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Tandem Living Insertion and Controlled Radical Polymerization for Polyolefin–Polyvinyl Block Copolymers

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Abstract: Practical synthesis of polyolefin–polyvinyl block copolymers remains a challenge for transition-metal catalyzed polymerizations. Common approaches functionalize polyolefins for post-radical polymerization via insertion methods, yet sacrifice the livingness of the olefin polymerization. This work identifies an orthogonal radical/spin coupling technique which affords tandem living insertion and controlled radical polymerization. The broad tolerance of this coupling technique has been demonstrated for diverse radical/spin traps such as 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO), 1-oxyl-(2,2,6,6-tetramethylpiperidine)-4-yl- α -bromoisobutyrate (TEMPO-Br), and *N*-tert-butyl- α -phenylnitron (PBN). Subsequent controlled radical polymerization is demonstrated with nitroxide-mediated polymerization (NMP) and atom transfer radical polymerization (ATRP), yielding polyolefin–polyvinyl di- and triblock copolymers ($\bar{D} < 1.3$) with acrylic, vinylic and styrenic segments. These findings highlight radical trapping as an approach to expand the scope of polyolefin-functionalization techniques to access polyolefin macroinitiators.

Introduction

The extensive investigation into the synthesis of functionalized polyolefins has led to a variety of techniques which polymerize olefins and polar vinyl monomers using functional group tolerant catalysts,^[1] combined polymerization techniques,^[2] and stimuli responsive reactions.^[3] Late-transition metal–organic coordination–insertion catalysts have served as an ubiquitous platform to explore functionalized polyolefins due to their control over olefin polymerization, functional group tolerance, and stimuli responsive behavior.^[4] Cationic α -diimine palladium(II) catalysts displayed a breakthrough in coordination–insertion polymerization due to their tolerance towards acrylic monomers which allowed for polyolefin syntheses with moderate polar monomer incorporations up to 10%.^[1c,5] Development of

functional group tolerant catalysts, however, has been restricted to random copolymer syntheses in a purely coordination–insertion method. As such, techniques to synthesize chain-end functionalized polyolefins for post-polymerization have risen and remain the dominant method to synthesize polar-polyolefin block copolymer architectures.

A predominant strategy to functionalize polyolefins is to incorporate a reactive molecule via the coordination–insertion pathway. Work by Chung et al. has demonstrated chain-end functionalization of polyolefins with metallocene catalysts by employing borane and *p*-methylstyrene capping units.^[6] Following post-transformation reactions to yield macroinitiators, free radical polymerization was performed to prepare diblock copolymers. Another example of chain-end functionalization with metallocenes has been shown by Scott et al., in which polyolefin macroinitiators capped with α -methylstyrene undergo free radical polymerization affording a mixture of homopolymers and diblock copolymers.^[7] An alternative functionalization approach was demonstrated by Guironnet et al., in which polyolefins with terminal alkenes were synthesized, and post-functionalization via cross-metathesis installed reactive handles capable of ring-opening polymerization (ROP).^[8] These methodologies largely suffer from multi-step syntheses, post-transformation, and/or generate side-products in the form of homopolymers. Recently, our group has demonstrated a one-pot approach to prepare polar-polyolefin block copolymers via a developed metal-organic insertion light-initiated radical (MILRad) polymerization.^[3a,9] The major advances of this approach is that a single catalyst accomplishes both the insertion and radical polymerization, avoiding multistep synthesis and post-functionalization, and prevents homopolymers from being generated during the radical polymerization. This technique employs a cationic palladium(II) diimine catalyst which polymerizes olefins in a living coordination–insertion manner ($\bar{D} < 1.1$). A polyolefin macroradical is generated through blue light irradiation, which undergoes free radical polymerization in the presence of vinyl monomers. This has established MILRad polymerization as a facile method for generating polar-polyolefin block copolymers. However, one of the drawbacks for all these aforementioned approaches is the sacrificed chain-end fidelity due to the free radical polymerization, which prevents multiple chain extensions. Therefore, approaches linking coordination–insertion polymerization to reversible-deactivation radical polymerization (RDRP) techniques such as ATRP,^[2a,c,10] and reversible addition–fragmentation

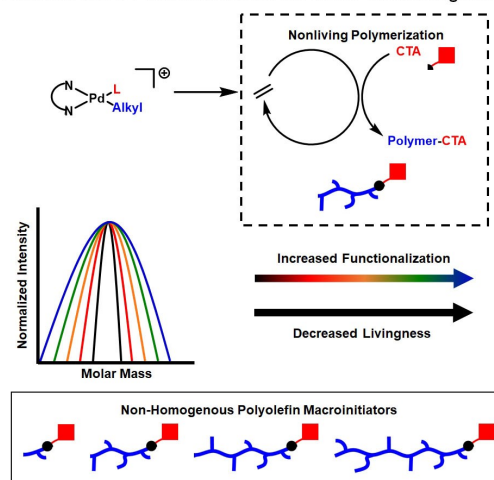
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chain-transfer (RAFT)^[11] polymerization have been investigated by several research groups.

Previous work from Matyjaszewski et al. has shown a method for the functionalization of polyethylene (PE) via degenerative chain-transfer yielding hydroxy functionalized linear polyethylene.^[10a] The crystalline hydroxy-polyethylene was subsequently transformed into an ATRP macroinitiator with molar mass ($< 2000 \text{ g mol}^{-1}$), narrow molecular weight distribution MWD, ($\bar{D} < 1.4$) and chain-end functionalization as high as 55 %. Subsequent ATRP extension resulted in block and graft copolymers with acrylic segments. Another approach by Mecking et al. demonstrated a direct incorporation of an alkoxyamine unit into polyethylene via a chain-transfer mechanism.^[12] Increasing the amount of the chain-transfer agent (CTA) up to 100 equivalents allowed for high functionalization (90 %), while generating broad MWD polyolefin macroinitiators ($\bar{D} = 1.6$). Subsequent NMP from the alkoxyamine afforded polyethylene block copolymers with styrenic and acrylic segments ($\bar{D} = 1.4\text{--}2.0$). While these approaches highlight access to living radical polymerization to give polar-polyolefin block copolymers, the multi-step synthesis and chain-transfer mechanism sacrifices the livingness of the coordination-insertion polymerization, emphasizing the need for alternative functionalization approaches in late-transition metal catalysts (Figure 1).

