

# Crystallization Behavior of Poly(Tetramethylene Oxide) Influenced by the Crystallization Condition of Poly(Butylene Succinate) in Their Copolymers

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**Abstract:** The effect of crystallization conditions of poly(butylene succinate) (PBS) component on the crystallization of poly(tetramethylene oxide) (PTMO) component in their segment block copolymer, with a higher PTMO content (PTMO mass fraction is 67%), was investigated by DSC and temperature-dependent FTIR. It is found that the isothermal crystallization time ( $t_c$ ) of PBS has an effect on the crystallization behavior of PTMO component. Perturbation correlation move-window two-dimensional (PCMW2D) correlation analysis and generalized 2D correlation analysis (2DIR) were performed to explore the origin of this phenomenon. The PCMW2D and 2DIR results show that the correlation intensity peak observed at around 20 °C for PTMO is due to the PTMO chains movements forced by the PBS chains folded movements. If  $t_c$  of PBS at temperature of 20 °C is prolonged, more PTMO components are incorporated in the region between PBS lamellae and the peak at -7.6 °C (belonging to less-constricted PTMO chains) changes smaller and even disappears, while the peak at -16.3 °C belonging to more-constricted PTMO chains gets bigger. A crystallization model was also established in this study. The results of tensile testing showed that tensile strength slightly increased and elongation at break decreased with increasing heat treatment time at 40 °C.

**Key words:** PBS/PTMO segment block copolymer; crystallization behavior; perturbation correlation move-window two-dimensional correlation analysis

## 1 Introduction

Aliphatic polyesters have attracted much attention because their final degradation products are non-toxic and can enter into the metabolic cycles of bio-organisms<sup>[1-4]</sup>. Among them, Poly(butylene succinate) (PBS) has been widely utilized in various applications because of its good mechanical properties and relatively high melting temperature<sup>[5]</sup>. Poly(tetramethylene oxide) (PTMO), which is more stable than PEO, is widely used as soft segments in the synthesis of thermoplastic copolyester elastomers or polyurethane elastomers. For example, an industrial important thermoplastic

elastomers (TPE) composed of PTMO and poly(butylenes terephthalate)(PBT)<sup>[6]</sup> have been widely used. Introducing PTMO or other polyether such as PEO into the backbone of PBS chains can improve biodegradability properties and mechanical properties of PBS. There are some reports about poly(ether-ester)s in which PBS as hard segment and polyether as soft segment, with the soft content low than 50% mass<sup>[2,7-9]</sup>. We also have synthesized a series of PBS/PTMO segment block polymers with the content of PTMO range from 10wt% to 70wt%<sup>[10]</sup>. We found that the crystallization temperature ( $T_c$ ) and melting temperature ( $T_m$ ) of the PBS block within poly(ether-ester)s decrease steadily until PTMO content reach 50wt%, and then  $T_c$  and  $T_m$  decrease sharply. Finally, the crystallization temperature of PBS and PTMO is close to each other. As we known, there are few studies on the crystallization behaviors of aliphatic segmented copolymer with close crystallization temperature.

In last decade, the crystallization behavior and morphology in crystallizable block copolymer were a hot subject, because they have a significant effect on the

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final optical and mechanical properties of a polymer. The most commonly studied of the semicrystalline block copolymer systems in the previous literature are diblock copolymers or triblock copolymers, where one block is amorphous and the other is semicrystalline. It is generally accepted that the final morphology is determined by three key transition temperatures: the order-disorder transition temperature ( $T_{ODT}$ ), the crystallization temperature ( $T_c$ ) of the crystallizable block, and the glass-transition temperature ( $T_g$ ) of the amorphous block<sup>[11-15]</sup>.

For double crystalline copolymers, there are some more complicated situations than for one crystalline copolymer since the first crystallization block may influence the crystallization and morphology of the second block<sup>[11]</sup>. For example, the second block could be nucleated, or its crystallization could be confined within the microdomain structure formed by the first block<sup>[11]</sup>. Confined crystallization can lead to fractional crystallization. The fractional crystallization phenomenon has been explained as the crystallization of a series of microdomains at specific and independent supercoolings<sup>[16,17]</sup>.

The crystallization temperatures of two blocks are the important parameters to the crystallization behavior and the morphology finally formed in the system<sup>[17-19]</sup>. When the crystallization temperature of one block is far from the other, the first block crystallizes and forms the crystallized lamellar morphology if two blocks are weakly segregated in the melt, and the second block crystallizes in the crystallized lamellar morphology formed by the first block<sup>[17]</sup>. When the crystallization temperatures of both blocks are close to each other, coincident crystallization of both blocks may be observed when the copolymer cooled from the melt. For example, PEO-b-PCL diblock copolymers have been frequently used to investigate the coincident crystallization behavior<sup>[13,20-23]</sup>. He and Sun<sup>[24]</sup> investigated the composition dependence of the crystallization behavior and morphology of the PEO-b-PCL diblock copolymers. They found that PCL chains crystallize or even can not fold to crystallize between the crystalline PEO lamellae when PEO was dominant in the diblock copolymer. As mentioned above in this section, the most commonly studied of the block copolymer systems in the literature are diblock copolymers or triblock copolymers. However, there are few studies that have been published on the crystallization behaviors of aliphatic segmented copolymer.

The temperature-dependent infrared spectroscopy can give us the information of structural evolution at the molecular level, and thus is widely used to reveal the structure and conformation changes during the crystallization and melting processes<sup>[25]</sup>. IR spectroscopy combined with generalized 2DIR correlation analysis, which was first proposed by Noda in 1993<sup>[26,27]</sup>, can provide important information on the molecular interactions and the movement of functional groups. In this study, perturbation correlation move-window two-dimensional (PCMW2D) correlation infrared spectroscopy was used to determine the phase transition or blocks temperature response in PBS/PTMO segment block copolymer. The theory about PCMW2D correlation infrared spectroscopy can be found in the literature<sup>[28]</sup>.

In this paper, we found that the isothermal crystallization time of PBS component has an effect on the crystallization behavior of PTMO component in their copolymer with relative higher PTMO content ( $m_{PTMO}=67\%$ ) by DSC measurement with a well designed thermal program. 2DIR correlation spectroscopy analysis and PCMW2D correlation analysis were applied to study the crystallization behavior and mutual blocks chain movements during cooling. A crystallization behavior mode was also discussed and established. We also used AFM to further testify the deduction.

