The conjugated plane formed in polyacrylonitrile during thermal stabilization

Shuai Lei, Weiyu Cao, Zeyu Fu, Lianghua Xu

Key Laboratory of Carbon Fiber and Functional Polymer, Ministry of Education, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China
Correspondence to: L. Xu (E-mail: xulh@mail.buct.edu.cn)

ABSTRACT: The formation process and mechanism of the pseudo-graphite sheets of polyacrylonitrile (PAN) during thermal treatment in inert atmosphere were investigated by thermo-gravimetry (TG) and X-ray diffraction (XRD). According to the results, the conjugated plane originally formed during stabilization was proposed as the basic planar structure of the pseudo-graphite sheets, and it was connected and stacked to form pseudo-graphite microcrystal through chain scission reaction and non-carbon atoms elimination reaction in 280–450 °C and 800–1300 °C respectively. The *in situ* measurements for time dependence of ultraviolet-visible (UV-vis) and Fourier transform infrared spectra (FTIR) were applied to study the conjugated plane of PAN during isothermal stabilization. It was found that with the higher temperature the conjugated plane forms more rapidly, and it has higher conjugated extent with the extending of heating time. The FTIR data showed that both cyclization and dehydrogenation are beneficial to the evolution of conjugated plane in the first 3 h, but only cyclization continues after 3 h at 250 °C. Further investigation indicated that stabilized PAN with large quantity and high conjugated extent of the conjugated plane would contribute to get large size of pseudo-graphite microcrystal after carbonization, which is consistent with the former assumption. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43890.

KEYWORDS: basic conjugated plane; polyacrylonitrile; pseudo-graphite crystal; thermal stabilization; UV-vis spectrum

INTRODUCTION

Polyacrylonitrile (PAN) is an ideal raw material for producing carbon fibers. Currently 90% of the global carbon fiber is produced by PAN precursor.[1] The transformational mechanism of the chemical structure during thermal treatment has attracted much research attention in the last few decades, because the chemical structure is diversified and complicated, and it directly determines the mechanical property of carbon fiber. For example, the Young's modulus of carbon fiber depends on the pseudo-graphite crystalline structure, and the large size of crystal results in the high modulus.[2–4] Therefore, a process that could improve the size of pseudo-graphite crystal would be extremely helpful to control the Young's modulus.

It is well-known that the pseudo-graphite sheet containing carbonic rings with π-conjugated bonds presents a carbonic conjugated plane, and the unsaturated double bonds were originally generated during stabilization.[5] Therefore, the big pseudo-graphite sheet of carbonized PAN probably derived from the relatively small one in the early stage of thermal treatment, but its basic structure was still puzzling.

Thermal stabilization, usually carried out at 180–300 °C, is an essential procedure for the organic–inorganic transformation of PAN.[6] In the past decades, many researchers dedicated to revealing the evolution mechanism of the chemical structure of PAN during thermal stabilization using FTIR and nuclear magnetic resonance (NMR). They recommended that the heat resistance of PAN could be improved by chemical reactions including cyclization of nitrile groups, dehydrogenation of the main chain, and oxidation, which generate C≡N, C≡C, and C≡O (or ─O─) respectively.[7,8] Several models for chemical structure of stabilized PAN have been proposed such as "ladder structure," "heteroaromatic cyclic structure," "polyenamine cyclic structure," and "conjugated polyene." Among them the "ladder structure" containing fully aromatic heterocyclic rings is accepted by most of the researchers.[8] Thus, we can make a conclusion from those reports that conjugated planes are formed by C≡N, C≡C, and aromatic heterocyclic rings, which can also explain the color change of PAN during stabilization.[9,10] Till now the evolution process of the conjugated plane with heating time and temperature, and its relationship with the pseudo-graphite crystal were not clarified.

Table I. PAN Samples with the Thermal Treatment Conditions

Samples (C-)	Temperature (°C)	Heating rate	Samples (T-)	Holding at 250 °C (h)	Carbonized	Heating rate
C-25	25	5 °C/min	T-0.5	0.5	1300 °C	10 °C/min
C-280	280		T-1	1		
C-450	450		T-3	3		
C-800	800		T-5	5		
C-1300	1300		T-7	7		
			T-10	10		

UV-vis spectrum is an effective method to characterize the conjugated system containing unsaturated bonds. The π-π^* electronic transition can be stimulated by relatively lower energy with the absorption wavelength in the range of 200–800 nm.[11] Kubasova N.A. mentioned that the conjugated system consisting of 5 or 6 double bonds was formed in PAN/dimethylformamide (DMF) solution at 153 °C based on the phenomenon that the UV-vis absorption band has a maximum absorption wavelength (λ_{max}) around 350 nm.[12,13] In fact, the stabilized PAN cannot be totally dissolved, so it is better to test it in solid state for the purpose of getting more accurate information about the conjugated plane.

