

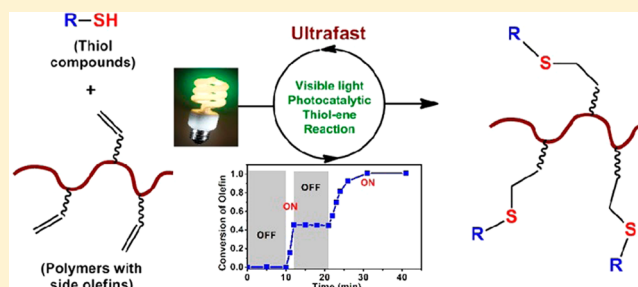
Visible Light Photocatalytic Thiol–Ene Reaction: An Elegant Approach for Fast Polymer Postfunctionalization and Step-Growth Polymerization

Jiangtao Xu and Cyrille Boyer*

Centre for Advanced Macromolecular Design (CAMD) and Australian Centre for NanoMedicine, School of Chemical Engineering, UNSW Australia, Sydney, NSW 2052, Australia

S Supporting Information

ABSTRACT: An elegant approach for fast polymer postfunctionalization and step-growth polymerization (via addition reaction) under aerobic condition was developed from visible light photocatalytic thiol–ene “click” reaction, employing $\text{Ru}(\text{bpy})_3\text{Cl}_2$ as photoredox catalyst and *p*-toluidine as redox mediator. The nature of the photoredox catalysts, thiol substrates, and solvents were extensively investigated for this reaction with two types of alkene polymers: polybutadiene and poly(allyl methacrylate)s. The use of *N*-methyl-2-pyrrolidone as the solvent and *p*-toluidine as redox mediator remarkably improved the reaction rates and limited the formation of side products. Finally, this highly efficient thiol–ene reaction was



INTRODUCTION

In 1912, Ciamician challenged the scientific community to develop “green” chemical reactions that will take advantage of abundant and renewable energy sources, such as “light”.¹ Since then, the utilization of UV light to initiate synthetic organic transformations and polymerizations has been investigated and developed for applications in polymer science, organic chemistry, and biological and material sciences.² Thiol–ene “click” chemistry is one of the most popular reactions in organic and polymer synthesis and is extensively employed for the synthesis of gels, thermosets, and the postmodification of polymers.³ One of the first examples was described by Goodyear, who reported the addition of elemental sulfur for the vulcanization of tires. His work was inspired by the earlier work of Hancock and Ludersdorf on the modification of natural latex by sulfur compounds. Braun and Murjahn⁴ extended thiol–ene reactions for the postmodification of various synthetic macromolecules. More recently, Hoyle⁵ and Bowman,⁶ Lowe,⁷ and other groups⁸ have successfully employed radical thiol–ene reactions for the preparation of functional polymer and polymeric networks with desired chemical and physical properties. In another recent example, Hawker and co-workers⁹ have successfully exploited the versatility and the high efficiency of thiol–ene and thiol–yne radical addition for the rapid preparation of dendritic polymers and polymer postmodification. Barner-Kowollik, Du Prez, and co-workers¹⁰ have investigated thiol–ene reaction to prepare complex architectures, such as star polymers and diblock copolymers. In all these cases, a photoinitiator or thermal initiator is required to produce a radical and subsequently generate a thiyl radical via

hydrogen abstraction from a thiol compound, which then has the ability to couple with an ene. This process is highly efficient and tolerant to a large range of functional groups. However, thermal initiation requires relatively high temperature and takes a few hours to achieve full conversion. In addition, thermal initiation does not offer spatiotemporal control as light does. Unfortunately, although UV light for initiating radical thiol–ene “click” reactions provides attractive properties for industrial applications, it can result in the formation of undesirable side products due to UV absorption of most chemical compounds.¹¹

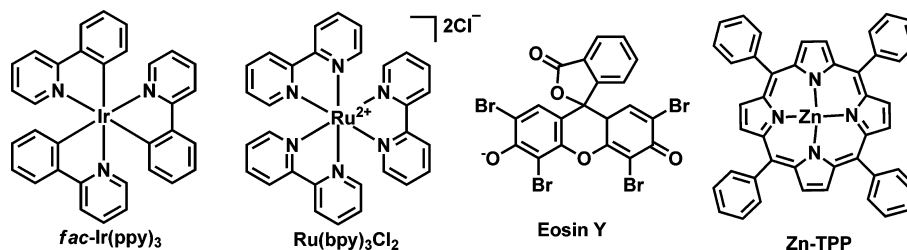
Motivated by seminal works of Stephenson,^{2j,12} MacMillan,¹³ and Yoon¹⁴ on photoredox catalysis for organic transformation, Hawker’s¹⁵ and our group¹⁶ proposed recently the use of visible light mediated atom transfer radical addition (ATRA) employing a photoredox catalyst, *fac*- $\text{Ir}(\text{ppy})_3$ (Scheme 1), to introduce various haloalkanes and α -halocarbonyls into polymer chains. Although the yield of this reaction is relatively high with some specific haloalkane compounds, such as iodoperfluoro compounds, the reaction requires several hours (typically 24 h) to reach high conversion (95%). Yoon and co-workers¹⁷ have recently reported successful thiol–ene coupling activated by a photoredox catalyst, $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$, for the preparation of functional organic compounds. This reaction can be performed under visible light using low doses of photoredox catalyst (typically, 0.25 mol %) in a few hours in acetonitrile via the photoinduced electron transfer (PET) process. Upon

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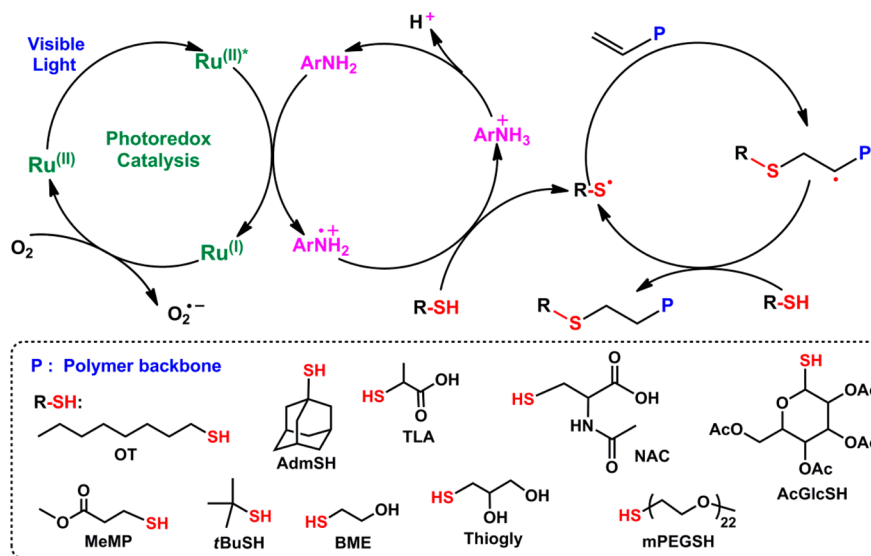
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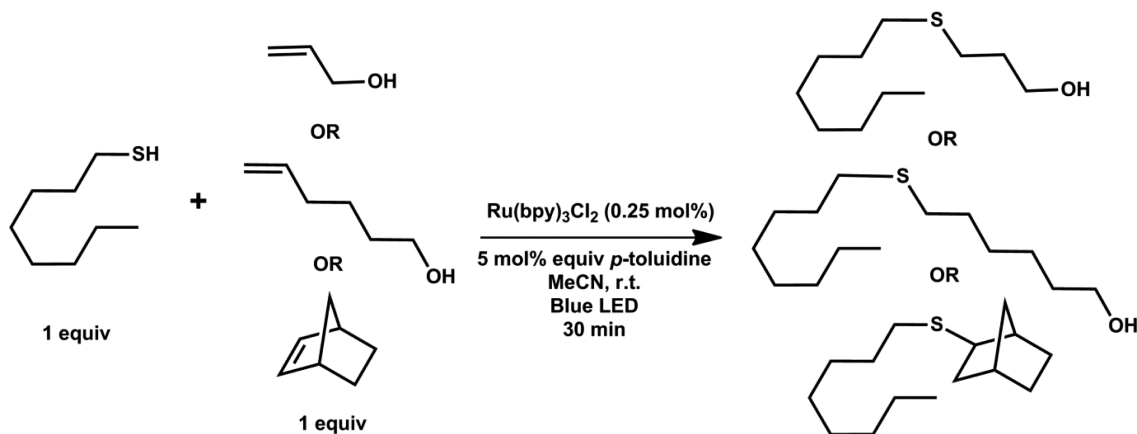
Scheme 1. Visible Light Photoredox Catalysts Investigated in This Study



