

Aspects on Interaction Between Multistage Stabilization of Polyacrylonitrile Precursor and Mechanical Properties of Carbon Fibers

P. H. WANG,* Z. R. YUE, R. Y. LI, and J. LIU

Institute of Polymer Materials, Anhui University, Hefei, Anhui 230039, People's Republic of China

SYNOPSIS

The progression of polyacrylonitrile (PAN) fibers on multistage stabilization stage has been monitored by following the variations in density, elemental composition, morphological aspect, and mechanical properties. The effects of various processing conditions during the multistage stabilization on the mechanical properties of final carbon fibers were evaluated in detail. To achieve an optimal extent of stabilization of PAN fibers is critical as the final mechanical properties of carbon fibers are concerned. This aim can be realized by adjusting and matching the temperatures in each step and the processing rates during multistage stabilization. Imposing stretching on multistage stabilization is beneficial to mechanical properties of carbon fibers. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Carbon fibers as reinforcements in the composites have gained wide range of applications from sports products to items used by the aerospace industry. Among the many precursors for making carbon fibers, polyacrylonitrile fibers (PAN) have been established as a most suitable precursor for producing high-performance carbon fibers.¹⁻⁵ The conversion of PAN fibers to carbon fibers usually include: (a) a low-temperature oxidative stabilization to yield a cyclized ladder structure, (b) higher temperature carbonization in inert environment to produce a graphitelike structure, and (c) an alternative "graphitization" treatment to improve the orientation of the carbon basal planes and the stiffness of fibers. Since the low-temperature stabilization (200–300°C) step is usually time consuming and has significant effect on not only the mechanical properties but also the manufacturing cost of carbon fibers, tremendous efforts have been accumulated to understand the complex transformations during this intermediate step and to choose optimal processing conditions on

the balance of economy and mechanical properties of resulting carbon fibers.⁶⁻¹⁰

In the usual practice of carbon fiber manufacture from PAN precursors, there are three alternatives for heat treatment during oxidative stabilization. First, isothermal stabilization, which was the first method for producing carbon fibers in a continuous process, is also the most time consuming. Second is a one-step stabilization with increasing temperature along a furnace. The third is a stepwise increase in stabilization temperature. This is employed industrially by having a sequence of ovens or separated sections of one oven. The basic consideration in the third method is to divide the stabilization of PAN precursors into several stages (termed multistage stabilization) with processing parameters such as temperature, residence time, etc. in each step to be chosen specifically according to the behavior of the precursors in each temperature zone.

Works on dimensional behavior (or stress generation), morphological transformations, as well as interactions between macroscopic constraints and morphological aspects of PAN precursors during oxidative stabilization appeared to further confirm the necessity and advantage of multistage stabilization. The principal outcome of these studies indicated that the stresses generated at any level of

* To whom correspondence should be addressed.

imposed deformation (or conversely, the deformation at any level of imposed stress) would change throughout the course of stabilization. The changes in deformation or stress were correlated with morphological arrangements along the progression of stabilization.¹¹⁻¹³ Thus, it was believed to be imperative to "tailor" different conditions to suit the rates of stabilization reactions and the deformation characteristics of the fibers in the course of the stabilization process so as to realize the maximum potential of a given precursor converted to carbon fibers.

In our laboratory, we have been adopting a multistage stabilization process to understand the physical and chemical aspects of PAN precursors during thermal oxidative stabilization, and the correlations between processing conditions as temperature, stretching ratios, etc. and resultant carbon fiber properties. The principal considerations underlying the division of stabilization into several steps in our setup were as following: (a) to realize the potential of morphological aspects of the original PAN precursors as fully as possible, (b) control the processing conditions in accordance with reaction rates in different temperature region so as to make most suitable intermediate fibers (stabilized PAN fibers) for conversion to carbon fibers, and (c) to balance the manufacturing cost and mechanical properties of final carbon fibers.

Based on these considerations, the stabilization was thus divided into five steps, with each step corresponding to a tubular furnace. The parameters for each furnace were different, especially the temperature and stretching ratio. The first zone was termed the prestabilization step, which was designed to explore the limits of improving the morphological order of PAN precursors before the onset of stabilization reactions. Therefore, the temperature employed in this region was comparatively lower in order to avoid significant initiation of chemical reactions. The remaining four zones were considered as stabilization, which meant significant stabilization reactions were proceeding through these regions. The temperatures for these furnaces were increased from one furnace to the next, with each furnace set to a specific constant temperature regime. The principles of choosing the temperatures were on one hand to fully "stabilize" the PAN fibers with less time as far as possible but on the other hand to minimize the structure inhomogeneities on cross sections of the fibers.

This setup for manufacturing carbon fibers from PAN precursors provides a unique potential to help in establishing the important link between the feature of the precursor fibers and the structure and properties of the carbon fibers which resulted from

them, and besides, to fully explore the correlation among the nature of a given PAN precursor, processing parameters on stabilization and mechanical properties of carbon fibers. In addition, the setup facilitates establishing optimal stabilization conditions for making high-quality PAN-based carbon fibers, and the conditions thus chosen provided direct guidance and effectiveness for the industrial scale of manufacturing PAN-based carbon fibers.

Based on this setup, we have been conducting a sequence of studies aimed at understanding the complicated physical and chemical transformations during the course of stabilization, and optimizing processing conditions to acquire best quality carbon fibers derived from PAN precursors. Part of these works has been or will be published.^{14,15} In this article, a wide range of aspects concerning the physical and chemical arrangements of PAN fibers during the continuous thermal, oxidative, multistage stabilization have been monitored. The effects of various processing conditions during the multistage stabilization upon the final mechanical properties of carbon fibers were surveyed and discussed in detail.