## 2 Experimental

### 2.1 Material and samples

The PBS/PTMO segment block copolymer were synthesized by a two-step transesterification reaction, starting from succinate, 1,4-butanediol, and  $\alpha$ ,  $\omega$ -hydroxyl-terminated PTMO ( $M_n=1000$  g/mol). The weight ratio of PBS and PTMO component in the investigated sample was about 33:67. These procedures were previously reported in detail<sup>[2,10]</sup>. The molecular weight  $M_n$  of the samples is approximately 53 000 g/mol. The  $M_w/M_n$  ratio of this copolymer is 2.5.

### 2.2 DSC measurements

Differential scanning calorimetric curves were obtained with NETZSCH DSC (204 F1) apparatus. The thermal program was shown in Fig.1. The thermal program was performed as follows: The sample was first melted at 120 °C for 3 min to erase the thermal history. Cooled the sample to 20 °C at rate of 30 °C/min, and held at 20 °C for  $t_{ic}$  min (step I). Cooled the sample from 20 °C to -40 °C at a cooling rate of 10

°C/min (step C) and held the temperature at  $-40\text{ }^{\circ}\text{C}$  for 3 min. Finally the sample was heated to  $120\text{ }^{\circ}\text{C}$  at a scanning rate of  $10\text{ }^{\circ}\text{C}/\text{min}$  (step H) and held the temperature at  $120\text{ }^{\circ}\text{C}$  for 3 min. v. Performed the steps of cooled and heated sample again.

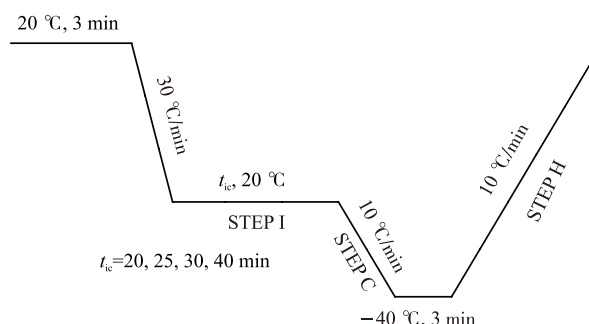


Fig.1 Thermal program designed in this study to investigate the effect of the isothermal crystallization time of PBS blocks on the crystallization and melting behaviors of the PTMO blocks

## 2.3 FTIR spectroscopy

The copolymer was spread on one side of a KBr disk by solvent casting from 20 g/L THF solution. The KBr disk covered with the copolymer sample was dried in a vacuum oven at  $70\text{ }^{\circ}\text{C}$  for 24 h with a  $-0.09\text{ MPa}$  vacuum degree. The copolymer film disk sample was placed in a homemade temperature control instrument including program heating cell and circulation liquid nitrogen cooling system. The temperature-dependent absorbance IR spectra in the  $4\ 000\text{--}400\text{ cm}^{-1}$  region were measured with Nicolet iS10 FTIR spectrometer. The spectral resolution was  $4\text{ cm}^{-1}$  and the number of the scans of each spectrum was 20. The copolymer film disk sample was heated from room temperature to  $120\text{ }^{\circ}\text{C}$  and kept the temperature for three minutes to erase thermal history. Then the sample was cooled from  $120\text{ }^{\circ}\text{C}$  to  $-40\text{ }^{\circ}\text{C}$  at the cooling rate of  $5\text{ }^{\circ}\text{C}/\text{min}$ . Ninety five IR spectra were collected from the corresponding cooling processing. In the whole measurement process, the test film sample was protected by dried high-purity nitrogen gas.

## 2.4 Perturbation correlation move-window two-dimensional (PCMW2D) correlation analysis

Before PCMW2D and generalized 2DIR correlation analysis, the intensity of each IR spectrum was normalized by dividing its intensity mean value. The PCMW2D and generalized 2DIR software were developed by one of the authors (Tao Zhou). The theory of 2D and PCMW2D correlation spectroscopy has been described elsewhere<sup>[26-29]</sup>.

## 2.5 AFM measurements

AFM experiments were performed by Nanoscope Multimode & Explore (America, Veeco Instruments) at room temperature in air with tapping mode. The method of preparing the samples for AFM observation is as follows: the copolymers were dissolved in chloroform to form a 0.5% (w/w) solution, and then the polymer solution was spin-coated at 500 rpm for 20 s onto the clean Si wafers. The Si wafers coated with sample were melt at  $120\text{ }^{\circ}\text{C}$  for 3 min, then cooled to room temperature immediately or followed by heat treatment at  $30\text{ }^{\circ}\text{C}$  for 2 h in a vacuum oven with a  $-0.09\text{ MPa}$  vacuum degree.

## 2.6 Tensile testing

Tensile strength and elongation at break of PBS copolymers were measured on an Instron Universal Testing Machine (Model 5567, Instron Engineering Corporation, Canton, MA) at a speed of  $50\text{ mm}/\text{min}$  at room temperature.

# 3 Results and discussion

## 3.1 DSC analysis

As mentioned in the introduction, the first crystallization block has an effect on the crystallization behavior of the second block as temperature decreases. In this paper, DSC analysis was employed to investigate the effect of PBS component on the crystallization behavior of PTMO. The designed DSC program is shown in Fig.1. The method was employed by prolonging the isothermal crystallization time of PBS block. The DSC cooling curves recorded at step C are summarized in Fig.2 for the PBS/PTMO segment block copolymer. For the sample directly cooled

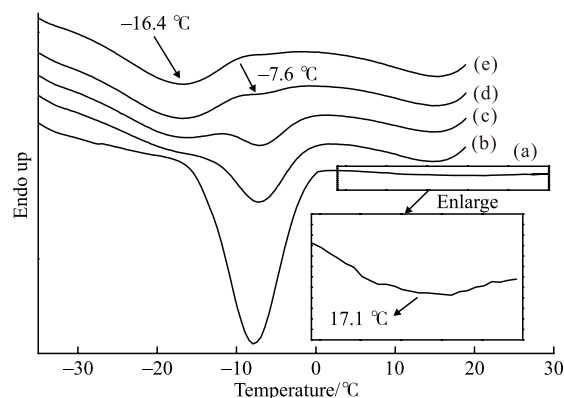


Fig.2 DSC curves of PBSPTMO67 cooling from  $20\text{ }^{\circ}\text{C}$  to  $-40\text{ }^{\circ}\text{C}$  at  $10\text{ }^{\circ}\text{C}/\text{min}$  (first melting in  $120\text{ }^{\circ}\text{C}$  for 3 min, then cooling to  $20\text{ }^{\circ}\text{C}$  at  $30\text{ }^{\circ}\text{C}/\text{min}$  and heating at the same temperature for different time  $t_c$ ) ( $t_c=20\text{ min}$ (b),  $25\text{ min}$ (c),  $30\text{ min}$ (d), and  $40\text{ min}$ (e)); a: cooling from  $120\text{ }^{\circ}\text{C}$  directly at  $10\text{ }^{\circ}\text{C}/\text{min}$