Scheme 2. Proposed Mechanism for Visible Light Photocatalytic Thiol–Ene Reaction



Scheme 3. Model Reactions Investigated in This Study



exposure to visible light, ruthenium polypyridyl complexes, e.g., Ru(bpy)₃(PF₆)₂ and Ru(bpy)₃Cl₂ (Scheme 1), afford a strong metal-to-ligand charge-transfer (MLCT) excited state with a redox potential of 1.4 V (for Ru(bpy)₃(PF₆)₂) that can undergo reductive quenching by a thiol (redox potential of 0.5 V) to generate a thiyl radical cation. This thiyl radical species reacts with electron-rich double bonds to yield thioether compounds. More recently, the authors have suggested the addition of *p*-toluidine, which plays the role of oxidative redox mediator and improves the reaction kinetics. *p*-Toluidine circumvents the slow rate of direct photooxidation of thiol by Ru(bpy)₃²⁺ and facilitates the transfer of electron from ruthenium catalyst to the thiol to generate a thiyl radical species (Scheme 2, top). Ru⁺

reacts with oxygen to regenerate Ru²⁺, which enables this process to be aerobic.

In this article, we optimized this reaction for polymer postfunctionalization and step-growth addition polymerization of dithiol and divinyl compounds using Ru(bpy)₃Cl₂ (ppm concentration relative to monomer) as photoredox catalyst under low-energy blue LED light and aerobic conditions. First, to illustrate the versatility of this approach, model polymers, i.e., poly(ethyl methacrylate-*r*-allyl methacrylate) and poly(butadiene), were tested to react with various thiols. The reaction was investigated using various photoredox catalysts, i.e., Ru(bpy)₃Cl₂, *fac*-Ir(ppy)₃, eosin Y, and Zinc tetraphenylporphyrin (Zn-TPP), in common solvents to reach high or full

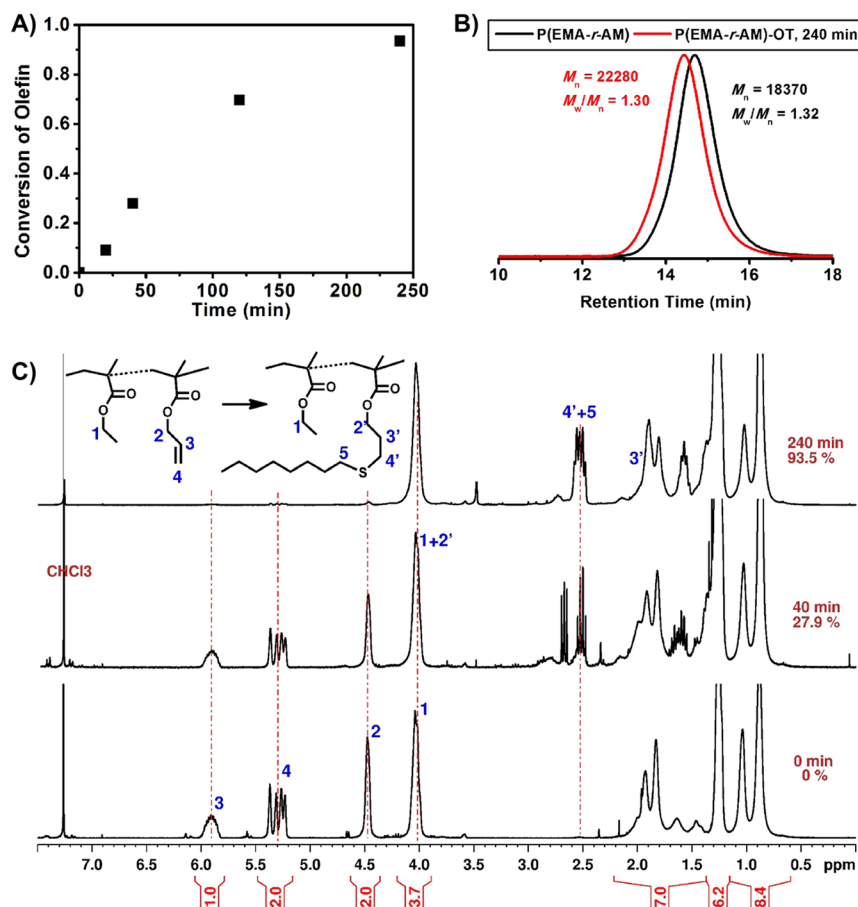


Figure 1. (A) Kinetic study for postfunctionalization of P(EMA-*r*-AM) by 1-octanethiol (OT) at different reaction times in MeCN. (B) GPC curves for P(EMA-*r*-AM) before and after postfunctionalization in MeCN. (C) Evolution of ^1H NMR spectra for postfunctionalized P(EMA-*r*-AM) at different reaction time points.

conversions in a few minutes. Second, the optimized conditions obtained for polymer postfunctionalization were exploited to produce linear thioether polymers via step-growth addition polymerization.

RESULTS AND DISCUSSION

1. Model Reactions. Yoon and co-workers¹⁷ have successfully demonstrated that photoredox catalyst, $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2$, could effectively activate radical thiol–ene additions in the presence of redox mediator, *p*-toluidine, under low-energy blue LED light. We decided to test this visible light photocatalytic thiol–ene reaction employing another widely used and low-cost catalyst, $\text{Ru}(\text{bpy})_3\text{Cl}_2$, prior to adapting this process for polymer postfunctionalization.

