

High-Temperature DSC Study of Polyacrylonitrile Precursors during Their Conversion to Carbon Fibers

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ABSTRACT: The evolution of structure, the changes of properties during the preoxidation, precarbonization, and carbonization of different polyacrylonitrile (PAN) precursors were firstly studied in detail by means of using high-temperature differential scanning calorimetry (DSC) to characterize with continuous heating from 25 to 1400°C. It was essential to study the thermal behavior of PAN precursors so that proper temperature was determined. Three precursors with different composition, P1: acrylonitrile/itaconic acid (AN/IA) = 98/2 (wt/wt); P2: acrylonitrile/acrylamide (AN/AM) = 98/2 (wt/wt); P3: acrylonitrile/ammonium salt of itaconic acid (AN/AIA) = 98/2 (wt/wt) were, respectively, selected in this study. Comparative results of the DSC

curves showed that the heating history influenced greatly the heat quantities released and exothermic position at low temperature of DSC curve, but influenced slightly at higher temperature. Aromatic index, carbon yield (W_c) and weight loss (η) can be calculated. After adjusting the temperature in preoxidation and precarbonization and carbonization technology depending on high-temperature DSC, the high performance carbon fibers were obtained that tensile strength is 3.56–4.16 GPa, modulus is 235–243 GPa. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1787–1792, 2007

Key words: DSC; precursor; fibers; thermal properties; strength

INTRODUCTION

It has been popularly accepted that high quality polyacrylonitrile (PAN) precursor fiber is a significant prerequisite for obtaining carbon fiber with excellent performance.^{1–5} There are many factors influencing the actual strength of PAN precursors, including interior conditions such as chemical structure, molecular weight and its distribution, crystallinity and orientation, defects, and exterior conditions such as temperature, tensile speed, and humidity. The large dipole moment is the distinguishing feature of the nitrile group, which is apt to increment polarity or generate hydrogen bond in PAN precursors, so their strength is determined by chemical bonding force of main chain and intermolecular force. Tensile strength will increase with the increase of molecular weight at a certain range. It is an essential step to improve the strength by enhancing their crystallinity and orientation degree. However, high tensile strength of PAN precursors is not sufficient condition to attain high-performance carbon fiber because of a series of complicated chemical reactions followed by stabilization and carbonization. Undoubtedly, it is advantageous to

prevent them from breaking because of their shrinkage behavior at subsequent step. Thermal stabilization is deemed an essential structural transformation process that converts the linear PAN molecular chains to aromatic ladder structure suitable for further carbonization.^{6,7} It is well known that differential scanning calorimetry (DSC) is a kind of multipurpose, high-effective, rapid, and sensitive testing method, which can be widely used to study physical changes, such as glass transition, melting and fusing, crystallization, crystal type transformation, and chemical changes such as decomposition, degradation, polymerization, and so on.^{8–14} The reports of DSC testing methods in many published literatures are carried out below 500°C, but there were a few discussions about the data attained by high temperature DSC method when the heating temperature varied from 20 to 1400°C in nitrogen gas. To the best of our knowledge, high-temperature DSC was firstly used to study the thermal behavior of PAN precursors, preoxidized fibers, and carbon fibers. Analyzing these distinctions may provide useful information for fabricating high property PAN precursor fibers that is more favorable for thermal stabilization and for obtaining high strength carbon fibers, and further extend to ascertain the influence factor of such precursors on the mechanical properties of the resulting carbon fibers.

