Well-Defined Polyisoprene-Grafted Silica Nanoparticles via the RAFT Process

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ABSTRACT: The preparation of well-defined polyisoprene-grafted silica nanoparticles (PIP-g-SiO$_2$ NPs) was investigated. Surface initiated reversible addition fragmentation chain transfer (SI-RAFT) polymerization was used to polymerize isoprene from the surface of 15 nm silica NPs. A high temperature stable trithiocarbonate RAFT agent was anchored onto the surface of particles with controllable graft densities. The polymerization of isoprene mediated by silica anchored RAFT with different densities were investigated and compared to the polymerization mediated by free RAFT agents. The effects of different temperatures, initiators, and monomer feed ratios on the kinetics of the SI-RAFT polymerization were also investigated. Using this technique, block copolymers of polyisoprene and polystyrene on the surface of silica particles were also prepared. The well-defined synthesized PIP-g-SiO$_2$ NPs were then mixed with a polyisoprene matrix which showed a good level of dispersion throughout the matrix. These tunable grafted particles have potential applications in the field of rubber nanocomposites. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *55*, 1493–1501

KEYWORDS: nanocomposites; nanoparticles; polyisoprene; reversible addition fragmentation chain transfer (RAFT)

INTRODUCTION Polymer-grafted nanoparticles are of great interest due to their applications in sensors, coatings, optoelectronics, and bioapplications.[1–4] RAFT polymerization has proven to be a powerful controlled radical polymerization technique for preparation of polymer-grafted particles due to the easy attachment and precise control over the grafting densities of RAFT agents. Since the first report on the application of SI-RAFT polymerization for the modification of silica particles using a surface-anchored RAFT agent by Tsujii et al.,[5] this technique has been widely utilized for the surface modification of various nanoparticles with a wide range of polymers.[6–15]

Polyisoprene and its copolymers have been recognized as an important class of rubber materials and are extensively used in the automotive and medical device industries.[16–19] Polyisoprene contains many double bonds in the polymer backbone which allows for further functionalization or chemical modifications. Isoprene-based polymers have been prepared by coordination, anionic,[20,21] cationic,[22,23] and radical polymerizations,[24,25] among which anionic polymerization has been the major method for the synthesis of such polymers. Anionic polymerization provides excellent control of the polymerization and produces polymers with predictable molecular weights and narrow polydispersities, however, it is expensive and not compatible with electrophilic and acidic functional groups and is challenging in the presence of contaminants.[26,27]

Surface polymerization of isoprene has been reported by living anionic polymerization from the surface of silica particles. Kir and Binder[28] applied anionic polymerization on the surface of silica nanoparticles. They modified the surface of particles with a diphenylethylene silane agent that served as the initiating site for the anionic polymerization of isoprene.

There have been significant reports on controlled radical polymerization (CRP) of isoprene by RAFT and nitroxide-mediated polymerization (NMP). Jitchum and Perrier[29] and Germack and Wooley[30] have reported RAFT polymerization of isoprene in bulk using high temperature stable trithiocarbonate RAFT agents. However, to the best of our knowledge, surface polymerization of isoprene has not been investigated by any of these CRP techniques. Herein, the SI-RAFT polymerization of isoprene on silica nanoparticle surfaces was investigated. The kinetics of isoprene surface graft polymerization mediated by RAFT agent anchored onto silica nanoparticles at different conditions was investigated and

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compared with the RAFT polymerization kinetics mediated by free RAFT agents. Homopolymer and block copolymers were also prepared and characterized. Well-defined PIP-*g*-SiO$_2$ NPs were then mixed with a polyisoprene matrix and the resulting composite was characterized.

EXPERIMENTAL

Materials

Isoprene was obtained from TCI America and was purified by passage over a neutral alumina prior to use. The RAFT agent 2-(((dodecylthio)carbonothioyl)thio)propanoic acid (DoPAT) (97%) was generously donated by Boron Molecular. Spherical SiO$_2$ nanoparticles with a diameter of 15 ± 4 nm were purchased from Nissan Chemical Co. Tetrahydrofuran (THF) (HPLC grade, Fisher), dicumyl peroxide (DCP) (Acros, 99%), di-*tert*-butyl peroxide (dTBP) (Acros, 99%), azobisisobutyronitrile (AIBN) (Acros, 98%), dicyclohexylcarbodiimide (Acros, 99%), 4-(dimethylamino)pyridine (Acros, 99%), 2-mercaptothiazoline (Acros, 98%), and 3-aminopropyldimethylethoxysilane (Gelest, 95%) were used as received.

Polymerization of Isoprene Mediated by Free DoPAT

In a typical polymerization, isoprene (2g, 30 mmol), DoPAT (35 mg, 0.1 mmol), dicumyl peroxide (2.7 mg, 0.01mol), and THF (2.8 mL) with a ratio between species of [monomer]:[CTA]:[initiator] = 300:1:0.1 were added to a Schlenk tube. The mixture was degassed by three freeze-pump-thaw cycles, filled with nitrogen, and then the Schlenk tube was placed in a 115 °C oil bath. The polymerization was stopped by quenching in ice water. Molecular weights were measured using gel permeation chromatography (GPC) in THF which was calibrated with polystyrene standards.

