21 (1938), 85; 23 (1941), 195.

copper foils and plates by dropping benzene solution of a specimen or by smearing the molten wax on them and examined with electron diffraction, one by transmission method and the other by reflection method respectively. These specimens were heated by a small electric furnace in the diffraction apparatus during observations.

Results obtained by reflection method agreed well with Tanaka's previous work. The pattern obtained by transmission method, on the other hand, showed six spots and this corresponded to single crystal of orthorhombic system characteristic to paraffin series. The crystal transformed from orthorhombic to hexagonal system as temperature rose, in agreement with Müller's X-ray examination.² This state of hexagonal crystal was maintained up to a certain definite temperature higher than its melting point and at that temperature the spot pattern vanished and there appeared a blurred ring, whose Bragg spacing was 4.6 Å which agreed well with the spacing obtained from molten paraffin by X-ray examination.³ This definite temperature for each specimen is tabulated in Table I together with the transition temperature by reflection method. These temperatures were plotted against the mean number of carbon atoms in the molecule estimated from its melting point for each specimen (Fig. 1). (For convenience the writer will call the transition temperature by reflection method "the first kind" and that by transmission method "the transition temperature of the second kind" hereafter.) It can be seen from the figure that the transition temperature of the second kind also increases linearly with increase of the number of carbon atoms in the molecule, but the rate of increase is not the same as that of the first kind. It is interesting that the spot pattern by transmission method was still maintained above the transition temperature of the first kind for the specimen whose melting point was 74° C. Indeed, the transmission

TABLE 1
Transition temperature of paraffin wax.

Specimen No.	Melting point	Mean number of carbon atoms	Transition temperature	
			The 2nd kind	The 1st kind
1	44° C	22	60~61° C	74~76° C
2	46.5	23	62~64	75~77
3	52	24	66~68	79~80
4	68	31	89~90	89~90
5	74	35	102.5	91~93

2. A. Müller: Proc. Roy. Soc., A, 138 (1932), 514.

3. A. Müller: *ibid.*

pattern obtained for this state showed a blurred ring inside the six spots. It is concluded from these facts that the crystalline state of the basal

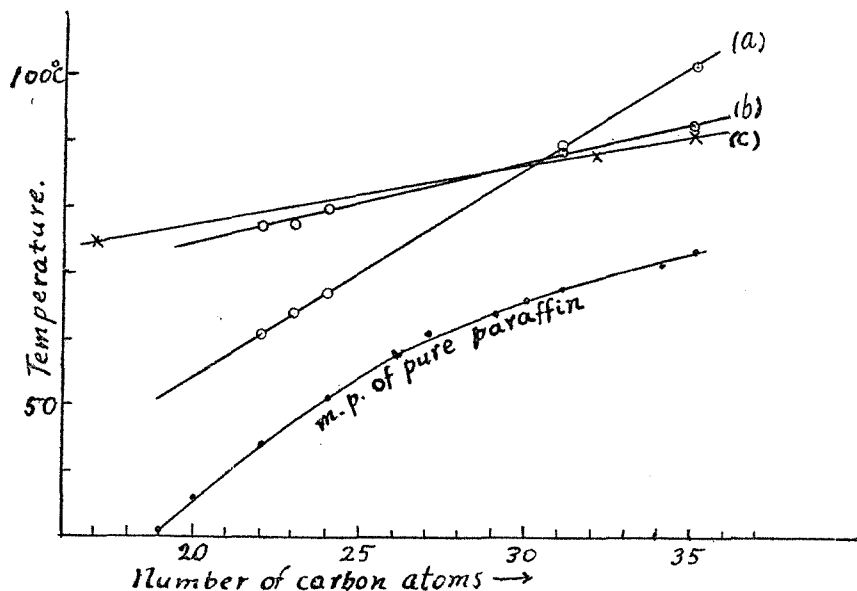


Fig. 1. (a) The transition temperature of the second kind, (b) that of the first kind for paraffin waxes. (c) The transition temperature of the first kind for pure paraffin quoted from K. Tanaka's paper.

part of the film is maintained up to the transition temperature of the second kind. Films formed on silver foils and plates were also examined, but it was found that transition temperatures of both kinds were not different from the corresponding values obtained for films on copper foils and plates.

Anomaly in reflection pattern.

Reflection pattern obtained from comparatively thick film of paraffin wax, whose transition temperature of the second kind was lower than that of the first kind, showed an anomaly as the temperature rose near the transition temperature of the second kind. Layer lines of the second and the third order became broad and blurred, and then the line of the second order split up into two lines as temperature rose and approached the transition temperature of the second kind (Plate 1). This state was maintained in the temperature range of 2~3° C, and then the outer one of the double line vanished and the line of the first order became faint as temperature rose. This phenomenon was reversible with temperature.

