JOURNAL OF MATERIALS SCIENCE 18 (1983) 3736–3742

Solubility and susceptibility of carbonaceous quinoline-insoluble substances including mesophase material in the co-carbonization process

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The solubility and susceptibility of carbonaceous quinoline-insoluble substances (QI) including mesophase material were studied in co-carbonizations with pitch-based materials by evaluating the homogeneity and the size of the anisotropic optical texture in resultant cokes. The efficacy of co-carbonization is attributed to the nature of both the QI substance and pitch-based materials. The order of the modifying ability of the partner is CP–BS < KP–BS < A240 < H-A240 and may be related to H/C ratios, *fa* values and *Rnus* (number of naphthenic rings per structural unit)/*Rtus* (number of total rings per structural unit). The hydrogen donating ability of the pitch material may be the most important property able to modify the non-fusible QI. The order of ability to be modified of the QI substances (susceptibilty) is KPQI–EtBS > soft mesophase > hard mesophase > KPQI. These abilities appear to be related to their fusibility and dependent upon their chemical structure defined by their origin and heat-treatment history. The molecular weight (extent of condensation) and the hydrogen content (favourably naphthenic hydrogen) of the components may be the most important factors. This approval is relevant to the preparation of suitable carbon fiber precursors from QI material including mesophase.

1. Introduction

Production of carbon fibres of high performance derived from mesophase pitch is one of the most attractive targets of modern carbon technology [1, 2]. The key step is the production of suitable mesophase which should show good orientation of the stacked condensed aromatic molecules, be stable and spinable at moderate temperatures below its thermal decomposition temperature and be reasonably reactive at temperatures below its melting point for oxidative condensation to induce the necessary thermosetting characteristic. In order to satisfy such contradictory requirements, various techniques have been reported. The basic ideas can be classified into three categories:

1. Simple condensation or carbonization of suitable sources such as acenaphthylene or tetrabenzophenazine.
2. Separation or fractionation of a suitable mesophase fraction formed during or after the condensation or carbonization reaction.
3. Modification of mesophase pitch prepared through conventional condensation or carbonization processes.

Some approaches using these ideas are reported in [3–6].

In this paper, the solubility and modifying ability of carbonaceous quinoline-insoluble substances (QI) including mesophase materials were studied in several systems at the elevated temperatures to examine the applicability of the above third approach. The homogeneity and the size of anisotropic textures in the resultant co-carbonized coke may indicate the solubility and susceptibility of QI in the system. The pitch-derived co-carbonization partner is able to modify the carbonization

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TABLE I Properties of pitch derived materials used in co-carbonizing

Sample	Preparative procedure	H/C	*fa**	*Rnus/Rtus*†
CP–BS	BS fraction of coal-tar pitch	0.72	0.91	0.00
KP–BS	BS fraction of Kureha pitch	0.66	0.94	0.00
A240	products of Ashland Petroleum Co.	0.75	0.88	0.09
H-A240	hydrogenated A240 using Li-ethylenediamine	1.22	0.55	0.38

*Carbon aromaticity.
†Rnus: number of naphthenic ring per unit structure.
Rtus: number of ring per unit structure.

properties of QI via dissolution and chemical reactions.

2. Experimental details

The co-carbonizing system of QI and pitch derived materials including mesophase used in the present study are listed in Tables I and II, respectively. Ashland A240 pitch (A240) and its hydrogenated derivative (H-A240) with Li–ethylenediamine [7–10] and benzene-soluble fractions of coal-tar pitch and Kureha pitch (abbreviated as CP–BS and KP–BS, respectively) were selected as co-carbonization partners and are soluble in quinoline. Preparative procedures of QI from Kureha pitch (KP–QI), its reductively ethylated derivative (KPQI–EtBS) [11, 12], and mesophase materials from Kureha pitch [8] (KPmeso400 and KPmeso480), heat-treated solvent refined coal pitch [13, 14] and its mesophase material (SRC410, SRCmeso420) are described in Table II.