Preparation of DoPAT-Functionalized Silica Nanoparticles

A solution (20 mL) of colloidal silica particles (30 wt % in methyl isobutyl ketone) was added to a two-necked round bottom flask and diluted with 35 mL of THF. Dimethylmethoxy-*n*-octylsilane (0.1 mL) was added to improve dispersibility along with 3-aminopropyldimethylethoxysilane (0.7 mL, 5 mmol) and the mixture was refluxed for 5 h under nitrogen protection. The reaction was then cooled to room temperature and precipitated in a large amount of hexanes (300 mL). The particles were then recovered by centrifugation and dispersed in THF using sonication, then precipitated in hexanes again. The amine-functionalized particles were then dispersed in 40 mL of THF for further reaction. Then 2.5 g (5.5 mmol) of activated DoPAT was prepared similarly to a procedure described previously[9] and added dropwise to a THF solution of the amine-functionalized silica nanoparticles (40 mL, 6 g) at room temperature. After complete addition, the solution was stirred overnight. The reaction mixture was then precipitated into a large amount of methanol (400 mL). The particles were recovered by centrifugation at 3000 rpm for 5 min. The particles were then redispersed in 30 mL THF and precipitated in methanol. This dissolution–precipitation procedure was repeated two more times until the supernatant layer after

centrifugation was colorless. The yellow DoPAT-functionalized silica nanoparticles were dried at room temperature and analyzed using UV-Vis spectroscopy to determine the chain density using a calibration curve constructed from standard solutions of free DoPAT. The RAFT agent density of the particles was calculated to be 100 μmol/g of grafted NPs (0.42 chains/nm^2).

RAFT Polymerization of Isoprene from DoPAT-Functionalized Silica Nanoparticles

In a typical polymerization, isoprene (1.42 g, 21 mmol), DoPAT-*g*-silica NPs with surface density of 0.10 mmol/g (0.7g, 70 μmol), THF (2.2 mL), and dicumyl peroxide initiator (7.0 μmol) with a ratio between species of [monomer]:[CTA]:[initiator] = 300:1:0.1 were added to a Schlenk tube. The particles were dispersed into the solution via sonication for 1 min and subsequently the mixture was degassed by three freeze-pump-thaw cycles, filled with nitrogen, and then the Schlenk tube was placed in an oil bath for the desired time and temperature. The polymerization was stopped by quenching in ice water. NMR spectroscopy was used to determine conversion of monomer comparing the monomer peak with the ones of internal standard (anisole). The resultant polymer grafted particles were then precipitated into a large amount of methanol and centrifuged at 8000 rpm for 5 min and the particles were dispersed back into THF.

### Preparation of Poly(Isoprene-*b*-Styrene)-Grafted Silica NPs

To make block copolymer-grafted particles, the surface polymerization of isoprene on 0.23 g of DoPAT-*g*-silica NPs with graft density of 79 μmol/g was performed similar to that described in the previous section. The resulting PIP-*g*-SiO$_2$ NPs were dissolved in 5 mL of THF and excess amount of styrene and AIBN (0.94 μmol) were added to a Schlenk tube. The mixture was degassed by three freeze-pump-thaw cycles, filled with nitrogen, and then the Schlenk tube was placed in a 65 °C oil bath for 8 h. The polymerization was stopped by quenching in ice water. The resultant polymer grafted particles were precipitated into a large amount of isopropanol and centrifuged at 5000 rpm for 8 min and the particles were dispersed back into 5 mL of THF. The precipitation and centrifugation steps were repeated one more time to obtain the block copolymer anchored particles.

General Procedures for Cleaving Grafted Polymer from Particles

In a typical experiment, 50 mg of polyisoprene-grafted silica particles were dissolved in 4 mL of THF. Aqueous HF (49%, 0.2 mL) was added, and the solution was allowed to stir at room temperature overnight. The solution was poured into a PTFE Petri dish and allowed to stand in a fume hood overnight to evaporate the volatiles. The recovered polymer was then dissolved in THF and analyzed by GPC.

Preparation of Polyisoprene Nanocomposite Filled with PIP-*g*-SiO$_2$ NPs

A PIP-*g*-SiO$_2$ NPs sample (M_n = 26 Kg/mol, Đ = 1.5) in THF was mixed with a solution of free polyisoprene (M_n = 77 Kg/
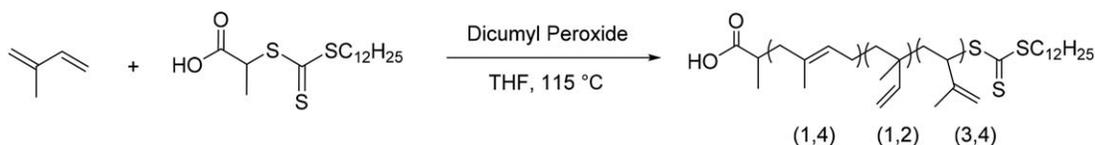
SCHEME 1 Polymerization of isoprene mediated by free DoPAT RAFT agent.

mol, $Đ = 1.4$) in THF in appropriate quantities at room temperature. The solution was stirred for 10 min and was cast in a Petri dish and dried in vacuum for 24 h. The final film was used for further characterizations.

Instrumentation

NMR spectra of products were recorded on a Varian 300 spectrometer using $CDCl_3$ as a solvent and anisole as internal standard. Molecular weights and dispersity ($Đ$) were measured using a Polymer Labs PL-GPC-120 gel permeation chromatograph (GPC) associated with a 515 HPLC pump, a 2410 refractive index detector, and three Styragel columns. The columns consisted of HR1, HR3 and HR4 which have corresponding effective molecular weight ranges of 100 to 5000, 500 to 30,000, and 5000 to 500,000, respectively. The GPC used tetrahydrofuran (THF) as eluent at 30 °C and a flow rate of 1.0 mL/min with the calibration of polystyrene standards obtained from Polymer Laboratories. TGA characterization was operated using a TA Instruments Q5000 with a heating rate of 10 °C/min form 25 °C to 1000 °C under nitrogen flow. Transmission electron microscopy (TEM) images were obtain using a Hitachi H8000 TEM operating at an accelerating voltage of 200 kV. The composite sample was cryomicrotomed at −120 °C into 100 to 150 nm slices using a diamond knife.