In this article, the formation process and mechanism of the pseudo-graphite sheets was investigated by TG and XRD, and the conjugated plane structures were proposed as the structural basis of pseudo-graphite sheets in stabilized PAN. In addition, PAN thin films were used to study the evolution process and mechanism of the conjugated plane by *in situ* FTIR and UV-vis measurements at different stabilized time and temperature. The suggested assumption was further proved by the investigation of the effect of stabilization on the pseudo-graphite microcrystalline size in carbonized PAN films.

EXPERIMENTAL

Materials
The white PAN copolymer powder containing less than a few percent of co-monomer (itaconic acid) was purchased from Jilin Chemical Fiber Co., (China) and it was prepared by free radical polymerization. The PAN powder was first dissolved in dimethyl sulfoxide (DMSO) by the concentration of 0.5 wt %, and then drop cast into glass trays. These trays were subsequently placed into a vacuum oven for vaporizing the solvent at 60 °C for 24 h. Later on PAN films were peeled off from the trays and washed by deionized water, and dried to get constant weight. Samples for *in situ* UV-vis test were prepared on a quartz substrate by the same solution casting method, because quartz has no absorption in the spectrum ranging from 200 to 800 nm. Only several drops were used to ensure the films were thin enough.

C1-labeled (nitrile groups) or C3-labeled (methylene groups) acrylonitrile (^{13}C, 99%) were purchased from Cambridge Isotope Laboratories. The C1-labeled or C3-labeled PAN copolymers were also synthesized although free radical polymerization with about 1 wt % itaconic acid (IA) as co-monomer, and used for ^{13}C-NMR test.

Thermal Treatment of PAN
The PAN films were thermal treated in a tube furnace under different conditions. They were heated to the objective temperature at a constant heating rate and cooled naturally. The pure nitrogen was used as atmosphere during the thermal treatment process to eliminate the effect of oxidation reaction on the conjugated system. The prepared PAN samples were listed in Table I together with the thermal treatment conditions.

The heat treatment process of ^{13}C labeled co-PAN powders was performed in the same furnace, and they were isothermal treated for 1 h at 250 °C in nitrogen and cooled naturally.

Characterization
Thermo-gravimetric (TG) measurement was carried out on a SDT Q600 (TA instrument) TG analyzer. About 5 mg PAN powder was put into a ceramic crucible, and it was heated at 5 °C/min in nitrogen (50 mL/min) up to 1300 °C.

An Empyrean wide angle X-ray diffractometer (Panalytical, Netherlands) was used to study the pseudo-graphite crystal of thermal treated PAN. The X-ray tube was operated at 40 KV and 250 mA with the Cu Kα radiation ($\lambda = 0.154$ nm). The 2θ scanning was carried out from 8° to 60° by 3°/min with the step width of 0.0263°. The diffraction bands were fitted by Lorentz and Gauss function, and the crystalline size of pseudo-graphite (L_a and L_c) was calculated by Scherrer formulae[14]:

$$L = k\lambda/\beta \cos\theta \tag{1}$$

where k is a constant 1.84 for L_a and 0.91 for L_c, λ is the wavelength of the X-ray (0.154 nm), θ is the diffraction angle, and β is the half-width of (10) diffraction for L_a and (002) diffraction for L_c, both β and θ needs to be transferred to radian.

Table II. X-ray Diffraction Parameters of Thermal Treated PAN at Different Temperatures

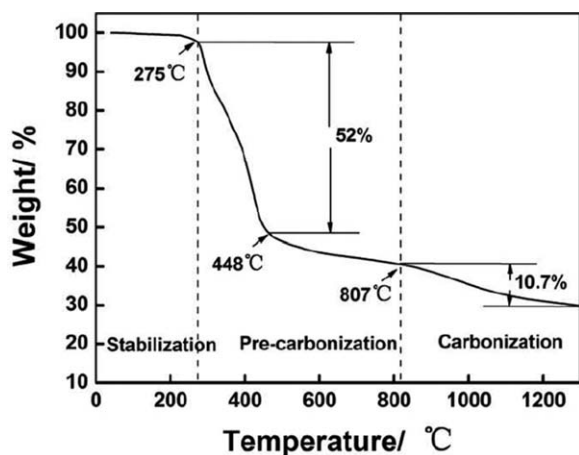| Temperature (°C)	2θ (°)				FWHM (°)
	(100)		(002)	(110)	(10)	(10)
25	16.8	25.8		29.3		
280	16.0		22.0		44.1	10.4
450	15.6		24.0		44.3	6.9
800			24.3		43.6	6.0
1300			25.1		43.6	4.2

Figure 1. TG curve of as-received PAN from room temperature to 1300 °C at 5 °C/min in pure nitrogen.

UV-vis spectroscopy measurement (Shimadzu UV-2450, wavelength range from 200 to 800 nm) was carried out to study the evolution of conjugated plane with the slit width of 2 nm and medium sweep speed. A Linkam FTIR600 hot platter with quartz windows was set into the light path of UV-vis spectrometer. The thin PAN film with its quartz substrate was quickly heating to 180, 220, 250, and 280 °C at 100 °C/min under the flow of nitrogen and holding for 10 h. The spectra were collected after different time scale (10 min/30 min/1 h/2 h... 10 h) and the air was used as the reference.

