

# The Rheological Behavior and Dynamic Mechanical Properties of Syndiotactic 1,2-Polybutadiene

Xiaofeng He,<sup>1</sup> Guangping Sun,<sup>1</sup> Jing Li,<sup>2</sup> Biao Wang,<sup>1</sup> Min Li,<sup>1</sup> Jingjiang Liu,<sup>3</sup> Jifu Bi,<sup>3</sup> Liansheng Jiang,<sup>3</sup> Xuequan Zhang<sup>3</sup>

<sup>1</sup>Key Laboratory of Automobile Materials Ministry of Education, Department of Materials Science and Engineering, Jilin University, Changchun 130025, People's Republic of China

<sup>2</sup>Teda Bio-X Research Center, College of Food Engineering and Biotechnology, Tianjin University of Science and Technology, Tianjin 300457, People's Republic of China

<sup>3</sup>State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

Received 12 October 2006; accepted 30 January 2007

DOI 10.1002/app.26439

Published online 8 May 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The rheological behavior and the dynamic mechanical properties of syndiotactic 1,2-polybutadiene (sPB) were investigated by a rotational rheometer (MCR-300) and a dynamic mechanical analyzer (DMA-242C). Rheological behavior of sPB-830, a sPB with crystalline degree of 20.1% and syndiotactic content of 65.1%, showed that storage modulus ( $G'$ ) and loss modulus ( $G''$ ) decreased, and the zero shear viscosity ( $\eta_0$ ) decreased slightly with increasing temperature when measuring temperatures were lower than 160°C. However,  $G'$  and  $G''$  increased at the end region of relaxation curves with increasing temperature and  $\eta_0$  increased with increasing temperature as the measuring

temperatures were higher than 160°C. Furthermore, critical crosslinked reaction temperature was detected at about 160°C for sPB-830. The crosslinked reaction was not detected when test temperature was lower than 150°C for measuring the dynamic mechanical properties of sample. The relationship between processing temperature and crosslinked reaction was proposed for the sPB-830 sample. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2468–2473, 2007

**Key words:** syndiotactic 1,2-polybutadiene; zero shear viscosity; dynamic mechanical properties; crosslinked reaction

## INTRODUCTION

Since syndiotactic 1,2-polybutadiene (sPB) was synthesized in 1955, considerable concerns have been aroused both industry and academia, but most research works were focused on polymer synthesis.<sup>1–3</sup> Only a few works were on the physical properties, Yang et al.<sup>4,5</sup> investigated the single crystal and morphological structure of sPB. Mo and co-workers<sup>6</sup> reported the crystallization and melting behavior of sPB. However, the rheological behavior and the dynamic mechanical properties have rarely been reported. It is well-known that the macromolecules are very easy to crosslinked at high temperature due to the abundant double bonds on the side chain, specially for highly sPB (melting temperature  $T_m = 204^\circ\text{C}$ ).<sup>7</sup> When  $T_m$  ( $>200^\circ\text{C}$ ) of the polymers is high, the amorphous region has already been crosslinked before the crystal region is melted. Thus, it is very difficult to investigate the developing structure

of this polymer. The properties of sPB are correlated with its syndiotactic content. Polymers with lower syndiotactic content show properties of characteristic elastomer, but that with higher syndiotactic content is a semicrystalline plastic, its crystallization plane is the  $\text{Pacm}^8$  space group which builds as the denticle orthogonal chain.

Since the rheological behavior and the dynamic mechanical properties of sPB are closely correlated with the experimental condition of material. As for sPB, it may present thermoplastic characteristic or thermosetting characteristic through choosing different experimental condition. In this paper, to propose the relationship between experimental temperature and crosslinked reaction, the rheological behavior and the dynamic mechanical properties of sPB were investigated by a rotational rheometer (MCR-300) and a dynamic mechanics analyzer (DMA-242C), respectively.

Correspondence to: J. J. Liu (jjliu@ciac.jl.cn).

Contract grant sponsor: Chinese Nation Science Foundation; contract grant number: 20274046.

