Hydrogenation of poly(myrcene) and poly(farnesene) using diimide reduction at ambient pressure

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Abstract

Ambient pressure chemical hydrogenation using *p*-toluene sulfonyl hydrazide (TSH) via thermal diimide formation (N_2H_2) permitted reduction of double bonds of poly(myrcene) (poly(Myr)) and poly(farnesene) (poly(Far)). Both pendent and backbone double bonds in poly(Myr) (M_n = 56 kg mol^{-1}) and poly(Far) (M_n = 62 kg mol^{-1}) synthesized by conventional free radical polymerization were hydrogenated to almost completion. Furthermore, TSH semi-batch addition efficiently hydrogenated double bonds, while avoiding undesired autohydrogenation of diimides that occurred in batch mode. Thermal stability improved for hydrogenated poly(Myr) and poly(Far), where temperature at 10% weight loss ($T_{10\%}$) increased from 188 °C to 404 °C for poly(Myr) and from 310 °C to 379 °C for poly(Far). T_gs of poly(Myr) and poly(Far) also increased by about 10-25 °C, indicating increased stiffness after hydrogenation. Lastly, viscosities of poly(Myr) and poly(Far) were also increased after hydrogenation, and a greater increase was observed for poly(Myr) (by two orders of magnitude from 10^2 to 10^4 Pa s) due to its M_n being much higher than its entanglement molecular weight. Poly(Far) viscosity only increased by 1.5 times after hydrogenation (~10^4

Pa s), comparable to the poly(Myr) after hydrogenation, suggesting unsaturated poly(Far) was more entangled than unsaturated poly(Myr) because of its longer side chains.

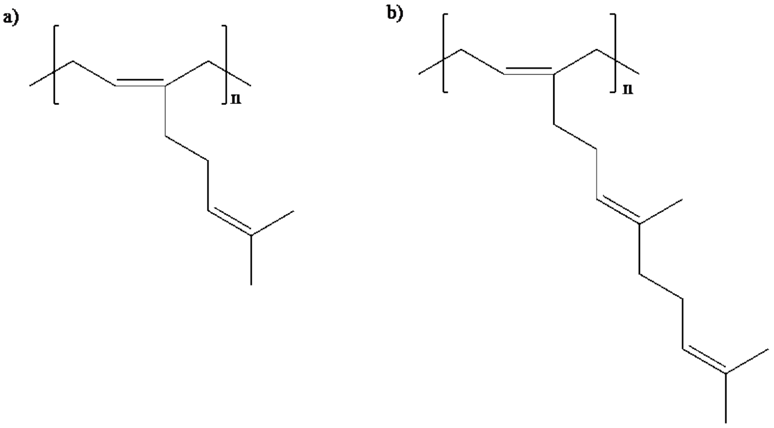
1. Introduction

1,3-Dienes are conjugated hydrocarbons that contain two double bonds separated by one single bond and can be easily polymerized. Common 1,3-dienes are butadiene (BD) and isoprene (IP), which are byproducts of crude oil cracking, and their polymers are used in many applications such as automotive parts, tires, and seals for O-rings, gaskets, and hoses.[1] Poly(BD) and poly(IP) are considered synthetic rubbers or elastomers because of their low glass transition temperatures (T_g) and viscoelastic properties. Poly(IP) is also known as natural rubber (mostly *cis*-1,4-poly(isoprene)) as it can be found naturally in tree sap.[2] Furthermore, the remaining double bond after polymerization allows for crosslinking, thereby forming thermosets that are resistant to chemical and thermal degradation.[3] Alternatively for poly(1,3-dienes) that are not chemically crosslinked, they can be blended with thermoplastics to obtain a final material with synergistic effects in mechanical and physical properties. 1,3-Dienes can also be copolymerized with mainly styrene (St), methyl methacrylate (MMA) and their derivatives to make thermoplastic elastomers (TPEs).[4] The glassy thermoplastic portion ($T_g > T_{room}$) acts as physical crosslinks, while maintaining viscoelastic properties of the rubbery portion ($T_g < T_{room}$), and TPEs can be processed at higher temperatures, like thermoplastics.

The remaining double bonds in poly(dienes) present several disadvantages, as they are susceptible to solvent and thermal degradation. The unsaturated compounds exhibit different mechanical and rheological properties, as well as polymer-polymer miscibility as their saturated analogs. Poly(styrene-*b*-butadiene-*b*-styrene) SBS triblock copolymers are TPEs and are often blended with crystalline poly(propylene) (PP) as a toughener to improve impact and tensile strength.[5] SBS can be partially hydrogenated and form poly(styrene-*b*-ethylene-*co*-butadiene-*b*-styrene) (SEBS), which can also be blended with PP.[6,7] Similarly, poly(styrene-*b*-isoprene-*b*-styrene) (SIS) can be hydrogenated to form poly(styrene-*b*-ethylene-*co*-propylene-*b*-styrene) (SEPS).[8] SEBS/PP blends showed improved impact strength compared to SBS/PP blends, as well as increased elongation at break due to the smaller droplets of TPE that are better dispersed in the matrix.[9] SEBS also has a higher T_g for the rubbery block at -50°C compared to a T_g of -86°C for SBS.[10] Moreover, hydrogenated poly(dienes) have lower hydrodynamic volumes compared to their unsaturated poly(dienes), and therefore require lower molecular weights in order to entangle and exhibit viscoelastic properties.[11,12]

Recently, there has been growing interest in replacing traditional petroleum-derived monomers with bio-derived monomers. Myrcene (Myr) and farnesene (Far) are terpenes that are found in nature and are also 1,3-dienes with longer sidechains and lower volatility compared to BD and IP. Myr can be produced by pyrolysis of *β*-pinene and Far can be produced from dehydration of terpenoids or fermentation using microorganisms.[13-16] Due to their lower volatility, these bio-based dienes are more easily polymerized at ambient pressures in numerous ways including ionic polymerization, redox emulsion, catalytic/coordination polymerization, reversible addition-fragmentation transfer polymerization (RAFT), and nitroxide-mediated polymerization (NMP).[17-31] The longer sidechains of poly(Myr) and poly(Far) provide great potential as promising elastomers due their bottlebrush-like structure. However their degree of unsaturation is higher compared to poly(BD) and poly(IP).[32] Indeed, a poly(Myr) repeating unit contains two double bonds and a poly(Far) repeating unit has three double bonds as shown in **Scheme 1**. As a result, the entanglement molecular weights (M_e) of poly(Myr) and poly(Far) are much greater than poly(BD) and poly(IP) (i.e.

$M_{e,Myr}$ = 18,000–25,000 g mol^{-1} and $M_{e,Far}$ = 50,000 g mol^{-1} versus $M_{e,BD}$ = 1,500–1,900 g mol^{-1} and $M_{e,IP}$ = 3,000–5,000 g mol^{-1}, where M_e depends on composition of *cis* and *trans* or 1,2- and 1,4-addition repeating units).[33,34] Therefore, the hydrogenation of poly(Myr) and poly(Far) is beneficial in order to lower their M_es and have comparable viscoelastic properties without achieving high molecular weights. In fact, the hydrogenation of poly(1,4-Myr) lowered the M_e from 18,000 g mol^{-1} to 12,000 g mol^{-1}.[33]



Scheme 1. Chemical structures of a) poly(Myr) and b) poly(Far) shown by 1,4-addition.

