

Anionic Bulk Polymerization to Synthesize Styrene-Isoprene Diblock and Multiblock Copolymers by Reactive Extrusion

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ABSTRACT: In this study, styrene-isoprene diblock and multiblock copolymers were synthesized with *n*-butyllithium as the initiator, in an intermeshing, corotating twin-screw extruder. The diameter (*D*) of this extruder was 36 mm, and the ratio of length/diameter was 56. The weight content of polyisoprene in these copolymers was above 50% although in the past studies it had not been possible to accomplish levels higher than 30%. Gel permeation chromatography results of samples and their degraded products show that there is only one long block polystyrene in the diblock copolymer chains; while in the multiblock copolymer molecules, there is a long block and large numbers of small blocks. Dynamic mechanical analysis and transmission electron microscopy show that the two phases in the diblock copolymer are completely incompatible, leading to sharp phase separation. In the multiblock copolymer, the two phases are partly compatible without an obvious phase boundary. The successful syntheses of styrene/isoprene diblock and multiblock copolymers with high-isoprene contents provide a novel method to synthesize polystyrene rubbers and styrene-diene-styrene thermoplastic elastomers. Traditionally, these products were mainly synthesized by solution polymerization. The present work in this article provides the possibility to synthesize them with very little or no solvent using bulk polymerization. This method fits the environmentally friendly trend to use low amounts of carbon while allowing commercial profitability. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 39429.

KEYWORDS: extrusion; polystyrene; copolymers

Received 21 February 2013; accepted 18 April 2013

DOI: 10.1002/app.39429

INTRODUCTION

Extruders are typical polymer processing and modification equipment. Their use as continuous polymerization reactors for polymer synthesis is growing rapidly. Compared with conventional polymerization reactors, extruders have the advantage of continuous bulk polymerization without any solvent. In addition, the polymerization in the screws is rapid allowing the possibility to apply the reactive extrusion technology toward production process in the manufacture plant. Moreover, the rotation of the screw ensures good mixing and heat transfer in spite of the high viscosity of the melt. Therefore, the reaction and the extrusion may take place simultaneously through the extrusion process.

Michaeli et al.^{1,2} used a corotating intermeshing twin-screw extruder with a diameter of 30 mm, reactor length/diameter (*L/D*) of 29 and *sec*-butyllithium as the initiator, to synthesize polystyrene. Subsequent characterization showed that this polymerization was extremely rapid. The conversion was almost 100% within a small distance traversed by the screw.

Based on the past 15 years of research by our group on anionic bulk polymerization by reactive extrusion, some theories and analysis methods have been proposed.³⁻⁹

Si et al.³ also synthesized ultrahigh molecular weight polystyrene by carrying out polymerization in an extruder reactor. By controlling the transfer of heat and mass and the mean residence time in twin-screw extruder, polystyrene with a weight-average molecular weight between 1.0×10^5 and 8.0×10^5 was synthesized.

Gao et al.^{4,5} conducted research on dynamic parameters of the reactive extrusion with a mixture of styrene/butadiene monomers, and subsequently synthesized a kind of styrene/butadiene copolymer. The polymerization mechanism in the screw was quite different from that in the solvent. In their opinion, when the mixture of the styrene/butadiene monomers was pumped into the extruder, with a boiling point of -4.5°C , the butadiene molecules immediately gasified and were prone to separate from the liquid phase that contains the initiator solution and the liquid styrene monomers. Therefore, the initiator attacked the

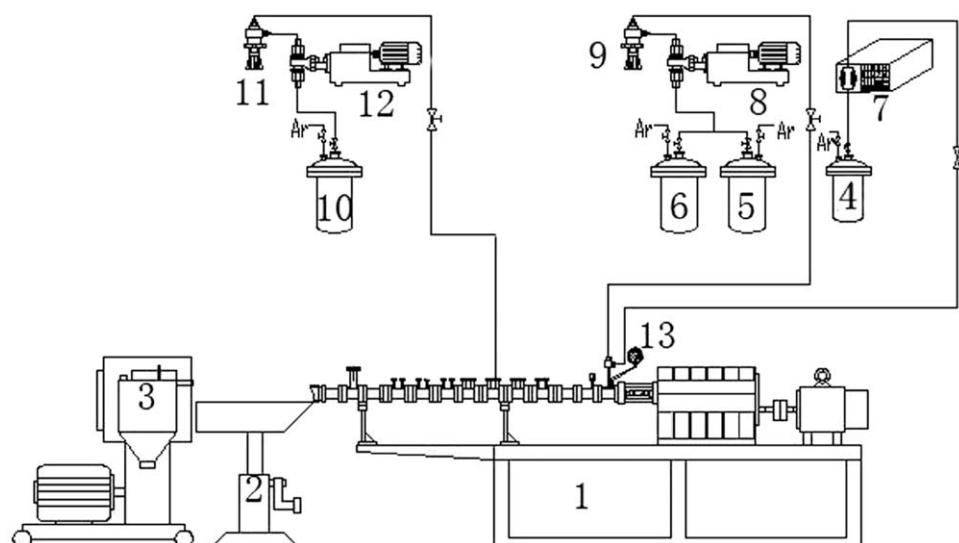


Figure 1. Experimental setup for reactive extrusion: 1 reactor, 2 water bath, 3 granulator, 4 initiator container, 5 styrene/isoprene mixed monomers container, 6 styrene monomer container, 7 initiator pump, 8,12 monomer pumps, 9,11 Back pressure valve, 10 isoprene monomer container, 13 pressure gauge.

styrene monomers first. As the polymerization of styrene continued, the viscosity in the screw increased along the screw axis; therefore, gaseous butadiene monomers diffused into the polymer melt subsequently and copolymerize with the activated styrene units. Based on this “bubble theory” was proposed.

