An X-Ray Study of Coal Tar Pitch

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The diffuse X-ray scattering from coal tar pitch has been investigated by using Fourier transformation for the 002 band and Diamond's least-squares method for the 11 band. From the results of this investigation, the layers were found to be stacked parallel to each other, partly in groups of 8—9 layers, the average number of the layers being 2.46. The distribution of the layer size showed a peak at the diameter of 8.4—10 Å, the average layer size was 8.9 Å, which corresponded to 25 atoms per layer.

It has been known that the properties of synthetic carbon depend largely on the structure of the starting materials and also on the condition of heating up to about 600 °C. However, not only the mechanism of the pyrolysis of the starting materials, but also the physical features of starting materials, have not yet been clarified. Therefore, it is valuable to clarify the structure of pitch from the viewpoint of the utilization of pitch as the starting material for synthetic carbon.

It has been known that the fundamental structure of coal tar pitch consists of various sizes of aromatic-ring systems.[1,2] However, the X-ray diffraction pattern of coal tar pitch shows only a small, diffuse scattering, corresponding to the 002, 100, and 110 reflections of graphite. The analysis of such diffuse scattering as is shown in coal and coal tar pitch is painstaking and difficult in the selection of its method.

In the present paper, the Fourier transformation, which Hirsch[3] used first and which Diamond[4] developed for the analysis of coal, was applied to the analysis of the 002 band of pitch. Moreover, Diamond's method[4,5] was used for the analysis of the 11 band of pitch. The size of the aromatic layer and the thickness of the aromatic layer stacking were estimated by using those methods.

Experimental

Sample. The sample was coal tar pitch which had already been treated at 390 °C. Table 1 shows some properties of the pitch used.

TABLE 1. SOME PROPERTIES OF PITCH USED

Ultimate analysis	C	92.1%
	H	4.5%
Specific gravity		1.31
Softening point		82.2 °C
Temperature of processing		390 °C

Experimental Procedure. The X-ray scattering was measured for a powdered sample using a diffractometer, a scintillation counter, a pulse-height analyser, and Cu$K\alpha$ radiation. Monochromation was carried out with balanced filters of Ni and Co.

The X-ray intensity was measured in two ranges, $0.01 \leqq s \leqq 0.44$ and $0.66 \leqq s \leqq 0.96$ Å^{-1} ($s = 2\sin\theta/\lambda$). The same experimental conditions of the slit system and of the electric power of the X-ray tube were adopted for both ranges of s.

The intensity of X-rays in the high-angle range ($0.66 \leqq s \leqq 0.96$ Å^{-1}) was measured by point counting or a fixed time method using the balanced filters. The intensity curve in the high-angle range was obtained by plotting the average value of two or more measurements. In the low-angle range ($0.01 \leqq s \leqq 0.44$ Å^{-1}), the X-ray intensity was recorded by a scanning method.

The observed intensity was then corrected for polarization, absorption, and geometrical factors. The absorption factor, $A(\theta)$, was obtained from Milberg's equation:[6]

$$A(\theta) = 1 - \frac{1}{\alpha}(1 - e^{-\alpha}) \tag{1}$$

$$\alpha = 2\rho'\left(\frac{\mu}{\rho}\right)\cdot A \cdot \mathrm{cosec}2\theta$$

with $A = 0.1614$ cm, $\rho' = 0.7$ g/cm^3, and $\mu/\rho = 4.60$ cm^2/g, where ρ' is the bulk density of the sample, where μ/ρ is the mass absorption coefficient for Cu$K\alpha$ and where A is the breadth of the X-ray beam.

Diamond's Method. The analysis derived by Diamond[4,5] was used for the 11 band, in which a linear combination of theoretical intensity curves from small layers of different sizes and from amorphous carbon atoms was fitted to the experimental curve over the range from 0.66 to 0.96 Å^{-1} by the method of least-squares. By means of a matrix transformation, the distribution, λ_i, in proportion by weight of the material, in each of the specified-layer-size groups, which are 5.8, 8.4, 10, 15, 20, and 30 Å in diameter, and of the amorphous atom, is derived by means of the following equation:

$$\lambda_i = \sum_j h_{ij} I_j \tag{2}$$

where h_{ij} is an element of the matrix calculated theoretically and where I_j is the observed intensity. The average layer diameter, $\bar{L}$, is defined by the relation:

$$\bar{L} = \sum_i{}' \lambda_i L_i / \sum{}' \lambda_i \tag{3}$$

where L_i is the specified layer size and where the prime denotes the omission of the term for amorphous carbon atoms. The relation between the layer size, L, and the number, N, of atoms in the layer of that size is given by the equation:

$$L = 2.5\sqrt{N/2} \tag{4}$$

Fourier Transformation. In the region of $s \leqq 0.40$ Å^{-1}, the main diffraction pattern is the 002 band, which is inter-

