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Communication

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Visible Light Photoinitiated Metal-Free Living Cationic Polymerization of 4-Methoxystyrene

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Supporting Information Placeholder

ABSTRACT: Metal-free, visible light-initiated, living cationic polymerization of 4-methoxystyrene using 2,4,6-tri(*p*-tolyl)pyrylium tetrafluoroborate and methanol is demonstrated. Molecular weight and dispersity are controlled by the concentration of methanol. Initial mechanistic analysis suggests that methanol likely serves to regulate propagation of the cation chain end via reversible chain transfer in a manner analogous to RAFT polymerization.

The ongoing development of new methods for the synthesis of polymers of complex architecture has led to a continuing interest in controlled/living polymerization.[1,2] Inspired by rapid progress in photoredox catalysis,[3] a few research groups have recently begun to explore the application of these systems for controlled polymerization.[4–7] Pioneering work by the Hawker group has seen the development of photoredox-promoted Atom Transfer Radical Polymerization (ATRP) for the controlled polymerization of acrylates making use of Ir(ppy)$_3$ as the single electron photoreductant.[4] Using similar visible light-activated catalysts, Boyer and coworkers have developed a Photoinduced Electron Transfer Reversible Addition-Fragmentation chain Transfer (PET-RAFT) polymerization system.[5] Hawker and coworkers have recently extended their photopromoted ATRP methodology to an organic system, making use of 10-phenylphenothiazine (**PTH**) in the place of Ir(ppy)$_3$ as the photoreductant (Figure 1).[7] While only very low loadings of Ir(ppy)$_3$ were necessary to carry out efficient ATRP, the elimination of transition metals entirely eases purification of the resulting materials, a necessary step for a wide variety of applications.

A recent report by the Boydston group furthers the nascent field of metal-free controlled photopolymerization by demonstrating the use of pyrylium salts in a visible light promoted ring-opening metathesis polymerization (ROMP).[6] Using substituted enol ethers as co-initiators and 2,4,6-tri(4-methoxyphenyl)pyrylium tetrafluoroborate (**1**) under visible light irradiation, an efficient and controlled ROMP of norbornene was demonstrated (Figure 1). The metathesis mechanism differs from traditional transition metal-alkylidene catalyzed ROMP as it involves the intermediacy of radical cationic species generated by the initial one-electron oxidation of the enol ether co-initiator by the excited state of **1**.

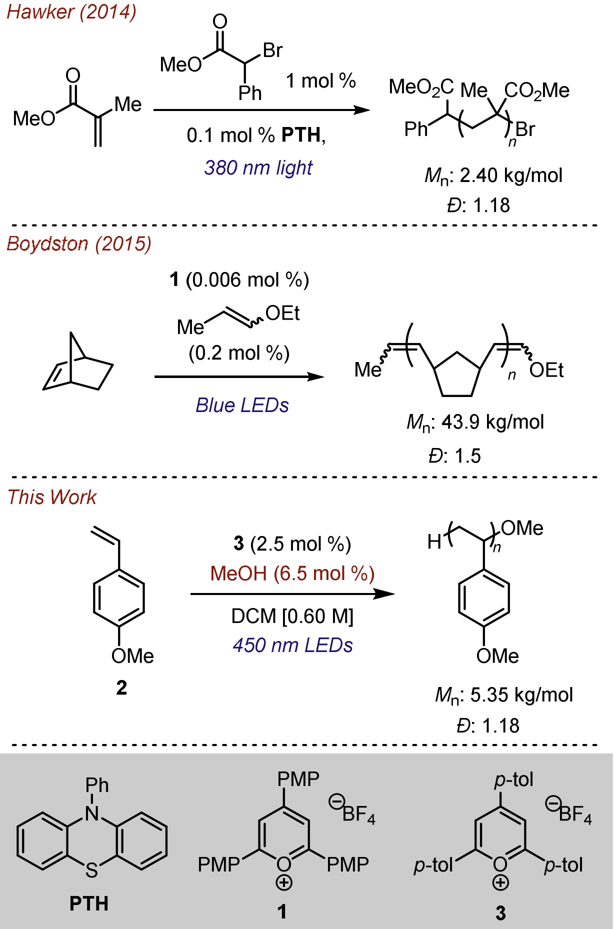
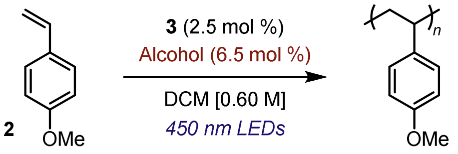


