

# Toughness Enhancement of High-Impact Polystyrene Based on $\gamma$ -Radiation Vulcanized Natural Rubber Latex by Using Block Copolymer

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**ABSTRACT:** Polyisoprene-*block*-polystyrene-*block*-polyisoprene (ISI) was synthesized by the iniferter route and its use, as compared to a commercial polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS), in the enhancement of the toughness of high-impact polystyrene (HIPS), prepared by the  $\gamma$ -radiation vulcanized natural rubber (RVNR) latex/phase transfer/bulk polymerization technique, was investigated. Addition of 5% SIS was adequate as an interfacial agent, which effectively increased the unnotched Izod impact energy of HIPS, whereas use of 10% of ISI was required. A long polyisoprene block with two polystyrene segments of SIS was favorable for compatibilization of HIPS. Transmission electron micrographs revealed the uniform distribution of the block copolymer at the shell region of the rubber particle. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1307–1316, 2002

**Key words:** high-impact polystyrene; natural rubber latex; block copolymers

## INTRODUCTION

Among several methods known for the preparation of high-impact polystyrene (HIPS) based on natural rubber (NR), the recent published method, that is,  $\gamma$ -radiation vulcanized natural rubber (RVNR) latex/phase transfer/bulk polymerization, is one of the simplest and, hence, therein lies its attractiveness.<sup>1,2</sup> In the process, a negatively charged RVNR latex particle is titrated with benzyldimethylhexadecylammonium chloride in the presence of a styrene monomer. At the critical transfer concentration (CTC), the rubber particles transfer from the aqueous phase into the styrene, which is, subse-

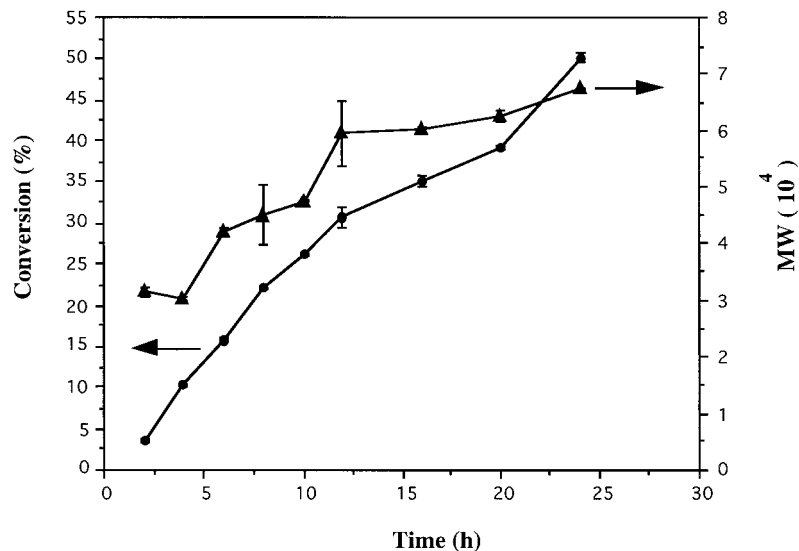
quently, polymerized, producing the HIPS-like product. The crosslink density of rubber is controlled by the irradiation dose, which is responsible for the size of the occluded polystyrene (PS) in the rubber particle. The unnotched Izod impact energy of the toughened PS prepared is higher than that of the unmodified PS depending on the rubber content and the amount of the initiator. Samples prepared from 5% of RVNR (14 kGy) showed maximum impact resistance, whereas the use of a lower benzoyl peroxide (BPO) concentration produced the higher molecular weight PS matrix with a higher impact energy.<sup>1,2</sup>

Since rubber–matrix adhesion is an important factor in influencing the toughness of a brittle polymer, it was the aim of this present study to investigate the effect of a block copolymer on the enhancement of the impact property of HIPS, prepared according to the RVNR latex/phase transfer/bulk polymerization technique.<sup>1,2</sup> It has been postulated that the effectiveness of the block co-

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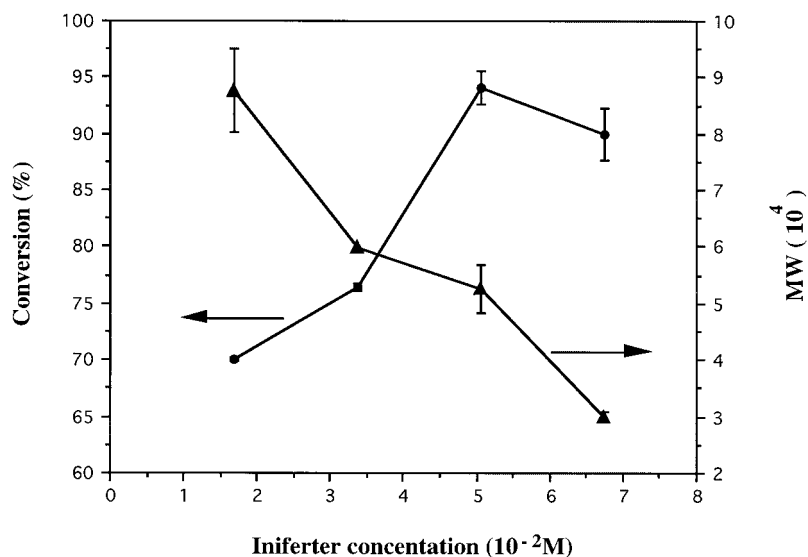
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**Figure 1** Conversion and average MW of the PS-macroiniferter as a function of polymerization time ( $[\text{styrene}] = 8.7$ ;  $[\text{TD}] = 1.12 \times 10^{-2} \text{ mol/L}$ ).