1) S. Otani and A. Yokoyama, This Bulletin, **42**, 1417 (1969).
2) The Coal Tar Data Book, 2nd Edition, The Coal Tar Research Association, Percy Lund, Humpheries & Co., London (1965).
3) P. B. Hirsch, *Proc. Roy. Soc. Ser., A*, **226**, 143 (1954).
4) R. Diamond, Ph. D. Dissertation, University of Cambridge, (1956), *Phil. Trans. Roy. Soc. London*, **A 252**, 193 (1959).
5) R. Diamond, *Acta Crystallogr.*, **10**, 359 (1957); **11**, 129 (1958).
6) M. E. Milberg, *J. Appl. Phys.*, **29**, 64 (1958).

preted by analogy with pure carbons as being due to the stacking of parallel layers. The scattering curve was analyzed by the Fourier transformation method of Hirsch[3] and Diamond.[4] The Fourier transform of the following form:

$$P(u) = 2\int_0^\infty \frac{I_{002}}{f^2}\cos 2\pi us\,ds \qquad (5)$$

gives the probability of finding a layer at a distance of u along the normal to a given layer. In Eq. (5), I_{002} is the intensity of the 002 band, f is the atomic scattering factor for the carbon atom, and s is the reciprocal distance. The interlayer spacing, d, was obtained from the periodicity in the transform $P(u)$. This function can be used to determine stacking distribution using the second differences of the peak weights above a smooth background curve following the minima in $P(u)$, in the manner of Hirsch.[3] If $P(n)$ is the weight of the nth peak from the origin in the transform, the probability, $f(n)$, that a given stack contains n layers ($n \geqq 2$) is given by the following equation:

$$f(n) = P(n) - 2P(n+1) + P(n+2) \qquad (6)$$

The following procedure was used to determine I_{002}. The experimentally-observed intensity was corrected for geometrical, polarization, and absorption factors. The intensity of I_{obs} in absolute units was obtained by dividing the above corrected intensity by the value of $\sum\lambda$ determined by Diamond's method. The Compton scattering was subtracted from I_{obs} in order to obtain the coherent scattering, I_{coh}. The Breit-Dirac recoil factor to the 2/3 power was considered to be correct for the Compton scattering. The minimum value of I_{coh}/f^2 in the neighourhood of $s=0.40$ Å^{-1} was subtracted from I_{coh}/f^2 in the region of $s \leqq 0.44$ Å^{-1}. I_{002} was estimated as the product of the above difference and s:[7]

$$I_{002} = s\cdot\left(\frac{I_{coh}}{f^2} - A\right) \qquad (7)$$

$$A = (I_{coh}/f^2)_{s\fallingdotseq 0.4}$$

Results

002 Band. In Fig. 1 the observed X-ray intensity, I_{obs}, is plotted in the range of s values smaller than 0.44 Å^{-1}. Fig. 1 shows that the corrected intensity of the 002 band reaches 55 electron units at $s \approx 0.29$ Å^{-1}. The intensity curve of the 002 band, I_{002}, obtained by Eq. (7), is given against s in Fig. 2.

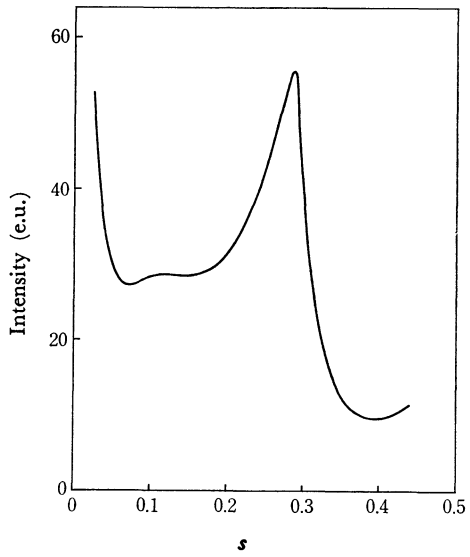

Fig. 1. X-ray intensity curve of coal tar pitch in low angle range.