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TABLE I
Properties of PAN Precursors with Different Composition

Precursor	Fineness (dtex)	Strength (cN/dtex)	Elongation at break (%)	Density (g/cm ³)	Oxygen content (wt %)	Crystallinity (%)
P1	1.05	7.36	11.80	1.13	2.30	61.43
P2	1.22	6.13	10.90	1.09	3.50	57.85
P3	0.85	8.75	12.30	1.17	2.78	72.33

EXPERIMENTAL

Preparation of PAN precursors

Free-radical solution copolymerization method was adopted to prepare PAN precursors. Different PAN precursors (named after P1, P2, P3, respectively) were selected in this study. For wet spun precursor P1, a 20 wt % dope was prepared in dimethyl sulfoxide (DMSO), by using a copolymer of acrylonitrile/itaconic acid (AN/IA is 98/2 w/w), with average molecular weight of 160,000 g mol⁻¹. For precursor P2, which were wet spun from a 21 wt % dope in DMSO of a copolymer of acrylonitrile/acrylamide (AN/AM is 98/2 w/w) with average molecular weight of 140,000 g mol⁻¹. For precursor P3, AIA was prepared by the neutralization of IA with NH₃, and was copolymerized to synthesize the ammonium-modified copolymer P (AN/AIA) using the same solvent and radical initiator, it was wet spun from a 20 wt % dope in DMSO of a copolymer of acrylonitrile/ammonium salt of itaconic acid (AN/AIA is 98/2 w/w) with average molecular weight of 150,000 g mol⁻¹. All there mentioned precursors contain 1000 filaments each single tow, the properties of PAN precursors were listed in Table I.

Stabilization and carbonization

The earlier obtained PAN precursors were stabilized by multistep heating process under a certain tension in air, with a temperature gradient in the range of 200–300°C, to achieve the preoxidized fibers. The fibers were firstly heated in ordinary nitrogen up to about 750°C, and then heated in high-purity nitrogen up to 1400°C to obtain the PAN-based carbon fibers. In this work, the preoxidized fibers and carbon fibers were also measured by DSC in comparison with PAN precursors.

High-temperature DSC measurements

DSC analysis was carried out using the NETZSCH DSC 404 thermal analyzer (Made in Germany). The samples, including the PAN precursors, preoxidized fibers, and carbon fibers, were chopped into short lengths, respectively, 10 mg of each was weighed by the model JA1003 nice scale (Made in Shanghai,

China), and encapsulated in crimped ceramic pans to obtain maximum thermal contact. An empty pan acted as the reference. The temperature ranges were chosen from ambient temperature to 1400°C. All measurements were made at a heating rate of 2.5°C/min under ordinary Argon atmosphere with a flow rate of 30 cm³/min.

Characterization

Bulk density of the fibers was determined by means of a density gradient column maintained at 25°C, carbon tetrachloride with a density of 1.57 g/cm³ was first introduced into the column. Xylene with a density of 0.90 g/cm³ was then added slowly to the column, carrying out to plotting the density of the calibrated floats against the position opposite the graduated scale of the column.

Element analyzer GmbH VarioEL (German) was employed to measure the elements in the PAN precursors and various heated fibers. About 3 mg of triturated samples was used. Atomic percentage of carbon, hydrogen, and nitrogen were determined by CHN column mode, atomic of percentage oxygen was then determined by difference.

The fineness was measured by a XD-1 fiber fineness machine, all the fibers were measured by a XQ-1 testing machine (both XD-1 and XQ-1 were made in Donghua University, Shanghai, China) at a cross-head speed of 0.5 mm/min with a testing length of 20 mm and load cell of 15 g, in each case, at least 30 sample filaments were tested, and taken for the average of 30 filaments in each experiment.

Mechanical properties of the carbon fibers were measured on an Instron Tensile testing machine with cross-head speed of 5 mm/min and gauge length of the single tow with 1000 filaments as 20 mm, an average of 20 reading for each sample is quoted in the text.

The degree of crystallization can be characterized by the aromatic index (AI), and can be calculated by the formula: $AI = 100 (H_v - H_o)/H_v$, where H_v and H_o are heats for the PAN precursor and the preoxidized fiber, respectively. In addition, carbon yield (W_c) can be measured for the PAN precursor by the model JA1003 nice scale, the final weight loss (η) can be obtained by the calculation: $\eta = (10 - W_c)/10$.

RESULTS AND DISCUSSION

DSC analysis of PAN precursors

Figure 1 showed the DSC curves of three PAN precursors from 25 to 1400°C, which several observed peaks, including several endothermic and exothermic. The relative parameters of thermal behavior taken on for heating PAN precursors were listed in Table II.

