

# Synthesis, Characterization, and Properties of Long-Chain Branched Poly(butylene succinate)

Guoli Wang,<sup>1</sup> Baohua Guo,<sup>1</sup> Rui Li<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, Institute of Polymer Science and Engineering, Tsinghua University, Beijing 100084, China

<sup>2</sup>China Textile Industrial Engineering Institute, Beijing 100037, China

Received 21 October 2010; accepted 25 December 2010

DOI 10.1002/app.34034

Published online 14 October 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Long-chain branched poly(butylene succinate) were synthesized through a two-step process of esterification and polycondensation, using 1,2,4-butanetriol (1,2,4-BT) as a long-chain branching agent. The effect of long-chain branches on the crystallization behaviors, rheological properties, and tensile properties was investigated systematically. The results of differential scanning calorimetry and polarized optical microscopy showed that with the increasing of 1,2,4-BT segments, the crystallization temperatures and glass transition temperatures increase slightly, while the relative crystallinity degree decreases gradually. Also, the double-banded extinction patterns with periodic distance along the radial direction were observed in the spherulites of long-chain branched poly(butylene succinate), similar to that of linear poly(butylene succinate) (PBS). The result of wide-angle X-ray diffraction indicated that the

incorporation of 1,2,4-BT segments had little effect on the crystal structure of PBS. However, based on data from rheology and tensile testing, the viscoelastic properties of long-chain branched PBS under shear flow were different from the linear PBS. For example, the complex viscosities, storage modulus, and loss modulus of long-chain branched PBS at low frequency were significantly enhanced in comparison with those of linear PBS. In addition, long-chain branched PBS showed higher tensile strength than that of linear PBS without notable decrease in the elongation at break when compared with linear PBS. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1271–1280, 2012

**Key words:** poly(butylene succinate); long-chain branches; crystallization behaviors; rheological properties; tensile properties

## INTRODUCTION

Poly(butylene succinate), as a biodegradable aliphatic polyester, has attracted more and more attention because of its particular properties. Compared to other aliphatic polyesters, such as poly(ethylene succinate), poly(ethylene adipate), poly(butylene adipate) (PBA), PBS possesses not only higher melting temperature, but also higher tensile strength and stiffness.<sup>1</sup> PBS has been commercialized (e.g., Biolle™) and used in many fields such as agriculture, packaging, fiber, and biomedicine.<sup>2,3</sup> However, PBS exhibits low melt strength and melt viscosity, because it is one of those polymers with highly linear chain structure, which limits its application in thermoplastic processing, foaming, and filming. The melt strength and melt viscosity of PBS can be enhanced through many ways, for example, by increasing molecular weight and introducing branches into the chain structure. Among these

methods, chain extension is widely used to increase the molecular weight of aliphatic polyesters.<sup>4</sup> For example, Zhao et al.<sup>5</sup> synthesized high-molecular weight PBS through chain extension reaction using octamethylcyclotetrasilazane and hexaphenylcyclotri-silazane as chain extenders. They<sup>6</sup> also studied the effect of catalyst on the intrinsic viscosity of chain-extended PBS and suggested that higher molecular weight PBS was obtained from the catalyzed chain extension than that from the noncatalyzed system. Under optimal conditions, the chain-extended PBS with intrinsic viscosity of 0.82 dL/g was synthesized by using 2,2'-(1,4-phenylene)-bis(2-oxazoline) as a chain extender and *p*-toluenesulfonic acid as a catalyst. However, this method has not been very successful due to the transesterification reactions during chain extending.

Introducing long-chain branches into linear polymer is another effective method to improve the melt strength and melt viscosity. Long-chain branched polyesters can be prepared via introducing multifunctional comonomer branching agents to polycondensation reactions. Unlike the short-chain branches, long-chain branches are long enough to increase the entanglement among polymer chains in melt and concentrated solutions, resulting in the improvement of the rheological properties.<sup>7</sup> Generally, long-chain

Correspondence to: B. H. Guo (bhguo@mails.tsinghua.edu.cn).  
Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50673050.

branched polymers show higher melt strength and melt viscosity than those of linear polymer. In addition, long-chain branching can produce a tension thickening effect, which improves uniform stretching property during the film blowing. Importantly, the large degrees of chain branches can enhance the horizontal tensile strength and tearing strength of polymer films.<sup>8–12</sup> Thus, many researchers have focused on modifying aliphatic polyesters through introducing long-chain branches into the polyesters backbone, and the preparation of long-chain branched PBS through copolycondensation of bifunctional acids/diols monomers with multifunctional monomers is relatively convenient and has attracted great interest over the past decades. Kim et al.<sup>13</sup> prepared long-chain branched PBS by introducing a chain-branching agent, trimethylol propane, to the polycondensation of succinic acid (SA) and 1,4-butanediol and led to the increase of complex viscosities and decrease of loss tangent with the increasing of chain-branching agent content, while the thermal and mechanical properties were not reported. Chae et al.<sup>14</sup> also investigated the rheological and crystallization behaviors of long-chain branched PBA and observed increased complex viscosities and storage modulus compared with linear polymers. Jin et al.<sup>15,16</sup> examined the effect of ethyl and *n*-octyl branches on the properties of PBS and concluded that the addition of ethyl branches as well as *n*-octyl branches into PBS improved the biodegradation properties, the elongation at break, and the tear strength without notable decrease of tensile strength and tensile modulus. However, the melt viscosity of branched PBS copolymers is lower than that of linear PBS, which is unfavorable for the processing properties of PBS.

In this work, long-chain branched PBS was prepared by a two-step process containing esterification and polycondensation, and the 1,2,4-butanetriol (1,2,4-BT) is used as a multifunctional monomer to form long-chain branched structure. The effect of long-chain branches on the crystallization behaviors, rheological, and tensile properties was studied in detail, aiming at correlating chains branches structure to macroscopic properties of long-chain branched PBS.

## EXPERIMENTAL

### Materials

SA was provided by Hexing Chemical Corp. (China) and was used as received. 1,4-Butanediol (1,4-BD) was supplied by Tianjin Jinke Fine Chemical Research Institute (China), and 1,2,4-BT was provided by Shanghai Experiment Reagent Corp. (China). Tetra-*n*-butyl-titanate (Ti(OBu)<sub>4</sub>) as a

catalyst was obtained from Beijing Chemical Co. (China). Other chemicals and solvents were used as received without further purification.

