Nanoscopic Structure and Properties of Mesophase Pitch

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1. Introduction

Understanding the structure of mesophase pitch, which is believed to be an important intermediate for graphitizable carbons, has been a most important task for the past 20 years. Brooks and Taylor [1] proposed that the mesophase sphere is a kind of nematic liquid crystal material, consisting of oligomers of planar aromatic rings stacked approximately parallel to each other to form an equatorial alignment. This review has summarized the structural concepts of mesophase pitch, as well as its derived carbon fibers of high graphitizability and preferred orientation along the fiber axis from the micro-, nano-, and macroscopic perspectives, emphasizing the novel features of the nanoscopic structural units. Such a series of structural concepts is applicable to both the liquid and the solid states of the carbonaceous substances, and their reversible inter-conversion and irreversible carbonization are consequently considered to show their mutual correlations.

2 Molecular Structure of Mesophase Pitch

Mochida et al.[2] proposed the Spider-Wedge Model for the structure of mesophase pitch, analyzing, after hydrogenation, quinoline-extractable components in the mesophase spheres, where aromatic units 0.6 to 1.5 nm in diameter are linked by aryl-aryl or methylene bridges to give molecular weights in the range of 400 to 4000 amu. The aromatic planes carry alkyl and naphthenic groups. Such groups assist in solubility and fusibility. A wide molecular weight distribution of the mesophase pitch is important to reveal the liquid crystal nature, because smaller molecules must be stacked through π-π interaction between large planar molecules. Smaller molecules are important to bring about the fusibility of the entire mesophase pitch. An average structure is often proposed, but, due to its complexity, is often useless because the contrasting nature of the constituent molecular species may yield a meaningless average.

The typical molecular structure of spinnable naphthalene-derived mesophase pitch is described in Figure 1.[3] ^{13}C NMR of fused mesophase pitch has been observed.[4],[5] The distributions of aromatic and aliphatic carbons indicate the average sizes and shapes of aromatic and naphthenic rings, and the shape, length, and number of alkyl side chains, as illustrated in Figure 2.

Figure 2 ^{13}C-melt-NMR spectrum of mesophase pitch catalytically prepared from naphthalene by HF/BF$_3$ at 347 °C.
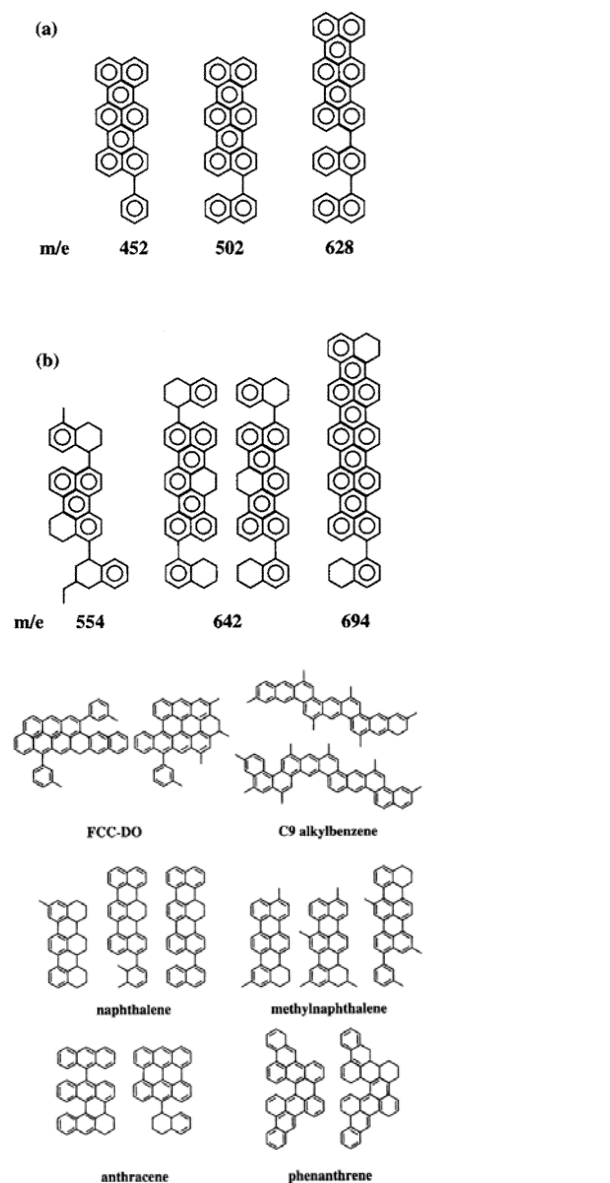
Figure 1 A: Typical molecular structures of benzene soluble (BS) fraction of naphthalene-derived AR-RESIN: (a) BS of naphthalene derived mesophase pitch; (b) BS of methylnaphthalene derived mesophase pitch. B: Typical molecular structures of mesogen molecules in several mesophase pitches.
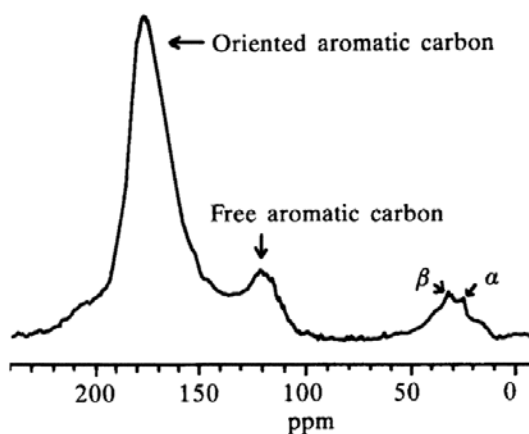
It has been established that the size and shape of aromatic planes, the number of alkyl substituents, and the naphthenic groups differ considerably depending on the precursor. Mesophase pitches derived from fluidized catalytic cracking-decant oil (FCC-DO) or coal-tar pitch is considered to have a greater variety of molecules, reflecting complex components in the starting feeds. Nevertheless, pitch derived from FCC-DO is rich in alkyl groups, whereas pitch derived from coal tar is highly aromatic. The differences in their properties are very specific. Mesophase pitches derived from aromatic hydrocarbon definitely inherit the structure of their initial molecules. Reaction conditions also influence the extents of oligomerization, ring closure and opening, and dehydrogenation. As indicated by FD-Mass (field desorption mass spectroscopy), the pitch certainly contains a variety of molecules in a limited range of molecular weights. Mesophase pitch derived from naphthalene has a molecular size distribution of 240 to 1500 m/e, as suggested by TOF-Mass (time of flight mass spectroscopy). The

