Review: Reversible Deactivation Radical Polymerization of Bio-based Dienes

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Abstract

Dienes such as isoprene and butadiene have long been used to impart rubbery character into polymeric materials, often by homopolymerization as blends with stiffer polymers or by copolymerization with other monomers. Examples of such products are styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR) and the triblock copolymer families such as the various poly(styrene)-*b*-poly(isoprene)-*b*-poly(styrene) (SIS) thermoplastic elastomers (TPEs). Isoprene and butadiene are derived from petroleum-based resources and like other products, emphasis on their production has shifted towards using renewable resources. Consequently, bio-based monomers such as myrcene and farnesene have been targeted as replacements for petroleum-based dienes in polymeric products and have been polymerized to make polymers with controlled microstructures via traditional ionic polymerizations. More recently, alternatives to living polymerization such as reversible deactivation radical polymerization (RDRP) offer the advantages of conventional radical polymerization without the stringent requirements required of living polymerizations. The application of bio-based dienes to RDRP has only recently started to emerge and this review will summarize the current state of applying RDRP to make polymeric materials with controlled microstructure and chain length, as well as an outlook on potential applications of bio-based dienes.

Keywords

Bio-based dienes, reversible deactivation radical polymerization, thermoplastic elastomers

1 Introduction

Dienes are conjugated hydrocarbons that contain two fixed double bonds (alkenes) and are typically byproducts, along with other olefins like ethylene and propylene, formed from steam cracking of crude oil [1]. These olefins are an integral part of the petrochemical industry as they can easily polymerize due to the double bond and enable production of polymeric materials at a large scale. Butadiene and isoprene are both dienes produced from the steam cracking process and are polymerized to make poly(diene) elastomers with viscoelastic properties and low glass transition temperature (T_g), -100ºC and -70 ºC for poly(butadiene) and poly(isoprene), respectively [2]. To improve the versatility and mechanical strength of these poly(diene) materials, they are often blended with thermoplastic polymers or copolymerized with styrene or acrylonitrile to make styrene-butadiene rubber (SBR) or nitrile-butadiene rubber (NBR) [3-5]. These added-value engineered materials make them suitable for automotive parts, disposable gloves, footwear, asphalt modifiers, and sealants [6-9].

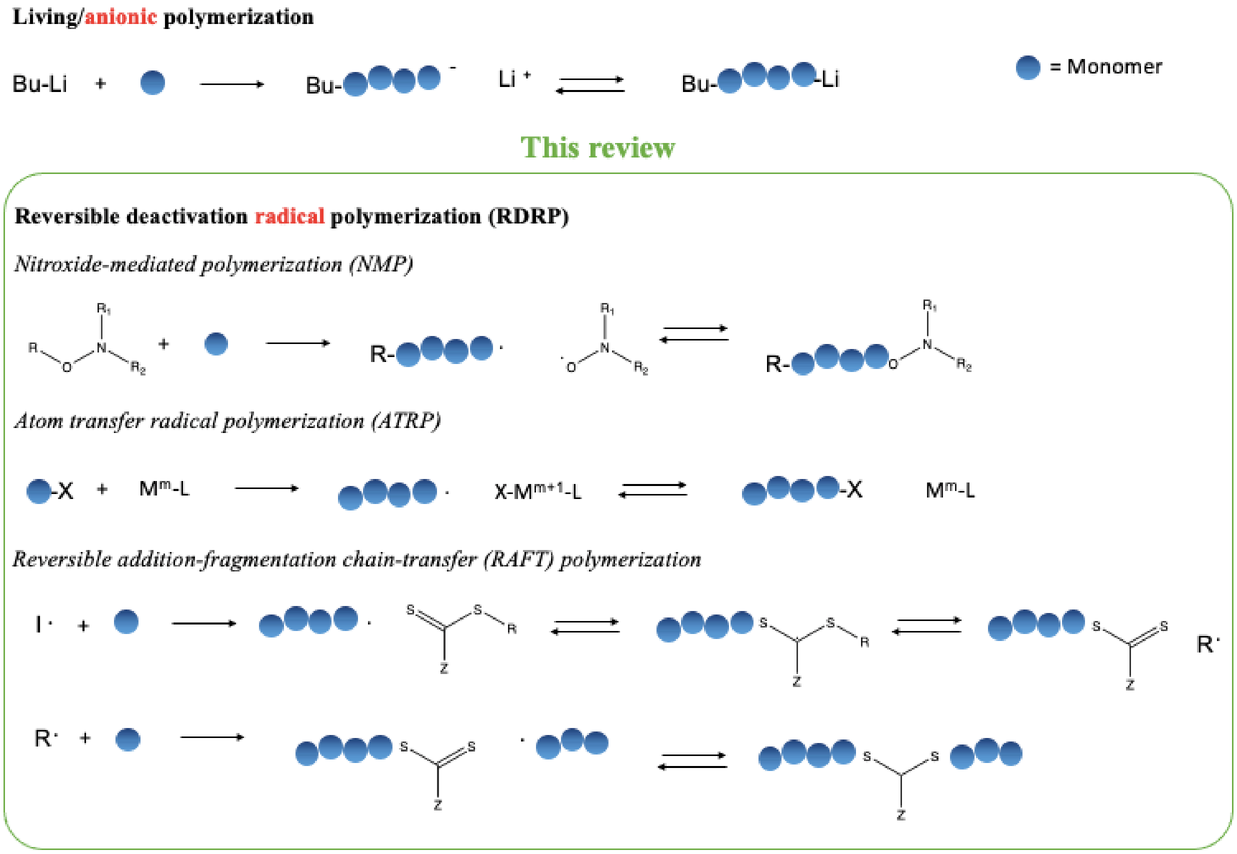
While SBR and NBR can be synthesized by conventional radical polymerization [10, 11], which is straightforward and inexpensive, triblock copolymers like styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS) are synthesized by anionic polymerization [12, 13]. Living or ionic polymerization proceeds through a propagating site that is ionic in nature – it may be an anion or cation, depending on the initiator used. Employing typically strong bases (e.g. organo-lithium compounds like *sec*-butyl lithium), which ensure almost instantaneous initiation, and copiously purified reagents and air-free transfers, propagation ensues in a linear fashion (degree of polymerization linear with monomer conversion) without any chain transfer or termination, resulting in "living" polymers [14, 15]. Ionic polymerizations can proficiently make polymers with narrow molecular weight distributions and precise microstructure. In fact, SBS, industrially known as Kraton^{TM}, is commercially produced by ionic polymerization [16].

However, due to the extremely high reactivity and sensitivity of the ionic groups to impurities, rigorous conditions must be met to achieve the desired polymer microstructure. It was long a goal to combine the control of microstructure obtained by living polymerizations and the simplicity and tolerance to impurities encountered with conventional radical polymerization. This was finally achieved with several landmark publications first reported in the early 1990s and generically referred to as controlled radical polymerization, more accurately termed by IUPAC as reversible deactivation radical polymerization (RDRP) [17]. In contrast to conventional free radical polymerization, concentration of radicals is controlled through a persistent radical effect (PRE), accomplished using reversible termination or chain transfer. Like living polymerizations, monomer can be added to an active propagating radical, approaching the linear degree of polymerization with monomer conversion and low dispersity, along with the ability to make block copolymers, as it would be in truly living polymerizations. Dispersity is much lower generally compared to conventional radical polymerizations but often are not as low as for living polymerizations, due to the inevitable irreversible radical associated reactions that are suppressed but not entirely eliminated.

Recently, great attention has been directed to the concept of sustainable development. The intensive use of non-renewable resources such as oil has a profound impact on the environment. This is an acute problem for the polymer industry as many commodity polymers and plastics are almost entirely based on fossil sources and 4% of the world's consumption of fossil fuels are used for plastics [18, 19]. Further, much publicity has focused on the effect on non-degradable plastics in the marine environment. Therefore, much research is increasingly working towards new ways to produce bio-based materials and which are readily biodegradable – this review will focus on the former. Several routes exist to create bio-based polymers. One method involves direct formation of polymers within the producing organisms (e.g. poly(hydroxyalkanoates) from microorganisms, algae, or plants), while others are manufactured from bio-based monomers, such as lactides or bio-based dienes [20, 21].

As alluded to earlier, butadiene, isoprene, and styrene have long been used to produce polymers and copolymers with interesting properties such as SBR and natural rubber, which are known for excellent abrasion resistance and better aging characteristics, and consequently are used in tires and in footwear [6, 8, 22]. It has been found that it is possible to obtain bio-based terpene-derived monomers such as myrcene and farnesene, that are able to produce polymers and copolymers with similar properties to the conventional petroleum-derived polymers. These terpene-based polymers have been shown to have comparable elastomeric properties [23]. Poly(farnesene) exhibits low T_g (-85ºC) and has relatively low viscosity but a higher entanglement molecular weight (M_e~50,000 g mol^{-1}) when compared to poly(butadiene) and poly(isoprene) (M_e ~ 6,000 and 13,000 g mol^{-1}, respectively) at the same molecular weight [24]. Poly(farnesene) finds uses in pressure sensitive adhesives, as an optically clear adhesive layer for touch screens on electronic devices, or can be converted to polyols to make polyurethanes [25-28]. Poly(myrcene) similarly has a low T_g (-73ºC) also with a higher entanglement molecular weight (M_e = 17,700 g mol^{-1}), and therefore finds similar applications as adhesives and thermoplastic elastomers [29-33]. However, all these polymers are either synthesized by anionic polymerization or conventional radical polymerization. Alternatively, there have even been some examples of catalytic/coordinative polymerization of myrcene and isoprene with high stereoselectivity for 1,4-*cis* or *trans* conformation [34-38].

Current advances have shown that these bio-based poly(diene) materials can be made by RDRP [39-44], which further simplifies the synthesis while still maintaining the precise molecular architecture of block copolymers for their applications. This review will introduce the different methods used currently while focusing particularly on three bio-based dienes: myrcene, farnesene and isoprene. Specifically, the polymerization of bio-based dienes using the various RDRP methods will be reviewed: nitroxide-mediated polymerization (NMP), atom-transfer radical polymerization (ATRP), and reversible addition-fragmentation chain-transfer polymerization (RAFT) to achieve desirable (co)polymers with the requisite rubbery character. The general mechanisms of RDRP methods focused in this review are shown in Scheme 1. But first, the synthesis of the precursors for these materials will be briefly examined.

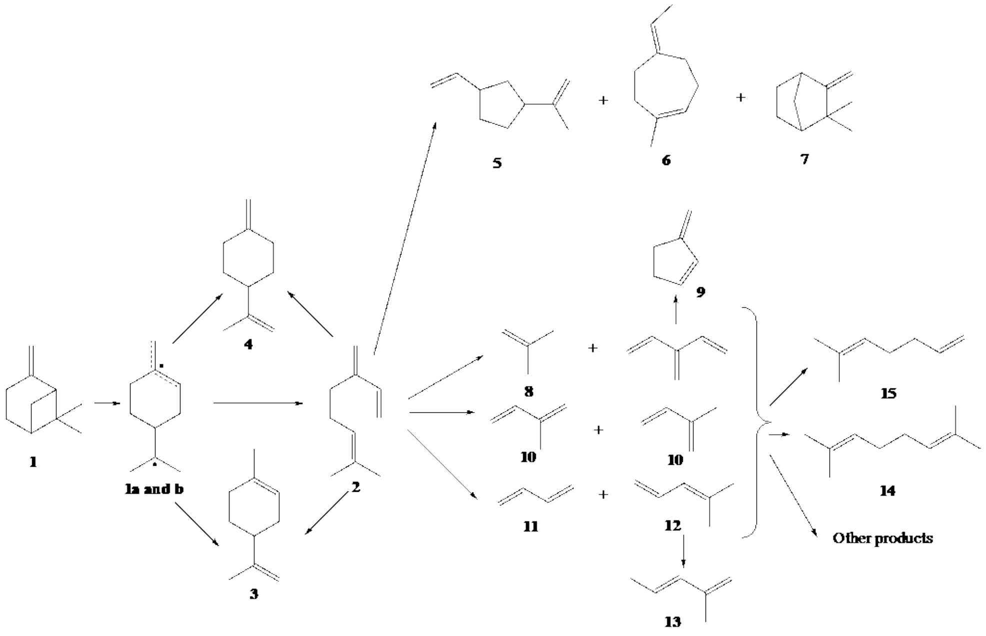


Scheme 1

2 Synthesis of bio-based dienes

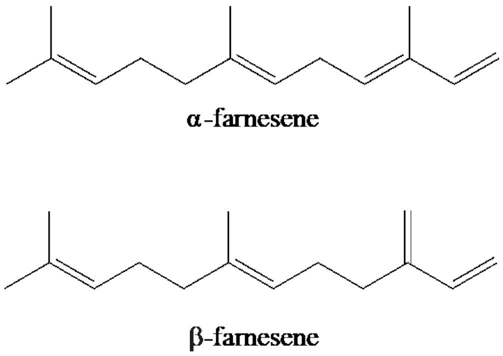
Terpenes are hydrocarbons made of isoprene building blocks naturally found in trees, plants, and essential oils, as well as produced by insects as an alarm pheromone [45, 46]. Because of their natural odors, they are often used in perfumes, cosmetics, aromatherapy, and food additives. Derivatives of terpenes that have hydroxyl functional groups are terpene alcohols, or terpenoids, that are used as building blocks for other chemicals [47]. For example, pinene is a cyclic terpene that is a major component of pine tree resin, as well as other coniferous trees [48, 49], however it can also be made from sugars by using genetically-engineered microorganisms [50].

One of the monomers of interest in this review is myrcene and it can be obtained by the pyrolysis of β-pinene [51]. Very high temperatures of 998 K can yield about 85% of myrcene, however it was found that a residence time of 0.4 s^{-1} at 743 K was the optimal condition for the highest yield of myrcene [52]. The yield is not 100% due to the isomerization of β-pinene at high temperatures forming byproducts, which include limonene and Ψ-limonene as seen in Scheme 2. Furthermore, decomposition of these products would form smaller alkenes and dienes, including isoprene, another monomer of interest.



Scheme 2

Other novel methods of producing myrcene involve terpenoids like geraniol and linalool, that are also naturally found in essential oils [47]. Acid-catalyzed hydration of geraniol can be employed to form myrcene with the highest selectivity being 43.5% after optimizing the concentration of weak acid boron zeolite catalyst, temperature and nitrogen flow [53]. Other terpenoids like farnesol and nerolidol can be found in grapes and wines, along with small amounts of *α*-farnesene isomers [54]. The acid-catalyzed dehydration of both farnesol and nerolidol using $KHSO_4$ at 170ºC can form trans-β-farnesene, another monomer of interest in this review, along with other farnesene isomers (chemical structures are shown in Scheme 3) [55]. Base-catalyzed dehydration of farnesol using KOH at 210ºC gave a slightly higher yield of trans-β-farnesene at 65%, which is similar to the catalytic dehydration using activated alumina which gave a yield of 65% as well [56]. Additionally, microbial pathways using genetically modified *Escherichia coli* can be employed to synthesize E-β-farnesene (at high selectivity of up to 98% and small amounts of myrcene) and isoprene [57, 58].

