

Preparations of Carbon Fibers from Precursor Pitches Synthesized with Coal Tar or Petroleum Residue Oil

Kap Seung Yang*, Young Ok Choi, Yong Min Kim, Sang Hee Park,
Cheol Min Yang¹, Yong Joong Kim², and Soon Young Soh³

Department of Textile Engineering, Faculty of Applied Chemistry, Chonnam National University,
300 Yongbong-dong, Puk-ku, Kwangju 500-757, Korea

¹Department of Chemistry, Faculty of Science, Chiba University, 1-33 Yayoi, Inage, Chiba 263, Japan

²Department of Electronical and Electric Engineering, Faculty of Engineering,
Shinshu University, 500 Wakasato, Nagano City 380, Japan

³Hanwha Chemical R & D Center, 6 Shinsung-Dong, Yusung-Ku, Taejeon 305-345, Korea

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Abstract: Pitch precursors were synthesized from coal tar(CT) and pyrolysis fuel oil(PFO, petroleum residue oil) at relatively low temperature of 250°C, in the presence of borontrifluoride/diethyletherate complex(BFDE) as a catalyst and nitrobenzene(NB) as a co-catalyst. The softening point, nitrogen content and carbon yield increased with an increase of concentration of NB. The pitch precursors with good spinnability were prepared by removing the volatile components through N₂ blowing. The precursor pitches were spun through a circular nozzle, stabilized at 310°C and finally carbonized at 1000°C. The optically anisotropic structure formed at the absence of NB was changed into isotropic structure, showing a decrease in size of the flow domain. The hollow carbon fiber could be prepared in the process of stabilization. The results proposed that the morphology of carbon materials could be controlled by changing the concentration of catalyst and/or co-catalyst and/or stabilization condition that affect on the mobility of molecules during carbonization.

Keywords: Coal tar, PFO, Borontrifluoride diethyletherate complex, Nitrobenzene, Isotropic carbon fiber

Introduction

The rapid progress in modern industrial technology depends in many ways on the development of new engineering materials capable of performing their functions under severe conditions. The development and use of carbon fibers(CFs) may satisfy many demands based on the superior properties of those[1,2].

CF can be prepared from various raw materials such as gas (methane, ethane and benzene), polymer(cellulose (rayon), polyacrylonitrile(PAN), polyvinylchloride, phenol resin), and pitch(isotropic and mesophase pitch). But commercial production has been achieved from only three kinds of precursors such as PAN, rayon and pitch[3-6].

Despite of its promising future based on its superior properties, large scale consumption of CF is still limited due to its high cost, which arises from high processing cost, low yield of precursor material and technical complexities of production processes. So CF production from petroleum or coal tar have been expected to be low priced under the assumption of low process-cost and high carbon yield.

The pitch-based carbon fibers were normally prepared from pitch precursors which were condensed from low residues. Mochida *et al.*[7-10] developed various catalysts for the condensation of polycyclic hydrocarbons. They reported that isotropic carbons could be prepared through condensations from naphthalene with catalyst of potassium

and the mesophase from that with catalysts of Lewis acids such as, AlCl₃ or HF/BF₃. The AlCl₃ in carbon would not be removed easily due to high viscosity of the condensed hydrocarbon and cause puffing in the process of carbonization. Even when it could be removed, it can not be recycled to be active because it is removed as the form of AlCl₃OH. The HF/BF₃ is difficult to process due to its strong acidity causing corrosion of metals.

Yang *et al.*[11-13] oligomerized, in the presence of *p*-nitroaniline[11], *p*-benzoquinone[12], nitrobenzene or halogen [13], the coal tar or aromatic heavy oil to prepare precursor pitches of high aromaticity for fiber spinning. In the carbonization process, an inhibition of molecular stacking was observed with an increase in molecular size of the precursors, which was explained on the basis of reduced mobility of the enlarged molecules as confirmed from ¹H-NMR and electron spin resonance data[12].

In this study, pitch precursors were prepared from PFO and CT in the presence of the catalyst of BFDE and the co-catalyst of NB, which do not need to be removed after reaction and have high enough boiling point to perform reaction at 250°C. The precursors were spun, oxidatively stabilized and carbonized to be CF. The properties of each prepared product were characterized.

Experimental

Materials

CT(POSCO Chem. Co., Korea) and PFO(Daelim Chem.

