Morphology and structure changes of aromatic copolysulfonamide fibers heat-drawn at various temperatures

Jinchao Yu, Rui Wang, Chunlei Yang, Shenghui Chen, Feng Tian, Huaping Wang and Yumei Zhang

Abstract

Pre-drawn aromatic copolysulfonamide (co-PSA) fibers were prepared by wet spinning and then heat drawing at temperatures varying from 350 to 390 °C, which are below the decomposition temperature. The fibers were then characterized using tensile testing, dynamic mechanical analysis, wide-angle X-ray diffraction and small-angle X-ray scattering. The relationship between structure and properties of the co-PSA fibers drawn at different temperatures was investigated. The heat-drawn co-PSA fibers displayed similar glass transition temperature of about 355 °C, which was higher than that of pre-drawn co-PSA fibers of 345 °C. The crystal orientation was high as a crystalline structure formed during heat drawing and the crystallinity increased with the heat-drawing temperature. However, the tenacity of the co-PSA fibers did not increase linearly with the draw temperature. When the drawing temperature was higher than the glass transition temperature, a decrease in tenacity was observed, which could be attributed to an increase of crystallite size of the (100) plane and a decrease of the long period of the lamellar structure.

INTRODUCTION

Fibers with the characteristics of high strength, high modulus, good thermostability and environmental resistance have attracted the increasing attention of scientists for several decades. In the early 1970s, Kevlar and Nomex, produced by Du Pont Company, emerged as the leading high-performance fibers. At approximately the same time, isomerically substituted aromatic polysulfonamides (PSAs) were identified as one group of heat-stable polymers.1 PSAs have found applicability in the fields of high-temperature filtration and flame retardancy2,3 due to their excellent chemical and thermal stability and large limiting oxygen index.4 Spinning experiments of some isomerically substituted PSAs were carried out as early as the 1970s.5,6 The first commercialized PSA fiber was produced by Shanghai Tanlon Fiber Co. Ltd in 2007 with the trade name of Tanlon®.7 Nevertheless, research on the spinning process as well as the properties and structures of PSA fibers has been insufficient. Many efforts have been focused on exploring the effect of the coagulation conditions during the wet-spinning process, such as coagulation bath composition and temperature, on the porous structure and mechanical behavior of PSA fibers or films.5,8,9 Only few reports have referred to the structural changes of PSA fibers during the spinning process. Muraveva and Konkin10 found that the structure of poly(3,3′-diphenylsulfonyl terephthalamide) fibers produced by wet spinning is amorphous during the forming and cold-drawing process, and significant structural conversions occur in hot stretching. These conversions result in further orientation and polymer crystallization, so that the tenacity of the fibers increases. Kuznetsov et al.1 found that even poly(4,4′-diphenylsulfonyl terephthalamide) (pt-PSA) with higher degree of symmetry of its molecules showed an amorphous state before heat treatment, and crystallization took place only during the annealing process. A similar phenomenon was also observed by our group previously.11 All these findings indicate that the crystalline structure of PSA fibers is formed only in the heat-stretching or annealing process, and certain mechanical properties can also be achieved. It could be suggested that heat stretching plays an important role in the improvement of the fiber performance.

Although studies on the structure and properties of PSA fibers are limited, we can draw inspiration from the achievements related to other aromatic polymeric fibers. Young et al.12 investigated the relationship between structure and mechanical properties of as-spun and heat-treated high-modulus poly(p-phenylenebenzobisoxazole) (PBO) fibers. It was concluded that,
when the temperature is lower than the degradation temperature \(T_d\), heat treatment of the fibers at elevated temperatures produces an improvement in the extent of crystallinity and better orientation leading to higher levels of stress and modulus. It was also reported by Allen et al.\(^{13}\) that the mechanical properties of poly(p-phenylenebenzobisthiazole) fibers are significantly enhanced by heat treatment at temperatures above 600 °C. When the heat treatment temperature is lower than \(T_d\), the tensile strength and modulus increase with temperature and applied tension resulting from the significant enhancement of the lateral molecular order of the rod-like poly(p-phenylenebenzobisthiazole) molecules. From the results of Lee et al.\(^{14}\), it is concluded that molecular reorientation is responsible for the modulus improvement of post-treated Kevlar fibers, and this reorientation occurs through the removal of pleats.