Three alkenes (Scheme 3), with diverse reactivity, i.e., 2-norbornene > allyl alcohol > 5-hexen-1-ol,⁵ were reacted with 1-octanethiol (OT) using a ratio of 1 to 1 in acetonitrile (MeCN) to yield corresponding thioether compounds. The reactions were performed in the presence of *p*-toluidine (5 mol %) and $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (0.25 mol %) under blue LED light ($\lambda = 461$ nm, 4.8 W). Near complete coupling (>98%) was detected from ^1H NMR spectra after 30 min (Supporting Information, Figures S2–S4) for all three alkenes, which confirmed the versatility of this approach regardless of the structure of alkenes, i.e., monosubstituted (allyl alcohol and 5-hexen-1-ol) or 1,2-disubstituted (2-norbornene) compounds. In the absence of *p*-toluidine as essential additive, the reaction yields are relatively

low (<10%), which is in good agreement with Yoon's results.^{17b} Additionally, the reactions did not work at all in the absence of light (data not shown).

2. Postfunctionalization of P(EMA-*r*-AM) and P-(OEGMA-*r*-AM) Random Copolymers. **2.1. Kinetics of Postfunctionalization.** Encouraged by the successful implementation of model photocatalytic thiol–ene reaction on small molecules, we turned our efforts to postfunctionalization of well-defined polymers. Since 1840, polymer postfunctionalization has attracted researchers' attention to prepare a library of functional polymers using specific parent polymers.¹⁸ Several efficient reactions, including azide–alkyne, epoxy–amine, activated ester–amine, tetrazine–norbornene, thiol–X reactions, and Diels–Alder, have been successfully implemented for the postfunctionalization of synthetic and natural macromolecules.¹⁹ Although these reactions are effective or fast in some case, severe conditions of UV light or high temperature are generally necessary to perform thiol–ene radical addition, which would initiate undesirable side reactions.¹¹

To launch our concept, a model polymer bearing allyl functionalities, poly(ethyl methacrylate-*r*-allyl methacrylate) (P(EMA-*r*-AM)), was synthesized via reversible addition–fragmentation chain transfer (RAFT) polymerization, with 4-cyanopentanoic acid dithiobenzoate (CPADB) as the chain transfer agent. By controlling the monomer conversion to less than 50%, we were able to successfully synthesize a P(EMA-*r*-AM) copolymers with a PDI ~ 1.3 , without obvious shoulder at

Table 1. Postfunctionalization of P(EMA-*r*-AM) with OT and P(OEGMA-*r*-AM) with Thiogly in the Presence of Photocatalyst and Blue LED Light in Different Solvents^a

no.	polymer or solvents	thiols	time (min)	conv of olefin (%)	M_n (g/mol) ^e	PDI
	P(EMA _{0.35} - <i>r</i> -AM _{0.65})				18370	1.32
1	MeCN	OT	20	9.1		
2	DMF	OT	20	80.3	21250	1.34
3	NMP	OT	20	99	23010	1.27
4	NMP ^b	OT	20	0		
5	NMP ^c	OT	20	27.2	ND ^d	ND ^d
6	NMP ^c	OT	120	67.3	20810	1.34
	P(OEGMA _{0.5} - <i>r</i> -AM _{0.5})				59000	2.1
7	MeOH	Thiogly	20	99	106460	3.2
8	H ₂ O	Thiogly	120	33.3	92000	2.5
9	NMP	Thiogly	60	95.5	88690	1.95

^aNote: the reactions were carried out at room temperature in the presence of air using blue LED light as light source. ^bIn the absence of additives.

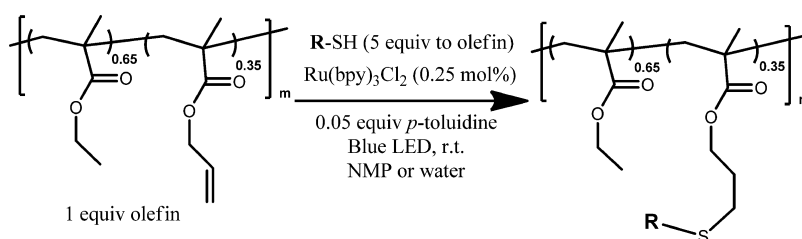
^cTriethylamine (TEA) as additive instead of *p*-toluidine. ^dND: not determined. ^eMolecular weights and polydispersities (PDI) were determined by GPC (DMAc) based on poly(methyl methacrylate) standard.

high molecular weight. The presence of allyl group was confirmed by ¹H NMR (signals at 5.9, 6.2, and 6.5 ppm). Subsequently, the dithiobenzoate end-group was removed via a cascade reaction of aminolysis with hexylamine and thiol–ene Michael addition in the presence of excess methyl acrylate, as reported in previous works.²⁰ The chemical structures of the final white powder (P(EMA-*r*-AM)) were confirmed by ¹H NMR: P(EMA_{0.65}-*r*-AM_{0.35}), $M_{n, GPC}$ = 18 370 g/mol, M_w/M_n = 1.32.

The postfunctionalization of P(EMA_{0.65}-*r*-AM_{0.35}) was initially investigated with OT in the presence of Ru(bpy)₃Cl₂ (0.25 mol % with respect to olefin functionality) and *p*-toluidine (5 mol %), using a molar ratio of [OT]:[olefin] = 5:1. Figure 1 exhibits the kinetic study of the thiol–ene reaction. The conversion of allyl group was monitored versus time via ¹H NMR (Figure 1A), clearly indicating that the reaction was proceeding smoothly. After 240 min, the conversion of allyl group reached as high as 93.5%. The stacking of ¹H NMR spectra at different time points (Figure 1C) showed the gradual decrease of allyl signal at δ 5.9, 5.3, and 4.5 ppm and the appearance of a new signal at δ 2.5 ppm attributed to the methylene group in adjacent position of sulfur atom, which indicates successful attachment of OT to the polymer chains. GPC traces (Figure 1B) for the final polymer showed complete shift of parent model polymer to high molecular weight product with monomodal distribution (M_n = 22 280, M_w/M_n = 1.30). The absence of tailing or shoulders at low retention time suggested radical–radical interpolymer coupling was not favorable, which is often observed in reported radical postmodification reaction, such as conventional thiol–ene reaction.^{10,11} Control experiments were carried out in the absence of redox mediator, light, or catalyst. In the absence of *p*-toluidine, the reactions proceeded very slowly with less than

20% of allyl conversion after 24 h light irradiation, while in the absence of Ru(bpy)₃Cl₂ or light, no conversion was observed (data not shown).

2.2. Different Solvents. Subsequently, the thiol–ene reaction efficiency was evaluated with various solvents, including *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), methanol (MeOH), and deionized water (Table 1). It is well-known that solvent polarity has a huge effect on radical reaction rates. As expected, compared to MeCN (9.1%, Table 1, no. 1), DMF and NMP exhibited higher conversions of olefin, i.e., 80.3% (Table 1, no. 2) and full conversion (Table 1, no. 3), respectively, after 20 min light irradiation. The difference of reactivity between MeCN, DMF, and NMP can be attributed to the difference of polarity indices, 5.8, 6.4, and 6.7, respectively, which improves the catalytic activity. This observation is in accord with our previous studies using Ru(bpy)₃Cl₂ for photoinduced electron transfer–reversible addition–fragmentation chain transfer (PET-RAFT) polymerization.²¹ In this early work, we demonstrated that the solvents had a strong effect on the apparent radical addition reaction rate. Most importantly, the final products after postmodification showed lower polydispersities in NMP than DMF and MeCN (1.34 and 1.27 for DMF and NMP, respectively), which suggested there was no cross-linking side reactions during the postfunctionalization. GPC analysis (Figure S5A) confirmed a clear shift of polymer peak from high to low retention time, while the ¹H NMR spectrum (Figure S5B) showed the absence of allyl groups (δ 5.9, 5.3, and 4.5 ppm) and the presence of new signals at δ 2.5 ppm attributed to the methylene group in adjacent position of sulfur atom. This “fast” postfunctionalization reaction, i.e., full conversion in less than 20 min, is unprecedented. Generally, most of the polymer postfunctionalization reactions, including azide–alkyne click chemistry,