EXPERIMENTAL

Setup for Continuous Multistage Stabilization and Carbonization

Figure 1 shows the setup for continuous multistage stabilization and carbonization for the conversion of PAN fibers to carbon fibers in our laboratory. It consists of prestabilization, stabilization, and carbonization steps. As described above, the function of prestabilization was designed to explore the feasibility and limits of increasing the original morphological order of precursors through stretching at low temperature. The stabilization phase comprises four furnaces designated as step A, B, C, and D, respectively, according to the sequence. The temperatures and stretching ratios for each furnace can be independently controlled. The drawing ratios were imposed by controlling the speed differences between feed and take-up rollers in each furnace. Compressed air was preheated and then tubed into the stabilization furnaces. The temperature on carbonization increased from 300 to about 1300°C. Purified argon was used as the protective atmosphere. A shrinkage of about 3% was allowed for carbonization. This setup provides the potential for conducting precisely controlled experiments at both the stabilization and carbonization stages in order to

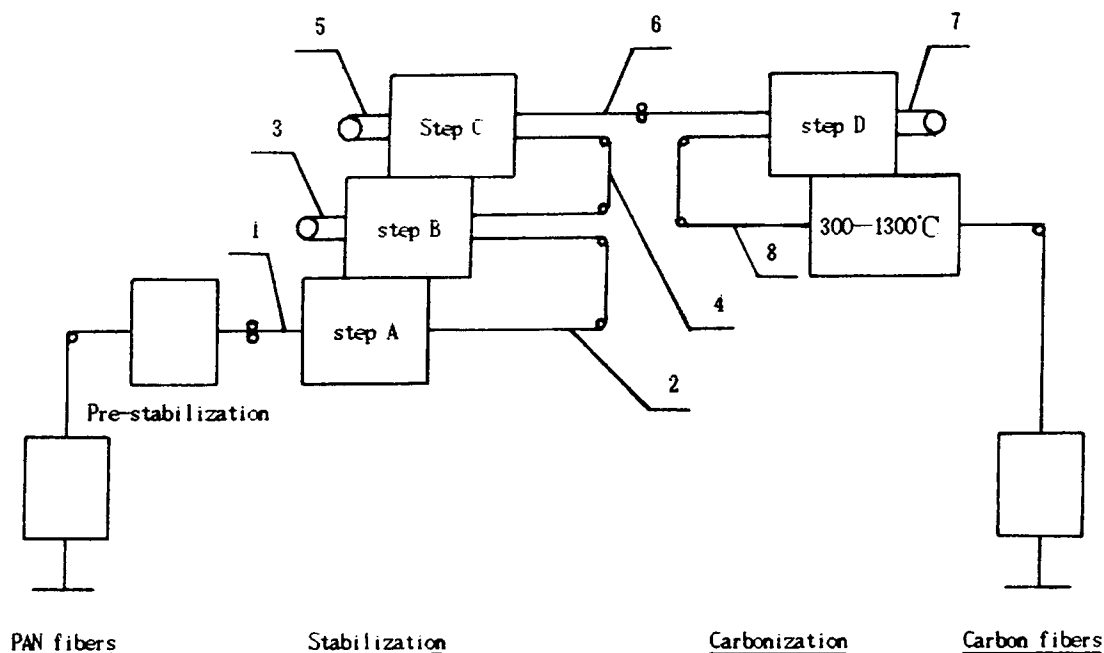


Figure 1 The setup for continuous preparation of carbon fibers from PAN fibers; (O) take-up roller.

establish the correlations among nature of a given precursor, processing conditions, structure, and properties of resulting carbon fibers.

Samples for the study of progression of continuous multistage stabilization were obtained with a three-point method for each furnace after steady state was reached, e.g., the inlet end, the middle point, and the delivery end. Numbers 1–8 in Figure 1 indicate the positions where samples were obtained, each corresponding to the temperature of the related furnace. The number 0 denotes the PAN precursor.

Materials

Studies were performed on a special commercially available acrylic fiber, Courtelle (Courtaulds Ltd. U.K.), which contains 3,000 filaments in each tow and each filament of 1.22 dtex.

Various Measurements

Densities of fiber samples were measured by the density gradient column method. A mixture of *n*-heptane with carbon tetrachloride was used.

Elemental analysis was carried out with a Perkin-Elmer 240C elemental analyzer. The fibers were characterized for carbon, hydrogen, and nitrogen. The oxygen content was derived by the difference.

The wide-angle X-ray diffraction (WAXD) measurements, which yielded information on size and orientation of lateral order fraction, were obtained with a Sinku Riko 2037 X-ray diffractometer using Ni-filtered CuK_α radiation. Details of experimental procedures and calculations were given in Ref. 14.

An Instron Model 1122 testing machine was employed to measure the tensile properties of PAN fibers during stabilization using the single-filament method and final carbon fibers by bundle impregnation method. For filament measurement, a gauge length of 2 cm and crosshead speed of 5 mm/min were used. An average of at least 30 independent measurements were recorded for the calculation. The diameter of individual filaments was measured by an optical microscope. For carbon fiber measurement, a gauge length of 20 cm and crosshead speed of 10 mm/min were used. The cross-sectional area was deduced by fiber density and linear density.

RESULTS AND DISCUSSION

Progression of Multistage Stabilization

Density and Elemental Composition

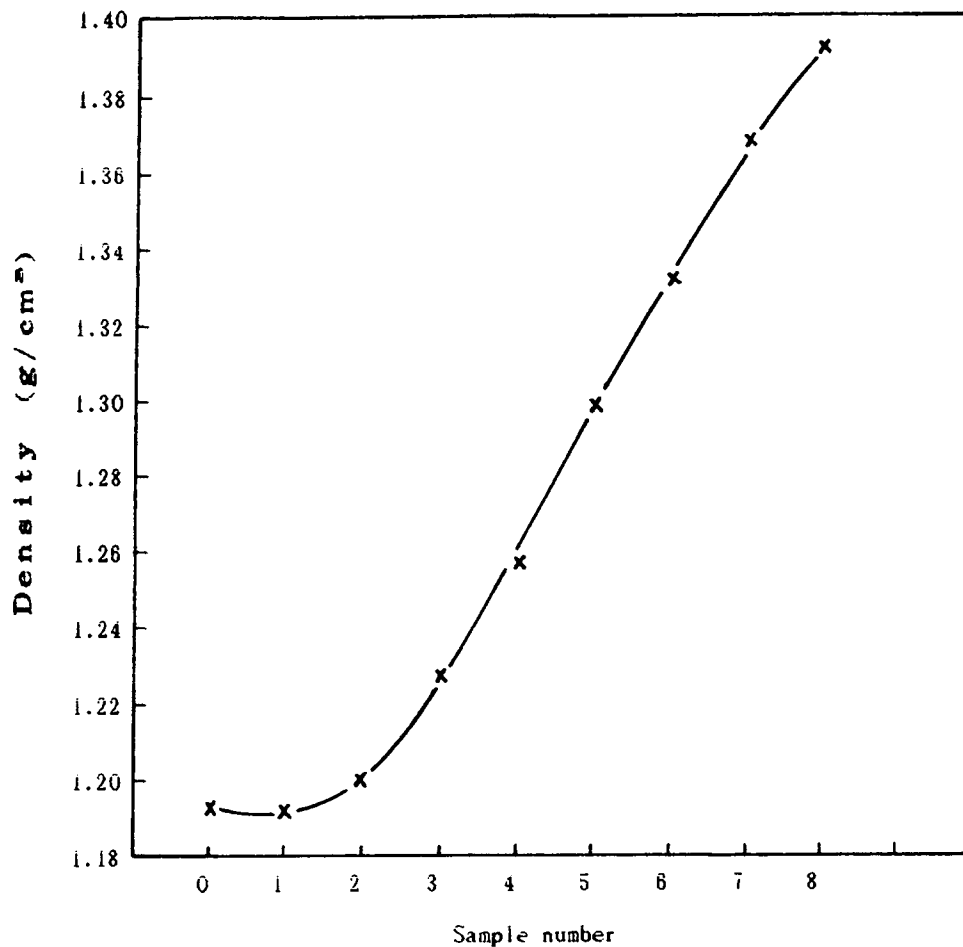
For the studies of progression of PAN fibers on multistage stabilization, the stabilization parameters are listed in Table I. During stabilization treatment,

