

# Effect of Electron Beam Irradiation on Polyacrylonitrile Precursor Fibers and Stabilization Process

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**ABSTRACT:** The electron beam was imposed on the polyacrylonitrile precursor fibers before the fibers were stabilized. The effect of electron beam irradiation on the chemical structure, transverse section, and surface morphology and thermal properties of the fibers in the process of stabilization was characterized by the use of Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), and differential scanning calorimeter, respectively. A parameter  $\eta = I(\text{C}=\text{N})/[I(\text{C}=\text{N}) + I(\text{C}\equiv\text{N})]$  was defined to evaluate the extent of cyclization in the stabilization process. The kinetic parameters, viz. activation energy ( $E$ ) and pre-exponential factor ( $A$ ) of the stabilization reactions, were calculated by Kissinger method. FTIR analysis indicated that the cyclization of nitrile groups was initiated at room temperature by electron beam irradiation. The transformation of  $\text{C}\equiv\text{N}$  groups

to  $\text{C}=\text{N}$  ones was accelerated in the process of stabilization. The extent of cyclization of the stabilized fibers was increased. SEM analysis indicated that irradiation could also decrease the internal and surface defects of the stabilized fibers treated at 300°C. The activation energy of cyclization reaction was reduced from 302 to 280 kJ/mol and 260 kJ/mol through 100 and 200 kGy electron beam irradiation, respectively. The reaction temperature range was expanded, and the exothermic rate was slowed down in the process of stabilization, which was the reason why the stabilized fibers have improved cyclization degree and less internal defects. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 90–96, 2011

**Key words:** electron beam irradiation; stabilization; morphology; activation energy

## INTRODUCTION

In comparison with conventional engineering materials such as metals and ceramics, carbon fibers have superior properties in strength, stiffness, and lightness.<sup>1</sup> They have gained a wide range of application from sport products to items used by the aerospace industry. Polyacrylonitrile (PAN) fibers have been found to be the most suitable precursors for making high-performance carbon fiber.<sup>2</sup> Presently, there still exists a large difference between the available and theoretical tensile strength of PAN-based carbon fibers even though they have a superior one. The reason of this difference can be attributed to some deviations from the regular form in a typical graphite crystal plane. It was suggested that misalignment of atomic plane around inclusions or voids can initiate the fracture of carbon fibers. The suppression of defects could be expected to provide a drastic improvement in the strength of carbon fibers.<sup>3</sup>

Three heat-treatment processes of stabilization and carbonization followed by graphitization are contained in the fabrication process of carbon fibers.<sup>4</sup> Stabilization of PAN precursor fibers is commonly performed in air between 180 and 300°C. During this process, PAN undergoes a number of physical and chemical changes due to a variety of exothermic chemical reactions, including cyclization, dehydrogenation, oxidation, and crosslinking. Among them, the cyclization reactions, which convert PAN into an infusible stable ladder polymer, are the most important.<sup>5</sup> The cyclization reactions can proceed in either an oxidizing atmosphere or an inert atmosphere. However, oxygen is necessary for the stabilization of PAN precursor fibers to get high-performance carbon fibers. The PAN precursor fibers must be stabilized in an oxidizing atmosphere, which is typically air.<sup>6</sup> These reactions, mainly including dehydrogenation and oxygen uptake reactions, are seriously influenced by the diffusion of oxygen; a limited oxygen diffusion rate results in requiring longer treatment time and forming inhomogeneous stabilized structure, namely skin-core structure.<sup>7</sup> Fitzer and Muller<sup>8</sup> have reported that the cyclization was a first-order reaction. Reducing the activation energy of cyclization can make the oxidation reaction ahead

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of schedule and make the exothermic peak wider, which can accelerate the oxygen diffusion and reduce the formation of skin-core structure.

The radiation chemistry of polymers has become of great interest in recent times. On account of conventional PAN, fibers display inhomogeneous structure, and these defects were generated due to inadequate crosslinking in the stabilization process.<sup>9</sup> The irradiation can generate free radicals in PAN, which aids crosslinking and cyclization. Radical-induced cyclization and intermolecular crosslinking through the nitrile groups have been reported for PAN via ion beam,<sup>10</sup> X-ray,<sup>11,12</sup> gamma,<sup>13–15</sup> and UV irradiation.<sup>10,16</sup> The research of Dietrich indicated that electron beam irradiation on PAN precursor fibers could generate free radical,<sup>17</sup> but the effect of electron beam on the stabilization process was not studied.

