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Hidemadas Honda [a]

[a] Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, Kaurazaka, Shinjuku-Ku, Tokyo, 162, Japan

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Mesophase Pitch and Meso-Carbon Microbeads

HIDEMASA HONDA

Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan.

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1. INTRODUCTION

Petroleum heavy residual oil, coal-tar, coal-liquefaction products and the like, being a mixture of heavy hydrocarbons, are used as the industrial resources of carbon materials which are not likely to be replaced easily.

These substances are economically carbonizable materials having a great deal of carbon content and obtainable with no difficulty, because these are liquids or semisolids at room temperatures, and these substances hold an important position in the resources of carbon materials.

Since the role of mesophase transformation in liquid-phase carbonization was recognized first by Brooks and Taylor[1] and studied by many other workers,[2–8] the understanding of the carbonization phenomena has improved substantially.

So mesophase transformation is becoming a compass needle in the manufacturing technique of carbonaceous raw materials and carbon products. The author will explain some topics in the utilization of mesophase pitch and meso-carbon microbeads.

2 MESOPHASE PITCH

2–1 Mesophase transformation

It is well known that mesophase transformation takes place in graphitizable organic materials, such as pitches, during pyrolysis at temperatures between 350°C and 500°C.

In the primary stages of mesophase formation, the carbonaceous mesophase appears as optically anisotropic small spherules suspended in the optically isotropic matrix.

The formed mesophase spherules grow progressively by putting the molecules into the matrix with an increase of residence time or heat-treatment temperature (HTT).

During the heat-treatment process of pitches, polycondensed aromatic hydrocarbons are formed due to thermal decomposition and thermal polymerization reactions, followed by orientation of polycondensed aromatic hydrocarbons in a fixed direction. By the accumulation of oriented polycondensed aromatic hydrocarbons in layers, the mesophase spherule is formed. The structural model of the mesophase spherule is illustrated in Figure 1.

When spherules meet each other, coalescence occurs to produce larger droplets, leading eventually to bulk mesophase. When the coalesced mesophase is further pyrolized, a plastic deformation produces fine textures of two types, fibrous and/or mosaic. This mesophase transformation is essential for the formation of precursors to be carbonized or graphitized, and the fibrous texture of bulk mesophase is essentially important in connection with graphitizability.

The heat-treated pitches containing mesophase spherules or bulk mesophase are named crystallized pitches or mesophase pitches.

It has been believed for a long time that the carbonaceous mesophase was insoluble in most solvents and particularly in quinoline which were usually used in its separation from the isotropic medium. Recent research results show that the mesophase solubility depends on the original material from

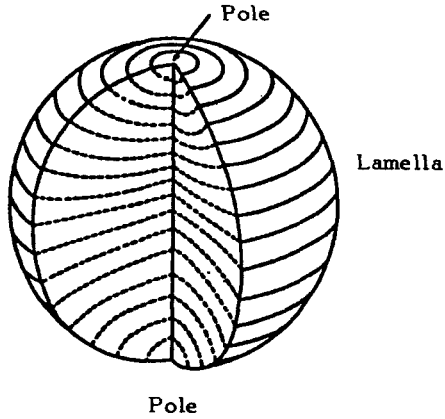


FIGURE 1 Structure model of mesophase spherule

which it is formed and that the percentage of the mesophase is not necessarily the same as that of insolubles. Thus, direct optical observations seem to be the way to evaluate this percentage.[9-11]

2-2 High performance carbon fiber

For carbon fibers, there are two main types of precursor materials. One is polymer yarns such as polyacrylonitrile (PAN) and the other is carbonaceous pitch. It is believed that the former are high performance fibers and that the latter are low modulus fibers.

In pitch-based carbon fibers, recently, it is known that the low modulus type is produced from isotropic pitch and the high performance type is prepared from anisotropic pitch (mesophase pitch). They are produced by Kureha Chemical Industry Co. and Union Carbide Corp. respectively.

