JOURNAL OF MATERIALS SCIENCE **21** (1986) 424–428

Preparation of anisotropic mesophase pitch by carbonization under vacuum

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Anisotropic mesophase pitch of high solubility and low melting temperature was prepared from petroleum pitch by carbonizing under vacuum conditions at 430° C for 5 h. The solubility and melting temperature were 55 wt% in quinoline and 270° C respectively, at complete development of anisotropic mesophase pitch. This solubility is much higher than that of mesophase pitch from the same feedstock using refluxing and gas blowing conditions. Yields of the mesophase pitch of complete anisotropic development were 60 wt% under vacuum. The structure of these mesophase pitches were analysed in terms of preparative procedures which create high solubility of a completly anisotropic material.

1. Introduction

Mesophase pitch, recognized as an essential precursor for high-performance carbon fibre [1], needs to be spinnable at low temperature, highly oriented, reactive for oxidation to promote thermosetting, and of high coking value. To satisfy these requirements mesophase pitch should be composed as discussed by Korai and co-workers [2, 3].

Mesophase pitch has been prepared via several stages of pitch modification and mesophase induction. Several researchers [2–7] have reported the development of anisotropy in pitches from petroleum and coal tar, using the Union Carbide patent [8, 9] where rapid gas blowing enhances the removal of lighter fractions in the parent pitch, so allowing stacking of the aromatic components of suitable size into anisotropic material with considerable solubility.

Thus, the efficiency of removal of light components is important for the preparation of mesophase pitch of high solubility and fusibility. The lighter molecular weight lamellar molecules are retained. The preparation of mesophase pitch by gas blowing would be time-consuming [10]. However, Yamada and Honda [11] prepared mesophase pitch from hydrogenated pitch at a relatively high temperature and with a short experimental time.

In the present study, mesophase pitch from petroleum pitch of relatively high hydrogen content was prepared under vacuum at a relative high temperature with short experimental times to achieve efficient removal of light components. Vigorous stirring was also applied to improve the efficiency. The comparative study of the properties and structure of mesophase pitch prepared under refluxing, gas blowing and vacuum conditions, discusses the origins of high solubility, low melting temperatures and formation of mesophase pitch.

2. Experimental details

2.1. Preparation of mesophase pitch

The petroleum pitch used and analyses are in Table I. Sample pitch (40 g) was heat-treated in a Pyrex glass tube at 430° C under refluxing, gas blowing or vacuum conditions as described below. The tube was placed in a brass block, and heated in a vertical electric furnace at a heating rate of 5° C min^{-1}.

1. Refluxing (RS): the pitch was heated in a Pyrex glass tube (35 mm diameter) attached to a condenser to allow refluxing.
2. Glas blowing (BS): the pitch was heated in a Pyrex glass tube (30 mm diameter) with a nitrogen gas blow from the bottom at a flow rate of 6 ml min^{-1} per gram of the initial sample weight.
3. Vacuum (VS): the pitch was heated in a Pyrex glass tube (35 mm diameter) connected to a vacuum pump to allow evacuation to below 5 mm Hg. On reaching the required temperature, pumping kept pressures to below 5 mm Hg.

The pitch was stirred vigorously during heat-treatment in all systems at 600 rpm with a stirring screw made of stainless steel. After the prescribed soak time, the mesophase pitch thus produced was cooled to room temperature at the rate of 3° C min^{-1} to develop anisotropy in an annealed form [2].

2.2. Anisotropic content and solubility of mesophase pitch

A portion of the mesophase pitch was mounted in resin. After the conventional polish, its anisotropic content was evaluated by point-counting using an optical microscope. The mesophase pitch was fractionated, after grinding to 60 mesh, by sequential Soxhlet extraction for 24 h, first with tetrahydrofuran (THF) and then with pyridine (P). The soluble fractions (THF–S and P–S) were recovered by removing the solvent in a rotary evaporator. The pyridine insoluble material (PI) was extracted with 200 ml of quinoline at 75° C for 0.5 h. The solution was filtered with a membrane filter (Sumitomo Electric Ind. Ltd, pore size 0.45 μm), and the residue (the quinoline insoluble fraction, QI) was washed with acetone. All fractions were

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TABLE I Analyses of parent pitch

Source	H/C	f_a*	R_{uns}†	R_{uns}/R_{tus}(%)‡
Petroleum	0.75	0.839	0.40	6.8

*Carbon aromaticitity.
†Naphthenic ring number per unit structure.
‡Naphthenic ring number/total ring number per unit structure [13].

