JOURNAL OF MATERIALS SCIENCE 26 (1991) 4836–4844

Structure and stabilization reactivity of mesophase pitch derived from f c c-decant oils

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Structure and stabilization reactivities of three mesophase pitches (MP-1–3) derived from fluid catalytic cracking (f c c)-decant oils were compared to reveal the structure–reactivity correlation in the stabilization reaction, which is the slowest step of the pitch-based carbon fibre production. Analyses of the toluene soluble fraction in mesophase pitches using ^{1}H-, ^{13}C-nuclear magnetic resonance (NMR), infrared and FD-mass spectroscopy suggested that the most abundant molecules in MP-2 and MP-3, which should have the highest and lowest softening points, respectively, consisted of a 7-ring aromatic skeleton with two phenyl groups, molecular weight 478 and a 10-ring aromatic skeleton with a phenyl and four methyl groups, molecular weight 556, respectively. MP-3 exhibited much more rapid stabilization and oxygen up take than MP-2. The analysis of stabilized fibre with Fourier transform-infrared spectroscopy indicated that the oxidative stabilization consisted of the following three steps: (1) oxygen up take to produce functional groups such as carbonyl, phenolic and ether groups; (2) growth of the aromatic ring; and (3) molecular association through hydrogen bonding. The first step of oxidation occurred at substituent alkyl, naphthenic and isolated aromatic hydrogens in the mesogen molecules regardless of the mesophase pitches. The reactivity of the mesophase pitch appears to be correlated to the number of such groups present.

1. Introduction

Pitch-based carbon fibres have been recognized as excellent fillers for the advanced composite. However, they still suffer the problems of high cost and insufficient properties [1]. The balance of the spinning properties and stabilization reactivity of the constituent molecules in the mesophase pitch is still a matter of much concern [2, 3]. It is most relevant to attempt to solve the structure of mesophase pitch at its molecular level in relation to its properties and to find procedures to synthesize the constituent molecules with designed structure.

In previous papers [4, 5] the authors compared the structure and reactivity of mesophase pitches derived from a coal tar and an f c c-decant oil (DO) and found significant differences in their structures in relation to their reactivity and the molecular shapes of the stabilized pitches with respect to stabilization temperature. The mesophase pitches, even from f c c-DOs, are known to be very different depending on the variety of f c c-DO and the method of mesophase pitch preparation. There are several reports on the mechanism of stabilization, however, the detailed structural analyses are not satisfactory [6–10].

In the present study, three mesophase pitches, all derived from f c c-DOs of different origin and through different procedures, were comparatively investigated in terms of the chemical structure of their constituents, spinning properties and stabilization reactivities. Because the structure of mesophase pitch is rather diverse, it may be appropriate to analyse the several fractions in the mesophase pitch separately, using a variety of analytical approaches suitable for the respective fraction. 400 MHz NMR for both ^{1}H and ^{13}C and FD-MS are very helpful. Fourier transform-infrared spectroscopy (FT-IR) provides additional information on the functional groups. Such procedures are also applicable to the definition of the stabilization scheme from the view of structural chemistry.

2. Experimental procedure

2.1. Mesophase pitches

The three kinds of mesophase pitches derived from f c c-DOs were analysed in the present study. Their general properties are summarized in Table I. The pitches were extracted with toluene and pyridine in Sohxlet for their detailed analyses.

The toluene soluble fractions were analysed by the elemental analysis, 400 MHz ^{1}H- and ^{13}C-NMR (Varian XL-400), FT-IR (Jeol 100) and FD-MS. ^{13}C-NMR was measured by the gated decoupling method using relaxation reagent chromium(III) acetylacetonate [11]. GASPE method [12] was used to quantify the internal quaternary carbons.

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Toluene insoluble–pyridine soluble (TI–PS) and pyridine insoluble (PI) fractions were analysed by FT-IR in addition to elemental analyses.

2.2. Stabilization and carbonization procedures

These mesophase pitches were spun into fibres (diameter 10 µm) from a steel spinneret (the length, L, and diameter, D, of nozzle were both 0.4 mm, $L/D = 1$) by applying a nitrogen pressure of 0.12 MPa. The pitch fibres were stabilized in an air flow at 543 K for variable periods of time. The heating rate was fixed at 5 K min^{-1}. The stabilized fibres were characterized by elemental analysis and FT-IR.

TABLE I Properties of mesophase pitches

	AP (%)	SP (K)	H/C	Solubility (%)		
				TS	TS–PS	PI
MP-1	100	518	0.54	30	14	56
MP-2	100	538	0.53	20	18	62
MP-3	100	508	0.56	49	6	45

SP = softening point, AP = anisotropic per cent, TS = toluene soluble, TI–PS = toluene insoluble–pyridine soluble, PI = pyridine insoluble.

The stabilized fibre was further carbonized at 873 K for 1 h to determine the time taken for complete stabilization.

3. Results

3.1. Properties and structures of mesophase pitches derived from fcc-DOs

Although the three mesophase pitches commonly exhibited 100% anisotropy with flow domain texture, their softening points were fairly different from 508 K for MP-3 (lowest) to 538 K for MP-2 (highest), reflecting their H/C values and solubilities (summarized in Table I). A larger H/C value and solubility in toluene corresponds to lower softening point.

