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Carbonization behavior of coal tar pitch modified with benzoquinone

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A soluble fraction of coal tar pitch (CP) in tetrahydrofuran (THF) was reacted with *p*-benzoquinone (BQ) at 160 and 180 °C and followed by carbonization and graphitization. The reaction and carbonization behavior were monitored *in-situ* by using differential scanning calorimeter, high-temperature ^{1}H NMR and high-temperature ESR. The reactions of CP and BQ resulted in an increase in molecular weight with an increase in BQ concentration. Such molecular weight increases led to the formation of a less ordered structure due to the reduced mobility of the molecules. The relative order of the carbonized materials was determined by using polarized light microscope and X-ray diffraction. The molecular size of the precursor was recognized as an important factor in determining the morphology of carbon materials. © *2000 Kluwer Academic Publishers*

1. Introduction

The molecular size of a pitch for the carbon industry has to be in the optimum range to exhibit enough processability and carbon yield. Some of the oxygen-containing compounds show dominant roles in the carbonization procedure. Marsh *et al.* [1] reported that aromatic compounds containing an optimum amount of oxygen had increased aromatic content and also carbon yield. On the other hand, if the compounds contain more oxygen than the optimum, the graphitizability is reduced because of the cross linking among the molecules. Yang *et al.* [2] reported that the naphthalene-based mesophase pitch transformed to an optically isotropic pitch after chemical modification with *p*-benzoquione(BQ) and the isotropic property remained even after carbonization at 2400 °C. The reaction mechanism between the BQ and polycyclic aromatic compounds was reported as a Diels-Alder reaction [3]. Fitzer *et al.* [4] investigated the cocarbonization of pitch with chloranil and found an enhanced yield of carbon with high porosity and reduced graphitizability.

The carbonization mechanisms were reported by several authors. When the polycyclic aromatic compounds were carbonized in the presence of alkali metal, the cokes exhibited optically isotropic because of the drastic reaction of the hydrocarbons [5]. Ota *et al.* [6] have shown that cocarbonization of quinone derivatives and dianthracenyl resulting in an increase in carbon yield. The carbonization was activated through reduction of the carbonyl group to be hydroxyl group and followed by dehydration of the hydroxyl groups.

High temperature ^{1}H-NMR and ESR spin probe method have been recognized to be useful methods for obtaining information about the molecular motion and chemical changes in coal and petroleum pitches in the early stage of carbonization [7, 8]. Andresen *et al.* [9] reported that high temperature ^{1}H NMR has shown that the softening point of a pitch is closely related to the toluene soluble fraction but that the beta-resin indeed becomes plastic on its own and can significantly contribute the total mobility of the pitch.

In the present study, coal tar pitch (CP) was reacted with BQ at various concentrations and then carbonized. The reaction and carbonization behaviors were monitored *in-situ* by DSC, high temperature ^{1}H NMR and ESR. The morphologies of the carbon resulted were characterized and explained on the basis of the behavior during reaction and carbonization.

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2. Experimental

2.1. Materials

The tetrahydrofuran(THF) soluble fraction of the coal tar pitch (softening point, 85 °C ; Jung Woo Coal Chem. Co., Korea) was used for chemical reaction with *p*-benzoquinone(BQ, 1st grade, Wako Pure Chemical Ind. Ltd., Japan).

2.2. Chemical reaction

A given amount of CP or BQ was ground to a fine powder and the mixture was evenly dispersed. The powder mixture was reacted in a three-neck flask installed in silicone oil bath at slightly over the respective reaction temperatures of 160 and 180 °C at heating rate of 1 °C/min and held for one hour at the each temperature. Reaction was performed by stirring the mixture with a magnetic stirrer under a nitrogen atmosphere and avoiding volatilization of the BQ with a reflux condenser. The unreacted BQ was washed out with methanol and followed by evacuation at 60 °C under vacuum, and the absence of BQ was verified on the basis of the absence of the characteristic IR peak of the BQ carbonyl group. The initial concentration of BQ was expressed as the weight ratio of BQ/CP.