TABLE II Analyses of mesophase pitches

Mesophase pitch	C	H	N	H/C	Melting point (°C)	Yield (wt %)
P–430–5RS	94.07	5.27	0.20	0.67	125	79
P–430–5BS	94.54	4.83	0.18	0.61	170	70
P–430–5VS	94.60	4.53	0.13	0.57	270	67
P–430–30RS	95.13	4.36	0.11	0.55	395	57
P–430–12BS	94.92	4.37	0.10	0.55	290	53

dried under vacuum to constant weight to ensure the removal of solvent. Solubilities were calculated from the weight of the respective insoluble material.

2.3. Analysis

^{1}H-NMR and the average molecular weight of THF-insoluble–pyridine-soluble material (THI–PS) were measured by using equipment for FT–NMR (JEOL FX-100) and a vapour pressure osmometer (Hitachi 177), respectively.

Infrared (IR) spectra of QI fractions from the mesophase pitches were observed using equipment for FT–IR (JEOL 03F). The aromatic and aliphatic C–H contents of the QI fractions in the mesophase pitches were estimated, the absorbances of their stretching bands at 3030 and 2920 cm^{-1}, respecively being used.

3. Results

3.1. Mesophase pitches prepared from a petroleum pitch under RS, BS and VS conditions

Optical micrographs of mesophase pitches for heat-treatment temperature (HTT) 430° C and 5 h soak (P–430–5RS, -5BS, -5VS), prepared under RS, BS and VS conditions are compared in Fig. 1. Mesophase pitches RS and BS consisted mainly of isotropic carbon with a small amount of anisotropic carbon. Anisotropic spheres were scattered within the isotropic matrix (Figs. 1a and b). In contrast, the VS mesophase pitch was totally anisotropic (Fig. 1c).

Optical micrographs of mesophase pitches (P–430–30RS, –12BS, -5VS) showed them all to be composed of broad flow-textured anisotropic carbon (Fig. 2).

The anisotropic contents and solubilities of the mesophase pitches are summarized in Fig. 3. The anisotropic content of P–430–5RS was only 15 vol %. A major portion (86%) was soluble in THF with 9% insoluble in quinoline. Thus, the anisotropic carbon corresponds to the THFI fraction. Blowing heat-treatment (P–430–5BS) increased the anisotropic content to 28 vol % and the QI to 26 vol %, again indicating that QI was anisotropic carbon. Heat-treatment under vacuum (P–430–5VS) was effective in enhancing the development of anistropic carbon (100 vol %) with a moderate increase in QI (45%). This anisotropic mesophase pitch contained soluble fractions of 40% THFS, 11% THFI–PS and 4% PI–QS. This optical anisotropy resembles that reported recently [3, 4, 6, 7, 12].

Longer treatment under refluxing and blowing conditions increased the anisotropic content, 30 and 12 h being required respectively to develop 100% anisotropy. At the same time, QI contents increased to 65 and 55%, with 30 and 23% of THFS remaining respectively.

The yields of mesophase pitches (starting pitch base) are summarized in Table II. When the mesphase pitches of 100% anisotropy are compared, the yield of P–430–5VS was 67% which is higher by 10 to 14% than the others. Melting points (Table II) rose along with the anisotropic and QI contents. The lowest melting point of all mesophase pitches was 270° C.

Thus, the mesophase pitch prepared under vacuum has the highest solubility, lowest melting point, and highest yield at 100% anisotropic development.