Table 2. Postmodification of P(EMA-*r*-AM) with a Variety of Thiol Compounds in the Presence of Photocatalyst and Blue LED Light^a

no.	R-SH	reaction time (min)	olefin conv (%)	M_n (g/mol) ^b	PDI
1	1-octanethiol (OT)	20	99	23010	1.27
2	methyl 3-mercaptopropionate (MeMP)	20	99	19860	1.32
3	<i>tert</i> -butyl mercaptan (<i>t</i> BuSH)	20	95	18860	1.34
4	1-adamantanethiol (AdmSH)	20	99	35830	1.32
5	β -mercaptoethanol (BME)	20	46.4	31830	1.42
6		60	99	41360	2.19
7	thiolactic acid (TLA)	20	99	93560	1.26
8	1-thioglycerol (Thiogly)	20	51.5	37660	1.33
9		60	76.1	39980	1.40
10	PEG-SH (M_n = 1000 g/mol)	120	59.6	57900	1.36
11	1-thio- β -D-glucose tetraacetate (AcGlcSH)	20	99	41120	1.25
12	<i>N</i> -acetyl-L-cysteine (NAC)	20	99	99100	1.22

^aNote: the reactions were carried out at room temperature in the presence of air using blue LED light as light source. ^bMolecular weights and polydispersities (PDI) were determined by GPC (DMAc) based on poly(methyl methacrylate) standard.

activated ester-amine, and Diels-Alder reactions, with different substrates required several hours to reach 100% conversion.¹⁹

These remarkable results in polar solvents motivated us to explore other common polar solvents, such as water and MeOH. Because of the limited solubility of P(EMA_{0.65}-*r*-AM_{0.35}) in water and MeOH, another model polymer, P(OEGMA_{0.5}-*r*-AM_{0.5}), was prepared by copolymerization of oligo(ethylene glycol) methyl ether methacrylate (OEGMA) and AM to yield P(OEGMA_{0.5}-*r*-AM_{0.5}), with $M_{n, GPC}$ = 59 000 g/mol and M_w/M_n = 2.1. This high PDI is attributed to the partial copolymerization of allyl group with methacrylates, which results in a branched polymer. However, NMR clearly shows the presence of an allyl group which can be employed for the postmodification. As OT is not water-soluble, another thiol compound, 1-thioglycerol (Thiogly), was tested instead. Under identical reaction conditions, the conversion of olefin displayed 100% in MeOH after 20 min and 30.2% in H₂O after 120 min light irradiation, respectively (Table 1, no. 7 and 8). Unfortunately, significant increases in PDI (3.2 and 2.5 for MeOH and H₂O, respectively; Figure S6) were observed after the reactions, which is most likely attributed to inter-cross-linking reactions. To confirm that the cross-linking was due to the nature of solvent and not the thiol compound (Thiogly), we performed the reaction under identical reaction conditions in NMP instead of MeOH or H₂O. In NMP, after 60 min, the final product presented a higher molecular weight but a comparable PDI (Table 1, no. 9). It is hypothesized that the polymer in MeOH and H₂O was not unimolecularly dissolved because of high content of hydrophobic allyl groups in polymer chains, which self-aggregated (confirmed by dynamic light scattering) and promoted radical-radical cross-coupling, while in NMP and DMF, the polymer was fully dissolved.

Consequently, NMP afforded the thiol-ene reaction fastest reaction kinetics among all investigated solvents, with full conversion in less than 20 min for most of thiol substrates

(Tables 1 and 2). For this reason, it has been chosen as the reaction solvent for the rest of this study. Additionally, we investigated the effect of the redox mediator (*p*-toluidine) on the reaction kinetics to verify its necessity. In the absence of *p*-toluidine, we did not observe conversion of olefin after 20 min (Table 1, no. 4). In the case *p*-toluidine was replaced by triethylamine (TEA) as external additive which is an efficient sacrificing electron donor in photoinduced living radical polymerization (PET-RAFT),²² a much slower reaction was noted (27.2% for 20 min and 67.3% for 120 min, Table 1, no. 5 and 6). According to our data, TEA could not play the same role of redox mediator as *p*-toluidine, in which arylamine radical cation could rapidly abstract hydrogen atom from thiol (Scheme 2, top, middle cycle).

2.3. Different Thiol Substrates. Conventional radical thiol-ene reaction is tolerant to a large range of functionalities, including alcohol, amine, carboxylic acid, etc.⁵ We decided to examine the versatility of our visible light photocatalytic thiol-ene reaction with a library of 10 thiol substrates (Scheme 2, bottom). In Table 2, most of the thiols could achieve 95+% conversion of olefin after 20 min light irradiation, except for β -mercaptoethanol (BME), Thiogly, and poly(ethylene glycol) methyl ether thiol (M_n = 1000 g/mol) (PEGSH) (Table 2, no. 5, 8, and 10). In the case of BME and Thiogly, the conversions could reach high conversion only after 60 min of light irradiation (99% for BME and 76.1% for Thiogly). Although the final polymer obtained for BME yielded a slightly cross-linked polymer with high polydispersity (2.19), it displayed good solubility in most of common solvents (chloroform, DMF, MeOH, and THF). In the case of PEG-SH, the relatively low yield is attributed to steric hindrance. However, it is still surprising to obtain 60% conversion of olefin and low polydispersity (1.36) after 2 h of light irradiation, which confirms further the high efficiency of this approach. GPC analysis (Supporting Information, Figures S7A–13A) for all products after modification showed a complete shift of polymer

Table 3. Postmodification of P(EMA-*r*-AM) with Octanethiol in the Presence of Different Photocatalyst and Blue LED Light in NMP^a

OT (5 equiv to olefin)
Catalyst (0.25 or 1 mol%)
0.05 equiv *p*-toluidine
Blue LED, r.t.
NMP

no.	polymer and catalysts	catalyst concn (%)	time	conv (%)	M_n^b (g/mol)	PDI ^b
	P(EMA _{0.35} - <i>r</i> -AM _{0.65})				18370	1.32
1	<i>fac</i> -Ir(ppy) ₃	0.25	15 h	41.1	21060	1.33
2	Ru(bpy) ₃ Cl ₂	0.25	20 min	99	23010	1.27
3	eosin	1	24 h	99	22800	1.32
4	Zn-TPP	1	24 h	63.5	22120	1.42

^aNote: the reactions were carried out at room temperature in the presence of air using blue LED light as light source. ^bMolecular weights and polydispersities (PDI) were determined by GPC (DMAc) based on poly(methyl methacrylate) standard.

