# Cycloolefin Copolymer Analogues from Styrene and Isoprene: Cationic Cyclization of the Random Copolymers Prepared by Living Anionic Polymerization

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ABSTRACT: This paper reports a novel and practical method for the synthesis of styrene-isoprene-derived cycloolefin copolymer analogues via the intramolecular Friedel–Crafts alkylation of well-defined random copolymers of styrene and isoprene prepared by living anionic copolymerization in the presence of a small amount of tetrahydrofuran as a randomizer. The random copolymers with an almost equimolar amount of the two monomers (styrene:isoprene = 48:52) and a predominant 1,4-isoprene-enchainment (1,4-:1,2-:3,4- = 67:1:32) were intramolecularly cyclized with $CF_3SO_3H$ efficiently to give the soluble cycloolefin copolymer analogues with a high glass transition temperature ($T_g$). The $T_g$ increased dramatically ($T_g = 20$ vs 130 °C) on cyclization between the aromatic ring of the styrene unit and the adjacent C=C bond in the isoprene unit via the intramolecular Friedel–Crafts alkylation that results in the tetrahydronaphtyl bicyclic unit in the backbone chain, for which the highest $T_g$ was observed at the equimolar content of isoprene and styrene. The predominant Friedel–Crafts cyclization between the styrene and the adjacent isoprene units was supported by the model reactions of the corresponding low molecular weight model compounds.

## Introduction

Amorphous hydrocarbon polymers with cyclic units in the main chain have attracted much attention especially in the optoelectronic field due to their good thermal properties, nonhygroscopic nature, and good transparency. One of the most typical methods to produce such amorphous polymers retaining the cyclic structures is to polymerize or copolymerize cycloolefins by adequate polymerizations such as cationic,[1] anionic,[2] coordination,[3] and ring-opening metathesis polymerizations depending on the monomer structure.[4] These cyclic monomers may sometimes be commercially available on a large scale, but others need to be prepared as the starting materials for such specialty polymers. Another promising route for the cycloolefin polymer analogues from an industrial viewpoint would be the polymerization of commercially available noncyclic hydrocarbon monomers followed by simple postpolymerization reactions, which can afford polymerized products with cyclic structures.[5,6]

One of the simplest methods for this purpose would be the cationic cyclization of unsaturated hydrocarbon polymers under acidic conditions via carbocationic intermediates. Since the 1910s, cyclization has been used for diene-polymer-based soft elastomers, such as natural rubber,[7] synthetic polyisoprene,[8] polybutadiene,[9] and their copolymers with styrene,[10,11] to produce hard and amber colored plastics. These polymers are commercially utilized as modifiers of natural rubber, adhesives, and photo resist materials.[12] However, cyclization occurs not only intramolecularly, but also intermolecularly, which often induces a cross-linking reaction to significantly increase the molecular weights, broaden the molecular weight distributions (MWDs), and make the products insoluble via gelation. A set of such uncontrolled reactions would cause brittleness and a low melt processability of the resultant polymers.

In this paper, we report a novel and practical method for the synthesis of styrene-isoprene-based cycloolefin copolymer analogues via the cationic cyclization of well-defined random copolymers prepared by living anionic copolymerization under the conditions specified in Scheme 1. The key for this method is to control the styrene-isoprene sequence distribution to favor intramolecular cyclization reactions along the chain to generate linear polymers with rigid cyclic repeating units. Upon protonation of the 1,4- or 3,4-isoprene units in the monomer sequence, the formed tertiary cationic carbon will preferentially attack the ortho-position of the adjacent benzene ring of the styrene unit via intramolecular Friedel–Crafts alkylation, which results in a tetrahydronaphtyl bicyclic unit in the backbone chain. The cyclization provides a higher glass transition temperature ($T_g$) than those of both poly(styrene) (PSt) and cyclized poly(isoprene) (PIp) and better thermal durability due to the aliphatic saturation of the olefin units.

## Experimental Section

**Materials.** Styrene (St: Kishida Chemical; purity 99.5%) was distilled from calcium hydride and stored at −25 °C. Isoprene (Ip: Tokyo Chemical Industry; purity >99.0%) was dried over calcium chloride before use. Cyclohexane (Wako Pure Chemical Industries; purity >99.5%) was distilled from calcium hydride. THF (tetrahydrofuran; Wako Pure Chemical Industries; purity >99.5%), *sec*-butyl lithium (Kanto Chemical; 1.0 mol/L in *n*-hexane), *n*-butyl lithium (Kanto Chemical; 2.6 mol/L in *n*-hexane), methanol (Wako Pure Chemical Industries; purity >99.5%), trifluoromethanesulfonic acid (Wako Pure Chemical Industries; purity >98%), sodium carbonate (Wako Pure Chemical Industries; purity >99.5%), Triphenylphosphine (Aldrich; purity 99%), isopropyl iodide (Aldrich; purity 99%), 3-phenylbutyraldehyde (Aldrich; purity 97%), sodium bis(trimethylsilyl)amide (Kanto Chemical; purity >98%), and ethyltriphenylphosphonium bromide (Kanto Chemical; purity >99%) were used as received.