The viscosity of mesophase pitch is larger than that of isotropic pitch, and the spinning of the former is more difficult than that of the latter. Moreover, the texture of the transverse section of mesophase pitch-based fibers in their as-spun state transforms into a radial structure more easily than that of isotropic pitch-based fibers. This readily causes longitudinal cracks in the carbon fibers made from mesophase pitch.[12]

In order to avoid these longitudinal cracks in the pitch-based carbon fibers, it may be natural that the transverse section texture of pitch fibers in their as-spun state has the onionskin and mid-radial, the onionskin and mid-random, and the onion-like structures, as shown in Figure 2.

The transverse texture of pitch fibers is controlled by the pretreatment of pitches, the constitution and the spinnability of spinning pitches, the spinning conditions, etc.

It is obvious that the preordered layer transformation,[13] the improvement of spinnability, and thermal stability are required in the spinning pitches by pretreatment and/or modification such as hydrogenation and degradation, separation of useless components, controlled condensation, etc. of raw pitches.

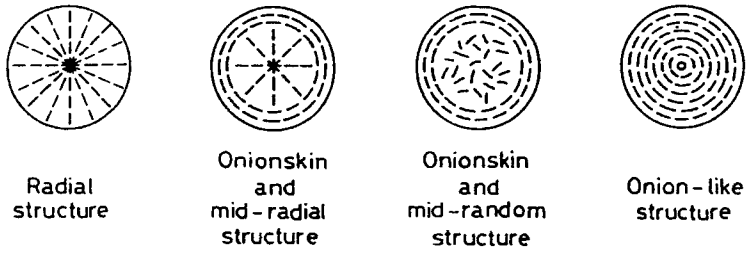


FIGURE 2 Transverse section texture of pitch fibers

The modified pitches are pseudomesophase pitches, such as the premesophase pitches by hydrogen transfer from THQ (1,2,3,4-tetrahydroquinoline) and heat-treatment[14] or the dormant mesophase pitches by Benkeser reduction and heat-treatment,[15] because the optical texture of pseudomesophase pitches is isotropic, although the constitution and orientation of pseudomesophase pitches are almost the same as those of mesophase pitches. The optical texture of dormant mesophase pitches, however, changes to an anisotropic pitch by shearing stress.

The premesophase and the dormant mesophase pitches have good spinnability and good thermal stability. The as-spun pitch fibers and/or the infusible fibers made from premesophase and dormant mesophase pitches show an isotropic and an anisotropic texture respectively. (Figure 3)

The premesophase and dormant mesophase pitch-based carbon fibers which are carbonized or graphitized have an anisotropic fibrill texture along the longitudinal axis like the mesophase pitch-based carbon fibers.

It is possible, therefore, that the tensile strength, modulus and elongation of premesophase pitch-based carbon fibers have the same orders or more as those of PAN-based carbon fibers as shown in Table 1.

3 MESO-CARBON MICROBEADS

3–1 Characteristics of meso-carbon microbeads

The heat-treated pitches containing mesophase spherules are named mesophase pitches. The mesophase spherules can be separated from the pitch matrix by solvent fractionation. The mesophase spherules separated as quinoline insolubles (QI) from the mesophase pitches are named meso-carbon microbeads (MC).[16] Components of the meso-carbon microbeads depend on the kind of raw pitch materials.

Meso-carbon microbeads separated from heat-treated quinoline soluble coal-tar pitch (C-pitch) are called C-MC, those from heat-treated coal-tar pitch containing metaphase (free carbons) (M-pitch) are M-MC, those from petroleum pitch (P-pitch) are P-MC, and those from naphtha-tar pitch (N-pitch) are N-MC.

The size of the C-MC was about 1–100 μm. The shape of C-MC larger than 5 μm was spherical and that of C-MC smaller than 3 μm was spindle or lemon-like. The size of M-MC was about 10 μm. The shape was irregular, and the surface was covered with metaphase (free-carbons) smaller than 1 μm. The size of P-MC was about 3 μm and the shape was almost spindle or lemon-like.

