

# Effect of heat treatment on the structure and properties of poly(2,6-benzothiazole) (ABPBT) and poly(2,5-benzoxazole) (ABPBO)

SHANFENG WANG, GAOBIN BAO, ZHIBAO LU, PINGPING WU\*, ZHEWEN HAN  
*Department of Polymer Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China*  
E-mail: zhwhan@ecust.edu.cn

Poly(2,6-benzothiazole) (ABPBT), poly(2,5-benzoxazole) (ABPBO) were synthesized and their fibers were prepared by dry-jet wet-spinning technique. The effect of heat treatment on the structure and properties of the fibers/films were studied in detail by the measurements using Fourier transform infrared (FTIR), scanning electron microscope (SEM), wide-angle X-ray diffraction (WAXD) and Instron tensile tester. The results not only showed that heat treatment had a significant effect on the macrostructure and microstructure of fibers, making fibers more regular and improving their mechanical properties, but also indicated that there was a suitable range of heat treatment conditions.

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## 1. Introduction

For many years, the development of aviation and space fields have been continuously pressing for novel materials with lightweight, high-modulus, high-strength, good thermostability and environmental resistance. Rigid-rod polymers have received much attention because of their superior properties resulted from their inherent molecular modulus and from their degree of molecular orientation, which was achieved by spinning process. In the early 70s, Du Pont's Kevlar, [poly(*p*-phenyleneterephthalamide) (PPTA)] was marketed and has emerged as the leading high performance polymer fiber for a whole variety of high specific strength applications; however, PPTA is liable to be hydrolyzed as a result of containing the amino group, its environmental stability cannot satisfy the need of aviation and space fields. On the base of long time studies, aromatic heterocyclic rigid-rod or stiff-chain polymers of the poly(benzazole) family have been synthesized to high molecular weight by Wolfe *et al.* [1]. Their modulus and strength are even higher than those of commercial Kevlar and similar to those of some graphite fibers. Besides their excellent mechanical properties, they also show a very good thermo-stability and environmental stability.

The preliminary approach of our lab mainly focused on the rigid-rod polymer structure and properties of poly(*p*-phenylenebenzobisthiazole) (PBZT) and poly(*p*-phenylenebenzobisoxazole) (PBO). Compared with poly(2,6-benzothiazole) (ABPBT) and poly(2,5-benzoxazole) (ABPBO) (Fig. 1): 1. the synthesis of PBO and PBZT was the polycondensation of two

monomers with dehydrochlorination, it is not easy to obtain high molecular weight polymers; 2. the synthetic process of PBO and PBZT is sophisticated and the cost is high; 3. the mechanical properties of ABPBT and ABPBO are close to those of PBZT and PBO, so it is of practical importance to study thoroughly the synthesis, structure and properties of ABPBT and ABPBO.

It is common practice in the spinning of high performance fibers to perform heat treatment. The effect of heat treatment on the morphology, properties [2, 3] and microfibrillar network [4] of PBO, PBZT and ABPBO has been reported. However, the effect of heat treatment on the completion of the cyclization reaction and the stress-strain behavior of ABPBO and ABPBT fibers has not been evaluated previously. So the goal of this work was to characterize such aspects with FTIR and Instron 1120 fiber tensile tester and to give an explanation of the effect of heat treatment on the structure and properties of ABPBO and ABPBT.

## 2. Experimental

### 2.1. Materials

ABPBO, ABPBT were synthesized in our own laboratory by polycondensation in poly(phosphoric acid) (PPA) according to the reference [5]. After polymerization, ABPBT/PPA or ABPBO/PPA dope was transferred to a bomb and fibers were spun by extruding the solution through a spinneret die into a water-coagulating bath. The fibers were dry-jet wet-spun, usually to a high draw ratio, in the air gap between the die and the coagulating bath. The residual dopes were

\* Author to whom all correspondence should be addressed.

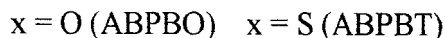
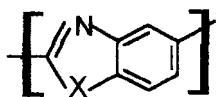


Figure 1 Chemical structure of ABPBO and ABPBT.

extracted on heated glass board to make ABPBT or ABPBO films. The fibers and films were immersed instantly in a large volume of cold water for at least three days in order to remove PPA completely, the water bath was checked with pH papers to assure that it was neutral. After that, the fibers and films were dried in air and then heat treated at different temperatures with different tensions for various durations, ready for the studies on the structure and properties.

