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Direct Preparation of Mesophase Pitch from Naphthalene by the Aid of HF/BF_3

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Direct preparation of mesophase pitch from naphthalene was studied using HF/BF_3 in an autoclave under autogeneous pressure at 260 °C. A mesophase pitch of 100% anisotropy was produced catalytically first at a yield above 60%. The pitch carried 52% of benzene soluble fraction, exhibiting softening temperature of as low as 215 °C. The pitch consisted principally of naphthalene oligomers which carried a large content of naphthenic hydrogens with some alkyl and phenyl groups. The pitch was smoothly spun into thin fiber, which was rapidly stabilized for 30 min at 270 °C.

Although several preparation procedures of the mesophase pitch as a precursor for the carbon fiber have been developed, pitch yield, spinning stability and oxidative reactivity were not fully sufficient to decrease the cost of the fiber.[1-3] It is partly because conventional thermal processes cannot fully controll the reactivity of components of diversed structure in the residual substances and convert only their small fraction into the mesophase pitch even after the pretreatment such as hydrogenation.[4-7] The present authors claimed the efficiency of HF/BF_3 for the cationic condensation of aromatic hydrocarbons into pitches of peculiar natures.[8] The most characteristic feature of this preparation is that the dehydrogenation hardly takes place during the condensation, allowing highly naphthenic structure induced in the carbonaceous product.[8]

In the present study, the direct preparation of the mesophase pitch through the catalytic process from naphthalene in one pot was examined using HF/BF_3 as a strong acidic catalyst at 260 °C. Highly naphthenic mesophase pitch can be expected at a high yield. The complete recovery of HF/BF_3 is still possible while the mesophase pitch is fusible. Thus, such a catalytic preparation can be applicable in the industrial process.

A mesophase pitch was prepared from commercial naphthalene by the aid of HF/BF_3 at 260 °C for 4 h under 2.1 MPa of autogenous pressure in an autoclave. After the reaction, the content in an autoclave was heattreated at 340 °C under a nitrogen gas flow with stirring to distill HF/BF_3, the unreacted starting monomer, and some volatile fractions, leaving the mesophase pitch. The yield of the pitch was above 60%.

The mesophase pitch was fractionated by sequential Soxhlet extraction. Extracts were analyzed with ^1H-NMR(VARIAN VXR-400) in the solvents ($CDCl_3$ or C_5D_5N). FT-IR(JEOL, JIR-100) spectra of the whole pitch were observed in the KBr disc, to clarify its functional groups. The FD-MS of the benzene soluble fraction in the mesophase pitch was measured with a JEOL INS-DX303 Mass spectrometer. Softening point and anisotropic content of the mesophase pitch were defined under a hot stage microscope(Leitz). The melt mesophase pitch was spun into fiber of 8-15 μm in diameter from a spinneret. The procedures for stabilization and carbonization of mesophase pitch fiber were described in previous papers.[6,7)]

The pitch exhibited 100% anisotropy under the optical microscope. Their softening point, solubility in benzene and H/C ratio were 215 °C, 52% and 0.67, respectively. Such properties should be noted because they are very different from those of the mesophase pitches prepared conventionally from FCC decant oil or coal tar.[5-7)] Figure 1 illustrates the IR spectra of naphthalene and the mesophase pitch. In comparison with naphthalene, the pitch exhibited intense bands at 2700-2970, 1450, 750-870 cm^{-1} which are identified as aliphatic C-H streching, methylene C-H(probably naphthenic C-H) bending and out-of-plane deformation of aromatic ring, respectively. The intense bands at 2800-2970 and 1450 cm^{-1}, indicated methylene or naphthene-rich structure. Rather intense three bands were observed at 870, 810, and 750 cm^{-1} which indicate a considerable substitution on the aromatic ring.

Table 1 summarizes the hydrogen distributions and Brown-Ladner parameters[9)] of benzene soluble and benzene insoluble-pyridine soluble fractions in the mesophase pitch. The benzene soluble fraction carried 49% of aliphatic hydrogens. The major aliphatic hydrogens were located in the α-position to the aromatic ring(H_α), while H_β and H_γ hydrogens decreased in this order, indicating that major hydrogens were naphthenic and that a few ethyl groups are substituted to the ring. The benzene insoluble-pyridine soluble fraction was certainly more aromatic and less naphthenic than the benzene soluble fraction, although it was still rather naphthenic.

Figure 2 exhibited FD-Mass spectrum of the benzene soluble fraction. Molecular weights of components in the benzene soluble fraction distributed from 226 to 1200 with the maximum abundance at 682-706, indicating that the fraction consisted of dimers to nonamers of naphthalene units. It is noted that the distribution was almost continuous, suggesting that continuous number of alkyl, and phenyl groups as well as naphthenic hydrogens are present in the constituent molecules.

The molecular weight of the benzene insoluble-pyridine soluble fractions was revealed by GPC to distribute from 100 to 6000 with the peak at 600 as shown in Fig. 3. Since the molecular weights of benzene soluble and benzene insoluble-pyridine soluble are rather comparable, the naphthenic hydrogens in the molecules appear to define the solubility in benzene.

The pitch was smoothly spun at a temperature from 285 to 300 °C, to give the

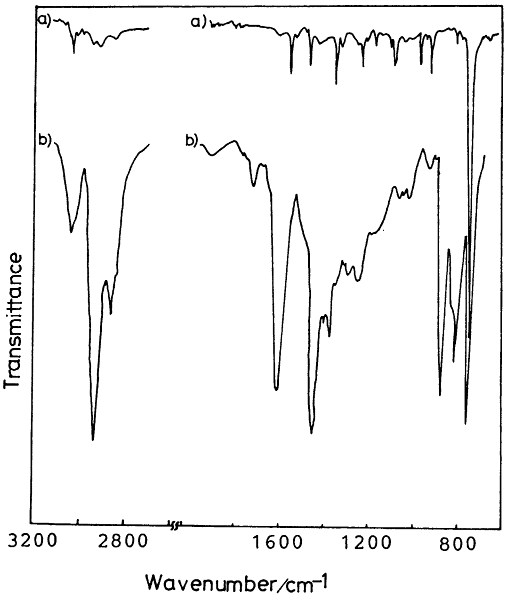

Fig. 1. IR spectra of naphthalene pitch(a) and the mesophase pitch(b).

