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Studies on the Development of Anisotropy of Carbonaceous Materials. Comparison of Carbonization Behavior between Methylene Bridged Naphthalene Oligomer and Biphenyl One

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Methylene bridged naphthalene oligomer was found to produce a carbonaceous material with optical anisotropy of a flow domain texture while corresponding biphenyl oligomer gave isotropic one. FD-MS measurements of oligomers and carbonized products revealed that the observed difference was originated from structural features whether condensed aromatic rings can develop or not.

The nature of the precursor pitch and the mechanism of its transformation to coke are believed to control the properties of the resulting carbonaceous materials.$^{1-2)}$ The chemical structure of petroleum and coal tar pitches are very complex, involving the portions either highly aromatic or extensively substituted by side chains. Although simple aromatic compounds, such as naphthalene, have been adapted as model compounds to get information about development of anisotropy,$^{1-4)}$ naphthalene has been carbonized under high pressure or by using acid catalyst to prepare anisotropic pitch or coke$^{5-6)}$ due to its rather low boiling point and sublimation properties.

Present authors found that anisotropic pitch having a flow domain texture can be obtained from carbonization of a mixture of methylene bridged naphthalene oligomers at 1 atm. Interestingly, naphthalene and biphenyl oligomers showed entirely different carbonization behavior. Their carbonization mechanisms were discussed based on FD-MS measurements.

Methylene bridged oligomers were prepared by condensation of naphthalene or biphenyl as follows.$^{7)}$ Naphthalene or biphenyl (5 g) and methylal (1 g) were dissolved in chloroform (20 g), into which sulfuric acid (95%, 10 g) was added slowly at 0 ^{o}C, and then stirred for 6 h at room temperature. Sulfuric acid was removed by washing repeatedly with deionized water. The organic phase was divided into chloroform-soluble and -insoluble fractions. In case of naphthalene, the chloroform-soluble fraction was further extracted with ether: the extraction yield was 75%. Carbonization reactions were carried out for chloroform-soluble fraction of biphenyl oligomer (**BPC**) and ether-soluble fraction of naphthalene oligomer (**NE**). A pyrex tube containing a oligomer fraction was immersed in a salt bath kept at 300 ^{o}C and then heated up to 470 ^{o}C at a rate of 5 ^{o}C min^{-1} under an atmospheric N_2 stream introduced to the tube throughout the reaction. Gas and sublimation products were collected and analyzed by GC. The optical texture of the carbonized sample was observed by polarized light microscopy after pelleted in an epoxy resin. FD-MS spectra were recorded using a JEOL DX303 under the conditions as follows : acceleration voltage 3.0 kV, emitter current elevated at a rate of 4.2 mA min^{-1}; 10 sec per 1 scan (m/z 50 - 1200).

Figure 1a shows the FD-MS spectrum of **NE**, which reveals that **NE** is a mixture of oligomers of **N**-(CH_2-**N**)$_n$-CH_2-**N**, where **N** is naphthalene nuclei and n=0 - 7 within m/z 1200. Figure 1b shows the FD-MS spectrum of **BPC**, which also reveals the structure as **BP**-(CH_2-**BP**)$_n$-CH_2-**BP**, where **BP** is biphenyl. Among possible isomers contained in **NE** and **BPC**, 1,5-bridged naphthalene oligomers and 4,4'-bridged biphenyl oligomers are demonstrated in Figs. 1a and 1b.

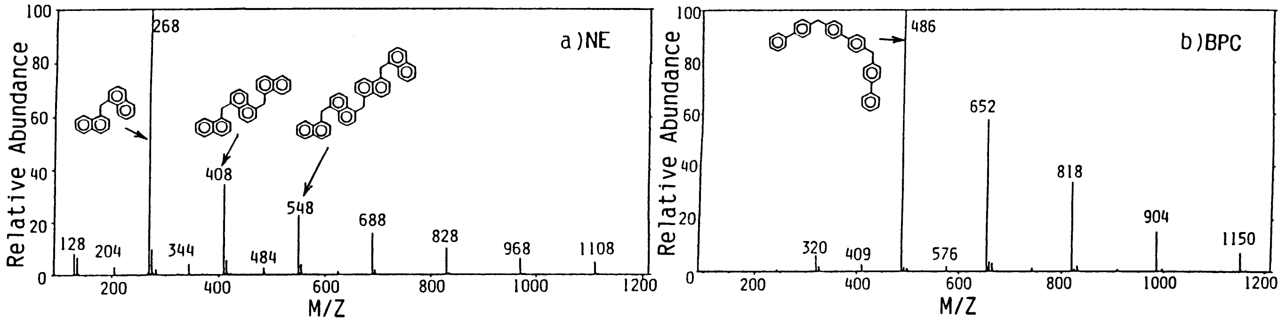

Fig. 1. FD-MS spectra of a)**NE** and b)**BPC**.

