Molecular Alignment and Domain Assembles in the Uni-chromic Mesophase Spherules Prepared from Synthetic Naphthalene Isotropic Pitch

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Molecular Alignment and Domain Assembles in the Uni-chromic Mesophase Spherules Prepared from Synthetic Naphthalene Isotropic Pitch

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Mesophase spherules produced at the initial stage of their formation in the synthetic isotropic pitch were observed microscopically as-produced in the pitch and after the isolation by the solvent extraction. The spheres which were all uni-chromic in the pitch became discuses after the isolation, to show blue or yellow elliptic and purple circular cross-section in the optical microscope. The solvent extracted discus had rod-like units which were arranged parallel with the shorter axis of discus. Based on above observation, alignment of hexagonal plane in the rod-like unit has been discussed. The extraction of the soluble fraction appears to shrink the length of rod, suggesting its location in the plane of the insoluble fraction.

1. INTRODUCTION

Since Brooks and Taylor found mesophase spherules in the carbonizing pitch or coal as an intermediate to graphitizable carbon[1) 2)], their structures in terms of molecular composition and alignment has been studied[3)-5)]. Honda et al. proposed their application as precursor for unique carbons after their isolation from isotropic matrix by solvent extraction[6)]. Recently mesophase spherules have attracted strong interests as an excellent carbon for anode of lithium-ion battery[7)8)], and their preparation procedures are studied to improve the yield and control the structure. The present authors have reported preparation from synthetic naphthalene pitch to increase the yield[9)] and mesoscopic units of microdomains of the mesophase spherules[10)11)]. The molecular alignment and domain assembles are considered to influence their anodic performance.

In the present study, we describe the molecular alignment and domain assembles in the mesophase spherules, which were produced from a synthetic mesophase isotropic pitch at the initial stage of its carbonization. The characteristic is that they are exclusively single color spherules of uni-chromatic arrangement. Their structure was studied by a polarized optical microscope (OM) and high resolution scanning electron microscope (HR-SEM).

Table 1 Some properties of Naphthalene isotropic pitch (EP-157).

S.P. (℃)	Solubility (%)				
	HS	HI-AS	AI-BS	BI-PS	PI
177	5	32	26	32	5

S.P. : Softening Point
HS : Hexane Soluble
HI-AS : Hexane Insoluble-Acetone Soluble
AI-BS : Acetone Insoluble-Benzene Soluble
BI-PS : Benzene Insoluble-Pyridine Soluble
PI : Pyridine Insoluble

2. EXPERIMENTAL

Isotropic pitch (EP-157) synthesized from naphthalene using HF/BF_3 catalyst[12)] was supplied by Mitsubish Gas Co. Some properties of this pitch are summarized in **Table 1**. Pitch was heated in a Pyrex glass tube at 380-400℃ by a heating rate of

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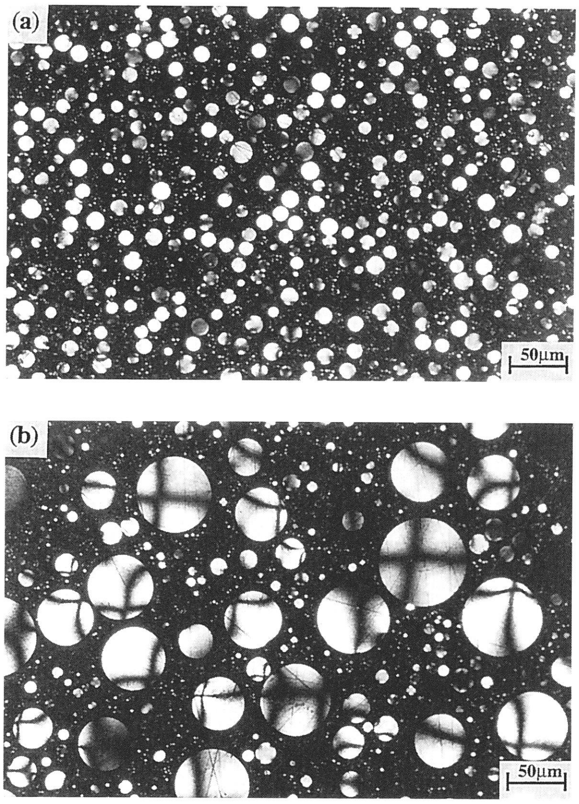

Fig. 1 Optical microphotographs of soaked pitches of (a) 380℃-2h and (b) 380℃-6h.