## 2.2. Measurements

Wide-angle X-ray diffraction (WAXD)  $2\theta$  scans were collected in a range of  $5^\circ$ – $60^\circ$  on a Rigaku D/max-rA rotating anode X-ray generator with Ni-filtered Cu  $K_\alpha$  radiation operated at 100 mA and 40 kV.

Fourier transform infrared (FTIR) studies provided qualitative information relative to the completion of cyclization from heat treatment. Thin ABPBT films were analyzed on a Nicolet Magna-IR 550 Fourier transform infrared spectrometer.

Philips SEM 550 was used at 15 kV to image both surface sections and tensile-fractured cross sections of the fibers for examining the effect of heat treatment and the fracture behavior. Fiber specimens were sputter coated with Au-Pd to enhance imaging contrast.

The stress-strain behavior of ABPBT and ABPBO fibers was determined on a Instron 1120 fiber tensile tester. The deformation rate was 5 mm per minute.

The mechanical properties of fibers were measured on a YG001A single fiber electronic tensile tester, produced by Taicang Textile Instruments Works of China National Textile Machinery Corp., with the deformation rate of 10 mm per minute.

Since there are variations in fiber diameter, which is thought to be the result of the exothermic diffusion and nonequilibrium hydrodynamic behavior existing in the coagulation of the polymer [2], it is necessary to test an adequate ensemble of fiber specimens for reliable mechanical properties. In this study, we tested 50 specimens from every group.

## 3. Results and discussion

Fig. 2 shows the FTIR spectra of ABPBT films heat treated at various temperatures with the same tension. The curves of the heat treated film have an intensity change of carbonyl group absorption peak at  $1710\text{ cm}^{-1}$ , the absorption peak of curve (a) (heat treated at  $200^\circ\text{C}$ ) is obviously stronger than those of the other three curves. There being no carbonyl group in the ABPBT molecular structure, the only possible explanation is that the carbonyl group is caused by the uncompleted cyclization reaction [6], i.e., there exists

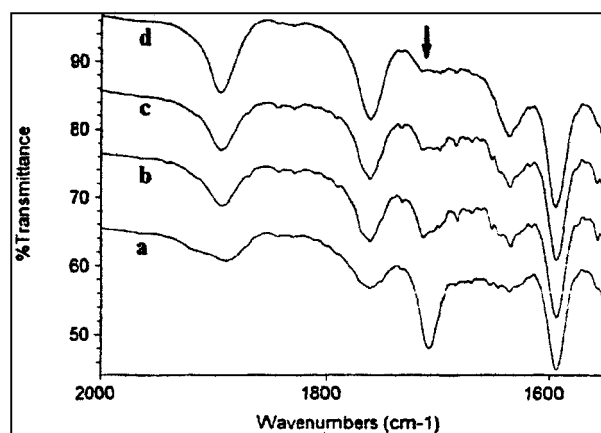
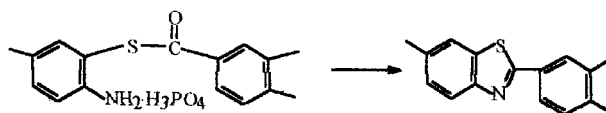


Figure 2 FTIR spectra of ABPBT treated under different temperatures. (a)  $200^\circ\text{C}$ ; (b)  $350^\circ\text{C}$ ; (c)  $450^\circ\text{C}$ ; (d)  $550^\circ\text{C}$ .

residual phosphoric acid partly in the form of free acid and partly in the form of associating with amino groups in the molecule. Heat treatment promotes the reaction of cyclization as Scheme 1.



Scheme 1 The completion of the cyclization reaction.