In the range of 25–400°C, for any one of P1, P2, and P3 precursors, there appears a exothermic peak, it can be seen that peak temperature sequence in terms of magnitude is $T_{pk}(P_1) < T_{pk}(P_2) < T_{pk}(P_3)$ below 350°C. The exothermic regime of both IA-containing and AM-containing PAN precursors is much broader and the cyclization reaction starts at lower temperature for P1 and P2 at 264 and 282.4°C, respectively, when compared with that of P3 precursors at 296.1°C. PAN tends to degrade well below about 350°C, because they undergo certain exothermic reactions, which lead to the formation of heat-resistant ladder structures and the disappearance of melting. The cyclization and cross-link reactions from —CN groups are exothermic followed by the oxidative reaction in the air.

It was reported that the exothermal peaks were 275°C in the DSC curve of PAN homopolymer in argon at 1°C min⁻¹, and were shifted to the higher temperature with elevating heating rate at the same medium atmosphere.⁹ In a sense, it can be deduced that P1 precursors contained IA comonomers shift peak temperature to lower value, P2 precursors contained AM comonomers or P3 precursors contained AIA comonomers shift peak temperature to higher value. In particular, for P3 precursor, there appears a slight endothermic peak at about 65°C, which may be due to the presence of water molecules and volatile small molecular monomers.

When the heating temperature was above 400°C, there are some common characterizations among the three curves, that is, exothermic peak appeared slightly in the range of 440–1100°C, for fibers developed from P1 precursor, the exothermic peak appears at 692.2°C and the endothermic peak appears at 865.6°C, which the corresponding energy of activation is 815.9 and 451 J g⁻¹, respectively, when compared with only 441 J g⁻¹ for cyclization initiation reaction. It could be possible the reaction under this environment could be either aromatization of the structure followed by dehydrogenation or the inner-molecular crosslinking reactions, because there is sufficient hydrogen still left in the fiber structure that can be removed at higher temperature in the presence of oxygen to attain further aromatization of the structure. This hydrogen would be driven off in the presence of nitrogen during carbonization as

