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Effects of hydrogenation of petroleum pitch on mesophase formation

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The effects of hydrogenation of petroleum pitch on mesophase formation have been studied in terms of the hydrogen donor (D_a) and acceptor (A_a) abilities of starting pitch, the temperature dependence of mesophase content, the thermal properties of the resultant mesophase pitches with differential scanning calorimetry (DSC), and ^{13}C-NMR spectra of the mesophase pitches in the liquid and solid states. Hydrogenation of petroleum-derived pitch causes a significant increase of (D_a) and a clear shift of the mesophase generation temperature to the high-temperature side. Measurement of the characteristics of molecular size for mesophase pitches using DSC has been successfully accomplished. The increase of D_a due to hydrogenation cause the production of mesophase having a smaller average molecular size and a more homogeneous molecular size distribution. The decrease of molecular size in the mesophase seems to cause the narrowing of the characteristic peak for mesophase around 180 p.p.m. in ^{13}C-NMR spectra in the liquid state.

1. Introduction

It has been widely recognized that the clarification of the mesophase formation process is a key point to optimize the properties of processed pitch, the so-called mesophase pitch, as a precursor for high-performance carbon materials [1, 2].

There have been many studies on chemical aspects of mesophase formation using model organic compounds as starting materials [3–8]. These studies have greatly contributed to an understanding of mesophase formation. However, an overall understanding of the changes of chemical structure of molecules and the molecular assembly during mesophase formation for industrially available pitch materials has not been completely achieved [2, 9]. This is largely due to the complex composition of these materials and the difficulty in analysing the molecular assembly of pitch molecules in a mesophase.

Lahaye *et al.* [10] have reported that differential scanning calorimetry (DSC) is useful for obtaining information about the molecular size of pitch. Recently, it has been reported that high-temperature ^{13}C nuclear magnetic resonance (NMR) is useful for characterizing mesophase formation of pitches [11]. In striving to reveal further details of molecular assembly in a mesophase by these methods, and to clarify the relationship among the properties of the starting pitch, the carbonization process and mesophase formation, one could develop tools for controlling the mesophase formation process.

The objective of this article is to clarify the effects of hydrogenation of petroleum-derived pitch as a starting material for early-stage carbonization, and the molecular assembly of pitch molecules during the mesophase formation process. In order to achieve this objective, we have measured the hydrogen donor and acceptor abilities of pitches, the temperature dependence of mesophase content, the thermal properties of the resultant mesophase pitches using DSC, and ^{13}C-NMR spectra of the mesophase pitches in the liquid state at high temperature and in the solid state.

2. Experimental procedure

2.1. Samples

A petroleum-derived pitch (pitch A) and a hydrogenated petroleum-derived pitch (pitch B: made from pitch A by hydrogenation) were selected. Table I shows the characteristics of the samples used in these experiments.

Mesophase pitch samples having various contents of mesophase were prepared by carbonizing pitches A and B. Carbonization was carried out in a Pyrex glass tube heated at 430 °C for pitch A and at 480 °C for pitch B. The content of mesophase in the carbonized samples was measured by optical microscopy with polarized light.

2.2. Measurement of temperature dependence of mesophase content

Carbonization of pitches A and B was carried out in a Pyrex glass tube heated to various temperatures at a rate of 5 °C min^{-1}. The content of mesophase in the

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TABLE I Elemental analysis, softening point and aliphatic carbon content of pitches

Pitch sample	Elemental analysis (wt %)			Softening point (°C)	Aliphatic carbon content (%)
	C	H	N		
A	93.3	6.2	< 0.2	115	16
B	92.6	6.5	< 0.2	80	25

carbonized samples was measured by optical microscopy with polarized light.