polymer depends on different structural characteristics, such as the chemical structure of the block, molecular weight of each block and of the copolymer, and the mode of addition of the compatibilizer.<sup>3-6</sup> Two types of triblock copolymers composed of relevant homopolymers [polyisoprene (PI) and PS], that is, PS-*b*-PI-*b*-PS (SIS) and PI-*b*-PS-*b*-PI (ISI), were, therefore, incorporated into HIPS. The former is a commercial copolymer under the trade name KRATON 1107,

while the latter was synthesized by applying the synthetic route involving living radical polymerization through the use of the iniferter (initiator-transfer agent-terminator) method.<sup>7-10</sup> A detailed synthesis of ISI, including the effects of the polymerization time and the iniferter concentration on yields and molecular weights of the resulting polymers, and a study of the impact resistance and morphology of HIPS incorporated with block copolymers are presented.



**Figure 2** Conversion and average MW of the PS-macroiniferter as a function of iniferter concentration (irradiation time, 27 h).

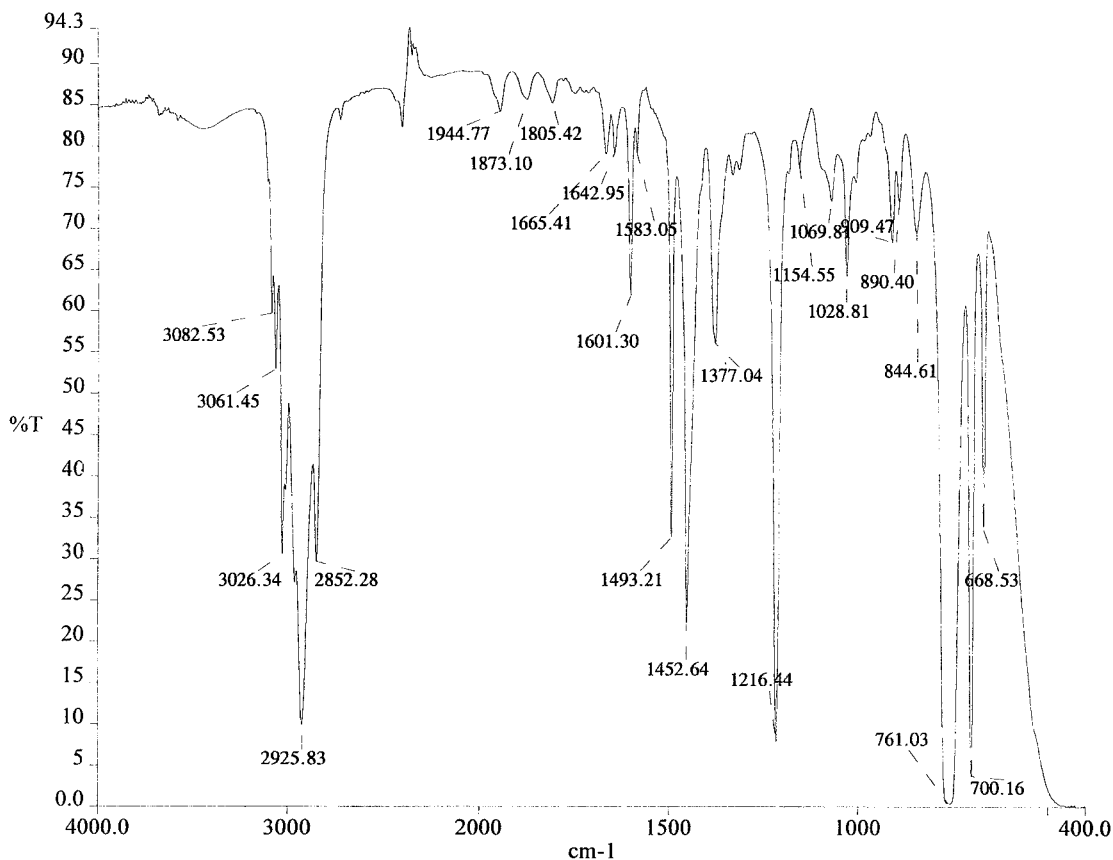


Figure 3 FTIR spectrum of ISI block copolymer.

