Transformation of Vulcanized Natural Rubber into Lower Molecular Weight Polymers and Their Application to Grafted Copolymer Synthesis with Some Vinyl Monomers

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ABSTRACT: Graft copolymerization of several vinyl monomers onto polyisoprene was carried out to explore the possibility to recycle waste rubber to useful functional materials. Synthetic polyisoprene, vulcanized natural rubber, and vulcanized natural rubber with carbon black were converted to lower molecular weight polymers at 300°C, under air or nitrogen atmosphere. The obtained low molecular weight natural rubber and polyisoprene were soluble in organic solvents, such as hexane, toluene, tetrahydrofuran (THF), chloroform, and monochlorobenzene. Radical copolymerization of styrene with a thermally fragmented natural rubber was carried out at 80°C in bulk for 2 h in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) under air atmosphere to give the corresponding grafted copolymer. The obtained polymer was a beige powdery copolymer at room temperature and consisted of isoprene (38 mol %) and styrene (62 mol %) units, respectively. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4003–4010, 2006

Key words: vulcanized natural rubber; vinyl monomer; graft copolymerization; crosslink; chemical recycle

INTRODUCTION

Among various polymeric wastes, spent vulcanized natural rubber is considered as a troublesome waste that is hard to be recycled in an environment-friendly method. Present disposal of waste vulcanized natural rubber is limited to simple incineration, thermal decomposition,[1–6] oil recovery,[7–14] and material recycle.[15–19] However, recent requirement on saving fossil fuel and decreasing the greenhouse effect require new environmentally-benign solutions, such as chemical recycling.

With this in mind, we focused on transformation of waste polyisoprene, which is the major component of vulcanized natural rubber, into useful functional substances. Some reports described modification of natural rubber by graft copolymerization of vinyl monomers, such as styrene, acrylonitrile, and methyl methacrylate (MMA).[20,21] The grafted copolymers may be expected to serve as polymer alloys or resin additive agents. However, recycle of waste polyisoprene by graft copolymerization will require much effect to attain elimination of contaminants such as modifiers. We describe here transformation of vulcanized natural rubber into low molecular weight polyisoprene, from which several vinyl monomers will be copolymerized to obtain graft copolymers as new functional materials from wastes.

EXPERIMENTAL

Measurements

FTIR spectra were obtained using a JASCO FT/IR-470 Plus instrument. ^{1}H-NMR spectra were recorded on a JASCO EX-270 spectrometer, using tetramethylsilane as internal standard. Estimation of the number–and weight–average molecular weights (M_n and M_w) by gel permeation chromatography (GPC) was carried out with a Tosoh SC-8020 system equipped with four consecutive polystyrene gel columns (TSK-$_{\mathrm{GM}}$HX, G4000HXL, G3000HXL, and G2500HXL), and refractive index detectors using tetrahydrofuran (THF) as an eluent with a flow rate of 1.0 mL/min by polystyrene calibration. Thermogravimetric analysis (TGA) curves were recorded on a TG/DTA 6200 instrument (Seiko Instruments) in N_2 atmosphere. Glass transition temperatures (T_g) of polymers were measured on a DSC 6200 instrument (Seiko Instruments) in N_2 atmosphere. TGA and DSC measurements were run at a heating rate of 10°C/min.

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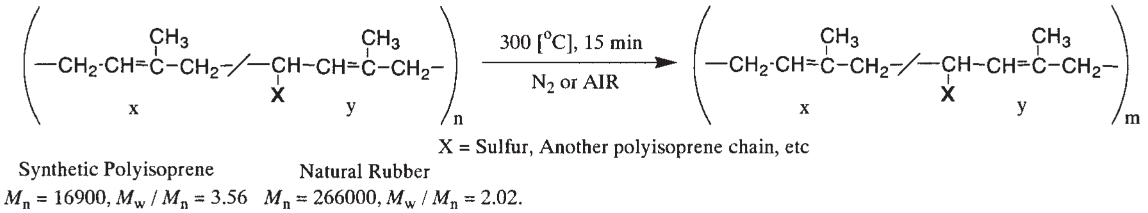


Scheme 1 Thermal fragmentation to low molecular weight synthetic polyisoprene and vulcanized natural rubber.