Generally, the enhancement of the properties of aromatic fibers is usually caused by a substantial improvement in structural perfection and chain alignment resulting from heat treatment. Following these assumptions, we have designed a heat-drawing experiment for pre-drawn aromatic copolysulfonamide (co-PSA) fibers to investigate the changes of the structure and properties of the fibers at various heat-drawing temperatures below \(T_d\). From our previous study, it is known that, unlike PBO and Kevlar fibers\(^{14–16}\) with extended chain structure in the crystal phase, pt-PSA has a twofold molecule with two monomeric units forming a zigzag conformation in the crystal lattice and forming a layer structure, which is stabilized by the hydrogen bond between \(-\text{NH}\) and \(-\text{C} = \text{O}\) and parallel-displaced \(\pi-\pi\) stacking from the distortional coplanarity of the benzene rings and amide groups.\(^{11}\) The relationship between the structures developed in the heat-stretching process and the performances of PSA fibers with such a special conformation is unknown yet.

In the work reported here, pre-drawn co-PSA fibers were prepared by wet spinning, which were then heat-drawn at various temperatures. Tensile testing, dynamic mechanical analysis (DMA), wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) studies were carried out to investigate the relationship between structure and properties of the co-PSA fibers drawn at various temperatures.

**EXPERIMENTAL**

**Materials**

The aromatic co-PSA was synthesized via polycondensation of 4,4′-dianidinodiphenylsulfone (4,4′-DDS), 3,3′-diaminodiphenylsulfone (3,3′-DDS) and terephthaloyl chloride with a molar ratio of 3:1:4 in dimethylacetamide (DMAc) at low temperature. The concentrated solution was used directly as spinning dope. The intrinsic viscosity, \(\eta_i\), of the prepared co-PSA was 0.7 dL g\(^{-1}\), measured in dimethylsulfoxide at 25 °C.\(^{11}\)

**Sample preparation**

The pre-drawn co-PSA fibers were prepared in our laboratory using wet-spinning technology. The spinning was performed by extruding the spinning dope into a first coagulation bath, containing DMAc–water (1:1 w/w) at 15 °C. The as-spun co-PSA fibers were then drawn between two draft rollers with a draw ratio of 3.7 in a second coagulation bath (DMAc–water, 6:4 w/w) at 60 °C. The pre-drawn co-PSA fibers were obtained by washing the drawn fibers in boiling water immediately and then drawing them using laboratory-scale multiple heat-drawing equipment, as shown in Fig. 1. From our previous study,\(^{17}\) PSA is thermally stable up to 420 °C before initiation of decomposition. Therefore, the temperature in the third stage was varied from 350 to 390 °C, i.e. below \(T_d\) to obtain the various samples.

**Characterization**

The co-PSA fibers were dried at 105 °C under vacuum to constant weight and then cut into powders. The compaction volume of weighed powders was measured using a densitometer (Ultrapycnometer 1000). The density of the fibers was calculated according to the measured weight and volume.\(^{11}\)

A bundle of co-PSA fibers was cut into a length of 2 cm and then weighed with a torsion balance. The fiber fineness was calculated according to the measured weight and the number of co-PSA fibers.

The stress–strain curves of a single fiber were recorded using a XQ-2 tensile tester with a gauge length of 20 mm and an extension rate of 20 mm min\(^{-1}\). At least 50 specimens were tested for each sample and the tenacity, elongation at break and initial modulus were calculated as average values.

DMA of the dried fibers was carried out using a TA Q800 V7.5 instrument to obtain the loss factor (\(\tan \delta\)). The frequency applied was 1 Hz over a temperature range from 40 to 400 °C in the temperature–frequency sweeping mode.