from melt to  $-40\text{ }^{\circ}\text{C}$ , two major exothermal peaks appeared in the curve (Fig.2(a)). One peak at about  $17.1\text{ }^{\circ}\text{C}$  is assigned to PBS hard blocks crystallization temperature, another at about  $-7.6\text{ }^{\circ}\text{C}$  is assigned to PTMO soft blocks crystallization temperature. The  $T_c$  of both blocks is much lower than that of the corresponding homopolymer. As the sample was heat treated at  $20\text{ }^{\circ}\text{C}$  for a while and then cooled to  $-40\text{ }^{\circ}\text{C}$ , a new exothermal peak at  $-16.3\text{ }^{\circ}\text{C}$  emerged in the curve (Figs.2(b)-2(e)). The new exothermal peak at about  $-16.3\text{ }^{\circ}\text{C}$  should also be assigned to the crystallization temperature of PTMO soft block. With the isothermal crystallization time of PBS component increasing, the exothermal peak at  $-7.6\text{ }^{\circ}\text{C}$  gets small. However, the exothermal peak at  $-16.3\text{ }^{\circ}\text{C}$  gets bigger at the same time.

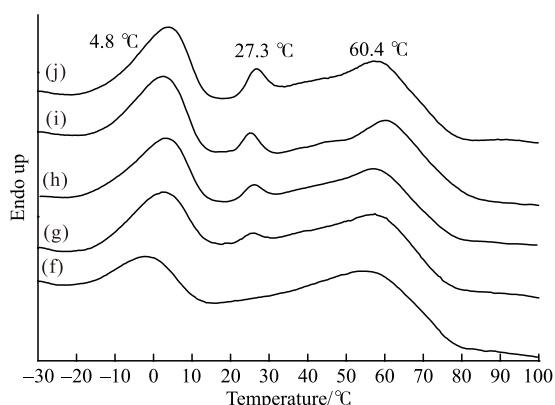


Fig.3 DSC heating curves (corresponding to DSC cooling curves in Fig.2)

Fig.3 shows the corresponding DSC heating curves recorded at step H (see Fig.1 for thermal program). Three major endothermic peaks are located at about  $4.8$ ,  $27.3$ , and  $60.4\text{ }^{\circ}\text{C}$ . The endothermic peaks located at about  $4.8\text{ }^{\circ}\text{C}$  and  $60.4\text{ }^{\circ}\text{C}$  are the melting temperature of PTMO blocks and PBS blocks, respectively. And they almost do not change as isothermal crystallization time changes. The peak at about  $27.3\text{ }^{\circ}\text{C}$  is assigned to the imperfect crystallites of PBS hard blocks, and it becomes bigger as the isothermal crystallization time increases. The bigger of the peak means more PBS chains take part in folding to form regular crystallites. In order to testify whether PTMO block chains can crystallize at  $20\text{ }^{\circ}\text{C}$  during isothermal crystallization step, we also employ the same heat program to PTMO homopolymer. And we find PTMO block almost can not crystallize at  $20\text{ }^{\circ}\text{C}$  (Fig.4). Now we can well deduce that the crystallization behavior of PBS hard blocks plays an important role in the crystallization behavior of PMTO

soft blocks. The new emergence of exothermal peak at  $-16.3\text{ }^{\circ}\text{C}$  is caused by the crystallization of PBS block. The phenomenon that two crystallization peaks appeared in cooling DSC curve was also reported in our another paper before<sup>[10]</sup>. Now we will think why two crystallization temperature of PTMO appeared in the cooling DSC curve after PBS block heat treatment at  $20\text{ }^{\circ}\text{C}$ , and why the peak at  $-7.6\text{ }^{\circ}\text{C}$  gets small, while the exothermal peak at  $-16.3\text{ }^{\circ}\text{C}$  gets bigger at the same time, as the isothermal crystallization time of PBS component increases.

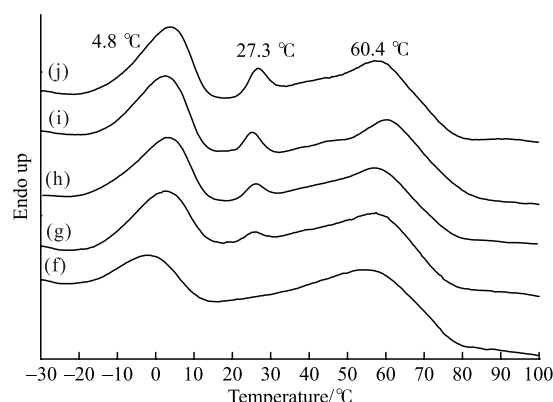


Fig.4 DSC curves of PTMO cooling from  $T_i$  to  $-30\text{ }^{\circ}\text{C}$  at  $10\text{ }^{\circ}\text{C}/\text{min}$  (first melting in  $100\text{ }^{\circ}\text{C}$  for 3 min, then cooling to  $T_i$  at  $30\text{ }^{\circ}\text{C}/\text{min}$  and holding at the same temperature for 40 min) ( $T_i=30\text{ }^{\circ}\text{C}$  (a),  $20\text{ }^{\circ}\text{C}$  (b), and  $15\text{ }^{\circ}\text{C}$  (c)); d: cooling from  $100\text{ }^{\circ}\text{C}$  directly to  $-30\text{ }^{\circ}\text{C}$  at  $10\text{ }^{\circ}\text{C}/\text{min}$ )