2.3. Analysis

2.3.1. Modified pitch

Elemental analysis of the modified pitch was performed to investigate the variations of composition through condensation reactions. The reaction profile of the BQ/CP mixture was investigated by using differential scanning calorimeter (DSC, Seiko SSC-5020) at a heating rate of 10 °C/min [2]. FT- IR spectroscopy (JIR-03F, Japan) was used to identify the functional groups of the products. The molecular weight of the modified CP, dissolved in pyridine, was measured by using vapor pressure osmometry and was determined on the basis of the calibration curve of polystyrene. The ^{1}H-NMR was conducted with $CDCl_3$ solvent using Varian XL 400. The hydrogen distribution was determined by means of ^{1}H-NMR and the aromaticity was calculated on the basis of the Brown-Ladner method [10].

2.3.2. Carbonization and graphitization

Carbonization behavior of the BQ/CP mixture was monitored *in-situ* by high temperature ^{1}H NMR (Pulse NMR, 36.4 MHz, Bruker, Germany) at a heating rate of 3 °C /min under a nitrogen atmosphere. The solid echo pulse sequence with refocusing time of 5 μs was used. As a parameter of the mobility of the consisting molecules, the width of line at half maximum intensity ($\Delta H_{1/2}$) of the aromatic hydrogen was measured [11]. In order to improve the resolution of the spectrum at high temperature, a home built shim system was used [12]. The variations of radical concentration were also monitored *in-situ* by high temperature electron spin resonance (ESR, Jeol JES-ME 3X, Japan) at a heating rate of 5 °C /min.

The modified pitches were carbonized in a horizontal type electrical furnace at 500 °C for one hour at a heating rate of 5 °C/min. The carbon yield was calculated by the Equation 1.

$$\text{Carbon yield}(\%) = \frac{\text{Wt. after carbonization}}{\text{Wt. before carbonization}} \times 100 \tag{1}$$

Optical textures of the cokes after carbonization were investigated using polarized light microscope (Nikon, AFX-II, Japan) after conventional polishing. Thermogravimetrical behavior of the BQ/CP mixture was investigated by TG/DTA (Seiko, Model SSC/5200) in the carbonization procedure at a heating rate of 5 °C/min under a nitrogen atmosphere. X-Ray diffractions were measured for the carbonized materials with X-ray diffractometer (Geigerflex, Rigaku, Japan) using CuKα radiation.

3. Results and discussion

The reaction profile was investigated on the basis of DSC thermal diagram (Fig. 1). DSC profile indicates that BQ is molten at 100 °C, reacts with CP at 155 and 168 °C. Though the reaction mechanisms are not definite, Diels-Alder and dehydration reactions would occur at the respective temperature. The reaction temperatures for naphthalene derived pitch with BQ were 115 and 158 °C which were identified with Diels-Alder and dehydration reactions respectively due to the ladder like structure of the pitch [2]. The heat of reaction of the BQ10/CP10 was measured as −442.5 J/g representing remarkable reactivity between BQ and CP.

The FT-IR spectra of CP and BQ5/CP10 are shown in Fig. 2. Though the CP contains only free water indicated at 3423 cm^{-1}, the BQ5/CP10 reacted at 160 °C formed phenolic group (1201, 3535 cm^{-1}) which was recognized the intensity of the peaks decreased at 180 °C representing the reduction of the content through dehydration. The dehydration is confirmed by a decrease in respective intensity of the peak ratios, i.e., $I_{\text{O-H}}/I_{\text{C=C}}$ and $I_{\text{C-O}}/I_{\text{C=C}}$, from 0.39 to 0.30 and from 1.41 to 1.33 with an increase of the temperature from 160 to 180 °C respectively. The trend described above were observed for all BQ/CP systems as far as studied. The BQ/CP

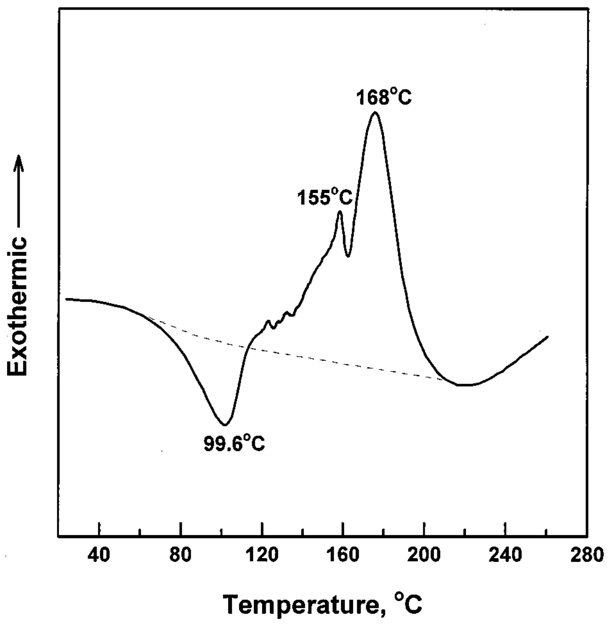


Figure 1 The DSC thermal diagram of BQ10/CP10 mixture; heating rate, 10 °C/min.

