

# Study on Nanometer-Size Styrene-Butadiene Multiblock Copolymer Synthesized by Reactive Extrusion

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**ABSTRACT:** In this study, a novel styrene-*b*-butadiene block copolymer was synthesized by bulk anionic polymerization in a corotating closely intermeshing twin-screw extruder. The structure of the S/B copolymer was determined by characterization methods including FTIR, NMR, dynamic mechanical analysis (DMA), and TEM. It is shown that the polymerized materials exhibit nanometer-size styrene and butadiene (S/B) multiblock structure and ultrahigh elongation at break, which differs considerably from that of tradi-

tional solution polymerizing methods. In terms of the structure of the polymerized products, the mechanism of living anionic polymerization of S/B in a corotating intermeshing twin-screw extruder is discussed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2265–2270, 2004

**Key words:** reactive extrusion; styrene; butadiene; anionic polymerization; twin-screw extruder

## INTRODUCTION

Traditionally, extruders are used to melt, homogenize, and pump polymer through dies. Nowadays, the use of extruders as continuous polymerization reactors for polymer synthesis is growing rapidly. Compared with the conventional polymerization reactors, such as the batch reactor, extruders have the advantage of continuous bulk-polymerizing without any solvent. Moreover, the rotation of the extruder screws ensures, even at a high viscosity, good mixing and heat transfer. Therefore, synthesis, and even modification of these polymers, may take place simultaneously with the finishing of the product.

In recent years, various investigations were reported on reactive extrusion areas, in which the reactions were performed successfully in twin-screw extruders, including step polymerization,<sup>1–2</sup> ring-opening polymerization,<sup>3–4</sup> and radical chain polymerization.<sup>5–6</sup> However, the polyreactive extrusion does not seem to reach to a level which is able to be used practically because of the quite low reaction time (up to a few minutes) and ultrahigh reaction temperature (more than 200°C) in the extruder.

More recently, living anionic polymerization, found to be very suitable for reactive extrusion, is adopted in the processing. Michaeli et al.<sup>7–8</sup> studied activated

anionic polymerization and copolymerization of styrene and found that the conversion of the reaction can reach 100% in a very short time in a twin-screw extruder. Menges et al.<sup>9</sup> also studied ring-opening anionic polymerization of  $\epsilon$ -caprolactam in a corotating intermeshing twin-screw extruder. The reaction is fast and less exothermic, so it can be controlled easily in the extruder. In our lab, polystyrene with ultrahigh molecular weight (UHMWPS) was also synthesized by living polymerization in an extruder reactor.<sup>10–12</sup> Based on the successful synthesis of UHMWPS, a styrene and butadiene (S/B) copolymer was subsequently developed.

In this article, the FTIR, NMR, dynamic mechanical analysis (DMA), and TEM were used to characterize the structure of a S/B copolymer synthesized by living anionic polymerization in a corotating intermeshing twin-screw extruder. The objective of the characterization was to investigate the living polymerization mechanism in an extruder reactor.

## EXPERIMENTAL

### Materials

The materials used in this study were industrial products. The styrene used was polymerization grade provided by the Shanghai Gaoqiao chemical plant and stabilized with tertiary butylcatechol. Destabilization of the monomers was performed with NaOH and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Butadiene, a commercial sample, was supplied by YueYang Petroleum-Chemical Co., Ltd. Butyl lithium as initiator was acquired from this laboratory. Argon, preparation, and processing of the raw materials was performed in a dry argon atmosphere.

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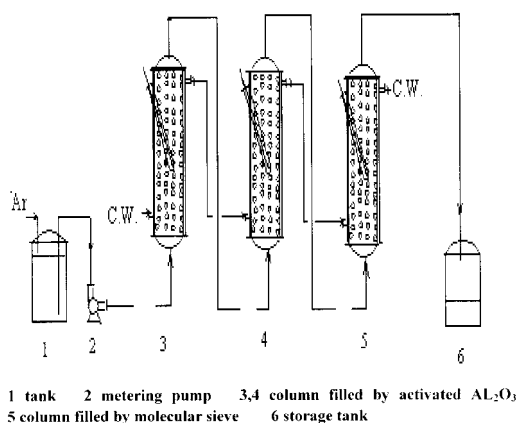


Figure 1 Flow chart of purification for St monomer.

