Mesophase Pitch Derived from Isotropic Anthracene Pitch Produced Catalytically with HF/BF$_3$

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The thermal preparation of the mesophase pitch from the isotropic anthracene pitch produced catalytically from anthracene with HF/BF$_3$ was studied through both single- and two-stage heat-treatments. The single stage under vacuum provided a mesophase pitch (SMAP-2) of 100% anisotropy and excellent spinnability at yield as high as 59%. The present mesophase pitch maintained the naphthenic structure to some extent, although thermal preparation, which tends to induce dehydrogenative aromatization, was employed. The two-stage preparation, comprising heat-treatments under pressure (2.1 MPa) and then under vacuum (1 Torr, 1 Torr≈133.322 Pa) increased the yield of the mesophase pitch to 64%. The resultant mesophase pitch (TMAP) of 100% anisotropy and excellent spinnability carried fewer aliphatic groups than that of the single stage. SMAP-2 was sufficiently stabilized for 30 min at 300 °C, superior to that of the mesophase pitches derived from FCC-DO and the isotropic naphthalene pitch. The complete stabilization of TMAP with a smaller aliphatic structure was achieved within a slightly longer time of 45 min. The number of aliphatic groups is closely related to the stabilization reactivity. It is worth noting that the present mesophase pitches prepared from the isotropic anthracene pitch retained the structure of the starting pitch to an extent which depended on the procedure, influencing the stabilization reactivity.

The mesophase pitch of high stabilization reactivity as well as highly oriented molecular alignment, low viscosity, high purity, and higher coking value has been recognized as an appropriate precursor for a pitch-based carbon fiber with high performance. Although preparation procedures for mesophase pitch have been proposed by a number of researchers,[1–7] its yield and properties have not necessarily been sufficient.

The properties of mesophase pitches are strongly related to those of precursor pitches,[7–9] hence, the pretreatment and modification (such as hydrogenation,[6,9] alkylation, and removal of the non-mesogen fractions) are very influential.[10–13] In previous papers[8,9] some favorable properties of the mesophase pitch were ascribed to its naphthenic group.

The present authors have reported novel preparative procedures of mesophase pitch from naphthalene by the aid of HF/BF$_3$ catalyst.[14–16] The mesophase pitch can be prepared via two procedures: in one, naphthalene is converted directly into mesophase pitch at relatively high temperatures of around 260—300 °C; in the second method naphthalene is converted first catalytically into an isotropic one at 80 °C and then thermally into the mesophase one. Both procedures have their advantages. The influence of the molecular structure on the mesophase pitch from naphthalene or anthracene may be of value to study how to establish a design for an excellent carbon fiber precursor.

In the present study, the preparation of a mesophase pitch was studied from the isotropic anthracene pitch[14] catalytically produced from anthracene by HF/BF$_3$. The properties of the mesophase pitches were examined in terms of their spinnability, stabilization reactivity and chemical structure, by comparing values to those of the mesophase pitches derived from the isotropic naphthalene pitch.

Experimental

Anthracene pitch was prepared from commercial-grade anthracene by the aid of HF/BF$_3$ at 80 °C for 3 h under 0.48 MPa autogenous pressure in an autoclave. The product was dissolved in benzene and HF/BF$_3$ was distilled out. The residual product was extracted with ethanol to remove any unreacted starting monomeric anthracene. Some analyses of the isotropic anthracene pitch are summarized in Table 1.

The isotropic anthracene pitch and its heat-treated derivatives (ca. 10—20 g) under pressure were heated in a Pyrex tube placed in a vertical electric furnace at a heating rate of 5 °C min^{-1} to 450 °C under a nitrogen flow with vigorous stirring (500 rpm). As soon as reaching 450 °C, a vacuum pump was started to gradually achieve 1 Torr within 5 min. After the reaction under vacuum for a prescribed time, the product was gradually cooled to 250 °C at a rate of 3 °C min^{-1}, and then rapidly to room temperature in order to fix the anisotropy in the resultant pitch.

A pitch of ca. 30 g was heat-treated at 450 °C for 50 min in a tube bomb under nitrogen pressure (2.1 MPa). After the treatment, the bomb was rapidly cooled down in water so as to recover the heat-treated pitch.

