Polymerization of Biobased Farnesene in Miniemulsions by Nitroxide-Mediated Polymerization

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ABSTRACT: Biobased farnesene (Far) was polymerized by nitroxide-mediated polymerization in miniemulsions using two different alkoxyamine initiators, the SG1-based and succinimidyl-modified BlocBuilder (NHS-BB) and Dispolreg 007 (D7). Stable emulsions were observed after 30 h of reaction at 90°C, where NHS-BB-initiated systems resulted in smaller particles (∼300 nm) than using D7 (∼400 nm). Successful chain extension of the poly(Far) macroinitiators (24,500−39,700 g mol⁻¹) with styrene were achieved using 15 wt % surfactant relative to monomer concentration. Compartmentalization effects were not observed in these emulsions as the polymerization rate was still much slower compared to the bulk, even though Z-averaged particle sizes were around 300−400 nm. Finally, all biobased diblock copolymers were synthesized by chain-extending poly(Far) macroinitiators with isobornyl methacrylate (iBOMA), where the D7 initiator showed more effective chain extension (less unreacted macroinitiator) than NHS-BB.

INTRODUCTION

There is increasing incentive to create materials from biorenewable resources, as well as modifying the processes in creating these materials to become greener. One such industrially relevant material is poly(styrene-block-butadiene-block-styrene) (SBS), which is a triblock copolymer used as a thermoplastic elastomer (TPE).1 This material can be processed at high temperatures such as thermoplastics and also have elastic properties without being chemically cross-linked, therefore making it a versatile material that is used in automotive parts, rubber soles for shoes, and asphalt modifiers.2−4 The elastomeric segment is made of a poly-(diene) (i.e., butadiene or isoprene5) sandwiched between thermoplastic segments made of poly(styrene). Traditionally, SBS is synthesized via anionic polymerization, which is done in organic solvents, and butadiene and styrene, which are both petroleum-derived monomers.6 Moreover, anionic polymerization is intolerant to functional groups and cannot be done in water. Although there have been recently reported methods to produce butadiene and isoprene from biorenewable resources, these monomers are still volatile and nevertheless require pressurized vessels for polymerizations to occur.7,8

Controlled radical polymerization, or more properly known as reversible deactivation radical polymerization (RDRP), combines the specificity of anionic/living polymerization to control the molecular architecture of polymer chains and the simplicity of radical chemistry that is robust and less stringent reactions conditions in comparison.9−11 There are several types of RDRP: atom transfer radical polymerization,12 reversible addition−fragmentation transfer polymerization (RAFT),12 and nitroxide-mediated polymerization (NMP).13 All these methods are able to incorporate functional groups into a polymer chain largely without need for protecting group strategies, and therefore, the resulting materials can be easily tailored to improve compatibilization and performance.

An added advantage of RDRP is its ability to be done in dispersed aqueous media (e.g., emulsion, miniemulsion, or dispersion polymerization), as well as in solution and bulk.14 This reduces the use of volatile organic compounds (VOCs) and lowers emissions while maintaining low viscosity, which can be important for latex coatings.15 Furthermore, depending on the particle size, there can be compartmentalization of the radicals, which could help attain higher polymer molecular weight and/or rate of polymerization compared to in bulk.16−18 For RDRP, partitioning of the chain-transfer agent between the organic and aqueous phase is another significant factor to consider.19−21

The polymerization of butadiene and isoprene has been explored by RAFT22,23 and NMP in solution/bulk polymerization, and NMP generally resulted in poly(diienes) that were...
lower in dispersity.\textsuperscript{24} Emulsion polymerization of butadiene and isoprene were mainly done by RAFT, and the resulting diblock copolymers consisting of poly(isoprene-b-styrene) showed micro-phase separation, as in differential scanning calorimetry, an important property for thermoplastic elastomers.\textsuperscript{25,26} Triblock SBS polymer latex was successfully synthesized by RAFT in miniemulsions and showed comparable mechanical properties to conventional SBS made by anionic polymerization.\textsuperscript{27}

Initially, NMP in emulsion proved to be difficult using a TEMPO alkoxyamine initiator as the polymerization loci would occur in the large monomer droplets, causing coagulation and emulsion instability.\textsuperscript{28} Additionally, TEMPO is hydrophobic and requires high temperatures for activation (∼135 °C). A second-generation alkoxyamine, the SG1-based BlocBuilder, is water-soluble when neutralized and has a higher rate of activation and allowed for NMP in emulsions.\textsuperscript{29} Even more recently, a newly developed alkoxyamine, Dispolreg 007 (D7), that is tailored for nitroxide-mediated homopolymerization of methacrylates, has been applied successfully in miniemulsions as well.\textsuperscript{30–32}