3.1.1. TS fraction

The FD-MS spectra of TS fractions in MP-2 and MP-3 pitches are illustrated in Fig. 1. The TS fraction of MP-2 pitch exhibited broader molecular weight distribution, its molecular weight ranging from 300–650. Major peaks were observed at 340, 404, 454,

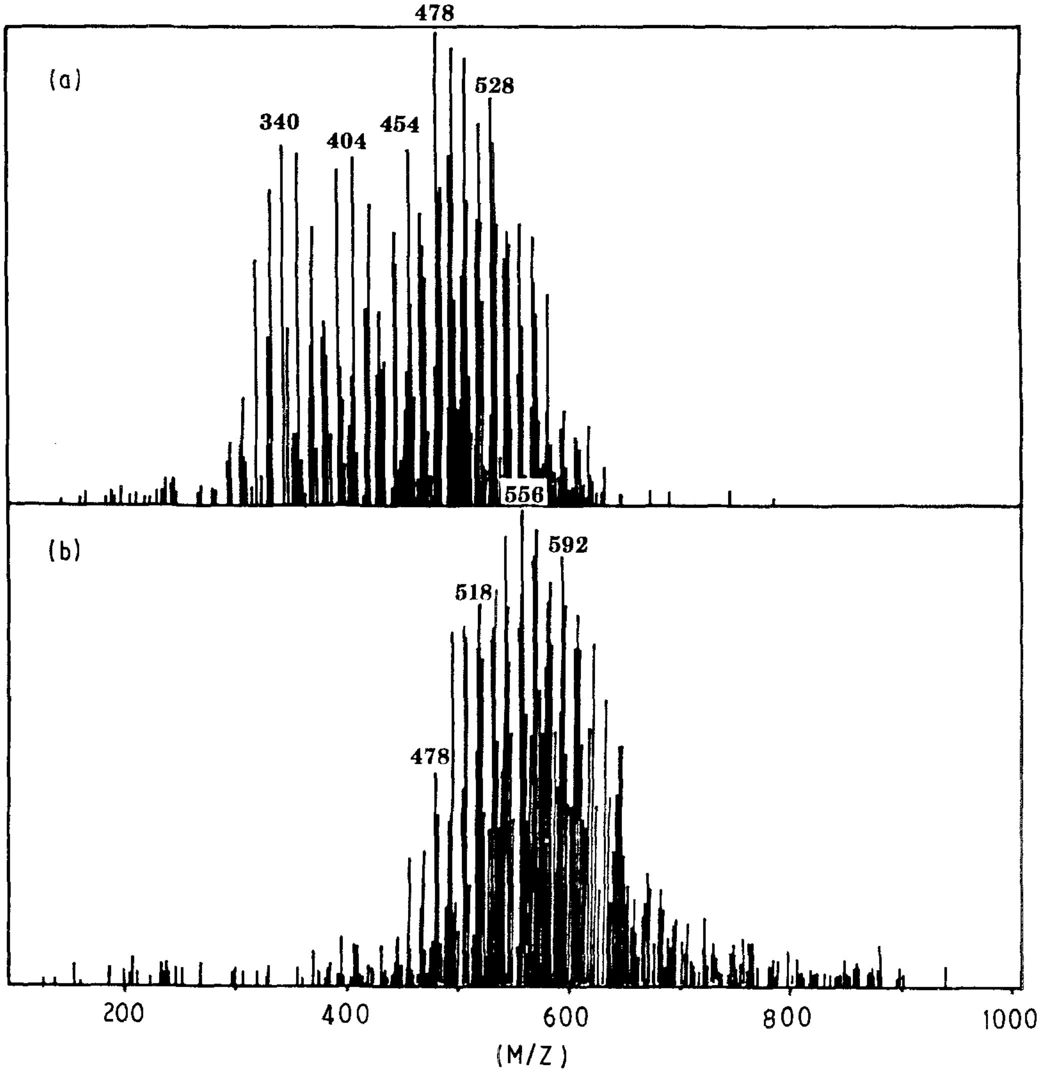

Figure 1 FD-MS spectra of TS fraction in pitches (a) MP-2, (b) MP-3.

478 and 528. These major peaks had satellite ones separated by 14 (M/Z).

The principal molecular weight of the fraction in MP-3 pitch was distributed in the similar manner but rather sharply in the range of 450–700 with minor peaks of higher molecular weight less than 900. Major peaks were found at 478, 518, 556 and 592.

The proton and carbon distributions of TS fractions by ^{1}H- and ^{13}C-NMR are summarized in Tables II and III, respectively. Both MP-1 and MP-2 carried the largest content of H_a, around 72%, leading to high f_a values of around 0.92. Aliphatic hydrogens in the fractions were mainly H_α (21%–23%), some H_β (4%–7%) and a little H_γ.

The TS fraction in MP-3 was much less aromatic, exhibiting H_a of 62% and an f_a value of 0.88. Its aliphatic hydrogens were mostly H_α (25%), H_β and H_γ occupying 12% and 1%, respectively. According to Brown–Ladner analyses [13], MP-3 pitch has the largest number of naphthenic hydrogens and alkyl substituents.

Carbon distributions of TS fractions by ^{13}C-NMR are illustrated in Fig. 2, where Car-4.1, Car-4.2, Car-4.3, Car-3, Cal-2 and Cal-1 are indicated "ar" indicating aromatic, and "al" aliphatic. They are identified [14] and quantified in Table III. Car-3 included inner quaternary aromatic carbon which is abbreviated as Car-3.2. It seems reasonable that a boarder peak at 127 p.p.m. is ascribed to Car-4.3 and Car-3 because aromatic molecules in the mesophase pitches may have some bent bonds as found in phenanthrene [15]. The present pitches showed very similar distributions, where the largest peak was for Car-3 and the second largest for internal quaternary Car-3.2 and Car-4.3. Rather limited quantities of Car-4.1 and Car-4.2 and a very little Cal-1,2 were common to pitches. Nevertheless some details were different. The ratio of Car-3.2/Car-4.3 as unity with MP-3, while MP-2 had the smallest ratio of 0.73. MP-1 and MP-3 showed similar values of Car-4.1 + Car-4.2 (18% and 17%, respectively). However, MP-1 carried for fewer aliphatic carbons and, hence, is estimated to have more phenyl–phenyl bonds. MP-2 had the smallest value of Car-4.1 + Car-4.2 and a larger one for Cal-1, hence the least number of phenyl–phenyl bonds.

