

## HIGH PERFORMANCE, MODERATE COST MESOPHASE PITCH BASED CARBON FIBERS

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### ABSTRACT

Mesophase pitch has been successfully prepared at very highly yield from aromatic hydrocarbons with low contaminant levels using HF/BF<sub>3</sub> as the catalyst. The derived carbon fiber is expected to be of high performance and to be produced at reasonable cost. The synthesis, structure, and properties of the mesophase pitches, which are strongly dependent upon the starting aromatic hydrocarbons and preparation conditions, will be described. The spinning process can control the shape and texture of the fiber, both of which are intimately related to performance. Fibers with a flat cross section, as thin as 1.5 μm, and round fibers with random texture can be produced when the spinning nozzle and the mesophase pitch are properly selected. Acceptable compression strength has been obtained with the random texture in the round fiber. Very high tensile strength as well as Young's modulus are realized by slow heating during stabilization. Some other applications of mesophase pitch will be addressed.

Key words: Mesophase pitch, Carbon fiber, HF/BF<sub>3</sub>

### INTRODUCTION

Mesophase pitch has been recognized as the most promising precursor for the carbon fiber of excellent properties and reasonable cost. Because of their low price, the residues from coal tar as well as petroleum have been selected as the starting substances. However, high cost of their refining, the lower yield, difficulty in spinning or the control of their molecular structure, and low reactivity lead to unacceptable price and insufficient quality. Carbon fibers produced from latter ones are of high price and their properties are unsatisfactory except for better Young's modulus which is better than that of PAN-based one<sup>1)-3)</sup>, limiting the broad application. Hence, lower price and better performances of the mesophase pitch are most relevant for the pitch based high performance carbon fiber.

Mitsubishi Gas Chemical company and Kyushu University proposed an application of HF/BF<sub>3</sub> as the catalyst for the condensation of aromatic hydrocarbon into mesophase pitch<sup>4)-11)</sup>. In the present paper, preparation conditions, structure, and physical and chemical properties of the mesophase pitch produced using HF/BF<sub>3</sub> were examined.

## EXPERIMENTAL

HF and  $\text{BF}_3$  are low boiling points of 19.9 and  $-101.1^\circ\text{C}$ , respectively. Such a liquid and a gas catalysts can promote the homogeneous reaction of monomer, being recovered and recycled completely by the distillation. HF has high dissolving power for organic compounds and can accelerate ionic reaction through the carbenium ion because of its high polarity. The ionic polymerization at lower temperatures is able to design the structure of mesophase pitch by virtue of the selective reaction under mild preparative conditions. Thus, mesophase pitches from naphthalene, anthracene and methylnaphthalene were prepared directly using HF/ $\text{BF}_3$  at a temperature range of 180 -  $300^\circ\text{C}$ .

These mesophase pitches were spun into fiber using mono hole spinneret of round, Y and slit shape under various conditions. After stabilization in air, fibers are carbonized in argon at 1300 to  $2500^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### 1. Preparation of mesophase pitch

Catalytic polymerization reactions of naphthalene are illustrated in Fig. 1. The protonated complex exists in excess HF as a suitable proton donor. It reacts with other monomer at the position of the highest electron density to produce dimeric structure without dehydrogenation. Such a non-dehydrogenative reaction will be repeated to produce aromatic oligomers such as trimers and tetramers, carrying hydrogens as many as a number of polymerization reaction. These hydrogens are finally stabilized in the produced pitch as naphthenic hydrogens.

Preparation conditions of pitches at a temperature range of 180 to  $300^\circ\text{C}$  are shown in Table 1. Mesophase pitch of 100 vol% anisotropy could be prepared catalytically from naphthalene at 210 -  $300^\circ\text{C}$ . Amount of HF and  $\text{BF}_3$  is important to develop the anisotropy, no anisotropy being observed when ratios of HF/naphthalene and  $\text{BF}_3$ /naphthalene were 0.30 and 0.15 in molar ratio at  $260^\circ\text{C}$ , respectively. However, a higher temperature ( $300^\circ\text{C}$ ) induced 100 vol% anisotropy even with a small amount of HF/ $\text{BF}_3$ . Mesophase pitch of 100 vol% anisotropy could be prepared directly from anthracene at  $220^\circ\text{C}$ . Anthracene is more reactive than naphthalene, providing the pitch of higher softening point with a small amount of the catalyst. The larger planar of anthracene may be favorable for its oligomer to develop anisotropy. Mesophase pitch of 100 vol% anisotropy could be prepared also from methylnaphthalene at  $265^\circ\text{C}$  for 5 h under autogenous pressure in an autoclave. Its softening point of  $205^\circ\text{C}$  should be noted very low, suggesting that methyl group of the monomer influences on properties of the resultant mesophase pitch. A pitch prepared from methylnaphthalene at  $260^\circ\text{C}$  by the same period carried 80 vol% of anisotropy. The methyl group may hinder cationic polymerization.