Materials

Synthetic polyisoprene (Aldrich Co.) was washed with methanol. Styrene, MMA, methyl acrylate, vinyl acetate, and *N*,*N*-dimethyl acrylamide were purified by distillation under reduced pressure prior to use. Toluene, hexane, chloroform, dichloromethane, acetone, THF, and *N*,*N*-dimethylformamide were purified by the general methods. Natural rubber used was obtained from Yokohama Rubber Co. Ltd. RSS 3, (M_n = 266,000, M_w/M_n = 2.02). Vulcanized natural rubber with carbon black was prepared by vulcanization of RSS 3. RSS 3 contained natural rubber (62.5 wt %), carbon black (31 wt %), flowers of zinc (2 wt %), stearic acid (1.5 wt %), antioxidants 6C (*N*-(1,3-dimethyl butyl)-phenyl-*p*-phenylenediamine, 0.5 wt %), antioxidants RD (poly(2,2,4-trimethyl-1,2-dihydroxinone), 1.5 wt %), sulfur (0.5 wt %), and a vulcanization accelerator (*N*-*t*-butyl-2-benzothiazylsulfenamide, 0.5 wt %).

Thermal fragmentation behavior of vulcanized natural rubber

Typical procedure

Natural rubber (RSS 3), vulcanized natural rubber, and vulcanized natural rubber with carbon black were cut into pieces smaller than 3 mm^2, and were heated at 300°C, under either air atmosphere or nitrogen atmosphere for 15 min in an electric furnace. After cooling to room temperature, the resulting viscous product toluene was poured in an excess amount of methanol (300 mL). The precipitated polymer was filtered off and dried under vacuum. Yield: 2.45 g (81.6%, under N_2 atmosphere) and 2.06 g (69.7%, under air atmosphere).

^{1}H-NMR ($CDCl_3$): δ/ppm 5.24–4.96 (1H, $=CH-$), 2.12–1.82 (4H, $-CH_2-C(-CH_3)=CH-CH_2-$), 1.74–1.66 (3H, $-CH_3$). IR (KBr): wavenumber/cm^{-1} 2968 ($-CH_3$, $-CH_2-$, C—H), 1716, 1455 (C=CH), 1103, 844, 479.

Graft copolymerization of styrene onto thermally fragmented natural rubber

Typical procedure

Thermally fragmented natural rubber (3.0 g, 44.0 mmol per unit), styrene (4.58 g, 44.0 mmol), and AIBN (0.72 g, 4.4 mmol) were charged into a flask. The copolymerization was carried out in air atmosphere at 80°C for 2 h with stirring. After the reaction, the reaction solution was diluted with toluene and the polymer was precipitated with methanol, separated by filtration, and dried *in vacuo*. A beige powdery copolymer was obtained in 80.8% (6.12 g) yield. Copolymer composition ([isoprene unit]/[styrene unit]) = 38/62.

^{1}H-NMR ($CDCl_3$): δ/ppm 7.20–6.89 (3H, phenylene protons), 6.53–6.39 (2H, phenylene protons), 5.20–5.04 (1H, $=CH-$), 2.10–1.96 (4H, $-CH_2-C(-CH_3)=CH-CH_2-$), 1.93–1.77 (1H, $-CH(Ph)-CH_2-$), 1.71–1.63 (3H, $-CH_3$), 1.55–1.27 (2H, $-CH(Ph)CH_2-$). IR

TABLE I
Transformation of Synthetic Polyisoprene and Vulcanized Natural Rubber into Low Molecular Weight Polyisoprene under Air and N_2 Atmosphere

	N_2 atmosphere		Air atmosphere	
Materials	Yield[a] (%)	M_n (M_w/M_n)[b]	Yield[a] (%)	M_n (M_w/M_n)[b]
Synthetic polyisoprene[c]	63.7	11,100 (3.78)	73.2	3,300 (5.94)
Natural rubber[d]	68.5	48,100 (2.44)	75.9	35,100 (1.84)
Vulcanized natural rubber with carbon black[e]	28.7	21,500 (2.97)	22.9	10,900 (2.65)
Vulcanized natural rubber[e]	81.6	37,600 (3.90)	69.7	23,600 (3.28)

[a] Isolated yield after precipitation into methanol.
[b] Estimated by GPC based on polyisoprene standards; eluent, THF.
[c] M_n = 16,900; M_w/M_n = 3.56.
[d] M_n = 266,000; M_w/M_n = 2.02.
[e] Rubber vulcanized from natural rubber (M_n = 266,000; M_w/M_n = 2.02).

TABLE II
Copolymerization of Synthetic Polyisoprene with Styrene in the Presence of Radical Initiators

Run	Radical initiator	Yield (%)[a]	[isoprene]/[styrene] $(x + y)/m$[b] (mol %)	M_n (M_w/M_n)[c]
1	Non	63.9	56/44	15,800 (3.13)
2	AIBN	93.9	45/55	11,000 (2.69)
3	BPO	90.4	46/54	10,400 (4.24)
4	BHP	49.9	60/40	17,500 (3.71)
5	CHP	76.7	57/43	10,900 (3.94)

Synthetic polyisoprene $M_n = 16{,}900$; $M_w/M_n = 3.56$.
[a] Isolated yield after precipitation into methanol.
[b] Estimated by ^{1}H NMR spectroscopy.
[c] Estimated by GPC based on polystyrene standards; eluent, THF.