There are two crystallization peaks appeared in cooling DSC curve for PTMO, suggesting the occurrence of fractionated crystallization. The fractionated crystallization has always been regarded as the results of confined crystallization. The phenomenon has been explained as the crystallization of a series of microdomains at specific and independent supercoolings, that is, the crystallization of the isolated domains of a semicrystalline polymer dispersed in an immiscible matrix, where the number of domains is higher than the number of active heterogeneous nuclei. Therefore, the different groups of domains may contain distinct type of heterogeneities with different efficiencies to induce nucleation or even can contain no heterogeneity at all, and thus they will crystallize at different supercoolings<sup>[16,17]</sup>. Few published works have reported fractionated crystallization in miscible systems<sup>[30,31]</sup>. He *et al*<sup>[30]</sup> first reported fractionated crystallization and even homogeneous nucleation for miscible blends of poly(ethylene oxide)/poly(butylene succinate). And they found that the crystallization behavior of the PEO component in the PBS/PEO blends with middle PEO content (30wt%-50wt%) is significantly affected by the isothermal



crystallization temperature of the PBS component ( $T_{IC}$ , PBS)<sup>[31]</sup>. It is suggested that  $T_{IC}$ , PBS controls the positional distribution of the PEO component after the crystallization of the PBS component. Higher  $T_{IC}$ , PBS favors the incorporation of the PEO component in the region between PBS lamellae, while lower  $T_{IC}$ , PBS favors the exclusion of the PEO component from the interlamellar region<sup>[31]</sup>. For our systems, the similar phenomenon is observed. From DSC results, it seems that the isothermal crystallization time of PBS ( $t_{IC}$ , PBS) significantly affects the crystallization behavior of the PTMO component. Longer  $t_{IC}$ , PBS favors the completely incorporation of the PTMO component in the region between PBS lamellae. We will discuss and demonstrate the deduction later in this paper.

### 3.2 The IR spectra of PBS/PTMO copolymer

Two interesting regions of normalized temperature-dependent (120-40 °C) FTIR spectra of the investigated PBS/PTMO copolymer sample are shown in Fig.5. For clarity, the whole spectra are not presented. As shown in Fig.5(a), the assignment of the C=O stretching region is very simple. Note that the C=O stretching band between 1 780-1 700  $\text{cm}^{-1}$  is split into three bands centered at 1 735, 1 723, and 1 714  $\text{cm}^{-1}$  below room temperature. The peak located at 1 735  $\text{cm}^{-1}$  is related to the hard segments in amorphous state, however 1 723 and 1 714  $\text{cm}^{-1}$  are related to the crystalline of hard blocks<sup>[11]</sup>. Fig.5(a) shows the change of the IR spectra in the C=O stretching region as a function of the cooling process. It is very obvious that during the cooling process, the band at 1 735  $\text{cm}^{-1}$  decreases while the 1 723 and 1 714  $\text{cm}^{-1}$  peaks

increase at the same time, which also means that the conformational transformation of PBS constituent happens. Fig.5(b) shows both temperature-dependent FTIR C-O-C stretching modes of PBS hard and PTMO soft segment. The peaks at 1 185 and 1 158  $\text{cm}^{-1}$  are assigned to the C-O-C stretching vibration in crystalline and amorphous regions of PBS hard segment respectively. With temperature decreasing, the peak at 1185  $\text{cm}^{-1}$  increase and 1 158  $\text{cm}^{-1}$  decreases at the same time. The peak at 1 111  $\text{cm}^{-1}$  assigned to the C-O-C stretching vibration of PTMO soft segment do not change intensively as the peak of 1 185 or 1 158  $\text{cm}^{-1}$  do. Obviously, the one-dimensional analysis is not able to provide sufficient information for transitions and movement order of group. We use both PCMW2D and 2DIR correlation spectroscopy in this study to elucidate the detailed crystallization mechanism of the block copolymer.

### 3.3 PCMW2D analysis

Fig.6 shows the PCMW2D correlation spectra based on autocorrelation calculations in the 1 780-1 700 and 1 200-1 000  $\text{cm}^{-1}$  regions. For PBS hard segment, at around 20 °C, one positive and two negative correlations intensity peaks are observed in the region of 1 780-1 700  $\text{cm}^{-1}$ . It is obviously an outcome of the PBS block crystallization transition. The crystallization temperature of PBS hard block by DSC measurement is 17.1 °C, and this value is close to the result obtained by PCMW2D. In the region of 1 200-1 000  $\text{cm}^{-1}$ , a new band at 1 173  $\text{cm}^{-1}$  is founded, which is assigned to the crystalline PBS hard segment. Three C-O-C peaks (1 185, 1 173, and 1 154  $\text{cm}^{-1}$ ) in PBS hard block are same to the region of 1 780-1 700  $\text{cm}^{-1}$ , which means

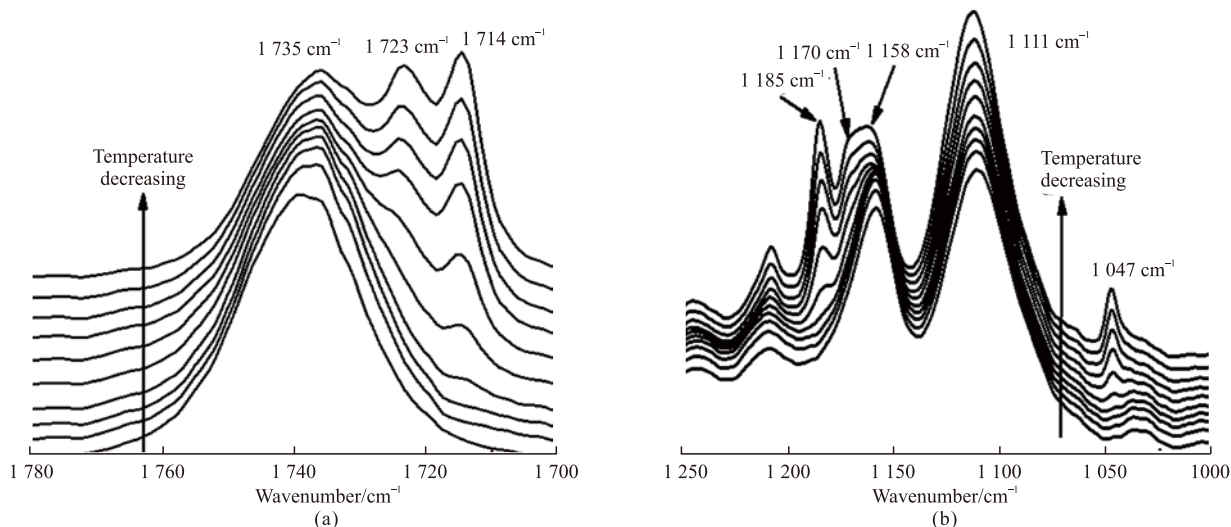


Fig.5 Temperature-dependent IR spectra of PBS/PTMO segment block copolymer in the range from 120 °C to -40 °C (a: 1 780-1 700  $\text{cm}^{-1}$ ; b: 1 250-1 000  $\text{cm}^{-1}$ )