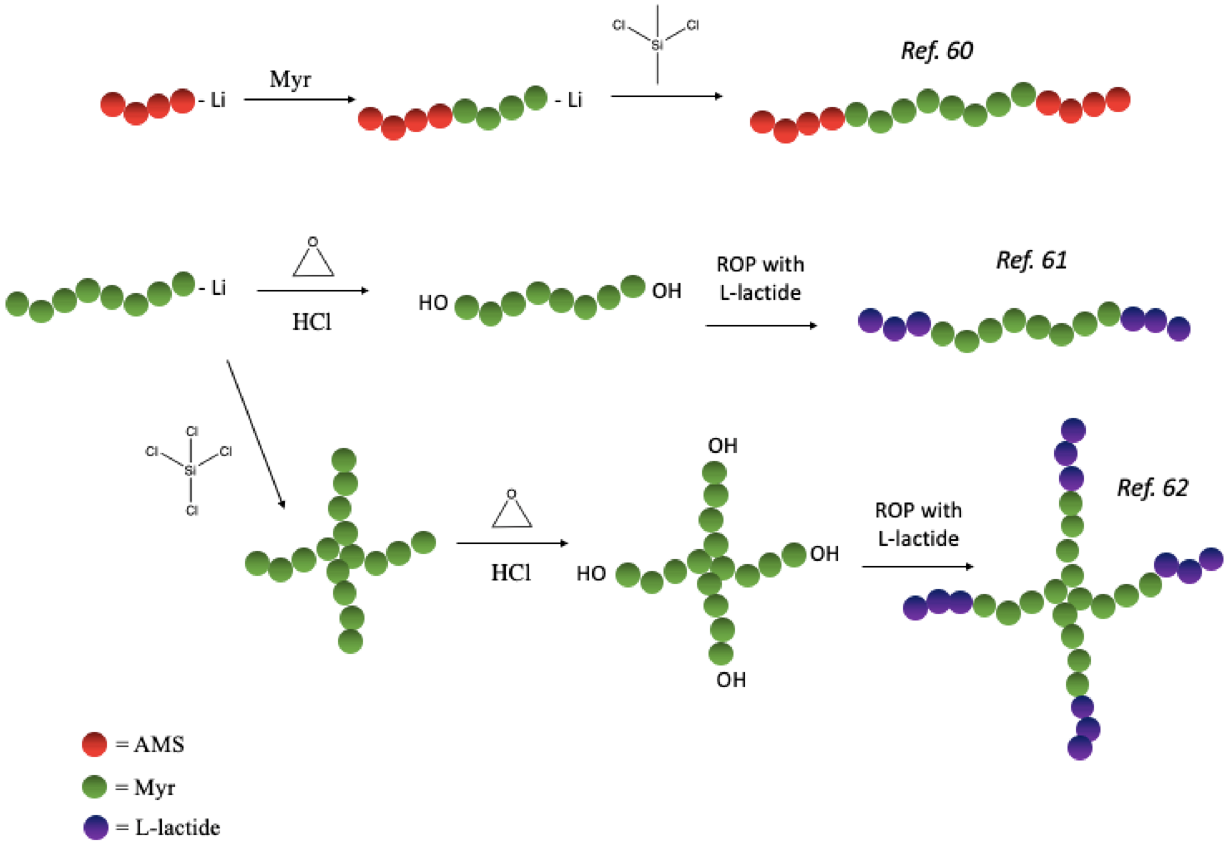


Scheme 3

3 Ionic polymerization of dienes

The carbon-carbon double bond of dienes can be polymerized either by free radical, controlled radical and ionic polymerization methods. It is instructive to start this discussion regarding controlled polymerizations by examining ionic polymerizations of bio-based dienes. Recognizing the close similarity in structure to isoprene (IP) and butadiene (BD), myrcene (Myr) and farnesene (Far) were explicitly polymerized by living anionic polymerization using *sec*-butyl lithium (sec-BuLi) in cyclohexane at 60ºC [59]. However, the molecular weight distribution for poly(Myr) was broad (M_n = 87 000 g mol^{-1}, M_w = 211 000 g mol^{-1}) and was far above the expected M_n of 46 000 g mol^{-1}. Using both ^{1}H and ^{13}C NMR, it was concluded that both poly(dienes) polymerized predominantly in a 1,4-*cis* configuration.

Later, polymerizations with myrcene proved more informative and successful (Scheme 4). Like IP or BD, Myr was targeted as the rubbery mid-block for bio-based thermoplastic elastomers. Instead of styrene (St), α-methyl-*p*-methylstyrene (AMS) was polymerized as the hard segment using *sec*-BuLi in THF [60]. The resulting PAMS-Li was re-initiated to polymerize myrcene forming PAMS-PMyr-Li, then subsequently coupled using dichloromethylsilane to form PAMS-PMyr-PAMS triblock ABA copolymers. A slightly different approach was done as well by sandwiching the rubbery poly(Myr) between hard poly(L-lactide) end blocks [61]. In this case, myrcene was polymerized anionically, then the end group was reacted with ethylene oxide and small amounts of hydrochloric acid such that the poly(Myr) midblock was hydroxyl terminated on both ends. This was then used as a macroinitiator for the ring-opening polymerization of L-lactide. Similarly, poly(Myr) synthesized using *sec*-BuLi was combined using $SiCl_4$, forming star-shaped poly(Myr), which was then hydroxylated for ring-opening polymerization of L-lactide. The result was a highly-branched poly(Myr)-*grafted*-poly(L-lactide) [62]. Furthermore, anionic polymerization of Myr followed by photo-initiated thiol-ene reactions was investigated to produce rubbery polyelectrolyte particles [63].



Scheme 4

Statistical anionic copolymerization of myrcene with common monomers like IP, St and AMS has also been reported [64]. After co- and terpolymerization using *sec*-BuLi, all polymers achieved high M_n (up to 161.5 kg mol^{-1}) and low dispersity (Đ ≤ 1.14). The polymerization is therefore well controlled considering narrow molecular weight distribution and linear M_n versus conversion were obtained. Block-like copolymers were obtained by gradient copolymerization. Two glass transition temperatures were observed for every gradient copolymer, corresponding to the glass transition temperature of the two homopolymers. Noticeable was the steep gradients encountered, due to the disparate reactivity ratios of Myr with St and AMS ($r_{Myr} = 36$, $r_{St} = 0.028$; $r_{Myr} = 140$, $r_{AMS} = 0.0074$) which essentially allowed for block copolymers. These experiments demonstrate the high potential of the bio-based monomer myrcene for the anionic synthesis of block and gradient copolymers to impart bio-based character into thermoplastic elastomers.

Poly(Far) was prepared anionically in heptanes using n-butyl lithium as the initiator resulting in a wide range of molecular weights (3,800 to 367,000 g mol^{-1}) with narrow molecular weight distributions ((Đ = 1.1 to 1.29) [24]. The polymerization was successfully conducted leading to poly(Far) of primarily 1,4-*cis* addition microstructure with T_gs around -73ºC. At high molecular weights, polymers displayed a transition in the slope of zero shear viscosities (η_0) from 1.2 to 3.1 at a critical entanglement molecular weight of $M_e \sim 10^5$ g mol^{-1}. This is considerably higher compared to other polydienes like poly(BD) ($M_e \sim 6000$ g mol^{-1}) and poly(IP) ($M_e \sim 13{,}000$ g mol^{-1}) as a function of weight average molecular weight (M_w), indicative of the transition to entangled chain dynamics, which is responsible for high viscosities.

Emulsion cationic polymerization of Myr was done using Lewis acid surface combined complexes (LASC) [65]. The subsequent poly(Myr) present the highest molecular weights ($M_n > 150{,}000$ g mol^{-1}) ever reported in the cationic polymerization of 1,3-dienes, however very high Đ (3.7 – 4.1) was also reported. The high Đ was an indication quasi-livingness was not achieved, further supported by the plateauing of M_n versus conversion starting early in the reaction at $X = 20\%$. In addition, instantaneous initiation did not occur as there were long induction times of 10 – 14 h, which was explained by the hydrophobicity of myrcene that required considerable time for the LASC to enter the monomer droplets. Furthermore, short polymer chains were formed on the interface of the droplets and were quickly terminated due to chain-transfer of the polymer chains with water. These short chains stabilized the droplets while polymerization continued inside the droplets forming high molecular weight chains, hence the broad distribution of molecular weight. Nonetheless, linear poly(Myr) chains were formed with mostly 1,4-addition units (almost equal part *cis* and *trans*), and statistical copolymerization of Myr and St was performed as well, but with similar kinetics. Interestingly, the reactivity ratios of Myr and St ($r_{\mathrm{Myr}} = 1.14$ and $r_{\mathrm{St}} = 0.74$) were very similar to those obtained from free radical polymerization ($r_{\mathrm{Myr}} = 1.12$ and $r_{\mathrm{St}} = 0.87$) [66], but very different from those obtained from anionic polymerization as seen earlier [64].

Thus, ionic polymerizations of bio-based dienes (Far and Myr), like those of conventional dienes (IP and BD), are well-controlled, but this technique encounters some major drawbacks. As seen with the anionic polymerization of Myr and AMS, crossover polymerization of the PAMS-PMyr-Li chains could not be done due to the ionic nature of the propagating chain, hence these polymer chains had to be coupled to form ABA block copolymers [60]. Emulsion cationic polymerization of Myr was attempted, but presence of water at the interface of the monomer droplets resulted in poor livingness of polymer chains [65]. Additionally, manipulation of IP and BD, being relatively volatile, requires some care when transferring reagents and solvents into the reactors. Therefore, some of these issues can be circumvented through the development of controlled radical polymerization for dienes that are essentially non-volatile, like Myr and Far.

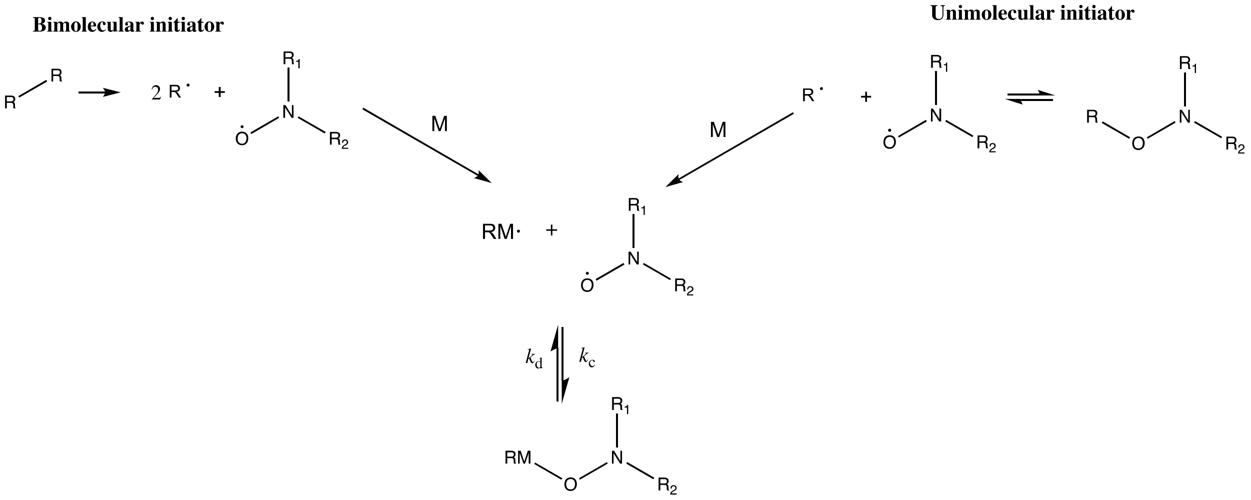
4 Reversible deactivation radical polymerization of dienes

A "living" polymerization can be seen as a chain polymerization that proceeds without the occurrence of chain transfer and termination events, through the establishment of a dynamic equilibrium between active and dormant species [67]. This method opened the door to well-defined polymers with precise and predetermined molar masses, compositions, topologies, and functionalities. Until 30 years ago, living anionic and cationic polymerizations were the only available methods to reach a high degree of structural and compositional homogeneity of polymers. Controlled/living radical polymerization (CLRP) or reversible deactivation radical polymerization (RDRP) techniques enable a high degree of control to be reached [17]. RDRP differs from ionic polymerization by its relative ease-of-use (only dissolved oxygen has to be generally eliminated), the broad range of vinylic monomers which can be polymerized, and the numerous processes that can be implemented (bulk, solution, emulsion, dispersion, etc.) [68]. Among the most well-established methods deriving from this concept are nitroxide-mediated polymerization (NMP), atom-transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT).

4.1 Nitroxide-mediated polymerization (NMP)

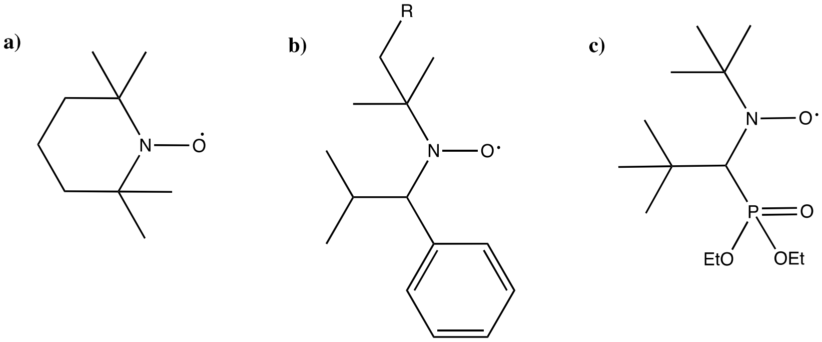
NMP is often considered the oldest controlled radical polymerization technique [69, 70]. Initial polymerizations employed (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) as the persistent radical to mediate the radical concentrations by a reversible termination step due to the low bond dissociation energy of TEMPO [71]. These systems were initiated using a bicomponent pathway by combining a conventional thermal initiator such as azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO) with TEMPO. The free radical generated by the thermal initiator would initiate monomer propagation, while the free nitroxide, TEMPO, would deactivate the propagating macroradicals in an activation-deactivation equilibrium ($K_{eq} = k_d/k_c$), where k_d is the dissociation rate constant and k_c is recombination rate constant. The equilibrium constant (K_{eq}) remains sufficiently low such that the macroradical species are mostly dormant and termination events are suppressed, therefore approaching “living” polymerization kinetics. It was found that a higher TEMPO/BPO ratio of 3.0 led to lower dispersity (1.19) in the NMP of St, but the rate of polymerization was slower due to the excess of free nitroxide [70]. Furthermore, successful NMP synthesis of SBR was shown by chain-extending the poly(St) macroradical with BD, and then again with St to make triblock copolymers [72]. There were some reports of statistical and block copolymers using dienes, but most were limited in copolymerizations with styrene and several vinyl monomers and even crosslinking divinyl monomers [73-76].