most abundant molecules in the pitches are illustrated in Figure 1(b). Methylnaphthalene and naphthalene appear very similar in providing the base oligomers of their respective units. A relatively high concentration of the methyl groups causes an important characteristic of the methyl-naphthalene-derived pitch, as described earlier.

A mixture of two aromatic hydrocarbons can be a precursor for another unique mesophase pitch. Block, alternative, and random oligomers can be designed as components of a particular mesophase pitch. A mixture of highly aromatic constituents, solid impurities, and heteroatoms are unique to the residue. Such problems are overcome by this novel procedure, because feeds can consist of distillable aromatic components of a much narrower range. Inclusion of heterocyclic species is designed to introduce unique properties to the mesophase pitch.

Aromatic hydrocarbons in diesel fuel are believed to cause black smoke through incomplete combustion. Their reduction or removal is believed to be a valuable approach in protecting the urban environment. Through these novel syntheses, the separation of a significant portion of rather small aromatic hydrocarbons from the fuel can be a reasonable feedstock for low-cost mesophase pitches having unique properties.

Molecular Weight and Molecular Weight Distribution of Mesophase Pitch

The molecular weight and molecular weight distribution of mesophase pitches are important structural concepts that determine their properties. The molecular weight of spinnable mesophase pitches, which depends on a variety of factors, such as hydrocarbon feeds and severity of preparation conditions, is often reflected in their softening point, falling in the range of 400 to 4000 amu. The exact determination of the molecular weight of a mesophase pitch has been considered a difficult task, because no solvent dissolves every molecule contained in the spinnable mesophase pitch. The complexity of the molecular compositions in the mesophase pitch derived from residues, which carry no monomeric units and very high aromaticity, is the reason for the difficulty. Nevertheless, several attempts to determine the molecular weights of mesophase pitches have been conducted using a series of analytical methods, such as light scattering, [6] gel permeation chromatography (GPC), [7] and FD-Mass. [8]

Recently, Watanabe et al. [9] applied TOF-Mass to measure the molecular weight of an entire molecular species in naphthalene-derived mesophase pitches, as shown in Figure 3. The monomeric structure is nearly maintained in the components, although some hydrogenated forms are present. Molecular weight and molecular weight distribution can be two of the most important factors to be controlled in processing the mesophase pitch.
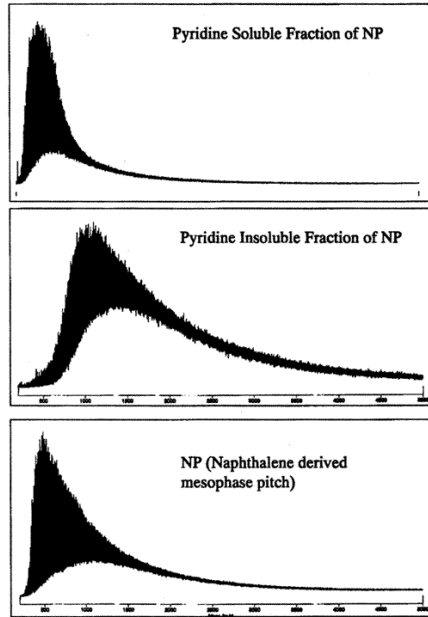
Figure 3 Molecular weight distributions of naphthalene-derived mesophase pitch and their fractions: (a) pyridine-soluble fraction; (b) pyridine-insoluble fraction; (c) mesophase as-received.