In an effort to replace petroleum-derived materials, farnesene (Far) and myrcene (Myr) have been investigated as biosourced dienes that are similar to butadiene and isoprene (see Scheme 1).\textsuperscript{33,34} Myr has been polymerized by conventional free radical polymerization and RAFT,\textsuperscript{35,36} and Far has been polymerized by anionic polymerization and redox free-radical polymerization in emulsion.\textsuperscript{37–39} Both Myr and Far have also been successfully polymerized by NMP in bulk for making thermoplastic elastomers with functionalized methacrylates (e.g., glycidyl methacrylate (GMA) and isobornyl methacrylate (iBOMA)).\textsuperscript{39} Statistical copolymers were also made using either Myr or Far with GMA and iBOMA to incorporate functional groups throughout the poly(diene) chain. Poly(Far-stat-GMA) and poly(Far-b-GMA) were made with succinimidy-modified BlocBuilder (NHS-BB) and D7 initiators, which are both used to better control polymerization of methacrylates.\textsuperscript{41} NHS-BB requires a small amount of the controlling comonomer, while D7 can homopolymerize methacrylates. Furthermore, Myr and Far are less volatile than butadiene and isoprene and therefore can be polymerized at atmospheric pressure, further simplifying the process and avoiding the use of more costly pressurized reactors. However, due to the long side chains of Myr and Far increasing their hydrodynamic volumes, higher molecular weights are required in order for the polymer chains to entangle and provide sufficient elastomeric properties. The entanglement molecular weight (\(M_c\)) for poly(Myrr) and poly(Far) are 17,700 and ∼50,000 g mol\(^{-1}\), respectively, whereas \(M_c\) for poly(butadiene) and poly(isoprene) are 1800 and 5400 g mol\(^{-1}\), respectively.\textsuperscript{42,43}

In this study, biosourced Far was polymerized by NMP using both NHS-BB and D7 initiators in miniemulsions for the first time. The sustainable aspect of this investigation is threefold: using a biosourced monomer to replace petroleum-derived monomers, performing the polymerization in aqueous media, eliminating VOCs, as well as performing the polymerization at atmospheric pressure, given the lower volatility of Far. Additionally, the goal was to utilize the compartmentalization effect in miniemulsions to lead to higher-molecular weight poly(Far) segments and improve the elastomeric properties by far exceeding the entanglement molecular weight of the rubbery block segment, which is the general approach applied for most TPEs (i.e., 10−20,000 g mol\(^{-1}\) for poly(styrene) block and 40−80,000 g mol\(^{-1}\) for poly(butadiene) block for SBS).\textsuperscript{1} The chain-end activity of the poly(Far) macroinitiators was investigated by chain extension with St to synthesize poly(Far-b-St) and with iBOMA to synthesize a completely biosourced poly(Far-b-iBOMA). The kinetics of nitroxide-mediated polymerizations in miniemulsions were also compared between the NHS-BB and D7 initiators. Furthermore, surfactant loading, particle size, and compartmentalization were comprehensively studied to understand how these factors affected the chain-end fidelity and molecular weight of poly(Far).

### RESULTS AND DISCUSSION

#### Comparing Surfactant Loading in Miniemulsions

Initially, the first two miniemulsion experiments were done with 5 wt % surfactant relative to the monomer using both initiators: D7 and NHS-BB. While both experiments showed linear kinetics in the ln(1/(1 – X)) versus time plots after 30 h of reaction (shown in Figure S.1), the poly(Far) macroinitiators did not chain-extend when polymerized with styrene (St) afterward. The dispersed particles appeared to remain stable at the end of the reaction as the particles did not coagulate and settle to the bottom; however, 5 wt % surfactant

### Table 1. Table of Poly(Far) Properties from Miniemulsion Polymerization Summarizing Final Conversion, Final Molecular Weight, Dispersity, Z-Averaged Particle Size, and Polydispersity Index of Particles

| experiment | initiator | \(M_{\text{target}}\) (g mol\(^{-1}\)) | surfactant loading (wt %) | final conversion (%) | final \(M_n\) (g mol\(^{-1}\)) | final \(M_d\) | final Z-averaged particle size (nm) | poly-dispersity index |
|-----------|-----------|-------------------------------|---------------------------|---------------------|-----------------|-------------|---------------------------------|---------------------|
| Exp 1     | D7        | 50,000                        | 5                         | 27.7                | 22,800          | 2.31        | 425                             | 0.287               |
| Exp 2     | NHS-BB    | 50,000                        | 5                         | 39.7                | 49,300          | 2.23        | 298                             | 0.297               |
| Exp 3     | D7        | 50,000                        | 15                        | 27.7                | 24,500          | 2.22        | 362                             | 0.386               |
| Exp 4     | D7        | 30,000                        | 15                        | 29.4                | 13,900          | 2.38        | 310                             | 0.286               |
| Exp 5     | NHS-BB    | 50,000                        | 15                        | 32.7                | 39,700          | 1.67        | 336                             | 0.286               |

