

# The development of mesophase in coal tar and petroleum pitches characterized by extrography

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*(Received 30 September 1992; revised 4 January 1993)*

A series of three coal tar and two petroleum pitches were characterized in terms of chemical composition by extrography combined with FT-i.r., g.c. and g.p.c. These pitches, along with another five pitches, were pyrolysed/carbonized isothermally at 425, 450 and 475°C for residence times of up to 180 min. Extents of mesophase formation, and size of mesophase growth units, were determined using an image-analysis system. Extents of formation of mesophase together with its characterization in terms of temperature and residence time are related to the extrography data. The process of homogeneous nucleation of mesophase from a pyrolysing system is described in detail, together with a discussion of the different growth mechanisms of mesophase. The 10 pitches represent a wide range of rates of growth of mesophase, 9PP being the slowest, 8CTP being the fastest, with the eight coal tar pitches being intermediate. These phenomena are discussed in terms of the obtained chemical analyses and of influences of primary QI materials within the coal tar pitches.

(Keywords: pitch; characterization; pyrolysis)

Carbonaceous materials derived from petroleum pitches and coal tar pitches have important industrial applications. Coal tar pitches are suitable binder materials for carbon anodes and graphitic electrodes, with petroleum pitches having a further application as impregnation agents to densify the graphite electrodes. When pitches are heated, they are converted from an isotropic liquid, through an intermediate liquid crystal phase (mesophase<sup>1</sup>), to the final solid coke. The characterization of mesophase as it is formed within the parent pitch, together with assessments of comparative rates of formation during heating processes, are important properties. They relate to how pitch materials perform in industrial applications.

It is generally accepted that formation and development of mesophase depends upon the chemical composition of the parent material and the reactivity of its components. Chemical and physico-chemical properties of pitches, such as aromaticity and hydroaromaticity, hydrogen transfer ability, molecular size distribution, heterofunctionalities, etc., are related to mesophase formation<sup>2-4</sup>. However, little is published which relates chemical characteristics with the chemical kinetics of mesophase formation<sup>5</sup>.

Important information about the chemical characteristics of pitches and related materials can be obtained by extrography. This is a technique of fractionation into compound classes<sup>6-8</sup> which provides information about chemical aspects closely related to reactivity and molecular size distribution of the pitch components<sup>9,10</sup>.

This work constitutes an attempt to widen the knowledge of kinetics of mesophase formation in pitches

using chemical analytical information obtained from extrographic fractionations. To this end, mesophase formation in 10 different pitches under different experimental conditions was studied. Kinetic data are correlated with chemical composition, and kinetic models for the different pitches were established. Extents and size of mesophase produced during carbonization were measured by image analysis based on an optical microscope.

## EXPERIMENTAL

Eight industrial coal tar pitches, six binder pitches (2CTP to 7CTP), an impregnating (1CTP) and a low temperature pitch (8CTP), and two petroleum pitches (9PP, 10PP) were used. Analysis and specifications are given in Table 1.

### Characterization of pitches

Five relevant pitches (1CTP, 4CTP, 8CTP, 9PP and 10PP) were fractionated by extrography and resultant fractions characterized by gas chromatography (g.c.), FT-i.r. and vapour pressure osmometry (v.p.o.). These pitches are considered to be representative of available industrial pitches.

Four grams of each pitch, <0.20 mm in particle size, was solubilized or suspended in dichloromethane, and 40 g of silica gel (63 to 200 µm) added to the solution. The silica gel was previously activated by heating at 120°C, and its activity adjusted by adding appropriate quantities of water. After mixing, the dichloromethane was removed by vacuum distillation in a rotary evaporator and the solid residue dried under nitrogen. The dried

**Table 1** Selected properties of studied pitches

Sample	Ultimate analysis (daf wt%)					SP <sup>b</sup> (°C)	QI (wt%)	TI (wt%)	Ash (wt%)
	C	H	N	S	O <sup>a</sup>				
1CTP	91.8	4.4	1.3	0.5	1.9	69	2.6	17.2	0.10
2CTP	92.8	4.6	1.0	0.4	1.0	90	11.8	34.7	0.15
3CTP	92.8	4.8	1.1	0.5	0.5	91	11.8	35.3	0.29
4CTP	92.8	4.8	1.1	0.6	0.5	92	11.6	33.1	0.16
5CTP	—	—	—	—	—	95	6.8	32.5	0.14
6CTP	—	—	—	—	—	97	2.1	29.7	0.03
7CTP	—	—	—	—	—	98	1.9	22.8	0.03
8CTP	86.0	7.0	1.3	0.8	4.6	96 <sup>c</sup>	0.7	5.9	0.30
9PP	92.0	6.0	1.0	0.5	0.5	—	0.5	—	0.03
10PP	92.2	5.1	0.3	2.3	0.2	208 <sup>c</sup>	0.4	17.5	0.04

<sup>a</sup> By difference<sup>b</sup> Kramer-Sarnow<sup>c</sup> Ramol-Mettler

material was placed in a glass column. At the bottom of the column, 18 g of silica gel were also placed to avoid overlapping of fractions. A sequence of six solvents was used<sup>8</sup>. The solvent volumes were those consumed until no further material was eluted<sup>8</sup>. Then, the solvent was removed from the collected fractions and the residues dried, weighed and analysed by g.c. and FT-i.r.. A further seventh fraction (No. VII) was obtained by Soxhlet extraction, using 300 ml of pyridine, from the residual material retained on the silica gel.

Gas chromatography of the fractions solved in dichloromethane or pyridine was carried out with a flame ionization detector and a fused silica capillary column (25 m length and 0.22 mm internal diameter), using nitrogen as carrier gas at a flow rate of 1.4 ml min<sup>-1</sup>, temperature programme 50 to 280°C at 4°C min<sup>-1</sup>. FT-i.r. spectra of the seven fractions were obtained with KBr pellets in a Perkin Elmer Fourier transform spectrometer. Molecular weights were determined by v.p.o. in a Knauer apparatus with dichloromethane as solvent, and standardized with benzil (diphenylglyoxal). V.p.o. results are given based on extrapolation to infinite dilution. Finally, gel permeation chromatography (g.p.c.) was carried out in a chromatograph consisting of a model 590 pump, a U6K injector and a model 481 absorbance detector operating at 254 nm, all from Waters Associates. The column used was PL-Gel (300 mm length and 7.5 mm internal diameter), using dichloromethane as solvent at a flow rate of 1 ml min<sup>-1</sup>.

#### Pyrolysis of pitches

About 0.4 g of each of the 10 pitches was placed into individual open-ended Pyrex tubes (50 mm × 5 mm) which were flushed with nitrogen. The 10 sample tubes were held together vertically in a graphite pot which was positioned in the centre of a horizontal tube furnace. The pitches were heated under nitrogen at 4°C min<sup>-1</sup> to 425, 450 and 475°C, and maintained at maximum temperature for residence times of 30, 60, 120 and 180 min. After the required residence time, the tubes were removed from the furnace and rapidly cooled under nitrogen.

#### Optical microscopy of heat-treated pitches

Each heat-treated pitch was mounted, with the Pyrex tube, in 'Metset' resin and then vertically cut into two

sections. These sections were polished and examined using a Vickers microscope fitted with parallel polars and a half-wave retarder plate to record the optical texture of the heat-treated pitches. A series of coloured micrographs was taken for each heated pitch at 25 × and 100 × magnifications.