Since MILRad polymerization is capable of generating polyolefin radicals while maintaining a living coordination-insertion polymerization, our group hypothesized light irradiation could serve as an ideal functionalization approach due to its innocuous effect on the coordination-insertion mechanism. Radical traps have been shown to prevent a free radical polymerization from these catalysts,^[13] yet installation of functional polymerization handles has never been shown via radical trapping methods for these late-transition metal catalysts. In key experiments that probed the mechanism, the radical trap TEMPO was employed to capture the macroradical for analytical compound characterization purposes.^[9a] The reaction products were found to include TEMPO-capped polyolefins and a cationic three membered ring Pd–N–O complex. These experiments served as inspiration for an alternative approach to polyolefin functionalization, where macroradical coupling with TEMPO was shown to be tolerant to the palladium complex, high in yield (90 %) and site specific. This discovery led to the development of a new strategy as outlined in Figure 2, where addition of radical/spin traps as opposed to vinyl monomers would achieve robust polyolefin functionalization with direct access to RDRP techniques. This would allow MILRad polymerization to not only function as a polymerization platform,^[3a,9] but would expand its uses to polyolefin functionalization. In an effort to explore the scope and effectiveness of radical functionalization for polyolefins, three nitroxide analogues were selected as radical/spin traps (Figure 2). Their reaction with polyolefin macroradicals would allow for immediate post-polymerization, obviating the need for further post-transformation reactions. This departure from classical approaches (CTAs) that rely solely upon insertion-coordination chemistry to install reactive groups ensures that the living-

A) Previous Work: Functionalization via Chain Transfer Agents



B) This Work: Functionalization via Radical Mechanism

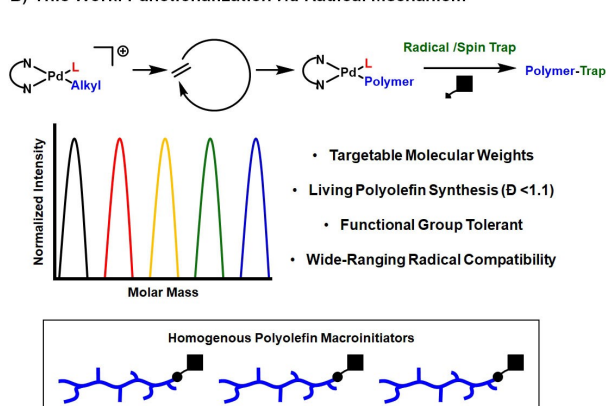


Figure 1. A) Overview of traditional approaches to functionalize polyolefins with chain-transfer agents (CTAs) which sacrifice the living insertion polymerization. B) Current work which identifies an orthogonal radical functionalization, allowing for well-defined, low-dispersity polyolefin macroinitiators.

ness of the polyolefin block is not sacrificed, while immediately yielding polyolefin macroinitiators suitable for block copolymer synthesis. Herein, we report the first functional group tolerant radical/spin coupling mechanism for polyolefins generated with cationic palladium(II) diimine complexes. Following the functionalization of polyethylene, subsequent RDRP techniques such as NMP and ATRP were performed yielding narrow molecular weight distribution polyolefin-polyvinyl di- and triblock copolymers, highlighting MILRad functionalization of polyolefins as a facile method which affords both living insertion and controlled radical polymerization for multiblock copolymer synthesis.

Results and Discussion

Two palladium diimine complexes were employed in the reactions detailed within the manuscript. A mononuclear Pd^{II} complex (**2a**) and a binuclear Pd^{II} complex (**bis-2a-DHFC**) were synthesized from our previous synthetic

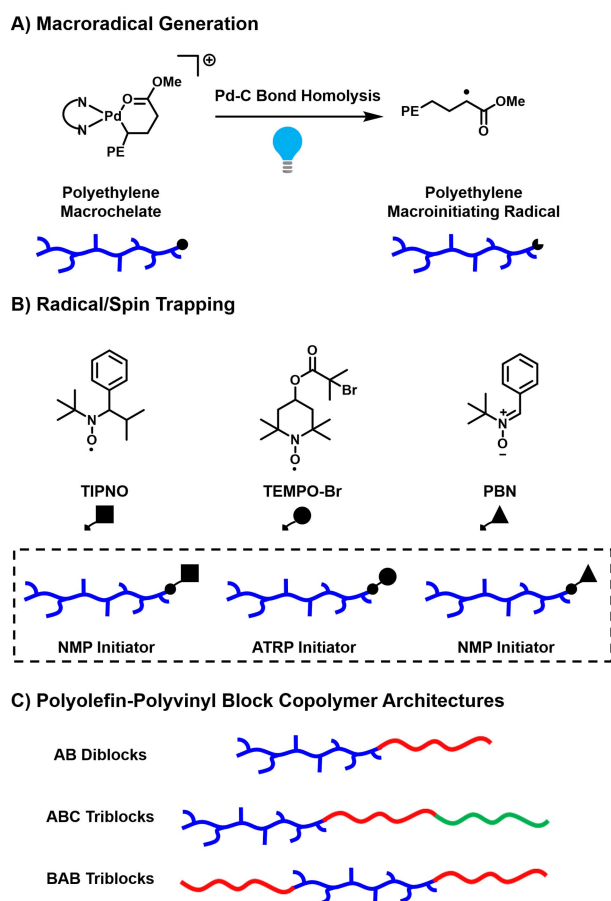


Figure 2. A) Overview of polyolefin macroradical generation. B) Capture of macroradical with radical/spin trap affords NMP and ATRP macroinitiators. C) Scope of polyolefin–polyvinyl block copolymers discussed in the text.

reports (Figure 3).^[9a] The mononuclear complex serves as a foundation to prepare AB diblocks as well as ABC triblocks, whereas the binuclear complex was selected to synthesize symmetrical BAB triblocks. Synthesis of the radical traps TIPNO^[12] and TEMPO-Br^[14] were performed with modified literature procedures. TIPNO was selected as an ideal radical trap which would yield a telechelic polyolefin capable of undergoing NMP (Figure 3A).^[15] NMP of styrene was demonstrated for the polyolefin macroinitiators, a monomer class that was not compatible with our previous established MILRad polymerization. To explore other complementary RDRP techniques, the TEMPO-Br radical trap was selected to install an α -bromoisobutyrate chain-end, which has been used as an initiator for both copper catalyzed ATRP and organocatalyzed atom transfer radical polymerization (O-ATRP) (Figure 3A).^[14,16] ATRP was demonstrated for MMA, a monomer class that NMP nor MILRad can polymerize in a controlled fashion. A key hallmark of NMP and ATRP is the chain-end fidelity exhibited by the radical polymerization, which allows for subsequent extensions to synthesize ABC triblock copolymers. This is another advantage over techniques which are limited to initiating free radical polymerization from poly-

