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Application study of styrene-isobutylene-styrene block copolymer as a new thermoplastic elastomer

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ABSTRACT

The properties of a new family of thermoplastic elastomers (TPEs) consisting of a polyisobutylene inner soft segment connected to two polystyrene outer hard segments (S-iB-S) has been investigated from the industrial point of view. The S-iB-S block copolymers exhibited excellent properties, especially in regard to gas permeability and damping behavior as compared to other commercialized block copolymers. These unique block copolymers are promising for gas barrier and/or damping materials.

INTRODUCTION

TPEs consisting of two glassy outer-blocks flanking an elastomeric inner-block are well-known to be very useful and various kinds of TPEs have already been commercialized. Among them, TPEs having polystyrene (PSt) as hard segments are one of the most popular TPEs because there exist numerous application fields for these block copolymers and also handling and performance of them are excellent. However, the performance of these PSt-based block copolymers are still insufficient for gas barrier materials and/or damping materials.

Recent developments of carbocationic polymerization have provided new avenues for block copolymer syntheses, which enables us to introduce polyisobutylene (PIB) as a new elastomer segment in PSt-based TPEs(1). Novel methodology for synthesizing block copolymers having PIB soft inner segment connected with various kinds of hard outer segments including PSt have already been reported in detail from the academic point of view(1-5). However, industrially oriented research with these block copolymers has not been reported so far.

The purpose of this study is to try to synthesize TPEs consisting of two PSt hard outer-blocks flanking a soft PIB mid-block (S-iB-S block copolymer) under convenient conditions for industrial practice compared to the earlier methods, and also to evaluate the performance and applicability of these block copolymers for gas barrier and damping materials. This paper concerns results of the synthesis, characterization and applicability of S-iB-S

block copolymers.

EXPERIMENTAL

A. Materials

The synthesis and purification of 1,4-di-(2-methoxy-2-propyl)benzene (DiCumOMe) and the sources and purification of CH_2Cl_2, styrene (St), n-hexane (nHX) and isobutylene (IB) have been described(1,2). Purification of cyclohexane (CHX) was carried out in the same manner as that of nHX. Anhydrous N,N-dimethylacetamide (DMA, Aldrich), $TiCl_4$ (Aldrich), deuterated chloroform($CDCl_3$, Aldrich) and methanol(Wako Chemicals) were used as received.

B. Procedures

Polymerization of S-iB-S block copolymers was carried out under a dry nitrogen atmosphere in a 300-500 mL round-bottomed flasks equipped with a mechanical stirrer, or in 3-liter stainless steel autoclaves equipped with a mechanical stirrer and a temperature control system in a temperature range of - 100 °C through + 50 °C . The general procedures for block copolymer syntheses were almost the same as those reported previously(1,3-5). The main difference of our procedure as compared to the previous ones was that polymerization equipments were in a conventional laboratory and not inside a special moisture-free dry box. Detailed conditions for block copolymer syntheses are summarized in Table 1.

Table 1.

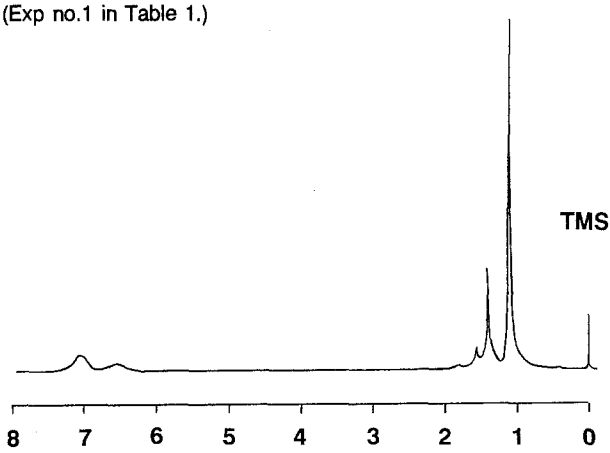
Synthesis of S-iB-S Block Copolymers

Exp no.	DiCumOMe (mmol)	$TiCl_4$ (mmol)	DMA (mmol)	IB (mol)	St (mol)	CH_2Cl_2 (ml)	nHX (ml)	CHX (ml)	Reaction (°Cxmin)	Yield (%)
1	0.356	6.0	0.4	0.38	0.17	75	---	75	-78x105	98
2	0.408	6.0	0.4	0.37	0.17	75	---	75	-78x 90	90
3	1.641	51.2	3.2	1.71	0.79	600	900	--	-80x 90	87

C. Characterization

Molecular weights and molecular weight distributions (MWDs) were obtained by a Waters GPC assembly. Calibration curves were obtained with narrow molecular weight polystyrene standards. Block copolymer compositions were determined by ^1H NMR spectroscopy. ^1H NMR spectra were taken on a JEOL JNM-EX90A spectrometer using $CDCl_3$ as solvent. Block copolymer compositions were calculated as reported previously(1). A representative ^1H NMR spectrum of a S-iB-S is shown in Figure 1. DSC measurements were performed on a DuPont instrument. The morphology of block copolymers was observed by Transmission Electron Microscopy(TEM). Detailed techniques of DSC and TEM were also reported previously(1).

