

## Styrene/Butadiene Copolymer Synthesized by Reactive Extrusion\*

Ji-ming Wang<sup>a</sup>, Bo Chen<sup>a</sup>, Sheng-jie Tang<sup>b</sup>, Dong Shan<sup>a</sup> and An-na Zheng<sup>a\*\*</sup>

<sup>a</sup>Shanghai Key Laboratory of Advanced Polymeric Materials, Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

<sup>b</sup>Department of Mechanical Engineering, University of Houston, Houston, Texas, USA

**Abstract** In this study, we present a method to synthesize styrene-butadiene copolymer, using anionic polymerization in a co-rotating closely intermeshing twin-screw extruder. The weight content of polybutadiene in these copolymers was above 50% although in the past studies it had been possible to accomplish levels higher than 30%. <sup>1</sup>H-NMR and GPC show that the molecular structure of the two polymers is different due to different feeding method. In terms of the structure of the polymerized products, the mechanism of polymerization in the bulk polymerization is discussed. TEM and DMA show that two phases in the block copolymer are completely incompatible, leading to sharp phase separation, while the case is complicated in the copolymer through the mixture feeding. Traditionally, styrene-butadiene rubber is mainly synthesized by solution polymerization. Reactive extrusion in this paper provides a possibility to synthesize these products in an environmentally friendly way.

**Keywords:** Reactive extrusion; Styrene; Butadiene; Anionic polymerization.

### INTRODUCTION

The thermoplastic elastomer made from styrene (St) and dienes, such as SBS and SIS, used to be synthesized by solution anionic polymerization, which was easy to cause the energy consumption and pollution. On the other hand, the extruders usually are used for polymer processing and modification. Recently, however, their application as reactors of polymerization drew wide attention. Up to now, a vast array of experimental data about the polymer synthesis using a twin screw extruder as a reactor has been published. Since the rotation of the screws ensures good mixing and heat transfer in spite of the high viscosity of the melt, the synthesis and modification of polymers can take place simultaneously, which leads to final products directly. In addition, as a kind of bulk polymerization, reactive extrusion doesn't need any solvent. Therefore, it means that the energy consumption and pollution would be avoided. However, the course of the reactive extrusion has been a matter of study for decades and the measurement and control of the polymerization process are very challenging due to the complexity of physical mechanisms and polymerization kinetics.

Stuber<sup>[1]</sup> and co-workers used a co-rotating intermeshing twin screw extruder with diameter of 34 mm to study the free radical polymerization of methyl methacrylate. They developed a model to forecast the polydispersity of the polymer and the extrusion efficiency through the resident time distribution and the

\* This work was financially supported by the National Natural Science Foundation of China for the Major Program (No. 50933002), the National High Technology Research and Development Program of China (863 Program, No. 2012AA040306) and Shanghai Leading Academic Discipline Project (No. B502).

\*\* Corresponding author: An-na Zheng (郑安呐), E-mail: zan@ecust.edu.cn

Received November 18, 2014; Revised January 8, 2015; Accepted January 22, 2015

doi: 10.1007/s10118-015-1659-2

molecular weight of the product.

The temperature in the extruder is required to be sufficiently high in order to make the polymerized reactant flowing during the reactive extrusion. At the same time, the residence time needed for the reaction is extremely short (about a few minutes). Therefore, the living polymerization, especially the anionic polymerization, is more suitable for the reactive extrusion of the polymerization. Furthermore, the extruder is a closed system away from H<sub>2</sub>O and O<sub>2</sub>, which is beneficial for the anionic polymerization.

Based on the above reasons, Michaeli<sup>[2]</sup> successfully synthesized polystyrene (PS) using a co-rotation twin screw extruder with diameter of 30 mm and reactor  $R/D$  of 29 using *s*-butyllithium as the initiator. The reaction temperature was 50 °C to 230 °C from zone 1 to zone 6 and the conversion was almost 100%. Then, Michaeli and co-workers<sup>[3]</sup> provided a new processing method to complete the synthesis of PS and its copolymers using *s*-butyllithium as the initiator. They found that the active center stayed “living” under high temperature and the temperature in the polymerization zone had a decisive influence on the product quality during sequential copolymerization.

