

Molecular organization of lignin during carbonization

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Thermotropic liquid-crystalline (LC) behaviour of lignin-like model compounds, lignin, (commercial) petroleum pitch and blends of lignin and pitch was studied using hot-stage optical microscopy. The results indicate that, while all the dimeric lignin-like model compounds representing β -O-4, β -5 and 5-5 intermonomer linkages exhibit thermotropic LC phenomena in some temperature range, the LC behaviour remains incomplete for lignin. At the temperature at which a maximum amount of LC behaviour is observed for lignin, large carbonized particles are observed as well. This prevents the formation of a molecularly organized fluid phase from ever developing. The inability to fluidize totally at elevated temperatures is likely to be responsible for lignin's (lignin derivative's) inability to produce high-strength, high-modulus carbon fibres.

(Keywords: lignin; carbonization; molecular organization; liquid-crystalline behaviour; fibres; characterization)

INTRODUCTION

Carbon fibres are the preferred reinforcing component of advanced composites owing to high strength, high stiffness, light weight, fatigue resistance and vibration damping. High strength and high modulus in carbon fibres requires flawless structure and development of highly anisotropic graphitic crystallites oriented along the fibre axis during the process of production¹. During carbon fibre production, the fibrous precursor is carbonized at 1200–2000°C in an inert atmosphere while maintaining its fibrous structure. This is aided by a stabilization stage in which the precursor fibres are heated under tension at 200–300°C in the presence of air. This causes crosslinking on the fibre surfaces, among other reactions, and this prevents shrinking, melting and fusing.

Carbon fibres are manufactured by thermally treating fibres composed of polyacrylonitrile (PAN), (petroleum and coal) pitch, or rayon^{1–3}. Carbon fibres from rayon suffer from low carbon yield (20–25%) owing to chain fragmentation, which eliminates the orientation of the precursor. Improvement of properties can be achieved by (expensive) stretch graphitization. PAN-based carbon fibres are by far the most important owing to their high carbon yield (50%) and good mechanical properties. However, the cost of these carbon fibres is high, and extensive work is being carried out to find new precursors.

Pitch is a complex mixture of thousands of mainly aromatic organic compounds with an average molecular weight of several hundred. Pitch is isotropic in both liquid and solid states. Brooks and Taylor⁴ found that, as pitch is heated above 400°C, small spheres appear, which gradually increase in size with time and temperature.

There is no change in the structure of the spheres when pitch is cooled to room temperature as the high viscosity permits the mesophase to cool with little disruption in microstructure⁵. Therefore the structure of high-temperature pitch materials can be studied at room temperature. The process of coalescence of mesophase spheres continues with simultaneous thermal dehydrogenative condensation reactions, leading to larger aromatic molecules⁵. When these molecules are sufficiently large (molecular weight ca. 1000) and flat, they favour the formation of a carbonaceous mesophase, which is a discotic nematic liquid crystal with parallel stacking⁶. Structurally, mesophase pitch is similar to conventional nematic liquid crystals, but, unlike nematic phases, they are formed through chemical processes. Fibres spun from mesophase pitch are highly oriented, with the molecular planes aligned along the fibre axis. These fibres are excellent precursors for manufacturing carbon fibres⁷. But pitch is a complex material that can certainly not be regarded as a single-component liquid-crystalline system. Among many current approaches to carbon fibre production, emphasis is now on the synthesis of pure, chemically stable, single-component systems of relatively simple disc-like molecules that exhibit striking analogies with carbonaceous mesophase pitch^{8–11}.

Carbon fibres have also been manufactured from lignin⁷. Lignin-based carbon fibres, Kayacarbon, were first developed and made commercially available by Nippon Kayaku Co. on a pilot scale. The process involves carbonization of dry-spun fibres from lignin dissolved in an alkaline solution with poly(vinyl alcohol) added as plasticizer^{12,13}. The lignin-based carbon fibres have the advantage of lower temperature and shorter period of stabilization stage since the crosslinking reactions are facilitated by oxygen-containing functional radicals^{12,13}.

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Although similar reactions may take place in pitch once stabilization begins, lignin stabilizes more rapidly. A short crosslinking stage and high carbonization yield contribute to reducing the production costs of carbon fibres from lignin. This makes lignin an attractive precursor.

However, electron microscopy studies on Kayacarbon showed poorly developed fibrillar structures and lack of homogeneity, orientation and interlinking between the crystalline planes. A large number of continuous and discontinuous graphitized inclusions were found owing to catalytic graphitization by impurities (e.g. sodium salts and other sodium compounds). These inclusions were effectively decoupled from the basic structure, thus weakening the fibres^{14,15}. Microvoids of complicated shapes and sizes were also observed^{16,17}. These flaws, and the lack of orientation, give rise to carbon fibres with low modulus and low tensile strength. This could be the reason for commercial abandonment of lignin-based carbon fibres by Nippon Kayaku Co. in 1973.

Sudo and his associates from the Forest Products Research Institute in Tsukuba, Japan, have demonstrated that carbon fibres can be produced from lignin by converting it into a pitch-like material using multi-step chemical modification^{18,19}. In the first process¹⁸, lignin was converted into a molten viscous material with suitable properties for melt spinning by hydrocracking followed by heat treatment in vacuum. This degradative process seems to induce flow in lignin by the removal of active functional groups (OH and CH₂OH). In the second process, the lignin pitch was prepared by phenolation of lignin followed by heat treatment in vacuum¹⁹. This process supposedly eliminates active functional groups by the condensation of phenol with lignin which otherwise interfere with the fluidity of lignin. The resultant carbon fibres from both processes were superior to Kayacarbon. However, owing to relatively low modulus and low tensile strength, these fibres fall into the category of general-purpose carbon fibres.

High-modulus, high-strength carbon fibres from lignin require that the molecules are organized in their melt state in an anisotropic, liquid-crystalline form prior to solidification. This molecular orientation, or the lack thereof, appears to be the primary limitation for the formation of high-modulus carbon fibres from lignin.

The main features that favour liquid-crystal formation are long, narrow, rod-shaped molecules with high aspect ratio (L/D). In addition, thin, flat molecules that allow discotic packing are probably also important in pitch. The presence of rigidity imparted by double bonds and ring structures along the long axis of molecules further enhances liquid-crystal formation. The majority of the liquid-crystalline structures possess two or more aromatic or heteroaromatic rings, one or more bridging groups that bind the rings together, and two terminal groups usually on the long axis of the molecule²⁰.

Lignin is one of the major components of the plant kingdom, and its basic repeat units are phenylpropane (C₆) structures in which the aromatic ring consists of 4-hydroxyphenyl, 3-methoxy-4-hydroxyphenyl (guaiacyl), or 3,5-dimethoxy-4-hydroxyphenyl (syringyl) groups. Liquid crystallinity has not been observed in lignin-derived compounds that were synthesized based on a homologous series of 4-n-alkoxybenzoic acid derivatives from vanillin and syringaldehyde²¹. This may have been due to the presence of methoxyl groups, since

the homologous series of 4-n-alkoxybenzoic acids does form thermotropic liquid-crystalline compounds. In order to reduce the effects of the methoxyl groups, benzyloxybenzoic acid derivatives, cholesteryl benzoate derivatives and benzylidene-*p*-aminobenzoic acid derivatives having the guaiacyl structure were synthesized from vanillin²¹⁻²³. All three acid derivatives exhibited thermotropic liquid-crystalline behaviour.

The goals of the present study were to investigate the thermotropic liquid-crystalline behaviour of lignin-like model compounds, lignin and lignin blends with pitch; and to examine the properties of carbon fibres made from hydroxypropyl lignin pitch.

EXPERIMENTAL

Materials

Lignin-like model compounds. The four dimeric lignin-like model compounds used in this study (Figure 1) represented two biphenyl (I, II), one β -ether (β -O-4) (III) and one phenyl coumaran (β -5) (IV) structure.

Lignin. The organosolv lignin was an experimental product similar to the one available from Aldrich Chemical Co. (product no. 37,101-7).