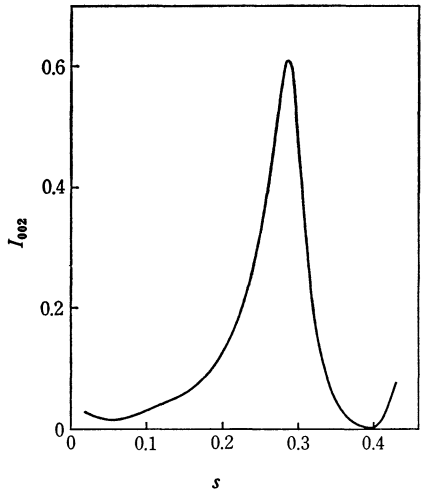

Fig. 2. X-ray intensity curve for 002 band of coal tar pitch.

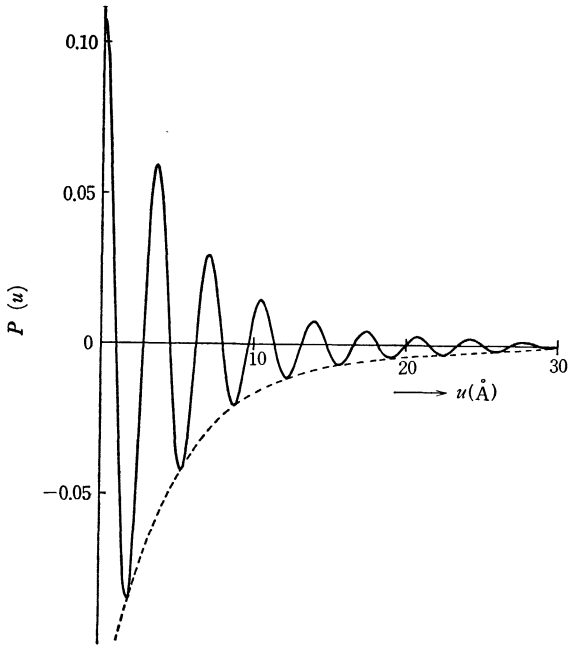

Fig. 3. Fourier transform of I_{002}.

The integration in Eq. (5) was replaced by a summation over the range from $s=0.01$ to $s=0.40$ corresponding to the minimum intensity of I_{002}. The results of the transform for coal tar pitch are shown in Fig. 3. The amplitude of oscillation is observed up to the 9th peak from the point of origin. The number of 9 corresponds to the maximum number of layers which may be considered to be packed parallel to each other at nearly equal distances. (Table 2)

A histogram of the stacking of the layers is given in Fig. 4. The layers per stack were observed up to 9 layers, but the fraction of stacks containing 8 and 9 layers was not obtained because $P(10)$ and $P(11)$ in Eq. (6) were unknown. Apart from the singly-occurring layers, the most frequently occurring groups contain two (55 wt%) or three (26 wt%) layers in the pitch

7) W. Ruland, *Carbon*, **2**, 365 (1965).

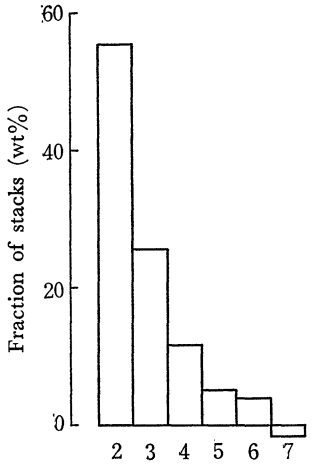

Fig. 4. Histogram of stack heights in coal tar pitch.

Table 2. Structural parameters of pitch used

Interlayer spacing	d	3.44 Å
Average number of layers per stack	$\bar{n}$	2.46
Thickness of stack	L_c	8.45 Å
Average layer size	$\bar{L}$	8.87 Å
Average number of atoms per layer	$\bar{N}$	25.2

used. The interlayer spacing, d, the average thickness of layer stack, L_c, and the average number of layers per stack other than the single layer, $\bar{n}$, are given in Table 2.

It is interesting to note that the interlayer spacing (3.44 Å) is equal to that in the non-graphitic carbons[8] and slightly smaller than that derived from the peak in Fig. 2.