The homogeneity and the size of the anisotropic textures in the resultant co-carbonized coke were evaluated using optical microscope. The co-carbonization was carried out in a pyrex tube. The heating rate, the soaking temperature and time were 600° C h^{-1}, and 580° C and 1 h, respectively. The partner and QI were well mixed before the co-carbonization.

3. Results

Micrographs of co-carbonized cokes from KP–QI and the modified QI (KPQI–EtBS) with partners are shown in Figs. 1 and 2, respectively. KP–QI was, when singly heat-treated, non-fusible to produce non-graphitizable isotropic carbon powders (Fig. 1a). When QI was co-carbonized with a large amount of partner (90 wt %), those remaining isotropic in the resultant cokes were in the order of CP–BS (Fig. 1b) > KP–BS (Fig. 1c) > A240 (Fig. 1d) H-A240 (Fig. 1e and f). The anisotropic development from the partners, which all exhibited flow texture when singly carbonized, was disturbed by the QI, the extent of disturbance being observed in the same order described above. Although the modifying activities of A240 and H-A240 were not apparently different when using 90 wt %, differences were detected by reducing the amount added. At 60 wt % of partner, QI particles, when co-carbonized with A240, dispersed totally in the resultant coke, with a major portion being found in the medium mosaic texture (Fig. 2a). In contrast, a considerable proportion was dissolved or deformed using HA240 (Fig. 2b), so allowing some development of flow type optical texture, although the major regions were of coarse grain mosaic.

When KPQI–EtBS, which was solubilized in benzene by the reductive ethylation, was co-carbonized with A240 (A240 content: 60 wt %), the regions of QI substance (fine mosaic texture) were surrounded by those of flow anisotropy from A240 pitch. When co-carbonized with H-A240, no trace of mosaic texture was observable in the resultant coke, the flow texture of relatively large

TABLE II Description of quinoline-insoluble (QI) materials

Sample	Preparative procedure	yield	H/C
KP–QI	QI fraction of Kureha pitch	30*	0.46
KP–QI–Et–BS	BS fraction prepared from KP–QI by reductive ethylation	60	0.82
KPmeso400	mesophase extracted from KP–QS, heat-treated at 400° C for 6.5 h	50*	0.48
KPmeso480	mesophase extracted from KP–QS, heat-treated at 480° C for 2 h	80*	0.44
SRC410	heat-treated SRC No. 2 pitch at 410° C for 2 h	94	0.59
SCRmeso420	mesophase extracted from SRC No. 2 heat-treated at 420° C for 2 h	18	0.54

*extraction solvent: quinoline.