RESULTS AND DISCUSSION

Polymerization of Isoprene Mediated by Free DoPAT
Before performing the RAFT polymerization of isoprene on the surface of NPs, detailed studies on the polymerization of isoprene mediated by free RAFT agents were conducted. Previous studies of the polymerization of isoprene by the RAFT

technique indicated that selecting a suitable RAFT agent is necessary for successful control. Jitchum and Perrier[29] compared the use of two types of RAFT agents in the polymerization of isoprene, a dithiobenzoate derivative 4-cyanopentanoic acid dithiobenzoate (CPDB) and a trithiocarbonate derivative 2-ethylsulfanylthiocarbonyl sulfanylpropionic acid ethyl ester (ETSPE) at 60 and 120 °C. At 60 °C both RAFT agents produced low monomer conversions and polymers with broad polydispersities. Upon increasing the temperature to 120 °C, degradation of CPDB was observed leading to an uncontrolled polymerization. However, ETSPE mediated polymerizations showed a continuous growth of polymer chains without any loss of RAFT agent suggesting that a high temperature stable RAFT agent is needed for this reaction. Herein, in this study, we employ 2-((dodecylthio)-carbonothioyl)thio)propanoic acid (DoPAT), a high temperature stable RAFT agent.

Scheme 1 shows the synthetic procedure of the RAFT polymerization of isoprene mediated by free DoPAT in solution. The polymerization was performed with the feed ratio of [monomer]/[CTA]/[initiator] = 300:1:0.1 at 115 °C under inert gas conditions. The kinetic results for the solution RAFT polymerization of isoprene are shown in Figure 1 (GPC data shown in Fig. 2). A linear relationship between monomer consumption and time over the conversion range studied implies a constant radical concentration throughout the polymerization. The controlled nature of the polymerization was demonstrated by the linear increase of M_n with respect to monomer conversion. Molecular weights were in general agreement with theoretical molecular weights, and molecular weight distributions were generally narrow (~1.2) These results were in agreement with previous studies
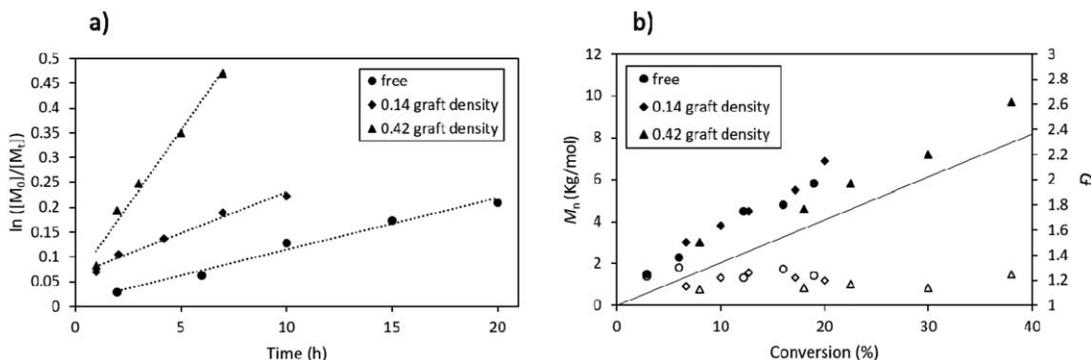

FIGURE 1 (a) First-order kinetic plots and (b) dependence of molecular weight (solid line, $M_{n, \text{theory}}$) on the conversion for the SI-RAFT polymerization of isoprene on silica nanoparticles; high surface density (triangle, 100 μmol/g, 0.42 ch/nm²); low surface density (diamond, 32 μmol/g, 0.14 ch/nm²); free DoPAT, (circle). All polymerizations were conducted under identical conditions with the ratio of [monomer]:[CTA]:[initiator] = 300:1:0.1.
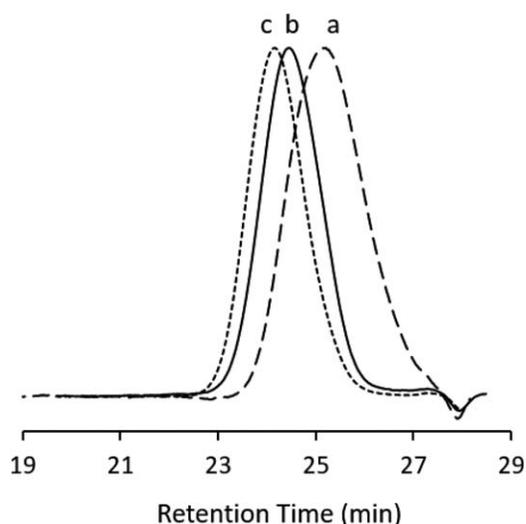
FIGURE 2 GPC traces of polyisoprene prepared from RAFT polymerization mediated by free DoPAT in THF for (a) 6% conversion, $M_n = 2500$; (b) 12.2% conversion, $M_n = 4500$; (c) 19% conversion, $M_n = 5800$; [monomer]:[CTA]:[initiator] = 300:1:0.1.

reported by Jitchum and Perrier[29] and Germack and Wooley[30] and confirmed that the trithiocarbonate RAFT agent selected for the current studies was suitable for high temperature RAFT polymerizations.
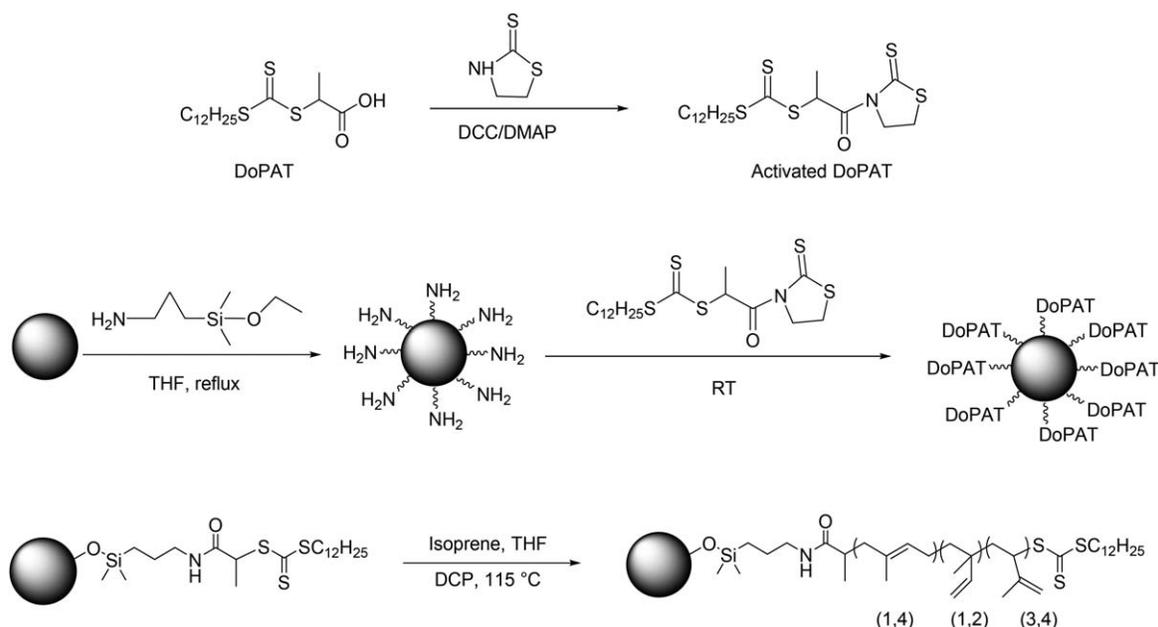
RAFT Polymerization of Isoprene from DoPAT-Functionalized Silica Nanoparticles