Extents of mesophase growth were determined using an Optomax V image-analysis system. The measurements were made by the 'feature-analysis' method to give the number of mesophase spheres examined, their mean area, perimeter, diameter and shape (form factor). Percentage of mesophase, as a percentage of the total area, and mesophase sphere size distributions were also determined. Such analyses were carried out on 10 fields from the bottom to the top of the tube and the step size of the stage was set to prevent overlapping of fields. Direct detection and an editor, for when the spheres were not well-defined, were used for all samples. This procedure measures about 2000 spheres within each pyrolysed pitch. For all samples, the use of the editor was necessary.

## RESULTS AND DISCUSSION

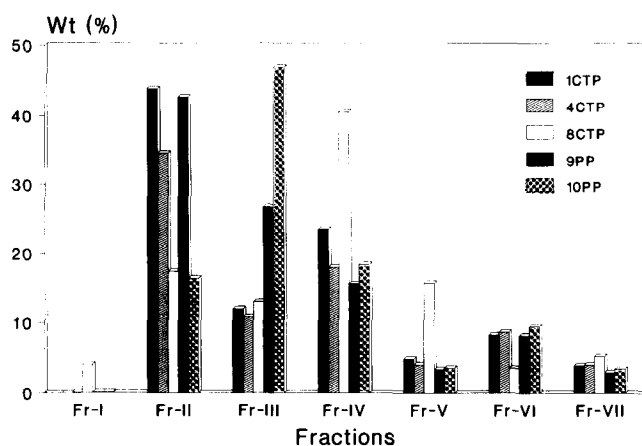
### Chemical characterization of pitches

Of the 10 carbonized pitches, five were selected for extrographic fractionation on the basis of significant differences in their composition. They were a low temperature pitch (8CTP), an impregnating coal tar pitch (1CTP), an industrial binder coal tar pitch (4CTP) and two petroleum pitches (9PP and 10PP).

Figure 1 shows the weight percentages within fractions I to VII obtained by extrography of pitches 1CTP, 4CTP, 8CTP, 9PP and 10PP. Except for 8CTP, fractions V, VI and VII are similar, with differences showing up in fractions II, III and IV. The 8CTP also contains significant amounts of aliphatic material, separated out in fraction I.

The control of the fractionations was carried out by g.c. and FT-i.r. spectroscopy of the fractions, by comparing chromatograms and spectra with those obtained in previous works<sup>11,12</sup> where the composition of fractions was studied by g.c.-m.s. and m.s.

The fractionation of coal-derived liquids consisting only of compounds able to be analysed by g.c.-m.s., shows



**Figure 1** Relative distribution of fractions obtained by extrography of pitches 1CTP, 4CTP, 8CTP, 9PP and 10PP

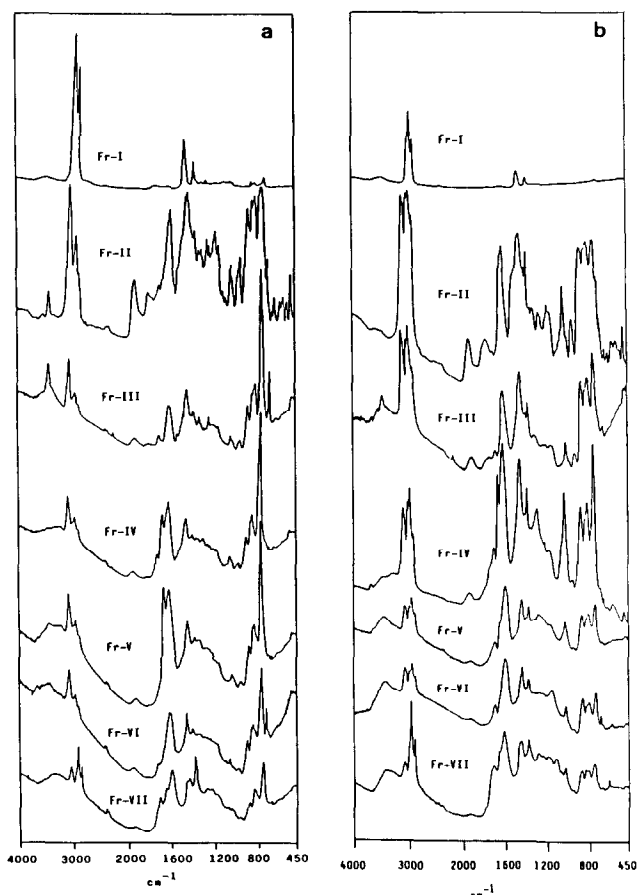
that extrography is an efficient technique for fractionation into compound classes<sup>11</sup>. Aliphatic hydrocarbons, neutral aromatic compounds (PACs), non-basic compounds (PANCs) and phenols were well separated out in fractions I, II, III and IV, respectively, whereas basic PANCs were distributed among fractions IV and V. In binder coal tar pitches, however, significant amounts of aromatic hydrocarbons with molecular weight ( $M_w$ ) over 300 amu were found in fraction III and minor amounts of more highly condensed hydrocarbons were even in fraction IV<sup>12</sup>. These results reveal that molecular size, and probably structural features of components affecting their solubility<sup>13</sup>, may modify the distribution into fractions.

FT-i.r. spectra of fractions I to VII obtained from 4CTP and 9PP are given in *Figures 2a* and *2b* respectively. They are shown as examples of CTPs and PPs, and confirm the good and reproducible fractionations into compound classes previously obtained by extrography<sup>8,11,12</sup>, specially for neutral PACs in fraction II, non-basic PANCs in fraction III (band at  $3450\text{ cm}^{-1}$ ), and basic PANCs in fractions IV and V ( $1650\text{ cm}^{-1}$ )<sup>12,14</sup>. Fractions of 9PP, as well as those of 10PP and 8CTP (whose spectra are not included), contain more aliphatic hydrogen than those of high temperature CTPs. Analyses of volatile compounds in fractions I to V (chromatograms not included) corroborate the above studied separations.

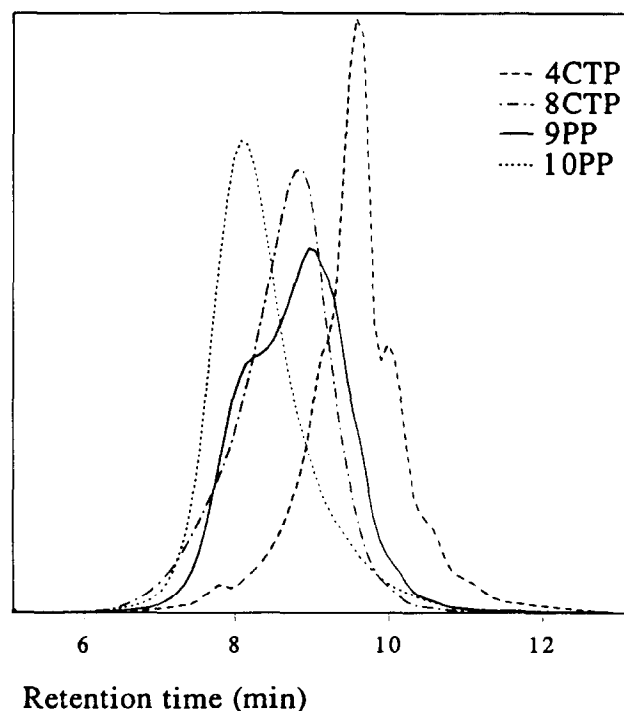
Possible doubts on the chemical composition of fractions were resolved using data of elemental analysis of pitches, and FT-i.r., g.p.c. and osmometry of fractions. In this way it can be assumed, for example, that the main components of fraction III of 10PP ( $\bar{M}_w = 522$ , 0.3% N and 0.1% O) are heavy PAH compounds. The same can be stated for most of the constituents of fraction IV. In the same way, the elemental composition of 8CTP corroborates that phenolic compounds and basic PANCs are the main components of fractions IV and V, respectively. The presence of important amounts of phenolic compounds in 8CTP was corroborated by extracting its toluene-soluble fraction with aqueous solution NaOH (10%).