The pitch was fractionated by sequential Soxhlet extraction: first with benzene, then with pyridine and finally with quinoline. The extract with quinoline was filtered with a membrane filter (pore size: 0.45 μm) at 80 °C. Fractions were benzene soluble (BS), benzene insoluble-pyridine soluble (BI-PS), pyridine insoluble-quinoline soluble (PI-QS), and quinoline insoluble (QI).

Extracts from pitches were analyzed with ^{1}H NMR

(Varian VXR-400) in the solvents ($CDCl_3$ or C_5D_5N), using tetramethylsilane as an internal standard. The BS fraction in the mesophase pitches was also measured with ^{13}C NMR (Varian VXR-400) in $CDCl_3$. A paramagnetic relaxation agent, chromium acethylacetonate $Cr(acac)_3$, was added to the deuteriochloroform solution (ca. 25wt%). ^{13}C NMR spectra were obtained under the following conditions: pulse width, 10.47 μs; spectrum width, 25000 Hz; pulse repetition, 6 s; flip angle, 52.1°; number of transients, 10000. In order to distinguish aromatic quaternary carbon from non-quaternary one, GASPE (gated spin-echo) method was applied.[17,18]

The FD-MS of the BS fraction was measured with a JEOL JNS-DX 303 mass spectrometer.

The softening point of the pitch was measured under a hot stage microscope (Leitz).

Mesophase pitches were annealed at temperatures about 50 °C higher than their softening points for 10 min under a nitrogen gas flow and then cooled to room temperature at 3 °C min^{-1}. Part of mesophase pitch, thus annealed, was mounted in the resin and then polished in order to evaluate its anisotropic content by counting the isotropic and anisotropic areas in the montage microphotograph.

The mesophase pitch was spun into fibers of ca. 8—12 μm in diameter under a nitrogen pressure of 0.11—0.12 MPa from a steel spinneret. The diameter and length of its nozzle were both 0.4 mm.

Mesophase pitch fibers were oxidatively stabilized at 300 °C for different periods. The heating rate to the stabilization temperature was 5 °C min^{-1}. The stabilized fibers were carbonized at 600 °C for 1 h in a Pyrex glass tube (30 mm diameter, 600 mm length). The heating rate was 10 °C min^{-1}.

The carbonized fibers were observed under an optical microscope to evaluate the extents of the adhesion and anisotropic orientation.

Results

Properties of Isotropic and Anisotropic Anthracene Pitches. Some properties of anthracene pitch produced with HF/BF_3 are summarized in Table 1. The anthracene pitch produced under autogenous pressure at 80 °C carried no anisotropy, its yield being higher than 90wt%. Its softening point was 180 °C, which was much higher than that of naphthalene pitch (63 °C) produced under similar conditions.[14] The pitch was mostly soluble in benzene, containing 16wt% of BI and 3% of PI. The H/C ratio of isotropic anthracene pitch was identical to that of the starting anthracene, suggesting that dehydrogenation did not take place during cationic polymerization by the aid of HF/BF_3.

Some properties of the mesophase pitches prepared from the isotropic pitch by the heat-treatment are also summarized in Table 1. Heat-treatment at 450 °C for 30 min under a vacuum (1 Torr) provided a mesophase pitch (SMAP-1) of 80 vol% anisotropy. A heat-treatment for an additional 30 min resulted in 100 vol% anisotropy in the resultant mesophase pitch (SMAP-2) with a softening point of 240 °C (H/C ratio: 0.59). Its yield was as high as 59 wt%. SMAP-2 contained 31wt% of BS and 21 wt% of QI, respectively.

The two-stage preparation, which involved heat-treatments under pressure (2.1 MPa) for 50 min and then under vacuum (1 Torr) for 30 min, provided a mesophase pitch (TMAP) of 100 vol% anisotropy with a softening point of 250 °C (H/C atomic ratio=0.57). Its H/C ratio was slightly smaller than that of SMAP-2. The yield increased to 64 wt%. TMAP possessed 38 wt% of BS and 29wt% of QI, respectively.

Spinning and Stabilization Properties on Mesophase Pitches. SMAP-2 was spinnable at 310—340 °C, exhibiting stable spinning for 5 min at 330 °C to give a pitch fiber of 8—12 μm diameter.

