

Heat Treatment of Carbon under Various Pressures

It has been said that the degree of graphitization of carbon depends chiefly on the highest temperature of heat treatment and that other conditions of heat treatment, such as holding time, are of secondary importance. However, it was previously reported¹ that the vacuum-evaporated carbon was scarcely graphitized in vacuum, although it was easily graphitized under atmospheric pressure. Therefore, we thought it necessary to study the effect of the gas phase of heat treatment on the graphitization of carbon. In order to investigate this effect, a calcined petroleum coke was heat-treated under various pressures and its lattice constant c_0 was measured by means of X-ray diffraction method using extra-pure silicon powder as an inner standard.

The change of lattice constant c_0 with the temperature of heat treatment is represented in Fig. 1.

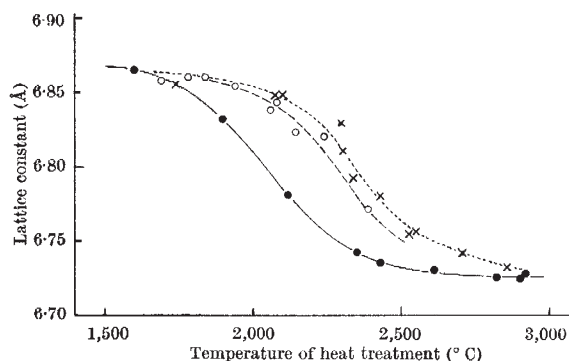


Fig. 1. Change of lattice constant, c_0 , with temperature of heat treatment. ●, Heat treatment under atmospheric pressure; ○, under reduced pressure; ×, in vacuum

Heat treatment under atmospheric pressure was made in a carbon granular resistance furnace of a type similar to an industrial graphitizing furnace. The details of this heat treatment were reported elsewhere². Heat treatment in vacuum of 10^{-2} mm mercury was made in a vacuum induction furnace. Heat treatment under reduced pressure (7–8 mm mercury) was made in a bell-jar type metallic chamber. In each case, the temperature of heat treatment was directly measured with the aid of an optical pyrometer.

The results of this work indicate that the relation between the degree of graphitization of carbon and the temperature of heat treatment is strongly affected by the gas phase of heat treatment. In this work, it was scarcely necessary to consider the catalytic action of metallic impurities, because the high-purity graphite (reactor grade) was used as a crucible. According to Mrozowski³, powdered coke was less graphitized than unpowdered. Therefore, the particle size distribution of the coke sample was controlled to the range of 1.4–0.2 mm in order to eliminate the possible effect of particle size on the graphitization. Holding time at the highest temperature was about 15 min in each case. Heating-rate was about 200° C/min in the heat treatment both under atmospheric pressure and in vacuum, and about 2,000° C/min in reduced pressure. But it was already reported that heating-rate has no effect on lattice constants of heat-treated carbon⁴. Accordingly, it was not the difference of heating-rate that caused the difference in the behaviour of lattice constant shown in Fig. 1.

The degree of graphitization of carbon therefore depends not only on the highest temperature but also on the gas phase of heat treatment, although it is not decisive whether the total pressure of gas phase or the partial pressure of any kind of existing gas, such as nitrogen or oxygen, has any effects on the graphitization.

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¹ Noda, T., and Matsuoka, H., *J. Chem. Soc. Japan, Indust. Chem. Sec.*, **64**, 2083 (1961).

² Inagaki, M., and Noda, T., *Bull. Chem. Soc. Japan*, **35**, 1652 (1962).

³ Mrozowski, S., *Proc. First and Second Conf. on Carbon*, 81 (Univ. of Buffalo, 1956).

⁴ Okada, J., et al., *Proc. Fifth Conf. on Carbon* (in the press).

Fractionation of Partially Isotactic Polypropylene Oxide

We have polymerized propylene oxide in dioxan with the zinc diethyl and water catalyst¹, dissolved the resulting high-molecular-weight polymer in iso-octane at 60° C and precipitated solid phases by lowering the temperature incrementally to 40° C. In this way we were able to obtain several fractions which were identical in average molecular weight and in the distribution of molecular weights about the average. By further lowering of the temperature we obtained liquid-liquid phase separation with fractionation occurring predominantly on the basis of molecular weight. A typical result of such a fractionation is shown in Fig. 1. Further analysis of that part of the polymer undergoing liquid-liquid phase separation (some 80 wt.-%), coupled with cryoscopic measurements on the fraction of lowest molecular weight, indicates that the ratio of the weight- to the number-average molecular weight for the polymer is greater than 1,000, the consequence of a large low molecular weight tail.

Other fractions produced in this way via solid-liquid phase separation from iso-octane have been investigated in more detail. Table 1 records, for

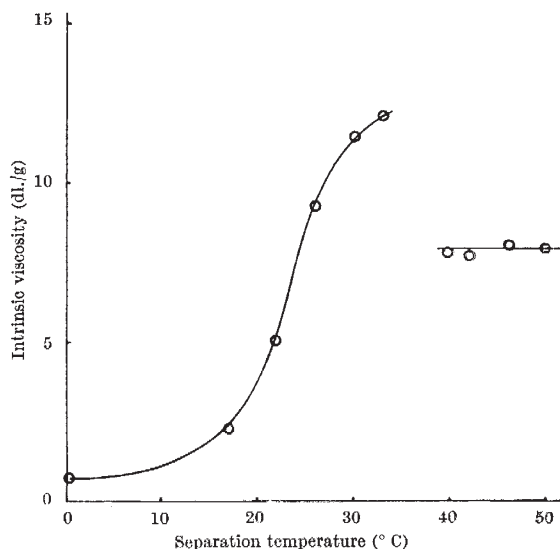


Fig. 1. The intrinsic viscosities (benzene at 25° C.) of fractions of polypropylene oxide versus their temperature of separation from iso-octane