Figure 1. ^{1}H NMR Spectrum of A Representative S-iB-S Block Copolymer
(Exp no.1 in Table 1.)



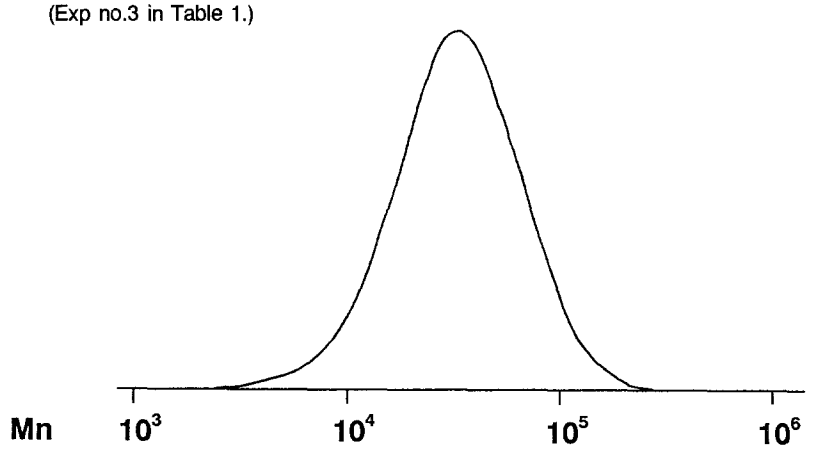
D. Measurement of Various Properties

Dynamic mechanical analyses were performed using a Polymer Laboratories dynamic mechanical thermal analyzer. Stress-strain measurements were carried out with an Instron tensile tester according to ASTM D412 and shore A hardness values were measured by a Shore Durometer according to ASTM D2240. Gas permeability measurements were performed according to ASTM D1434.

RESULTS AND DISCUSSION

The first purpose of this study was to synthesize S-iB-S by a convenient procedure. A representative GPC trace of a S-iB-S sample is shown in Figure 2.

Figure 2. GPC Trace of A Representative S-iB-S Block Copolymer
(Exp no.3 in Table 1.)



Evidently a monodisperse S-iB-S could be obtained by our simplified method. Characterization and stress-strain measurements of S-iB-Ss are summarized in Table 2.

Table 2.

Characterization and Stress-Strain Results of S-iB-S Block Copolymers

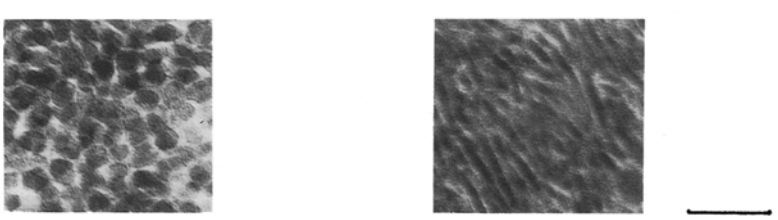
Exp no.	Characterization			Stress-Strain Results			
	Mn	MWD	PSt content (wt%)	300% Modulus (MPa)	Tensile Strength (MPa)	Elongation (%)	Hardness (Shore A)
1	45,700	1.69	39	4.5	6.4	450	42
2	46,100	1.59	41	6.3	8.3	400	54
3	25,200	1.61	38	---	4.3	300	42

Ths MWDs of S-iB-Ss were relatively broad compared to S-iB-Ss reported previously(1). Impurity level (mainly moisture) in our system might be higher than that in the previous method which may explain the finding that the MWDs of our S-iB-Ss were slightly broad. The hardness of S-iB-Ss were in the range of 42 - 54 (see Table 2), which is much lower than the hardness of poly(styrene-b-butadiene-b-styrene) (SBS)(~90) of the same PSt content. This softness is the result of the presence of the PIB segment in the TPE. Tensile properties of our S-iB-Ss were fair and a little lower than the reported values(1). Number average molecular weight (Mn) of S-iB-Ss were lower than those reported previously(1), which could explain the lower tensile properties. The other reason could be the broadness of the S-iB-S (see above).

It has been reported that the PSt segment should be at least of Mn = 6,000 ~ 10,000 to obtain SBSs having good tensile properties. Also, the mechanical properties of TPEs depend on phase separation between the two type of block polymer segments(6-8). The PSt segment length of the S-iB-S (Exp no.2 in Table 1 and 2) is Mn ~ 9,000, which has already been achieved minimum Mn of PSt segment.

Figure 3. TEM Micrographs of S-iB-Ss

(a) Exp no.2 in Table 1. (b) Exp no.3 in Table 1.