### Characterization

The characterization procedures adopted were FTIR, NMR, DMA, and TEM.

#### FTIR spectroscopy

A Nicolet 5SXC spectrometer was used to record the FTIR spectra of the polymerized materials. Samples were dissolved in a mixture of trifluoroacetic acid and chloroform (1:3) and then cast onto a KBr disc to obtain a thin film. These discs were then dried in a chamber under a current of nitrogen before the spectra were taken.

#### NMR spectroscopy

The microstructure of the polymerized materials was characterized with the help of  $^{13}C$ - and  $^1H$ -NMR spectroscopy. Both the  $^{13}C$  spectra and the  $^1H$ -NMR spectra of the polymers were obtained by using a DRX-500 spectrometer ( $^{13}C = 125$  MHz and  $^1H = 499.869$  MHz); the spectra were calibrated by using tetramethylsilane (TMS) as an internal standard. All the samples were prepared in deuterated chloroform ( $^{13}C = 5\%$  w/v and  $^1H = 10\%$  w/v).

#### Dynamic mechanical analysis

The dynamic mechanical measurements were carried out by using a Netzsch DMA242 rheometric mechanical spectrometer. The geometry of the solid-state rectangular samples is  $10.0 \times 6.25 \times 3.97$  mm. The samples were scanned at temperatures ranging from  $-150$  to  $150^\circ C$  with a frequency of 1 rad/s. The temperature was increased at a rate of 2 K/min.

#### Transmission electron microscope (TEM)

Ultrathin sections were prepared to analyze the phase structure by TEM. After cutting the sections at low

temperature ( $-130^\circ C$ ) with a glass knife using ultramicrotome Ultratome III (LKB), the ultrathin sections were stained in  $OsO_4$  vapor. For observation and micrographing, TEM Hitachi H-600 was used.

#### Mechanical properties

The mechanical properties of the copolymers were examined after injection-molding by using a Boy 22S injection-molding machine. The temperatures in the three zones of the injection-molding machine were 140, 170, and  $200^\circ C$  with a pressure of 4 MPa. The mold temperature was kept at  $25^\circ C$  with a screw speed of 100 rpm. Tensile strength, flexural strength, and impact properties of the samples were obtained according to the DIN53455, DIN53452, and DIN53453 test methods.

### Experimental setup

Styrene and butadiene monomers were purified and destabilized before polymerization by using an argon atmosphere in the unit shown in Figure 1. Water content was cut to less than 10 ppm. There was a freezing system to keep butadiene monomers in a liquid state. Purified styrene and butadiene were stored in a tank able to endure high pressure; then, the S/B monomer mixtures were added directly into the extruder by a metering pump (Fig. 1).

The reactor was a corotating closely intermeshing twin-screw extruder with 35 mm diameter ( $D$ ) and a ratio of 42 for the length ( $L$ )/ $D$ . The feeding system was made up of two meter pumps A and B. A was for the styrene/butadiene monomer mixture and B was for the initiator. The whole line (see Fig. 2) was operated in an argon atmosphere to prevent contamination of the reaction system by oxygen and moisture (Fig. 2).