## EXPERIMENTAL

### Materials and Reagents

RVNR was prepared from concentrated high ammonia-preserved NR latex having about a 60% dry rubber content (DRC) by the described method.<sup>1,11</sup> The block copolymer SIS (KRATON 1107) was kindly provided by the Shell Co. of Thailand Ltd. (Bangkok). Its molecular weight noted in the literature was  $10^4$ – $1.2 \times 10^5$ – $10^4$  (ref. 12), while the value verified by using gel permeation chromatography (GPC; 150 CV, Waters) was  $\sim 10^5$ .

Styrene (Fluka, Switzerland, puriss) and isoprene (Fluka, purum) were purified by passing them through an aluminum oxide column.<sup>1,11</sup> Methanol, ethanol, and toluene were distilled before use, whereas carbon tetrachloride (Merck, GR), tetrahydrofuran (Lab Scan, AR), and benzyldimethylhexadecylammonium chloride (Fluka, purum) were used as received. Tetraethylthiuram disulfide (TD; Fluka, purum) was recrystallized twice from ethanol.

### Living Radical Polymerization

A required amount of the TD iniferter was mixed with styrene (8.7 mol/L) in a tube and purged with

nitrogen for 5 min. The sealed tube was irradiated with UV (Mercury HPLN 1000W UV lamp; Philips) at a fixed distance of 30 cm at ambient temperature for the given time. The macroiniferter, that is, PS–TD, was isolated by precipitation with methanol and the product dried under reduced pressure. The conversion (percent) of the polymer was determined from weight of the dried product and its molecular weight was measured by GPC using tetrahydrofuran (THF) as a solvent.<sup>7–10</sup>

A solution of a known weight of PS–TD in toluene (15 mL) was placed in a reaction tube followed by the addition of isoprene (30 mL). The preparation of the ISI block copolymer was carried out as described above by UV irradiation at a distance of 10 cm. Infrared (FTIR; 2000, Perkin–Elmer), nuclear magnetic resonance (NMR; DPX300, Bruker), and GPC were used for polymer characterization.

### Incorporation of Block Copolymer in HIPS

The SIS or ISI block copolymer (5, 10, 20, or 40%) was dissolved in the styrene monomer (30 g) and then poured into an Erlenmeyer flask containing

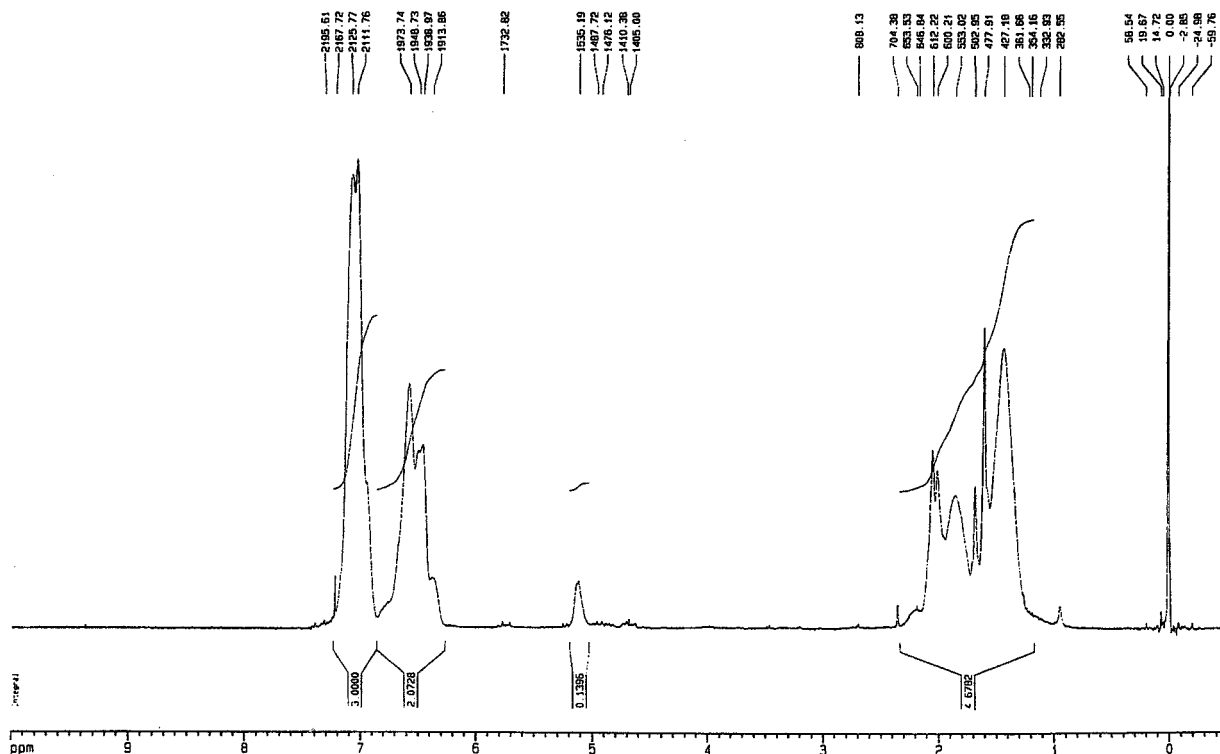


Figure 4 <sup>1</sup>H-NMR spectrum of ISI block copolymer.