3.2. Structure of mesophase pitch

Atomic ratios (H/C) of P–430–5RS and P–430–5BS, with anisotropic contents of 20 and 28% respectively, were higher than that of P–430–5VS (100% anisotropy). The former two values decreased to the lower value with formation of 100% anisotropy.

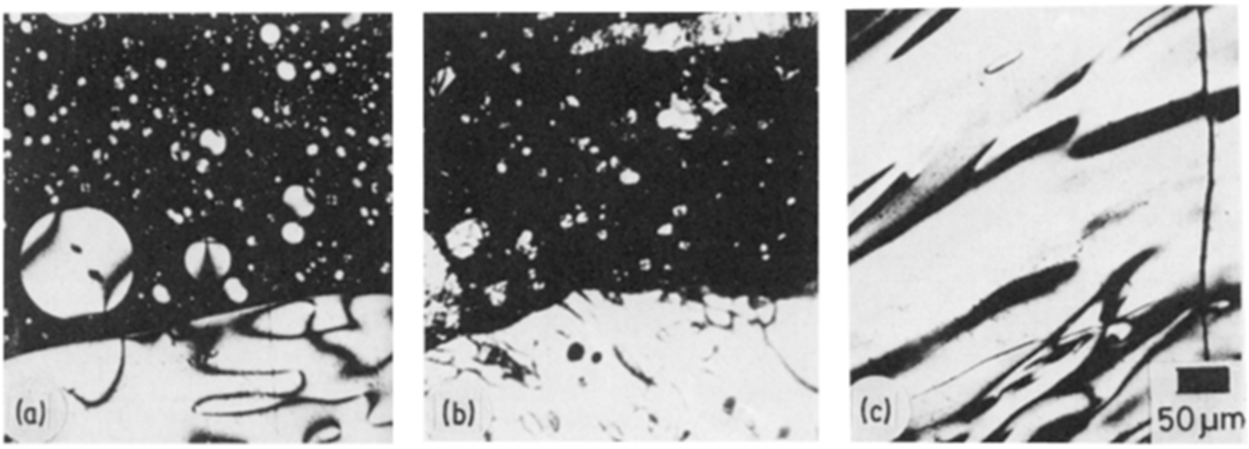

Figure 1 Optical micrographs of mesophase pitches prepared with 5 hour soak: (a) P–430–5RS, (b) P–430–5BS, (c) P–430–5VS.

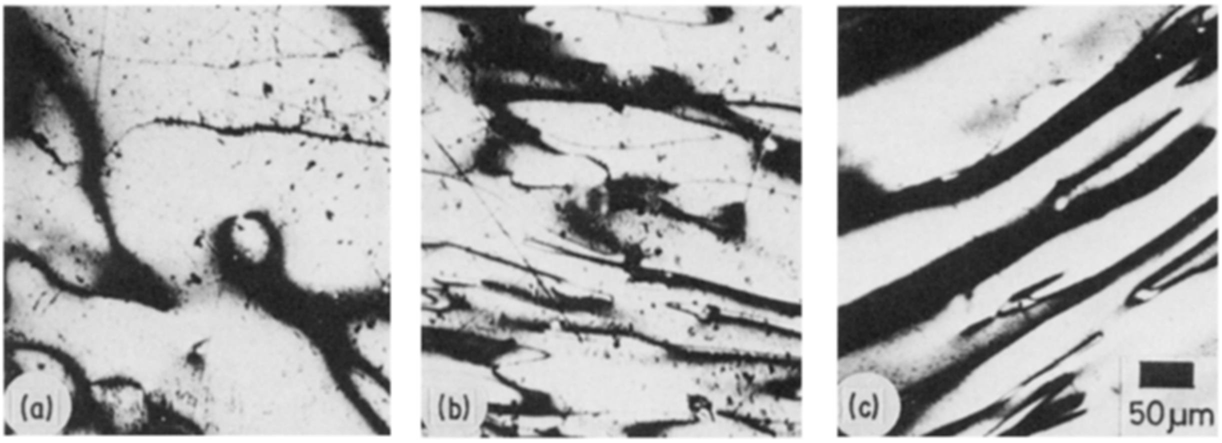

Figure 2 Optical micrographs of mesophase pitches prepared under optimum conditions: (a) P–430–30RS, (b) P–430–12B, (c) P–430–5VS.