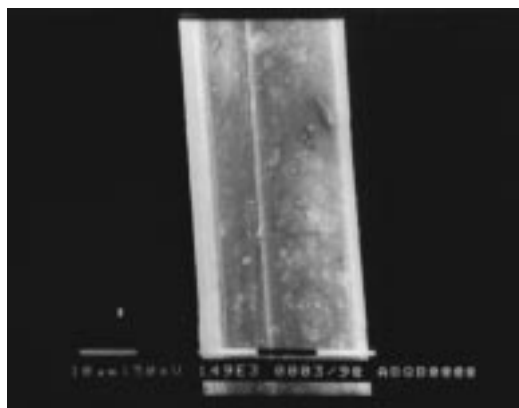
Heat treatment over  $300^\circ\text{C}$  can make free phosphoric acid decompose, followed by the sublimation of  $\text{P}_2\text{O}_5$ ; heat treatment over  $460^\circ\text{C}$  can make phosphoric acid associated with amino groups release from the fiber, so the reaction of cyclization advances further and the carbonyl group content decreases with the rise of temperature. After the completion of the cyclization reaction, the molecular chain regularity and the length of the conjugated system in the polymer chain were improved, and the packing of the stiff chains became more compact and more orderly, which must be helpful to improve the mechanical properties of ABPBT fiber.

ABPBT fibers were fabricated from ABPBT/PPA dopes by dry-jet wet-spinning and coagulation. Voids were formed in the fibers, especially on the surface (Fig. 3a) during the coagulation when a drastic volume reduction occurred in the dissolution of PPA. As the solvent PPA was leaking out from the fiber, the residual stress was then brought about in the as-spun fiber, which will affect the mechanical properties of ABPBT fiber significantly. As we know, when heat treated and given enough energy under certain conditions, the molecular chain will slide along the stress direction, which will reduce the void content (Fig. 3b) and relax the residual stress, and consequently lead to higher mechanical properties.

The determination of the crystalline structure of oriented fibers of ABPBT and ABPBO was described in the reference [7]. Both units cells are metrically orthorhombic, with the parameters:  $a(100)=0.6044$  (17),  $b(010)=0.3417$  (7),  $c$  (fiber axis) = 1.2194 (18) nm for ABPBT and  $a(100)=0.6061$  (17),  $b(110,010)=0.3417$  (13),  $c$  (fiber axis) = 1.1575 (6) nm for ABPBO. Changes induced by the heat treatment



(a)



(b)

Figure 3 SEM images of as-spun ABPBT fiber (a) and ABPBT fiber heat-treated at 550 °C (b).

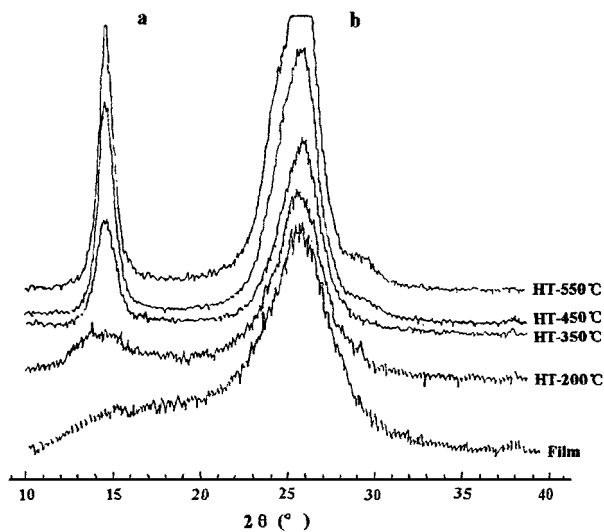


Figure 4 WAXD equatorial scan of ABPBT film and heat-treated fibers with tension ((a)  $2\theta = 14.75^\circ$ ; (b)  $2\theta = 26^\circ$  "HT" used in this paper means heat-treatment).

in the chain packing with the crystallites are evident in the wide-angle X-ray diffraction patterns. The diffraction patterns of the ABPBT film and fibers heat treated under different temperatures with tension are shown in Fig. 4. All curves have two peaks at the interplanar spacing corresponding to  $2\theta = 14.75^\circ$  (0.6006 nm) and  $26^\circ$  (0.3427 nm), which correspond to the (100) plane and (010) plane respectively. The peaks observed in the patterns of ABPBT fibers are much sharper

than those of ABPBT film, indicating their more ordered structure. And with the rise of heat treatment temperature, the change of the half-peak width of peak at  $26^\circ$  is negligibly small, suggesting that the face-to-face interplanar distance and the degree of order in the (010) plane of ABPBT fiber does not vary. As to the peak (a) at  $14.75^\circ$ , the intensity is raised and the half-peak width reduces considerably with increase of the heat treatment temperature, which shows that the periodicity and the degree of order in the plane (100) were changed significantly, especially above  $350^\circ\text{C}$ .