## EXPERIMENTAL

### Materials and sample preparation

sPB with less crystalline content (sPB-830) was developed by Japan Synthetic Rubber and sPB with

*Journal of Applied Polymer Science*, Vol. 105, 2468–2473 (2007)  
© 2007 Wiley Periodicals, Inc.

**TABLE I**  
Parameters of Syndiotactic 1,2-Polybutadienes

Code	$M_w$ ( $10^5$ )	$M_w/M_n$	$X_c$ (%)	$T_m$ ( $^{\circ}\text{C}$ )	Syndiotactic content (%)
sPB-830	1.4	2.1	20.1	105	65.1
sPB-9	6.9	2.8	72.9	171	82.8

higher crystalline content (sPB-9) was synthesized by own laboratory. The main physical parameters of sample were listed in Table I.

The degree of crystallinity ( $X_c$ ) and the melting temperature ( $T_m$ ) were tested by DSC. The consummate crystalline enthalpy of sPB is 60.7 J/g.<sup>9</sup> The syndiotactic content of sample was determined with NMR.<sup>10</sup>

Film samples with thickness of about 1 and 0.6 mm for rheology tests and DMA tests were prepared by compression molding at 120 $^{\circ}\text{C}$  (sPB-830) and 180 $^{\circ}\text{C}$  (sPB-9), with a pressure of 15 MPa, then cooled to room temperature in the air under the pressure.

### Properties test

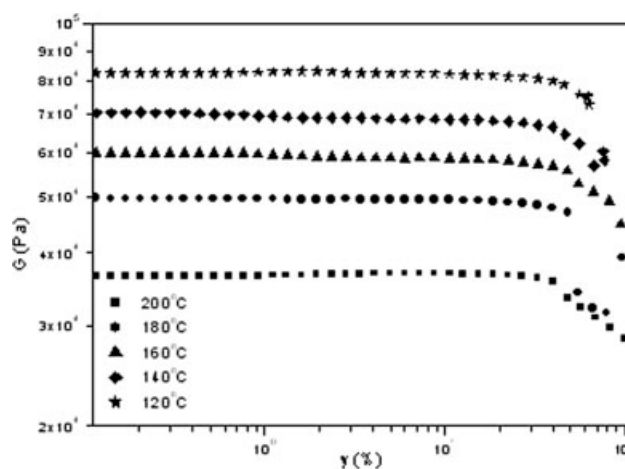
Rheological measurement was performed with a paar physica rotational rheometer (MCR 300) using 25 mm parallel geometry with a fixed plate-plate gap of 0.8 mm. Angle frequency range from 0.1 to 100 rad/s and shear rate range from 0.01 to 100  $\text{s}^{-1}$  were used for dynamic and steady state shearing measurements, respectively. All the tests were run under nitrogen atmosphere. The measurements of dynamic mechanical properties were made using a dynamic mechanics analyzer (DMA-242C) (Netzsh) on rectangular specimens of the following dimensions: length 20 mm, width 4 mm, and thickness around 0.6 mm. The measurements were made at different frequency (2, 5, 10, 20, 33 Hz, respectively) with the largest oscillation amplitude of 120  $\mu\text{m}$  and the largest oscillation force of 3 N. The temperature dependences of storage tensile modulus  $E'$ , loss modulus  $E''$ , and loss tangent ( $\tan \delta$ ) were measured from -150 to 150 $^{\circ}\text{C}$  at a heating rate of 2 $^{\circ}\text{C}/\text{min}$  under nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Rheological properties