Zhou et al.⁶ and Zhang et al.⁷ also synthesized styrene/butadiene and styrene/isoprene multiblock copolymers. To study the microstructure of the copolymers by gel permeation chromatography (GPC), a degradation reaction was carried out. The data suggested that the polymer chains can be considered to comprise of a long polystyrene block and many micro blocks of both polystyrene and polydiene. This result substantiates the “bubble theory.”

Zhang et al.⁸ and Sun et al.⁹ studied the relationship between polar additives and microstructure. They also tested the influence of microstructure on physical properties.

However, in all of these reports, the content of butadiene or isoprene was lower than 25 wt %. In order to reach high-diene content, some additives needed to be added into the polymerization process to suppress the gel formation.¹⁰ However, the additives would decrease the 1, 4-structural element of the polydiene significantly. Hence, there was need of further research to increase the diene content without any modifying the 1, 4 structure.

In this study, by controlling the temperatures of various barrels alone without supplying additives, two kinds of styrene/isoprene copolymer with high isoprene content were successfully synthesized using reactive extrusion. Although the styrene–isoprene copolymers were not widely used as the styrene–butadiene copolymers, their synthetic method and polymerization mechanism were quite similar. As a result, isoprene, which was convenient to store and purify, was used to study the bulk polymerization of dialkene and styrene in extruder. ¹H-NMR analysis showed that weight contents of isoprene in both

copolymers were higher than 50%. GPC, transmission electron microscopy (TEM), and dynamic mechanical analysis (DMA) analyses proved that one of the styrene/isoprene copolymers is a neat diblock copolymer, and the other one is a kind of multi-block copolymer.

EXPERIMENTAL

Materials

The chemicals used in this research were industrial products. Styrene and isoprene used were polymerization grade provided by the Sinopec Shanghai Petrochemical Company (Shanghai, China) and stabilized with tertiary butylcatechol. The inhibitor in the monomers was eliminated by distillation. Molecule sieve was utilized to adsorb the moisture 10 h prior to polymerization. Moisture meter analysis showed that the moisture content was lower than 20 μg/mL.

The *n*-butyl lithium solution (2.4 mol/L in hexane) was provided by J&K Scientific Company, China. Cyclohexane was used to dilute the initiator to about 0.1 mol/L and the initiator solution was stored in airtight steel cans away from light.

Polymerization

The reactor was a corotating closely intermeshed twin-screw extruder with diameter (D) of 36 mm and ratio of L/D of 56, manufactured by Nanjing Ruiya Extrusion Machinery Co (Nanjing, China). The feeding system included three metering pumps 7, 8, and 12 (see Figure 1), all manufactured by Hangzhou Zhijiang Petrochemical Equipment Co (Hangzhou, China). When the S/I multiblock copolymer was synthesized, pumps 8 and 7 were used to transport the styrene/isoprene monomer mixture and initiator, respectively. Pump 12 was not used. When the diblock copolymer was synthesized, pumps 8, 7, and 12 were used to transport the styrene, the initiator, and the isoprene monomers, respectively. The whole line (see Figure 1) was

operated in an argon atmosphere to prevent contamination of the reaction system by oxygen and moisture.

Oxidative Degradation of the Copolymer

In order to study the microstructure of the final products, complete degradation of the polymers has been studied.¹¹ The copolymer samples were dissolved in 50 mL orthodichlorobenzene at 90°C. The solution was stirred for 30 min to make sure that the samples were dissolved completely. Then, the solution was cooled down to 25°C; 1 mL OsO₄ aqueous solution at a concentration of 0.003 mol/L and 12 mL H₂O₂ were added into the solution. Then, the solution was heated to 90°C and stirred for 120 min. Finally, the solvent and small molecules created by the degradation reaction were removed by reduced pressure distillation. The remaining solids were polystyrene segments which were not destroyed during the degradation reaction.⁷

Analysis of Gel Content

In order to measure gel content of the copolymer, the samples were dissolved in tetrahydrofuran (THF). After sufficient stirring, the solution was leached through filter paper. Gel content was tested by measuring changes in the quality of the filter paper.

Gel Permeation Chromatography (GPC)

Absolute molecule weight was determined by Waters Model 244 GPC spectrometer connected with Wyatt Technology DAWN EOS small-angle light scattering detector. The measuring range of molecule weight was from 10³ to 10⁶. THF was used as the solvent, with a sample content of 5 mg/mL and the test was carried out at 25°C.

Proton Nuclear Magnetic Resonance (¹H-NMR)

Microstructure of the polymerized materials was characterized with the help of ¹H-NMR spectroscopy. NMR spectra of the polymers were obtained by using a Bruker DRX-400 spectrometer; the spectra were calibrated by using tetramethylsilane (TMS) as an internal standard. All the samples were dissolved in deuterated chloroform.