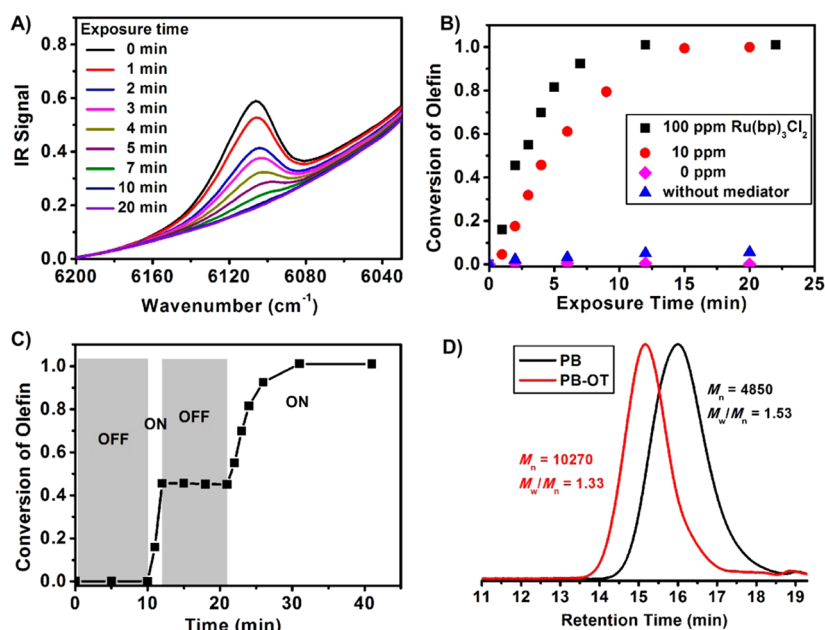


Figure 2. FTNIR spectroscopy for kinetic study of PB modification with 1-octanethiol (OT) in NMP using Ru(bpy)₃Cl₂ (0–100 ppm relative to olefin concentration) as photocatalyst and *p*-toluidine (5% to olefin concentration) as redox mediator. (A) FTNIR spectra for the reaction solution at different exposure time points. (B) Kinetic plots for conversion of olefin vs exposure time with different concentration of catalysts (100 (square), 10 (circle), 0 (diamond) ppm) and in the absence of redox mediator (triangle). (C) “ON–OFF” study for the postmodification. (D) GPC traces for PB before and after postfunctionalization with OT in NMP for 20 min.

distributions from high to low retention times. ¹H NMR spectra (Supporting Information, Figures S7B–14B) for the final products after purification confirmed the successful incorporation of functional groups along the polymer chains.

2.4. Different Photoredox Catalysts. Motivated by our previous research experience on photopolymerization of acrylates and methacrylates using different photoredox catalysts,^{21,21–23} we decided to assess different photocatalysts, including *fac*-Ir(ppy)₃, eosin Y (EY), and zinc tetraphenylporphyrine (Zn-TPP), to perform the thiol–ene reaction. The results shown in Table 3 indicated low catalytic efficacy for *fac*-Ir(ppy)₃ and Zn-TPP; even 1% of Zn-TPP could only reach 63.5% conversion after 24 h light irradiation. The low efficiency of these catalysts, for *fac*-Ir(ppy)₃^{13b} and Zn-TPP,²⁴ is attributed to their lower oxidation potentials [(E_{M^*/M^-}) =

0.66 and 0.62 V versus the saturated calomel electrode (SCE), respectively] than Ru(bpy)₃Cl₂ [(E_{M^*/M^-}) = 0.77 V].^{13b} However, in the case of EY, a complete conversion with 1% catalyst after 24 h irradiation was observed, which is explained by the high oxidation potential [(E_{M^*/M^-}) = 1.18 V versus SCE].²⁵ Nevertheless, EY presents a lower efficiency to perform a PET process due to its short excitation lifetime, which is usually observed for organophotoredox catalyst.²⁶ These results show that other photoredox catalysts can be employed to perform photocatalytic thiol–ene reaction, although improvement of reaction rates is required. It is worthy to note that EY presents the advantages to avoid the introduction of transition metals into the system, which could be beneficial for bioapplications for example.

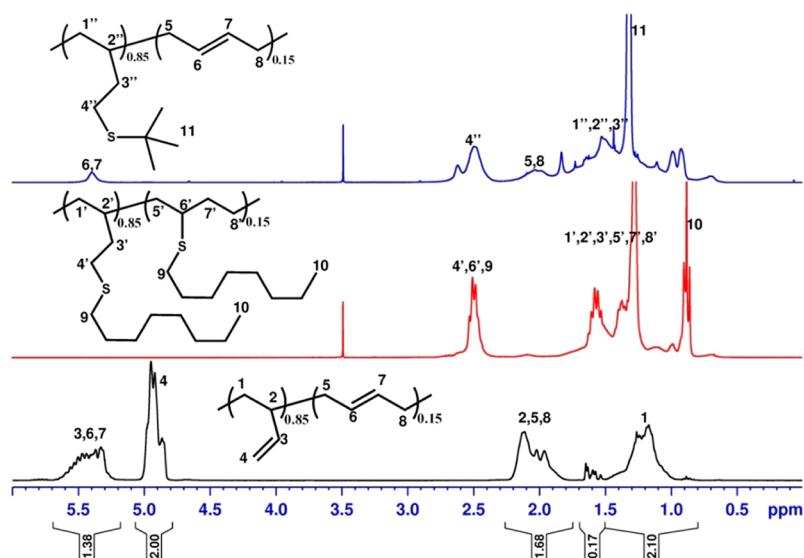


Figure 3. ^1H NMR spectra for commercial polybutadiene (black curve), the products after postmodification with OT (red curve), and *t*BuSH (blue curve).

3. Postfunctionalization of Polybutadiene (PB, 85% 1,2-Vinyl, 15% 1,4-Addition). Further investigation of this technique for the postfunctionalization of polybutadiene (1,2-vinyl PB) was performed. The modification via radical thiol–ene reaction has been reported by several authors²⁷ using rather harsh or uneconomic conditions (high temperature or UV light). Applying oxygen tolerant, visible light catalytic reaction at room temperature can offer more eco-friendly and milder conditions, which could tremendously limit side reactions.¹¹ Additionally, a fast preparation will be advantageous and practical for industrial applications.

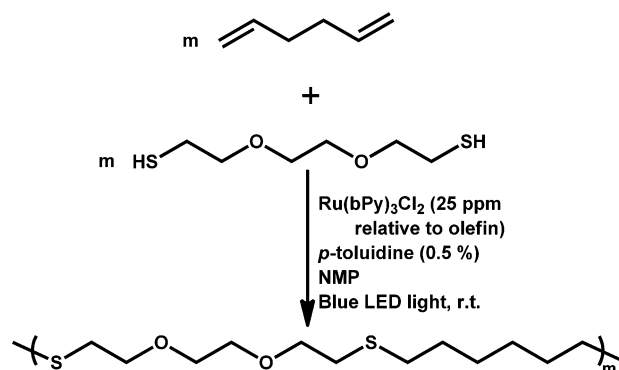
The online Fourier transform near-infrared (FTNIR) spectroscopy was invoked to investigate the reaction kinetics for PB ($M_n = 4850$, $M_w/M_n = 1.53$, 85% 1,2-vinyl, 15% 1,4-addition) modification with OT. The vinylic stretching signal of olefin at $6160\text{--}6080\text{ cm}^{-1}$ decreased gradually with the reaction time, which was utilized to determine conversion of olefin based on signal intensity (Figure 2A). Although the olefin functionalities in PB are dense along the polymer backbone and in-chain double bonds are 10 times less reactive than pendant double bonds, our results unexpectedly showed that all double bonds were converted through thiol–ene reaction with OT in few minutes in the presence of 100 ppm catalyst (with respect to olefin concentration), shown in Figure 2B. Successful reaction was also demonstrated by the ^1H NMR spectrum (Figure 3) after purification of polymer via precipitation. The reaction remained highly efficient; nearly 100% conversion within 15 min, even when the catalyst concentration was reduced to be 10 ppm. The control experiments in the absence of photocatalyst ($\text{Ru}(\text{bpy})_3\text{Cl}_2$) or mediator (*p*-toluidine) showed negligible conversions, which demonstrate that both compounds are vital to perform this reaction. Most importantly, the reaction can be switched “ON” and “OFF” by turning the light “ON” and “OFF”, respectively (Figure 2C). In the absence of light, the reaction stopped immediately, while the reaction resumed when the light was “ON”. Moreover, GPC analysis showed monomodal distribution with lower polydispersity (1.33) than the parent polymer (1.53) (Figure 2D), which suggests that no intermolecular cross-linking occurred during the postmodification. All the double bonds