WAXD of the fibers was carried out at Shanghai Synchrotron Radiation Facility (SSRF) on beam line BL14B with an X-ray wavelength of 0.124 nm. A bundle of co-PSA fibers was put on a sample holder with the fiber direction perpendicular to the X-ray beam (shown in Fig. 1 of the supporting information). The specimen-to-detector (Mar345) distance was calibrated using the standard sample LaB\(_6\). All data analysis (background correction, radial and azimuthal integration) was carried out using Xpolar software (Precision Works Inc., NY, USA).

The crystal orientation along the fiber axis (Z) was calculated using Hermann’s orientation parameter (\(f_c\)):

\[
f_c = \frac{3 \left( \cos^2 \varphi_{cZ} \right) - 1}{2}
\]

The values of \(f_c\) can range from –0.5 (planes arranged parallel to the fiber axis) to 1 (planes arranged perpendicular to the fiber axis). The crystal is randomly oriented when \(f_c\) equals zero.

The orientation parameter \(\left( \cos^2 \varphi_{cZ} \right)\) was determined according to the Wilchinsky model.\(^{18}\) For the reflections (002), the
where (version 4.12, Seasolve Co., San Jose, CA) to calculate respectively. The profile fitting was conducted by peakfit software of all the crystal peaks and the peak area of amorphous phase, $\theta$ is shown in Fig. 2, and intensity variation of the azimuthal angle of the (002) reflection, as particularly integrating the WAXD patterns. The crystallinity of fibers was calculated according to the Scherrer equation:

$$W_{c,x} = \frac{I_c}{I_c + I_a} \times 100\%$$

(3)

where $W_{c,x}$ is the crystallinity and $I_c$ and $I_a$ are the total peak area of all the crystal peaks and the peak area of amorphous phase, respectively. The profile fitting was conducted by peak fit software (version 4.12, Seasolve Co., San Jose, CA) to calculate $I_c$ and $I_a$.

The average crystal size $L_{hkl}$ perpendicular to plane (hkl) was calculated according to the Scherrer equation:

$$L_{hkl} = \frac{K\lambda}{\beta\cos\theta}$$

(4)

where $\lambda$ is the wavelength of X-rays, $\theta$ is half of the diffraction angle (2$\theta$), $\beta$ is the integral width of reflection peak (hkl) and $K = 1$.

The SAXS experiments on the fibers were carried out at SSRF on beam line BL16B with an X-ray wavelength of 0.124 nm (shown in Fig. 1 of the supporting information). The sample-to-detector (Mar CCD 165) distance was 1980 mm. All data analysis was carried out using Xpolar software (Precision Works).

The equatorial streak of small-angle diffuse scattering is generally attributed to the presence of voids or fibrils elongated along the fiber axis.19 The ‘needle-shape’ model for co-PSA fibers can be adopted20 and the fibrils or micro-voids extend longitudinally along the fiber axis. Figure 3(a) shows a schematic of scattering objects. The radius of the scattering objects can be determined using21

$$I(q) = I(0) \exp\left(-\frac{q^2R^2}{5}\right)$$

(5)

where $R$ is the radius of scattering objects with circular cross-section, $I(q)$ is the scattering intensity and $q (q = 4\pi \sin \theta/\lambda)$, where $2\theta$ is the scattering angle and $\lambda$ is the wavelength) is the scattering vector. The average scattering object length and the scattering object misorientation from the fiber axis were calculated based on the method of Ruland.22 For co-PSA fibers, it is found that the azimuthal scans of the equatorial streak at different scattering vectors $s$ ($s = q/2\pi$) can be described by Lorentzian/Cauchy-type functions. The scattering object length ($l_l$) and the misorientation width ($B_\phi$) can be obtained using the following equation:

$$sB_{obs} = \frac{1}{l_l} + sB_\phi \text{ (Cauchy–Cauchy)}$$

(6)

where $B_{obs}$ is the actual full width at half maximum of the azimuthal profile from the equatorial streak fitted with a Lorentzian function.

