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Authors

Areephong, J
Mattson, KM
Treat, NJ
et al.

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Triazine-mediated controlled radical polymerization: new unimolecular initiators†

J. Areephong,^a K. M. Mattson,^{a,b} N. J. Treat,^{a,c} S. O. Poelma,^{a,b} J. W. Kramer,^d H. A. Sprafke,^a A. A. Latimer,^{a,b} J. Read de Alaniz^{a,b} and C. J. Hawker^{*a,b,c}

Triazine-based unimolecular initiators are shown to mediate the controlled radical polymerization of several monomer classes, yielding polymers with low dispersities, targeted molecular weights, and active chain ends. We report the modular synthesis of structurally and electronically diverse triazine-based unimolecular initiators and demonstrate their ability to efficiently control the radical polymerization of modified styrene monomers. Copolymerizations of styrene with butyl acrylate or methyl methacrylate were conducted to highlight the monomer family tolerance of this system. Notably, in the case of methyl methacrylate and styrene, up to 90 mol% methyl methacrylate comonomer loadings could be achieved while maintaining a controlled polymerization, allowing the synthesis of a range of block copolymers. This class of triazine-based mediators has the potential to complement current methods of controlled radical polymerization and marks an important milestone in ongoing efforts to develop initiators and mediators with high monomer tolerance that are both metal and sulfur-free.

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Introduction

Controlled radical polymerizations (CRP) are of paramount importance to the field of polymer chemistry. Their ability to access well-defined polymers with rich chemical functionality makes them critical to many state-of-the-art applications. While there are a variety of CRP techniques,^{1–3} three dominate due to their simplicity and functional group tolerance: atom transfer radical polymerization (ATRP),^{4,5} reversible addition-fragmentation chain transfer polymerization (RAFT),⁶ and nitroxide-mediated polymerization (NMP).^{7,8} Of these, NMP is particularly useful because of both its inherent simplicity (*i.e.* needing only monomer and unimolecular initiator) and its avoidance of sulfur and metal catalysts found in the RAFT and ATRP processes.⁸ This is achieved through the use of a stable nitroxide radical (Fig. 1a) that reversibly caps the growing polymer chain end, establishing a low radical concentration in solution, and minimizing deleterious termination events (Fig. 2a). Over the last 20 years, NMP has evolved to be a viable technique for the production of a variety of functional

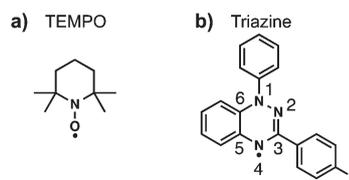


Fig. 1 (a) 2,2,6,6-Tetramethylpiperidinyl-1-oxyl (TEMPO) and (b) benzo-1,2,4-triazinyl (triazine) stable radicals.

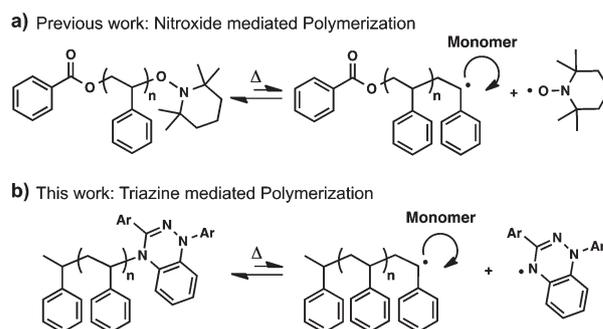


Fig. 2 (a) Mechanism of NMP and (b) proposed mechanism for triazine-mediated polymerization.

^aMaterials Research Laboratory, University of California, Santa Barbara, 93106, USA. E-mail: hawker@mrl.ucsb.edu

^bDepartment of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, USA

^cMaterials Department, University of California, Santa Barbara, 93106, USA

^dThe Dow Chemical Company, Midland, MI 48674, USA

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materials.^{8–14} However, limitations still exist. For example, NMP's monomer scope does not match those of RAFT and ATRP, with the controlled polymerization of methacrylates only recently being reported using specialized mediators.^{15–17}