Table I Stabilization Conditions

	Prestabilization	Stabilization			
		Step A	Step B	Step C	Step D
Temperature (°C)	180	215	230	245	265
Feeding rate (m/h)	14			14	
Residence Time (min)		8.6	17.2	17.2	17.2
Total Stabilization Time (min)				60.2	
Air flow (L/min)			4		

PAN fibers underwent a series of chemical reactions which transformed the original linear polymer structure to a partially cyclized ladder structure¹⁶ and, in addition, caused a significant change in elemental composition of the structure.¹⁷ As a result of denser packing and stacking of these created cyclized species and mass changes of the polymer backbones by dehydrogenation, oxygen incorporation, etc., acrylic fibers exhibited a monotonic in-

crease in density on stabilization.¹⁸ Figures 2 and 3 show a typical variation in density and elemental composition of PAN precursor, respectively, during multistage stabilization employed in our laboratory. It can be seen from Figure 2 that on the prestabilization and step A of stabilization (215°C), the density increase is very gradual. It is therefore inferred that during this part of stabilization, PAN fibers mainly undergo physical transformation, e.g., the

**Figure 2** Density variation on multistage stabilization.

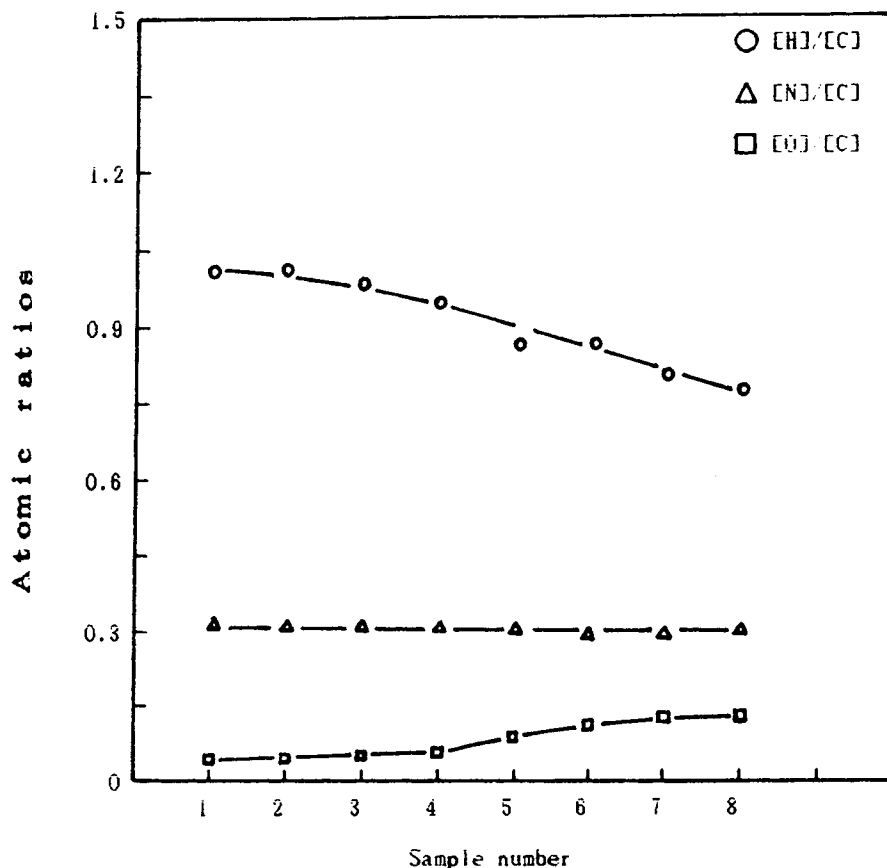


Figure 3 Variation of the atomic ratios H/C, N/C, and O/C on multistage stabilization.

morphological rearrangements, whereas the chemical reactions, which cause the chain structure to change, are not a significant consideration. Thereafter, high stretching is usually imposed on this initial part of the stabilization stage in order to induce additional orientation and order.^{14,15} During the following stages from sample number 2–7 in Figure 2, which includes steps B, C, and D (temperature zones 230, 245, and 265°C, respectively), the fiber density displays dramatic and linear increase, an indication that significant chemical reactions associated with stabilization were occurring within the fiber structure. The final density for the stabilized PAN fibers is predominantly determined by the temperature and processing rate employed on stabilization. It was found in our experiments that this final value of density has a marked impact on the mechanical properties of resulting carbon fibers. This aspect will be further discussed later.

With the progression of density on multistage stabilization, elemental composition as indicated by atomic ratios of PAN fibers also demonstrates significant variation (Fig. 3). The hydrogen ratio de-

creases gradually on whole stabilization. However, the decrease in hydrogen ratio begins from step B and continues to step C. The oxygen ratio, on the other hand, increases during stabilization. In contrast, the nitrogen ratio keeps approximately a constant value. This indicates, as pointed out by Standa et al.,¹⁹ that any chain scission occurring during the reactions largely results in the removal of whole number multiples of acrylonitrile units.