Fig. 5 demonstrates the change in the chain packing of ABPBO fibers with the rise of heat treatment temperature studied by WAXD. The result is similar to that of ABPBT fibers.

The interplanar distance of ABPBO, calculated from the angle of the diffraction peak by employing the following well-known Bragg's equation, as a function of the number of units:

$$2d \sin \theta = n\lambda \quad (1)$$

where  $d$  is the interplanar distance,  $\theta$  is the scattering angle,  $n$  is the order of the reflection, and  $\lambda$  is the wavelength of the X-ray used. In the present case,  $n$  is 1 and  $\lambda$  is 0.15418 nm for nickel-filtered Cu  $K_\alpha$  radiation.

The size of the ordered structure can be estimated from the breadth of the Equatorial peaks using the Debye-Scherrer formula which states that:

$$L_{hkl} = \frac{K\lambda}{B \cos \theta_{hkl}} \quad (2)$$

where  $L_{hkl}$  is the lateral size of the crystallite, i.e., the size of the ordered structure, as measured from the breadth of the ( $hkl$ ) reflection at a scattering angle  $2\theta$ , for which the half-peak width is  $B$ .  $K$  is a constant of value equal to 0.89. The results are listed in Table I.

The results show that the interplanar distance, representing the period of the ordered structure, of peak (a) ( $2\theta = 14.1^\circ$ ) reduces and the size of ordered structure increases with the rise of the heat treatment temperature. Moreover, the intensity of peak (a) is raised considerably, which is in accord with the effect of heat treatment on ABPBT fibers.

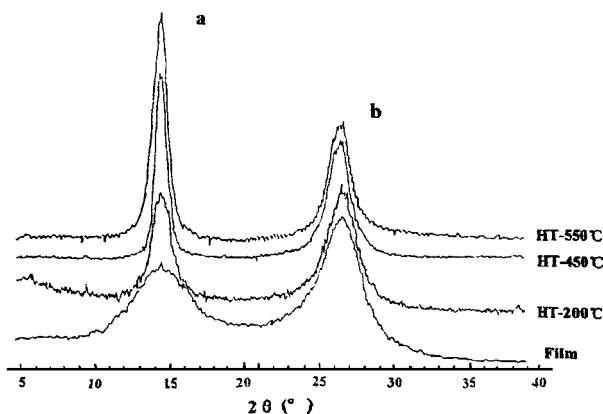


Figure 5 WAXD equatorial scan of ABPBO film and heat-treated fibers with tension ((a)  $2\theta = 14.5^\circ$ ; (b)  $2\theta = 26.4^\circ$ ).

TABLE I X-ray results of ABPBO fibers and film

Sample	$2\theta(^{\circ})$		$d$ (nm)		$L$ (nm)	
	peak a	peak b	peak a	peak b	peak a	peak b
film	14.3	26.3	0.619	0.339	1.30	2.02
HT-200 $^{\circ}\text{C}$	14.1	26.5	0.628	0.336	1.18	2.31
HT-550 $^{\circ}\text{C}$	14.6	26.6	0.607	0.335	10.04	4.75

As revealed in Fig. 5, film extruded from the ABPBO/PPA dope and fibers spun by the dry-jet wet-spinning technique all have a high degree of orientation. But the diffraction parameters of the fiber heat treated a 550 $^{\circ}\text{C}$  with tension (Table I) show that the half-peak width reduces sharply and the size of ordered structure increases from 1.18 nm to 10.04 nm, suggesting that the conformation of ABPBO molecular chain changes drastically. Moreover, there is a weak shift of the peak (a) from 14.1 $^{\circ}$  to 14.6 $^{\circ}$ , which means that the side-by-side interplanar distance is reduced from 0.628 nm to 0.607 nm. According to Fratini's calculation [7], there is a transformation from coil-like conformation (*cis*) to extended-chain conformation (*trans*) around 300 $^{\circ}\text{C}$ , as illustrated in Fig. 6, and this extended-chain conformation is fixed after 550 $^{\circ}\text{C}$  heat treatment. The dynamic mechanical property of ABPBO film also aids to explain this phenomenon [8].