### 2. Some properties of mesophase pitches

General properties of mesophase pitches prepared from naphthalene, anthracene, methylnaphthalene are summarized in Table 2. Their softening point, solubility, H/C

ratio varied according to preparation temperature and starting materials. Anthracene mesophase pitch tends to exhibit higher softening point and a low solubility. Methyl naphthalene pitch has a softening point of as low as 205°C and 57 % solubility in benzene.

**Table 3** summarizes the hydrogen distribution in the BS and BI-PS fractions of the mesophase pitches. The higher preparation temperature tends to provide a more aromatic mesophase pitch. Aromaticity of anthracene mesophase pitch (AP-220) and naphthalene mesophase pitch (NP-260) are similar. The methyl naphthalene mesophase pitch is most aliphatic, carrying many methyl groups in spite of the severest preparation conditions. The representative molecular species of BS fraction of each mesophase pitches are illustrated in **Fig. 2**.

### **3. Molecular assembly of the mesophase pitches**

Molecular assembly of the mesophase pitches at their fused states is examined using a high temperature horizontal X-ray diffractometer<sup>12</sup>. Changes in Lc values of some pitches calculated from the half width of C(002) are shown in **Fig. 3**. MNP-265 shows the largest Lc value of 5.8 nm at room temperature which stays almost constant up to 210°C of its softening point. Then, Lc decreases sharply at higher temperatures than its softening point. At 350°C, Lc of MNP-265 decreases to less than a half of that at room temperature. These results reveal that the mesogen molecules in the mesophase pitch are certainly stacked as observed with conventional liquid crystals, the thickness or number and d-space of the layers being temperature-dependent and different from one pitch to another. Among the mesophase pitch, MNP-265, exhibits the largest Lc (average thickness).

The values of Lc change according to the temperature especially above the softening point. The thermal motion of molecules above the softening point may compete the intermolecular interaction to liberate the stacking and to enlarge the d-space. Lc in MNP-265 decreases most sharply and those of NP-265-5 and AP-220 do gradually. The molecular motion should influence the stacking thickness and d-space in the similar manners, however, the former should be also influenced by the solubility of the stacking fraction in the isotropic matrix which is more strongly molecular structure - dependent.

### **4. Viscoelastic properties of mesophase pitches**

The mesophase pitch exhibited viscoelastic properties, reflecting its molecular structure and assembly. Typical viscoelastic properties of MNP-265 and NP-265-5 are shown in **Fig. 4**. Very different profiles may be due to the different assembling structure described above. The viscoelastic properties define the alignment in the spinning nozzle, dieswelling at the outlet of nozzle, and alignment at the extension. Hence such properties influence strength, shape, and texture of the resultant carbon fiber.

### **5. Carbon fiber from the mesophase pitch**

A variety of mesophase pitches provide various pitch based carbon fibers, which can achieve high tensile strength, Young's modulus<sup>1,2</sup> and compressive strength. Shapes of molecules and their stacking influence alignment of aromatic planes in

the pitch fiber under the spinning conditions which are fixed by stabilization. The alignment, thickness, and length of the graphite units along the fiber axis are recognized as the common origin of these strengths, the thicker the stacking the higher the modulus or stiffness of the carbon fiber. This occurs at a sacrifice of compressive strength. Hence, the complete controls of molecular shape and its alignment during the preparation of mesophase pitch and spinning are major targets to be achieved for the development of higher performance pitch-based carbon fiber. Table 4 summarizes the mechanical properties of carbonized fibers from naphthalene(NP-260-3) and anthracene(AP-220) mesophase pitches. Tensile strength of their carbonized fiber from NP-260-3 was 2.60 GPa at 1500°C and gradually increased with graphitization, reaching higher than 3.0 GPa by 2550°C. In contrast, tensile strength of carbonized fiber from AP-220 was limited to around 2.0 GPa, even after graphitization at 2550°C, indicating defects at its spinning. Tensile modulus of both fibers are very high, achieving 800 GPa by 2550°C. AP-220 tends to give higher values of Young's modulus than NP-260-3 when the graphitization temperature is lower. It may be due to the constituent molecules of the former mesophase pitch which consist of anthracene units tend to have wider planar structure for developing better graphitization and orientation. Because the spinning properties of AP-220 is inferior to that of NP-260-3, tensile strength of the former fibers may be limited due to micro-defects introduced at spinning. Careful preparation of AP-220 for its better spinning is expected to increase the tensile strength of its resultant carbon fiber.