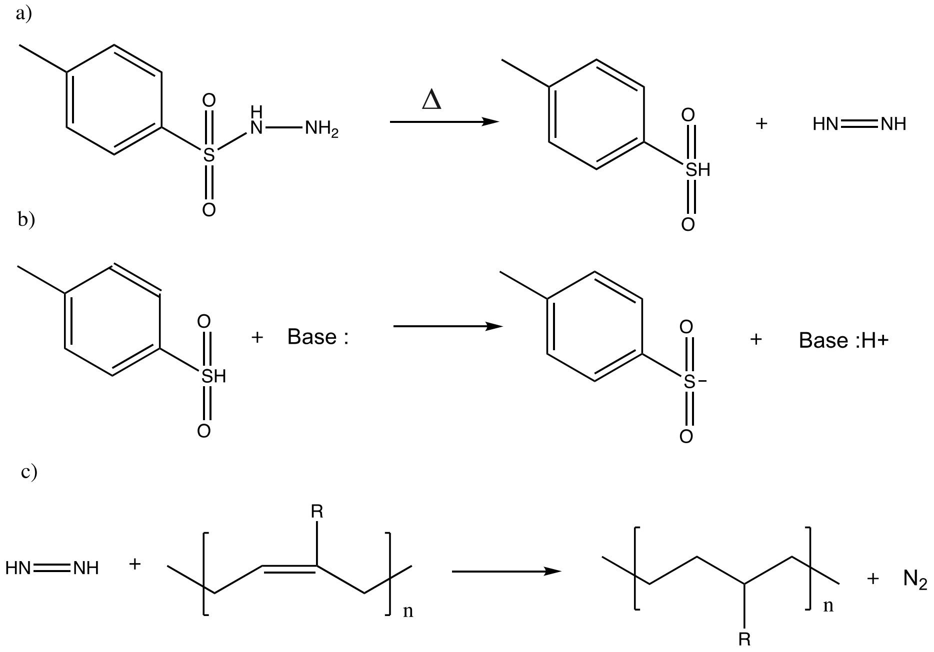
Hydrogenation of poly(dienes) is straightforward and is commonly done industrially using metal catalysts (homogeneous or heterogeneous).[12,35-37] However, catalytic addition of hydrogen gas requires specialized high pressure reactors. Another method developed by Hahn employs thermal degradation of *p*-toluene sulfonyl hydrazide (TSH) to generate diimides in order to chemically hydrogenate poly(dienes) without the use of pressurized reactors, but requires at least stoichiometric amounts of TSH for complete hydrogenation.[38] Early hydrogenation studies of poly(BD) and poly(IP) using TSH showed incomplete hydrogenation due to side reactions like degradation and cyclization. Eventually, modification of the Hahn method was done by adding a base like tripropylamine (TPA) with TSH, which helped minimize side reactions and chain cleavage of polymers.[38-41] Chemical hydrogenation using TSH/TPA has successfully hydrogenated poly(BD) and poly(IP) block copolymers and homopolymers, while showing good tolerance for functional groups.[42-46] Diimides have also been used to hydrogenate polymers synthesized via ring opening metathesis polymerization of various substituted cyclooctenes.[47-50]

There are several examples of catalytic hydrogenation of Myr monomer and one example of hydrogenation of poly(β-pinene) using diimides.[51-55] However, the chemical hydrogenation of bio-based poly(dienes) has not yet been explored. The goal of this study is to optimize the hydrogenation of poly(Myr) and poly(Far) to almost completion using diimides at ambient pressure. Poly(Myr) and poly(Far) were synthesized via free radical polymerization in bulk such that their average molecular weights are above their M_e. Several modes of operation for hydrogenation were investigated (i.e. batch reaction, semi-batch addition of TSH, and with and without solvent) and suggested conditions for high hydrogenation degree of bio-based poly(dienes) was provided for the first time. Additionally, their thermal and rheological properties were compared before and after hydrogenation to assess the change due to the additional processing steps.

2. Results and discussion

2.1. Hydrogenation of poly(Myr) in batch mode

Preliminary hydrogenation experiments done with poly(Myr) were based on similar studies of hydrogenation of poly(dienes) using diimides found in literature.[38,41-45] In these studies, TSH would undergo thermal degradation to form a *p*-tolylsulfinic acid and a diimide, the latter which would chemically hydrogenate an alkene (**Scheme 2**). However, early studies of hydrogenation using TSH resulted in side reactions such as cyclization and chain cleavage due to nucleophilic attack of *p*-tolylsulfinic acid on the polymer backbone.[39-41] Hahn modified this method by adding a base like tripropylamine (TPA) that would deprotonate *p*-tolylsulfinic acid, and therefore avoid chain cleavage by protonation of the polymer backbone.[38] SBS and SIS triblock copolymers were hydrogenated with TSH/TPA, and SBS reached almost 100% hydrogenation whereas SIS reached at maximum of 69% hydrogenation using 6 molar equivalent of TSH/TPA per double bond.



Scheme 2. Hahn's modified chemical hydrogenation of poly(dienes) using diimide (N_2H_2).[38] a) Thermal degradation of TSH to form diimide in the presence of b) a base to deprotonate the acidic *p*-tolylsulfinic acid, and c) diimide hydrogenation of poly(diene). The *R* group can represent an H for butadiene, CH_3 for isoprene, or other alkyl groups.

In this study, poly(Myr) was hydrogenated using TSH with tributylamine (TBA) in slight excess (1:1.2 TSH:TBA molar ratio) as a base to deprotonate the acidic TSH byproduct. Like the studies in literature, hydrogenation reactions were done in batch, where all reagents were added initially into the reactor. Furthermore, BHT was added to prevent oxidative degradation of the polymer chains. Two hydrogenation reactions were done in batch using 2.0 and 4.0 molar equivalents of TSH per double bond of poly(Myr) and their hydrogenation degrees over 4 hours of reaction are shown in **Figure 1**. Because poly(Myr) has a double bond in the backbone due to mostly 1,4-addition and a pendent double bond in its side chain, the hydrogenation of both the backbone and pendent double bonds were quantified using ^{1}H NMR.

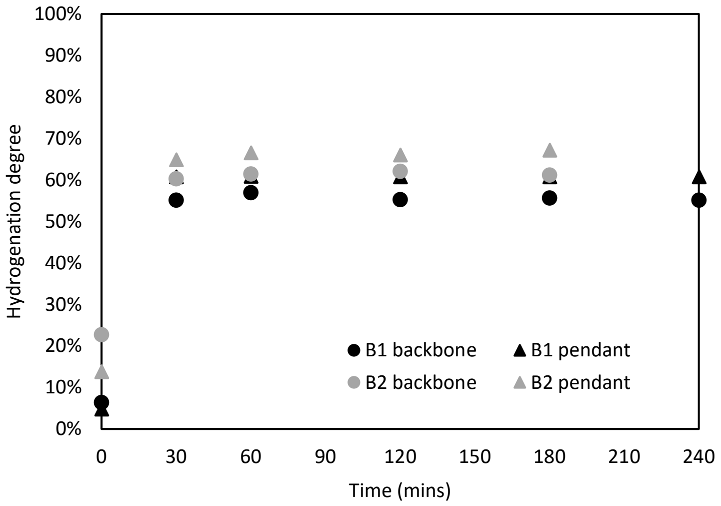
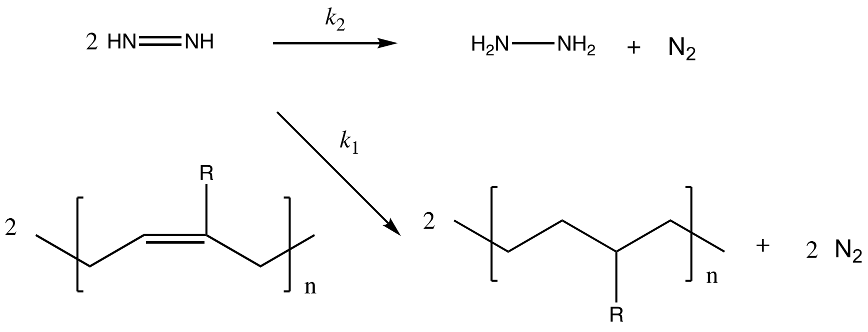


Figure 1. Hydrogenation of poly(Myr) in batch using 2.0 (B1) and 4.0 (B2) mol eq. of TSH per double bond.

The final hydrogenation degrees when using initially 2.0 molar eq. of TSH per double bond (hydrogenation reaction abbreviated B1) were 55% and 61% for the backbone and pendent double bonds, respectively. With 4.0 molar eq. of TSH per double bond used in the feed (hydrogenation reaction abbreviated B2), the hydrogenation degrees were 63% and 65% for the backbone and pendent double bonds, respectively. By increasing from 2.0 to 4.0 mol eq. of TSH per double bond, it only increased the hydrogenation degree of poly(Myr) slightly. Furthermore, the hydrogenation of the backbone is slightly higher than that of the pendent double bond, but also not very significant, which suggests that the pendent double bond is almost as accessible as the backbone for hydrogenation and the steric hindrance are comparable for both double bonds.

In Hahn's study of the hydrogenation of SBS and SIS triblock copolymers, the double bonds of isoprene units could not be completely hydrogenated in comparison to butadiene double bonds, which reached complete hydrogenation.[38] This was attributed to steric hindrance from the methyl group of IP, which then favoured the undesired autohydrogenation of diimide (**Scheme 3**). It can be seen in **Figure 1** that the hydrogenation degree increased significantly in the first 30 mins of the reaction, and then essentially remained constant. In the beginning of the batch reaction, a high concentration of diimide led to fast hydrogenation of the double bonds of poly(Myr). However, as the reaction progressed and the double bonds became less available for hydrogenation, k_2 became more favourable than k_1. Due to the lowered concentration of double bonds, any excess TSH remaining in the batch reaction would inevitably lead to autohydrogenation, such that increasing TSH from 2.0 to 4.0 mol eq. had negligible improvement on the hydrogenation degree of poly(Myr).