Thermal initiators suffer from incomplete efficiency in forming primary radicals and they often undergo rearrangement and fragmentation. Therefore, unimolecular alkoxyamine initiators were developed so that it would dissociate into an initiating radical and a nitroxide at high temperatures, as opposed to a bimolecular system that required both thermal initiator and free nitroxide [77, 78]. The initiation mechanisms using unimolecular and bimolecular initiators are shown in Scheme 5. It was found that α-methyl groups were necessary for unimolecular initiators with benzylic derivatives to exhibit good control of polymerization [78]. Unimolecular initiators gave comparable low dispersity and molecular weight polymers to bimolecular systems, however unimolecular initiators were able to maintain good control even at higher molecular weight. Both initiating systems still required high temperatures (120 – 125ºC) and long reaction times (~20 hours) to reach high conversions.



Scheme 5

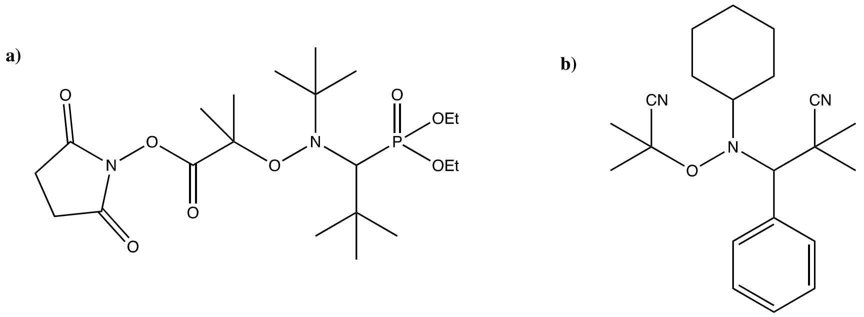
Hence, this led to further development to improve the cleavage of the nitroxide to carbon bond at lower temperatures. It was discovered that larger cyclic rings and acyclic nitroxides had lower bond dissociation energies, specifically referring to another widely used nitroxide, 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxyl (TIPNO) [79, 80]. Soon after, it was found that β-phosphonylated nitroxides afforded stable nitroxides as well, which led to the synthesis of *N*-tert-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1-based) initiators and the eventual commercialization of BlocBuilder^{TM} by Arkema [81-83]. The chemical structures of the various commonly used commercially available nitroxides are shown in Scheme 6.



Scheme 6

Homopolymerization of 1,3-dienes including BD and IP using unimolecular TIPNO showed better control than using TEMPO, where poly(IP) reached an M_n of 100,000 g mol^{-1} and Đ < 1.20 and poly(BD) had an M_n of 5,200 g mol^{-1} and Đ = 1.14 [84]. Random copolymerization of IP with various styrenic monomers and *tert*-butyl acrylate (tBA) also showed good control with low Đ all below 1.30. Block copolymers made of different monomer compositions such as poly(*t*BA-*b*-IP-*co*-*t*BA), poly(St-*b*-IP-*co*-St), and poly(IP-*b*-IP-*co*-St) all had low Đ values < 1.30. Random copolymerizations of IP with 1 – 10 wt% of glycidyl methacrylate (GMA) were done with unimolecular TIPNO, as well as with bimolecular OH-TEMPO and TIPNO [85]. The bimolecular polymerizations tended to yield higher Đ ~2 – 3.3, but copolymerizations with up to 10 wt% GMA using unimolecular TIPNO still gave reasonable Đ of 1.26 and M_n = 57,000 g mol^{-1}. Similarly, NMP of IP was done with several SG1-based alkoxyamines and they showed low Đ ~1.10 at high conversions [86]. Furthermore, difunctional TIPNO alkoxyamine was used to polymerize IP with dimethylacrylamide (DMA) and tBA and successfully synthesized ABA triblock copolymers, poly(IP-*b*-tBA-*b*-IP) and poly(DMA-*b*-IP-*b*-DMA) with Đ < 1.26 [87].

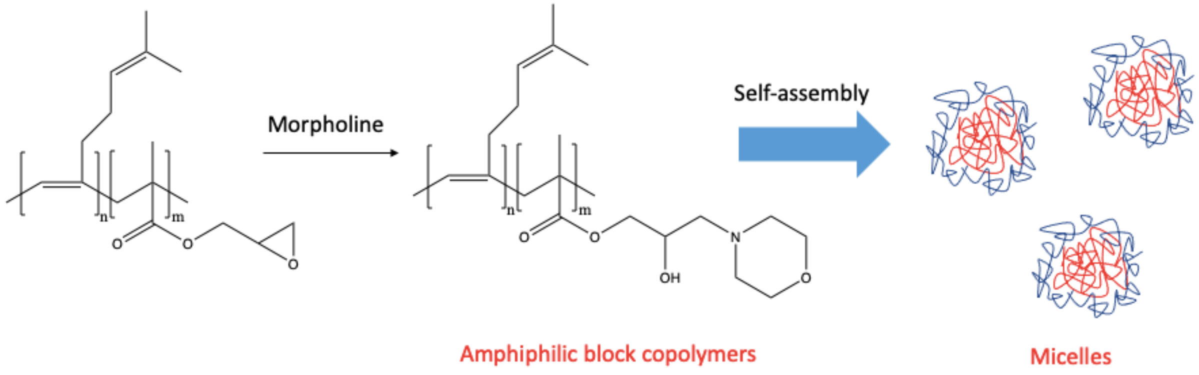
Nitroxides such as TIPNO and SG1-based initiators were very effective when polymerizing functional monomers like acrylates and acrylamides, and also conventional dienes like BD and IP. However, one drawback of NMP is its inability to homopolymerize methacrylates while maintaining active chain-ends due to steric stability provided by the methacrylate propagating radical and steric hindrance from the bulky SG1-based nitroxide. This leads to a slow rate of recombination (k_c) which leads to termination of the macroradicals by disproportionation [88, 89]. One way to mitigate this problem is to add a small amount (5 – 10 mol%) of controlling comonomer like St, acrylonitrile, or even IP to decrease the overall K_{eq} and better maintain active chain-ends [84, 90-92]. The SG1-based BlocBuilder^{TM} can be modified with a succinimidyl group (NHS-BB) to further improve the polymerization of methacrylates (since it does not rely on additional free nitroxide) but controlling comonomer is still needed [93]. More recently, a new alkoxyamine, Dispolreg 007 (D7), was developed that was able to homopolymerize methacrylates without controlling comonomer and could also be easily synthesized [94-96]. Chemical structures of the succinimidyl ester-modified BlocBuilder and Dispolreg 007 alkoxyamines are shown in Scheme 7.



Scheme 7

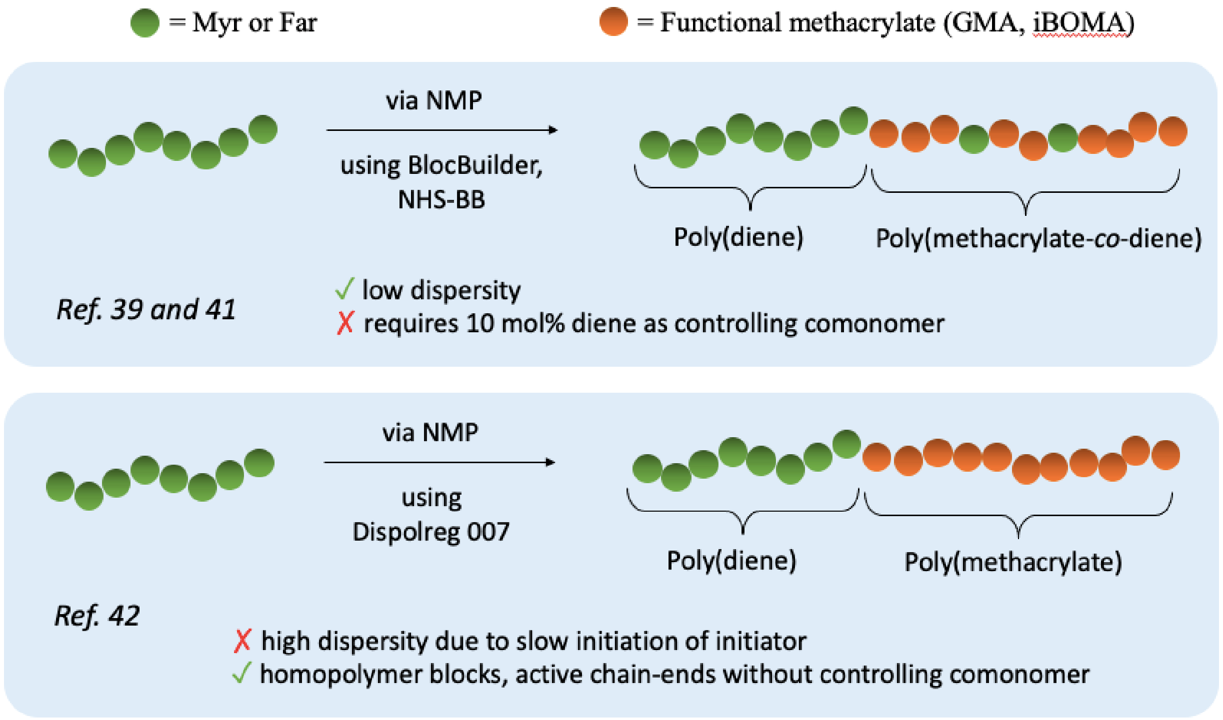
In an effort to synthesize a greener alternative to SBR, Myr was substituted in place of BD to make block and random copolymers with St using SG1-based NHS-BB initiator [40]. For the homopolymerization of Myr, well-defined polymers with M_n ~ 15,000 g mol^{-1} were made with both BlocBuilder and NHS-BB, while NHS-BB resulted in lower Đ = 1.26 (versus Đ = 1.45 using BlocBuilder). Poly(Myr) made with NHS-BB showed high SG1 chain-end fidelity and were successfully chain-extended with St making poly(Myr-*b*-St) with two distinct T_gs of the two respective homopolymers. Statistical copolymerization of Myr and St by NMP gave similar reactivity ratios compared to free radical copolymerization (r_{Myr} = 1.88 and r_{St} = 0.25) [66]. Copolymers with high composition of either Myr or St were successfully chain-extended, as well, with both Myr and St indicating good chain-end fidelity with final Đ < 1.60 [40].

Other examples of block and statistical copolymers with Myr and functional methacrylates like glycidyl methacrylate (GMA) and isobornyl methacrylate (iBOMA) have also been reported [39, 41]. Statistical copolymerization of Myr and GMA using NHS-BB showed that at high compositions of GMA (f_{GMA} < 0.50), Đ values became greater than 1.45 [39]. However, at low compositions of GMA, the polymerization was better controlled with final Đ ~ 1.30 which indicates myrcene can also act as a controlling comonomer. The epoxy groups in the GMA block of poly(Myr-*b*-GMA) (the chain-extension with GMA included 10 mol% of Myr as controlling comonomer) were modified with morpholine groups, and the diblock copolymers became amphiphilic and were able to self-assemble into aggregates in water at 45 – 65°C (Scheme 8). Similarly, random copolymerization of Myr and iBOMA showed that myrcene could act as a controlling comonomer for NMP of iBOMA [41]. Furthermore, the reactivity ratios for iBOMA and Myr (r_{Myr} = 2.16 and r_{iBOMA} = 0.07) were quite different resulting in gradient-like copolymers. Poly(Myr-*grad*-iBOMA), one rich in Myr and one rich in iBOMA, had Đ of 1.32 and 1.51, respectively, and were chain-extended with Myr and iBOMA/Myr mixture with final Đ ~ 1.60. Triblock copolymers, poly(iBOMA-*b*-Myr-*b*-iBOMA), were also synthesized using an SG1-terminated dialkoxyamine (M_n = 51,000 g mol^{-1} and Đ = 1.91) and two distinct T_g's were shown at -51 and 181°C.



Scheme 8

Likewise, Far was polymerized using NHS-BB and D7 initiators to make block and statistical copolymers with GMA [42]. The reactivity ratios for Far and GMA (r_{Far} = 0.54 and r_{GMA} = 0.25) were very similar to Myr and GMA (r_{Myr} = 0.49 and r_{GMA} = 0.50) [39], where both systems resulted in essentially random copolymers. Poly(Far-*co*-GMA) rich in Far made with NHS-BB also showed lower Đ = 1.33 compared to a copolymer rich in GMA (Đ = 1.63) at similar M_n of ~20,000 g mol^{-1}. In an equimolar statistical copolymerization of Far and GMA using D7, the resulting Đ was high ~2.5, which was explained by both the great differences in rate of propagation between Far and GMA and the slow initiation of D7 (therefore not instantaneous initiation, a criteria for RDRP). Despite the homopolymerization of Far using D7 resulting in a high Đ of 1.60, the chain-ends were still active and chain-extension with GMA was successful. Poly(Far) made with NHS-BB had a Đ of 1.17, but required 10 mol% of Far as a controlling comonomer when chain-extended with GMA. Nonetheless, poly(Far-*b*-GMA) block copolymers were synthesized using both NHS-BB and D7 initiators. A schematic comparing the synthesis of poly(diene-*b*-methacrylate) block copolymers using SG1-based and D7 initiators is shown in Scheme 9.



Scheme 9

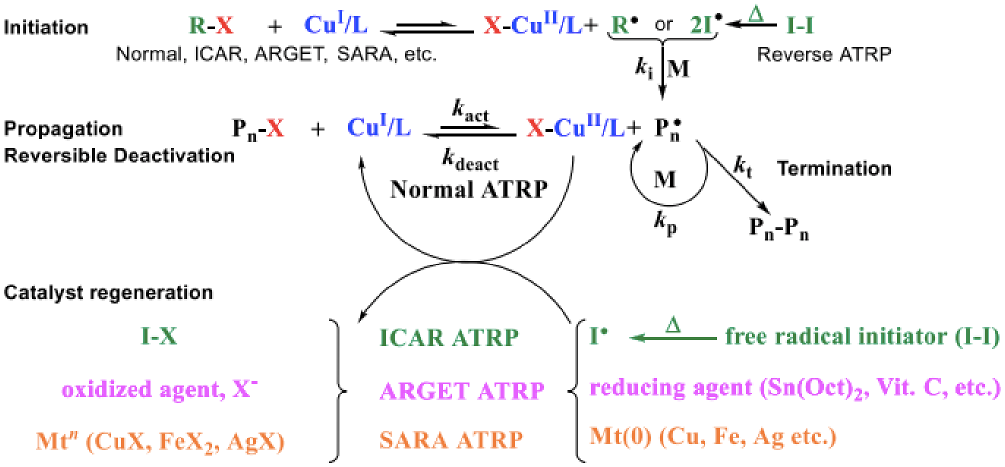
The synthesis of St-IP-St (SIS) copolymers was revisited by using a difunctionalized SG1-based alkoxyamine (PEG-SG1$_2$) [97]. The resulting poly(IP) midblocks had high molecular weight with M_n = 52 – 59 kg mol^{-1} and Đ ~ 1.5. Furthermore, they were able to be re-initiated after adding St monomer producing poly(St-*b*-IP-*b*-St) triblock copolymers. The polymers with higher composition of St (F_{St} = 0.49) showed hard brittle behaviour, while the polymers with F_{St} = 0.30 showed much better elongation and micro-phase separation into cylindrical/lamellar morphologies. The same method was used to produce an analogous poly(iBOMA-*b*-IP-*b*-iBOMA) triblock copolymer, where the chain-extension with iBOMA included 10 mol% of St. The final Đs of these polymers were lower (1.76) compared to the styrene analogous polymers (Đ ~2.2), and the increased hardness provided by the iBOMA segments improved the toughness and elongation at break of the final polymer.