Fig. 3 shows the infrared spectrum of the TS fractions which were again very similar. Some differences were still observable in the relative intensities of bands at 3030 and 2930 cm^{-1}, at 1600 and 1440 cm^{-1} and at 880 and 750 cm^{-1}, which are identified as aromatic and aliphatic C–H (stretching); aromatic C=C and aliphatic C–H (bending); and isolated and 1,2-di-substituted aromatic C–H, respectively [16, 17]. Hence the intensity ratios of 3040/2930, 1600/1440 and 880/750 indicate the aromaticity (former two) and the number of substituents. The intensity ratios of 1600/1440 and 880/750 increased in the order of MP-1 < MP-2 < MP-3, and MP-2 < MP-3 < MP-1, respectively, indicating increasing amounts of alkyl side chains and number of aromatic substituents.

3.1.2. TI–PS and PI fraction

TI–PS fractions were minor in the mesophase pitches of the present study. Their H/C values were 0.54, 0.56

TABLE II Proton distribution and Brown-Ladner [13] parameters of the mesophase pitches

	H_a	H_α	H_β	H_γ	f_a	σ	R_{nus}	C_{side}
MP-1								
TS (%)	72.5	22.6	4.3	0.7	0.92	0.13	0.54	1.73
TI–PS (%)	70.8	20.8	7.0	1.5	0.93	–	–	–
MP-2								
TS (%)	71.8	21.0	6.5	0.7	0.91	0.13	0.33	2.23
TI–PS (%)	71.6	19.2	6.7	2.5	0.92	0.11	–	–
MP-3								
TS (%)	61.8	24.7	12.4	1.1	0.88	0.16	1.15	1.91
TI–PS (%)	55.5	25.5	14.8	4.1	0.88	0.17	–	–

H_a = aromatic hydrogen (6–9 p.p.m.), H_α = α-hydrogen (2–4 p.p.m.), H_β = β-hydrogen (1.1–2 p.p.m.), H_γ = γ-hydrogen (0.3–1.1 p.p.m.), f_a = aromaticity, σ = degree of substitution of aromatic nucleus, R_{nus}: number of naphthenic rings per unit structure, C_{side}: number of side chains per unit structure.

TABLE III Carbon distribution of TS fractions in the mesophase pitches

	Aromatic (%)^a					Aliphatic (%)^b		f_a
	Car-4.1	Car-4.2	Car-4.3	Car-3.1	Car-3.2	Cal-2	Cal-1	
MP-1	8	10	16	60	13	2	3	0.95
MP-2	5	9	15	64	11	3	4	0.93
MP-3	6	11	14	61	14	3	5	0.92

[a] Car-4.1 = internal benzonaphthenic carbon (138.0–150.1 p.p.m.), Car-4.2 = substituted carbon (133.1–138.0 p.p.m.), Car-4.3 = outer quaternary carbon (127.0–133.1 p.p.m.), Car-3.1 = protonated carbon (116.9–127.0 p.p.m.), Car-3.2 = inner quaternary carbon (116.9–127.0 p.p.m.).

[b] Cal-2 = methylene carbon (21.9–54.2 p.p.m.), Cal-1 = methyl carbon (8.5–21.9 p.p.m.).

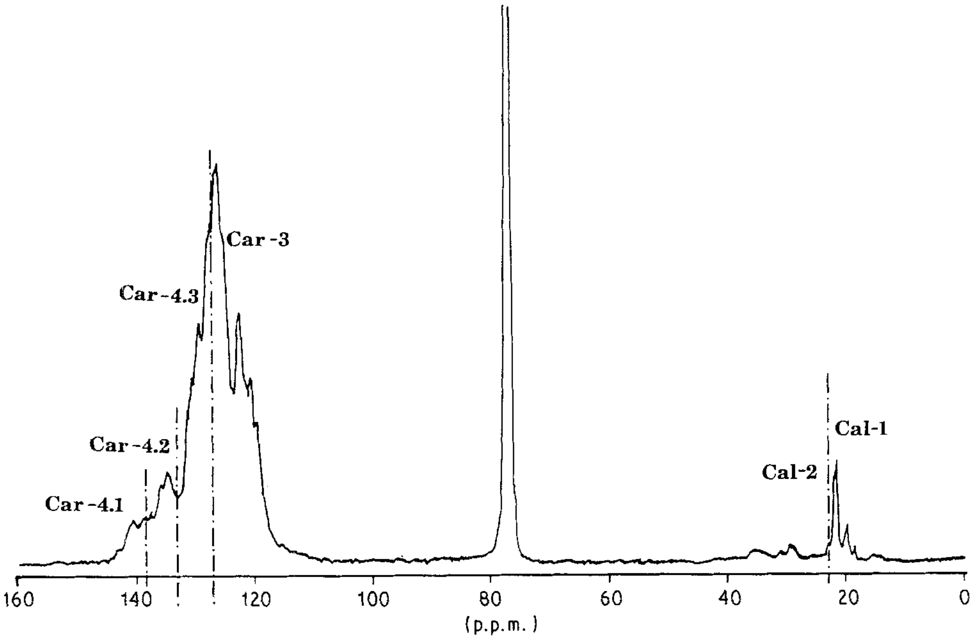

Figure 2 ^{13}C-NMR spectrum of TS fraction of MP-2.