Our lab<sup>[4–12]</sup> has conducted researches on anionic bulk polymerization of St and dienes with reactive extrusion for over ten years and focused at the mechanism and kinetics of the polymerization and the textural structure and analysis methods of the products. Gao *et al.*<sup>[8, 9]</sup> carried out the anionic polymerization of St and butadiene (Bd) using *n*-butyllithium as the initiator. They studied the polymerization mechanism and proposed a “bubble theory”. According to this theory, when monomers of St and Bd are pumped into the extruder, all the Bd gasified and only the St could be polymerized and form the polystyryl reactive species. The Bd did not participate into copolymerization until the viscosity of reactant was large enough to wrap Bd gas. Therefore, a novel St-*b*-Bd multi-block copolymer was synthesized. Yuan *et al.*<sup>[10, 11]</sup> and Shan *et al.*<sup>[12]</sup> got some St-isoprene copolymers by reactive extrusion in which the weight content of isoprene was up over 50%.

In this work, two kinds of St-Bd copolymers are synthesized using a intermeshing co-rotating twin-screw extruder with reactor  $L/D$  of 56, diameter of 36 mm and *n*-butyllithium as the initiator through the addition of a special polarity regulator and strictly controlling the screw speed and the temperature of every zone. GPC, <sup>1</sup>H-NMR, DMA, DSC and TEM are used to analyze the molecular structure and the micromorphology of the products. The aim of this research is at establishing a new method to synthesize the St-Bd copolymers with different structures and properties without need of any solvent.

## EXPERIMENTAL

### Materials

The St used in the polymerization was polymerization grade provided by the Sinopec Shanghai Petrochemical Company Limited with tertiary butylcatechol as polymerization inhibitor. Bd, a commercial sample, was supplied by YueYang Petroleum-Chemical Co., Ltd.. The inhibitors in the St and the Bd were removed respectively by distillation for the former and by adsorption of Al<sub>2</sub>O<sub>3</sub> for the latter. The moisture in the monomers was removed through adsorption of molecular sieve and the water content should be less than 0.01%. The initiator provided by J&K Chemical was diluted to 0.08 mol/L using cyclohexane. The monomers and the initiators were all stored in tanks away from light. The storage and the processing of the polymerization were always in a dry argon atmosphere. Tetrahydrofuran (THF) provided by J&K Chemical was distilled to remove the moisture.

### Synthesis of S/B Copolymer

The rapid polymerization of St and Bd was carried out in a co-rotating intermeshing twin-screw extruder containing 13 zones, shown in Fig. 1. At first, the extruder was heated to set temperatures of the various zones and cleaned with dry argon to remove moisture in the extruder before polymerization. The screw speed was 100 r/min. During the synthesis of SBR1, pump 1 was used to feed the initiator with THF ( $n_{\text{THF}}/n_{\text{BuLi}} = 3$ ) as regulator into zone 1 of the extruder and the S/B monomer mixture ( $m_{\text{S}}/m_{\text{B}} = 38/62$ ) was added into the same zone by pump 2. The feeding rate of monomer and the initiator is 40 g/min and 5 mL/min. However, PS could be

prepared as SBR1 only by replacing S/B monomer mixture with St. While SBR2 was synthesizing, pumps 1, 2 and 3 were used to feed the initiator, St and Bd respectively into zone 1, 1 and 4 of the extruder. The feeding speed of St, Bd and the initiator was 15.2 g/min, 24.8 g/min and 5 mL/min, respectively. The temperature of extruder was set as Table 1<sup>[13]</sup>.