RVNR latex having a 10% solid content (15 g) and distilled water (45 g). The mixture was then titrated with an aqueous solution of benzyldimethylhexadecylammonium chloride (5 g/L) according to the method previously described.<sup>1,2,11</sup>

After allowing the mixture to stand for 24 h at room temperature, the styrene phase containing the transferred rubber particle and the block copolymer was gently centrifuged using a Supraspeed centrifuge (Centaur 2, Sanyo) at 3000

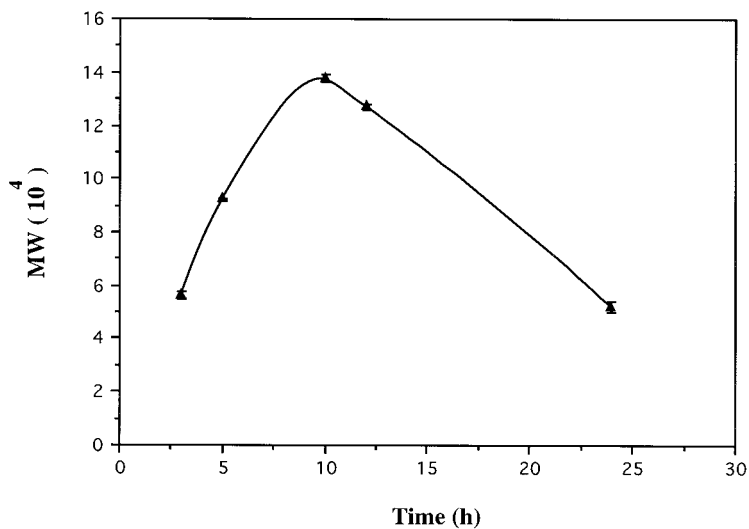


Figure 5 Average MW of ISI block copolymer as a function of polymerization time ([isoprene] = 6.66; [PS-TD] = 1.33 × 10<sup>-3</sup> mol/L).

**Table I** Yield, MW, and MWD of Synthesized PS-TD Macroiniferter and ISI Block Copolymer

Macroiniferter/Block Copolymer	Yield (%)	MW ( $\times 10^5$ )	MWD
PS-TD	94.1	0.5	2.8
ISI-1	25.3	0.95	3.9
ISI-2	26.3	1.39	3.9
ISI-3	13.3	1.83	3.9
ISI-4	15.0	2.07	3.5

[Isoprene] = 6.66 mol/L and reaction time 10 h.

rpm for 10 min to eliminate any trace of water. The next step of bulk polymerization in a Teflon-coated steel mold using 1% of BPO as an initiator was also described in the previous work.<sup>1,2</sup>

#### Determination of Impact Resistance and Morphology

The impact resistance of an unnotched sample ( $63.5 \times 12.7 \times 3.2$  mm) was measured by using an Izod apparatus (Zwick 5102) according to ASTM D4812-93. The average value of 20 specimens was reported for each measurement.

The morphology of HIPS was determined on a transmission electron microscope (TEM; H 300, Hitachi). Specimens were prepared according to the osmium staining principle.

## RESULTS AND DISCUSSION

### Characterization of PS-Macroiniferter

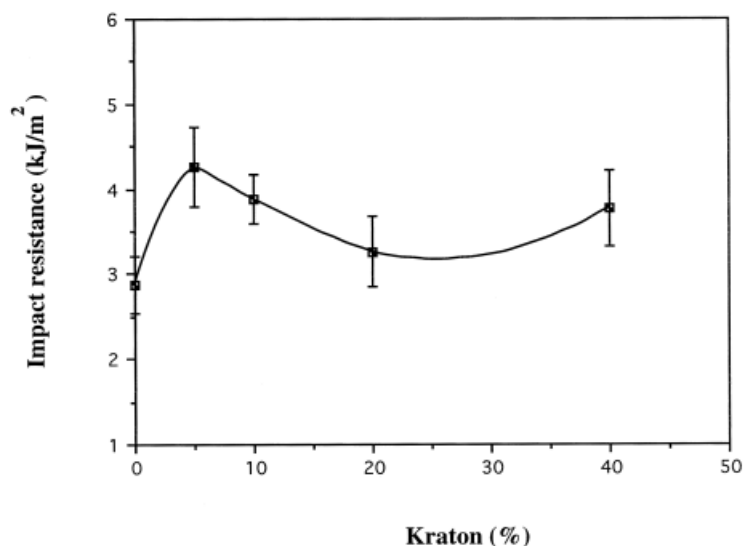
The first block, that is, the PS-macroiniferter prepared by using  $1.12 \times 10^{-2}$  mol/L of TD, was characterized by the determination of the percent conversion and the average molecular weight (MW). The data plotted versus the irradiation time are presented in Figure 1.