Hydroxypropyl lignin (HPL). Organosolv Red Oak HPL was obtained in accordance with earlier reports²⁴.

Petroleum pitch. The pitch was obtained from Ashland Oil Co. under the designation Ashland A-240.

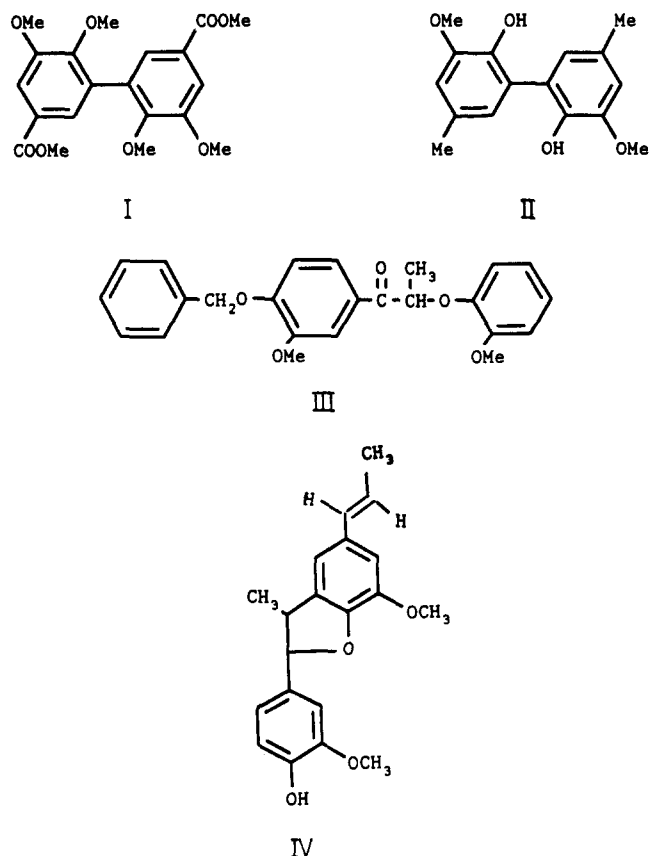


Figure 1 Chemical structures of lignin-like model compounds: non-phenolic biphenyl (5-5) model (I); phenolic biphenyl (5-5) (II); β -ether model (III); phenyl coumaran (β -5) model (IV)

Methods

Acetylation of lignin. Lignin was acetylated according to the procedure of Gierer and Lindberg²⁵ with some minor changes.

Preparation of mesophase pitch from A-240. Mesophase pitch was prepared by following the procedure of previous investigators²⁶⁻²⁸ with some changes. A-240 was heated under nitrogen flow in a Pyrex jar to 425°C. The pitch was continuously stirred throughout the heating process to keep the material homogeneous. The temperature was maintained at 425°C for 3 h (residence time). After 1 h of residence time, a drop of pitch was placed on a microscope slide, and was covered by a cover slip. A similar sample was prepared after 2 h. It was difficult to prepare such samples after 3 h as the pitch became too viscous. The slides were examined for mesophase formation on the optical microscope stage with cross-polarizers.

Preparation of pitch and carbon fibres from HPL. The preparation of pitch and carbon fibres from HPL was performed at the Forest Products Research Institute in Tsukuba, Japan, in accordance with standard procedures developed earlier^{18,19}. About 20 g of HPL were hydrocracked in the presence of 1 g (based on lignin) of Raney nickel catalyst in 200 ml of 5% aqueous sodium hydroxide. The initial hydrogen pressure was 5 MPa, and the reaction time and temperature were 1 h and 250°C. After cooling the reaction mixture, the solution was filtered to remove the catalyst and the residue. The yield of hydrocracked lignin was 61% based on starting material. The hydrocracked HPL was heat treated at 250°C for 70 min in a stream of nitrogen to remove volatile and/or thermally unstable compounds, and to prepare HPL pitch. Total yield of lignin pitch was 50.3%. The pitch was spun into fibres by melt spinning through a single-hole spinnerette under nitrogen pressure at 153–165°C. The fibres were wound onto a bobbin at a winding speed of about 100 m min⁻¹. These as-spun fibres (also called green fibres) were thermostabilized in air by heating up to 210°C at a rate of 1–2°C min⁻¹. After the heat treatment, the fibres were carbonized in nitrogen by heating at a rate of 5°C min⁻¹ up to 1000°C. The yield of the carbon fibres based on the starting material was 26%. (This compares to ca. 50% based on pitch.)

Preparation of blends. Blends of lignin and A-240 pitch were prepared by mixing weighed amounts of lignin and A-240 in a mortar using a pestle.

Gel permeation chromatography. Molecular weights were determined using a gel permeation chromatograph system consisting of a differential viscometer (Viscotek, model 100) in series with a refractive index monitor (Waters Assoc., model 410), and three Ultrastyrigel columns (Waters Assoc.) with pore sizes of 10³, 10⁴ and 10⁶ Å. Similar systems have been described elsewhere²⁹.

Hot-stage optical microscopy. Lignin-like model compounds, lignin, HPL, A-240 pitch and blends of lignin and A-240 samples (few milligrams) were placed between microscope slide and cover slip. This set was heated in the hot stage of a Zeiss Axioplan optical microscope before being examined between cross-polarizers. The heating and cooling rate was 5 and 2.5°C min⁻¹,

respectively. The hot-stage compartment containing the sample was continuously flushed with dry nitrogen in order to maintain an inert atmosphere, and to remove pyrolysis gases.

Differential scanning calorimetry (d.s.c.). The thermal analysis of the lignin-like model compounds was carried out on a Perkin-Elmer DSC-System 2 interfaced to a Thermal Analysis Data Station (TADS). All the compounds were analysed at a heating and cooling rate of 5 and 2.5°C min⁻¹, respectively, under a purge of dry nitrogen.

¹³C n.m.r. spectroscopy. The ¹³C n.m.r. spectra of HPL, hydrocracked HPL and heat-treated HPL (concentration, 150 mg/0.75 ml deuterated dimethylsulfoxide) solutions were recorded on a Varian 400 FT n.m.r. spectrometer operated at 100 MHz and spectral width of 25 000 Hz. The observed spectra for HPL, hydrocracked HPL and heat-treated HPL solutions were obtained after 3500, 1550 and 1550 repetitions, respectively, at 25°C in 5 mm n.m.r. tubes using the polarization transfer standard 'distortionless enhancement polarization transfer' (d.e.p.t.) technique.

Scanning electron microscopy. The carbon fibres from HPL were observed on a JEOL JSM-35C scanning electron microscope with an accelerating voltage of 15 kV. The carbon fibres were mounted on aluminium specimen mounts (EMSL) at 45° angle. The fibres were coated at the bottom by Ladd silver conducting paint, and they were then sputter-coated with pure gold for 1 min (9 nm thickness) in an SPI sputter coater.

Transmission electron microscopy. The carbon fibres were embedded in Poly/Bed 812 (Polysciences Inc.) and cured at 60°C for 48 h in flat moulds. Sections (80–90 nm) were microtomed across the cross-section from the embedded fibres. All sections were mounted on copper grids, and they were observed on a Philips STEM EM-420 electron microscope.

RESULTS AND DISCUSSION

The molecular characteristics of lignin, HPL, hydrocracked HPL and HPL pitch (Table 1) reveal effective depolymerization during hydrocracking. Relevant data describing commercial petroleum pitch are given in Table 2.

Lignin-like model compounds

A thermotropic liquid-crystal-forming substance is, in general, expected to transform upon heating from a crystalline (K) phase into a nematic liquid-crystalline (N) phase, and, at higher temperatures, it undergoes melting with the formation of an isotropic liquid phase (N→I phase change). K→N and N→I phase changes can normally be detected by differential scanning calorimetry (d.s.c.) as two separate thermal events, often separated by several degrees on the temperature scale. Both transitions have their own specific latent heat (ΔH_f) values, with the ΔH_f value for the N→I phase transition usually being significantly smaller than that for the K→N transition.