In hopes of overcoming these issues, many other stable radicals have been evaluated for controlled polymerization, including (aryloxy),¹⁸ borinate,¹⁹ triazolyl,^{20–23} and verdazyl^{24–28} radicals. Of these, only triazolyl and verdazyl radicals have been shown to control polymerizations, and these only for styrene and acrylates. Thus, there is significant potential for the development of new radical mediators that may overcome limitations of NMP and expand the field of controlled radical polymerizations. With this in mind, we began our search for a new radical mediator, eventually identifying the benzo-1,2,4-triazinyl (triazine) moiety first reported by Blatter in 1968 as a highly stable radical (Fig. 1b).²⁹

The triazine moiety interested us in particular because it had previously been explored for controlled radical polymerization in combination with thermal initiators, but the performance of the corresponding unimolecular initiator and associated structural variations had not been studied.³⁰ Further, the triazine unit is a versatile building block, easily tunable from a synthetic standpoint, and triazine-mediated polymerizations would be analogous to NMP in avoiding sulfur and metal contamination (Fig. 2).

Results and discussion

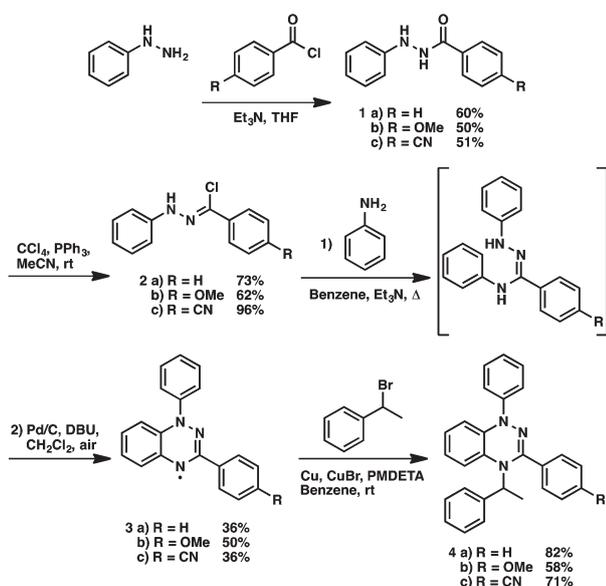
After identifying the triazine radical as a nitroxide equivalent in an NMP-like system, synthesis of the stable radical **3a** was achieved in three steps starting from low cost commercially available phenyl hydrazine and benzoyl chloride (Scheme 1).

For our initial screen, we combined **3a** with styrene and benzoyl peroxide at 125 °C and observed controlled polymerization at low conversions with good agreement between theoretical and experimental molecular weights, as well as low

dispersities (see Table S1†). However, at conversions above *ca.* 14%, the polymerization became uncontrolled. To overcome this, atom transfer radical addition was carried out to convert triazine radical **3a** into the unimolecular initiator (**4a**, see Scheme 1) in analogy with NMP literature where unimolecular initiators exhibit improved polymerization behavior over their stable free radical counterparts.^{31,32} Accordingly, the parent triazine-based unimolecular initiator **4a** displays superior control over the bulk polymerization of styrene up to high conversions (~80%), with low dispersities ($M_w/M_n = 1.15–1.23$, see Table S2†). These initial results encouraged us to prepare a series of triazine-based unimolecular initiators and explore their potential in controlled radical polymerizations.

In a systematic study examining the influence of the electronic nature of the triazine radical, we therefore synthesized unimolecular initiators **4b** and **4c** (Scheme 1). The synthesis was analogous to that of **1a** but used *para*-substituted benzoyl chlorides in the initial condensation step to obtain **1b–c**. Treatment of **1b–c** with triphenylphosphine and carbon tetrachloride gave the corresponding chlorohydrazones **2b–c**, which were then condensed with aniline to give the desired stable triazine radical following oxidative cyclization.³³ Coupling with (1-bromoethyl)benzene under a modified atom transfer radical addition step then provides the corresponding unimolecular initiators **4a–c** in moderate to high yields. Single crystal X-ray analysis of **4a** confirmed the attachment of the 2-methyl benzyl unit on the N-4 position (Fig. 3).

It is important to note that this synthetic strategy provides a platform for producing a wide variety of triazine structures, many of which may be easily accessible from the large number of commercially available aryl amines and substituted benzoyl chlorides and acids. Further, we found that these molecules are inherently chromophoric (Fig. S5†). Both the electron-neutral and donating (**4a–b**) triazines have absorption maxima (λ_{max}) of 315 nm, while the electron-withdrawing derivative (**4c**) has a significant red-shift ($\lambda_{max} = 430$ nm) (see Fig. S5†). Compared to other CRP techniques, these tunable chromophoric properties are a distinct advantage as they allow for facile



Scheme 1 Synthetic platform for triazine unimolecular initiators.