**Measurements.** The $^1H$ NMR spectra were recorded on a JEOL JNM-LA400 (400 MHz). The number-average molecular weight ($M_n$) and polydispersity index ($M_w/M_n$) were determined by size-exclusion chromatography in tetrahydrofuran (THF) at 40 °C on

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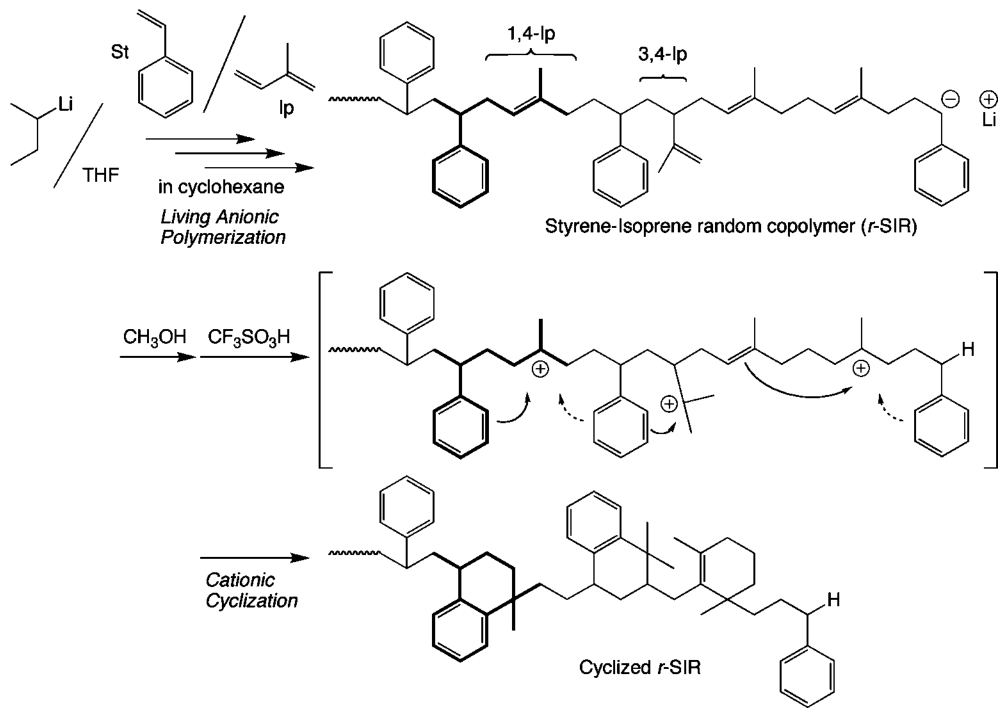
**Scheme 1. Living Anionic Copolymerization of Styrene and Isoprene and Subsequent Cationic Cyclization of the Copolymer**



three polystyrene gel columns [TSKgel GMH-M (exclusion limit, $4 \times 10^6$; bead size, 5 $\mu$m; 7.8 mm i.d. × 30 cm) × 2 and TSKgel G2000H (exclusion limit, $1 \times 10^4$; bead size, 5 $\mu$m; 7.8 mm i.d. × 30 cm); flow rate 1.0 mL/min] connected to Tosoh HLC-8020 system including refractive index and UV detectors. The columns were calibrated against 9 standard polystyrene samples (GL sciences; $M_p = 580-600000$; $M_w/M_n = 1.02-1.12$) with refractive index detectors. Glass transition temperature ($T_g$) of the polymer was recorded on DSC30 differential scanning calorimetry (Mettler Toledo). Certified indium and tin were used for temperature and heat flow calibration. Samples were first heated to 200 °C at 10 °C/min, and cooled to −80 °C at 10 °C/min and then reheated to 200 °C at 10 °C/min. All $T_g$ (midpoint of the transition) values were obtained from the second scan, after removing the thermal history. The absolute weight-average molecular weight ($M_w$) of the polymers was determined by multiangle laser light scattering in THF at 40 °C on a Wyatt Technology DAWN HELEOS photometer ($\lambda = 658$ nm). The refractive index increment (d*n*/d*c*) was measured in THF at 25 °C on a Wyatt Optilab rEX refractmeter ($\lambda = 658$ nm), the d*n*/d*c* values were 0.166 and 0.183 mL/g for *r*-SIR and its cyclized derivative, respectively.