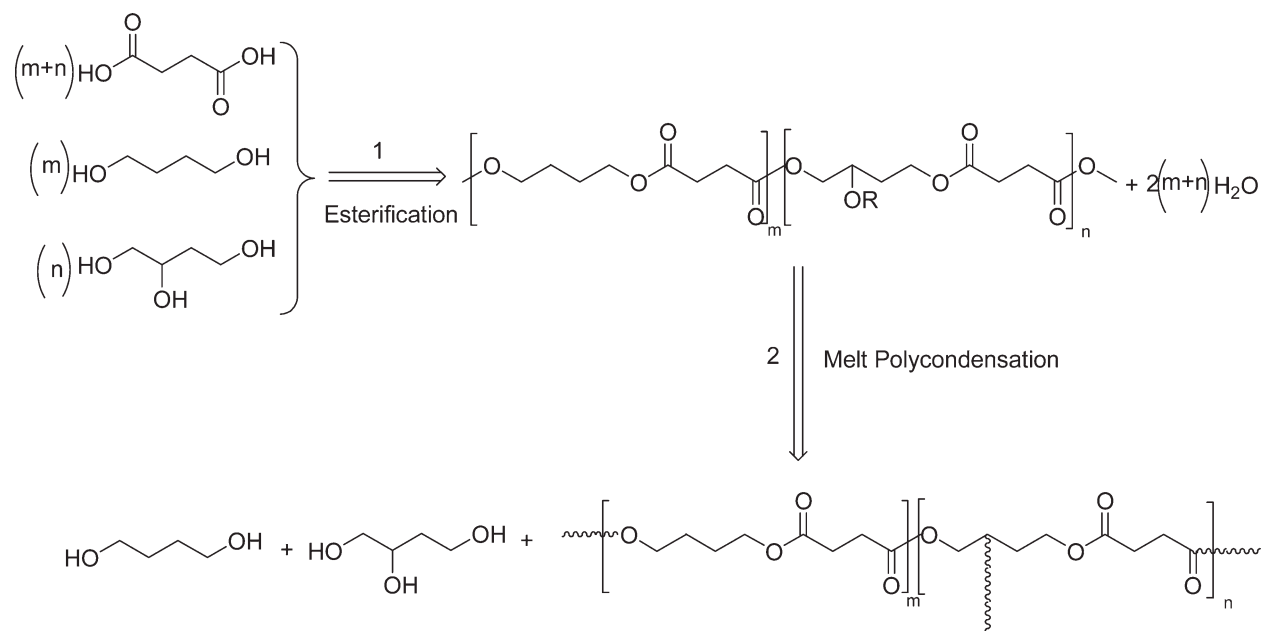
### Synthesis of samples

Linear PBS and long-chain branched PBS were synthesized through a two-step reaction of esterification and polycondensation in the melt state. As an example, the synthesis of long-chain branched PBS containing 0.5 mol % of 1,2,4-BT segments is described as follows: in the process of esterification, the reactor was a three-necked flask with a mechanical stirrer, nitrogen inlet, and a condenser in a temperature-controlled oil bath. The reaction mixtures, 1,4-BD (39.40 g, 0.4378 mol), 1,2,4-BT (0.2335 g, 0.0022 mol), and SA (47.3 g, 0.40 mol), were added into the reactor. The temperature was increased slowly to 145°C until the acid component melted completely under N<sub>2</sub> atmosphere. Water resulted from the reaction was collected using a trap device. The reaction was assumed completed when no more water was distilled out under the atmospheric pressure. The weight of H<sub>2</sub>O collected was about 95% of its theoretical maximum value. In the following polycondensation process, catalyst Ti(OBu)<sub>4</sub> was added first, and the temperature was gradually raised to the final reaction temperature of 220°C at pressure below 0.5 mm Hg and maintained at this condition for 2 h. After the polymerization, the highly viscous product was cooled in the flask under nitrogen atmosphere.

The obtained long-chain branched PBS was dissolved in chloroform and then added dropwise into ice-cold methanol. The precipitate was washed with methanol and dried in vacuum at room temperature for 24 h. All the other polyesters were synthesized following the similar procedure. The synthesized polyesters are denoted as PBSBT-0.5, PBSBT-0.75, and PBSBT-1, respectively, where "BT" in the sample code represents the 1,2,4-BT segments and the numbers following "BT" represent the mol fraction percents of 1,2,4-BT segments.

### Characterization

The number-average molecular weight ( $M_n$ ) and molecular weight distribution (MWD,  $M_w/M_n$ ) for linear PBS and long-chain branched PBS were determined by gel permeation chromatography (GPC; Waters 1515 isocratic HPLC pump, Waters 717 plus autosampler, and Waters 2414 refractive index detector) at 30°C with a calibration curve constructed using polystyrene standards. Chloroform was used as solvent and eluent with a flow rate of 1.0 mL/min. DSC experiment was performed using a Shimadzu DSC-60 differential scanning calorimeter



**Figure 1** Scheme synthesis of long-chain branched PBS.

under nitrogen atmosphere in the temperature range from 30 to 160°C. All long-chain branched PBS were scanned from 30 to 160°C (Run I), remained at 160°C for 5 min to eliminate the thermal history, and then cooled to 30°C at a rate of 10°C/min; after that, the samples were reheated to 160°C at a rate of 10°C/min (Run II). Spherulite morphology of linear PBS and long-chain branched PBS was observed using a polarizing optical microscope (Olympus BH-2). The dynamic rheological measurements of linear PBS and long-chain branched PBS were performed in an Anton Paar MCR301 stress/strain controlled rheometer, using 25-mm diameter parallel plates in oscillatory shear mode under laboratory environment at 140°C. Two different types of test were conducted: (i) the strain sweep at frequency  $\omega = 1$  rad/s, for strain,  $\varepsilon = 0.01$  to 100; (ii) the frequency sweep at  $\varepsilon = 0.5\%$  within the  $\omega$  range from 0.05 to 120 rad/s. Wide-angle X-ray diffraction (WAXD) analysis was performed at room temperature using an X-ray diffractometer (Rigaku, D/max-RB) with Cu K $\alpha$  radiation at a scanning rate of 6°C/min. The tensile properties of linear PBS and long-chain branched PBS were obtained with a Gotech tester at room temperature and at a crosshead speed of 10 mm/min according to ASTM D638. To measure the tensile properties and WAXD analysis of long-chain branched PBS and linear PBS, the synthesized long-chain branched PBS and linear PBS were molded into testing samples by the small injector (DACA instruments, Santa Barbara, CA), and the obtained samples were not only used to test tensile properties but also used to characterize the WAXD experiment.