In this work, a new and highly effective method of pretreatment PAN precursor fibers was described. The method consists of exposure the PAN precursor fibers to high-energy electron beam for different doses. And then the fibers are stabilized by heating in pure air for various times at temperatures in the range 180–300°C. The effect of the electron beam on the PAN precursor fibers was investigated using Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimeter (DSC). The effect of the electron beam on the stabilization process of the fibers was investigated using FTIR and scanning electron microscope (SEM). The value of activation energies ( $E$ ) was calculated by Arrhenius relationship.

## EXPERIMENTAL

### Materials

The PAN precursor fibers were 3 K supplied by Jilin chemical fiber Co. (Changchun, China). They were made by ternary water suspension polymerization method with *N,N*-dimethylacetamide as solvent. Epoxy resin LX6101 was provided by Lanzhou Bluestar resin Co. (China). Triethylenetetraamine was obtained from Chengdu Kelon Chemical Factory (China). *N,N*-dimethyl formamide (DMF) was purchased from Tianjing Hongshun Chemical Co. (China).

### Pretreatment of irradiated PAN precursor fibers

The electron beam was produced by JJ-2 static electricity accelerator in the Institute of Nuclear Science and Technology Sichuan University at room temperature. The electron beams were produced through the emission of electrons from a pointed glow cathode in a vacuum. With the application of a high voltage, the electrons were accelerated toward the anode and distributed by a scanner system into a surface area of the Lenard window. After they penetrated the thin

titanium foil of the Lenard window, the electrons hit the specimens moved by the dolly car. As the speed of the dolly car is well proportioned, the specimens could be irradiated evenly. From previous tests, it was known that the radicals produced by the irradiation pretreatment in PAN precursors were very stable. The irradiated precursor fibers can be stored as required for several days until stabilization without any significant loss in reactivity.<sup>17</sup>

The energy of the electrons used in this experiment is 1.7 MeV, and the electron beam current is 32 mA. The doses of energy used in this experiment were 100 and 200 kGy.

### Stabilization process for the precursor fibers

A heating furnace, which was made by Tianjin Central Experimental Furnace Company (China), was used to stabilize the fibers. The PAN precursor fibers could be stabilized at a heating rate of 4/3°C/min from 180 to 300°C in continuously flowing pure air (20 L/h). It was carried out by constant tension modes, wherein one end of the fibers was rigidly fixed, and the other end of the fiber was attached to the set of weights. The extend tension is 0.16 g/d from 180 to 260°C and 0.05 g/d from 260 to 300°C. The desired heat-treatment temperatures were 180, 200, 220, 240, 260, 280, and 300°C. Sample collection involved heating the precursor fibers to the desired heat-treatment temperature and holding at the temperature for 5 min and then rapidly quenching the stabilized fibers in the desired atmosphere.