The same hot platter with ZnSe windows was also used on FTIR spectrometer (Nicolet 5700, scanning from 400 to 4000 cm^{-1} with the resolution of 8 cm^{-1}) to detect the generation of double bonds and the degradation of nitrile groups. The test conditions were same as UV-vis measurements.

The ^{13}C solid-state NMR spectra were recorded with a Bruker AV III 400WB spectrometer operating at a ^{13}C resonance frequency of 100.6 MHz. A 2.5 mm MAS H/F/X triple resonance probe was also applied. The samples were packed into 2.5 mm Zirconia rotor with magic-angle scanning (MAS) at a spinning speed of 20 kHz. ^{13}C DP/MAS spectra were acquired with a 200 s recycle delay, and 256 scans with ^{13}C 90° pulse of 3.9 μs.

RESULTS AND DISCUSSION

Formation Process of the Planar Structure

Commonly, two thermal treatment steps including stabilization (or pre-oxidation) and carbonization are necessary for the production of carbon fiber, which is consisting of pseudo-graphite microcrystal.[1,15] Stabilization process is very complex especially in the oxidizing atmosphere. According to the previous studies on the extent of stabilization by FTIR,[16–18] the nitrile groups were gradually decreased as the stabilization proceeding and were not totally reacted. That is to say the stabilized PAN must be composed of two parts differing in chemical structure, the heat-resistant aromatic ring and the heat-labile polymer chain. The later was decomposed during pre-carbonization (<700 °C), molecular segments with several carbon atoms were eliminated as tar,[19] and most of the weight loss happened. As a consequence, we need to find out when dose the pseudo-graphite

sheets appear to study the structural basis of it and the transfer mechanism. A TG test had been performed in nitrogen atmosphere before the thermal treatment of PAN to determine the temperature ranges.

The TG curve of PAN shown in Figure 1 exhibits two main stages of weight loss. The greatest weight loss was 52% happened in the temperature range of 280–450 °C, which corresponds to the precarbonization, and chain scissions reaction dominates in this temperature range with the emission of HCN, NH$_3$, and oligomers.[19–22] Relatively, 10.7% of the weight lost in the temperature range of 800–1300 °C, which corresponds to the high temperature carbonization, and non-carbon atoms elimination reaction dominates in this temperature range with the emission of N$_2$, etc.[22] However, only a little weight lost before 280 °C, which corresponds to stabilization.

XRD patterns of thermal treated PAN, as shown in Figure 2(a), were applied to study the formation of the pseudo-graphite crystal at different thermal treatment steps based on the temperature ranges of TG results. The typical sharp peaks at 16.8° and 29.3° are belonged to (100) and (010) diffraction of the as-received PAN, respectively, which is accepted by most of the researchers. While the dispersed peak at 25.8° is controversial, some researchers ascribed it to the diffraction of amorphous molecular chain.[23,24] With the temperature increasing, the peaks at 25.8° and 29.3° disappear at 280 °C, and the peak at 16.8° disappear at 800 °C, that means the molecular chain structure was totally decomposed at 800 °C. Similarly, there are also two sharp peaks at 25.1° and 43.6°, which are assigned to (002) and (10) diffraction of pseudo-graphite crystal in carbonized PAN at 1300 °C respectively.[14] It is worth noting that both the (002) and (10) diffraction are firstly appeared at 280 °C (marked by black triangle), which demonstrates the pseudo-graphite sheets were formed since stabilization. However, the diffractions at 280 °C are broad and dispersive, this phenomenon indicated that the pseudo-graphite sheets are very small and arranged randomly. This also can explain the quasi (002) diffraction of stabilized PAN appeared at 22.0° at 280 °C, which is not uniform with the (002) diffraction of carbonized PAN.

