

Diimide Hydrogenation of Isoprene–Styrene Diblock Copolymers

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ABSTRACT: Isoprene–styrene diblock copolymers of various molecular weights were prepared by anionic polymerization with *n*-BuLi in cyclohexane. Hydrogenation of the unsaturated backbone of the block copolymers was performed with diimide generated *in situ* by the thermolysis of *p*-toluenesulfonylhydrazide (TSH). The reaction was carried out in xylene at 135°C. A molar ratio of TSH to double bonds equal to 4:1 was found to be the optimum ratio, which provided the highest percentage of hydrogenation. The percentage of hydrogenation analyzed by ¹H-NMR, IR spectroscopy, and iodine value (the Wijs method) were compared. Evidence from ¹H-NMR also revealed a change in the

ratio of the cis–trans configuration after hydrogenation. The thermal stability of the hydrogenated products was improved as shown by the results from thermogravimetric analysis. From differential scanning calorimetry measurements, the glass-transition temperatures of the hydrogenated products were found to increase about 10–20°C above those of the original block copolymers. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 76–82, 2003

Key words: anionic polymerization; diblock copolymers; elastomers; modification

INTRODUCTION

Chemical modification of polymers has long been an active field of research because modified polymers with new or improved properties compared with the base polymers can be obtained. Hydrogenation is one of the most important methods for improving and changing the properties of unsaturated elastomers to provide greater stability against thermal and oxidative degradation.^{1,2} For instance, hydrogenated nitrile rubber (HNBR) is famous for its properties as an oil-resistant elastomer with superior abrasion resistance at elevated temperatures. Its ozone, oxygen, and chemical resistances at high temperatures are better than the original nitrile rubber.^{1,3,4} Hydrogenation of SBR and SBS elastomers results in new materials with high temperature stability and excellent resistance to oxygen and ozone. These properties make it available for a wide range of applications, particularly as a new class of thermoplastic elastomers and an impact modifier for polymer blending systems.^{5–7}

Catalytic and noncatalytic hydrogenations of diene-containing polymers have been widely studied.^{1,2} Classical catalytic hydrogenation, which is the reaction of unsaturated substrates with transition-metal-activated hydrogens, is usually quite expensive. It re-

quires special equipment because the reaction is normally carried out under high pressure and at a high temperature. Noncatalytic hydrogenation of low molecular weight olefins by diimide (N₂H₂) has been extensively studied over the past 20 years. The reaction is homogeneous and generally performed under nitrogen gas at atmospheric pressure with a relatively simple apparatus. Diimide can be produced by various methods, such as the oxidation of hydrazine,⁷ the thermal decomposition of arenesulfonylhydrazides,^{2,8–10} and the photochemical irradiation of 1-thia-3,4-diazolidine-2,5-dione.¹¹ Among these hydrogen-releasing agents, the thermal decomposition of *p*-toluenesulfonylhydrazide (TSH) has been successfully applied to the hydrogenation of various butadiene- and isoprene-containing polymers. Mango and Lenz reviewed the use of diimide for hydrogenating unsaturated polymers.²

Isoprene–styrene diblock and styrene–isoprene–styrene triblock copolymers are interesting materials because they have the potential to be used as compatibilizers in polymer blends.^{12,13} It is known that diene polymers cannot resist high temperature treatment because their unsaturation could initiate degradation reactions through the formation of a radical at allylic positions of double bonds. Reduction of unsaturated parts in the block copolymer can improve the thermal and oxidative stability and produce new elastomeric materials. The hydrogenated product of the styrene–isoprene copolymer can also be potentially used as an