*Corresponding author: ksyang@chonnam.ac.kr

Co., Korea) were used. THF-soluble CT was prepared by dissolving in tetrahydrofuran(THF) and followed by removing through filtration of insoluble components. BFDE (Aldrich, first-grade) and NB(Duksan, first-grade) were used as received for catalyst and co-catalyst, respectively. The chemical structures of BFDE and NB are shown in Scheme 1.

Preparation of pitch precursors and fibers

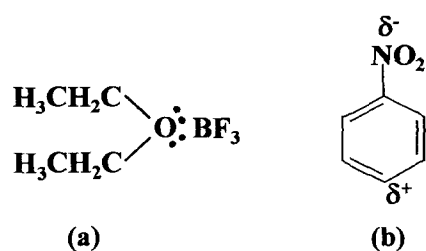
Pitch precursors were synthesized from PFO or CT in the presence of 10 wt. % BFDE as catalyst and 0~50 wt. % NB as co-catalyst at relatively low temperatures of 200 or 250°C for 2 hrs in nitrogen atmosphere. Product yield of the pitch precursor was calculated from equation (1).

$$\text{Yield}(\%) = \frac{\text{weight of the product after reaction}}{\text{weight of the raw materials}} \times 100 \quad (1)$$

The softening point of pitch precursor was raised to be enough for oxidative stabilization by nitrogen blowing at 350°C for 3 hrs by removing the volatile components. CT precursor used for spinning was CT/BFDE10-NB10, representing CT reacted in the presence of 10 wt. % BFDE and 10 wt. % NB and followed by nitrogen blowing to reduce volatile components. PFO precursor used for spinning was PFO/BFDE10-NB10, which represents that PFO was condensed in the presence of BFDE 10 wt. % and NB 10 wt. % at 250°C for 2 hrs.

Preparations of carbon fibers

Pitch fiber was spun at 290~305°C through the round-



Scheme 1. The chemical structure of BFDE (a) and NB (b) used as a catalyst and a co-catalyst, respectively.

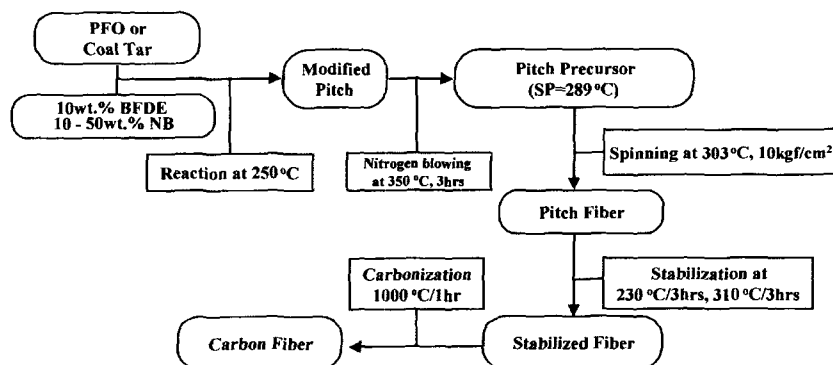


Figure 2. The schematic diagram of overall experiment.

shaped single hole spinneret(L/D = 0.6/0.3 mm) by pressurized nitrogen of 10 kgf/cm². Figure 1 shows the schematic diagram of spinning apparatus. The pitch fibers were oxidatively stabilized stepwise at 230°C and 310°C for 3 hrs in the air atmosphere to avoid fusion in the carbonization process.

The stabilized fibers were carbonized at 600°C and/or 1,000°C for 1 hr under argon atmosphere. The carbon yield was calculated from the equation (2). Heating rate was 5°C/min for both stabilization and carbonization. The overall diagram of experiment is shown in Figure 2.

$$\text{Carbon yield}(\%) = \frac{\text{weight of sample after carbonization}}{\text{weight of sample before carbonization}} \times 100 \quad (2)$$

Characterizations

Softening points of the precursors were measured by sensing the melt flow using Mettler FP90 (Mettler-Toledo, Switzerland). The functional groups of the samples were characterized by using an FT-IR (Nicolet 520p, USA) and an NMR (Varian XL-400, USA) in KBr disc and dissolved in