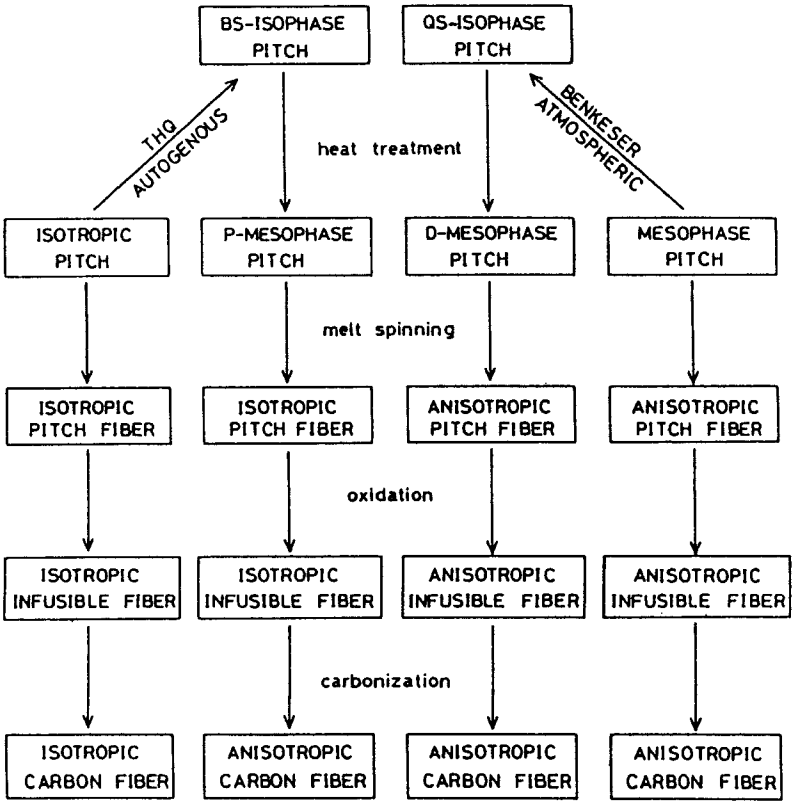


FIGURE 3 Fundamental procedure for pitch-based carbon fibers

From the results of ultimate analysis, infra-red spectra and pyrolysis gas chromatography of the microbeads,[17] the constituents of the meso-carbon microbeads are considered as follows:

The meso-carbon microbeads are composed of high molecular weight aromatic hydrocarbons. The components of C-MC and of M-MC are almost the same, and are polynuclear aromatic hydrocarbons having short side chains of aliphatic hydrocarbons. On the other hand, the components of P-MC and N-MC are aromatic hydrocarbons of a small ring number

TABLE I

Characteristics of Premesophase and Dormant Mesophase Pitch-based Carbon Fibers

		Strength kg/mm^2	Modulus 10^3 kg/mm^2	Elongation %
Premesophase pitch-based carbon fiber	Low modulus	300	20	1.8
	High modulus	350	60	0.7
Dormant mesophase pitch-based carbon fiber	Low modulus	250	20	
	High modulus	200	40	
PAN-based carbon fiber	Low modulus	350	20	1.5
	High modulus	250	40	0.6

having long side chains of aliphatic hydrocarbons. Components of the meso-carbon microbeads and mesophase spherules in the pitch depend on the kind of raw pitch materials.

The meso-carbon microbeads do not melt or fuse with heat treatment and do not dissolve in any organic solvent such as quinoline, pyridine, benzene, etc. at room temperature. When the meso-carbon microbeads were heat-treated at 500–3000°C, the shape of the spherical unit did not change.

From the changes of density and X-ray parameters[18] with heat treatment, the MC belongs structurally to the graphitizing carbon.

Although the MC has an internal texture presented by Brooks and Taylor[1] as shown in Figure 1, an average molecular structure model organizing the MC has been presented as a spider wedge model by Mochida[19] as shown in Figure 4. This model is strictly of an average structure and it, in fact, appreciably varies with the differences of the starting materials and the conditions of the formation of the MC.

From the chemical reactivity,[20] the pore structure,[21] the adsorption-desorption isotherms and the heat of immersion[22] of the MC, an internal structure of the MC has been presented as shown in Figure 5. That is, the constituent unit of the MC is a micell composed of the molecules as shown in Figure 4 and the micells lie perpendicular (a bit loosely) to a pole of the sphere as in Taylor's model (Figure 1).