**Synthesis of 2-Methyl-5-phenyl-2-hexene (1).** First, isopropyltriphenylphosphonium iodide was prepared from triphenylphosphine (107 mmol, 28.06 g) and isopropyl iodide (118 mmol, 20 g) in toluene (84 mL) under reflux for 21 h at 76 °C. The reaction mixture was cooled and the precipitates were filtered. Then the precipitates were washed with 50 mL of $Et_2O$ twice and vacuum-dried to give isopropyltriphenylphosphonium iodide (75.9 mmol; 32.8 g; yield = 71%). *n*-butyl lithium solution (9.69 mL, 2.6 M in hexane) was added into the suspension of isopropyltriphenylphosphonium iodide (23 mmol, 10 g) in $Et_2O$ (40 mL) at 0 °C and stirred overnight at room temperature. 3-Phenylbutyraldehyde (24 mmol, 3.60 g) was added into the reaction mixture at 0 °C and stirred for 6 h at room temperature. Water (20 mL) and *n*-hexane (30 mL) were added into the mixture and the insoluble parts were removed by filtration. The organic layer was diluted another 30 mL of *n*-hexane, washed twice with 50 mL of water, and then evaporated to give the crude product as a liquid. The crude product was purified by silica column chromatography with *n*-hexane to give 2-methyl-5-phenyl-2-hexene (**1**: 13.8 mmol, 2.4 g; yield = 60%, purity >99%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$7.23−7.32 (m, 2H), 7.12−7.22 (m, 3H), 5.03−5.13 (m, 1H), 2.65−2.78 (m, 1H), 2.15−2.33 (m, 2H), 1.66 (s, 3H), 1.54 (s, 3H), 1.23 (td, 3H).

**Synthesis of 2,6-Dimethyl-2,6-octadiene (2).** A Wittig reagent of (ethylidene)triphenylphosphorane was prepared from the reaction between sodium bis(trimethylsilyl)amide (220 mmol, 40 g) and ethyltriphenylphosphonium bromide (220 mmol, 82 g) in *n*-hexane (800 mL) under reflux for 3 h at 70 °C. The reaction mixture was cooled to −20 °C and the precipitates were filtrated to give the crude Wittig reagent including NaBr. To remove NaBr, the product was dissolved with 750 mL of THF and then filtrated. The THF solution of (ethylidene)triphenylphosphorane was cooled to −78 °C and mixed with a THF solution (200 mL) of 6-methyl-5-hepten-2-one (28 g, 220 mmol) for 1 h and then stirred overnight at room temperature. After THF was evaporated, the crude product was diluted with *n*-hexane, filtered, washed with water two times, and then dried with $Na_2SO_4$ overnight. The solution was further cooled to −20 °C and filtered to remove the residual $Ph_3P = O$. The crude was purified by silica column chromatography with *n*-hexane to give 2,6-dimethyl-2,6-octadiene (**2**: 24.3 g, 176 mmol; yield = 80%, purity >99%) as a clear liquid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$5.16−5.25 (q, 1H), 5.05−5.16 (m, 1H), 2.04 (s, 2H), 1.94−2.11 (dt, 2H), 1.68 (s, 6H), 1.61 (d, 3H), 1.56 (d, 3H).

**Polymerization Procedures.** The polymerizations were carried out by the syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for St/Ip random copolymerization is given below. The copolymerization was initiated by adding solutions of premixed St/Ip mixture (St, 1.2 mol, 138 mL; Ip, 1.2 mmol, 120 mL) at 3.3 mL/min by a syringe pump into a *sec*-butyl lithium solution containing cyclohexane (840 mL), THF (6.0 mmol, 0.49 mL), and *sec*-butyl lithium (2.0 mmol) at 40 °C. After adding all the St/Ip mixture, the polymerization mixture was kept stirred for 1 h at 40 °C. The polymerization was terminated with methanol (1 mL). The quenched solutions were washed with 300 mL of water three times to remove the initiator residues, dropped into methanol and acetone mixture (600/400 mL), decanted off any liquid, and vacuum-dried to give the product styrene−isoprene random copolymers (*r*-SIR: random styrene−isoprene rubber) [yield = 93% (192 g), $M_n$ = 119 400, $M_w/M_n$ = 1.03, St content = 48 mol %, Ip 3,4-unit content = 28 mol %]. The St and Ip 3,4-unit

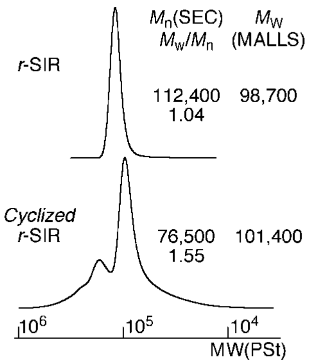


**Figure 1.** Size-exclusion chromatograms of styrene−isoprene copolymers (*r*-SIR: code 5 in Table 1) and its cyclized derivative (cyclized *r*-SIR: code 5 in Table 2) obtained with *r*-SIR (60 g), $[CF_3SO_3H]_0 = 1.9$ mM in cyclohexane (2.34 L) for 1 h at room temperature.