The diffraction angle (2θ) and the full width at half maximum (FWHM) of (10) diffraction were listed in Table III. According to the data in Table III, the shape of (10) diffraction turned more and more sharp as the temperature increasing, which indicates the growth of the pseudo-graphite sheets. The lateral size (L_a) calculated by Scherrer formulae was depicted in Figure 2(b). The growth of pseudo-graphite sheets is also emerged two main stages, and the temperature ranges are consistent with the TG curve. Consequently, the evolution mechanism of pseudo-graphite sheets was proposed in Figure 3. The pseudo-graphite sheets composed of heterocyclic rings and double bonds was originally formed during stabilization, but the plane was very small and containing non-carbon atoms at 280 °C, accordingly it appeared as a conjugated plane structure. The chain scissions reaction (280–450 °C) resulted in the growth of L_a from 1.68 to 2.55 nm, while the non-carbon atoms elimination reaction (800–1300 °C) resulted in the growth of L_a from 2.89 to 4.13 nm.
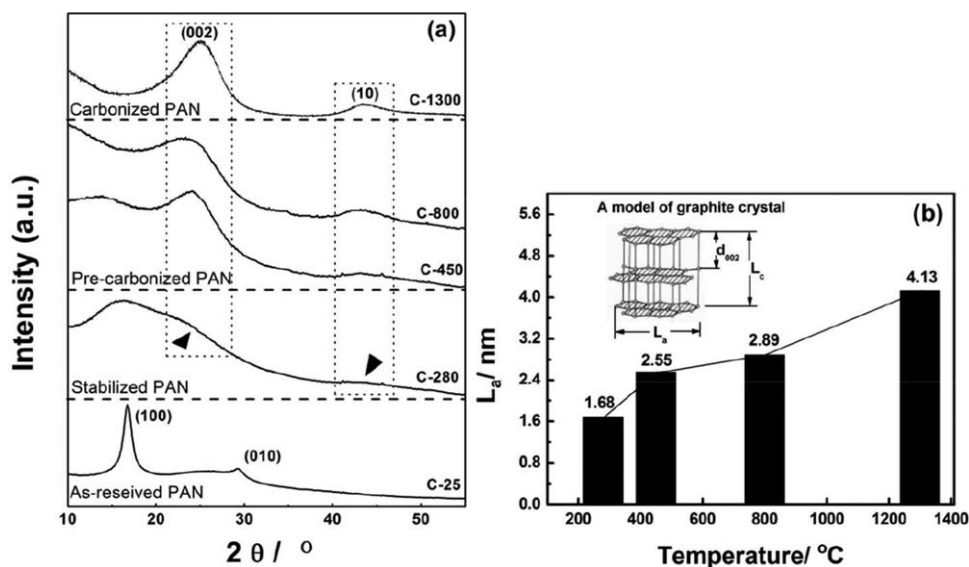
Figure 2. (a) XRD patterns of thermal treated PAN at different temperatures; (b)the lateral size of carbonic conjugated planes calculated by Scherrer formulae. All of these patterns are fitted by Lorentz and Gauss mixed functions.
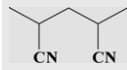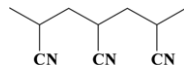
Formation and Evolution of the Basic Conjugated Structure during Stabilization

Figure 4 shows the *in situ* UV-vis spectra of isothermal stabilized PAN with different heating time at a series of temperature. There appears two bands with the wavelength of maximum absorption (λ_{max}) at around 250 nm (band I) and 360 nm (band II), which stand for two kinds of conjugated plane structure consisting of C=C and C=N groups,[8,11–13] and they have different conjugated extent. The conjugated extent of conjugated plane II is higher, because it has higher λ_{max}. With the heating time extending, the position of band I do not change; in the case of band II, it keeps constant around 360 nm at lower temperature180 and 220 °C [Figure 4(a,b)], and shifted to 400 nm at 250 °C after 4 h [Figure 4(c)], while at 280 °C it shifted to 407 nm after 2 h [Figure 4(d)].

According to those model structures mentioned in the introduction part of this article, these two conjugated planes are partly consisting of aromatic heterocyclic rings. Wang *et al.*[25] found that the isolated pyridine units were formed at relatively low temperature thermal treatment of PAN in nitrogen using selective ^{13}C labeling and solide-state NMR spectroscopy. Similar method was also used to study the samples isothermal treated at 250 °C for

1 h in nitrogen as depicted in Figure 5. The ratio of the integral values of C1 (149 ppm and 154 ppm): C3 (136 ppm) for the isolated aromatic heterocyclic ring should be 2:1, but the calculated ratio is about 1.84:1 according to the data in Figure 5. In other word, there were still some structures containing more than one aromatic heterocyclic ring. It has been reported that the formation of aromatic heterocyclic ring is related with the configuration of the original PAN molecular chain, the neighboring nitrile group of the isotactic unit will easily take place the cyclization reaction.[25] The free radical polymerized PAN has an atactic configuration, but also contains some isotactic units with several monomers, and the relatively long isotactic units are less than short ones (see Table III). Namely, the probability of forming polycyclic aromatic structure with higher conjugated extent is extremely low. Consequently, it is reasonable to conclude that conjugated plane I and II are composed of single and double aromatic rings respectively, and the quantity of conjugated plane I is more than that of conjugated plane II in theoretical. The difference of 52 nm between observed bands and reference bands in Table III reveals that these conjugated planes contain not only aromatic rings but also about two double bonds linked to the rings as shown in Figure 3. The bathochromic-shift phenomenon happened only on band II

Table III. UV-Vis Absorption Bands of the Conjugated Planes and its Theoretical Reference Structures

Atactic-PAN chain		Reference structure	Reference bands[28] (primary, π-π*)[a]	Observed bands
Isotactic configuration	Radio[26,27]			
CN CN	50.6%		198 nm	250 nm
CN CN CN	25.3%		308 nm	360–407 nm