The exterior of the meso-carbon microbeads melts in the medium of polynuclear aromatic hydrocarbons or pitch materials during heat treatment; and the meso-carbon microbeads in liquids similar to pitch under heat treatment behave in a similar manner to mesophase spherules produced in pitch during heat treatment.

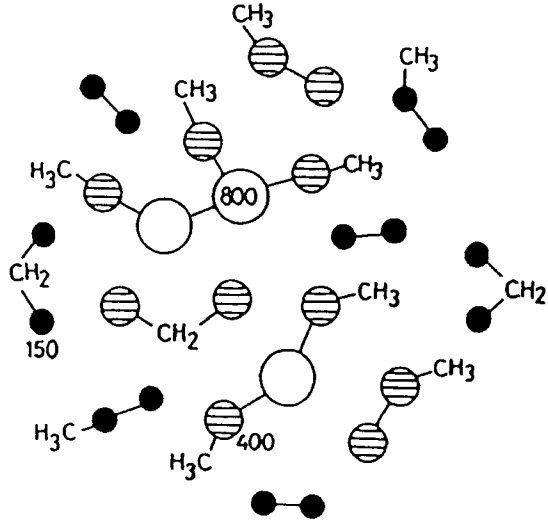


FIGURE 4 A model for the component molecules in the spheres (Numbers in the circle represent the molecular weight)

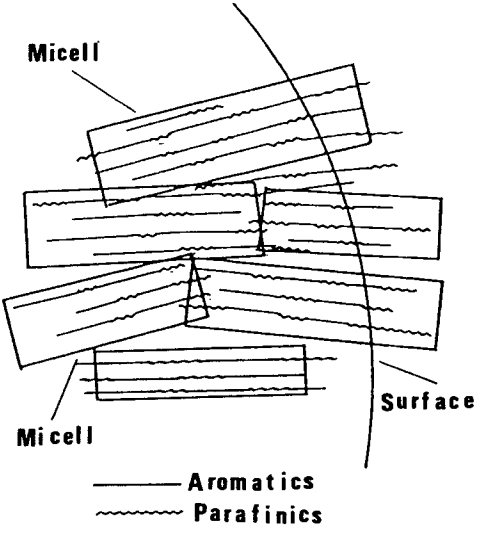


FIGURE 5 The internal structure model of the microbeads

3–2 Filler of high performance liquid chromatography

It is no exaggeration to say that the carbonaceous mesophase sphere (MC) is a very interesting carbon material which has no precedent so far, because it has an internal texture and its morphology is of a single spherule as shown in Figure 1.

In polycyclic aromatics, the reactivity of the edge carbon atom at its periphery is very high, as is well known. The surface of the MC, therefore, is interesting from the viewpoint of the surface chemistry of solids.

As a possible way for the use of the MC as a fine carbon, the MC can be considered as a filler (column-packing material) of a high liquid-chromatography performance.[22,23] The carbon-packing material has almost never been obtained even though it is expected because of its characteristic properties.

For example, the following properties are required for the fillers: (1) being able to be used in either strong acidic or basic solutions, (2) having construction to swell a little is permissible, although no-swelling construction is most preferable, (3) withstanding the use at high temperature, *e.g.* 150–250°C, (4) being possible to be complete unactivation, (5) having no change of the separating capability in water, etc.

The MC can satisfy such requirements because of its characteristics. In addition, the MC can fix a more uniform and steady liquid phase on the surface due to its morphology and texture, and if an MC with a sharp particle-size distribution is obtained, even the closest packing column is expected.

The MC used is N-MC (Figure 6). Its particle-size distribution is very wide and it should be practically classified. However, in the present work, since the amount of the specimen was very small, specimens which have a very wide particle-size distribution (from 8 to 14.3 μm) could not be used.

In the use of original N-MC as the filler, its separating capability for polycyclic aromatics as solutes was excellent and the capability was similar to that of commercial Hitachi gel #3010 (styrene porous polymer), whereas basic aromatics were not separated, perhaps because the basic solutes were fixed on acidic sites of the carbon surface.