*Figures 3* and *4* are profiles of  $M_w$  distributions with retention times obtained by g.p.c., for fractions II and III of 4CTP, 8CTP, 9PP and 10PP, respectively. Curves of 1CTP were not included because they were similar to those of 4CTP. *Table 2* contains the average molecular weights ( $\bar{M}_w$ ) of these fractions of the five pitches. For

9PP, 10PP and 8CTP the  $\bar{M}_w$  of fraction II is higher than that found for the high temperature CTPs (*Table 2*) and higher than 300 amu, suggesting lower aromaticity and higher solubility of PAH compounds in these



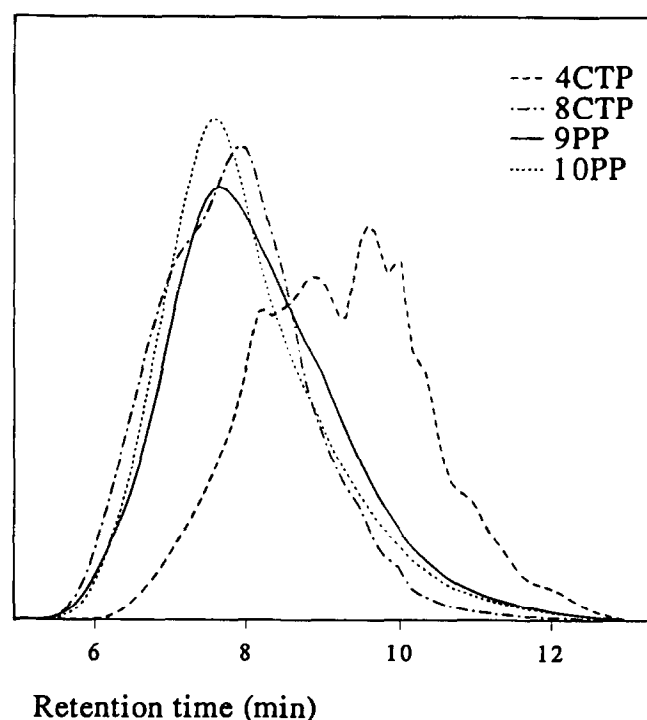
**Figure 2** FT-i.r. spectra of fractions obtained by extrography of (a) 4CTP, and (b) 9PP



**Figure 3** Profiles of molecular weight distribution with retention time, obtained by g.p.c., for fraction II of 4CTP, 8CTP, 9PP and 10PP

**Table 2** Average molecular weight of fractions II, III and IV for five pitches

Fraction	1CTP	4CTP	8CTP	9PP	10PP
II	274	269	350	352	452
III	386	421	402	491	522
IV	—	—	438	—	—

**Figure 4** Profiles of molecular weight distribution with retention time, obtained by g.p.c., for fraction III of 4CTP, 8CTP, 9PP and 10PP

pitches<sup>15</sup>. The  $\bar{M}_w$  of fraction III of 10PP is the highest, ~520 amu. Fractions of 10PP have the narrowest molecular size distribution, see *Figures 3 and 4*. On the other hand, the g.p.c. curves of the binder CTP and the impregnating CTP fractions show several peaks and, consequently, a wider molecular size distribution.

The two high temperature CTPs (1CTP and 4CTP), with constituents of similar structure and molecular size, differ from each other in the content of light PAH compounds (fraction II) and phenols/basic PANCs (fraction IV). In terms of reactivity of the constituent molecules, 1CTP should be more reactive than 4CTP, meaning that pyrolysis processes of increase in  $\bar{M}_w$  should begin at lower temperature for 1CTP. Furthermore, the higher weight loss on thermal treatments, could also contribute to a faster concentration in mesogenic molecules. Consequently, one can expect an early formation of mesophase for this pitch.

The low temperature pitch 8CTP contains a relatively high amount of aliphatic hydrogen, a low content in fraction II, with  $\bar{M}_w$  350 amu, and the largest amounts of phenols and basic compounds (fractions IV and V). It should be the most reactive of the studied pitches.

The two PPs are different from CTPs and from each other in terms of molecular size of PAH compounds (fractions II and III), with 10PP mainly consisting of PAH compounds with high molecular weight (*Table 2*). On the other hand, elemental analysis and FT-i.r. spectra show that 9PP and 10PP contain more aliphatic

hydrogen than high temperature CTPs. Therefore, one can suppose that they are rich in alkyl substituents and/or hydroaromatic and naphthenic structures. This composition suggests, according to Korai and Mochida<sup>15</sup>, that they will form a well-structured and fusible mesophase, especially 10PP due to its high molecular weight.

#### *Effects of residence time and temperature during heat treatment of the pitches*

*Figure 5* shows the variation of weight loss with residence time during pyrolysis of pitches 1CTP to 8CTP, 9PP and 10PP, at 425, 450 and 475°C under nitrogen. The variations of weight loss with residence time follow the same order for the three temperatures. The low temperature pitch 8CTP followed by the impregnating pitch 1CTP, has the highest weight loss and 10PP has the lowest. Processes of volatile loss (distillation) relate to the softening point of the pitch except for 8CTP (*Table 1*). Pitch 10PP has the highest softening point with 1CTP having the lowest softening point.

During pyrolysis, pitch 8CTP is the fastest to form a mesophase at any of the temperatures tested in this study. At 425°C and 120 min soak-time it is totally converted into a multitude of small mesophase spheres, whereas from among the other pitches only 3CTP, 5CTP, 6CTP and 10PP produce mesophase in amounts of about 10% after 180 min soak-time. At 450°C, 8CTP is totally transformed into mesophase after only 30 min soak-time. Increases in soak-time produce increases in the size of mesophase spheres, the optical texture of semi-cokes changing from fine-grained mosaics (30 min) to medium mosaics (120, 180 min). The spheres are of small size, most of them (~90%) being smaller than ~1 µm. This value is an approximation because some spheres are grouped together.

The high loss of 8CTP during thermal treatment, which amounts to about 60% at 450 and 475°C (*Figure 5*), cannot only be due to the volatility of its constituents because its fractions have a  $\bar{M}_w$  higher than those of 1CTP and 4CTP (*Table 2*). It seems more likely to attribute the weight loss also to the instability of its components, particularly those with phenol groups and/or aliphatic structures. The early and fast formation of mesophase by 8CTP, together with the generation of small spheres, is undoubtedly connected with the high weight loss and the reactivity of its components which makes possible a fast increase of its  $\bar{M}_w$  and viscosity.