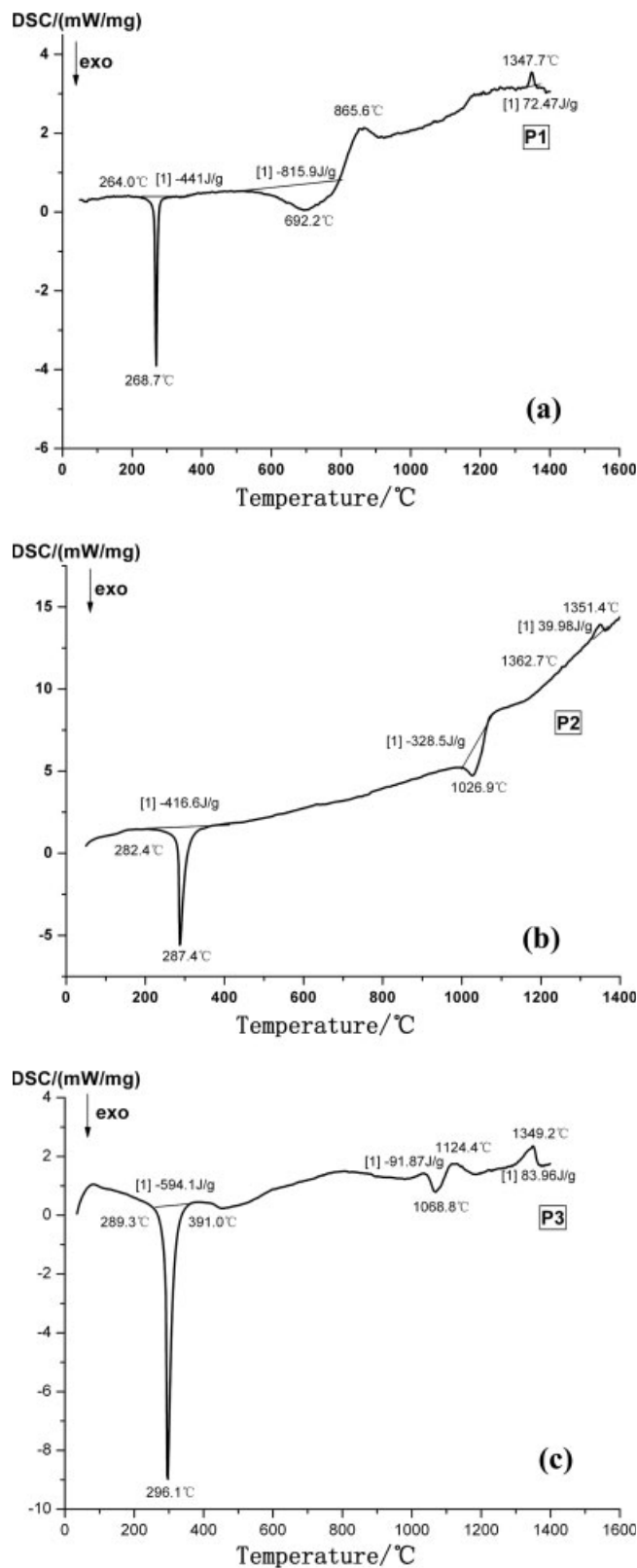


Figure 1 DSC curves in nitrogen atmosphere of (a) P1 precursors, (b) P2 precursors, and (c) P3 precursors.

well, but perhaps undergoing other chemical reactions, such as forming excessive tar and condensable hydrocarbons.

TABLE II
The Relative Data of High Temperature DSC from Figure 1

Sample code	Temperature distribution							
	1 (25–400°C)		2 (400–700°C)		3 (700–1200°C)		4 (1200–1400°C)	
	T_{pk} (°C)	ΔH (J g ⁻¹)	T_{pk} (°C)	ΔH (J g ⁻¹)	T_{pk} (°C)	ΔH (J g ⁻¹)	T_{pk} (°C)	ΔH (J g ⁻¹)
P1	268.7	-441	692.2	-815.9	865.6	+451	1347.7	+72.47
P2	287.4	-416.6	-	-	1026.9	-328.5	1351.4	+39.96
P3	296.1	-594.1	-	-	1068.8	-91.87	1349.2	+83.96

–, is represented as the exothermic reaction; +, is represented as the endothermic reaction.

The peak shapes of curves of P2 and P3 precursors were similar (exothermic reaction followed by endothermic reaction) between 1000 and 1200°C except that P1 precursor has only the endothermic peak at 1347.7°C. In particular, carbon fibers developed from P2 and P3 precursors have the strong endothermic peak at 1026.9 and 1068.6°C, respectively, which is attributed to the rereaction between the end groups, side chains and –CN groups without cross-linked and the release of volatiles (i.e., HCN, N₂, NH₃, etc), it may be an important factor to facilitate dealing with the carbonization process. A possible reason is that the endothermic peak can alleviate the breakage of a filament because of denitrogenation during the final carbonization. The ladder structures in polymers cross-link at about 1350°C originate from the further pyrolysis reaction and the removal of the pyrolysis non-carbonous exhausts from the fibers. It followed by the formation of the dense heterocyclic aromatic structures, and thus results in the production and release of N₂ and NH₃. The microscopic structure converts from the random graphite-like layer to the random graphite structure. All of the characteristic differences would have great effect on the carbonization processes.

Density analysis

The variation of densities of PAN fibers after stabilization and carbonization was shown in Figure 2, during the stabilization, PAN fibers underwent a series of physical and chemical changes, which transformed the original linear polymer structure into partially cyclized ladder structure, as demonstrated in Figure 1. For any one of P1, P2, and P3 precursors as a result of consolidation and densification occurring within these fibers, it was found that the densities rapidly increases with increase of oxidation temperature in the range of 190–300°C in air, then increases to an extreme value at about 1200°C, then after the maximum there is a slight drop because of the conversion of open pores to closed pores, which resulting in the density and surface area of carbon fibers decreased when temperature rises above 1200°C, this was the similar phenomenon has been studied by Ko and Lin.¹⁵

Compared the data on the densities changes of different fibers developed from different P1, P2, and P3 precursors after treatment, it seem appreciable that the density of P3 is higher than that of P1 or P2. This may be the reason that the P3 precursors have the highest tensile strength and elongation possibly as a result of their higher density and higher crystallinity, as have been listed in Table I.