TABLE I Elemental analysis data

Elements (%)	CP	BQ3/CP10 180 °C	BQ5/CP10 140 °C	BQ5/CP10 180 °C
C	93.02	87.98	85.97	86.87
H	5.08	4.53	4.92	4.24
N	1.05	0.98	0.94	0.97
O	0.67	6.51	8.17	7.92
H/C(mol)	0.66	0.62	0.69	0.59
O/C(mol)		0.058	0.071	0.068
f_a^*	0.96	—	0.98	0.98

* Calculated on the basis of Brown-Lander method [10].

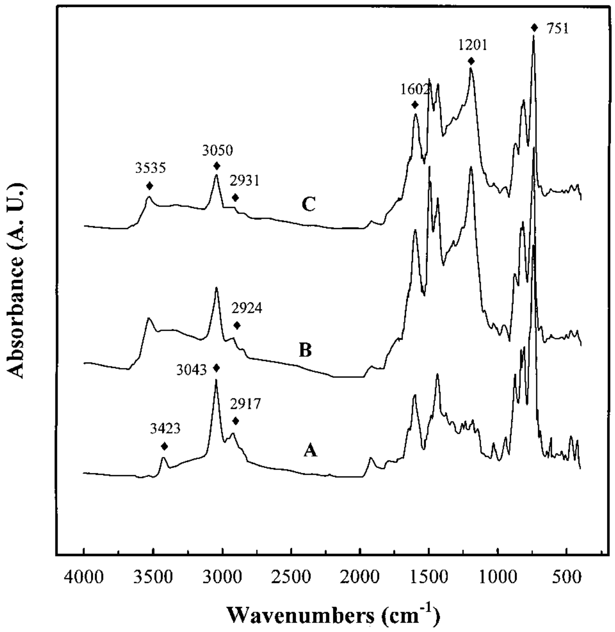


Figure 2 FT-IR spectra of the samples heat-treated at various temperatures; (A), CP; (B), BQ5/CP10 at 160 °C; (C), BQ5/CP10 at 180 °C.

reaction increased hydrogen aromaticity from 0.96 of CP to 0.98 of BQ5/CP10 irrespective of the reaction temperatures as shown in Table I.

The elemental analysis of the chemically modified CP was tabulated in Table I. Slight decrease of O/C and H/C values were observed for the BQ5/CP10 with temperature increase and the oxygen concentration was increased with an increase in BQ concentration. Remarkable evidence that the reaction occurred between BQ and CP is that the molecular weight was increased from 480 to 1400 with an increase in BQ concentration up to BQ5/CP10 as shown in Fig. 3. The molecular weight 1400 implies that the 2–3 CP molecules were oligomerized with BQ. The increase in molecular weight rises in softening point from 85 °C to 150 °C at the same composition range. The carbon yield at 500 °C increased from 60% to 80% when the BQ concentration increased up to BQ5/CP10. Such an increase would come from the enhanced thermal stability from increased molecular weight of resultant product at the early stage of carbonization.

Figs. 4 and 5 show the ^{1}H NMR peak intensity and the temperature dependence of the $\Delta H_{1/2}$ obtained from ^{1}H NMR measurement for CP and BQ5/CP10 respectively. The value of the $\Delta H_{1/2}$ is inversely proportional to the spin-spin relaxation time, T_2. Therefore the T_2

