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Synthesis and Characterization of Syndiotactic Polystyrene-Polyisoprene-Syndiotactic Polystyrene ABA Type Triblock Copolymer

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Synthesis and Characterization of Syndiotactic Polystyrene-Polyisoprene-Syndiotactic Polystyrene ABA Type Triblock Copolymer

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The synthesis of a model ABA type triblock copolymer, consisting of syndiotactic polystyrene (SPS) (A) and polyisoprene (PIP) (B) blocks is demonstrated. The 3,4-vinyl carbon on the polyisoprene side chain in the SPS-graft-PIP was effectively lithiated with sec-butyllithium, which was subsequently utilized for further living anionic polymerization of isoprene. Propagating polyisoprenyl anions were terminated with 1,3-diiodopropane to make the ABA type triblock copolymer. From the ^{1}H NMR and GPC measurements, the composition ratio of ABA block was found to be almost 1:3:1.

Keywords syndiotactic polystyrene, triblock copolymer, lithiation, living anionic polymerization

Introduction

ABA type triblock copolymers, such as polystyrene-polyisoprene-polystyrene and polystyrene-polybutadiene-polystyrene, are known to be typical thermoplastic elastomers (TPE) (1–6). Polystyrene (PS) plays an important role as a segment to form hard-segment domains. PS is usually amorphous and has a high glass transition temperature. However, the domain consisting of amorphous polystyrene chains has a lower rigidity than that consisting of crystalline PS because of its low cohesive energy. If an ABA triblock copolymer with a crystalline **A** block can be synthesized, heat-, weather- and oil-resistance properties would be much improved as compared with a conventional styrene type TPE. It is, however, difficult to make a crystalline **A** block in the synthesis of ABA type copolymer because the propagating chain end of the crystalline polymer tends to be in the heterogeneous condition in a solvent.

Syndiotactic polystyrene (SPS) is a semi-crystalline polymer with a high melting point around 270°C due to its stereoregularity (7). In our previous paper, we have reported that SPS-*graft*-PIP was synthesized from the copolymerization of styrene and a PIP macromonomer with a homogeneous cyclopentadienyl titanium trichloride in

combination with methylaluminoxane (CpTiCl$_3$/MAO) catalyst (8–10). The resulting SPS-*graft*-PIP was found to be a graft copolymer with a well-defined branch structure, due to the PIP macromonomer which was pre-synthesized using a living anionic polymerization method. Generally, it is difficult for SPS to modify some functional groups chemically because of a heterogeneous reaction. In other words, it is hard to dissolve SPS in solvents under mild conditions due to its considerable cohesive energy arising from its crystallinity. The PIP side chain in the SPS-*graft*-PIP, however, can be easily dissolved in the usual solvents, indicating that the PIP side chain was easy to react with other chemicals under the mild conditions, which results in the generation of the reacting active site in the SPS-*graft*-PIP.

In this report, the synthesis of a novel ABA triblock copolymer consisting of SPS-PIP-SPS is demonstrated in accordance with the route shown in Scheme 1. In particular, we focus on the further living anionic polymerization of isoprene by utilizing the PIP side chain in the SPS-*graft*-PIP as an initiating active site.