For heat-drawn co-PSA fibers, there is detectable scattering along the meridional direction, which indicates the existence of lamellar morphology. The structure model for this SAXS pattern can be described as follows.23 The crystalline lamellae within each fibril are separated by interlamellar amorphous chain segments. A schematic of the structure, including long period and amorphous regions corresponding to SAXS patterns, is shown in Fig. 3(b). In

**Figure 3.** Schematic of the structure corresponding to SAXS patterns.

**Figure 4.** Stress–strain curves of the co-PSA fibers heat-drawn at various temperatures.
Aromatic copolysulfonamide fibers

RESULTS AND DISCUSSION

Mechanical properties of co-PSA fibers heat-drawn at various temperatures

The stress–strain curves for the co-PSA fibers are shown in Fig. 4. The stress–strain curve of co-PSA-0 fibers demonstrates a prominent deviation from linearity at strain values of about 2% followed by a region with a weak dependence of the stress on the strain. During the heat-drawing process, the pre-drawn co-PSA fibers consisting of weakly oriented chains transform into a better-oriented fibrillar structure. Thus, the heat-drawn co-PSA fibers exhibit unobvious yielding with a steep slope transition compared to co-PSA-0 fibers in the stress–strain curves, which shows an improved strength and modulus for the heat-drawn co-PSA fibers.

The strength of heat-drawn co-PSA fibers is dependent on the stretching temperature, as shown in Table 1. The maximum strength achieved of heat-drawn co-PSA fibers is 4.6 cN dtex⁻¹, and the modulus is about 40 cN dtex⁻¹ at a stretching temperature ranging from 350 to 370 °C. However, it can be observed that the strength of heat-drawn co-PSA fibers shows an obvious decrease when drawn at higher temperature (380 and 390 °C). Such a marked change in the strength of co-PSA fibers could be due to morphological and structural changes that occur during the heat-drawing process, which will be discussed in the following section.

DMA of co-PSA fibers heat-drawn at various temperatures

Previously, Ding et al. investigated the influence of copolymer composition on the glass transition temperatures of PSA, which range from 280 to 370 °C with various monomer ratios of 4,4′-DDS and 3,3′-DDS. In fact, it has been observed that the thermal properties of co-PSA fibers not only depend on the chemical structure of the polymer, but also on the process technology. From the DMA data for co-PSA fibers in Fig. 5, only the α transition corresponding to the glass transition of co-PSA is observed in the tan δ–temperature curves, which is consistent with previous results. It is generally known that the α transition corresponding to segmental motion is attributed to a motion in the amorphous region of polymers. In our study, a continuous α transition from 300 to 400 °C was observed due to the coexistence of para- and meta-motion units in co-PSA. In addition, it is worth noting that the α transition peak is partly suppressed during the heat-stretching process, suggesting that the disordered domain decreases and more ordered and dense phase forms during this process. A similar phenomenon has been observed in other aromatic polyimide fibers, such as 3,3′,4,4′-biphenyltetraacarbonyl dianhydride–2,2′-dimethyl-4,4′-diaminobiphenyl fibers, of which the tan δ peak of the α relaxation seems to disappear at a degree of crystallinity of 80%. Meanwhile, the glass transition temperature of heat-drawn co-PSA fibers is higher than that of pre-drawn co-PSA fibers. However, the heat-drawn co-PSA fibers display similar glass transition temperature of about 355 °C, illustrating that the co-PSA fibers heat-drawn at 350–390 °C have similar molecular mobility in the amorphous regions. Therefore, it can be speculated that a similar amorphous structure of heat-drawn co-PSA fibers forms at different stretching temperatures.

