

# Effect of Adding Sulphur to the Dope on Properties of Modified Polyacrylonitrile Fibers

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**ABSTRACT:** Ammonium-modified polyacrylonitrile (PAN) dope was prepared by free-radical solution copolymerization of acrylonitrile (AN) and ammonium itaconate (AIA), adding different weight percent amount of sulphur into quantitative dope and then the dope was spun into precursor fibers. Effects of sulphur on the characteristics of the copolymers and precursor fibers even the oxidated fibers or the resultant carbon fibers were studied. It has been found that the adding sulphur could obviously increase the hydrophilicity of the copolymer. But in the spinning processes, with the concentration of the adding sulphur increasing, the apparent minus jet stretch of as-spun fibers varied from  $-21\%$  to  $-66\%$ , the crystallinity increased from 21.2% to 40.5%, the void volume, fineness, tenacity and

elongation at-break of the ammonium-modified precursors all decreased, which could result in the increase of the comprehensive properties of the resultant precursors. It was testified that the precursors developed from the copolymer with the higher concentration of adding sulphur have higher degree of orientation. The resultant carbon fibers developed from precursors of the adding sulphur show an improvement in tensile strength of about 30%. The activation energy of cyclization can be reduced from the original  $150 \text{ kJ mol}^{-1}$  to about  $110 \text{ kJ mol}^{-1}$ . © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3773–3779, 2007

**Key words:** copolymerization; fibers; precursors; thermal properties; sulphur

## INTRODUCTION

Among the precursors available for producing carbon fibers, PAN fibers are the most commonly used and promising precursors.<sup>1–3</sup> The conversion from PAN solution to high-strength carbon fiber contains three key stages: spinning, stabilization, and carbonization. Each stage is a very important process because of the mechanical properties of the ultimate carbon fiber depending greatly upon each other. PAN homopolymer as precursor results in carbon fiber of poor quality because of its low thermal property.<sup>1</sup> With acidic monomers acting as comonomers, such as methacrylic acid (MA) or itaconic acid (IA), PAN copolymers possess high thermal property because the acidic groups in the PAN copolymer can catalyze the cyclization of nitrile groups during the heat stabilization treatment of PAN precursors. It settles the problem of comonomer but not its later adverse effect on the process of producing the resultant carbon fibers. Many ways have been attempted to resolve this problem, Watt and coworkers<sup>4</sup> realized the process of streaming to restretch PAN precursors to improve the mechanical properties of the

resultant fibers. Blakslee et al.<sup>5</sup> utilized the neutron irradiation technique to increase the Young's modulus of carbon fibers. Raškovic and Marinkovic<sup>6</sup> filled boron into carbon fibers, while Bahl et al.<sup>7</sup> and Ko et al.<sup>8–12</sup> respectively, utilized various solutions such as CuCl, potassium permanganate (KMnO<sub>4</sub>) to modify PAN fibers so as to promote the mechanical properties of the resultant carbon fibers. Nevertheless, most of the previous work was focused on the influence of the modified precursors on the properties of carbon fibers, besides many studies carried out in laboratory conditions using such a modifying mode, which have many differences from the step-wise ways used in industrial manufacture. The effect of sulfur on the thermal and physical properties of the final PAN precursor fibers—even that of the resultant carbon fibers—have not been discussed in the published literature so far. In this study, a series of experiments were conducted on a continuous production line and the effect of adding sulfur into the dope on the properties of modified PAN fibers investigated in detail.