As discussed above, heat treatment with tension can provide relevant energy and make the molecular chain adjust and slide along the fiber axis. As the result of the completion of the cyclization reaction promoted by heat treatment, the molecular chain regularity, the length of the conjugated system in the polymer chain and the orientation of the ABPBT or ABPBO fiber were improved. Together with the reduction of defects in the fibers and the transformation of the molecular chain conformation from coil-like conformation (*cis*) to extended-chain conformation (*trans*) around 300 $^{\circ}\text{C}$ , which is a preferable conformation for packing and regularity, heat treatment with tension surely results in the improvement of the mechanical properties of ABPBO and ABPBT fibers.

The stress-strain behavior of both as-spun and heat-treated ABPBT/ABPBO fibers is shown in Fig. 7. As fibers are obtained from the polymerization solution

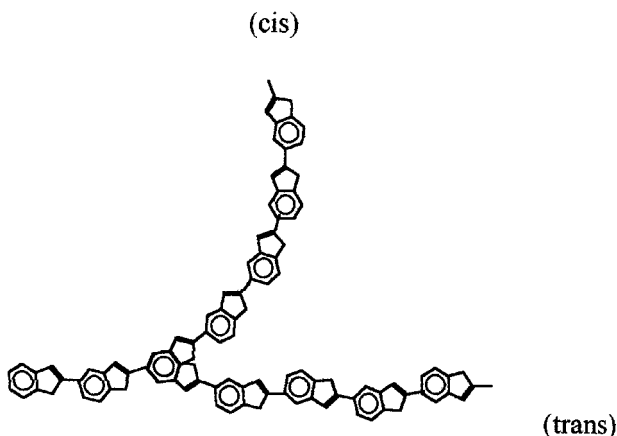


Figure 6 Conformation transformation of ABPBO chain.

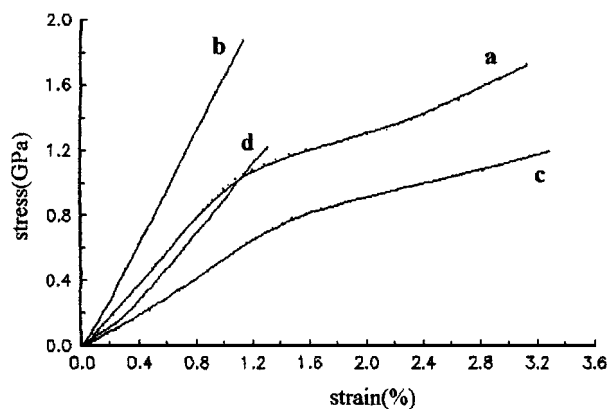


Figure 7 Stress-strain behavior of as-spun and heat-treated ABPBT and ABPBO fibers at ambient temperature. ((a) as-spun ABPBT fiber ( $D = 28.4 \mu\text{m}$ ); (b) ABPBT fiber ( $D = 26.3 \mu\text{m}$ ); (c) as-spun ABPBO fiber ( $D = 64.6 \mu\text{m}$ ); (d) ABPBO fiber ( $D = 62.5 \mu\text{m}$ )).

by dry-jet wet-spinning and water coagulating bath, there should have been some voids and residual stress in the as-spun fibers, which lead to ductile fracture with the nonlinear character of the stress-strain behavior and make as-spun fibers yield before fracture. Contrasted with as-spun fibers, heat-treated fibers demonstrate fragile fracture with the linear-elastic stress-strain behavior [9], characterized as higher modulus, strength and lower elongation than those of their counterparts. Evidently it is because that heat treatment enhances the regularity and orderness of the molecular chain.