By assuming that the original and heat-treated fibers have three carbon atoms per repeat unit on average, the molecular weight and molecular volume per repeat unit were calculated from densities and elemental compositions. The results are shown in Figure 4 where the relative molecular weight denotes the ratio of the molecular weight per repeat unit for the heat-treated fibers against that for the reference fibers (PAN fibers after prestabilization stage, e.g., sample number 1, the same for the relative molecular volume) and the relative molecular volume denotes the ratio of the molecular volume per repeat unit for the ongoing stabilization fibers against that for the reference fibers. The purpose of these compar-

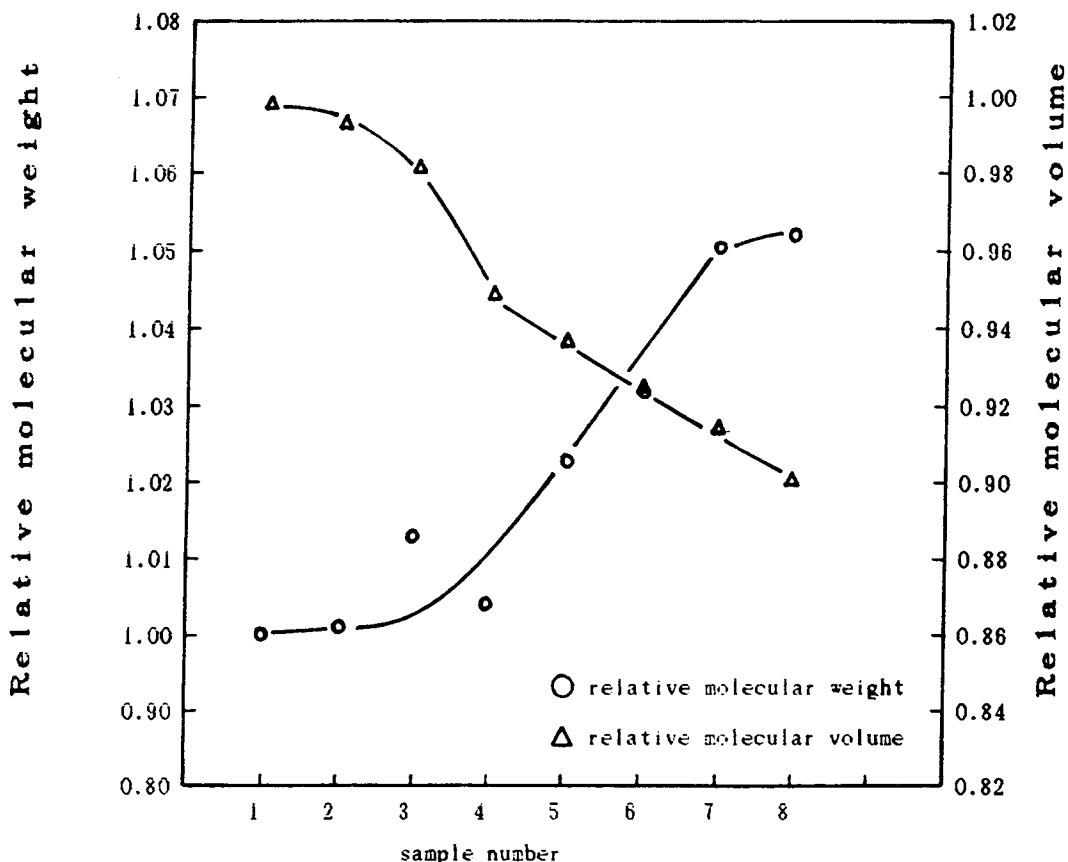


Figure 4 Variations of the relative molecular weight and relative molecular volume per repeat unit on multistage stabilization.

isons is to reveal some aspects related to the contributions of stacking of newly formed cyclized structure and mass change of polymer backbones to the density increase. From Figure 4, it can be seen that with the progression of multistage stabilization, the unit volume of molecular segments is decreasing, which is primarily attributed to the formation and denser packing of cyclized ladder structures. Whereas, the unit weight of molecular chain is significantly increased largely due to the dehydrogenation and oxygen incorporation of the polymer backbones. Comparing the two curves in Figure 4, the change of the relative molecular weight seems to lag behind that of the relative molecular volume. It is thus estimated that the density increase at initial stabilization stage is mainly contributed by the denser packing of the cyclized structures while at later stabilization stage by the mass change.

Morphological Aspects

Figure 5 shows a typical diagram of variation of the orientation and size for the laterally ordered domains

on the continuous multistage stabilization. It can be seen that both the lateral size and lateral orientation display a similar trend in changes. The initial significant increase during early stages of stabilization (mainly prestabilization and step A of stabilization) is due to the plastic deformation of molecular segments of PAN fibers under macroscopic constraints such as constant length or stretching. This deformation of molecular chains leads to marked increase in morphological order and orientation level.

Following the initial part of morphological improvements, and with the occurrence of dramatic chemical reactions within the fibers, both the lateral size and lateral orientation demonstrate rapid decline. However, it should be mentioned that the decrease of orientation evidently lags behind that of lateral size (Fig. 5). This aspect can be explained as due to the chemical reactions, was initiated at boundaries of the laterally ordered fractions, and gradually proceeded inward, leading to a transfer of lateral order to lateral disorder, but without significantly decaying the lateral orientation initially.¹⁴