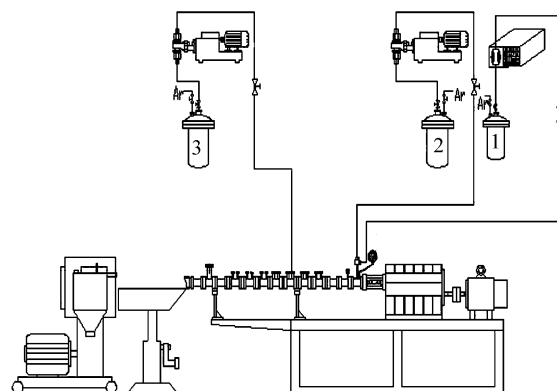


Fig. 1 Process for reactive extrusion of St-Bd copolymers

Table 1. Temperature setting for extruders

Barrel	1	2	3	4	5	6	7	8	9	10	11	12	13
$T_{\text{SBR1}}$ (°C)	30	40	50	60	80	90	100	100	140	150	150	180	180
$T_{\text{SBR2}}$ (°C)	100	140	80	30	40	50	70	90	100	140	150	150	180
$T_{\text{PS}}$ (°C)	100	140	180	180	180	180	180	180	180	180	180	180	180

#### <sup>1</sup>H Nuclear Magnetic Resonance (<sup>1</sup>H-NMR) Analysis

The microstructure of the polymer was analyzed with <sup>1</sup>H-NMR using a DRX-500 spectrometer with tetramethylsilane as the internal standard. All the samples were dissolved in deuterated chloroform.

#### Gel Permeation Chromatography (GPC) Analysis

The molecule weight and molecule weight distribution were characterized with Waters Model 244 GPC spectrometer connected with Wyatt Technology DAWN EOS small-angle light scattering detector using THF as the solvent. In order to analyze the structure of the polymer chain, complete degradation of the samples was conducted using OsO<sub>4</sub> under the catalysis of H<sub>2</sub>O<sub>2</sub> before measurements<sup>[14]</sup>. After degradation, all double bonds were cut off, therefore the left polymer should be PS blocks in the copolymer.

#### Dynamic Mechanical Analysis

The dynamic mechanical data were recorded with Netzsch DMA242 rheometric mechanical spectrometer. The samples, with a size of 10.0 mm × 30.0 mm × 4.0 mm, were analyzed at the heating rate of 2 K/min from -100 °C to 150 °C using the oscillation frequency of 1 rad/s.

#### Transmission Electron Microscope Observation

Joel JEM-1400TEM was used for the observation of the micromorphology of samples. In order to distinguish the PS domain region and the polybutadiene (PB) domain region, the sample film was stained with OsO<sub>4</sub> for 35 min.

## RESULTS AND DISCUSSION

#### Microstructure of the Polymer Chain

<sup>1</sup>H-NMR spectra of the two polymers, SBR1 and SBR2, are shown in Fig. 2, whose computing method and data are listed in Table 2 and Table 3, respectively. The absorption peaks at  $\delta = 6.35\text{--}7.25$  belong to <sup>1</sup>H at ortho, meta and para position of the benzene ring of the St in the polymers. The absorption peaks at  $\delta = 4.75\text{--}5.05$  and  $\delta = 5.05\text{--}5.45$  belong to <sup>1</sup>H at 1,2-structure and  $\delta = 5.45\text{--}5.75$  belong to <sup>1</sup>H at 1,4-structure. As shown in Table 3, the