From Figure 1, both the conversion and the MW of the polymer increased with the reaction time, indicating that the polymerization proceeded via a mechanism similar to living radical polymerization in a homogeneous system.<sup>7-10</sup> The results agreed well with those reported in the literature.<sup>7-9</sup>

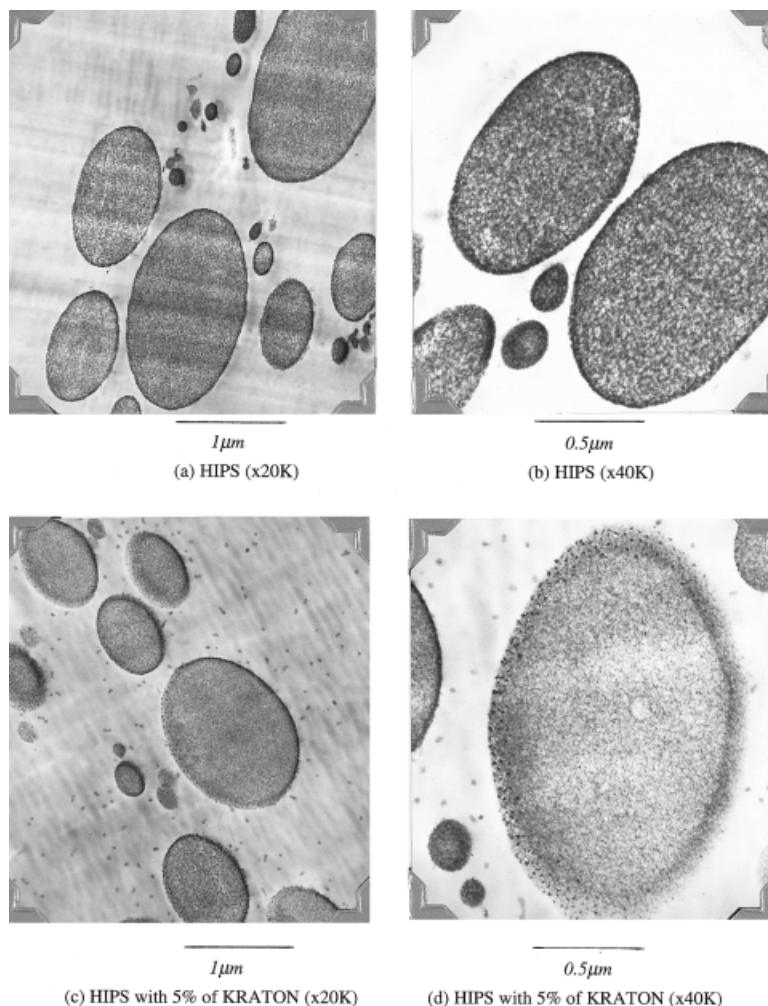
The effect of the iniferter concentration on the percent conversion and the MW of PS-TD irradiated for 27 h was then studied and the data are presented in Figure 2. It was observed that a higher iniferter concentration resulted in a lower MW of the polymer.<sup>10</sup> In addition, the conversion increased and attained its optimum value of about 95% when the concentration of TD was  $5.06 \times 10^{-2}$  M.

### Characterization of ISI Block Copolymer

It was reported that PS-TD serves as a good polymeric photoiniferter for the polymerization of a vinyl monomer such as vinyl alcohol and methyl methacrylate.<sup>8</sup> In our case, the isoprene monomer



**Figure 6** Effect of KRATON concentration on unnotched Izod impact resistance of HIPS, containing 5% of RVNR (14 kGy), polymerized by using 1% of BPO.



**Figure 7** TEM of HIPS (a,b) without block copolymer and (c,d) with 5% of KRATON.

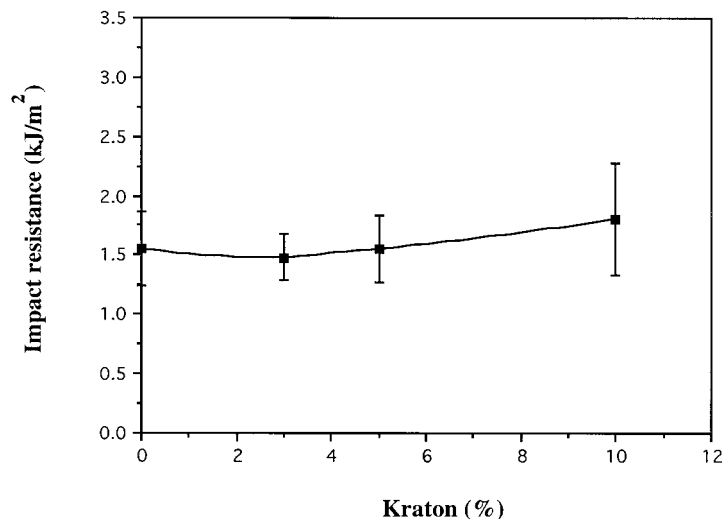
was selected for polymerization with the bifunctional macroiniferter, that is, PS-TD ( $MW = 5 \times 10^4$ ), to produce the ISI triblock copolymer. The presence of two end groups in PS-TD was confirmed by measuring its UV absorbance (Spectronic Genesis 2).<sup>7-10</sup>