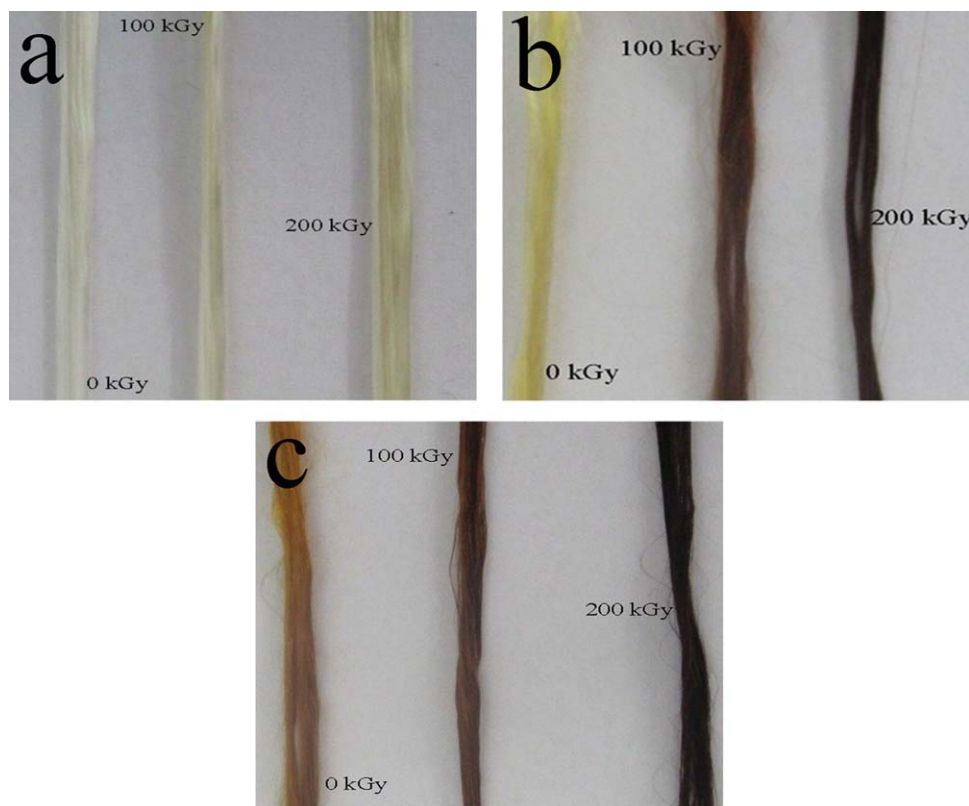
### Characterization

#### Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectroscopy was used for analyzing functional groups formed on PAN fibers with the electron beam pretreatment and different temperature stabilization. Treated fibers were cut and mixed with KBr. The mixture was analyzed with Nicolet 560 made by Nicolet Company in the range 400–4000  $\text{cm}^{-1}$ .

#### Scanning electron microscopy

The transverse section and surface morphology of stabilized fibers were observed through SEM. The equipment was Inspect. F made by FEI Company (Netherlands) with the field emission at an accelerating voltage of 20 kV. The samples used to observe transverse section morphology must be coated with epoxy resin with triethylenetetraamine as the curing agent, and then they were cryogenically fractured in liquid nitrogen. The fractured surfaces of the specimens were sputter coated with a thin gold layer before SEM observation.



**Figure 1** The color of PAN fibers with different doses of electron beam irradiation in different heating temperature; (a) room temperature, (b) 180°C, and (c) 200°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

#### Differential scanning calorimetry

The thermal stability of the precursor powder samples was evaluated by DSC with DSC204 Phoenix made by Netzsch Company. Calorific scans were conducted over a temperature range of 30–400°C. Constant rate scans were performed at heating rates of 5, 10, 15, and 20°C/min in oxygen atmosphere. The kinetic parameters of reaction were evaluated by analyzing thermograms obtained at various heating rates according to Kissinger's method.<sup>18,19</sup> The shape factor of the exothermic peak gives the kinetic order of the reaction.<sup>19</sup> The formulae are as follows:

$$-\frac{E}{R} = \frac{d \ln(\phi/T_m^2)}{d \ln(1/T_m)} \quad (1)$$

$$\ln \frac{\phi}{T_m^2} = -\frac{E}{R} \frac{1}{T_m} + \ln \frac{RA}{E} \quad (2)$$

where formulae  $E$  is the activation energy (kJ/mol),  $A$  the pre-exponential constant ( $s^{-1}$ ),  $\phi$  the heating rate ( $^{\circ}C/min$ ),  $T_m$  the exothermic peak temperature (K), and  $R$  the ideal gas constant.

The slopes of  $\ln[\phi/T_m^2]$  versus  $1/T_m$  plots were used to calculate activation energy for the cyclization reaction.

#### RESULTS AND DISCUSSION

The exposure of PAN precursor fibers to high-energy electron beam was carried out for different doses. The irradiated fibers became insoluble in DMF. The color of the fibers with different doses of electron beam pretreatment and different temperature treatment was shown in Figure 1. The results indicated that the original white fibers turned to yellow in the case of electron beam irradiation. The greater the irradiation doses, the more obviously the color of the fibers changes. With the heat temperature increasing, the color generation was dramatic for irradiated fibers. Takata and Hiroi<sup>20</sup> showed that, for model di-, tri-, and tetrameric acrylonitrile compounds, the visible light absorption appeared after intramolecular cyclization reaction. Thus, the change of the color showed in Figure 1 suggests that the irradiated fibers readily form ring structure compared to nonirradiated fibers.