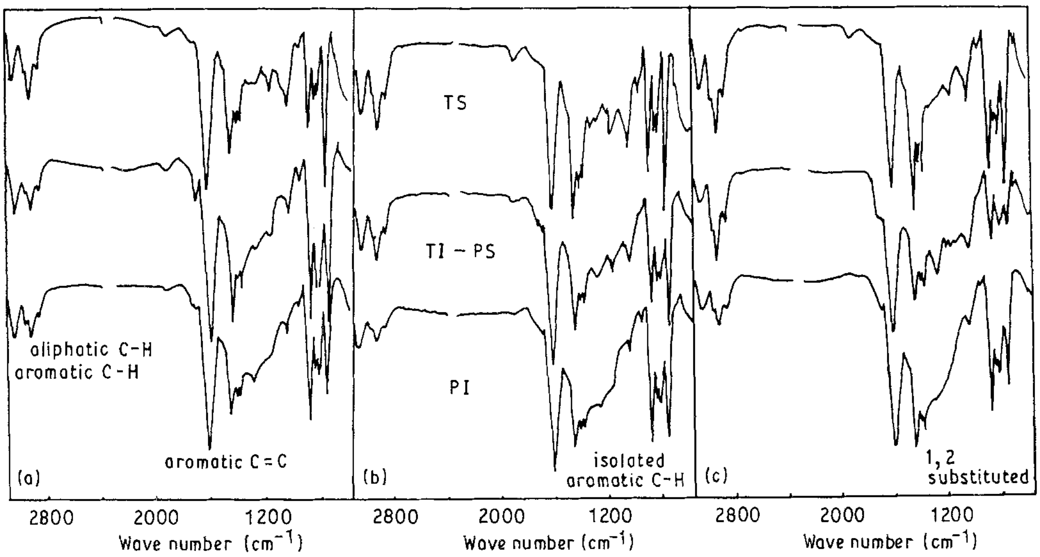

Figure 3 FR-IR spectra of fractionated mesophase pitches. (a) MP-1, (b) MP-2, (c) MP-3.

and 0.54 for MP-1, 2 and 3, respectively, and certainly less than those of corresponding TS fractions.

Proton distributions of the fractions in MP-1 and 2 (shown in Table II) were very similar. MP-3 carried much larger H_α and H_β and slightly larger H_γ contents. The aliphatic nature of MP-3 was definite.

Fig. 3 illustrates the infrared spectra of the fractions. The relative intensities of bands at 3040/2970, 1600/1440, and 880/750 cm^{-1} were larger than those of the TS fraction, indicating less aliphatic substitution and high aromaticity.

These tendencies were further emphasized in PI fractions. MP-1 pitch exhibited a large increase of relative intensity at 880/750 cm^{-1} and a small increase at 1600/1440 cm^{-1}, while MP-2 pitch exhibited a large increase of relative intensity at 1600/1440 cm^{-1} and a small increase at 880/750 cm^{-1}. MP-3 pitch showed some increase of relative intensities at both 1600/1440 and 880/750 cm^{-1}.

3.2. Reactivity and structural changes of the mesophase pitch fibre during stabilization

Fig. 4 shows the oxygen uptake profiles of MP-1, 2 and 3 during their stabilization at 543 K. MP-1 and MP-2 required 60 min for complete stabilization when 5.4% and 5.6% O_2 were taken up, respectively. MP-3 required 45 min for complete stabilization when 6.8% O_2 was taken up. Thus, oxygen uptake was much more rapid with MP-3 than with other mesophase pitches. It is of value to point out that the profiles

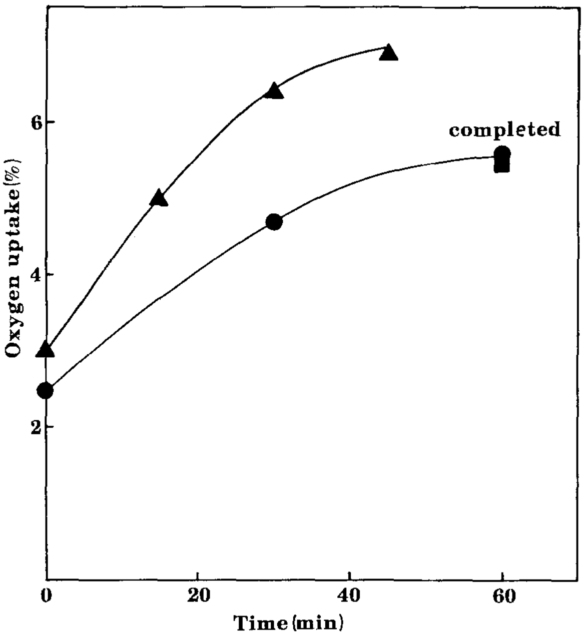

Figure 4 Oxygen up take profile during oxidative stabilization at 543K. (■) MP-1, (●) MP-2, (▲) MP-3.

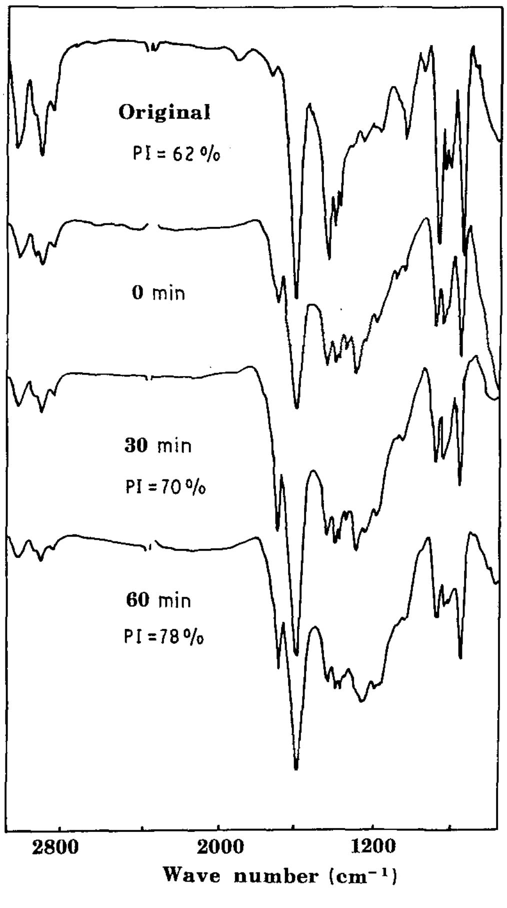

Figure 5 FT-IR spectra of MP-2 pitch fibres stabilized at 543 K.