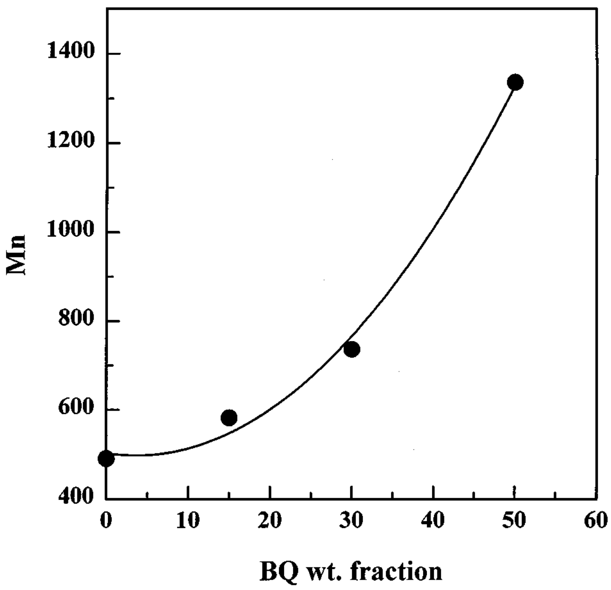


Figure 3 Molecular weight dependence of the products reacted at 180 °C on BQ/CP weight fraction.

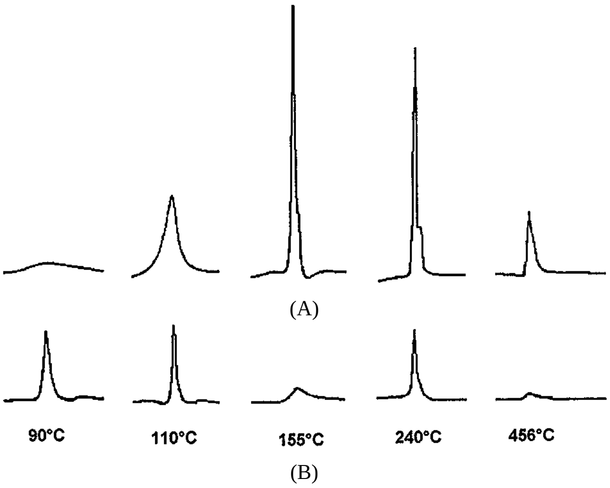


Figure 4 High temperature ^{1}H NMR spectra; (A), CP; (B), BQ5/CP10.