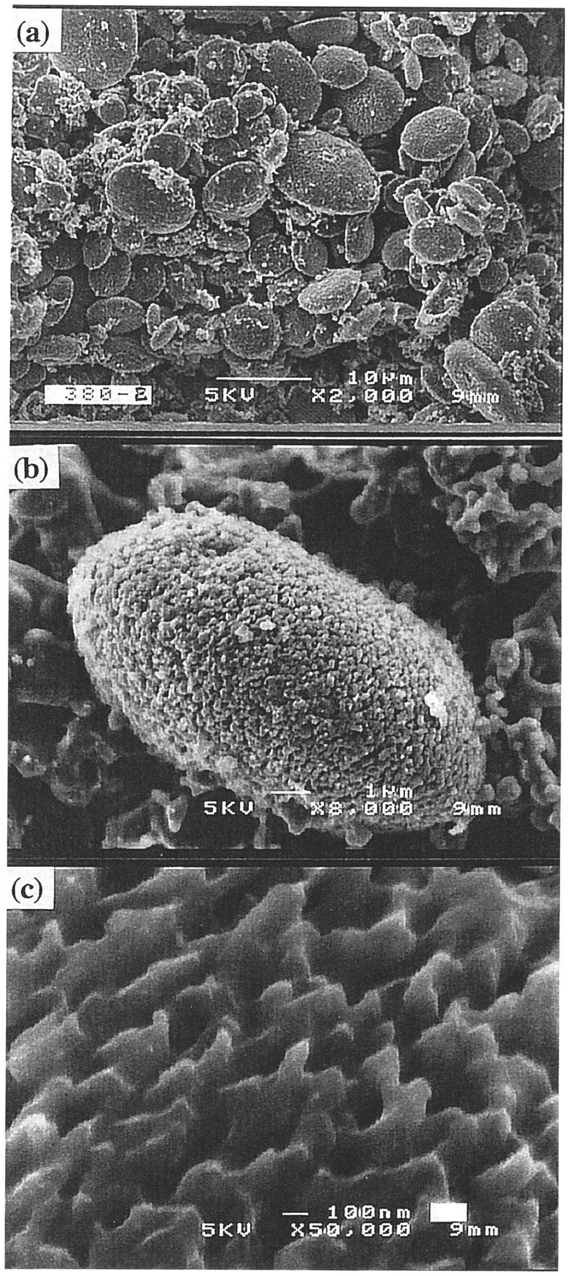

Fig. 2 SEM photographs of unichromic sphere of isolation by pyridine extraction.

2℃ /min with mild stirring of 200rpm. After annealing for 0.5h-6h, the soaked pitch was cooled to room temperature under nitrogen flow. The soaked pitch was extracted by pyridine to isolate mesophase spherules. The isolated spherules were oxidatively stabilized in air at 270℃ for 90 min at a heating rate of 2℃ /min, and then the stabilized spheres were heat-treated to 1000℃ under argon at a heating rate of 5℃/min.

The soaked pitch and isolated mesophase sphere by pyridine were mounted with epoxy resin and polished to be observed under the optical microscope. The isolated spheres heat-treated at 1000℃ were observed by HR-SEM.