The substances released during carbonization reactions of **NE** and **BPC** are summarized in Table 1: a large amount of **ArH** (**Ar** is **N** or **BP**) were produced whereas the yields of Ar(CH_3)$_n$ (n=1 and 2) were relatively low, and gas predominantly consists of H_2 (more than 99%). Therefore, it is assumed that -CH_2- groups almost remained in the pitch.

Table 1. Results of carbonization of **NE**[a)] and **BPC**[b)]

	Substances released during reaction(wt%)					Residue(wt%)
	Gas[c)]	**ArH**[d)]	**Ar**-CH_3	**Ar**-(CH_3)$_2$	Others[e)]	
NE	3	63	10	1	10	13
BPC	4	20	8	1	17	50

a) **NE** was carbonized at 470 °C for 1 h.

b) **BPC** was carbonized at 470 °C for 4 h.

c) H_2 more than 99 mol% in Gas.

d) **Ar** = naphthalene or biphenyl group.

e) Substances having high boiling points.

Figure 2a shows the photomicrograph of carbonized **NE** (**C-NE**; carbonized for 1 h, yield 13 wt%). The sample exhibited an anisotropic texture of flow domain type. On the other hand, the texture of carbonized **BPC** (**C-BPC**; carbonized for 4 h, yield

50 wt%) is isotropic (Fig. 1b). Due to high boiling points of **NE** and **BPC**, they are considered to be carbonized in liquid states. Therefore, the difference in optical anisotropy of the carbonized products would be originated from their structural features: it should be concerned whether planar condensed aromatic rings can develop or not. **NC**, the chloroform-soluble fraction of naphthalene oligomer, also produced the anisotropic texture similar to that from **NE**. However, the carbonization properties of **NE** was further investigated and compared with **BPC** because of its narrower range of molecular weights of oligomers than that of **NC**.

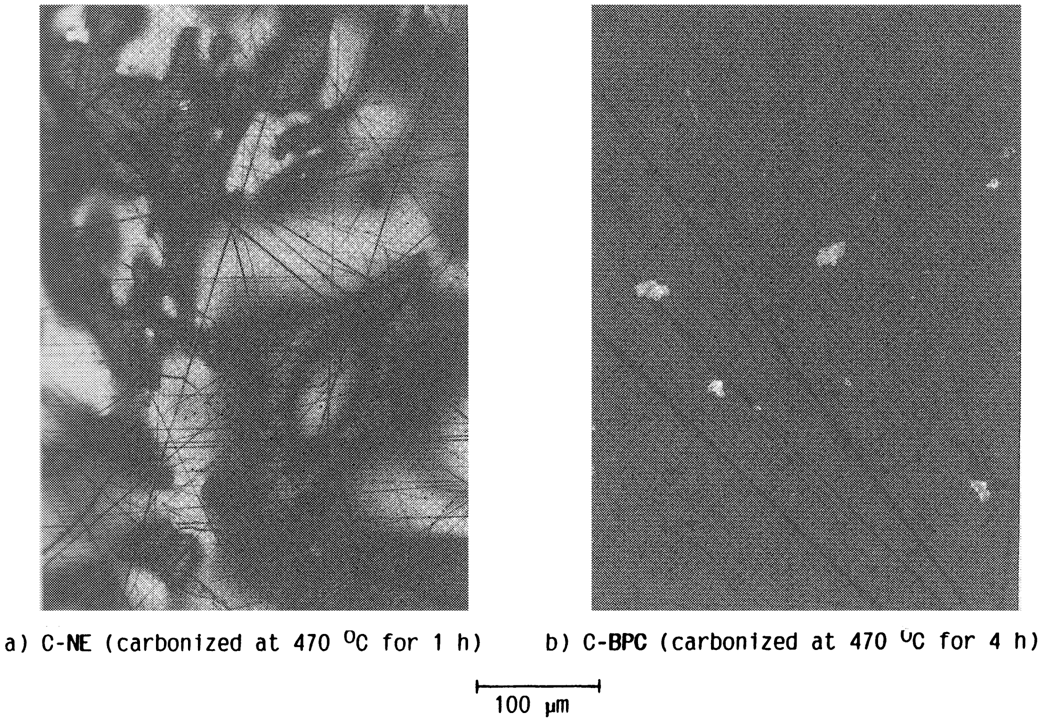
a) C-**NE** (carbonized at 470 °C for 1 h) b) C-**BPC** (carbonized at 470 °C for 4 h)

Fig. 2. Photomicrographs of carbonized a)**NE** and b)**BPC**.