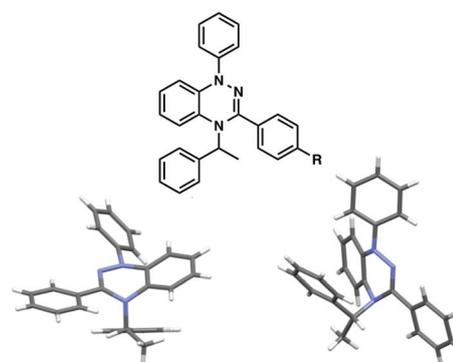


Fig. 3 Top: General structure of triazine-based unimolecular initiator. Bottom: Crystal structure of triazine unimolecular initiator **4a** determined by X-ray crystallography.

chain-end verification *via* UV-vis spectroscopy. Further, they also provide application capabilities for optical imaging and biological signal enhancement.³⁴

Following the synthesis of unimolecular initiators **4a–c**, bulk polymerization of styrene was investigated at 125 °C, thoroughly monitoring the reaction progress over time. Significantly, controlled behavior was observed for each triazine derivative, as indicated by a linear increase in molecular weight with conversion, and low dispersities ($M_w/M_n = 1.1–1.3$) (Fig. 4a and b). Additionally, the linear semi-logarithmic plot of $\ln([M_0]/[M_t])$ versus time (Fig. S7†) indicates first order reaction kinetics and a constant radical concentration over the course of the polymerization. Interestingly, introducing electron-donating (**4b**, OMe) or electron-withdrawing (**4c**, CN) groups into the C-3 position (Fig. 1b) gave very little difference in the polymerization kinetics or control, though they do provide a valuable handle for tuning chain-end absorption properties (*vide supra*). Controlled polymerization was also observed at temperatures as low as 110 °C (Table S2†), although a marked decrease in rate occurred.

Having established a controlled chain-growth process for unimolecular initiators **4a–c**, we targeted a range of molecular weights by adjusting the ratio of **4a** to styrene (1–45 kg mol⁻¹, Fig. 5 and Table S3†). Indeed, low dispersity and good agreement between experimental and theoretical molecular weights were consistently observed under bulk conditions. This demonstrates the ease in preparation of a range of materials, and provides evidence for the potential of triazine-mediated controlled polymerization.

To further illustrate the living radical nature of this process, chain end control was studied using a combination of

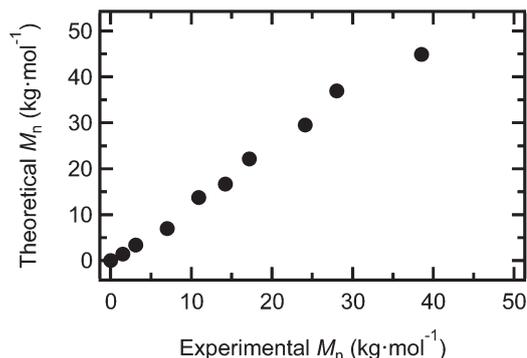


Fig. 5 Relationship between experimental and theoretical molecular weights for the polymerization of styrene targeted at different molecular weights, initiated with **4a**, run at 125 °C for 8 h.

methods. First, a polystyrene homopolymer was grown using unimolecular initiator **4b** and investigated by ¹H NMR. The methoxy group of **4b** has a diagnostic ¹H NMR signal at 3.8 ppm, which was used as a handle for molecular weight calculation (Fig. 6). The theoretical molecular weight as well as experimental molecular weights determined by both ¹H NMR and SEC were all in good agreement, verifying controlled polymerization and high retention of the triazine chain ends. Moreover, SEC monitoring of UV-vis absorption and comparison of RI and UV-vis detection confirmed that the triazine moiety was present across the entire weight-range (Fig. S9†).

Excellent chain end fidelity naturally led to examining the use of these homopolymers as stable macroinitiators for block copolymer formation. We employed unimolecular initiator **4a** to extend isolated polystyrene homopolymers to give poly(styrene-*b*-styrene) and poly(styrene-*b*-4-vinylanisole) diblock copolymers (Fig. 7) with minimal tailing in the low molecular weight region of their respective SEC chromatographs, validating the retention of triazine end-groups throughout the polymerization. These experiments clearly demonstrate that a living process is occurring, and that triazine-based mediators have the ability to control the synthesis of multiblock copolymers.