Although the carbonized fiber from SMAP-2 adhered after stabilization at 300 °C for 20 min, no adhesion was no longer observable when the stabilization time exceeded 30 min; the transverse section of the carbonized fibers exhibited a homogeneous fine mosaic texture. The oxygen uptake of SMAP-2 reached 6.5 wt% at 20 min, and 11.1 wt% at 30 min when complete stabilization was achieved. Large oxygen uptake should be noted.

TMAP prepared by a two-stage process also exhibited similar a spinnability at temperatures from 335 to 355 °C as SMAP-2, though its stabilization reaction took 45 min for complete stabilization.

Such spinnability and stabilization reactivities of the mesophase pitches derived from an isotropic anthracene pitch are much better than those of thermally prepared type from a naphthalene pitch[16] and may be comparable, or even slightly better, than those

Table 1. Preparation Conditions and Properties of the Mesophase Pitches Prepared from Synthesized Pitch

Pitch	HTC[a] Temp	HTC[a] Time	Residue Yield	S.P.[b]	A.C.[c]	Solubility/wt% BS	Solubility/wt% BI-PS	Solubility/wt% PI(QI)	Coke Yield	H/C
	°C	min	wt%	°C	vol%				wt%	
AP	—	—	—	180	0	81	16	3(—)	63	0.71
SMAP-1	450	30	61	225	80	51	20	29(—)	—	0.61
SMAP-2	450	60	59	240	100	31	32	37(21)	77	0.59
TMAP	Two stage[d]		64	250	100	38	18	44(29)	86	0.57

a) Heat-treatment conditions. b) Softening point. c) Anisotropic content. d) First stage: 450 °C, 50 min, 2.1 MPa. Second stage: 450 °C, 30 min. 1 Torr.

of petroleum-derived mesophase pitches examined in our laboratories.9,10) The much higher yield, purity and lower price of the present pitches can be their main advantages.

Structure of Isotropic and Anisotropic Anthracene Pitch. Figure 1a illustrated the FT-IR spectra of the isotropic anthracene pitch. The isotropic pitch showed strong bands at 2920 and 2860 cm^{-1} (C-H stretching of methylene groups) without the band at 2960 cm^{-1} (methyl C-H). The intense band at 1450 cm^{-1} (methylene or naphthenic C-H bending) was correspondingly observed, suggesting the presence of naphthenic rings. Aromatic C-H bands were much less intense. Three intense bands were observed at 870, 810,. and 750 cm^{-1}, reflecting the types of substitution on the aromatic ring. The more intense bands at 870 and 750 cm^{-1}, can be assigned to an isolated and 4 neighboring aromatic C-H bonds on the aromatic ring, respectively.