At 450°C, 5CTP and 6CTP follow 8CTP in mesophase formation (*Figure 6a*), but the transformation of 10PP into mesophase undergoes a sharp increase after 120 min. 9PP is the slowest, reaching only 4% conversion after 180 min.

At 475°C the mesophase formation starts at a lower soak-time and rates of formation are higher for all pitches, some of them tending to a maximum value of mesophase after 180 min soak-time. 10PP quickly forms mesophase, becoming totally anisotropic before 120 min soak-time. 3CTP also starts early but the increase of mesophase falls after 90 min. 4CTP seems to stop mesophase formation at 150 min with only 38% transformation. 6CTP and 9PP follow a different trend, with mesophase formation still increasing after 180 min.

Kinetic changes in mesophase formation promoted by increases in temperature are to be expected, at least qualitatively, because rising temperature increases weight loss and reactivity of constituent molecules, leading to

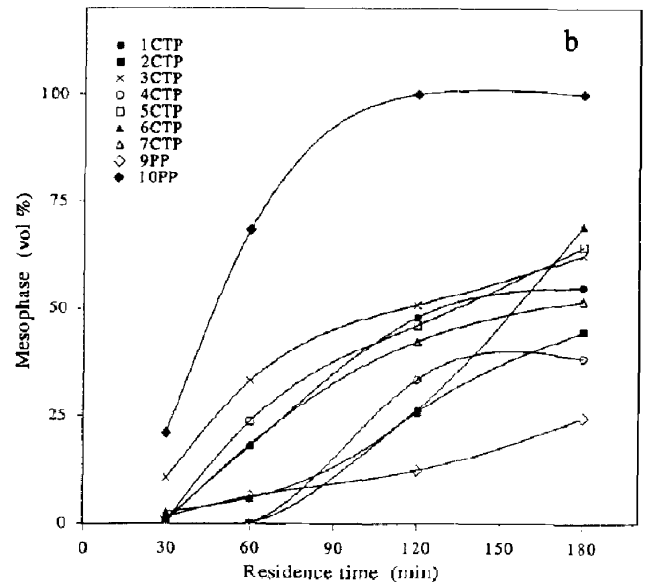
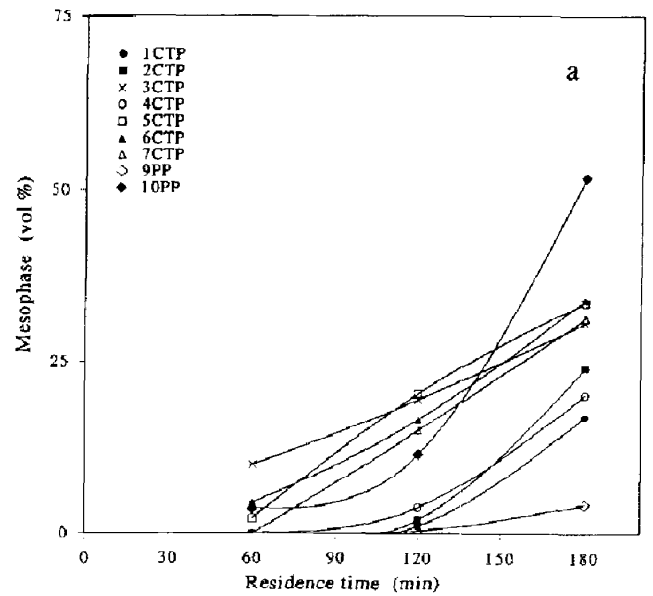
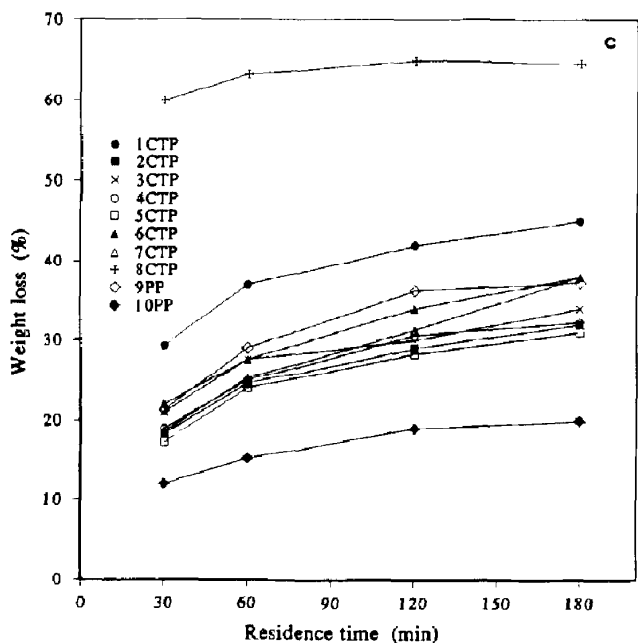
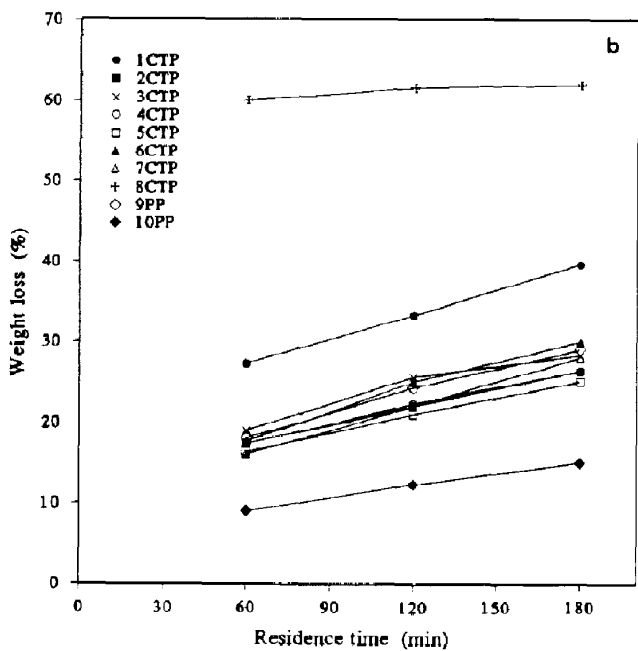
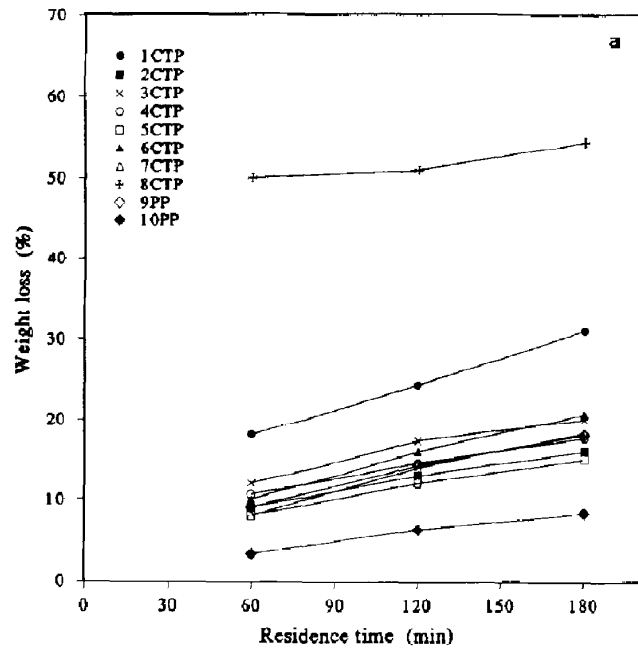


Figure 6 Variation of the extent of mesophase development (vol%) with residence time (min) during pyrolysis of pitches 1CTP to 7CTP, 9PP and 10PP at (a) 450°C, and (b) 475°C

pitch systems with increased  $\bar{M}_w$ . In addition, the fall in viscosity also improves the ability of the system to form and develop mesophase. Limits in the volume of mesophase formed at a given temperature mean that most of the constituent molecules are almost unreactive at that temperature as the same pitches, at 500°C and 60 min soak-time, are totally converted into an anisotropic semi-coke.