Dynamic Mechanical Analysis (DMA)

The DMA was carried out by using a Netzsch DMA242 rheometric mechanical spectrometer. The samples were scanned at temperatures ranging from -100 to 150°C, with a frequency of 1 Hz. The temperature was increased at the rate of 3 K/min.

Transmission Electron Microscopy (TEM)

The polymer samples were dissolved in toluene at the concentration of 1 wt %. The solution was dripped on the copper grid. When the solvent was evaporated completely a polymer film was obtained. The sample film was stained in OsO₄ vapor for 20 min. Joel JEM-1400 TEM was used for observation and micrographing.

RESULTS AND DISCUSSION

Synthesis of S/I Copolymer

Very rapid anionic polymerization was performed in the corotating, closely intermeshed twin-screw extruder. Despite the ultrahigh reaction temperatures at the barrels near the die, the anionic polymerization was performed successfully within the extruder reactor. The melt proceeding out of the die showed

an intense red color, indicating the presence of reactive polystyryl and polyisoprene anions. Moreover, the main screw profile included conveying elements and different types of kneading blocks. They were designed to effectively transfer the heat and mass more easily for monomer polymerization and melt conveyance.

Both the diblock and multiblock copolymers were synthesized by the same extruder. The extruder had 11 barrels, and the set temperature of each barrel was set according to the polymerization process parameters. When the copolymer was synthesized, the temperatures were set from 40 to 200°C, in a slow gradient along the screw from the feeding hole to the die.

Polymerization Mechanism

Using two different monomer feeding systems, the polymerization mechanism in the extruder was monitored and two kinds of block copolymer were made from styrene and isoprene monomers.

To synthesize the styrene/isoprene diblock copolymer, styrene monomers were fed into the extruder in the first barrel, but isoprene monomers were not fed into the extruder until the fifth barrel. Therefore, the initiator attacked the styrene monomers first because there were no isoprene monomers in the first barrel. When the isoprene monomers were later added, a long polystyrene block had been polymerized. Therefore, the final copolymer was a neat diblock copolymer.

On the other hand, to synthesize the styrene/isoprene multiblock copolymer, styrene monomers and isoprene monomers were fed into the extruder simultaneously in the first barrel. However, the polymerization mechanism of styrene/isoprene in this study is different from that in a previous study on synthesizing styrene/butadiene multiblock copolymer.⁵ First, the boiling point of isoprene is 34.3°C, which is much higher than that of butadiene (-4.5°C). Second, in this study, the weight content of isoprene was above 50%, while in the previous studies, the weight content of butadiene was lower than 30%.⁵

As a result, in this study, when the monomer mixture was added into the screw, the isoprene monomers could not gasified completely as in the case of butadiene because the barrel temperature (40°C) was only slightly higher than the boiling point of isoprene, and because of the much higher weight content of isoprene. Hence, some of the liquid isoprene monomers dissolved in the styrene monomers. As soon as the initiator was added into the screw, the isoprene monomers in liquid phase began to polymerize. Styrene monomers followed after the liquid isoprene monomers were completely consumed. Along with the polymerization, when the viscosity of the styrene/isoprene copolymer would be sufficient to contain the small isoprene bubbles, the short polystyrene and polyisoprene segments would be further polymerized into a longer chain. Consequently, there would be a polyisoprene block at one end, a polystyrene block at the middle, and many short polystyrene and polyisoprene blocks at the other end of the final copolymer chain, according to the "bubble theory." In contrast, there were only a long polystyrene block and many short polystyrene and polybutadiene blocks on the styrene/butadiene copolymer.⁵

Control of Gel Content

The key to successfully synthesize styrene/isoprene multiblock copolymer with high isoprene weight content is strict control of the temperature. From large number of experiments, it was found that the gel mainly appeared at the beginning of the polymerization. Previous studies on anionic bulk polymerization of styrene¹² and the solution polymerization of butadiene¹³ proved that when *n*-butyl lithium initiated the polymerization, the association of *n*-butyl lithium still existed. Insertion of styrene monomers into the space between the carbanion and the lithium cation would result in building of a supramolecular structure consisting of living polystyryllithiums. Along with the polymerization, the polymer chain in the supramolecular structure would become closely intertwined, making it difficult for styrene monomers to enter into that structure to polymerize. As a result, the polymerization would end up in a stationary-conversion platform (SCP). The supramolecular structure would not dissociate except when the polymerization had passed the SCP stage. In this study, when the polymerization of the monomer mixtures was in the SCP phase, most of the double bonds could be attacked by the living anions in the supramolecular structure were on the polymer chains but not the monomers because the latter were almost outside of this structure. It is obvious that living anions would not be able to attack the double bonds on the polymer chain as easily as those on the monomers. However, if the temperature was high enough, this reaction would be possible. During polymerization of the styrene, the supramolecular structure could dissociate into many living polymer chains. However, during the polymerization of the monomer mixtures, if the double bonds on the polymer chain are attacked and subsequently formed polymer branching, the supramolecular structure is not able to dissociate but can release a macromolecule with many living anions. These living anions are placed close enough to make it easy to polymerize into a network polymer. This would result in increase in the gel content. Therefore, strict control of the reaction temperature when the polymerization is initiated, or before reaching the SCP stage, can reduce gel content significantly. Through several experiments, it was possible to control the gel content of the final product to be lower than 0.5 wt %.