(KBr): wavenumber/cm^{-1} 2980 (—CH_3, —CH_2—, C—H), 1733, 1420 (C$=$CH), 1127 (Ph).

Grafted copolymerization of styrene onto thermally fragmented natural rubber obtained from vulcanized natural rubber with carbon black

The thermally fragmented natural rubber with carbon black (1.87 g, 27.5 mmol per polyisoprene unit), styrene (4.58 g, 44.0 mmol), and AIBN (0.590 g, 3.6 mmol) were charged into a flask. The copolymerization was carried out in air atmosphere at 80°C for 2 h with stirring. After the reaction, the reaction solution was diluted with toluene and the polymer was precipitated with methanol, separated by filtration, and dried in vacuo. A beige powdery copolymer was obtained in 60.3% (3.89 g) yield. Copolymer composition ([isoprene unit]/[styrene unit]) = 31/69.

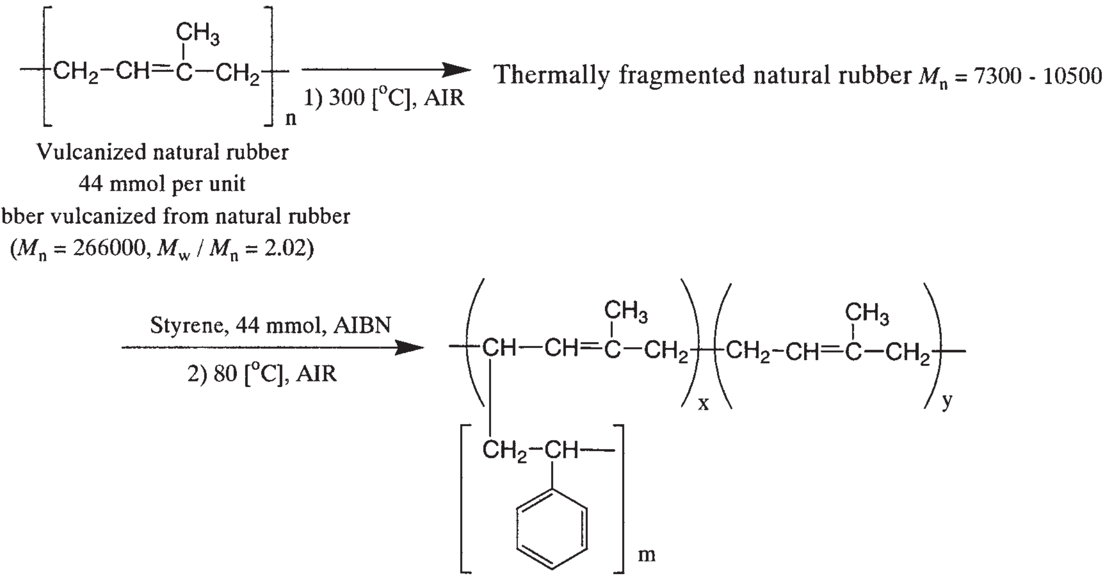
^{1}H-NMR ($CDCl_3$): δ/ppm 7.30–6.87 (3H, phenylene protons), 6.77–6.29 (2H, phenylene protons), 5.24–4.96 (1H, —CH—), 2.10–1.94 (4H, —CH_2—C(—CH_3)$=$CH—CH_2—), 1.91–1.78 (1H, —CH(Ph)—), 1.72–1.62 (3H, —CH_3), 1.54–1.22 (2H, —CH_2—). IR (KBr): wavenumber/cm^{-1} 2978 (—CH_3, —CH_2—, C—H), 1723, 1427 (C$=$CH), 1130 (Ph).

Grafted copolymerization of various vinyl monomers onto synthetic polyisoprene

Typical procedure

Synthetic polyisoprene (1.02 g, 15.0 mmol per unit), styrene (1.56 g, 15.0 mmol), and AIBN (0.25 g, 1.5 mmol) were charged into a flask. The copolymerization was carried out in an air atmosphere at 80°C for 1 h with stirring. After the reaction, the reaction solution was diluted with THF and the polymer was precipitated with methanol, separated by filtration, and dried in vacuo. A white powdery copolymer was obtained in 93.9% (2.42 g) yield.

^{1}H-NMR ($CDCl_3$): δ/ppm 7.02–6.99 (3H, phenylene protons), 6.69–6.40 (2H, phenylene protons), 5.17–5.06



Scheme 2 Graft copolymerization of styrene onto thermally fragmented natural rubber.