DSC analysis of the preoxidized fibers

Figure 3 shows the DSC curve of the preoxidized fibers from room temperature to 1400°C. The relative parameters of thermal behavior taken on for heating PAN precursors were listed in Table III.

There are an endothermic peak at about 95°C for P1 fibers followed by a baseline shift downward, a broad exothermic peak at about 330°C followed by a baseline shift upward, a shoulder-like exothermic peak near 1172°C, a sharp endothermic peak at about 1341.5°C, and an exothermic peak. For P2 fibers, there are an endothermic peak at about 72°C followed by a baseline shift downward, a broad exothermic peak at about 318°C followed by a baseline shift upward, a shoulder-like exothermic peak near

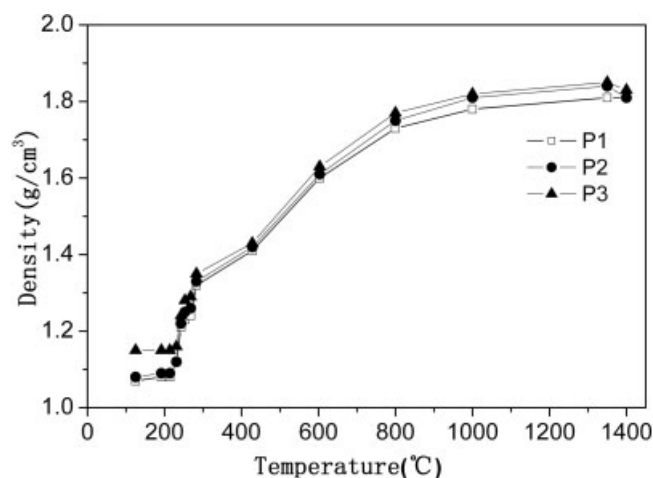


Figure 2 The variation of densities of PAN fibers after stabilization and carbonization.