Figure 1. Recent advances in metal-free controlled photopolymerization. PMP = 4-(OMe)C$_6$H$_4$; *p*-tol = 4-(Me)C$_6$H$_4$

On the other hand, while photoinitiated cationic polymerization has been known for decades,[8–11] there has been little attention to the development of variants which facilitate controlled, or even living, polymerization beyond procedures for *in situ* photochemical generation of organohalide co-initiators for subsequent Lewis acid mediated living polymerization of vinyl ethers.[12–14] Given our experience in the field of visible light photoredox catalysis, and particularly our research into the controlled dimerization of electron rich styrenes, we were intrigued by the possibility of harnessing this reactivity for controlled photopolymerization.[15] In particular, we set out to develop a procedurally simple method for a metal-free controlled/living photopolymerization using visible light. Reported herein is a system for the controlled cationic photopolymerization of 4-methoxystyrene (**2**) using low concentrations of methanol in combination with 2,4,6-tri(*p*-tolyl)pyrylium tetrafluoroborate (**3**) as a photoinitiator.[16] To our knowledge, this is the first report of a living cationic polymerization controlled by methanol.

Specifically, we commenced our investigations with irradiation of **2** and substoichiometric loadings of **3** in dichloromethane (DCM) using blue light-emitting diodes (LEDs). Poly(4-methoxystyrene) of moderately high molecular weight was produced with greater than 95% conversion after only a few minutes (^{1}H NMR). Initial studies via additive probes intended to elucidate the predominant mode of polymerization revealed an interesting effect. Small amounts of methanol resulted in markedly lower number average (M_n) and weight average (M_w) molecular weights, unexpectedly accompanied by much lower than anticipated dispersity ($Đ$, M_w/M_n) (Table 1, entry 2). Proton NMR analysis of the resulting poly(4-methoxystyrene) indicated the presence of methoxy end groups at the chain termini. Resonances centered around δ 2.95 ppm were identified and found to be in agreement with methoxy-capped poly(4-methoxystyrene) synthesized by a different living cationic polymerization (Figure 2, **A**).[17] Substitution of methanol-*d3* in the standard conditions verified that the methoxy end-group was coming from the methanol added to the reaction mixture, and not from subsequent precipitation and purification steps (Figure 2,**B**). Further, resonances centered around δ 1.00 ppm are indicative of a methyl end group, likely resulting from initiation via protonation. This provided strong evidence that the polymerization propagation mode is cationic in nature, and is in agreement with previous literature reports on pyrylium initiated polymerization.[18,19]

Table 1. Alcohol Additive Study



Entry	Alcohol	M_n (kg/mol)[a]	$Đ$[a]	Yield (%)[b]
1	–	72.5	3.04	92
2	MeOH	5.41	1.18	92
3	EtOH	6.12	1.22	96
4	*i*-PrOH	10.5	1.31	96
5	*t*-BuOH	26.0	1.86	97
6	CF_3CH_2OH	33.7	2.05	97
7[c]	MeOH	6.18	1.21	86

[a]Determined by GPC, relative to polystyrene standards, average of three experiments. [b]Yield after precipitation, average of three experiments. [c]0.25 mol % **3**.