2.3. Measurement of hydrogen donor and acceptor abilities

In order to evaluate the hydrogen donor ability (D_a) of pitches A and B, anthracene was used as a hydrogen acceptor [12], while their hydrogen acceptor ability (A_a) was assessed by using 9,10-dihydroanthracene (9,10-DHA) as a hydrogen donor molecule [13]. Anthracene or 9,10-DHA and the sample were mixed (weight ratio 1:1) and heat-treated using a vertical infrared image furnace. The heating rate, the soaking temperature and soaking period were 10 °C min^{-1}, 400 °C and 5 min, respectively. The resulting specimen was dissolved in $CDCl_3$ and examined using ^{1}H-NMR. D_a was estimated from the intensity at 3.9 p.p.m. ($I_{3.9}$) due to the 9,10 positions of 9,10-DHA which are produced by the transfer of hydrogen from the sample. A_a was evaluated from the intensity at 8.4 p.p.m. ($I_{8.4}$) due to the 9,10 positions of anthracene derived from 9,10-DHA. For quantitative measurement, the intensities $I_{3.9}$ and $I_{8.4}$ were calibrated against the intensity of acenaphthene ($I_{3.4}$) as an internal standard.

2.4. DSC measurements

DSC measurements for mesophase pitches were carried out using a Perkin-Elmer DSC-4. A powdered mesophase pitch sample (~ 15 mg) was put into an aluminium sample pan of 6.8 mm outer diameter and 1.5 mm depth with no cover. To prepare a film-like specimen appropriate for measurement of the glass transition, the sample was heated at a rate of 40 °C min^{-1} from 50 °C up to 350 °C, held at 350 °C for 1 min and then quenched to 50 °C under a nitrogen gas flow in the DSC sample chamber. The thermogram of the specimen was measured at a heating rate of 40 °C min^{-1} from 50 °C up to 350 °C. The glass transition temperature distribution of the sample was obtained by differentiating the thermogram.

2.5. High-temperature NMR measurements

High-temperature ^{13}C-NMR measurements for mesophase pitches were carried out using a Bruker MSL-300 FT-NMR with a high-temperature probe (^{13}C resonance frequency of 75 MHz). The magnetic field used was 7.0 T. A ^{13}C-NMR spectrum of 10% ethylbenzene in $CDCl_3$ was measured at room temperature to calibrate the chemical shifts of peaks. A pitch sample (~ 500 mg) was put into an NMR tube of 10 mm diameter. Glass wool was softly packed into the sample tube at a position about 3 cm from the bottom to keep an insulating zone of about 1 cm thickness. Samples were heated at a rate of 5 °C min^{-1} up to 300 °C and then held at 300 °C under a nitrogen gas flow. At 300 °C, free induction decays (FIDs), were accumulated for 1 h. FIDs were obtained with a 45° pulse of 5 μs, a pulse repetition time of 2 s, and complete proton decoupling. Spectra were obtained through Fourier transformation of the accumulated FIDs, with a line broadening factor of 100 Hz.

2.6. Solid-state high-resolution NMR

A powder sample (~ 90 mg) was packed in a sample container of 3 mm inner diameter and 17 mm depth. Cross-polarization-magic-angle spinning CP–MAS ^{13}C-NMR spectra were obtained using a Bruker MSL-300 FT-NMR with a rotation rate of 10 kHz, a contact time of 2 ms, a repetition time of 6 s, an accumulation of 1000 times, and a line broadening factor of 50 Hz. Chemical shifts of peaks for the sample were calibrated using glycine as an external reference.

3. Results and discussion

3.1. Hydrogen transfer and the mesophase formation process

Fig. 1 shows the temperature dependence of optically anisotropic mesophase content for pitches A and B, when the pitch samples were heated at a rate of 5 °C min^{-1}. Mesophase transformation occurred at about 430 °C for pitch A and about 490 °C for pitch B. The temperatures corresponding to a mesophase content of 20% are about 475 °C for pitch A and about 505 °C for pitch B. Thus hydrogenation of the starting pitch shows a clear effect of shifting the temperature of mesophase generation to the high-temperature side. It has been reported that the hydrogen donor ability D_a, and acceptor ability A_a, of pitches and coals are important factors governing mesophase development in the co-carbonization of low-rank coal and pitch systems [13–15]. We applied the concept of D_a and A_a to understand the mechanism of the difference in mesophase generation. As shown in Table II, values of D_a and D_a/A_a of pitch B are much larger than those of pitch A. Hydrogen transfer occurring at the pyrolysis temperature would reduce radicals and depress polymerization [13]. The authors have reported that hydrogenation of the starting petroleum pitch shows a clear effect of a significant decrease of spin concentration at high temperatures [16]. Hence it is clear that for pitch B inter- or intra-molecular hydrogen transfer