*Final measurements were taken after 30 h of reaction.*
was not sufficient to maintain active chain ends of the polymer chains as the molecular weight distributions did not shift to higher molecular weights after the intended chain extension with St (Figure S.2). The final conversion of these two experiments initiated by D7 and NHS-BB were 28 and 40%, respectively. The final properties of all poly(Far) made by miniemulsions in this study are summarized in Table 1.

The remaining miniemulsion experiments were done with 15 wt % surfactant using different initiators and different target molecular weights ($M_{n,\text{target}}$). First, the experiments done using the D7 initiator and 5 versus 15 wt % surfactant (Exp 1 vs Exp 3) were compared. The $\ln(1/(1 - X))$ with time followed a linear trend in both cases, as seen in Figure 1, which shows good simultaneous chain growth for most polymer chains. The rates of polymerization in both cases were also the same, so it was not affected by increasing the surfactant loading. Similarly, the molecular weight and dispersity versus conversion plots were not affected by surfactant loading, as shown in Figure 2. Molecular weights also increased linearly with conversion, further indicating steady growth, suggestive of a controlled polymerization. Dispersities remained high, typically ~2, likely due to the slow rate of propagation and initiation at a relatively low polymerization temperature of 90 °C. However, polymer chains continued to grow, and dispersity decreased at $X > 10\%$, as seen in Figure 2b, so the high dispersity can also be due to the polymerization being in the early stages with the low conversions reported. Perhaps, dispersity could continue to decrease as the conversion increases (until irreversible termination occurs).

The experimental $M_n$ values were consistently higher than the theoretical $M_n$ values, which is expected as D7 has a slower rate of activation ($k_{\text{act}}$) compared to TEMPO and SG1-based initiators and is known to create longer polymer chains due to fewer alkoxyamines initiating chain growth from the beginning.30,31 This also explains the higher dispersity values of ~2.3, although they are considerably higher than previously reported for polymerization of Far using D7 in bulk.41 Despite the high dispersity, which should indicate a significant concentration of inactive chain ends, poly(Far) synthesized using 15 wt % surfactant successfully chain-extended with styrene, as opposed to poly(Far) made using 5 wt % surfactant. In Figure 3, the molecular weight distributions (MWDs) shifted to the right as the molecular weights increased with reaction time after 120 min of chain extension from 24,500 to 35,100 g mol$^{-1}$. The resulting poly(Far-b-St) diblock copolymer had a dispersity of 2.20. Final copolymer composition along with other block copolymer properties are summarized in Table 2. The kinetics of the two miniemulsions were very similar, but increasing the surfactant loading maintained more active chain ends. This will be discussed more fully in a later section.

All the miniemulsion experiments were analyzed after 30 h of reaction and achieved relatively low conversions of ~30–40%. One miniemulsion study was done with 15 wt % surfactant using the D7 initiator, and the reaction time was extended to 72 h. The conversion achieved was not much higher and the final $M_n$ and $D$ were 32,300 g mol$^{-1}$ and 2.19 (Figure S.3), respectively. Therefore, the reaction time was...
chosen to be 30 h in this study for convenience. However, the 72 h emulsion reaction remained visibly stable without coagulation and chain extension with St was successful, indicating high chain-end fidelity (Figure S.4). The low conversions from the 30 h reaction were also ideal as most polymer chain ends would remain active for chain extension, with the long-term goal of deriving high-molecular-weight block copolymers.

Comparing Target Molecular Weights in Miniemulsions. The effect of changing $M_{n,target}$ of the farnesene homopolymerizations in miniemulsions was studied as well using the D7 alkoxyamine. By varying $M_{n,target}$, it effectively varies the monomer-to-nitroxide ratio in the system. The $\ln(1/(1-X))$ versus time plots of the miniemulsions done with $M_{n,target} = 30,000$ versus 50,000 g mol$^{-1}$ (Exp 3 vs Exp 4) are shown in Figure 4. With $M_{n,target} = 30,000$ g mol$^{-1}$, the plot showed linear kinetics in the range studied, which indicate that most polymer chains were growing simultaneously at the same rate, similar to the previous experiment with $M_{n,target} = 50,000$ g mol$^{-1}$. The molecular weight also increased linearly with conversion, as seen in Figure 5, as the final molecular weight was 13,900 g mol$^{-1}$ and the final $D = 2.38$.

