

# Study on PET Fiber Modified by Nanomaterials: Improvement of Dimensional Thermal Stability of PET Fiber by Forming PET/MMT Nanocomposites

Weizhen Xiao,<sup>1</sup> Huimin Yu,<sup>2</sup> Keqing Han,<sup>2</sup> Muhuo Yu<sup>2</sup>

<sup>1</sup>SINOPEC Yizheng Chemical Fiber Co., Ltd, Yizheng 211900, People's Republic of China

<sup>2</sup>State Key Laboratory of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai 200051, People's Republic of China

Received 10 May 2004; accepted 3 November 2004

DOI 10.1002/app.21703

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Poly(ethylene terephthalate) (PET) and PET/montmorillonite (MMT) (2.5 wt %) nanocomposites with high molecular weight were prepared by solid-state polycondensation and their fiber was spun and drawn under various conditions. The influence of MMT nanomaterials on the thermal shrinkage of PET fiber was investigated and the structure was studied using the methods of WAXD, DSC, fiber orientation measurement, etc. The results showed that the MMT nanomaterials improved the thermal stability of microstructure of PET fiber. The fusion heat of PET/MMT was higher than that of PET, which generally implied the

high orientation or high crystallinity. However, the degree of orientation and the crystallinity of PET/MMT fiber measured by WAXD were lower than that of pure PET fiber. It is suggested that the strong interaction between MMT layer and PET restricted the motions of PET molecular chains, which developed "a special continuous network structure" and prohibited the thermal shrinkage of PET fiber. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2247–2252, 2005

**Key words:** nanocomposites; solid-state polymerization; thermal stability; fibers; PET; montmorillonite

## INTRODUCTION

Poly(ethylene terephthalate)/montmorillonite (PET/MMT) is a new class of layered nanocomposites. In terms of layered nanocomposites, especially PET/MMT, most investigations mainly concern the engineering plastic application. However, the fiber application is the most important market for PET. When PET fiber is used as tire cords, high tensile strength, high modulus, and low thermal shrinkage are expected properties; the fiber dimensional thermal stability especially is a key factor that influences the application of PET industrial fiber. Many researchers study the processing conditions, interior structures, thermal properties, and their relations. Some research shows that high crystallinity and high degree of orientation of fiber are structural bases for its excellent mechanical properties, while high degree of orientation is the main internal structure causing the thermal shrinkage of fiber.<sup>1–6</sup> During the processes of fiber formation, such as spinning, drawing, etc., important strains appear, resulting in the accumulation of internal stresses, which constitute elements of instability in the fiber microstructure and properties.<sup>7</sup> In this article,

the effect of MMT, as well as related process conditions on the thermal shrinkage and the microstructure of the fiber will be studied.

## EXPERIMENTAL

### Materials

Pure PET ( $[\eta] = 0.64$ ) and PET/MMT nanocomposites with MMT content of 2.5 wt % ( $[\eta] = 0.65$ ), which were supplied by Yanshan Petrochemistry Inc., China, were used for this study.

### Solid-state polycondensation (SSP) and the intrinsic viscosity measurements

The SSP of pure PET and PET/MMT was carried out in a tumble reactor. Nitrogen gas was heated before passing through the tumble reactor and the nitrogen flow was controlled by a gas flow meter. The reactor was heated slowly to make the PET fully precrystallize until the temperature reached 230°C. The SSP of pure PET and PET/MMT chips was carried out for 20 h.

The relative viscosity ( $\eta_r$ ) of PET in tetrachlorethane/phenol (1 : 1 by weight) at concentration ( $c = 0.5\text{g/dL}$ ) was determined using a Ubblohde viscometer at 25°C. The solution was kept steady for more than 48 h to eliminate the effect of nanoparticles on viscosity measurement by particle deposition. The

Correspondence to: M. Yu (yumuhuo@dhu.edu.cn).

intrinsic viscosity of PET was calculated using the following approximation for linear flexible chains:

$$[\eta] = \frac{\sqrt{1 + 1.4\eta_{sp}} - 1}{0.7c}$$

where  $\eta_{sp} = \eta_r - 1$  and  $c$  (g/dL) is the concentration of PET deducting the MMT content.