TABLE III
Radical Copolymerization of Styrene onto Thermally Fragmented Vulcanized Natural Rubber

Run	AIBN (mol %)	Time (h)	Yield[a] (%)	[isoprene]/[styrene] $(x + y)/m$[b] (mol %)	Thermally fragmented natural rubber M_n (M_w/M_n)[c]	Grafted copolymer M_n (M_w/M_n)[c]
1	0.05	48	39.8	>99/Trace	7,300 (2.67)	7,800 (2.38)
2	0.5	6	63.5	41/59	10,500 (3.04)	23,700 (3.13)
3	5.0	2	80.8	38/62	9,900 (3.79)	13,300 (4.30)

[a] Isolated yield after precipitation into methanol.
[b] Estimated by ^1H NMR spectroscopy.
[c] Estimated by GPC based on polystyrene standards; eluent, THF.

(1H, $=CH-$), 2.12–1.97 (4H, $-CH_2-C(-CH_3)=CH-CH_2-$), 1.95–1.73 (1H, $-CH(Ph)-$), 1.71–1.62 (3H, $-CH_3$), 1.56–1.25 (2H, $-CH_2-$). IR (KBr): wavenumber/cm^{-1} 2926 ($-CH_3$, $-CH_2-$, $C-H$), 1601, 1492, 1453 ($C=CH$), 1130 (Ph), 1027, 837.

The copolymer composition ([isoprene unit]/[styrene unit]) was determined to be 45/55 by ^1H-NMR spectroscopy. The copolymerization of polyisoprene with other comonomers was carried out by the same procedure.

Methyl methacrylate. A white oily copolymer. Yield, 64.7% (methanol insoluble part); copolymer composition ([isoprene unit]/[methyl methacrylate unit]), 79/21; ^1H-NMR ($CDCl_3$): δ/ppm 5.18–5.05 (1H, $=CH-$), 3.66–3.55 (3H, $-O-CH_3$), 2.14–1.96 (4H, $-CH_2-C(-CH_3)=CH-CH_2-$), 1.91–1.78 (3H, $-C(CH_3)-CH_2-$), 1.73–1.59 (3H, $-CH_2-C(-CH_3)=CH-$), 1.34–1.20 (2H, $-C(CH_3)-CH_2-$). IR (KBr): wavenumber/cm^{-1} 2960 ($-CH_3$, $-CH_2-$, $C-H$), 2855, 1733 ($C=O$), 1449 ($C=CH$), 1375, 1269, 1242, 1193, 1150, 987, 889, 839.

Methyl acrylate. A yellow oily copolymer. Yield, 57.3% (methanol insoluble part); copolymer composition ([isoprene unit]/[methyl acrylate unit]), 61/39; ^1H-NMR ($CDCl_3$): δ/ppm 5.17–5.06 (1H, $=CH-$), 3.70–3.61(3H, $-O-CH_3$), 2.40–2.23 (1H, $-CH(C=O)$), 2.12–1.92 (4H, $-CH_2-C(-CH_3)=CH-CH_2-$), 1.70–1.62 (3H, $-CH_2-C(-CH_3)=CH-$), 1.36–1.21 (2H, $-CH_2-$). IR (KBr): wavenumber/cm^{-1} 3448, 2961 ($-CH_3$, $-CH_2-$, $C-H$), 1737 ($C=O$), 1450 ($C=CH$), 1375, 1164, 1085, 888, 831.

TABLE IV
Thermally Fragmented Natural Rubber with Polystyrene, by Soxhlet's Extraction

	Yield (%)	[isoprene]/[styrene] $(x + y)/m$[a] (mol %)	M_n (M_w/M_n)[b]
Acetone soluble part	15.1	15/85	8,000 (1.92)
Chloroform soluble part	75.4	54/46	11,600 (3.06)

Natural rubber with grafted polystyrene; M_n = 10,700; M_w/M_n = 3.32; [isoprene]/[styrene] = 38/62.
[a] Estimated by ^1H NMR spectroscopy.
[b] Estimated by GPC based on polystyrene standards; eluent, THF.