The versatility of NMP has been shown from its initial conception for SBR synthesis using St and BD to adding functionality and polymerizing bio-based dienes through the development of next-generation nitroxide initiators. Although Đ values using NMP are typically higher than those achieved using ionic polymerization, chain-end activity was maintained, and block copolymers were successfully synthesized. Also, triblock copolymers were more efficiently synthesized by using difunctionalized alkoxyamines. The family of diene triblock copolymers has been extended by incorporating functionalized monomers like *t*BA, dimethylacrylamide [87], and iBOMA [41], the last case demonstrating improved mechanical strength of the material compared to styrene analogs.

4.2 Atom transfer radical polymerization (ATRP)

ATRP is one of the most efficient synthetic techniques allowing for controlled radical polymerizations with predetermined molecular weights, narrow molecular weight distributions, and high degrees of chain-end functionalities. Like other RDRP methods, ATRP utilizes the persistent radical effect (PRE) [98]. Primary radicals are formed when a transition metal complex (M^m-L) abstracts the halogen atom from an alkyl halide (R-X) to form an oxidized metal complex (X-M^{m+1}-L), which acts as the radical deactivator. The radical R· reacts with an alkene monomer and propagation proceeds, and termination of the propagating radical is supressed by the reversible deactivation of X-M^{m+1}-L in an equilibrium process (characterized by K_{act}). The general mechanism for ATRP using a copper metal catalyst is shown in Schematic 6. In the early conception of ATRP, several metallic catalysts were studied including ruthenium, copper, and nickel complexes and their ability to polymerize St and methacrylates resulted in low Đ and linear M_n versus conversion [99-101].

Typically, in all types of RDRP, every polymer chain is simultaneously initiated by an initiator, and hence the metal catalyst concentration in the final polymer for ATRP can be very high. As a result, there is discoloration and other negative effects possible with the metallic species, so catalyst removal is essential [102, 103]. In order to minimize catalyst concentration to ppm amounts, methods have been developed to regenerate or lower the oxidation state of the metal catalyst such that less than the stoichiometric amount of catalyst is needed. Using activators generated by electron transfer (AGET) or activators regenerated by electron transfer (ARGET) methods, reducing agents are added to continually activate or regenerate the metal catalyst by electron transfer without initiating polymer chains on their own [104]. Some examples of reducing agents include FDA-approved tin(II) 2-hexanoate, ascorbic acid, glucose, silver metal, and hydrazine [105-109]. Another technique is the supplemental activation reducing agent (SARA) or single-electron transfer (SET), where a zero oxidation state metal (i.e. Cu(0) or Fe(0)) is utilized to reduce the activated catalyst concentration [110, 111]. The proposed mechanisms for both SARA and SET include the same components and reactions, but differ in which competitive equilibria is responsible for activation and deactivation between oxidation states [112, 113]. Alternatively, initiators for continuous activator regeneration (ICAR) employs free radical initiators to continuously reduce the oxidation state of the metal catalyst [114-116]. The different mechanisms for catalyst regeneration are also shown in Scheme 10.



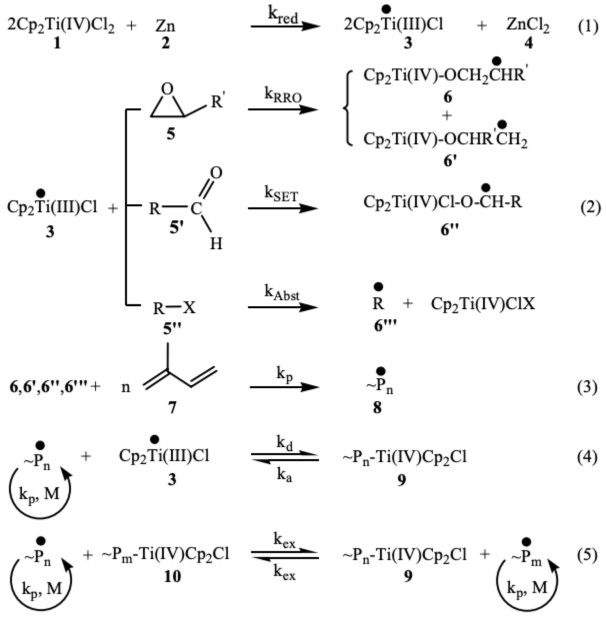
Scheme 10

An advantage of using AGET/ARGET reducing agents is that it can also eliminate dissolved oxygen in the medium, so polymerizations can be done with a limited concentration of air [104-106]. As with most metal reducing agents, they can partake in competitive complexation with ligands, monomer, and polymer, or substitution/elimination of the halide chain-ends causing irreversible termination and poor livingness of polymer chains [117-119]. Therefore, it is common to add excess ligands in order to limit the complexation of monomer/solvent/reducing agent with the catalyst. As with the addition of free radical initiators, there will be a small portion of polymer chains that are initiated by free radicals, hence the rate of addition has to be slow in order to avoid rapid polymerization and loss of control [114, 120].

ATRP has proven to be very effective in polymerizing vinylic monomers like St and (meth)acrylates using different catalyst regeneration techniques and in synthesizing various topologies including star, graft, and highly branched polymers [121]. However, ATRP of dienes using copper catalysts remains a challenge and it was believed to be due to the coordination of dienes to CuX, which is not observed with monomers like methyl (meth)acrylates or styrene [122-124]. Later on, it was discovered that the diene-copper complexes (i.e. BD and IP) were actually not very stable at common polymerization temperatures, especially compared to strong coordinating ligands like amines or phosphines [125-127]. In fact, it is the low bond dissociation energy of the poly(diene)-halide (PD-X) that leads to fast activation and slow deactivation of the propagating radical, and therefore loss of halide chain-end functionality (CEF) and loss of control [122].

Furthermore, polymerization temperatures are kept relatively low as BD and IP have low boiling points in addition to slow rates of propagation (k_p) compared to methacrylates and St, both of which aid in loss of CEF [121]. The slow polymerization rate and slow deactivation of the propagating radical also lead to side reactions such as quaternization of diene with metal catalyst and Diels-Alder dimerization [128-131]. Indeed, in an attempt to polymerize isoprene using CuBr catalyst with tris-[2-(dimethylamino)ethyl] amine ligands (CuBr/Me_6TREN) initiated by ethyl bromoproprionate in bulk, very low yields < 5% were obtained [132]. The lack of polymerization was mainly attributed to low solubility of CuBr/Me_6TREN in the non-polar monomer, therefore methyl ethyl ketone was used as a solvent (up to 40 vol%) but yield did not improve. Some progress was made in the ATRP of IP using copper halide and nitrogenous ligands (bipyridine and dinonyl bipyridine) due to a much lower rate of catalyst activity (k_{act}) [133]. Much higher temperatures were used (100°C, 130°C, and 150°C) to compensate for the low rate of propagation. As a result, low molecular weight poly(IP) were synthesized (M_n < 10,000 g mol^{-1}) but high conversions were achieved (88.8% at 150°C).

It was clear that conventional copper catalysts such as CuBr/Me_6TREN was not sufficient in controlling the polymerization of dienes. The choice of metal catalyst, ligands, alkyl halide, temperature, reagent ratios, and ATRP method are all important factors to consider. There has been some success with the polymerization of IP using Ti-based catalysts (Cp_2TiCl-catalyst). Titanocene dichloride, $Cp_2Ti(IV)Cl_2$, is often used in epoxide ring opening reactions, aldehyde reduction, and halide abstraction [134, 135]. $Cp_2Ti(IV)Cl_2$ is first reduced by Zn and undergoes radical ring opening, single electron transfer reduction, and halide abstraction with epoxides, aldehydes, and halides, respectively, to initiate CRP of IP (Scheme 11) [136-138]. It seemed the key to obtaining low Đ values was ensuring fast initiation by adding the initiator (e.g. epoxide, aldehyde, or halide) after most of the $Cp_2Ti(IV)Cl_2$ had been reduced and having an excess of Ti to initiator. Aldehyde-initiated polymerizations of IP gave reasonable Đ values of 1.4 – 1.5 compared to epoxy-initiated polymerizations, and 110°C was the optimal temperature compared to 90 or 130°C [136]. However, M_n was typically low, being $< 10{,}000$ g mol^{-1}. Statistical and block copolymers of St and IP synthesized using Cp_2TiCl-catalyst and epoxy initiator were reported, as well, but final polymer characteristics and synthesis of block copolymers were unclear [139].



Scheme 11

Some recent studies reported ATRP of BD using less conventional metal complexes like molybdenum, iron, nickel, palladium, and platinum [140-142]. One report used 1-octanol substituted $MoCl_5$ metal catalyst with triphenyl phosphine (PPh_3) ligands to polymerize BD [140]. Although high conversions were achieved ($X \sim 60\%$), Đ remained at 1.7 throughout the reaction, which was attributed to the slow establishment of the equilibrium between active propagating radicals and dormant species using $MoCl_3(1\text{-octanol})_2$ catalyst.

Another study used iron metal complexed with a large series of ligands including carbon, nitrogen, halide, oxygen, and phosphorus-supported ligands [141]. It ultimately reported that one phosphorus-supported ligand, $P[Ph(OMe)_3]_3$, was far superior in controlling the polymerization of BD, and $FeCl_2$ and $FeCl_3$ provided much more stable PBD-X chain-ends and better deactivators than $FeBr_2$ and $FeBr_3$. Furthermore, ICAR and photo-initiated ATRP using $FeCl_3$/ $P[Ph(OMe)_3]_3$ significantly increased the rate of polymerization compared to normal ATRP, where the rate of photo-initiated ATRP was 10 times that of normal ATRP and higher conversion (X = 70% vs. 50%) and chain-end functionality (CEF = 0.9 vs. 0.65) were achieved.

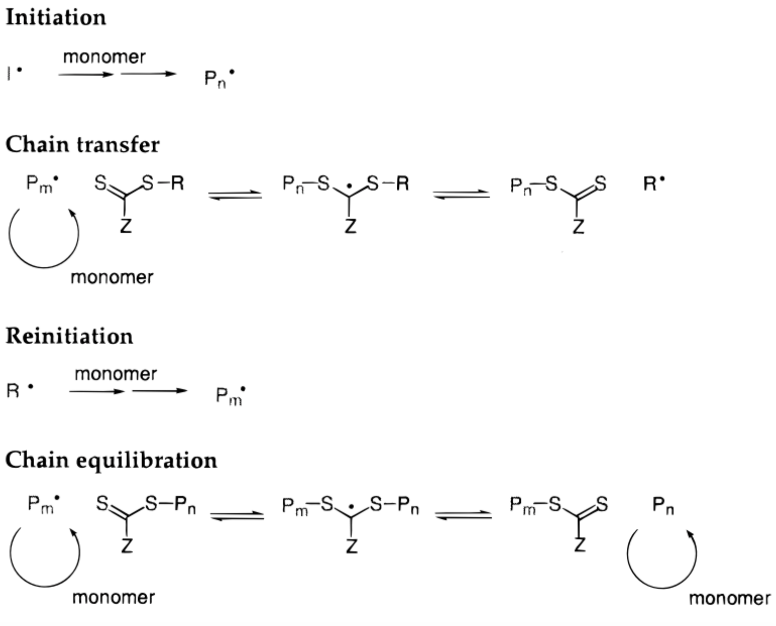
Comparing between Ni, Pd, and Pt metal complexes and the effect of ligands initiated with bromoesters, it was found that ICAR-ATRP of BD using $(PPh_3)Ni(CO)_2$ and $(PPh_3)NiCl_2$ resulted in better initiator efficiency, Br chain-end functionality, and higher conversion [142]. With the exception of Mo metal complex, phosphine-supported ligands seemed to be the most suitable for ATRP of BD as they were nucleophilic enough to reduce the metal catalyst but not too much that they would quaternize with PBD-X and lower CEF. Unlike the previous example of ATRP of IP [132], a non-polar solvent like toluene aided in the solubility of the metal catalyst in order to facilitate controlled polymerization.

Moving towards conventional Cu-mediated ATRP of BD in the most recent study, similar conditions were found to lead to successful controlled polymerizations [143]. Tertiary bromoester (as opposed to benzyl) initiators combined with low nucleophilicity ligands and non-polar solvents resulted in poly(BD) with a wide range of M_n values (1000 – 100,000 g mol^{-1}) and low Đ of 1.2 – 1.5. Furthermore, ICAR-ATRP proved to be much more efficient at increasing the rate of polymerization and minimizing side reactions compared to normal, SARA, and ARGET ATRP. Triblock ABA copolymers were synthesized with St and MMA making poly(BD-*b*-St-*b*-BD) and poly(MMA-*b*-BD-*b*-MMA). Initially, a poly(St) midblock was made with a difunctional alkyl bromide initiator in normal ATRP, as St would make a more reactive propagating radical. Br-poly(St)-Br was then chain-extended with BD and the final CEF of the triblock polymer was ~40%. Therefore, poly(BD)-Br was shown to have a high enough CEF for subsequent chain-extension. A poly(BD) midblock was then synthesized with a CEF of ~90% and was successfully chain-extended with MMA with the final CEF being >50%. However, relatively short polymer chains were achieved for both triblock copolymers. M_n for poly(St) was 2000 g mol^{-1} and increased to 13,000 g mol^{-1} after chain-extension with BD, and M_n for poly(BD) was 4600 g mol^{-1} and increased to 11,700 g mol^{-1} after chain-extension with MMA.

