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Interaction among fractions in mesophase pitches derived from $AlCl_3$-modified ethylene tar

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The anisotropic development is studied of mesophase pitches prepared from modified ethylene tar (ETP) using $AlCl_3$, of fractions separated by benzene, tetrahydrofuran (THF) and pyridine, and of mixed fractions, to find structural factors affecting fusibility and optical anisotropy of mesophase pitch. Annealing was carried out at 360° C for 10 min. Each fraction developed a unique optical anisotropy quite different from that of the parent mesophase pitch. The lightest fraction (soluble in benzene) was highly fusible with small numbers of small anisotropic spheres. The heaviest fraction (insoluble in pyridine) was infusible and exhibited a total mosaic anisotropy. In contrast, mixed fractions behaved like the parent mesophase pitch in terms of liquid crystal behaviour. The extent of anisotropy and fusibility after annealing were strongly dependent on the preparatory conditions of the parent mesophase pitch. The fusibility of mixed fractions is ascribed to the dissolving ability of the fusible fraction and the solubility of the infusible fraction at the annealing temperature. Small molecules in the lighter fractions also contribute to anisotropy when they are located in interlayer positions between the larger aromatic molecules which constitute liquid crystals. Such co-operative properties of constituent molecules of the mesophase pitch can be described in terms of a practical compatibility.

1. Introduction

Carbonaceous mesophase pitch is recognized as a precursor for carbon fibres of high performance [1, 2]. Patents have been issued for its preparation [3–5]. However, the origins and physicochemical understanding of mesophase pitch as a liquid crystal is not fully elucidated. Recently, Diefendorf and co-workers [6–8] have used phase diagrams to describe carbonaceous mesophase by analogy with liquid crystals, allowing for some characteristic aspects of carbonaceous mesophase as distinct from traditional liquid crystals.

In previous work [9, 10] the authors prepared highly soluble mesophase pitches from A240 petroleum pitch and examined the anisotropic development and chemical structure of their fractions relative to formation of mesophase. The authors also succeeded in preparing a soluble mesophase pitch from ethylene tar (ETP) modified with $AlCl_3$ [11]. Chemical structures created in the modified pitches under different conditions influenced significantly the properties of the resultant mesophase pitches [11].

In the present study, the authors have examined fractions of mesophase pitches prepared from modified ETP with special reference to interactions between fractions to describe the behaviour of the entire pitch in

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terms of liquid crystals. This is because dissolution of the infusible in the fusible fraction, and the interlayer stacking of the smaller aromatic molecules between the layered aromatic components of the infusible fraction, may affect the fusibility and optical anisotropy of the resultant mesophase pitches, respectively. Knowledge of how the fractions combine may allow prediction of the properties of carbonaceous mesophase pitch. The dissolving ability of a carbonization distillate for residual mesophase pitch has been reported [12, 13]. Interaction between fractions can be accurately described as compatibility of two fractions as in co-carbonization systems [14–17].

2. Experimental details

2.1. Material and procedures

Properties of mesophase pitches from ETP (provided by Koa Oil Co, Yamaguchi-Ken, Japan) are summarized in Table I together with conditions for acid modification of ETP and mesophase development from modified pitches. ETP was heat-treated with $AlCl_3$ (5 to 10 wt %) in a Pyrex tube (50 mm diameter) under flowing nitrogen with vigorous stirring at 250 to 320° C for 2 to 7 h. The modified pitch was washed repeatedly with dilute HCl and then with water to remove the catalyst. To prepare mesophase pitch, ETP and the modified pitches (10 to 20 g) were heat-treated at 380° C for 15 h in a Pyrex tube (30 mm diameter) under vigorous stirring (600 rpm) with nitrogen gas bubbling (1.0 to 1.5 ml sec^{-1}) from the bottom of the tube [10, 11] according to a British patent [4]. The heating and cooling rates were 5 and 3° C min^{-1}, respectively.

2.2. Solubility of mesophase pitch

Solubility of the mesophase pitch was examined using benzene (B), tetrahydrofuran (THF), quinolene (Q) and pyridine (P). The mesophase pitch was fractionated into soluble (S) and insoluble (I) fractions by Soxhlet apparatus.