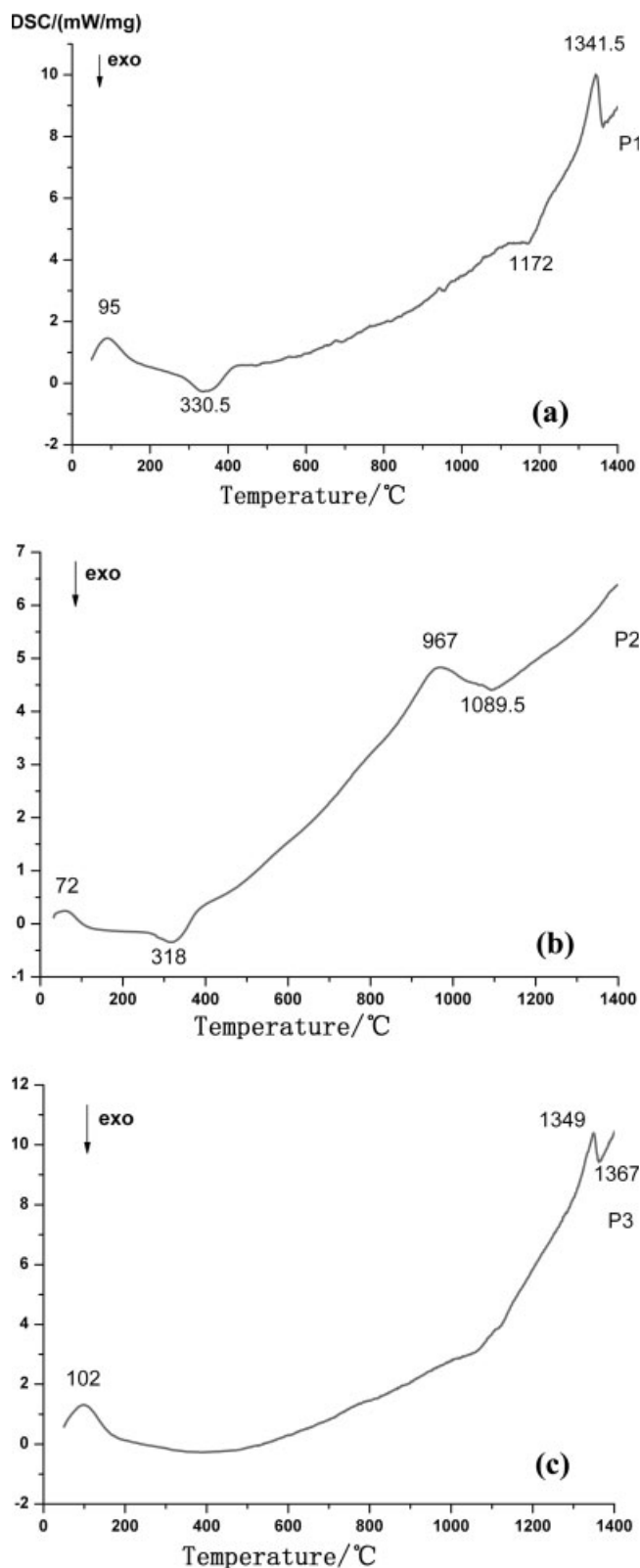


Figure 3 DSC curves of (a) stabilized fibers developed from P1 precursors, (b) stabilized fibers developed from P2 precursors, and (c) stabilized fibers developed from P3 precursors.

967°C, but there is no a sharp endothermic peak at about 1350°C. For P3 fibers, there are an endothermic peak at about 102°C followed by a baseline shift downward, followed by a baseline shift upward, a sharp endothermic peak at about 1349°C, and an exothermic peak. It was found that the glass transition temperature, the intermolecular cyclization and intermolecular cross-link chemical reactions from the residual $-\text{CN}$ groups shift to higher temperatures, and the corresponding peaks broaden, which may be attributed to the new amorphous region in the preoxidized fibers and the reduction of their quantities. The original endothermic peak near 700°C seems to disappear, demonstrating that the PAN precursors have produced structural changes and the stabilized ladder structures may form in the amorphous region after the preoxidation in the temperature ranges of 200–300°C in air. These structural changes also influence the subsequent ones, which may be shown by the changes of peaks position and shape in the DSC curve. It is clear that the peak positions between 1300 and 1400°C are hardly changed, indicating that the reaction types do not change except that the amount of reactant decreases.

All of the three processes ($-\text{C}\equiv\text{N}$ groups reaction, conjugated $-\text{C}=\text{N}-$ formation and oxidation reaction) occur during the early stages of stabilization in air.¹² The nitrile reaction generates the conjugated structures containing groups $-\text{C}\equiv\text{N}$, which may be either intramolecular and result in cyclization,¹³ or intermolecular and result in cross-linking. The conjugated $-\text{C}=\text{N}-$ may result from dehydrogenation,¹⁴ or from imine-enamine tautomerization and subsequent isomerization. The oxidation reaction gives rise to the carbonyl groups.

According to the gases released, the turning point between high-temperature and low-temperature reactive zone is 750°C. The unreactive linear PAN chains cyclize further, the intermolecular chains dehydrate, dehydrogenate and cross-link, the main chains, the pendant chains and the end groups decompose during the preoxidation in middle-temperature zone. Nitrogen and hydrocyanic acid are the main gases released in high-temperature zone. It is estimated that the intermolecular chains produce cross linking, the planes of carbon network expand further. Nitrogen is bonded with the aromatic structure in fibers, preventing the formation of thick layer molecules during further heat treatment. The aromatic rings begin to rupture above 500°C and give out the hydrocyanic acid at 750°C or so.