mass fractions of the Bd in the two polymers can be calculated according to Table 2, being 61% in SBR1 and 59% in SBR2, respectively. Although the mass fraction of the monomers in the two kinds of polymers is almost equal, their structures are quite different as shown by  $^1\text{H-NMR}$  spectra. In SBR2, the absorption peak at 6.55 belonging to the ortho proton of St is clearly presented, which means PS is the homopolymer or the block polymer in the co-polymer. However, this absorption peak almost don't appear in SBR1, which means there hardly exists the continuous St links. Furthermore, because of the influence of the complicated chemical environment of the alternated units of St and Bd, the chemical shift of the  $^1\text{H}$  in Bd drifted and the peaks of 1,2-structure and 1,4-structure merged each other. On the other hand, the absorption peaks of St unit and Bd unit in the SBR2 are almost the same as those in PS and PB, which means there hardly exists the alternated unit of two monomers in SBR2. The addition of THF also changed the insert structure of Bd and the proportion of 1,2-Bd became larger<sup>[15, 16]</sup>.

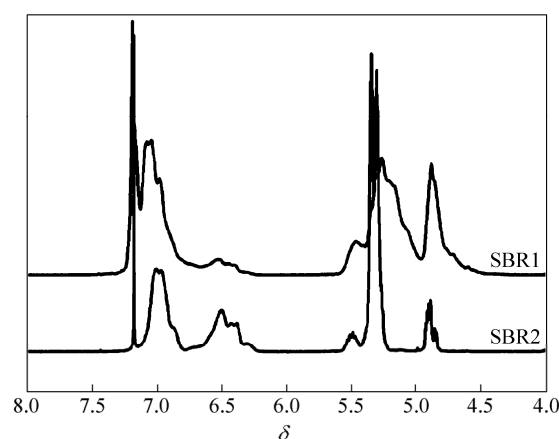


Fig. 2  $^1\text{H-NMR}$  spectra of SBR1 and SBR2

Table 2. Chemical shift of  $^1\text{H}$  and the computing method of structural contents

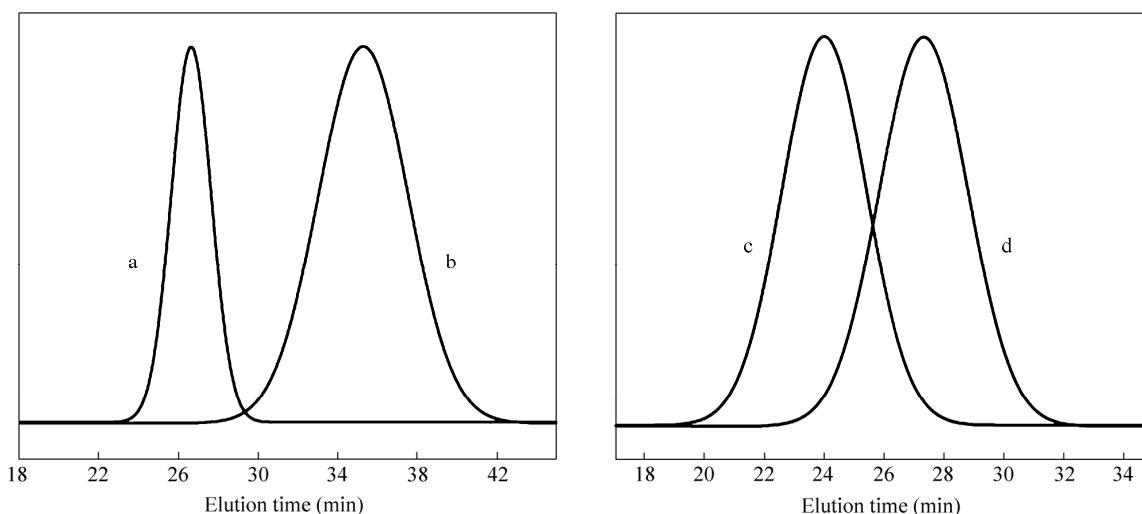
Chemical shift	Peak area	belongingness	Computing method
6.35–7.25	$A_1$	St	$\frac{20.8 \times A_1}{27 \times A_4 + 54 \times A_3 + 20.8 \times A_1}$
4.75–5.05	$A_2$	1,2-Bd	$\frac{27 \times A_2}{27 \times A_4 + 54 \times A_3 + 20.8 \times A_1}$
5.45–5.75	$A_3$		
5.05–5.45	$A_4$	1,4-Bd	$\frac{27 \times A_4}{27 \times A_4 + 54 \times A_3 + 20.8 \times A_1}$
4.75–5.75	$A_2 + A_3 + A_4$	Bd	$\frac{27 \times A_4 + 54 \times A_3}{27 \times A_4 + 54 \times A_3 + 20.8 \times A_1}$