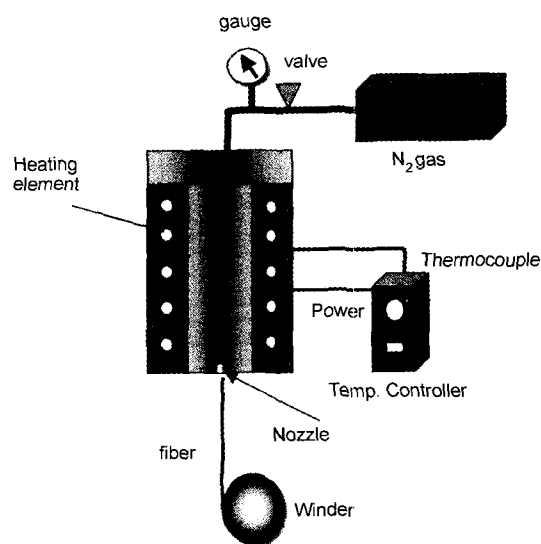


Figure 1. Schematic diagram of spinner.

CDCl_3 , respectively. C, H, N contents in samples were determined from elemental analysis, and the O content was calculated from subtracting the sum of C, H, N % from 100.

Thermogravimetric analysis (TGA) was performed under air or nitrogen atmosphere to find optimized stabilization condition or to measure thermal stability of the samples respectively.

The optical properties of stabilized and carbonized samples imbedded in an unsaturated polyester resin and polished were observed under a polarized-light microscope (AFX-II, Type-104, Nikon, Japan). SEM (Hitachi, S-4700, Japan) was used to investigate the surface and cross sectional features of the fibers. X-ray diffractometry (Dmax 1200, Rigaku, Japan) was also used to characterize the microstructures.

Results and Discussion

Table 1 shows the characteristics of the raw materials of CT and PFO and their reaction products. Though the carbon content of CT is lower than that of PFO, the aromaticity of CT is higher than that of PFO, indicating the larger molecular size of PFO with lower aromaticity than CT. With increasing concentrations of BFDE and NB, the softening point of precursor was increased, representing the increase of molecular sizes. H/C value shows decreasing trend with an increase in BFDE or NB concentration, indicating increase in molecular size through condensation reaction. Some exceptional cases of CT/BFDE10-NB50 and PFO/BFDE10 resulted probably from the result of competition reaction between the condensation and the addition reactions of hydrogen-rich compound of NB or diethyl ether.

Table 2 shows the characteristics of pitch precursors that

exhibited good spinnability of 700 m/min in take-up speed. The precursor pitches with appropriate softening points for fiber formation were prepared through nitrogen blowing of the reaction products. Both the CT/BFDE10-NB10 (N_2) and PFO/BFDE10-NB10 (N_2) exhibited the carbon contents above 92%, which may give high carbon yield in carbonization. The lower H/C ratio of the CT/BFDE10-NB10 than PFO/BFDE10-NB10 represents that the CT-source sample consists mainly of aromatic components while the PFO-source sample consists mainly of aliphatic components. In general, the precursor with high aromaticity leads to high carbonization yield.

TGA thermograms of the samples (Figure 3) were used for investigating the thermal stability under N_2 atmosphere and finding an optimum stabilization condition under air atmosphere. CT-source precursor starts to lose weight from about 200°C with somewhat gentle slope, on the other hand, the PFO-source precursor starts to lose weight from 400°C with a steep slope. The weight losing tendency of the two samples was reversed above 600°C. The PFO-source precursor would be larger size of molecule than CT-source precursor but exhibiting lower aromaticity. The oxygen uptake of PFO-source precursor was much higher than that of CT. The behavior can be explained that the PFO with higher alkyl content (lower f_a value) is more reactive to oxygen under air atmosphere.

The polarized light microphotographs of samples carbonized at 600°C are shown Figures 4 and 5. CT/600 and CT/BFDE10-NB10 (or NB30)/600 showed the optically anisotropic morphology but CT/BFDE10-NB50/600 was isotropic. The molecular size of the pitch was increased by condensation reaction with an increase NB concentration. The molecules with increased sizes are expected to exhibit

Table 1. Some properties of the reaction products

Sample ID	Softening Point(°C)	Elemental Analysis (wt. %)					Atomic Ratio		f_a^*
		C	H	N	S	O	H/C	N/C	
CT	Liquid at RT	91.21	5.08	3.06	0.65	-	0.68	0.029	0.9
CT/BFDE10-NB0	100	89.89	4.69	1.21	0.78	3.43	0.63	0.012	0.9
CT/BFDE10-NB10	134	89.68	4.27	1.48	0.59	3.78	0.60	0.014	0.9
CT/BFDE10-NB50	203	83.51	4.39	3.62	0.48	8.0	0.63	0.037	-
PFO	40	91.92	7.10	0.59	0.39	-	0.93	0.005	0.75
PFO/BFDE10	155	88.86	7.14	-	0.25	3.75	0.96	0	0.67
PFO/BFDE10-NB10	214	88.24	6.07	0.99	0.24	4.46	0.83	0.01	0.77

* f_a : aromaticity calculated on the basis of Brown-Lander equation[14].