It shows that the difference of original structures results in the different DSC thermographs. In other words, the heat history has great effect on stabilization process. The AI, carbon yield (W_c), the final weight loss (η), the tensile strength and modulus of the resultant carbon fibers were listed in Table IV.

TABLE III
The Relative Data of High Temperature DSC from Figure 3

Sample code	Temperature distribution							
	1 (25–300°C)		2 (300–700°C)		3 (700–1200°C)		4 (1200–1400°C)	
	T_{pk} (°C)	ΔH (J g ⁻¹)	T_{pk} (°C)	ΔH (J g ⁻¹)	T_{pk} (°C)	ΔH (J g ⁻¹)	T_{pk} (°C)	ΔH (J g ⁻¹)
P1	95	+378.1	330	-776.4	1172	-432	1341.5	+71.34
P2	72	+256.7	318	-685.3	967 (1089.5)	+328.5 (-497.6)	-	-
P3	102	+537.6	-	-	-	-	1349 (1367)	+83.96 (-34.56)

-, is represented as the exothermic reaction; +, is represented as the endothermic reaction.

TABLE IV
The Aromatic Index, Carbon Yield, Final Weight Loss, Tensile Strength and Modulus of the Resultant Carbon Fibers

Sample code	AI (%)	η (%)	Tensile strength (GPa)	Modulus (GPa)
P1	48	96.5	3.56	243
P2	65	97.7	3.88	236
P3	77	98.2	4.16	235

CONCLUSION

High-temperature DSC method was firstly used to characterize the thermal properties of PAN precursors. There were several exothermic reactions and one endothermic reaction with respect to the PAN precursor, demonstrating that several structural transitions occurred.

The technical parameters can be designed for PAN precursors according to the range of the respective endothermic and exothermic temperature on the DSC curve. The preoxidation temperature range is from 200 to 300°C. The carbonization is divided into two stages, the middle-temperature (350–750°C) and high-temperature (above 1300°C) carbonization.

Heating history had great effects on the DSC curves during 200 and 300°C, and different heating history had different effects, but they tend to shift to higher temperature. The carbonization is not completed enough up to 1400°C.

The AI can be calculated according to the DSC curves; carbon yield can also be obtained. The higher is carbon yield, the higher is the tensile strength of the resultant carbon fibers.

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References

- Sen, K.; Bahrami, S. H.; Bajaj, P. *Macromol Chem Phys C* 1996, 36, 1.
- Bajaj, P.; Roopanwal, A. K. *Macromol Chem Phys C* 1997, 37, 97.
- Wang, M. Z. *New Carbon Mater* 1998, 13, 79.
- Wang, Y. Z.; Zhu, B.; Wang, Y. X. *New Carbon Mater* 2001, 16, 12.
- Wu, G. P.; Lu, C. X.; Li, Y. H. *New Carbon Mater* 2003, 18, 25.
- Kalashnik, A. T. *Fibre Chem* 2002, 34, 10.
- Zhang, S. C.; Wen, Y. F.; Yang, Y. G. *New Carbon Mater* 2003, 18, 315.
- Pan, Z. R. *Macromolecular Chemistry*, 2th ed.; Chemical Industrial Press: Beijing, 2000; p 3.
- Wang, M. Z.; He, F. *Production, Properties and Application of Carbon Fibers*, 1st ed.; Science Press: Beijing, 1984; p 29.
- Gupta, A. K.; Paliwal, D. K.; Bajaj, P. *J Appl Polym Sci* 1998, 70, 2703.
- Grove, D.; Desai, P.; Abhiraman, A. S. *Carbon* 1988, 26, 403.
- Dalton, S.; Heatley, F.; Budd, P. M. *Polymer* 1999, 40, 5531.
- Xue, T. J.; Mckinney, M. A.; Wilkie, C. A. *Polym Degrad Stab* 1997, 58, 193.
- Usami, T.; Itoh, T.; Ohtani, H.; Shin, T. *Macromolecules* 1990, 23, 2460.
- Ko, T. H.; Lin, C. H. *J Appl Polym Sci* 1998, 70, 2409.