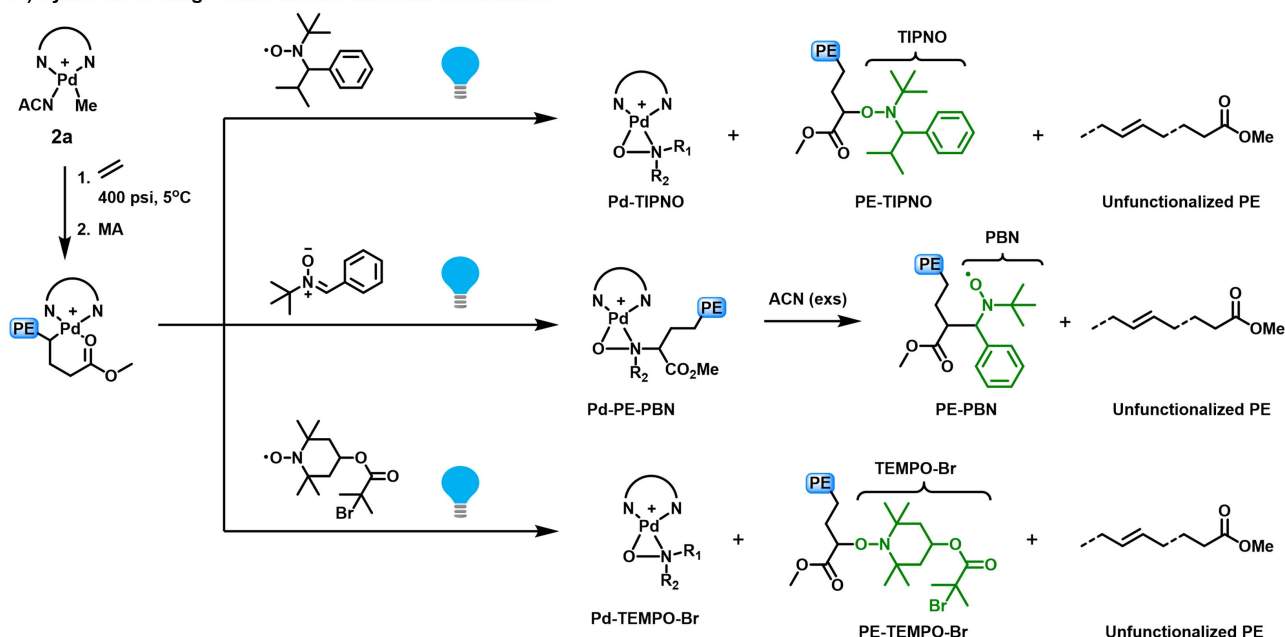
olefins, as multiblock architectures would not be achieved. Lastly, PBN was selected as another radical coupling reagent that functions as a spin trap (Figure 3). The benefits of employing PBN as a spin trap is not only the capability to perform NMP, but PBN has also been utilized for radical coupling reactions to synthesize block copolymers.^[17] The radical/spin traps selected for this work provide a framework for the scope of reagents suitable to generate telechelic polyolefins.

Established conditions for the living coordination–insertion polymerization of ethylene were used.^[9a] The living polymerization allows for targetable molecular weights of the polyolefin block by adjusting the reaction time. This has been demonstrated by synthesizing polyolefin blocks with molar masses ranging from 4–37 kDa, all with narrow molecular weight distributions ($\mathcal{D} < 1.1$). Once the targeted polyolefin molecular weight was achieved, addition of methyl acrylate (MA) followed by removal of volatiles yields a stable macrochelatate. Characterization of the macrochelatate (**2a-PE-MA**) was performed via ¹H NMR, confirming the connectivity of the Pd^{II} species to all polyethylene chains formed (Figure S9). Following characterization, the macrochelates are immediately used for radical/spin trapping reactions.

The mechanism for radical generation from the aforementioned polyolefin macrochelates has been thoroughly investigated.^[9a,18] Addition of an ancillary ligand to the reaction mixture in the presence of blue light irradiation facilitates the palladium–carbon bond homolysis for non-sterically hindered diimine complexes. An ancillary ligand is not necessary for palladium(II) diimine complexes with added steric rotation barriers to benzhydryl substituents of the diimine backbone and homolysis can occur solely via photoirradiation.^[18] Radical traps have been used to probe and confirm the generation of radicals from the palladium catalyst,^[13] yet further utilization of this single-site radical transformation had not been shown until now. As opposed to CTA functionalization approaches^[10a,12] which require a multistep synthesis of novel reagents for every desired functional handle, immediate application of known radical and spin traps is achieved without transformation prior to use.

In a typical reaction to synthesize the polyolefin macroinitiators, macrochelates are dissolved in degassed chlorobenzene in a round bottom flask equipped with a stir-bar in a glove bag. To start the reaction, methyl acrylate and acetonitrile are injected into the flask with the selected radical/spin trap. The reaction is then irradiated with blue light (455 nm) and run at room temperature. Large-scale reactions were successfully demonstrated to immediately yield gram quantities of polyolefin macroinitiators. The tolerance of this radical coupling technique allows all macroinitiators to be synthesized in identical conditions, and removal of the generated Pd–N–O complexes is achieved via filtration. Interestingly, the nature of the radical trap directly influences the degree of functionalization. A 81 % and 50 % functionalization is achieved with TIPNO and TEMPO-Br traps respectively, compared to the 90 % functionalization previously demonstrated for TEMPO.

A) Synthesis of Single-Site Functionalized Macroinitiators



B) Synthesis of Dual-Site Functionalized Macroinitiators

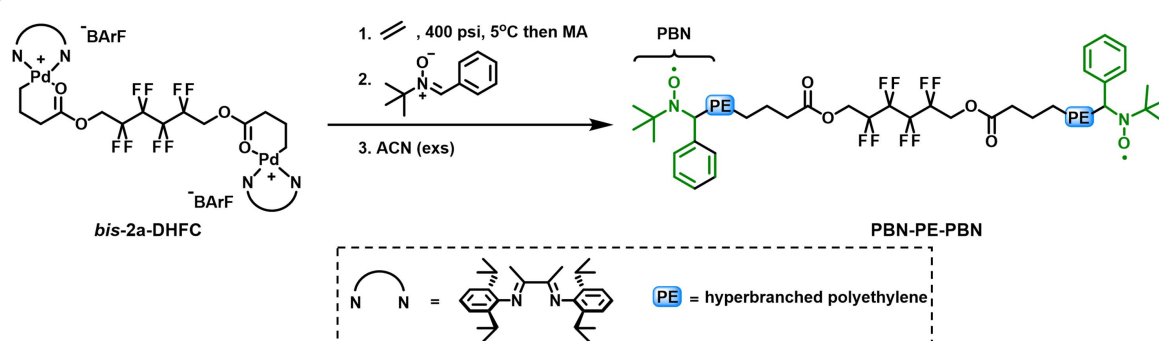


Figure 3. Overview of polyolefin macroinitiator synthesis which yields the macroinitiator, three-membered ring Pd–N–O complex, and chain-transfer polyethylene side product. A) Single-site functionalized macroinitiators capable of generating AB diblock and ABC triblock copolymers. B) Dual-site functionalized macroinitiator capable of generating symmetrical BAB triblock copolymers.