$[\eta]$  is related to  $M_n$  using the Mark-Houwink relationship:<sup>8</sup>

$$[\eta] = 2.1 \times 10^{-4} M_n^{0.82}$$

### Fiber spinning and drawing

The materials were dried *in vacuo* for 48 h at 120°C prior to spinning. Melt spinning of pure PET and PET/MMT were carried out using a model ABE-25 spinning machine. Drawing of as-spun fiber was carried out using a model Barmag 3013 drawing machine at different drawing temperatures (160, 170, and 180°C).

### Fiber orientation measurements<sup>9</sup>

Orientation factor of fiber was obtained using a model SCY-IV sound velocity apparatus.

### Thermal shrinkage test

One end of each fiber sample was fixed, and another end was loaded certain stress that related to fiber's denier, the original length,  $L$  (mm), of fiber being marked. All fiber samples were kept at various environmental temperatures (100, 120, 140, and 160°C) for 30 min, and then the length,  $L_1$  (mm), between the two marks of each fiber sample was measured. The thermal shrinkage was calculated according to the following equation:

$$\text{Thermal shrinkage (\%)} = \frac{L - L_1}{L} \times 100$$

### DSC measurements

The DSC experiments were performed with a Mettler Toledo® System DSC 822<sup>e</sup> differential scanning calorimeter in a nitrogen gas environment at a flow rate of 20 mL/min. All samples were heated to 290°C at 10°C/min.

### Wide-angle X-ray diffraction measurements (WAXD)

The WAXD experiments were performed using a Rigaku model D/max-B automatic diffractometer

with Cu target. The generator was operated at 40 KV and 40 mA. Samples were scanned from  $2\theta = 5$  to  $40^\circ$ .

### Average crystal size measurements

From WAXD curves, the average axial crystal size  $A_i$  in the  $A$  axis direction vertical to the 010 crystal face will be<sup>10</sup>

$$A_i = \lambda \frac{180}{\pi} \frac{1}{\sqrt{H_i^2 - 0.01} \cos(x_{\theta i}/2)}$$

where  $\lambda$  is the wavelength of the X-ray (0.1542nm);  $x_{\theta i}$  is the  $2\theta$  value of the 010 diffraction peak;  $H_i$  is the peak width at half height of the 010 diffraction peak. In our research,  $H_i$  was automatically calculated by computer software based on the peak division method according to WAXD patterns.

### Crystallinity measurements

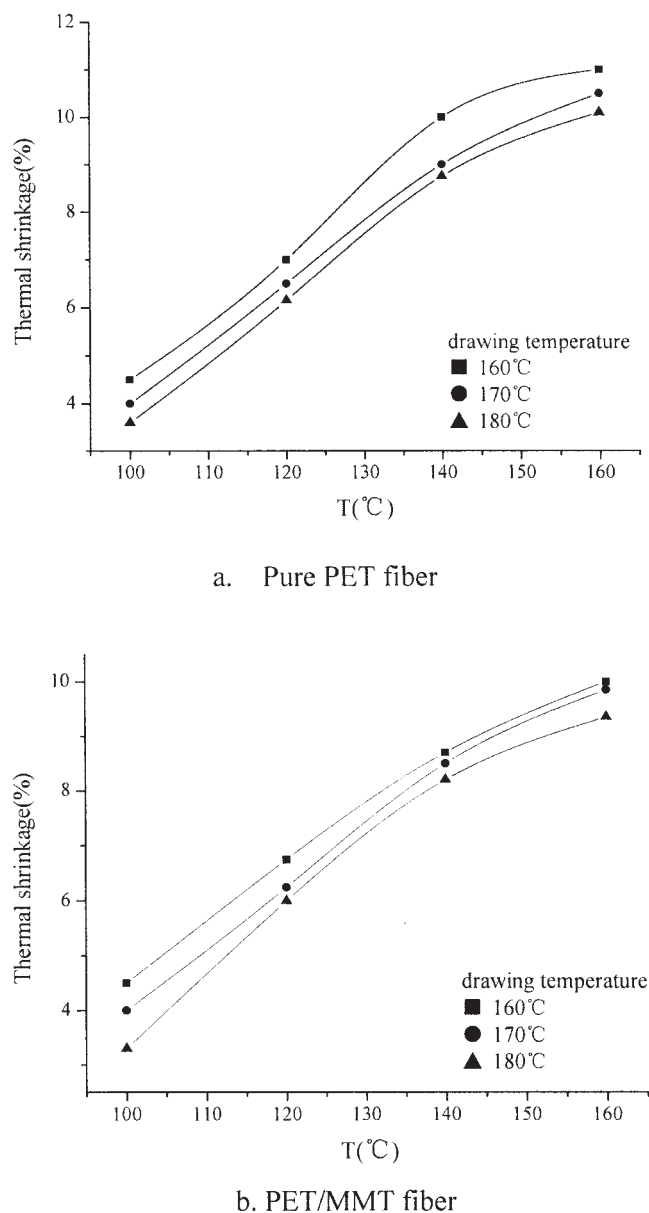
The crystallinity measurement by WAXD is based on the Vainshtein intensity conservation law. The total intensity of diffraction is the summation of intensity both in crystalline region and in amorphous region; thus the crystallinity of fiber is calculated as follows:<sup>11</sup>

