REACTIONS OF COAL TAR PITCH WITH P-BENZOQUINONE AND ITS CARBONIZATION

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IINTRODUCTION

The polycondensation of a pitch through heat treatment is a method of high energy consumption which leads to an uncontrollable of molecular structure. The polymerization through chemical reaction of the pitch could be a solution of the problems. The morphology of the carbon products also could be modified by the chemical modification of the molecular structure of the precursor pitch. A porous, non-graphitisable coke was obtained with marked increase in coke yield when the chloranil was added in pitch pylolysis (1). Endo et al. reported that the morphology with minimum crystalline thickness in the carbon fiber showed maximum capacity to lithium cation which could be used as a high capacity electrode of lithium secondary battery (2).

In the present study, the reaction of coal tar pitch (CP) was performed with p-benzoquinone (BQ) containing 4 symmetrical functional groups which may provide Diels-Alder and/or electrophilic aromatic substitution reaction with pitch. The products reacted and carbonized were characterized.

EXPERIMENTAL

The soluble fraction of coal tar pitch in tetrahydrofuran (THF) was reacted with BQ of various concentrations at 180 ^{o}C for one hour. The BQ unreacted in the MCP was washed with methanol and the molecular weight of the product was measured with using VPO after dissolving the products in pyridine. The reaction products were carbonized by the program, heating rate of 5 ^{o}C/min up to 500 ^{o}C, holding 1 hour at the temperature and cooling at 10 ^{o}C/min. The carbon yields were calculated by dividing the sample weight after carbonization by the original weight. The textures after carbonizations were visualized with using a polarizing microscope. The carbonization behavior of the CP/BQ mixture was monitored in *In-situ* using high temperature NMR.

RESULTS AND DISCUSSION

The thermal behavior of the CP/BQ (10/10) mixture was presented in Fig. 1. The BQ crystal melts at ca. 99 ^{o}C showing endotherm, CP and BQ react at two distinctive temperatures with rather large heat of reaction, -423 mJ/mg. Through the reaction, the molecular weight (Mn)was increased by three times at 10/5 wt. ratio comparing with the control (Fig.2).

The morphology of the carbonized products could be changed by varying the BQ concentration. The large flow-texture in the absence of BQ varied to mosaic texture at 10/3 and eventually became isotropic texture at 10/5. These results would come from inhibited mobility introduced by polymerization. The mobility of the molecules, indicated as the ratio of peak-height/half-width (PH/HW), at the carbonization process was monitored with high temperature NMR. As shown in Fig. 3, the mobility was minimum at 150 ^{o}C independently with CP/BQ weight ratio, representing reaction temperature, and increased drastically with an increase in temperature up to maximum, and decreased with a further increase in temperature showing occurrence of pyrolysis.

The increased Mn would give an effect of an increase in carbon yield through polymerization. The 61% of carbon yield in the absence of BQ increased to 80 % at 10/5 (Fig.4).

CONCLUSIONS

The Mn of CP increased with the reactions of BQ. The increase in Mn varied the texture of the pitch from flow domain, mosaic, and eventually to isotropic texture with an increase in BQ concentration after carbonization. The Mn

increase would also contribute to an increase in carbon yield.

REFERENCES

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2. M. Endo, J. Nakamura, Y. Sasabe, T. Takahashi and M. Inagaki, Tanso (Japan), No. 165 pp. 282-287 (1994).

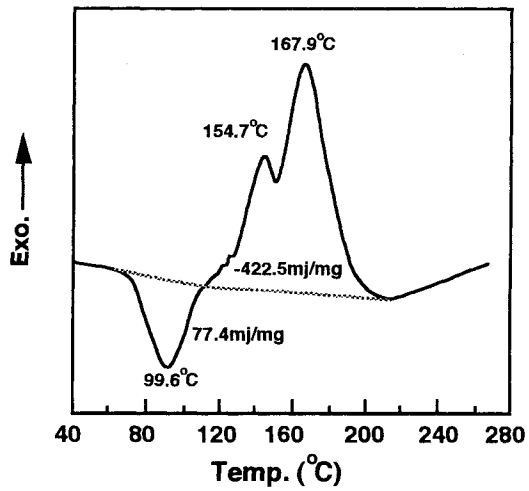

Fig. 1. DSC thermal diagram of CP/BQ (1/1 by weight, heating rate; 10°C/min).

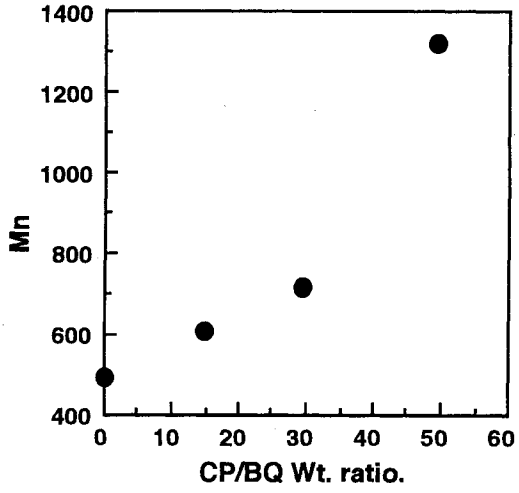

Fig. 2 Molecular weight dependence of coal tar pitch on CP/BQ wt ratio ; reaction Temp., 180°C.

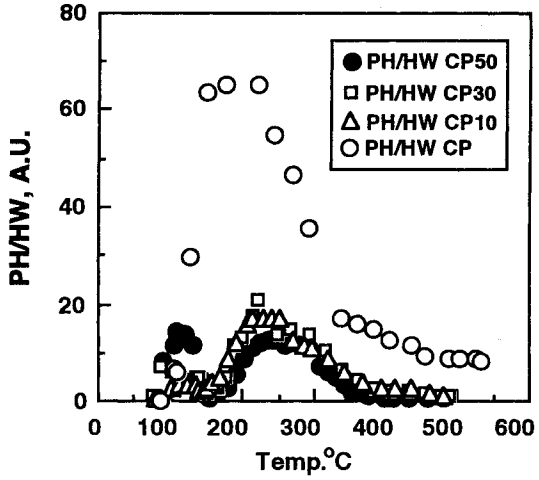

Fig. 3. PH/HW vs. temperature of high temperature ^{1}H NMR.

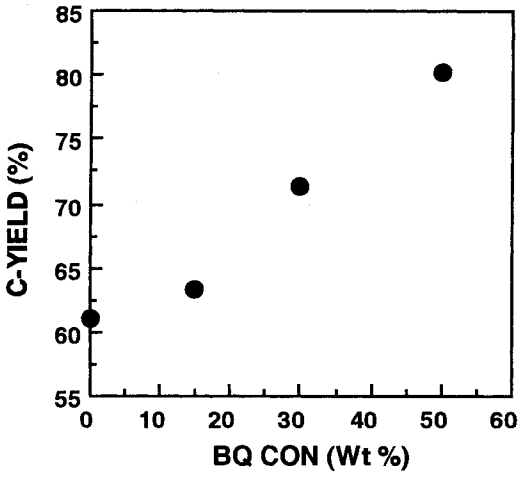

Fig.4. Carbon yield dependence on CP/BQ wt ratio at 500°C; heating rate, 5°C/min; hold for 1hr, cooling rate, 10°C/min.