Now, the MC was heat-treated and hydrogenated at 1000°C, followed by alkylation and its separating capability as liquid-partition chromatography was measured.

The hydrogen site of the benzenoidal ring is easily alkylated by the Friedel-Crafts reaction, as it is well known; that is, the reaction of the hydrogen site on the hydrogenated surface with octadecyl chloride proceeds in the presence of Lewis acid as follows:

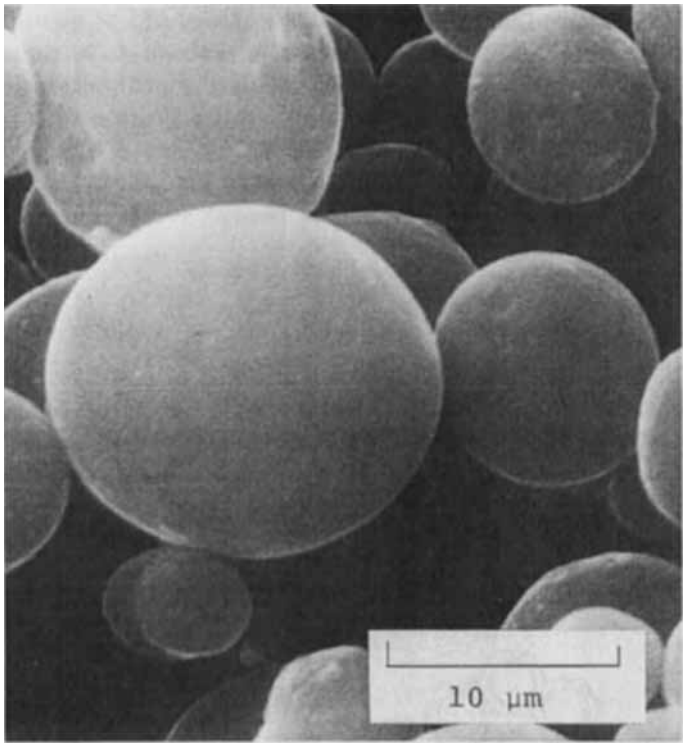
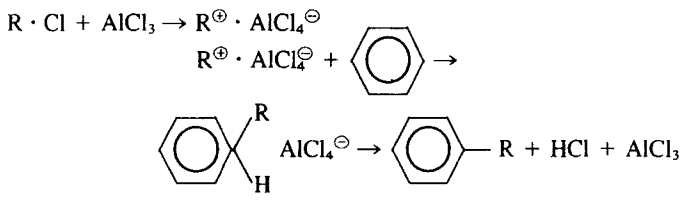


FIGURE 6 The scanning electron micrograph of type N microbeads



(R: octadecyl radical)

(where the solvent used is nitromethane).

Since the C-C linkage formed with such reactions is thermochemically stable, the specimen prepared may satisfy the requirements for the filler as described above. The specific surface area of this specimen from benzene-adsorption at 298°K agreed with its geometrical surface area. The agreement suggests that the adsorbate molecule no longer penetrated into the MC.

The separation capabilities of the octadecylated MC as the filler were measured for polycyclic aromatics, benzene derivatives, its isomers and acidic, basic aromatics. Some chromatographs obtained are exemplified in Figure 7 and Figure 8. Though the particle-size distribution of specimens used was very wide and the column length (100 mm) was very short, the separation characteristics for the solutes used were on the whole very remarkable, and the fact that the isomers could be separated was worth noting.