## EXPERIMENTAL

### Materials

Monomer AN was industrial polymerization-grade and distilled to remove inhibitors before use. Comonomer IA was recrystallized from acetone. Azobisi-

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TABLE I  
Important Parameters of Copolymerization<sup>a</sup>

AN/AIA (w/w)	Oxygen concentration in copolymer (wt %)	AIA concentration in copolymer (wt %)	Conversion (%)	$M_w \times 10^4$
99/1	0.45	1.997	92	14

<sup>a</sup> The conditions are as follows: DMSO/(AIA+AN+AIBN+DMSO) = 78.5% (w/w);  $C_{AN} = 4.5 \text{ mol L}^{-1}$ ;  $C_{AIBN} = 0.007 \text{ mol L}^{-1}$ ;  $t = 6 \text{ h}$ ;  $T = 60^\circ\text{C}$ ;  $M_w$  is calculated by  $[\eta] = 2.83 \times 10^{-4} M_w^{0.758}$ .

sobutyronitrile (AIBN) was recrystallized from ethanol. DMSO was distilled to remove moisture. IA was firstly placed in a flask and dissolved in ethanol. Then the  $\text{NH}_3$  gas was slowly blown into the solution. Neutralization took place and IA turned into AIA. AIA precipitated when there was enough  $\text{NH}_3$  blown in. Precipitated AIA was filtered and dried under vacuum.

### Polymerization and spinning

Firstly, the amounts of AN, IA, AIBN, DMSO were precisely measured out, AN and AIA were carried out the free-radical solution copolymerization in a 20-L pilot-scale stainless reactor, using dimethyl sulfoxide(DMSO) as solvent and azodiisobutyronitrile (AIBN) as radical initiator. Some important parameters and polymerization conditions of the copolymer are shown in Table I.

After the copolymerization was over, the sulfur was added into the dope, and the concentrations of sulfur were changed from 0.0, 0.3, 0.6, ..., to 2.1 wt %, then stirred for half an hour to attain the homogeneous solution; but the total concentration of monomers (including AN and AIA) was controlled at 20 wt %, the obtained spinning dope was controlled at  $70^\circ\text{C}$  and spun into a coagulating bath of 60% DMSO with a spinneret through 1000 holes, each hole having a diameter of 0.06 mm. The coagulated filaments were drawn via three steps in a water bath, followed by soakage with the heat-resistant amine silicone oil. The resultant filaments were dried to be compact, then further drawn in steam set to eliminate stresses and wound to obtain PAN precursors.

### Stabilization of precursors and carbonization of stabilizing fibers

Samples were prepared by stabilizing the PAN precursor in air in different temperature zones in sequences as 190, 220, 240, 250, 260, 270, and  $280^\circ\text{C}$ . The stabilized fibers were carbonized in nitrogen atmosphere at a heating rate of  $400^\circ\text{C}/$

min with a temperature range of  $300\text{--}800^\circ\text{C}$  and at a heating rate of  $500^\circ\text{C}/\text{min}$  with a temperature range of  $800\text{--}1200^\circ\text{C}$ , up to  $1400^\circ\text{C}$  under a drawing ratio of 0.56.

### Characterization

Hydrophilicity of the copolymer is determined by the contact angle. The contact angle can be calculated by the following equation,<sup>13</sup>

$$\cos \theta = 1 - \rho g h_m^2 / 2\sigma \quad (1)$$

where  $\theta$  is the contact angle,  $h_m$  is the maximal height of the liquid,  $\sigma$  is the surface tension,  $\rho$  is the liquid density, and  $g$  is a constant.

The activation energy of any chemical reaction has been calculated using the Arrhenius equation given as literature,<sup>14</sup>

$$K = K_0 \exp(-E_a/RT) \quad (2)$$

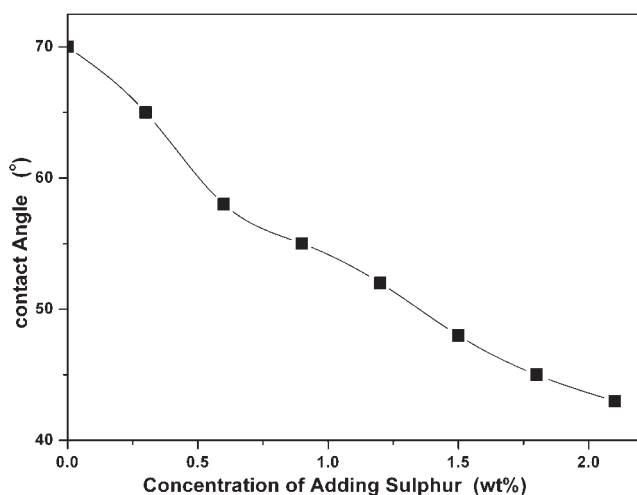
where  $K$  ( $\text{s}^{-1}$ ) is the reaction rate constant,  $E_a$  ( $\text{kJ mol}^{-1}$ ) is the activation energy and  $R$  is the gas constant.