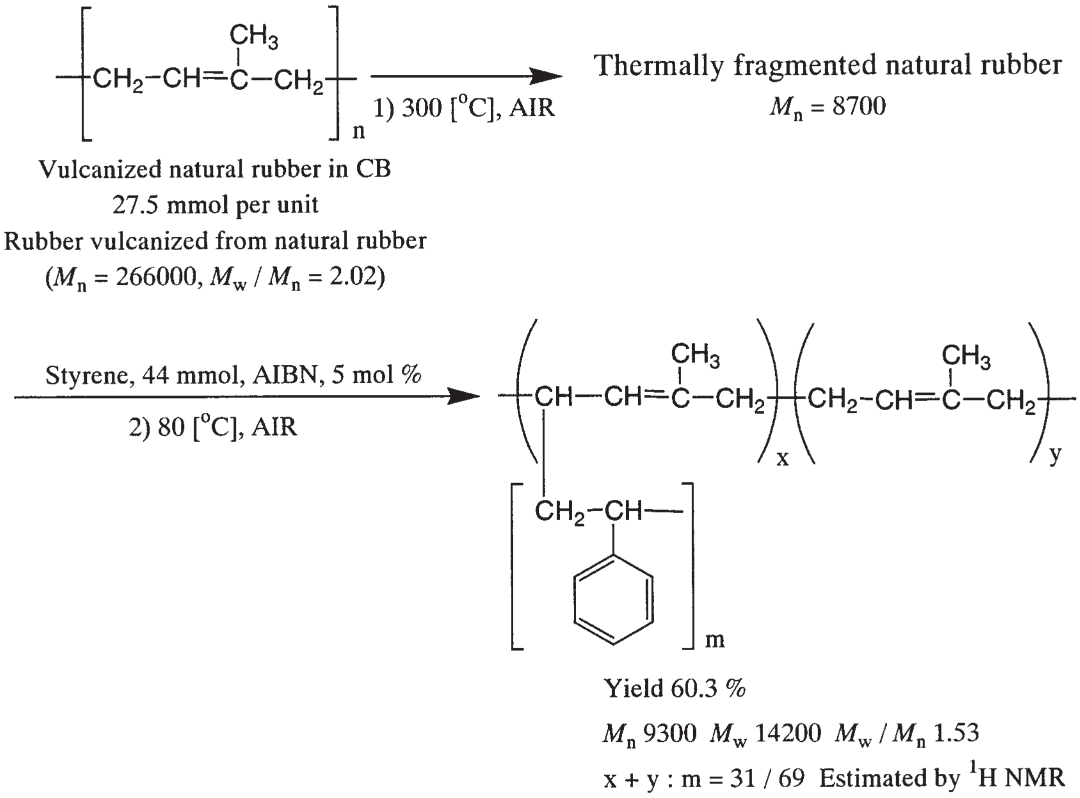
Vinyl acetate. A colorless viscous copolymer. Yield, 59.8% (methanol soluble part); copolymer composition ([isoprene unit]/[vinyl acetate unit]), 25/75; ^1H-NMR ($CDCl_3$): δ/ppm 5.16–5.08 (1H, $=CH-$), 4.89–4.81 (1H, $-CHO-$), 2.10–2.01 (3H, $C(=O)-CH_3$), 2.01–1.95 (4H, $-CH_2-C(-CH_3)=CH-CH_2-$), 1.89–1.71 (2H, $-CH_2-$), 1.69–1.66 (3H, $-CH_2-C(-CH_3)=CH-$). IR (KBr): wavenumber/cm^{-1} 2961 ($-CH_3$, $-CH_2-$, $C-H$), 1740 ($C=O$), 1665, 1601, 1492, 1451, 1375, 1246 (CH_3COO), 1083.

N,N-*Dimethyl acrylamide.* White powdery copolymer. Yield, 65.7% (methanol soluble part); copolymer composition ([isoprene unit]/[*N*,*N*-dimethyl acrylamide unit]), 33/67; ^1H-NMR ($CDCl_3$): δ/p.p.m. 5.17–5.08 (1H, $=CH-$), 3.01–2.83 (6H, $-N(CH_3)_2$), 2.10–1.97 (4H, $-CH_2-C(-CH_3)=CH-CH_2-$), 1.96–1.86 (1H, $-CH-$), 1.71–1.64 (3H, $-CH_2-C(-CH_3)=CH-$), 1.63–1.56 (2H, $-CH_2-$). IR (KBr): wavenumber/cm^{-1} 3478, 2930 ($-CH_3$, $-CH_2-$, $-N(Me)_2$), 1632, 1503, 1402, 1357, 1256, 1144, 1097, 1056.