for the oxygen uptake of MP-1 and MP-2 were much the same.

Fig. 5 shows the FT-IR spectra of a series of whole MP-2 pitch fibres stabilized at 543 K for variable times. In the initial stage of stabilization during the heating to stabilization temperature, the intensity of the band at 1440 cm^{-1} which is ascribed to bending of C–H in CH_2 and CH_3 groups decreased, while bands at 1700 cm^{-1} of C=O and 1280 cm^{-1} of C–O started to appear. In the next step of stabilization, the intensity of the band at 750 cm^{-1} of aromatic C–H on 1,2-disubstituted rings decreased and the band at 1600 cm^{-1} of aromatic C=C increased. In the final step of stabilization, the intensity of band at 830 cm^{-1} (isolated aromatic C–H) decreased and the bands at 1300–1100 cm^{-1} which are identified as the C–O in the oxygen functional groups such as phenol and ether were intensified and broadened to complete the stabilization.

Fig. 6 also illustrates the FT-IR spectrum of PS and PI fractions separated from MP-2 fibres stabilized for a series of times. The PS fraction showed a decrease of intensity at 1440 cm^{-1} and an increase at 1700 cm^{-1} in the initial step. In contrast, the intensity at 3040 cm^{-1} (aromatic C–H) decreased, while intensity at 1280 cm^{-1} (C–O) increased in PI. In the next step (30 min), the intensity at 880 cm^{-1} was reduced and the oxygen functional group appeared in the PS fraction and the PI fraction began to obtain the band at 1700 cm^{-1} (C=O).

Fig. 7 shows the FT-IR spectra of MP-3 fibres stabilized at 543 K. Changes in the spectra during stabilization was very similar but much more rapid than that of MP-2. MP-3 took up oxygen much more rapidly to intensify the oxygen functional groups. However, the increase of PI content was rather slow as indicated in Fig. 6.

4. Discussion

4.1. Structure of mesophase pitches

Three mesophase pitches derived from fcc-DOs exhibited very different reactivity for their stabilization, although they were all much more reactive than those from coal tar pitch [4]. Such reactivities should reflect their chemical structure.

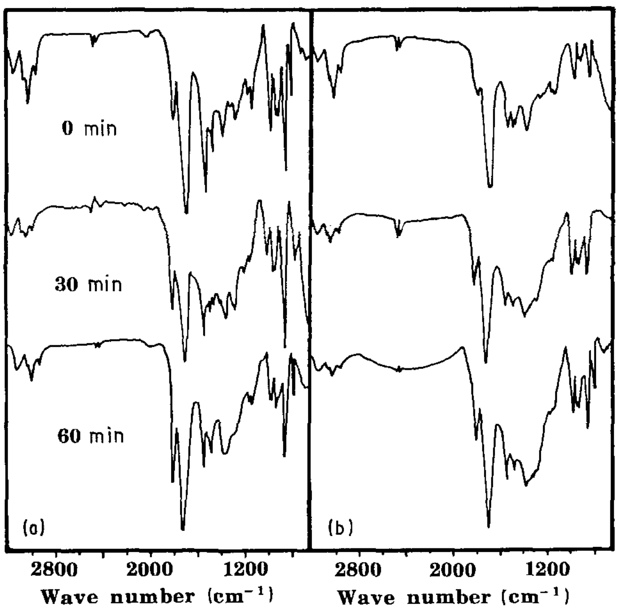

Figure 6 FT-IR spectra of fractionated MP-2 pitch fibres stabilized at 543 K. (a) PS, (b) PI.

Because the mesophase pitch and even its fractions consisted of a large variety of molecules as clearly indicated by FD-MS, adequate structural description is never easy. ^{1}H- and ^{13}C-NMR can be most informative on the structure of its soluble fraction. However, only averaged parameters are obtainable for the mixture of molecules in the fraction. Hence, in the present study, the most abundant molecules of the TS fraction revealed by FD-MS are assumed to carry the structural characteristics suggested by NMR and infrared spectroscopy. It is certain that many of the major peaks in FD-MS are distributed by the intervals of 14 (M/Z), suggesting that constituent molecules may have a series of structures only differentiated by the number of alkyl side chains or methylene bridges. From ^{13}C-NMR, more than 90% of methyl carbon is located in 21.9–17.2 p.p.m., suggesting its direct linkage to the aromatic carbon [15]. Major methyl carbons are ascribed to the peaks at 19 and 21 p.p.m., suggesting their location at the 1 and 2 positions of the aromatic ring.