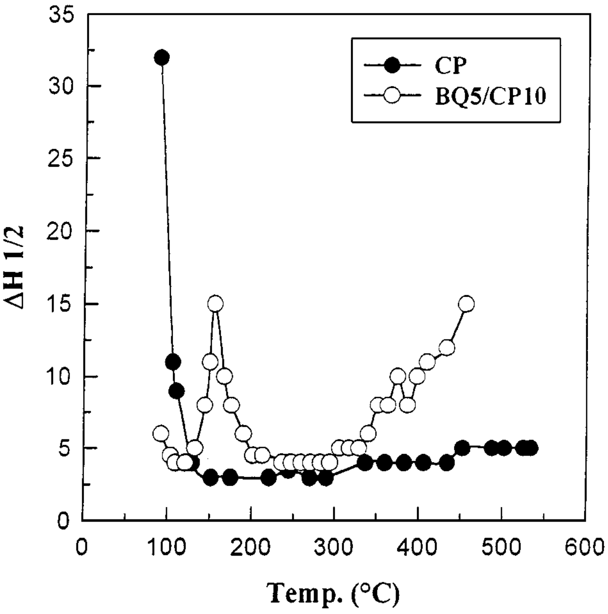
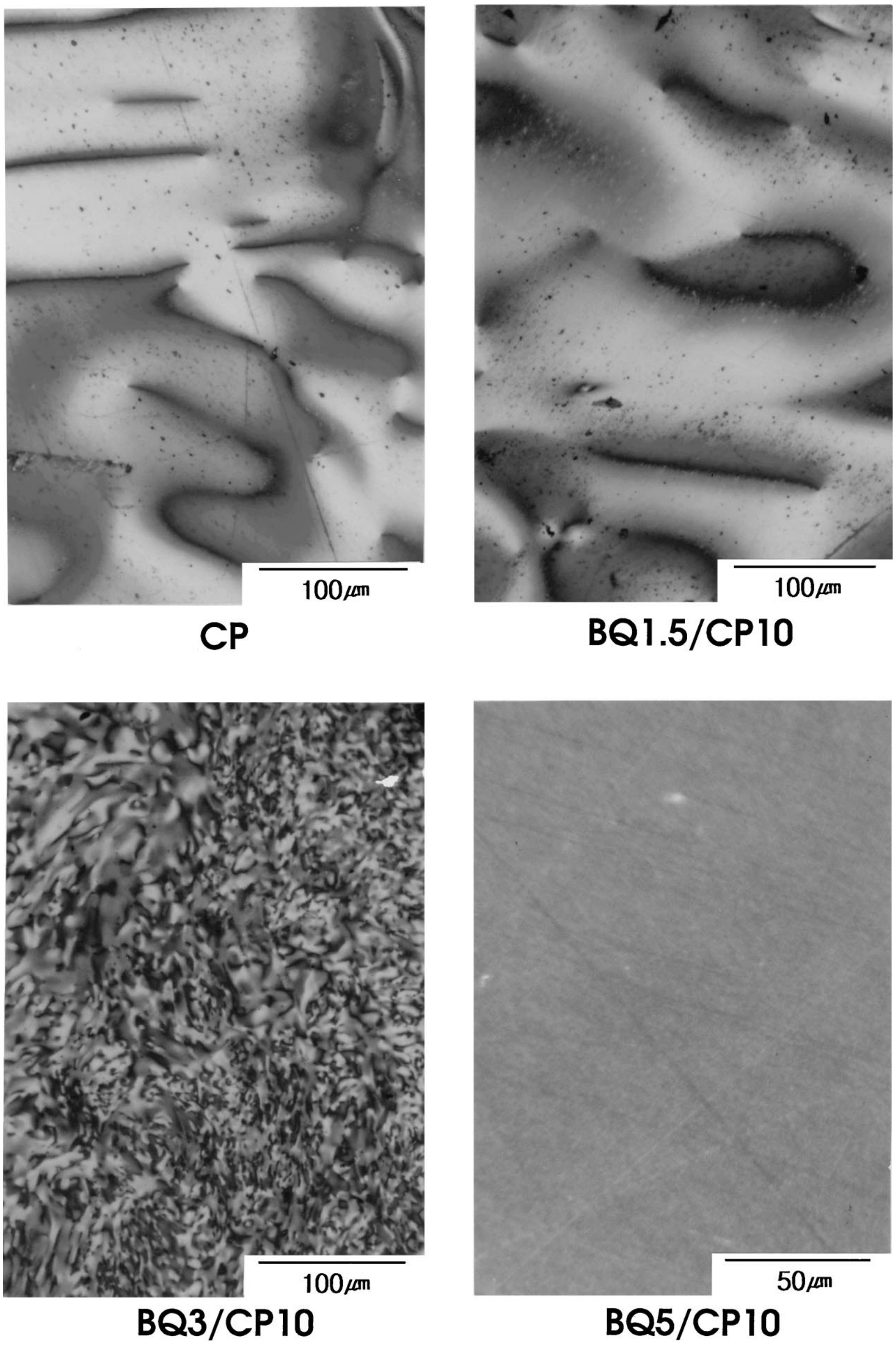


Figure 5 Temperature vs. $\Delta H_{1/2}$ of the peak of ^{1}H NMR.

value is a parameter of the mobility of the constituent molecules, i.e., the higher the mobility the larger the T_2 value [11]. The mobility is determined by competitions between the reversible thermoplastic character and irreversible effect of the reactions of the pitches. The value of $\Delta H_{1/2}$ for CP decreases drastically at about the softening point of the pitch due to the reduction of viscosity and then increases slowly with temperature due to the dominant effect of the enhanced molecular size to the mobility. On the other hand, the $\Delta H_{1/2}$ values for BQ5/CP10 vary with the temperature reflecting the reaction and carbonization behaviors. The lower value of BQ5/CP10 than that of CP at around 100 °C is due to the reduced viscosity from fusion of BQ. The maximum at about 155 °C is coincided with the oligomerization at the reaction temperature (ref. Fig. 1), and then rather sharp increase from 350 °C is indicative of the initiation of rapid growing in molecular size.

The molecular mobility of coal tar pitch is, in general, relevant to its size, i.e., the smaller the molecule, higher the mobility. This fact allows explanation of the optical textures of the samples heat treated in the early stage of carbonization because the stacking process of the molecules in a mesophase formation occurs early at high fluidity resulting in a well developed optical texture (below 450 °C). Fig. 6 shows polarized light microscopic photographs for the samples modified with various concentrations BQ heat treated at 500 °C. The increase in BQ concentration resulted in a decrease in size of flow domain and finally in isotropic texture for



CP

BQ1.5/CP10

BQ3/CP10

BQ5/CP10

Figure 6 Polarized light microscopical photographs of the reaction products of BQ/CP heat-treated at 500 °C.