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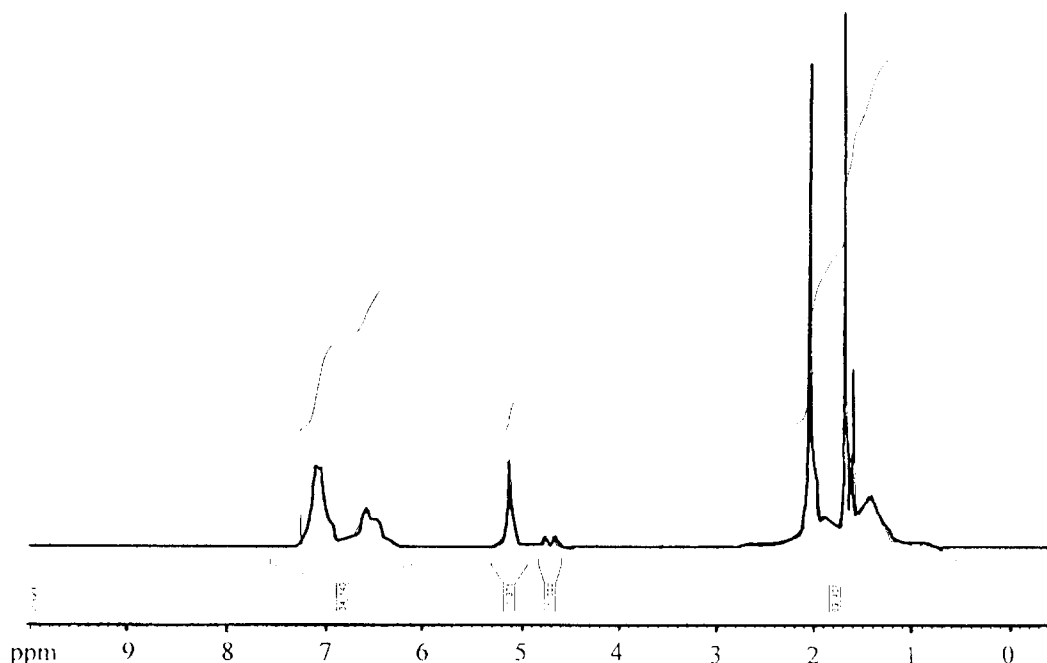


Figure 1 $^1\text{H-NMR}$ spectrum of the isoprene-styrene diblock copolymer.

additive in coating and a viscosity index improver.¹ Velichkova et al. studied the hydrogenation of styrene-isoprene block copolymers with different degrees of monomer distribution, using homogeneous catalytic hydrogenation. They found that the solubility of the hydrogenated products in base lubricating oil was higher than for their parent copolymers.¹⁴

In this study, various molecular weights of isoprene-styrene diblock copolymers with relatively equal block length were prepared by anionic polymerization with *n*-BuLi as an anionic initiator in cyclohexane. TSH was employed as the noncatalytic hydrogen-releasing agent. The microstructure of the isoprene-styrene diblock copolymers before and after hydrogenation was investigated by $^1\text{H-NMR}$ and IR spectroscopy. Different techniques for the determination of degree of hydrogenation, that is, $^1\text{H-NMR}$, IR spectroscopy, and iodine value (IV), were compared. Thermal behaviors of the hydrogenated products were also analyzed with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques.

EXPERIMENTAL

Materials

Isoprene and styrene monomers (Fluka, Phillipsburg, NJ) were purified by extraction of the inhibitor with 10% NaOH aqueous solution before distillation as reported elsewhere.¹⁵ Cyclohexane obtained from JT Baker (Buchs, Switzerland) was dried by refluxing with CaH_2 for 3 h and was then distilled under nitro-

gen gas. TSH, practical grade (Fluka), and xylene (JT Baker) were used.

Polymerization procedure

Poly(isoprene-*b*-styrene) (IS) with a block ratio of isoprene to styrene of about 50:50 was prepared in cyclohexane by the sequential living anionic polymerization of isoprene and styrene, respectively, with *n*-BuLi as an initiator under a nitrogen atmosphere. The polymerization of isoprene monomer was carried out at 40°C for 3 h. The purified styrene monomer was then added, and the reaction was allowed to proceed for another 3 h. The ratios of monomer to initiator were varied to produce four different molecular weights of the diblock copolymers. This was done on the basis of traditional anionic living polymerization.¹⁶ Methanol was used as a terminating agent and nonsolvent for the copolymer.

Hydrogenation procedure

Hydrogenation of IS was carried out under nitrogen gas in a 2-L three-necked round-bottomed flask equipped with a magnetic bar, a reflux condenser, and a nitrogen inlet tube. The solution of 2% (w/v) polymer in xylene was used with different molar ratios of TSH to unsaturation sites in the block copolymer. The reaction took place at 135°C for 4 h under nitrogen gas. At the end of the reaction, the mixture was washed with distilled water and filtered through a sinter glass

TABLE I
Hydrogenation Condition of IS^a

Sample	Isoprene: styrene (%) ^b	TSH/d.b. (by mole)	Hydrogenation ^b (%)
IS-1	55:45	1:1	85.9
IS-2	55:45	2:1	95.8
IS-3	55:45	4:1	98.4
IS-4	55:45	6:1	98.4

d.b., double bonds.