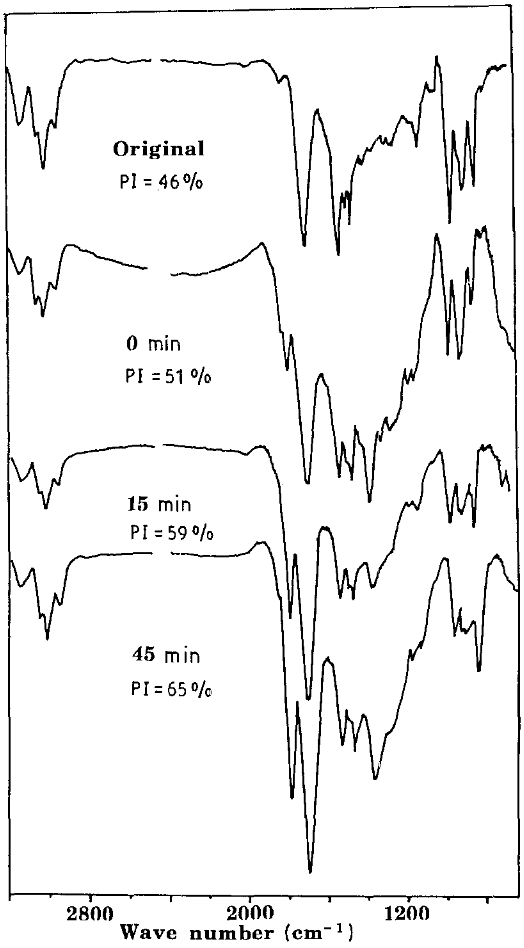

Figure 7 FT-IR spectra of MP-3 pitch fibres stabilized at 543 K.

The most abundant molecules in the TS fraction of MP-2 had mass numbers of 454, 478 or 492. According to ^{13}C-NMR, and H/C atomic ratio, a particular molecule should have carbon of the particular criteria whose contents are summarized in Table III. More methyl groups are found at the 2 position in the TS fraction of MP-2. Very small numbers of methyl carbons are located at 17.2–10.0 p.p.m. compared to the methylene, indicating that major parts of Cal-2 are identified as methylene bridge or naphthene carbons. Thus, ethyl or longer alkyl side chains are ruled out.

The ratio of inner/outer quaternary carbons in Table III suggests condensed rings of six or seven in the molecule of MP-2. When the number of condensed aromatic rings is seven, two or three phenyl groups need to be connected to the condensed ring to account for the number of protonated carbons, Car-3. Two phenyl groups are most probably connected to the major aromatic ring directly or through a methylene bridge. The model-A structure thus estimated, having 478 (M/Z), is illustrated in Fig. 8a(i). When one methyl group connects to an A molecule, the molecular weight becomes 492 which is another abundant one. Other molecular weights are adjusted by adding CH_3 and/or CH_2 groups. If the number of condensed aromatic rings is six and two phenyl groups are connected by methylene bridges as illustrated in Fig. 8a(ii), the molecular weight becomes 454 which is another abundant one. Other molecular weights are again adjustable by adding CH_3 and or CH_2 groups. Calculated carbon distributions of model structures are summarized in Table IV. The model reproduces satisfactorily the distribution observed. Such a series of model structures are consistent with results of infrared spectroscopy. Other molecular weights in the FD-MS suggest other model structures through a similar procedure.

Model molecules of the TS fraction of MP-3 estimated by a similar procedure are illustrated in Fig. 8b. Molecules in MP-3 have a large nucleus of central aromătic rings (about 8) which has an inner/outer quaternary ratio of unity, carrying more phenyl, methyl, methylene and isolated aromatic C–H groups than the molecules in other mesophase pitches. More methyl groups are located at the 1 position. Several molecular models are imaginable. For example, when six central aromatic rings are connected to two phenyl rings and two methyl groups, a naphthalene ring is assumed to be connected by a cyclohexyl ring, as illustrated in Fig. 8b(i), which accounts for the molecular weight of 518. There is another molecule of 10 aromatic rings connected to a phenyl and four methyl groups, which accounts for the molecular weight of 556.

TABLE IV Calculated carbon distribution of estimated model molecules

	Car-4.1	Car-4.2	Car-4.3	Car-3.1	Car-3.2	Cal-2	Cal-1
MP-2	1.9	3.4	5.6	24.0	4.1	1.1	1.5
MP-3	2.6	4.8	6.1	26.7	6.1	1.3	2.2

Estimated molecular weight by FD-MS: MP-2, $M_w = 478$, MP-3, $M_w = 556$.