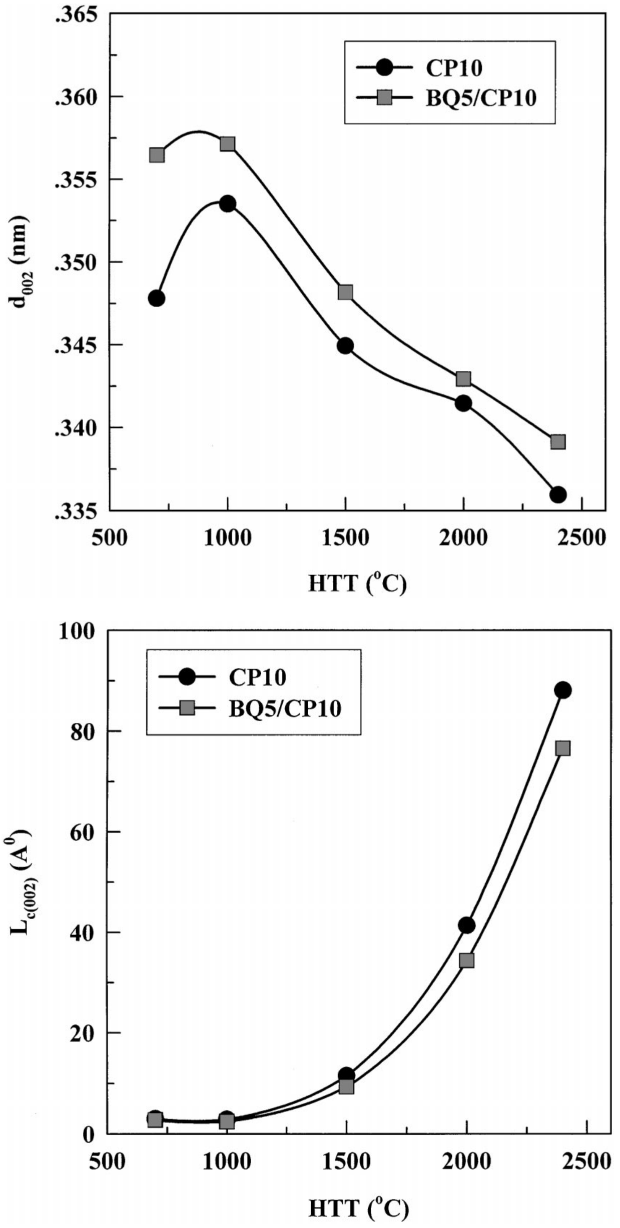


Figure 7 Heat treatment temperature effects of CP and BQ5/CP10 on d_{002} and L_c values.

the BQ5/CP10. The less ordered texture would result from the restricted mobility of the molecules in stacking with an increased size from the BQ/CP reactions. The carbonized ones up to 2400 °C showed the same trend as optical texture of the samples expressed in d_{002} and L_c values as shown in Fig. 7. The d_{002} and L_c values for the BQ5/CP10 represent that CP is more easily graphitizable than BQ5/CP10.

The radical concentration, N_s, of the BQ/CP mixture during the carbonization was monitored *in-situ* by using high temperature ESR and compared with CP in Fig. 8. Though the radical concentrations of all the three samples do not show any significant differences up to the reaction temperature of 155 °C, it becomes more significant for BQ/CP sample above the reaction temperature comparing with CP alone. The N_s values for the BQ3/CP10 and BQ5/CP10 exhibit inflection point at ca. 350 °C at which the mobility of the molecules starts to decrease drastically (refer Fig. 5). The evidence would be interpreted as radical formation on the aromatic carbons. In general, σ-radical is very active

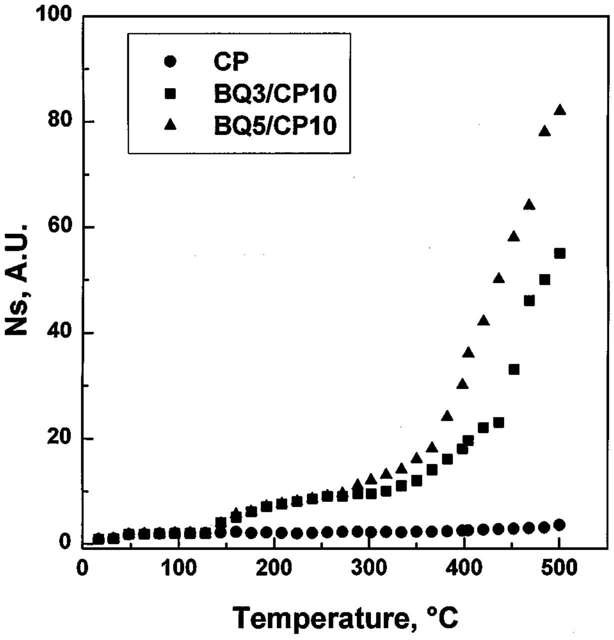


Figure 8 ESR spin concentration dependence on the temperature.