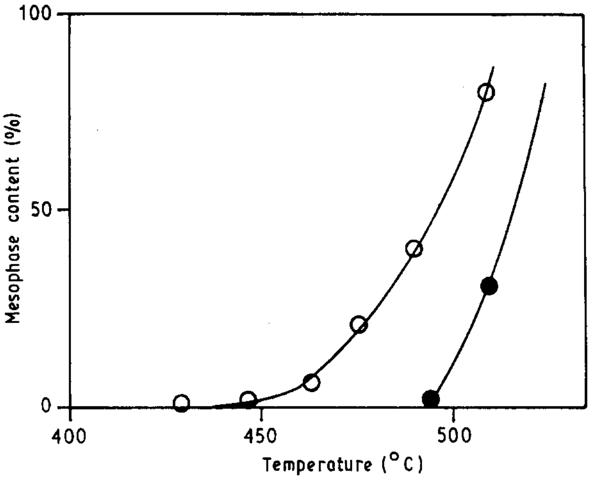

Figure 1 Temperature dependence of mesophase content for pitches (○) A and (●) B.

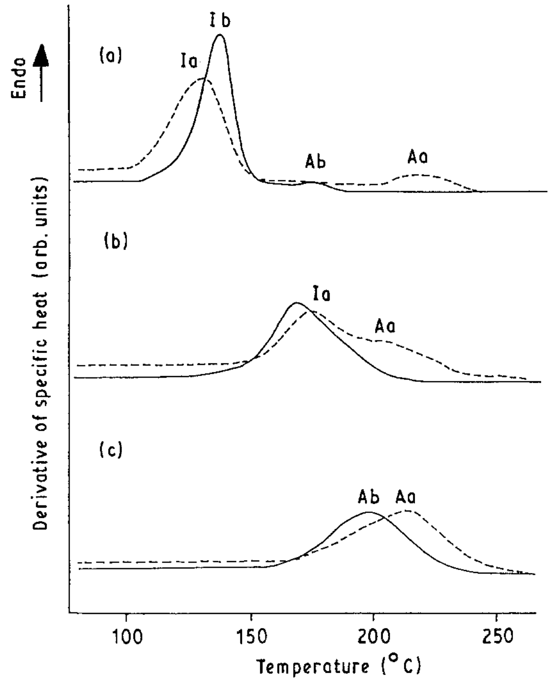

Figure 2 Glass transition temperature distribution of mesophase pitches made from pitches (---) A and (——) B. Mesophase content: (a) 10%, (b) 50%, (c) 100%.

TABLE II Hydrogen donor abilities (D_a) and hydrogen acceptor abilities (A_a) of pitches

Pitch sample	D_a (mg H_2/g pitch)	A_a (mg H_2/g pitch)	D_a/A_a
A	0.44	1.4	0.31
B	1.27	1.1	1.15

suppresses radical generation during heating. Suppression of radical generation leads to the depression of extreme polymerization. Therefore a much more severe heat treatment is required for pitch B to produce macromolecules having enough size to be able to form a mesophase.

3.2. Molecular size distribution of mesophase pitches

Fig. 2 shows the results of measurements of the glass transition temperature distribution for mesophase pitches. As shown in Fig. 2a, two peaks were observed for both pitches A and B. It is thought that peaks on the low-temperature side correspond to the isotropic phase (Ia and Ib indicated in Fig. 2a) and peaks on the high-temperature side correspond to the mesophase (Aa and Ab as indicated in Fig. 2a). The peak temperature of Ib is higher than that of Ia, and the peak width of Ib is narrower than that of Ia as shown in Fig. 2a; the peak temperatures of Ib and Ia are about 139 and 131 °C and the half-widths about 16 and 25 °C, respectively.

Fox and Flory [17] have reported that there is a good correlation between the glass transition temperature and the average molecular size for polyethylene. Lahaye *et al.* [10] have studied the glass transition characterization of pitches by DSC and reported that in the case of a series of pitches with similar intermolecular forces and compactness, the width of the glass transition is expected to be correlated with the molecular size distribution [10]. Both intermolecular forces and compactness depend on chemical structure of molecules. It has been reported that the chemical structures of petroleum pitches in terms of hydrogen aromaticity [16] and carbon aliphaticity [11] are similar around the mesophase transformation. Therefore, in the early stage of mesophase generation, the matrix for pitch B consists of molecules having a larger average molecular size and a more homogeneous molecular size distribution than those for pitch A.