Gel-permeation chromatograms of THFS fractions of mesophase pitches are compared in Fig. 4, where molecular weights of fluoranthene, decacyclene and polystyrene are marked as references. Although the molecular weights of the fractions in all mesophase pitches were between 200 and 800, the fraction of P–430–5VS had the highest average molecular weight. It is of value to note that the THFS fraction of mesophase pitches prepared under refluxing and blowing conditions had lower average molecular weights after extended treatments to develop 100% anisotropy. However, their PI contents increased significantly, indicating considerable broadening of their molecular weight distributions.

The H/C atomic ratios and structural parameters of THFI–PS fractions in mesophase pitches are given in Table III, where parameters were calculated by the Brown–Ladner method [13]. The fraction of P–430–5VS had larger carbon aromaticity f_a (see Table I) and smaller H/C values and a lower average molecular weight than the other mesophase pitches. The extended treatments (RS, BS) increased H/C and f_a and decreased the molecular weight and σ value (Table III), indicating that the components became smaller in molecular weight although aromatization (dehydrogenation) and dealkylation had taken place.

When the fractions of pitches of 100% anisotropy were compared, significantly larger R_{nus}/R_{tus} ratios (Table I) and molecular weights of P–430–5VS were noted. The elemental analyses and f_a values of QI fractions in the mesophase pitches are summarized in Table IV, the f_a value being calculated from IR absorbances at 3030 and 2920 cm^{-1} [14]. The QI of P–430–5VS showed similar H/C and slightly larger f_a values than those of P–430–5RS and P–430–5BS. However, the former values were considerably lower and greater respectively than those of P–430–30RS and P–430–12BS which exhibited 100% anisotropy.

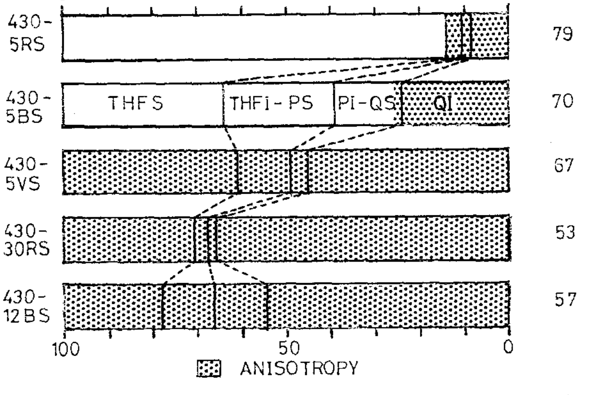

Figure 3 Solubilities and anisotropy contents of mesophase pitches.

IR spectra of QI at 3000, 1600 and 800 cm^{-1} are illustrated in Fig. 5. The QI fractions of the pitch prepared for 5 h under different conditions exhibited similar features despite different anisotropic contents. The extended treatments under refluxing and gas blowing conditions decreased markedly the intensity of the 2940 cm^{-1} band ascribed to alkyl C–H stretching [15].

4. Discussion

The mesophase pitch prepared under vacuum and vigorous stirring exhibited higher solubility and lower melting point at 100% anisotropic development than pitches prepared under refluxing and gas blowing conditions. Such properties may make it favourable as a precursor for carbon fibres because of its distribution of molecular size. Such molecules should have an optimum size of aromatic sheet, large enough for ordered stacking in the mesophase but not too large to prevent solubility and fusibility. Naphthenic or alkyl groups may enhance solubility or fusibility in mesophase pitch as discussed elsewhere [3, 16–20].

Mesophase pitch prepared under vacuum has a more homogeneous distribution of molecular size at

TABLE III Analyses of the THFI–PS fraction from mesophase pitches

Mesophase pitch	H/C	f_a*	R_{nus}*	R_{nus}/R_{tus} (%)	σ†	AWM‡
P–430–5RS	0.61	0.90	1.36	14.9	0.24	1800
P–430–5BS	0.64	0.90	0.59	9.0	0.20	1600
P–430–5VS	0.56	0.93	2.47	11.1	0.16	1000
P–430–30RS	0.65	0.93	0.04	1.0	0.17	800
P–430–12BS	0.63	0.95	0.02	0.4	0.16	600

*See Table I.
† Number of substitution groups per unit structure.
‡ Average molecular weight.