11 Band. The X-ray intensity curve in electron units, obtained by dividing the collected X-ray intensity by $\Sigma\lambda_i$, is shown in Fig. 5 over a range extending from $s=0.66$ to 0.96 Å^{-1}. As is shown in Fig. 5, the intensity of the 11 band is weak in comparison with

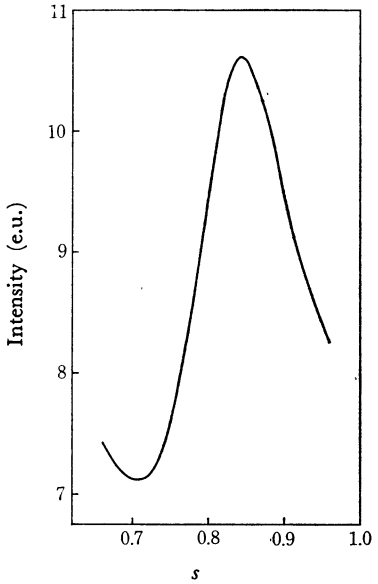

Fig. 5. X-ray intensity curve of coal tar pitch in high angle range.

8) R. E. Franklin, *Acta Crystallogr.*, **4**, 253 (1951).

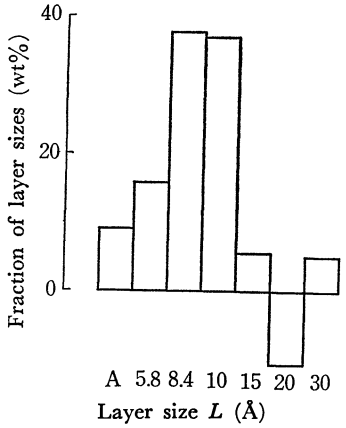

Fig. 6. Layer size histogram for coal tar pitch. The size group A is amorphous (single) carbon atoms.

the background scattering. The peak has a value of about 10.7 e.u.

A layer-size histogram of the coal tar pitch is given in Fig. 6. The fraction of amorphous matter is about 9%, and the fractions of the layer size in 8.4 and 10 Å are 38% and 37% respectively. The fraction of the layer size in 20 Å shows a minus value. The average layer size was 8.87 Å, and the number of carbon atoms per layer, $\bar{N}$, was 25.2.

Discussion

The transform, $P(u)=2\int(I_{002}/f^2)\cos 2\pi us ds$, is in principle the most general way for estimating the stacking distribution. There is a problem, however, in the determination of I_{002}. Diamond[4] derived two transforms as follows:

$$P_1(u) = 2\int \frac{s^2 I}{f^2}\cos 2\pi us ds \tag{8}$$

and

$$P_2(u) = 2\int \frac{I}{f^2}\cos 2\pi us ds \tag{9}$$

The first gives the probability of finding a layer at a distance of u along the normal to a given layer; it thus represents a projection of the density of the interatomic vectors to the normal to the layers at any given point in the specimen. The second function corresponds to a projection of the density of the interatomic vectors along an arbitrary radius with random orientation.

Franklin[9] and Diamond[4] considered that the function, s^2I/f^2, in Eq. (8) was the best plot for the evaluation of the 002 reflection and the stacking distribution determined. However, when an undistorted profile is desired, an sI/f^2 plot is preferable to an s^2I/f^2.[7] Therefore, Eq. (7) was adopted for the best evaluation of the 002 reflection in this paper.

On the other hand, Fig. 1 shows a weak peak of $s\approx 0.1$ Å^{-1}, the existence of which implies that there may be a variation in the density in this region. There are two possible explanations of the variation in density.[3,10] First, the spacing of the peak may be due to some repeat distance of the structure; secondly, the peak may be due to the internal structure of the unit, which, for ex-

9) R. E. Franklin, *Acta Crystallogr.*, **3**, 107 (1950).

10) J. K. Brown and P. B. Hirsch, *Nature*, **175**, 229 (1955).

Table 3. Properties of pitch used by van krevelen and by cartz

Van Krevelen			Cartz		
Ultimate analysis	C	92.7%	Interlayer spacing	d	3.53 Å
	H	4.4%	Average number of layers per stack	$\bar{n}$	1.59 Å[a)]
Aromaticity	f_a	0.89	Average layer size	$\overline{L}$	7.0 Å
Number of aromatic carbon atoms	C_{ar}	27	Average number of atoms per layer	$\overline{N}$	15.7