**Table 1. Copolymers (*r*-SIR) of Styrene (St) and Isoprene (Ip) Prepared by Anionic Polymerization**[a]

| | | | | | microstructure in Ip, %[b] | | | |
|---|---|---|---|---|---|---|---|---|
| code | *r*-SIR | $F_{st}$, mol %[b] | $M_n$[c] | $M_w/M_n$[c] | 1,4 | 1,2 | 3,4 | $T_g$, °C[d] |
| 1 | *r*-SIR15 | 16 | 150 100 | 1.03 | 82 | 0 | 18 | −36 |
| 2 | *r*-SIR30 | 29 | 114 700 | 1.03 | 73 | 1 | 26 | −7 |
| 3 | *r*-SIR40 | 39 | 112 700 | 1.02 | 71 | 1 | 28 | 4 |
| 4 | *r*-SIR50−1 | 48 | 119 400 | 1.03 | 68 | 1 | 31 | 16 |
| 5 | *r*-SIR50−2 | 48 | 112 400 | 1.04 | 67 | 1 | 32 | 20 |
| 6 | *r*-SIR55 | 55 | 61 900 | 1.11 | 73 | 1 | 26 | 28 |
| 7 | *r*-SIR65 | 66 | 131 100 | 1.02 | 64 | 0 | 36 | 39 |
| 8 | *r*-SIR75 | 74 | 110 200 | 1.02 | 65 | 1 | 34 | 45 |
| 9 | PIp | 0 | 117 000 | 1.02 | 74 | 0 | 26 | −65 |
| 10 | PSt | 100 | 197 500 | 1.03 | | | | 100 |

[a] The copolymerization was initiated by adding solutions of premixed St/Ip mixture (St: 1.2 mol; Ip: 1.2 mol) at 3.3 mL/min by syringe pump into a *sec*-butyl lithium solution containing cyclohexane (840 mL), tetrahydrofuran (6.0 mmol), and *sec*-butyl lithium (2.0 mmol) at 40 °C. [b] Determined by $^1$H NMR. [c] The number-average molecular weight ($M_n$) and distribution ($M_w/M_n$) were determined by size-exclusion chromatography against PSt standards. [d] The glass transition temperature ($T_g$) was determined by differential scanning calorimetry.

contents were determined by $^1$H NMR spectroscopy using the peak intensities of aromatic (6.5−7.5 ppm), 1,4-Ip (4.75−5.15 ppm), and 3,4-Ip protons (4.0−4.75 ppm).

**Cyclization Procedures of *r*-SIR.** The cyclizations were carried out by the syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for *r*-SIR cyclization is given below. The cyclization was initiated by adding $CF_3SO_3H$ (4.4 mmol, 0.39 mL) into a *r*-SIR solution, containing *r*-SIR (60 g) and cyclohexane (2.34 L) at room temperature. After a predetermined period (60 min), the cyclization was terminated with 1% aqueous solution of $Na_2CO_3$ (500 mL). The quenched solutions were washed with 500 mL of water three times to remove $CF_3SO_3H$ and $Na_2CO_3$ residues, dropped into methanol and acetone mixture (3/2 L), filtered and vacuum-dried to give the product [yield = 97% (58 g), $M_n = 76\,500$, $M_w/M_n = 1.55$].

**Cyclization Reaction of 2-Methyl-5-phenyl-2-hexene (1) and 2,6-Dimethyl-2,6-octadiene (2).** The cyclizations of the model compounds (**1** and **2**) were also carried out by the syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the cyclization of **1** is given below. The cyclization was initiated by adding $CF_3SO_3H$ (0.44 mmol, 0.039 mL) into a solution, containing 2-methyl-5-phenyl-2-hexene (**1**: 344 mmol, 6 g) and cyclohexane (234 mL) at room temperature. After a predetermined period, the cyclization was terminated with 1% aqueous solution of $Na_2CO_3$ (50 mL). The quenched solutions were washed with 50 mL of water three times to remove $CF_3SO_3H$ and $Na_2CO_3$ residues, evaporated to remove the solvent, to give the cyclized product [**3**: yield = 90% (5.38 g)]. The conversion was almost quantitative (>99%) determined by $^1$H NMR spectroscopy using the peak intensities of −CH(Ar)− and =CH− protons (*b*, *b*′, and *e* in Figure 5, respectively). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$7.30 (d, 1H), 7.03−7.20 (m, 3H), 2.87 (q, 1H), 1.86−1.99 (m, 1H), 1.70−1.80 (m, 1H), 1.49−1.61 (m, 2H), 1.28 (s, 3H), 1.26 (d, 3H), 1.24 (s, 3H).

## Results and Discussion

**1. Cycloolefin Copolymer Analogues by Cationic Cyclization of *r*-SIR.** Prior to the cationic cyclization, we first prepared *r*-SIR with various compositions of styrene and isoprene by the living anionic polymerization technique in a nonpolar solvent, cyclohexane, using *sec*-butyl lithium as the initiator. This is one of the most popular industrial methods for producing SIR.[13] For making the monomer sequence random and less blocky, the premixed styrene and isoprene monomers were incrementally and continuously added to the reaction mixture throughout the reaction in the presence of a small amount of THF as the randomizer (see the Experimental Section), because the batch polymerization of the two monomers in nonpolar solvents without polar compounds usually forms the blocky copolymers. It was reported that small amounts of Lewis bases as additives enhance the copolymerizability of styrene and diene to result in formation of random copolymers,[13,14] while much different reactivity ratios were obtained in the absence of additives ($r_{Ip} = 16.6$ and $r_{St} = 0.046$ in cyclohexane at 40 °C).[15] For all the comonomer feed ratios, the obtained copolymers had relatively high and controlled molecular weights ($M_n \sim 10^5$) with narrow MWDs ($M_w/M_n \le 1.1$) (Table 1). The comonomer composition ratio in the obtained copolymers determined by $^1$H NMR spectroscopy agreed well with those in the feed. The regiospecificities in the isoprene units were predominantly 1,4-rich (1,4-:1,2-:3,4- = 64−82: 0−1:18−36), which are almost the same as the reported values.[10] The randomness of the repeating styrene and isoprene units was also evaluated by $^{13}$C NMR spectroscopy, which indicates less consecutive styrene−styrene units in the *r*-SIR (see Figure S1 in the Supporting Information).