were converted (Figure 3) to thioether or possibly five- or six-member ring structures from intramolecular cyclization of two butadiene pendant groups, although intramolecular cyclization is less favorable because of the random distribution of double bond in position 1,2 and 1,4 in the polybutadiene.

Finally, we decided to test less reactive thiol, i.e., *tert*-butyl thiol (*t*BuSH). Interestingly, this thiol preferentially reacts with pendant double bonds, while the in-chain double bonds were partially left unreacted after 20 min light irradiation (Figure 3). This specificity was explained by the steric hindrance of *tert*-butyl group, resulting in slow reactivity.

4. Step-Growth Addition Polymerization of Dithiol and Diene Compounds via Visible Light Photocatalytic Thiol–Ene Reaction. After these successful results, we envisaged to use this photocatalytic thiol–ene reaction for the preparation of linear polymers by step-growth addition polymerization of dithiol with diene compounds (Scheme 4). Stoichiometric monomers, 1,5-hexadiene (HD) and 2,2'-(ethylenedioxy)diethanethiol (EDDT), 25 ppm $\text{Ru}(\text{bpy})_3\text{Cl}_2$, and *p*-toluidine (0.5%) were mixed in NMP and then irradiated with blue LED light (4.8 W) without degassing. The conversion of olefin was monitored by online FTNIR by tracking the

Scheme 4. Reaction Condition for Visible Light Photocatalytic Thiol–Ene Polycondensation of Dithiol and Diene



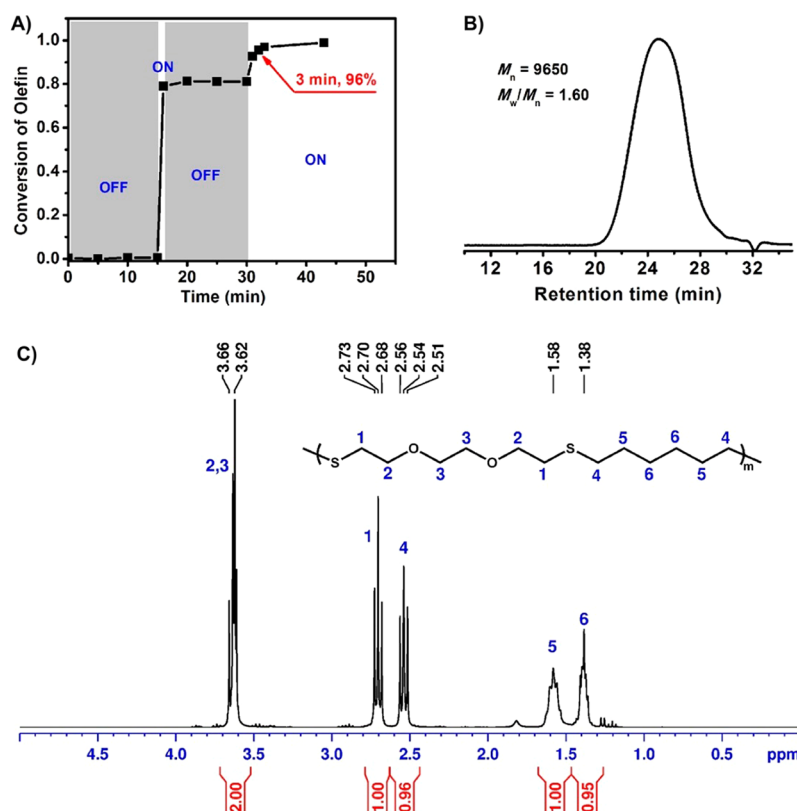


Figure 4. (A) FTNIR spectroscopy for “ON/OFF” study of visible light photocatalytic thiol–ene polycondensation in NMP using $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (25 ppm relative to olefin concentration) as photocatalyst and *p*-toluidine (0.5% to olefin concentration) as redox mediator. (B) GPC trace and (C) ^1H NMR spectrum for final purified product by thiol–ene polycondensation.

signals at $6200\text{--}6300\text{ cm}^{-1}$. Surprisingly, 96% conversion of olefin was observed after 3 min irradiation (Figure 4A) using blue LED light to yield a copolymer with a molecular weight of $M_n = 9650\text{ g/mol}$ (Figure 4B). This thiol–ene reaction could also be switched “ON” and “OFF”, as demonstrated by negligible conversion of olefin during the “OFF” periods. The final product was characterized by ^1H NMR (Figure 4C), which shows the characteristic spectrum of ethylenedioxy thioether.

CONCLUSION

In this work, an original visible light photocatalytic thiol–ene reaction was employed for fast polymer postfunctionalization and step-growth addition polymerization under aerobic conditions. Model polymers, polybutadiene and poly(allyl methacrylates), were successfully modified with a large range of functional thiols in several minutes (typically, in 20 min). The use of *N*-methyl-2-pyrrolidone as the solvent and *p*-toluidine as redox mediator remarkably improved the reaction rates and limited the formation of side products. Finally, the photoredox thiol–ene was successfully employed for the preparation of linear polymers by step-growth addition reactions in few minutes using 25 ppm photocatalyst relative to olefin concentration. This highly efficient reaction was performed under low-energy (blue LED, 4.8 W) and eco-friendly visible light in the presence of air, affording important industrial implications with mild reaction conditions and easy scale-up. Furthermore, this approach could be an alternative to existing thermal and UV-promoted radical thiol–ene chemistry.

ASSOCIATED CONTENT

Supporting Information

Experimental details, fluorescence spectrum, UV–vis spectra, NMR spectra, and GPC traces (Figures S1–S15). This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: cboyer@unsw.edu.au (C.B.).