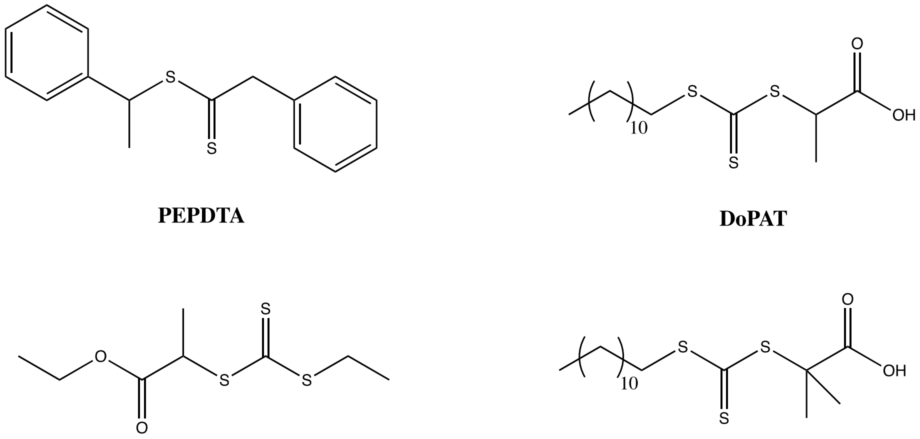
Since successful studies for ATRP of BD were only very recently reported, it is understandable no reports of ATRP of bio-based dienes like Myr and Far were found. Even with studies of ATRP of BD using Mo, Fe, and Ni metal complexes, multi-block copolymers were not synthesized [140-142]. Triblock ABA copolymers were only reported in the latest Cu-mediated ATRP of BD [143]. By optimizing the selection of ligands, initiator, solvent, and metal catalyst, the control of ATRP of dienes has improved greatly. This is hopeful for possible future studies for ATRP of Myr and Far, as both bio-based dienes have higher boiling points compared to IP and BD. Therefore, polymerization temperatures can be increased to further increase rate of initiation and rate of polymerization with hopefully an ability to minimize side reactions.

4.3 Reversible addition-fragmentation chain-transfer polymerization (RAFT)

The emergence of RAFT came shortly after NMP and ATRP, and is viewed as the most versatile amongst RDRP techniques [144]. Where NMP shows lack of control for polymerization of methacrylates and ATRP for dienes, RAFT is able to polymerize a diverse group of vinylic monomers including St, (meth)acrylates, and dienes [145-147]. The mechanism for RAFT differs slightly from NMP and ATRP and employs chain transfer agents (CTA) that reversibly react with propagating radicals instead of using radical deactivators. The CTA is often a dithioester with Z and R substituent groups. Polymerization begins with free radical initiation using common thermal initiators, which begins propagation of a polymer chain ($P_n\cdot$). The CTA reversibly adds onto the propagating radical and subsequently through chain transfer would release the initiating radical $R\cdot$. The initiating radical would initiate propagation as well, forming another propagating polymer chain ($P_m\cdot$). Finally, in the chain equilibration step, the CTA reversibly transfers between the two propagating polymer chains ($P_n\cdot$ and $P_m\cdot$) and irreversible termination is supressed. The RAFT polymerization mechanism is shown in Scheme 12, along with chemical structures of common RAFT CTAs in Scheme 13.



Scheme 12

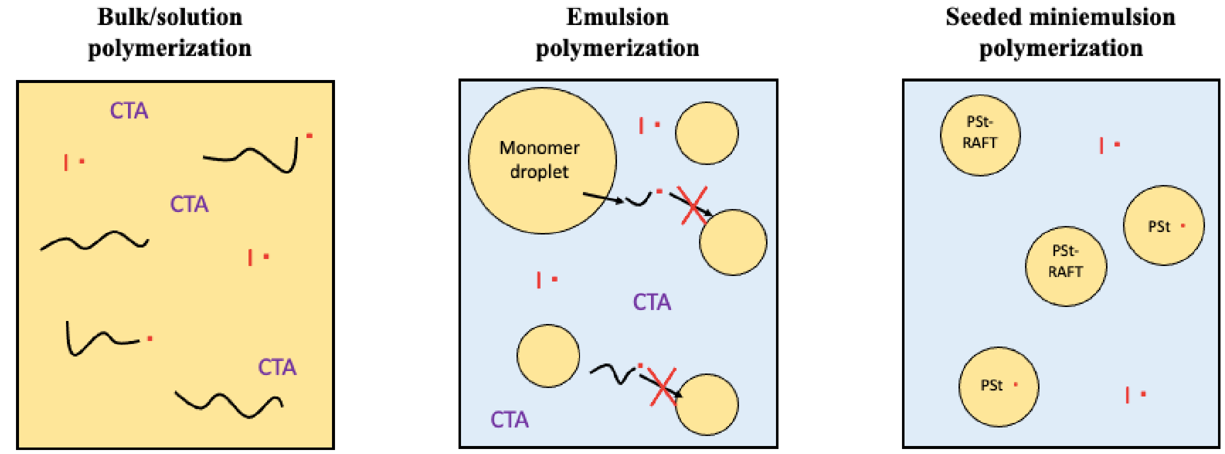


PEPDTA **DoPAT**

ETSPE **DDMAT**

Scheme 13

Early RAFT polymerizations of BD were mostly done in dispersed aqueous media as solution or bulk polymerizations yielded very slow rates (Scheme 14) [148, 149]. Emulsion polymerization *ab initio* was employed in order to utilize compartmentalization effects (i.e. segregation of radicals such that every particle has either one or zero radicals) to increase polymerization rate. However, in conventional emulsion, the chain-extension of poly(St) using RAFT with BD was unsuccessful, as the k_p of BD is very low and was unable to form hydrophobic oligomers in the aqueous phase to enter particles [148]. However, seeded miniemulsion showed much better success using 1-phenylethyl phenyl dithioacetate (PEPDTA), potassium persulfate (KPS) initiator, and SDS surfactant at 70°C [149]. BD was added to the PSt-RAFT seed latex and continued to polymerize at 70°C. Although gelation started to occur after 20% conversion of butadiene, poly(St-*b*-St-*co*-BD) copolymers were synthesized with varying compositions of BD (F_{BD} = 0.37 to 0.92) and relatively low Đ from 1.20 – 1.58. This work was expanded to synthesize triblock SBS copolymers by purging away BD and adding St again to make the third poly(St) block, although final Đ were quite high (>2.2) [150]. Another industrially relevant material, BD and acrylonitrile copolymer (NBR), was also successfully attained using RAFT in emulsion *ab initio* [151]. Polymerizations were done with 2-(((dodecylsulfanyl)carbonothioyl)sulfanyl)propanoic acid (DoPAT) and KPS, and showed good control up to 55% with M_n = 20,400 g mol^{-1} and Đ = 1.6. NBR copolymers were successfully chain-extended with St, as well, after re-initiation using AIBN.



✗ Very slow polymerization rates

✓ Faster polymerization rates due to segregation of radicals
✗ Poor entry of oligomers due to slow propagation

✓ Active loci are already inside monomer droplets

Scheme 14

Following the success of RAFT polymerization of BD, there have been a few reports of RAFT polymerization of IP as well. One report used the RAFT CTA, 2-ethylsulfanylthiocarbonyl-sulfanylpropionic acid ethyl ester (ETSPE) combined with thermal initiator dicumyl peroxide (DCP) for the polymerization of IP [152]. The optimal temperature of 115°C was chosen to maintain reasonable polymerization rates without loss of control. Block copolymers were made by first synthesizing poly(St) and poly(tBA) via RAFT, then chain-extended with isoprene making poly(St-*b*-IP) with final M_n = 44,300 g mol^{-1} and Đ = 1.19 and poly(tBA-*b*-IP) with final M_n = 21,500 g mol^{-1} and Đ = 1.20. Similarly, RAFT polymerization of IP was done using *S*-1-dodecyl-*S*'-(*r*,*r*'-dimethyl-*r*''-acetic acid)trithiocarbonate (DDMAT) and *t*-butyl peroxide at 125°C [153]. Control of polymerization was shown by linear M_n versus conversion, and CTA-chain end was maintained by successful chain-extension of poly(IP) with St (final M_n = 15,600 g mol^{-1} and Đ = 1.28). In both cases, increased thermal initiator helped to increase polymerization rate, as well as lower Đ. These polymerizations were both done in bulk, and similar to BD, polymerization rates were very slow, where reaction times were at least 20 hours.

Emulsion polymerization of IP using RAFT was also studied and much faster rates were achieved due to compartmentalization. In the same study that investigated *ab initio* emulsion polymerization of BD, IP was also added to poly(St) in emulsion [148]. Unlike the BD in emulsion, there was some St monomer left in the emulsion such that the k_p of copolymerization was increased to form oligomers that would eventually enter particles to continue polymerization. At the time of the study, there was no k_p data of IP and the authors speculated slow polymerization according to k_p of BD, and indeed k_p of IP is comparable and even lower than BD ($k_{p,BD}$ = 135 L mol^{-1} s^{-1} and $k_{p,IP}$ = 99 L mol^{-1} s^{-1} at 50°C) [154, 155]. However, the resulting copolymers included insoluble, crosslinked material. Seeded emulsion was done, where poly(St) particles were swollen with IP before polymerization began. After 2 h of reaction, poly(AA_{10}-St_{40}-IP_{80}) was synthesized reaching X = 58% and showed two distinct T_g's [148]. Poly(acrylic acid) (poly(AA)) was the hydrophilic stabilizing block in the emulsion.

RAFT polymerization was then successfully applied to Myr. In a study also using ETSPE and AIBN, similar poly(Myr-*b*-St) block copolymers were made, where chain-extension of poly(Myr) with St increased from 2490 to 11,100 g mol^{-1} and final Đ = 1.40 [43]. However, distinct T_gs of the two homopolymers were not obtained, likely due to the relatively short blocks in the polymer chain therefore phase separation was not achieved. In a more recent study, it showed that regioselectivity of poly(Myr) was affected by choice of thermal initiator more so than CTA [44]. In general, higher temperatures yielded lower percentage of 1,4-configuration, and dibenzoyl peroxide (DBPO) initiators yielded lower percentage of 1,4 configuration than AIBN. Since DBPO has a slower rate of dissociation than AIBN, the polymerization temperature was increased from

90 to 130°C, and evidence of crosslinking started to occur. Furthermore, change in regioselectivity was plotted as a function of conversion for the first time, and it showed that the 1,4-configuration was initially favoured at 95% but decreased to 76% as 3,4-configuration increased by the end of the polymerization.

Although good chain end fidelity was achieved with RAFT of Myr, the polymerizations rates were very slow. Polymerizations of Myr were done at a low temperature of 65°C and $X \sim 50\%$ after 125 hours, and even at a higher temperature of 130°C conversion reached 50-60% after ~50 hours [43, 44]. Another example used UV instead of a thermal initiator to initiate RAFT polymerization of Myr in bulk and at room temperature [156]. Similarly, polymerization rate was slow reaching $X = 20\%$ after 160 hours with M_n of 12,000 g mol^{-1} and Đ ~ 1.6. However, triblock copolymers were synthesized with St and poly(ethylene glycol) methacrylate (PEG-MA). In a very recent study, ABA triblock poly(St-*b*-Myr-*b*-St) copolymers were made via a bifunctional RAFT CTA in aqueous dispersion [157]. High conversions ($X > 68\%$) were achieved in 48 h at 75°C, and the block copolymers had high M_n (>40,000 g mol^{-1}) with relatively low Đ (highest Đ being 1.75) considering triblock copolymers were synthesized with vary compositions of St and Myr.

RAFT continues to show its versatility by successful synthesis of block copolymers made of IP with other monomers like *N*-vinyl pyrrolidinone and ethylene oxide [158, 159], as well as statistical copolymerization with St and hydroxyl-functionalized (meth)acrylates and dienes [160-162]. Polymerization temperatures were generally kept relatively low to prevent crosslinking and loss of control, and therefore polymerization rates were very slow. Seeded emulsions and miniemulsions seemed to be a good solution as compartmentalization was achieved to increased polymerization rates and successful block copolymers were synthesized using isoprene and myrcene. However, examples of RAFT polymerization of Far were not found and can be further investigated, especially in dispersed aqueous media.

5 Outlook for bio-based poly(dienes) in real-world applications

Understandably, bio-based dienes find applications predominantly in the same sector as conventional dienes. They are used as feedstocks to impart rubbery character into polymers in the form of homopolymers, statistical, block and gradient copolymers. It is expected that in the foreseeable future that monomers like Myr and Far will be touted as candidates for replacement of petroleum-based dienes and evidence suggests that these monomers can be readily adapted to various chemistries already established for dienes. Further, the key advantage of handling bio-based dienes like Myr and Far is their relatively lower volatility compared to IP or BD, which makes manipulation in polymerization processes much easier (for example, pressurized reactors are not required). However, like in other cases where a bio-based alternative is proposed (e.g. replacements for poly(ethylene terephthalate)) [163], there must be a compelling case for improvement or enhancement of properties in addition to a sound economic basis.

One major application for BD and IP is thermoplastic elastomers (TPEs) and many examples in this review showcased RDRP of Myr or Far with St to make block copolymers. In comparison, these Myr and Far analogous TPEs do not exhibit the same elongation to break properties due to the high hydrodynamic volume which requires high molecular weights for chains to entangle and form rubbery materials. However, using RDRP has allowed the hard segment (that would traditionally be made of St) to be replaced by functionalized methacrylates that introduced hydrophilicity (i.e. PEG-MA) [156], post-polymerization compatibilization and modification (i.e. GMA) [39], and increased thermal stability and hardness (i.e. iBOMA) [41].

Nonetheless, high entanglement molecular weights may be an advantage in low temperature applications. To take advantage of the low T_g of poly(Myr) and poly(Far), there have been several patents, as mentioned briefly in the introduction, that found new applications for these materials. Amyris Inc., filed a patent reporting the polymerization of Far to use in pressure sensitive adhesives (PSAs). Their patent describes the polymerization of Far using ionic polymerization or metal catalysts (Ziegler-Natta, Kaminsky, or metallocene) and copolymerization with other olefinic monomers to make statistical or block copolymers [25]. Poly(Myr) was copolymerized with sulfur dioxide by free radical polymerization and showed good adhesion to various surfaces such as glass, wood, aluminum and copper [31].

Fina Technology Inc. owns several patents using poly(Far) in many applications. One patent describes the use of Friedel-Craft catalysts to make low molecular weight poly(Far) as tackifying resins to be blended with elastomers [26]. Another patent details anionic polymerization of Far with at least one hydroxyl-terminated chain-end for further modification such as hydrogenation or acrylation [28]. The resulting polymer is a liquid optically clear adhesive to use in laminated screen assemblies in electronic devices. Alternatively, Far can be modified with a terminal hydroxyl, amino, epoxy, isocyanato, or carboxylic acid group which can be reacted with a (meth)acrylate to make a macromonomer, and then be further polymerized radically [164]. This bottlebrush polymer can be used as an additive in lubricants, hydraulic fluids, cosmetics, or adhesives. Far homopolymer (or copolymer with other dienes or vinyl aromatics) with terminal hydroxyl groups (a Far polyol) can also be reacted with diisocyanates to make a polyurethane prepolymer, which can further react with polyols to lower the isocyanate content in the final polyurethane product while increasing molecular weight [27]. Such materials would find application in markets where polyurethanes are often used such as sealants, caulking, sponge, foam, coatings, and binders.

There is one example of RAFT polymerization of Myr used as an anti-fouling membrane for oil/water separation [165]. Cellulose membrane (CM) is modified with DoPAT RAFT agent via acid/hydroxyl esterification with a hydroxyl group on the cellulose. Subsequently, grafting-from polymerization of 3-(trimethoxysilyl)-propyl acrylate formed the first block, followed by polymerization of Myr to form the second block. The modified CMs showed exceptional hydrophobicity with a contact angle >160° and was able to separate crude oil contaminants from water effectively. Odorous thiol contaminants can also be removed through their thiol-ene interactions with the double bonds in the poly(Myr) block. These materials can find uses in many chemical processes and environmental remediation. Furthermore, they are made of mostly bio-derived sources, namely CM and Myr, and the cellulose component is bio-degradable.