During the polymerization of diblock copolymer, the styrene monomers were first polymerized. The supramolecular structure was dissociated when isoprene monomers were added. Therefore, there was almost no gel phenomenon during the polymerization.

Microstructure Analysis

¹H-NMR Spectra of S/I Copolymers. Molecular structure of the S/I copolymer was revealed by ¹H-NMR spectra.

In Figure 2, two absorption peaks at chemical shifts of about 6.55 and 7.05 ppm were observed. These two peaks are characteristic of a polystyrene block structure: Resonances at approximately 6.55 ppm are from ortho protons,¹⁴ while resonances near 7.05 ppm are from meta and para protons. The spectra also showed three characteristic polyisoprene absorption peaks at 5.13, 4.76, and 4.68 ppm.¹⁵ The double bond protons on the 1, 4 polyisoprene units produced resonances at 5.13, while the

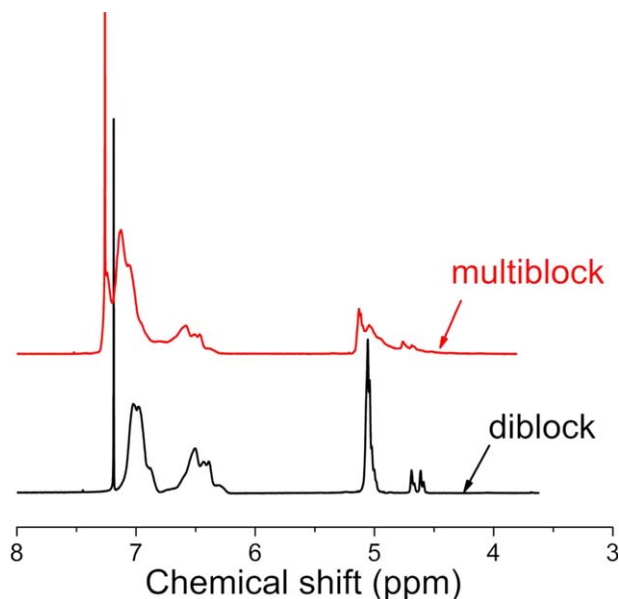


Figure 2. ¹H-NMR spectrum of S/I diblock and multiblock copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

3, 4 units produced them at 4.76 and 4.68 (there were two double bond protons at the 3, 4 units). The content for each component can be calculated from the ¹H-NMR spectra. Based on Figure 2, the calculated polyisoprene weight content was 56.3% for the diblock copolymer and 52.3% for the multiblock copolymer. In the synthetic elastomers, the weight content of diolefin was always above 60%. Therefore, in the further works, a higher diolefin content (about 75 wt %) was reached by using the techniques developed in the current work. It is also possible to calculate the weight content of the 3, 4 structure in the polyisoprene units. Results of such calculations showed that the weight content of the 3, 4 polyisoprene units was 8.2% in the diblock copolymer and 9.0% in the multiblock copolymer.

Although the isoprene contents in the two copolymers are similar, the characteristics of proton absorption peaks corresponding to isoprene units are somewhat different. In the diblock copolymer, the isoprene units and styrene units are almost mutually exclusive, and there are no chemical bonds between them except at the linking position of the two blocks. Therefore, the ¹H-NMR spectra of the isoprene units in the diblock copolymer and in the isoprene homopolymer are identical. In the multiblock copolymer, the distribution of the two components is more random, and a considerable part of the isoprene units is connected with the styrene units, in accordance with the “bubble theory.” Because of the complicated chemical environment around the double bond of the polyisoprene units, the absorption peaks of the double bond protons in the multiblock copolymer are more complicated than those in the diblock copolymer. As a result, the absorption peaks of double bond proton in the diblock copolymer are more intense than those of the multiblock copolymer.

GPC of S/I Copolymers. ¹H-NMR analysis of degradation products showed that the absorption peaks from 4.60 to 5.20

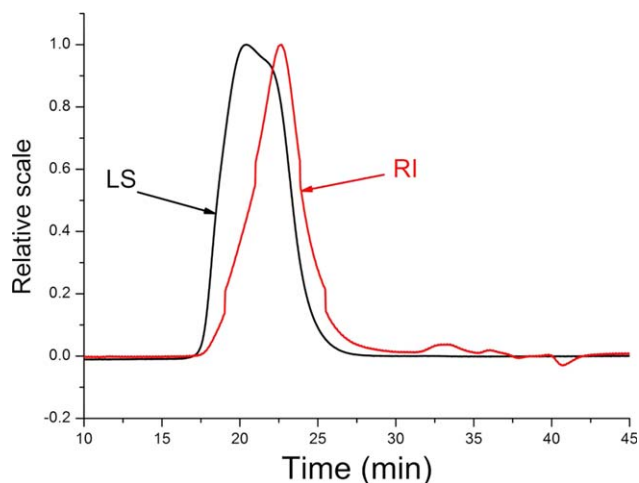


Figure 3. GPC profile of S/I multiblock copolymer before degradation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ppm of the copolymer samples disappeared completely after degradation, while no differences were observed for the peaks from 6.50 to 7.10 ppm.⁷ This suggests that the double bonds in the polyisoprene units broke completely during degradation. From the study of the remaining polymer fragments, it was possible to obtain an accurate microstructure of the polystyrene units.