3. RESULTS AND DISCUSSION

Fig. 1 shows the microphotographs of the soaked pitches at 380℃ -2h and 380℃ -6h, respectively. **Fig. 1 (a)** exhibits mesophase spherules of 10-15μm in diameter which were exclusively unichromically blue or yellow regardless of diameter. Longer soaking provided larger spheres (ca. 20-60μm) with a purple cross which divided regions of different colors.

Higher temperatures of 390℃ and 400℃ similarly provided two kinds of spheres according to the soaking time, 1h at 390℃ and 0.5h at 400℃ providing unichromic spheres, while 4h at 390℃ and 2h at 400℃ spheres with a purple cross. It should be noted that the optical photographs showed the perfect circular shape of mesophase spheres without any indication of elliptic shape at all.

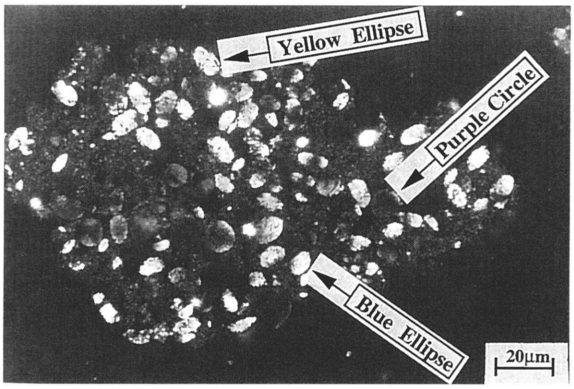

Fig. 3 Optical microphotographs of unichromic sphere of isolation by pyridine extraction.

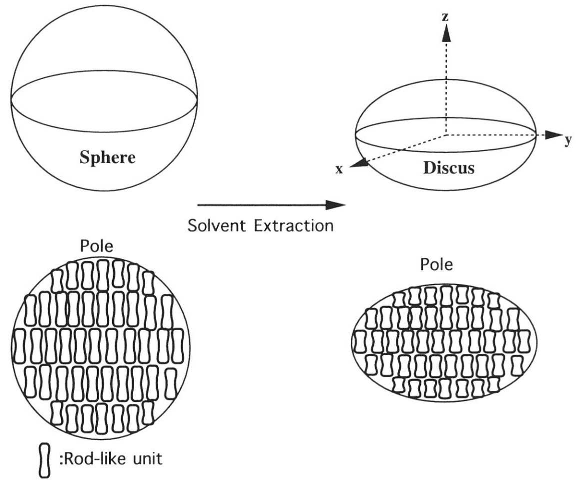

Fig. 4 Structure of unichromic mesophase sphere and its shrinkage by solvent extraction.