Scheme 3. Desired hydrogenation of poly(diene) using diimide (k_1) versus the competing autohydrogenation reaction of diimide (k_2).

Although hydrogenation of SIS triblock copolymers using Hahn's modified method did not reach complete hydrogenation, later studies showed that high degrees of hydrogenation (> 95%) can be obtained by batch hydrogenation of poly(isoprene-*b*-styrene) diblock copolymer and liquid natural rubber.[38,42,45] Another study used the semi-batch approach and added TSH in three separate batches throughout the reaction, and achieved complete hydrogenation of poly(IP) and poly(1,3-pentadiene).[46] Therefore, semi-batch hydrogenation of poly(Myr) would be advantageous since the concentration of diimide is kept low in the reaction medium, which would minimize the unwanted autohydrogenation reaction. Furthermore, a constant supply of diimide would ensure that the limited amount of diimide available would favour towards the hydrogenation of the double bonds.

2.2. Hydrogenation of poly(Myr) in semi-batch mode

Hydrogenation of poly(Myr) was studied in a semi-batch operation, and the first two semi-batch reactions were done by adding a TSH solution continuously into the reaction using a dropping funnel. TSH was dissolved in two different solvents, 1,4-dioxane and pyridine (i.e. SB1 and SB2), although TSH was not completely soluble in either solvent. A peristaltic pump was originally used to add the TSH solution to the reaction, but the partially insoluble TSH powder in 1,4-dioxane and pyridine caused blockages in the tubing. Additionally, poly(Myr) was not dissolved in xylene in the first two semi-batch reactions to minimize the use of organic solvents and because a solvent would be added with the TSH solution. Therefore, excess TBA was added initially to dissolve the poly(Myr) in the reactor. The hydrogenation degrees of poly(Myr) in SB1 and SB2 are shown in **Figure 2**, where 2.0 mol eq. of TSH was added per double bond.

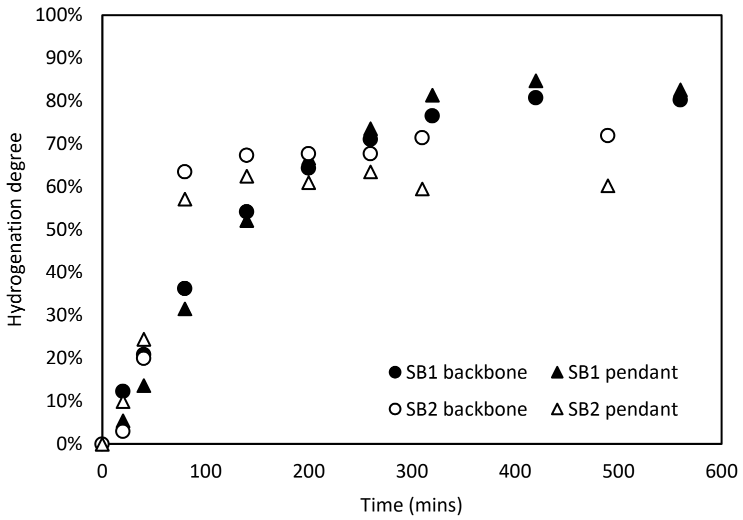


Figure 2. Hydrogenation of poly(Myr) in semi-batch using 2.0 mol eq. of TSH per double bond, where TSH was dissolved in 1,4-dioxane (SB1) and pyridine (SB2) and added continuously throughout the reaction.

Semi-batch hydrogenation was more successful than the batch case, as higher hydrogenation degrees were achieved as seen in **Figure 2**. SB1 achieved hydrogenation degrees of 80% and 83% for the backbone and pendent double bonds, respectively, and the hydrogenation showed a gradual increase using 1,4-dioxane, unlike hydrogenation in batch. Even though higher degrees of hydrogenation were achieved, poly(Myr) was still not completely hydrogenated. One issue was due to the low boiling point of 1,4-dioxane (T_b = 101°C), which effectively lowered the reaction temperature to 101°C – 104°C even though the reaction temperature was set at 125°C.

Therefore, pyridine was used as a solvent to dissolve TSH because it has a higher boiling point (T_b = 115°C). Final hydrogenation degrees by adding TSH in pyridine reached 72% and 60% for backbone and pendent double bonds, respectively, which was lower than what was achieved using TSH in 1,4-dioxane. Furthermore, hydrogenation seemed to increase steadily up until 100 min, then plateaued as seen in **Figure 2**. The reaction mixture also turned orange at the end of reaction and side degradation reactions were suspected. An earlier study for hydrogenation of poly(isoprene) used TSH and pyridine as a base suppressant for chain cleavage, however it resulted in severe chain degradation. Furthermore, higher concentrations of pyridine led to slower rates of hydrogenation.[40] Evidently, pyridine does not act as a base like TBA to deprotonate the TSH acid by-product, but rather accelerated chain cleavage. Since a suitable solvent could not be found to fully dissolve TSH into solution for semi-batch addition, dry TSH powder was added in small batches (1 g for every 15 min) throughout the reaction instead. Similar to SB1 and SB2, SB3 did not include any xylene to dissolve poly(Myr) initially, but the dry TSH powder was not fully soluble in the poly(Myr)/TBA mixture, and therefore hydrogenation did not occur. The reaction mixture turned yellow, then brown, and eventually purple towards the conclusion of the experiment. Consequently, the remaining semi-batch reactions included xylene as a solvent, which was required to dissolve both poly(Myr) and TSH into a homogenous mixture.

In SB4, poly(Myr) was dissolved in xylene and TBA, and 2.0 mol eq. of dry TSH powder per double bond was added throughout the reaction. The hydrogenation degrees of SB4 are shown in **Figure 3**, and high degrees of hydrogenation were achieved (89% and 88% for the backbone and pendent double bonds, respectively). The ratio of TSH to double bond was increased to 2.5 and 3.0 mol eq. and the highest degrees of hydrogenation were achieved using 3.0 mol eq. of TSH, reaching 97% and 94% for the backbone and pendent double bonds, respectively. The semi-batch reactions with continuous addition of dry TSH powder also maintained the reaction temperature at 125°C unlike SB1 and SB2 where the temperatures were lowered due to the low boiling points of the solvents. Therefore, adding dry TSH powder had the most success in achieving almost complete hydrogenation of poly(Myr) for both the backbone and pendent double bonds.

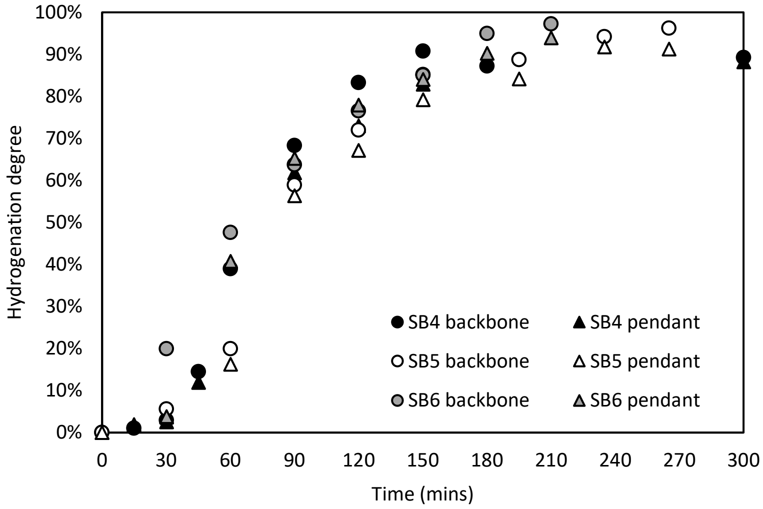


Figure 3. Hydrogenation of poly(Myr) in semi-batch by adding dry TSH powder (1 g for every 15 min) at 2.0 (SB4), 2.5 (SB5), and 3.0 (SB6) mol eq. of TSH per double bond.

The progression of the hydrogenation reactions of poly(Myr) were quantified by ^{1}H NMR. As an example, the series of ^{1}H NMR spectra for SB6 is shown in **Figure 4**. The doublet at 1.6 ppm (A) represents the two unsaturated methyl groups of the Myr repeating unit, which disappear as the hydrogenation reaction occurs. The appearance of the doublet at 0.8 ppm (B) represents the saturated methyl group protons of backbone double bonds as they become hydrogenated. Lastly, the disappearance of the peak at 5.1 ppm (C) represents the hydrogenation of the pendent double bonds of the poly(Myr). At the end of the reaction, it is evident that there is a minimal fraction of pendent and backbone double bonds remaining.