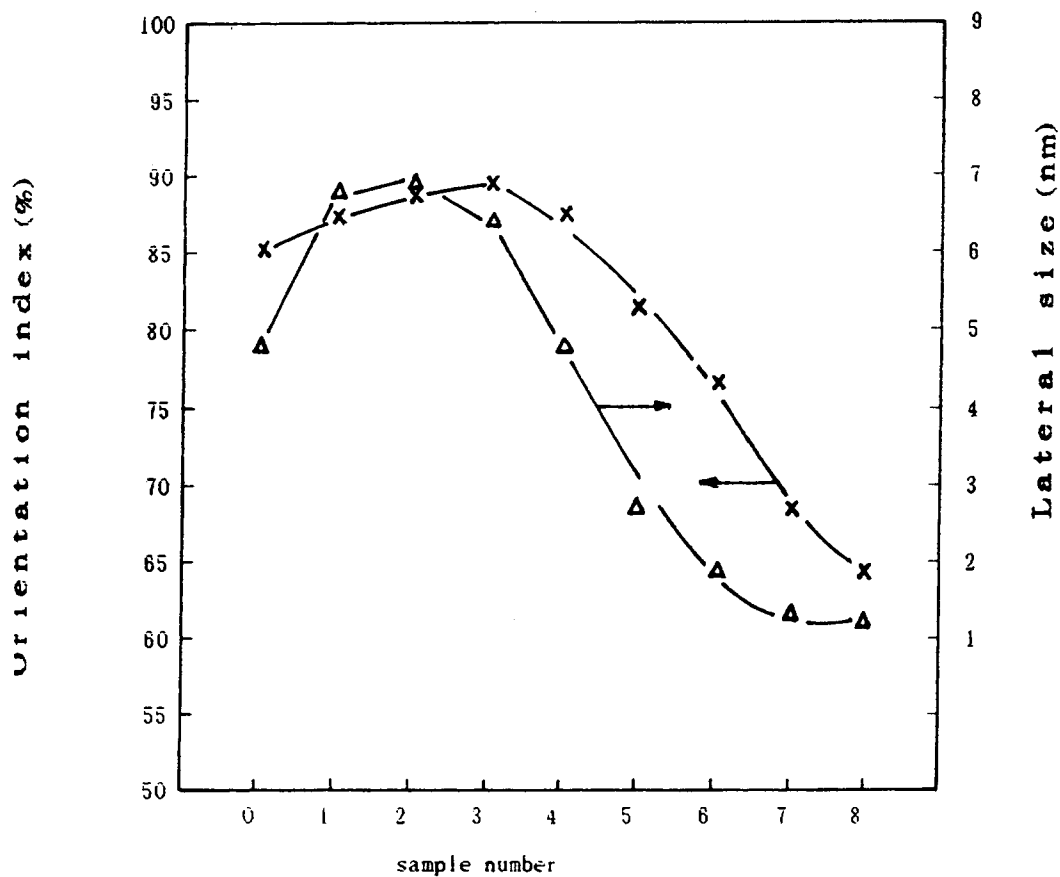


Figure 5 Variation of morphological aspects on multistage stabilization.

At the later stage of stabilization, the decrease in lateral size and lateral orientation becomes gradual and slow.

Mechanical Properties

The variation of fiber diameter along the continuous multistage stabilization is shown in Figure 6. Continual decrease in diameter is observed. This decrease in diameter and simultaneous increase in fiber density (Fig. 2) imply significant volume contraction taking place with progression of stabilization (Fig. 4). The variation in tensile strength and initial Young's modulus of PAN fibers is shown in Figure 7. Tensile strength displays a dramatic and continual decline with stabilization. This observation has been generally attributed to the chemical reaction induced decrease in "cohesive energy" between molecular chains due to the decrease in pendent cyanide groups. However, it should be considered that in addition to the chemical reactions, physical reasons such as morphological aspects and other factors, for example, possible disruption of microfibrillar struc-

ture under outside stretching,²⁰ may also have an impact on the behavior of tensile strength. The change in Young's modulus of PAN fibers is different from that of tensile strength. With the increase in morphological order and orientational level during the early stage of stabilization, the Young's modulus is markedly increased. Then, with the ongoing chemical reactions and decrease in morphological order, the Young's modulus sees a dramatic decrease. At the later stage of stabilization, the Young's modulus experiences a small extent of increase. This second increase can be explained as due to the stacking and ordering of cyclized structures in the material.

Influence of Stabilization Conditions on the Mechanical Properties of Resultant Carbon Fibers

Characterizing Index for Optimal Stabilization Extent

As the mechanical properties of resulting carbon fibers are concerned, the stabilization stage has significant influence on the outcome of carbon fiber

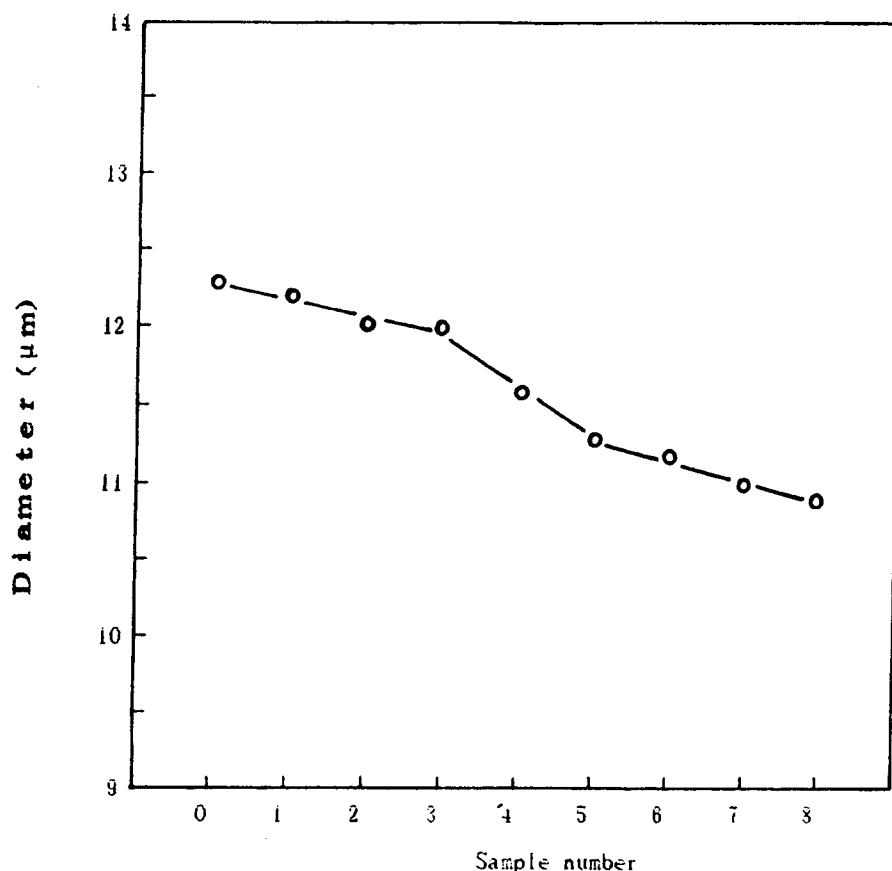


Figure 6 Variation of fiber diameter on multistage stabilization.

properties. Thus, various methods have been tried to characterize the extent of stabilization, and to correlate the stabilization extent with final carbon fiber properties.^{21,22} Among those, the density appears to be the most effective and simplest indicator for characterizing the extent of stabilization. The reason might be that the variation in density of PAN fibers during stabilization shares direct correlation with the progression of chemical reactions and morphological transformations. Figure 8 shows a relation between the density of stabilized PAN fibers and the tensile strength of carbon fibers derived from them. The various density values were reached through adjusting either the temperatures in each step or the processing rate during multistage stabilization. Higher temperature profile employed on the multistage stabilization or lower processing rates resulted in higher densities of stabilized PAN fibers and vice versa. It can be seen from Figure 8 that in order to prepare carbon fibers with high tensile strength, the densities for the stabilized fibers have to be controlled at certain ranges. Overstabilized PAN fibers (which yields higher densities) or un-

derstabilized PAN fibers (which yields lower densities) lead to decay in carbon fiber strength.