In addition to the α transition, a sub-glass transition ranging from 100 to 250 °C is observed for pre-drawn co-PSA fibers; however, it does not appear for heat-drawn co-PSA fibers. As we know, a porous structure of fibers is inevitable in the wet-spinning process, which leads to weak interactions between molecular chains in pre-drawn fibers, and therefore provides enough space for the motion of small segments like side and end groups. In the subsequent heat-stretching process, the ordering of the structure and intermolecular interactions in the amorphous region increase, suggesting an increase in molecular packing density. Therefore, the motion of small segments is confined and the sub-glass transition cannot be detected for the heat-drawn co-PSA fibers in the DMA experiment. From the above analysis, it is concluded that heat stretching is beneficial for improving the thermal stability of the co-PSA fibers.

Microstructure of co-PSA fibers heat-drawn at various temperatures

WAXD patterns of the pre-drawn and heat-drawn co-PSA fibers are shown in Fig. 6. The pattern of the pre-drawn fibers consists of a strong diffuse halo, indicative of an amorphous state. It should be noted that the equatorial and meridional reflections and off-axis (hkl) reflections develop following the heat drawing, and become sharper with an increase of heat-stretching temperature, indicating the development of crystalline structure within the fibers. Although the crystalline structural parameters for co-PSA fibers have not been reported, the same WAXD pattern of pt-PSA can be seen and the d-spacings of co-PSA are identical to those of pt-PSA, from which it can be deduced that only the symmetric segments of 4,4′-diphenylsulfonyl terephthalamide are packed in the crystalline phase of co-PSA. It is suggested that the co-PSA with a monomer ratio of 4,4′-DDS to 3,3′-DDS of 3:1 has the same crystalline structure as pt-PSA, which has a zigzag conformation in the lattice. The index reflections of co-PSA are identified as shown in Fig. 6. For the heat-drawn co-PSA fibers, the strong equatorial reflections (100) and multiple meridional reflections (002), (004) and (006) indicate a high degree of crystallite orientation along the fiber axis and suggest a good lateral packing of the molecules within the co-PSA fibers.
Table 1. Mechanical properties of co-PSA fibers heat-drawn at various temperatures

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Heat-drawing temperature (°C)</th>
<th>Linear density (dtex)a</th>
<th>Tenacity (cN dtex&lt;sup&gt;−1&lt;/sup&gt;)b</th>
<th>Initial modulus (cN dtex&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>co-PSA-0 (pre-drawn fiber)</td>
<td>–</td>
<td>3.5</td>
<td>2.1</td>
<td>22</td>
<td>23</td>
</tr>
<tr>
<td>co-PSA-350</td>
<td>350</td>
<td>1.8</td>
<td>4.6</td>
<td>40</td>
<td>16</td>
</tr>
<tr>
<td>co-PSA-360</td>
<td>360</td>
<td>1.8</td>
<td>4.6</td>
<td>40</td>
<td>17</td>
</tr>
<tr>
<td>co-PSA-370</td>
<td>370</td>
<td>1.8</td>
<td>4.6</td>
<td>38</td>
<td>16</td>
</tr>
<tr>
<td>co-PSA-380</td>
<td>380</td>
<td>1.8</td>
<td>3.2</td>
<td>31</td>
<td>18</td>
</tr>
<tr>
<td>co-PSA-390</td>
<td>390</td>
<td>1.7</td>
<td>2.9</td>
<td>32</td>
<td>15</td>
</tr>
</tbody>
</table>

a 1 dtex = 0.1 g km<sup>−1</sup>.  
b 1 cN = 0.01 N.

Figure 6. WAXD patterns of the co-PSA fibers heat-drawn at various temperatures.