Factors contributing to the difference in the efficiency of macroinitiator formation were investigated in two experiments. Firstly, the rate at which the nitroxides react with the **2a** palladium (II) diimine complex under light irradiation was studied by monitoring the reaction over six hours by ^1H NMR spectroscopy. The kinetics showed that the order of reactivity decreases from $\text{TEMPO} > \text{TEMPO-Br} > \text{TIPNO}$, suggesting that the structure of the nitroxides directly influences the rate of radical generation to yield the three-membered ring Pd–N–O complex (Figure 3, Figure S8). Secondly, the rate at which the nitroxides promote chain transfer was monitored in the dark for synthesized macrochelates. These results showed that TEMPO and TIPNO do not promote chain transfer, while the polar ester moiety in the TEMPO-Br nitroxide promoted chain transfer evidenced by the new peak observed at the olefinic region (Figure S11B, Table S2). Taken together, the bulkiness of the nitroxide plays a minor role in radical generation (90 % vs. 81 % functionalization for TEMPO vs. TIPNO), while

the presence of polar groups is thought to have a more dominant effect on functionalization (90 % vs. 50 % functionalization for TEMPO vs. TEMPO-Br). Notwithstanding, all radical/spin traps effectively generated macroinitiators in a one-pot reaction. Macroinitiators were characterized via a combination of techniques including electron paramagnetic resonance (EPR), NMR, matrix-assisted laser desorption/ionization time of flight (MALDI-ToF) and GPC analyses. The alkoxyamines are readily characterized by NMR, while the paramagnetic macroradicals were subjected to EPR analysis. Controlled radical polymerizations were lastly demonstrated for all synthesized macroinitiators, yielding block copolymers with molar masses ranging from 28–161 kDa and molecular weight distributions ranging from $\bar{D} = 1.2$ –1.5.

Initially, NMP was demonstrated with PE-TIPNO macroinitiators as a way to investigate controlled radical polymerization from functionalized polyolefins. Typical NMP conditions were utilized for the polymerization of

Table 1: Selected polyolefin–polyvinyl block copolymers.^[d]

Entry	Sample	Polyolefin Block				Vinyl Block	Polyolefin- <i>b</i> -polyvinyl		
		Macro-initiator	M_n [kg mol ⁻¹]	M_w [kg mol ⁻¹]	\bar{D}		M_n [kg mol ⁻¹]	M_w [kg mol ⁻¹]	\bar{D}
1 ^[a,c]	PE-PS	PE-TIPNO	10.3	10.6	1.03	PS	45.6	56.5	1.24
2 ^[a,c]	PE-PI	PE-TIPNO	13.9	14.2	1.02	PI	57.6	82.4	1.43
3 ^[a,c]	PE-P(nBA)	PE-TIPNO	7.9	8.2	1.04	P(nBA)	28.3	39.3	1.39
4 ^[a,c]	PE-PS-P(nBA)	PE-TIPNO	10.5	11.0	1.05	PS-P(nBA)	49.8	64.2	1.29
5 ^[a,c]	PH-PBN	PH-PBN	4.0	4.1	1.02	—	—	—	—
6 ^[a,c]	PE-PS	PE-PBN	11.7	12.2	1.04	PS	38.8	47.0	1.21
7 ^[b,c]	PS-PE-PS	PBN-PE-PBN	36.8	39.9	1.09	PS	160.5	273.2	1.70
<i>Hydrolyzed Sample</i>							80.5	143.3	1.78
8 ^[a,c]	PE-PMMA	PE-TEMPO-Br	13.9	14.2	1.02	PMMA	32.9	38.8	1.18
9 ^[a,c]	PE-PMMA	PE-TEMPO-Br	13.9	14.2	1.02	PMMA	66.5	101.5	1.53
10 ^[a,c]	PE-PMMA-PMMA	PE-PMMA-Br	66.5	101.5	1.53	PMMA	155.5	238.0	1.53

[a] Complex used for the syntheses: **2a**. [b] Complex used for the syntheses: **bis-2a-DHFC**. [c] Molecular weight and dispersity index (\bar{D}) were determined by GPC analysis with samples run in THF at 40 °C calibrated to poly(methyl methacrylate) standards. [d] Samples correspond to polyolefin–polyvinyl block copolymers synthesized as described in the text with a variety of block compositions. Abbreviations; PE = poly(ethylene), PH = poly(1-hexene), PS = poly(styrene), PI = poly(isoprene), P(nBA) = poly(*n*-butyl acrylate), PMMA = poly(methyl methacrylate).

styrene, isoprene and *n*-butyl acrylate from PE-TIPNO macroinitiators yielding di- and triblock copolymers (Figure 4). Results from the crude products show the formation of the block copolymers as well as unreactive polyolefin precursors (Figure S17A). Block copolymers were obtained utilizing Soxhlet extraction to remove the unreacted polymer, and monomodal traces were obtained (Figure S17B). This separation is possible due to the fact that the incorporation of the more polar monomers decreased the block copolymer solubility in non-polar alkanes, and extraction with pentanes allowed for selective removal of the unreactive polyolefin chains. The lower molecular weight polymer was identified as unreacted polyethylene, while the peak which shifted to a higher molecular weight is the block copolymer. This is supported by the ¹H NMR for the PE-TIPNO macroinitiator which identified that the macroinitiator was 82 % functionalized, while the chain-transfer side product exists as non-functionalized polyethylene incapable of chain extension (Figure S12, Table 1 Entry 1).

To further confirm that the block copolymerization was successful, ¹H diffusion-ordered NMR spectroscopy (DOSY) was employed for PE-*b*-PS diblock copolymers (Figure 5, Table 1 Entry 1). The PE-TIPNO macroinitiator and the purified PE-*b*-PS in which unreacted PE was removed were both analyzed. The 2D spectrum of the PE-TIPNO polymer exhibits a diffusion coefficient of 5.97×10^{-11} (cm²sec⁻¹) (Figure 5A). The purified PE-*b*-PS sample exhibited a single resonance where the signals of PE (1.26–0.9 ppm) and PS (7.4–6.3 ppm) are aligned at the same diffusion coefficients, confirming the block copolymer architecture (Figure 5B). A diffusion coefficient of 1.76×10^{-11} (cm²sec⁻¹) was obtained for the block copolymer, which was expected to diffuse at a slower rate than that of the PE-TIPNO macroinitiator. The purified block copolymer was submitted for small-angle X-ray scattering (SAXS) analysis, and exhibited principal scattering peaks, also confirming the existence of block copolymer structures (Figure S17C). To probe the self-assembly of these poly-