## RESULTS AND DISCUSSION

### Synthesis of S/B copolymer

The very rapid anionic polymerization of S/B monomer mixtures was performed in the corotating in-

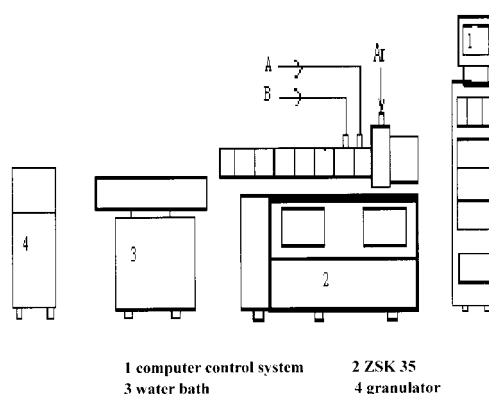


Figure 2 Experimental setup for reactive extrusion.

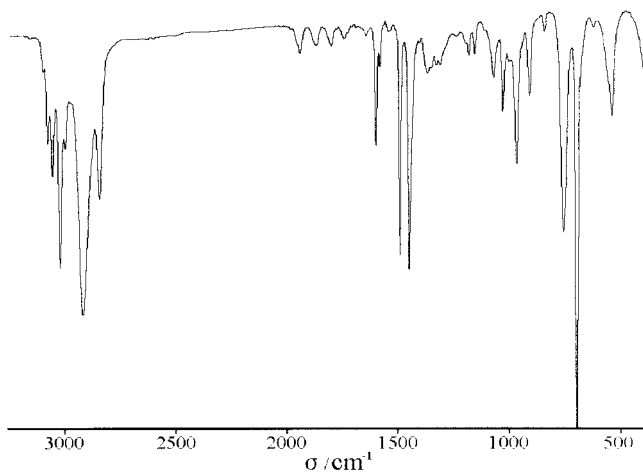


Figure 3 FTIR spectrum of S/B copolymer.

termeshing twin-screw extruder, which was divided into eight zones. The temperature for every zone was constant. The temperature range was from 40 to 220°C. Despite this ultrahigh reaction temperature, the living anionic polymerization of S/B monomer mixtures was performed successfully in the extruder reactor. On leaving the extruder, the melt showed an intense red color, which indicated the presence of reactive polystyryl anions. Moreover, the main screw profile included conveying elements and different types of kneading blocks, which were designed technically for monomer polymerization and melt conveyance.

### Structure characterization

#### Molecule structure of S/B copolymer

Figure 3 shows the FTIR spectrum of the S/B copolymer. In the spectrum, the bands at 700 and 760  $\text{cm}^{-1}$  arise from the bending mode of the hydrogen atoms, attached to the phenyl ring. Those characteristic bands, together with bands at 1670, 1740, 1800, 1870, and 1940  $\text{cm}^{-1}$ , indicate a monosubstituted phenyl ring: there are no additional bands indicative of other functional groups. Therefore, the phenyl ring is attributed to the polystyrene structure. Moreover, strong bands at 967 and 910  $\text{cm}^{-1}$ , respectively, indicate the presence of olefinic C=C units, suggesting that a diene has been incorporated into the copolymer chains (Fig. 3).

The molecular structure of the S/B copolymer was further revealed by  $^1\text{H-NMR}$  spectra and  $^{13}\text{C-NMR}$  spectra. In Figure 4,  $^1\text{H-NMR}$  results show that two absorption peaks appear at chemical shifts of about 6.5 and 7.0 ppm. Usually, blocks of styrene units produce separate resonances for the *ortho* protons at approximately 6.5 ppm, while the *meta* and *para* protons produced a resonance near 7.0 ppm.<sup>13</sup> Therefore, the two

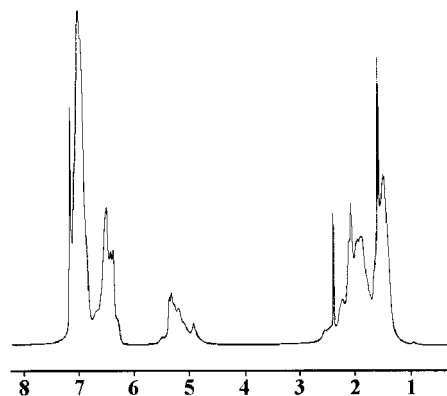


Figure 4  $^1\text{H-NMR}$  spectrum of S/B copolymer.

peaks at 6.5 and 7.0 ppm were characteristic of a polystyrene block structure (Fig. 4).