Experimental

Materials

Isoprene (IP), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) and 1,3-diiodopropane (commercially available reagents) were used after distillation before use. *sec*-BuLi diluted with cyclohexane (Kanto Chemical Co.) was used without further purification. Solvents and other reagents were purified by conventional methods.
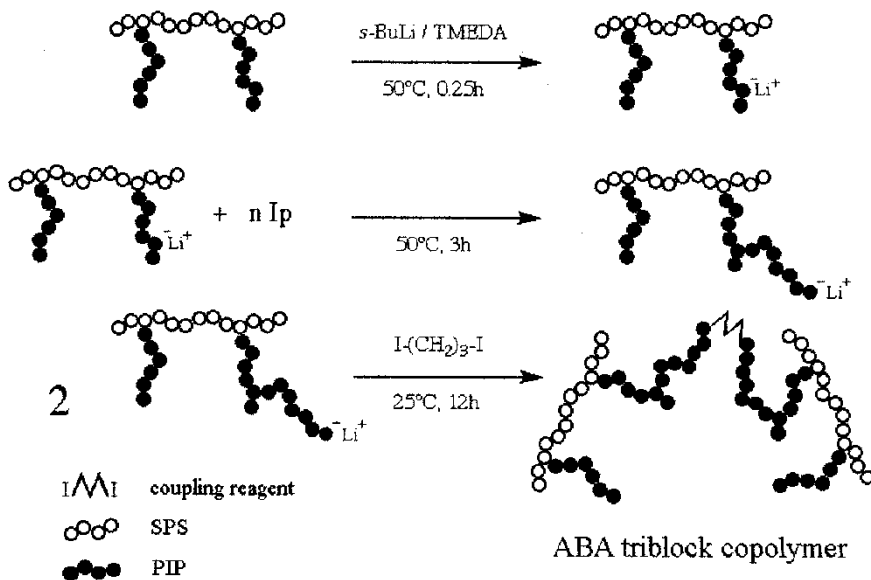
Scheme 1.

Synthesis of ABA Triblock Copolymer

Syndiotactic graft copolymer consisting of the SPS unit as the main chain and poly-isoprene as the side chain was previously synthesized, (8) which contained 10.2% of the 3,4-vinyl type isoprene unit. The 3,4-vinyl moiety was subsequently reacted with *sec*-butyllithium, in combination with TMEDA, in the glass reactor at 50°C for 0.25 h. A living anionic polymerization of IP, initiated with vinylene lithium on the PIP chain in the SPS-*graft*-PIP, was carried out in the glass reactor. The required amounts of reagents were charged by syringes through a septum. The coupling reaction of 1,3-diiodo-propane and polyisoprenyllithium was carried out at −78°C for 12 h. After the reaction, the contents in the reactor were poured into a large amount of methanol and toluene to precipitate a product. The product was extracted by methyl ethyl ketone (MEK) for 12 h to obtain the SPS-PIP-SPS ABA type triblock copolymer in the insoluble fraction. The yield was determined by gravimetry.

Characterization

Microstructures of the SPS-*graft*-PIP and the resulting ABA block copolymers were deter-mined by NMR spectra recorded on a JEOL GX-400 spectrometer in *o*-dichlorobenzene/C_6D_6 at 120°C. M_n and M_w/M_n of the copolymer(s) were estimated by GPC, using *o*-dichlorobenzene solvent at 120°C and a Waters GPC 150CV unit, calibrated with standard polystyrenes (Figure 1).
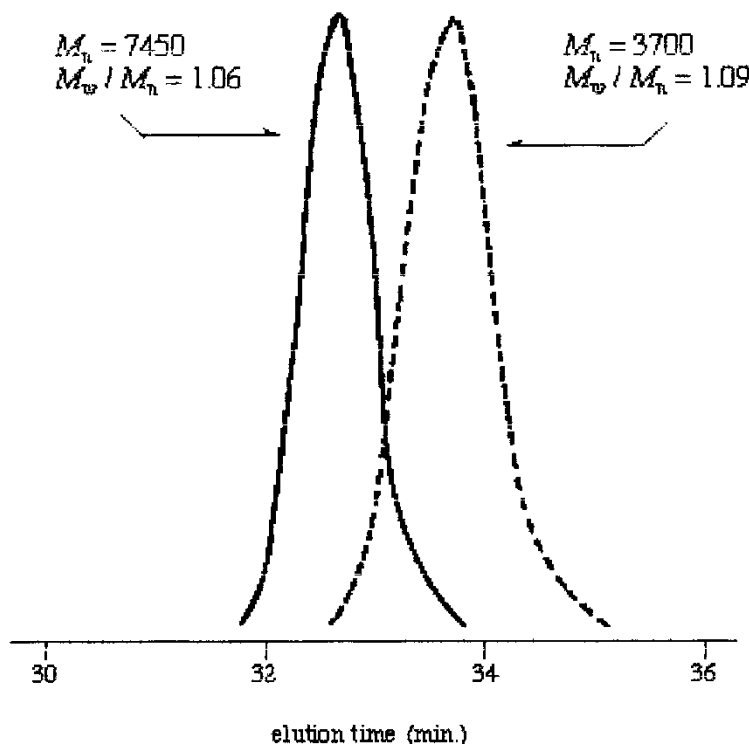