Figure 7 shows the extent of mesophase formation with temperature between 425 and 475°C and 180 min soak-time. A linear relationship exists for all pitches with the highest gradient for 10PP followed by 1CTP and 6CTP. 9PP again shows the lowest gradient of mesophase increase together with 2CTP and 4CTP.

With regard to the expected relationship between weight loss and mesophase formation, Figures 5 and 6

Figure 5 Variation of percentage weight loss with residence time (min) during pyrolysis of pitches 1CTP to 8CTP, 9PP and 10PP at (a) 425°C, (b) 450°C, and (c) 475°C under nitrogen

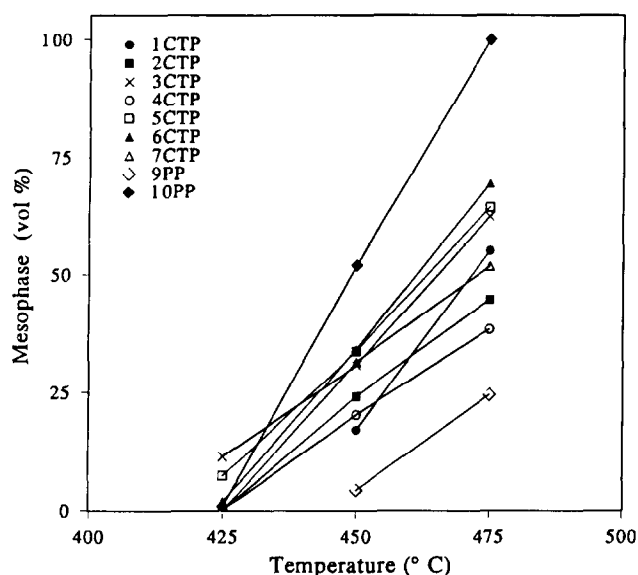


Figure 7 Variation of the extent of mesophase development (vol%) with temperature (°C) during pyrolysis of pitches 1CTP to 7CTP, 9PP and 10PP after 180 min soak-time

do not show any clear connection between them. Neither the beginning of the mesophase formation, nor its later increase with soak-time, state the contribution of weight loss to mesophase growth.

Figure 8 shows variations of mesophase sphere size, expressed as mean perimeters ( $\mu\text{m}$ ) with residence time at 450°C (Figure 8a) and 475°C (Figure 8b). 8CTP was not considered because of the total pitch conversion into anisotropic material at lower temperature. At 450°C increasing residence time does not greatly affect the sizes of the spheres, increase in the amount of mesophase being related more to the generation of new spheres than to the process of coalescence. Only 10PP exhibits a considerable increase in size from 36 to 189  $\mu\text{m}$  mean perimeter. With increasing residence time to 120 min, some spheres coalesce, new ones are produced and this results in a wider range of sizes being predominantly larger with greater residence times. At 475°C, effects of residence time on mesophase size development are more pronounced and consequently, the dependence of mesophase evolution on the characteristics of parent pitches is more in evidence. At this temperature 9PP, 6CTP, 7CTP and 5CTP show an increase from 15–30  $\mu\text{m}$  to 225–240  $\mu\text{m}$ , whilst 2CTP, 3CTP and 4CTP show smaller increases from 30 to about 60  $\mu\text{m}$ . The behaviour of 1CTP is quite surprising, because fast growth up to 60 min is followed by stabilization of the sphere size.

It is interesting to note the relationship between primary quinoline insolubles (QI) content and mesophase development. Figure 9 displays the mean perimeter of spheres at 475°C and 120 min residence time vs. QI; a close relation between them is shown and agrees with general acceptance of the prevention of growth and mesophase coalescence by QI.

Mesophase sphere size depends on the rheological properties of pitches, and their evolution, in the temperature interval in which the development of mesophase takes place. In turn, rheological properties depend on the composition and reactivity of pitches. Relations between composition, provided by extrography and mesophase development, will be discussed later.

Figures 10a, 10b and 10c are histograms of the

percentage formation of mesophase against the distribution of sphere diameter for 5CTP after heating at 475°C for 60, 120 and 180 min, respectively. The distribution of mesophase sphere size ranges becomes wider as the residence time increases. This is the general trend for all the pitches, with the maximum broadening for 5CTP, 7CTP and 9PP.

As an example, Figures 11 shows the optical micrographs, using polarized light, of polished surfaces of pyrolysed pitch/mesophase systems from 5CTP at 475°C, with different residence times. They show the initiation, growth and coalescence of mesophase spheres. 5CTP after 180 min shows mesophase coalesced at the bottom of the reaction tube making it difficult to quantify a distribution of sphere size. The impregnating pitch 1CTP shows a peculiar behaviour, which differs from the rest. After 60 min at 475°C, the mean perimeter has changed little