3. Cluster and Domain Structures in the Mesophase Pitch

3.1 Molecular Assembly and Nanoscopic Units

The aromatic planes in mesophase pitch are stacked parallel to one another, as indicated by polarized light optical microscopy. The pitch has been evaluated by optical microscopy in terms of anisotropic (stacked) and isotropic (nonstacked) contents, and the shape and size of the isochromatic areas. Microscopic description was attempted to evaluate the molecular stacking or assemblies within the cross-section of carbon fibers derived from the mesophase pitch by extension of the concept used for needle coke. However, the much smaller size 10-μm-diameter carbon fiber makes it difficult to describe the details. Nevertheless, Zimmer and White [10] conjectured on the stacking properties of the mesophase pitch, and suggest that the heterogeneity of the anisotropic distribution has been missed in a fiber.

Korai and Mochida [11] found definite d_{002} diffraction by a method using *in situ* XRD. Such a stacking of aromatic rings is compared to the graphite-like units. We defined it as a cluster of aromatic mesogens. It is important to note that a liquid crystal mesogen may carry the cluster units of larger stacking in the mesophase pitch than in the isotropic pitch. According to the line position and width, the interlayer distance and height of the stack can be calculated. The results are summarized in Table 1. The stacking heights are dependent on the initial organic species and the preparation conditions, although the d spacing was much the same. High stacking of methylnaphthalene-derived mesophase pitch was noted. Further higher stacking was observed with dimethylnaphthalene-derived mesophase pitch. Larger aromatic rings should not be a reason for the higher stacking of the methylnaphthalene-derived mesophase pitch. Vorpagel and Lavin[12] suggest that methyl groups located over the aromatic plane of the neighboring molecule stabilize the stacking.

Table 1 Lc (002) Values of Mesophase Pitches and Their Solvent Fractions.

Sample	MNP (nm)	NP (nm)
Mesophase pitch as-received	7.5	2.4
Pitch annealed	8.3	2.3
Pitch quenched	6.5	2.3
PyS as extracted	1.3	<1
PyS annealed	1.6	<1
PyS quenched	1.4	<1
THFs as extracted	4.8	<1
THFs annealed	3.2	<1
THFs quenched	2.6	<1
PyI as extracted	2.2	ND
PyI annealed	3.3	ND
PyI quenched	3.1	ND

ND: not detected; NP: naphthalene-derived mesophase pitch; MNP: methylnaphthalene-derived mesophase pitch; PyS: pyridine-soluble fraction; PyI: pyridine-insoluble fraction; THFs: tetrahydrofuran-soluble fraction.

The height decreased very rapidly above the softening point, as shown in Figure 4. Nevertheless, some stacking 1- to 3-nm high, which was still subject to the initial feeds, is observable even at 300 °C, indicating the liquid crystal properties of the mesophase pitch at the spinning temperature.
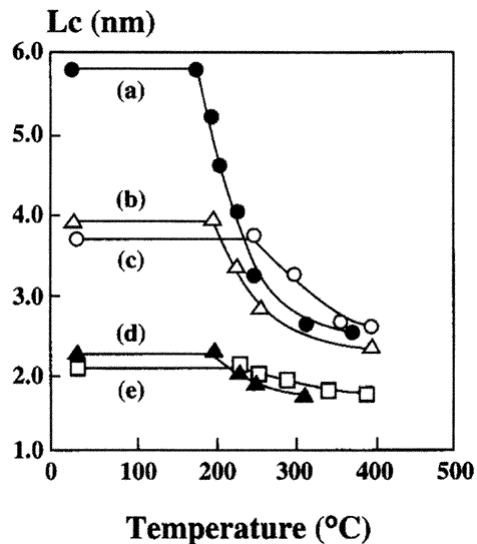

Figure 4 Change of Lc values (nm) of mesophase pitches with increasing temperature: (a) methylnaphthalene-derived mesophase pitch; (b) coal tar-derived mesophase pitch; (c) anthracene-derived mesophase pitch; (d) naphthalene-derived mesophase pitch; (e) petroleum residue-derived mesophase pitch.