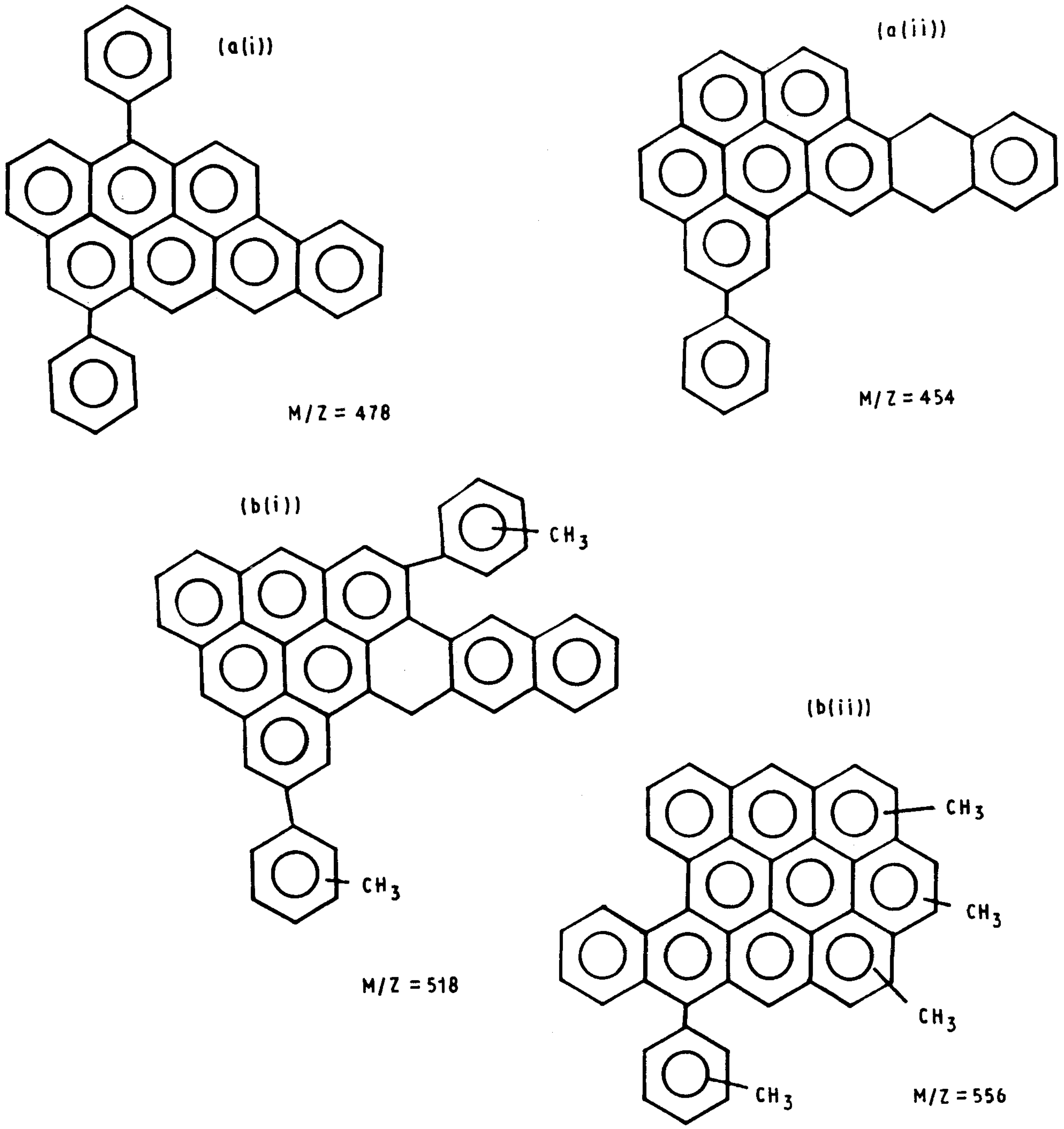

Figure 8 Model structures of TS fractions in mesophase pitches: (a) MP-2, (b) MP-3.

The structure of the insoluble fraction in mesophase pitches is very difficult to determine directly because information based on their FD-MS and high resolution NMR is lacking. Hence, their structure is estimated by assuming that the central nucleus of their structural unit inherits that found in the molecules of TS fraction in the same mesophase pitch. Infrared spectroscopy is believed to indicate the differences between two corresponding molecules. Then the structure model molecules of PI fractions are discussed. It should be noted that we have no information on their molecular weight.

The infrared spectra of the PI fraction exhibited marked decreases of CH_2 and CH_3 groups and four neighbouring aromatic C–H bonds by the reduced intensities of the bands at 2930, 1440 and 750 cm^{-1} respectively, suggesting a decrease in aromatic substitutions such as alkyl side chains, methylene and aryl–aryl bridges.

The PI fraction in MP-2 lost markedly the intensity of the band at 1440 cm^{-1}, taking account of a number of alkyl side chains, suggesting a model molecule in Fig. 9a. The fraction in MP-3 showed the most moderate reduction, although its aromatic ring is certainly more condensed. The model molecule maintains the most alkyl side chains and isolated aromatic C–H among the molecules of the PI fractions as its TS fraction does.

4.2. Scheme and reactive sites of the stabilization reaction

The stabilization reaction of the present mesophase pitches at 543 K proceeds via oxygenation and