[a] The π-π* transition of the reference structures has the maximum of absorption coefficient (ε), so it's the primary band.
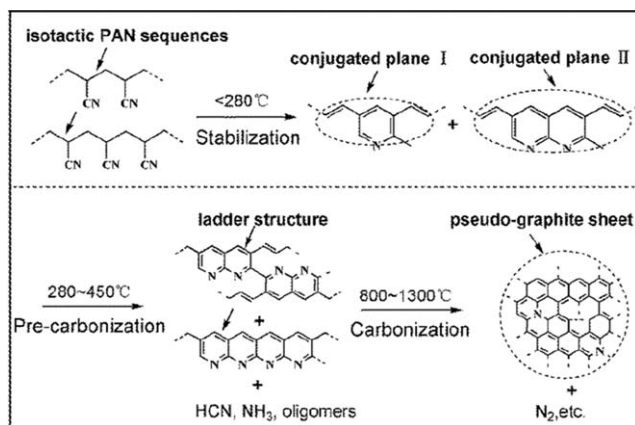
Figure 3. Scheme for chemical reaction pathways of the planar structure.[1,8,20–22]

Figure 5. [13]C DP/MAS spectra for nitrile (C1) and methylene (C3) group ^{13}C-labeled co-PAN stabilized at 250 °C for 1 h in nitrogen. The insert spectra shows the original polymer as reference, and every individual peak was fitted by Lorentz and Gauss mixed functions to calculate the integral values which were list at the peaks.

could be interpreted by the different quantity of these two kinds of structures. Under the same thermal treatment conditions, the conjugated extent of most conjugated plane II increased, which lead to the bathochromic-shift and the extending of the end absorption to visible light region (>500 nm). In contrast, only a small part of conjugated plane I changed, thus no bathochromic-shift happened on band I.

The absorption intensity of the two bands increases in different ways at various temperatures. It shows almost linearly increasing
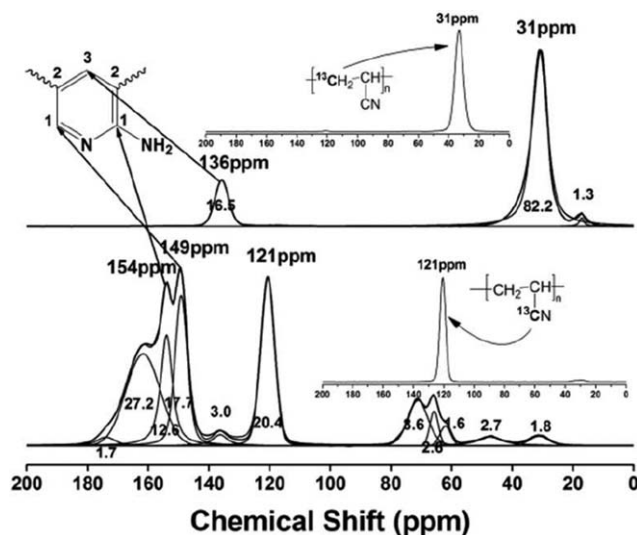
at 180 °C [Figure 4(a)], however, at 220, 250, and 280 °C the increasing tendency is slowdown after a period of heating time [Figure 4(b–d)], and the higher temperature leads to the shorter
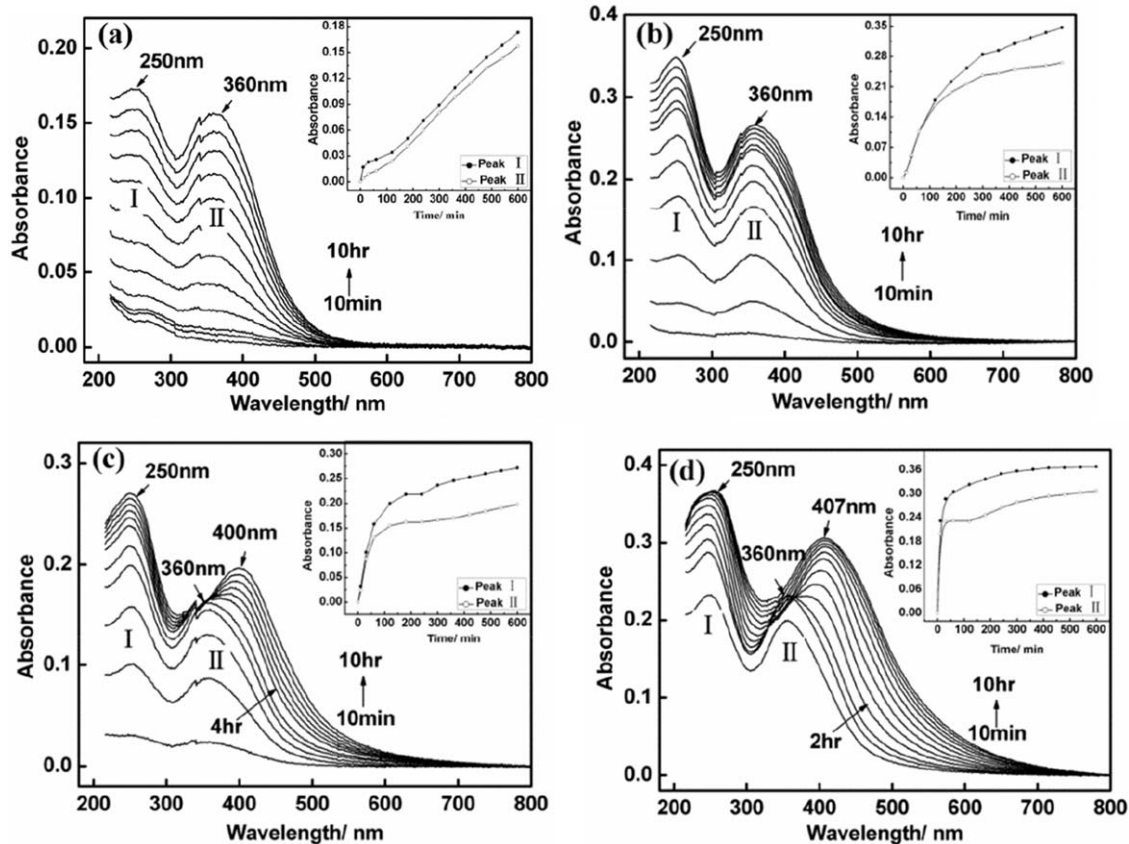