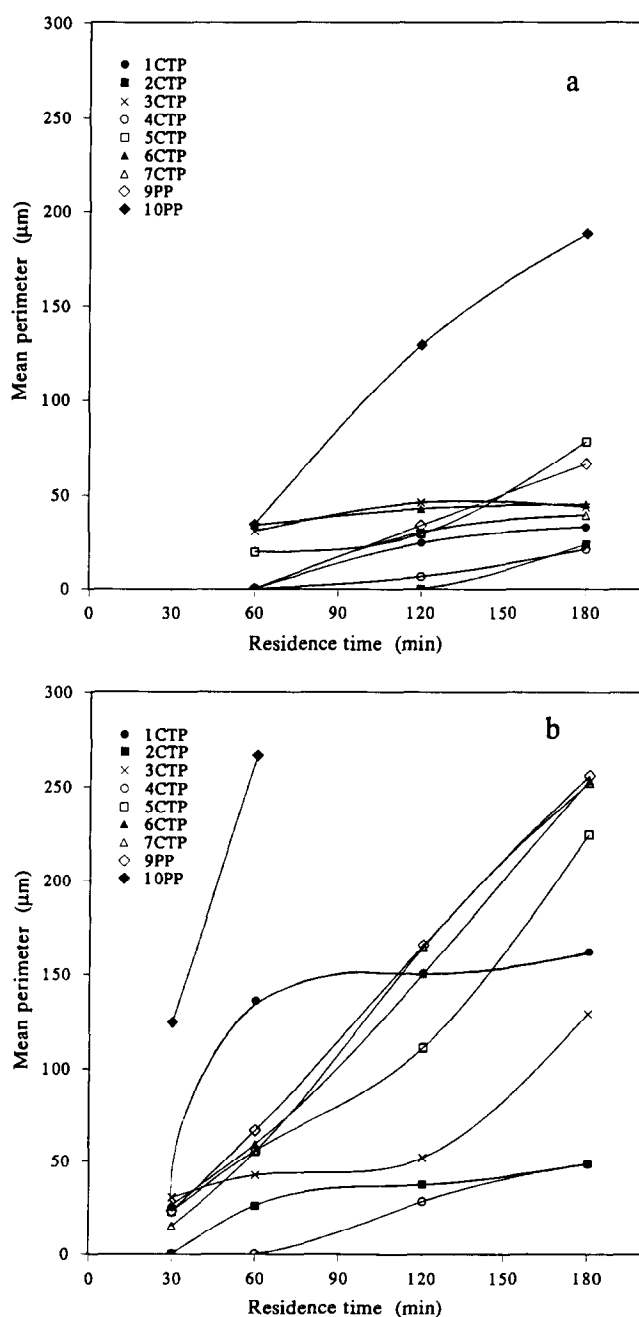
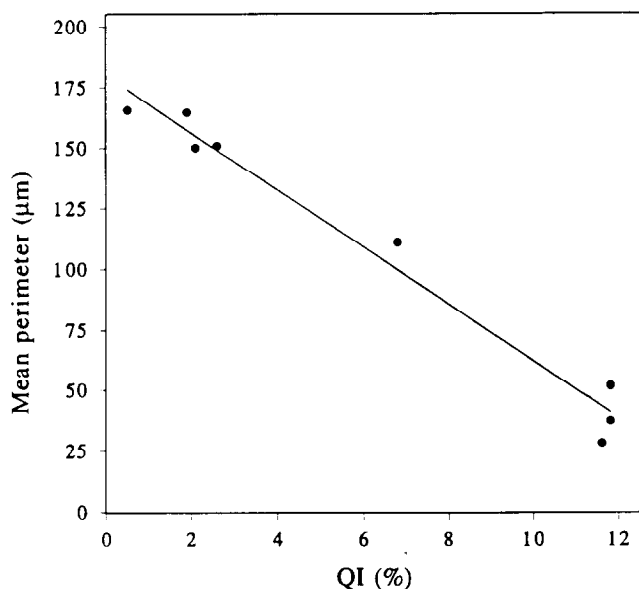


Figure 8 Variation of mean perimeter ( $\mu\text{m}$ ) of mesophase spheres with residence time (min) during pyrolysis of pitches 1CTP to 7CTP, 9PP and 10PP at (a) 450°C, and (b) 475°C



**Figure 9** Variation of mean perimeter ( $\mu\text{m}$ ) of mesophase sphere size with the QI (%) content of pitches at  $475^\circ\text{C}$  after 120 min soak-time

for this pitch, in this aspect resembling the behaviour of 8CTP. The mesophase of 10PP is totally coalesced after 120 min at  $475^\circ\text{C}$ .

#### Modelling of mesophase development

The aim of this study is to explain differences in the observed kinetics of mesophase formation from several different pitch systems in terms of their chemical composition as assessed using extrography. To this end, this paper examines several pitches, in terms of the effectiveness of the extrography technique as an analytical tool, to gain insight into pitch composition and its relationship to mesophase formation and properties. Initially, rather than describing each pitch individually, the approach is to set out a general model of the mechanism of mesophase formation and then to discuss each pitch in terms of variation in the dominant controlling parameters introduced into the model.

Mesophase is a liquid-crystal system which, as with conventional nematic and smectic liquid crystals, owes its special properties to the size and shape of molecules and to the high intensity of the polar forces which exist between the molecules. However, pyrolysing pitch systems differ from conventional liquid-crystal systems in that an essential part of the molecules which form the liquid crystal (called mesogens) have to be synthesized within the pitch. In pitches, liquid crystals appear with increasing temperature because of the need to generate, chemically, the mesogens, whereas in conventional liquid crystals, structural order is created by cooling to a temperature where the intermolecular cohesion energy overcomes the molecular kinetic energy. Furthermore, these as-synthesized liquid crystals are chemically reactive and, from the mesophase, they eventually polymerize to a hard green coke. In addition, the conditions of formation of mesophase have to be considered. The pyrolysing pitch may be in open or closed systems. In the former, significant volatile loss may occur; in the latter, all components of the pitch are essentially transformed into mesophase. Also, the pitch may be heated isothermally (as in delayed coking) or non-isothermally (as in the

carbonization of composite electrodes for the aluminium and steel industries, and carbon/carbon fibre composites). These factors modify the controlling parameters of mesophase formation in the model. Lastly, pitches exist with a wide range of physical and chemical properties and these must also be included in the considerations of the model. Pitches may be compared with a mixture of conventional liquid-crystal materials where eutectic formations are known.

As a result, variations in these several factors of mesophase formation produce variations in the physical properties of the resultant mesophase. These include:

1. Temperature or time of onset of mesophase formation.
2. Size and number of mesophase growth units.
3. The optical texture (size and shape) of resultant coalesced mesophase.
4. Rates of formation of mesophase and temperature and completion time of mesophase coalescence.
5. In coal tar pitches in particular, the presence of QI materials should be recognized.

In molecular terms, the processes of formation of mesophase can be modelled as follows. As pitch materials have been prepared at temperatures approaching  $400^\circ\text{C}$  the formation of mesophase on further heating up to this temperature is of small interest for the aim of this study. Above  $400^\circ\text{C}$ , the processes of molecular growth of the system occur, usually by dehydrogenative polymerization and elimination of smaller molecules by distillation. Thus, there are generated within the pitch, and concentrated in it, types of discotic, aromatic mesogens. Mesophase formation depends upon the ability of constituent molecules to associate to each other sufficiently strongly to maintain cohesion, but at the same time to maintain liquid-crystal properties. When the size (molecular weight) is such that inter-molecular cohesive energies are sufficiently strong, then the beginnings of mesophase growth occur. The further growth of mesophase may incorporate molecules smaller in size than the envisaged initial mesogens<sup>16</sup>.

On the basis of constant values of  $M_w$  distribution,  $\bar{M}_w$ , solubility in pyridine and the glass transition temperature<sup>17</sup> of the mesophase during the transformation of an isotropic petroleum pitch (into homogeneous mesophase under isothermal heating at  $400^\circ\text{C}$ ), Grienke and Singer<sup>16</sup> propose a mechanism of mesophase formation. This involves continuous transfer of smaller size molecules from the isotropic phase to mesophase, restoring in this way the molecular equilibrium in the mesophase; as, in other ways, the  $M_w$  would continually increase, because pitch molecules with  $M_w$  between 400 and 1100 amu are reactive<sup>5</sup>.

This mechanism cannot be applied to all pitches, and to all conditions of mesophase formation, without new further detailed experimentation. In non-isothermal studies, the thermotropy of mesophase with increasing temperature has never been observed; thus, it is essential to accept a mechanism of physical mesophase stabilization involving the creation of new or stronger associative forces by polymerization or cross-linking. Perhaps the cross-linking is mobile, not localized, such that flow properties can be maintained.