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Ciamician, G. *Science* **1912**, 36, 385–394.
- (2) (a) Roy, D.; Sumerlin, B. S. *Macromol. Rapid Commun.* **2014**, 35, 174–179. (b) Bella, F.; Bongiovanni, R. *J. Photochem. Photobiol., C* **2013**, 16, 1–21. (c) Tasdelen, M. A.; Uygun, M.; Yagci, Y. *Macromol. Rapid Commun.* **2011**, 32, 58–62. (d) Ligon, S. C.; Husár, B.; Wutzel, H.; Holman, R.; Liska, R. *Chem. Rev.* **2013**, 114, 557–589. (e) Ribelli, T. G.; Konkolewicz, D.; Bernhard, S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2014**, 136, 13303–13312. (f) Chuang, Y.-M.; Ethirajan, A.; Junkers, T. *ACS Macro Lett.* **2014**, 3, 732–737. (g) Xiao, P.; Dumur, F.; Zhang, J.; Gigmes, D.; Fouassier, J. P.; Lalevee, J. *Polym. Chem.* **2014**, 5, 6350–6357. (h) Fors, B. P.; Hawker, C. J. *Angew. Chem., Int. Ed.* **2012**, 51, 8850–8853. (i) Xu, J.; Jung, K.; Atme, A.; Shanmugam, S.; Boyer, C. *J. Am. Chem. Soc.* **2014**, 136, 5508–5519. (j) Narayanan,