The marked effect of added methanol implicated a nucleophilic interaction with the propagating chain end. If this were the case, M_n and $Đ$ should be sensitive to changes in the nucleophilicity of the alcohol additive. A series of polymerizations were then carried out under identical conditions varying only the added alcohol (Table 1). Alcohols of decreasing nucleophilicity were chosen: methanol, ethanol, *iso*-propanol, *tert*-butanol and trifluoroethanol. As the steric environment of the additive becomes more demanding, concomitant with decreasing nucleophilicity (entries 2 through 5), both M_n and $Đ$ of the resulting poly(4-methoxystyrene) increases. This trend is indicative of a nucleophilic interaction between the propagating chain end and the alcohol additive. If this effect were indeed nucleophilic in origin (rather than simply steric), then alcohols of similar steric environments around the hydroxyl group, but with differing nucleophilicity due to electronic factors, should give dissimilar results. This is indeed the case when comparing ethanol (entry 3) to trifluoroethanol (entry 6); the latter is less nucleophilic than ethanol due to the potent electron-withdrawing nature of the trifluoromethyl group thereby leading to the observed loss of control over the polymerization (entry 6).

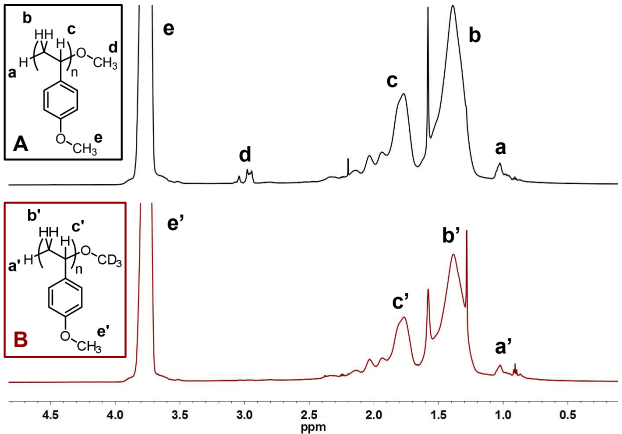


Figure 2. ^{1}H NMR spectra of poly(4-methoxystyrene). Conditions: 2.5 mol % **3**, 6.5 mol % methanol (A) or methanol-*d3* (B), [0.60 M] **2** in DCM, blue LED irradiation. **A:** M_n = 5.35 kg/mol, $Đ$ = 1.18 or methanol-*d3*, **B:** M_n = 6.26 kg/mol, $Đ$ = 1.15.

Furthermore, methanol loading exhibited a strong influence over M_n and $Đ$ (Figure 3). Increased methanol loading is associated with decreased $Đ$ up to loadings of approximately 6.5 mol %. At this concentration of methanol and above, $Đ$ remains relatively constant at approximately 1.2. Increased methanol loadings were also associated with decreased M_n, which suggests that methanol likely plays a key role in the number of chains initiated. On the other hand, the loading of the photooxidant **3** had a relatively small influence on the resulting poly(4-methoxystyrene), similarly exhibiting low $Đ$ around 1.2 and only a modest increase in M_n at lower loadings of **3** (Table 1 entry 7, see Figure S1 and Table S1 in SI).

The kinetics of the polymerization were studied using ^{1}H NMR and gel permeation chromatography via quenching after varying irradiation times (Figures 4 and 5). The polymerization exhibits an induction period of several minutes during which monomer conversion is very low and no polymer is produced. After this induction period, polymerization is rapid and follows first order kinetics (Figure 4). Furthermore, the molecular weight increases steadily with monomer conversion, exhibiting