a) Included single layers

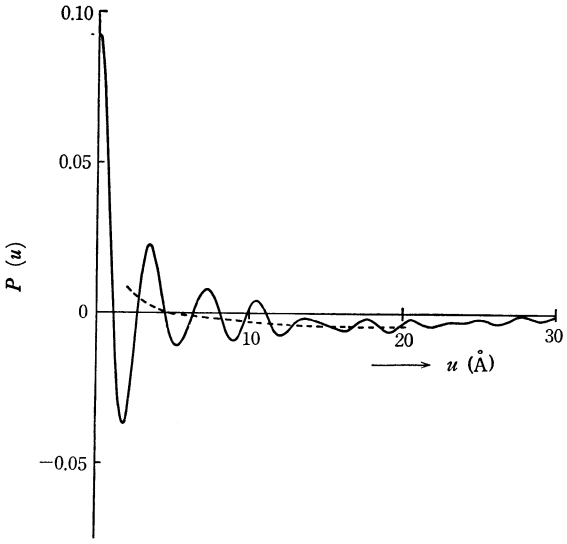

Fig. 7. Fourier transform of I_{coh}/f^2.

ample, has a greater than average density in its core and a less than average density in its peripheral regions. Therefore, the transform, $P_2(u)$, in Eq. (9) of this pitch was tried. As is shown in Fig. 7, there appear about five rapid oscillations due to the layers, but no maximum of the slow modulation of the transform appears. (The modulation is a dotted curve on Fig. 7) Accordingly, although Fig. 1 shows a peculiar region of $s \approx 0.1$, a distinct order with a distance of *ca.* 10 Å is not observed in this pitch from an analysis of the Fourier transformation.

Cartz[11] has examined a specimen of pitch for which structural parameters had been determined by Van Krevelen, using the statistical structure analysis. (Table 3). The carbon and hydrogen contents of the coal tar pitch used in the present experiment are nearly equal to those of the sample used by Van Krevelen and Cartz. However, the histograms of the stacking of the layers and the layer sizes are different in shape. Although the histogram of the layer size obtained by Diamond's method contains a negative term and does not give directly the true proportion of layers of the sizes indicated, the comparison with the shape of the histogram is more significant[4] and the average layer size, $\overline{L}$, is quite accurate.[12] Since C_{ar} stands for the average number of aromatic carbon atoms per cluster unit, the value of C_{ar} is compared with the number of atoms in a coherently-diffracting layer as deduced from X-ray data, $\overline{N}$. The average number of atoms per layers (25.2) in this pitch is found to be larger than the result, $\overline{N}$, by Cartz and slightly smaller than that, C_{ar} obtained by Van Krevelen.

Since the layers deduced from the high-angle diffraction pattern are diffracted effectively coherently in the 11 and the 20 region, all that may be said about the average layer size, $\overline{L}$, is that it represents the lower limit of the actual size of the imperfect sheet and the upper limit of the size of the perfect region of the layer. Therefore, the average layer size, $\overline{L}$, cannot necessarily be identified with the aromatic molecule as determined by statistical structural analysis. Notwithstanding the above reservation, the average number of atoms per layer, $\overline{N}$, is rather closer to the number of aromatic carbon atoms, C_{ar}, obtained by the statistical structural analysis than the $\overline{N}$ obtained by Cartz using X-ray analysis. The above discussion indicates that the average layer size, $\overline{L}$, obtained in this pitch is smaller than the aromatic molecule in this pitch.

On the other hand, the number of layers in the stacks were obtained from the area under the peaks of the Fourier transform by a second difference method. The proportion of single layers can not, however, be derived by the same method, since the origin peak in the transform is not accurate. In view of the height of the minima in the experimental curve, it seems that an appreciable proportion of the layers are unassociated.

Conclusion

On the basis of the results of the present experiments, the aromatic layers of the coal tar pitch used can be said to be distributed mostly at layer sizes of 8.4—10 Å. The average layer size which diffracts effectively coherently had a diameter of 8.9 Å and contained 25 atoms per layer. It was found that such aromatic layers stacked parallel to each other up to 8—9 layers. The average number of layer stacking was 2.46, excluding an isolated single layer and the interlayer spacing was 3.44 Å.

Therefore, it can be concluded that the crystallite size of the coal tar pitch was 8.9 Å in diameter and 8.5 Å in thickness.

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11) L. Cartz and P. B. Hirsch, *Phil. Trans. Roy. Soc.* (London), **A252**, 557 (1960).

12) M. Shiraishi and K. Kobayashi, *Nippon Kagaku Kaishi*, **1972**, 1135.