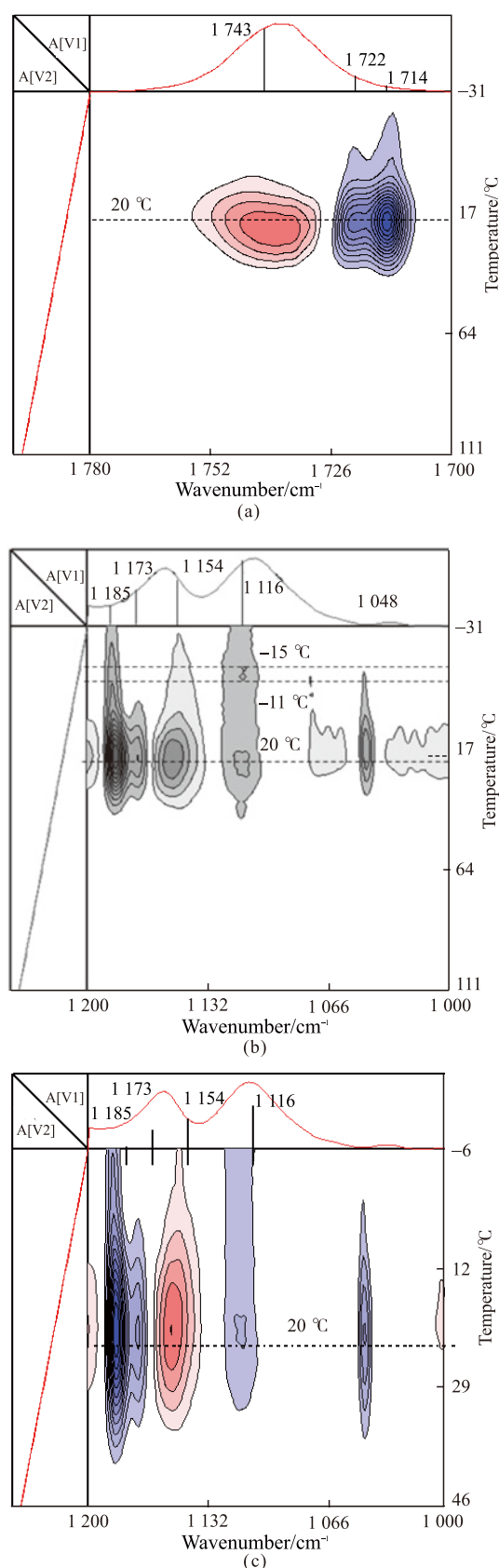


Fig.6 PCMW2D correlation spectra based on autocorrelation calculated from the temperature-dependent IR spectra of copolymer ((a: 1 780-1 700  $\text{cm}^{-1}$  (120-40  $^{\circ}\text{C}$ ); b: 1 250-1 000  $\text{cm}^{-1}$  (120-40  $^{\circ}\text{C}$ ); c: 1 250-1 000  $\text{cm}^{-1}$  (60-10  $^{\circ}\text{C}$ ))

there are have at least three types C-O-C in the sample. At 20  $^{\circ}\text{C}$ , three peaks are observed and one is positive and two are negative, which is also attributed to the crystallization transition of PBS hard block. The peaks at 1 116  $\text{cm}^{-1}$  is assigned to C-O-C stretching vibration of PTMO soft block. As mentioned before, PTMO can also crystallize at the condition of lower temperature in the PBS/PTMO segment block copolymer with relatively high weight of soft block. Two negative correlation intensity peaks at -11  $^{\circ}\text{C}$  and -15  $^{\circ}\text{C}$  are observed at band of 1 116  $\text{cm}^{-1}$ , which are assigned to C-O-C stretching vibration of PTMO soft block. The correlation intensity peak at about -15  $^{\circ}\text{C}$  was detected by the PCMW2D correlation analysis but was not observed obviously in the DSC curve. The possible reason is that the exothermal peak is overlapped by the major exothermal peak at about -7.6  $^{\circ}\text{C}$ . The two peaks at -11 and -15  $^{\circ}\text{C}$  are obviously ascribed to the crystallization transition of PTMO. Two correlation intensity peaks mean fractionated crystallization happens in the system. It is well known that fractionated crystallization is the consequence of confined crystallization, which has been the hot topic in the last decades<sup>[15,16]</sup>.

Another notable and interesting phenomenon we should take attention is that one correlation intensity peak is observed at around 20  $^{\circ}\text{C}$  (corresponding to PBS hard block crystallization temperature) for C-O-C stretching vibration of PTMO soft block. Of course, it can not be easily detected by the usual ways such as DSC, DMA *et al.* This responding at around 20  $^{\circ}\text{C}$  for PTMO soft block means the notable movement of PTMO chains at this temperature. However, it is well known that PTMO homopolymer can not crystallize at 20  $^{\circ}\text{C}$  (PTMO homopolymer crystallization temperature is about 0  $^{\circ}\text{C}$  and we have also testified this result in above section)<sup>[7,8]</sup>. How and why this interesting phenomenon happens? Because of the chemical joint between PBS and PTMO blocks, we can deduce that the movement of the PBS chains at 20  $^{\circ}\text{C}$  involves a fraction of PTMO blocks movement at the same time.

### 3.4 2D FTIR correlation analysis

Fig.7(a) and (b) show synchronous and asynchronous 2D correlation spectra in the 1780-1 700  $\text{cm}^{-1}$  region constructed from the IR spectra in the temperature range from 120 to -40  $^{\circ}\text{C}$ . The synchronous spectra in Fig.7(a) are dominated by three auto-peaks at about 1 742, 1 722, and 1 714  $\text{cm}^{-1}$ , respectively. As mentioned before, 1 742  $\text{cm}^{-1}$  is assigned to C=O stretch modes in amorphous, and

1 722 and 1 714  $\text{cm}^{-1}$  are assigned to crystalline region of PBS hard segment respectively. The negative cross-peaks at (1 742, 1 722)  $\text{cm}^{-1}$ , (1 742, 1 714)  $\text{cm}^{-1}$ , and positively (1 722, 1 714)  $\text{cm}^{-1}$  reveal that the direction of the bond intensity change at 1 742  $\text{cm}^{-1}$  is opposite to that of the intensity change at 1 722  $\text{cm}^{-1}$ , 1 714  $\text{cm}^{-1}$ , and the direction of the bond intensity changes at 1 722  $\text{cm}^{-1}$  is same to that at 1 714  $\text{cm}^{-1}$  with temperature decreasing. The results are similar to the observation in the 1D IR analysis.