The cationic cyclizations of the obtained *r*-SIR were then examined using a commercially available strong Brönsted acid, $CF_3SO_3H$, in cyclohexane at ambient temperature under moderate polymer concentration (4 wt %). The obtained products were completely soluble in THF without gelation. Figure 1 shows a typical example of the size-exclusion chromatography (SEC) curves of the *r*-SIR with 48 mol % styrene contents (code 5 in Table 1) before and after the cyclization under the optimized conditions. Although the main peak of the SEC curves shifted to a lower molecular weight after the postpolymerization reactions due to the reduced hydrodynamic volume on the cyclization, the absolute molecular weight of the main peak was almost the same as that before the reactions [$M_W$(MALLS) = 98 700 (before) vs 101 400 (after)]. The higher molecular weight small peak of the cyclized *r*-SIR showed some intermolecular linking and/or cross-linking reactions, which became more pronounced on increasing the polymer concentration (see Figure S2 in the Supporting Information).

Figure 2 shows the $^1$H NMR spectra of *r*-SIR and the product polymers after the postpolymerization reactions (parts A and B of Figure 2, respectively). Before the cyclization of the copolymers, the spectrum showed the typical signals of the styrene-isoprene random copolymers, in which all the peaks were relatively broad compared to the corresponding homopolymers. The signals (*e*, *j*, *n*, and *o*) at 3.8−5.3 ppm assigned to the olefinic protons of the isoprene unit showed a predominant 1,4-enchainment (*e*: 67%), 3,4-structure (*j*: 32%), and a negligible amount of 1,2-strucutre (*n* and *o*: ≤1%) due to the presence of a small amount of THF during the copolymerization. After the reactions, these double bond signals dramatically decreased, and the peaks of the aromatic protons (*c*′) at the 6.5−7.5 ppm became broader. These results indicate that the cyclization most

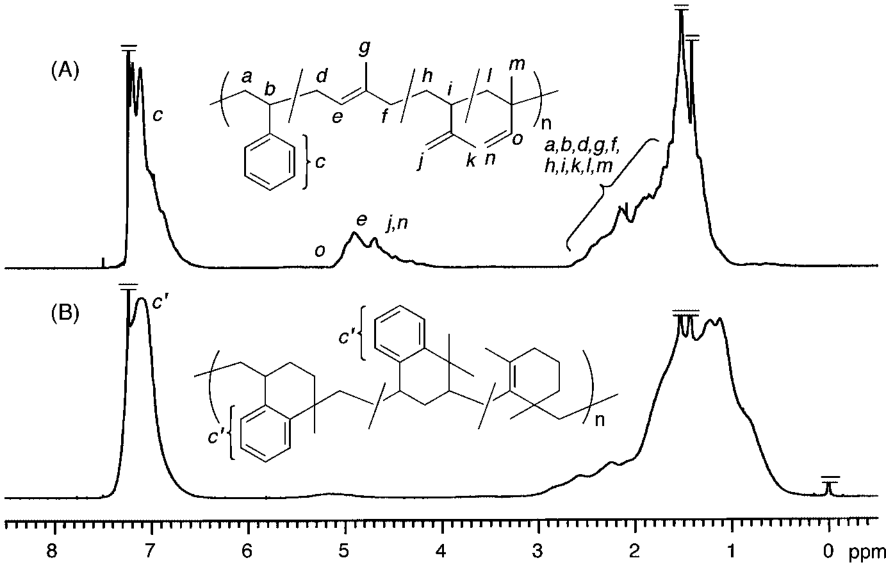


**Figure 2.** $^1$H NMR spectra ($CDCl_3$, 25 °C) of (A) *r*-SIR (code 5 in Table 1) and (B) cyclized *r*-SIR obtained with $CF_3SO_3H$ in cyclohexane at room temperature (code 5 in Table 2).

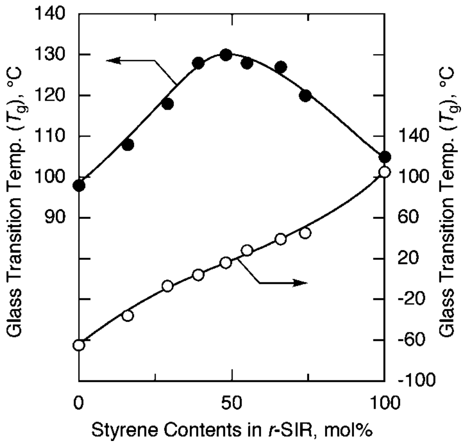


**Figure 3.** Glass transition temperature ($T_g$) of *r*-SIR (○) and their cyclized derivatives (●) as a fraction of styrene contents in the copolymers.