^a $M_n = 6.1 \times 10^3$.

^b Calculated from ¹H-NMR.

funnel packed with aluminum base to remove by-products. After evaporation of the solvent, the product was purified by several reprecipitations in methanol and dried in vacuum at room temperature.

Characterization

The chemical structure of the copolymers and hydrogenated products was analyzed by ¹H-NMR (Bruker DPX-300 NMR spectrometer) and IR (PerkinElmer System 2000 Fourier transform infrared spectrometer) spectroscopy. The molar percentage of isoprene to styrene of the block copolymer was determined by ¹H-NMR. IV (the Wijs method), defined as the number of centigrams of iodine equivalent to the unsaturation present in 1 g of sample, was used as a quantitative method to measure the unsaturation present in samples.^{17,18}

The number average molecular weight (M_n) of the copolymer was determined by GPC [Waters 150-CV equipped with styragels (HT3 and HT4) with THF as

a mobile phase at a flow rate of 1.0 mL/min]. Thermal behaviors of the diblock copolymers before and after hydrogenation were investigated with a PerkinElmer TGA7 and a PerkinElmer DSC7. TGA was performed from 50 to 600°C at a scanning rate of 40°C/min. The DSC measurement was performed under the scanning temperature from -90 to 120°C at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Characterization of isoprene and styrene diblock copolymer

The isoprene-styrene diblock copolymer (IS) could be successfully prepared without the occurrence of alternating or random copolymers because of the different propagation rate constants of isoprene and styrene monomers. The homopolymerization rate constant of isoprene (k_{ii}) is higher than the crosspolymerization rate of isoprenyl anion to styrene monomer (k_{is}).¹⁹ Isoprene should be homopolymerized until depletion; then, crosspolymerization will occur. Four different molecular weights of IS determined by GPC were prepared: M_n 's = 4.5×10^3 , 6.1×10^3 , 8.2×10^3 , and 16.2×10^3 .

The ¹H-NMR spectrum of the prepared IS copolymer is shown in Figure 1. Two characteristic peaks of polyisoprene (PI) were found at 5.1 and 4.75 ppm, which could be assigned to the protons adjacent to double bonds of the 1,4-PI and 3,4-PI units, respectively. The peaks at 6.5–7.2 ppm were of the protons of benzene rings in the polystyrene (PS) block. The amount of PI and PS blocks could, therefore, be cal-

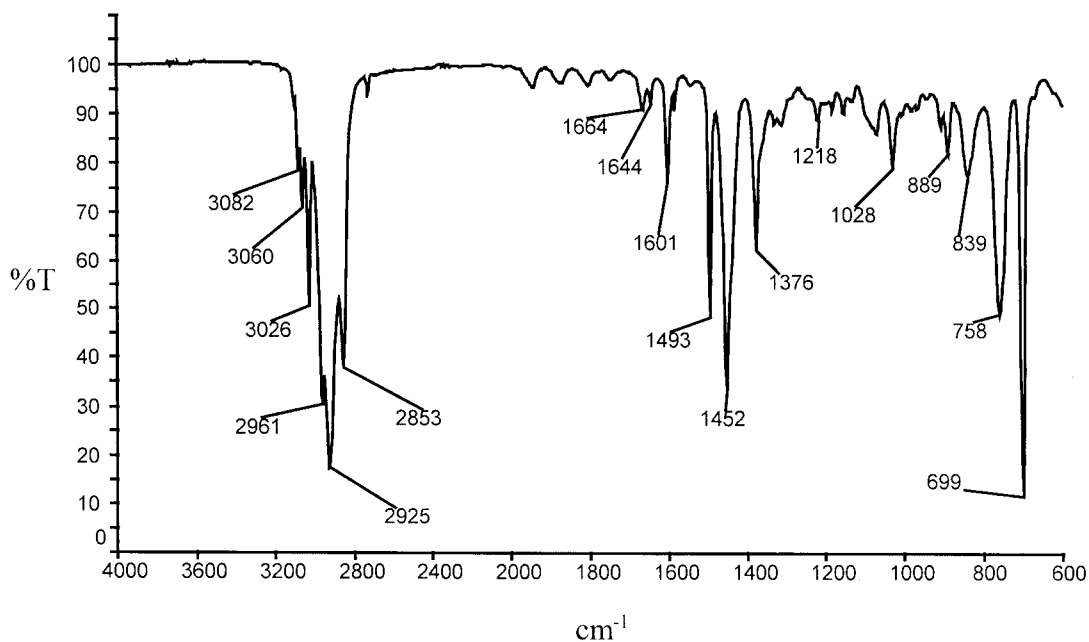


Figure 2 IR spectrum of the isoprene-styrene diblock copolymer.