Viscosity of the copolymers solutions was measured using the NDJ-4 rotary viscosimeter under the different shearing rate at  $30^\circ\text{C}$ . The shearing rate is proportionable to the rotor speed. The shearing rate can be calculated from the following:<sup>15</sup>

$$\gamma = \frac{2\omega R^2}{(R^2 - r^2)} \quad (3)$$

where  $\gamma$  is the shearing rate,  $\omega$  is the rotor speed, and  $r$  and  $R$  are the radius of the rotor and the beaker, respectively.

Bulk density of the fibers was determined by means of a density gradient column maintained at  $25^\circ\text{C}$ , the columns were prepared in the 250-mL graduated cylinders, carbon tetrachloride with a density of  $1.57 \text{ g/cm}^3$  was first introduced into the column. Xylene with a density of  $0.90 \text{ g/cm}^3$  was then added slowly into the column, carrying out to plotting the density of the calibrated floats against the position opposite the graduated scale of the column.



**Figure 1** Relationship between hydrophilicity and the concentration of adding sulfur.

Element analyzer GmbH VarioEL (Germany) was employed to measure the elements in the PAN polymers or precursors and various treated 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.

DSC curves of the precursors were recorded on NETZSCH DSC404C thermal analyzer in air flow using a heating rate of 5°C/min with the temperature range from 30 to 450°C.

A Rigaku X-ray diffractometer (D/MAX-rA, Japan) with Ni-filtered  $\text{CuK}\alpha$  radiation as the source was used to study the wide angle at 40 KV and 60 mA, the sample was in the disc form prepared by compressing the randomly aligned short fibers, then the crystalline-related properties of the sample were measured, the scanning speed was 6 deg  $\text{min}^{-1}$ , scanning step was 0.02 deg.

Crystallinity  $C = (S_c/S_t)100\% = S_c/[(S_a + S_c)]100\%$ ;  $S_t$  is the total peak area;  $S_a$  is the amorphous peak area;  $S_c$  is the crystalline peak area.

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  $\text{min}^{-1}$  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.

## RESULTS AND DISCUSSION

### Effect of adding sulfur on the hydrophilicity of the copolymer

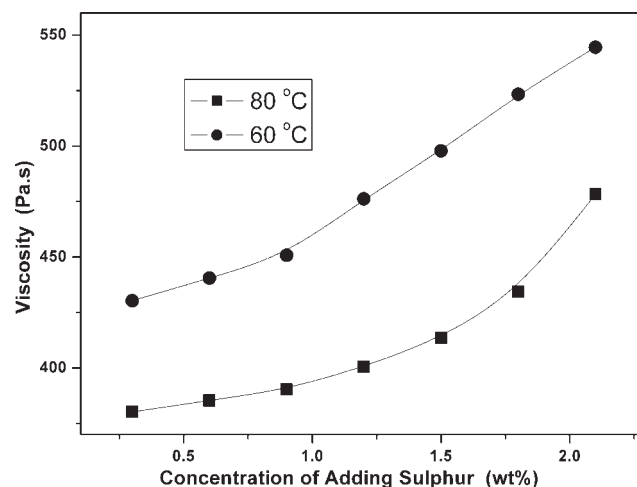
The contact angle between a polymer layer and water can be used to demonstrate the hydrophilicity

of the polymer.<sup>13</sup> The relationship between the hydrophilicity of the discussed dope and the concentration of the adding sulfur is shown in Figure 1. From the changes of the values of the contact angle, it can be found that the contact angle increase, that is to say, the hydrophilicity of copolymer shows an obvious trend of increase with the increase of amount of adding sulfur.