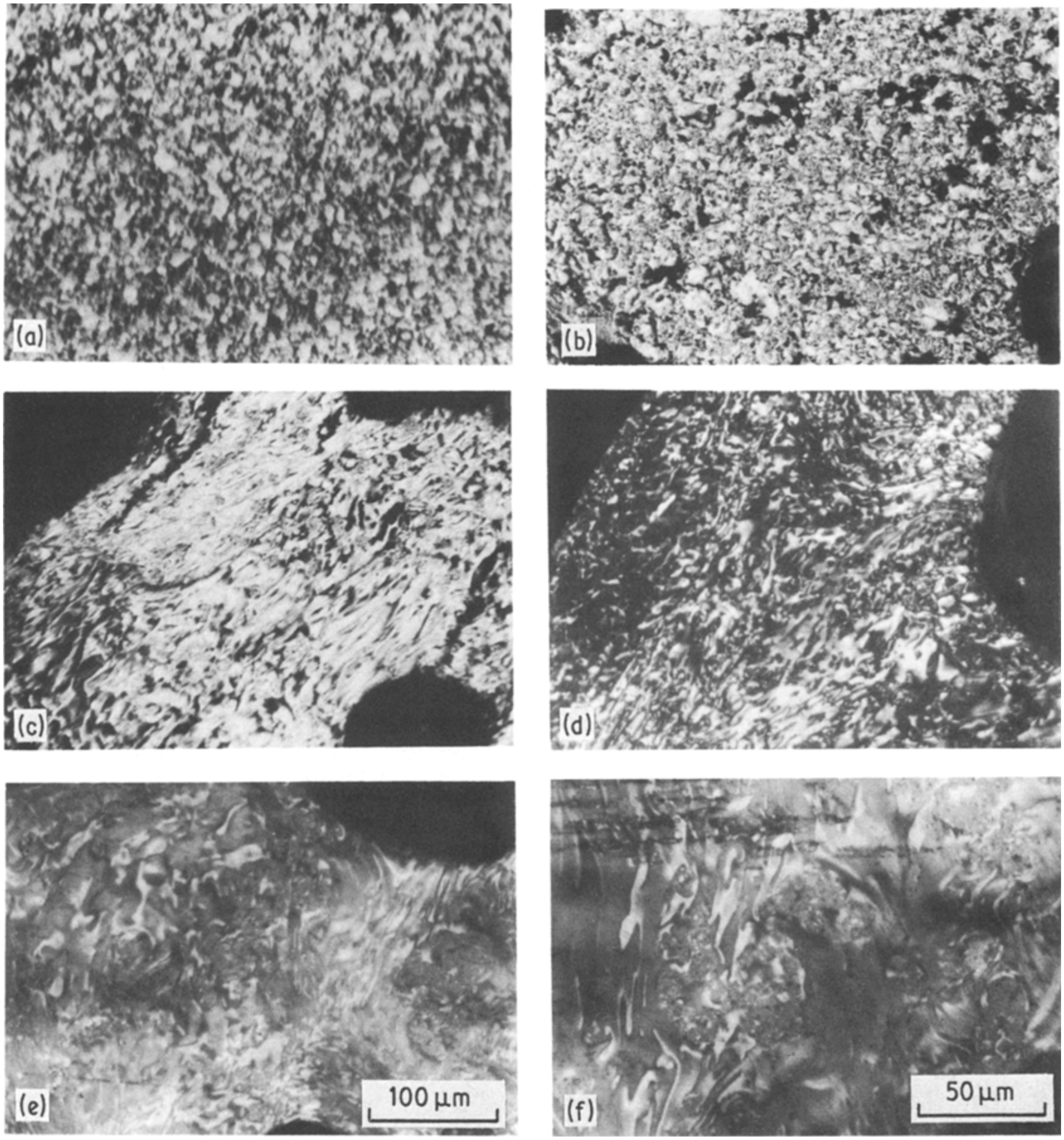

Figure 1 Microphotographs of coke surfaces obtained by the co-carbonization of KP–QI with various partners. Amount of partners: 90 wt%, HTT: 580° C. Partners: (a) none, (b) CP–BS, (c) KP–BS, (d) A240, (e) and (f) H-A240.

size prevailing over the overall surface as shown in Figs. 2d and e.

Figs. 3a and d show the microphotographs of the co-carbonized coke of the mesophase materials extracted from the heat-treated quinoline soluble fraction of Kureha pitch (KP–QS) at 400 and 480° C (KPmeso400 and KPmeso480), respectively. KPmeso400 can be named "soft mesophase", consisting principally of the bulk mesophase immediately after the coalescence with a small amount of anisotropic spheres. On the other hand, KPmeso480 was "hard mesophase" which exhibited completely coalesced anisotropy in the surface. Both materials were non-fusible so that their optical texture and shapes after grinding were not changed by further heat-treatment. The soft mesophase (KPmeso400), however, had the homogeneous appearance of flow texture by following co-carbonizations with both A240 and H-A240 (60 wt%) as shown in Figs. 3b and c, indicating its dissolution and high susceptibility with both partners. In contrast, the hard mesophase particles neither dissolved nor fused, staying as anisotropic units in the resultant coke (Figs. 3e and f), so pro-