The experimental $M_n$ for $M_{n,target} = 30,000$ g mol$^{-1}$ was also significantly higher than the theoretical $M_n$ but not as significant compared to $M_{n,target} = 50,000$ g mol$^{-1}$. Furthermore, the rate of polymerization for $M_{n,target} = 30,000$ was faster than $M_{n,target} = 50,000$, as seen in Figure 4, although in bulk or solution polymerization, the rate of polymerization would be slower when the target molecular weight is lower. This is due to the lower monomer-to-nitroxide ratio, which means a higher concentration of nitroxides to deactivate the propagating polymer chains, thereby decreasing the rate of polymerization. However, the faster rate of polymerization is likely due to the smaller particle size in the emulsion, which is discussed in a later section. Additionally, the dispersity was not affected by the change in $M_{n,target}$ even though higher concentration of nitroxides should maintain more active chain ends and effectively lower the dispersity.

The chain-end activity of poly(Far) made with $M_{n,target} = 30,000$ g mol$^{-1}$ was investigated by doing a chain extension with styrene. The MWD is shown in Figure 6, and an increase in molecular weight is seen as the distribution shifted to the right with reaction time. The molecular weight increased from 13,900 to 28,900 g mol$^{-1}$, indicating most of the polymer chains remained active. There is also a clear disappearance of the slightly low molecular weight shoulder from 0 to 120 min, therefore decreasing the $D$ from 2.38 to 2.22. Block copolymer properties are summarized in Table 2.

| Chain extension | Macroinitiator alkoxamine | poly(Far) macroinitiator $M_n$ (g mol$^{-1}$) | $f_{St}$ | $f_{iBOMA}$ | final $M_n$ (g mol$^{-1}$) | final $D$ | $P_{pol}$ estimated by NMR |
|----------------|---------------------------|---------------------------------------------|--------|-----------|--------------------------|--------|---------------------------|
| CX-1           | D7                        | 24,500                                     | 1.0    | 0         | 35,100                   | 2.20   | 0.38                      |
| CX-2           | D7                        | 13,990                                     | 1.0    | 0         | 28,900                   | 2.22   | 0.27                      |
| CX-3           | NHS-BB                    | 39,700                                     | 1.0    | 0         | 70,400                   | 2.15   | 0.31                      |
| CX-4           | D7                        | 24,500                                     | 0      | 1.0       | 30,645                   | 3.19   | 0.30                      |
| CX-5           | NHS-BB                    | 39,700                                     | 0.1    | 0.9       | 44,300                   | 2.24   | N/A                       |

“Final copolymer compositions were estimated by $^1$H NMR. $^b$Final $M_n$ of the diblock copolymers were estimated by GPC and are relative values using PMMA standards; therefore, copolymer compositions were more accurately estimated using $^1$H NMR.”

Figure 4. Linearized conversion vs time plot for the homopolymerization of farnesene in miniemulsions using D7 at 90 °C in 20 wt % monomer with 15 wt % surfactant and $M_{n,target} = 30,000$ and 50,000 g mol$^{-1}$.

Figure 5. (a) Molecular weight and (b) dispersity vs conversion plots for the homopolymerization of farnesene in miniemulsions using D7 at 90 °C in 20 wt % monomer with 15 wt % surfactant and $M_{n,target} = 30,000$ and 50,000 g mol$^{-1}$. The solid line in (a) represents the theoretical $M_n$ for $M_{n,target} = 50,000$ g mol$^{-1}$, and the dashed line represents the theoretical $M_n$ for $M_{n,target} = 30,000$ g mol$^{-1}$.
Figure 6. MWD of poly(Far-b-St) after 120 min of chain extension of poly(Far) made with 15 wt % surfactant and \(M_{\text{target}} = 30,000 \text{ g mol}^{-1}\).

Figure 7. Z-averaged particle size of miniemulsions for homopolymerizations of farnesene in 5 and 15 wt % surfactant using D7 and NHS-BB initiators at 90 °C with a \(M_{\text{target}} = 50,000 \text{ g mol}^{-1}\).

Scheme 2. Diagram of Conventional Emulsion Polymerization (Left) vs Miniemulsion Polymerization (Right)\(^{a}\)

\(^{a}\)Droplets are stabilized by surfactants, and the red arrows in the right show mass transfer of monomer from monomer reservoir into the aqueous phase and then into the micelles for polymerization to occur. Initiator is represented by \(I^*\) either in the aqueous or oil phase.