Effects of heat treatment temperature, tension and duration on the mechanical properties (i.e. modulus, strength and elongation) of ABPBT fibers are plotted in Fig. 8a–c respectively. According to time-temperature equivalence well known to us, these three parameters above are correlated to one another in the effect. The higher the heat treatment temperature, the easier the adjustment and slide were performed, giving more ordered structure and inducing higher mechanical properties. Considering that ABPBT will degrade at about 600 $^{\circ}\text{C}$  in air, one can conclude that heat treatment at 550 $^{\circ}\text{C}$  is a suitable temperature for ABPBT and ABPBO. Tension can not only ensure the process of heat treatment, but impel the molecular chains to adjust and slide along the stress direction (i.e., fiber axis) for further orientation. With the increase of tension, the adjustment and movement of molecular chains become easier and the mechanical properties, especially modulus, are improved obviously. But tension should not be increased without limit; otherwise, it will destroy the molecular chain of the ABPBT fibers or even break the fibers, which will do harm to the fiber properties. Fig. 8b shows the relationship of mechanical properties with heat treatment tension: the fiber modulus and strength first increase and then decrease as the tension rises. As to the fiber we obtained, 300 MPa is a suitable tension.

It was reported that the properties and the structure of this type of fibers were insensitive to the duration of heat treatment [10], but we found that heat treatment duration also have similar effect on the properties of the fibers, as shown in Fig. 8c. The goal of the heat treatment is to transform from low-property state

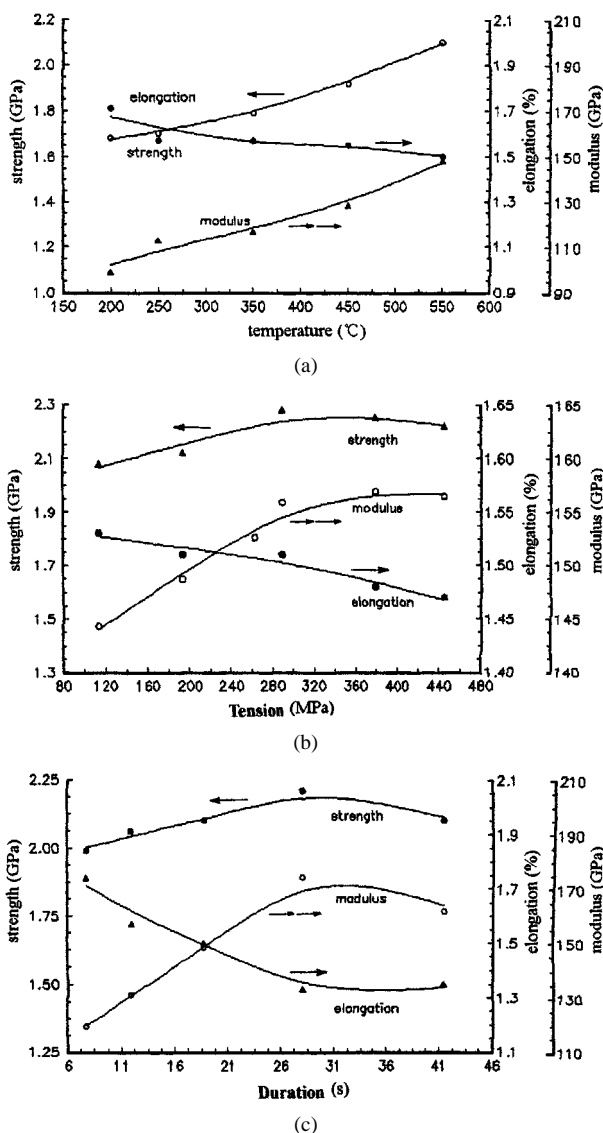


Figure 8 Effects of heat treatment factors ((a) temperature (b) tension (c) duration) on ABPBT mechanical properties.

to high-property state. Polymeric movement is a relaxation process, requiring a certain long period. Too short heat treatment duration is not enough for fibers to transform to the high-property state. But long time gives the same result as high temperature does, which will be deleterious to fiber structure and the mechanical properties.

#### 4. Conclusion

Heat treatment can reduce void content and residual stress in the as-spun ABPBT or ABPBO fiber. The completion of the cyclization reaction was promoted by heat treatment, which is advantageous to the molecular regularity, the length of the conjugated system in the polymer chain and the packing of the chains. Together with the transformation from coil-like conformation (*cis*) to extended-chain conformation (*trans*) around 300°C, these factors induced by heat treatment improve the mechanical properties of fibers. Under a suitable heat treatment condition, ABPBT fiber with better mechanical properties can be obtained.

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