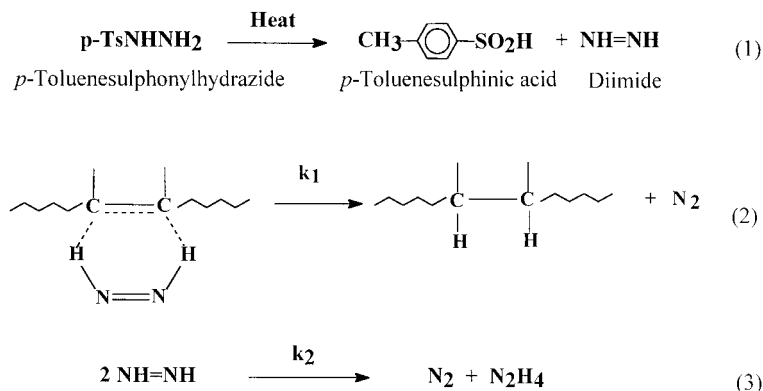


Figure 3 Hydrogenation reaction of the unsaturated polymer by TSH: (1) generation of diimide from the thermal decomposition of TSH, (2) syn addition of diimide on the olefinic site, and (3) disproportionation reaction of diimide, giving nitrogen and hydrazine.

culated with the integrated area ratio of these signals. For the block copolymer of $M_n = 6.1 \times 10^3$, the ratio of isoprene to styrene was 55:45 (see Table I).

The PI block in the copolymer was composed of 1,4-PI and 3,4-PI microstructures with a ratio of 94:6, which is typical for anionic polymerization of isoprene in a nonpolar solvent. The appearance of the signals at 1.68 and 1.60 ppm could be assigned to *cis*-1,4-PI and *trans*-1,4-PI, respectively. By enlarging these two signals, we found the approximate ratio of the *cis* to *trans* microstructure to be 75:25. This result is in accordance with the high percentage of *cis* configuration (70–90%) of PI obtained by alkyllithium-initiated polymerization in a nonpolar solvent.²⁰

The characteristic absorption bands in the IR spectrum (shown in Fig. 2) of the synthesized IS exhibited two important characteristic peaks at 1664 and 1644 cm^{-1} , corresponding to C=C stretching of 1,4 addi-

tion and 3,4-PI, respectively. The deformation signals of =C—H of 1,4-PI and 3,4-PI at 839 and 889 cm^{-1} also confirmed the existence of 1,4 and 3,4 microstructures, respectively. The presence of a PS segment in the block copolymer was shown by characteristic peaks at 1601, 1493, and 1452 cm^{-1} , corresponding to the benzene rings of PS; vibrational frequencies of =C—H aromatic summation bands at 1943, 1870, 1802, and 1745 cm^{-1} ; and peaks at 758 and 699 cm^{-1} , relating to monosubstituted benzene rings. For the PS block, atactic configuration was obtained, revealed by a broad band at 1100–1040 cm^{-1} with 250 scans and resolution of 2 cm^{-1} .²¹

Effect of TSH content

TSH is one of the most popular reagents for releasing a diimide (N_2H_2) intermediate under thermal decom-