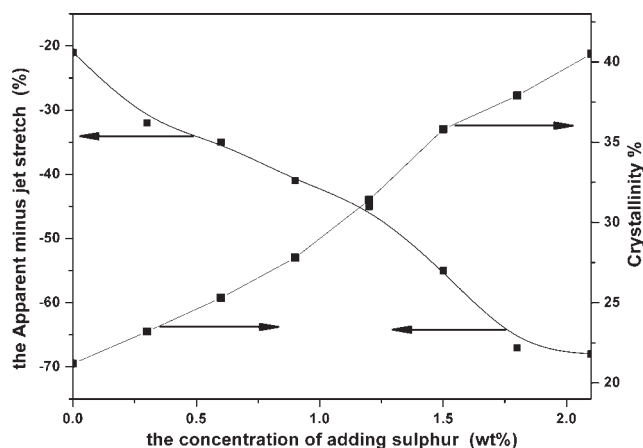
The increase of the said copolymer hydrophilicity gives advantages to the spinning processes of the precursor fibers. The contact angle is a direct measure method for wettability. In the coagulation process where the polymer solution is converted into gel fibers because of the phase separation, the adding sulfur segments in the polymer can improve the microenvironment where the microphase separation is taking place. When water is plasticizer in the stretching process of the precursor fiber spinning, the extent of the stretching of precursor fibers is higher and the orientation of the fibers can be increased. Therefore the physical properties of the precursor fibers are improved.

### Effect of adding sulfur on the viscosity of the copolymer

An influence of adding sulfur on the viscosity of the copolymer solutions was studied by varying concentration of adding sulfur. Figure 2 shows the changes of viscosity with the concentration of addition of sulfur. The viscosity of copolymer solution decreases continuously as the concentrations of adding sulfur increases, when the concentration of adding sulfur is in the range of 0–0.9 wt %, whether at 60°C or at 80°C, the viscosity increases slowly, but when the



**Figure 2** Relationship between viscosity and the concentration of adding sulfur.



**Figure 3** Effect on the spinnability of the as-spun fibers developed from the copolymer with different concentration of adding sulfur.

concentration of adding sulfur is above 0.9 wt %, it increases faster at 80°C than that at 60°C.

It is physical interaction that increases the viscosity of copolymer solution with the increase of concentration of sulfur. The presence of sulfur in AN copolymer solutions is also considered as an important factor for yellowing acrylic fibers.

Intermolecular interaction is reduced by adding sulfur, which leads to the decrease of association degree of high molecular. Entanglement networks of high molecular chain are destroyed. Disentanglement and slippage of entanglement crosslink begin to occur. With an increase of adding sulfur concentration, the rate of disentanglement and slippage is faster compared to that of entanglement, and entanglement networks of high molecular chain are becoming less and less. Disentanglement and slippage of entanglement crosslink relatively easily occur because of better dissolvability of sulfur, on the other hand, the coordinated complexation ability of sulfur is great, and sulfur may form sulfur com-

plex with nitrile radical of the two polyacrylonitrile molecular bordering on each other.