## RESULTS AND DISCUSSION

### Synthesis of long-chain branched PBS

The synthesis of long-chain branched PBS was outlined in Figure 1. In the first step, long-chain branched PBS oligomers were obtained via esterification reaction using SA, 1,4-BD, and 1,2,4-BT, which was used as a long-chain branching agent. In the second step, the long-chain branched PBS oligomers were then mixed and went through a melt polycondensation to obtain long-chain branched PBS. The molecular weight of linear PBS and long-chain branched PBS was measured by GPC, and the data are summarized in Table I. Compared to that of linear PBS, the number-average molecular weight ( $M_n$ ) of long-chain branched PBS first increased gradually and then decreased slightly with the increasing of 1,2,4-BT segments. The molecular weight distribution curves are shown in Figure 2. It is shown that there was a small shoulder at higher molecular weight region for the samples of long-chain branched PBS. In addition, the peak height decreased with the addition of 1,2,4-BT segments. The reason of widened molecular weight distribution is likely due to the existence of long-chain branches.<sup>17</sup>

### Crystallization behaviors of long-chain branched PBS

DSC was used to evaluate the crystallization and thermal properties of linear PBS and long-chain branched PBS. The first heating, the cooling, and the subsequent reheating curves are shown in Figure 3.

**TABLE I**  
**The Molecular Weight and Thermal Parameters of Linear PBS and Long-Chain Branched PBS**

Sample	$M_w$ ( $\times 10^4$ g/mol)	$M_n$ ( $\times 10^4$ g/mol)	$M_w/M_n$	$T_m$ ( $^{\circ}$ C)		$\Delta H_m$ (J/g) run I/run II	$T_c$ ( $^{\circ}$ C)	$T_g$ ( $^{\circ}$ C) <sup>a</sup>	$X_c$ (%)
				Run I/run II	Run I/run II				
PBS	14.2	4.8	2.95	115.2/114.1	96.8/76.9	73.5	-31.8	69.9	
PBSBT-0.5	15.7	5.0	3.12	115.2/114.3	67.7/56.1	72.3	-31.5	50.8	
PBSBT-0.75	19.8	5.2	3.84	116.2/114.4	82.7/57.9	74.5	-27.7	52.4	
PBSBT-1	12.8	4.5	2.83	115.1/113.9	80.9/54.8	78.2	-29.9	49.6	

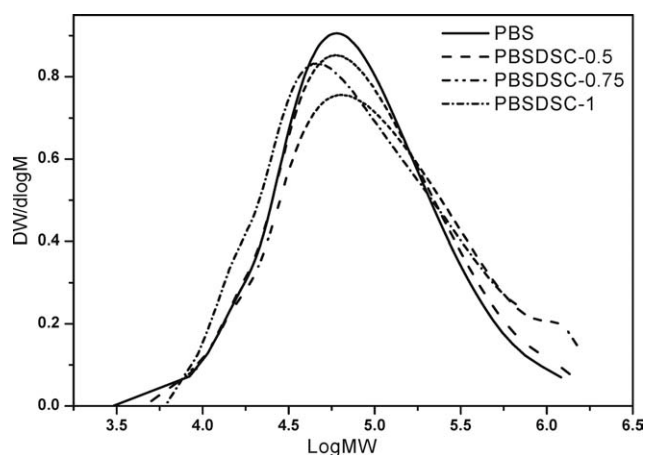
<sup>a</sup> Determinated by dynamic-mechanical thermal analyzer (Anton Paar, MCR301) with a strain of 0.1%, the temperature range was between  $-80^{\circ}$ C and  $60^{\circ}$ C with a heating rate of  $2^{\circ}$ C/min.

The obtained thermal parameters including the melting temperatures ( $T_m$ ), crystallization temperatures ( $T_c$ ), glass transition temperatures ( $T_g$ ), the enthalpies of melting ( $\Delta H_m$ ), and the relative crystallization degree ( $X_c$ ) are summarized in Table I. From Figure 3 and Table I, it can be seen that the addition of 1,2,4-BT segments has almost no effect on  $T_m$ . The linear PBS exhibits a single cooling exothermic peak at  $73.5^{\circ}$ C, while the value of  $T_c$  of long-chain branched PBS first decreases slightly and then increases with the increasing of 1,2,4-BT segments loading. This enhancing effects become more and more significant with the increasing of 1,2,4-BT segments content and suggest that the long-chains branches are beneficial to the enhancement of crystallization temperature and acceleration of crystallizability. The above results can be interpreted that the addition of higher content of 1,2,4-BT segments can produce more branching points, which served as nucleating agents during the crystallization process. Similar results have been reported by other researchers.<sup>18,19</sup>