#### Linear viscoelasticity

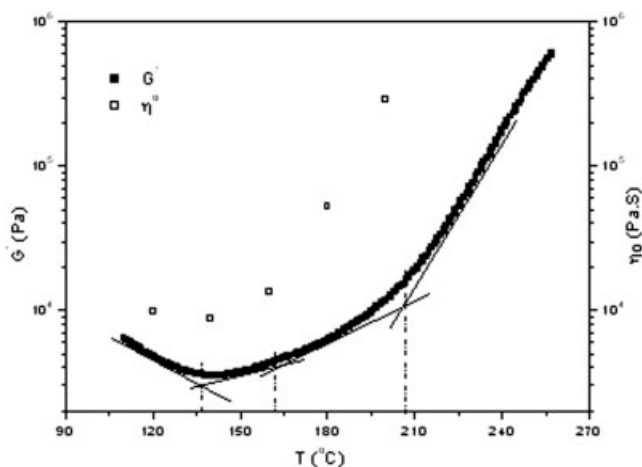
The plots of  $G'$  versus amplitude for sPB-830 1,2-polybutadiene at different temperatures are shown in Figure 1. The storage modulus ( $G'$ ) almost remains constant when the amplitude is less than



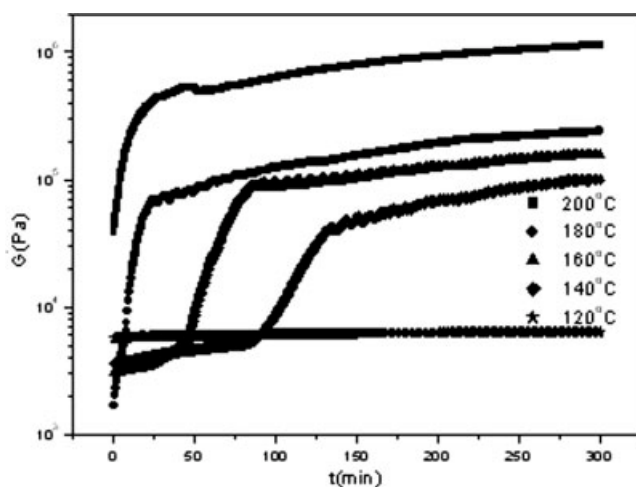
**Figure 1** The plots of  $G'$  versus amplitude for sPB-830 at different temperatures.

20%, the strain value of 5% was consequently chosen in present the study to ensure that the linear viscoelastic test of polymer was in its linear viscoelasticity region.

The storage module ( $G'$ ) and the zero shear viscosity ( $\eta_0$ ) of syndiotactic 1,2-polybutadiene (sPB-830) as a function of temperature are shown in Figure 2. The heating rate and shear rate were 4 $^{\circ}\text{C}/\text{min}$  and 10 rad/s, respectively. Obviously, the value of  $G'$  and  $\eta_0$  firstly decreased and then increased with temperature increase. Three crosslinking reaction temperatures for this experiment were detected as shown in Figure 2, the temperature of 137 $^{\circ}\text{C}$  can be defined as initial crosslinking temperature, the temperature of 160 $^{\circ}\text{C}$  is crosslinking reaction temperature, the temperature of 207 $^{\circ}\text{C}$  is rapidly crosslinking reaction temperature. The zero shear viscosity ( $\eta_0$ )



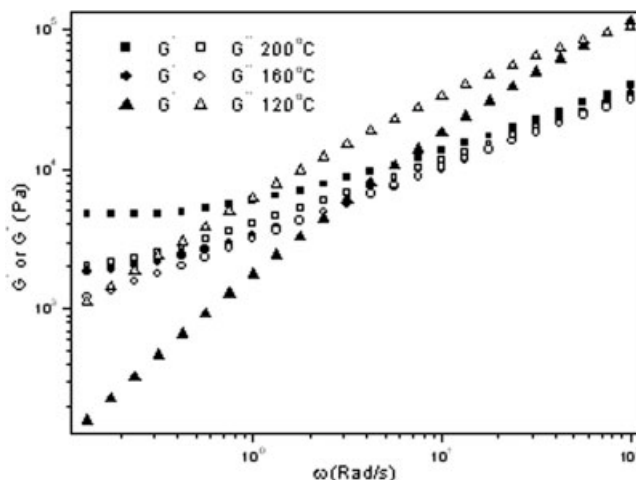
**Figure 2** The plots of  $\log G'$  and  $\eta_0$  versus temperature for sPB-830.