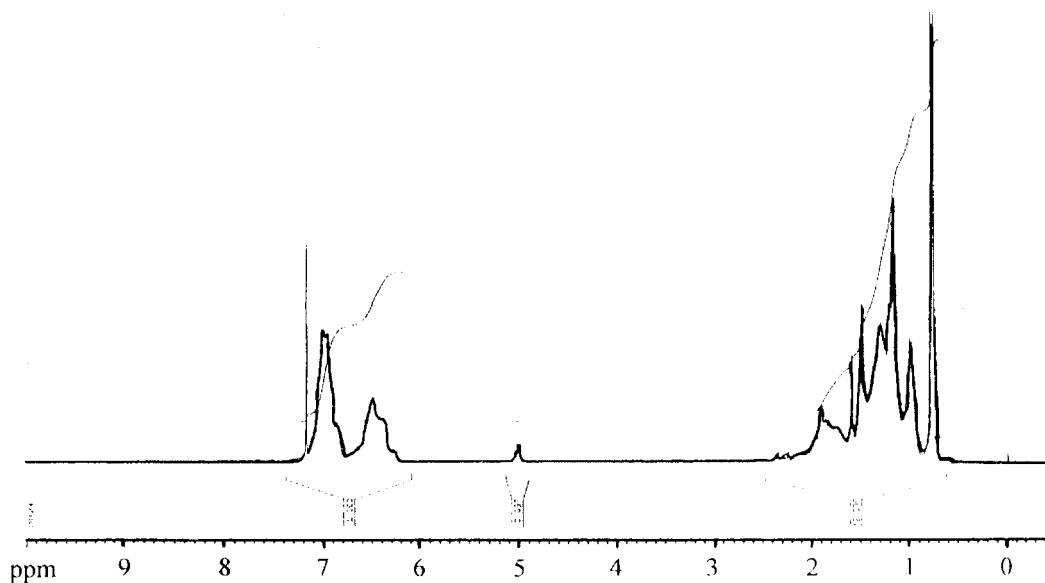


Figure 4 $^1\text{H-NMR}$ spectrum of the partially hydrogenated isoprene-styrene diblock copolymer.

TABLE II
Percentage Hydrogenation of Various Molecular Weights of IS Determined by $^1\text{H-NMR}$, IR, and IV

Sample	$M_n (\times 10^3)$ before hydrogenation	$M_n (\times 10^3)$ after hydrogenation	H (%)		
			By $^1\text{H-NMR}$	By IR	By IV
HIS1	4.5	5.6	87.7	90.5	67.0
HIS2	6.1	4.8	85.0	92.3	75.5
HIS3	8.2	10.9	85.3	85.5	74.3
HIS4	16.2	14.1	77.3	92.1	72.2

position reaction [eq. (1) in Fig. 3]. To investigate the optimum ratio of TSH to double bonds of the copolymer, we hydrogenated the IS with a M_n of 6.1×10^3 with various molar ratios of TSH to double bonds, as shown in Table I. The TSH was slightly soluble in xylene at room temperature, but it could be totally dissolved on heating. As the reaction proceeded, the reaction mixture changed from colorless to deep yellow with the release of diimide molecules. The diimide was then conducted to highly specific hydrogen addition in a syn configuration [eq. (2) in Fig. 3]. Theoretically, a 1:1 molar ratio should give complete hydrogenation. Harwood et al. reported that approximately 5 mol of hydrazide per mole of butadiene or isoprene units are required to complete hydrogenation.²² It is shown in Table I that the utilization of a 1:1 molar ratio of TSH to double bonds gave only 85% hydrogenation, as determined by $^1\text{H-NMR}$. The reason could be that not all the diimides generated reacted with the $\text{C}=\text{C}$ of isoprene units at the decomposition temperature, but the diimide could also undergo disproportionation, giving unreactive nitrogen and hydrazine [eq. (3) in Fig. 3]. The rate of disproportionation (k_2) was reported to be faster than the reaction rate of diimide with double bonds of a polymer (k_1); that is, $k_2 > k_1$.⁹ Mango and Lenz reported that the rate of hydrogenation depends on the microstructure of the PI segments. They found that the vinyl segments were hydrogenated at a greater rate than either the cis or trans 1,4 units ($k_{\text{vinyl}} > k_{\text{cis}} \sim k_{\text{trans}}$).² Poshyachinda and Kanithanon reported that the rate of addition of hydrogens to the butadiene sites in the cis configurations was likely to be faster than that of the trans unit because of only one-side steric effect.²³ The $^1\text{H-NMR}$ spectrum in Figure 4 shows the disappearance of the signal of protons adjacent to $\text{C}=\text{C}$ of 3,4-PI, whereas the signal of protons adjacent to $\text{C}=\text{C}$ of 1,4-PI still remained. This indicated that the less steric fraction of PI (i.e., 3,4-PI configuration) should have reacted with the diimide much faster than the 1,4-PI configuration.