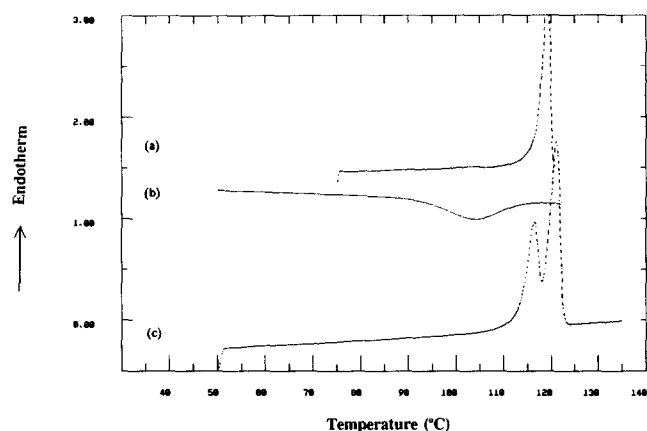
In addition, these thermal events can be observed by polarized optical microscopy (p.o.m.) when a sample is heated on a hot-stage microscope while being observed

Table 1 Chemical and molecular characteristics of lignin, HPL, hydrocracked HPL and heat-treated HPL

	Lignin	HPL	Hydrocracked HPL	Heat-treated HPL
$\langle M_n \rangle$	2900	1900	400	780
$\langle M_w \rangle$	12 000	5600	600	2000
$\langle M_w \rangle / \langle M_n \rangle$	4.1	2.9	1.5	2.5
MHS constant, a	0.41	0.24	0.17	0.21
Log K	-2.81	-2.21	-1.9	-2.1
Intrinsic viscosity, $[\eta]$ (dl g ⁻¹)	0.056	0.044	0.034	0.036

Table 2 Typical properties of commercial petroleum pitch^a

	Test method	A-240 pitch
Glass transition temperature (°C)	ASTM D-3104	120
Density, 25°C (g cm ⁻³)	Beckman pycnometer	1.23
Benzene insolubles (%)	ASTM D-2317	5.0
Quinone insolubles (%)	ASTM D-2318	nil
Carbon (wt%)	ASTM D-2416	51.8
Ash (wt%)	ASTM D-2415	0.10
Sulfur (wt%)	ASTM D-1552	2.2
Viscosity, 163°C (Pa s)	Brookfield	0.70
Viscosity, 177°C (Pa s)	Brookfield	0.27
Viscosity, 188°C (Pa s)	Brookfield	0.14

^aSource: Ashland Oil Co.**Figure 2** Heating and cooling d.s.c. scans of non-phenolic biphenyl (5-5) model (II): (a) as received; (b) sample in (a) cooled from isotropic melt; (c) sample in (b) heated at 5°C min⁻¹

between crossed polars. A typical thermotropic liquid-crystalline substance is expected to reveal its K→N phase transition (i.e. the appearance of disclination lines) after the crystalline structure has disappeared. All order disappears when the N→I transition is reached and an isotropic non-birefringent fluid is formed.

In samples in which the K→N and the N→I transitions are located in close proximity, the transitions can often be made more distinct by cooling and heating the sample at an extremely slow rate so as to allow the system to remain close to equilibrium during all phase transitions. This helps to accentuate the K→N and N→I transitions.

Several dimeric lignin-like model compounds that represent intermonomer linkages present in isolated lignin (Figure 1) were subjected to observations by d.s.c. and p.o.m. during heating from ambient temperature to the isotropic melt state. The results with the 5-5 linked model compound I reveal two melting endotherms when heated from room temperature: a small (extremely faint) transition at 104°C and a sharp peak at 119°C

(Figure 2a). Upon cooling, this sample reveals crystallization through an exothermic event taking place between 115 and 80°C (Figure 2b). When the sample is heated again, very slowly, following complete crystallization, two sharp endotherms appear, at 116.5 and at 122°C (Figure 2c). The K→N transition is located at a higher temperature (by 12.5°C) than that of the corresponding unannealed sample. This difference could be due to the presence of smaller or less perfect crystals in the unannealed sample. These observations are in agreement with those made by p.o.m. (not shown). The specific latent heat of the 116.5°C transition (K→N) is lower than that of the 122°C transition (N→I). This is unusual behaviour for liquid-crystal-forming substances.

Biphenyl compound II represents a phenolic substance capable of hydrogen bonding (Figure 1). On cooling from the isotropic melt at 135°C, spherulites appeared and grew in size at 98°C (Figure 3a). On reheating, the spherulitic texture remained stable until disclination lines characteristic of a nematic liquid-crystalline phase appeared at 118°C (Figure 3b). The K→N transition is complete at 120°C (Figure 3c). This nematic phase was stable up to 128°C, and it became isotropic at 129°C. D.s.c. results reveal an exothermic transition upon cooling the sample from its isotropic state, between 95 and 50°C (Figure 4a), in agreement with p.o.m. observations. Upon reheating, compound II reveals a broad exothermic peak at ca. 75°C, and a small endothermic peak at 113°C, which is immediately followed by a sharp endothermic transition at 123°C (Figure 4b). This compound appears to crystallize slowly, which causes additional crystallization to occur during reheating following cooling at a rate of 2.5°C min⁻¹. Since the optical microscopy results suggested that the higher endothermic peak between 114 and 128°C corresponds to both a K→N and a N→I transition, it was suspected that the lower-temperature endothermic transition (shoulder at 114°C) must be attributed to the melting of less perfect crystals. Repeating the cooling and reheating cycle at a faster rate (Figure 4c), however, did not result in a different endothermic peak appearance. In order to distinguish the K→N and N→I phase transitions more clearly, d.s.c. experiments were therefore conducted on a sample subjected to an extremely slow cooling cycle (cooling rate of 0.31°C min⁻¹) followed by heating at a rate of 0.31°C min⁻¹. The results (Figure 4d) indicate a K→N transition at 124°C followed by a (small but distinct) N→I transition at 129°C. This scan was strikingly devoid of the lower-temperature endothermic shoulder. This confirms that the lower endotherm was indeed due to the melting of less perfect crystals formed on dynamic heating. These results suggest that II exhibits thermotropic liquid-crystalline behaviour; and ΔH_f for the K→N transition is greater than that of the