This pattern was analysed by the usual method (Fig. 2) and it was found that this pattern was the superposition of two "grease patterns," one of which was not affected by refraction, while the other was subjected to the effect of inner potential of about 5 volts. The writer will call the former "C" pattern and the latter "L" pattern for convenience.

"L" pattern agrees well with the one for higher temperatures (Table 2) and it is obvious that this pattern is due to free molecules arranged perpendicularly to the free surface.

TABLE 2. Spacing and inner potential
(for the specimen whose melting point is 44° C)

Temperature	d (Å)	ϕ (volts)
17° C	2.58±0.02	c. a. 1.7~4.8
59 'C'	2.60~2.61	—
'L'	2.52~2.54	4.8~5.1
64	2.53~2.55	5.0~5.5

"C" pattern is rather close to the one for lower temperatures and the side spacings measured for spots on the first order line by Murison's method⁴ agree well with those obtained for spot pattern by transmission method at the same temperature (Table 3). Layer lines of "C" pattern often appeared as arcs, especially on heating, which seems to be due to the orientated crystalline state. From these considerations it is concluded that "C" pattern is due to quasi-crystalline state whose *c*-axis is perpendicular to the surface.

TABLE 3. Side spacings for "C" pattern.

Side spacings measured for spot on the 1st order line.	Spacing & indices obtained by transmission method. (hexagonal system)	Indices estimated
4.16 Å	4.17 Å (100)	(10 <i>l</i>)
2.40	2.40 (110)	(11 <i>l</i>)

The line of the fourth order of "C" pattern coincided with that of "L" pattern and consequently there exists the discrepancy of about 0.08 Å between the measured value of spacing d , which corresponds to the distance of alternate carbon atoms in a molecule, for "C" pattern and that for "L" pattern (cf. Fig. 2, also Table 2.). It is well known that the normal paraffin takes two crystalline forms⁵ and the long spacing,

4. C. A. Murison: *Phil. Mag.*, **17** (1934), 204.

5. A. Müller: *Proc. Roy. Soc., A*, **127** (1930), 417.

which corresponds to the chain-length of a molecule, increases by 1.25 Å and 1.203 Å per carbon atom for each form respectively. The twice of the difference of these two increments is nearly equal to the discrepancy mentioned above and this fact seems to suggest that there exists some connection between these two crystal forms and the state which produced "C" and "L" patterns.

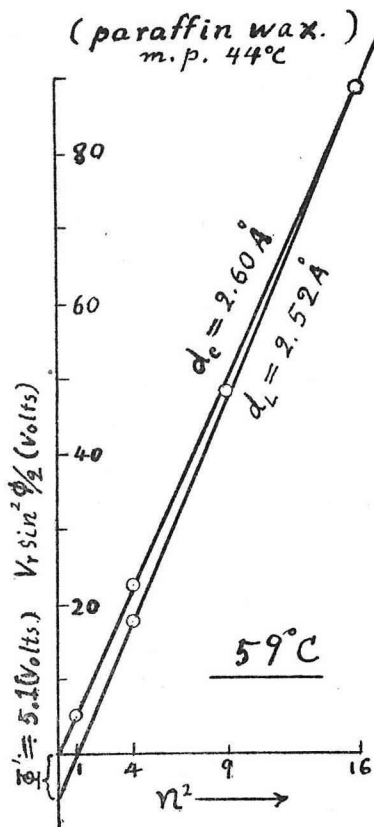


Fig. 2. n , order of reflection, ϕ , angle of reflection, ϕ , inner potential, $V_r = V(1 + V \cdot 10^{-6})$, where V is the accelerating potential in volts. d is the spacing calculated from the inclination of straight line.



Plate 1.

Setting aside that problem, the writer wishes to interpret the process of transformation of pattern as follows: The quasi-crystalline state in the surface layer of film is maintained above the melting point, and then texture loosening begins, resulting in the unevenness of the surface. This state causes the broadening of layer lines. Then, a part of quasi-crystalline aggregate is decomposed into aggregates of free molecules (but the regularity of molecular arrangement is still maintained). These aggregates compose the flat part of the surface which produces "L" pattern. The remaining aggregate of crystallites produces "C" pattern. On cooling, crystal seeds are formed on the surface of film at the transition temperature of

the second kind and they grow larger till quasi-crystalline aggregates cover up the whole surface as the temperature lowered.