**Figure 3** Variation of  $G'$  during the oscillation time sweeps for sPB-830 at an angular frequency of 10 rad/s at different temperatures.

has also the same trends process along with temperature change.

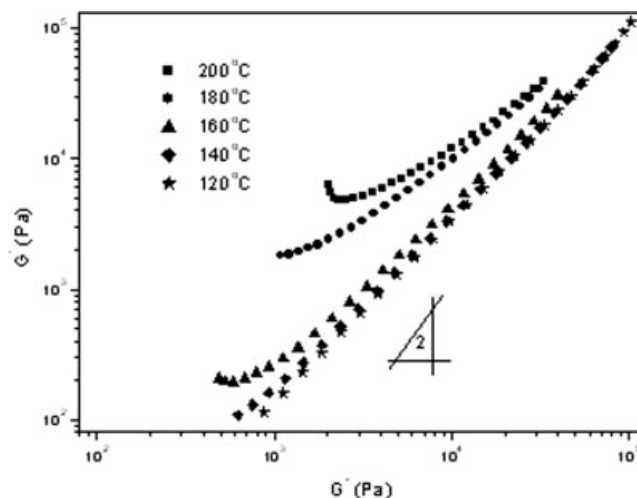
Figure 3 gives the time sweeps under oscillation shearing for sPB-830 at different temperatures. Obviously, the storage modulus ( $G'$ ) almost remains constant over the time at 120°C. At 140°C, the value of  $G'$  also remains constant for 80 min, after that,  $G'$  rapidly increases, and then, it steadily increases as time prolonging. The process at 160°C is the same trends to that of at 140°C, only  $G'$  remains constant for 25 min. When the temperatures are higher than 160°C, such as 180°C and 200°C, the value of  $G'$  rapidly increases firstly and steadily increases as time prolonging. In conclusion, when the temperatures are lower than 160°C, the material viscoelasticity is stable in 25 min.



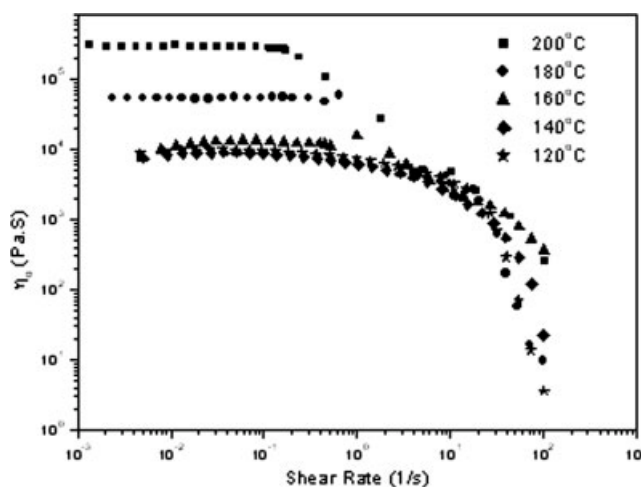
**Figure 4** The plots of  $\log G'$  and  $\log G''$  versus angular frequency  $\omega$  for sPB-830 at different temperatures.

The linear viscoelastic response as measured by storage module ( $G'$ ) and loss module ( $G''$ ) for sPB-830 is shown in Figure 4. It is known that  $G'$  and  $G''$  represent elastic and viscous responses of the polymer, respectively. When temperatures are lower than 160°C (140°C are not shown here for abbreviation), the polymer exhibits a viscoelastic liquid (where  $G' < G''$ ) in the low frequency region, and a viscoelastic solid (where  $G' > G''$ ) in the high frequency region. Storage module ( $G'$ ) and loss module ( $G''$ ) are almost overlapped over all range of frequencies at 160°C, and most range of frequencies at temperatures higher than 160°C (220°C are not shown here for abbreviation), the  $G'$  value is greater than the  $G''$  value and no intersection of the two module is found, which suggest that sPB-830 exhibits viscoelastic solid characteristics.