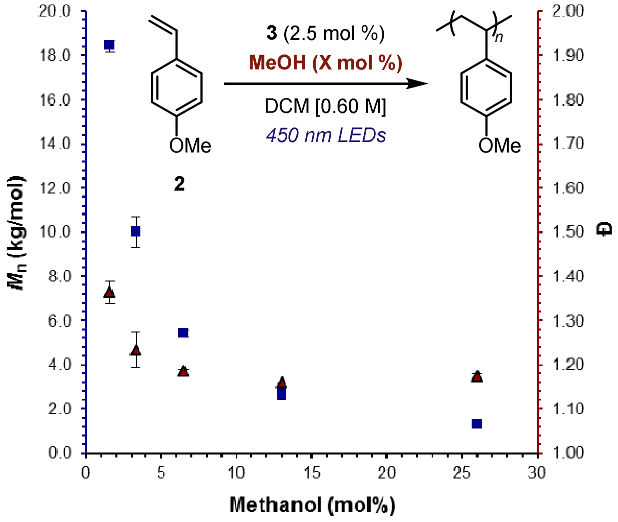


Figure 3. Influence of methanol loading on M_n (■) and $Đ$ (▲) of poly(4-methoxystyrene). M_n and $Đ$ were determined by GPC relative to polystyrene standards, average of three experiments. Conditions: 2.5 mol % **3**, [0.60 M] **2** in DCM, blue LED irradiation.

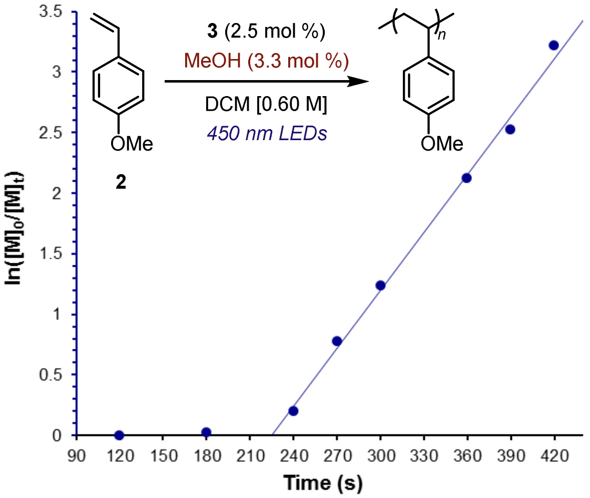


Figure 4. A plot of $\ln([2]_0/[2]_t)$ versus reaction time (●). Conversions were determined by ^{1}H NMR analysis of reaction aliquots, after quenching with trimethylamine, using an internal standard. Conditions: 2.5 mol % 3, 3.3 mol % methanol, [0.60 M] 2 in DCM, blue LED irradiation, quenched with triethylamine after varying irradiation times.

a linear relationship to monomer conversion after a short initial period of non-linear growth (Figure 5). Similarly, *Đ* increases up to this same conversion and then remains nearly constant. Altogether, these data suggest that after an induction period, this photopolymerization becomes a well-controlled cationic polymerization exhibiting the characteristics of living polymerization.