DLS analysis, there was evidence of a low fraction of larger droplets (102 nm) likely due to the high hydrophobicity of farnesene, but the majority of the droplets were \(~10^3\) nm (Figures S.5 and S.6). The emulsions appeared to remain stable without obvious visible coagulation (even after 72 h of reaction). At above the critical micelle concentration (CMC) of DOWFAX 8390 (3 mM),\(^{46}\) there is likely the presence of small micelle-sized (<100 nm) droplets even though it was not observed from DLS analysis. There is also likely excess surfactant at the interface. The Z-averaged particle sizes for the homopolymerizations with \(M_{\text{target}} = 50,000 \text{ g mol}^{-1}\) are shown in Figure 7. The particle sizes mostly remained constant and slightly decreased after 30 h. This was more evident with NHS-BB experiments, which could indicate some homogeneous nucleation of new particles in the aqueous phase.

The original intent on increasing surfactant concentration was to decrease particle size, which would help with maintaining active chain ends and perhaps lead to compartmentalization, therefore enabling higher molecular weights to be achieved. It is evident in Figure 7 that surfactant loading did not quite have an effect on the particle size and polymerization rate, and final \(M_n\) also did not increase as discussed previously. However, using NHS-BB initiator led to smaller particles than using D7, which led to faster rates of polymerization and higher final \(M_n\). Final particle sizes and polydispersity index are summarized in Table 2.

Increasing surfactant loading from 5 to 15 wt % did not significantly decrease the Z-averaged particle size for both D7 and NHS-BB miniemulsions, but as seen previously, it improved chain-end fidelity of the poly(Far) macroinitiators for chain extension. Looking at the particle size distributions more closely, specifically the volume-averaged distributions, there was a higher percentage of large droplets (103 nm in size) nearing the end of the reaction when there was only 5 wt % surfactant compared to 15 wt % surfactant (Figure 8). Although the difference is not obvious, there seems to be a smaller left-hand side shoulder at higher surfactant concentration.

Nitroxides partition between the aqueous and oil phases in an equilibrium and continuously enter and exit the particles.\(^{20}\) When there is a distribution of particle sizes, nitroxides are much more likely to enter smaller micron-sized droplets than larger droplets due to the higher surface area-to-volume ratio. Therefore, there is a lower concentration of nitroxides in the larger droplets such that the likelihood of irreversible termination is increased when there is only 5 wt % surfactant present, which perhaps lowered the overall chain-end fidelity in the system. However, a faster rate of nitroxide entry also means a faster rate of nitroxide exit. Nonetheless, it is uncertain what phenomena caused increased livingness at increased surfactant concentration, and more studies would need to be done to conclusively determine the cause for better chain end fidelity at such conditions.

Although surfactant concentration did not have a significant effect on particle size, alkoxamine concentration did. In the
miniemulsion using D7 and $M_{\text{target}} = 30,000$ g mol$^{-1}$, the particle size was consistently smaller than the miniemulsion with $M_{\text{target}} = 50,000$ g mol$^{-1}$ and it was similar to the particle size achieved using NHS-BB. In Figure 9, the particle size with conversion is plotted for both experiments using different $M_{\text{target}}$. Because the particle size was smaller with $M_{\text{target}}$ of 30,000 g mol$^{-1}$, the rate of polymerization was more rapid as a result, as seen earlier in Figure 4.

**Compartmentalization Versus Confined Space Effects.** It was estimated that for NMP in dispersed systems, compartmentalization occurs when particles are <110 nm in diameter, and a confined space effect was observed when particles are <60 nm diameter.17 Compartmentalization is observed when particle size is in a range where each particle has an average radical concentration of 0.5, where the propagating radicals are segregated from one another and irreversible termination is minimized. Therefore, the rate of polymerization is increased, leading to higher conversions and degrees of polymerization. However, any type of RDRP and specifically NMP, the partition of nitroxides between the aqueous and the oil phase is also very important. When the particle size is further decreased, then the rate at which nitroxides enter the particle is much faster and more effectively deactivates the propagating radicals, such that rate of polymerization is decreased.20 In this case, the confined space effect is observed when the polymerization rate is slower than that in bulk.