### Effect of adding sulfur on the spinnability of the dope developed from copolymer

The spinnability of dope is mainly affected by the properties of the spinning solution. There is no report in the published literature about the effect of adding sulfur on the spinnability of the dope developed from the copolymer. When talking about the spinnability of the dope, several parameters including the apparent minus ratio jet stretch, crystalline structure and molecular orientation of the as-spun fibers are critical to evaluate it. Keeping the spinning environment and other experimental parameters constant such as the temperature is 60°C and the concentration of coagulation at 60/40(DMSO/H<sub>2</sub>O)wt %, the effect on the spinnability of the as-spun fibers developed from the copolymer with different concentration of adding sulfur is shown in Figure 3. With an increase of the concentration of the adding sulfur, the apparent minus jet stretch varies from -21% to -66%, the crystallinity increases from 21.2% into 40.5%. The minus ratio jet stretch is generally accepted as a comprehensive index of the rheology and hydrodynamic process of wet spinning. When the proto-fiber was extruded from the spinneret, the initial phase of stretching involves deformation of the fibrillar structure with concurrent orientation of the fibrils, and sulfur in the dope can hinder the interaction of the groups, which results in the occurring of the weak action; on one hand it gives rise to the adverse effect, but on the other hand, the increase of crystallinity of the as-spun fibers results in increasing of the degree of orientation, which predict the tensile strength increasing of the corresponding precursors.

**TABLE II**  
Physical Properties of the Precursor Fibers<sup>a</sup>

Precursor code	Optimized draw-ratio	Fineness (dtex)	Tenacity (cN/dtex)	Elongation at break (%)	Bulk density (g cm <sup>-3</sup> )
P0	8.1	1.32	6.0	10.6	1.16
P1	8.0	1.26	7.2	11.1	1.17
P2	8.8	1.22	7.4	11.4	1.17
P3	9.5	1.16	7.6	11.9	1.18
P4	10.2	1.15	8.3	12.2	1.18
P5	11.0	1.12	8.2	12.5	1.18
P6	11.5	1.12	8.2	12.5	1.19
P7	12.0	1.12	8.6	13.1	1.18

<sup>a</sup> P0, P1, P2, P3, P4, P5, P6, and P7 were numbered as the dope with the concentrations of adding sulphur being changed from 0.0, 0.3, 0.6, 0.9, 1.2, 1.5, 1.8 to 2.1 wt %.