Depression of extreme polymerization due to the high ability of hydrogen transfer for pitch B, as mentioned above, is the reason that pitch B has a more homogeneous molecular size distribution than pitch A. The average molecular size of a pitch matrix having a homogeneous molecular size distribution at mesophase generation ought to be larger than that of a pitch matrix having a wider molecular size distribution, because the pitch matrix around mesophase transformation has to contain molecules large enough to be able to form a mesophase. The peak temperature of Ab is lower than that of Aa as shown in Fig. 2a and c: the peak temperatures of Ab and Aa are about 178 and 221 °C, respectively, in Fig. 2a, and about 198 and 213 °C, respectively, in Fig. 2c. The peak width of Ab is narrower than that of Aa as shown in Fig. 2c: the half-widths of Ab and Aa are about 37 and 42 °C, respectively.

Therefore, the mesophase produced from pitch B has a smaller average molecular size and a more homogeneous molecular size distribution than that produced from pitch A. The homogeneous molecular size distribution in the mesophase is obtained from the pitch matrix having a homogeneous molecular size distribution produced by depression of extreme polymerization due to the high ability of hydrogen transfer. It has been reported that the molecular size distribution for isotropic pitches can be evaluated using DSC [10]. The present study has successfully accomplished measuring the characteristics of molecular size for the first time for mesophase pitches using DSC. It has been reported that D_a and A_a of pitches are important factors governing the extent of development of optically anisotropic texture [13–15]. The present study has revealed that D_a and D_a/A_a for petroleum pitch are important factors governing the molecular size in the mesophase.

3.3. NMR spectra of mesophase pitches

In order to examine the characteristics of mesophase pitches in the liquid state beyond the glass transition region, ^{13}C-NMR spectra of mesophase pitches obtained from pitches A and B were measured at 300 °C. Fig. 3 shows spectra for mesophase pitches having a mesophase content of 100%. A peak around 180 p.p.m. corresponds to a characteristic peak for the mesophase [11]. The mesophase pitch from pitch B has a narrower line-width of the characteristic peak for mesophase around 180 p.p.m. than that from pitch A: the half-widths for the mesophase pitches from pitches A and B are 1.9 and 1.5 kHz, respectively. Generally, the narrower the line width is, the higher the mobility of the molecules becomes (see e.g. [18]). The molecules in the mesophase pitch from pitch A are relatively rigid in the mesophase. In contrast, mesophase-composing molecules in the mesophase pitch from pitch B have a high mobility.

It has been reported that aliphatic carbon in a mesophase causes an increase of mesophase mobility [11]. Accordingly, the aliphatic carbon content in the mesophase pitches obtained from pitches A and B were measured using high-resolution solid-state ^{13}C-NMR spectra. Fig. 4 shows spectra for petroleum-derived and hydrogenated petroleum-derived mesophase pitches. However, aliphatic carbon contents for both mesophase pitches are almost at the same level: the area intensities of the aliphatic carbon region around 10–50 p.p.m. (see e.g. [19]) for mesophase pitches from pitches A and B are 12 and 11%, respectively. Hence, it is thought that the high mobility for the mesophase pitch from pitch B mainly resulted from interaction with weak intermolecular forces due to the relatively small molecular size of molecules in mesophase as characterized by DSC (section 3.2). It has been reported that there is a relation between the aliphatic carbon in a mesophase and the narrowing of the characteristic peak around 180 p.p.m. for the mesophase [11]. The present study has shown a relation for the first time between the molecular size of the mesophase and the narrowing of the characteristic peak around 180 p.p.m.

Summarizing the results, we can draw a schematic model of molecular size for mesophase-composing molecules as shown in Fig. 5. The molecules in hydrogenated petroleum-derived mesophase pitch have a rather small molecular size and a homogeneous molecular size distribution, and are rather mobile.