FTIR and <sup>1</sup>H-NMR spectra of an example of the synthesized ISI block copolymer are presented in Figures 3 and 4, respectively. The peaks at 3062, 1601, 1493, and 1453  $\text{cm}^{-1}$  in Figure 3 correspond to the benzene ring of PS, while those at 1665 and 1643  $\text{cm}^{-1}$  reveal the presence of PI in the block copolymer as *trans*-1,4 and *cis*-1,4-PI. The <sup>1</sup>H-NMR spectrum in Figure 4 indicates the presence of protons in the monosubstituted aromatic ring at 7.30–6.46 and in the C=C of 1,4-PI at 5.13 ppm.<sup>13</sup> Although the existence of PS and PI in the product were disclosed, the actual block structure was still ambiguous. Therefore, the MW of ISI prepared us-

ing [isoprene] = 6.66 and [PS-TD] =  $1.33 \times 10^{-3}$  mol/L as a function of the reaction time was measured and the plot is shown in Figure 5.

It is observed in Figure 5 that the MW of the block copolymer initially increased with the reaction time, passed through a maximum (10 h), and then decreased. The possible explanation is that, at the early stage, living radical polymerization in a homogeneous solution took place by a successive insertion of monomer molecules into the dissociated bond. After 10 h, destruction of double bonds in the PI segment in the copolymer, caused by thermal energy from the reaction and UV light, possibly followed.<sup>14</sup> Because the MW obtained was higher than that of the PS-TD iniferter ( $5 \times 10^4$ ), it could be deduced that an ISI block copolymer was formed.

Four ISI copolymers having different MWs were prepared using 6.66 mol/L of isoprene with



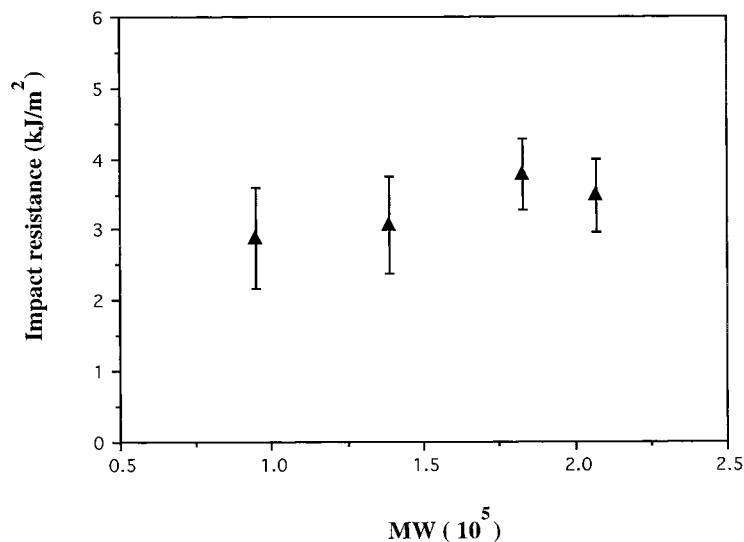
**Figure 8** Effect of KRATON content on impact resistance of unmodified PS polymerized using 1% of BPO.

various concentrations of PS-TD for 10 h of irradiation time. Their percentage yields, MW, and molecular weight distribution (MWD) are summarized in Table I. It was noticed that their MWD was considerably high because a bimolecular termination was not totally prevented, which implied a nontruly living mechanism.<sup>15,16</sup> The highest yield of ISI obtained with  $3.8 \times 10^{-3}$  mol/L of [PS-TD] for 10 h of UV irradiation was 26%. The results agreed well with the previous work in which the maximum yield of 25% of PI was ob-

tained when the benzyl *N,N*-diethyldithiocarbamate (BDC) iniferter was used at 44 h irradiation time.<sup>15</sup>

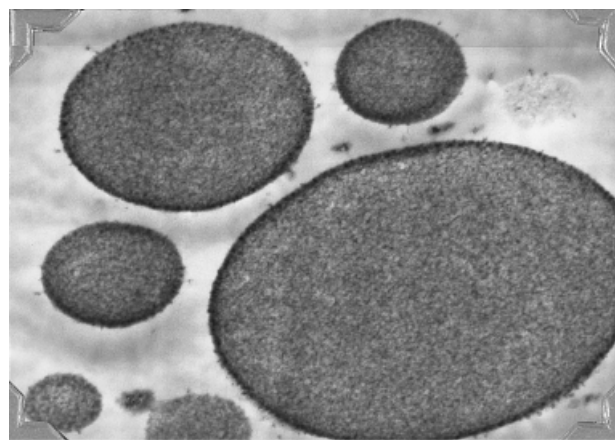
#### Effect of KRATON on Impact Resistance of HIPS

The effect of KRATON 1107 incorporated into HIPS containing 5% of transferred RVNR (14 kGy) on its unnotched Izod impact resistance was studied. Values of the impact resistance of HIPS polymerized using 1% of BPO plotted with the KRATON content are presented in Figure 6.