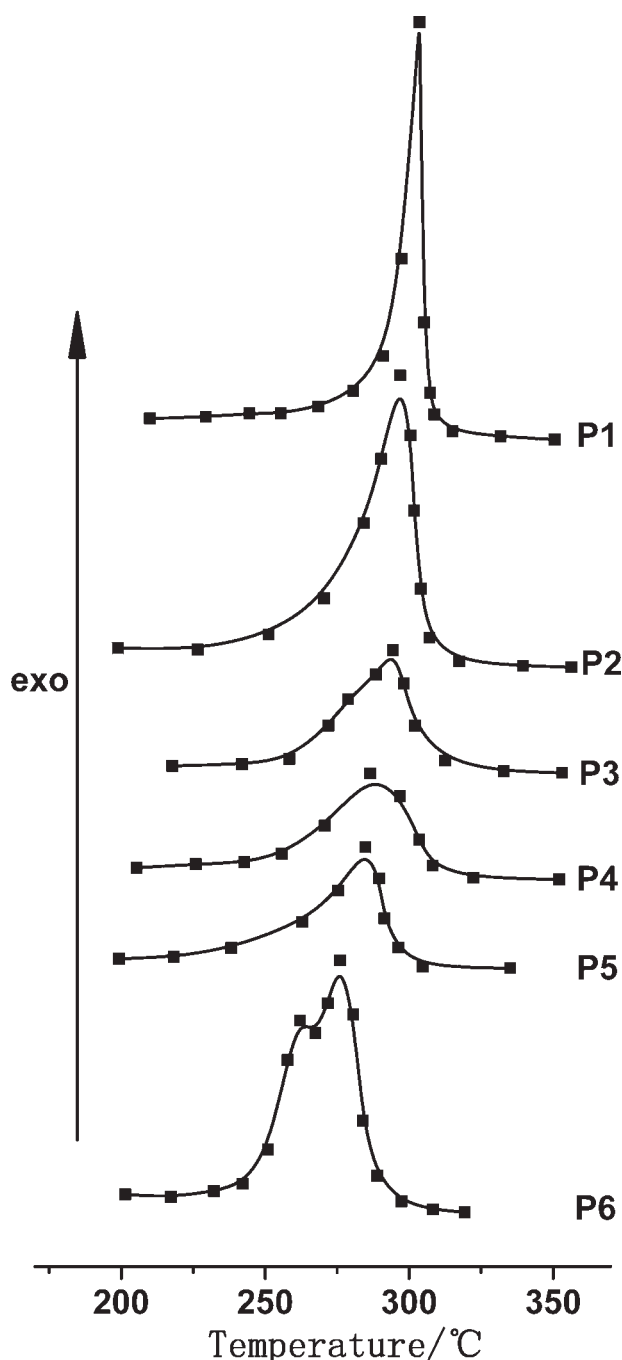


Figure 4 DSC plot of different PAN precursors.

### Effect of adding sulfur on physical properties of the precursor fibers

It is very important to study the physical properties of the precursor fibers. The comonomers play a key role in the factors that affect the physical properties of the precursor fibers. Table II shows effects of the adding sulfur on physical properties of the precursor fibers.

From Table II, it can be shown that the fineness of the precursor fibers decreases with the increase of the concentration of the adding sulfur. But in the spinning processes, the optimized draw-ratio, the tenacity, the bulk density and elongation at-break of the precursors all improve and enhance. In addition, there are no fluffs, broken and adhered fibers in them. The reason and the physical property improvements is the preferable hydrophilicity of the adding-sulfur copolymers, and sulfur in fibers acts as plasticizer in the stretching processes of spinning. It appears that improvement of fiber density in the protofiber also results in improvement in the tensile strength of the protofiber.

### Thermal properties

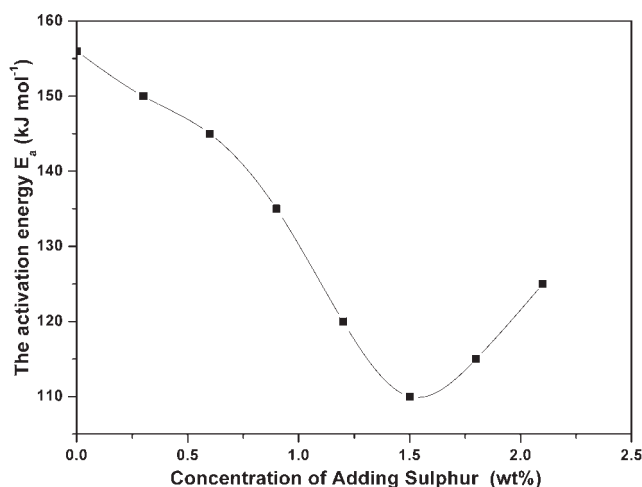
There have been many reports about the stabilization process of the polyacrylonitrile precursors by using DSC method, but there is no discussion about the effect of adding the sulfur to the precursors on its properties by means of DSC. To study the effect of adding sulfur on the thermal properties of precursor fibers, the DSC curves of the adding sulfur precursor fibers are recorded and shown in Figure 4. Some important DSC parameters of the curves are shown in Table III. It was found that there are the following phenomena taking place. With the concentration of adding sulfur in the copolymers increasing, the initial temperatures ( $T_i$ ) are gradually reduced, but the decrease of  $T_i$  becomes less prominent, when the concentration of adding the sulfur is more than 0.9 wt %. The finish temperature ( $T_f$ ), the peak temperature ( $T_p$ ), and the width of exothermic peaks ( $\Delta T = T_i - T_f$ ) also decrease, but the heat liberated during the reaction ( $\Delta H$ ) and the ratio of heat liberated