RESULTS AND DISCUSSION

Thermally fragmented behavior of vulcanized natural rubber

Because the vulcanized natural rubber and that with carbon black were insoluble in organic solvents, their solubilization may need from recycle point of view, for example, transformation to lower molecular weight polymers. Vulcanized natural rubber is obtained by vulcanization of natural rubber (M_n = 266,000, M_w/M_n = 2.02). Transformation of vulcanized natural rubber, that with carbon black, and synthetic polyisoprene into low molecular weight polymers were carried out by following procedure: the vulcanized natural rubber cut into small pieces was heated at 300°C, under either air atmosphere or nitrogen atmosphere for 15 min (Scheme 1). As a result, thermally fragmented polymers were obtained more efficiently under air than under nitrogen atmosphere, as shown in Table I. The low yields in the thermal fragmentation of vulcanized natural rubber with car-



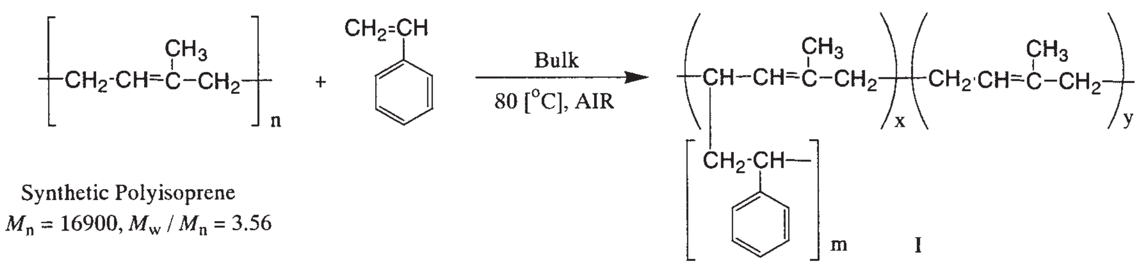
Scheme 3 Grafted copolymerization of styrene onto thermally fragmented natural rubber from vulcanized natural rubber with carbon black.

bon black may have originated from absorption of rubber onto celite during filtration to remove carbon black. The obtained low molecular weight natural rubber and polyisoprene were soluble in organic solvents, such as hexane, toluene, THF, chloroform, and monochlorobenzene.

Effect of radical initiators on grafting of styrene onto polyisoprene

Bulk copolymerization of vinyl monomers with synthetic polyisoprene was achieved in the presence of 2,2′-azobis(isobutyronitrile)(AIBN), benzoylperoxide (BPO), *t*-butyl hydroperoxide (BHP), and cumene hydroperoxide (CHP) as radical initiators in bulk at 80°C for 2 h. Since polyisoprene is easily oxidized at high temperature (e.g., 140°C) under air atmosphere, we examined the copolymerization at 80°C. The synthetic polyisoprene with grafted polystyrene was purified by precipitation of THF solution of the resulting products into methanol. The results are summarized in Table II. But since BHP and CHP are used at high temperature, they may not be desirable for use in this research.

When graft copolymerization of styrene with synthetic polyisoprene was carried out in the presence of BPO under nitrogen atmosphere, the grafted copolymer was obtained as networked polymer, which accordingly are employed AIBN as a radial initiator in the following experiments.



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Scheme 4 Grafted copolymerization of styrene onto synthetic polyisoprene.

TABLE V
Thermal Copolymerization of Synthetic Polyisoprene and Styrene

Run	Charge ratio (mol %) [isoprene]/[styrene]	Time (h)	Yield[a] (%)	[isoprene]/[styrene] $(x + y)/m$[b] (mol %)	M_n (M_w/M_n)[c]
1	25/75	24	63.9	37/63	7,700 (1.49)
2	33/67	24	68.3	54/46	31,000 (1.93)
3	50/50	36	68.9	56/44	15,800 (3.13)
4	67/33	72	70.2	79/21	26,900 (2.95)
5	75/25	96	60.1	90/10	13,000 (3.15)

[a] Isolated yield after precipitation into methanol.
[b] Estimated by ^{1}H NMR spectroscopy.
[c] Estimated by GPC based on polystyrene standards; eluent, THF.

Graft copolymerization of styrene onto thermally fragmented natural rubber

On the basis of the aforementioned results, we carried out graft copolymerization of styrene onto thermally fragmented natural rubber with lower molecular weight (Scheme 2). The grafted copolymerization of styrene onto the thermally fragmented natural rubber was carried out under air atmosphere to give the corresponding grafted copolymer (Table III). Higher amounts of AIBN were effective to obtain polymers with higher styrene contents in high yield. GPC analysis of the obtained polymers showed unimodal peaks with increased molecular weight, suggesting formation of graft copolymers. The obtained thermally fragmented natural rubber with grafted polystyrene was soluble in organic solvents, such as toluene, THF, and chloroform.

Soxhlet's extraction of thermally fragmented natural rubber with grafted polystyrene was accomplished sequentially with acetone to remove polystyrene, for 24 h (Table III, Run 3). Although natural rubber is insoluble in acetone to a lesser extent, acetone soluble part contained polyisoprene unit ([isoprene]/[styrene] = 15/85, Table IV). There results may suggest the formation of grafted copolymers with styrene-rich composition and polystyrene homopolymer. The acetone insoluble part was soluble in chloroform, and that contained almost 54/46*M* content of polyisoprene and polystyrene moieties.