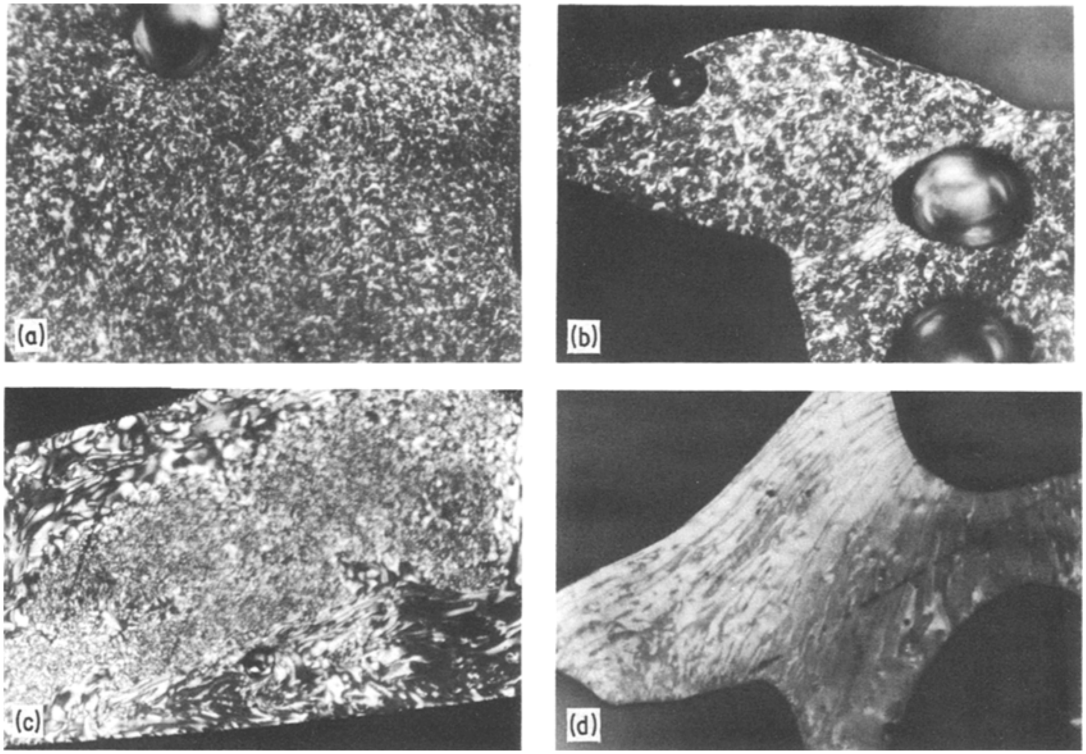

Figure 2 The modification effects on KP–QI during the co-carbonization with A240 and H-A240. Amount of partner: 60 wt %, HTT: 580° C; (a) KP–QI with A240, (b) KP–QI with H-A240, (c) KP–QI–Et–BS with A240, (d) and (e) KP–QI–Et–BS with H-A240.

viding a hetereogenous appearance, although regions of flow texture probably originating from the partners were also observable.

The heat-treated SRC-No. 2 pitch at 410° C (SRC410), which consisted of some small coalesced spheres in the major isotropic matrix (Fig. 4a), provided the flow texture in the co-carbonization with H-A240 (60 wt %, Fig. 4c), although the pitch gave fine mosaic texture when singly carbonized (Fig. 4b), indicating its complete solubility in H-A240 even after heat-treatment.

The heat-treatment at the slightly higher temperature of 420° C increased considerably the anisotropic content in the SRC pitch. Fig. 5a is a microphotograph of the mesophase extracted from SRC-No. 2 pitch heated at 420° C (SRCmeso420). This mosaic mesophase was co-carbonized with A240 (60 wt %) to give fine mosaic cokes, although coarse mosaic textures were observed locally (Fig. 5b). With H-A240 (60 wt %), the enlargement of the size and the elongation of anisotropic units were observed throughout the cokes, although some heterogeneous appearance still remained in the flow texture regions which may derive from H-A240.

Thus, the modifying ability of heat-treated pitch with a co-carbonizing partner was very sensitive to the temperature of treatment as well as carbonaceous sources.