Table 3. Structural contents of SBR1 and SBR2

Sample	<i>b</i> -St	<i>r</i> -St	St (%)	Bd (%)	1,2-Bd (%)	1,4-Bd (%)
SBR1	7	32	39	61	16	45
SBR2	40	1	41	59	7	52

The structure of the two polymers was quite different only for that two different kinds of feeding sequence were used. However, according to the analysis of  $^1\text{H-NMR}$  results above-mentioned, it is clear that the reactivity ratios of St and Bd approached equal during the polymerization of the SBR1. Furthermore, it means that the homo-polymerization of St had almost completed before the polystyryl radicals reacting with Bd according to the feeding sequence in SBR2.

In order to analyze the structure of the chain links of the two polymers, GPC was adopted to measure the polymer samples before and after degradation. The designed number average molecular weight of the polymers was  $10^5$  and the actual molecular weight of both polymers before degradation corresponded with this designed value (Table 4). However, the molecular weight distribution and chain links of SBR1 and SBR2 were quite different after degradation, as shown in their GPC curves (Fig. 3) and the weight percentage of different molecular weight of PS chains (Table 5). During the degradation of SBR-1, polymer with 1,2-butadiene could not be cut off because the double bond was not in the backbone which led to the increase of  $M_n$  of PS. Even so, the PS oligomer with low molecular weight was the significant proportion of PS chains in the SBR1, while this case did not exist in SBR2, in which PS blocks with the molecular weight of  $0.8-8 \times 10^4$  occupied the significant proportion. The results are consistent with the  $^1\text{H-NMR}$  analyses given above.



**Fig. 3** GPC profiles of SBR1 and SBR2 (a: SBR1 before degradation, b: SBR1 after degradation, c: SBR2 before degradation and d: SBR2 after degradation)

**Table 4.** GPC data for SBR1 and SBR2

Sample	SBR1		SBR2	
	Before degradation	After degradation	Before degradation	After degradation
$M_n$	$1.13 \times 10^5$	$4.13 \times 10^4$	$1.02 \times 10^5$	$2.32 \times 10^3$
MWD	1.35	1.85	1.59	1.56

**Table 5.** Data of the integral curves of molecular weight of SBR1 and SBR2 after degradation

Sample	Weight percentage of different molecular weight of PS chains			
	Below $2 \times 10^3$	$2 \times 10^3-8 \times 10^3$	$8 \times 10^3-2 \times 10^4$	$2 \times 10^4-8 \times 10^4$
SBR1	25.1%	70.3%	2.8%	0.4%
SBR2	1.0%	1.7%	17.0%	78.6%

### Micromorphology of the Polymers

TEM images of SBR1 and SBR2 are shown in Fig. 4. In TEM images, PS and PB domains appear as white and black regions, respectively, because of the double bond left in PB being dyed by osmium tetroxide. In spite of the similar chemical composition, the morphology of SBR1 appears to be significantly different with that of SBR2. In the morphology of SBR1, PS domains also existed which meant that there were PS blocks in the copolymer. However, the percentage of PS domain was much smaller in SBR1 than in SBR2 which meant that there were St units existing in the PB phase. On the other hand, in the morphology of SBR2, black PB and white PS regions had sharp and clear interface between the two phases, and PB was the continuous phase PS was the discrete phase, embedding in PB phase. Therefore, the morphology of SBR1 and SBR2 as indicated by TEM is

consistent with the results shown above by  $^1\text{H-NMR}$  and GPC analyses. These further indicate that the structure of the polymer chain plays an important role in the morphology formation. However, it is worth to note when SBR1 was synthesized through the mixture feeding of St and Bd, even THF was added into the reaction system, block structure, either PS blocks or PB blocks with a certain scale still formed, which clearly indicates that the anionic polymerization by the reactive extrusion is quite different to that by traditional solution polymerization because of some dynamic factors<sup>[17]</sup>.