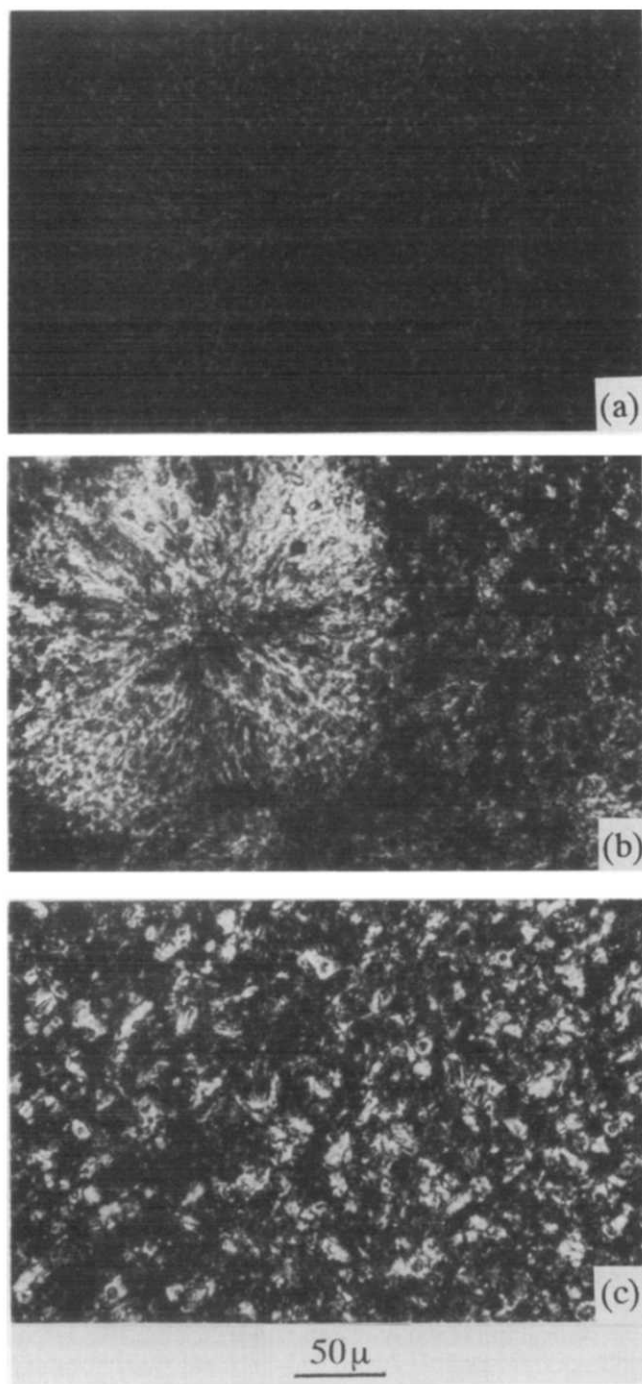


Figure 3 Polarized optical micrographs of phenolic biphenyl (5-5) model (II) crystallized isothermally at 98°C and heated on hot stage as a function of temperature: (a) 98°C; (b) 118°C; (c) 120°C

corresponding N→I transition, as is usual for liquid-crystal-forming substances.

Compound III (Figure 1) revealed a melting transition at 102.5°C on the hot-stage microscope (Figure 5a) and disclination lines typical of a nematic phase were found at 103.5°C (Figure 5b). The N→I transition was complete at 105°C. The d.s.c. thermogram (Figure 6) shows a broad endotherm ranging from 85 to 106°C. This broad endotherm includes both the K→N (~93°C) and the N→I transition (~105°C), and there is no possibility to distinguish the two owing to failure of the sample to crystallize upon cooling. By both d.s.c. and p.o.m., the sample failed to crystallize (exothermic transition or development of birefringence, respectively) upon an

isothermal annealing between 50 and 85°C for 24 h. This suggests that compound III exhibits thermotropic LC behaviour only during the first heating run, and that the nematic mesophase is unstable. The K→N and N→I transitions seem to be separated by only a few degrees Celsius.

The phenyl coumaran model compound IV underwent K→N and N→I transitions within 3°C, between 131.2

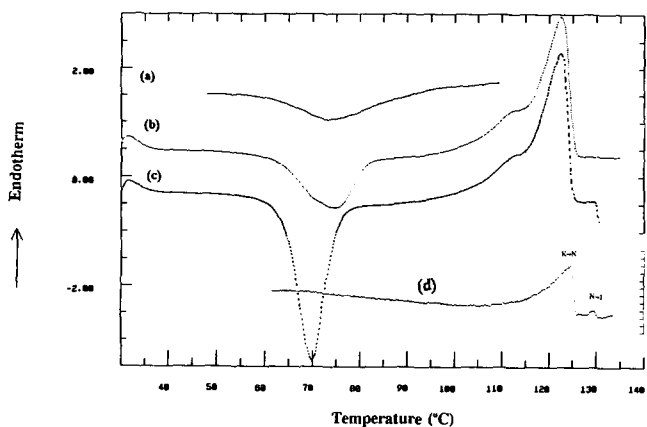


Figure 4 Heating and cooling d.s.c. scans of phenolic biphenyl (5-5) model (II): (a) cooled at 2.5°C min⁻¹ from isotropic melt; (b) sample in (a) heated at 5°C min⁻¹; (c) sample quenched from 135°C to room temperature and heated at 5°C min⁻¹; and (d) sample in (a) heated at 0.31°C min⁻¹

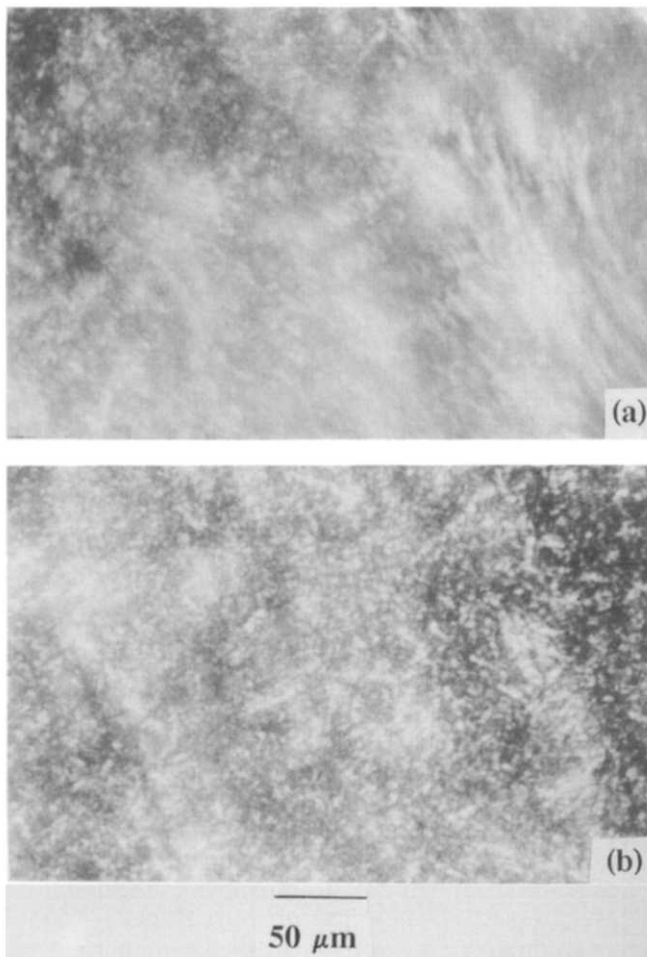


Figure 5 Polarized optical micrographs of β-ether model (III) heated on hot stage as a function of temperature: (a) 102.5°C; (b) 103.5°C

and 133.8°C by both d.s.c. and p.o.m. (not shown). Results from both experiments, d.s.c. and p.o.m., suggest that IV undergoes K→N transition at around 115°C and N→I transition at around 132°C; and that IV forms stable thermotropic LC structures with the specific latent heat, ΔH_f , greater for the N→I transition than for the K→N transition. These observations parallel those made with model compound I.

Table 3 summarizes the results of both d.s.c. and p.o.m.

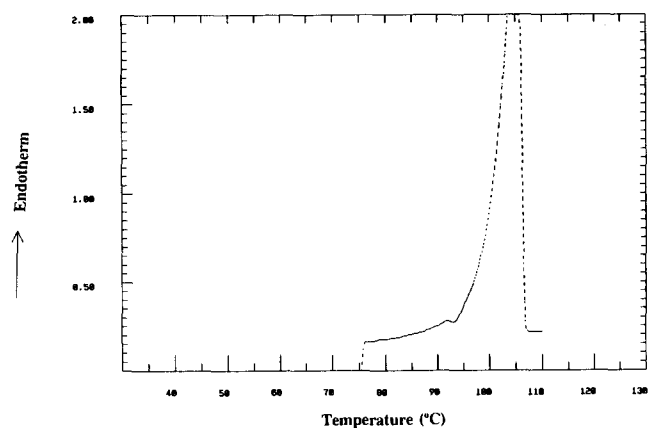


Figure 6 D.s.c. scan of as-received β -ether model compound (III)

Table 3 Summary of LC behaviour of lignin-like model compounds

Observation	Transition temperature (°C) ^a for model compound			
	I	II	III	IV
P.o.m. ^b (heating)				
T_m	105	118	102.5	105
K→N	120	120	103.5	115
N→I	128	129	104	131.8
P.o.m. ^b (cooling)				
T_c	95	98		
D.s.c. (heating)				
T_c		75		85
K→N	116.5	113	103.5	113
N→I	122	123	105	131
D.s.c. (cooling)				
T_c	115–80	95–50		