In order to check if the degradation reaction affects the polystyrene units, the degradation reaction was also carried out on the polystyrene homopolymer. The GPC analysis of homopolymer before and after degradation showed no differences.⁷ This indicates that the degradation reaction did not destroy the polystyrene units.

Figures 3–6 show the GPC curves of the diblock and multiblock copolymers before and after degradation. The Light Scattering (LS) curves in the graphs refer to the signal of laser light

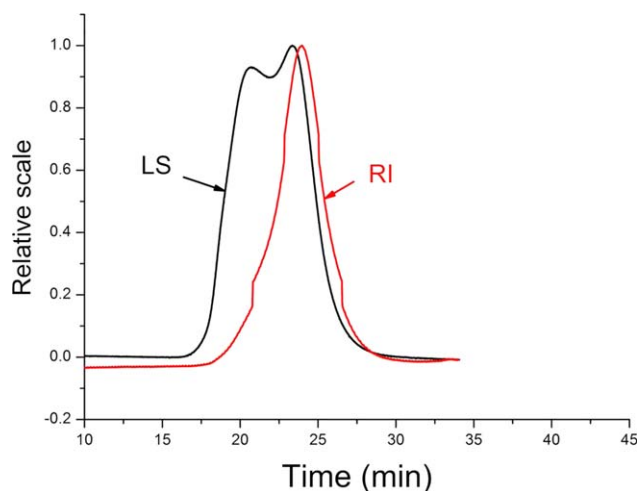


Figure 4. GPC profile of S/I diblock copolymer before degradation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

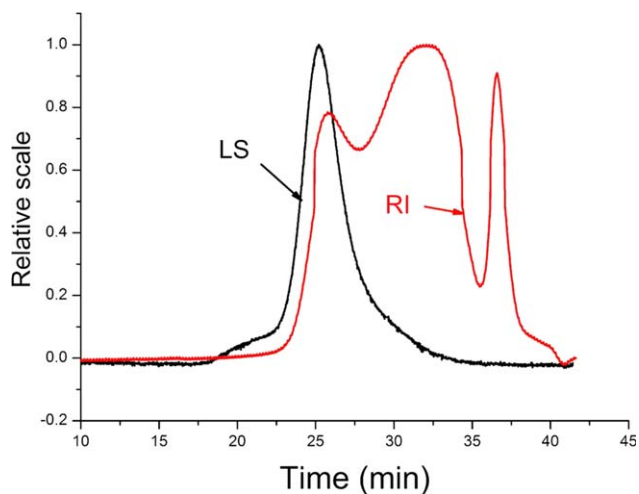


Figure 5. GPC profile of S/I multiblock copolymer after degradation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

scatterometer, which provides relatively high test sensitivity for larger molecular weight polymers. The Refractive Index (RI) curves refer to the differential refractive signal, which provides high test sensitivity for the smaller molecular weight polymers. Based on data in Table I, the number-average molecular weight of both the diblock and multiblock copolymers are about 1.0×10^5 and their molecular weight distributions are similar. However, from Table II, the molecule weights of the remaining polystyrene fragments are quite different after degradation. Based on the differential refractive signal curve of the diblock copolymer after degradation, the peak intensity of the long block is much higher than the intensities of others. During the polymerization of the diblock copolymer, the styrene and isoprene monomers were added into the extruder at different positions; the styrene was at the first barrel while the isoprene was at the fifth. The speed of polymerization of styrene monomers was very high because of the high temperature of the barrels.

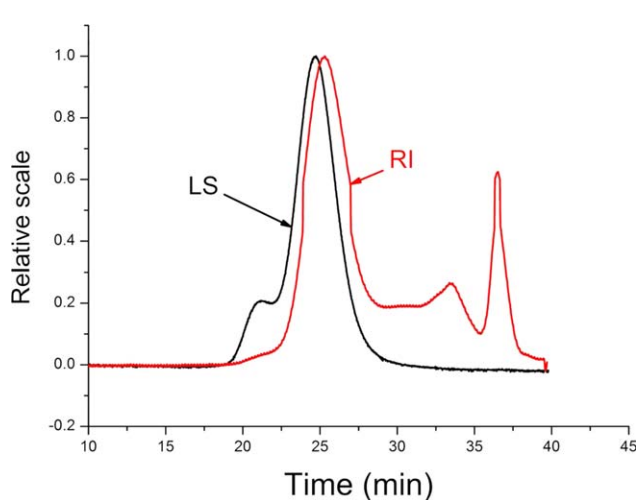


Figure 6. GPC profile of S/I diblock copolymer after degradation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. GPC Data for the Diblock and Multiblock Copolymers

Samples	Before degradation		After degradation			
	$M_n \times 10^{-4}$	M_w/M_n	Long block		Micro block	
			$M_n \times 10^{-4}$	M_w/M_n	$M_n \times 10^{-4}$	M_w/M_n
Diblock	11.1	1.7	2.7	1.9	0.12	1.2
Multiblock	10.5	1.8	2.8	1.3	0.09	3.9

Table II. Analysis of GPC Integral Curves for the Diblock and Multiblock Copolymers after Degradations