According to linear viscoelasticity theory, storage module ( $G'$ ) and loss module ( $G''$ ) of thermosplastic polymer increase monotonously with frequency in a given temperature. The intersection of the two modulus ( $G'$ ,  $G''$ ) is usually associated with relaxation characteristic of polymer chains, characteristic relaxation time:  $\tau = 1/\omega$ . The intersection is a general transition from viscoelastic solid (solid-like) (where  $G' > G''$ ) to viscoelastic liquid (liquid-like) (where  $G' < G''$ ), which is related with the movement of polymer chains. The characteristic relaxation time reduces initially and rises with increasing temperature as shown in Figure 4. This phenomenon is generally attributed to the effect of both melting and crosslinking. With increasing temperature, macromolecules flowing becomes easy, therefore characteristic relaxation time shortens, whereas, with increasing temperature further, the



**Figure 5** The relationship of  $\log G'$  and  $\log G''$  for sPB-830.



**Figure 6** The plots of zero shear viscosity  $\eta_0$  against shear rate for sPB-830 at different temperatures.

crosslinked response is dominant, macromolecules flowing becomes difficultly, characteristic relaxation time becomes longer.

The  $\log G' - \log G''$  curve of sPB-830 is shown in Figure 5, which was used to investigate the change of microscopic structure of homopolymer, block copolymer and polyblend.<sup>11,12</sup> Thus, the tendency of  $\log G' - \log G''$  curve should be consistent as temperature changes, if microscopic structure of polymer has not been altered. This curve is also available used to explain the change of polymer structure at a given temperature. For example, Harrell and Nakayama<sup>13,14</sup> used the  $\log G' - \log G''$  curve to investigate the change of polyethylene microscopic structure made by branched chains and wide molecular weight distribution, it was found that  $G'$  value increased with increase of long branched chain at the constant  $G''$  value. As shown in Figure 5, when temperatures are lower than 160°C, the tendency of  $\log G' - \log G''$  curves of the polymer are quite similar and the slope value is about 2. Therefore, the molecular chain structure of sPB-830 is homogeneous, the molecular structure has not changed when temperature is lower than 160°C. On the contrary, the tendency of  $\log G' - \log G''$  curve of polymer deviates linear relationship in the terminal region of the relaxation spectrum when temperatures are higher than 160°C. In other words, the homogeneity of polymer system is destroyed and have crosslinked.

### Nonlinear rheological properties

Comparing the linear viscoelastic response at small strains in frequency sweeps, steady shear response of sPB-830 usually provides useful information on the material dealing processing. Steady shear viscos-

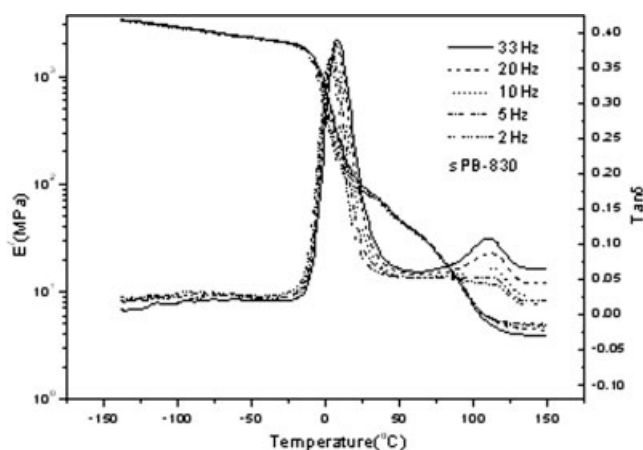
ity as a function of shear rate for sPB-830 is shown in Figure 6 with different temperatures. Each flowing curve displays a similar profile with independent shear viscosity plateau at lower shear rate region and shear thinning at higher shear rate region. The plateau viscosity at lower shear rates is defined as the zero shear viscosity ( $\eta_0$ ), it is only a function of temperature.