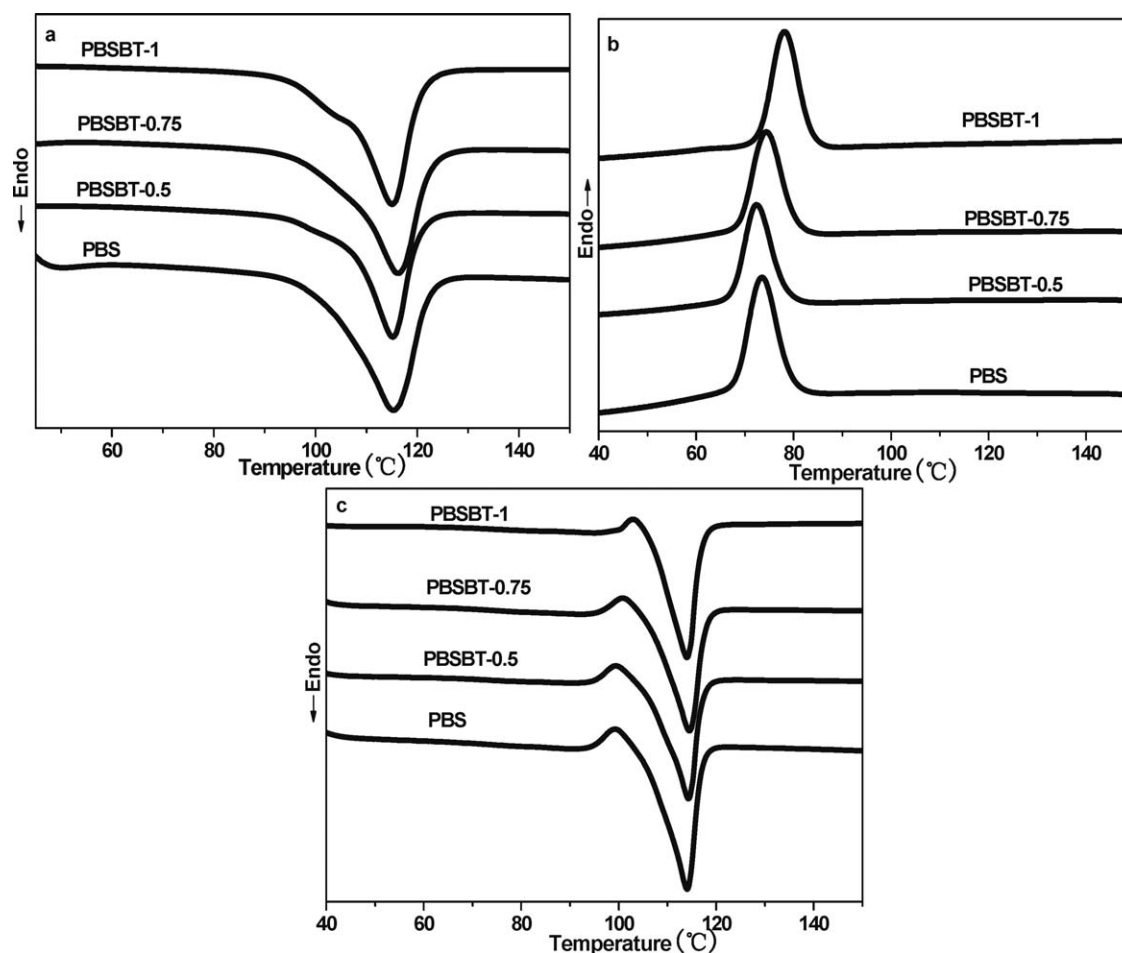
From Table I, it is shown that the glass transition temperature ( $T_g$ ) of long-chain branched PBS increases significantly with the addition of 1,2,4-BT segments and indicated that a decrease in the chain segments mobility because of the existence of long-chain branches. From Figure 3(c), it can be seen that long-chain branches have little effect on  $T_m$  of linear PBS. In addition, the melting peak of long-chain branched PBS is sharper than that of linear PBS as shown in Figure 3(c), suggesting that the crystals in long-chain branched PBS are more regular than those of linear PBS. It is also shown that the value of  $X_c$  of long-chain branched PBS is lower than that of linear PBS, and it is decreased with the increasing of 1,2,4-BT segments content, indicating that the long-chain branches may affect the structural regularity of PBS chains and resulting in the decrease of  $X_c$  of long-chain branched PBS. Also, it is necessary to study the effect of 1,2,4-BT segments on the crystal structure of linear PBS. The X-ray diffractograms of linear PBS and long-chain branched PBS are shown in Figure 4. It is clear that long-chain branched PBS exhibits the same diffractions peak locations as those

of linear PBS, suggesting that the addition of 1,2,4-BT segments does not affect the crystal structure of linear PBS, and the 1,2,4-BT segments are excluded from the crystalline region of the lamellae in the crystallized polyesters. The main diffraction peaks appear at  $2\theta = 19.61^{\circ}$ ,  $22.18^{\circ}$ , and  $22.67^{\circ}$ , assigned to (020), (021), and (110) planes of  $\alpha$ -form crystal of PBS, respectively.<sup>20</sup> In addition, from Figure 4, it is also shown that the peak intensity changes with the increasing of long-chain branches content. The reason for this can be probably due to the testing samples preparation such as sample orientation, samples size, and sample surface rough, which will affect the peak intensity of long-chain branched PBS in the WAXD curve.

The above DSC and WAXD results suggest that the crystallizability of linear PBS can be enhanced with the incorporation of 1,2,4-BT segments. Also, the addition of 1,2,4-BT segments has little effect on the crystal of linear PBS. It is necessary to further research the effect of long-chain branches on the spherulite morphology of linear PBS at different crystallization temperature. Figure 5 shows the typical polarized optical micrographs of linear PBS and long-chain branched PBS after melt-crystallization at three different temperatures. From Figure 5(a), it is shown that for linear PBS after melt-crystallized at



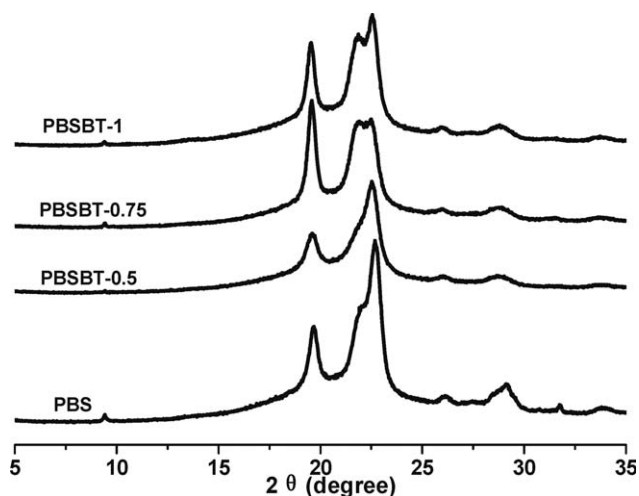
**Figure 2** MWD curves of linear PBS and long-chain branched PBS.



**Figure 3** DSC thermograms of linear PBS and long-chain branched PBS with different content of 1,2,4-BT segments. (a) The first heating curves, (b) the cooling curves, and (c) the second heating curves.

75°C, the small spherulites with an apparent Maltese cross was formed owing to the large supercooling degree and fast crystallization rate. When the crystallization temperature increase to 85°C, the large spherulites were found due to the small supercool-