Samples	Molecule weight scale			
	Below 4×10^3 (%)	4×10^3 to 10×10^3 (%)	10×10^3 to 70×10^3 (%)	Above 70×10^3 (%)
Diblock	5.1	3.6	80.6	10.7
Multiblock	59.5	14.6	25.9	0

When the polystyryllithium came in contact with the isoprene monomer, a long polystyrene chain had already been created. The GPC analysis indicates that the number-average molecule weight of the long block polystyrene fragments is about 2.7×10^4 , and the molecule weight distribution is 1.9. From the integral curve in Figure 8 and the data in Table II, the polystyrene fragments from 1.0×10^4 to 7.0×10^4 constituted 80.6 wt % of the whole sample while the fragments under 1.0×10^4 constituted only 8.7 wt %. This GPC analysis indicates that the polystyrene units in the diblock copolymer were mainly in the form of a long block.

On the contrary, a very different molecular structure was obtained for the multiblock copolymer because a different feeding sequence was used. During the polymerization of the multiblock copolymer, the two monomers were mixed at first, and then added into the extruder before the multiblock copolymer was synthesized. The reaction in the extruder was a bulk polymerization. The “bubble theory” proves that the process of the anionic bulk polymerization in the extruder is different from that of solution polymerization. As shown in Table I, the number-average molecule weight of the multiblock copolymer before degradation is 10.5×10^4 , and the molecule weight distribution is 1.8. Both these characteristics are similar to those of the diblock copolymer. However, their RI curves, which typically have high test sensitivity to smaller molecules of the polystyrene fragments, are quite different. The peak area of long polystyrene block in the degraded multiblock copolymer is much smaller than that of the micro block. This indicates that the polystyrene in the multiblock copolymer degradation sample is mainly composed of micro block. The GPC measurements also indicate that the number-average molecule weight of the long polystyrene is 2.8×10^4 , and molecule weight distribution is 1.3, while these parameters in the smaller block have values of about 900 and 3.9, respectively. From Figure 7 and Table II, the integral curve also provides similar results: Short blocks below 1.0×10^4 (Mw) constituted 74.1 wt % of the whole sample. These results indicate that reactive extrusion of styrene/isoprene monomer

mixture results in synthesis of a multiblock copolymer in which the polystyrene is composed of a long block and many short blocks. These results fit the bubble mechanism.^{5,7}

TEM of S/I Copolymers. TEM analyses were carried out as illustrated in Figure 8. The microstructures of diblock and multiblock copolymers were found to be significantly different. The black part in the photograph is polyisoprene phase after being stained with OsO_4 vapor, while the white part is polystyrene phase which could not be stained. According to the graph of the diblock copolymer, the two phases represent columnar distribution. This distribution suggests that the two phases are incompatible, leading therefore to sharp phase separation.

On the other hand, as observed in TEM photograph of the multiblock copolymer, polyisoprene units in the copolymer represent globular distribution. The GPC discussion indicates that

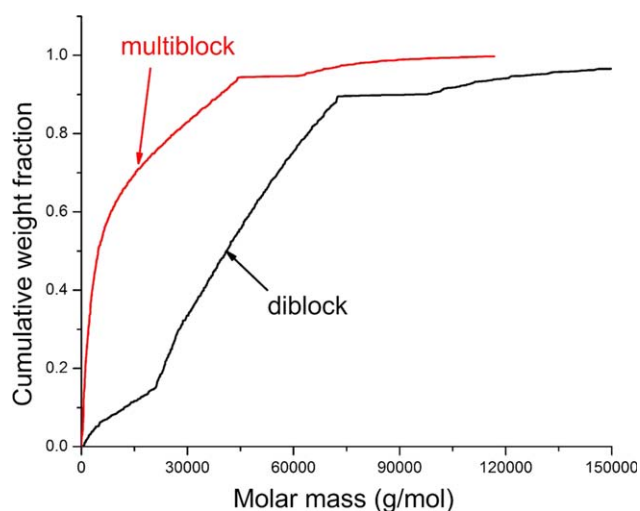


Figure 7. Molecule weight integral profile of S/I diblock and multiblock copolymers after degradations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

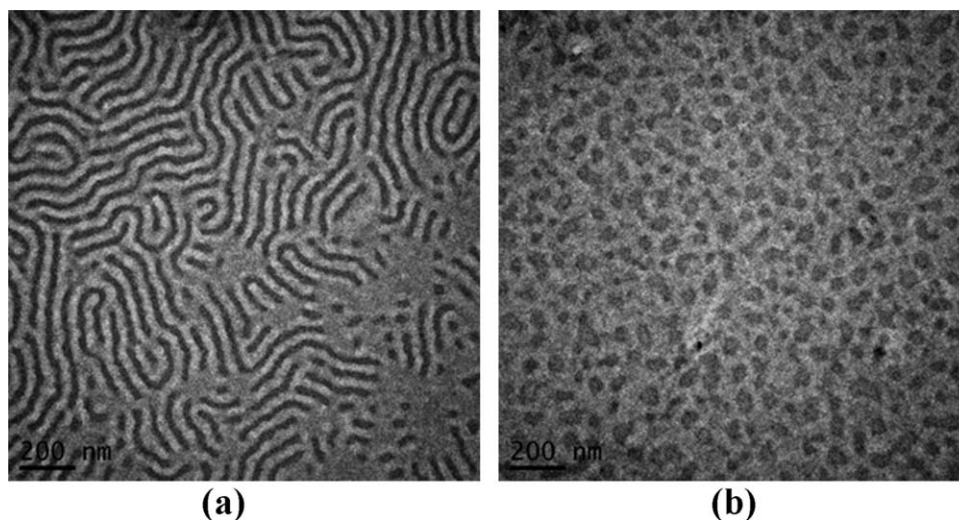


Figure 8. TEM graphs for S/I diblock (a, 56.3wt% of isoprene) and multiblock (b, 52.3wt% of isoprene) copolymers.