Influence of Feeding Rates

Figure 9 shows the effect of feeding rate (or processing rate) during multistage stabilization on the tensile strength of carbon fibers while keeping the temperatures and other conditions constant. The residence time of PAN fibers on stabilization stage under different feeding rate is also shown in Figure 9. It can be found that low processing rates are unfavorable to the strength of carbon fibers. The highest tensile strength is arrived at relatively high processing rate (around 12–16 m/h), which corresponds to a soaking time of about 1 h. Obviously, low processing rates resulted in longer stabilization time of PAN fibers, which lead to overstabilization of PAN fibers. As a consequence, more oxygen might be incorporated into the polymer structures. During the subsequent high-temperature carbonization, more dramatic elimination of small oxide moleculars like CO and CO₂, etc. and more disruption of polymer

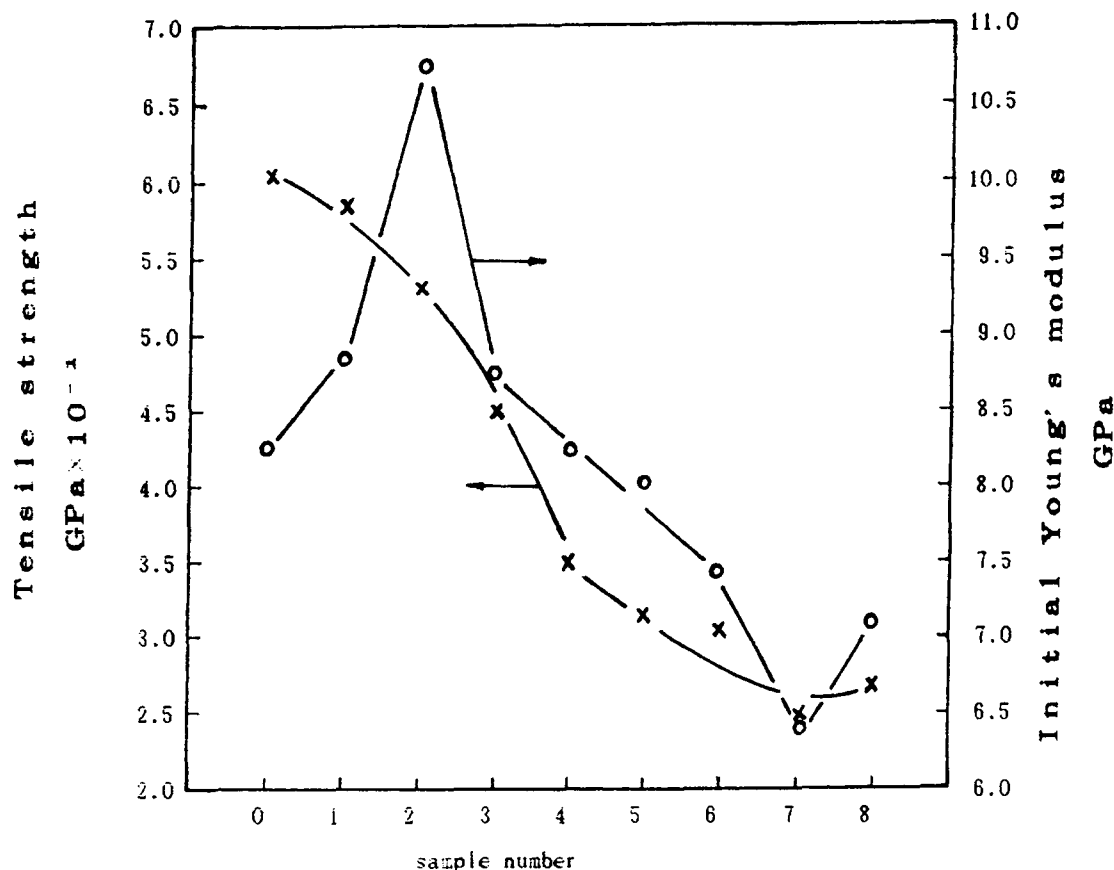


Figure 7 Variation of tensile properties of PAN fibers on multistage stabilization.

chains would be expected, thus creating more defects and flaws within the condensed carbon structures, and therefore, deteriorating the final mechanical properties of carbon fibers. Compared with the isothermal stabilization process as employed in early carbon fiber manufacture, the multistage stabilization as used in our laboratory greatly shortens the required stabilization time. However, it should be noted that the temperatures applied in each step and the processing rates must be correlated and matched with each other in order to balance between stabilization time and optimal stabilization extent.

Influence of Temperatures

On stabilization stage of PAN fibers, temperature and duration time are the two important parameters that affect the extent of stabilization and thus the mechanical properties of resulting carbon fibers. In a process of multistage stabilization, the temperatures in each step will have significant but different effects upon the overall extent of stabilization. Therefore, the temperature profiles employed in

each step have to be chosen to arrive at optimal extent of stabilization. Table II shows the effects of different combinations of temperatures in each step and processing rates on the mechanical properties of final carbon fibers. Under all these stabilization conditions, tensile strengths over 3.0 GPa are produced, an indication that these stabilization conditions are quite suitable and optimal for the precursor used and the multistage stabilization setup employed in our laboratory. The characteristics of these combinations of temperatures and feeding rates are as follows: higher temperature profiles with higher feeding rates and lower temperature profiles matching lower feeding rates. Or put another way, higher temperatures need shorter duration time and lower temperatures require longer duration time. In five sets of experiments, the temperature in step A was kept relatively lower than those in other steps. This is because the stabilization reactions of PAN comonomer fibers (especially with acid monomer) is predominantly diffuse controlled, thereafter, if initial reaction temperature is quite high, rapid chemical reactions will occur around the outermost