Table 2. Some properties of pitch precursor for spinning

Sample ID	Softening Point(°C)	Elemental Analysis (wt. %)					Atomic Ratio	
		C	H	N	S	O	H/C	
CT/BFDE10-NB10 (N_2)	289	92.70	3.72	1.90	0.34	1.34	0.48	
PFO/BFDE10-NB10 (N_2)	267	93.78	6.07	-	0.17	-	0.78	

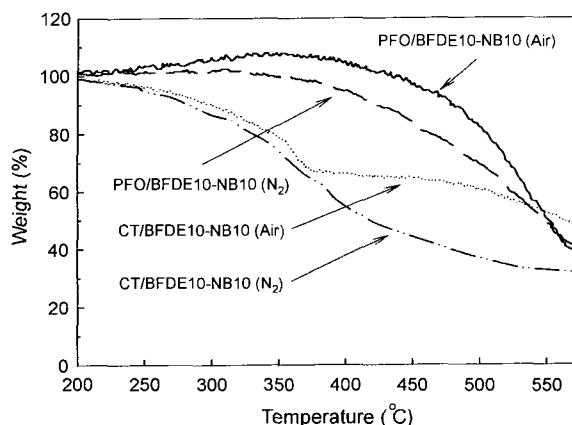


Figure 3. TGA curves of samples under air and N₂ atmosphere.

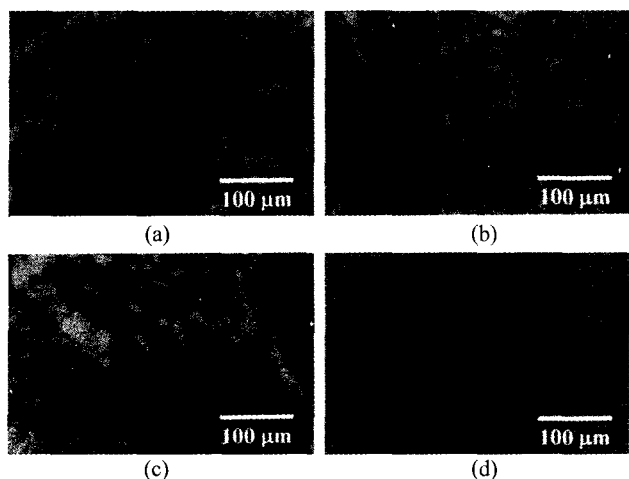


Figure 4. Polarized light microphotographs of samples carbonized at 600°C: (a) CT/600; (b) CT/BFDE10-NB10/600; (c) CT/BFDE10-NB30/600; (d) CT/BFDE10-NB50/600.

relatively low mobility during carbonization procedure, which may then cause the inhibition of molecular stacking to result in optically isotropic texture. This phenomenon would be supported by the study of Yang *et al.*[12] who reported that the optical structure is related on molecular size at early

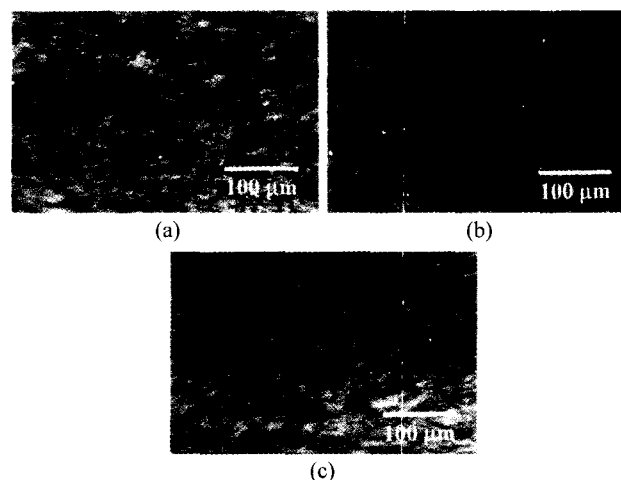


Figure 5. Polarized light microphotographs of samples carbonized at 600°C: (a) PFO/600; (b) PFO/BFDE10/600; (c) PFO/BFDE10-NB10/600.

stage of heat treatment. In Figure 5, the carbonized samples prepared from PFO are optically anisotropic, but PFO/BFDE10-NB10/600 has the smaller domain sizes in comparison with corresponding CT-source sample (Figure 4(b)). In general, the domain size of CT-source sample is larger than that of PFO-source sample, indicating the smaller size of component molecules of CT sample.