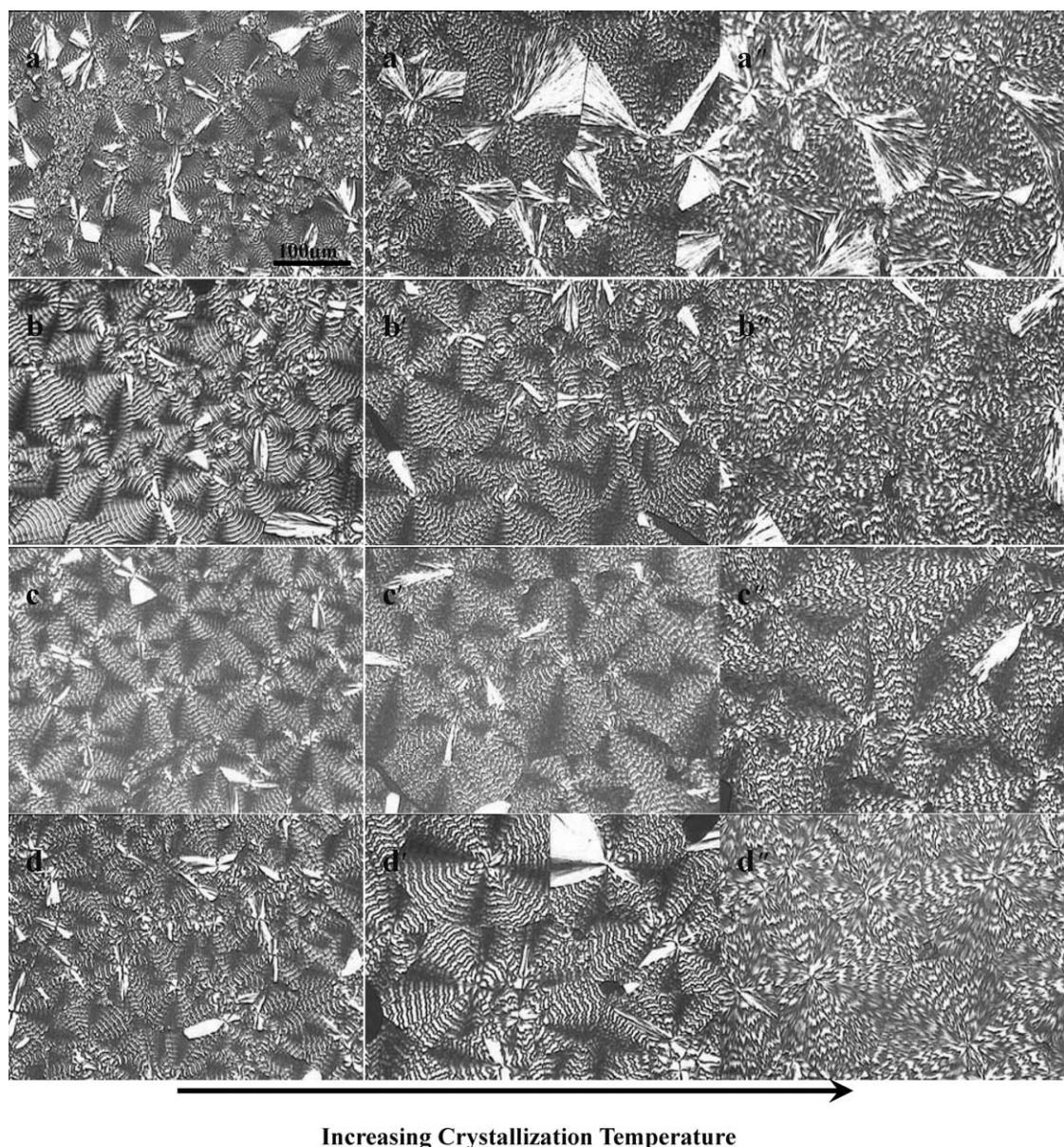
ing degree, the double-banded extinction patterns with periodic distance along the radial direction were observed in the spherulites of linear PBS and long-chain branched PBS at all measured crystallization temperatures. In addition, the banded distance increases with the increasing of crystallization temperature. Although the long-chain branches have a different influence on the spherulites morphology when compared with linear PBS, for example, the banded spherulites of long-chain branched PBS are more regular than those of linear PBS at the same crystallization temperature, also, the formation of banded/ringed spherulites is generally ascribed to the lamellar twisting in the direction of radical growth.<sup>21,22</sup> The origin of lamellar twisting of branched PBS will be investigated in the further work.



**Figure 4** X-ray diffractograms of linear PBS and long-chain branched PBS.

**Rheological properties of long-chain branched PBS**

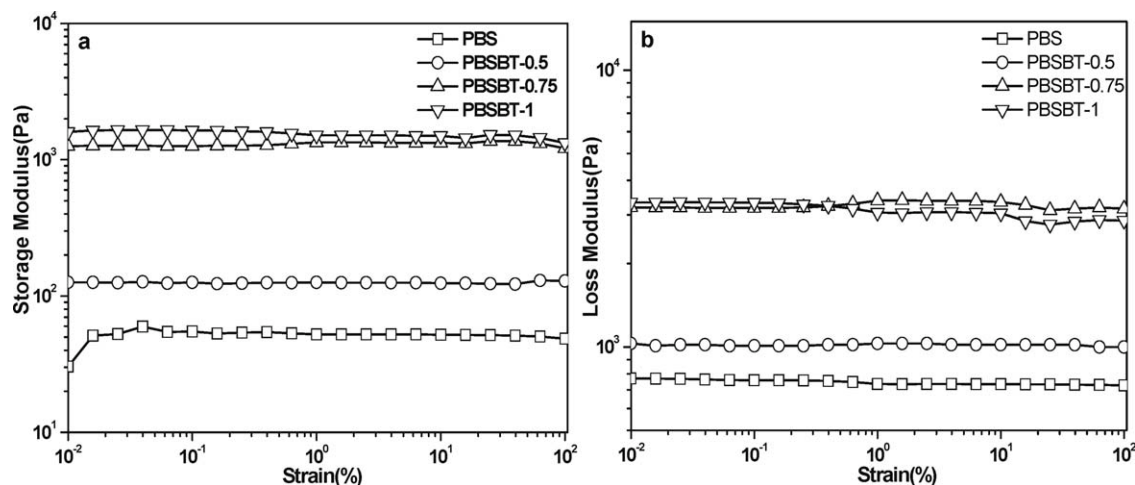
The effect of 1,2,4-BT segments on the structural change of long-chain branched PBS with varying strain amplitude was investigated to characterize the linear viscoelastic regime and the strain-dependent



**Figure 5** The crystalline morphology of linear PBS and long-chain branched PBS after melt-crystallized at 75°C, 80°C, and 85°C: (a) linear PBS, (b) PBST-0.5, (c) PBST-0.75, and (d) PBST-1. The scale bar is 100  $\mu\text{m}$ .

viscoelastic properties of these samples. The storage modulus ( $G'$ ) and loss modulus ( $G''$ ) as a function of strain at  $\omega = 1$  rad/s for linear PBS and long-chain branched PBS are shown in Figure 6(a,b), respectively. It is shown that the moduli of long-chain branched PBS consistently increase with the incorporation of 1,2,4-BT segments, indicating that the addition of 1,2,4-BT segments can increase the stiffness of linear PBS, resulting in the improvement in moduli values. In addition, the 1,2,4-BT segments have almost no effect on the onset of nonlinear viscoelastic region when compared with the linear PBS, presenting that both linear PBS and long-chain branched PBS have a relative wide linear viscoelastic region.