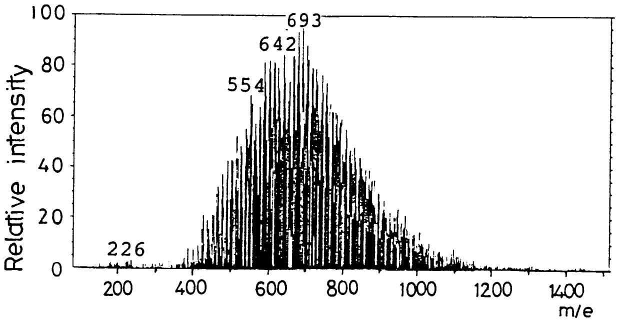

Fig. 2. FD-Mass spectrum of the benzene soluble fraction in the mesophase pitch.

Table 1. Hydrogen distribution of BS and BI-PS fractions in mesophase pitches

		% a)				
		Haro	Hα	Hβ	Hγ	fa b)
Mesophase	BS	50.7	36.0	12.7	0.6	0.82
pitch	BI-PS	66.4	24.7	7.9	1.0	0.90

BS:benzene soluble, BI-PS:benzene insoluble-pyridine soluble. a)Haro:6-10ppm, Hα:2-4.5ppm, Hβ:1.1-2ppm, Hγ:0.3-1.1ppm. b)carbon aromaticity.

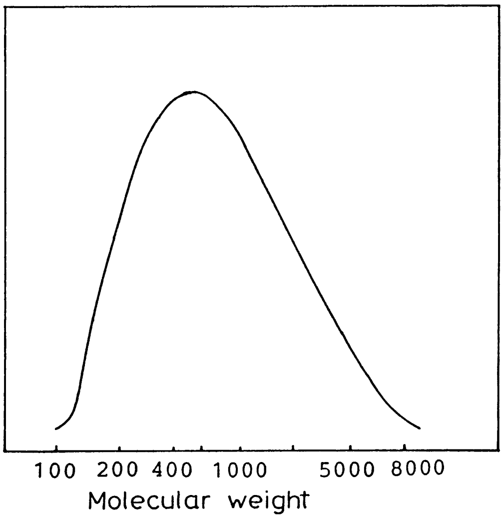

Fig. 3. The GPC profiles of benzene insoluble-pyridine soluble fractions.

pitch fiber of 8 to 15 μm diameter. It took 22 min at 270 °C to stabilize fibers from the present pitch not to adhere and deform, however definite skin-core structure was observable in the carbonized fiber. The fine mosaic texture prevailed in the transverse section, indicating complete stabilization when the stabilization time exceeded 30 min.

Mesophase pitch of 100 vol% anisotropy can be produced directly from naphthalene through the catalytic condensation by the aid of HF/BF_3 at a high yield. The mesophase pitch carried a significant amount of hydrogens as indicated by H/C atomic ratio of 0.67, and exhibited considerable high solubility and lower softening point. It was noted that the constituent molecules of the mesophase pitch were very rich in naphthenic hydrogens with some alkylgroups as revealed by ^{1}H-NMR, FD-Mass, and FT-IR. It has been experienced rather difficult to maintain a significant content of aliphatic groups in the mesophase pitch since alkyl and naphthenic groups are easily removed thermally through the heat treatment.10) The mesophase pitch was prepared in the present study by the aid of the super acid HF/BF_3 through the cationic condensation which was not caused by the dehydrogenation during the polymerization,8) as observed in the similar reaction with $AlCl_3$.11-13) Lower temperature of the polymerization due to super acidity favors more naphthenic structure to be retained. Estimated structures of some representative molecules(554, 642, 694 m/e) are illustrated in Fig. 4. A considerable ring-opening is suggested to take place during the polymerization via hydrogenation under the present conditions providing alkyl and phenyl groups on the oligomers.

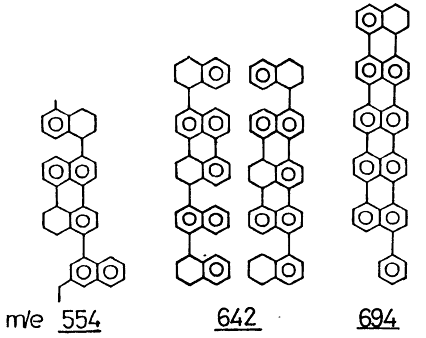

Fig. 4. Some of representative molecules of the benzene soluble fraction in the mesophase pitches.

It is one of most important advantage of HF/BF_3 that its complete recovery and repeated use are possible. Hence the product is essentially free from any impurity such as, S, N, and inorganic substances. The highly soluble mesophase pitch showed the excellent spinnability and its oxidative reactivity was very high compared to those of conventional mesophase pitches derived from such as coal tar or petroleum residues.6,7) The high oxidative reactivity of the present pitch appears to reflect structure rich in naphthenic groups. The rapid losses of such groups by oxidation may lead to the rapid and sufficient stabilization, up-taking 8% of oxygen within 30 min.

Further polymerization in the linear forms of naphthalene linkage without dehydroganation can be designed in the present catalytic preparation by assuring more turn-over of the catalyst.

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