To perform the polymerization of isoprene onto the surface of particles, modification of the surface was required. Attachment of DoPAT chain transfer agent was carried out in two steps according to the literature. Following the attachment of aminosilane molecules onto the particles' surface, the amino-

functionalized silica particles were reacted with activated DoPAT to give DoPAT-grafted SiO$_2$ NPs (DoPAT-g-SiO$_2$) (Scheme 2). The attachment of DoPAT onto silica nanoparticles was confirmed by UV-Vis spectrometry. The amount of RAFT agent anchored onto the modified silica nanoparticles was determined quantitatively by comparing the absorption at about 300 nm for the DoPAT anchored silica nanoparticles to a standard absorption curve made from known amounts of the free DoPAT. Using this method DoPAT-g-SiO$_2$ NPs with densities of 100 μmol/g (0.42 chains/nm^2) and 32 μmol/gr (0.14 chains/nm^2) were synthesized and used to study the SI-RAFT polymerization of isoprene.

To perform the surface polymerization of isoprene, DoPAT-g-SiO$_2$ particles need to be dispersed in a solvent medium that should be polar enough to disperse silica particles and yet able to dissolve nonpolar polyisoprene chains. In this work, tetrahydrofuran (THF) was used as a suitable solvent for the dispersion of silica particles combined with excess monomer as a solvent for the polyisoprene chains. It was found that when the THF to monomer ratio (v/v) was smaller than 1, partial gelation of the polymerization occurred. This gelation could be due to the inter-particle polymeric radical coupling which normally occurs at high concentration of particles.[31] Therefore, a solvent to monomer ratio of 1 was maintained in all polymerizations.

The molar ratio of [initiator]/[CTA] was set to 0.1. This ratio is low enough to minimize termination by surface anchored polymeric radical recombination and also helped minimize the amount of free polymer derived from the initiator and yet maintains a moderate polymerization rate.[5,6,9] When a reaction was conducted with a higher ratio of initiator ([initiator]/[CTA] = 0.3), partial gelation of the polymerization solution was observed after 4 h and complete gelation was

SCHEME 2 Preparation of PIP-g-SiO$_2$ NPs.

TABLE 1 Data for the SI-RAFT Polymerization of Isoprene on DoPAT-*g*-SiO$_2$ NPs (0.42 ch/nm^2) Using Different Initiators at Various Temperatures and Conditions

Sample No.	Initiator	[M]:[CTA]:[I]	Temp. (°C)	Reaction Time (h)	Conversion (%)	M_n (kg/mol)	Đ
1	AIBN	300:1:0.1	75	7	8	2.7	1.1
2	AIBN	300:1:0.1	75	23	23	4.9	1.09
3	DCP	300:1:0.1	95	7	15	4.6	1.17
4	DCP	300:1:0.1	115	7	38	9.7	1.25
5	DCP	300:1:0.3	115	7		Gelation	
6	DCP	10,000:1:0.1	115	24	–	44	1.4
7	dTBP	300:1:0.1	135	7	27	8.1	1.17
8	dTBP	2,000:1:0.1	135	8	–	27	1.45

observed after 7 h (Sample 5 in Table 1). This experiment showed that a low ratio of [initiator]/[CTA] is essential for controlling the graft polymerization of isoprene.