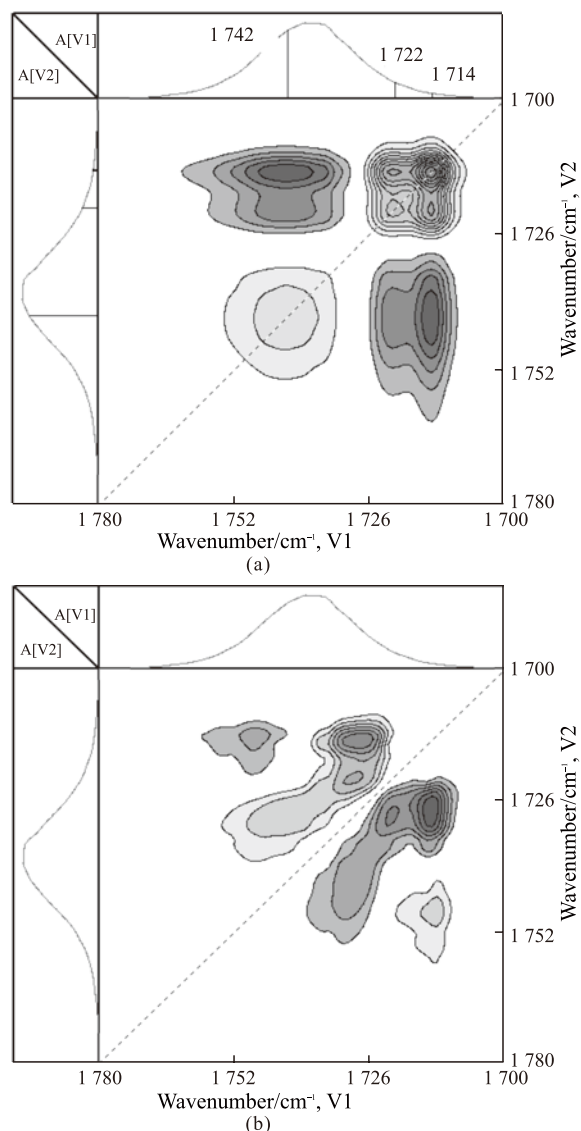


Fig.7 Synchronous (a) and asynchronous (b) 2D IR correlation spectra (120- -40  $^{\circ}\text{C}$ ) in region 1 780-1 700  $\text{cm}^{-1}$

Asynchronous correlation spectra 2D correlation spectra in Fig.7(b) give us more information on the sequential order of intensity changes between these peaks. According to Noda rules, if  $\Phi(v_1, v_2) \times \psi(v_1, v_2) > 0$ , band  $v_1$  varies prior to band  $v_2$ . Contrarily, if  $\Phi(v_1, v_2) \times \psi(v_1, v_2) < 0$ , band  $v_2$  varies prior to the band  $v_1$ . If  $\Phi(v_1, v_2) \times \psi(v_1, v_2) = 0$ , band  $v_1$  varies at same time as the band  $v_2$ . All peaks discussed in this paper are the peaks

appearing in the top-left region of the synchronous and asynchronous 2D correlation spectra maps. Based on the Noda rules, we find that the band at 1 742  $\text{cm}^{-1}$  varies in first, then 1 722  $\text{cm}^{-1}$ , and the band at 1 714  $\text{cm}^{-1}$  varies at last as temperature decreases. Now we can safely deduce that peaks at 1 722 and 1 714  $\text{cm}^{-1}$  are assigned to the C=O stretch modes in the region of less and more perfect crystallites respectively. The processing can be explained as follows: as temperature decreases, the PBS chains in the melt fold to form the less perfect crystallites in the first, and then form the more perfect crystallites. Moreover, similar to previous study<sup>[25]</sup>, there is a so-called “butterfly pattern” in the C=O stretching region in the asynchronous correlation spectra. Usually, the appearance of this pattern is attributed to a peak shift combined with the intensity changes or band splitting<sup>[25]</sup>.

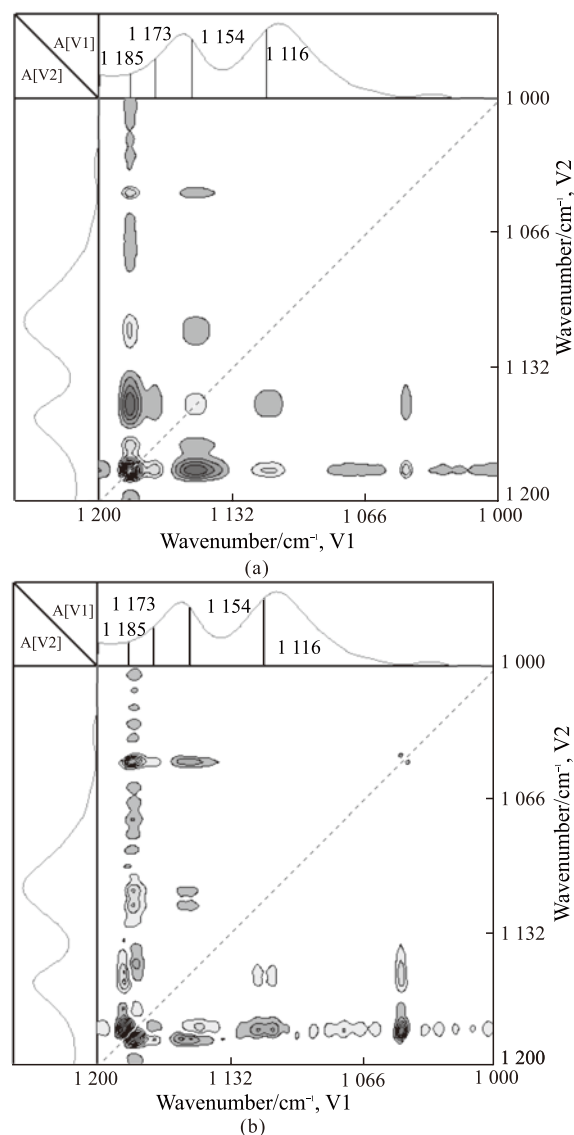


Fig.8 Synchronous (a) and asynchronous (b) 2D IR correlation spectra of PBSPTMO60 (60-10  $^{\circ}\text{C}$ ) in region 1 200-1 000  $\text{cm}^{-1}$