In terms of a general model, these processes of (a) mesogen generation, (b) adsorption or assimilation of mesogens into existing mesophase, and (c) growth of the mesophase spheres, continue until mesophase spheres

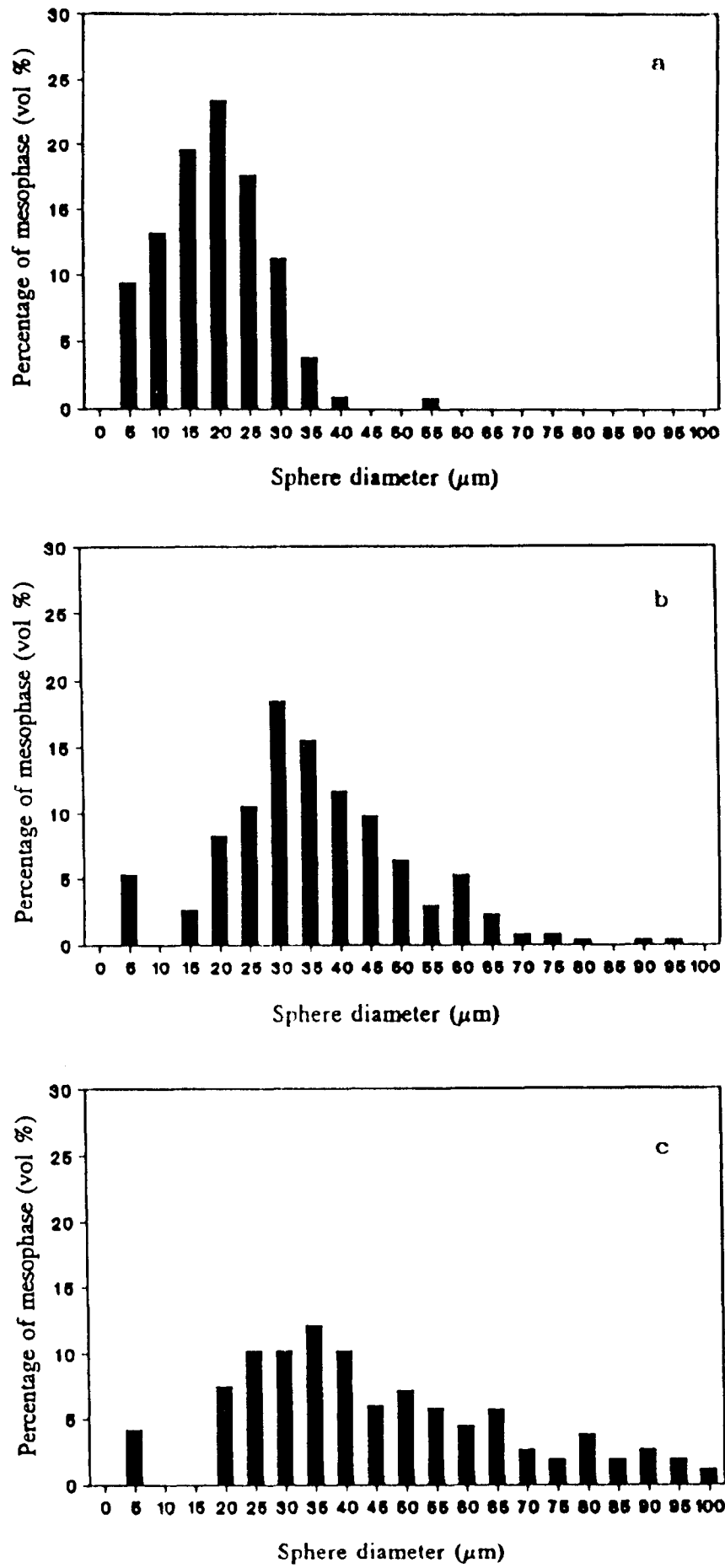
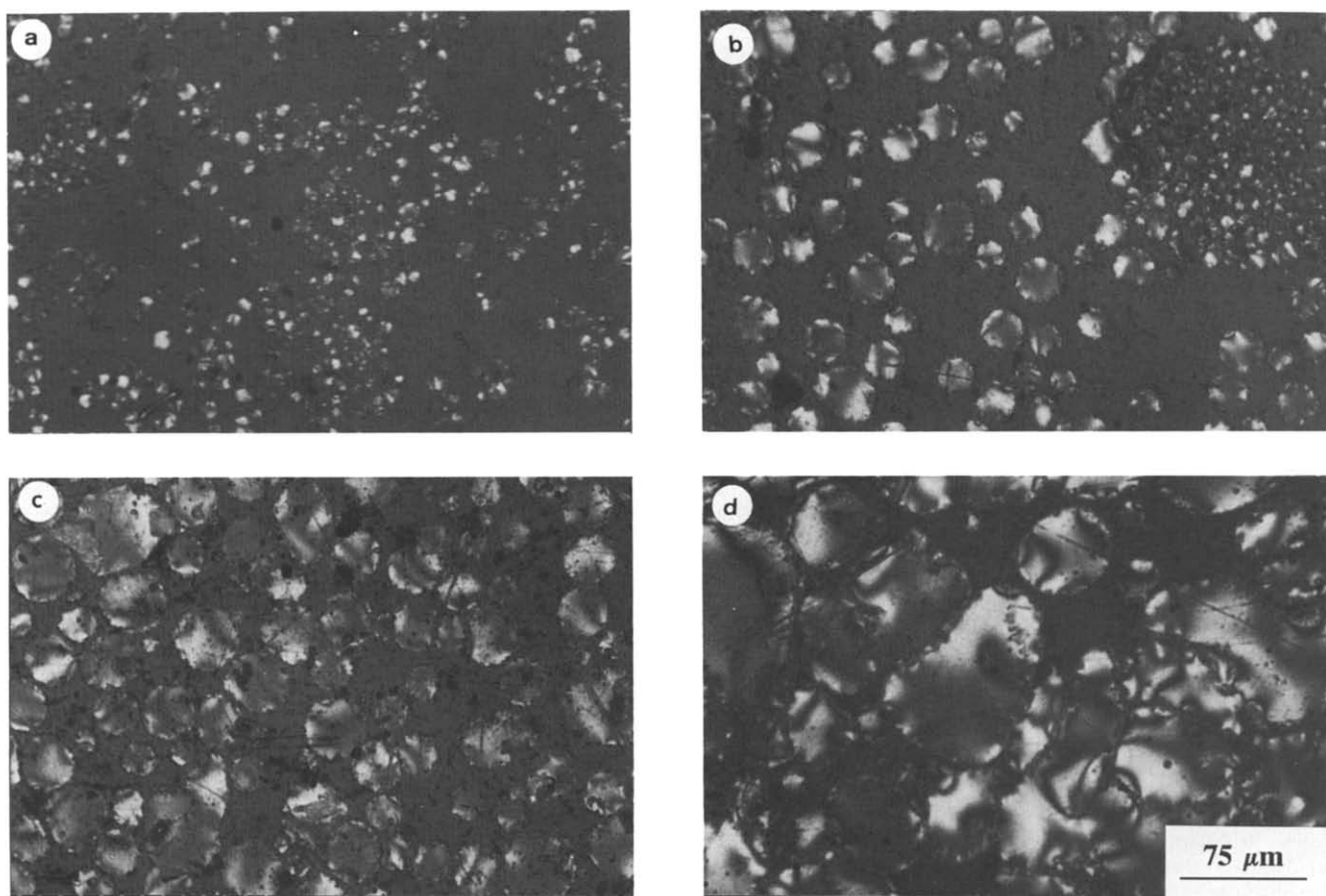


Figure 10 Histograms of percentage formation of mesophase vs. distribution of sphere diameter (μm) for 5CTP after reaction at 475°C for (a) 60 min, (b) 120 min, and (c) 180 min





**Figure 11** Optical micrographs, using polarized light, of polished surfaces of pyrolysed pitch/mesophase systems of 5CTP, at 475°C, with residence times of (a) 30 min, (b) 60 min, (c) 120 min, and (d) 180 min

touch and coalesce such that in the end, all the pitch is converted to mesophase.