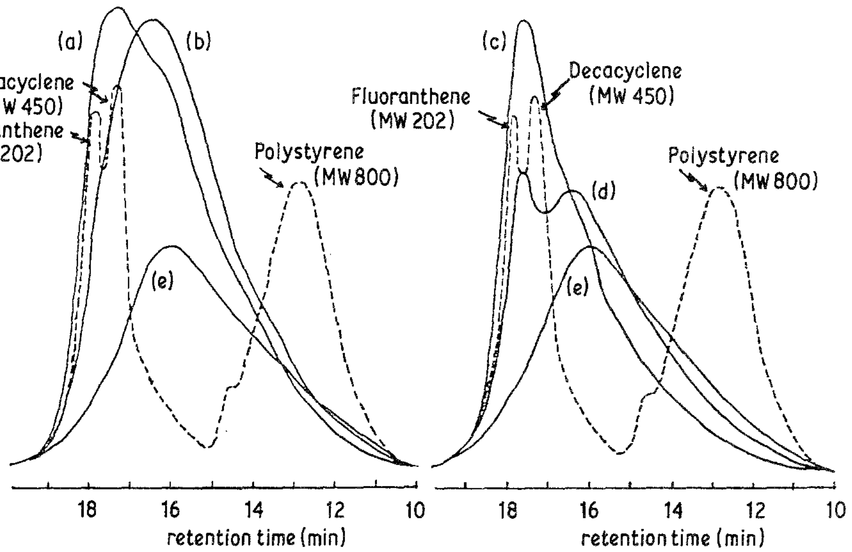

Figure 4 Gel-permeation chromatograms of THFS fractions from mesophase pitches: (a) P–430–5RS, (b) P–430–5BS, (c) P–430–30RS, (d) P–430–12BS, (e) P–430–5VS.