$M_n = 7450$
$M_w / M_n = 1.06$

$M_n = 3700$
$M_w / M_n = 1.09$

elution time (min.)

Figure 1. GPC elution curves of PIP terminated with 1,3-diiodepropane (—) and methanol (---)

Results and Discussion

SPS-*graft*-PIP, which has about two PIP side chains per one molecule, was employed as a starting material. The molar mass of the SPS backbone and the PIP side chain in SPS-*graft*-PIP were 4.6×10^3 and 2.0×10^3 g/mol, respectively. Microstructures of the PIP side chain consisted of 11.4% of 3,4-vinyl, 55.7% of *cis*-1,4-, and 32.9% of *trans*-1,4-type isoprene unit. In the ^{1}H NMR spectrum of the SPS-*graft*-PIP, the peak intensities at 4.8 ppm, due to the methylene proton of 3,4-vinyl units of polyisoprene side chains, and at 1.4 ppm, due to the methylene proton of the SPS main chain, were used to calculate the peak intensity ratio of 3,4-vinyl and St units. Initially, the ratio of 3,4-vinyl and St units in the SPS-*graft*-PIP were calculated to be 10.2, indicating that the 6.9 units of the 3,4-vinyl isoprene per one molecule of the SPS-*graft*-PIP existed. The number of 3,4-vinyl units calculated from the peak intensity ratio of 3,4-vinyl and St units was consistent with that calculated from the microstructure and the molar mass of PIP side chains.

The 3,4-vinyl units in the PIP side chain are expected to be subject to chemical modification by lithiation, since reactivity of these moietes are much higher than that of the internal *cis*- and *trans*-1,4-PIP double bond units (11). The lithiated 3,4-vinyl units will be useful as a macroinitiator for a living anionic polymerization. Table 1 shows the results of the reaction of the SPS-*graft*-PIP with *sec*-butyllithium in combination with TMEDA. The peak intensity ratio of 3,4-vinyl and St units was decreased from 10.2 to 3.7 by the reaction in cyclohexane while the IP unit content and the other microstructures were not changed much in either n-hexane or cyclohexane. This indicates that the 3,4-vinyl units were lithiated selectively in cyclohexane. Lithiation of 3,4 vinyl units reached almost 36.3%. Taking the number of IP units of the side chain into consideration, 1.3 units of 3,4-vinyl structure per a side chain was found to be lithiated. Sen *et al.* reported that the bromination of SPS by *N*-bromosuccinimide reached 18.9 mol% of the bromine content, despite the insolubility of SPS in CCl_4 (12). In our case, the local solubility of the PIP side chain resulting in homogeneous state in cyclohexane led to an increase of lithiation despite the insolubility of SPS.

Table 1

Lithiation of syndiotactic graft copolymer with s-BuLi/TMEDA[a]

Code	Solvent	IP content[b] (%)	3,4 unit/St[c] (%)
SPS graft copolymer	—	36.7	10.2
1	*n*-hexane	37.5	9.9
2	cyclohexane	32.0	3.7

[a]Reaction conditions: graft copolymer, 0.2 g, solvent, 90 mL, [*sec*-BuLi] = 0.04 mol/L, [*sec*-BuLi]/[TMEDA] = 1.0. The reaction was carried out at 50°C for 0.25 h.

[b]The IP unit content was calculated from the peak intensity ratio of ^{1}H NMR spectra at 5.2 ppm due to the methylene proton of PIP side chain and at 1.4 ppm due to the methylene proton of the SPS.