Pitch materials are not homogeneous in terms of chemical composition and vary considerably between themselves. The molecular constituents vary in terms of their pyrolysis 'reactivity'; that is, the rates at which they begin to polymerize into larger molecules. These molecular reactivities are crucial in understanding the detail of differences in the formation condition and resultant properties of the mesophase. Relatively, the most unreactive of the molecular systems are the polynuclear aromatics as generated from, e.g. anthracene or acenaphthylene. These systems maintain molecular stability to the highest of temperatures, when the viscosity of the isotropic pitch liquid is at a minimum. This imparts minimum viscosity and maximum stability in the mesophase, resulting in the largest optical texture domain sizes of coalesced mesophase. On the other hand, for the pitches with the highest molecular constituent reactivities (associated with functionality and aliphatic content), polymerization and growth in molecular size, relatively, commence at a lower temperature. Under these conditions, the viscosity of the system is higher. When these reactive mesogens come together to form mesophase the latter assumes the higher reactivity of its constituent molecules and its viscosity increases relatively rapidly. Consequently, the process of further mesogen assimilation is restricted, mesophase growth is retarded, coalescence between spheres does not occur and the optical texture is reduced in size, down to a few

micrometres and, with increasing reactivity, to an isotropic solid.

When the mesogen growth process is slow (relatively) in the pitch of lowest viscosity, there is a tendency for a smaller number of larger-size spheres to form. Alternatively, when a high concentration of reactive molecules exists with a rapid increase in concentration of reacting species, there is a tendency for a larger number of smaller-sized spheres to form, and have limited coalescence ability.

In consideration of the pyrolysis of entire pitch systems, under standard conditions of pyrolysis, the properties and structure of resultant mesophase are determined, dominantly, by the chemical composition, i.e. reactivity of the molecular constituents.

It is against this model of mesophase formation that the results of this kinetic and analytical study of pitch pyrolysis are interpreted.

#### *Correlations of extrographic with kinetic data*

The following relates extrographic with kinetic data for the pitches 1CTP, 4CTP, 8CTP, 9PP and 10PP. The kinetic behaviour of these five pitches are significantly different from each other, as seen from their pyrolyses at 475°C (*Figure 6b*). 9PP reacts the slowest; 4CTP (11.6 wt% QI) does not initiate mesophase until after 60 min residence time; 1CTP (2.6 wt% QI) has about 18 wt% mesophase after 60 min at 475°C, reaching a total of 55% after 180 min; pitch 10PP has the second most rapid mesophase formation with 100% conversion after

only 120 min residence time. 8CTP has a rate of mesophase formation well in excess of the other four pitches.

Figures 1, 2, 3, 4, 6 and 8 can be compared to relate extrography and g.p.c. data to kinetic data. Dominantly, the formation of mesophase, as seen in Figures 6a and 6b, cannot be extrapolated to zero time for the pitches. In particular, for pitch 10PP there is an induction period of about 60 min at 450°C and 20 min at 475°C before mesophase can be seen in the optical microscope. During this time mesophase will be growing by nanometres. Presumably, during this time the centres of growth are being established, but the sigmoidal shape of the curve requires further explanation.

The principal fractions of 1CTP are Fr-II (PAHs <300 amu) and IV (phenols and basic compounds). The principal fractions of 4CTP are the same. For 8CTP the principal fraction is Fr-IV (phenols and basic compounds). For 9PP the principal fractions are Fr-II and III (containing PAH and neutral heteroatomic compounds). For 10PP the principal fractions are Fr-III and IV (mainly constituted by heavy PAHs). Average molecular weights are highest in 10PP, 522 amu (most rapid rates of mesophase formation) and lowest in 4CTP, 269 amu.

Petroleum pitches (9PP and 10PP) can be compared, both having <1 wt% QI. 9PP contains a significant amount of fraction II. The proportion of phenols and basic nitrogen compounds is relatively low. The poly-aromatic nature of these smaller molecules accounts for the slow growth rate of mesophase formation, reaching only 20 wt% at 475°C after 180 min. The larger mean perimeter (~260 µm) of the spheres is indicative of a low viscosity, unreactive mesophase. Pitch 10PP has a dominance of fraction III. The lowest relative weight losses are a consequence of its high average molecular weight. In the industrial preparation of this pitch, by the Ashland Chemical Company, molecules have been created which are closer to the mesogens. Thus, the mesophase formation could begin as soon as the system reaches the minimum viscosity. Hence, the rapid formation of mesophase at 475°C. A much reduced reactivity in the mesophase is illustrated by the total coalescence (low viscosity) of the mesophase system.

Comparing 4CTP with 1CTP, 4CTP produces mesophase at a slower rate. Fractions III, V, VI and VII are very similar; 4CTP has smaller fractions of II and IV. 4CTP has higher TI and QI contents. 4CTP has less oxygen. Prediction of the rate of mesophase growth in these pitches is somewhat blurred. The detail, required in the above model, of molecular size and temperature range of molecular reactivity, cannot be accurately provided, but the higher reactivity of the 1CTP could be associated with the higher content in fraction IV (mainly basic compounds) of 1CTP.

The highest reactivity of 8CTP is clearly associated with its fraction IV, having a high content of reactive phenols and basic compounds, suggested by the analyses of Table 1, so causing extensive formation of mesophase at 425°C. The smallest size of resultant coke optical texture confirms this.

The role of QI in mesophase growth (initiation) requires further investigation. The above results indicate a trend that the slowest rates of formation are, for coal tar pitches, of highest QI content (Figure 9). A suggestion

is that small associations of mesogens could be adsorbed on surfaces of QI so taking growth units initially out of the isotropic pitch phase and introducing an induction period. But, differences between QI materials, shape, size and agglomeration could be additional controlling parameters.

In summary, the approaches of Greinke<sup>5</sup> and Greinke and Singer<sup>16</sup> describe the change in composition of a given pitch system. Such studies are detailed and time-consuming. This alternative approach of predicting the pitch/mesophase transition from pitch analyses is indicative. The above model of mesophase formation can be understood in general terms of that description, with extrography providing information consistent with the model.

## CONCLUSIONS

Extrography, as a technique, shows differences in chemical composition between coal tar pitches of different origin and between petroleum-derived pitches.

The pitches used exhibit a wide range of mesophase formation rates in the temperature range 425 to 475°C. The variation of rate with temperature is a specific property related to pitch composition.

The correlation of extrography data with kinetic data further assists the understanding of those chemical factors which control rates of mesophase growth and the physical characteristics of the mesophase as it is developed.

QI in coal tar pitches may influence both mesophase growth processes as well as mesophase coalescence processes, but further studies, involving QI characterization are required.

## ACKNOWLEDGEMENTS

The authors would like to thank DGICYT, Project No. PB87-0456 and FICYT for financial support.

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