2.3. Annealing and co-annealing of the mesophase pitches and their fractions

The mesophase pitch and fractions were separately annealed to quantify their anisotropic content. The THFS and PI fractions of the mesophase pitches (weight ratio: THFS/PI = 1/2) were ground and mixed in a mortar and pestle before annealing to examine their compatibility. Mesophase pitches, their fractions, and their combined fractions were reheated at 360° C (lower by 20° C than the mesophase development temperature) for 10 min (heating rate: 5° C/min^{-1}), and then cooled to room temperature at the rate of 3° C min^{-1} under flowing nitrogen.

The annealed pitch was mounted in resin and polished for microscopic examination by the point-counting technique using an optical microscope (Leitz). Anisotropic content and the shapes of isochromatic particles were used to evaluate anisotropic development and fusibility during the annealing.

2.4. Structural analysis

THF-soluble fractions of mesophase pitches were analysed by ^1H nuclear magnetic resonance (NMR), using a JEOL FX–100. Average structural indices were calculated according to the Brown and Ladner method [18] based on elemental analyses and proton distribution. Infrared (IR) spectra of pyridine-insoluble fractions were observed by FT–IR, using a JEOL JIR–03F.

3. Results

3.1. Optical anisotropy developed by the fractions of a mesophase pitch

Photographs of the fractions separated from

TABLE I Preparative conditions of mesophase pitches and their various properties

Material	Acidic modification conditions		Preparation of mesophase pitches	Anisotropy		Solubility (wt %)		
	$AlCl_3$ (wt %)	Heat treatment (° C, h)	Heat treatment (° C, h)	Yield (wt %)	Content (vol %)	THFS	PS	QS
ETP/380–15	–	–	380, 15	11	10	38	51	71
M1–ETP/380–15	5	250, 12	380, 15	22	70	50	64	69
M2–ETP/380–15	5	320, 2	380, 15	30	90	14	31	34
M3–ETP/380–15	10	250, 7	380, 15	33	100	29	42	52

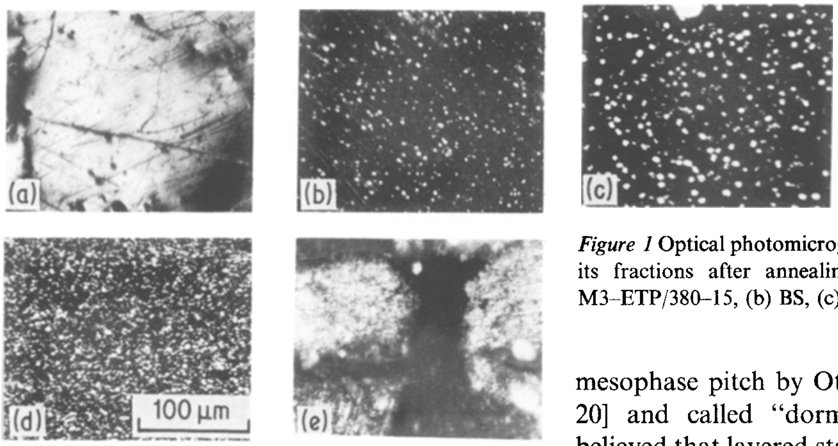

Figure 1 Optical photomicrographs of M3–ETP/380–15 and its fractions after annealing at 360° C for 10 min: (a) M3–ETP/380–15, (b) BS, (c) THFS, (d) THFI–PS, (e) PI.

M3–ETP/380–15 are shown in Fig. 1: that of the parent mesophase pitch is also included for comparison. Each fraction showed different features of anisotropy which appeared after the removal of the respective solvent and the annealing. The size of anisotropic unit and the content of anisotropic material increased in the following order: BS, THFS, THFI–PS, IS. The optical texture of each fraction was very different from that of the parent pitch (Fig. 1a). It is noted that the solvent-soluble materials, even the benzene-soluble fraction, can show some optical anisotropy.

The BS-fraction showed some peculiar behaviour of optical anisotropy (Fig. 2). As shown in Fig. 1b, this fraction showed very fine anisotropic units in the isotropic matrix after conventional polishing. The rubbing of the polished surface with paper allowed an anisotropic development oriented in the rubbing direction. The brightness under the microscope changed according to the rotation angle of the stage of the microscope (Figs. 2a to c). Such an anisotropy has been reported for hydrogenated mesophase pitch by Otani and co-workers [19, 20] and called "dormant mesophase". It is believed that layered stacking of aromatic molecules at the surface is induced by the rubbing, although the scratches may also bring about such an optical appearance.