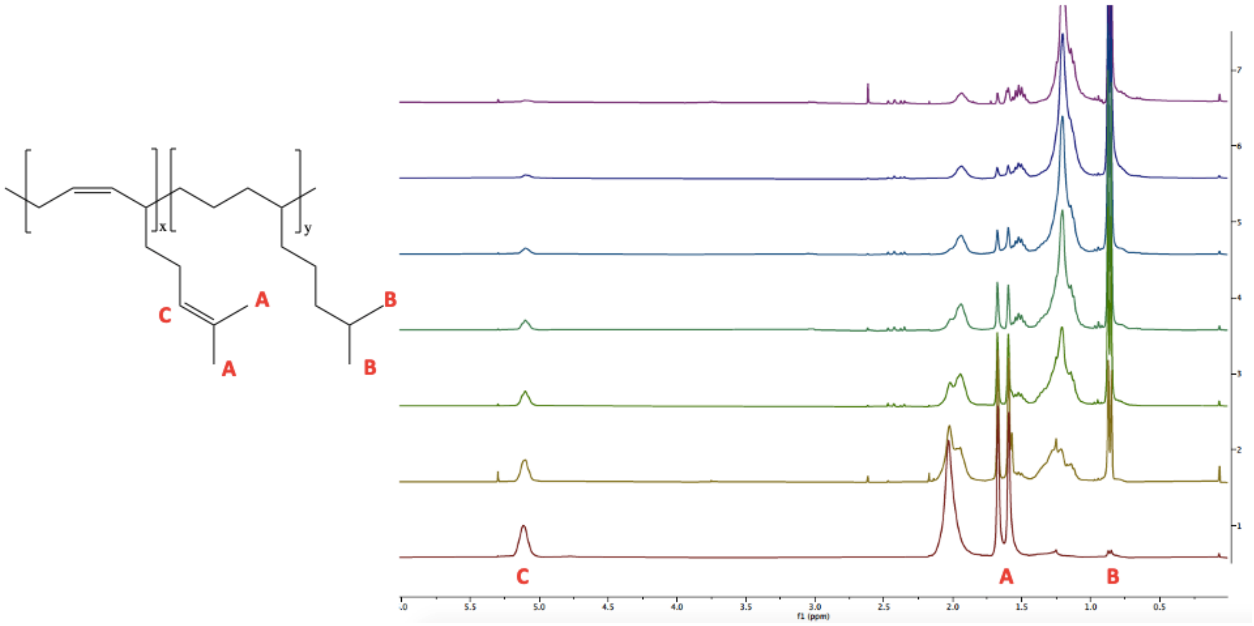


Figure 4. ^{1}H NMR ($CDCl_3$) spectra of SB6 hydrogenation reaction of poly(Myr) from time = 0 min (bottom, red) to time = 210 min (top, purple).

The molecular weight distribution (MWD) of poly(Myr) synthesized by free radical polymerization is compared with the MWDs of the hydrogenated poly(Myr) made by the semi-batch method. As seen in **Figure 5**, the molecular weights of poly(Myr) measured from GPC did not change significantly after hydrogenation, indicating there was no chain cleavage from TSH acidic by-products, or from any thermal or oxidative degradation.

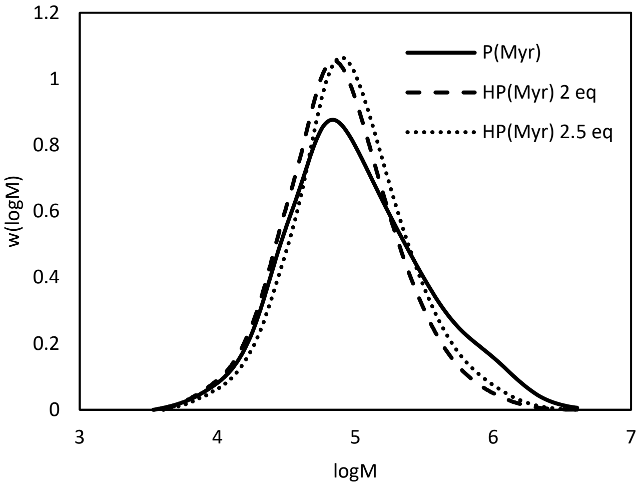


Figure 5. Molecular weight distributions of poly(Myr) before and after hydrogenation in semi-batch using 2.0 and 2.5 mol eq. of TSH per double bond.

2.3. Hydrogenation of poly(Far) in semi-batch mode

Since the hydrogenation of poly(Myr) was optimized by adding dry TSH powder in semi-batch operation, the hydrogenation of poly(Far) was done using the same method. In SB7, SB8, and SB9, poly(Far) was hydrogenated with 2.0, 2.5, and 3.0 mol eq of TSH per double bond of poly(Far), except now there are three double bonds per repeating unit instead of two. The hydrogenation degrees with reaction time are shown in **Figure 6**. Similar to the hydrogenation of poly(Myr) in semi-batch mode, the highest degrees of hydrogenation for poly(Far) was achieved using 3.0 mol eq of TSH. Almost complete hydrogenation was reached for poly(Far) at 97% and >99% of hydrogenation for the backbone and pendent double bonds, respectively.

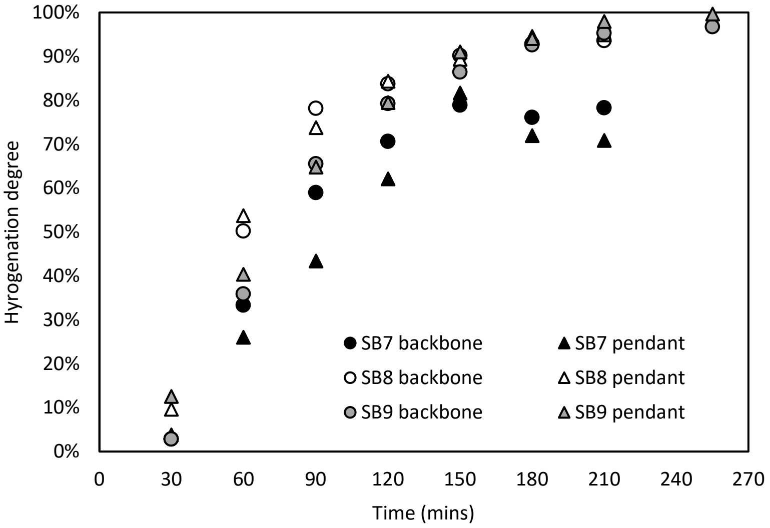


Figure 6. Hydrogenation of poly(Far) in semi-batch by adding dry TSH powder (1 g for every 15 min) at 2.0 (SB7), 2.5 (SB8), and 3.0 (SB9) mol eq. of TSH per double bond.

A series of ^{1}H NMR spectra for the hydrogenation of poly(Far) in semi-batch is shown in **Figure 7**. Similar to the hydrogenation of poly(Myr), there is the disappearance of the doublet peak representing the three unsaturated methyl group protons at 1.6 ppm (A), and appearance of the saturated methyl groups at 0.8 ppm (B) from the hydrogenation of the backbone double bond. There is also the disappearance of the unsaturated proton peak at 5.1 ppm (C), which represents the hydrogenation of the pendent double bonds in the side chains of poly(Far).

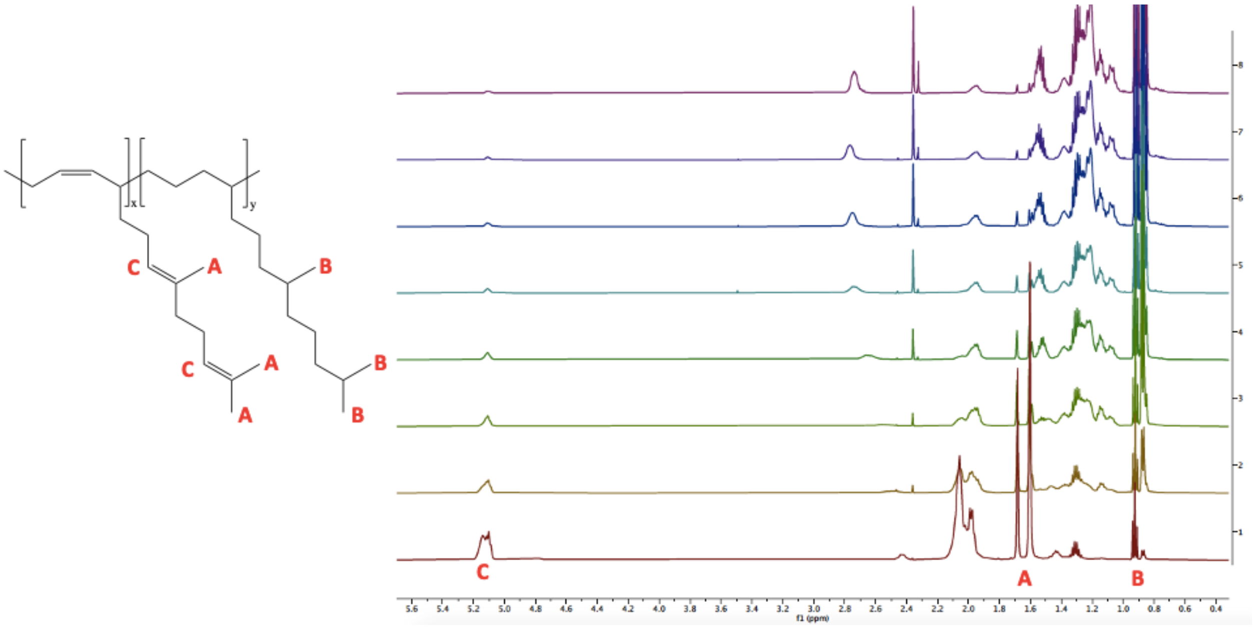


Figure 7. ^{1}H NMR ($CDCl_3$) spectra of SB9 hydrogenation reaction of poly(Far) from time = 0 min (bottom, red) to time = 255 min (top, purple).