[c]The 3,4-vinyl units of PIP side chain were calculated from the peak intensity ratio of the vinyl proton of 3,4-vinyl units and the methylene proton of the SPS determined by ^{1}H NMR spectroscopy.

Table 2 shows the results of a living anionic polymerization of the IP monomer initiated with the lithiated SPS-*graft*-PIP as a macroinitiator. The IP content and the microstructure of the lithiated SPS-*graft*-PIP was described in code 2 (Table 2) in order to compare with that of the chain extended SPS-*graft*-PIP. After the reaction, the contents in the reactor were poured into a large amount of methanol and toluene to precipitate a product. Polyisoprene homopolymer dissolved in toluene at room temperature was obtained, which indicates that IP monomer was polymerized with the excess *sec*-BuLi without using the lithiated SPS-*graft*-PIP. After the fractionation procedure, the resulting polymer was extracted by methyl ethyl ketone (MEK) using a Soxhlet extractor. The IP content of the MEK insoluble part was increased in comparison with that of SPS-*graft*-PIP. This indicates that the macroinitiator prepared by a lithiation of the SPS-*graft*-PIP initiated the polymerization of IP. However, only 0.06 g of MEK insoluble parts was obtained against 0.2 g of the SPS-*graft*-PIP in the feed. It shows that the yield of the resulting MEK insoluble part was 30%, which seemed to be low. The yield of MEK soluble parts was almost 65% of the lithiated SPS-*graft*-PIP as shown in code 3 (Table 2). It was suspected that the MEK soluble part included the chain extended SPS-*graft*-PIP, which has heterogeneously extended the PIP side chains due to the generation of a large amount of 1,2-vinyl structure. However, the peak attributed to SPS main chain was hardly observed in the ^{1}H NMR spectra of the MEK soluble part. On the other hand, the peak intensity ratio of the vinyl structure consisting of 3,4 and 1,2-microstructure was increased in the MEK-soluble part. These findings indicate that TMEDA has a strong ability for chelating the growing chain end (13).

It is possible that the MEK insoluble part contained the chain extended SPS-*graft*-PIP and a small amount of unreacted SPS-*graft*-PIP. Since the molar mass of the ABA type triblock copolymer obtained was almost consistent with that calculated from SPS-*graft*-PIP in the feed stoichiometrically, the unreacted SPS-*graft*-PIP in MEK insoluble part would be a negligible quantity.

To elucidate the mechanism of the coupling reaction of polyisoprenyl anions, a living anionic polymerization of IP monomer initiated with *sec*-BuLi/TMEDA was terminated with 1,3-diiodopropane or methanol. Figure 1 shows the GPC elution curves of

Table 2
Polymerization of IP initiated by macroinitiator[a]

Code	Solvent extraction[b]	Yield (g)	IP content[c] (%)	Microstructure (%)[d]			
				cis-1,4	*trans*-1,4	3,4	1,2
2	—	—	32.0	60.9	29.3	9.8	0
3	MEK sol.	0.13	—	14.0	14.2	60.5	11.3
	MEK insol.	0.06	36.1	42.0	40.5	17.0	0.5

[a]Reaction conditions; graft copolymer: 0.2 g, solvent: 90 mL, [*sec*-BuLi] = 0.04 mol/L, [*sec*-BuLi]/[TMEDA] = 1.0, [IP] = 1.47 mol/L (10.0 g), [IP]/[*sec*-BuLi] = 36.7. Reaction was carried out at 50°C for 3 h.
[b]Fractionated by toluene at r.t. followed by boiling MEK for 12 h.
[c]IP content was calculated from the peak intensity of IP unit of graft copolymer by ^{1}H NMR spectroscopy.
[d]The microstructure of PIP was determined by the ^{1}H NMR spectroscopy.

the resulting polymers. The molar mass of the reaction product terminated with 1,3-diiodopropane was twice higher than that of the original polymer terminated with methanol. A narrow molecular weight distribution was observed in these cases. The efficiency of coupling reaction between the polyisoprenyl anions and 1,3-diiodopropane was found to be almost 100%. From these results, we suggest that the coupling reaction of the polyisoprenyl anion with 1,3-diiodopropane proceeded through a living system without any side reactions.