Natural rubber-monitored grafted polystyrene could also be obtained from vulcanized natural rubber containing carbon black that could be easily removed by simple precipitation procedure. Efficient carbon black removal was easily confirmed by the color of the polymers (Scheme 3).

Thermal polymerization

Grafted copolymerization of styrene onto synthetic polyisoprene was carried out at 80°C in a flask under

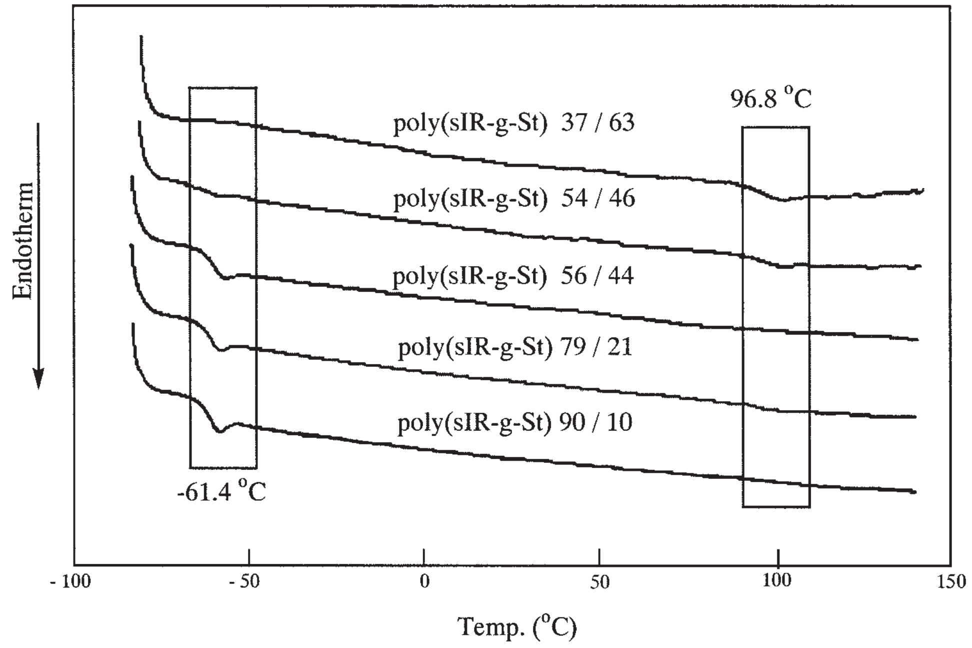


Figure 1 DSC curves of styrene onto synthetic polyisoprene grafted copolymer.

TABLE VI
Radical Copolymerization of Synthetic Polyisoprene and Styrene under Air Atmosphere or N_2 Atmosphere

Atmosphere	Yield[a] (%)	[isoprene]/[styrene] $(x + y)/m^b$ (mol %)	M_n $(M_w/M_n)^c$	GPC curve[c]
Air	93.9	45/55	11,000 (2.69)	Unimodal
N_2	72.3	57/43	9,300 (4.07)	Bimodal

Synthetic polyisoprene; $M_n = 16{,}900$; $M_w/M_n = 3.56$.
[a] Isolated yield after precipitation into methanol.
[b] Estimated by ^{1}H NMR spectroscopy.
[c] Estimated by GPC based on polystyrene standards; eluent, THF.

air atmosphere (Scheme 4) to obtain a powdery polymer in every case, by precipitation with methanol, in good yield as summarized in Table V. The composition of the copolymers was evaluated by ^{1}H-NMR spectra. All the polymerizations under examined feed ratios gave the corresponding copolymers (I) with synthetic polyisoprene as a trunk polymer and polystyrene chain as a grafted polymer. All polymers showed a unimodal peak on their GPC analysis.