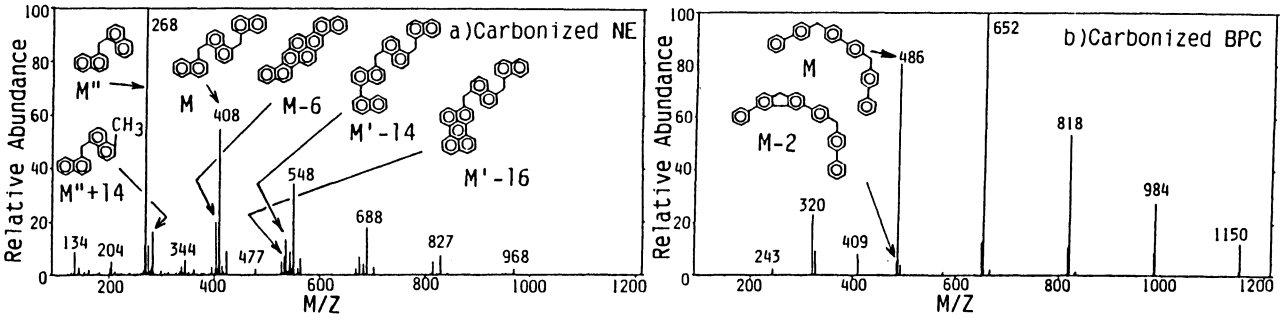

Fig. 3. FD-MS spectra of a)C-**NE** and b)C-**BPC** (carbonized at 470 °C and immediately cooled).

Figure 3a shows the FD-MS spectrum of C-**NE** (carbonized up to 470 °C and immediately cooled). In addition to a series of main peaks of starting oligomers (m/z=M=268, 408, 548, 688, etc.) several peaks having m/z=M-14, M-6 and M+14 appear on its FD-MS spectrum (Fig. 3a), which are expected to be formed by coupling of naphthyl radicals, dehydrogenation, and elimination of naphthalene, respectively, as shown in Fig. 4. Since **NE** has methylene bridges between all the naphthalene groups, the possible structures of condensed aromatic rings of m/z=M-6 are different from that of perylene, which was proposed in the carbonization of naphthalene with catalysts such as $AlCl_3$ or potassium.$^{5-6)}$ In contrast, the FD-MS spectrum of C-**BPC** (Fig. 3b) shows only a slight difference from feed **BPC** (Fig. 1b): peaks of m/z=M-2 are observed. These peaks suggest the presence of fluorene structure formed by coupling of phenyl groups (Fig. 3b). Low reactivity of **BPC** is also indicated by the fact that no pitch was produced from **BPC** when carbonized for 2 h.

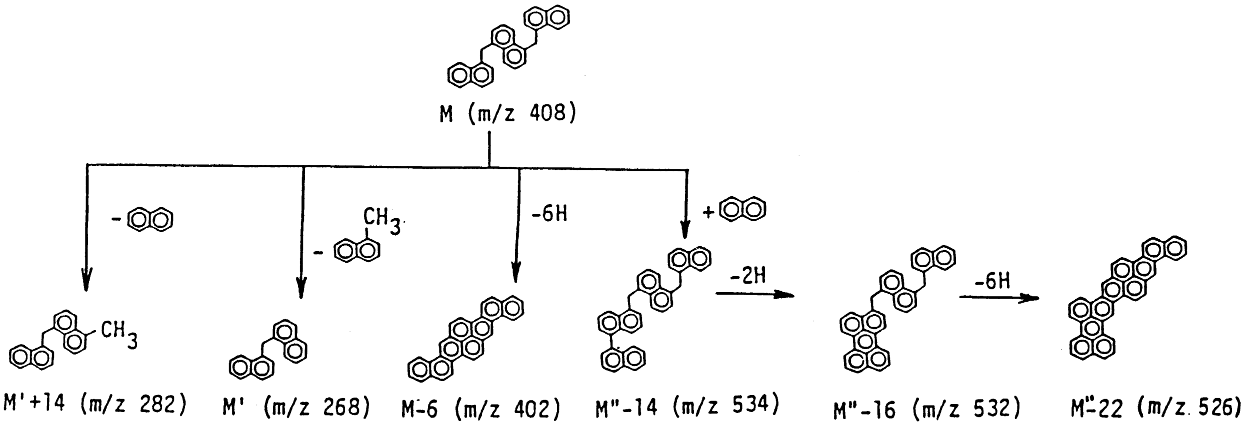

Fig. 4. Possible reaction scheme for carbonization of **NE**.

In summary, both naphthalene and biphenyl can be carbonized in a liquid phase by oligomerizing them with methylene bridges. However, the optical properties of the carbonized products primarily depend upon their chemical structures. When phenyl groups in **BPC** undergo coupling with each other, they would form fluorene structure as shown in Fig. 3b, which is assumed to produce isotropic texture leading to non-graphatizing carbon.$^{8)}$ In contrast, naphthalene groups in **NE** could undergo coupling to produce condensed aromatic rings as proposed in Fig. 3a.

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