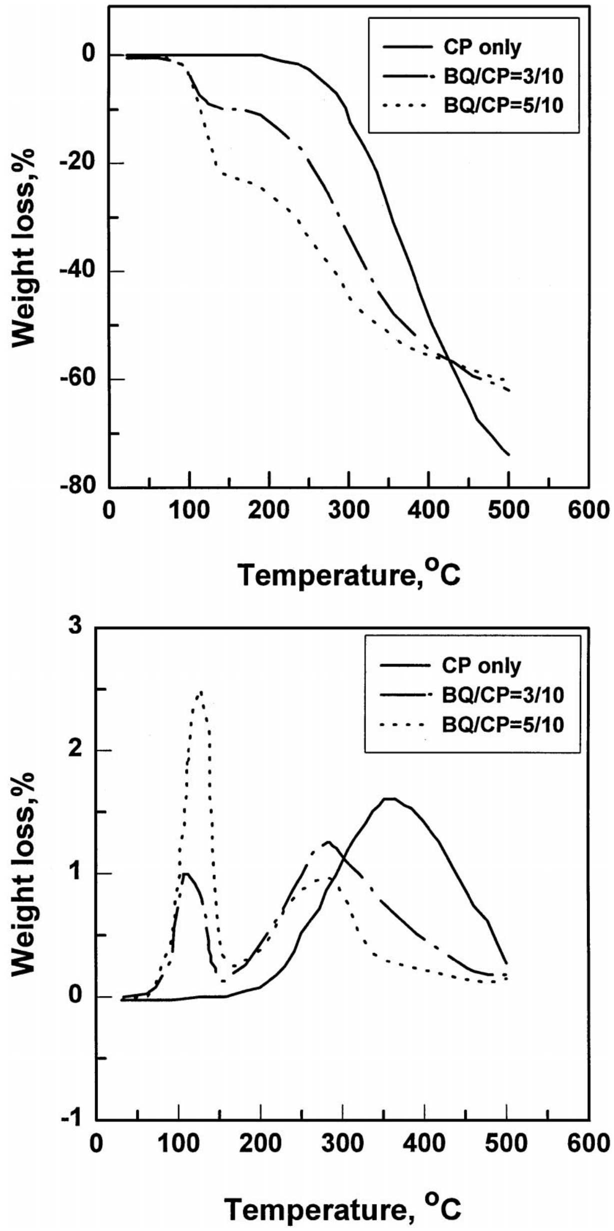


Figure 9 TG, DTA of the BQ/CP mixtures at various compositions.

with very short life-time. On the other hand, π radicals are less active with longer life-time than σ-type radical and the stability of the radical increases with in crease of the size of the conjugated aromatic ring [13]. The investigations suggest that the molecular size increased through the Diels-Alder reaction at 155 °C and then radicals were stabilized. The stabilized σ-radicals in the temperature range of 155–350 °C , and π-radicals above 350 °C were combined resulting further increase in molecular size. The cross-linking formation is considered to be significant after the drastic increase in radical concentration above 350 °C.

Thermogravimetrical behavior of the BQ/CP mixture is shown in Fig. 9. Sudden weight loss at ca. 150 °C would be resulted from the evolution of water after reaction introduced. Once oligomerization and dehydration occurred in the BQ/CP mixture, the oligomerized one became thermally more stable with increasing temperature in comparison with the control. The TDA thermal diagram represents that the temperature of the weight loss moved to lower temperature with the higher BQ concentration above the reaction temperature.

4. Conclusions

The reactions of CP and BQ resulted an increase in molecular weight with an increase in BQ concentration. Such molecular weight increase led to form less ordered carbon materials due to restricted mobility of the consisting molecules. The molecular weight of the precursors was recognized as an important factor in determining the morphology of carbon materials.

Acknowledgement

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