Figure 4. Time dependence of in situ UV-vis spectra for stabilized PAN film with different heating time (10 min/30 min/1 h/2 h . . . 10 h) at (a) 180 °C; (b) 220 °C; (c) 250 °C; (d) 280 °C.
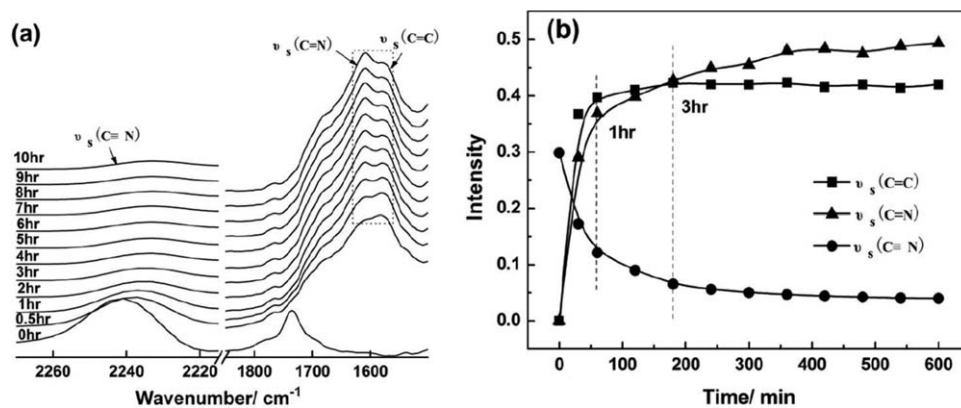
Figure 6. (a) FTIR spectra around 1600 and 2240 cm^{-1} of stabilized PAN film with different heating time (10 min/30 min/1 h/2 h ... 10 h) at 250 °C, (b) the evolution of absorption intensity of v_s (—C≡N), v_s (C=C), and v_s (C=N) fitted by Lorentz and Gaussian method.

of the transition time. According to the Lambert–Beer's Law (2), there are two reasons for the increase of the absorption intensity, one is the generation of conjugated plane, and the other is the growth of conjugated extent:

$$A = \varepsilon l c, \qquad (2)$$

where A is the absorption intensity, ε is the absorption coefficient which is related to the conjugated extent, l is the thickness of the film (cm), and c is the mole concentration of conjugated plane (mol/cm). Therefore, the increase of band I is attributed to the generation of conjugated plane I, and that of band II is attributed to the same reason at 180 °C and 220 °C. But at higher temperature the increase of band II is due to both the generation of conjugated plane II and the growth of conjugated extent, because the bathochromic-shift stops at the later stage of the isothermal treatment in Figure 4(d), while the intensity of band II still increased slowly. This phenomenon implies the generation of the conjugated plane happening simultaneously with the growth of conjugated extent.

The case of stabilization at 250 °C was taken as an example to investigate the influence of double bonds to the evolution of con-

jugated plane by FTIR. The spectra containing 2220–2270 cm^{-1} region and 1500–1800 cm^{-1} region is depicted in Figure 6(a). Based on the previous research, the single peak at 2240 cm^{-1} should be ascribed to the absorption of nitrile group [v_s (—C≡N)], and the broad absorption band around 1600 cm^{-1} should be ascribed to the absorption of mixed double bonds [v_s (C=C) and v_s (C=N)], which were derived from dehydrogenation and cyclization respectively.[17,29] The broad absorption band was fitted to two individual peaks at 1580 and 1620 cm^{-1}, and the evolution of the peak intensity of these three peaks are shown in Figure 6(b). Generally, the absorption intensity of —C≡N decreased with the extending of heating time, and the decreasing rate was gradually slowdown, which was coincidently matched with the increasing rate of 1620 cm^{-1} peak intensity. This coincidence can be interpreted by the cyclization of —C≡N with forming of C=N. Therefore, the peak of 1620 cm^{-1} must be assigned to v_s (C=N), while the peak of 1580 cm^{-1} must be assigned to v_s (C=C). The C=C also increased with the extending of heating time in the early stage, but it stopped increase after a period of time, which implied there was a limitation of dehydrogenation. We can also see from Figure 6(b), both C=C and C=N generate rapidly in the first 1 h, and then slowdown in the next 2 h, which is coincident with the increase of conjugated planes in the first 3 h [Figure 4(c)]. Nevertheless, after 3 h C=C do not generate anymore, and C=N still keeps generating slowly. This indicates that the evolution of conjugated plane is due to cyclization reaction after 3 h.