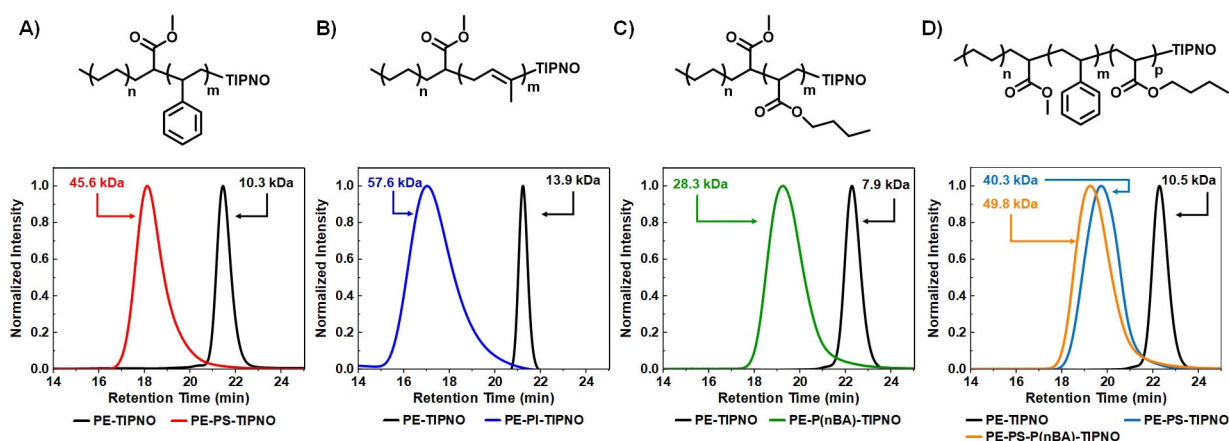


Figure 4. Collection of GPC traces for block copolymers synthesized from PE-TIPNO macroinitiators via NMP. A) PE-*b*-PS diblock copolymer. B) PE-*b*-PI diblock copolymer. C) PE-*b*-PS(*n*BA) diblock copolymer. D) PE-*b*-PS-*b*-P(*n*BA) triblock copolymer.

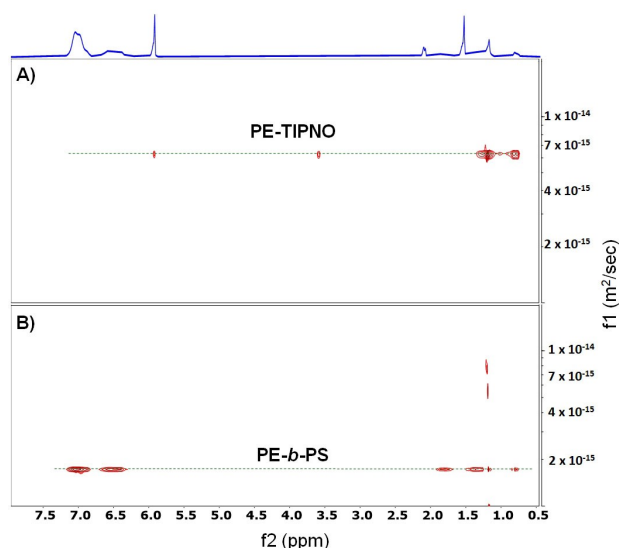


Figure 5. ^1H DOSY NMR (600 MHz, $\text{TCE-}d_2$, 298 K): A) PE-TIPNO macroinitiator; B) purified PE-*b*-PS. The resonances corresponding to the PE block and the PS block show similar diffusion behavior. No unreacted PE is detected in the purified sample.

mers, transmission electron microscopy (TEM) was applied. PE-*b*-PS block copolymers yielded light cloudy solutions at a concentration of 2 mg mL^{-1} in both polar (acetone) and nonpolar (hexane) solvents (Figure S20A). The dispersion samples were analyzed by TEM, confirming the ability of the block copolymers to self-assemble into micelles in selective solvents of their homopolymer compartments (Figure 6). To highlight the chain-end fidelity of the PE-*b*-PS block copolymers, polymerization of *n*-butyl acrylate was performed to form PE-*b*-PS-*b*-PnBA triblock copolymers (Figure 4D, Table 1 Entry 4). A complete shift toward the higher molecular weight region is observed, showing that all diblock copolymers are capable of subsequent radical polymerization reactions, and the ABC triblock copolymer does not require further purification (Figure S19).

Of the potential products generated from the radical trapping of polyethylene with TIPNO, only the alpha-TIPNO product is suitable for NMP (Figure 7A). Studer et al. confirmed that the strength of the C–ON bond when bound to a methylene unit in a polyolefin is not suitable for

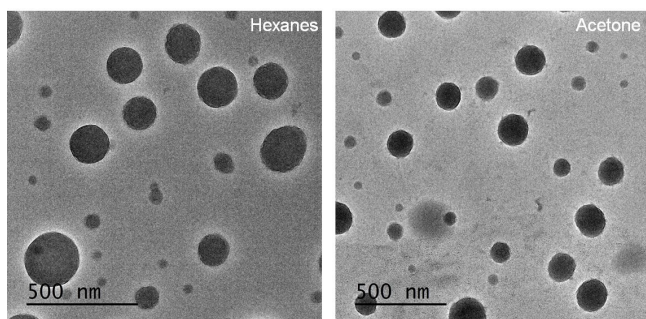
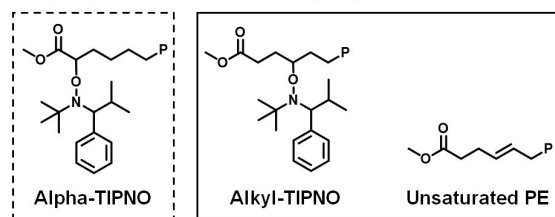
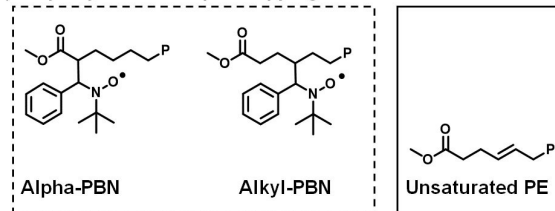


Figure 6. TEM imaging shows self-assembly of PE-*b*-PS block copolymers in hexanes and acetone, respectively.

A) Polyethylene-TIPNO Radical Trapping Products



B) Polyethylene-PBN Spin Trapping Products



----- Products Suitable for NMP

————— Products Not Suitable for NMP

Figure 7. A) Products generated during the radical trapping of polyethylene macrochelates with TIPNO. B) Products generated during the spin trapping of polyethylene macrochelates with PBN.