Comparison of various techniques for the determination of the degree of hydrogenation

The hydrogenation of IS diblock copolymers with various molecular weights was carried out with a TSH to

double bonds molar ratio equal of 4:1. The hydrogenated products were symbolized as HIS1, HIS2, HIS3, and HIS4 as shown in Table II. The determination of the degree of hydrogenation of the copolymers has been widely carried out by spectroscopic methods such as $^1\text{H-NMR}$ and IR spectroscopy.^{9,13} The determination of the degree of unsaturation of olefinic molecules with the IV/Wijs method has been recommended for industrial and commercial analysis.^{17,18} This method was reported to be applicable only for the determination of the residual unsaturation of HNBR.¹⁸ It was, therefore, interesting to extend the IV method to hydrogenated isoprene-styrene copolymers and to compare the results to spectroscopic methods. From $^1\text{H-NMR}$, the integrated area ratio of the protons adjacent to isoprenic structures (4.75 and 5.1 ppm) to the protons of benzene rings (6.5–7.2 ppm) was used to calculate the percentage hydrogenation. For IR spectroscopy, the peak ratios of isoprene units at 839 and 889 cm^{-1} to the styrene units at 1601 cm^{-1} before and after hydrogenation were used to determine the percentage of hydrogenation. Determination of the double bonds of the diene units was performed with the IV/Wijs method before and after hydrogenation was carried out.

The results of the hydrogenation of four different molecular weights of the diblock copolymers are shown in Table II. The degrees of hydrogenation determined by $^1\text{H-NMR}$ and IR were higher than those determined with the IV technique. The different results obtained by IR spectroscopy might have been errors from baseline adjusting before the calculation of area under peaks. For $^1\text{H-NMR}$, the integrated area of signal also depends on the baseline adjusting and molar concentration of the sample analyzed. The IV

TABLE III
Percentage Cis and Trans of Polyisoprene Block in IS Copolymers Before and After Hydrogenation (Calculated from $^1\text{H-NMR}$)

Sample	Before hydrogenation		After hydrogenation	
	Cis (%)	Trans (%)	Cis (%)	Trans (%)
HIS1	76.0	24.0	33.3	66.7
HIS2	75.0	25.0	64.5	35.5
HIS3	75.4	24.6	23.1	76.9
HIS4	75.8	24.2	42.9	57.1

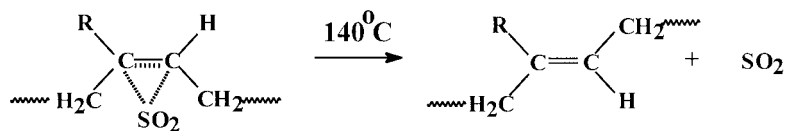


Figure 5 Cis-trans isomerization of 1,4-polydiene by sulfur dioxide.

method is considered a direct technique for evaluating the double bonds of the unsaturated units. Therefore, the IV method might be theoretically an accurate method to determine the amount of residual double bonds of the hydrogenated isoprene-styrene diblock copolymers, even though it is time consuming. Table II shows that the hydrogenation altered the M_n 's of the polymers. The change in the molar mass of the hydrogenated product was also seen with the hydrogenation of polybutadiene.²⁴ It is unclear whether the changes in molecular weight during the hydrogenation involved the degradation reaction caused by the relatively high reaction temperature used or oxidative degradation of residual unsaturation. It is possible that after hydrogenation, the fewer C=C bonds in the backbone should have behaved in GPC differently from the starting material; that is, the hydrodynamic dimensions of the substrate changed after hydrogenation. All block copolymers in this study were of low molecular weight. The copolymers before and after hydrogenation were also dissolved easily in solvents such as hexane and chloroform. Therefore, we assumed that no gel or crosslinking occurred in the samples.