$$X_c = \frac{\int_0^\infty S^2 I_c(s) ds}{\int_0^\infty S^2 I(s) ds}$$

where  $X_c$  is the crystallinity of fiber;  $S = 2\sin\theta/\lambda$ ;  $I(s)$  is the total intensity of diffraction;  $I_c(s)$  is the intensity of diffraction in crystalline region.

## RESULTS AND DISCUSSION

After 20 h SSP, the intrinsic viscosity of pure PET and PET/MMT (2.5 wt %) was, respectively, 0.92 and 0.95, and  $M_n$  was, respectively,  $28 \times 10^3$  and  $29 \times 10^3$ , which indicated that the molecular weight of PET reached the requirement of PET industrial fiber used as tire cords. Figure 1 shows that the thermal shrinkage of fiber increases as the environment temperature increases. This was because the disorientation of PET molecular chains occurred more easily while the environmental temperature was increased. Also, it could be seen in Figure 1 that a higher drawing temperature led to lower thermal shrinkage, which would improve



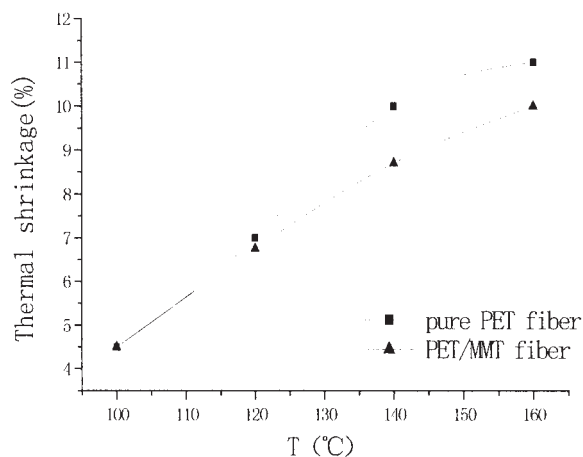
**Figure 1** Thermal shrinkage of fiber at various environmental temperatures.

the dimensional thermal stability. As we know, during the drawing of fiber, the molecular orientation increases in the amorphous phase and the molecular chains transform from random entangled state to extension, which results in the decrease of entropy. Therefore the system is unstable in thermodynamics and has an internal drive to disorient. On the other hand, high crystallinity and proper crystal size as well as good crystal distribution of fiber can lead to higher dimension stability. As the temperature increases, the system is further apart from the equilibrium with more active molecular motion, so its entropy will be increased by disorientation of the oriented chain segment or its free energy will be decreased by transforming to crystal.<sup>10</sup>

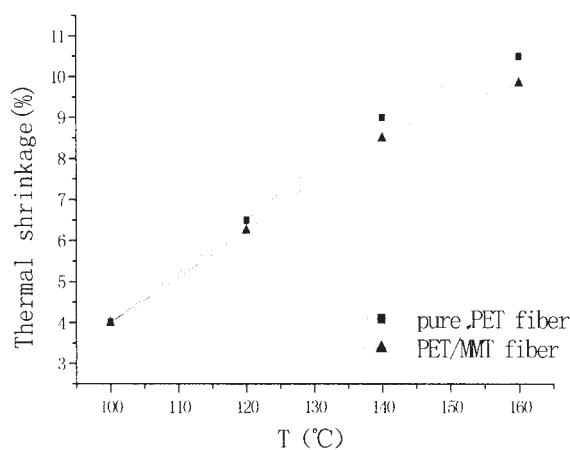
To investigate the difference of thermal shrinkage between the PET/MMT fiber and pure PET fiber, the relation of thermal shrinkage of fiber with different drawing temperatures versus environmental temperatures was plotted in Figure 2, in which the deviation for each data point is  $\pm 0.1\%$ . It was observed that the thermal shrinkage of PET/MMT fiber was lower than that of PET fiber, which can be explained in terms of strong interaction of the MMT layer and PET molecules.