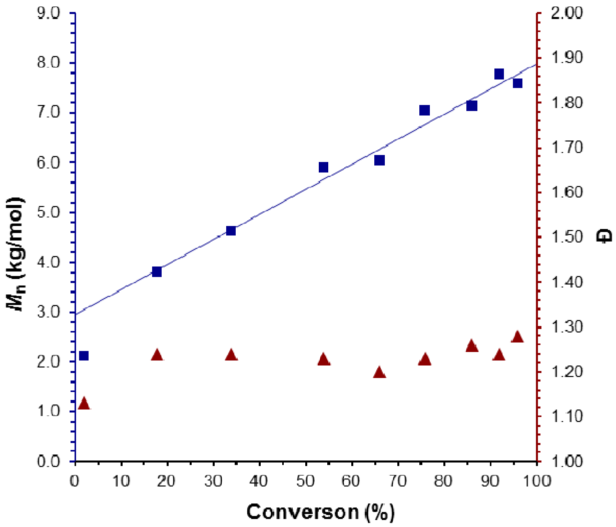
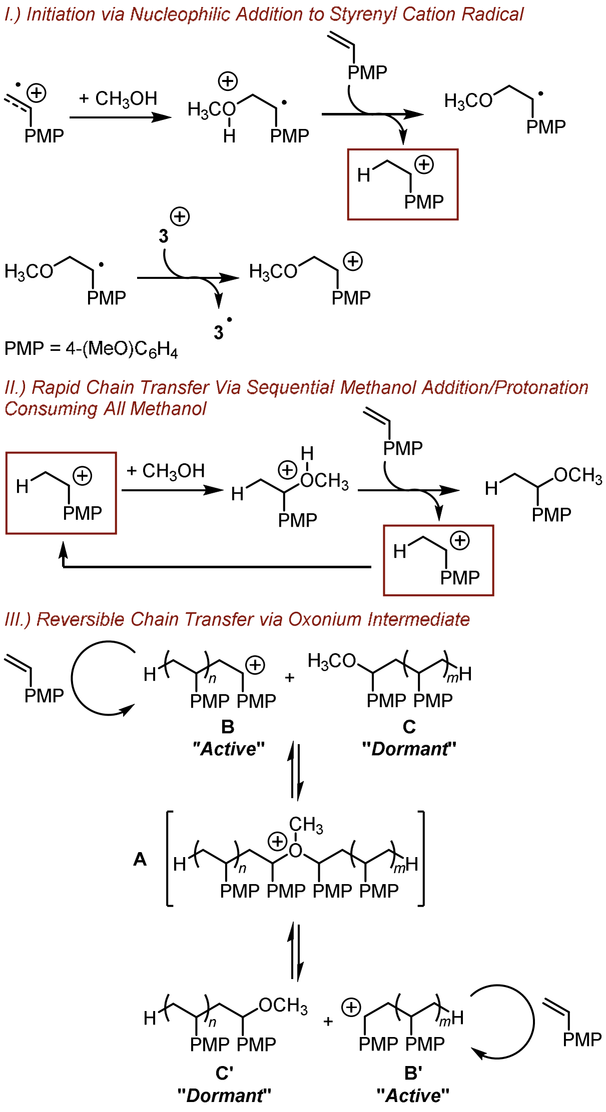


Figure 5. M_n (■) and *Đ* (▲) of poly(4-methoxystyrene) as a function of monomer conversion. M_n and *Đ* were determined by GPC relative to polystyrene standards. Conversions were determined by ^{1}H NMR analysis of aliquots after quenching with triethyamine using an internal standard. Conditions: 2.5 mol % **3**, 3.3 mol % methanol, [0.60 M] **2** in DCM, blue LED irradiation, quenched with triethylamine after varying irradiation times.

Given these data and observations, we propose the following mechanism (Scheme 1): photoredox catalyst **3** serves as the initiator upon visible light illumination, likely via initial single electron oxidation of **2** generating a styrenyl cation radical (Scheme 1, I).[20] The subsequent initiation steps are still under study, but likely involve anti-Markovnikov nucleophilic addition of methanol to the styrenyl cation radical.[21] End group analysis of poly(4-methoxystrene) using 2D NMR techniques indicates correlations which support some proportion of methoxy end groups resulting from initial anti-Markovnikov addition (see Figure S8 in SI). The resulting methanol captured cationic radical could protonate an additional monomer, generating an active cationic chain end, followed by rapid oxidation of the resulting benzylic radical by **3** to the corresponding cation (Scheme 1, II).[22,23] Once a cation has been formed, nucleophilic capture by methanol generates an additional proton that goes on to protonate an additional monomer, which is itself intercepted by methanol. This proceeds until all methanol in the reaction has been converted into methoxy groups and a relatively small number of active cationic chain ends remain. The observation of deuterium enrichment on the methyl end groups of poly(4-methoxystyrene) prepared using methanol-*d4* provides additional support for this mechanism (see Figure S9 in SI). In this manner, the concentration of methanol determines the number of chains rather than the loading of **3** (for an elaborated mechanistic proposal see Scheme S1 in SI). Control of the polymerization then occurs via a mechanism analogous to Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization wherein the methoxy group serves as the chain transfer agent by transient formation of an oxonium ion intermediate through nucleophilic capture of a cationic chain end (**A**, Scheme 1, III).[2] This oxonium ion can fragment via carbon-oxygen bond heterolysis to produce a new active chain end (**B**) and a new dormant methoxy-capped chain (**C**). The new cationic chain end then propagates until it recombines with the methoxy end group of another chain, again generating an oxonium ion intermediate,