#### FTIR characterization

A Fourier transform infrared spectroscopy (FTIR) measurement was most commonly used to characterize the chemical reaction taking place in PAN fibers upon heat treatment. A comparison of FTIR

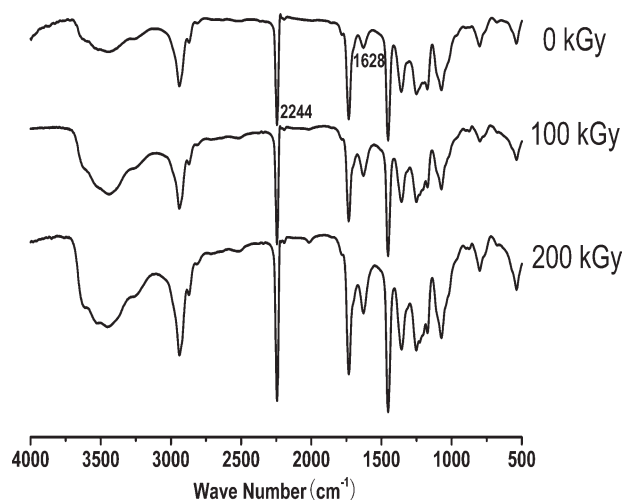


Figure 2 FTIR spectra of PAN precursor fibers.

spectra between the original, 100 and 200 kGy irradiated PAN precursor fibers can be seen in Figure 2. The FTIR spectra between them after heat treatment with the temperature of 180 and 200°C are shown in Figures 3 and 4, respectively. The spectrum of PAN fibers contained some characteristic peaks at 2936, 2244, and 1628  $\text{cm}^{-1}$  due to the stretch vibration of the methylene ( $\text{CH}_2$ ), nitrile ( $\text{C}\equiv\text{N}$ ), and  $\text{C}=\text{N}$  groups, respectively. The cyclization reaction would involve reaction of the nitrile unit. Therefore, we defined a parameter ( $\eta$ ) to evaluate the extent of cyclization.

$$\eta = \frac{I(\text{C}=\text{N})}{I(\text{C}=\text{N}) + I(\text{C}\equiv\text{N})} \quad (3)$$

In eq. (3),  $I(\text{C}=\text{N})$  and  $I(\text{C}\equiv\text{N})$  meant the intensity of the characteristic peak of  $\text{C}=\text{N}$  and  $\text{C}\equiv\text{N}$ , respectively. The change of the extent of cyclization  $\eta$  was

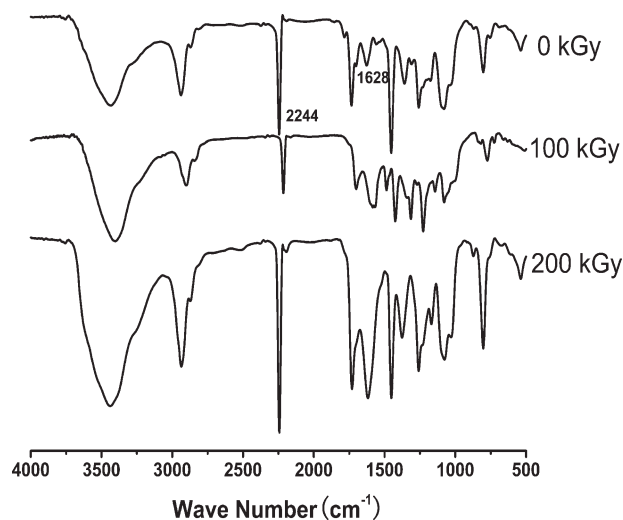


Figure 3 FTIR spectra of PAN fibers treated at 180°C.