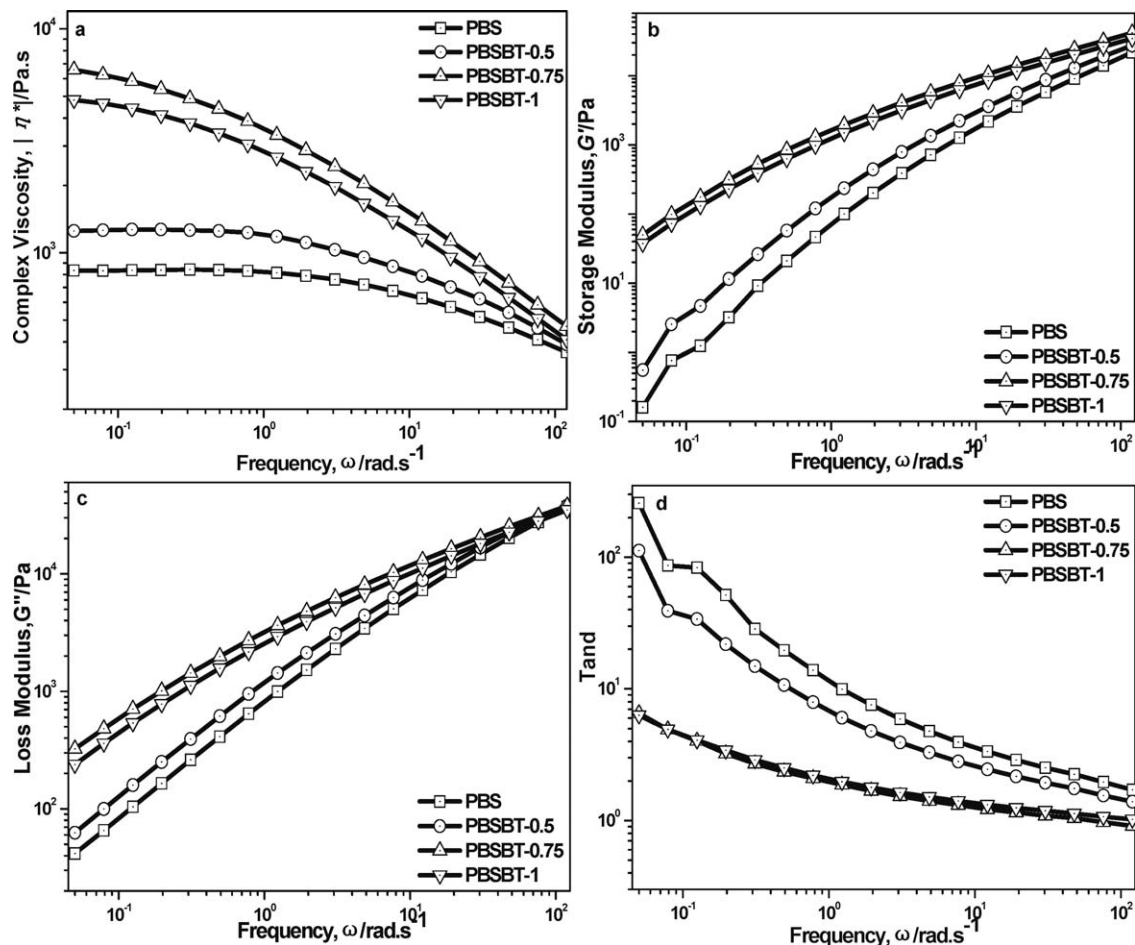
The complex viscosity ( $|\eta^*|$ ), storage modulus ( $G'$ ), loss modulus ( $G''$ ), and damping factor ( $\tan \delta$ ) as a function of frequency for a typical response are shown in Figure 7. The values of  $|\eta^*|$  of linear PBS and long-chain branched PBS are decreased with increasing frequency, indicating a non-Newtonian behavior and pseudoplastic characteristics over the entire testing frequency range. Also, the incorporation of a small quantity of 1,2,4-BT segments into PBS matrix increase the value of  $|\eta^*|$  compared to linear PBS, especially at low frequency, and shown that the existence of more entanglement of long-chain branches leads to the longer relaxation mechanism. Also, the  $|\eta^*|$  values of long-chain branched PBS increase at first and then slightly decrease with



**Figure 6** Dynamic storage modulus ( $G'$ ) (a) and loss modulus ( $G''$ ); (b) versus strain of linear PBS and long-chain branched PBS.

the increasing of 1,2,4-BT segments content, suggesting that the addition of excessive 1,2,4-BT segments concentration is not favorable for long-chain branching reaction, as it will result in low branching level. The shear thinning of long-chain branched PBS starts

at lower frequency than that of linear PBS and becomes more and more apparent with the increasing of 1,2,4-BT segments content, indicating that a large number of long-chain branches existed in the backbone of PBS. Although at high frequency, long-



**Figure 7** Dynamic complex viscosity ( $|\eta^*|$ ) (a), storage modulus ( $G'$ ) (b), loss modulus ( $G''$ ) (c), and damping factor ( $\tan \delta$ ) (d) as a function of frequency of linear PBS and long-chain branched PBS.

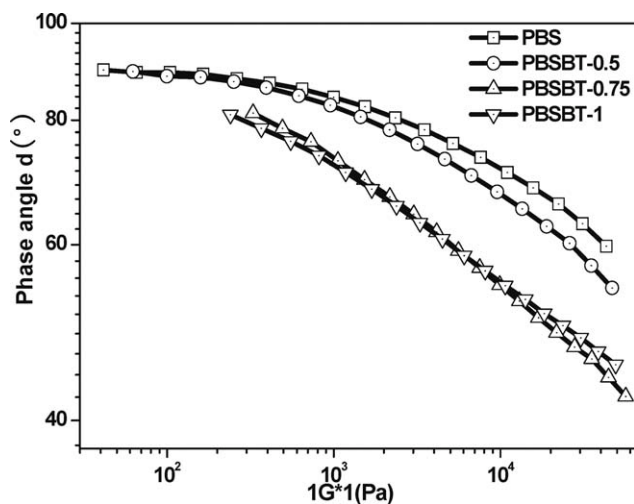
**TABLE II**  
Variations of Low Frequency Slopes of  $|\eta^*|$ ,  $G'$ , and  $G''$  Versus  $\omega$  of Linear PBS and Long-Chain Branched PBS

Samples	Slope of $ \eta^* $ versus $\omega$	Slope of $G'$ versus $\omega$	Slope of $G''$ versus $\omega$
PBS	0.0007	1.99	1.00
PBSBT-0.5	-0.0056	1.88	0.99
PBSBT-0.75	-0.192	1.19	0.77
PBSBT-1	-0.167	1.18	0.80

chain branched PBS exhibit similar complex viscosity when compared with linear PBS owing to a higher degree of shear thinning behaviors. Similar results have been reported that long-chain branched PP have a higher viscosity and more distinct shear thinning behavior than its linear counterpart.<sup>23,24</sup>