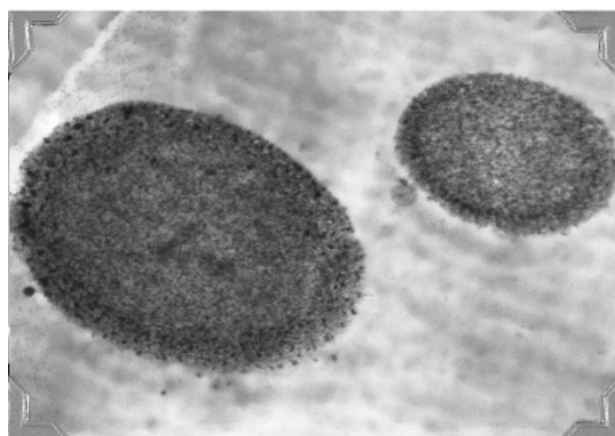


**Figure 9** Effect of synthesized ISI block copolymer MW on unnotched Izod impact resistance of HIPS, containing 5% of RVNR and 5% of ISI, polymerized using 1% of BPO.





0.5  $\mu\text{m}$   
(a) HIPS with 5% of ISI



0.5  $\mu\text{m}$   
(b) HIPS with 10% of ISI

**Figure 10** TEM of HIPS (a) with 5% of ISI and (b) with 10% of ISI ( $\times 40\text{K}$ ).

The presence of KRATON caused an increase in the impact energy of HIPS over the uncompatibilized PS, indicating the role of KRATON as a compatibilizer. This block copolymer provided good interfacial adhesion by the attachment of a long PI block length to the NR particle, due to its high MW, which is entangled enough in the homopolymer,<sup>3,4</sup> while two short PS blocks of KRATON protruded into the PS matrix. The maximum impact resistance was obtained using 5%

KRATON, an amount which possibly caused the exact saturated rubber/PS interface. The result agreed well with the previous report that the optimum impact resistance is ideally provided when the interface is exactly saturated with the block copolymer.<sup>3</sup> The distribution of KRATON at the interface between the rubber particle and the PS matrix was observed under TEM. Micrographs at two magnifications of HIPS and HIPS incorporated with 5% of KRATON are shown in Figure 7(a–d).

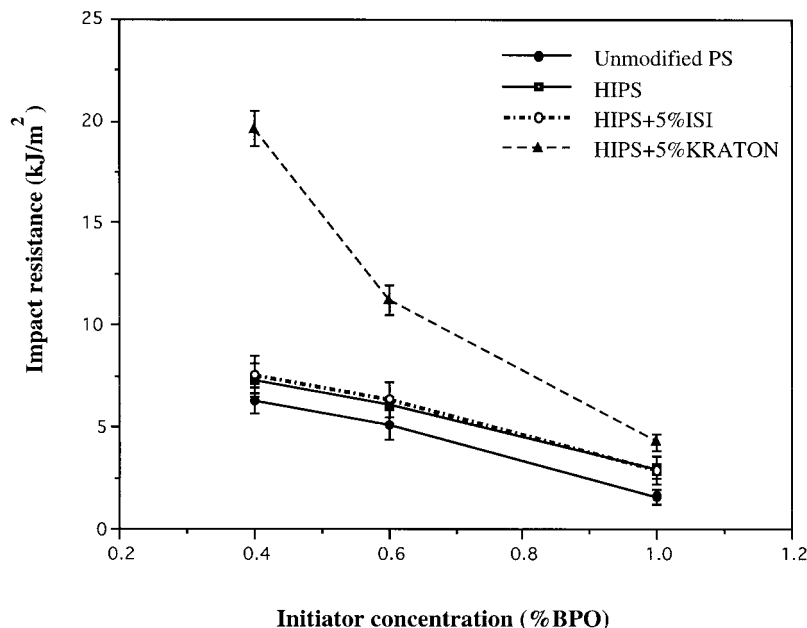
All micrographs revealed two-phase morphology of the crosslinked rubber particles (dark), containing PS occlusions, dispersed in the PS matrix (light). It is important to point out in Figure 7(a,b) that the RVNR particles in HIPS were surrounded by a membrane layer, possibly derived from a protein–lipid complex as previously reported.<sup>1,2,11</sup> Compared to Figure 7(a), the less clear-cut membrane or the lighter interfacial region with a higher thickness was noticed in HIPS containing KRATON in Figure 7(c). From the high magnification micrograph in Figure 7(b,d), the dark spots in the shell region of RVNR in Figure 7(d) should be assigned to KRATON molecules stained by  $\text{OsO}_4$ . It was concluded that KRATON located at the rubber–PS interface as a compatibilizer greatly improved the impact resistance of HIPS.