Clusters gather to form larger collective units of molecular ordering to be defined as microdomains (Σ 1-10 nm). Korai et al.,[13] using high-resolution SEM, first found two basic structural units of microdomains and domains (30 to 80 nm) on the longitudinal surface of the as-spun mesophase pitch fiber after solvent extraction. The soluble fraction surrounds the microdomain in the mesophase pitch and its as-spun fiber to hide the shape of the latter unit. The soluble fraction may also be located in the microdomains. Extraction with a series of solvents makes the location and shape distribution of the microdomain more precise. The domain corresponds to the optical unit as described above; however, high-resolution SEM clarifies more details of its shape and size and the distribution. The extraction also reveals the microdomains in the mesophase pitch, which are randomly arranged, although their fishbone shape is basically uniform.

3.2 Reorganization of Molecular Assembly of Mesophase Pitch

Several interesting features at the reorganization of molecular assemblies in the mesophase pitches and their fractions from heating/cooling cycles were found by Fortin et al.[14] using XRD and TEM analyses. The mesophase pitches tended to maintain their texture, domain, and microdomain regardless of the resolidification procedures, although this was not the case for molecular stacking in

the cluster. Regardless of the mesophase pitches, Lc (002) values of the entire pitches were always larger than those of their fractions, suggesting that the fractions play cooperative roles. [15] The relaxation mobility and stacking stability of planar molecules during the solidification procedure in which the temperature fell at variable rates may play an essential role in determining the height of the molecular stacking. The tetrahydrofuran (THF)-soluble fraction with smaller molecular components showed larger Lc (002) values than the pyridine-soluble fraction, although the latter provided larger Brooks-Taylor-type spheres, as shown in Figure 5 and Table 1. Recently, the Lc (002) values were found to be recovered by successive relaxation at an elevated temperature, above the glass transition (Tg) below the melting point (Ts). Depending on the rate of cooling, mobility should have a major effect on the stacking order.
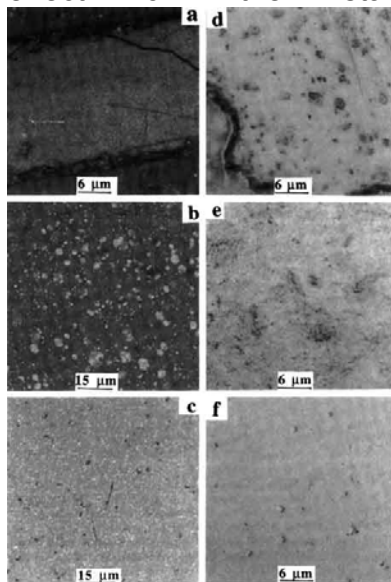

Figure 5 Optical micrographs of THF fractions and spheres: (a) THFs of MNP as extracted; (b) THFs of MNP annealed; (c) THFs of MNP as quenched; (d) THFs of NP as extracted; (e) THFs of NP annealed; (f) THFs of NP as quenched.

TEM failed to distinguish differences in the molecular stacking of the mesophase pitches, as shown in Figure 6(a), although XRD indicated obvious differences in their stacking. TEM revealed more ordered molecular stacking to form lattice fringes in the pyridine-insoluble fraction, as shown in Figure 6(b). The thermal fructuation of relatively small hexagonal planes may disturb TEM observation of molecular stacking in the mesophase pitch.
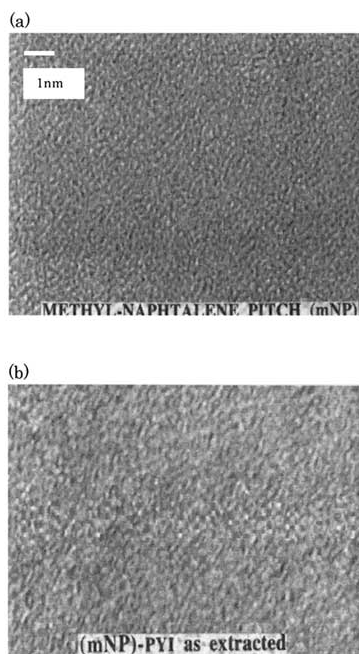

Figure 6 (a) TEM 002 lattice fringe images of methylnaphthalene-derived mesophase pitches; (b) TEM 002 lattice fringe images of pyridine insoluble fraction.

4. Thermal Properties of Mesophase Pitch

4.1 Glass Transition Temperature (Tg) and Softening Point (Ts) of Mesophase Pitch

When thermoplastic polymer is cooled below a particular temperature characteristic of the respective polymer, it becomes hard and brittle. This temperature is called the glass transition temperature (Tg). The applications of some polymers, such as polystyrene and polymethylmethacrylate, are usually in their glass state, below their Tg's, whereas the applications of other polymers, including rubbers and elastomers, are in their rubbery state, above their Tg's, in which they are soft and flexible. Polymeric chains are resolved from their crystal assembly to become disordered liquid at the melting point for crystalline or semicrystalline polymers and at the Ts for amorphous polymers. Glass transition only happens with amorphous polymers in which all polymer chains are not necessarily ordered in their crystal forms, but rather are entangled randomly, although they are in their solid state. Usually thermoplastic polymers consist of a 40-70% amorphous portion. Such a composition provides the polymer with both Tg and Ts. Some crystalline polymers whose polymer chains have complete lamellar folding are present with no Tg observed.