4. Discussion

A co-carbonization technique has been reported to be successful to provide flow or anisotropic texture from poor carbonaceous sources in the production of the needle and blast furnace cokes, respectively, using proper co-carbonization partners or additives [13–18]. This technique relies on

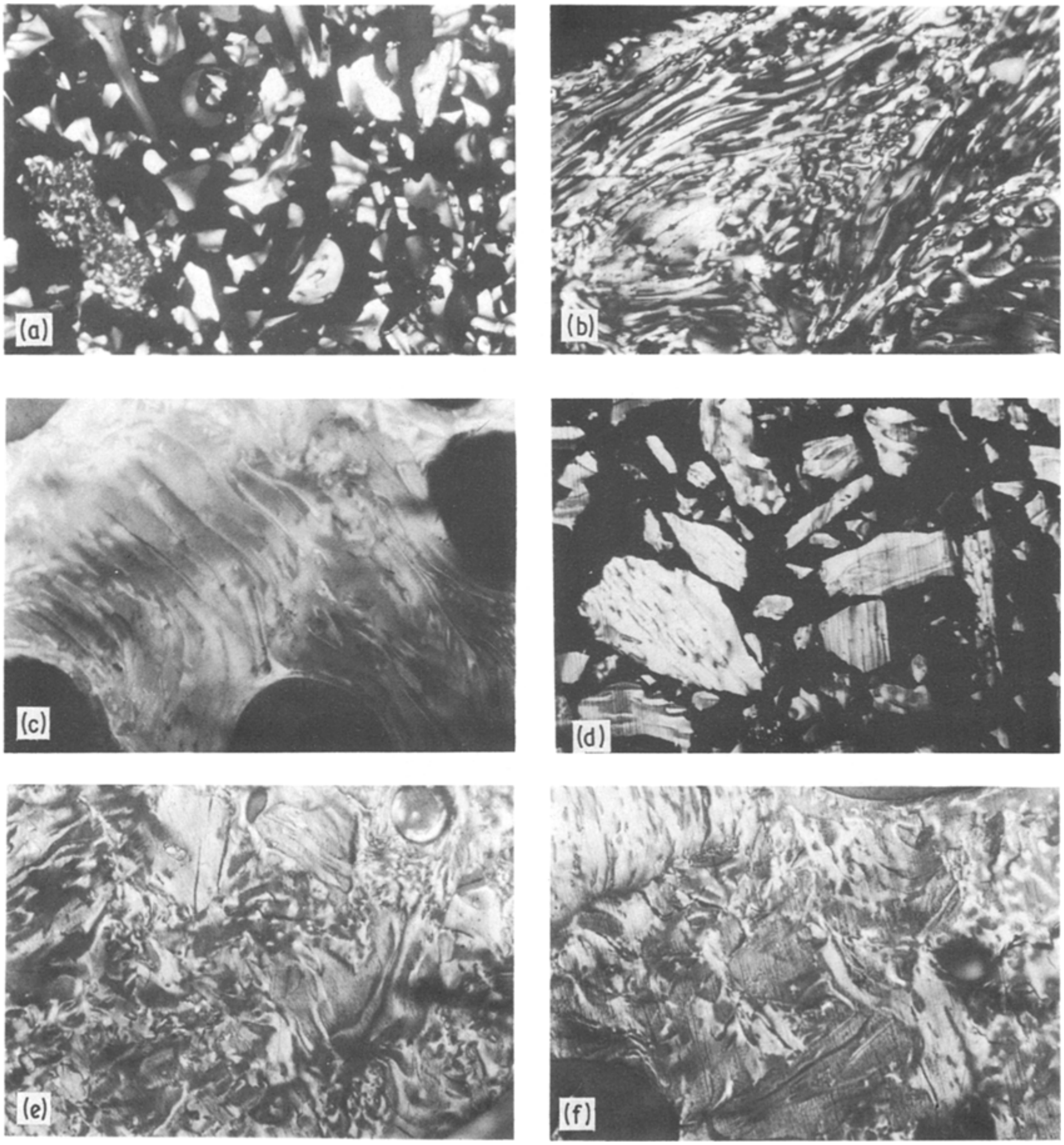

Figure 3 Microphotographs of coke surface obtained by the co-carbonization of KPmeso with partners. Amount of partner: 60 wt%, HTT: 580° C; (a) KPmeso400, (b) KPmeso400 with A240 (c) KPmeso400 with H-A240, (d) KPmeso480 (e) KPmeso480 with A240, and (f) KPmeso480 with H-A240.