This review highlights some of the particular advantages of using bio-based dienes in RDRP processes that have emerged over the past decade. Although many current applications using poly(Far) and poly(Myr) that are synthesized via ionic, free radical, or catalytic polymerization, recent developments highlighted here can positively lead to more applications using RDRP. Continued activity is expected to concretely evaluate the merit of replacing petroleum-based dienes with their bio-based alternatives.

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6 References

[1] A. Chauvel, G. Lefebvre, L. Castex, Steam cracking, Petrochemicals processes, Editions Technip, Paris, 1989.

[2] J. Brandrup, E.H. Immergut, E.A. Grulke, Polymer handbook, 4th ed. ed., Wiley, New York, 1999.

[3] I. Kopal, P. Koštial, Z. Jančíková, J. Valíček, M. Harničárová, P. Hybler, M. Kušnerová, Modifications of Viscoelastic Properties of Natural Rubber/Styrene-Butadiene Rubber Blend by Electron Beam Irradiation, in: A. Öchsner, H. Altenbach (Eds.), Improved Performance of Materials: Design and Experimental Approaches, Springer International Publishing, Cham, 2018, pp. 219-229.

[4] M.-P. Bertin, G. Marin, J.-P. Montfort, Viscoelastic properties of acrylonitrile-butadiene-styrene (ABS) polymers in the molten state, Polymer Engineering & Science 35(17) (1995) 1394-1406.

[5] T. Masuda, A. Nakajima, M. Kitamura, Y. Aoki, N. Yamauchi, A. Yoshioka, Viscoelastic properties of rubber-modified polymeric materials at elevated temperatures, Pure and Applied Chemistry, 1984, p. 1457.

[6] J.G. Drobny, 15 - Applications of Thermoplastic Elastomers, in: J.G. Drobny (Ed.), Handbook of Thermoplastic Elastomers, William Andrew Publishing, Norwich, NY, 2007, pp. 281-315.

[7] J.M. Degrange, M. Thomine, P. Kapsa, J.M. Pelletier, L. Chazeau, G. Vigier, G. Dudragne, L. Guerbé, Influence of viscoelasticity on the tribological behaviour of carbon black filled nitrile rubber (NBR) for lip seal application, Wear 259(1) (2005) 684-692.

[8] W.C. White, Butadiene production process overview, Chemico-Biological Interactions 166(1) (2007) 10-14.

[9] R. Varma, H. Takeichi, J.E. Hall, Y.F. Ozawa, T. Kyu, Miscibility studies on blends of Kraton block copolymer and asphalt, Polymer 43(17) (2002) 4667-4671.

[10] T.O. Broadhead, A.E. Hamielec, J.F. MacGregor, Dynamic modelling of the batch, semi-batch and continuous production of styrene/butadiene copolymers by emulsion polymerization, Die Makromolekulare Chemie 10(10-11) (1985) 105-128.

[11] V.I. Rodríguez, D.A. Estenoz, L.M. Gugliotta, G.R. Meira, EMULSION COPOLYMERIZATION OF ACRYLONITRILE AND BUTADIENE. CALCULATION OF THE DETAILED MACROMOLECULAR STRUCTURE, International Journal of Polymeric Materials and Polymeric Biomaterials 51(6) (2002) 511-527.

[12] A.F. Johnson, D.J. Worsfold, Anionic polymerization of butadiene and styrene, Journal of Polymer Science Part A: General Papers 3(2) (1965) 449-455.

[13] A.F. Halasa, J.E. Hall, A. Para, Process for the preparation of block copolymers, U.S., 1980.

[14] M. Morton, L.J. Fetters, E.E. Bostick, Mechanisms of homogeneous anionic polymerization by alkyllithium initiators, Journal of Polymer Science Part C: Polymer Symposia 1(1) (1963) 311-323.

[15] M. Morton, L.J. Fetters, Homogeneous anionic polymerization of unsaturated monomers, Journal of Polymer Science: Macromolecular Reviews 2(1) (1967) 71-113.

[16] R. Bening, D. Handlin, L. Sterna, C. Willis, Novel block copolymers and method for making same, Kraton Polymers US LLC, 2003.

[17] D. Jenkins Aubrey, G. Jones Richard, G. Moad, Terminology for reversible-deactivation radical polymerization previously called "controlled" radical or "living" radical polymerization (IUPAC Recommendations 2010), Pure and Applied Chemistry, 2009, p. 483.

[18] R.C. Thompson, C.J. Moore, F.S. vom Saal, S.H. Swan, Plastics, the environment and human health: current consensus and future trends, Philosophical Transactions of the Royal Society B: Biological Sciences 364(1526) (2009) 2153-2166.

[19] Oil Consumption, 2019. https://www.bpf.co.uk/Press/Oil_Consumption.aspx. (Accessed November 26 2020).

[20] T.A. Hottle, M.M. Bilec, A.E. Landis, Sustainability assessments of bio-based polymers, Polymer Degradation and Stability 98(9) (2013) 1898-1907.

[21] K. Satoh, Controlled/living polymerization of renewable vinyl monomers into bio-based polymers, Polymer Journal 47(8) (2015) 527-536.

[22] B. Davies, Natural rubber — Its engineering characteristics, Materials & Design 7(2) (1986) 68-74.

[23] P. Sahu, A.K. Bhowmick, G. Kali, Terpene Based Elastomers: Synthesis, Properties, and Applications, Processes 8(5) (2020).

[24] C. Iacob, T. Yoo, J. Runt, Molecular Dynamics of Polyfarnesene, Macromolecules 51(13) (2018) 4917-4922.

[25] D.J. McPhee, M.J. Graham, Adhesives compositions comprising a polyfarnesene, Amyris Inc., United States, 2010.

[26] K.A. Nelson, A. Pierre-Justin, N.P. Hansen, Farnesene-based tackifying resins and adhesive compositions containing the same, Fina Technology Inc., United States, 2018.

[27] N. Tian, H. Chao, Polyols derived from farnesene for polyurethanes, Fina Technology Inc, United States, 2018.

[28] T. Yoo, H. Chao, S.K. Henning, Farnesene-based polymers and liquid optically clear adhesive compositions incorporating the same, Fina Technology, United States, 2018.

[29] P. Sarkar, A.K. Bhowmick, Synthesis, characterization and properties of a bio-based elastomer: polymyrcene, RSC Advances 4(106) (2014) 61343-61354.

[30] R.P. Quirk, Triblock polymers of a monovinyl aromatic compound and myrcene, Michigan Molecular Institute, United States, 1981.

[31] X. Guo, X. Liu, S. Shan, W. Zhao, H. Su, Q. Jia, Green approach toward sustainable adhesive: Synthesis and characterization of poly(myrcene sulfone), Journal of the Taiwan Institute of Chemical Engineers 95 (2019) 208-216.

[32] C. Zhou, Z. Wei, C. Jin, Y. Wang, Y. Yu, X. Leng, Y. Li, Fully biobased thermoplastic elastomers: Synthesis of highly branched linear comb poly(β-myrcene)-graft-poly(l-lactide) copolymers with tunable mechanical properties, Polymer 138 (2018) 57-64.

[33] L.J. Fetters, D.J. Lohse, D. Richter, T.A. Witten, A. Zirkel, Connection between Polymer Molecular Weight, Density, Chain Dimensions, and Melt Viscoelastic Properties, Macromolecules 27(17) (1994) 4639-4647.

[34] S. Loughmari, A. Hafid, A. Bouazza, A. El Bouadili, P. Zinck, M. Visseaux, Highly stereoselective coordination polymerization of β-myrcene from a lanthanide-based catalyst: Access to bio-sourced elastomers, Journal of Polymer Science Part A: Polymer Chemistry 50(14) (2012) 2898-2905.

[35] B. Liu, D.-t. Liu, S.-h. Li, G.-p. Sun, D.-m. Cui, High trans-1,4 (co)polymerization of β-myrcene and isoprene with an iminophosphonamide lanthanum catalyst, Chinese Journal of Polymer Science 34(1) (2016) 104-110.

[36] S. Georges, M. Bria, P. Zinck, M. Visseaux, Polymyrcene microstructure revisited from precise high-field nuclear magnetic resonance analysis, Polymer 55(16) (2014) 3869-3878.

[37] S. Georges, A.O. Touré, M. Visseaux, P. Zinck, Coordinative Chain Transfer Copolymerization and Terpolymerization of Conjugated Dienes, Macromolecules 47(14) (2014) 4538-4547.
[38] S. Georges, O.H. Hashmi, M. Bria, P. Zinck, Y. Champouret, M. Visseaux, Efficient One-Pot Synthesis of End-Functionalized trans-Stereoregular Polydiene Macromonomers, Macromolecules 52(3) (2019) 1210-1219.
[39] A. Métafiot, J.-F. Gérard, B. Defoort, M. Marić, Synthesis of β-myrcene/glycidyl methacrylate statistical and amphiphilic diblock copolymers by SG1 nitroxide-mediated controlled radical polymerization, Journal of Polymer Science Part A: Polymer Chemistry 56(8) (2018) 860-878.
[40] A. Métafiot, Y. Kanawati, J.-F. Gérard, B. Defoort, M. Marić, Synthesis of β-Myrcene-Based Polymers and Styrene Block and Statistical Copolymers by SG1 Nitroxide-Mediated Controlled Radical Polymerization, Macromolecules 50(8) (2017) 3101-3120.
[41] A. Métafiot, L. Gagnon, S. Pruvost, P. Hubert, J.-F. Gérard, B. Defoort, M. Marić, β-Myrcene/isobornyl methacrylate SG1 nitroxide-mediated controlled radical polymerization: synthesis and characterization of gradient, diblock and triblock copolymers, RSC Advances 9(6) (2019) 3377-3395.
[42] S.B. Luk, M. Marić, Nitroxide-Mediated Polymerization of Bio-Based Farnesene with a Functionalized Methacrylate, Macromolecular Reaction Engineering 13(3) (2019) 1800080.
[43] J. Hilschmann, G. Kali, Bio-based polymyrcene with highly ordered structure via solvent free controlled radical polymerization, European Polymer Journal 73 (2015) 363-373.
[44] N. Bauer, J. Brunke, G. Kali, Controlled Radical Polymerization of Myrcene in Bulk: Mapping the Effect of Conditions on the System, ACS Sustainable Chemistry & Engineering 5(11) (2017) 10084-10092.
[45] E. Breitmaier, Terpenes: Importance, General Structure, and Biosynthesis, Terpenes2006, pp. 1-9.
[46] M.B. Isman, Plant essential oils for pest and disease management, Crop Protection 19(8) (2000) 603-608.
[47] W. Chen, A.M. Viljoen, Geraniol — A review of a commercially important fragrance material, South African Journal of Botany 76(4) (2010) 643-651.
[48] F. Englund, R.M. Nussbaum, Monoterpenes in Scots Pine and Norway Spruce and their Emission during Kiln Drying, Holzforschung 54(5) (2000) 449.
[49] L.L. Ingram, Jr., S. Rubin, A.T. Dalton, F.W. Taylor, M.C. Templeton, The measurement of volatile organic emissions from drying southern pine lumber in a laboratory-scale kiln, Forest Products Journal 50(4) (2000) 91-94.
[50] S. Sarria, B. Wong, H.G. Martín, J.D. Keasling, P. Peralta-Yahya, Microbial Synthesis of Pinene, ACS Synthetic Biology 3(7) (2014) 466-475.
[51] M.B. Kolicheski, L.C. Cocco, D.A. Mitchell, M. Kaminski, Synthesis of myrcene by pyrolysis of β-pinene: Analysis of decomposition reactions, Journal of Analytical and Applied Pyrolysis 80(1) (2007) 92-100.
[52] H. Zheng, J. Chen, C. Li, J. Chen, Y. Wang, S. Zhao, Y. Zeng, Mechanism and kinetics of the pyrolysis of β-pinene to myrcene, Journal of Analytical and Applied Pyrolysis 123 (2017) 99-106.
[53] M. Eisenacher, S. Beschnitt, W. Hölderich, Novel route to a fruitful mixture of terpene fragrances in particular phellandrene starting from natural feedstock geraniol using weak acidic boron based catalyst, Catalysis Communications 26 (2012) 214-217.

[54] Z. Li, K. Howell, Z. Fang, P. Zhang, Sesquiterpenes in grapes and wines: Occurrence, biosynthesis, functionality, and influence of winemaking processes, Comprehensive Reviews in Food Science and Food Safety 19(1) (2020) 247-281.

[55] G. Brieger, T.J. Nestrick, C. McKenna, Synthesis of trans, trans-.alpha.-farnesene, The Journal of Organic Chemistry 34(12) (1969) 3789-3791.

[56] G. Brieger, Convenient preparation of trans-β-farnesene, The Journal of Organic Chemistry 32(11) (1967) 3720-3720.

[57] J. Crock, M. Wildung, R. Croteau, Isolation and bacterial expression of a sesquiterpene synthase cDNA clone from peppermint (Mentha X Piperita L.) that produces the aphid alarm pheromone (E)-β-farnesene, Proceedings of the National Academy of Sciences 94(24) (1997) 12833.

[58] A.R.C. Morais, S. Dworakowska, A. Reis, L. Gouveia, C.T. Matos, D. Bogdał, R. Bogel-Łukasik, Chemical and biological-based isoprene production: Green metrics, Catalysis Today 239 (2015) 38-43.

[59] R.A. Newmark, R.N. Majumdar, 13C-NMR spectra of cis-polymyrcene and cis-polyfarnesene, Journal of Polymer Science Part A: Polymer Chemistry 26(1) (1988) 71-77.

[60] J.M. Bolton, M.A. Hillmyer, T.R. Hoye, Sustainable Thermoplastic Elastomers from Terpene-Derived Monomers, ACS Macro Letters 3(8) (2014) 717-720.

[61] C. Zhou, Z. Wei, X. Lei, Y. Li, Fully biobased thermoplastic elastomers: synthesis and characterization of poly(l-lactide)-b-polymyrcene-b-poly(l-lactide) triblock copolymers, RSC Advances 6(68) (2016) 63508-63514.

[62] C. Zhou, Z. Wei, Y. Wang, Y. Yu, X. Leng, Y. Li, Fully biobased thermoplastic elastomers: Synthesis of highly branched star comb poly(β-myrcene)-graft-poly(l-lactide) copolymers with tunable mechanical properties, European Polymer Journal 99 (2018) 477-484.

[63] A. Matic, H. Schlaad, Thiol-ene photofunctionalization of 1,4-polymyrcene, Polymer International 67(5) (2018) 500-505.

[64] E. Grune, J. Bareuther, J. Blankenburg, M. Appold, L. Shaw, A.H.E. Müller, G. Floudas, L.R. Hutchings, M. Gallei, H. Frey, Towards bio-based tapered block copolymers: the behaviour of myrcene in the statistical anionic copolymerisation, Polymer Chemistry 10(10) (2019) 1213-1220.