3.2. Optical anisotropy from the combined fractions after annealing

Optical photomicrographs of the mixture of THFS and PI (both fractions from M3–ETP/380–15) after annealing are shown in Fig. 3, where the mixing ratio was 1:1 by weight. The shape of optical anisotropy developed after the annealing was an elongated mosaic, being quite different from those of each fraction alone as shown in Fig. 1c and e, where anisotropic spheres in the isotropic matrix (THFS) and a cluster of fine grained mosaic (PI) were observed, respectively. The very much increased extent of anisotropy from the mixture indicated that the PI fraction was deformed in the mixture during annealing.

The anisotropic contents in the respective fractions are compared in Fig. 4. The THFS-fraction alone showed a limited anisotropic content (15 vol %) as shown in Fig. 4a. However, the mixture exhibited anisotropy as high as

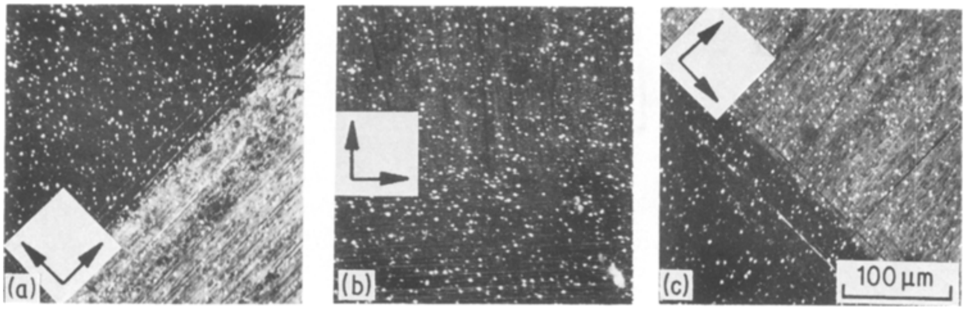

Figure 2 Optical photomicrographs of annealed BS fraction after rubbing. The arrows represent the rubbing direction. Rotation angle of stage: (a) 0°, (b) 45°, (c) 90°.

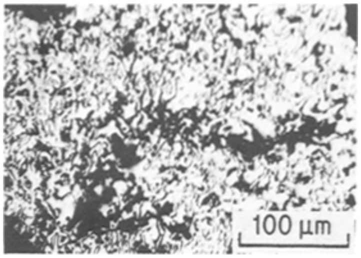

Figure 3 Optical photomicrograph of the mixture of THFS and PI fractions after annealing at 360° C for 10 min. Sample: M3–ETP/380–15.

95 vol % (mixture volume base) as shown in Fig. 4c, indicating that 75 vol % of the THFS fraction became anisotropic in the presence of PI. It is worth mentioning that the extent of optical anisotropy developed from the mixture is smaller than that of the parent pitch.

3.3. Annealing of PI fractions from different mesophase pitches with one fixed THFS fraction

Optical photomicrographs of annealed mixtures of the PI fractions from various mesophase pitches with the THFS fraction from M3–ETP/380–15 are shown in Fig. 5. The size and area of anisotropic units after the annealing strangely varied with the PI fraction, indicating different susceptibilities. An increasingly larger size of anisotropic units developed in the following order of PI: ETP, M1–ETP, M2–ETP, M3–ETP.

3.4. Annealing of one fixed PI fraction with the THFS fractions from different mesophase pitches

Photomicrographs of the mixtures of THFS fractions from various mesophase pitches with one only PI fraction from M3–ETP/380–15 are shown in Fig. 6. The size and shape of optical anisotropic units were quite different from each other, indicating the order of annealing ability of THFS fractions against the PI fraction for better anisotropic development. The order of increasing annealing ability of THFS fractions is: ETP, M1–ETP, M2–ETP, M3–ETP.

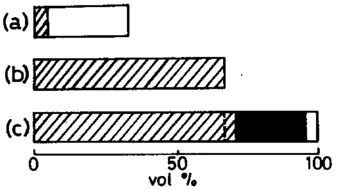

Figure 4 Anisotropic contents in THFS, PI, and their combined mixture prepared from M3–ETP/380–15: ▨ anisotropy, ■ interlayer stacking. (a) THFS, (b) PI, (c) THFS + PI (mixing ratio: 1/2).