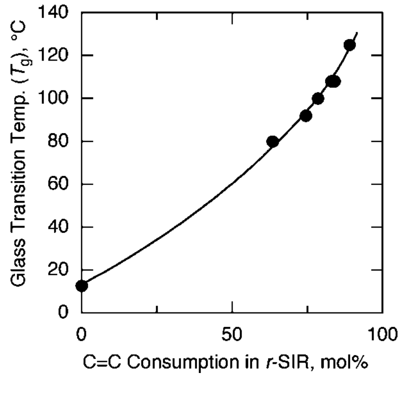


**Figure 4.** Glass transition temperature ($T_g$) of cyclized *r*-SIR as C=C bond consumption in the original *r*-SIR copolymers ($F_{st}$ = 48%, $M_n$ = 128 400, $M_w/M_n$ = 1.05).

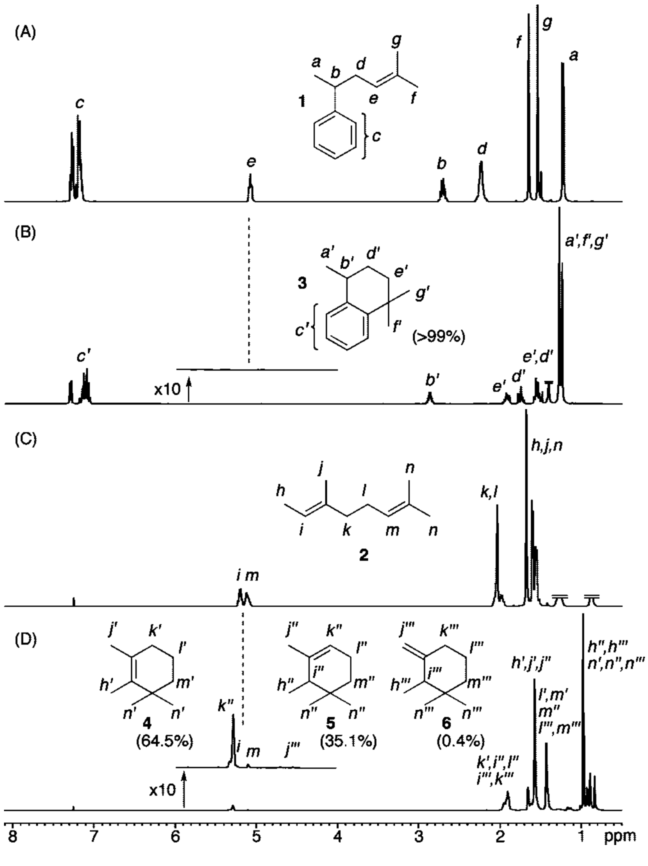


**Figure 5.** $^1$H NMR spectra ($CDCl_3$, 25 °C) of (A) 2-methyl-5-phenyl-2-hexene (**1**), (B) the cyclized derivative of **1** (**3**), (C) 2,6-dimethyl-2,6-octadiene (**2**), and (D) the cyclized derivatives of **2** (**4**−**6**) obtained with $CF_3SO_3H$ in cyclohexane at room temperature.

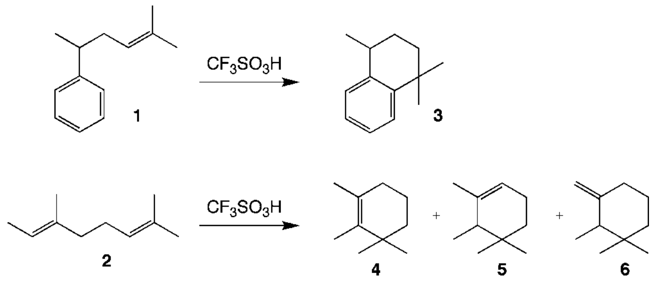
probably proceeded between the C=C double bond of the isoprene unit and the phenyl group of the adjacent styrene units via the Friedel−Crafts reaction.

The consumption of the olefinic protons was then evaluated from the decrease of the peak intensity ratios of the =CH protons to all the peaks of the polymers for various *r*-SIR and PIp. As shown in Table 2, most of the vinyl groups in the polymers underwent the acid-induced reactions to be consumed in high conversions (≥80%). For all the *r*-SIR, the $M_n$ based on the polystyrene calibration by SEC slightly became lower due to the decrease of the hydrodynamic volume on the intramolecular Friedel−Crafts cyclization between the neighboring isoprene and styrene units. However, the SEC curves showed small peaks in the higher molecular weight regions, indicating a small amount of intermolecular linking reaction, the ratio of which decreased from 25 to 9% as the styrene contents in the original *r*-SIR increased. Such intermolecular linking products were more pronounced in the acid-promoted reaction of homopolyisoprene with no styrene units, where much broader molecular weight distributions ($M_w/M_n > 2.0$) were observed. These results also support that the favorable intramolecular Friedel−Crafts cyclization between the neighboring isoprene and styrene units in *r*-SIR.