With increasing temperature, it can be found from Figure 6 that the zero shear viscosity ( $\eta_0$ ) firstly reduces slightly and then obviously increases, this critical temperature value is quite similar to that of storage modulus ( $G'$ ), as discussed earlier in Figure 4. Above the critical temperature, the zero shear viscosity obviously increases with increasing temperature, this observation is generally attributed to the crosslinked of polymer. With crosslinked reaction aggravating, the polymer chains formed network architecture, which would hold up the movement of the polymer chains. The network architecture leads to the flexibility of the polymer chains reduced and the zero shear viscosity increased.

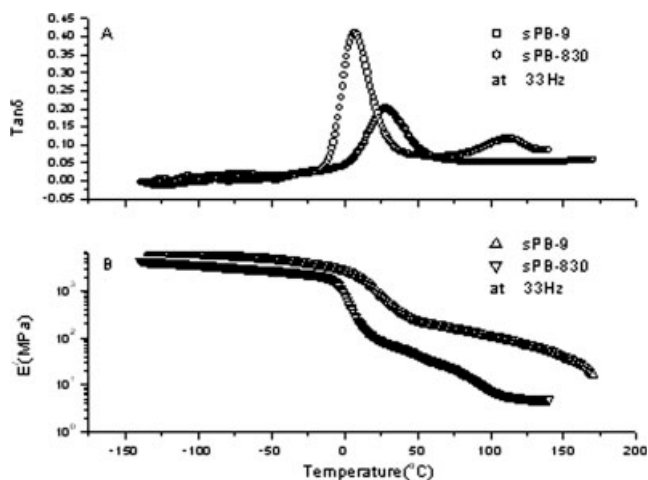
It is very difficult to investigate rheological properties of sPB-9 because the crystal region have not melted when temperatures are lower than 170°C, while the sample has obviously crosslinked, losing flowing properties when temperatures are higher than 170°C.

### Dynamic mechanical behavior

The polymer relaxation is strongly influenced by variables that describe macromolecular movement, such as glass transition, crystallinity, molecular orientating, crosslinking, and phase separation, which sensitively influence dynamic mechanical properties. Therefore, dynamic mechanical analysis (DMA) is a useful method to investigate microcosmic structure,



**Figure 7** The storage module  $E'$  and the loss tangent as a function of temperature for sPB-830.



**Figure 8** The storage module  $E'$  and the loss tangent versus temperature measured for sPB-9 and sPB-830 at 33 Hz.

macromolecular movement and other properties of polymer. Figure 7 summarizes the DMA data in which dynamic storage modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) of sPB-830 are presented as a function of temperature.

Double peaks at lower and higher temperature region can be observed in the curves of  $\tan \delta$  versus temperature, the temperature of the peak at lower temperature region located is the glass transition temperature ( $T_g$ ) of amorphous region, while the temperature of the peak at higher temperature region located is the melting temperature of crystalline region. The melting points measured by DMA are quite similar to the value determined by DSC in Table I. These phenomena were also observed in investigating linear polyethylene by Nitta et al.<sup>15</sup> The DMA data in which dynamic storage modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) of sPB-9 (here for abbreviation) are similar to that of sPB-830, but only a single peak was observed on the plot of  $\tan \delta$  versus temperature for sPB-9. The peak in high temperature region was not discovered because the melting point of sPB-9 is higher than test temperature.

The dynamic storage modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) data for sPB-9 and sPB-830 at 33 Hz are shown in Figure 8. The glass transition temperature ( $T_g$ ) of sPB-9 is 28°C, and for sPB-830 is 7°C. With increasing crystallinity, glass transition temperatures of sPB increases remarkably, while mechanical internal friction is greatly reduced. These observations are due to amorphous chain relaxation and ratio between amorphous phase and crystalline phase. It can be seen from Figure 8(B),  $E'$  value of sPB-9 and sPB-830 is quite similar before glass transition, because storage module of amorphous phase and