The SI-RAFT polymerizations of isoprene were studied at two different RAFT agent densities of 100 μmol/gr (0.42 chains/nm^2) and 32 μmol/gr (0.14 chains/nm^2) to investigate the effect of grafting densities on the polymerization and were compared with the polymerization mediated by free DoPAT. All reactions were conducted under identical conditions using dicumyl peroxide as the initiator at 115 °C and with the ratio between species of [monomer]:[CTA]:[initiator] = 300:1:0.1. The polymerizations were conducted at low conversion range to avoid possible gelation or interparticle radical coupling.[31] The results of the kinetic studies for the SI-RAFT polymerization of isoprene mediated by surface anchored RAFT agents (two graft densities) and free RAFT agent are shown in Figure 1. The graphs show a linear relationship between monomer consumption and time for all cases over the range of conversion studied, which indicates a constant free radical concentration during the polymerization. The results in Figure 1 also show that the molecular weight increased linearly with monomer conversion for all polymerizations, measured molecular weights were in general agreement with the theoretical molecular weights, and molecular weight distributions were generally narrow. However, the rates of the polymerizations mediated by surface anchored RAFT agents were apparently higher than the polymerization mediated by free RAFT agent under identical conditions. Also, in the case of anchored RAFT agent systems, the polymerization with higher DoPAT density proceeded at a higher rate compared to the system with lower DoPAT density. This trend is opposite that observed in the RAFT polymerization of styrene where the polymerization rate decreased at increasing RAFT agent density. In another comparison between the free and graft RAFT polymerization rates, isoprene behaved similar to styrene where free polymerization rates were lower than grafted polymerization rates but opposite that of methyl methacrylate.[9] From the limited data available in the literature at this time, it is still difficult to discern definitive trends in polymerization rates in these systems. Another difference between the grafted and free RAFT polymerization of isoprene was observed in the GPC results. A collection of GPC traces of polyisoprene prepared by free RAFT (Fig. 2) and grafted RAFT polymerization (after cleaving from the NPs) (Fig. 3) are shown. In previous works on the graft polymerization of styrene from nanoparticle surfaces using RAFT, considerable low molecular weight tailing and high molecular weight humps were observed due to the surface radical migration effect and termination by recombination.[5,6] In our work, no apparent high molecular weight hump is observed for the graft polymerization even at monomer conversions up to 38%. However, an apparent low molecular weight shoulder peak was observed at about 26 min elution time which is equivalent to 900 Da molecular weight. Our first hypothesis was that this low molecular peak could be due to the presence of the surfactants used in the manufacture of silica particles which were cleaved along with the grafted polymer chains from the particles. To evaluate the origin of this peak, the eluents were collected after passing through the GPC columns, separated, and analyzed by FTIR spectroscopy.
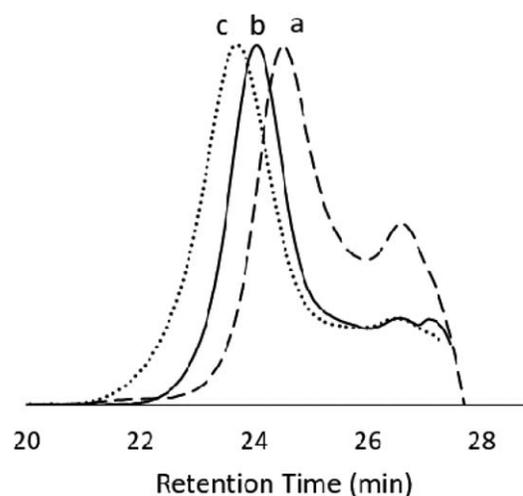

FIGURE 3 GPC traces of polyisoprene prepared from RAFT polymerization mediated by grafted RAFT agents in THF for (a) 18% conversion, M_n = 4600; (b) 30% conversion, M_n = 7200; (c) 38% conversion, M_n = 9700; [monomer]:[CTA]:[initiator] = 300:1:0.1.
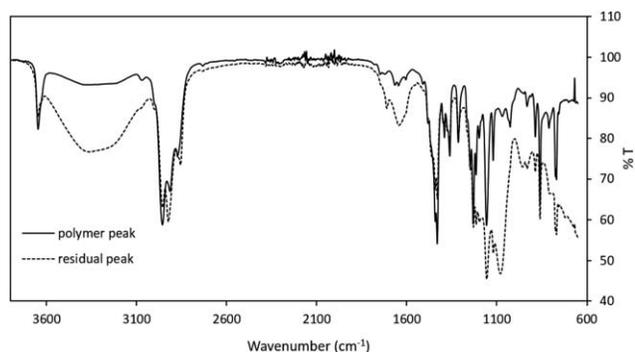
FIGURE 4 FTIR spectra of the collection of two different eluent peaks from the GPC of cleaved polyisoprene.

Figure 4 shows the FTIR spectra of the polymer and the residual peaks. The strong peaks at 1000 to 1150 cm^{-1} in the residual sample are ascribed to the Si—O—Si bonds probably from small molecules emanating from the etched particles after chain cleavage by HF. The broad peak at 3200 to 3600 cm^{-1} could also be ascribed to the OH moieties from the silica particles and/or surfactants present on particles. To further evaluate and ensure this hypothesis, a sample of bare silica particles was etched by HF with the same method for polymer chain cleavage explained earlier and analyzed by GPC. The GPC trace of this sample is shown in Figure 5 and compared with the cleaved polyisoprene and clearly shows a strong peak that matches the low molecular weight shoulder peak observed in the GPC of the cleaved polyisoprene sample. These results indicate that the shoulder peak could be ascribed mostly to the surfactants and stabilizers used in the manufacture of silica and small molecules produced from the silica particles during the polymer cleavage and not from the SI-RAFT process.

The SI-RAFT polymerization of isoprene was conducted at different temperatures using different initiators with ratios between species of [monomer]:[CTA]:[initiator] = 300:1:0.1 under identical conditions. We observed that polymerization at 75 °C using AIBN as the initiator after 7 h showed low
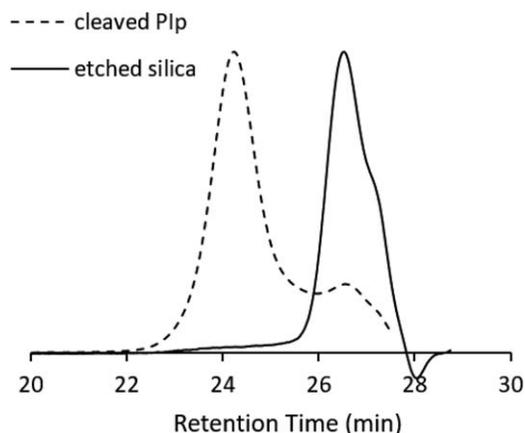

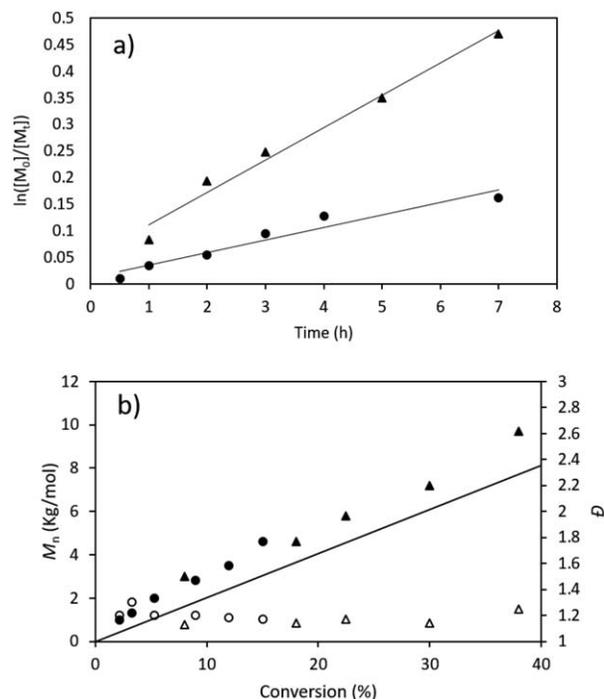**FIGURE 5** GPC traces of cleaved polyisoprene (dashed line) and etched silica (solid line).