^a T_m and T_c are the melting and crystallization temperature. K→N and N→I refer to crystal to nematic transition and nematic to isotropic transition, respectively

^b Polarized optical microscopy

experiments, by heating and cooling, of all model compounds studied. It is evident: (a) that all dimeric lignin-like model compounds show two transitions, K→N and N→I; (b) that these transitions occur within a 2°C range (β -O-4 model, III) while others cover an 8 to 10°C (5-5 models, I and II) or 15°C range (β -5 model, IV); (c) that a lower-temperature endothermic transition (shoulder on main melt endotherm) is due to the melting of less perfect crystals; (d) that dimeric lignin-like model compounds form nematic thermotropic LC mesophases that differ in stability and distinctiveness in relation to their chemical structure; (e) that ΔH_f for the K→N transition may be greater (model II) or smaller (models I and IV) than that representing the N→I transition; and (f) that crystallization rates vary between model compounds, with II being slower than I. This is the first report of the formation of thermotropic LC behaviour of lignin-like model compounds. It is apparent that the biphenyl (5-5) intermonomer bond contributes rigidity³⁰ and unidimensionality to the structures, and this promotes the formation of LC structures. 1,4-Disubstituted benzene rings usually form the standard building block from which the majority of the LC molecular structures are derived²⁰. The β -O-4 type dimeric lignin-like model compound (III) contains an alkyl ether bridge, which imparts more molecular flexibility than is required for the formation of stable LC structures. The phenyl coumaran compound (IV) represents a rigid multi-ring molecular arrangement conducive to the formation of nematic mesophases. The propensity for the formation of LC structures of dimeric lignin-like model compounds promises that the formation of an organized fluid phase may indeed be possible. Fibres from this phase may form high-modulus carbon fibres following carbonization.

Lignin

Lignin is an amorphous, aromatic biopolymer consisting of phenylpropane units (C_9) that are linked together by ether and carbon-carbon bonds³¹. Many of the units are trifunctional, which makes it possible for lignin to form branched and three-dimensional structures. A schematic representation has previously been proposed for organosolv lignin (Figure 7). Experimental evidence on lignin monolayers suggests that the structure is moderately flexible, possibly elongated and crosslinked³². There is no change in monolayer film thickness with molecular weight, which supports two-dimensional, planar conformation.

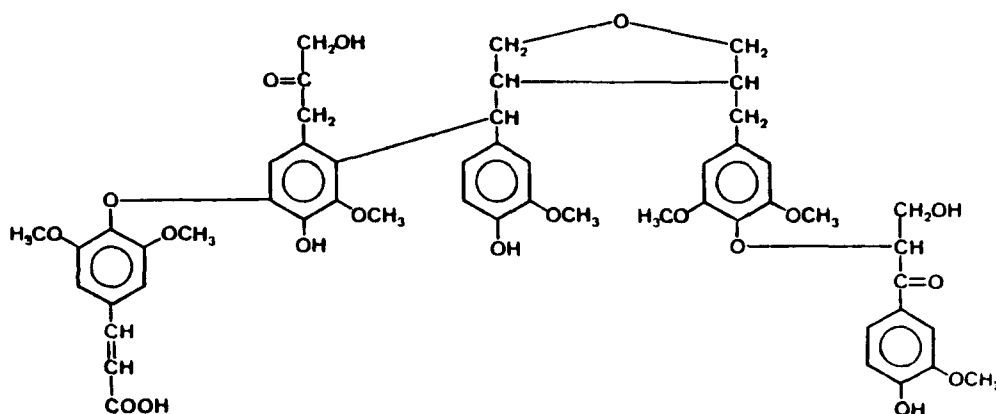


Figure 7 Chemical structure scheme of organosolv lignin

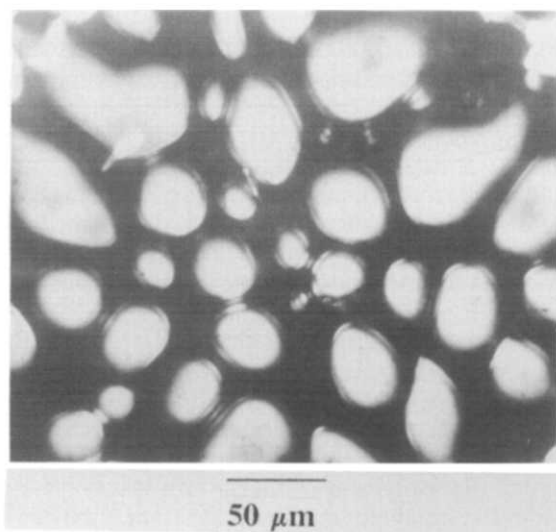


Figure 8 Polarized optical micrograph of lignin at 200°C when heated on hot stage

Table 1 represents the chemical and molecular characteristics of the organosolv lignin used in this study. Upon heating, this lignin flowed at about 110°C. At 200°C, clear anisotropic droplets were observed (Figure 8), which persisted for ca. 1 h. As the temperature was raised to 300°C, these droplets gradually faded and disappeared at 400°C. The lignin became completely carbonized above 440°C.

The anisotropic droplets observed at approximately 200°C during the hot-stage experiment (Figure 8) are consistent with the view that lignin's planar conformation favours the formation of anisotropic melts. The molten lignin fails, however, to organize fully into an anisotropic fluid and instead remains non-uniform. This may possibly be due to three-dimensional molecular diversity and a partially crosslinked structure. Molecular breadth is considered an important feature in the correlation between thermal stability and chemical constitution of mesophases³³. An increase in molecular breadth would normally reduce the anisotropy, thus depressing the stability of both nematic and smectic liquid-crystalline formations. Lignin is a spherical molecule (large diameter), which reduces the anisotropy (i.e. L/D ratio) of the structure. Low-molecular-weight lignin fractions should form liquid-crystalline systems as the structures will be more well defined and narrow. The observation of liquid-crystalline behaviour in the dimeric lignin model compounds supports this hypothesis.

Pitch

Table 2 shows typical properties of the pitch sample used. When pitch was heated on the hot-stage microscope, optically anisotropic spheres were observed, which began to develop at 120°C. Sphere formation gradually increased by coalescence as the temperature rose to 425°C. Figures 9a and 9b show the micrographs of pitch samples kept at 425°C for 1 and 2 h, respectively. A clear indication of carbonaceous mesophase formation and molecular organization is indicated, which becomes uniform and continuous with time (not shown). Textures of this nature have been reported earlier for pitch when *in situ* observations were made by optical microscopy^{34,35}.

Figures 10a and 10b show the micrographs of

pitch that was heated in a Pyrex jar and then quenched to room temperature from 425°C after a residence time of 1 and 2 h, respectively. After 2 h, the mesophase structure is fibrous, and wedge-like disclinations become apparent (Figure 10b). This type of morphology was also observed when the structure of carbonaceous mesophase was investigated by conventional metallographic methods^{6,36,37}. The difference in the morphology detected between Figures 9 and 10 may be due to continuous stirring of the pitch while being heated; this transforms the system into a homogeneous carbonaceous mesophase.