Mesophase pitches, which are generally glass-like materials at room temperature, consist of very stiff, two-dimensionally spaced molecules that do not form lamellar-type folding but rather planar stacking of aromatic sheets. Mesophase pitch has a Tg over room temperature that is about two-thirds of Ts.

Mesophase pitch has the following Tg features: (1) relatively high molecular weight, even though it is much smaller than that of ordinary polymers; (2) relatively wide temperature range of Tg,

indicating heterogeneity and broad molecular weight distribution; (3) relatively smaller changes of free volume or heat capacity measured by thermo mechanical analysis (TMA) and differential scanning calorimeter (DSC), compared to those of ordinary polymers; and (4) molecular stacking of the pitch that decreases with increased temperature starting around Tg, and increasing sharply above Ts.

We measured Tg's (the starting point of Tg) of mesophase pitches derived from naphthalene, methylnaphthalene, and dimethylnaphthalene, using TMA, as shown in Table 2 and Figure 7. The Tg's of naphthalene, methylnaphthalene, and dimethylnaphthalene mesophase pitches appeared at 163 °C, 143-144 °C, and 183 °C, respectively, which were around 75% of their softening points. The Tg of methylnaphthalene-derived mesophase pitch of a relatively lower molecular weight was lower than those of the other mesophase pitches. Dimethylnaphthalene-derived mesophase pitch with a higher Lc (002) value showed a higher Tg than those of the other mesophase pitches. The stacking height of the mesogen molecules in the mesophase pitch molecules is suggested as another important factor in determining Tg.

Table 2 Tg's and Ts of Naphthalene-, Methylnaphthalene-, and Dimethylnaphthalene-Derived Mesophase Pitches.

NP		MNP		dMNP	
Tgs (°C)	Ts (°C7rpar;	Tgs (°C)	Ts (°C)	Tgs (°C)	Ts (°C)
163	228	144	225	183	249

DMNP: dimethylnaphthalene-mesophase pitch; MNP: methylnaphthalene-derived mesophase pitch; NP: naphthalene-derived mesophase pitch; Tg's:
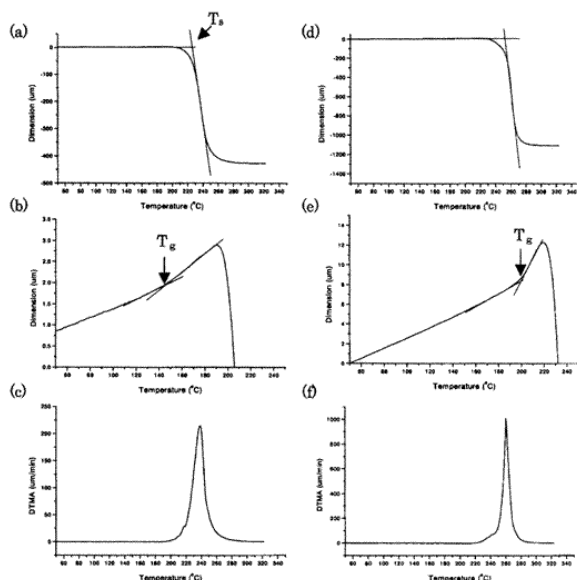
Figure 7 Thermo mechanical analysis (TMA) and Differential thermo mechanical analysis of methylnaphthalene-and dimethylnaphthalene-derived mesophase pitches: (a), (b), (c): Methylnaphthalene-derived mesophase pitch (MNMP); (a) TGA curve of MNMP; (b) enlarged TGA curve of MNMP; (b) DTGA curve of MNMP; (d), (e), (f): Dimethylnaphthalene-derived mesophase pitch (DMNMP); (d) TGA curve of DMNMP; (e) enlarged TGA curve of DMNMP; (f) DTGA curve of DMNMP.

4.2 Stacking Recovery of Mesophase Pitch by Solid-State Annealing

In the fiber formation stage (spinning) of mesophase pitch, the clusters of mesophase pitch molecules sustain strong shear force from the wall of the spinning capillary to align the molecules or clusters along the spinning axis. Such phenomena result in shear thinning (removal of strain) macroscopically, deforming the cluster to reduce the stacking height of the mesophase pitch to some extent. In addition, rapid quench from the fused state in the nozzle to the solid state at the nozzle outlet may not allow the relaxation to recover the stacking height in the solid state of the mesophase pitch. Mesophase pitches with larger Lc values were found usually to suffer greater lowering of Lc in their as-spun fibers because of more rapid quenching due to their higher stacking.