Once again, it is interesting that increasing the surfactant concentration had a minimal effect on $Z$-averaged particle size unlike what is observed in conventional free radical miniemulsions.47 This was supported by the polymerization rates and $M_n$ versus conversion results that remained the same after increasing surfactant concentration. In a miniemulsion study for NMP of styrene using TEMPO, where surfactant concentration ranged from below to above CMC, the polymerization rate and $M_n$ also remained the same.48 The initial particle size ranged from 40–100 nm by decreasing the surfactant concentration from 15 to 1.25 mM. This was justified by the fact that the average number of radicals per particle is much lower than 0.5 due to the high concentration of nitroxides that are present per particle. Therefore, the rate of polymerization is dominated by the deactivation of propagating chains from the nitroxides, such that even with smaller particles, the rate did not increase, and compartmentalization was not achieved. Even with particle sizes up to 180 nm, compartmentalization was not observed.50 Similarly, much larger particle size was required for compartmentalization in particles with low macroinitiator concentration.50 Further-
more, it has been simulated that with a lower \( k_{act} \), which is the case for the D7 initiator, larger particle sizes are required for compartmentalization to occur.\(^{20} \) This is because radical concentration is decreased at lower \( k_{act} \).

Hence, in nitroxide-mediated polymerizations combined with a lower \( k_{act} \), the particle size would have to be larger to increase the average radical concentration per particle to 0.5 and allow for compartmentalization. Although the \( Z \)-average particle sizes in this study were ~300–400 nm, the number-averaged particle sizes showed that the majority of the particles were ~150–200 nm in size. However, the rate of polymerization was still much slower than compared to bulk, (\( X_{\text{bulk}} = 85\% \) after 4 h\(^{41} \) vs \( X_{\miniemulsion} = 28\% \) after 30 h both using D7 initiator). Similar to previous studies, not only is compartmentalization not observed but also the confined space effect seems to be in effect even with relatively large particle sizes, partly due to the slower activation of D7 and the presence of nitroxides in these miniemulsions.

**Molecular Weight Distributions of Poly(Far) Macro-initiators.** The molecular weight distributions (MWDs) of the miniemulsion homopolymerizations of Far done with \( M_{n,\text{target}} = 50,000 \text{ g mol}^{-1} \) are shown in Figure 10. As discussed earlier, the \( D \) of the experiments done with the D7 initiator are high (~2.3). Looking at the MWDs in Figure 10a,b, there is a slight low molecular weight shoulder, which is expected as the activation of D7 is slow and not all polymer chains were initiated in the beginning of the polymerization, leading to shorter chains that were formed later. The low molecular weight shoulder was also seen in homopolymerization of Far using D7 in bulk.\(^{41} \) Moreover, comparing to MWDs of the experiments done with NHS-BB in Figure 10c,d, they are narrower and more monomodal, which indicate all polymer chains were initiated simultaneously.

Figure 11 is the MWD of the miniemulsion homopolymerization of Far done with \( M_{n,\text{target}} = 30,000 \text{ g mol}^{-1} \). The dispersities are slightly higher compared to \( M_{n,\text{target}} = 50,000 \text{ g mol}^{-1} \) (2.38 vs 2.22, respectively), and this is evident from the more apparent low molecular weight shoulder in the MWD. Although a lower \( M_{n,\text{target}} \) should mean better control of polymerization (as there is a higher concentration of nitroxides), in this case it is likely due to the delay in initiation of polymer chains that is more apparent at a higher concentration of D7. As a result, there is a higher number of short polymer chains being formed.

**All Biosourced Diblock Copolymers.** It has been shown in this study that farnesene, a biosourced monomer, can be polymerized in dispersed aqueous media by nitroxide-mediated polymerization. These poly(Far) materials were chain-extended earlier with styrene to make diblock copolymers (somewhat resembling SBS materials which are triblock copolymers), and now they are chain-extended with another biosourced monomer, iBOMA, to make an virtually all-biosourced and more sustainable material compared to SBS. Poly(Far) made with both D7 and NHS-BB initiators, 15 wt %
surfactant, and $M_{n,\text{target}} = 50,000 \text{ g mol}^{-1}$ was used as the macroinitiator (poly(Far)-D7 and poly(Far)-NHS-BB, respectively).

Poly(Far)-NHS-BB was chain-extended with an iBOMA/Far mixture (10 mol % Far relative to iBOMA) as NHS-BB requires a small amount of the controlling comonomer to control the polymerization of a methacrylate.\(^3\) Dienes such as isoprene, myrcene, and farnesene have been shown to be effective controlling comonomers in nitroxide-mediated polymerizations of methacrylates.\(^24,39,41\) The resulting poly-(Far-b-iBOMA-ran-Far) was essentially a diblock copolymer, where the molecular weight increased from 38,900 to 44,300 g mol\(^{-1}\) and $D$ increased from 1.83 to 2.24. The MWDs of the chain extension is shown in Figure 12. As seen in the MWD, high $D$ was observed, but chain extension did continue to proceed. As seen in Figure 13, the initial MWD had a low molecular weight shoulder. Perhaps the chain extension started with very fast polymerization of iBOMA, and only a portion of the macroinitiators were initiated. However, despite the high $D$, the polymer chains continued to grow and eventually $D$ decreased with the disappearance of the low molecular weight shoulder. In fact, poly(Far)-D7 showed better chain extension compared to poly(Far)-NHS-BB as expected as there was a significant increase in molecular weight in the same reaction time without controlling comonomer despite the high dispersity. Furthermore, chain extension of poly(Far) made with D7 after 72 h of reaction was also successful, as shown in Figure S.7.