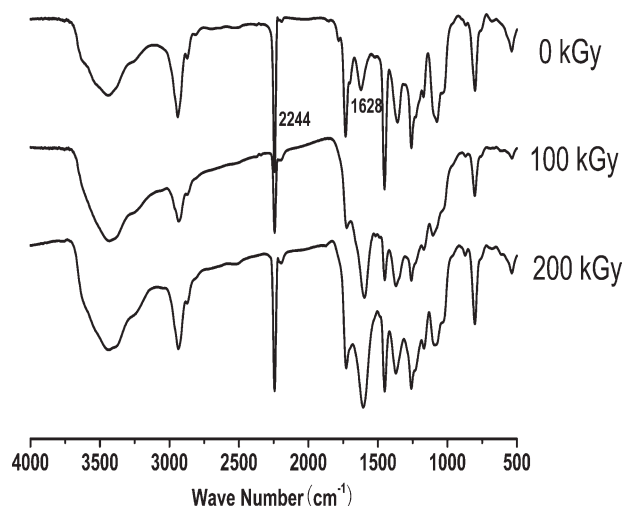


Figure 4 FTIR spectra of PAN fibers treated at 200°C.

showed in Table I. The FTIR spectra of the original and 100 kGy irradiated PAN fibers after stabilization at 300°C can be seen in Figure 5.

From the spectral changes in the figures and tables, it was shown that electron beam irradiation can induce cyclization of the PAN precursor fibers in the room temperature before heat treatment. The extent of cyclization of irradiated fibers increased significantly after heat treatment in the stabilization process compared to the original fibers. These results were in agreement with the results of color change. The spectral changes indicated that electron beam irradiation could improve the ability of PAN molecular cyclization in the stabilized process.

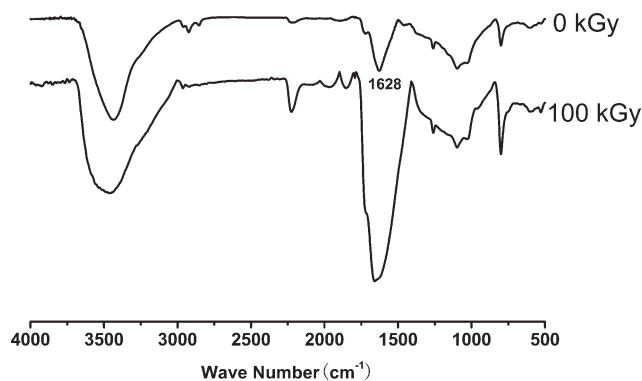
### Effect on morphological structure

The transverse section morphology of thermally stabilized fibers developed from the original, 100 and 200 kGy irradiated PAN precursor fibers, was examined under an SEM, and the results were shown in Figure 6. The irradiated and original PAN precursor fibers were thermally stabilized at identical heat-treatment temperature of 300°C. The fibers developed from original precursor fibers easily displayed a skin-core structure, that is, to say that there was a different thermal stabilization degree between the

TABLE I  
The Effect of Different Doses of Electron Beam Irradiation on the Extent of Cyclization of PAN Fibers in Different Heating Temperature

Irradiation doses (kGy)	Room temperature	180°C	200°C
0	0.16	0.27	0.32
100	0.27	0.62	0.76
200	0.26	0.60	0.66





**Figure 5** FTIR spectra of stabilized fibers at 300°C.

outer and inner part of the fibers, but the thermally stabilized fibers developed from irradiated precursor fibers did not have clear skin-core structure. As the core part of fibers contained in the skin-core structure was not thermally stabilized enough to sustain a higher carbonization temperature, the carbon fiber containing macrovoid was easily obtained, which was developed from thermally stabilized fibers, which contained the skin-core structure.<sup>21</sup> From this point, it was presumed that electron beam irradiation determinately can accelerate oxygen diffusion to the interior of fiber. Irradiation could demonstrate a catalytic effect on the thermal stabilization of PAN precursor fibers.

The surface morphology of thermally stabilized fibers developed from the original, 100 and 200 kGy irradiated PAN precursor fibers, was shown in Figure 7. The thermally stabilized fibers, developed from irradiated PAN precursor fibers, had smoother surface than that developed from the original fibers. The more doses of electron beam irradiation with the PAN precursor fibers, the smoother the surface of the stabilized fiber, which was stabilized at 300°C.