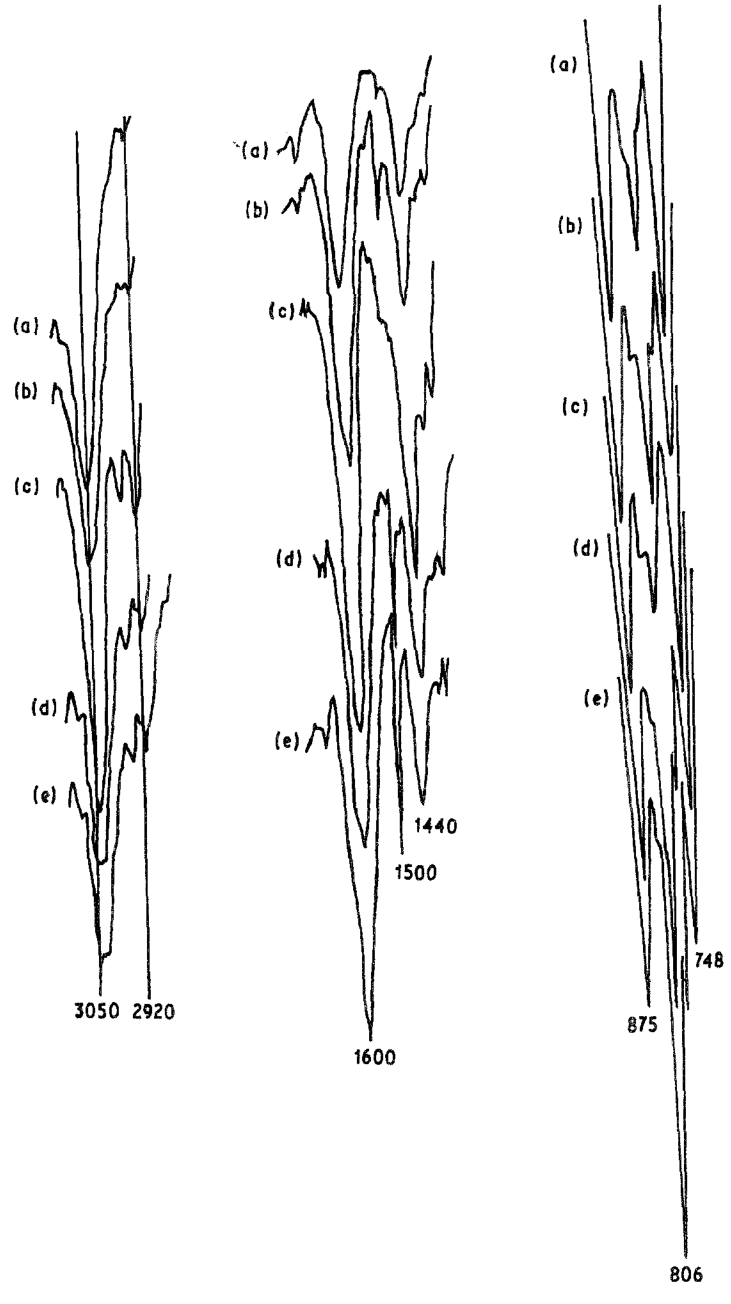

Figure 5 FT–IR spectra of QI fractions from mesophase pitches: (a) P–430–30RS, (b) P–430–12BS, (c) P–430–5VS, (d) P–430–5BS, (e) P–430–5RS.

TABLE IV Analyses of QI fractions from mesophase pitches

Mesophase pitch	C	H	H/C	f_a*
P–430–5RS	92.72	4.21	0.55	0.96
P–430–5BS	92.24	4.22	0.54	0.98
P–430–5VS	94.50	4.36	0.55	0.98
P–430–30RS	94.64	4.00	0.51	1.00
P–430–12BS	94.04	4.11	0.52	1.00

*$f_a = 1-(H/C)/(1 + H_a/H_{al})$; $H_a/H_{al} = (D_{3030}/D_{2920})\varepsilon$; $\varepsilon = 0.5$ [14].

100% anisotropy than pitches prepared under RS and BS conditions; the soluble fraction of the former pitch has a larger average molecular weight than the latter. The insoluble fraction appears of smaller molecular weight as indicated by H/C ratios. Such distributions are schematically illustrated in Fig. 6, together with solubilities.

The larger amounts of naphthenic and alkyl groups in the soluble as well as infusible fractions of the former mesophase pitch as deduced by NMR and IR respectively also favour higher solubility and fusibility. The limited f_a value for QI may also contribute to a lower melting point.

The structure of the mesophase pitch prepared under vacuum is created during its preparation. Vacuum pyrolysis with vigorous stirring assures the efficient removal of the lightest components, allowing anisotropic development with a relatively short soak time at a relatively high temperature. The shorter time suppresses excess condensation and cracking which lead to the formation of more QI and lighter fractions, so maintaining a more homogeneous distribution of components and improving the pitch yield. Dehydrogenation is kept to a minimum to maintain naphthenic groups.

In contrast, the relatively poor efficiency of removal under the refluxing condition necessitates a longer soaking time for complete anisotropy, and this causes excessive condensation and cracking during the extended heat-treatment.

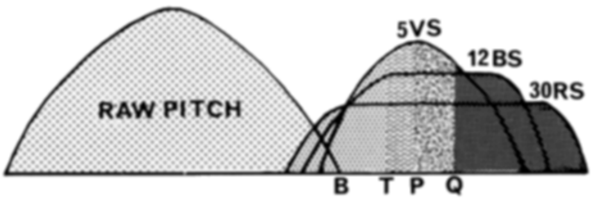

Figure 6 Schematic illustration for the mesophase pitches of molecular weight distribution and solubility. Solubility index shown for (B) benzene, (T) tetrahydrofuran, (P) pyridine and (Q) quinoline.

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Received 18 May 1984
and accepted 28 February 1985