The pattern did not show any anomaly when the film was thin enough, and only a temporary broadening of layer lines was observed near that temperature. Perhaps crystal grains formed were small in this case and projections of these crystal grains were not large enough to be free from refraction, on account of the thinness of the film. Specimen whose transition temperature of the second kind was higher than that of the first kind did not show this phenomenon.

Temperature-time curve.

It was expected that some latent heat would be absorbed or released at these transition temperatures, so that the writer intended to examine the cooling curve.

The film of paraffin wax was formed on an aluminium foil (thickness : 0.007 mm, area : $12 \times 12 \text{cm}^2$) by smearing molten wax or pouring benzene solution of the specimen on it. This foil was supported horizontally in a bronze box and heated from outside by electric heater. The thermo-couple used was made of manganin and constantan wire whose diameter was 0.1 mm. Temperature was read by the galvanometer in every ten seconds. Temperature-time curve obtained showed small swellings at transition temperatures, but no singularity was seen at the melting point.

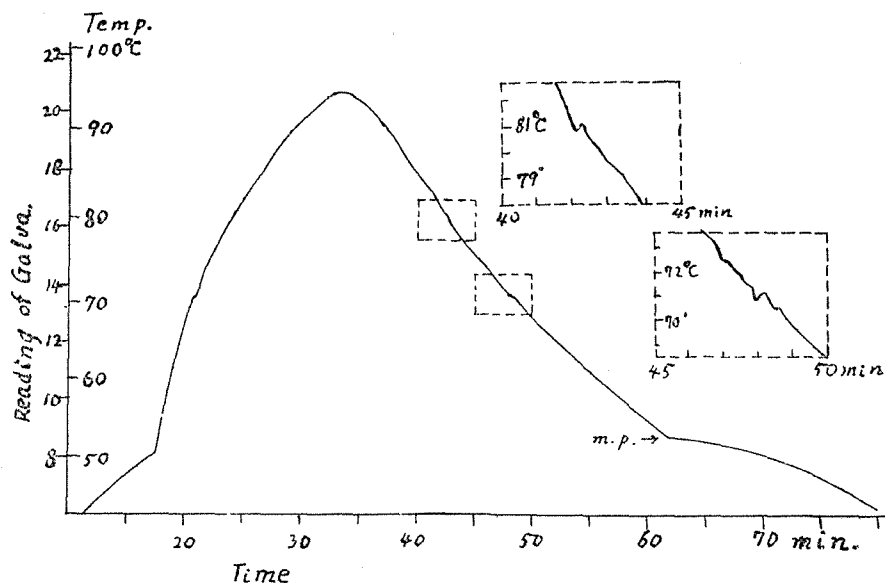
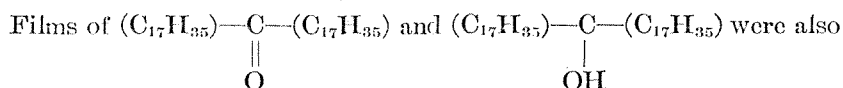


Fig. 3. Temperature-time curve of the surface layer of paraffin wax in bulk. (m. p. 52°C)

Then the same paraffin wax was melted and poured in a shallow pan made of tin-plate about 1 mm. in depth and the thermo-couple was touched lightly on the surface of the specimen. This pan was inserted in the same bronze box and measurement was carried out as before. Curve obtained also showed small swellings at these two transition temperatures (Fig. 3). It indicates that the phenomenon mentioned in the previous paragraph occurred even on the free surface of molten paraffin in bulk. Similar results were obtained with other specimens, but definite results were not obtained for specimens whose melting points were 68° C and 74° C respectively, since their purities were not so high as others.

Extremely thin films and others.

A small flake of paraffin wax was melted on copper plate and wiped off thoroughly with tissue paper while it was still in molten state. Reflection pattern obtained from this specimen, when once heated above its transition temperature and cooled, showed fibre structure whose fibre axis was nearly parallel to the normal of (110) plane and perpendicular to the surface of base metal, and the pattern due to the base metal superposed on it. Origin of this pattern would be as follows: Such film becomes too thin to be able to cover the whole surface of the base metal by evaporation of a part of film during heating process, and the remainder separates into many small groups of crystals whose *c*-axes are parallel to the surface of the base metal.



prepared from their benzene solutions and examined as before. Molecules were arranged with their long-chain axes parallel to the normal of the surface as in the case of paraffin. When once heated and cooled, molecular arrangement was not so regular as before. Tendency to form fibre structure mentioned above was stronger for these substances. Further researches on these substances are now in progress.

In conclusion, the writer wishes to express his sincere thanks to Professor K. Tanaka for his kind guidance.