the multiblock polymer chain is mainly composed of short polyisoprene and polystyrene blocks. In this TEM photograph, these short polystyrene blocks appeared as black rubber balls with the largest diameter of about 50 nm. Although the sizes of the black rubber balls varied, these balls were rather uniformly surrounded by the light colored matrix. This TEM graph confirms that blocks in the multiblock copolymer synthesized by reactive extrusion are not completely incompatible with each others. However, this multiblock copolymer is not a completely random copolymer, either.

DMA of S/I Copolymers. According to the traditional theory of phase separation in the styrene/isoprene block copolymer, there would be a phase separation if the molecule weight of each block was high enough. As a result, this copolymer would have two separate glass transition temperatures.^{16,17} The following DMA analysis with results shown in Figures 9 and 10, including loss factor, loss modulus, and storage modulus, suggests that there are huge differences between the diblock and multiblock

copolymers. Both the loss modulus and loss factor curves of diblock copolymer have two peaks, corresponding to the glass transition temperatures (T_g) of polyisoprene and polystyrene, respectively.

Due to the large differences in solubility parameters of polystyrene and polyisoprene ($17.5 \text{ MPa}^{1/2}$ for polystyrene and $16.0 \text{ MPa}^{1/2}$ for polyisoprene, respectively), the polystyrene block and polyisoprene block are incompatible. Two distinct peaks located at the T_g s of polystyrene and polyisoprene indicate that the diblock copolymer synthesized by reactive extrusion was completely phase separated.

However, according to the loss factor and loss modulus curves of the multiblock copolymer, there is mainly one glass transition temperature, which is between the two T_g s of polyisoprene and polystyrene. The multiblock copolymer is mainly composed of large numbers of polystyrene and polyisoprene microblocks. As a result, the two phases are compatible and form one phase

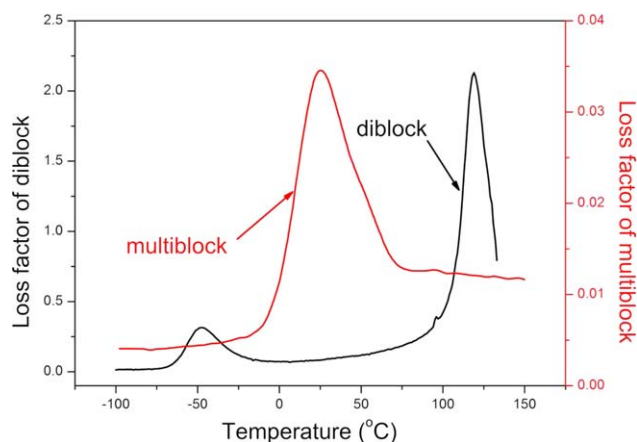


Figure 9. Temperature dependence of loss factor on S/I diblock and multiblock copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

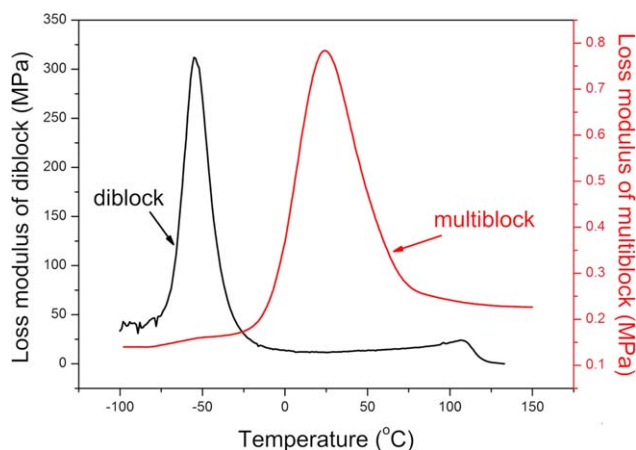


Figure 10. Temperature dependence of loss modulus for S/I diblock and multiblock copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