3.5. Structural analysis of THFS and PI fractions

Some structural indices of THFS fractions from mesophase pitches are summarized in Table II. They have similar H/C atomic ratio and f_a (aromaticity) values. However, differences were observable in values of R_{tus} (total number of rings per structural unit), R_{aus} (number of aromatic rings per structural unit), R_{nus} (number of naphthalene rings per structural unit), C_{side} (number of carbon atoms of side chain per structural unit), MW_{us} (molecular weight per structural unit) and AMW (average molecular weight). Smaller R_{aus}, R_{nus}, MW_{us} and C_{side} may differentiate the THFS fractions of ETP/380–15 from the other THFS fractions of the modified ETP. Larger R_{aus} and R_{tus} values may distinguish the THFS fraction in M1–ETP/380–15 from the other fractions derived from modified ETP.

Limited structural information about PI fractions is summarized in Table III. The PI in ETP/380–15 was different in the QS/PI ratio (QS content in PI) and smaller aliphatic C–H intensity, the latter differentiating probably the PI fractions of ETP and M1–ETP from those of M2– and M3–ETP.

4. Discussion

Recently, the liquid crystal behaviour of carbonaceous mesophase pitch has been emphasized [6–9, 21]. Chen and Diefendorf [8] state that mesophase pitch consists of mesogen and non-mesogen components, these having the characteristic properties of lyotropic liquid crystals. Mochida and Korai [9] report that select fractions isolated from mesophase pitch behave as typical liquid crystals. The present study reveals that a mixture of two fractions from mesophase pitch behaves as liquid crystals during annealing even if, singly, they do not behave as typical liquid crystals, suggesting another mechanism for liquid crystal behaviour. The BS fraction can be either almost an isotropic liquid or glass-like, depending on temperature, whereas the PI remains as an anisotropic glass

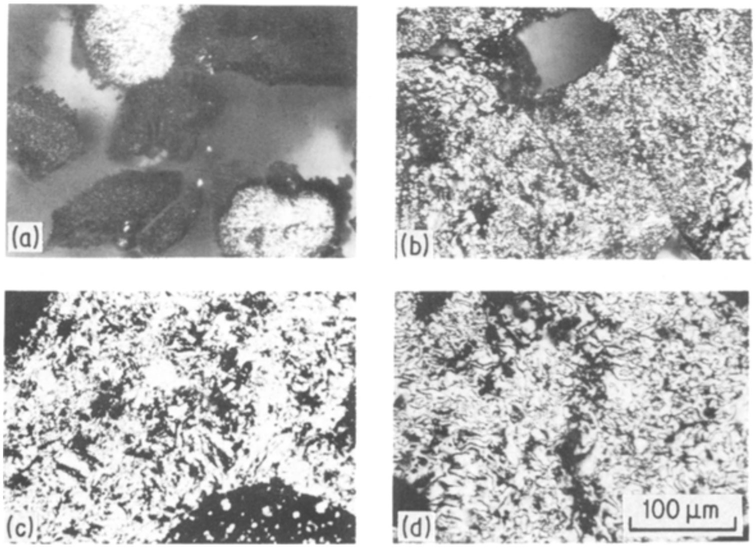

Figure 5 Optical photomicrographs of the mixtures of one fixed THFS (M3–ETP/380–15) with variable PI fractions, annealed at 360° C for 10 min. Mixing ratio: THFS/PI = 1/2 (by weight). PI from: (a) ETP/380–15, (b) M1–ETP/380–15, (c) M2–ETP/380–15, (d) M3–ETP/380–15.

without fusing at all temperatures examined. The infusible fraction of anisotropy (PI in the present case) may become soluble in the fusible isotropic fraction at annealing temperatures and is then deformed. On the other hand, the fusible fraction exhibited anisotropy in the presence of the infusible fraction of anisotropy, probably because of its intermediate position in the layered stacking of PI molecules.

The susceptibility of the infusible fraction and the dissolving ability of the fusible fraction will ultimately determine the fusibility of the mixture, and this will significantly influence the size of anisotropic optical texture developed after the annealing process. Amounts and nature of the isotropic fusible fraction in the stacked structure of the infusible fraction may influence strongly the extent of development of anisotropy and the fusibility of the mixture. Thus, the compatibility of the two fractions may be a useful concept to understand the above mentioned behaviour of mesophase pitch, as reported in the co-carbonization process of pitches [14–17] and QIs with additives [22].