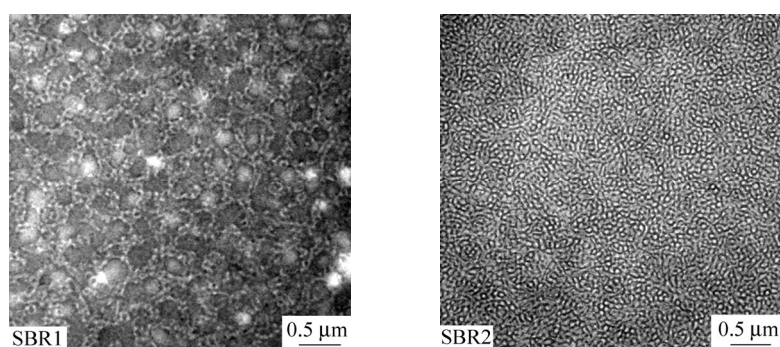


Fig. 4 TEM images of SBR1 and SBR2

The glass transition temperatures ( $T_g$ ) of SBR1 and SBR2 can be clearly observed from their DMA curves, as shown in Fig. 5 and Fig. 6. Comparing with normal PS and PB,  $T_g$ s of PB blocks and PS blocks are close to each other, that is,  $T_g$  of PB blocks increases by about 70 K, in contrast,  $T_g$  of PS blocks decreases by about 50 K. According to the Fox equation for a random copolymer, the compatibility of the two phases is greatly improved. The reason is that in SBR1, there are many St units embedding in PB phases, vice versa<sup>[18–20]</sup>.