The orientation factor ( $f_s$ ) of fiber samples measured by sound velocity apparatus was listed in Table I, which confirmed that the degree of orientation of PET/MMT fiber was lower than that of pure PET fiber. Moreover, the orientation of pure PET fiber decreased a little, and the orientation of PET/MMT (2.5 wt %) fiber had no distinct change as the drawing temperature increased. It was suggested that the addition of MMT and the increase of drawing temperature indeed weakened the disorientation ability of molecular chains and improved the dimensional stability of fiber, which were in agreement with the results shown in Figures 1 and 2.

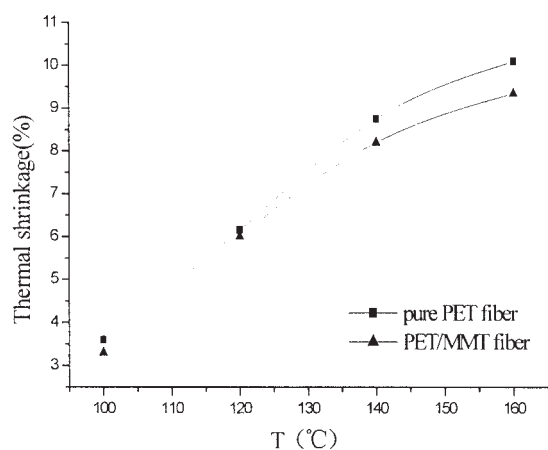
In WAXD patterns (see Figure 3), the narrow reflection suggested the great crystal size and the few crystal defects<sup>12</sup> for the width of the reflection depend on both the size of crystallites and the local lattice fluctuations (defects). The smaller the crystallites, the more the diffraction appears to scatter. Very small crystallites are therefore extremely difficult to detect by X-ray.<sup>13</sup> The crystallinity and the crystal size of fiber were calculated and are listed in Table II. It could be seen that both crystallinity and crystal size of fiber increased as the drawing temperature increased. Crystal size and crystalline structure are important factors for dimensional stability of fiber at high temperature.<sup>1</sup> The enhancement of crystallinity will result in the decrease of the disorientation of molecular chains in the amorphous region, which represents the macroscopic improvement of dimensional stability of fiber. However, in comparison with pure PET fiber, PET/MMT fiber showed lower crystallinity and smaller crystal size at the same drawing temperature, which was coincident with the characteristics of materials before spinning, as shown in polarizing microscope images (see Figure 4). In the crystallization process, the distinct large spherulite in pure PET formed, while only small-sized crystals appeared in PET/MMT nanocomposites. This was probably due to the MMT nanoparticles dispersed in PET matrix acting as the nucleating agent in the PET crystallization process. At the same time the strong interaction between PET and MMT restricted the motions of the PET molecular segment and prohibited the growth of PET



a. Drawing temperature of 160°C



b. Drawing temperature of 170°C



c. Drawing temperature of 180°C

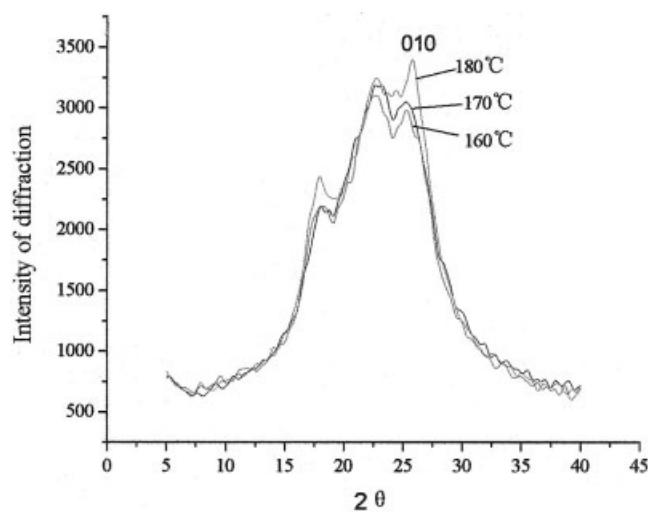
**Figure 2** Thermal shrinkage of fiber at different environmental temperatures.

crystalline structure.<sup>14</sup> Therefore smaller and more incomplete crystals formed in PET/MMT nanocomposites.