Table 3 shows the carbon yield and elemental analysis of samples carbonized at 1000°C. The carbon yield of CT/1000 and PFO/1000 were 22% and 20.5%, respectively. But they increased with the presence of BFDE and NB that improve the thermal stability by increasing molecular weight. The participation of NB in the reaction may be confirmed by the increase of N/C values with an increase in NB concentration. The carbon yield of CT-source sample is still higher than that of PFO-source sample, indicating high aromaticity of the former sample. This preparation method could be applicable to preparation of nitrogen-containing ACF, which can be used as catalyst support with high dispersion and adsorbents of polar materials including SO_x or NO_x.

Figure 6 shows the X-ray diffraction curves of samples

Table 3. Some properties of the samples carbonized at 1000°C

Sample ID	Yield (%)	Elemental Analysis (wt. %)					Atomic Ratio	
		C	H	N	S	O	H/C	N/C
CT/1000	22.0	98.68	0.25	0.76	0.31	0	0.030	0.007
CT/BFDE10/1000	42.0	98.15	0.37	1.10	0.38	0	0.046	0.010
CT/BFDE10-NB10/1000	50.0	98.13	0.25	1.27	0.35	0	0.031	0.011
CT/BFDE10-NB50/1000	46.0	96.79	0.34	2.48	0.39	0	0.043	0.012
PFO/1000	20.5	99.24	0.38	0	0.38	0	0.05	0
PFO/BFDE10/1000	31.0	99.57	0.29	0	0.14	0	0.03	0
PFO/BFDE10-NB10/1000	33.7	98.04	0.34	0.76	0.19	0.67	0.04	0.007

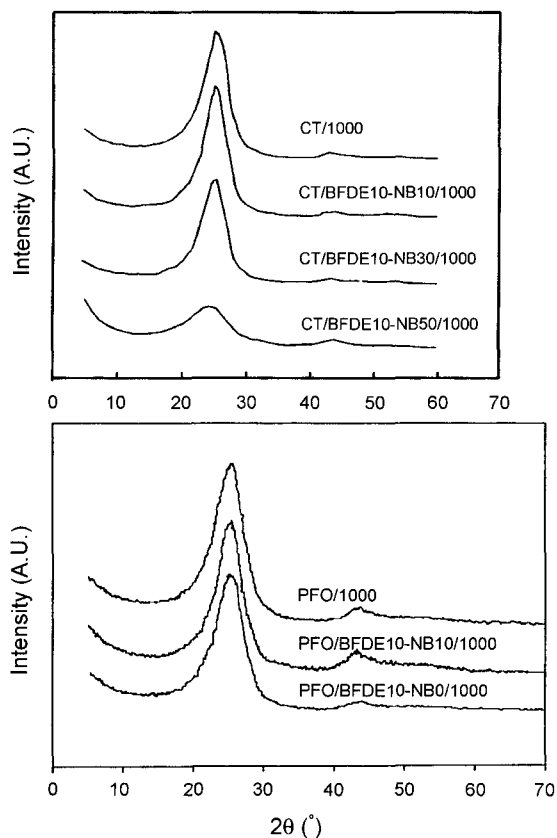


Figure 6. X-ray diffraction curves of samples carbonized at 1000°C.

carbonized at 1000°C. The intensities of the carbonized samples decreased with an increase in the NB concentration, indicative of poor crystallinity and small stacking height (Lc). Table 4 summarized the X-ray parameters calculated from the Figure 6. In general, the stacking height(Lc) decreased with the increasing NB concentration. Especially CT/BFDE10-NB50/1000 shows almost amorphous state and the lowest Lc value.