Annealing as-spun mesophase pitch fibers in the solid state at a temperature range between Tg's and Ts restored the Lc (002) value of the as-spun fiber to the value of the mesophase pitch, without any distinct change in the nano- and macroscopic morphologies. This is an important case in the industrial stabilization.

5. Dynamic Property and Liquid Crystalline Nature of Mesophase Pitch

5.1 Capillary Rheometry of Mesophase Pitch

Above its Ts, mesophase pitch flows in a liquid state, maintaining its molecular ordering. Nazem [16] reported that the viscosity of a mesophase pitch strongly depends on the temperature of measurement, the anisotropic content, and the initial materials of the pitch. However, the flow properties of mesophase pitches in their molten state, under variable shear rates at the temperature of spinning, are rarely measured, and dependence on structure has still not been resolved in spite of several studies. [17-19]

Because they are different from ordinary polymers and isotropic pitch, mesophase pitches show the typical features of liquid crystal polymers in their viscosity and shear rate correlation curves, as shown in Figure 8.[20] The viscosity decreases rather sharply with an increased shear rate, where spinning is often conducted (region a). At that point, the viscosity becomes almost constant, within a limited range, being independent of shear rate (region b: Plateau region). A further increase in the shear rate continues to decrease the viscosity, which always approaches a constant value as the shear rate approaches zero. The reduction of viscosity at higher shear rates is explained in terms of deformation of the domain and microdomain, finally decreasing the extent of molecular stacking in the cluster according to the value of the shear rate.
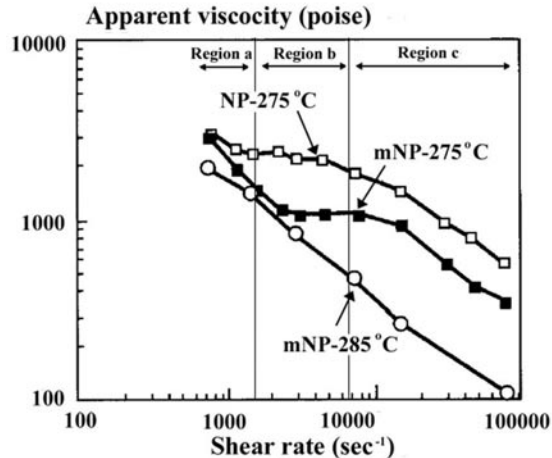

Figure 8 Viscosity-shear rate correlation curves of naphthalene- and methylnaphthalene-derived mesophase pitches: NP: naphthalene-derived mesophase pitch; MNP: methylnaphthalene-derived mesophase pitch.

The shape of the viscosity-shear rate correlation curves depends on the chemical and physical properties of the mesophase pitches.41 The mesophase pitch from naphthalene exhibited more or less Newtonian behavior in regions a and b, where viscosity decreases very slightly with an increased shear rate. The sharp decrease of viscosity in region c is also observable in this pitch.

The methylnaphthalene-derived mesophase pitch exhibited a different viscosity-shear rate correlation than that of the naphthalene-derived mesophase pitch, reflecting the difference in size of the microdomains and the stacking height of the planar molecules in the liquid crystal state. Structure-property correlations in this area are still open for further study.

5.2 Die Swell Phenomenon of Mesophase Pitch in Spinning

When a viscoelastic fluid is extruded through a tube, the extruded jet usually increases in diameter, sometimes even to three or four times that of the tube. This phenomenon is called "die swell." The die swell ratio is defined as the ratio between the maximum diameter of the extruded jet and the diameter of the tube. Die swell, a general phenomenon occurring in any viscoelastic fluid, is an important issue in industry, because so many forming processes involve the extrusion of viscoelastic fluids. One example with wide application is the extrusion of plastics in their molten state. The die swell phenomenon may be explained by elastic recovery. The molecules are stretched by the shear forces in the tube, and the average axial stress at the exit is a tension. The Weissenberg and

Reynolds numbers of the fluid itself govern dimensional parameters.