Furthermore, the MWDs of poly(Far) before and after hydrogenation are shown in **Figure 8**. There is a prominent molecular weight shoulder for poly(Far) as a result of the free radical polymerization at low initiator loading, hence the high Đ of 6.6. Similarly, there is a negligible difference in the MWD after almost complete hydrogenation using 2.5 and 3.0 eq TSH per double bond, indicating there was no polymer chain degradation.

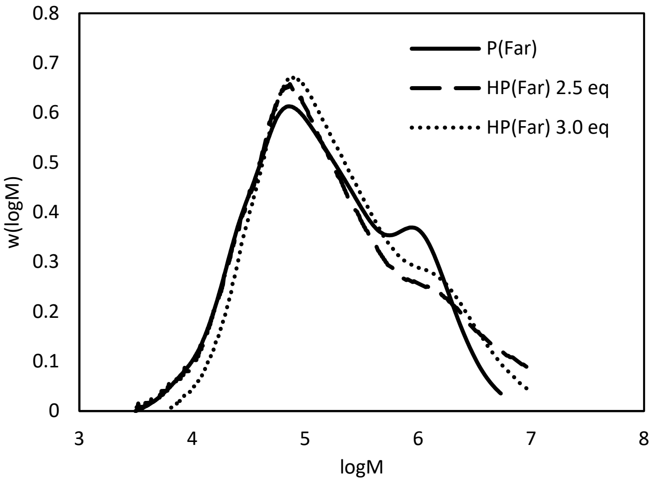


Figure 8. Molecular weight distributions of poly(Far) before and after hydrogenation in semi-batch using 2.5, and 3.0 mol eq. of TSH per double bond.

It is apparent that the semi-batch addition of dry TSH powder was very effective in almost completely hydrogenating the double bonds of both poly(Myr) and poly(Far). The most efficient hydrogenation was achieved by adding 3.0 mol eq. of TSH per double bond. The final hydrogenation degrees for all experiments for poly(Myr) and poly(Far) are summarized in **Table 1**. Furthermore, the hydrogenated poly(dienes) were not expected to have any stereochemistry, as they become saturated alkyl chains comprised of σ-bonds. Although the manual addition of TSH required opening the reactor every time, N_2 gas generated by the reaction itself was able to maintain a nitrogen atmosphere for the reaction. Although the addition of dry TSH powder could have been automated by using a powder dispenser, manual addition of the powder was still sufficient as shown by the semi-batch experiments in this study.

Table 1. Summary of final hydrogenation degrees of poly(Myr) and poly(Far) for both pendent and backbone double bonds.

Experiment ID	**Poly(diene)**	**Molar eq. of TSH**[a)]	**Hydrogenation degree of pendent double bonds**[b)]	**Hydrogenation degree of**

				backbone double bonds c)
B1	Poly(Myr)	2.0	61%	55%
B2	Poly(Myr)	4.0	65%	63%
SB1	Poly(Myr)	2.0	83%	80%
SB2	Poly(Myr)	2.0	60%	72%
SB4	Poly(Myr)	2.0	88%	89%
SB5	Poly(Myr)	2.5	91%	96%
SB6	Poly(Myr)	3.0	94%	97%
SB7	Poly(Far)	2.0	81%	79%
SB8	Poly(Far)	2.5	95%	94%
SB9	Poly(Far)	3.0	99%	97%

a) Molar equivalent of TSH was added per double bond per repeating unit of poly(Myr) or poly(Far); b) Hydrogenation degrees were determined using ^{1}H NMR.

2.4. Thermal behaviour of hydrogenated poly(Myr) and poly(Far)

The thermal stability of the bio-based polymers was analyzed before and after hydrogenation. The thermal degradations of poly(Myr) and the hydrogenated poly(Myr) in semi-batch mode with 2.5 and 3.0 mol eq. of TSH per double bond were measured using TGA as shown in **Figure 9**. The degradation of poly(Myr) shows an initial degradation at 170°C and its weight decreased by 25 wt% until a second degradation occurred at 360°C. This two-step degradation is consistent with the thermal degradation of poly(Myr) in literature, as well as for poly(BD).[21,56] Poly(BD) homopolymer showed a two-step degradation for polymers containing the 1,4-addition (*cis* or *trans*) conformation, however there was only one degradation step for poly(BD) polymerized by 1,2-addition.[57] Poly(Myr) polymerized by redox emulsion mostly consisting of 1,4-addition units also showed a distinct two-step degradation.[21] The initial degradation of poly(BD) is attributed to its depolymerization into butadiene and vinylcyclohexene by-products, and the second step is the degradation of cyclized and crosslinked polymer units.[56] Since poly(Myr) in this study was also mostly comprised of 1,4-addition units, it is not surprising that it exhibited a two-step degradation as well.

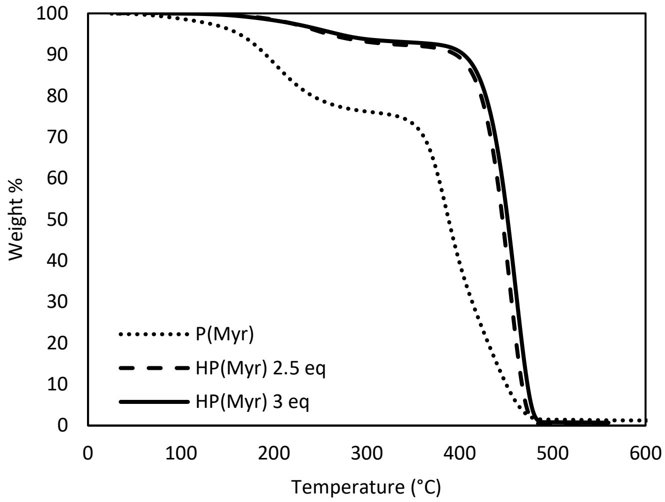


Figure 9. Thermal degradation of poly(Myr) showing weight loss with temperature before (dotted line) and after semi-batch hydrogenation using 2.5 (dashed line) and 3 mol eq (solid line) of TSH per double bond.

The thermal degradation of poly(Myr) showed great improvement after almost complete hydrogenation as seen in **Figure 9** (HP(Myr) 2.5 eq and HP(Myr) 3 eq). The initial degradation lessened to 7 wt% loss, and the degradation temperature at 10 wt% loss ($T_{10\%}$) is at 404°C. This suggests that after saturation of the backbone double bonds, the depolymerization of the polymer units by 1,4-addition was minimized. Furthermore, the saturation of the pendent double bonds likely decreased the cyclization between monomer units. Therefore, the thermal stability of the hydrogenated poly(Myr) is significantly improved. This is consistent with other poly(dienes), where an increase in thermal stability was shown after hydrogenation of the double bonds.[42,43,45]

Poly(Far) also shows an initial degradation at 125°C but only 4 wt% of its initial mass had degraded, therefore it is not as severe as poly(Myr) where 20 wt% of its initial mass degraded. Furthermore, poly(Far) exhibited a $T_{10\%}$ at 310°C (**Figure 10**). The low initial thermal degradation of poly(Far) is similar to the work recently done by our group showing the degradation of poly(farnesene-*b*-ethylene glycol dicyclopentenyl methacrylate) (poly(Far-*b*-EGDEMA).[58] The diblock copolymer had a very short block of poly(EGDEMA) and was mostly comprised of poly(Far), and it also had a 4 wt% decrease at 125°C. Even though both poly(Far) and poly(Myr) were polymerized by 1,4-addition, the lower initial degradation of poly(Far) suggests the longer side chains may have helped to prevent the depolymerization degradation, and therefore has better thermal stability compared to poly(Myr). Nonetheless, much improvement in thermal stability was shown after almost complete hydrogenation using 2.5 and 3.0 mol eq. of TSH per double bond, where $T_{10\%}$ increased to 379°C.