NMP.^[19] The alpha-TIPNO product is suitable for NMP as the resultant radical generated from the C–ON homolysis is stabilized by resonance with the acrylic moiety. To avoid generating unreactive macroinitiators for NMP, spin trapping with PBN, as opposed to TIPNO, was explored, as the synthesized polymers would not generate strong C–ON bonds that are incapable of NMP (Figure 7B). All spin-trapped products were expected to be suitable for subsequent polymerization in which the alkoxyamine would be generated in situ affording labile C–ON bonds necessary for NMP.

To characterize the spin products which would result stable macroradicals, a combination of EPR and MALDI-ToF experiments were performed to confirm the macroradical nature and connectivity of the nitron to the synthesized polymer (Figure 8). A mixture of two products (Pd-PE-PBN complex and PE-PBN macroradical) are produced following the light initiated radical production in the presence of PBN, where upon treatment with dimethyl sulfide afforded a single carbon-centered stable radical.^[9a] A milder purification process has now been established through treatment with acetonitrile for two hours, which gives a single radical species (Figure 8A and S13). The strong binding affinity of the acetonitrile efficiently complexes with the PE-PBN-Pd product, yielding Pd byproducts and releasing stable macroradicals of PE-PBN that can be easily extracted with hexanes (Figure 7B). The PE-PBN macroradical exhibited measured coupling constants of $a_{\text{H}} = 3.20 \text{ G}$ and $a_{\text{N}} = 14.53 \text{ G}$, which is consistent with values measured for Me-PBN adducts.^[20] Following confirmation of the stable free radical, low molecular weight poly(1-hexene)-PBN (PH-PBN) macroinitiators were synthesized so that they could be characterized by MALDI-ToF (Table 1 Entry 5). 1-Hexene was used as opposed to ethylene so that

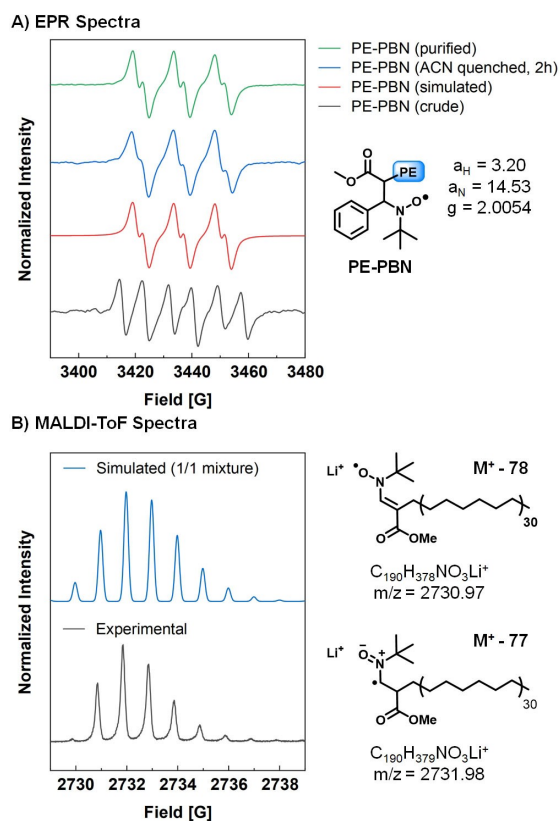


Figure 8. A) CW X-band (9.5 MHz, rt) EPR spectra of the spin trapping of polyethylene macroradicals with PBN. The crude product (black) shows a mixture of polyolefin macroradicals PE-PBN-Pd and PE-PBN. Addition of acetonitrile releases the palladium and yields a single PE-PBN radical signal (green). B) Expansion of the MALDI-ToF spectra of PH-PBN macroinitiator, with major fragments shown for DP=30.

the larger peak-to-peak mass difference (Δ value) results in a better resolution in the mass spectrum. The ability to use ethylene and α -olefins is another avenue in which block copolymer development can be tuned. The MALDI-ToF spectrum of the resultant polymer shows a main distribution (Figure S15) with a Δ of 84 corresponding to the 1-hexene monomer. Additionally, molecular weight agreement between the predicted structure and experimental results again support chain-end functionalization with PBN (Figure 8B). To our best knowledge, this is the first polyolefin-nitroxide stable radical which was fully isolated and characterized by EPR and MALDI-ToF.

To demonstrate the viability of living radical polymerization from stable polyolefin macroradicals, NMP was demonstrated with the characterized PE-PBN macroinitiators in a similar manner to PE-TIPNO. Successful extension with styrene was demonstrated, and PE-*b*-PS block copolymers with a molar mass of 39 kDa and $D=1.21$ were generated (Table 1 Entry 6). Following these studies, double headed initiators were prepared via spin trapping of macrochelates stemming from the **bis-2a-DHFC** complex, allowing direct access to symmetrical BAB triblock copolymers.

To generate telechelic macroinitiators, catalyst **bis-2a-DHFC** was selected due to the binuclear Pd^{II} complex

allowing for selective dual-site functionalization along the polyolefin chain (Figure 3A). The macrochelat **bis-2a-DHFC-PE-MA** was synthesized corresponding to the **2a** catalyst equivalent, with addition of MA and removal of volatiles after the targeted molecular weight was achieved. The double headed macrochelat was then subjected to photo-induced bond homolysis in a similar fashion to prepare difunctional telechelic polyethylene PBN-PE-PBN macroinitiators. Following synthesis of the double headed initiator (Table 1 Entry 7), successive extension was demonstrated with styrene in an effort to synthesize polystyrene-*b*-polyethylene-*b*-polystyrene triblock copolymers. These styrenic block copolymers (SBCs) are unique for their thermo-plastic elastomeric properties, and are commonly synthesized by anionic polymerization followed by hydrogenation.^[21] An advantage to this method is both segments are synthesized with tolerant polymerization techniques, and also do not require post-polymerization hydrogenation to achieve an elastomeric olefin block. NMP of styrene for the PBN-PE-PBN macroinitiator (37 kDa) gave the PS-PE-PS triblock copolymer (Table 1 Entry 7). A key component of the **bis-2a-DHFC** complex is the fluorinated ester linkage which is susceptible to transesterification. As evidence of simultaneous chain growth from both ends of the polymer, the obtained triblock copolymer (161 kDa) was subjected to hydrolysis (Figure 9). The hydrolyzed triblock product exhibits a halved molar mass of 81 kDa, and disappearance of the ester linkage protons at 4.56 ppm confirms the complete hydrolysis of the parent polymer.