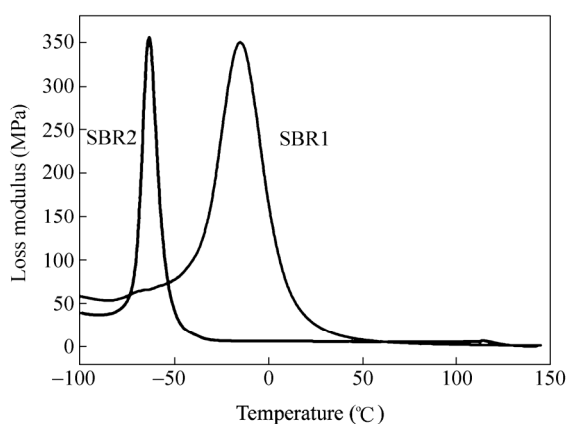


Fig. 5 Loss modulus versus temperature curves of SBR1 and SBR2

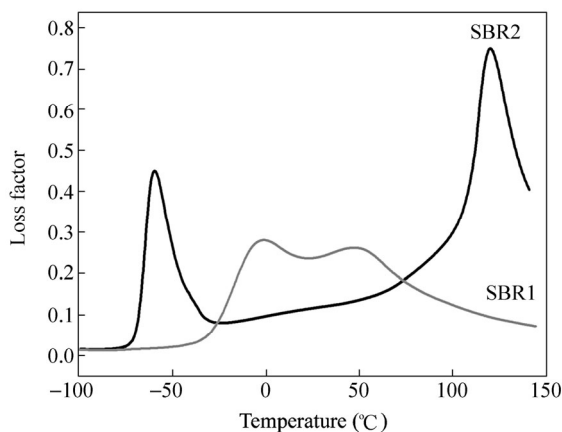


Fig. 6 Loss factor versus temperature curves of SBR1 and SBR2

According to the traditional theory, when average molecular weight ( $M_n$ ) of the polymer increases up to a certain value, its  $T_g$  will be equal to  $T_g^\infty$  (the  $T_g$  while the  $M_n$  of the polymer being infinitely great), that is, the effect of  $M_n$  on  $T_g$  can be ignored. The certain value of  $M_n$  of the PS block is higher than 8000. When the two kinds of blocks in the St-Bd random polymer are shorter,  $T_g$ s of the two parts will both reduce<sup>[21]</sup>. Therefore, it is quite natural that the  $T_g$  of PS blocks in SBR1 is much lower than 105 °C, the  $T_g$  of homo PS, because the  $M_n$  of the PS phase over 80 wt% in SBR1 is lower than 8000, as shown in Table 5 and Fig. 6. Furthermore, the  $T_g$  of PB phase is greatly higher than that of normal PB homo-polymers, though some weak signals can be seen at about -68 °C, as shown in Fig. 5 and Fig. 6. This means there are many St units existing in PB links. This is in

keeping with Fox equation (1), in which  $W_S$  and  $W_B$  are the mass fraction of St and Bd in the copolymer and  $T_{gS}$  and  $T_{gB}$  are the  $T_{gS}$  of PS and PB, respectively. In contrast, the  $T_{gS}$  of the PS block and PB block in SBR2 is as high as those of each homopolymers<sup>[22-24]</sup> (at about  $-68$  °C and  $120$  °C in Fig. 6), as shown in Fig. 5 and Fig. 6, which means that in SBR2, there hardly exist monomer units of another kind in any homopolymer blocks.

$$\frac{1}{T_g} = \frac{W_S}{T_{gS}} + \frac{W_B}{T_{gB}} \quad (1)$$

According to the thermodynamics, the phase separation depends on the disparity between the solubility parameters of the two kinds of polymers, PS and PB, being 8.7–9.1 and 8.1–8.6. Though the disparity between the solubility parameters of PS and PB is not great, the phase separation of SBR2 appears so sharp, as shown in Fig. 6. However, the phase separation of SBR2 is still controlled to a certain extent, so as to form the micro-phase separation with nanometer scale, as shown in Fig. 4(b), because the two blocks are linked through chemical bond. This kind of micro-phase separation cannot form in the blend of two polymers for lack of links between two polymers. In contrast, the bond of St-Bd is so many that the interface between two polymers is too wider in the SBR1. Therefore, if the polymer is an entirely random polymer, the width will be infinite and there will be only one phase in the polymer<sup>[25]</sup>.

### Conversion

The sample collected after the extruding process were stable and the conversion  $\alpha$  of St and Bd was calculated using the formula:

$$\alpha = \frac{a}{b} \times 100\% \quad (2)$$

where  $a$  is the weight of the St/Bd in the sample obtained in 10 min and  $b$  is the weight of the St/Bd pumped in the extruder. In SBR1 the conversion of St and Bd was 98.9% and 94.8%, respectively. While in SBR2, the conversion was 99.2% and 87.5%. The boiling point of Bd is  $-4.5$  °C and part of Bd would gasify when pumped into the extruder. The conversion of Bd was lower than St because the reaction between liquid and gas was slow.

## CONCLUSIONS

Styrene-butadiene rubbers with different molecular weight, molecular weight distribution, structure of link and completely different aggregation structure can be polymerized by anionic polymerization using reactive extrusion through the controlling of feeding method and parameters. The new production mode has paved the way for the industrialization path of energy conservation and environmental protection.

Using once feeding method with THF as the polarity regulator, the copolymer had short St and Bd blocks embedding in the opposite matrix and formed a two-phase elastomer. Using twice feeding method, the polymer similar to the solution polymerization product with clear phase separation was obtained. The nanoscale microphase separation was formed because of the chemical bonds between the two phases.