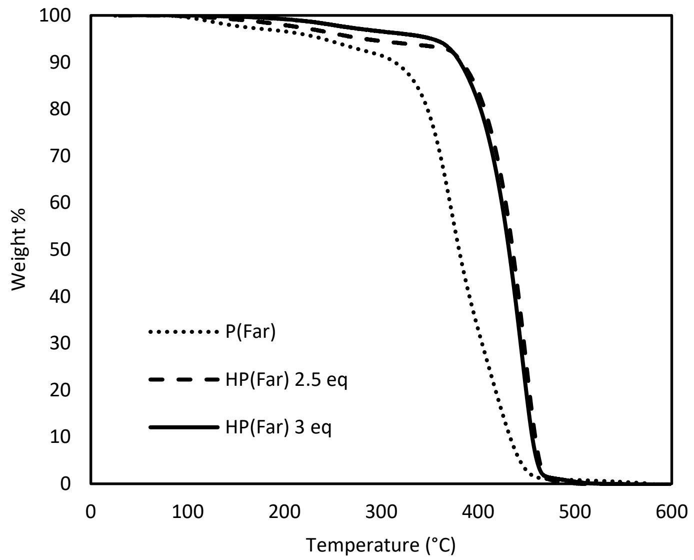


Figure 10. Thermal degradation of poly(Far) with temperature before (dotted line) and after semi-batch hydrogenation using 2.5 (dashed line), and 3.0 mol eq (solid line) of TSH per double bond.

Glass transition temperatures of the hydrogenated poly(Myr) and poly(Far) were measured using DSC and are summarized in **Table 2**. With increased degrees of hydrogenation (by increasing TSH per double bond), the T_g also increased compared to their respective unsaturated poly(dienes). T_gs of the unsaturated poly(Myr) and poly(Far) were not detected using the DSC in this study. This could be due to the high dispersity of the polymers made by free radical polymerization such that the presence of shorter chains could have plasticized the polymer and lowered the T_g to below or very close to the lowest possible temperature of -90°C for the DSC that was used. There are several reported T_gs of poly(Myr), where homopolymerization of Myr via nitroxide-mediated polymerization exhibited a T_g of -77°C and homopolymerization of Myr by persulfate-initiated emulsion exhibited a T_g of -73°C.[21,29] However, poly(Myr) synthesized by redox emulsion and RAFT polymerization both had a T_g of -60°C.[21,24] Evidently, poly(Myr) with highly ordered microstructures (>90 mol% 1,4-*cis*) and/or higher molecular weight exhibit higher T_gs.[59] Although T_g of poly(Myr) before hydrogenation was not detected using DSC, the T_gs of the hydrogenated poly(Myr) are all higher than the reported values of unsaturated poly(Myr). Furthermore, it has been shown that poly(Myr) polymerized with predominantly 1,4-addition had a T_g of -68°C compared to a T_g of -54°C after hydrogenation.[60] T_g of poly(Far) in this study was also not observed in DSC but it is reported to be -73°C.[34] Similarly, T_gs of the hydrogenated poly(Far) also increased compared to the unsaturated analog. An increase in T_g suggests an increase in stiffness of polymer chains as a result of the saturation of double bonds, and this is consistent with other hydrogenated poly(diene) homopolymers and copolymers in literature.[10,42,43,46,61]

Table 2. Glass transition temperatures of poly(Myr) and poly(Far) before and after hydrogenation.

	T_g of unsaturated poly(diene) [°C]	**T_g of hydrogenated poly(dienes) [°C]**	
		2.5 mol eq. TSH	**3.0 mol eq. TSH**
Poly(Myr)	-77[a)]	-54	-52
Poly(Far)	-73[b)]	-66	-63

[a)] Obtained from references 20 for poly(Myr) mostly made of 1,4-addition units; [b)] Obtained from reference 32

The thermal behaviour of these bio-based poly(dienes) was certainly affected after hydrogenation of the double bonds. A significant improvement in thermal stability was shown after the hydrogenation of poly(Myr), where the initial depolymerization degradation was greatly decreased. Furthermore, an increase in $T_{10\%}$ for both hydrogenated poly(Myr) and poly(Far) compared to the unsaturated poly(dienes) was also observed. Their T_gs also increased after hydrogenation, which indicate stiffer polymer chains.

2.5. Rheology of hydrogenated poly(Myr) and poly(Far)

To further investigate the change in the properties of the bio-based poly(dienes) after hydrogenation, their steady shear viscosities were measured as a function of shear rate using the rheometer. In **Figure 11**a, the viscosity of the unsaturated poly(Myr) decreased slightly from 1.41×10^2 Pa s to 1.15×10^2 Pa s by increasing the shear rate from 0.1 to 10 s^{-1}. After hydrogenation, the viscosity of the hydrogenated poly(Myr) increased significantly by two orders of magnitude to 2.53×10^4 Pa s (HP(Myr) 3 eq in Figure 11a), which confirms that hydrogenated poly(Myr) did increase in stiffness. By increasing shear rate from 0.1 s^{-1} to 10 s^{-1}, the viscosity of hydrogenated poly(Myr) decreased by an order of magnitude to 2.70×10^3 Pa s, which demonstrates more shear-thinning behaviour. Conversely, the viscosity of poly(Far) only increased slightly after hydrogenation as seen in **Figure 11**b (HP(Far) 2.5 eq and HP(Far) 3 eq). The viscosity of poly(Far) at low shear rates < 1 s^{-1} is about 1×10^4 Pa s and decreased an order of magnitude at a shear rate of 10 s^{-1} indicative of shear-thinning behaviour.

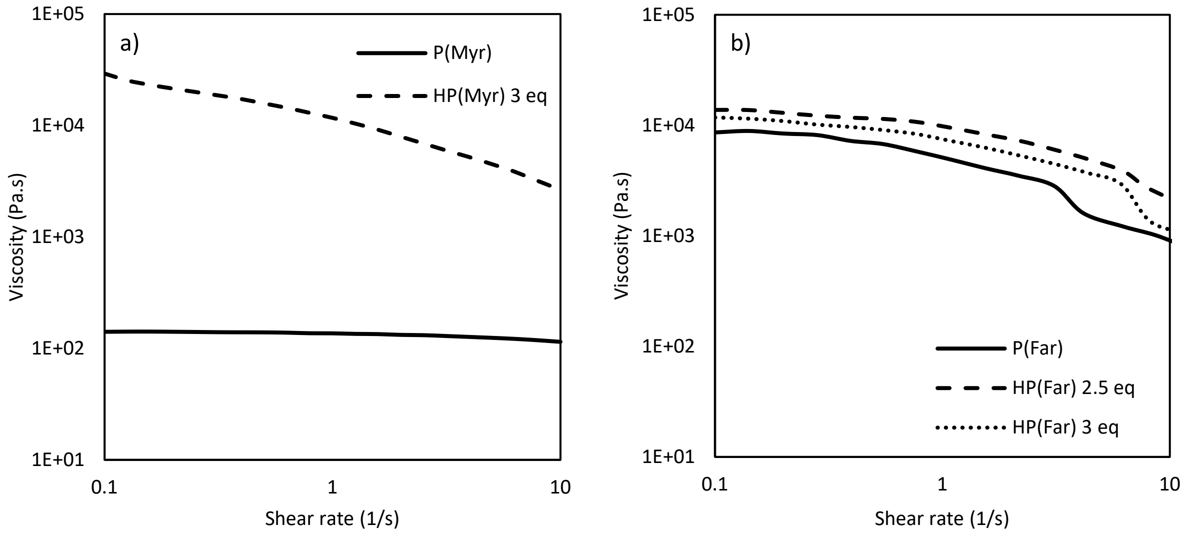


Figure 11. Viscosity as a function of steady shear rate for a) poly(Myr) and b) poly(Far) before and after hydrogenation.

The difference in viscosities before and after hydrogenation is much greater for poly(Myr) than for poly(Far). Rheological studies of bottlebrush polymers have shown that the length of side chains have a great effect on the conformation of the polymer chains, as well as the ratio between the length of the backbone and the length of the side chains.[62,63] For bottlebrush polymers with compact side chains, viscosity has a weak dependence on molecular weight even after the molecular weight has surpassed the critical or entanglement molecular weight. This is due to the one-dimensional growth of the polymer chain as DP_n of the backbone increases, while the length of the side chains remains fixed, meaning that the polymer chains change from a spherical to a cylindrical shape. Furthermore, the high density of side chains reduces the frictional effects of the side chains on the backbone. Therefore, increased molecular weight has little effect on viscosity such that higher molecular weight bottlebrush polymers can behave similarly to linear unentangled polymers.