Figure 5 shows a  $^{13}\text{C-NMR}$  spectrum; the assignment of the individual peaks to carbons of specific dyads is summarized in Table I. The assignments obtained from literature<sup>14</sup> for polystyrene and polybutadiene are also given in Table I for comparison. Among those peaks, Peaks II and IV were associated with block 1,4-linked butadiene units: Peak II at 27.3 ppm is assigned to block *cis*-1,4-linked butadiene units ( $cc^*$ ,  $c^*c$ ,  $c^*t$ , and  $tc^*$ ), whereas Peak IV at 32.7 ppm arose from block *trans*-1,4-linked butadiene units ( $tt^*$ ,  $t^*t$ ,  $t^*c$ , and  $ct^*$ ). Those peaks further demonstrate the presence of polybutadiene block.

From all the above-mentioned results (FTIR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$ ), it is clear that the S/B block copolymer was successfully synthesized by reactive extrusion.

#### DMA of S/B copolymer

DMA is one of the most useful means of investigating the macrostructure of copolymer, which can provide

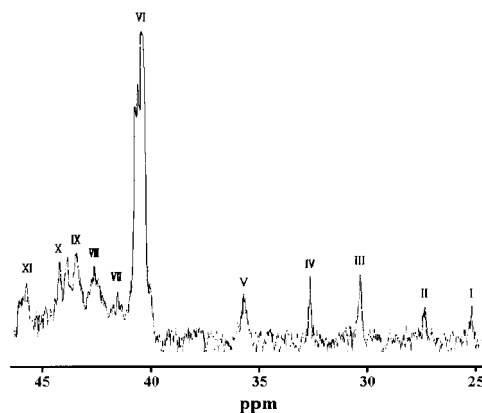


Figure 5  $^{13}\text{C-NMR}$  spectrum of the alkane region of S/B copolymer.

TABLE I  
Spectral Peaks of the Alkane Region and Their Assignments

Peak	Chem. shift		Methylene number	Sequences
	Experiment	Literature		
I	25.2	25.2	CH <sub>2</sub> 1	sc*s
II	27.3	27.3	CH <sub>2</sub> 14	cc* c*c c*t tc*
III	30.5	30.7	CH <sub>2</sub> 1	st* t*s
IV	32.7	32.7	CH <sub>2</sub> 4	tt* t*t t*c ct*
V	35.8	35.8	CH <sub>2</sub> 1	sv*1,4(r) vv*1,4(r)
VI	40.4	40.4	CH 2	vs*v sv*1,4
	40.6	40.6	CH 2	ss*v vs*s
	40.8	40.8	CH 2	ss*s
	41.6	41.7	CH <sub>2</sub> 1	sv*vs vv*vs sv*vv
VIII	42.7	42.6	CH <sub>2</sub> 1	1.4s*v 1.4v*s
IX	43.5	43.1	CH <sub>2</sub> 1	vv*s sv*s
X	44.2	44.5	CH <sub>2</sub> 1	ss*s
XI	45.3	45.0	CH 2	1.4v*

Chemical shift expressed in ppm.

Note: \*, resonance corresponding carbon: m, meso; r, racemation; s, styrene; v, 1,2-linked; c, *cis*-1,4-linked; t, *trans*-1,4-linked; 1,4, *cis*- or *trans*-1,4-linked.

direct information on the difference between block copolymer and random copolymer. In principle, S/B random copolymer has only one glass transition temperature ( $T_g$ ), which locates usually between the  $T_g$  of polystyrene (100°C) and the  $T_g$  of polybutadiene (-108°C, *cis*-1,4-linked), while there exist two  $T_g$  for S/B block copolymer corresponding to the  $T_g$  of polystyrene and the  $T_g$  of polybutadiene, respectively. Therefore, the peak which appeared at -51.3°C ( $\tan \delta = 0.0076$ ) in Figure 6 confirms the presence of polybutadiene block. However, the peak observed in the figure is relatively small, implying the polybutadiene block might be very short in block length. Further evidence will be provided by TEM results (Fig. 6).