In general, cyclization in the main-chain provides better thermal properties such as a high $T_g$. The thermal properties of a series of cyclized *r*-SIR were then evaluated by differential scanning calorimetry (DSC). Figure 3 shows the relationship between the styrene contents ($F_{st}$) in the *r*-SIR and the $T_g$ values of the *r*-SIR (open circles) and the cyclized products (filled circles). Each DSC of the *r*-SIRs showed only one $T_g$ value, which increased in nearly direct proportion to the styrene content, suggesting again the formation of the random copolymers in the living anionic copolymerizations. After the acid-induced reactions, the $T_g$ values dramatically increased irrespective of the styrene contents, indicating again the cyclization. Upon similar cyclization of homopolyisoprene ($F_{st} = 0\%$) via the carbocationic intermediates, known as cyclized rubber,[7] the $T_g$ increased to 98 °C, whereas no reaction occurred for the homopolystyrene ($F_{st} = 100\%$) with the $T_g$ constant at 105 °C, as expected. As the styrene contents in the copolymers increased, the $T_g$ value of the cyclized polymer increased and reached the maximum value ($T_g = 130$ °C) at an almost 50% styrene content ($F_{st} = 48\%$), whereas it decreased over a 50% styrene content. This suggests the formation of the bicyclic structure between the isoprene and the adjacent styrene units, which would be more rigid than the monocyclic structures originating from the adjacent isoprene-isoprene units. In addition, the styrene-styrene sequence cannot produce any cyclic structures under such reaction conditions and thus the $T_g$ values decreases over $F_{st} = 50\%$. Therefore, the highest $T_g$ was observed at the equimolar content of isoprene and styrene, which should result in the highest probability of the styrene−isoprene sequence in the random copolymers for the intramolecular Friedel−Crafts cyclization. These results again indicate that the incorporation of the adjacent styrene-isoprene sequence into the prepolymer is important for the formation of the cyclic repeating units having good thermal properties.

Figure 4 shows the $T_g$ dependence on the consumptions of the C=C double bond in the *r*-SIR containing the nearly equimolar amount of isoprene and styrene units. As the C=C double bond consumed, the $T_g$ of the copolymers increased gradually. Furthermore, the consumptions of the C=C bonds as well as the increase of $T_g$ took place much faster than the intermolecular linking and/or cross-linking reactions (see Figure S3 in the Supporting Information). These indicate little dependence of $T_g$ on the intermolecular linking reaction. A similar result was also obtained with the cyclized *r*-SIR with different contents (25−50%) of intermolecular linking products obtained from the same *r*-SIR, in which the $T_g$ values of the obtained products were almost the same (124−125 °C) (see Figure S2 in the Supporting Information). Thus, *r*-SIR undergoes the acid-promoted intramolecular Friedel−Crafts cyclization efficiently to result in cycloolefin copolymer analogues with a wide range of $T_g$'s that depend on the comonomer compositions and C=C consumptions.

**Scheme 2. Cationic Cyclization of the Model Compounds (1 and 2) for the *r*-SIR Copolymer**



**2. Cyclization Reactions of Model Compounds.** To elucidate the cyclization mechanism, the model reactions of the cationic cyclization were examined with 2-methyl-5-phenyl-2-hexene (**1**) and 2,6-dimethyl-2,6-octadiene (**2**), which corresponds to the models of the styrene-isoprene and isoprene-isoprene sequence with 1,4-isoprene enchainments, respectively (Scheme 2).

These model compounds were treated with $CF_3SO_3H$ in cyclohexane under the same conditions as those for *r*-SIR. Figure 5 shows the $^1H$ NMR spectra of the model compounds **1** and **2** (Figure 5, parts A and C, respectively) and their products after the reaction by $CF_3SO_3H$ (Figure 5, parts B and D, respectively). The reaction of **1** gave the intramolecularly cyclized tetrahydronaphthyl bicyclic compound (**3**) in almost quantitative yield along with the complete consumption of the olefinic protons in the $^1H$ NMR spectrum.[16] On the other hand, the reaction of **2** was slower and afforded the mixture of the unsaturated compounds (**4**−**6**).