In an effort to expand the scope of polymer structures that can be generated in a living manner, ATRP from polyolefins with terminal bromine handles was explored (Figure 3A). Both traditional copper-catalyzed and metal-free approaches were explored. Supplemental activation reducing agent (SARA) ATRP was first selected as it has been demonstrated to react faster than normal ATRP conditions and at much lower catalyst concentrations (1–50 ppm).^[22] Polymerization was demonstrated for methyl methacrylate, a monomer that the NMP macroinitiators

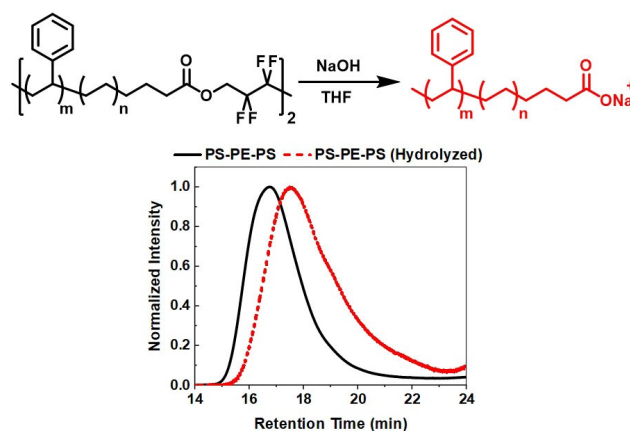


Figure 9. GPC trace of the PS-*b*-PE-*b*-PS triblock copolymer synthesized from PBN-PE-PBN macroinitiator and hydrolyzed product.

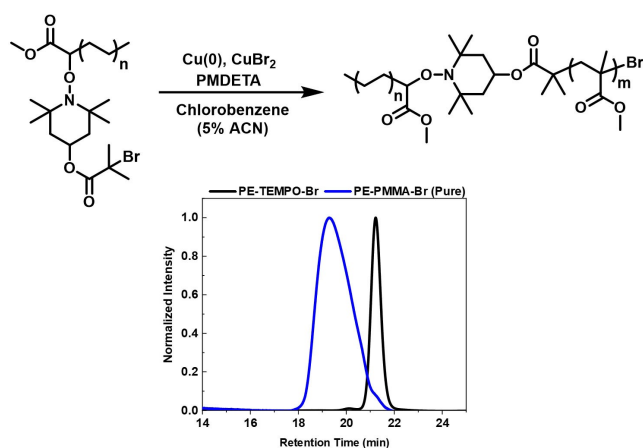


Figure 10. GPC trace of PS-*b*-PMMA diblock copolymer synthesized from PE-TEMPO-Br macroinitiator.

were not suitable for.^[23] A functionalization of up to 50 % was achieved for the TEMPO-Br capping of macrochelates (Figure S16). As opposed to the structures of TIPNO and PBN, the TEMPO-Br radical trap has a strongly coordinating ester moiety that can promote chain transfer of the macrochelates. Despite this observed effect on the capping efficiency, the generated polyolefins (\bar{D} =1.02) and PE-*b*-PMMA block copolymers (\bar{D} =1.18) remained narrow in their molecular weight distribution reaching molar masses of 33 kDa (Figure 10, Table 1 Entry 8). SARA ATRP operates with ppm-level concentration of catalyst, and the presence of residual palladium and diimine ligand following purification could affect the polymerization and might cause the lower initiation efficiency which will be further investigated in future studies. O-ATRP functions as a metal-free approach to polymerizing monomers in a visible-light photoredox catalytic manner.^[24] For our system, an oxygen-doped anthracene (ODA) photocatalyst was selected which functions in non-polar organic solvents, ideal for polyolefin macroinitiators.^[25] The PE-PMMA diblock copolymers reached molar mass of 66 kDa (Table 1 Entry 9), and a successful chain-extension was shown (Table 1 Entry 10, Figure S24), highlighting the chain-end fidelity for these polymers. Both metal-catalyzed and photoredox-catalyzed systems were successful in forming block copolymers with methacrylic segments. In all, these results again highlight the important role of functional group tolerance exhibited by the palladium diimine complex which allows for a wide variety of radical/spin traps to be applied, while also demonstrating that orthogonal controlled polymerizations yielding well-controlled block copolymers.

Conclusion

Expansion of new techniques which can bridge coordination-insertion with radical polymerization has accelerated the ability to synthesize functional polyolefin block copolymers for the development of next-generation materials. Herein, we report a versatile radical/spin trapping technique

in which tailorable chain-end functionalization of polyolefin is achieved with synthetic and commercial radical/spin traps. In this study, the reactivity of the different radical/spin traps to undergo C–C and C–X bond formation yielding functional polyolefins were explored and all coupling reactions afforded macroinitiators in a one-pot method. We anticipate these findings will pave the way for further coupling reactions with polyolefins promoted by metal–carbon bond homolysis. The major breakthrough of this polyolefin functionalization, named MILRad functionalization, can be summarized as; 1) the tolerance towards nitroxides and nitrones allows for a variety of reagents to install reactive chain-ends; 2) since a chain-transfer agent is not employed, functionalization via a radical pathway is achieved without sacrificing the livingness of the polyolefin blocks; 3) mono- and binuclear palladium diimine complexes can undergo a triggered radical homolysis to create a polyolefin macro-radical, enabling precise tuning of polyolefin properties with well-established catalysts. Taking advantage of this approach, controlled NMP and ATRP were demonstrated from functional polyolefins with acrylic, styrenic, and vinylic monomers which expands the chemical and physical properties of polyolefins to generate post-modern materials. Additionally, the tandem living system permits a precise macromolecular design, which has been demonstrated by the novel ABC and BAB triblock copolymer architectures. With importance given to the largely unnoticed compatibility of coordination-insertion and radical chemistry, a new outlook toward functionalizing polyolefins can be applied to other established techniques, further expanding the scope of coordination-insertion catalysts towards polyolefin-polyvinyl block copolymers.

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Conflict of Interest

The authors declare no conflict of interest.