TABLE III  
Important DSC Parameters of Different PAN Precursors

Precursor code	$T_i$ (°C)	$T_f$ (°C)	$T_p$ (°C)	$\Delta T$ (°C)	$\Delta H$ (J g <sup>-1</sup> )	$\Delta H/\Delta T$ (J g <sup>-1</sup> °C <sup>-1</sup> )
P1	234.1	300.2	290.3	66.1	824.8	12.47
P2	227.2	310.5	285.4	83.3	816.4	9.80
P3	220.0	320.7	280.2	100.7	780.5	7.75
P4	209.3	325.3	276.7	116.0	760.2	6.55
P5	206.2	327.4	270.8	121.2	754.3	6.22
P6	195.4	330.5	265.7	135.1	744.8	5.51

and the time taken during the exotherm ( $\Delta H/\Delta T$ ) increase. It is indicated that the sulfur could greatly lower the initial temperature ( $T_i$ ) and the rate of exothermic reaction ( $\Delta H/\Delta T$ ). Clearly, the presence of oxygen plays a significant role in the initiation of cyclization, so it can be inferred that the diffusion of oxygen into the reaction site would be important in determining the initiation of cyclization. The lateral order of molecular chains resulting from sulfur barricaded the diffusion of oxygen, therefore, slowing down the initiation of cyclization, results the peak temperature shift to the left.

The values of activation energies listed in Figure 5 are based on eq. (2). Because the value of  $-E_a/R$  is the slope of the straight line curve between  $\log K$  and  $1/T$ , the values reported are based on six measurements for each sample. As shown in Figure 5, a wide range of activation energies is exhibited by PAN fibers depending on the pretreatment of adding sulfur. The value of activation energy decrease with the increase of the concentration of adding sulfur from  $150 \text{ kJ mol}^{-1}$  at zero to  $110 \text{ kJ mol}^{-1}$  at 1.5 wt %, but beyond the concentration of 1.5 wt % it increased. The low value of activation energy suggests that the reaction should be initiated at a lower temperature, which is reflected in the time taken for completion the cyclization reaction at a single temperature. The time taken for completion should be low for a reaction and whose  $E_a$  is low compared with a reaction whose  $E_a$  is high, as shown in Table III, and the time taken for completion of reaction for the precursor with the concentration of 1.5 (wt %) adding sulfur was only 25 min, which shorten time of the oxidation process. It can be attributed to the interactions among CN,  $\text{CONH}_2$ , and COOH groups of polymers as a result of the introduction of segmental mobility below 1.5 wt % of adding sulfur,



**Figure 5** The relationship between values of activation energies and concentration of adding sulfur.

**TABLE IV**  
The Mechanical Properties of the Resultant Carbon Fibers Developed from Different Precursors

Sample code	Tensile strength (GPa)	Elongation at break (%)	Carbon yield (%)
P0	2.76	1.21	94.44
P1	2.88	1.35	95.56
P2	3.18	1.37	95.71
P3	3.36	1.41	95.89
P4	3.48	1.45	96.21
P5	3.60	1.48	96.48
P6	3.53	1.52	97.21
P7	3.50	1.52	97.55

but beyond 1.5 wt % that may be due to the exothermic cyclization reaction.

#### Evaluation of mechanical properties of carbon fibers

The mechanical properties of carbon fibers developed from different precursors with the different concentration of adding sulfur are shown in Table IV. It is noted that there appears to be an increase trend in the tensile strength, the elongation at break, and in the carbon yield with the increase of the concentration of adding sulfur.

#### CONCLUSIONS

Different weight percent amount of sulfur was added into quantitative dope and then it was spun into precursor fibers. It has been found that adding sulfur could obviously increase the hydrophilicity of the copolymer. But in the spinning processes, with an increase of the concentration of the adding sulfur, the apparent minus jet stretch of as-spun fibers varies from  $-21\%$  to  $-66\%$ , but the crystallinity increases from 21.2% to 40.5%, and the void volume, fineness, tenacity, and elongation at-break of the ammonium-modified precursors all decrease, which can result in the increase of the comprehensive properties of the resultant precursors. It is testified that the precursors developed from the copolymer with the increasing of concentration of adding sulfur have higher degree of orientation. The resultant carbon fibers developed from precursors of the adding sulfur show an improvement in tensile strength of about 30%, and the activation energy of cyclization can be reduced from the original  $150 \text{ kJ mol}^{-1}$  to about  $110 \text{ kJ mol}^{-1}$ .

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