From the WAXD profiles, the peak position, peak height, peak width and integrated intensity (peak area) for each crystal reflection and the amorphous diffraction were fitted (Fig. 7). Then, the crystallinity and crystallite size of all the samples were determined, as shown in Fig. 8. It is evident that the crystallinity of heat-drawn co-PSA fibers increases with increasing stretching temperature, which results in an increase of the density as the fibers are drawn. Once the crystalline phase is formed, the crystal orientation of the heat-drawn co-PSA fibers is found to be high. It is interesting that the crystallite sizes of (002) and (100) show different trends at different stretching temperatures. It is generally known that the normal direction of crystal plane (002) is parallel to the fiber axis while that of (100) is perpendicular to the fiber axis. The results may imply that the crystallites tend to grow in the radial direction with larger crystallite size of plane (100) and smaller size of plane (002) at higher stretching temperature, i.e. at 380 and 390 °C. From the conformation and molecular packing in the crystal phase, it could be that the transformation of the random coil to a largely zigzag conformation is not easy. It could be understood that only the oriented chain segments can be packed into the crystal lattice under the tension along the fiber axis due to the low mobility of the chain segments at lower stretching temperature. And the movement of the chain segments increases with stretching temperature which results in the packing of molecular chains perpendicular to the fiber axis due to the hydrogen bond interaction between NH<sub>2</sub> and C=O.

The analysis of the morphology of the co-PSA fibers was done using SAXS at large scale as shown in Fig. 9. A characteristic diamond-shaped small-angle scattering pattern is obtained for pre-drawn co-PSA fibers. To determine the scattering objects causing the streak along the equator in SAXS patterns, we also used wet heat-drawn fibers (fibers soaked in water for 1 h and the water on the fiber surface removed with filter paper) for SAXS experiments (Fig. 2 of the supporting information). As expected, the equatorial scattering intensity decreases a little. For the heat-drawn co-PSA fibers with denser structure, it is reasonable to deduce that the slight change in intensity is mainly due to the absorption of water in disordered regions, decreasing the electron density difference within the fibers. This does not imply that voids have to be the cause of the scattering. Therefore, the scattering objects in heat-drawn co-PSA fibers are mainly associated with the microfibrillar structure, not with the void morphology. However, there is no apparent scattering along the meridian, indicating that the pre-drawn co-PSA fibers have no trace of periodic structure along the fiber axis. After heat-stretching, the equatorial streak of the heat-drawn co-PSA fibers becomes sharper and grows in intensity, indicating a higher orientation of the heat-stretched co-PSA fibers. In addition, the SAXS patterns of heat-drawn co-PSA fibers show a
meridional arc-shape pattern. This demonstrates the existence of a periodic structure in the draw direction which has a certain deviation from the fiber axis.\textsuperscript{26} This SAXS pattern is quite different from that of other heat-resistant fibers, e.g. Kevlar\textsuperscript{27} and PBO.\textsuperscript{28,29}

Based on the SAXS patterns of heat-drawn co-PSA fibers, the size of the fibrils was determined. The radius of the fibrils in cross-sections of heat-drawn co-PSA fibers were calculated according to Eqn (5), which indicates that the size of fibrils in the cross-section exhibited multi-order characters within the margin of error of around 6, 12 and 21 nm. The average fibril length and the fibril misorientation were determined by the method of Ruland, as listed in Table 2. For co-PSA-0 fibers, the fitting curve gives a negative intercept. In this case, we can only say that the objects are large enough, over a certain length. As for heat-drawn co-PSA fibers, it is seen that the fibril length of co-PSA fibers drawn at higher temperatures is smaller than that of fibers drawn at lower temperatures, although the misorientation varies within a small range. Because all of the heat-drawn co-PSA fibers were drawn with the same draw ratio, it is reasonable to exclude that fibril breakage occurs resulting in the decrease of the average fibril length. As mentioned above, the orientation of molecules along the fiber axis is mainly connected with the realization of forced deformation under the tension due to the low mobility of the chain segments at lower stretching temperature, e.g. 350 °C. Only a very small amount of lamellae form within the fiber, seen from Fig. 9. In contrast, the chain segments with higher mobility at higher stretching temperature tend to pack into the crystal lattice with a marked zigzag conformation. Therefore, it is conceivable that the formation of fibrils with a smaller average length at higher stretching temperature is related to the crystal structure, as observed earlier using WAXD. In addition, the scattering intensity of the arc-shape on the meridian line increases as the heat-stretching temperature increases. This indicates that the contrast between the domains of the crystalline and amorphous phases increases. From the meridional component of the reflection scattering angle, the long period (L) in the fiber direction was calculated via the Bragg equation (Table 2). For co-PSA-350 and co-PSA-360, the scattering intensity of the meridional direction is too low for quantitative calculations. The long period of other heat-drawn co-PSA fibers obtained from Bragg function analysis is ca 22–25 nm, which is larger than that of pt-PSA fibers of ca 18 nm.\textsuperscript{30} It is observed that the long period of co-PSA fibers heat-drawn at higher temperature is smaller, which corresponds to the smaller size of crystallite (002). It can be understood that the amorphous regions of the co-PSA fibers drawn at different temperatures are similar, which also corresponds to the conclusion from DMA.