### Thermal analysis of PAN precursor

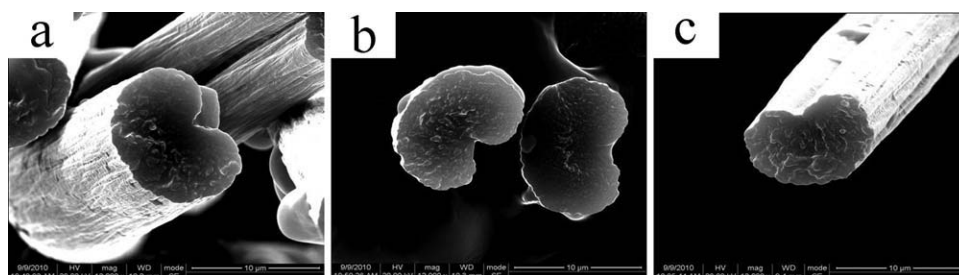
Figure 8 shows the DSC patterns of the fibers with different heating rates of 5, 10, 15, and 20°C/min

under oxygen atmosphere. The results of activation energies of cyclization reaction can be calculated using Kissinger method<sup>19</sup> as in Table II. From Figure 8 and Table II, we can conclude that the activation energy of PAN precursor fibers was reduced by irradiation. As alkyl radicals could be produced in PAN precursor fibers, which had been exposed to electron beams,<sup>17</sup> electron beam irradiation could improve the cyclization ability of acrylonitrile and decrease the intermolecular force of C≡N. The cyclization could occur, and trapezoidal structure was formed at low temperature. Therefore, the cyclization energy of PAN structural transformation in stabilization process is relatively low after electron beam irradiation, and PAN molecules cyclization can be induced at low temperature.

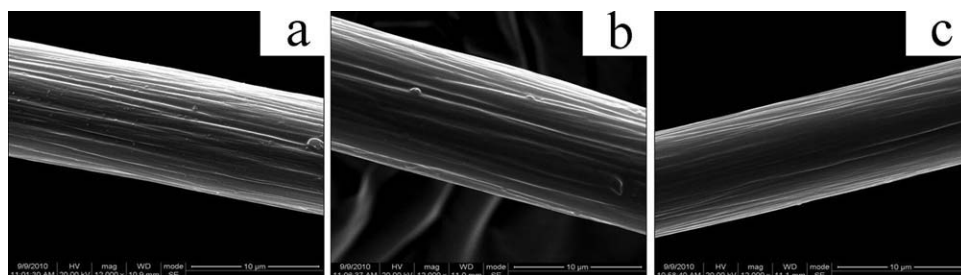
From the DSC curves in Figure 8(a), there was a narrow exothermic peak of original precursor fibers, which started at 224.3°C, ended at 289.3°C, and centered at 275.1°C. But the exothermic peak of irradiated fibers was not narrow. It started at 165.8°C, ended at 271.1°C, and centered at 267.6°C with 100 kGy irradiation, and started at 160.0°C, ended at 267.4°C, and centered at 263.1°C with 200 kGy irradiation. So, the cyclization reaction temperature of PAN was reduced, and the exothermic reaction was tended to be assuasive. As the intensive heat liberation was greatly caused by the cyclization of nitrile groups during heating treatment in the stabilized process.<sup>22,23</sup> Peak width was controlled by the rate of diffusion of oxygen through the skin into the core of fiber.<sup>24</sup> This results mean that the imposition of electron beam on fibers can control the exothermic reaction rate. We also can conclude that the control of the reaction rate results in the decrease of the internal defects such as skin-core structure.

### CONCLUSIONS

PAN precursor fibers were exposed to different dosage of electron beam irradiation and then to thermal treatment with the temperature up to 300°C to study