Scheme 1. Mechanistic Proposal



which can itself undergo further fragmentation (e.g to **B'** and **C'**).

If our mechanistic proposal is accurate, then the poly(4-methoxystyrene) chain ends should still be active once all monomer has been consumed. To test this, monomer addition experiments were carried out. After polymerization was complete, irradiation was ceased and an additional equivalent of **2** was added directly to the solution (Figure 6). A nearly monomodal molecular weight shift was observed via GPC which retained a low *Đ*, a strong indication that the poly(4-methoxystyrene) chain ends are still active at the end of polymerization. While the increase in M_n was less than the theoretically expected doubling, an isolated yield of 90% was observed after precipitation of the poly(4-methoxystyrene). The GPC trace did indicate a small higher molecular weight shoulder, suggesting some loss of control. Given the apparent rapid rate of the polymerization, this may be a result of initial small differences in monomer concentration at the moment of addition.

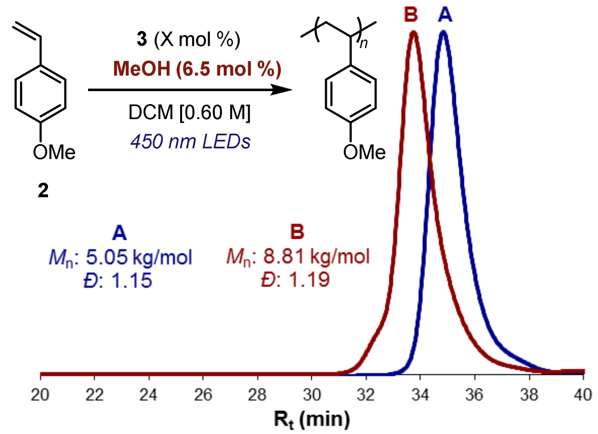


Figure 6. GPC trace showing monomodal molecular weight shift after monomer addition. Conditions: 2.5 mol % **3**, 6.5 mol % methanol, [0.60 M] **2** in DCM, blue LED irradiation. **A**: Quenched with triethylamine after 10 minutes irradiation. **B**: Irradiation ceased at 10 minutes, immediate addition of a further equivalent of **2**.

In conclusion, we have carried out initial studies into the methanol-controlled visible light photoinitiated polymerization of 4-methoxystyrene using pyrylium salts. First order kinetic behavior, linear M_n growth with respect to monomer consumption, narrow *Đ*, and continued polymerization upon monomer addition all indicate the controlled/living nature of the polymerization. The accumulated data suggest methanol plays a role as a reversible chain transfer agent, analogous to that of dithiocarbamates in RAFT polymerization. The polymerization does not require the use of strong Lewis or Brønsted acids or the prior synthesis or formation of small molecule co-initiators. Poly(4-methoxystyrene) of low *Đ* can be prepared, with M_n controlled by the concentration of methanol. Further development of this methodology will focus on reducing the induction period made apparent via kinetic study, and elucidation of the precise steps involved in initiation will likely be of key importance in this endeavor. Expansion of the scope of this methodology to further monomers and towards the preparation of block copolymers and polymers of more complex architecture is also planned. Further tuning of the protic additive should allow for reduced loadings and greater control over the polymerization. In principle, a matching of protic additive and monomer should be possible such that a wide range of monomers could be amenable to controlled polymerization via this method.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Funding Sources

The authors declare no competing financial interests.