The mechanical properties can be understood from the changes of crystalline structure of co-PSA fibers heat-drawn at different temperatures. From the above analysis, it should be noted that the heat-drawn co-PSA fibers have much denser structure with higher orientation and crystallinity compared to the pre-drawn co-PSA fibers. This is the reason why the strength of all the heat-drawn co-PSA fibers is higher than that of pre-drawn co-PSA fibers. However, a decrease in the strength of heat-drawn co-PSA fibers is observed at higher stretching temperatures despite the intensive
tallinity of co-PSA resulted in a decrease in tenacity although the crystallinity in tensile strength. However, an overly high stretching temperature, a crystalline structure formed gradually causing an increase in drawing temperature lower than the glass transition temperature. Mechanical properties are sensitive to the temperature. At a fibers drawn at various temperatures, it can be said that the increase in crystallinity of co-PSA is not the primary determinant of strength improvement during heat stretching.

CONCLUSIONS
From the analysis of the structure and properties of the co-PSA fibers drawn at various temperatures, it can be said that the mechanical properties are sensitive to the temperature. At a drawing temperature lower than the glass transition temperature, a crystalline structure formed gradually causing an increase in tensile strength. However, an overly high stretching temperature resulted in a decrease in tenacity although the crystallinity increased. The results demonstrate that the increase of crystallinity of co-PSA fibers is not the primary determinant of tenacity improvement during the heat-stretching process because of the special conformation of co-PSA packing in the crystal lattice.

ACKNOWLEDGEMENTS
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SUPPORTING INFORMATION
Supporting information may be found in the online version of this article.

REFERENCES

Table 2. Results from SAXS analyses

<table>
<thead>
<tr>
<th>Parameter</th>
<th>co-PSA-0</th>
<th>co-PSA-350</th>
<th>co-PSA-360</th>
<th>co-PSA-370</th>
<th>co-PSA-380</th>
<th>co-PSA-390</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_1 ) (nm)</td>
<td>5.7</td>
<td>5.6</td>
<td>6.5</td>
<td>5.6</td>
<td>5.4</td>
<td>5.6</td>
</tr>
<tr>
<td>( R_2 ) (nm)</td>
<td>11.8</td>
<td>11.4</td>
<td>14.2</td>
<td>12.1</td>
<td>11.6</td>
<td>11.8</td>
</tr>
<tr>
<td>( R_3 ) (nm)</td>
<td>21.2</td>
<td>19.4</td>
<td>24.1</td>
<td>21.4</td>
<td>20.6</td>
<td>20.5</td>
</tr>
<tr>
<td>Fibril length ( l_f ) (nm)</td>
<td>–</td>
<td>833</td>
<td>707</td>
<td>574</td>
<td>495</td>
<td>398</td>
</tr>
<tr>
<td>Misorientation ( \phi_\delta ) (°)</td>
<td>–</td>
<td>13.1</td>
<td>12.5</td>
<td>14.4</td>
<td>12.8</td>
<td>10.1</td>
</tr>
<tr>
<td>Long period ( L ) (nm)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>25.8</td>
<td>24.8</td>
<td>22.4</td>
</tr>
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</table>

Figure 9. SAXS patterns of the co-PSA fibers heat-drawn at various temperatures.