the modification of the carbonization system by the partners because of improved fusibility and reactivity of the carbonizing system for the anisotropic development. This technique should be applicable to the preparation of carbon fibre precursor by careful selection of carbonaceous sources and partners. Since QI including mesophase materials often consists of large, highly aromatic molecules suitable for ordered stacking, it can be an excellent precursor when the fusibility at the spinning temperature can be created by proper treatment. With this objective, Otani *et al.* [5] and Yamada *et al.* [6] hydrogenated heat-treated pitches, using Li–ethylenediamine and tetrahydroquinoline, respectively. These procedures include separation steps of hydrogen donative reagents. In contrast, the present partner need not be removed since it can be a component of the precursor. The fusibility endowed by the co-carbonization is evaluated, simply in the present study, by observing the homogeneity and size of anisotropic development in the resultant coke. The co-

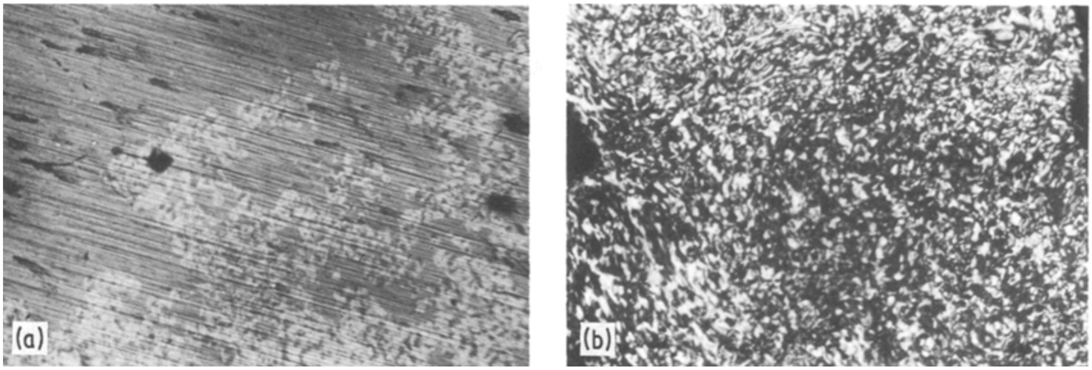

Figure 4 Microphotgraphs of coke surface obtained by the co-carbonization of heat-treated SRC pitch. (SRC410) with H-A240, HTT: 580° C; (a) SRC410 (as prepared), (b) SRC410, and (c) SRC410 with H-A240 (60 wt %).

carbonized product can be a precursor by control of heat-treatment temperature and soaking time.

The efficacy of co-carbonization can be attributed to the nature of both the QI substance and the partner. The modifying ability can be a measure of the efficacy of the co-carbonization [17, 18]. The order of modifying ability against QI including mesophases is CP–BS < KP–BS < A240 < H-A240, as deduced above. It may be related to the H/C ratio, *fa* value, and *Rnus*/*Rtus* as described previously [19]. Above all, the naphthenic hydrogens appear most influential since CP–BS with the least naphthenic hydrogens exhibited the lowest ability. The hydrogen-donating ability may be the most important factor for the modifying ability against the non-fusible QI because partial hydrogenation can induce fusibility

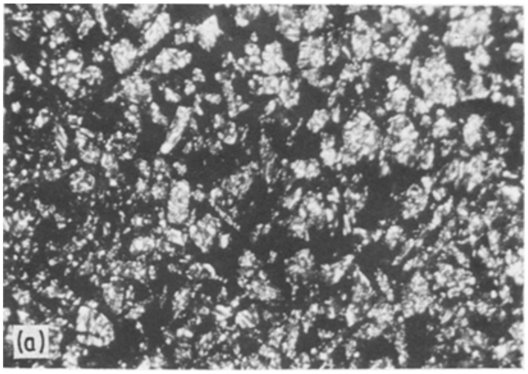

Figure 5 Microphotographs of coke surface obtained by the co-carbonization of SRCmeso420 with partners. Amount of partner: 60 wt %, HTT: 580° C; (a) SRCmeso420, (b) SRCmeso420 with A240, and (c) SRCmeso420 with H-A240.