FIGURE 6 (a) First-order kinetic plots and (b) dependence of molecular weight (solid line, $M_{n, theory}$) on conversion for the SI-RAFT polymerization of isoprene on DoPAT-g-SiO$_2$ NPs with RAFT agent density of 100 µmol/g, 0.42 ch/nm^2 at 95 °C (circle) and 115 °C (triangle) using dicumyl peroxide as initiator. All polymerizations were conducted under identical conditions with the ratio of [monomer]:[CTA]:[initiator] = 300:1:0.1.

conversion and molecular weight with dispersities as low as 1.10 and at longer times this reaction showed higher conversion and molecular weight (M_n = 4.9 Kg/mol) with low dispersity (Samples 1 and 2 in Table 1). When the polymerization was conducted at 95 °C with dicumyl peroxide as the initiator, the reaction proceeded to higher percent conversion without loss of control (Sample 3 in Table 1). These results are interesting when compared to the results of Jitchum and Perrier[29] and Germack and Wooley[30] for the bulk RAFT polymerization of isoprene at similar temperatures (76 and 90 °C) where they observed low conversions and molecular weights (1.5–2 kg/mol) at these temperatures even after much longer reaction times.

The investigation of the effects of reaction temperature on the graft polymerization was further conducted by choosing two temperatures, 95 and 115 °C using dicumyl peroxide as the initiator. The kinetic studies of the SI-RAFT polymerization of isoprene at different temperatures is shown in Figure 6. Both polymerizations showed a linear relationship between monomer consumption and time over the conversion range studied. Also a linear increase in molecular weight as a function of conversion was observed. However, at 115 °C conversion of 38% was reached within 7 h, while polymerization at 95 °C yielded only 15% conversion within the same time. Relatively low dispersities (Đ < 1.25) were maintained at both temperatures for all conversions
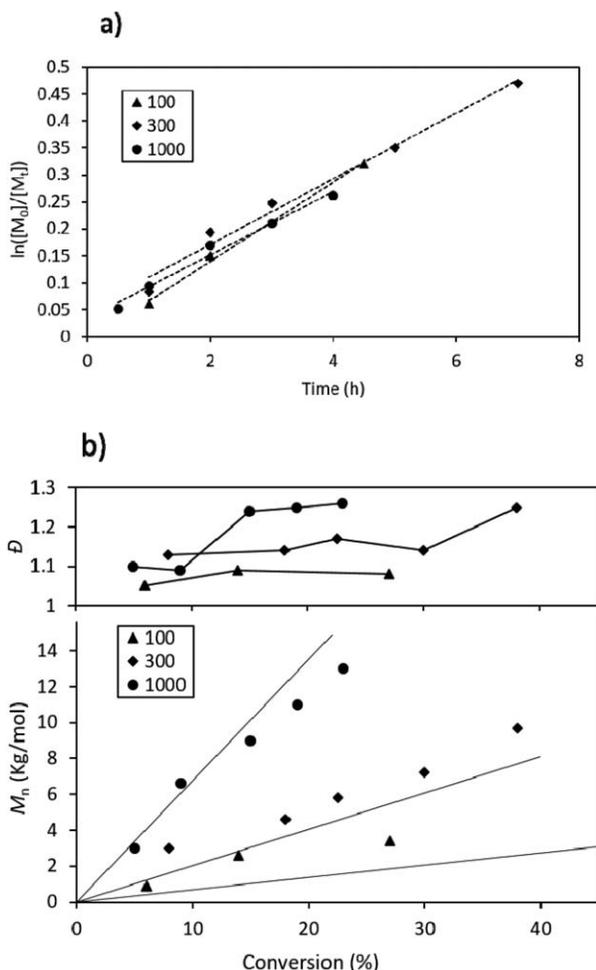
FIGURE 7 (a) First-order kinetic plots and (b) dependence of molecular weight (solid line, $M_{n, \text{theory}}$) on conversion for the SI-RAFT polymerization of isoprene on DoPAT-*g*-SiO$_2$ NPs with RAFT agent density of 100 μmol/g, 0.42 ch/nm^2 at 115 °C with the ratio of [monomer]:[CTA] of 100 (triangle), 300 (diamond), and 1000 (circle). All polymerizations were conducted at identical conditions with the ratio of [CTA]:[initiator] = 10.

investigated in this work. The graft polymerization of isoprene was also performed at 135 °C using di-*tert*-butyl peroxide as the initiator and resulted in PIP-*g*-SiO$_2$ NPs with similar low dispersity (Sample 7, Table 1). These results suggest that the SI-RAFT polymerization of isoprene can be performed at a wide range of temperatures with relatively good control over the molecular weight and dispersity. To test if this method is able to produce high molecular weight PIP-*g*-SiO$_2$, a polymerization reaction with high ratio of [monomer]:[CTA] = 2000:1 was conducted at 135 °C using di-*tert*-butyl peroxide as initiator (Sample 8, Table 1). PIP-*g*-SiO$_2$ with polymer molecular weight of 27 kg/mol and Đ of 1.45 was obtained. In another experiment, a polymerization reaction with [monomer]: [CTA] = 10,000:1 using dicumyl peroxide as initiator at 115 °C was performed for 24 h which resulted in PIP-*g*-SiO$_2$ with M_n = 44 Kg/mol and Đ = 1.4. Note that the molecular weight distribution for the RAFT polymerization of isoprene is generally higher than that of

styrenic and acrylic monomers and this could probably be due to the presence of double bonds in the polymer chains which could increase the chance of chain-chain couplings, particularly at higher temperatures and conversions.[30]