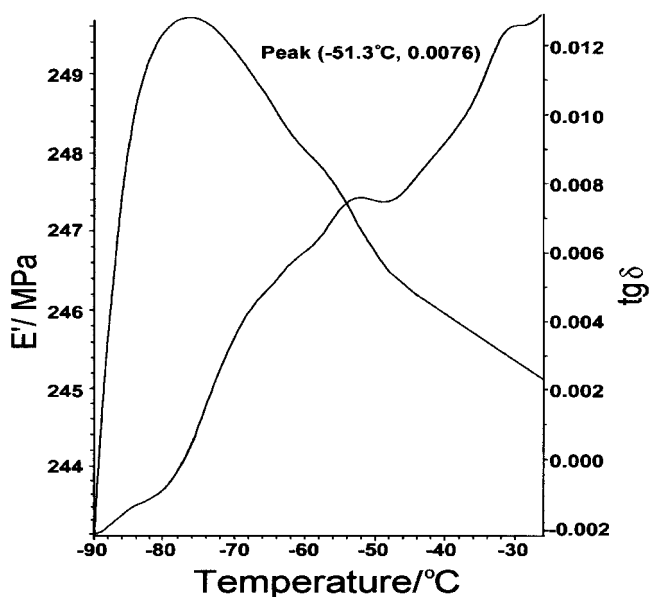


Figure 6 DMA curve of copolymer (zoom).

It has been reported that  $T_g$  of the polybutadiene phase of S/B block copolymer, prepared by traditional solution polymerization, ranges from -58 to -78°C. However, the glass transition temperatures of the resulting copolymer, as illustrated in Table II (e.g., for B% = 24 wt %  $T_g = -51.3^\circ\text{C}$  and for B% = 13 wt %  $T_g = -45^\circ\text{C}$ ), are generally higher than that of the block copolymer from solution polymerization. Meanwhile, the  $\Delta T_g$  of the S/B copolymer is about 140°C, which is lower than that from traditional solution polymerization. This might also be attributed to the short polybutadiene block, which improves the compatibility of two phases in the S/B copolymer prepared in this work (Table II).

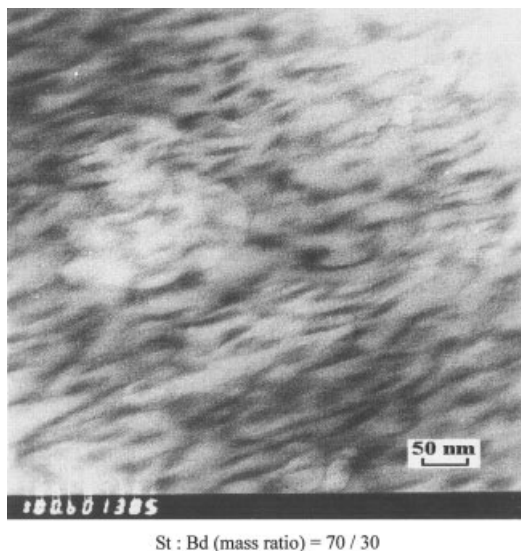
#### TEM of S/B copolymer

To obtain a deeper insight into the microphase separation of the resulting copolymers, TEM analyses were carried out by using ultrathin chips, as illustrated in Figure 7. It can be clearly seen that the microstructure of the copolymer shows evident two-phase structure: bright continuous polystyrene phase and dark dispersed polybutadiene phase. A close inspection of the micrograph also indicates the polybutadiene phase has been elongated with a size of less than 100 nm in