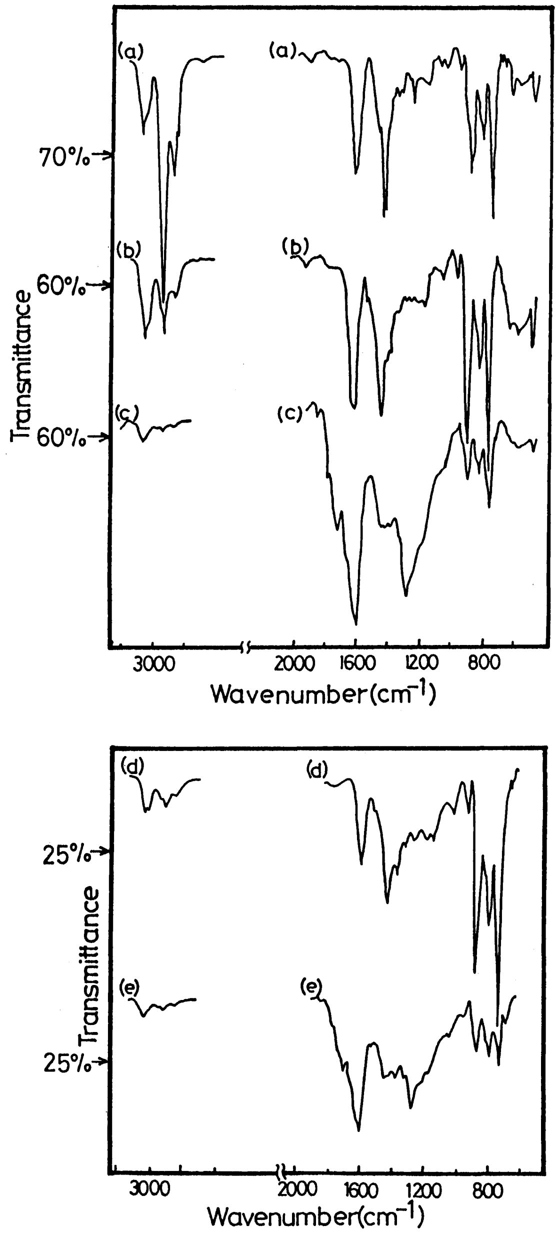

Fig. 1. FT-IR spectra of the pitches. (a) Anthracene pitch. (b) SMAP-2. (c) Sufficiently stabilized fiber(SMAP-2). (d) TMAP. (e) Sufficiently stabilized fiber (TMAP).

Figure 2 shows the ^{1}H NMR spectra of the BS and BI-PS fractions in the pitch. The isotropic pitch (Fig. 2a) exhibited intense peaks at δ=1.6—2.1 and 3.0, and minor ones at δ=3.1 and 3.4 in the aliphatic region. Essentially no resonance was found at δ=1.1—1.5, which is ascribed to methyl groups. A distinct peak at δ=4.0—4.5 was observed, which is also found in 9,10-dihydroanthracene. The three dominant peaks were observed at δ=8.4, 7.9, and 7.5, reflect the aromatic hydrogens of anthracene. The BI-PS fractions were certainly more aromatic and less naphthenic than were the BS fractions.

Table 2 summarizes the hydrogen distributions and structural parameters of the BS and BI-PS fractions according to Brown and Ladner.19) The isotropic anthracene pitch was fairly aromatic according to ^{1}H NMR, although it carried a significant amount of Hα and Hβ hydrogens. A smaller amount of Hγ was noted.

Table 3 summarizes the carbon distributions in the BS fractions of the isotropic pitch. The types of carbons were classified into seven categories (A_1—A_7),

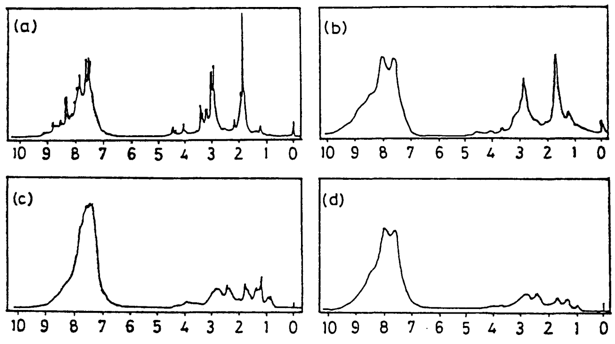

Fig. 2. ^{1}H NMR spectra of BS and BI-PS fractions. (a) BS of anthracene pitch. (b) BI-PS of anthracene pitch. (c) BS of SMAP-2. (d) BI-PS of SMAP-2.

Table 2. Hydrogen Distribution of BS and BI-PS Fractions in the Mesophase Pitches[a]

		%				f_a
		Haro	Hα	Hβ	Hγ	
AP	BS	55.7	29.6	14.4	0.3	0.84
	BI-PS	65.5	22.4	11.1	1.0	0.89
SMAP-2	BS	73.9	15.7	8.4	2.0	0.91
	BI-PS	81.9	12.8	4.6	0.7	0.95
TMAP	BS	77.0	15.1	6.0	1.9	0.93
	BI-PS	82.4	10.5	4.8	2.3	0.96

a) Haro: δ=6—10, Hα: δ=2—4.5 Hβ: δ=1.1—2, Hγ: δ=0.3—1.1. Identification according to Brown and Ladner.19)

Table 3. Carbon Distribution of BS Fractions in the Mesophase Pitches[a)]

Run. No.	A_1	A_2	A_3	A_4	A_5	$A_6(A_7)$
AP	5	19	15	36	10	15(0.1)
SMAP-2	6	15	19	37	16	7(1.2)
TMAP	4	14	15	52	12	5(1.2)

a) Identification according to Refs 17 and 18. A_1: Aromatic carbons substituted by aromatic groups or methylene groups $-CH_2-$ between aromatic rings δ=150.1—138.0. A_2: Aromatic carbons substituted by saturated groups or naphthenic $-CH_2-$ δ=138.0—133.1. A_3: Outer quaternary aromatic carbon δ=133.1—129.2. A_4: Unsubstituted aromatic carbon δ=129.2—116.9. A_5: Inner quaternary aromatic carbon δ=129.2—116.9. A_6: Aliphatic carbon of methylene $-CH_2-$ δ=54.2—21.9. A_7: Aliphatic carbons of methyl $-CH_3$ δ=21.9—10.0.