#### **6. Improvement of mechanical properties of pitch based carbon fiber**

Because the physical properties and mechanical properties of carbon fibers strongly depend on their transversal shape and texture<sup>(3)-15)</sup>, it is believed that controls of transversal shape and texture of carbon fiber during the spinning is most relevant<sup>14)</sup>. The present authors examined some methods to change the flow pattern of molten pitches during spinning in order to control the transversal texture. Fig. 5 shows transversal sections of carbon fibers from methylnaphthalene derived mesophase pitch (MNP-265), using circular or non-circular shaped spinning nozzles at 285°C. It is noted that circular shaped fiber is obtainable at this temperature regardless of the nozzle shapes. Transversal texture of carbon fibers from Y and slit shaped spinning nozzles exhibited random or random-onion textures, respectively. In contrast, circular shaped spinning nozzle gives a radial one with open wedge, even though melt viscosities of molten pitches are much the same at the spinning temperature. This indicates that the flow pattern of molten mesophase pitch is changed and distorted against fiber axis during extrusion before solidification.

Table 5 shows mechanical properties of carbon fibers. Tensile strengths of graphitized carbon fibers spun with Y and slit shaped spinning nozzles are improved by 0.25 and 0.55 GPa, respectively. Young's modulus and compressive strengths of graphitized fibers spun with Y and slit shaped spinning nozzles are also improved by 160 and 0.13 GPa, and 120 and 0.04 GPa, respectively. Importance to control the texture is suggested to improve the mechanical properties of the resultant fiber. Slow heating rate of 0.5°C at the stabilization was found to improve very significantly the tensile strength up to 5 GPa.

Fig. 6 shows the transversal shape and texture of graphitized tape, which is spun through the slit nozzle. The thickness of the tape is as thin as  $1.6\ \mu\text{m}^{15}$ . Its excellent mechanical properties are noted. Tensile strength, Young's modulus and compressive strength of the graphitized tape are as high as 3.65 GPa, 810 GPa, and 0.71 GPa, respectively.

### 7. Further application of the mesophase pitch

The present mesophase pitches with moderate softening points and naphthenic hydrogens can be used as precursor pitches for a variety of carbon materials. The following are some examples: Carbon fiber-mesophase pitch prepreg<sup>17</sup>, high density carbon materials, binder of MgO brick<sup>18</sup>, porous carbonaceous materials, precursor for the solid lubricant, and oxidation prohibitors.

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Table 1 Preparation conditions of pitches and their some properties.

Sample	HF (mol%)	BF <sub>3</sub> (mol%)	Temp. (°C)	Yield (wt%)	A. C. (vol%)	S. P. (°C)
NP-180	0.67	0.25	180	52	0	202
NP-200	0.81	0.30	200	52	15	199
NP-210	0.83	0.30	210	74	98	216
NP-260-1	0.59	0.15	260	71	95	219
NP-260-2	0.30	0.25	260	37	0	95
NP-260-3	0.47	0.20	260	68	100	212
NP-300	0.64	0.10	300	58	100	285
AP-220	1.00	0.20	220	90	100	238
AP-260	1.00	0.10	260	82	100	275
MNP-260	0.52	0.15	260	>80	80	205
MNP-265	0.52	0.15	265	76	100	205

NP: naphthalene derived pitch., AP: anthracene derived pitch.

MNP: methylnaphthalene derived pitch.

The amount of aromatic hydrocarbon: 1 mol.

Preparation time is 4 hr except for MNP-265(5 hr)

Table 2 Some properties of mesophase pitches.

Sample	S.P. (°C)	A. C. (vol%)	Solubility(wt%)				H/C
			BS	BI-PS	PI-QS	QI	
NP-260-4	215	100	52	19	6	23	0.67
NP-260-5	212	100	57	15	12	16	-
NP-300	285	100	12	29	6	53	0.58
AP-220	238	100	44	12	19	25	0.62
AP-260	275	100	19	32	16	33	0.65
MNP-260	205	80	72	10	10	8	0.68
MNP-265	205	100	57	13	4	26	0.69

Table 3 Hydrogen distribution of BS and BI-PS fractions in the mesophase pitches.

		Hydrogen distribution(%)				
		Haro	H <sub>α</sub>	H <sub>β</sub>	H <sub>γ</sub>	fa
NP-260-4	BS	50	36	13	1	0.82
	BI-PS	66	25	8	1	0.90
NP-300	BS	65	23	10	2	0.89
	BI-PS	71	15	9	5	0.92
AP-220	BS	56	26	15	3	0.85
	BI-PS	57	20	19	4	0.87
MNP-265	BS	44	40	13	3	0.81
	BI-PS	47	35	15	3	-

Haro: aromatic hydrogen(6-10 ppm), H<sub>α</sub>: α-position hydrogen(2.1-5.0 ppm)

H<sub>β</sub>: β-position hydrogen(1.1-2.1 ppm), H<sub>γ</sub>: γ-position hydrogen(0.3-1.1 ppm)

fa: aromaticity

Table 4 Mechanical properties of carbon fiber produced from NP and AP.