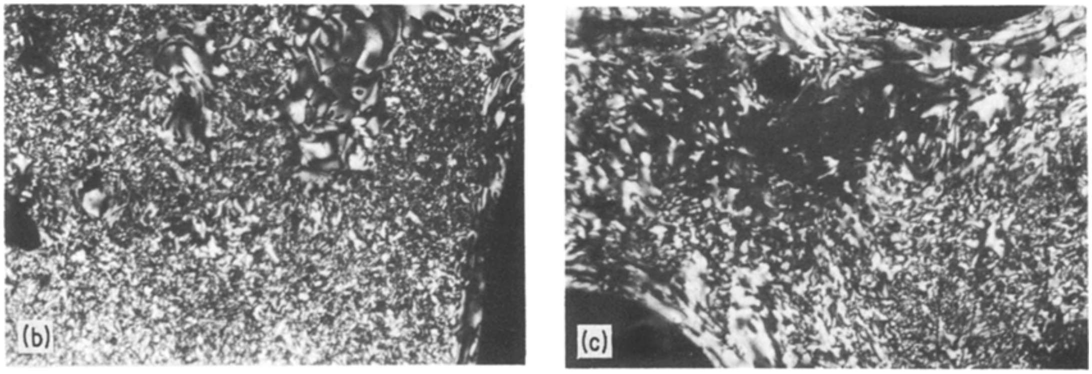

TABLE III Properties of solubilized fractions from QI by reductive ethylation [8, 9, 12]

Sample	Yield (wt %)	H/C	AMW†
KP–QI	63	0.82	3000
KPmeso400	89	0.81	2790
KPmeso480	47	0.88	1550

*Yield of solubilized fraction after reductive ethylation.
†Average molecular weight.

from non-fusible coals [20] and QI fractions [10, 11].

The present QI substances are arranged in the following order of modifying susceptibility, KP–QI–Et–BS > KPmeso400 > SRC410 > SRCmeso420 > KPmeso480 > KP–QI. As the structural comparison of mesophase spheres and KP–QI in previous papers [8, 9, 21] indicates the average molecular weight, molecular weight distribution (the size of unit structure and the degree of condensation), hydrogen content, and the extent of substitution may be different among QI substances including mesophase materials used in the present study. Table III summarizes yields and analyses of solubilized fractions by the reductive ethylation of KP–QI, KPmeso400 and KPmeso480. Significant difference in yield is correlated with susceptibilities by A240. Although the analyses of the solubilized fractions appear much the same, the non-solubilized fraction, which is dominant, for example, in the KPmeso480, may be highly condensed (higher molecular weight) and severely dehydrogenated as its H/C ratio before the ethylation indicates and hence is hard to modify. Thus, the material, heat-treated severely or more extensively carbonized tends to lose its co-carbonization susceptibility.

The co-carbonization susceptibility of the QI substances can be improved by chemical treatment. Increased solubility of a QI substance by the reductive ethylation clearly improved it with the hydrogen donating H-A240, although non-hydrogenated A240 failed to be modified. Hydrogen transfer may take place effecively while the alkylated QI is soluble in the partner during the co-carbonization. Dealkylation in the non-hydrogen donative partner eliminates the solubility from the ethylated QI [12], so no effective modification occurs.

Preparative procedures of the mesophase may also influence its susceptibility to be modified. Fusibility may be most important for the reasons given above. Lower molecular weight and/or higher hydrogen content (favourably naphthenic hydrogen) of the components appear to be essential.

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Received 6 December 1982
and accepted 22 April 1983