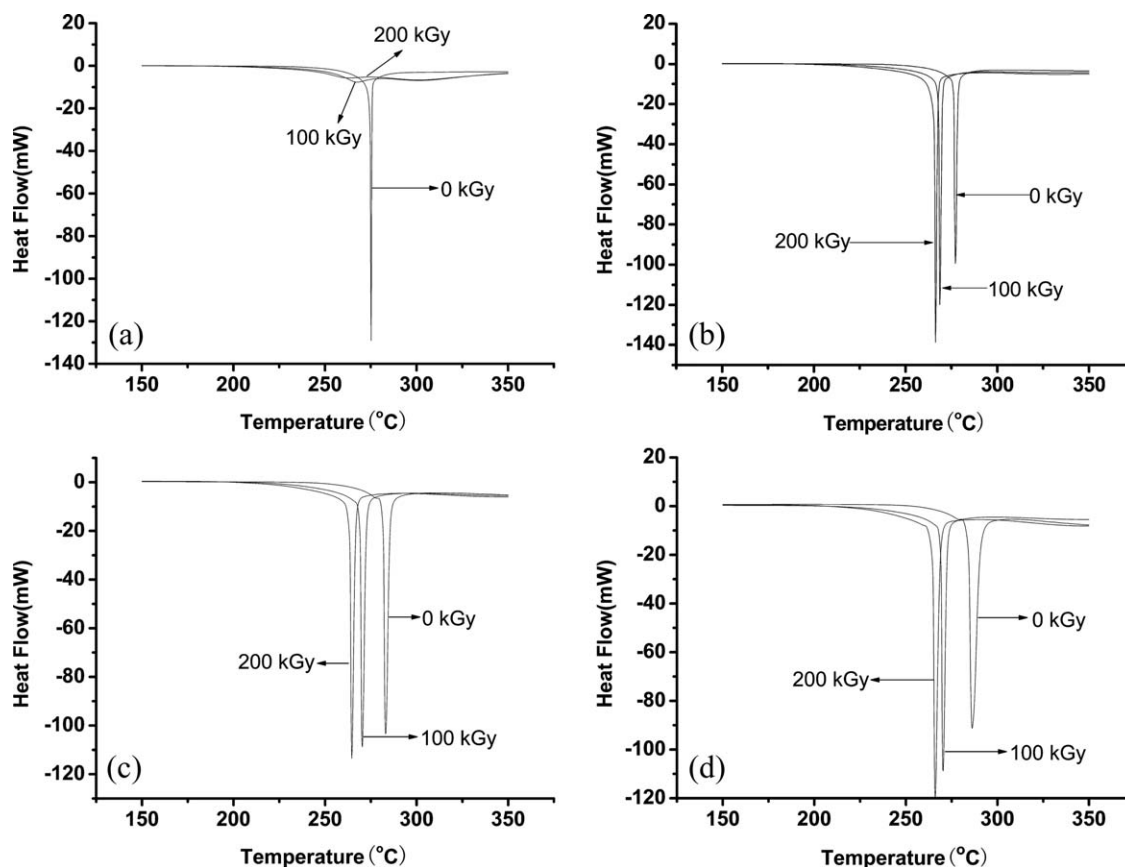
**Figure 6** SEM photo of the transverse section of thermal stabilized fibers obtained at 300°C with different doses of electron beam energy pretreatment; (a) original PAN precursor fibers, (b) 100 kGy irradiated PAN fibers, and (c) 200 kGy irradiated PAN fibers.



**Figure 7** SEM photo of the surface of thermal stabilized fibers obtained at 300°C with different doses of electron beam energy pretreatment; (a) original PAN precursor fibers, (b) 100 kGy irradiated PAN fibers, and (c) 200 kGy irradiated PAN fibers.

the effect of irradiation on PAN precursor fibers and the process of stabilization. The chemical structure, surface transformation, and thermal properties of PAN fibers were examined by FTIR, SEM, and DSC. The following results have been obtained:

1. The pretreatment of PAN precursor fibers with electron beam can induce cyclization at room temperature. The transformation of  $C\equiv N$  to  $C=N$  could be accelerated, and the intensity of  $C=N$  increased significantly in the stabilization process.
2. The transverse section morphology of thermally stabilized fibers developed from original PAN precursor fibers display apparent skin-core structure. The more doses of electron beam treatment, the more serious the skin-core structure was. It can also eliminate surface defects of the stabilized fibers.
3. The PAN precursor fibers with irradiation of electron beam have lower activation energy when they were stabilized. Irradiation of the precursor fibers can expand the reaction temperature range and reduce the onset and



**Figure 8** DSC curve of PAN precursor fibers at different heating rates in an oxygen atmosphere; (a) 5, (b) 10, (c) 15, and (d) 20°C/min.

**TABLE II**  
**Activation Energy of PAN Precursor Fibers Calculated**  
**by the Kissinger Method**

	$d\ln(\Phi/T_m^2)/dT_m^{-1}$	$E$ (kJ/mol)	$A$ (s <sup>-1</sup> )
0 kGy	-36.32	302	$7.19 \times 10^{25}$
100 kGy	-33.68	280	$1.28 \times 10^{24}$
200 kGy	-31.33	260	$2.23 \times 10^{22}$

middle temperature. It can also slow down the reaction rate and the exothermic rate in the process of stabilization, which is the reason for decreasing the internal defects.

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