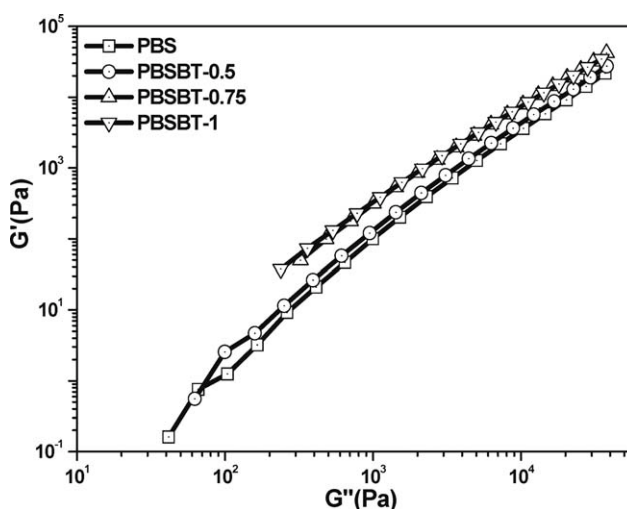
In addition to the complex viscosity, other properties including  $G'$  and  $G''$  were also influenced by long-chain branches.  $G'$  and  $G''$  of linear PBS and long-chain branched PBS as a function of frequency are plotted in Figure 7(b,c). The incorporation of 1,2,4-BT segments has a distinct effect on the rheological behaviors, even at loading level as low as 0.5 mol %. The values of  $G'$  and  $G''$  of long-chain branched PBS are significantly improved compared to linear PBS, especially at low frequency, indicating that the truly existence of the long-chain branches and resulting in the longer relaxation time of their chains. The slopes of the terminal zone of  $G'$  and  $G''$  for long-chain branched PBS are shown in Table II. Linear PBS exhibits the typical terminal flow behaviors, while long-chain branched PBS deviate from the terminal behaviors. The decrease in the slopes of  $G'$  and  $G''$  for long-chain branched PBS with the increasing of 1,2,4-BT segments content, for example, the terminal slope of  $G'$  decreases from 1.99 of linear PBS to 1.18 of PBSBT-1 (Table II), which can be ascribed to the existence of long-chain branches in the PBS chains, resulting in the increased dynamic moduli at low frequency and the longer relaxation mechanism of their chains. It is also shown that the increasing degree in  $G'$  of long-chain branched PBS is higher than that of  $G''$  over whole frequency range, resulting in more elasticity than that of linear PBS.

The variation of  $\tan \delta$  with frequency for long-chain branched PBS is shown in Figure 7(d). From Figure 7(d), it is shown that for linear PBS, the  $\tan \delta$  values rapidly decrease as the frequency increased, and this indicated that a typical terminal behavior of liquid-like material for the linear chains structure. Although with the addition of 1,2,4-BT segments, the value of  $\tan \delta$  decreases obviously at low frequency, which was much lower than that of linear PBS, indicating that the long-chain branches have formed in



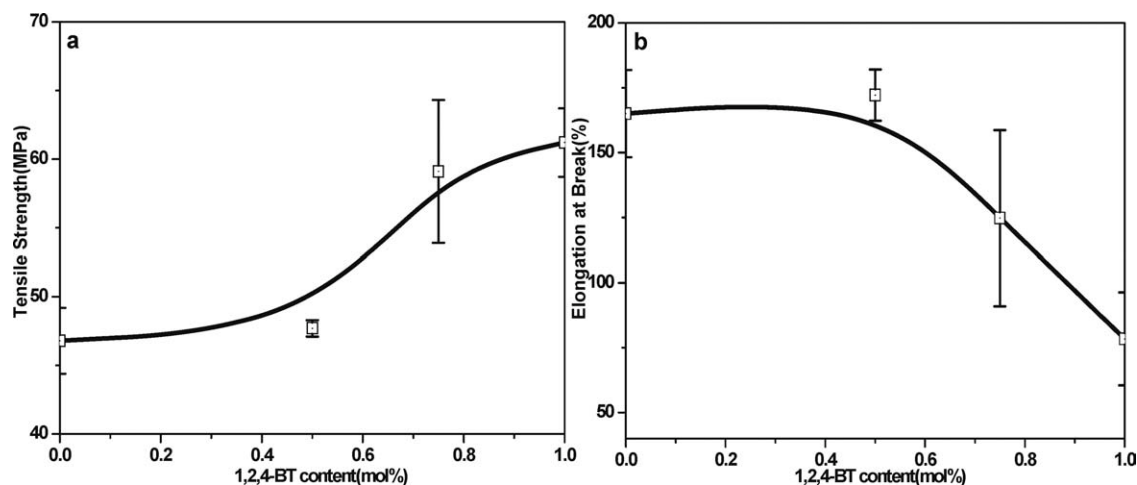
**Figure 8** Plots of phase angle versus complex modulus of linear PBS and long-chain branched PBS.

the backbone of PBS. Similar results have been reported by Graebing<sup>25</sup> and Tang,<sup>26</sup> who explained this result as the grafting of long-chain branches onto PP skeleton and increasing the terminal relaxation time. The plots of the phase angle versus the absolute value of complex modulus for long-chain branched PBS, which is known as the Van Gurp–Palmen plot, are shown in Figure 8. It is clear that long-chain branched PBS exhibited smaller phase angle values in the whole scope of measurement when compared with linear PBS and shown that the long-chain branches did exist in their backbone, and the elastic properties was improved with the addition of 1,2,4-BT segments. Hatzikiriakos et al.<sup>27</sup> have found that the Van Gurp curve shifts to a smaller value of the phase angle with the increasing of LCB content in polyethylene. Meanwhile, it is found that the



**Figure 9** Plots of  $G'$  and  $G''$  for linear PBS and long-chain branched PBS.





**Figure 10** The tensile properties of linear PBS and long-chain branched PBS with different content of 1,2,4-BT segments.

decreasing degree of Van Gurp plots increased initially and then decreased with the 1,2,4-BT segments content increased, suggesting that the amount of long-chain branches level increased at first and then decreased with the increasing of 1,2,4-BT segments loadings.

The values of  $G'$  and  $G''$  for long-chain branched PBS were higher than those of linear PBS, and this reinforcement effect was more significant with the increasing of 1,2,4-BT segments content, and the Cole–Cole plots of linear PBS and long-chain branched PBS are shown in Figure 9. Generally, if the polymer melt is isotropic and homogeneous, the Cole–Cole plot provides a master curve with a slope of 2, irrespective of temperature.<sup>28</sup> The long-chain branched PBS exhibit the shifting and change of the slope of the plot with the incorporation of 1,2,4-BT segments. The slopes in the terminal regime of long-chain branched PBS were less than 2 (1.69, 1.45, and 1.40, respectively), indicating that a long relaxation mechanism occurred in long-chain branched samples. In addition, when the 1,2,4-BT segments content attain to 1 mol %, the slope of long-chain branched PBS is lower than that of linear PBS and others, presenting the existence of good interfacial interactions between PBS and 1,2,4-BT segments. On the other hand, when the  $G''$  value is over  $10^4$ , the slopes of long-chain branched PBS increase and attain to the similar slope of linear PBS, indicating long-chain branches have almost no effect on the relaxation mechanism of PBS.