TABLE II  
Dynamic Properties of S/B Block Copolymer

	Bd% (wt %)		
	13%	24%	34%
$T_{g1}, ^\circ\text{C}$	-45.0	-51.3	-53.8
$T_{g2}, ^\circ\text{C}$	94.2	95.8	94.7
$\Delta T_g =  T_{g2} - T_{g1} $	139.2	147.1	148.5





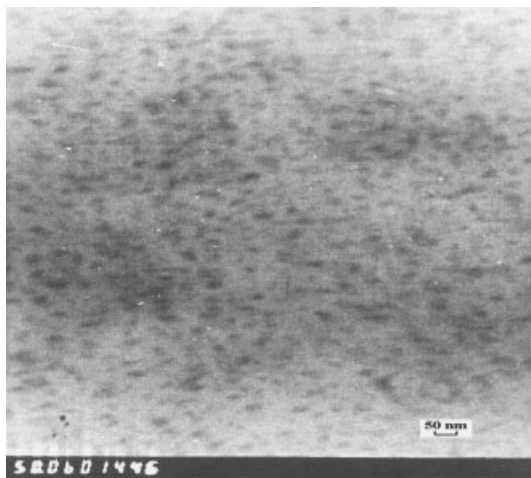
St : Bd (mass ratio) = 70 / 30

Figure 7 TEM photographs of S/B copolymer ( $\times 100,000$ ).

length (Fig. 7). Such morphology was formed by the polymer chain orientation at the die. After being heated at  $100^{\circ}\text{C}$ , the polybutadiene phase retracted into spherical particles 20–30 nm in diameter and dispersed homogeneously in the copolymer, as shown in Figure 8. The TEM observations strongly support the conclusion that the copolymer possesses a multi-S-B-block structure with the dispersed phase in a nanometer range.

**Reaction mechanism**

When anionic copolymerization of styrene and butadiene is conducted in a conventional tank reactor, butadiene monomers tend to polymerize first according to the reactivity ratio of the two monomers. Sty-



St : Bd (mass ratio) = 85 / 15

Figure 8 TEM photographs of S/B copolymer ( $\times 50,000$ ).

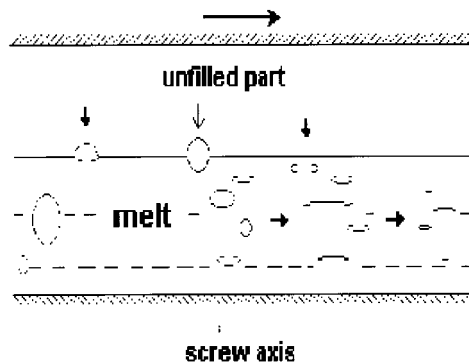


Figure 9 Schematic of the polymerization process in extruder.

rene polymerization does not proceed until the butadiene monomers have been consumed.<sup>7</sup> As a result, S-B diblock copolymer or S-B-S triblock copolymer is formed. However, the reaction conditions in the extruder reactor are different, which lead to a copolymer with multi-S-B-block structure. Accordingly, the mechanism of living anionic polymerization of S/B monomer mixtures in a corotating intermeshing twin-screw extruder also differs from that involved in a tank reactor.