[65] M.I. Hulnik, I.V. Vasilenko, A.V. Radchenko, F. Peruch, F. Ganachaud, S.V. Kostjuk, Aqueous cationic homo- and co-polymerizations of β-myrcene and styrene: a green route toward terpene-based rubbery polymers, Polymer Chemistry 9(48) (2018) 5690-5700.

[66] P. Sarkar, A.K. Bhowmick, Terpene Based Sustainable Elastomer for Low Rolling Resistance and Improved Wet Grip Application: Synthesis, Characterization and Properties of Poly(styrene-co-myrcene), ACS Sustainable Chemistry & Engineering 4(10) (2016) 5462-5474.

[67] M. Szwarc, Living Polymers, Nature Nature 178(4543) (1956) 1168-1169.

[68] D.A. Shipp, Living Radical Polymerization: Controlling Molecular Size and Chemical Functionality in Vinyl Polymers, Journal of Macromolecular Science, Part C 45(2) (2005) 171-194.

[69] D.H. Solomon, E. Rizzardo, P. Cacioli, Polymerization process and polymers produced thereby, Google Patents, 1986.

[70] M.K. Georges, R.P.N. Veregin, P.M. Kazmaier, G.K. Hamer, Narrow molecular weight resins by a free-radical polymerization process, Macromolecules 26(11) (1993) 2987-2988.

[71] P.M. Kazmaier, K.A. Moffat, M.K. Georges, R.P.N. Veregin, G.K. Hamer, Free-Radical Polymerization for Narrow-Polydispersity Resins. Semiempirical Molecular Orbital Calculations

as a Criterion for Selecting Stable Free-Radical Reversible Terminators, Macromolecules 28(6) (1995) 1841-1846.

[72] M.K. Georges, G.K. Hamer, N.A. Listigovers, Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process, Macromolecules 31(25) (1998) 9087-9089.

[73] C. Burguière, M.-A. Dourges, B. Charleux, J.-P. Vairon, Synthesis and Characterization of ω-Unsaturated Poly(styrene-b-n-butyl methacrylate) Block Copolymers Using TEMPO-Mediated Controlled Radical Polymerization, Macromolecules 32(12) (1999) 3883-3890.

[74] T. Fukuda, T. Terauchi, A. Goto, Y. Tsujii, T. Miyamoto, Y. Shimizu, Well-Defined Block Copolymers Comprising Styrene−Acrylonitrile Random Copolymer Sequences Synthesized by “Living” Radical Polymerization, Macromolecules 29(8) (1996) 3050-3052.

[75] M. Baumert, J. Fröhlich, M. Stieger, H. Frey, R. Mülhaupt, H. Plenio, Styrene-vinylferrocene random and block copolymers by TEMPO-mediated radical polymerization, Macromolecular Rapid Communications 20(4) (1999) 203-209.

[76] E. Tuinman, N.T. McManus, M. Roa-Luna, E. Vivaldo-Lima †, L.M.F. Lona, A. Penlidis, Controlled Free-Radical Copolymerization Kinetics of Styrene and Divinylbenzene by Bimolecular NMRP using TEMPO and Dibenzoyl Peroxide, Journal of Macromolecular Science, Part A 43(7) (2006) 995-1011.

[77] C.J. Hawker, Molecular Weight Control by a "Living" Free-Radical Polymerization Process, Journal of the American Chemical Society 116(24) (1994) 11185-11186.

[78] C.J. Hawker, G.G. Barclay, A. Orellana, J. Dao, W. Devonport, Initiating Systems for Nitroxide-Mediated “Living” Free Radical Polymerizations: Synthesis and Evaluation, Macromolecules 29(16) (1996) 5245-5254.

[79] G. Moad, E. Rizzardo, Alkoxyamine-Initiated Living Radical Polymerization: Factors Affecting Alkoxyamine Homolysis Rates, Macromolecules 28(26) (1995) 8722-8728.

[80] D. Benoit, V. Chaplinski, R. Braslau, C.J. Hawker, Development of a Universal Alkoxyamine for “Living” Free Radical Polymerizations, Journal of the American Chemical Society 121(16) (1999) 3904-3920.

[81] S. Grimaldi, J.-P. Finet, F. Le Moigne, A. Zeghdaoui, P. Tordo, D. Benoit, M. Fontanille, Y. Gnanou, Acyclic β-Phosphonylated Nitroxides: A New Series of Counter-Radicals for “Living”/Controlled Free Radical Polymerization, Macromolecules 33(4) (2000) 1141-1147.

[82] D. Bertin, F. Chauvin, J.L. Couturier, P.E. Dufils, D. Gigmes, O. Guerret, S. Marque, P. Tordo, Alkoxyamines originating from beta-phosphorylated nitroxides and use thereof in radical polymerisation, Google Patents, 2005.

[83] F. Chauvin, J.-L. Couturier, P.-E. Dufils, P. Gérard, D. Gigmes, O. Guerret, Y. Guillaneuf, S.R.A. Marque, D. Bertin, P. Tordo, Crowded Phosphonylated Alkoxyamines with Low Dissociation Temperatures: A Milestone in Nitroxide-Mediated Polymerization, Controlled/Living Radical Polymerization, American Chemical Society2006, pp. 326-341.

[84] D. Benoit, E. Harth, P. Fox, R.M. Waymouth, C.J. Hawker, Accurate Structural Control and Block Formation in the Living Polymerization of 1,3-Dienes by Nitroxide-Mediated Procedures, Macromolecules 33(2) (2000) 363-370.

[85] D. Contreras-López, M. Albores-Velasco, E. Saldívar-Guerra, Isoprene (co)polymers with glycidyl methacrylate via bimolecular and unimolecular nitroxide mediated radical polymerization, Journal of Applied Polymer Science 134(29) (2017) 45108.

[86] S. Harrisson, P. Couvreur, J. Nicolas, SG1 Nitroxide-Mediated Polymerization of Isoprene: Alkoxyamine Structure/Control Relationship and α,ω–Chain-End Functionalization, Macromolecules 44(23) (2011) 9230-9238.

[87] J. Ruehl, A. Nilsen, S. Born, P. Thoniyot, L.-p. Xu, S. Chen, R. Braslau, Nitroxide-mediated polymerization to form symmetrical ABA triblock copolymers from a bidirectional alkoxyamine initiator, Polymer 48(9) (2007) 2564-2571.
[88] C. Dire, J. Belleney, J. Nicolas, D. Bertin, S. Magnet, B. Charleux, β-Hydrogen transfer from poly(methyl methacrylate) propagating radicals to the nitroxide SG1: Analysis of the chain-end and determination of the rate constant, Journal of Polymer Science Part A: Polymer Chemistry 46(18) (2008) 6333-6345.
[89] Y. Guillaneuf, D. Gigmes, S.R.A. Marque, P. Tordo, D. Bertin, Nitroxide-Mediated Polymerization of Methyl Methacrylate Using an SG1-Based Alkoxyamine: How the Penultimate Effect Could Lead to Uncontrolled and Unliving Polymerization, Macromolecular Chemistry and Physics 207(14) (2006) 1278-1288.
[90] E. Guégain, Y. Guillaneuf, J. Nicolas, Nitroxide-Mediated Polymerization of Methacrylic Esters: Insights and Solutions to a Long-Standing Problem, Macromolecular Rapid Communications 36(13) (2015) 1227-1247.
[91] B. Charleux, J. Nicolas, O. Guerret, Theoretical Expression of the Average Activation−Deactivation Equilibrium Constant in Controlled/Living Free-Radical Copolymerization Operating via Reversible Termination. Application to a Strongly Improved Control in Nitroxide-Mediated Polymerization of Methyl Methacrylate, Macromolecules 38(13) (2005) 5485-5492.
[92] J. Nicolas, C. Dire, L. Mueller, J. Belleney, B. Charleux, S.R.A. Marque, D. Bertin, S. Magnet, L. Couvreur, Living Character of Polymer Chains Prepared via Nitroxide-Mediated Controlled Free-Radical Polymerization of Methyl Methacrylate in the Presence of a Small Amount of Styrene at Low Temperature, Macromolecules 39(24) (2006) 8274-8282.
[93] J. Vinas, N. Chagneux, D. Gigmes, T. Trimaille, A. Favier, D. Bertin, SG1-based alkoxyamine bearing a N-succinimidyl ester: A versatile tool for advanced polymer synthesis, Polymer 49(17) (2008) 3639-3647.
[94] N. Ballard, M. Aguirre, A. Simula, A. Agirre, J.R. Leiza, J.M. Asua, S. van Es, New Class of Alkoxyamines for Efficient Controlled Homopolymerization of Methacrylates, ACS Macro Letters 5(9) (2016) 1019-1022.
[95] N. Ballard, M. Aguirre, A. Simula, J.R. Leiza, S. van Es, J.M. Asua, High solids content nitroxide mediated miniemulsion polymerization of n-butyl methacrylate, Polymer Chemistry 8(10) (2017) 1628-1635.
[96] N. Ballard, A. Simula, M. Aguirre, J.R. Leiza, S. van Es, J.M. Asua, Synthesis of poly(methyl methacrylate) and block copolymers by semi-batch nitroxide mediated polymerization, Polymer Chemistry 7(45) (2016) 6964-6972.
[97] A. Métafiot, S. Pruvost, J.-F. Gérard, B. Defoort, M. Marić, Synthesis of isoprene-based triblock copolymers by nitroxide-mediated polymerization, European Polymer Journal 134 (2020) 109798.
[98] K. Matyjaszewski, J. Xia, Atom Transfer Radical Polymerization, Chemical Reviews 101(9) (2001) 2921-2990.
[99] M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, Polymerization of Methyl Methacrylate with the Carbon Tetrachloride/Dichlorotris-(triphenylphosphine)ruthenium(II)/Methylaluminum Bis(2,6-di-tert-butylphenoxide) Initiating System: Possibility of Living Radical Polymerization, Macromolecules 28(5) (1995) 1721-1723.

[100] J.-S. Wang, K. Matyjaszewski, Controlled/"living" radical polymerization. atom transfer radical polymerization in the presence of transition-metal complexes, Journal of the American Chemical Society 117(20) (1995) 5614-5615.

[101] C. Granel, P. Dubois, R. Jérôme, P. Teyssié, Controlled Radical Polymerization of Methacrylic Monomers in the Presence of a Bis(ortho-chelated) Arylnickel(II) Complex and Different Activated Alkyl Halides, Macromolecules 29(27) (1996) 8576-8582.

[102] Y. Shen, H. Tang, S. Ding, Catalyst separation in atom transfer radical polymerization, Progress in Polymer Science 29(10) (2004) 1053-1078.

[103] K. Matyjaszewski, T. Pintauer, S. Gaynor, Removal of Copper-Based Catalyst in Atom Transfer Radical Polymerization Using Ion Exchange Resins, Macromolecules 33(4) (2000) 1476-1478.

[104] W. Jakubowski, K. Matyjaszewski, Activator Generated by Electron Transfer for Atom Transfer Radical Polymerization, Macromolecules 38(10) (2005) 4139-4146.

[105] W. Jakubowski, K. Min, K. Matyjaszewski, Activators Regenerated by Electron Transfer for Atom Transfer Radical Polymerization of Styrene, Macromolecules 39(1) (2006) 39-45.

[106] W. Jakubowski, K. Matyjaszewski, Activators Regenerated by Electron Transfer for Atom-Transfer Radical Polymerization of (Meth)acrylates and Related Block Copolymers, Angewandte Chemie International Edition 45(27) (2006) 4482-4486.

[107] K. Min, H. Gao, K. Matyjaszewski, Use of Ascorbic Acid as Reducing Agent for Synthesis of Well-Defined Polymers by ARGET ATRP, Macromolecules 40(6) (2007) 1789-1791.

[108] V.A. Williams, K. Matyjaszewski, Expanding the ATRP Toolbox: Methacrylate Polymerization with an Elemental Silver Reducing Agent, Macromolecules 48(18) (2015) 6457-6464.

[109] K. Matyjaszewski, W. Jakubowski, K. Min, W. Tang, J. Huang, W.A. Braunecker, N.V. Tsarevsky, Diminishing catalyst concentration in atom transfer radical polymerization with reducing agents, Proceedings of the National Academy of Sciences 103(42) (2006) 15309.

[110] K. Matyjaszewski, S. Coca, S.G. Gaynor, M. Wei, B.E. Woodworth, Zerovalent Metals in Controlled/"Living" Radical Polymerization, Macromolecules 30(23) (1997) 7348-7350.

[111] V. Percec, T. Guliashvili, J.S. Ladislaw, A. Wistrand, A. Stjerndahl, M.J. Sienkowska, M.J. Monteiro, S. Sahoo, Ultrafast Synthesis of Ultrahigh Molar Mass Polymers by Metal-Catalyzed Living Radical Polymerization of Acrylates, Methacrylates, and Vinyl Chloride Mediated by SET at 25 °C, Journal of the American Chemical Society 128(43) (2006) 14156-14165.

[112] K. Matyjaszewski, N.V. Tsarevsky, W.A. Braunecker, H. Dong, J. Huang, W. Jakubowski, Y. Kwak, R. Nicolay, W. Tang, J.A. Yoon, Role of Cu0 in Controlled/"Living" Radical Polymerization, Macromolecules 40(22) (2007) 7795-7806.

[113] B.M. Rosen, V. Percec, Single-Electron Transfer and Single-Electron Transfer Degenerative Chain Transfer Living Radical Polymerization, Chemical Reviews 109(11) (2009) 5069-5119.

[114] M. Zhong, K. Matyjaszewski, How Fast Can a CRP Be Conducted with Preserved Chain End Functionality?, Macromolecules 44(8) (2011) 2668-2677.

[115] A. Plichta, W. Li, K. Matyjaszewski, ICAR ATRP of Styrene and Methyl Methacrylate with Ru(Cp*)Cl(PPh3)2, Macromolecules 42(7) (2009) 2330-2332.

[116] S. Okada, S. Park, K. Matyjaszewski, Initiators for Continuous Activator Regeneration Atom Transfer Radical Polymerization of Methyl Methacrylate and Styrene with N-Heterocyclic Carbene as Ligands for Fe-Based Catalysts, ACS Macro Letters 3(9) (2014) 944-947.

[117] A. Simakova, S.E. Averick, D. Konkolewicz, K. Matyjaszewski, Aqueous ARGET ATRP, Macromolecules 45(16) (2012) 6371-6379.