Blends of pitch and lignin

A mixture of pitch containing 25% (w/w) lignin was heated on the hot stage. The lignin portion of the blend was found to begin to flow at 110°C, and spheres were seen to develop at 120°C as pitch molecules were undergoing molecular organization. Pitch and lignin seemed to form a compatible blend at temperatures between 120 and 180°C. At 200°C, droplets of lignin were seen to develop, and there was a simultaneous growth of mesophase formation from pitch. The micrograph of the blend that was kept at 425°C for 2 h (Figure 11) clearly reveals that there is mesophase formation

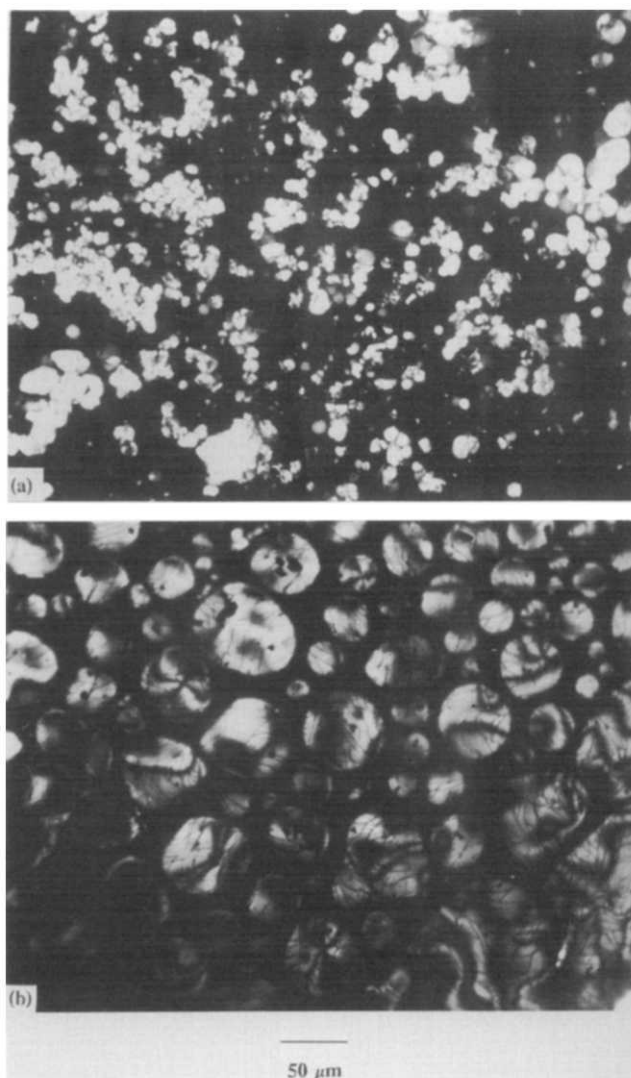


Figure 9 Polarized optical micrographs of A-240 pitch when heated isothermally at 425°C on hot stage as a function of time: (a) 1 h; (b) 2 h

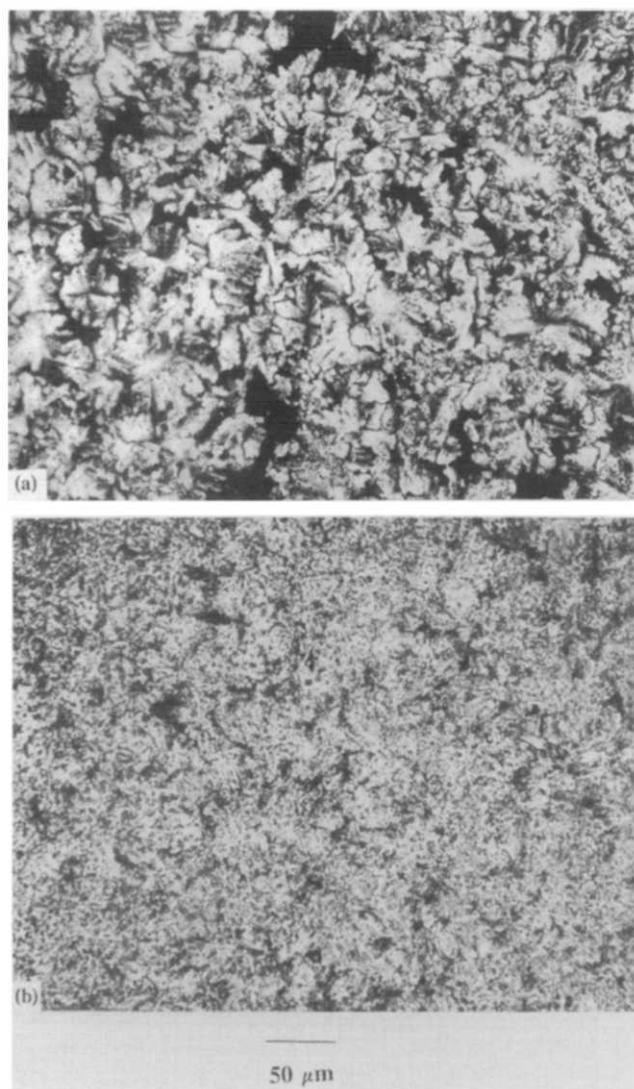


Figure 10 Polarized optical micrographs of quenched A-240 pitch at room temperature after isothermal heat treatment at 425°C with varying residence time: (a) 1 h; (b) 2 h

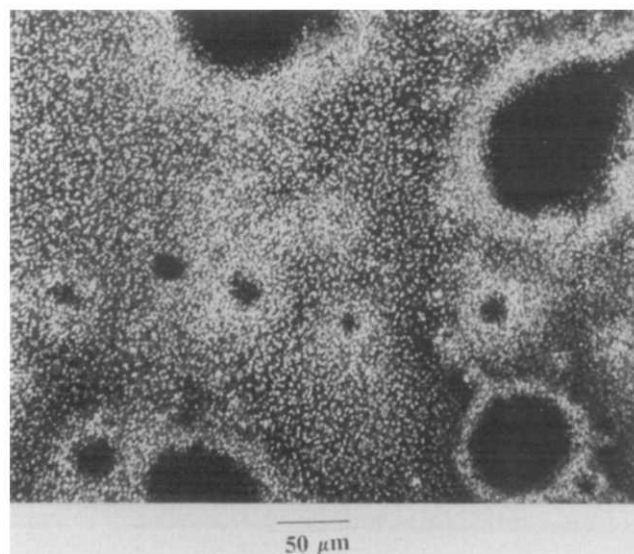


Figure 11 Polarized optical micrograph of the blend of A-240 pitch and lignin containing 25% (w/w) lignin after isothermal heating at 425°C for 2 h on hot stage

due to pitch (75% w/w), but the development of a continuous, homogeneous, anisotropic fluid is prevented by the premature carbonization of lignin as, at higher temperature, lignin and pitch remain a physically separated mixture (i.e. incompatible blend). Similar observations were made for the blend containing 50 and 75% (w/w) lignin.

From these observations of blends of pitch and lignin it appears that lignin interferes with the development of a homogeneous carbonaceous mesophase during heat treatment due to premature carbonization. The development of a continuous and homogeneous carbonaceous mesophase sphere is hindered by the formation, at an early stage, of carbon particles³⁸. This premature vitrification can probably be retarded by degradation, such as hydrocracking^{18,19}. This route produces a lignin pitch that continues to flow, and which is processable at high temperature. This approach has been pursued by Sudo *et al.*^{18,19}. Another method of improving lignin's flow characteristics involves chemical modification, such as alkoxylation.

Hydroxypropyl lignin (HPL)

The chemical and molecular characteristics of HPL are summarized in *Table 1*. HPL is obtained by reacting lignin with propylene oxide²⁴ (*Figure 12*). This chemical modification improves the flow characteristics of lignin without degradation. On heating, HPL transforms into a homogeneous liquid, at around 100°C, which ultimately becomes carbonized at higher temperature (>400°C) without any signs of mesophase formation. While propoxylation does increase the molecular flexibility, the possibility of intramolecular hydrogen bonding and the increased molecular substitution with alkylene ether groups both seem to contribute to an interference with effective mesophase formation.

Hydroxypropyl lignin pitch

Attempts were made to improve the mesophase-forming characteristics of HPL by conventional hydrocracking and heat treatment^{18,19}. *Table 1* shows the molecular characteristics of hydrocracked and heat-treated HPL. It is evident that, on comparing with HPL, $\langle M_n \rangle$ and $\langle M_w \rangle$ values for hydrocracked lignin decrease whereas the values for heat-treated HPL increase owing to the removal of low-molecular-weight, thermally unstable compounds and condensation (*Figure 13*).