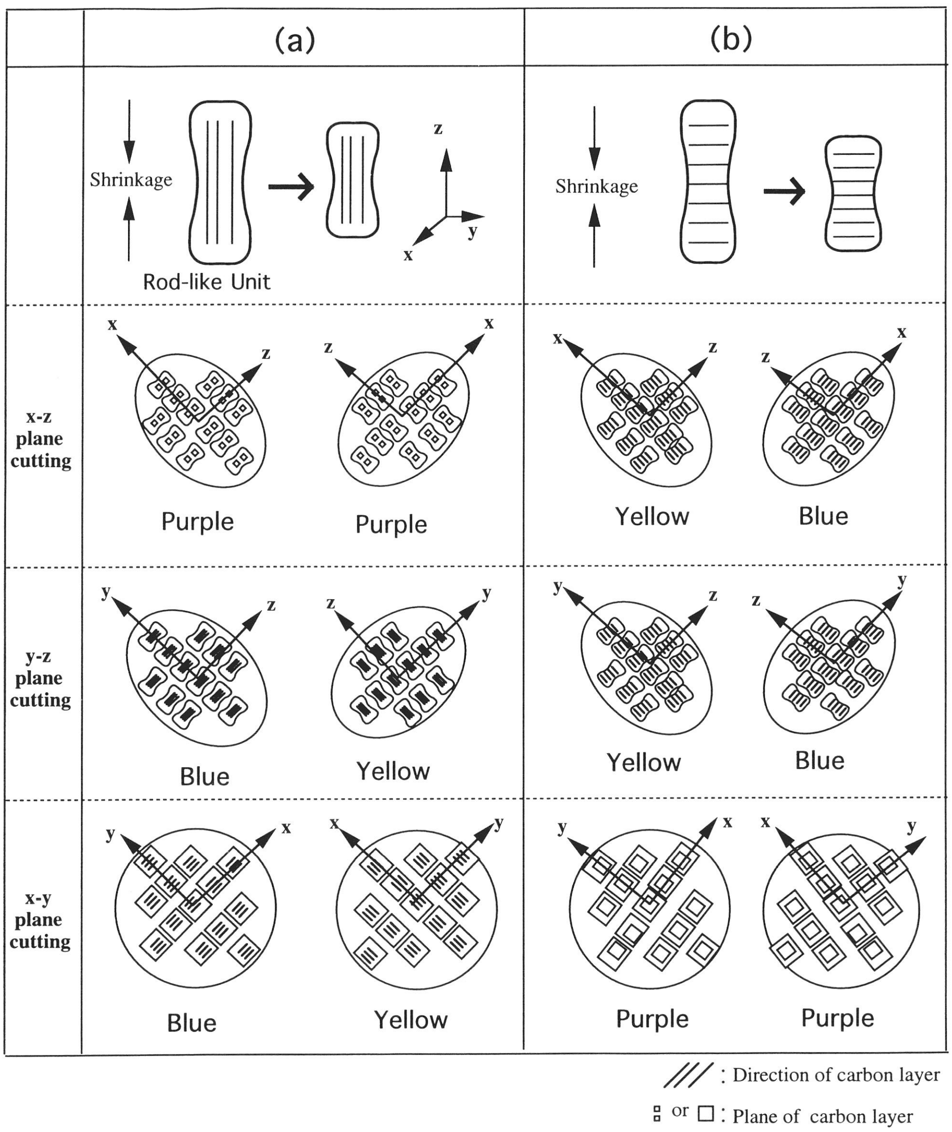

Fig. 5 Models of carbon layer alignment in rod-like unit, (a) parallel to longer axis of rod-like unit, (b) perpendicular to longer axis of rod-like unit.

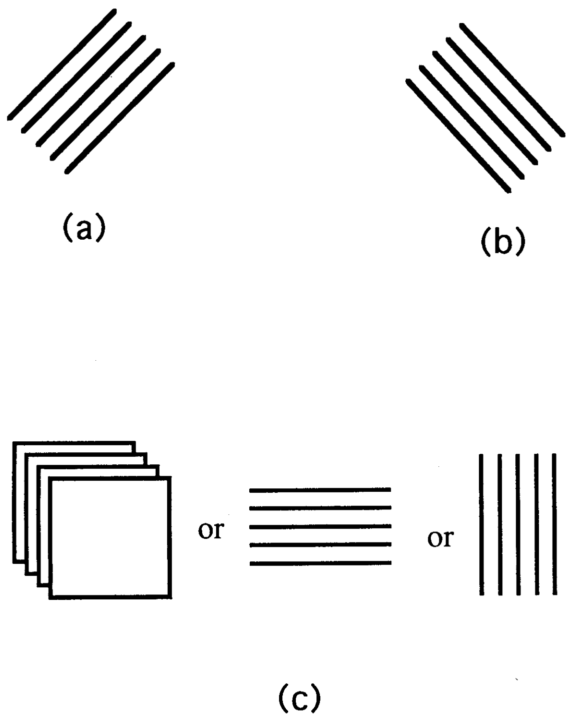

Fig. 6 Polarized light optical microscopy and interference colors. (a) blue, (b) yellow and (c) purple.