Although both poly(Myr) and poly(Far) in this study were synthesized above their entanglement molecular weights, poly(Myr) has an M_n of 56 kg mol^{-1}, which is more than three times its literature M_e of 18 kg mol^{-1}. After hydrogenation, the entanglement spacing in between branches becomes more compact, and effectively lowers the M_e to 12 kg mol^{-1}.[33] Therefore, entanglement of poly(Myr) is significantly increased and it is reflected in the significant increase in viscosity. On the other hand, poly(Far) has an M_n of 62 kg mol^{-1}, which is only slightly above its M_e of 50 kg mol^{-1}. However, poly(Far) has longer sidechains which would exhibit a higher degree of entanglement, and thus the unsaturated poly(Far) has a higher viscosity compared to unsaturated poly(Myr). Nonetheless, its entanglement was only slightly improved even after hydrogenation as seen by the slight increase in viscosity. Therefore, the DP_n of poly(Far) would likely have to be much higher in order to see a significant increase in entanglements and subsequently viscosity, after hydrogenation.

3. Conclusion

Hydrogenation of poly(dienes) has been well-studied for homopolymers and copolymers containing butadiene or isoprene. However, hydrogenation of bio-based poly(Myr) and poly(Far) has not been reported. Furthermore, the hydrogenation was done at ambient pressure using diimide generated by thermal degradation of TSH and was optimized in a semi-batch process to efficiently hydrogenate the backbone and pendent double bonds of poly(Myr) and poly(Far). By adding 3.0 mol eq. of TSH per double bond in a semi-batch fashion, almost complete hydrogenation was achieved for poly(Myr) (97% and 94% for the backbone and pendent double bonds, respectively) and poly(Far) (97% and >99% for the backbone and pendent double bonds, respectively). The thermal stability of poly(Myr) and poly(Far) also improved after hydrogenation as the depolymerization and cyclization degradations were reduced and $T_{10\%}$ degradation temperatures were increased. Glass transition temperatures also increased after hydrogenation, suggesting stiffer polymer chains after saturation of the double bonds, which was also shown by the increase in viscosities of the hydrogenated polymers. Although a greater increase in viscosity for poly(Myr) was observed compared to poly(Far) due to the molecular weight of poly(Myr) being much higher than its M_e, the hydrogenated poly(Myr) and poly(Far) possessed greater thermal stability and higher glass transition temperatures, which is consistent with the hydrogenation of poly(BD) and poly(IP) found in in literature. Furthermore, these hydrogenated bio-based poly(dienes) can substitute midblocks of TPES such as SEBS and SEPS, or copolymerized with bio-based outer thermoplastic blocks made of different methacrylates or acrylates, for example.

4. Experimental Section/Methods

Materials. β-Myrcene monomer (Myr, ≥95%) was purchased from Millipore Sigma. Trans-*β*-farnesene monomer (Far, ≥95%) was obtained from Amyris Inc. Monomers were purified using 1.0 g of aluminum oxide (basic Al_2O_3, activated, Brockmann I) and 0.05 g calcium hydride (CaH_2, ≥90%) per 50 mL of monomer, which were used as received from Millipore Sigma. Dicumyl peroxide (DCP, 98%) initiator, *p*-toluene sulfonyl hydrazide (TSH, 97%), tributylamine (TBA, ≥98.5%), 3,5-di-*tert*-butylhydroxytoluene (BHT, ≥99%) were purchased from Millipore Sigma and used as received. Xylene (≥ 98.5%), methanol (MeOH, ≥ 99.8%), tetrahydrofuran (THF, 99.9% HPLC grade), 1,4-dioxane (≥ 99%), and pyridine (≥ 99%) were purchased from Fisher Chemicals and used as received. Deuterated chloroform ($CDCl_3$, 99.9% D) was purchased from Cambridge Isotope Laboratories, USA and used as received.

Free radical polymerization of Myr and Far in bulk. The synthesis of poly(Myr) was done by free radical polymerization in bulk. DCP thermal initiator (0.18 g) and Myr monomer (117 g) were added into a 250 mL three-neck round bottom flask, with a condenser attachment to prevent evaporation of monomer during polymerization. The reaction mixture was purged with nitrogen for 30 mins, and polymerization proceeded at 120°C with stirring for 6 h and reached a conversion of X_{myr} = 76% (see Supporting information Figure S.1), final number-average molecular weight (M_n) of 57 kg mol^{-1} and dispersity (Đ) of 3.6. Poly(Myr) was confirmed by ^{1}H NMR to be mostly polymerized by 1,4-addition (86 mol%) with some units of 1,2- and 3,4-addition (7 mol% each) (Figure S.2). However, *cis*- or *trans*- stereochemistry was not confirmed via ^{13}C NMR. Poly(Far) was synthesized in a similar manner using DCP initiator (0.05 g) and Far monomer (10 g) in bulk at 120°C for 2 h. The reaction mixture was purged with nitrogen for 30 mins, and the polymerization proceeded at 115°C with stirring for 2 h, reaching a conversion of X_{Far} = 64% (Figure S.3) and final M_n of 62 kg mol^{-1} , Đ = 6.6. The Poly(Far) was more predominantly polymerized by 1,4-addition (96.8 mol% 1,4-addition, 1.9 mol% 1,2-addition, and 1,3 mol% 3,4-addition) compared to Myr as seen in Figure S.4. The final polymers were precipitated using methanol, then dried under air overnight and in the vacuum oven at room temperature for a day.

Hydrogenation of poly(Myr) in batch mode. Hydrogenation experiments of poly(Myr) (obtained from free radical polymerization in bulk) were done in batch, where all reagents were added initially into the reactor. In a 250 mL three-neck round bottom flask equipped with a condenser, magnetic stir bar, and nitrogen influx, poly(Myr) was dissolved in xylene at approximately 3.3 – 4.0% w/v. The amount of TSH added was based on 2.5 or 4.0 molar equivalent of TSH per double bond of poly(Myr), which was estimated based on the number average degree of polymerization (DP_n) of poly(Myr) measured from gel permeation chromatography (GPC). Every repeating unit of poly(Myr) has 2 double bonds (**Scheme 1**), therefore the number of double bonds is two times the DP_n. TBA was also added in slight excess relative to TSH to neutralize the acidic by-product of TSH thermal degradation.

Finally, a very low concentration of BHT was also added to prevent oxidative degradation of the poly(Myr) chains. A summary of hydrogenation experiments in batch are shown in **Table 3**. Hydrogenation reactions took place at 125°C for up to 4 h, and samples were taken periodically to be analyzed by ^{1}H NMR to quantify hydrogenation degree. The final polymer after hydrogenation was also analyzed by GPC to check for polymer chain degradation.

Table 3. Summary of experiments for hydrogenation of poly(Myr) in batch.

Experiment ID	**$m_{\text{poly(Myr)}}$ [g]$^{a)}$**	**V_{xylene} [mL]**	**Mol eq. of TSH$^{b)}$**	**m_{TSH} [g]$^{c)}$**	**m_{TBA} [g]$^{c)}$**	**m_{BHT} [g]**
B1	2.0	50	2.5	6.80	6.85	0.01
B2	2.0	60	4.0	10.9	11.0	0.01

$^{a)}$ Concentration of poly(Myr) in xylene solution is 3.3 to 4.0% w/v; $^{b)}$ Molar equivalent amount of TSH added for hydrogenation is per double bond per repeating unit of poly(Myr), calculated based on molecular weight measured from GPC; $^{c)}$ Mass of TSH is determined based on molar equivalent amount of TSH required, and mass of TBA is added in slight excess.

Hydrogenation of poly(Myr) in semi-batch mode. Hydrogenation experiments of poly(Myr) were done in semi-batch, where TSH was slowly added throughout the reaction. Similarly, the hydrogenation reactions were done in a 250 mL three-neck round bottom flask equipped with condenser, magnetic stir bar, nitrogen influx. Several experimental setups were investigated including only dissolving poly(Myr) in TBA and no xylene, dissolving TSH in a solvent and adding the TSH solution to reaction mixture by a dropping funnel, and adding dry TSH powder manually to the reaction mixture. The flow rate of TSH addition by dropping funnel was calculated based on total volume of solution added over the total time of TSH addition. The addition of dry TSH powder was 1 g for every 15 mins until the total amount has been added to the reaction mixture. A summary of the semi-batch experimental formulations is shown in **Table 4**. In the experiments where poly(Myr) was not dissolved in xylene, excess TBA was added to solubilize the polymer. In all cases, reaction mixtures were purged with nitrogen for 30 mins and hydrogenation of poly(Myr) was done at 125°C for up to 9 h depending on the rate of TSH addition.