storage module of crystalline phase are similar, the  $E'$  value of entire system is almost not influenced by crystallinity.<sup>16</sup> Near glass transition temperature, the  $E'$  value of entire system is remarkably influenced by crystallinity, storage module of crystalline phase is higher than that of amorphous phase, therefore, the  $E'$  value of sPB-9 with highly crystalline is higher than that of sPB-830 with less crystalline. This is because now macromolecular chains of amorphous region have already started to move, and amorphous phase transforms from glass state to high stretch state, while macromolecular chains of crystalline region have not changed, crystalline phase of system become similar to physical crosslinked bond. Another characteristic is that sPB-9 starts to appear the melting phenomenon at 170°C in DMA test, sPB-830 starts to appear the rubber platform at 125°C, but the crosslinked reaction did not appear. These phenomena are quite similar to rheological results as discussed above.

## CONCLUSIONS

The rheological behavior and the dynamic mechanical properties of sPB have been studied in this paper. It is found that a critical crosslinked reaction temperature for sPB-830 with lower syndiotactic content was detected at about 160°C. Below the critical crosslinked reaction temperature,  $G' > G''$ , system shows mainly elasticity at high frequency region. At low frequency region,  $G' < G''$ , system shows mainly viscosity. Above critical temperature, the  $G'$  value is higher than  $G''$  in all the frequency range, crosslinked reaction has occurred. Below critical crosslinked reaction temperature, the zero shear viscosity  $\eta_0$  reduces with increasing temperature, whereas above critical crosslinked reaction temperature,  $\eta_0$  increases with increasing temperature. Moreover, at higher shear rates, the shear thinning phenomenon is more and more obvious, system presents pseudo-plastic fluid characteristic. The glass transition temperature of sPB is remarkably increased with increasing crystalline degree, storage module ( $E'$ ) is remarkably influenced by crystalline degree. Especially, above glass transition temperature, material properties are mainly dominated by crystalline phase. The relationship between processing temperature and crosslinked reaction is proposed for sPB-830 sample.

## References

1. Natta, G. *Macromol Chem* 1955, 16, 213.
2. Ashitaka, H.; Ishikawa, H.; Ueno, H. *J Polym Sci Part A: Polym Chem* 1983, 21, 853.
3. Ricci, G.; Battistella, M.; Bertin, F. *Polym Bull* 2002, 48, 25.
4. Ye, Chen; Decai, Yang; Yanming, Hu; Xuequan, Zhang. *Chem J Chin Univ* 2003, 24, 2119.

5. Ye, Chen; Decai, Yang; Yanming, Hu; Xuanquan, Zhang. *Chem J Chin Univ* 2003, 24, 2321.
6. Minqiao, Ren; Qingyong, Chen; Zhishen, Mo. *J Polym Sci Part B: Polym Phys* 2005, 43, 553.
7. Sugiura, S.; Ueno, H.; Kono, M.; Hamada, H.U.S. Pat. 3,778,424 (1970).
8. Natta, G.; Corradini, P. *J Polym Sci* 1956, 20, 251.
9. Obata, Y.; Tosaki, C.; Ikeyama, M. *Polym J* 1975, 7, 207.
10. Montiel, V.; Bastero, A.; Mecking, S. *Macromolecules* 2005, 38, 5393.
11. Han, C. D.; Kim, J.; Kim, J. K. *Macromolecules* 1989, 22, 383.
12. Chuang, H. K.; Han, C. D. *J Appl Polym Sci* 1984, 29, 2205.
13. Harrell, E. R.; Nakajima, N. *J Appl Polym Sci* 1984, 29, 995.
14. Nakayama, N.; Harrell, E. R. In *Current Topics in Polymer Science, Rheology and Polymer Processing/Multi-Phase Systems*, Vol. 2; Ottenbrite, R. M., Utracki, L. A., Inous, S., Eds; Carl Hanser: Munich, 1987; pp 149–165.
15. Nitta, K.-h; Tanaka, A. *Polymer* 2001, 42, 1219.
16. Meili Guo. *Dynamic Mechanical Thermal Analysis of Polymers and Composites*; Chem Industry: Beijing, 2002; p 8.