[118] S.R. Woodruff, B.J. Davis, N.V. Tsarevsky, Selecting the Optimal Reaction Conditions for Copper-Mediated Atom Transfer Radical Polymerization at Low Catalyst Concentration, Progress in Controlled Radical Polymerization: Mechanisms and Techniques, American Chemical Society2012, pp. 99-113.
[119] N.V. Tsarevsky, W. Jakubowski, Atom transfer radical polymerization of functional monomers employing Cu-based catalysts at low concentration: Polymerization of glycidyl methacrylate, Journal of Polymer Science Part A: Polymer Chemistry 49(4) (2011) 918-925.
[120] W. Jakubowski, Adapting Atom Transfer Radical Polymerization to Industrial Scale Production: The <italic>Ultimate ATRP^{SM} </italic> Technology, Progress in Controlled Radical Polymerization: Mechanisms and Techniques, American Chemical Society2012, pp. 203-216.
[121] K. Matyjaszewski, Atom Transfer Radical Polymerization (ATRP): Current Status and Future Perspectives, Macromolecules 45(10) (2012) 4015-4039.
[122] M.B. Gillies, K. Matyjaszewski, P.-O. Norrby, T. Pintauer, R. Poli, P. Richard, A DFT Study of R−X Bond Dissociation Enthalpies of Relevance to the Initiation Process of Atom Transfer Radical Polymerization, Macromolecules 36(22) (2003) 8551-8559.
[123] W.A. Braunecker, T. Pintauer, N.V. Tsarevsky, G. Kickelbick, M. Krzysztof, Towards understanding monomer coordination in atom transfer radical polymerization: synthesis of [CuI(PMDETA)(π-M)][BPh4] (M=methyl acrylate, styrene, 1-octene, and methyl methacrylate) and structural studies by FT-IR and 1H NMR spectroscopy and X-ray crystallography, Journal of Organometallic Chemistry 690(4) (2005) 916-924.
[124] W.A. Braunecker, N.V. Tsarevsky, T. Pintauer, R.R. Gil, K. Matyjaszewski, Quantifying Vinyl Monomer Coordination to CuI in Solution and the Effect of Coordination on Monomer Reactivity in Radical Copolymerization, Macromolecules 38(10) (2005) 4081-4088.
[125] P.J. Hendra, D.B. Powell, Co-ordination complexes of butadiene with platinum-II, palladium-II and copper-I, Spectrochimica Acta 18(9) (1962) 1195-1199.
[126] M. Håkansson, K. Brantin, S. Jagner, Copper(I) complexes with conjugated dienes, Journal of Organometallic Chemistry 602(1) (2000) 5-14.
[127] M. Haakansson, S. Jagner, D. Walther, A complex between isoprene and copper(I) chloride: synthesis and structural characterization, Organometallics 10(5) (1991) 1317-1319.
[128] W.v.E. Doering, M. Franck-Neumann, D. Hasselmann, R.L. Kaye, Mechanism of a Diels-Alder reaction. Butadiene and its dimers, Journal of the American Chemical Society 94(11) (1972) 3833-3844.
[129] G. Huybrechts, L. Luyckx, T. Vandenboom, B. Van Mele, Thermal dimerization of 1,3-butadiene: Kinetics of the formation of cis, cis-cycloocta-1,5-diene, International Journal of Chemical Kinetics 9(2) (1977) 283-293.
[130] E.C.F. Ko, K.T. Leffek, Studies on the Decomposition of Tetra-alkylammonium Salts in Solution. V. Rates and Activation Parameters of Salts Containing Substituted-benzyl or Other Active Groups, Canadian Journal of Chemistry 50(9) (1972) 1297-1302.
[131] A. Anastasaki, C. Waldron, P. Wilson, R. McHale, D.M. Haddleton, The importance of ligand reactions in Cu(0)-mediated living radical polymerisation of acrylates, Polymer Chemistry 4(9) (2013) 2672-2675.
[132] J. Wootthikanokkhan, M. Peesan, P. Phinyocheep, Atom transfer radical polymerizations of (meth)acrylic monomers and isoprene, European Polymer Journal 37(10) (2001) 2063-2071.

[133] Y.-F. Zhu, F.-J. Jiang, P.-P. Zhang, J. Luo, H.-D. Tang, Atom transfer radical polymerization and copolymerization of isoprene catalyzed by copper bromide/2,2′-bipyridine, Chinese Chemical Letters 27(6) (2016) 910-914.
[134] T.V. RajanBabu, W.A. Nugent, Selective Generation of Free Radicals from Epoxides Using a Transition-Metal Radical. A Powerful New Tool for Organic Synthesis, Journal of the American Chemical Society 116(3) (1994) 986-997.
[135] R.J. Enemærke, J. Larsen, T. Skrydstrup, K. Daasbjerg, Revelation of the Nature of the Reducing Species in Titanocene Halide-Promoted Reductions, Journal of the American Chemical Society 126(25) (2004) 7853-7864.
[136] A.D. Asandei, G. Saha, Toward Cp2TiCl-Catalyzed Living Radical Polymerization of Isoprene, Polym. Prepr 46(2) (2005) 474-475.
[137] A.D. Asandei, O. Adebolu, H.S. Yu, C.P. Simpson, M. Gilbert, Carbonyl initiated Cp2TiCl-catalyzed controlled radical polymerization of isoprene, Polymer Preprints 50(1) (2009) 177.
[138] A.D. Asandei, C.P. Simpson, H.S. Yu, Cp2TiCl-catalyzed controlled radical polymerization of isoprene initiated from epoxides, aldehydes and halides, Polym. Prepr. Am. Chem. Soc 49 (2008) 73-74.
[139] A.D. Asandei, C.P. Simpson, Cp2TiCl-catalyzed synthesis of styrene/isoprene copolymers by controlled radical polymerization, Polym. Prepr. Am. Chem. Soc 49 (2008) 75-76.
[140] J. Hua, H. Xu, J. Geng, Z. Deng, L. Xu, Y.-l. Yu, Atom transfer radical polymerizations of styrene and butadiene as well as their copolymerization initiated by benzyl chloride / 1-octanol-substituted MoCl5 / PPh3, Journal of Polymer Research 18(1) (2011) 41-48.
[141] V. Vasu, J.-S. Kim, H.-S. Yu, W.I. Bannerman, M.E. Johnson, A.D. Asandei, Normal, ICAR and photomediated butadiene-ATRP with iron complexes, Polymer Chemistry 9(18) (2018) 2389-2406.
[142] V. Vasu, J.-S. Kim, H.-S. Yu, W.I. Bannerman, M.E. Johnson, A.D. Asandei, Toward Butadiene-ATRP with Group 10 (Ni, Pd, Pt) Metal Complexes, Reversible Deactivation Radical Polymerization: Mechanisms and Synthetic Methodologies, American Chemical Society2018, pp. 205-225.
[143] H.-S. Yu, J.-S. Kim, V. Vasu, C.P. Simpson, A.D. Asandei, Cu-Mediated Butadiene ATRP, ACS Catalysis 10(12) (2020) 6645-6663.
[144] T. Le, G. Moad, E. Rizzardo, S. Thang, PCT Int. Appl. Number PCT/US/97/12540. Int. Publ. Number WO 98/01478. Al. 15 January, (1998).
[145] J. Chiefari, Y.K. Chong, F. Ercole, J. Krstina, J. Jeffery, T.P.T. Le, R.T.A. Mayadunne, G.F. Meijs, C.L. Moad, G. Moad, E. Rizzardo, S.H. Thang, Living Free-Radical Polymerization by Reversible Addition−Fragmentation Chain Transfer: The RAFT Process, Macromolecules 31(16) (1998) 5559-5562.
[146] Y.K. Chong, T.P.T. Le, G. Moad, E. Rizzardo, S.H. Thang, A More Versatile Route to Block Copolymers and Other Polymers of Complex Architecture by Living Radical Polymerization: The RAFT Process, Macromolecules 32(6) (1999) 2071-2074.
[147] G. Moad, Reversible addition–fragmentation chain transfer (co)polymerization of conjugated diene monomers: butadiene, isoprene and chloroprene, Polymer International 66(1) (2017) 26-41.
[148] G. Bar-Nes, R. Hall, V. Sharma, M. Gaborieau, D. Lucas, P. Castignolles, R.G. Gilbert, Controlled/living radical polymerization of isoprene and butadiene in emulsion, European Polymer Journal 45(11) (2009) 3149-3163.

[149] R. Wei, Y. Luo, Z. Li, Synthesis of structured nanoparticles of styrene/butadiene block copolymers via RAFT seeded emulsion polymerization, Polymer 51(17) (2010) 3879-3886.
[150] R. Wei, Y. Luo, W. Zeng, F. Wang, S. Xu, Styrene–Butadiene–Styrene Triblock Copolymer Latex via Reversible Addition–Fragmentation Chain Transfer Miniemulsion Polymerization, Industrial & Engineering Chemistry Research 51(47) (2012) 15530-15535.
[151] L. Hlalele, D.R. D'hooge, C.J. Dürr, A. Kaiser, S. Brandau, C. Barner-Kowollik, RAFT-Mediated ab Initio Emulsion Copolymerization of 1,3-Butadiene with Acrylonitrile, Macromolecules 47(9) (2014) 2820-2829.
[152] V. Jitchum, S. Perrier, Living Radical Polymerization of Isoprene via the RAFT Process, Macromolecules 40(5) (2007) 1408-1412.
[153] D.S. Germack, K.L. Wooley, Isoprene polymerization via reversible addition fragmentation chain transfer polymerization, Journal of Polymer Science Part A: Polymer Chemistry 45(17) (2007) 4100-4108.
[154] S. Deibert, F. Bandermann, Rate coefficients of the free-radical polymerization of 1,3-butadiene, Die Makromolekulare Chemie 194(12) (1993) 3287-3299.
[155] B. van Büren, F. Brandl, S. Beuermann, Propagation Kinetics of Isoprene Radical Homopolymerization Derived from Pulsed Laser Initiated Polymerizations, Macromolecular Reaction Engineering 14(1) (2020) 1900030.
[156] L. Niedner, G. Kali, Green Engineered Polymers: Solvent Free, Room-Temperature Polymerization of Monomer From a Renewable Resource, Without Utilizing Initiator, ChemistrySelect 4(12) (2019) 3495-3499.
[157] U. Kalita, S. Samanta, S.L. Banerjee, N.C. Das, N.K. Singha, Biobased Thermoplastic Elastomer Based on an SMS Triblock Copolymer Prepared via RAFT Polymerization in Aqueous Medium, Macromolecules (2021).
[158] J.W. Bartels, P.L. Billings, B. Ghosh, M.W. Urban, C.M. Greenlief, K.L. Wooley, Amphiphilic Cross-Linked Networks Produced from the Vulcanization of Nanodomains within Thin Films of Poly(N-vinylpyrrolidinone)-b-Poly(isoprene), Langmuir 25(16) (2009) 9535-9544.
[159] J.W. Bartels, S.I. Cauët, P.L. Billings, L.Y. Lin, J. Zhu, C. Fidge, D.J. Pochan, K.L. Wooley, Evaluation of Isoprene Chain Extension from PEO Macromolecular Chain Transfer Agents for the Preparation of Dual, Invertible Block Copolymer Nanoassemblies, Macromolecules 43(17) (2010) 7128-7138.
[160] M. Langer, J. Brandt, A. Lederer, A.S. Goldmann, F.H. Schacher, C. Barner-Kowollik, Amphiphilic block copolymers featuring a reversible hetero Diels-Alder linkage, Polymer Chemistry 5(18) (2014) 5330-5338.
[161] M. Langer, J.O. Mueller, A.S. Goldmann, F.H. Schacher, C. Barner-Kowollik, α,ω-Reactive Building Blocks Based on a Dual Functional RAFT Agent for Thermal and Light-Induced Ligation, ACS Macro Letters 5(5) (2016) 597-601.
[162] W.M. Gramlich, G. Theryo, M.A. Hillmyer, Copolymerization of isoprene and hydroxyl containing monomers by controlled radical and emulsion methods, Polymer Chemistry 3(6) (2012) 1510-1516.
[163] X. Fei, J. Wang, J. Zhu, X. Wang, X. Liu, Biobased Poly(ethylene 2,5-furancoate): No Longer an Alternative, but an Irreplaceable Polyester in the Polymer Industry, ACS Sustainable Chemistry & Engineering 8(23) (2020) 8471-8485.
[164] S.K. Henning, T. Yoo, H.S. Chao, Farnesene-based macromonomers and methods of making and using the same, Google Patents, 2020.

[165] R.H. Kollarigowda, S. Abraham, C.D. Montemagno, Antifouling Cellulose Hybrid Biomembrane for Effective Oil/Water Separation, ACS Applied Materials & Interfaces 9(35) (2017) 29812-29819.

7 Figure Captions

Scheme 1: General mechanisms for living/anionic polymerization, and different types of RDRP methods focused in this review (including NMP, ATRP, and RAFT polymerization)

Scheme 2: Proposed products from the pyrolysis of β-pinene (1) to form isomers myrcene (2), limonene (3), and Ψ-limonene (4). The possible byproducts from decomposition reactions include 1-ethenyl-3-methylethenyl-cyclopentane (5), 5-ethylidene-1-methylcycloheptene (6), camphene (7), 2-methyl-1-propene (8), 3-methylenecyclo-pentene(9), isoprene (10), 4-methyl-1, 3-pentadiene (12), 2-methyl-1, 3-pentadiene (13), 2, 7-dimethyl-2, 6-octadiene (14) and 2-methyl-2, 6-heptadiene (15) [51].

Scheme 3: Chemical structure of farnesene isomers.

Scheme 4: Schematic of several syntheses of poly(Myr) block copolymers via anionic polymerization.

Scheme 5: General mechanism for bimolecular and unimolecular initiation in nitroxide-mediated polymerization. R· represents the initiating radical formed at high temperature from either the thermal initiator or the unimolecular initiator. M represents a single monomer unit that would become initiated by the radical. R1R2NO· is the free nitroxide that would deactivate the propagating radical.

Scheme 6: Chemical structures of a) TEMPO, b) TIPNO, and c) SG1-based nitroxides.

Scheme 7: Chemical structures of a) succinimidyl-modified SG1-based BlocBuilder^{TM} and b) Dispolreg 007 alkoxyamines.

Scheme 8: Schematic of poly(Myr-*b*-Myr-*co*-GMA) modified with morpholine groups to make amphiphilic block copolymers that self-assembled into micelles in aqueous solution [39]. The red represents the hydrophobic poly(Myr) block, and the blue represents the hydrophilic poly(GMA) block modified with morpholine, which acts as the steric stabilizer in aqueous solution.

Scheme 9: Schematic of chain-extension of poly(Myr) or poly(Far) with functional methacrylates using SG1-based (BlocBuilder and NHS-BB) and Dispolreg 007 initiators.

Scheme 10: General mechanism for ATRP using copper as the metal catalyst. Catalyst regeneration mechanisms are included for ICAR, ARGET, and SARA. [143]

Scheme 11: Cp2TiCl (3) initiated controlled radical polymerization of isoprene (7) using epoxides (5), aldehydes (5'), alkyl halides (5'') [138].

Scheme 12: General polymerization mechanism for RAFT using dithioester chain transfer agent.[141]

Scheme 13: Chemical structures of common RAFT CTAs discussed in this review.

Scheme 14: Schematic of RAFT polymerization of bio-based dienes in bulk/solution, conventional emulsion, and in seeded miniemulsion.