To investigate the effects of monomer loading on the SI-RAFT polymerization of isoprene, polymerizations with [monomer]:[CTA] of 100, 300, and 1000 were conducted at 115 °C. A ratio of [CTA]:[DCP] = 10 was kept for all polymerizations. Polymerizations were performed on the particles with the RAFT agent density of 100 μmol/gr (0.42 chains/nm^2) under identical reaction conditions. Note that the concentration of monomer remained the same since a volume ratio of monomer/solvent = 1 was maintained for all polymerizations. The results of the kinetic studies are shown in Figure 7 including previous data at 115 °C. All the polymerizations showed a linear relationship between the monomer consumption and time and relatively the same rate was observed in all polymerizations. All polymerizations were well controlled as the number-average molecular weights increased in a linear fashion with monomer conversion with relatively low molecular weight distributions (<1.25).

^{1}H NMR spectroscopy of PIP-*g*-SiO$_2$ NPs indicated the presence of products of three types of additions, 1,4-addition, 1,2-addition, and 3,4-additon as shown in Figure 8. The peak at ∼5.3 ppm is attributed to 1 H of –C*H*=C(CH$_3$)$_3$ from the 1,4-addition (both *cis* and *trans*), the broad peak at 5.7 to 5.9 ppm to 1 H of –C*H*=CH$_2$ from the 1,2-addition, the one at 4.7 to 4.9 ppm to 2 H of –C(CH$_3$)$_3$=C*H*$_2$ from the 3,4-addition, and the peak at 4.9 to 5.2 ppm to 2 H of –CH=C*H*$_2$ from the 1,2-addition. In a previous report on the bulk RAFT polymerization of isoprene by Jitchum and Perrier,[29] the product isomer ratios were 75% (1,4), 25% (1, 2 and 3, 4) isomers obtained from the ^{1}H NMR. However, in our study the major product was ∼88% 1, 4 isomer and the 1, 2 and 3, 4 isomers were together ∼12% of product which was independent of monomer conversion. RAFT polymerization

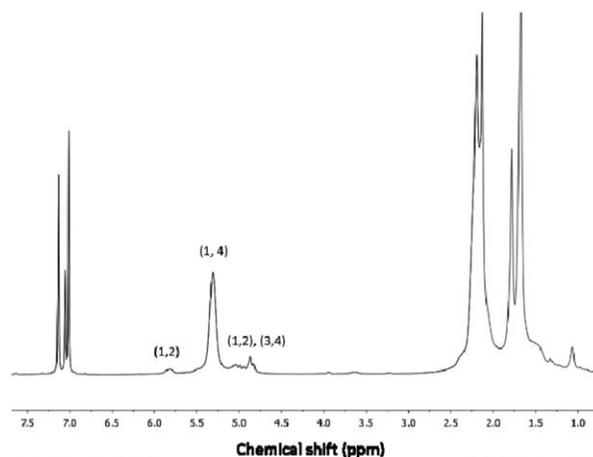**FIGURE 8** ^{1}H NMR spectrum of PIP-*g*-SiO$_2$ particles in CDCl$_3$ with indication of polyisoprene isomers prepared by SI-RAFT polymerization.
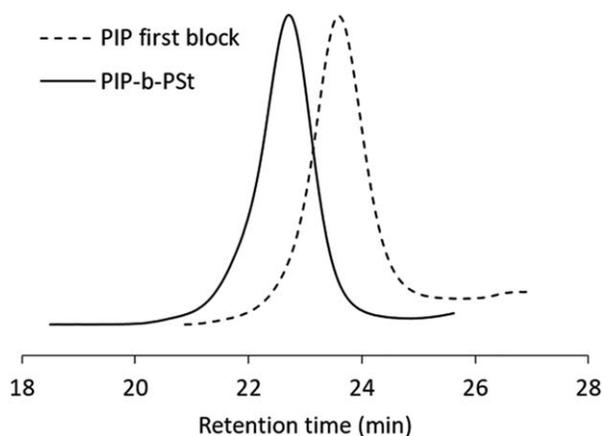
FIGURE 9 GPC traces of the cleaved polyisoprene and polyisoprene-*b*-polystyrene chains.

of isoprene mediated by free DoPAT gave the same ratio of isomers (Supporting Information Fig. S1).

Block Copolymerization

Chain extension reaction was carried out on PIP-*g*-SiO$_2$ NPs. To accomplish this, a recovered sample of PIP-*g*-SiO$_2$ (79 µmol/gr, $M_n = 9.4$ kg/mol, Đ = 1.14) was dissolved in THF and added to a Schlenk tube along with an excess of styrene with AIBN (0.1 equivalent relative to macro-chain transfer agent). Polymerization was conducted at 65 °C to afford a diblock copolymer of (PSt-*b*-PIP)-*g*-SiO$_2$ NPs ($M_n = 23.5$ kg/mol, Đ = 1.16). Figure 9 shows the shift of molecular weight distribution in GPC after addition of the second block demonstrating the chain extension polymerization. The formation of the block copolymer could be used as a qualitative indication of the livingness of the polymerization from the particle surface. The complete shift of the GPC trace and low polydispersity of the final block copolymer confirmed the living character and high efficiency of the polyisoprene macro-RAFT agents grafted onto silica nanoparticles. TGA analysis was also used to examine the formation of the homopolymer and block copolymer. Figure 10 shows the TGA analysis of the PIP-*g*-SiO$_2$ first block and the (PSt-*b*-PIP)-*g*-SiO$_2$ NPs. A
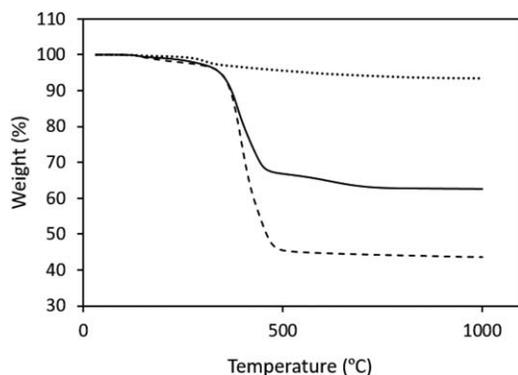