In the extruder reactor, barrel temperature is far higher than the vaporization temperature of butadiene monomers ( $-4^{\circ}\text{C}$ ). Consequently, most butadiene monomers in monomer mixtures diffuse into the gas phase immediately after being fed into the screw. Only a small portion of butadiene in monomer mixtures is kept in the liquid phase. As soon as an initiator is added, butadiene monomers in liquid phase start to polymerize, while styrene polymerization follows after the complete consumption of liquid butadiene monomers. Because the twin-screw extruder was partially filled for reactive extrusion, butadiene monomer in gaseous phase occupied the unfilled part of the barrel. The viscosity of the polymer in the screw increased along the screw axis because of the styrene polymerization. Therefore, the occupied volume of the gaseous butadiene in the barrel decreased, and part of the gaseous butadiene diffused into the polymer melt because of the powerful mixing. As shown in Figure 9, circles represent the gaseous butadiene phases and the bottom represents the polymer melt, the top part being the unfilled part in the barrel. It is easy to understand that the powerful mixing of the screw divides the gaseous butadiene into a lot of small parts, and some of them diffuse into the polymer melt. Because of high reactivity, butadiene, that diffused in to polymer melt, polymerized immediately. As a result, the polybutadiene block is small. Because of powerful mixing of the twin screw, small butadiene blocks in copolymer are very homogeneous (Fig. 9).

TABLE III  
The Mechanical Properties of S/B Copolymers

	St content, wt %				
	100	91.9	85.7	81.6	68.4
Tensile strength, MPa	47.9	52.1	43.5	40.4	34.1
Flexural strength, MPa	78.8	94.3	83.9	75.8	56.8
Elongation at break, %	6.7	21.3	76.1	128.3	215.5
Simple beam impact strength					
Notched, kJ/m <sup>2</sup>	1.35	2.56	2.68	2.85	3.79
Unnotched, kJ/m <sup>2</sup>	6.3	—	10.1	13.7	19.5

<sup>a</sup> DIN standard.

### Mechanical properties

Mechanical properties of the S/B copolymer depend on the components in the polymer. As expected, the rigidity of the material is reduced gradually, or the toughness of the material is improved steadily, with the increase of butadiene content (see Table III). Furthermore, the resulting polymer shows an ultrahigh elongation at break (see Fig. 10). When the butadiene content is 31.6%, the impact strength of the copolymer is about three times that achieved by pure polystyrene; however, the elongation at break is increased by more than 30 times. These findings can be explained in terms of the toughening mechanism of rubber particles. Generally, the size of the rubber phase, dispersed in the polystyrene matrix, ranges from 1 to 10  $\mu\text{m}$  for conventional toughened PS such as HIPS. The rubber particles are able to limit the propagation of cracks through the material. However, nanometer-dispersed butadiene phase in the S/B copolymer cannot play the same role because of its extremely small particle size. That could be the reason the impact property of the block copolymer was not improved significantly. Furthermore, in the S/B copolymer, there are a lot of small polybutadiene blocks which are dispersed homogeneously. As a result, it is difficult for the continuous phase of polystyrene to limit the plastic deformation of all the dispersed rubber particles. Accordingly, the elongation at break was improved greatly.

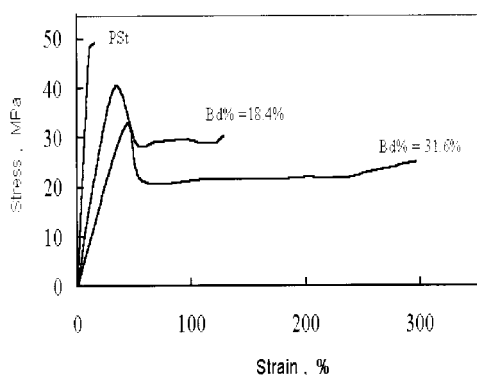


Figure 10 The effect of butadiene content on elongation at break of S/B copolymer.

### CONCLUSION

Using an anionic initiator system and twin-screw extruder as reactor for addition of styrene/butadiene monomer mixtures, nanometer-size multiblock copolymers were synthesized by bulk polymerization.

The analyses of <sup>1</sup>H-NMR, IR, DMA, and TEM indicate that the copolymer was a nanometer-size multiblock structure, the size of butadiene block ranging from 20 to 30 nm.

With the increase of butadiene content in copolymer, the elongation at break of the material was improved greatly. When the content of butadiene in copolymer was 31.6%, the impact of the copolymer was three times higher than the pure polystyrene, and elongation increased more than 30 times.

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