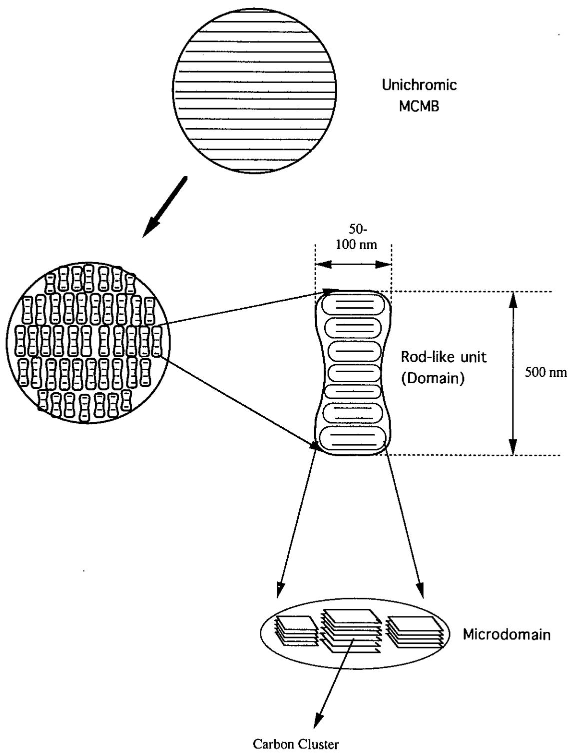

Fig. 7 Structure model of unichromic mesophase sphere.

Fig. 2 shows the SEM photographs of unichromic spheres after the isolation, stabilization, and heat-treatment at 1000℃. The photographs show that most of the isolated particles were not sphere any more but discus in the shape regardless of the size as shown in Fig. 2(a). The particle was composed of rod-like units as a basic structural units, of which longer axis parallel appeared to be aligned to the shorter axis of the discus as shown in **Figs. 2** (**b**) and (**c**), and their size was about 0.05-0.1μm wide and 0.5μm long.

Fig. 3 shows the optical microphotograph of pyridine extracted mesophase spheres. The shapes of cross-section were elliptic and circular according to cutting direction to the axis of discus. The elliptic cross-sections were unichromically either yellow or blue and their size was 10-15μm in the longer axis and 5-10μm in the shorter axis, while the circular sections were purple and their size was about 10-15μm. The shrinkage can be thought to occur about 30% just in the direction of shorter axis.

Based on the above observations, unichromic sphere in the soaked pitch before the extraction has alignment of rod-like unit as shown in **Fig. 4**. Such sphere particles in the soaked pitch change into discus by shrinkage in z-direction (the shorter axis of discus) due to the shrinkage along the longer axis of rod-like unit.

Fig. 5 illustrates the alignment of hexagonal carbon plane in the rodlike unit. Model (a) in which hexagonal carbon planes are aligned parallel and model (b) perpendicular to the longer axis of the rod-like unit. The alignment of model (a) allows development of purple ellipse and yellow or blue circle, respectively, according to the alignment of hexagonal planes as shown in **Fig. 6**. However, such a set of color development was not observed in optical microphotographs as shown in **Fig. 3**. In contrast, the alignment of **Fig. 5** (**b**) allows the development of yellow or blue ellipse regardless of cutting direction and purple circle, which are well consistent to the optical microphotographs of **Fig. 3**. Hence, the alignment in the unichromic mesophase spherule which is different from that of Brooks and Taylor mesophase spherule as shown in **Fig. 7**.

The shrinkage of clusters by solvent extraction suggests the location of soluble components. The soluble component can be placed among the insoluble components in the same plane, or form own planes among planes of insoluble components. The shrinkage observed in the present study suggests the latter case The molecular alignment in the sphere appears unique to the synthetic pitch. The components of narrow molecular size and shape allow the definite molecular stacking in the clusters which form the rod-like unit. The assembles of rod-like units forms the present sphere. In contrast, only very large molecules form the spheres in the coal tar, the domain being not definite in sphere.

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