Figure 7 shows the SEM microphotographs of stabilized fiber and carbon fibers carbonized at 1000°C. (a), (b), and (c) are prepared from CT/BFDE10-NB10 and (d) is prepared from PFO/BFDE10-NB10. The average diameter of fibers was decreased by carbonization from (a) to (b), indicating mass loss through carbonization. The carbon fiber from CT/BFDE10-NB10 had the 12.25 Å of Lc and 5.24 Å of d₀₀₂, representing the low ordered isotropic carbon fiber. The

Table 4. The X-ray diffraction data of the samples carbonized at 1000°C

Sample ID	X-ray parameters		
	2θ	d ₀₀₂ (Å)	Lc (Å)
CT/1000	25.00	3.559	22.89
CT/BFDE10/1000	25.30	3.517	20.56
CT/BFDE10-NB10/1000	25.35	3.511	22.62
CT/BFDE10-NB50/1000	25.95	3.431	13.94
PFO/1000	24.90	3.573	37.61
PFO/BFDE10/1000	25.45	3.497	35.86
PFO/BFDE10-NB10/1000	25.05	3.552	21.68

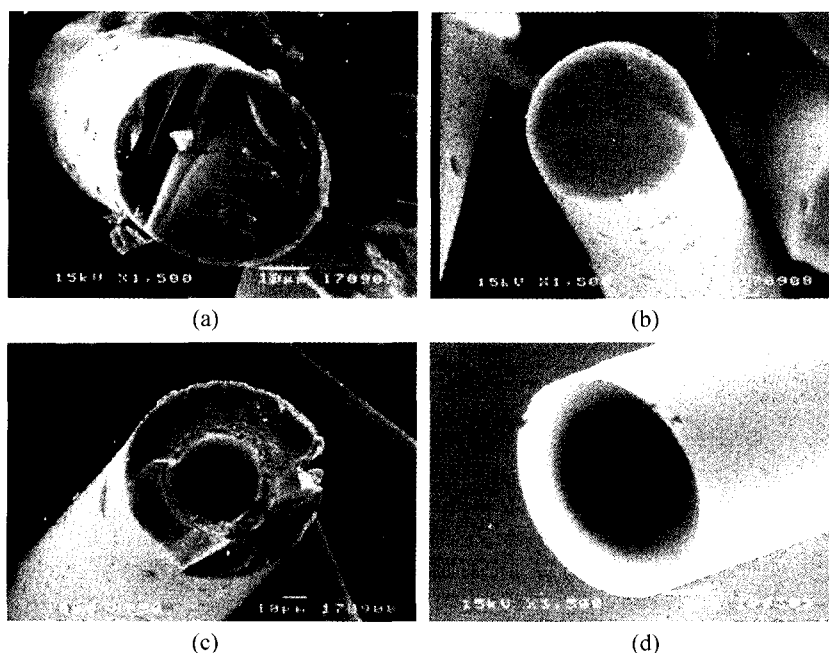


Figure 7. SEM microphotographs of stabilized fiber and carbonized fibers: (a) CT/BFDE10-NB10-stabilized fiber; (b) CT/BFDE10-NB10/1000; (c) CT/BFDE10-NB10/1000-hollow fiber; (d) PFO/BFDE10-NB10/1000.

hollow fiber was formed from the pitch fiber with the relatively large diameter (60 μm). The difficulty of diffusion of oxygen into inner center of fiber would stabilize only outer portion of the fiber, setting the structure of the outer part of the fiber and remaining to be volatile in the central part. The part with enough fluidity would form hollow shape through mass loss in the carbonization procedure. This behavior could be used for preparation of hollow CF through selective stabilization. CF prepared from PFO/BFDE10-NB10 also shows the skin-core structure caused by the insufficient stabilization.

Conclusions

Pitch precursors were prepared from coal tar and PFO at relatively low temperature (250°C) in the presence of BFDE as a catalyst and NB as a co-catalyst. Precursors show an increase in aromaticity and softening point from the raw materials, when the molecular weight was raised through chemical reaction with BFDE and NB. Both of the precursors showed the good spinnability with the winding speed of above 700 m/min. Though PFO precursors showed higher reactivity to air than the CT precursors did, they showed lower thermal stability than that of CT precursors above 600°C. The higher concentration of NB, the higher carbon yield and the more glassy carbon structure were obtained. It was proposed that the morphology of carbon materials could be controlled by changing the concentration of catalyst and/or co-catalyst and/or stabilization condition that affect on the mobility of molecules during carbonization.

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