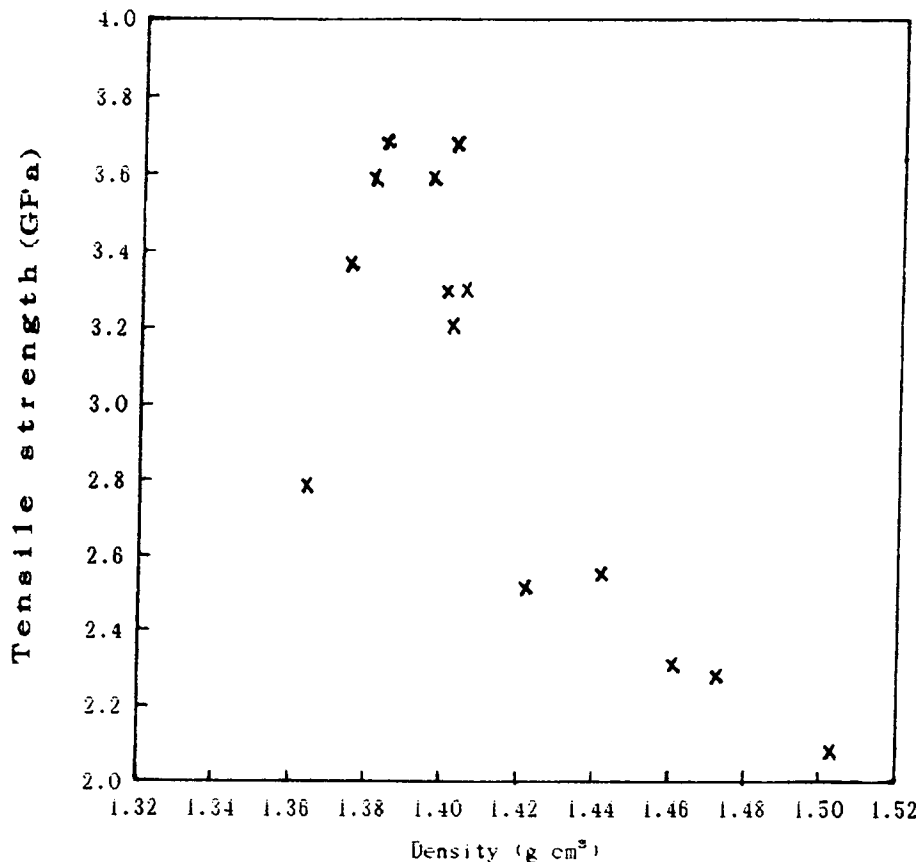


Figure 8 Tensile strength of resulting carbon fibers as a function of the density of stabilized PAN fibers.

skin of PAN fibers where oxygen is sufficient, and as a result, a stabilized sheath will form. This sheath will delay the diffusion of oxygen into the interior of fibers, and thus lead to significant inhomogeneity of structure over the cross sections.

The temperatures in the following steps of stabilization were varied in five different runs. The underlying basis for these combinations is to control the final extent of stabilization. From the viewpoint of the practical manufacture of carbon fibers, the experimental condition in run 4 appears to be most attractive because it gives the highest tensile strength of carbon fibers but needs very short duration time (about 50 min) on stabilization stage.

Effect of Stretching Ratios

The necessity to impose outside stretching and its benefits upon the morphological aspects of PAN fibers during stabilization stage have been subjects of many studies.^{14,23,24} In this section the effects of im-

posed stretching during multistage stabilization process on the mechanical properties of resultant carbon fibers are discussed. The results are listed in Table III. With the increase in stretching ratio on stabilization, the orientation level of carbon basal planes of carbon fibers is increased. The ratio of linear density against density, which characterizes the cross-sectional area of carbon fibers, decrease with increase in stretching ratio, an indication of concurrent decrease in fiber diameter. The tensile strength and the Young's modulus of carbon fiber increase significantly as the stretching ratio increases. These results prove that imposed outside stretching during stabilization stage has beneficial effects upon the mechanical properties of carbon fibers.

However, overstretching during both the pre-stabilization and the stabilization stage may cause disruption of some molecular chains and thereafter induce defects and flaws, which would deteriorate the carbon fiber properties.

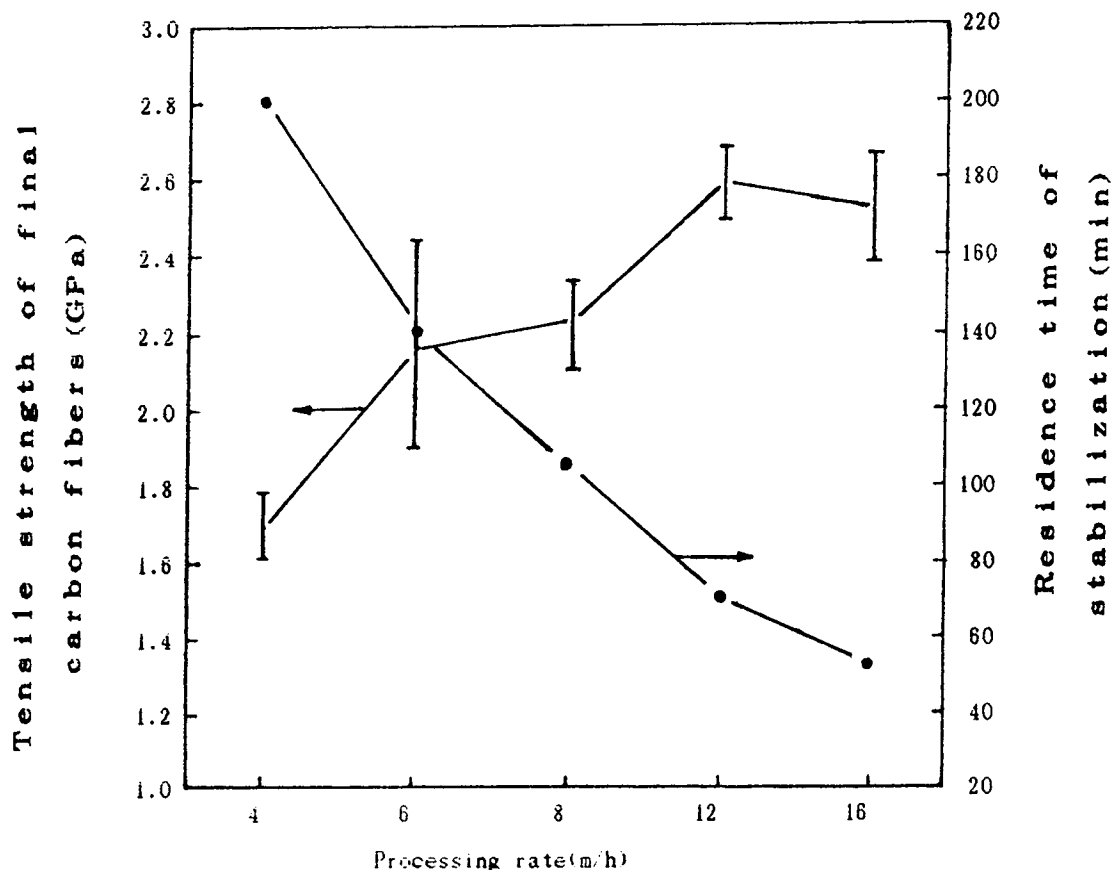


Figure 9 Tensile strength of resultant carbon fibers as a function of processing rate of stabilization.