Table IV. The X-ray Diffraction and Structural Parameters of Pseudo-Graphite Crystal in Carbonized PAN Film

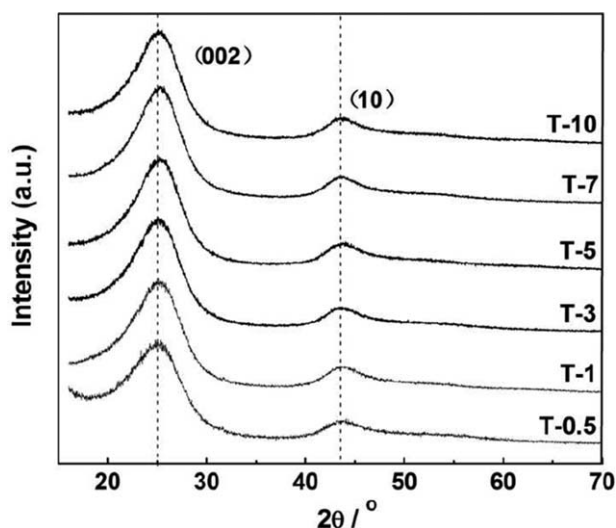| Sample number	(002)			(10)		
	2θ/°	FWHM/°	L_c/nm	2θ/°	FWHM/°	L_a/nm
T-0.5	24.86	6.11	1.39	43.92	5.20	3.37
T-1	24.88	5.99	1.42	44.01	4.84	3.62
T-3	24.85	5.81	1.46	43.88	4.52	3.87
T-5	24.99	5.67	1.50	43.96	4.41	3.97
T-7	25.04	5.53	1.54	43.93	4.34	4.03
T-10	24.95	5.45	1.56	43.73	4.29	4.08

Figure 7. XRD patterns of carbonized PAN for different stabilized time, all of these patterns are fitted by Lorentz and Gauss mixed functions.

Effect of the Basic Conjugated Plane on the Pseudo-Graphite Crystal

To evaluate the effect of stabilized time on the pseudo-graphite crystalline structure, the PAN samples were firstly thermal treated at 250 °C for various periods of time and subsequently carbonized at 1300 °C under nitrogen atmosphere. XRD patterns of the samples are shown in Figure 7, which presents two peaks around 25° (002) and 44° (10),[14] and the peaks turned to be sharp with the extending of stabilized time. The crystalline size of pseudo-graphite structure was calculated by Scherrer formulae, and the diffraction parameters and calculated structural parameters are listed in Table IV. According to the data in Table IV, the lateral size (L_a) and the stacking height (L_c) were increased significantly, but the increase rate was slowed down with the extending of stabilized time. The diffraction angle (2θ) is approximate the same, the tiny difference may be caused by the error of peak fitting. So the interlayer spacing was not changed according to the Bragg equation ([2]d sin $\theta = \lambda$). That means the increase of L_c was resulted from stacking amount of the pseudo-graphite sheets. This result was further proved the assumption of the evolution process of pseudo-graphite microcrystal and the structural basis it, which was proposed in Figure 3.

CONCLUSIONS

The structural basis of the pseudo-graphite sheets is the conjugated plane, which is originally formed in stabilization. With the connecting and stacking of the small conjugated plane through chain scission reaction (280–450 °C) and non-carbon atoms elimination reaction (800–1300 °C), the size of pseudo-graphite crystal increases significantly. Two kinds of conjugated planes containing single or double aromatic rings with about two double bonds are formed in PAN during stabilization in nitrogen atmosphere because of cyclization and dehydrogenation reactions. The quantity of conjugated plane I is more than that of conjugated structure II theoretically based on the analysis of the configuration of atactic-PAN molecular chain. The conjugated extent of most conjugated plane I did not change with the extending of heating time, but that of most conjugated plane II increased at 250 °C and 280 °C after a certain time due to cyclization reaction. Increasing the temperature and extending the heating time are beneficial to generate conjugated planes with high conjugated extent, so PAN isothermal stabilized for a long time tends to obtain large size of pseudo-graphite crystal after carbonization. From above, we can conclude that PAN-based carbon fibers with different graphite crystalline structure can be obtained by strictly controlling the stabilized temperature and time.