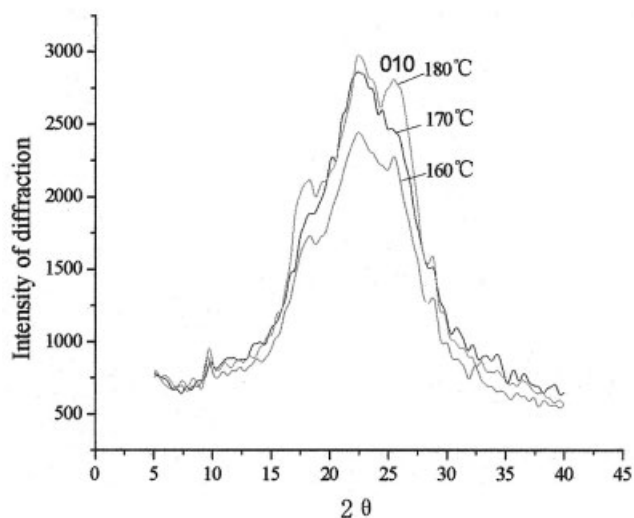
**TABLE I**  
Orientation Factor ( $f_s$ ) of the Fiber with Various Drawing Temperatures

Samples	160°C	170°C	180°C
Pure PET fiber	0.911	0.906	0.888
PET/MMT fiber	0.893	0.898	0.893

The melting point ( $T_m$ ) and the fusion heat ( $\Delta H$ ) can both reflect the thermal properties of fiber. In other words, the excellent thermal dimensional stability is reflected in  $T_m$  and  $\Delta H$ .<sup>12</sup> The melting points and the fusion heat of pure PET and PET/MMT fiber drawn at 160°C were measured by DSC, as presented in Table



a. Pure PET fiber



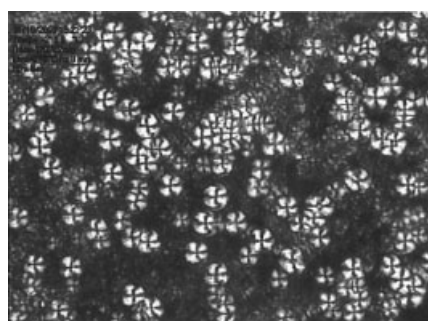
b. PET/MMT fiber

**Figure 3** The WAXD patterns of fiber with various drawing temperatures.

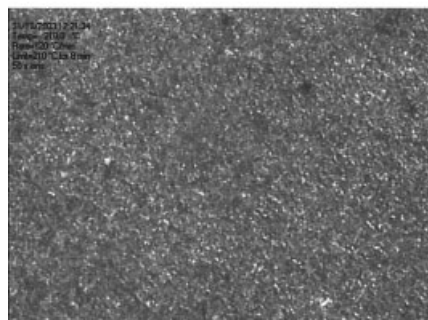
**TABLE II**  
Data of the Crystallinity and Crystal size of Fibers

Samples	Drawing temperature (°C)	$X_c$ (%)	$A_j$ (nm)
Pure PET fiber	160	52.65	6.39
	170	53.70	6.87
	180	55.81	6.96
PET/MMT fiber	160	47.40	4.27
	170	50.18	4.38
	180	54.93	4.58

III. It was shown that the melting point of PET/MMT fiber was lower than that of pure PET fiber, which implied that the crystal of PET/MMT fiber was less stable than that of pure PET fiber. The fusion heat is the energy that is necessary for the partially crystalline polymer to overcome van der Waals' force to transform to disorder when heated, so  $\Delta H$  is acknowledged as a scale measuring the crystalline portion of polymer.<sup>11</sup> As discussed above (from Table II), the crystallinity of PET/MMT fiber gained by WAXD was lower than that of pure PET fiber, so PET/MMT fiber should have lower fusion heat. However, the fusion heat of PET/MMT fiber obtained by DSC, as shown in Table III, was higher than that of pure PET fiber. These inconsistent data suggested that there was some other kind of structure in PET/MMT fiber, which played an active role in restraining the thermal shrinkage of fiber.