### CONCLUSIONS

Farnesene, a biobased diene monomer, was successfully polymerized for the first time in miniemulsions via nitroxide-mediated polymerization. Although there was evidence of large oil droplets present, stable emulsions were achieved after 30 h, reaching a final conversion of $\sim$30–40%. The resulting poly(Far) made with both D7 and NHS-BB initiators had active chain ends when 15 wt % surfactant was added to the system. This was attributed to a higher fraction of micron-sized droplets present in the emulsion. Particle size had an effect on the rates of polymerization, but they were still slow compared to rates in bulk, and so compartmentalization was still not achieved. Therefore, the molecular weights of poly(Far) homopolymers did not exceed the entanglement molecular weight to create sufficiently elastomeric materials. However, entirely biosourced diblock copolymers were synthesized by

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**Figure 12.** MWD of poly(Far-b-iBOMA-ran-Far) after 90 min of chain extension of poly(Far) made with NHS-BB, 15 wt % surfactant, and $M_{n,\text{target}} = 50,000 \text{ g mol}^{-1}$.

**Figure 13.** MWD of poly(Far-b-iBOMA) after 90 min of chain extension of poly(Far) made with D7, 15 wt % surfactant, and $M_{n,\text{target}} = 50,000 \text{ g mol}^{-1}$.

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The shift in molecular weight was not significant and $D$ increased slightly, indicating some irreversible termination in the chain extension with iBOMA even with 10 mol % of Far as the controlling comonomer. This is consistent with poly(Far) made in bulk with NHS-BB when chain-extended with glycidyl methacrylate and 10 mol % Far.\(^4\)

Next, poly(Far)-D7 was also chain-extended with iBOMA for comparison, and no controlling comonomer was added with this macroinitiator as D7 does not require a controlling comonomer. The final poly(Far-b-iBOMA) polymer properties can be found in Table 3. The molecular weight increased from 15,400 to 30,600 g mol\(^{-1}\), $D$ decreased from 4.90 to 3.19, and the shift in MWD is seen in Figure 13. It is unclear why the initial $D$ was so high as the poly(Far)-D7 macroinitiator had a $D$ of 2.08. This chain extension was done twice and similar (Based on Monomer Content)

| experiment | initiator | target $M_n$ (g mol\(^{-1}\))\(^a\) | surfactant loading (wt %)\(^b\) | $m_{\text{initiator}}$ (g) | $m_{\text{exo}}$ (g) | $m_{\text{costabilizer}}$ (g) | $m_{\text{water}}$ (g) | $m_{\text{surfactant}}$ (g) |
|------------|-----------|-------------------------------|-----------------------------|-----------------|-----------------|----------------------|-----------------|-----------------|
| Exp 1      | D7        | 50000                         | 5                           | 0.10            | 14.77           | 0.12                 | 59.09           | 0.74            |
| Exp 2      | NHS-BB    | 50000                         | 5                           | 0.10            | 13.12           | 0.10                 | 52.49           | 0.66            |
| Exp 3      | D7        | 50000                         | 15                          | 0.10            | 14.77           | 0.12                 | 59.09           | 2.22            |
| Exp 4      | D7        | 30000                         | 15                          | 0.10            | 8.86            | 0.07                 | 35.45           | 1.33            |
| Exp 5      | NHS-BB    | 50000                         | 15                          | 0.10            | 13.12           | 0.10                 | 52.49           | 1.97            |

\(^a\)Target $M_n$ is determined based on the initial monomer-to-alkoxyamine concentration ratio. \(^b\)Surfactant loading amounts are relative to monomer amounts. \(^c\)Costabilizer amounts were added at 0.8 wt % relative to the monomer.
EXPERIMENTAL METHODS