- J. M. R.; Stephenson, C. R. J. *Chem. Soc. Rev.* **2011**, *40*, 102–113.
- (k) Wang, X.; Liu, G.; Hu, J.; Zhang, G.; Liu, S. *Angew. Chem., Int. Ed.* **2014**, *53*, 3138–3142. (l) Hu, X.; Tian, J.; Liu, T.; Zhang, G.; Liu, S. *Macromolecules* **2013**, *46*, 6243–6256.
- (3) (a) Beria, L.; Gevrek, T. N.; Erdog, A.; Sanyal, R.; Pasini, D.; Sanyal, A. *Biomater. Sci.* **2014**, *2*, 67–75. (b) Hearon, K.; Nash, L. D.; Rodriguez, J. N.; Lonacker, A. T.; Raymond, J. E.; Wilson, T. S.; Wooley, K. L.; Maitland, D. J. *Adv. Mater.* **2014**, *26*, 1552–1558. (c) van den Berg, S. A.; Tu, J.; Slidregt, K. M.; Kros, A.; Wennekes, T.; Zuilhof, H. *Adv. Mater. Interfaces* **2014**, DOI: 10.1002/admi.201300061. (d) Ware, T.; Jennings, A. R.; Bassampour, Z. S.; Simon, D.; Son, D. Y.; Voit, W. *RSC Adv.* **2014**, *4*, 39991–40002. (e) Sawicki, L. A.; Kloxin, A. M. *Biomater. Sci.* **2014**, *2*, 1612–1626. (f) Tucker-Schwartz, A. K.; Farrell, R. A.; Garrell, R. L. *J. Am. Chem. Soc.* **2011**, *133*, 11026–11029. (g) Rossi, F.; van Griensven, M. *Tissue Eng., Part A* **2013**, *20*, 2043–2051. (h) Chung, W. J.; Griebel, J. J.; Kim, E. T.; Yoon, H.; Simmonds, A. G.; Ji, H. J.; Dirlam, P. T.; Glass, R. S.; Wie, J. J.; Nguyen, N. A.; Guralnick, B. W.; Park, J.; SomogyiÁrpád; Theato, P.; Mackay, M. E.; Sung, Y.-E.; Char, K.; Pyun, J. *Nat. Chem.* **2013**, *5*, 518–524. (i) Flores, M.; Foix, D.; Serra, A.; Ramis, X.; Sangermano, M. *Macromol. Mater. Eng.* **2014**, *299*, 495–503. (j) Calle, M.; Lligadas, G.; Ronda, J. C.; Galià, M.; Cádiz, V. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 3017–3025. (k) Choudhary, U.; Northrop, B. H. *Chem.—Eur. J.* **2014**, *20*, 999–1009. (l) Bian, S.; Zieba, S. B.; Morris, W.; Han, X.; Richter, D. C.; Brown, K. A.; Mirkin, C. A.; Braunschweig, A. B. *Chem. Sci.* **2014**, *5*, 2023–2030. (m) Claudino, M.; Mathevet, J.-M.; Jonsson, M.; Johansson, M. *Polym. Chem.* **2014**, *5*, 3245–3260. (n) Tan, J.; Li, C.; Zhou, J.; Yin, C.; Zhang, B.; Gu, J.; Zhang, Q. *RSC Adv.* **2014**, *4*, 13334–13339. (o) Brosnan, S. M.; Schlaad, H. *Polymer* **2014**, *55*, 5511–5516. (p) Le Neindre, M.; Nicolay, R. *Polym. Chem.* **2014**, *5*, 4601–4611. (q) Kumpfer, J. R.; Rowan, S. J. *J. Am. Chem. Soc.* **2011**, *133*, 12866–12874. (r) Roth, P. J.; Boyer, C.; Lowe, A. B.; Davis, T. P. *Macromol. Rapid Commun.* **2011**, *32*, 1123–1143. (s) Liu, Z.; Ou, J.; Lin, H.; Liu, Z.; Wang, H.; Dong, J.; Zou, H. *Chem. Commun.* **2014**, *50*, 9288–9290. (t) Xi, W.; Scott, T. F.; Kloxin, C. J.; Bowman, C. N. *Adv. Funct. Mater.* **2014**, *24*, 2572–2590. (u) Prasath, R. A.; Gokmen, M. T.; Espeel, P.; Du Prez, F. E. *Polym. Chem.* **2010**, *1*, 685–692. (v) Walker, C. N.; Sarapas, J. M.; Kung, V.; Hall, A. L.; Tew, G. N. *ACS Macro Lett.* **2014**, *3*, 453–457. (w) Zhang, Q.; Li, G.-Z.; Becer, C. R.; Haddleton, D. M. *Chem. Commun.* **2012**, *48*, 8063–8065. (x) van der Ende, A.; Croce, T.; Hamilton, S.; Sathiyakumar, V.; Harth, E. *Soft Matter* **2009**, *5*, 1417–1425. (y) Stevens, D. M.; Tempelaar, S.; Dove, A. P.; Harth, E. *ACS Macro Lett.* **2012**, *1*, 915–918. (z) Stevens, M. M.; Mecklenburg, G. *Polym. Int.* **2012**, *61*, 680–685.
- (4) v. Braun, J.; Murjahn, R. *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 1202–1209.
- (5) Hoyle, C. E.; Lee, T. Y.; Roper, T. J. *Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5301–5338.
- (6) (a) Hoyle, C. E.; Bowman, C. N. *Angew. Chem., Int. Ed.* **2010**, *49*, 1540–1573. (b) Cramer, N. B.; Couch, C. L.; Schreck, K. M.; Carioscia, J. A.; Boulden, J. E.; Stansbury, J. W.; Bowman, C. N. *Dent. Mater.* **2010**, *26*, 21–28. (c) Cole, M. A.; Jankousky, K. C.; Bowman, C. N. *Polym. Chem.* **2013**, *4*, 1167–1175. (d) Peng, H.; Nair, D. P.; Kowalski, B. A.; Xi, W.; Gong, T.; Wang, C.; Cole, M.; Cramer, N. B.; Xie, X.; McLeod, R. R.; Bowman, C. N. *Macromolecules* **2014**, *47*, 2306–2315.
- (7) (a) Lowe, A. B. *Polym. Chem.* **2010**, *1*, 17–36. (b) Lowe, A. B.; Liu, M.; van Hensbergen, J. A.; Burford, R. P. *Macromol. Rapid Commun.* **2014**, *35*, 391–404.
- (8) (a) An, S. Y.; Hwang, J. W.; Kim, K. N.; Jung, H. W.; Noh, S. M.; Oh, J. K. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 572–581. (b) Tunca, U. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 3147–3165. (c) Hermann, A.; Mruk, R.; Roskamp, R. F.; Scherer, M.; Ma, L.; Zentel, R. *Macromol. Chem. Phys.* **2014**, *215*, 32–43. (d) Desroches, M.; Caillol, S.; Lapinte, V.; Auvergne, R. m.; Boutevin, B. *Macromolecules* **2011**, *44*, 2489–2500. (e) Liu, B.; Quirk, R. P.; Wesdemiotis, C.; Yol, A. M.; Foster, M. D. *Macromolecules* **2012**, *45*, 9233–9242.
- (9) (a) Kade, M. J.; Burke, D. J.; Hawker, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 743–750. (b) Sprafke, J. K.; Spruell, J. M.; Mattson, K. M.; Montarnal, D.; McGrath, A. J.; Pötzsch, R.; Miyajima, D.; Hu, J.; Latimer, A. A.; Voit, B. I.; Aida, T.; Hawker, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, DOI: 10.1002/pola.27345. (c) Lee, B. F.; Kade, M. J.; Chute, J. A.; Gupta, N.; Campos, L. M.; Fredrickson, G. H.; Kramer, E. J.; Lynd, N. A.; Hawker, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 4498–4504. (d) Killops, K. L.; Campos, L. M.; Hawker, C. J. *J. Am. Chem. Soc.* **2008**, *130*, S062–S064. (e) Gupta, N.; Lin, B. F.; Campos, L. M.; Dimitriou, M. D.; Hikita, S. T.; Treat, N. D.; Tirrell, M. V.; Clegg, D. O.; Kramer, E. J.; Hawker, C. J. *Nat. Chem.* **2010**, *2*, 138–145. (f) Campos, L. M.; Killops, K. L.; Sakai, R.; Paulusse, J. M. J.; Damiron, D.; Drockenmuller, E.; Messmore, B. W.; Hawker, C. J. *Macromolecules* **2008**, *41*, 7063–7070.
- (10) Koo, S. P. S.; Stamenović, M. M.; Prasath, R. A.; Inglis, A. J.; Du Prez, F. E.; Barner-Kowollik, C.; Van Camp, W.; Junkers, T. J. *Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 1699–1713.
- (11) Derboven, P.; D’hooge, D. R.; Stamenovic, M. M.; Espeel, P.; Marin, G. B.; Du Prez, F. E.; Reyniers, M.-F. *Macromolecules* **2013**, *46*, 1732–1742.
- (12) (a) Nguyen, J. D.; Tucker, J. W.; Konieczynska, M. D.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2011**, *133*, 4160–4163. (b) Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem.* **2012**, *77*, 1617–1622. (c) Wallentin, C.-J.; Nguyen, J. D.; Finkbeiner, P.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2012**, *134*, 8875–8884.
- (13) (a) Nicewicz, D. A.; MacMillan, D. W. C. *Science* **2008**, *322*, 77–80. (b) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322–5363.
- (14) Yoon, T. P.; Ischay, M. A.; Du, J. *Nat. Chem.* **2010**, *2*, 527–532.
- (15) Fors, B. P.; Poelma, J. E.; Menyo, M. S.; Robb, M. J.; Spokoiny, D. M.; Kramer, J. W.; Waite, J. H.; Hawker, C. J. *J. Am. Chem. Soc.* **2013**, *135*, 14106–14109.
- (16) Xu, J.; Atme, A.; Marques Martins, A. F.; Jung, K.; Boyer, C. *Polym. Chem.* **2014**, *5*, 3321–3325.
- (17) (a) Tyson, E. L.; Ament, M. S.; Yoon, T. P. *J. Org. Chem.* **2012**, *78*, 2046–2050. (b) Tyson, E. L.; Niemeyer, Z. L.; Yoon, T. P. *J. Org. Chem.* **2014**, *79*, 1427–1436.
- (18) (a) Günay, K. A.; Theato, P.; Klok, H.-A. *Functional Polymers by Post-Polymerization Modification*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2012; pp 1–44. (b) Espeel, P.; Du Prez, F. E. *Macromolecules* **2015**, *48*, 2–14.
- (19) (a) Hansell, C. F.; Espeel, P.; Stamenović, M. M.; Barker, I. A.; Dove, A. P.; Du Prez, F. E.; O’Reilly, R. K. *J. Am. Chem. Soc.* **2011**, *133*, 13828–13831. (b) Oehlenschlaeger, K. K.; Mueller, J. O.; Brandt, J.; Hilf, S.; Lederer, A.; Wilhelm, M.; Graf, R.; Coote, M. L.; Schmidt, F. G.; Barner-Kowollik, C. *Adv. Mater.* **2014**, *26*, 3561–3566. (c) Pauloehrl, T.; Delaitre, G.; Winkler, V.; Welle, A.; Bruns, M.; Börner, H. G.; Greiner, A. M.; Bastmeyer, M.; Barner-Kowollik, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 1071–1074. (d) Barner-Kowollik, C.; Du Prez, F. E.; Espeel, P.; Hawker, C. J.; Junkers, T.; Schlaad, H.; Van Camp, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 60–62. (e) Iha, R. K.; Wooley, K. L.; Nyström, A. M.; Burke, D. J.; Kade, M. J.; Hawker, C. J. *Chem. Rev.* **2009**, *109*, 5620–5686. (f) Theato, P. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6677–6687.
- (20) Boyer, C.; Granville, A.; Davis, T. P.; Bulmus, V. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 3773–3794.
- (21) (a) Xu, J.; Jung, K.; Boyer, C. *Macromolecules* **2014**, *47*, 4217–4229. (b) Xu, J.; Jung, K.; Corrigan, N. A.; Boyer, C. *Chem. Sci.* **2014**, *5*, 3568–3575.
- (22) Xu, J.; Shanmugam, S.; Duong, H. T.; Boyer, C. *Polym. Chem.* **2015**, DOI: 10.1039/c4py01317d.
- (23) Shanmugam, S.; Xu, J.; Boyer, C. *Chem. Sci.* **2015**, DOI: 10.1039/C4SC03342F.
- (24) Huang, C.-Y.; Su, Y. O. *Dalton Trans.* **2010**, *39*, 8306–8312.
- (25) Hari, D. P.; König, B. *Chem. Commun.* **2014**, *50*, 6688–6699.
- (26) Majek, M.; Filace, F.; Wangelin, A. J. v. *Beilstein J. Org. Chem.* **2014**, *10*, 981–989.
- (27) (a) Decker, C.; Nguyen Thi Viet, T. *Polymer* **2000**, *41*, 3905–3912. (b) Lotti, L.; Coiai, S.; Ciardelli, F.; Galimberti, M.; Passaglia, E.

Macromol. Chem. Phys. **2009**, *210*, 1471–1483. (c) ten Brummelhuis, N.; Diehl, C.; Schlaad, H. *Macromolecules* **2008**, *41*, 9946–9947. (d) Bai, J.; Shi, Z.; Yin, J.; Tian, M. *Macromolecules* **2014**, *47*, 2964–2973. (e) Silverstein, J. S.; Casey, B. J.; Natoli, M. E.; Dair, B. J.; Kofinas, P. *Macromolecules* **2012**, *45*, 3161–3167.