a. Neat PET



b. PET/MMT

**Figure 4** Polarizing microscope images of crystallization.

The macroscopic thermal shrinkage of oriented and semicrystalline synthetic fiber is probably due to the entropic deformation trend of the local extended molecular chains, the internal stress produced when the molecular chains transform to random state, and the axial internal stress frozen in fiber in the process of spinning. The local internal stress can be transferred to the whole material via the molecular network, which will support the stress when a sufficient quantity of heat is supplied.<sup>3</sup> The molecular orientation stability and the macroscopic dimensional stability of fiber depend on the internal structure of materials, the outside conditions, and the internal stress. Oriented and semicrystalline polymer is composed of various constitutional units with different orientation stability as follows:<sup>1</sup>

1. greatly stable and complete crystalline portion,
2. relatively unstable and incomplete crystal including the effect of lattice distortion and surface energy,
3. the transition layer between relatively unstable crystal and the amorphous region, and
4. unstable oriented amorphous phase.

The orientation stability of oriented and semicrystalline polymer mainly relies on the completeness and continuity of the molecular network formed by the above four kinds of structure.

According to the existing research, the interaction between PET and the nanosized layer of MMT was fairly strong.<sup>15</sup> Therefore it was deduced that the interaction between PET and MMT worked as crosslinked points of the PET molecular network. These similar physical crosslinked points made the molecular network more complete and more continuous and effectively restricted the motions of the molecular segment. So the contribution by the constitutional units 3 and 4 listed above to thermal shrinkage was insignificant, which led to the improvement of the heat resistance and dimensional stability of fiber. In comparison with the contribution to thermal shrinkage by incomplete crystal, the motion restraint of molecular segment by MMT nanomaterials was more significant and effective. Therefore it can be acknowledged that the thermal stability of PET fiber was improved by MMT nanomaterials.

**TABLE III**  
DSC Thermodynamics Parameters of Pure PET Fiber and PET/MMT Fiber Drawn at 160°C

Samples	$T_m$ (°C)	$\Delta H$ (J/g)
Pure PET fiber	256.52	42.76
PET/MMT fiber	245.28	46.60

## CONCLUSIONS

The thermal dimensional stability of PET fiber was improved as a result of the addition of nanoscaled MMT. The results of microstructure investigations suggested that the strong interaction existed on the interface between MMT layer and PET, which restricted the motions of PET molecular chains and accordingly developed the more perfect and more continuous molecular network.

## References

1. Chen, Z.; Xiang, Q.; Li, J.; Cheng, S.; Zhang, Y.; Wei, Y.; Ma, R. *Acta Polym Sinica* 1997, 5, 530.
2. Samules, R. J. *Structure and Polymer Properties*. Wiley: New York, 1974.
3. Trznadel, M.; Kryszewski, M. *J Macromol Sci: Rev Macromol Chem Phys* 1992, 32, 259.
4. Rim, P. B.; Nelson, C. J. *J Appl Polym Sci* 1991, 42, 1807.
5. Gupta, V. B.; Radhakrishnan, J.; Sett, S. K. *Polymer* 1994, 35, 2560.
6. Hristov, H. A.; Schultz, J. M. *J Polym Sci: Polym Phys Ed* 1990, 28, 1647.
7. Melinte, S.; Jeflea, A. *Macromol Mater Eng* 2001, 286, 196.
8. Ma, Y.; Agarwal, U. S.; Sikkema, D. J.; Lemstra, P. J. *Polymer* 2003, 44, 4085.
9. Chen, X.; Huang, X. *Chem Fiber Exp Textile Industry Press: Beijing*, 1988.
10. Li, X.; Li, R.; Wu, D.; Sun, L.; Song, Q.; Guo, F.; Wu, L. *Acta Polym Sinica* 2001, 1, 84.
11. Ren, X.; Meng, J. *Synth Technol Appl* 1998, 13, 1.
12. Chen, Z.; Guo, X.; Li, Z.; Sui, K.; Ma, R.; Guo, B. *Acta Polym Sinica* 1999, 2, 134.
13. Elias, H.-G. *Macromolecules. 1. Structure and Properties*, Plenum Press: New York, 1984; 2<sup>nd</sup> ed.
14. Zhang, G.; Yi, G.; Wu, L.; Xu, X.; Song, Q.; Yang, Y.; Jin, J.; Zhong, S. *Acta Polym Sinica* 1999, 3, 309.
15. Bai, X.; Wang, Y. *J Zhengzhou Univ (Eng Sci)* 2002, 23, 91.