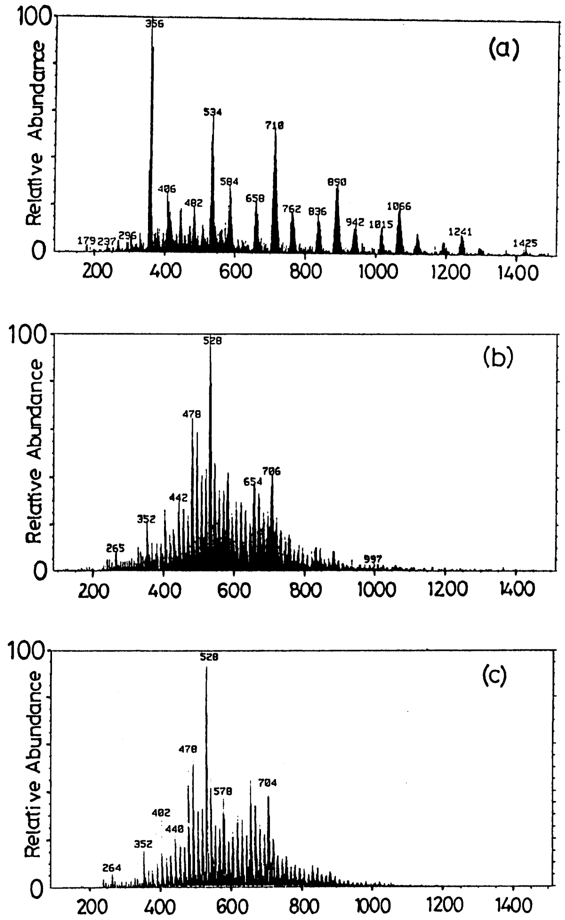

Fig. 3. FD-Mass spectra of BS fraction. (a) Anthracene pitch. (b) SMAP-2. (c) TMAP.

as summarized in Table 3. The isotropic pitch carried as much as 14% of aliphatic carbon (A_6+A_7), though the alkyl side chain was essentially absent, since a very weak resonance was observed in the range δ=21.9—10.0 (A_7) assignable to alkyl side chains. It is suggested that a cleavage of naphthenic structure, as well as dehydrogenation, hardly took place during cationic polymerization at 80 °C with HF/BF_3. The pitch carried inner quaternary aromatic carbon of only 10% among aromatic carbons substituted with an aromatic ring (A_1, 5%) and saturated (alkyl and naphthenic) groups (A_2, 19%), as well as outer quaternary aromatic carbon (A_4, 36%). The most condensed form of anthracene trimers was calculated to have the following carbon distribution: 28.6% of A_3, 42.9% of A_4, and 28.6% of A_5. Thus, the present pitch was estimated to have less condensed forms, since the content of A_5-carbon in the pitch was about one third of the most condensed anthracene trimer. A considerable content of both naphthenic and aryl-aryl bondings should be present in the oligomers of the pitch.

Figure 3 exhibits FD-Mass spectra of the BS fractions in the pitch. The molecular weight of the constituents in the isotropic pitch distributed from 178 to 1500 with a maximum abundance at 356 (exhibiting major peaks around m/z 356, 534, 710, 890, 1066, 1241 and 1425, as summarized in Table 4). These peaks are ascribed to dimers, trimers, tetramers, pentamers, hexamers, heptamers, and octamers, respectively. It is noted that they were observed at a regular molecular weight interval of m/z 178, suggesting that ring degradation hardly took place during cationic polymerization with HF/BF_3.

The FT-IR spectra of SMAP-2 and TMAP are also illustrated in Fig. 1(b, c, d). They are very similar, except for minor differences in the intensities of some bands. The bands related to aromatic C-H and C=C (3050, 1600, 870—750 cm^{-1}) were relatively intensified, and those related to aliphatic C-H (2960—2700 cm^{-1}) were weakened by the mesophase pitches.