The rates of the cyclization reaction of **1** and **2** as well as that of *r*-SIR were then compared. Figure 6 shows the consumption of the C=C bonds in **1**, **2**, and *r*-SIR ($F_{st} = 58\%$) in cyclohexane at ambient temperature (23 °C). The C=C double bond of **1** was consumed very fast to afford the cyclized compound almost quantitatively, whereas the consumption of C=C for **2** was very slow. This indicates that the styrene-isoprene unit (**1**) cyclizes easily via the intramolecular

**Table 2. Cationic Cyclization of Copolymers (*r*-SIR) of Styrene (St) and Isoprene (Ip)[a]**

| code | *r*-SIR (prepolymer) | =C*H* ratio in $^1H$ NMR[b] *x* | *y* | C=C consumption, %[c] | $M_n$[d] | $M_w/M_n$[d] | intermolecular linking, %[e] | $T_g$, °C[f] |
|---|---|---|---|---|---|---|---|---|
| 1 | *r*-SIR15 | $1.22 \times 10^{-1}$ | $2.49 \times 10^{-2}$ | 80 | 93 500 | 1.48 | 25 | 108 |
| 2 | *r*-SIR30 | $1.13 \times 10^{-1}$ | $1.75 \times 10^{-2}$ | 85 | 67 400 | 1.50 | 24 | 118 |
| 3 | *r*-SIR40 | $9.31 \times 10^{-2}$ | $1.10 \times 10^{-2}$ | 88 | 61 800 | 1.63 | 20 | 128 |
| 4 | *r*-SIR50−1 | $8.35 \times 10^{-2}$ | $7.87 \times 10^{-3}$ | 91 | 66 300 | 1.60 | 19 | 130 |
| 5 | *r*-SIR50−2 | $8.37 \times 10^{-2}$ | $7.08 \times 10^{-3}$ | 92 | 76 500 | 1.55 | 19 | 129 |
| 6 | *r*-SIR55 | $6.54 \times 10^{-2}$ | $6.00 \times 10^{-3}$ | 91 | 50 800 | 1.30 | 15 | 128 |
| 7 | *r*-SIR65 | $5.33 \times 10^{-2}$ | $2.41 \times 10^{-3}$ | 95 | 81 900 | 1.45 | 13 | 127 |
| 8 | *r*-SIR75 | $4.15 \times 10^{-2}$ | $3.04 \times 10^{-3}$ | 93 | 75 800 | 1.32 | 9 | 120 |
| 9 | PIp | $1.58 \times 10^{-1}$ | $2.87 \times 10^{-2}$ | 82 | 51 000 | 2.08 | *multimodal* | 98 |
| 10 | PSt | | | | 197 500 | 1.03 | 0 | 105 |

[a] The cyclization was carried out by adding $CF_3SO_3H$ to the cyclohexane solution of *r*-SIR (60 g), $[CF_3SO_3H]_0 = 1.9$ mM in cyclohexane (2.34 L) for 1 h at room temperature. [b] The peak intensity ratio of the olefinic protons to all the peaks of the polymers in the $^1H$ NMR spectra before (*x*) and after (*y*) the cyclization. [c] Determined from the =C*H* ratio in the $^1H$ NMR. [d] The number-average molecular weight ($M_n$) and distribution ($M_w/M_n$) were determined by size-exclusion chromatography (SEC) against PSt standards. [e] Determined by the peak intensity ratio of the higher molecular weight peaks in the SEC curves. [f] The glass transition temperature ($T_g$) was determined by differential scanning calorimetry.

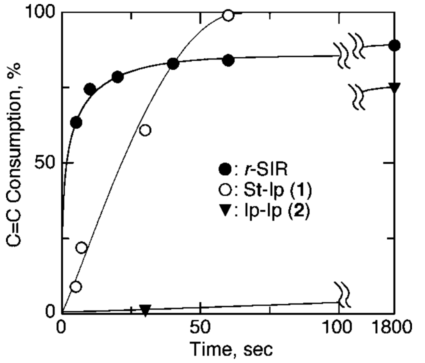


**Figure 6.** Consumption of C═C bonds in the reaction of **1**, **2**, and *r*-SIR with $CF_3SO_3H$ in cyclohexane at ambient temperature: **1**, **2**, or *r*-SIR (6.0 g), $[CF_3SO_3H]_0 = 1.9$ mM in cyclohexane (0.23 L) at 23 °C.

Friedel−Crafts alkylation to yield the well-defined cyclic unit, while the reaction between the isoprene-isoprene unit (**2**) is less efficient and more complex. A fast consumption of C═C for *r*-SIR also supports the acid-promoted reaction of *r*-SIR mainly proceeds via a similar intramolecular Friedel−Crafts cyclization between the neighboring styrene and isoprene units in the *r*-SIR to result in the rigid tetrahydronaphtyl bicyclic structure in the main chain.

## Conclusion

The optimization of the cationic cyclization of the styrene−isoprene random copolymers as well as the design of the living anionic copolymerizations for the prepolymers are important for the construction of novel *r*-SIR-derived cycloolefin copolymer analogues. The acid-promoted postpolymerization reaction afforded copolymers with a higher glass transition temperature (∼130 °C) than both those of PSt and cyclized PIp, indicating the formation of the bicyclic structure via the intramolecular Friedel−Crafts reaction. Further studies are now in progress for the evaluation of the various properties of the cyclized copolymers.

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**Supporting Information Available:** Figures showing $^{13}C$ NMR spectra of polystyrene and *r*-SIR, size-exclusion chromatograms of cyclized *r*-SIR obtained with $CF_3SO_3H$ in cyclohexane, and size-exclusion chromatograms and $^1H$ NMR spectra for the cyclization of *r*-SIR at varying reaction times. This material is available free of charge via the Internet at http://pubs.acs.org.

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