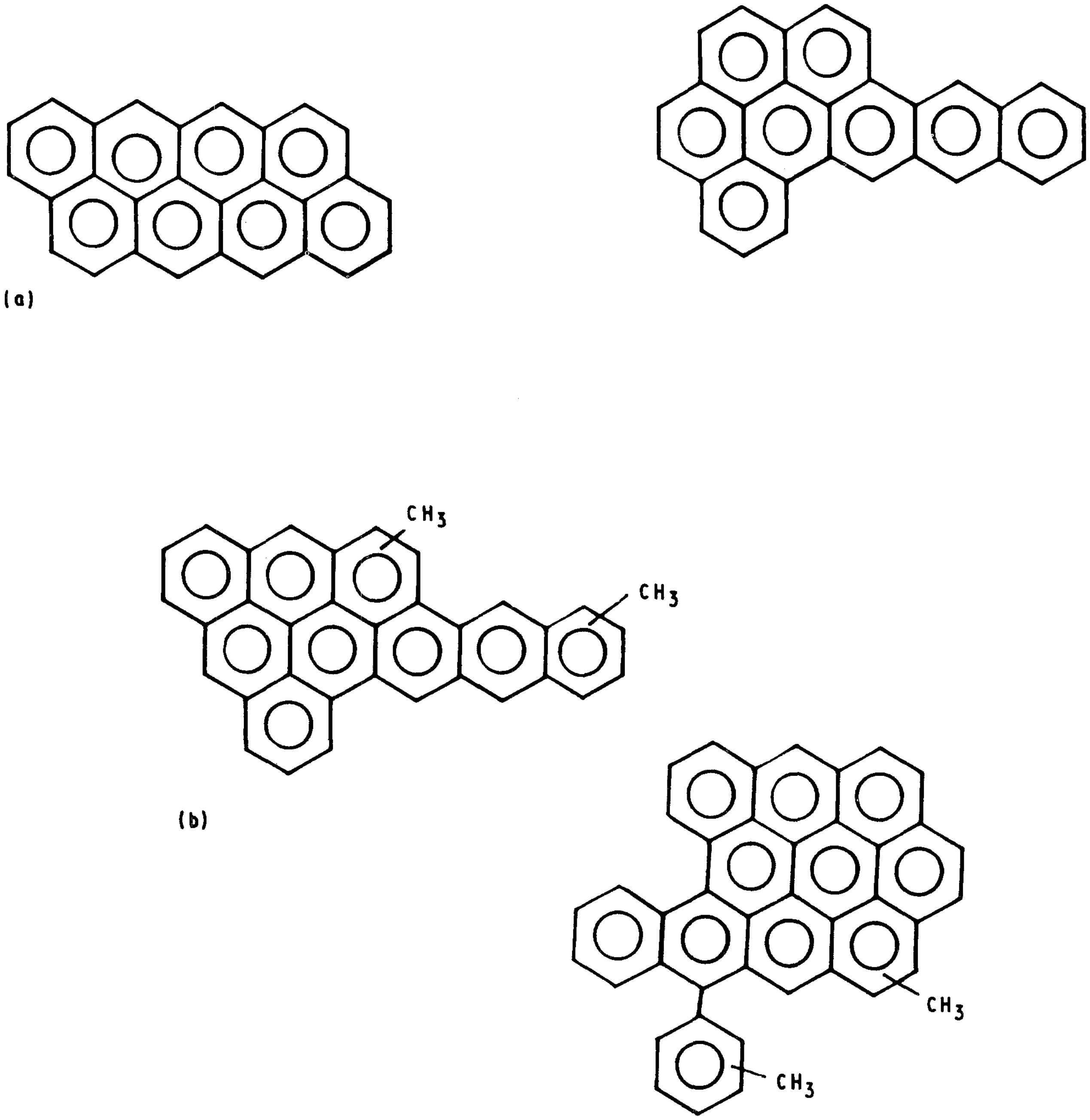

Figure 9 Model structures of TI fractions in mesophase pitches: (a) MP-2, (b) MP-3.

oxidative dehydrogenation, increasing oxygen content in and removing the hydrogens from the mesophase molecules. The reactions convert fusible TS and soluble TI into non-fusible or less-soluble TI to complete the stabilization [5]. The progress of stabilization is followed by infrared spectroscopy as structural changes in the mesophase. Detailed structure analysis of the starting mesophase allows such an approach. The mesophase pitch first loses alkyl C–H and isolated aromatic C–H to obtain carbonyl and C–O single bonds. The loss of aromatic C–H on the 1,2-disubstituted ring may lead to the condensation of the aromatic rings [5]. Finally, isolated aromatic C–H is substituted by a large number of C–O groups which should interact with each other to complete the stabilization. Thus, the stabilization is achieved by reduced fusibility through molecular association as well as the oxygenation and dehydrogenative condensation.

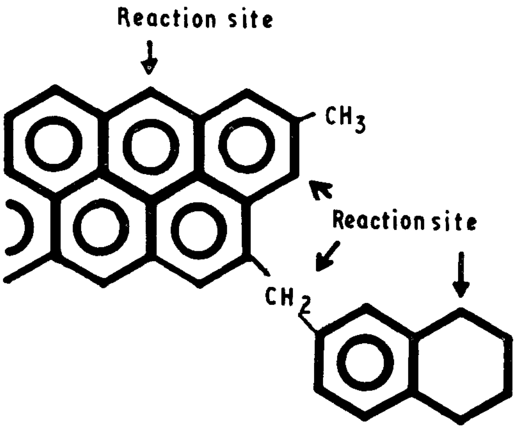

Figure 10 Reaction sites of mesophase molecules for the oxidative stabilization.

These reaction sites in the molecules are illustrated in Fig. 10.

The reactions for PS and PI appear to contrast. According to infrared spectroscopy, PS easily loses aliphatic C–H to obtain carbonyl groups in the first step, loses aromatic C–H on the 1,2-disubstituted ring in the second step and finally obtains ring condensation and strong interaction among C–O groups. The PS fraction has more alkyl side chains but less isolated aromatic C–H so that it easily loses aliphatic C–H to obtain carbonyl groups. In contrast, the PI loses easily isolated aromatic C–H to obtain single C–O bonds, and obtains, in the second step, the condensation of aromatic ring structure. The PI fraction has more isolated aromatic C–H and fewer alkyl side chains so that it obtains single C–O bonds which are connected mostly to aromatic carbons. In the case of mesophase pitch derived from coal tar, isolated aromatic C–H is very scarce because it has a little alkyl side chain and its aromatic ring is peri-type so that the single C–O bond is produced slowly or only at high temperature [4]. It is suggested that isolated aromatic C–H is the reaction site for the formation of the single C–O bond. It is time to note that isolated aromatic C–H is the reaction site for the oxidative stabilization.

The progress of the stabilization is much the same regardless of the mesophase pitch as far as fcc-DO derived ones are concerned, although their reactivities are still very different. The number of reactive sites, reflecting their structure, may define their reactivity. It is of value to note that MP-3 took up oxygen much more rapidly. However the conversion of PS into PI was rather slow. More reactive sites may contribute to the rapid oxygen up take as well as to the solubility of the constituent molecules. The latter factor may be unfavourable for the completion of stabilization.

It is concluded that the ideal molecules in the mesophase pitch should have a larger molecular size with alkyl, naphthenic and isolated aromatic C–H groups. Such groups may contribute to the oxidation reactivity and fusibility for smooth spinning while they stay in the molecule.

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Received 22 January
and accepted 30 November 1990