Fig.8 shows the synchronous and asynchronous 2D correlation spectra of the highly overlapped 1 200-1 000  $\text{cm}^{-1}$  region in the temperature range of 60-10  $^{\circ}\text{C}$ . The band regions of 1 200 to 1 132  $\text{cm}^{-1}$  are assigned to C-O-C stretch modes of PBS hard blocks. Similar to C=O stretch modes (1 780-1 700  $\text{cm}^{-1}$ ), three types bands of C-O-C of PBS hard blocks are observed in the 2DIR correlation spectrum map. Bands at 1 154, 1 173, and 1 185  $\text{cm}^{-1}$ , are assigned to the C-O-C stretch modes of PBS in the region of amorphous state, less and more perfect crystallites state respectively. And based on the Noda rules, we find that the band at 1 154  $\text{cm}^{-1}$  varies in first, then 1 173  $\text{cm}^{-1}$ , and the band at 1 185  $\text{cm}^{-1}$  varies at last as temperature decreases. The band at 1 116  $\text{cm}^{-1}$  is assigned to the C-O-C stretch modes of PTMO soft blocks. As mentioned before, there is one responding peak at 20  $^{\circ}\text{C}$  for PTMO, although its homopolymer can not crystallize at the same temperature. Also there is one auto peak located at about 1 116  $\text{cm}^{-1}$  in the synchronous spectra in Fig.8(a). Because of  $\Phi(1\ 154$

$\text{cm}^{-1}, 1\ 116\ \text{cm}^{-1}) \times \psi(1154\ \text{cm}^{-1}, 1116\ \text{cm}^{-1}) > 0$  and  $\Phi(1\ 185\ \text{cm}^{-1}, 1\ 116\ \text{cm}^{-1}) \times \psi(1\ 185\ \text{cm}^{-1}, 1\ 116\ \text{cm}^{-1}) > 0$ , band at 1 184 or 1 154  $\text{cm}^{-1}$  varies prior to band at 1 116  $\text{cm}^{-1}$ . As the results discussed above, it can well deduce that the folded PBS chains movement force PTMO blocks chemical linked by PBS hard blocks to move at the same time. We can also imagine that by changing the crystallization condition of PBS hard blocks, the PTMO soft blocks should show different crystallization behavior.

### 3.5 Mechanism model of crystallization behavior

According to the analyses of the DSC, IR, PCMW2D, and 2DIR, we constructed a mechanism model of crystallization behavior about the copolymer. The mechanism model of crystallization behavior of the copolymer is illustrated in the Fig.9. Because of the chemical links between PBS hard blocks and PTMO soft blocks, PTMO has an effect on the PBS chains movements. Unlike aromatic esters such as