The morphology of S-iB-Ss were observed by TEM. Figure 3 shows TEM micrographs of S-iB-Ss. The PSt domain size of S-iB-S (Exp no.2 in Table 1 and 2; Mn of PSt domain was ~9,000) was 20 ~ 40 nm, which is consistent with the reported value(9). As shown in Figure 3, phase separation was clearly observable, however the tensile strength was not so good. SBSs having the same PSt segments exhibited higher tensile strength than S-iB-S materials.
S-iB-S with the same PSt content exhibited different morphology. The shape of the PSt domain was changed from cylindrical to spherical by increasing the total Mn of S-iB-S. We would be the first to report this phenomenon.

Figure 4. DMTA Spectrum of A Representative S-iB-S Block Copolymer

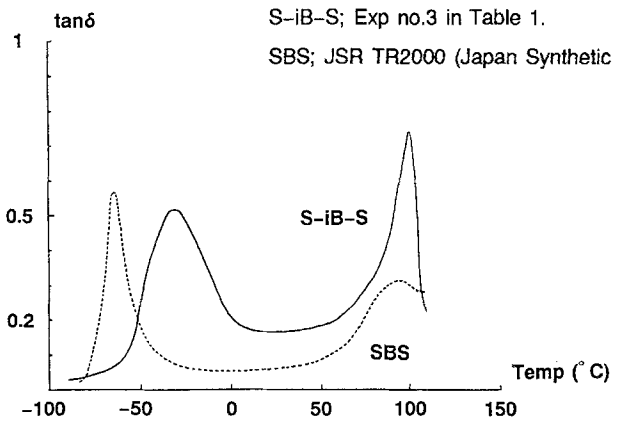
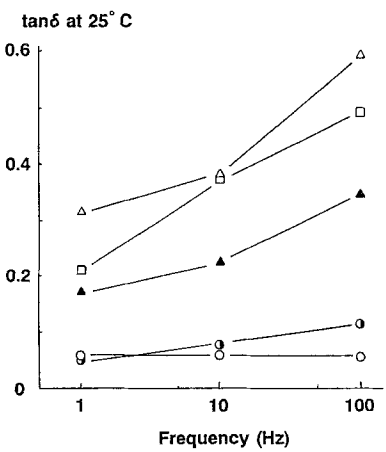


Figure 4 shows representative dynamic mechanical analysis data of S-iB-S and SBS. Two peaks of tan δ were observed in each sample, which would correspond to two block polymer segments of each triblock copolymer. The tan δ level of S-iB-S was relatively high over the whole temperature range shown in Figure 4.

Figure 5. Frequency Dependence of the Mechanical Loss Tangent (tanδ)



(○); SBS (JSR TR2000)
(◑); SEBS (Shell, Kraton G1650)
(△); S-iB-S (Exp no.2 in Table 1.)
(▲); S-iB-S (Exp no.3 in Table 1.)
(□); IIR vulcanizate
Formulation:

Polymer	100
HAF Carbon Black	50
Stearic Acid	1
Zinc Oxide	3
Sulfur	3

Vulcanized at 150°C for 40 min

The frequency dependence of tan δ at 25 °C is plotted in Figure 5 for a variety of block copolymers. The figure caption identifies the block copolymers used. The tan δ levels of S-iB-Ss are excellent as compared to those of SBS and hydrogenated SBS (SEBS) and are of almost the same level as IIR over a wide frequency range. These S-iB-Ss may be useful for various kinds of damping materials, and our S-iB-S might be better than conventional vulcanized IIRs because vulcanization is not necessary in our system.
The gas permeability of S-iB-Ss was also determined. Results are summarized in Table 3.

Table 3.

Determination of Gas Permeability Characteristics of TPE Materials

Material	Permeability of O_2 (fmol/m·s·Pa)			Permeability of CO_2 (fmol/m·s·Pa)
	35°C	50°C	65°C	35°C
S-iB-S (Exp No.2 in Table 1)	1.01	2.15	3.69	4.45
SBS (JSR TR2000;Japan SYnthetic RUbber Co.,Ltd.)	10.1	15.8	22.4	73.1
SEBS (Kraton G1650;Shell Chemical Co.,Ltd.)	23.3	---	---	37.9
IIR 365 (JSR IIR 365; Japan Synthetic Rubber Co.,Ltd.)	0.807	1.83	3.83	3.07

According to the data, S-iB-S exhibits excellent gas barrier properties. Thus, S-iB-Ss are promising new TPEs for a variety of gas barrier materials.
As stated above, the morphology of S-iB-Ss could be changed dramatically. The gas permeability may be affected by the change of the morphology of the block copolymer system, and the study of the relationship of these phenomena would be very interesting.

CONCLUSIONS

(1) S-iB-S having narrow MWDs could be synthesized under industrially convenient condition.

(2) We have been the first to observe a morphology change of S-iB-S caused by different molecular weights under the same PSt content.

(3) S-iB-S exhibits excellent dynamic mechanical behavior and gas permeability; as a consequence, S-iB-Ss may be useful for gas barrier materials and/or damping materials.

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measuring gas permeabilities of S-iB-Ss and other polymers.

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