In Figure 6, it is noticed that increasing the concentration of KRATON (i.e., more than 5%) resulted in a decrease of the impact resistance of HIPS. This was possibly due to the lamella at the interface formed by the excess copolymer causing weak interfacial adhesion.<sup>3,4</sup> The use of higher than 20% of KRATON resulted in an increase in the impact resistance of HIPS. This could be explained in terms of the formation of a microdomain of KRATON molecules, a thermoplastic elastomer, in the PS phase owing to the high viscosity of the block copolymer.<sup>17,18</sup> However, when PS containing various concentrations of KRATON in the absence of RVNR were prepared for use as the control, it was observed in Figure 8 that the impact resistance values of PS were slightly increased. Hence, it might be deduced that the microdomain of KRATON in PS without the addition of rubber, if it existed, did not greatly toughen the PS.

#### Effect of Synthesized ISI Block Copolymer on Impact Resistance of HIPS

The curve in Figure 9 shows the change in the impact resistance of HIPS, polymerized using 1%





**Figure 11** Effect of concentration of BPO on unnotched Izod impact resistance of unmodified PS, HIPS, and HIPS with 5% of KRATON or ISI (MW of  $9.5 \times 10^4$ ) block copolymer.

of BPO, having 5% of RVNR and 5% of synthesized ISI, when the block copolymer MW was varied. Even though the MWs of each block segment in all the copolymers used were greater than their corresponding homopolymer entanglement MWs,<sup>3,4</sup> it was observed that the impact resistance of HIPS with an ISI MW of  $9.5 \times 10^4$  was comparable to that without the addition of the copolymer. A slightly positive effect was obtained with a higher block MW of  $1.39\text{--}2.07 \times 10^5$ , that is, each PI block ranged from  $4.5\text{--}7.9 \times 10^4$  (at a fixed PS block MW of  $5 \times 10^4$ ). The presence of one PS and two PI blocks in ISI was, therefore, less favorable to effectively serve as an anchor between the NR particle and the PS matrix than that of KRATON.<sup>19</sup>

To attain the maximum impact resistance of HIPS based on RVNR in our study ( $4.26 \text{ kJ/m}^2$ ) using 1% of BPO, it was found that 10% of ISI (MW of  $9.5 \times 10^4$ ) was required instead of only 5% in the case of KRATON. It could also be explained that the rubber/PS interface was exactly saturated when using 10% of ISI. At this concentration, the dark spots corresponding to ISI molecules stained by  $\text{OsO}_4$  were observed in the shell region of the NR particle as presented in Figure 10(b), whereas the uniform distribution of ISI at the interface could not be detected in the HIPS containing 5% of ISI as shown in Figure 10(a).

The results indicated that it was reasonable to assume that the areal chain density (the number of chains per unit area) at the interface greatly influenced the enhancement of HIPS toughness.<sup>3</sup>

#### Efficiency of Block Copolymer on Impact Resistance Enhancement

The impact resistance of HIPS, containing 5% of RVNR without and with 5% of the block copolymer, polymerized using 0.4, 0.6, or 1% of the initiator (BPO), was determined and compared with that of unmodified PS. The data obtained are presented in Figure 11.

As expected, it was observed that the impact resistance of the materials increased with a decrease of the BPO concentration. This was due to the higher MW PS matrix produced at a lower BPO content as already explained in the previous work.<sup>1,2</sup> The efficiency of KRATON (MW of  $10^5$ ) in improving the impact resistance of HIPS at all initiator concentrations was greatly noticed, whereas the presence of the synthesized ISI block copolymer (MW of  $9.5 \times 10^4$ ) insignificantly affected the resistance. Our results confirm that the compatibilization effectiveness depends on the block sequence and structure.<sup>4–6</sup> Although both SIS and ISI could be considered as symmetric block copolymers, which theoretically prefer to

locate at the interface,<sup>20</sup> the long PI block length of KRATON seemed to be well attached to the NR particle, while two PS blocks protruded into the styrene monomer and, subsequently, into the PS matrix (“Y-shape”). On the contrary, the attachment of two PI shorter blocks in ISI on the rubber chain in the NR particle (“inverse Y-shape”) might take place with less efficiency. In addition, the broad MWD of the synthesized ISI block copolymer using living radical polymerization might also be responsible for its lower activity as compared to KRATON.

## CONCLUSIONS

In conclusion, we successfully prepared a PI-*b*-PS-*b*-PI (ISI) triblock copolymer using the iniferter method. We also found that the amount of synthesized ISI added to HIPS to attain its maximum impact resistance was higher than that of PS-*b*-PI-*b*-PS (KRATON 1107; SIS). This indicated that the attachment of long PI on the rubber chain in the NR particle with two PS blocks of KRATON (“Y-shape”) favorably took place, providing less areal chain density (the number of chains per unit area) at the interface and, hence, greatly enhanced the toughness of HIPS.

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