Exhibition of a die swell phenomenon indicates that mesophase pitch contains viscoelastic, polymer-like materials, as described above. Figure 9 is a schematic diagram of the die swell phenomenon in the spinning process of a mesophase pitch. [21] The attenuation point, which depends on the spin speed, nozzle diameter, and cooling properties of the mesophase pitch, was observed to be 2 to 4 mm from the nozzle outlet. The attenuation point of methylnaphthalene-derived mesophase pitch, ~ 2 mm from the nozzle outlet, is shorter than that of the naphthalene-derived mesophase pitch at a shear rate of around 800 sec^{-1}. This means that the methylnaphthalene-derived mesophase pitch may have a shorter cooling time for resolidification than that of the naphthalene-derived mesophase pitch. The rapid cooling may result from its larger thermal conductivity. The size of the die swell increased with an increased spinning temperature. [22] Mochida et al. [23] successfully prepared a transverse-shaped carbon fiber with random cross-sectional textured slit- and Y-shaped spinning nozzles at a relatively high spinning temperature. This die swell relaxed the shear induced by the nozzle wall on the molten pitch at the outlet of the spinning nozzle and changed the fiber shape to round. Usually, a certain amount of elastic energy can be stored in all viscoelastic fluid, leading to the Barus effect.[24] The die swell effect increases with the amount of stored energy (increasing with shear stress, and decreasing with capillary length). If the amount of stored energy exceeds a certain limit, the fiber breaks. Such a break is called a " cohesive break, " because it depends on the cohesive

energy (or surface energy) of the material, as well as on the viscosity of the liquid, the fiber production rate, and the modulus of elasticity. Turpin et al.46 reported that the storage modulus of a mesophase pitch in low-frequency range increases as temperature increases. The shape of the fibers at the nozzle outlet reflects the shear of the planar molecules on the wall of the nozzle. This, in turn, defines the cooling rate according to the surface area and thermal conductivity of the mesophase pitch.
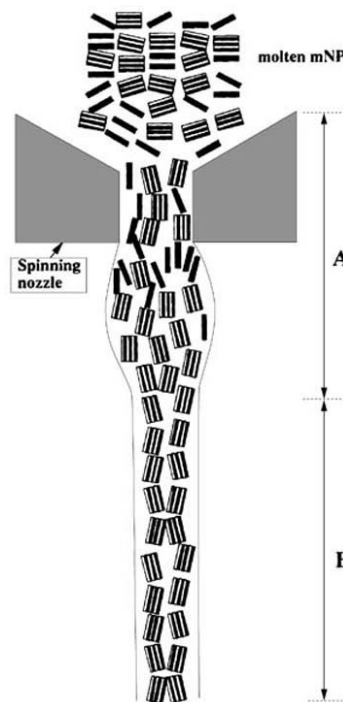

Figure 9 Schematic model of the formation of pitch fiber from molten mesophase pitch.

6. Structural Inheritance of Carbon Fiber from the Mesophase Pitch

Carbon fibers derived from mesophase pitch usually exhibit a higher Young's modulus and greater thermal and electric conductivity than those derived from PAN. The mesophase-based carbon fibers

were highly evaluated due to their very high graphitizability and the ordered alignment of graphite units along the fiber axis, and are expected to become strategic materials. Such high degrees of performance are considered to be closely related to their nano- and microstructures, which are inherited from the same structures of mesophase pitch.

We have studied the origin of the microdomains and domains of carbon fibers based on mesophase pitch. A series of solvent-extracted mesophase pitch fibers (solvent-extracted, as-spun fibers), stabilized fibers, and carbonized and graphitized fibers were observed systematically using HR-SEM.

Korai et al. [25] observed HR-SEM of the transverse sectional surfaces of pyridine-extracted fibers using a tilted view (10 °). The as-spun fiber had a wavy texture but did not show the fibrils or pleats of ordered alignment. Solvent extraction was found to introduce the fibrils (100-nm wide) and pleat structures (30-nm wide) in the spun fibers. HR-SEM photographs of the longitudinal surfaces of the stabilized, carbonized, and graphitized fibers revealed that although the stabilized fiber exhibits the wavy surface as observed on the as-spun fiber, the carbonized and graphitized fibers close up the fibril (domain) and nanofibril (microdomain, pleat) units. These units have basically the same shapes as those observed in the extracted spun fiber. The sizes appear to be slightly reduced by the carbonization and graphitization because of shrinkage during the heat treatment processes. The transverse sectional surface of the carbonized fiber exhibits microdomains ~30-nm long and 100-nm thick.