	HTT (°C)	$\Delta l$ (%)	T.S. <sup>1)</sup> (GPa)	Y.M. <sup>1)</sup> (GPa)
NP-260-3	1500	1.0	2.60	250
	2000	0.6	2.50	500
	2550	0.4	3.50	800
AP-220	1500	0.6	1.70	270
	2000	0.3	2.00	570
	2550	0.3	2.00	810

1) JIS R7601 monofilament method

HTT: heat-treatment temperature,

T.S.: tensile strength,

$\Delta l$ : strain to break,

Y.M.: Young's modulus

Table 5 Mechanical properties of graphitized fibers.

nozzle	fiber. shape	texture	diameter ( $\mu\text{m}$ )	$\Delta l$ (%)	DO (%)	Lc (nm)	T.S. (GPa)	Y.M. (GPa)	CS (GPa)
circular	circular	radial-crack	7.0	0.35	95.4	21	2.85	740	0.58
Y	triangle	random	9.0	0.40	94.2	39	3.10	900	0.71
slit	circular	random-onion	9.0	0.45	95.4	23	3.40	860	0.62

DO: degree of orientation

CS: compressive strength tested by composit method( $V_f=60\%$ )  
proposed by H. M. Hawthorne et. al. (ref. 15)

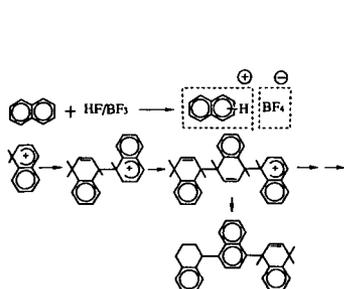


Fig. 1 Catalytic polymerization of naphthalene with  $\text{HF}/\text{BF}_3$ .

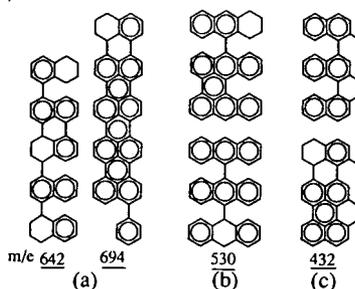


Fig. 2 Model structure of BS in the mesophase pitches.  
(a)NP-260, (b)AP-220, (c)MNP-265

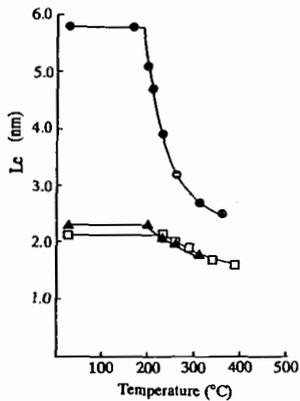


Fig. 3 Change in Lc at higher temperatures.  
 ○:MNP-265, ▲:NP-265-5,  
 □:AP-220

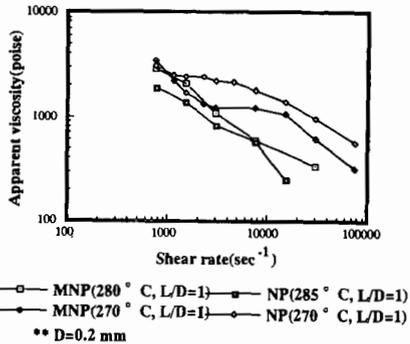


Fig. 4 Typical viscoelastic properties of MNP-265 and NP-265-5

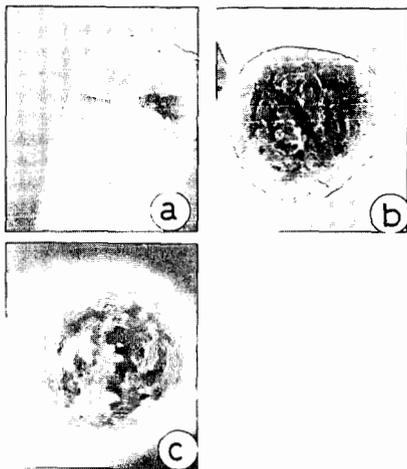


Fig. 5 SEM photographs of carbon fibers spun with circular or non-circular shaped spinning nozzles.  
 (a) circular-shaped nozzle  
 (b) Y-shaped nozzle  
 (c) slit-shaped nozzle

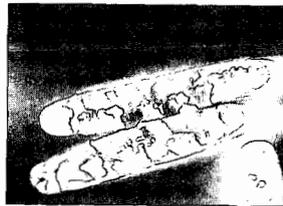


Fig. 6 SEM photograph of carbon tape graphitized at 2500°C