The microstructures of the four hydrogenated products were also analyzed by $^1\text{H-NMR}$. The percentage of cis and trans configuration, calculated from the integrated area of $^1\text{H-NMR}$ peaks at 1.68 and 1.60 ppm, respectively, before and after hydrogenation is shown in Table III. The ratio of cis to trans configura-

tion changed after hydrogenation. It was reported that catalytic cis-trans isomerization of 1,4-PI could be carried out with thiol acids, sulfur dioxide, and other related materials that function as catalysts.²⁵ The isomerization of *cis*-PI and *trans*-PI with sulfur dioxide could occur via the formation of an unstable complex at 140°C, as shown in Figure 5. In our system, *p*-toluenesulfonic acid by-product was generated during the thermal decomposition of TSH [eq. (1) in Fig. 3]. It can be postulated that the by-product acting as a catalyst for cis-trans isomerization was the cause of the change of the percentage of cis and trans configuration. It was also reported in the literature that utilization of TSH for hydrogenation promotes the cis-trans isomerization of 1,4-polydiene.²⁶ Evidence of the cis-trans isomerization of *cis*-1,4-polybutadiene after hydrogenation by TSH was also shown by Poshychinda and Kanithanon.²³

Thermal characterization

The thermal stability of the modified isoprene-styrene diblock copolymers should increase as the degree of unsaturation decreases. The resistance to heat of the copolymers was measured by the weight loss at increasing temperature with TGA. Additionally, the heat required for polymer molecules to deform; that is, the glass-transition temperature (T_g), was measured by DSC. A sample TGA thermogram in Figure 6 reveals that the starting temperature for weight loss of

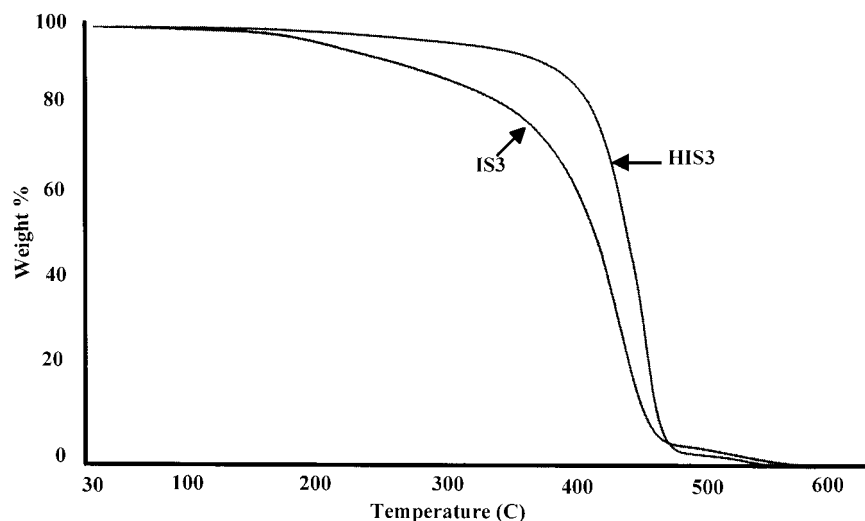


Figure 6 TGA thermograms of the isoprene-styrene diblock copolymer (IS3) and its hydrogenated product (HIS3).

TABLE IV
 T_g of IS Before and After Hydrogenation

Sample	T_g (°C)	
	Before hydrogenation	After hydrogenation
IS1	53	62
IS2	42	65
IS3	46	69
IS4	52	60

the hydrogenated copolymer was higher than that of the original copolymer. The hydrogenated products tended to degrade at much higher temperatures than the original copolymer, that is, an improvement of thermal stability. T_g 's of the hydrogenated products were higher than those of the starting copolymers by about 10–20°C (Table IV). All the block copolymers prepared were low molecular weight products; there was no extra-endothermic peak from DSC thermograms of the hydrogenated block copolymers indicating cyclization. We propose that no cyclization reaction occurred during the hydrogenation reaction. If the cyclization had occurred, it would have had such a small percentage of cyclization that it would not have affected the thermal property of the final products.

CONCLUSIONS

The noncatalytic diimide hydrogenation of isoprene-styrene diblock copolymer with TSH was a mild condition because it was carried out at atmospheric pressure and moderate temperature. The 3,4 structure of the PI unit hydrogenated faster than the 1,4 unsaturated structure. The percentage hydrogenation could be determined by various techniques (i.e., $^1\text{H-NMR}$, IR spectroscopy, and IV). From the alteration of the ratio of cis to trans configuration after hydrogenation, quantitatively analyzed from $^1\text{H-NMR}$ spectra, we postulate that the TSH hydrogenation promoted the cis-trans isomerization. The thermal stability of the hydrogenated products, examined by TGA, was improved, and the T_g 's of hydrogenated block copolymers were 10–20°C higher than those of the original block copolymers.

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