ACKNOWLEDGMENTS

REFERENCES

1. Rahaman, M. S. A.; Ismail, A. F.; Mustafa, A. *Polym. Degrad. Stabil.* **2007**, *92*, 1421.

2. Qin, X. Y.; Lu, Y. G.; Xiao, H.; Wen, Y.; Yu, T. *Carbon* **2012**, *50*, 4459.

3. Xiao, H.; Lu, Y. G.; Zhao, W. Z.; Qin, X. Y. *J. Mater. Sci.* **2014**, *49*, 794.

4. Hanna, S. B.; Yehia, A. A.; Ismail, M. N.; Khalaf, A. I. *J. Appl. Polym. Sci.* **2012**, *123*, 2074.

5. Xue, Y.; Liu, J.; Liang, J. Y. *J. Appl. Polym. Sci.* **2013**, *127*, 237.

6. Paiva, M. C.; Kotasthane, P.; Edie, D. D.; Ogale, A. A. *Carbon* **2003**, *41*, 1399.

7. Fu, Z. Y.; Gui, Y.; Liu, S.; Wang, Z.; Liu, B. J.; Cao, C. L.; Zhang, H. X. *J. Appl. Polym. Sci.* **2014**, *14*, 363.

8. Dalton, S.; Heatley, F.; Budd, P. M. *Polymer* **1999**, *40*, 5531.

9. Zargham, S.; Bazgir, S.; Katbab, A. A.; Rashidi, A. *e-Polymer* **2014**, *14*, 363.

10. Molnar, K.; Szolnoki, B.; Toldy, A.; Vas, L. M. *J. Therm. Anal. Calorim.* **2014**, *117*, 1123.

11. Tian, Y. C.; Han, K. Q.; Zhang, W. H.; Zhang, J. J.; Rong, H. P.; Wang, D.; Yan, B.; Liu, S. P.; Yu, M. H. *Mater. Lett.* **2013**, *92*, 119.

12. Kubasova, N. A.; Shishkina, M. V.; Zaliznaya, N. F.; Geiderikh, M. A. *Polym. Sci. USSR* **1968**, *10*, 1537.

13. Kubasova, N. A.; Din, D. S.; Heiderich, M. A.; ; Shishkina, M. V. *Polym. Sci. USSR* **1971**, *13*, 184.

14. Kim, C.; Park, S. H.; Cho, J. I.; Lee, D. Y.; Park, T. J.; Lee, W. J.; Yang, K. S. *J. Raman. Spectrosc.* **2004**, *35*, 928.

15. Kaburagi, M.; Bin, Y.; Zhu, D.; Xu, C.; Matsuo, M. *Carbon* **2003**, *41*, 915.

16. Arbab, S.; Mirbaha, H.; Zeinolebadi, A.; Nourpanah, P. *J. Appl. Polym. Sci.* **2014**, *131*, DOI: 10.1002/app.40343.

17. Ouyang, Q.; Cheng, L.; Wang, H. J.; Li, K. X. *Polym. Degrad. Stab.* **2008**, *93*, 1415.

18. Esrafilzadeh, D.; Morshed, M.; Tavanai, H. *Synth. Met.* **2009**, *159*, 267.

19. Yusof, N.; Ismail, A. F. *J. Anal. Appl. Pyrolysis* **2012**, *93*, 1.

20. Usami, T.; Itoh, T.; Ohtani, H.; Tsuge, S. *Macromolecules* **1990**, *23*, 2460.

21. Jing, M.; Wang, C. G.; Wang, Q.; Bai, Y. J.; Zhu, B. *Polym. Degrad. Stabil.* **2007**, *92*, 1737.

22. Daranyi, M.; Sarusi, I.; Sapi, A.; Kukovecz, A.; Konya, Z.; Erdohelyi, A. *Thin Solid FILMS* **2011**, *520*, 57.

23. Nguyen-Thai, N. U.; Hong, S. C. *Carbon* **2014**, *69*, 571.

24. Fazlitdinova, A. G.; Tynmentsev, V. A.; Podkopayev, S. A.; Shveikin, G. P. *J. Mater. Sci.* **2010**, *45*, 3998.

25. Wang, Y. S.; Xu, L. H.; Wang, M. Z.; Pang, W. M.; Ge, X. W. *Macromolecules* **2014**, *47*, 3901.

26. Zhang, Y. Y.; Minus, M. L. *Macromolecules* **2014**, *47*, 3987.

27. Wang, Y. S.; Pang, W. M.; Xu, G. Y.; Wu, W. T.; Zhu, Q. R.; Lu, F.; Xu, L. H. *Chin. J. Magn. Reson.* **2008**, *25*, 176.

28. Huang, L.; Yu, D. Q. UV Spectrum: Application in Organic Chemistry; Science Press: Beijing, **1988**; Vol. *1*, Chapter 6, p 211.

29. Karbownik, I.; Fiedot, M.; Rac, O.; Suchorska-Wozniak, P.; Rybicki, T.; Teterycz, H. *Polymer* **2015**, *75*, 97.