4 CONCLUSION

For the production of high performance carbon fibers from pitches, it is necessary to get spinning pitches in which the constitutions and their

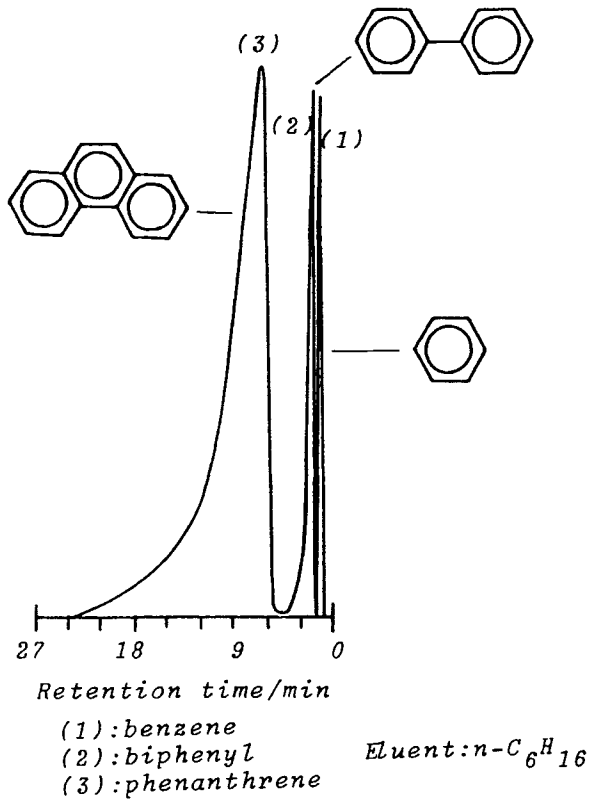


FIGURE 7 The chromatograms by octadecylated type N microbeads

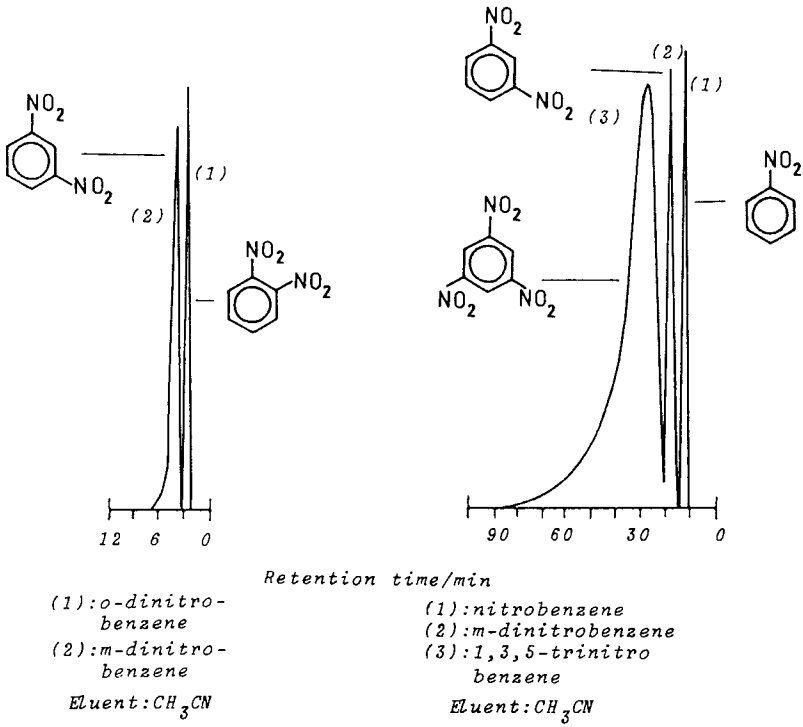


FIGURE 8 The chromatograms by octadecylated type N microbeads

orientations are almost the same as those of mesophase pitches, having good spinability and good thermal stability by pretreatment and/or modification such as hydrogenation and degradation, separation of useless components, and controlled condensation of raw pitches. The transverse texture of as-spun pitch fibers may be controlled by the characteristics of spinning pitches and spinning conditions. Moreover, the control in infusibilization and carbonization of pitch fibers is important. In order to realize excellent and high productivity, however, many problems still remain to be solved.

The meso-carbon microbead is a very interesting carbon material, because its morphology is of a single spherule having an internal texture with loose-packing lamellar micells. In the utilization of meso-carbon microbeads, however, it is desired that the particle-size distribution is narrow. The size and distribution of mesophase spherules in the mesophase pitch may be controlled on the basis of investigation.

The mass production technique of high-performance carbon fibers and/or meso-carbon microbeads having the same size will be done with the support of research in the field of disc-like liquid crystals.

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