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REFERENCES

(1) Matyjaszewski, K. *Macromolecules* **2012**, *45*, 4015.

(2) Moad, G.; Rizzardo, E.; Thang, S. H. *Acc. Chem. Res.* **2008**, *41*, 1133.

(3) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322.

(4) Fors, B. P.; Hawker, C. J. *Angew. Chem. - Int. Ed.* **2012**, *51*, 8850.

(5) Xu, J.; Jung, K.; Atme, A.; Shanmugam, S.; Boyer, C. *J. Am. Chem. Soc.* **2014**, *136*, 5508.

(6) Ogawa, K. a; Goetz, A. E.; Boydston, A. J. *J. Am. Chem. Soc.* **2015**, *137*, 1400.

(7) Treat, N. J.; Sprafke, H.; Kramer, J. W.; Clark, P. G.; Barton, B. E.; Read de Alaniz, J.; Fors, B. P.; Hawker, C. J. *J. Am. Chem. Soc.* **2014**.

(8) Sangermano, M. *Pure Appl. Chem.* **2012**, *84*, 2089.

(9) Crivello, J. V. *J. Polym. Sci. Part Polym. Chem.* **1999**, *37*, 4241.

(10) Kahveci, M. U.; Yilmaz, A. G.; Yagci, Y. In *Photochemistry and Photophysics of Polymer Materials*; Allen, N. S., Ed.; John Wiley & Sons, Inc.: Hoboken, New Jersey, 2010; pp 421–478.

(11) Yagci, Y.; Durmaz, Y. Y.; Aydogan, B. *Chem. Rec. N. Y. N* **2007**, *7*, 78.

(12) Kwon, S.; Chun, H.; Mah, S. *Fibers Polym.* **2004**, *5*, 253.

(13) Kahveci, M. U.; Tasdelen, M. A.; Yagci, Y. *Polymer* **2007**, *48*, 2199.

(14) Higashimura, T.; Kojima, K.; Sawamoto, M. *Polym. Bull.* **1988**, *19*, 7.

(15) Riener, M.; Nicewicz, D. A. *Chem. Sci.* **2013**, *4*, 2625.

(16) For examples of electroinitiated styrene polymerization, see: a.) Funt, B. L.; Blain, T. J. *J. Polym. Sci. [A1]* **1970**, *8*, 3339.; b.) Toppare, L.; Eren, S.; Özel, ö.; Akbulut, U. *J. Macromol. Sci. Part - Chem.* **1984**, *21*, 1281; c.) Akbulut, U.; Fernandez, J. E.; Birke, R. L. *J. Polym. Sci. Polym. Chem. Ed.* **1975**, *13*, 133

(17) De, P.; Faust, R. *Macromolecules* **2004**, *37*, 7930.

(18) Bawn, C. E. H.; Carruthers, R.; Ledwith, A. *Chem. Commun.* **1965**, *21*, 522.

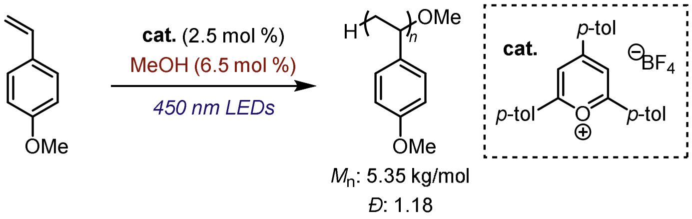
(19) Ledwith, A. *Polym. Prepr.* **1982**, *23*, 323.

(20) Miranda, M. A.; Gar, H. *Chem. Rev.* **1994**, *94*, 1063.

(21) Hamilton, D. S.; Nicewicz, D. A. *J. Am. Chem. Soc.* **2012**, *134*, 18577.

(22) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

(23) Kamachi, M.; Guo, H.-Q.; Kajiwara, A. *Macromol. Symp.* **1997**, *118*, 149.



Living Photopolymerization Controlled by Alcohol Cocatalysts