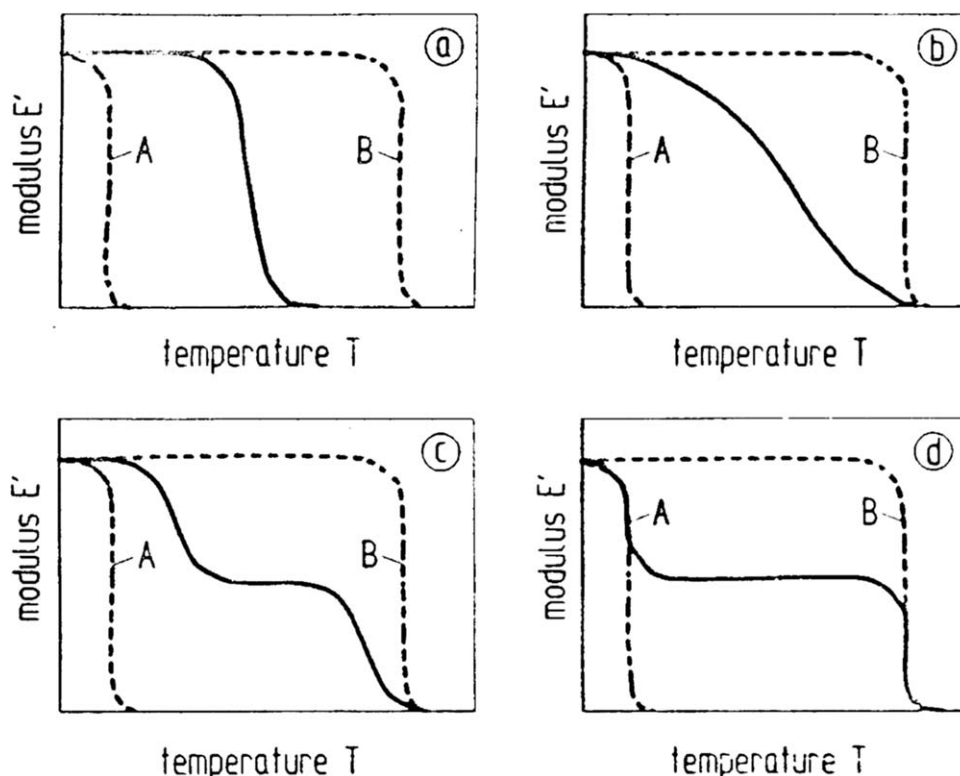


Figure 11. Temperature dependence of the storage modulus for four typical copolymers.

although there appears to be a small peak at -50°C (Figure 10) corresponding to the T_g of polyisoprene. Despite the presence of small amount of long polystyrene blocks, there was no obvious peak near the T_g of polystyrene. Therefore, the multiblock styrene/isoprene copolymer synthesized by reactive extrusion mainly displays a single phase, being neither the phase of polystyrene nor that of polyisoprene.

Figure 11¹ shows temperature dependence of the storage modulus E' for four typical copolymers composed of two components A and B.

Curve a: A and B are completely compatible without any phase separation.

Curve b: A and B are partly compatible without clear phase separation.

Curve c: Intermediate stage with phase separation and diffuse phase boundary. The narrower the flat region of the modulus, the more diffuse is the phase boundary.

Curve d: A and B are completely incompatible and a complete phase separation takes place.

The storage modulus curve of the multiblock copolymer (see Figure 12) is similar to curve b, due to there is mainly a single phase copolymerized by small blocks of polystyrene and polyisoprene although some trace phases of polystyrene and polyisoprene appear to exist at -50°C and 100°C , corresponding to the T_g s of polyisoprene and polystyrene, respectively. On the other hand, the blocks of polystyrene and polyisoprene in the diblock copolymer are completely incompatible as a result of their sufficient length. Therefore, the storage modulus curve of the diblock copolymer is similar to curve d.

CONCLUSIONS

A neat styrene/isoprene diblock copolymer and a single-phase styrene/isoprene multiblock copolymer were synthesized by reactive extrusion. GPC, TEM, and DMA analyses prove that polystyrene and polyisoprene phases in the diblock copolymer are completely incompatible. This study on the diblock copolymer, synthesized by reactive extrusion, has provided an

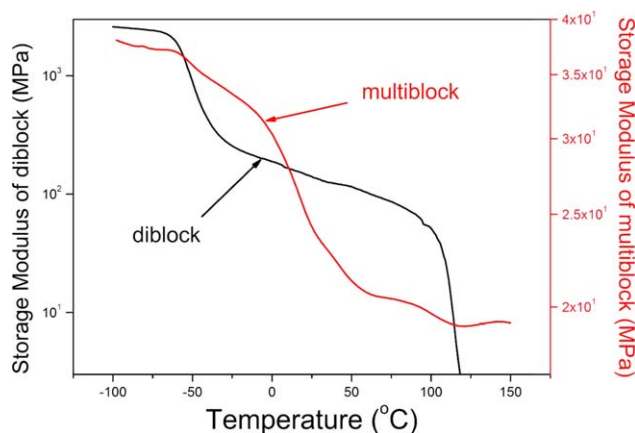


Figure 12. Temperature dependence of storage modulus on S/I diblock and multiblock copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

improved way for producing styrene–isoprene–styrene or styrene–butadiene–styrene thermoplastic elastomer although there were still a little polystyrene short blocks on the polymer chain. However, the further study proved that this amount of short blocks would not influence the properties of the final products and the related work is under submitting. These studies also provide a novel method for producing polystyrene rubbers by adding randomization reagent in the reactor. Traditionally, the polystyrene elastomers were produced by solution polymerization which consumed vast amounts of solvent and energy. The current study provides a new bulk polymerization method which utilizes very little or no solvent. Further research on styrene/isoprene copolymer should be continued to help develop new methodologies for industry that are effective in reducing costs and pollution by replacing the method of anionic solution polymerization.

ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (No. 50933002).

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