Evenly spaced pleats (microdomain, nanofibril) and fibrils (domain) making up the longitudinal section of the graphitized fiber must inherit the same units of the mesophase pitch. Figure 10 (A-C) shows schematic diagrams of such nanoscopic structures and their routes of formation from mesophase pitch. [26] Such nanoscopic structures should be formed by the assembly of units (clusters) of aromatic molecules in the mesophase pitch. Their rearrangement occurred through deformation during the spinning of the mesophase pitch. Hence, the structure observed in the fiber reflects the original self-assembly of the mesogen molecules in the mesophase pitch.
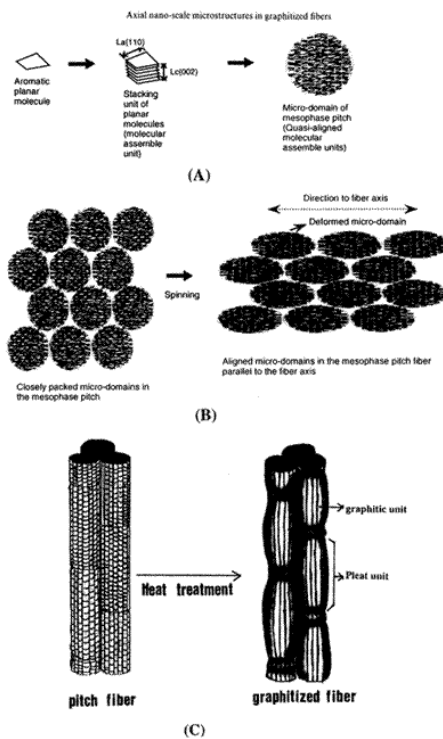

Figure 10 Formation mechanism of graphitized fiber from liquid crystal mesophase pitch: (A) formation of the molecular stacking and microdomain units from aromatic planar molecules in mesophase pitch; (B) deformed alignment of microdomains in

mesophase pitch under shear; (C) formation of graphitic and pleat units in graphitized fiber.

7. Concluding Remarks for Further Development

The basic unit of carbonaceous materials is commonly sp^2 carbon hexagonal planes, which are aromatic sheets of mesogen molecules in the mesophase pitch, and graphene sheets in the graphite. The size and shape of the hexagon is the key factor, although the mesogen molecules also carry sp^2 substituents that influence its stacking. The stacking of the hexagonal planes forms the clusters in the mesophase pitch and the graphitic units in the graphite. The clusters assemble into microdomains that form domains. The size, shape, and alignment of such nanoscopic structural units govern the properties of the mesophase pitch and its derived graphites.

The structure of mesogen molecules is proved to determine the stacking height in the cluster. A larger hexagon tends to yield a greater height. It is interesting to observe that more methyl groups on the hexagon remarkably enhance the stacking. Dimethylnaphthalene give a stacking height as high as 10 nm at room temperature. Higher temperature reduces the stacking height; nevertheless, the pitch shows some stacking height even in the melted state, its liquid crystal nature being proved microscopically. Thus, clusters, microdomains, and domains appear to be present in the liquid crystal state. In other words, liquid crystal characteristics such as melt flow and thermal properties are basically governed by such a series of structures. Deformation during shear thinning might define the flow properties, whereas cluster stacking and alignment govern the thermal properties. In the mesophase pitch itself, it is difficult to show microdomains. However, solvent extraction proves the presence of a uniform grain of an insoluble fraction ∼20-100 nm in size, which corresponds to the microdomain.

The structure of the mesophase pitch at any level is inherited by its derived carbon fiber, even though spinning, stabilization, carbonization, and graphitization deform the structural units and allow significant growth of the hexagon size, according to the extent of graphitization. The structural consequences for converting mesophase pitch to graphitized fiber are nearly straightforward. Extraction has revealed that the nanoscopic units in the spun fiber basically stay unchanged during the successive carbonization. Carbonization of the soluble fraction appears to follow morphologically the nanoscopic shapes of the insoluble fraction.

There are several interesting features in the formation of fibers from mesophase pitch. One is die swelling, which deforms the diameter and shape of the fiber from that of the nozzle. The shear stress charged through the nozzle is released at the outlet of the spinning nozzle to allow the rectangular shape of the fiber to expand into a round shape while the pitch is still soft. If the pitch were cooled rapidly, there would be no time to allow the deformation. Slow cooling allows relaxation and recovery of the maximized stacking at room temperature. Rapid cooling inhibits such relaxation. Annealing above the Tg below the Ts restores the stacking of the mesophase pitch. Such relaxation was clearly observed with the methylnaphthalene- and

dimethylnaphthalene-derived mesophase pitches. The presence of the Tg indicates that the mesophase pitch consists of semicrystalline aromatic oligomers.

Finally, nanoscopic units observed in the mesophase pitch and its derived carbon fibers indicate that they are a nanostructural material. Their properties probably can be improved through optimization of nanostructures. The nanostructure can be isolated through extraction and swelling, providing novel types of nanocarbonaceous materials.

The nanoscopic views of mesophase pitch and its derived carbon materials suggest novel types of structures, improvements of their properties based on the structures, and applications for novel uses of their high-performance characteristics.

Very recently, the semi- and photoconductive properties of polymeric molecules were again recognized as being expected to provide new types of electronic devices. A variety of aromatic mesogen molecules synthesized as precursors of carbon fiber can be promising candidates for such applications. The molecular structure and self-assembly of the mesogen must be studied further for these purposes.

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