¹³C n.m.r. spectra of the various lignin preparations provide evidence for the chemical changes taking place during hydrocracking and heat treatment (*Figure 14*). The peaks at ~20, 64–68 and 72–80 ppm represent the CH₃, CH and CH₂ groups, respectively, of propylene oxide. These peaks almost disappear during hydrocracking (*Figure 14b*) and heat treatment (*Figure 14c*). However, the methoxyl peak (~56 ppm) of lignin exists even after heat treatment. The peaks in the range of 100–120 ppm are assigned to the aromatic carbons of lignin. These peaks are very evident in hydrocracked HPL (*Figure 14b*), and they decline somewhat during heat treatment (*Figure 14c*). These spectra indicate that, upon hydrocracking and heat treatment, there is cleavage of propylene oxide from HPL, and HPL pitch contains heavily condensed structures with an abundance of aromatic moieties.

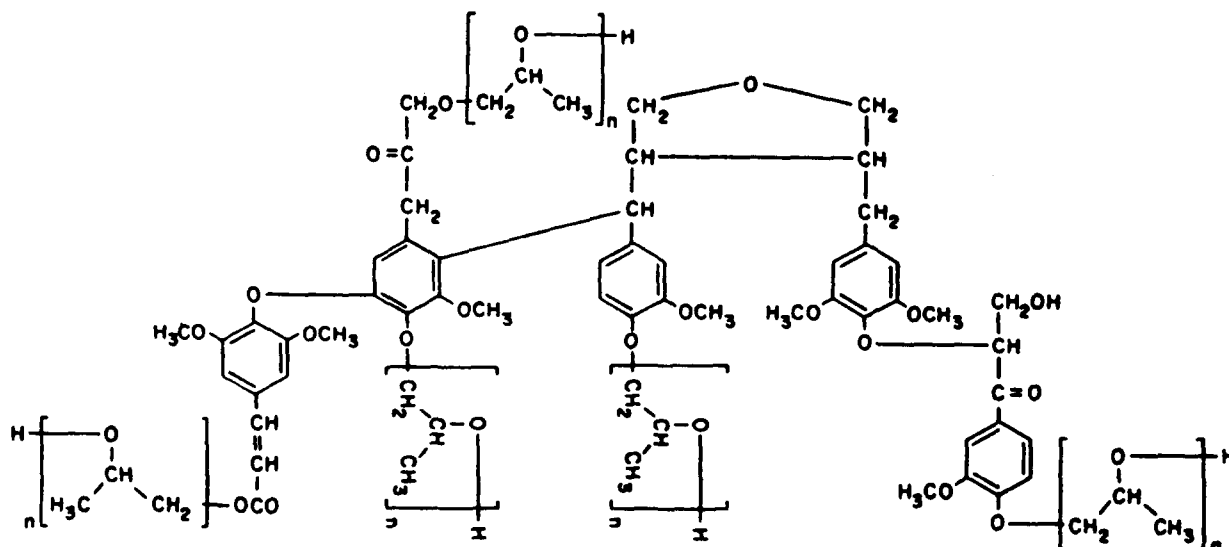


Figure 12 Schematic representation of hydroxypropyl (organosolv) lignin derivative ($n=1$)

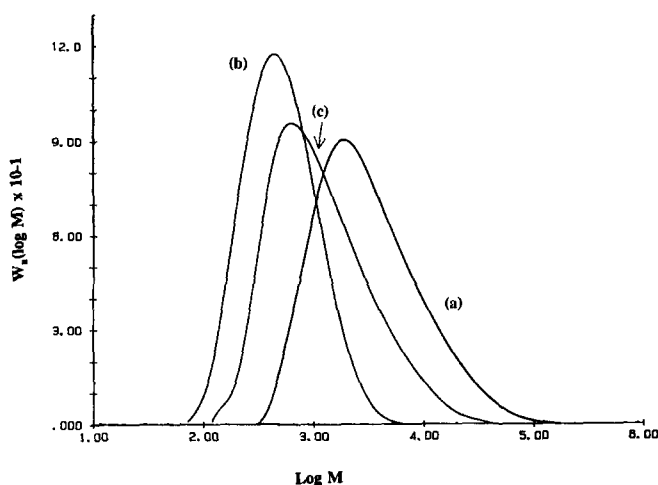


Figure 13 Molecular-weight distributions: (a) HPL; (b) hydrocracked HPL; and (c) heat-treated HPL

Table 4 Physical properties of carbon fibres (CF) from different precursors

Carbon fibre type	Tensile strength (GPa)	Tensile modulus (GPa)	Diameter (μm)	ϵ_b (%)
Polyacrylonitrile (PAN) ^a	3.65	231	5–7	1.3–1.8
Mesophase pitch ^b	2.1	520	10	0.4
Rayon ^c	0.4–0.7	20–55		
After hot stretching	3.1	620		
Kayacarbon				
(i) 1500°C ^d	0.25	27.0	12–14	1.0
(ii) 2000°C	0.29	24.0	12–14	1.0
Lignin pitch ^e				
(i) Process I	0.66	40.7	7–9	1.63
(ii) Process II	0.52	48.9	21–26	1.06
HPL pitch	0.33	–	6–15	–

^a T-300, Thornel Product Information, Amoco Performance Products

^b P-75S, Thornel Product Information, Amoco Performance Products

^c From ref. 1

^d Carbonization temperatures

^e From ref. 18

Mechanical properties

The mechanical properties of carbon fibres from PAN, mesophase pitch, rayon, Kayacarbon (lignin/PVA), lignin pitch and HPL pitch are compared in Table 4. The fibres from PAN and mesophase pitch are comparable in strength, but the fibres from rayon (without hot stretching) are inferior to the commercial products. They are comparable to lignin pitch carbon fibres. HPL pitch fibres were even weaker than lignin pitch fibres.

Scanning electron microscopy

The surface morphologies of green and carbon fibres from heat-treated HPL pitch (Figure 15) are quite smooth. Whereas green fibres reveal the presence of some particulate depositions on the surface, carbon fibres from HPL pitch are extremely smooth, and the absence of any structural defects on the surface produces fibres that have a higher tensile strength than Kayacarbon (Table 4).

Transmission electron microscopy

The TEM micrograph of the cross-section of the carbon fibre (Figure 16) fails to reveal any sign of molecular organization at low molecular weight. The cross-section of carbon fibres from HPL did not show any layered arrangement of carbon lattice fringes along the fibre axis at high magnifications. This indicates that the fibres are amorphous. The lack of orientation, primarily, is responsible for the inferior mechanical properties.

The fibre spinning temperature (i.e. 153–165°C) of the heat-treated HPL was above the N→I transition of the model compounds. This suggests that the green fibres, spun from an isotropic melt state, have low orientation and are isotropic. This, presumably, is responsible for the observed low orientation of the carbon fibres (Figure 16). No attempts were made to study the structure of the green fibres as they were too fragile to handle. Electron microscopy of green fibres would be of interest for further advancing the understanding of processing parameters of lignin into carbon fibres³⁹.

CONCLUSIONS

Dimeric lignin-like model compounds representing β -O-4, 5-5 and β -5 intermonomer bonding are capable of