CONCLUSIONS

The progression of PAN fibers on the multistage stabilization has been investigated by variations in density, elemental composition, morphological aspects, and mechanical properties. Fiber density

showed significant increase during stabilization due to denser stacking of cyclized structures and mass change of polymer backbone. Initial improvements in morphological order and orientation were observed during the early steps of multistage stabilization. Then, with the occurrence of chemical re-

Table II Influence of Stabilization Conditions on the Mechanical Properties of Carbon Fibers

Run No.	Stabilization Conditions		Tensile Properties of Carbon Fibers	
	Temperatures ^a $T_1-T_2-T_3-T_4$ (°C)	Feeding Rate (m/h)	Tensile Strength (GPa)	Young's Modulus (GPa)
1	215-215-225-240	4	3.38	202.9
2	215-215-235-250	6	3.60	193.1
3	215-230-245-260	10	3.19	192.1
4	215-230-245-270	16	3.68	185.2
5	215-235-255-275	20	3.25	181.3

^a $T_1-T_2-T_3-T_4$ refer to the temperature in steps A, B, C, D, respectively, in the multistage stabilization unit. Prestabilization temperature 180°C, total draw ratio on stabilization: approximately 10%. Air flow: 4 L/min.

Table III Influence of Stretching During Multistage Stabilization on the Morphological Structure and Mechanical Properties of Resultant Carbon Fibers^a

Total Drawing Ratio (%)	Orientation Index (%)	Linear Density/ Density	Tensile Strength (GPa)	Young's Modulus (GPa)
0	78.7	11.7	3.00	182.5
11	79.2	10.8	3.49	187.2
22	79.4	9.1	3.63	200.9

^a Temperature profile in multistage stabilization: 215–230–245–265°C. Prestabilization temperature: 180°C. Feeding rate: 14 m/h. Air flow: 4 L/min.

actions, the order and orientation declined significantly. The diameter of PAN fibers decreased throughout the stabilization stage, indicating a simultaneous volume contraction occurring within the material. Tensile strength displayed continual decrease whereby the Young's modulus showed a similar pattern of change to that of lateral orientation during progression of stabilization.

The effects of various stabilization conditions on multistage stabilization on the mechanical properties of resulting carbon fibers have been evaluated. It was found that in order to achieve high mechanical properties of carbon fibers, to control an optimal stabilization extent is critical. This end can be realized by adjusting and matching the temperatures in each step and the processing rates. The density of stabilized PAN fibers was found to be effective indicator of the stabilization extent. Imposing outside stretching during multistage stabilization was proved quite beneficial to the mechanical properties of resultant carbon fibers.

We wish to thank professor J. H. Yu for many useful suggestions and discussions during this work. Help from G. X. Shi in X-ray measurements is gratefully acknowledged.

REFERENCES

- W. Watt and W. Johnson, *Appl. Polym. Symp.*, **9**, 215 (1969).
- O. P. Bahl and R. B. Mathur, *Fiber Sci. Technol.*, **12**, 31 (1979).
- O. P. Bahl, R. B. Mathur, and K. D. Kundra, *Fiber Sci. Technol.*, **13**, 199 (1980).
- E. Fitzer, W. Frohs, and M. Heine, *Carbon*, **24**, 387 (1986).
- T. H. Ko, *J. Appl. Polym. Sci.*, **42**, 1949 (1991).
- O. P. Bahl and L. M. Manocha, *Carbon*, **12**, 417 (1974).
- N. Grassie, I. C. Mcneill, and J. N. Hay, *J. Polym. Sci.*, **56**, 189 (1962).
- N. Grassie and R. McGuchan, *Eur. Polym. J.*, **8**, 257 (1972).
- S. B. Warner, L. H. Peebles, Jr., and D. R. Uhlmann, *J. Mater. Sci.*, **14**, 565 (1979).
- S. B. Warner, L. H. Peebles, Jr., and D. R. Uhlmann, *J. Mater. Sci.*, **14**, 556 (1979).
- M. K. Jain, M. Balasubramanian, P. Desai, and A. S. Abhiraman, *J. Mater. Sci.*, **22**, 301 (1987).
- G. S. Bhat, F. L. Cook, and A. S. Abhiraman, *Carbon*, **28**, 377 (1990).
- P. H. Wang, R. Y. Li, and J. Liu, to appear.
- P. H. Wang, J. Liu, Z. R. Yue, and R. Y. Li, *Carbon*, **30**, 113 (1992).
- P. H. Wang, J. Liu, and R. Y. Li, to appear.
- W. Watt, *Carbon*, **10**, 121 (1972).
- K. Miyamichi, Y. Saito, and M. Katayama, *Seni-Gakkaishi*, **23**, 239 (1976).
- J. W. Bell and R. K. Mulchadani, *J. Soc. Dyers Colour*, **81**, 55 (1965).
- A. E. Standage and R. D. Matkowsky, *Eur. Polym. J.*, **7**, 775 (1971).
- J. Ferguson and B. Mahapatro, *Fiber Sci. Technol.*, **9**, 161 (1976).
- W. Watt, *Nature*, **257**, 210 (1975).
- S. B. Warner, L. H. Peebles, Jr., and D. R. Uhlmann, *J. Mater. Sci. Lett.*, **14**, 2764 (1979).
- W. G. Zheng, MA Thesis, Anhui University, China (1990).
- J. S. Tsai, *J. Mater. Sci. Lett.*, **11**, 140 (1992).

Received May 24, 1994

Accepted October 19, 1994