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- [1] a) L. H. Guo, W. J. Liu, C. L. Chen, *Mater. Chem. Front.* **2017**, *1*, 2487–2494; b) L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414–6415; c) C. M. Killian, D. J. Tempel, L. K. Johnson, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 11664–11665; d) S. Mecking, L. K. Johnson, L. Wang, M. Brookhart, *J. Am. Chem. Soc.* **1998**, *120*, 888–899; e) B. P. Carrow, K. Nozaki, *Macromolecules* **2014**, *47*, 2541–2555; f) C. Tan, C. Chen, *Angew. Chem. Int. Ed.* **2019**, *58*, 7192–7200; *Angew. Chem.* **2019**, *131*, 7268–7276.
- [2] a) S. C. Hong, S. Jia, M. Teodorescu, T. Kowalewski, K. Matyjaszewski, A. C. Gottfried, M. Brookhart, *J. Polym. Sci. Part A* **2002**, *40*, 2736–2749; b) G. H. Chen, D. Huynh, P. L. Felgner, Z. B. Guan, *J. Am. Chem. Soc.* **2006**, *128*, 4298–4302; c) K. Zhang, J. Wang, R. Subramanian, Z. Ye, H. Lu, Q. Yu, *Macromol. Rapid Commun.* **2007**, *28*, 2185–2191.
- [3] a) A. Keyes, H. E. Basbug Alhan, U. Ha, Y.-S. Liu, S. K. Smith, T. S. Teets, D. B. Beezer, E. Harth, *Macromolecules* **2018**, *51*, 7224–7232; b) C. K. A. Gregson, V. C. Gibson, N. J. Long, E. L. Marshall, P. J. Oxford, A. J. P. White, *J. Am. Chem. Soc.* **2006**, *128*, 7410–7411.
- [4] A. Keyes, G. R. Jones, H. E. Basbug Alhan, E. Ordonez, U. Ha, H. Dau, D. B. Beezer, E. Tsogtgerel, Y.-S. Liu, E. Harth, *Angew. Chem. Int. Ed.* **2019**, *58*, 12370–12391; *Angew. Chem.* **2019**, *131*, 12498–12520.
- [5] A. M. LaPointe, M. Brookhart, *Organometallics* **1998**, *17*, 1530–1537.
- [6] T. C. M. Chung, *Macromolecules* **2013**, *46*, 6671–6698.
- [7] C. J. Kay, P. D. Goring, C. A. Burnett, B. Hornby, K. Lewtas, S. Morris, C. Morton, T. McNally, G. W. Theaker, C. Waterson, P. M. Wright, P. Scott, *J. Am. Chem. Soc.* **2018**, *140*, 13921–13934.
- [8] D. J. Walsh, E. Su, D. Guironnet, *Chem. Sci.* **2018**, *9*, 4703–4707.
- [9] a) H. Dau, A. Keyes, H. E. Basbug Alhan, E. Ordonez, E. Tsogtgerel, A. P. Gies, E. Auyeung, Z. Zhou, A. Maity, A. Das, D. C. Powers, D. B. Beezer, E. Harth, *J. Am. Chem. Soc.* **2020**, *142*, 21469–21483; b) A. Keyes, H. Dau, H. E. Basbug Alhan, U. Ha, E. Ordonez, G. R. Jones, Y.-S. Liu, E. Tsogtgerel, B. Loftin, Z. Wen, J. I. Wu, D. B. Beezer, E. Harth, *Polym. Chem.* **2019**, *10*, 3040–3047.
- [10] a) H. Kaneyoshi, Y. Inoue, K. Matyjaszewski, *Macromolecules* **2005**, *38*, 5425–5435; b) K. Zhang, Z. Ye, R. Subramanian, *Macromolecules* **2008**, *41*, 640–649.
- [11] X. Shi, Y. Zhao, H. Gao, L. Zhang, F. Zhu, Q. Wu, *Macromol. Rapid Commun.* **2012**, *33*, 374–379.
- [12] S. M. Stadler, I. Göttker-Schnetmann, A. S. Fuchs, S. R. R. Fischer, S. Mecking, *Macromolecules* **2020**, *53*, 2362–2368.
- [13] A. C. Albéniz, P. Espinet, R. López-Fernández, *Organometallics* **2003**, *22*, 4206–4212.
- [14] W. Song, J. Huang, C. Hang, C. Liu, X. Wang, G. Wang, *Polym. Chem.* **2015**, *6*, 8060–8070.
- [15] a) D. Benoit, V. Chaplinski, R. Braslau, C. J. Hawker, *J. Am. Chem. Soc.* **1999**, *121*, 3904–3920; b) A. Nilsen, R. Braslau, *J. Polym. Sci. Part A* **2006**, *44*, 697–717.
- [16] a) R. Nicolaÿ, L. Marx, P. Hémerly, K. Matyjaszewski, *Macromolecules* **2007**, *40*, 9217–9223; b) C. Bian, Y.-N. Zhou, J.-K. Guo, Z.-H. Luo, *Macromolecules* **2018**, *51*, 2367–2376.
- [17] a) E. H. H. Wong, C. Boyer, M. H. Stenzel, C. Barner-Kowollik, T. Junkers, *Chem. Commun.* **2010**, *46*, 1959–1961; b) E. H. H. Wong, M. H. Stenzel, T. Junker, C. Barner-Kowollik, *J. Polym. Sci. Part A* **2011**, *49*, 2118–2126.
- [18] Y.-S. Liu, E. Harth, *Angew. Chem. Int. Ed.* **2021**, *60*, 24107–24115; *Angew. Chem.* **2021**, *133*, 24309–24317.
- [19] C. B. Wagner, A. Studer, *Macromol. Chem. Phys.* **2010**, *211*, 2510–2516.
- [20] a) G. R. Buettner, *Free Radical Biol. Med.* **1987**, *3*, 259–303; b) L. D. Haire, P. H. Krygsman, E. G. Janzen, U. M. Oehler, *J. Org. Chem.* **1988**, *53*, 4535–4542.
- [21] F. Lin, C. Wu, D. Cui, *J. Polym. Sci. Part A* **2017**, *55*, 1243–1249.
- [22] a) K. Matyjaszewski, N. V. Tsarevsky, W. A. Braunecker, H. Dong, J. Huang, W. Jakubowski, Y. Kwak, R. Nicolay, W. Tang, J. A. Yoon, *Macromolecules* **2007**, *40*, 7795–7806; b) P. Krysz, Y. Wang, K. Matyjaszewski, S. Harrisson, *Macromolecules* **2016**, *49*, 2977–2984; c) C. M. R. Abreu, L. Fu, S. Carmali, A. C. Serra, K. Matyjaszewski, J. F. J. Coelho, *Polym. Chem.* **2017**, *8*, 375–387.
- [23] Y. Guillauneuf, D. Gigmes, S. R. A. Marque, P. Tordo, D. Bertin, *Macromol. Chem. Phys.* **2006**, *207*, 1278–1288.
- [24] a) J. C. Theriot, C.-H. Lim, H. Yang, M. D. Ryan, C. B. Musgrave, G. M. Miyake, *Science* **2016**, *352*, 1082–1086; b) X. Pan, C. Fang, M. Fantin, N. Malhotra, W. Y. So, L. A. Peteanu, A. A. Isse, A. Gennaro, P. Liu, K. Matyjaszewski, *J. Am. Chem. Soc.* **2016**, *138*, 2411–2425; c) B. L. Buss, C.-H. Lim, G. M. Miyake, *Angew. Chem. Int. Ed.* **2020**, *59*, 3209–3217; *Angew. Chem.* **2020**, *132*, 3235–3243.
- [25] Q. Ma, J. Song, X. Zhang, Y. Jiang, L. Ji, S. Liao, *Nat. Commun.* **2021**, *12*, 429–436.

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