#### Tensile properties of long-chain branched PBS

The effect of mol fraction of 1,2,4-BT segments on the tensile properties of linear PBS is shown in Figure 10. From Figure 10(a), it is shown that long-chain branched PBS exhibits higher tensile strength than that of linear PBS and increases gradually with

increasing the 1,2,4-BT segments content. Upon addition of 1 mol % 1,2,4-BT segments, long-chain branched PBS can have a tensile strength by 31% higher than the linear PBS, indicating that long-chain branches can enhance the stiffness of linear PBS. From Figure 10(b), it can be seen that the elongation at break of long-chain branched PBS is lower than that of linear PBS and decreases gradually as the concentration of 1,2,4-BT segments increased. The above results showed that the long-chain branches can enhance the tensile strength of linear PBS; however, the elongation at break decreases gradually with the increasing of 1,2,4-BT segments content. The reason of enhanced tensile properties is probably due to the existence of long-chain branches structure.

#### CONCLUSIONS

In this study, long-chain branched PBS were synthesized by a two-step process of esterification and polycondensation in the presence of a long-chain branching agent, 1,2,4-BT. The crystallization behaviors, rheological properties, and tensile properties of long-chain branched PBS were investigated in detail. The main results were summarized as follows:

1. The introduction of 1,2,4-BT segments can increase the crystallization temperature, glass transition temperature, while decrease the relative crystallinity of linear PBS. Besides the normal extinction crosses, the double-banded extinction patterns are observed in the spherulites of linear PBS and long-chain branched PBS. In addition, the crystal pattern of linear PBS is not affected with the addition of 1,2,4-BT segments.
2. The 1,2,4-BT segments have a distinct effect on the rheological behaviors of linear PBS. The

rheological characteristics such as higher  $|\eta^*|$ ,  $G'$ , and  $G''$  at low frequency, lower  $\tan \delta-\omega$  plot, the lower values of the phase angle versus  $G^*$  in the Van Gurp plots, deviating from the scaling  $G'-G''$  of linear PBS in Cole-Cole plot were found in long-chain branched PBS, the different relaxation mechanism of long-chain branched PBS is the reason for this.

- The addition of 1,2,4-BT segments can enhance the tensile strength of linear PBS, that is, with the addition of 1 mol % 1,2,4-BT segments, and the tensile strength of long-chain branched PBS is improved by 31% when compared with linear PBS.

## References

- Shih, Y. F.; Chen, L. S.; Jeng, R. J. *Polymer* 2008, 49, 4602.
- Fujimaki, T. *Polym Degrad Stab* 1998, 59, 209.
- Pan, P. J.; Ionue, Y. S. *Prog Polym Sci* 2009, 34, 605.
- Zhao, J. B.; Li, K. Y.; Yang, W. T. *J Appl Polym Sci* 2007, 106, 590.
- Zhao, J. B.; Wu, X. F.; Yang, W. T. *J Appl Polym Sci* 2004, 92, 3333.
- Huang, C. Q.; Luo, S. Y.; Xu, S. Y.; Zhao, J. B.; Liang, S. L.; Yang, W. T. *J Appl Polym Sci* 2010, 115, 1555.
- Mckee, M. G.; Unal, S.; Wilkes, G. L.; Long, T. E. *Prog Polym Sci* 2005, 30, 507.
- Shroff, R. N.; Mavridis, H. *Macromolecules* 1999, 32, 8454.
- WoodAdams, P. M.; Dealy, J. M. *Macromolecules* 2000, 33, 7489.
- Nagata, M.; Ibuki, H.; Sakai, W.; Tsutsumi, N. *Macromolecules* 1997, 30, 6525.
- Malmberg, A.; Kokko, E.; Lehmus, P.; Löfgren, B.; Seppälä, J. V. *Macromolecules* 1998, 31, 8448.
- Bikiaris, D. N.; Karayannidis, G. P. *Polym Int* 2003, 52, 1230.
- Kim, E. K.; Bae, J. S.; Im, S. S.; Kim, B. C.; Han, Y. K. *J Appl Polym Sci* 2001, 80, 1388.
- Chae, H. G.; Kim, B. C.; Im, S. S.; Han, Y. K. *Polym Eng Sci* 2001, 41, 1133.
- Jin, H. J.; Park, J. K.; Park, K. H.; Kim, M. N.; Yoon, J. S. *J Appl Polym Sci* 2000, 77, 547.
- Kim, M. N.; Kim, K. H.; Jin, H. J.; Park, J. K.; Yoon, J. S. *Eur Polym J* 2001, 37, 1843.
- Li, S. Z.; Xiao, M. M.; Wei, D. F.; Xiao, H. N.; Hu, F. Z.; Zheng, A. N. *Polymer* 2009, 50, 6121.
- Nam, G. J.; Yoo, J. H.; Lee, J. W. *J Appl Polym Sci* 2005, 96, 1793.
- Su, F. H.; Huang, H. X. *J Appl Polym Sci* 2009, 113, 2126.
- Ihn, K. J.; Yoo, E. S.; Im, S. S. *Macromolecules* 1995, 28, 2460.
- Xu, Y. X.; Xu, J.; Liu, D. H.; Guo, B. H.; Xie, X. M. *J Appl Polym Sci* 2008, 109, 1881.
- Lim, J. S.; Lee, Y. I.; Im, S. S. *J Polym Sci Part B: Polym Phys* 2008, 46, 925.
- Su, F. H.; Huang, H. X. *J Appl Polym Sci* 2010, 116, 2557.
- Su, F. H.; Huang, H. X. *Adv Polym Technol* 2009, 28, 16.
- Graebling, D. *Macromolecules* 2002, 35, 4602.
- Zhang, Z. J.; Xing, H. P.; Qiu, J.; Jiang, Z. W.; Yu, H. O.; Du, X. H.; Wang, Y. H.; Ma, L.; Tang, T. *Polymer* 2010, 51, 1593.
- Hatzikiriakos, S. G. *Polym Eng Sci* 2000, 40, 2279.
- Han, C. D.; Kim, J.; Kim, J. K. *Macromolecules* 1989, 22, 383.