## REFERENCES

- 1 Stuber, N.P. and Tirrell, M., *Polym. Process Eng.*, 1985, 3: 71
- 2 Michaeli, W., Frings, W., Höcker, H. and Berghaus, U., *J. Appl. Polym. Sci.*, 1993, 48: 871
- 3 Michaeli, M., Grefenstein, A. and Frings, W., *Adv. Polym. Technol.*, 1993, 12(1): 25
- 4 Zhang, Y., Yan, W., Gao, S., Zheng, A. and Han, Z., *Acta Polymerica Sinica (in Chinese)*, 2002, (5): 677
- 5 Si, L., Zheng, A., Zhu, Z. and Zhang, Y., *J. Appl. Polym. Sci.*, 2002, 85(10): 2130
- 6 Sun, G., Zhou, Y., Zhang, K., Liu, C. and Zheng, A., *Acta Polymerica Sinica (in Chinese)*, 2007, (9): 790

- 7 Zhang, K., Zhou, Y., Sun, G., Hu, F. and Zheng, A., *Polym. Mater. Sci. & Eng.* (in Chinese), 2009, 3: 42
- 8 Gao, S., Zhang, Y., Zheng, A. and Xiao, H., *Polym. Adv. Technol.*, 2004, 15: 185
- 9 Gao, S., Zhang, Y., Zheng, A. and Xiao, H., *J. Appl. Polym. Sci.*, 2004, 91: 2265
- 10 Yuan, X., Guan, Y., Li, S. and Zheng, A., *J. Appl. Polym. Sci.*, 2014, 15(2): 131
- 11 Yuan, X., Wang, J., Shan, D. and Zheng, A., *Polym. Eng. Sci.*, 2014, DOI: 10.1002/pen.23987
- 12 Shan, D., Yang, L., Wang, J. and Zheng, A., *Chem. J. Chin. U.* (in Chinese), 2014, 35: 2698
- 13 Marino, X., "Reactive extrusion: principles and practice", Chemical Industry Press, Beijing, 1999, p. 266
- 14 Yu, Y.S., Jerome, R., Fayt, R. and Teysse, P., *Macromolecules*, 1994, 27: 5958
- 15 Chen, B., Wang, J. and Shu, M., *Chin. J. Chem.*, 2014, 32:1128
- 16 Zheng, A., Chen, B., Hu, D., Guan, Y., Wei, D., Li, S. and Jin, D., *Chin. J. Chem.*, 2013, 31: 393
- 17 Rameshwar, A. and Goerg, H.M., *Prog. Polym. Sci.*, 2004, 29: 949
- 18 Trinh, A.H., Le, H.H., Rameshwar, A., Roland, W., Goerg, H.M. and Konrad, K., *Polymer*, 2003, 44: 1237
- 19 Masato, M., Taku, U., Hiroshi, H., Sayuri, C. and Harumi, A., *Polymer*, 1968, 9: 425
- 20 Trinh, A.H., Rameshwar, A. and Goerg, H.M., *Polymer*, 2003, 44: 1247
- 21 Adel, F.H., Chad, J., Wen, L.H. and David, J.Z., *Eur. Polym. J.*, 2010, 46: 2013
- 22 Takeji, H., Mineo, F. and Hiromichi, K., *Macromolecules*, 1980, 13(6): 1660
- 23 Rameshwar, A., Goerg, H.M., Trinh, A.H., Elena, I., Reinhold, G., Werner, L. and Konrad, K., *Macromol. Chem. Phys.*, 2003, 204(3): 488
- 24 Mochel, V.D. and Claxton, W.E., *J. Polym. Sci., Part A: Polym. Chem.*, 1971, 9: 345
- 25 Sato, H. and Tanaka, Y., *J. Polym. Sci. Polym. Chem. Ed.*, 1979, 17: 3557