Table 3 shows the results of the coupling reaction of polyisoprenyl anions initiated by the lithiated SPS-*graft*-PIP with 1,3-diiodopropane. The reaction was carried out at room temperature for 12 h. The white precipitation due to the LiI complex was recognized during the reaction. After the reaction, the product was precipitated from a large amount of methanol and toluene. The resulting polymer was extracted by MEK for 12 h, using a Soxhlet extractor. Considering that the SPS-*graft*-PIP has 2.6 initiating points in two PIP side chains, the molar mass of PIP terminated with methanol was estimated to be 2.0×10^3 g/mol. It was a little smaller than that calculated from the molar ratio of [IP]/[Li] in the feed, which was 2.5×10^3 g/mol. The molecular weight distribution of the branched polymer in code 3 (Table 2) was 2.76, which was broader than that of the SPS-*graft*-PIP in the feed. From these results, we suggest that 2.0 lithiated 3,4-vinyl units in the two PIP side chains contributed to the extended polymerization of isoprene.

After the coupling reaction using 1,3-diiodopropane, the higher molar mass of the resulting polymer was observed in the GPC elution curves of the MEK-insoluble part, in comparison with that of the original living polymer (code 3, Table 2). The molecular weight distribution was monomodal and a relatively small ($M_w/M_n = 1.41$). Considering that the SPS-*graft*-PIP has 2.0 initiating points in two PIP side chains, the molar mass of the resulting polymer (2.77×10^4 g/mol) was consistent with that calculated from the molar ratio of [IP]/[Li] in the feed. The latter suggests that the ABA triblock copolymer was obtained by the polymerization of IP initiated with the macroinitiator followed by termination with 1,3-diiodopropane. The molar ratio of ABA components was found to be almost 1:3:1. Note that the ^{1}H NMR spectra of the resulting polymers indicated no difference between the coupling and the termination reaction products because of the same composition profile.

Table 3
Coupling reaction between isoprenyl anions by $I(CH_2)_3I^a$

Code	$I(CH_2)_3I$ (mol/L)	$I(CH_2)_3I/$ sec-BuLi	Yield[b] (g)	IP content[c] (%)	Reaction product	
					$M_n \times 10^{-4}$	M_w/M_n
3[d]	0	0	0.06	36.1	1.36	2.76
4	1.89×10^{-2}	0.5	0.14	35.8	2.77	1.41

[a]Coupling reaction at r.t. for 12 h using the macroinitiator: $M_n = 8.6 \times 10^3$, number of branch = 2.0.
[b]MEK insoluble part.
[c]IP content was calculated from the peak intensity of IP unit in graft copolymer by ^{1}H NMR spectroscopy.
[d]Polymerization of IP initiated with the macroinitiator and terminated with methanol.

Conclusion

In this paper, we have demonstrated the synthesis of the model ABA type triblock copolymer consisting of SPS-*graft*-PIP-*graft*-SPS through a living anionic polymerization of IP, using the SPS-*graft*-PIP as a macroinitiator. The PIP side chain was lithiated efficiently by *sec*-BuLi/TMADA under a local homogeneous condition. It was soluble in common solvents, suggesting that a modification of the PIP side chain in a homogeneous condition is much easier than that of the SPS main chain in a heterogeneous system. It can be a good model for the modification of the SPS-based polymer under a homogeneous condition. The lithiated PIP side chain of the SPS-based graft polymer can be utilized for anionic polymerizations of a wide variety of monomers such as 1,3-butadiene, ethylene oxide, and MMA. This will render the synthesis of quite a few novel triblock and even ABCBA penta-block copolymers possible (14, 15) In addition, modifications of PIP, such as epoxidation and hydrogenation, enables SPS-*graft*-PIP to have improved physical and chemical properties, as well as processability (16–18).

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