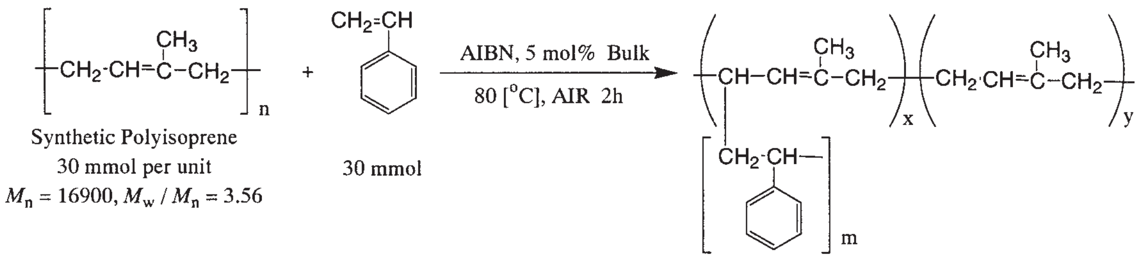
Phase transition of the synthetic polyisoprenes with grafted polystyrene was examined by differential scanning calorimetry (DSC). Figure 1 shows the DSC curves of the grafted synthetic polyisoprene and mixture of polyisoprene and polystyrene. The DSC thermograms of copolymers with polyisoprene-rich composition showed T_g's originated from polyisoprene backbone at approximately −61°C, whereas those of copolymers with polystyrene-rich composition showed T_g's originated from polystyrene grafted chain at approximately 97°C.

Copolymerization under air or N_2 atmosphere

Grafted copolymerization of styrene onto synthetic polyisoprene was carried out at 80°C in a flask under air atmosphere or N_2 atmosphere. Powdery polymers in both cases were obtained by the precipitation of THF solution of the resulting products into methanol in good yields (Table VI). GPC analysis of these polymers showed a unimodal elution peak for the polymer obtained under air atmosphere and a bimodal elution peak for the polymer obtained under N_2 atmosphere. The product obtained under N_2 was precipitated with hexane, when the soluble part was polyisoprene homopolymer, which was confirmed by ^{1}H-NMR spectra. Because ^{1}H-NMR analysis revealed that the hexane soluble part contained polyisoprene structure, the obtained product under air atmosphere consisted of graft copolymer and polyisoprene homopolymer.

Grafted copolymerization of various vinyl monomers onto synthetic polyisoprene

To clarify the grafted copolymerization behavior, synthetic polyisoprene was subjected to grafted copolymerization with various vinyl monomers. Styrene, MMA, methyl acrylate, vinyl acetate, and *N,N*-dimethyl acrylamide were used as comonomers. Grafted copolymerization was carried out at 80°C in bulk under air for 2 h using AIBN as an initiator (Scheme 5). The resulting grafted copolymers were characterized by ^{1}H-NMR spectroscopy, GPC measurements, and TGA (Table VII). Grafted copolymers of various monomers with polyisoprene were successfully synthesized, and their copolymer composition was dependent upon the comonomers. As shown in Table VII, polymerizations producing methanol insoluble part as main products were those using styrene, MMA, methyl acrylate, while other polymerizations produced methanol soluble polymers as their corresponding main products. This tendency depended upon the solubility of the homopolymers. The copolymerization of styrene with polyisoprene graft copolymer gave highest yield.



Scheme 5 Grafted copolymerization of various vinyl monomers onto synthetic polyisoprene.

TABLE VII
Graft Copolymerization of Various Vinyl Monomers onto Synthetic Polyisoprene

Materials	Yield[a] (%)	[isoprene]/[styrene] $(x + y)/m$[b] (mol %)	M_n (M_w/M_n)[c]	T_{d10}[d]
Methanol soluble part				
sIR/styrene	5.9	86/14	200 (4.14)	145
sIR/MMA	34.8	19/81	4100 (1.46)	190
sIR/methyl acrylate	40.8	16/84	10000 (2.01)	143
sIR/vinyl acetate	59.8	25/75	6000 (2.24)	170
sIR/*N*,*N*-dimethylacrylamide	65.7	33/67	18400 (2.00)	230
Methanol insoluble part				
sIR/styrene	93.9	45/55	11000 (2.69)	353
sIR/MMA	64.7	79/21	12400 (3.20)	133
sIR/methyl acrylate	57.3	61/39	3900 (2.19)	343
sIR/vinyl acetate	38.9	85/15	1900 (1.20)	332
sIR/*N*,*N*-dimethylacrylamide	22.5	71/29	10000 (2.07)	155

Synthetic polyisoprene; $M_n = 16{,}900$; $M_w/M_n = 3.56$.
[a] Isolated yield after precipitation into methanol.
[b] Estimated by ^{1}H NMR spectroscopy.
[c] Estimated by GPC based on polystyrene standards; eluent, THF.
[d] Determined by TGA, under N_2 atmosphere.

TGA revealed that copolymers from styrene and methyl acrylate have high heat resistance than the homopolymers.

Summary

Thermal fragmentation of vulcanized natural rubber was accomplished by heating at 300°C under air or nitrogen atmosphere. The thermally fragmented natural rubber and polyisoprene could be transformed into natural rubber-based grafted copolymers by copolymerization with various vinyl monomers. Further, thermally fragmented natural rubber with grafted polystyrene was also obtained from vulcanized natural rubber with carbon black in a simple procedure.

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