It is worthwhile to attempt to relate structural aspects of the fusible and infusible fractions to their compatibility. Although the structural information is limited at this stage, the structural parameters of the fusible (THFS) and infusible (PI) fractions using NMR and IR can be related

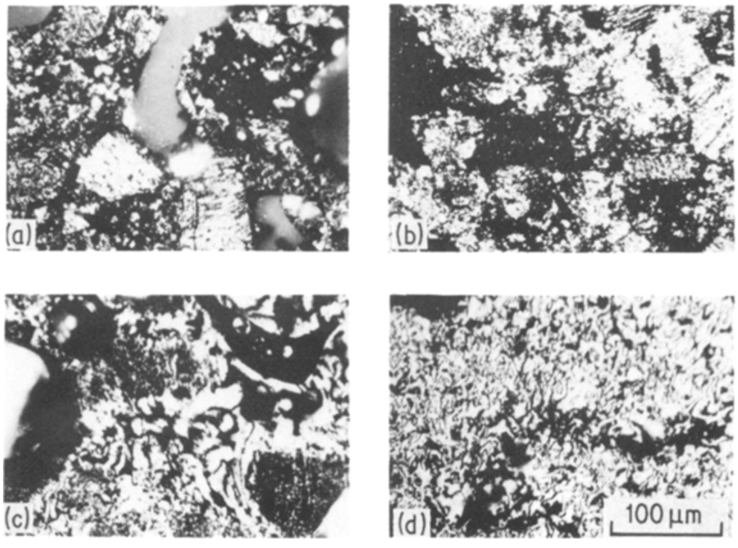

Figure 6 Optical photomicrographs of mixtures of various THFS fractions with one fixed PI (M3–ETP/380–15), annealed at 360° C for 10 min. Mixing ratio: THFS/PI = 1/2 (by weight). THFS from: (a) ETP/380–15, (b) M1–ETP/380–15, (c) M2–ETP/380–15, (d) M3–ETP/380–15.

TABLE II Structural parameters of THFS from mesophase pitches

Parameter*	ETP/380–15	M1–ETP/380–15	M2–ETP/380–15	M3–ETP/380–15
H/C	0.82	0.83	0.85	0.84
AMW	480	460	620	
f_a	0.81	0.79	0.79	0.80
R_{aus}	2.17	3.13	2.24	2.55
R_{tus}	2.41	3.49	2.50	2.78
R_{nus}	0.24	0.36	0.26	0.23
C_{side}	1.74	2.71	2.18	2.37
MW_{us}	180	240	190	200

*For abbreviations see text.

TABLE III Structural parameters of PI from mesophase pitch

	ETP/380–15	M1–ETP/380–15	M2–ETP/380–15	M3–ETP/380–15
H/C	0.59	0.59	0.61	0.60
QS/PI*	0.41	0.14	0.04	0.17
$CH_{al}/CH_a^{\dagger}$	2.11	2.11	2.40	2.42

*The ratio of QS in PI (PI base).
†IR band intensity ratio: $CH_{al} = 2920\,cm^{-1}$, $CH_a = 3050\,cm^{-1}$.

to their annealing properties. The PI fraction consists of quinoline-soluble (QS) and quinoline-insoluble (QI) components. Although the larger content of QI is expected to lead to less solubility, the order of susceptibility of PI to the better annealing properties is not related to its QI content (Table III), suggesting that the nature of QI may be more important at higher temperatures.

The size and kind of substitution group of constituent molecules may be related to the extent of molecular association, although for insoluble substances this is difficult to estimate. Alkyl groups remaining in the PI fraction after heat-treatment provide for a suitable association of constituent molecules to promote annealing. The alkyl C–H intensity observed by IR correlates well with the annealing properties of PI fractions.

The dissolving ability of the fusible fraction may be controlled by total aromaticity, presence of alkyl groups etc. The quantity as well as quality of the fusible fraction in the mesophase pitch have an influence on the dissolving ability. Such an understanding suggests how to improve fusibility by the blending of an adequate additive. This idea can be applicable for the preparation of carbon fibre precursors.

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