Mesophase pitches were also found by ^1H NMR to be more aromatic, as shown in Fig. 2 and Table 2. The relative intensity of Hγ, a broadening of the aromatic hydrogen resonance, and a decrease in the intensity at δ=8.5 were noted. The mesophase pitch

Table 4. m/z Numbers of the Major FD-Mass Peaks from BS Fraction in the Pitches[a)]

	Monomer (178)	Dimer (356)	Trimer (534)	Tetramer (712)	Pentamer (890)	Hexamer (1068)	Heptamer (1246)
Anthracene pitch	—	356	534	710	890	1068	1246
SMAP-2	—	352	528	706	882	—	—
TMAP	—	352	528	704	—	—	—

a) Numbers in parenthesis are calculated values.

of two-stage preparation (TMAP) gained slightly, but significantly, more Haro and Hγ.

The carbon distributions in the BS fractions of the mesophase pitches are also summarized in Table 3. The A_6 methylene group of SMAP-2 (7%) was much less than that of the isotropic pitch (15%), while the A_7 (methyl) carbon increased, although its content was still very low. Naphthenic ring was principally dehydrogenated into an aromatic ring during the heat-treatment. A small amount of the naphthenic groups may have cleaved into methyl groups. Compared to the starting isotropic pitch, SMAP-2 gained A_5 considerably and A_3 slightly, indicating that both dehydro-aromatization and condensation took place during the heat-treatment. TMAP gained markedly A_4, while increases of A_3 and A_5 were very minor. The anthracene unit may be reproduced through dehydrogenation.

The FD-Mass peaks of the BS fraction in the SMAP-2 distributed almost continuously from 220 to 1100, as shown in Fig. 3. The peaks around *m/z* 356, 534 and 710 (Table 4) markedly reduced their intensity, while the peaks at around *m/z* 528 and 706 were relatively intensified. The latter two peaks may correspond to the trimer and tetramer of the anthracene units, respectively, which suffer dehydrogenation. The BS fraction in the TMAP distributed from 230 to 1100 with a maximum abundance at 528, as shown in Fig. 3c, the distribution and intensity of the peaks being similar to those of SMAP.

Structure of Stabilized Mesophase Pitch Fiber. Figure 1(c, e) illustrates the FT-IR spectra of sufficiently stabilized mesophase pitch fibers. Stabilized SMAP-2 exhibited new bands at 1690—1650 cm^{-1} (C=O specifically for quinone or aryl-aryl lactone groups), 1300—1000 cm^{-1} (C-O stretching), and the bands at 1280 cm^{-1} (phenoxy group C-O, aromatic ketone C=O) and/or 1180 cm^{-1} (ether Ar-O-Ar) increased their intensities, while the bands at 1450 cm^{-1} (methylene and naphthenic $-CH_2-$ bending), 2960—2720 cm^{-1} (aliphatic C-H stretching) and 870—675 cm^{-1} (aromatic C-H bending) lost markedly their intensities. Oxygenation was significant. The FT-IR spectrum of TMAP stabilized for 45 min in air at 270 °C was similar to that of SMAP-2.

Discussion

An isotropic pitch prepared catalytically from anthracene with HF/BF_3 provided through the heat-treatment mesophase pitches of excellent spinnability and fair stabilization reactivity comparable or slightly better to those derived from decant oils.[10] The final yield of the mesophase pitch from anthracene reached as high as 64%. Hence, using the present procedure where the catalytic condensation of anthracene with HF/BF_3 and the thermal induction of liquid crystal natures can be industrially competitive in terms of both cost and quality of mesophase pitch. It is an advantage that corrosive HF/BF_3 was applied at relatively low temperatures.