Table 4. Summary of experiments for hydrogenation of poly(Myr) in semi-batch conditions.

Experiment ID	$m_{poly(Myr)}$ [g]	V_{xylene} [mL]	Mol eq. of TSH[b]	m_{TSH} [g]	TSH solvent	$V_{TSH\ solvent}$ [mL]	TSH addition rate	m_{TBA} [g]	m_{BHT} [g]
SB1	2.0	0.0	2.0	10.9	1,4-Dioxane	63.6[c]	0.30 mL/min[d]	30.9[f]	0.01
SB2	2.0	0.0	2.0	10.9	Pyridine	48.7[c]	0.43 mL/min[d]	22.5[f]	0.01
SB3	2.0	0.0	2.0	10.9	--	--	1g/15min[e]	34.3[f]	0.01
SB4	2.0[a]	56	2.0	11.0	--	--	1g/15min[e]	14.2[g]	0.01
SB5	2.0[a]	72	2.5	14.0	--	--	1g/15min[e]	21.0[g]	0.01
SB6	2.0[a]	60	3.0	16.4	--	--	1g/15min[e]	23.4[g]	0.01

[a] Concentration of poly(Myr) in xylene solution is 2.8 to 3.3% w/v; [b] Molar equivalent amount of TSH added for hydrogenation is per double bond per repeating unit of poly(Myr), calculated based on molecular weight measured from GPC; [c] Volume of solvent for TSH solutions is based on approximately 20% w/w of TSH in 1,4-dioxane or pyridine; [d] Flow rate of TSH solution was calculated based on total volume of solution added over total time of addition; [e] Dry TSH powder was added in small batches throughout the reaction at 1 g for every 15 min until all of the required TSH is added; [f] Excess TBA was added to solubilize poly(Myr) in absence of xylene as solvent; [g] TBA was added in slight excess (1:1.2 TSH:TBA molar ratio)

Hydrogenation of poly(Far) in semi-batch mode. After optimization of the semi-batch hydrogenation of poly(Myr), hydrogenation of poly(Far) was also done in semi-batch. Similar to the hydrogenation experiments of poly(Myr), poly(Far) (obtained from free radical polymerization in bulk) was dissolved in xylene (about 3.3% w/v) in a 250 mL three-neck round bottom flask equipped with a condenser, magnetic stirring, and nitrogen influx. The amount of TSH added was calculated based on three double bonds per repeating unit of poly(Far) (**Scheme 1**), which was estimated based on the DP_n from GPC. In these semi-batch hydrogenation experiments, 2.0 – 3.0 molar equivalent of TSH was added per double bond in poly(Far). TBA in slight excess relative to TSH (1:1.2 TSH:TBA) was also added to the polymer solution, as well as small amounts of BHT. The polymer solution was then purged with nitrogen for 30 mins. TSH dry powder was added manually (1 g for every 15 min) to the reaction mixture, and the hydrogenation reaction was done at 125°C for up to 4.5 h. A summary of the semi-batch experimental recipes for hydrogenation of poly(Far) is shown in **Table 5**.

Table 5. Summary of experiments for hydrogenation of poly(Far) in semi-batch.

Experiment ID	$m_{poly(Far)}$ [g]$^{a)}$	V_{xylene} [mL]	Mol eq. of TSH$^{b)}$	m_{TSH} [g]	TSH addition rate$^{c)}$	m_{TBA} [g]$^{d)}$	m_{BHT} [g]$^{d)}$
SB7	2.4	60.0	2.0	13.0	1g/15min	15.5	0.01
SB8	1.9	60.0	2.5	12.6	1g/15min	15.1	0.01
SB9	1.9	60.0	3.0	15.4	1g/15min	18.4	0.01

a) Concentration of poly(Far) in xylene solution is approximately 4.0% w/v; b) Molar equivalent amount of TSH added for hydrogenation is per double bond per repeating unit of poly(Far), calculated based on molecular weight measured from GPC; c) Dry TSH powder was added in small batches throughout the reaction at 1 g for every 15 min until all of the required TSH is added; [d)] Mass of TSH is determined based on molar equivalent amount of TSH required, and mass of TBA is added in slight excess (1:1.2 of TSH:TBA molar ratio).

Polymer characterization. Conversions and hydrogenation degrees of the poly(Myr) and poly(Far) samples were determined using ^{1}H NMR (Bruker AVIIIHD 500 MHz spectrometer, 16 scans). For the hydrogenation experiments, 1 mL samples were taken periodically, and the polymers were precipitated from solution using excess methanol. The dried polymer samples were redissolved in $CDCl_3$ for ^{1}H NMR analysis. Hydrogenation degree calculations can be found in Supporting Information (Figure S.5 and S.6). Number average molecular weight (M_n) and dispersity ($Đ = M_w/M_n$) of polymer samples were characterized using gel permeation chromatography (GPC, Water Breeze) with HPLC grade THF as an eluent at a flow rate of 0.3 mL min^{-1}. The GPC has three Waters Styragel HR columns (HR1 with a molecular weight measurement range of 10^2 to 5×10^3 g mol^{-1}, HR2 with a molecular weight measurement range of 5×10^2 to 2×10^4 g mol^{-1}, and HR4 with a molecular weight measurement range of 5×10^3 to 6×10^5 g mol^{-1}), a guard column, and a refractive index (RI 2414) detector. The columns were heated to 40°C during analysis. The molecular weights were determined relative to poly(styrene) calibration standards from Scientific Polymer Products Inc. (ranging from 570 to 2,754,000 g mol^{-1}).

Thermal stability and glass transition temperature analysis. Polymer samples were analyzed by thermogravimetric analysis (TGA) to evaluate their thermal degradation before and after hydrogenation using Discovery 5500 TGA (TA Instruments). Polymer samples weighing between 5 – 10 mg were placed in platinum pans and they were analyzed from room temperature to 600°C under nitrogen flow at a heating rate of 10°C min^{-1}. Differential scanning calorimetry (DSC) was also done using Discovery 2500 from TA instruments.

Polymer samples were heated up from room temperature to 50°C to remove any thermal history, then cooled to -95°C, then heated up to 20°C again to determine T_g. The heating rate used for all three cycles was 10°C min^{-1}.

Rheology. Dynamic viscosity of polymer samples before and after hydrogenation was measured using the MCR302 rheometer from Anton Paar Instruments. Polymer samples were placed between parallel plates with a 1 mm gap, and the viscosity was measured at steady shear from 0.1 to 10 s^{-1} at room temperature.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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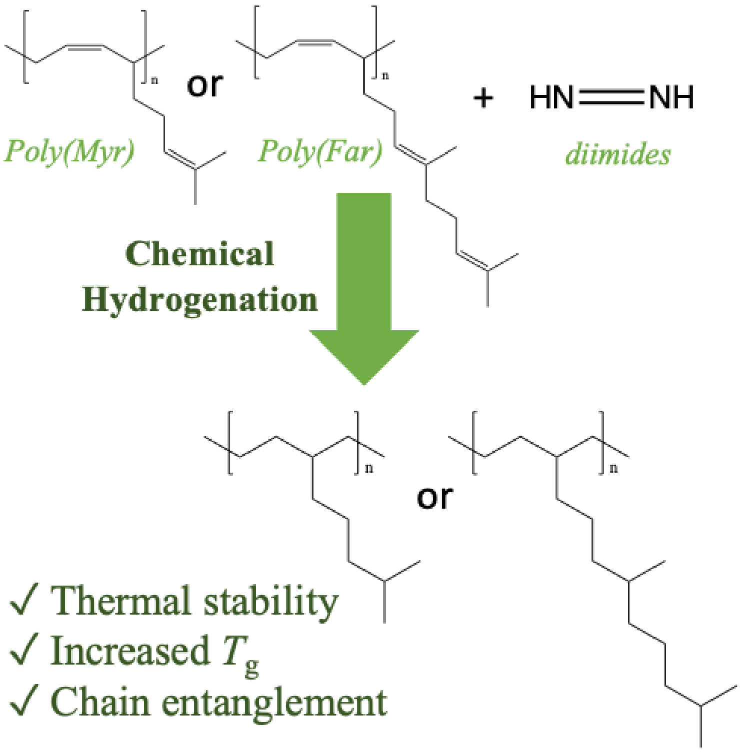
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