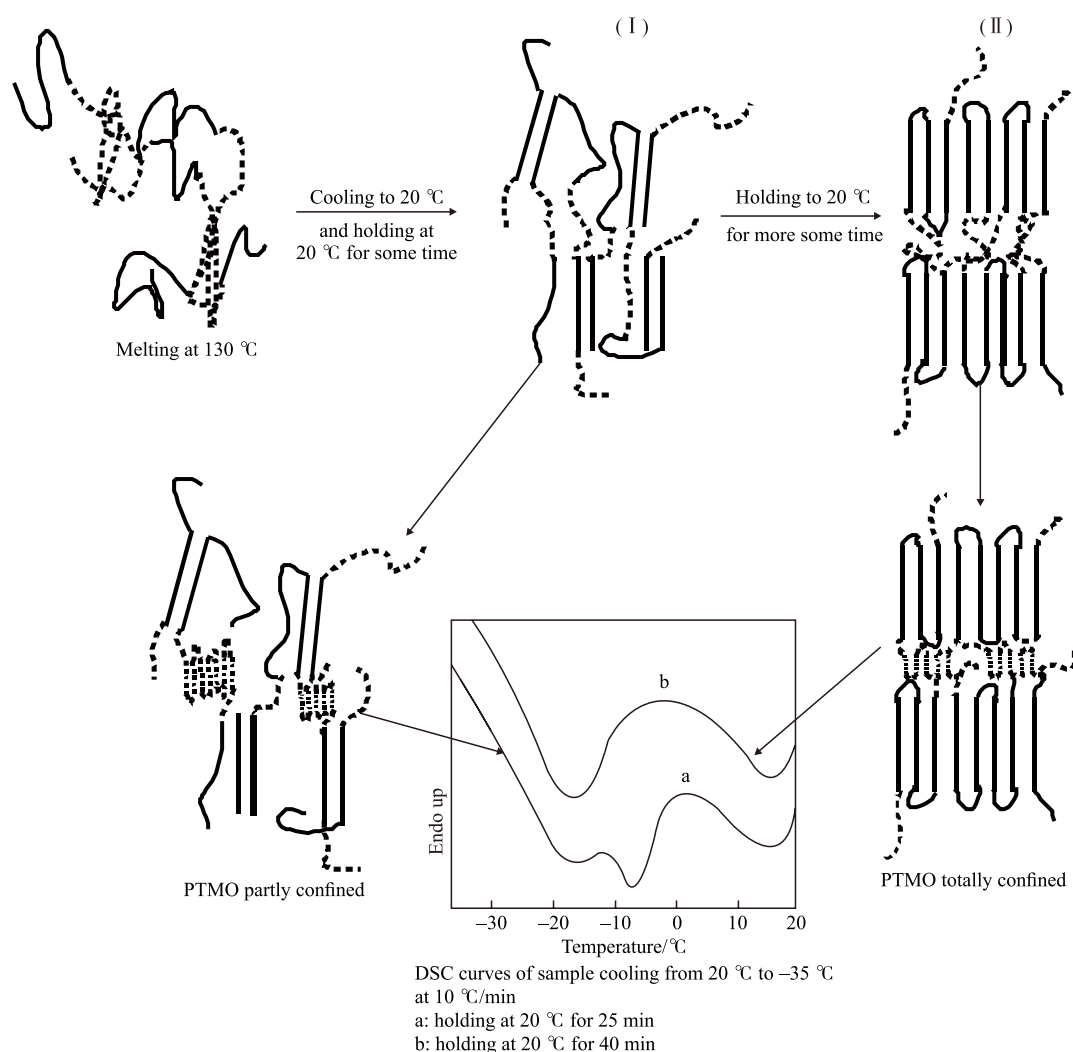


Fig.9 Mechanism models of isothermal crystallization



PBT, the ability of PBS chains movements or folding is weaker than that of PBT, especially with higher PTMO soft content. At usual cooling rates for example 10 °C/min, PBS chains have no enough time to move and fold to form complete crystallites, so PTMO chains are excluded from the interlamellar region, which makes PTMO in the sample shows only one crystallization temperature (with relatively higher temperature, Fig.2(a)) during cooling process. If isothermal crystallization time of PBS is prolonged but shorter, PBS chains have enough time to move and fold. As mentioned before in this paper, PBS chains movements force PTMO chains to move at the same time. So the PTMO chains are partly confined (Fig.9(I)) within the crystalline lamellar formed by PBS blocks, making PTMO in the sample shows two crystallization temperatures (Fig.9(a), or Figs.2(b)-2(d)) during cooling process. If for more isothermal crystallization time, more PTMO chains are forced to move, even finally are totally incorporated (Fig.9(II)) within the crystalline lamellar formed by PBS blocks, and of course PTMO in the sample will show one crystallization temperature (with relatively lower temperature, Fig.9(a) or Fig.2(e)). So as the isothermal time of PBS prolongs, the peak at  $-7.6$  °C belonged to less constricted PTMO chains changes smaller and even disappears, while the peak at  $-16.3$  °C belonged to more constricted PTMO chains gets bigger (shown in Fig.2).

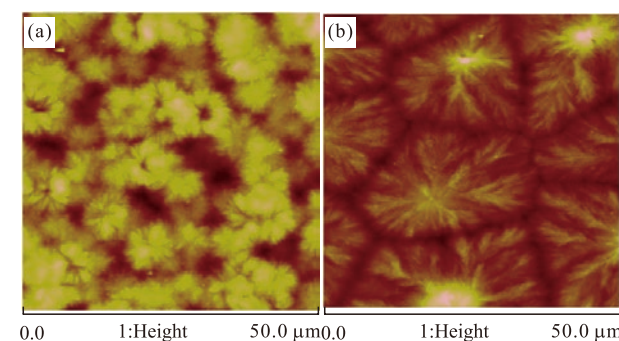


Fig.10 Atomic force microscope images of PBS/PTMO67 (a: heating to 120 °C and cooling to room temperature immediately; b: heating to 120 °C and heating treatment at 30 °C for 2 h)

In order to further testify the results obtained above, atomic force microscope analysis was applied in this paper. Fig.10(a) shows the atomic force microscope image of sample without heat treatment (heating to 120 °C and cooling to room temperature immediately). Fig.10(b) shows the atomic force microscope image of sample with heat treatment (heating to 120 °C, then cooling to 30 °C and holding the sample at the same temperature for two hours, finally cooling it to room

temperature immediately). As shown in Fig.10(a) and Fig.10(b), the morphology of the sample both shows the type of spherulites. However, the morphology of the sample with heat treatment shows bigger size of spherulites than that of untreated. This result has demonstrated that with isothermal crystallization time increasing, more PBS chains fold and force the chemical linked PTMO to move, finally more PTMO soft blocks are confined into the lamellar structure formed by PBS crystallization. This results also resolve the reason that why the higher crystallization temperature of PMTO gets small while the lower crystallization temperature of PMTO becomes bigger (see Fig.2) as  $t_{ic}$  of PBS prolongs.

### 3.6 Mechanical properties

Table 1 Mechanical properties

Sample	1	2	3	4
Tensile strength/MPa	16.7	16.8	17.2	18.5
Elongation at break/%	975.6	923.7	862.5	602.8

Samples 1-4 are obtained respectively by heat treatment at 40 °C for 0 min, 30 min, 2 h, 24 h

Mechanical properties of polymers are more important than any other properties with respect to practical applications. The tensile properties of the PBS/PTMO sample heat treated for different time at 40 °C are summarized in Table 1. A trend of slightly increasing in tensile strength and decreasing in elongation at break was observed with increasing heat treatment time. Tensile strength and elongation at break are 16.7 MPa and 975.6% respectively as the sample is cooled directly to room temperature. However, tensile strength and elongation at break are 18.5 MPa and 602.8% respectively as the sample was annealed for 24 h. As discussed above, chemical links between PBS and PTMO have an impact on the mobility of PBS chains, especially in the samples with higher PTMO content. If cooling directly to room temperature, PBS chains have no enough time to move and fold to form complete crystallites. However, longer heat treatment time, more perfect crystallites are formed, and also more PTMO chains are forced to move, even finally are totally incorporated in the crystalline lamellar formed by PBS blocks. The formation of more complete PBS crystallites is beneficial to the increase of tensile strength, but not to elongation at break.

## 4 Conclusions

The crystallization behavior of PBS/PTMO

segment block copolymer with 67% mass PTMO content was investigated in this paper. The crystallization of PBS has an effect on the crystallization behavior of PTMO component as isothermal crystallization time of PBS chains increases. A crystallization model was also established in this study.

a) By the DSC results, as isothermal crystallization time of PBS chains increases, the peak at  $-7.6\text{ }^{\circ}\text{C}$  belonged to less constricted PTMO chains changes smaller and even disappears, while the peak at  $-16.3\text{ }^{\circ}\text{C}$  belonged to more constricted PTMO chains gets bigger.

b) The crystallization transition of PBS hard block is  $20\text{ }^{\circ}\text{C}$ , and three temperature responses (at  $20\text{ }^{\circ}\text{C}$ ,  $-11\text{ }^{\circ}\text{C}$ , and  $-15\text{ }^{\circ}\text{C}$ ) are observed for PTMO soft block detected by PCMW2D.  $-11\text{ }^{\circ}\text{C}$  and  $-15\text{ }^{\circ}\text{C}$  assigned to the fractional crystallization transition of PTMO. The response at  $20\text{ }^{\circ}\text{C}$  is assigned to PTMO chains movement forced by the PBS chains corresponding to the crystallization of PBS. By the 2DIR results, as temperature decreases, the PBS chains in the melt fold to form the less perfect crystallites in the first, and then form the more perfect crystallites, and the PBS chains folded movement force PTMO blocks chemical linked by PBS hard blocks to move at the same time.

c) The isothermal crystallization time of PBS ( $t_{\text{IC}}$ , PBS) significantly affects the crystallization behavior of the PTMO component. For longer  $t_{\text{IC}}$ , PBS favors the completely incorporation of the PTMO component in the region between PBS lamellae. Tensile strength slightly increased and elongation at break decreased with the increasement of heat treatment time at  $40\text{ }^{\circ}\text{C}$ .

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