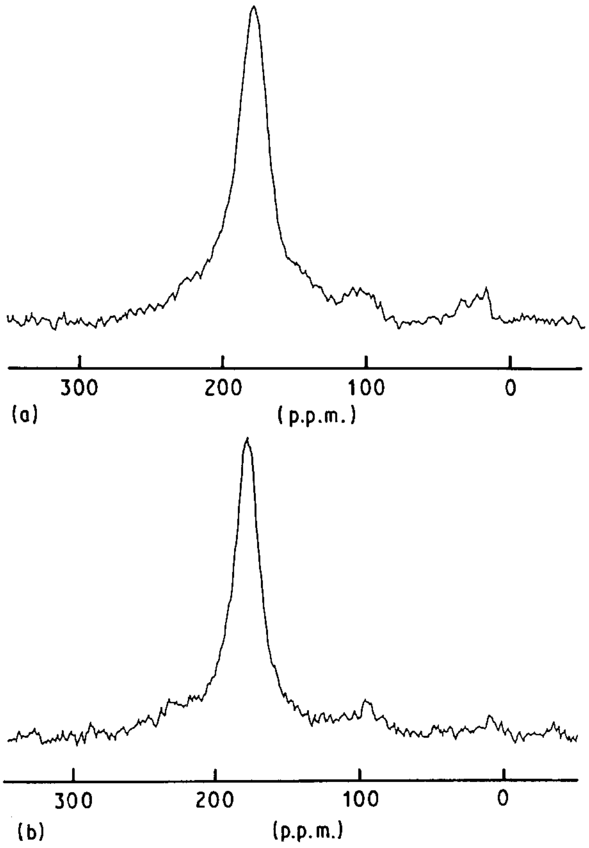

Figure 3 High-temperature ^{13}C-NMR spectra of mesophase pitches (a) A and (b) B at 300 °C.

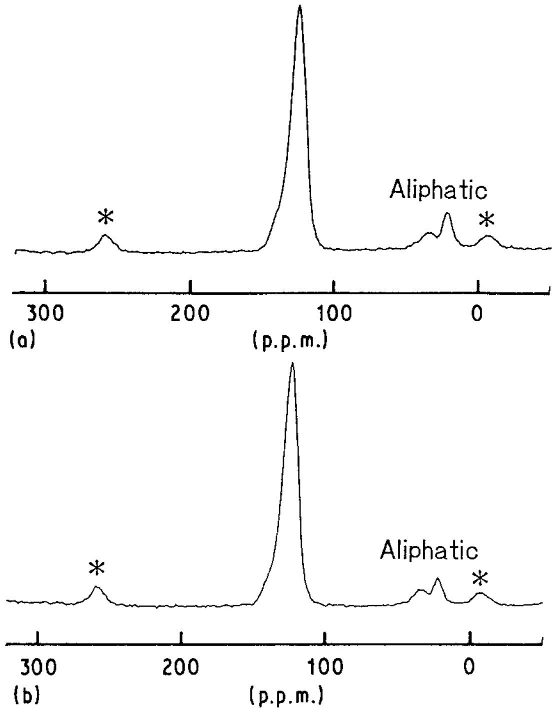

Figure 4 High-resolution solid-state ^{13}C-NMR spectra of mesophase pitches (a) A and (b) B; (*) spinning sidebands of peak around 130 p.p.m.

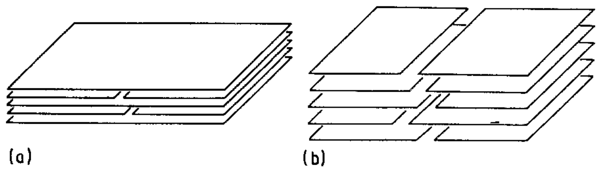

Figure 5 Model of molecular size for mesophase-composing molecules in pitches (a) A and (b) B.

4. Conclusions

1. Measuring the characteristics of the molecular size distribution for mesophase pitches has been successfully accomplished using DSC.

2. The significant increase of D_a due to hydrogenation for petroleum pitch causes the production of a mesophase having a smaller average molecular size and a more homogeneous molecular size distribution.

3. The decrease of molecular size in the mesophase causes an increase of mesophase mobility and a narrowing of the characteristic peak for mesophase around 180 p.p.m. in ^{13}C-NMR spectra in the liquid state.

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