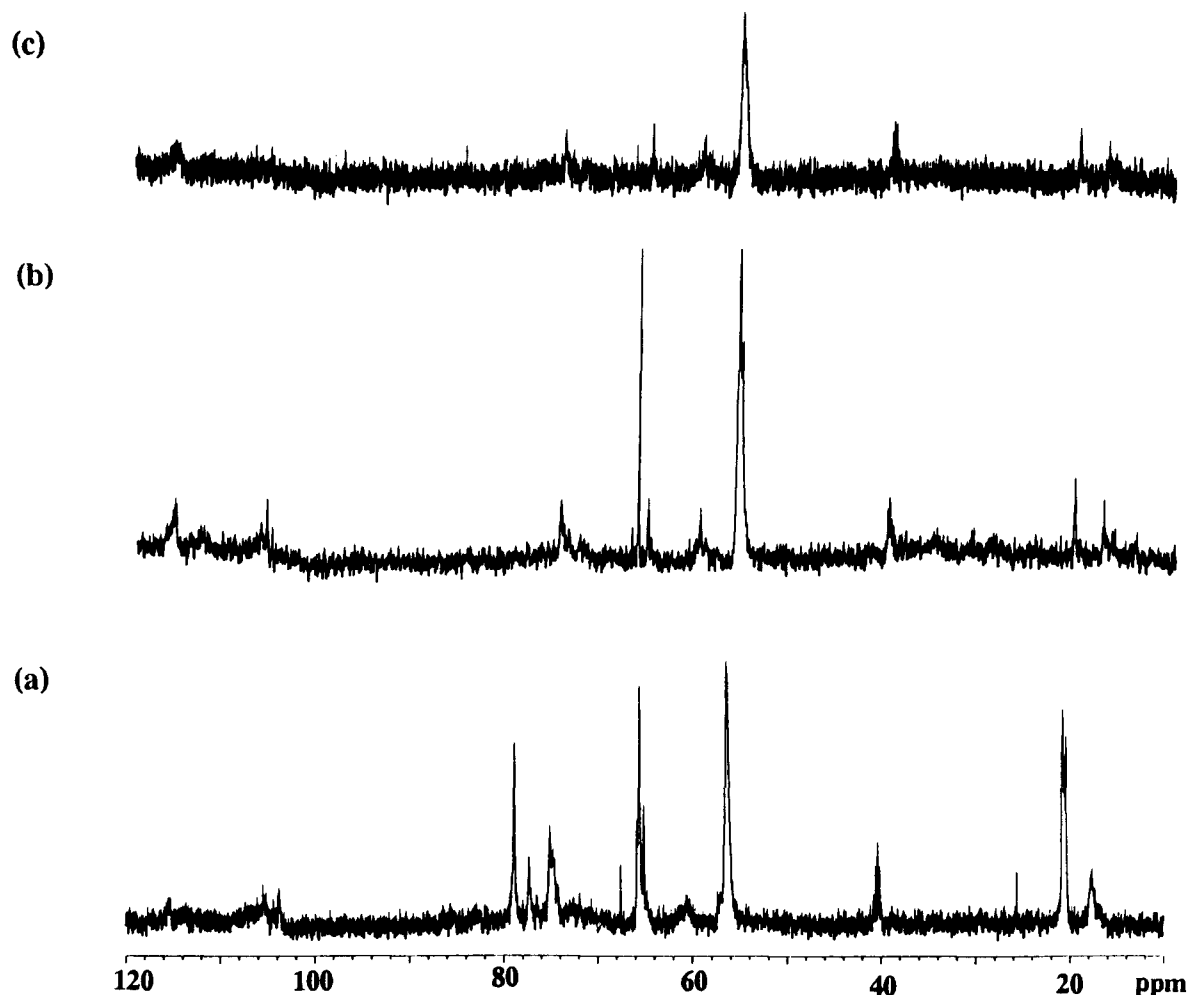


Figure 14 ^{13}C n.m.r. spectra: (a) HPL; (b) hydrocracked HPL; and (c) heat-treated HPL

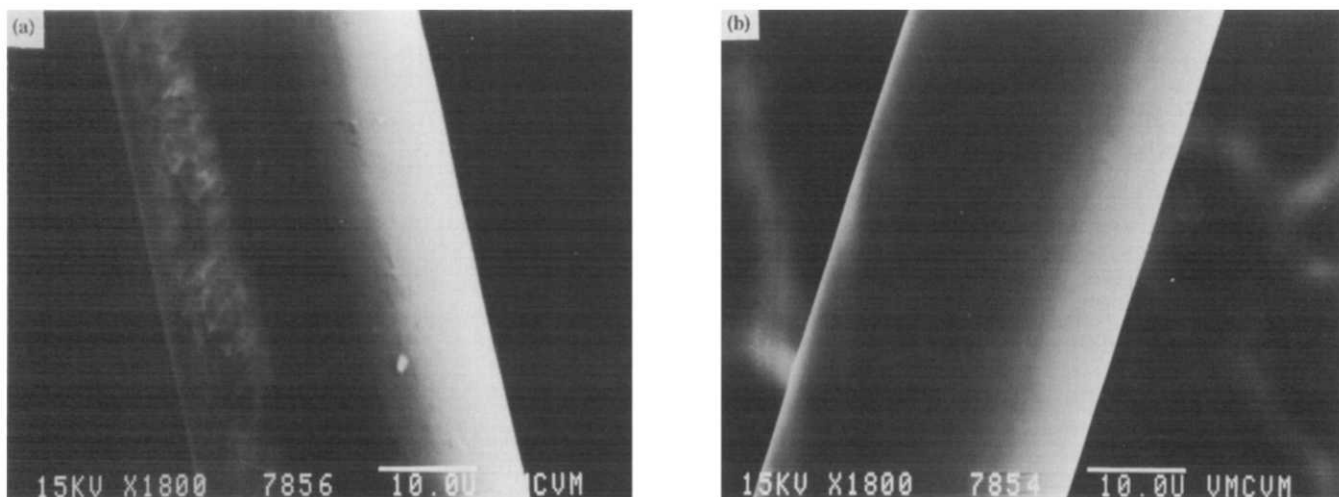


Figure 15 Scanning electron micrographs of the surface of fibres spun from heat-treated HPL: (a) green fibres; (b) carbon fibres

developing thermotropic liquid-crystalline phases as observed by hot-stage optical microscopy and differential scanning calorimetry.

The stability of the nematic phase declines in the order of 5-5 (most stable), β -5 and β -O-4 (least stable).

The temperature range over which K \rightarrow N and N \rightarrow I transitions are observed is extremely narrow, generally $<10^\circ\text{C}$, and, in the case of the β -O-4 model, $<3^\circ\text{C}$.

Lignin, having chemistry similar to that of pitch,

appears to possess the necessary ability for molecular organization during heating while in the fluid phase. Restraints are recognized for the formation of organized fluids that are related to significant non-uniformity in terms of response to heating (i.e. the presence of solid particulates that never undergo fluidization and carbonize while surrounded by an anisotropic solution). If it were possible to eliminate those substances which resist fluidization during heating, it might be possible for

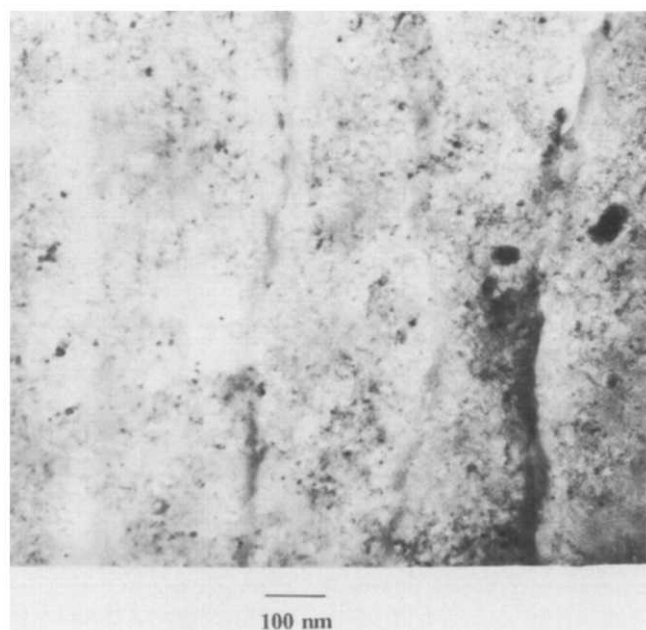


Figure 16 Transmission electron micrograph of the cross-section of carbon fibres from heat-treated HPL

lignin to display pitch-like carbonaceous mesophase behaviour. If an organized lignin fluid phase, however, is characterized by the same low thermal stability as that of several lignin-like model compounds, the formation of highly oriented fibres would become impossible.

The degradative process of hydrocracking and heat treatment eliminates the active functional groups that reduce molecular interactions and increase fluidity in lignin and hydroxypropyl lignin. Carbon fibres from hydroxypropyl lignin pitch have a defect-free surface morphology but, owing to the lack of molecular orientation, the properties are inferior to those of other carbon fibres.

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