FIGURE 10 TGA analysis of the prepared DoPAT-*g*-SiO$_2$ (dotted line), PIP-*g*-SiO$_2$ (solid line), and (PSt-*b*-PIP)-*g*-SiO$_2$ NPs (dashed line).
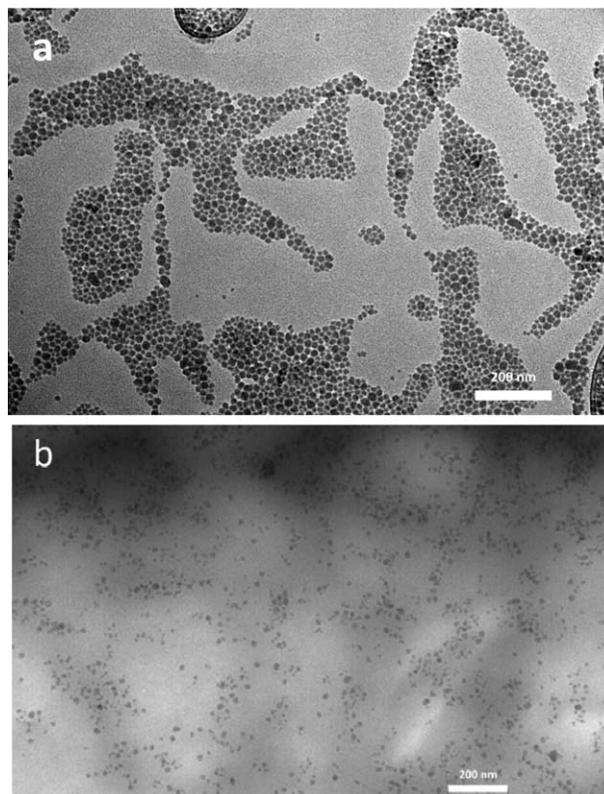

FIGURE 11 TEM micrographs of (a) as prepared PIP-*g*-SiO$_2$ NPs and (b) polyisoprene ($M_n = 62$ Kg/mol) nanocomposite filled with 4% loading of PIP-*g*-SiO$_2$ NPs ($M_n = 22$ kg/mol, Đ = 1.4) with chain density of 0.17 ch/nm^2 (scale bars are 200 nm).

weight gain was observed after addition of each block. Using this method, nanocomposites could be designed so that the outer block would be compatible with the matrix and the inner block could impart specific interphase properties.

Polyisoprene Nanocomposite Filled with PIP-*g*-SiO$_2$ NPs

The morphology of the grafted silica particles and the dispersion of these particles was examined using transmission electron microscopy (TEM). Figure 11(a) shows the TEM image of a thin layer of PIP-*g*-SiO$_2$ NPs prepared by casting a drop of dilute suspension of the grafted NPs in THF onto a copper grid and evaporating the solvent. To investigate the compatibility of the grafted particles with polyisoprene matrix, a sample of PIP-*g*-SiO$_2$ NPs ($M_n = 22$ kg/mol, Đ = 1.4) with a chain density of 0.17 ch/nm^2 was synthesized and mixed with polyisoprene matrix ($M_n = 62$ kg/mol, Đ = 1.4) through solution mixing and cast in a petri dish. After solvent evaporation, the nanocomposite was sectioned by a cryo-microtome and analyzed by TEM. The chain density of 0.17 ch/nm^2 corresponds to about 110 chains per particle. As shown in the TEM image in Figure 11(b) this density appears to be sufficient to screen the core-core interactions between silica particles leading to randomly dispersed particles throughout the matrix.

While our initial studies show that the PIP-*g*-SiO$_2$ NPs were miscible with polyisoprene matrices and have the potential to be used as fillers in the rubber industries, the investigation of the effect of these well-defined particles on different types of rubber nanocomposites is an interesting matter which shall be continued as the focus of our future work.

CONCLUSIONS

A facile method was demonstrated for the synthesis of polyisoprene grafted on silica NPs using a surface-initiated RAFT polymerization technique. A high temperature stable chain transfer agent (DoPAT) was anchored onto the surface of silica particles with controllable graft densities. Controlled radical polymerizations were conducted that produced polymers with low dispersities and predictable molecular weights, and it was found that the surface anchored DoPAT showed excellent control over the surface graft polymerization of isoprene. The kinetics of the isoprene surface polymerizations mediated by the DoPAT-grafted silica nanoparticles at two different surface densities were studied and compared with isoprene polymerization mediated by free DoPAT. Our experiments revealed that the SI-RAFT polymerization of isoprene from particles proceeded with higher rate when compared to polymerization mediated by free RAFT agent and also proceeded at higher rates as the surface density of the RAFT agent increased. The effects of polymerization temperature employing various initiators and also the effects of the [monomer]:[CTA] ratio on the polymerization kinetics were investigated. Chain extension polymerization was performed to produce block copolymer of (PSt-*b*-PIP)-grafted silica nanoparticles. ^{1}H NMR of the product confirmed the presence of ∼88% of 1,4-addition isomer along with ∼12% of 1, 2 and 3, 4 isomers. Well-defined PIP-*g*-SiO$_2$ NPs were mixed with a polyisoprene matrix to prepare a nanocomposite. The final nanocomposite was analyzed by TEM and revealed thorough dispersion and miscibility of silica nanoparticles throughout the polyisoprene matrix. We conclude that this method is an efficient technique for interfacial design of polyisoprene and isoprene copolymers on nanoparticle surfaces. These particles have potential applications in reinforced rubber nanocomposites where the dispersion and the compatibility of nanoparticles are crucial in achieving enhanced properties.

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