Materials. Trans-β-farnesene, known as Biofene (Far, ≥95%) was obtained from Amyris. Styrene (St, ≥99%) monomer was purchased from Millipore Sigma. Isobornyl methacrylate (VISIONMER Terra iBOMA) was obtained from Evonik. Monomers were purified using 1.0 g of aluminum oxide (basic Al₂O₃, activated, Brockmann I) and 0.05 g of calcium hydride (CaH₂, 99%) per 50 mL of the monomer, which were used as purchased from Millipore Sigma. 2-((tert-Butyl)[(1-diethoxy-phosphoryl)-2,2-dimethylpropyl]amino]-oxy)-2-methylpropionic acid or BlocBuilder was kindly provided by Arkema and modified with an N-succinimidyl ester group by following a method used in literature to synthesize 2-methyl-2-[[N-tert-butyl-N-(1-diethoxphosphoryl-2,2-dimethylpropyl)-amino]-N-propionylxosuccinimide or NHS-BlocBuilder (NHS-BB). 44 3-(((2-Cyanopropan-2-yl)-oxy) (cyclohexyl)amino)-2,2-dimethyl-3-phenylpropenitrile, Dispolreg 007 (D7) was synthesized according to the method described by Ballard et al. 30 Toluene (≥99%), methanol (MeOH, ≥99%), and tetrahydrofuran (THF, 99.9% HPLC grade) were obtained from Fisher Scientific and used as received. Deuterated chloroform (CDCl₃, 99.9% D) was purchased from Cambridge Isotope Laboratories, USA, and used as received. DOWFAX 8390 was purchased for The Dow Chemical Company and used as purchased. Hexadecane (99%) was used as purchased from Millipore Sigma.

Homopolymerization of Farnesene in Miniemulsions. The miniemulsions were done with 20 wt % monomer in water (20% solids content) purified by reverse osmosis (RO) (see Table 3 for miniemulsion recipes). DOWFAX 8390 surfactant was dissolved in water and stirred for 10 min in a 100 mL glass beaker. The Far monomer, initiator, and hexadecane (used as the costabilizer) were dissolved and stirred separately in a 20 mL vial for 10 min. The oil phase was added to the aqueous phase and stirred with a magnetic stir bar for another 15 min before being sonicated for 10 min at 70% amplitude and 0.50 duty cycle using the Hielshcer sonicator UP200S. The milky emulsified mixture was added into a 100 mL three-neck round-bottom flask and purged with nitrogen for 30 min before being heated up to 90 °C with stirring for polymerization to occur for 30 h. A reflux condenser was attached to the reactor to ensure all volatile components remain in the reactor. Samples were taken intermittently for gravimetric conversion calculation and molecular weight analysis.

Chain Extension of the Poly(Far) Macroinitiator. Purified poly(Far) macroinitiators (~0.5–0.75 g) were dissolved in toluene with either St and/or iBOMA monomer added to the solution (50 wt % monomer and macroinitiator in toluene). The reaction mixture was added to a 10 mL three-neck round-bottom flask and purged with nitrogen for 30 min with stirring. The chain-extension reactions were done at 120 °C for 90–120 min with a reflux condenser attached. Similarly, samples were taken intermittently for gravimetric or 1H NMR conversion calculation and molecular weight analysis.

Polymer Characterization. Monomer conversion was determined gravimetrically. The samples (~3 mL) taken from the miniemulsions were weighed and dried under air for 24 h to remove most of the water and then placed in the vacuum oven at room temperature to ensure residual water was removed. Afterward, the polymer/monomer mixture was redissolved again in small amounts of toluene (~2 mL) and precipitated in excess methanol. The polymer samples were then dried under air for several hours before being dried in the vacuum oven completely at room temperature overnight. The final dried polymers were weighed and used to determine the conversion. The conversion calculations of the chain-extension reactions with St and iBOMA were done by 1H NMR (see Figures S.8 and S.9 in Supporting Information). Copolymer compositions were analyzed by 1H NMR as well (Figure S.10).

Number-average molecular weight (Mₙ) and dispersity (D = Mₙ/M̅) of polymer samples were measured 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 Styrage HR columns (HR1 with a molecular weight measurement range of 10² × 10⁵ g mol⁻¹, HR2 with a molecular weight measurement range of 5 × 10⁵ to 2 × 10⁶ g mol⁻¹, and HR4 with a molecular weight measurement range of 5 × 10⁶ to 6 × 10⁷ 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(methyl methacrylate) (PMMA) calibration standards from Varian Inc. (ranging from 875 to 1,677,000 g mol⁻¹). The reported molecular weights were all relative to the PMMA standards and not adjusted with Mark–Houwink parameters.

Particle Size Characterization. Particle size distributions of the miniemulsion experiments were measured by dynamic light scattering (DLS) using the Malvern Zetasizer Nano-ZS. The instrument has a 4 mW He–Ne laser at 633 nm and an avalanche photodiode detector. The original dispersed samples were further diluted with water (0.01–1000 mg mL⁻¹) for analysis. Samples were analyzed with a measurement angle of 173° at 25 °C, and each sample measurement was repeated five times.
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Notes
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