The mesophase pitch derived from an isotropic anthracene pitch exhibited interesting features regarding both structure and properties. Model structures for typical constituents in the BS fractions of isotropic and anisotropic pitches based on both NMR and FD-Mass are illustrated in Fig. 4. The mesophase pitch certainly carries less naphthenic hydrogens than does the starting isotropic pitch. Nevertheless, the mesophase pitch retained more naphthenic hydrogens and suffered much less bond cleavage of ring structures than did the naphthalene pitch reported in a previous paper.[16] More aryl-aryl bonds are found in the present mesophase pitch. These characteristics of the former pitch brought about advantages as a precursor of the carbon fiber which are superior to those of the latter-mentioned pitch. Higher yield is another advantage of the anthracene pitch. The two-stage preparation increased the yield of mesophase pitch

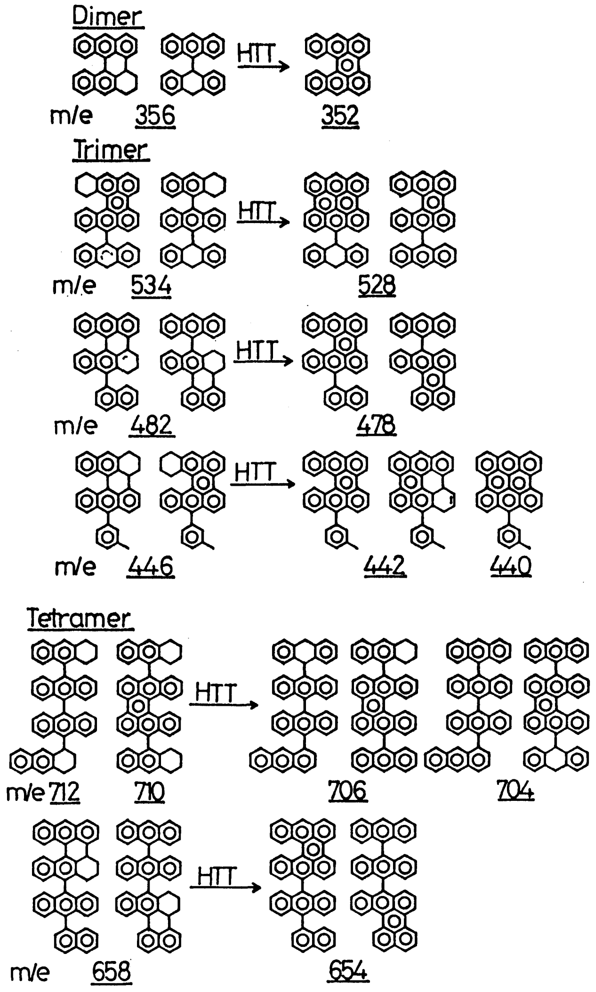

Fig. 4. Some of the representative model structures in the BS fractions of the anthracene and mesophase pitches (SMAP-2 and TMAP). HTT: Heat-treatment at 450 °C for mesophase induction.

because of the pressurized reaction for a long time during the first stage, which introduces more aryl-aryl linkages. A smaller amount of highly condensed forms was found in the anthracene pitch than in the naphthalene pitch.

Such differences in the properties and structures of the mesophase pitches of anthracene from those of naphthalene are due to their original structure. Anthracene has reactive sites at 9 and 10 positions, where condensation takes place first, while increasing the pitch yield. The hydrogens at the condensation sites may not stay at the same positions but, rather, move to other sites of higher stability, since the 9,10-dihydroanthracene-type naphthenic hydrogens are reactive. More naphthenic rings tend to survive in the anthracene oligomers than do naphthalene oligomers. The lower temperature and shorter heat-treatment time for mesophase induction may be other reasons why the pitch carries more hydrogens on the ring. Thus, the mesophase pitch from anthracene can maintain more naphthenic hydrogens, even after the thermal process of mesophase preparation, although their quantity is lower than that of the starting pitch.

Facile conversion of the anthracene oligomers to mesophase pitch is due to the larger aromatic ring of anthracene, and probably to the high reactivities of 9,10-positions. The high reactivities of these positions may lead to some preferential formation of aryl-aryl bonds in the oligomers during condensation with HF/BF_3 under such milder conditions. The aryl-aryl bonds may survive in the mesophase pitch to lower its softening point, in spite of the larger size of the aromatic ring.

The aliphatic C-H groups in the mesophase pitch derived from the anthracene exhibited oxidation reactivity during the initial stage of stabilization to produce a carbonyl bond of the quinone group. The oxygen uptake of the anthracene pitch was very rapid, reaching 11% within 30 min; this was much faster than that of naphthalene pitch. The 9,10 positions may be easily oxidized to give quinone. Such a high rate of oxygen uptake is another characteristic of the present anthracene mesophase pitch, completing stabilization within a reasonable time.

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