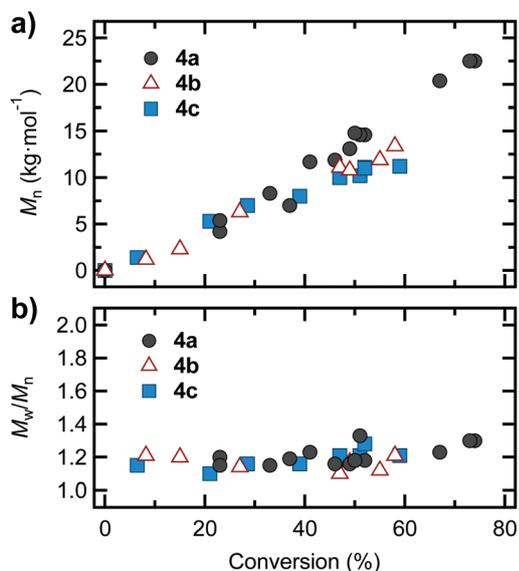


Fig. 4 (a) Evolution of experimental molecular weight versus conversion for the polymerization of styrene using unimolecular initiators **4a**, **4b**, and **4c** and (b) the corresponding M_w/M_n values demonstrate controlled polymerization for all triazines tested.

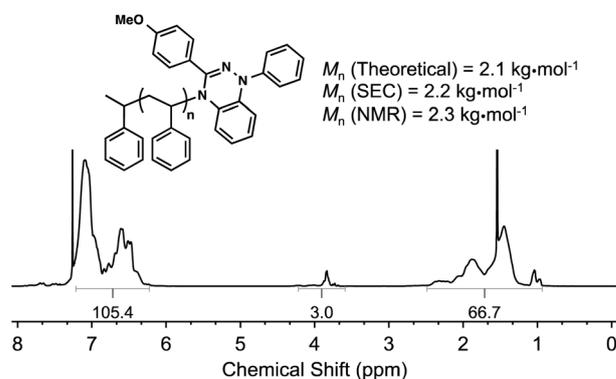


Fig. 6 ¹H NMR spectrum of polystyrene synthesized using triazine unimolecular initiator **4b** demonstrating high retention of triazine chain ends.

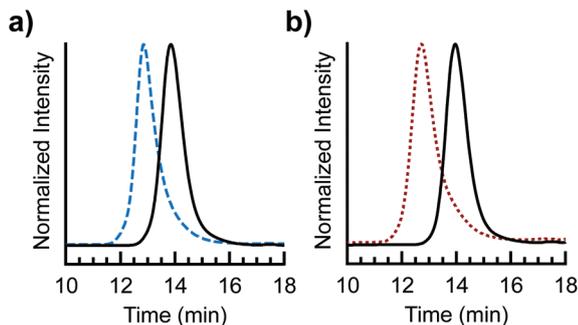
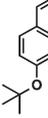
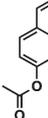


Fig. 7 SEC traces of block copolymer syntheses; (a) (black solid line) polystyrene macroinitiator ($M_n = 13.1 \text{ kg mol}^{-1}$, $M_w/M_n = 1.16$), (blue dashed line) poly(styrene-*b*-styrene) ($M_n = 25.1 \text{ kg mol}^{-1}$, $M_w/M_n = 1.26$); (b) (black solid line) polystyrene macroinitiator ($M_n = 11.9 \text{ kg mol}^{-1}$, $M_w/M_n = 1.16$), (red dotted line) poly(styrene-*b*-4-vinylanisole) ($M_n = 28.5 \text{ kg mol}^{-1}$, $M_w/M_n = 1.27$).

The triazine system was then evaluated for functional group tolerance through copolymerization experiments, with a focus on comonomers containing functional groups commonly used for post-polymerization modifications (Table 1). Thus, using unimolecular initiator **4a**, copolymerizations with styrene were conducted with high comonomer loadings (50–90 mol%) of halogenated styrenics, including chlorides and bromides, as well as protected phenols. In all cases, polymerizations

Table 1 Dispersities and experimental molecular weights (M_n) for bulk random copolymerizations of styrene and styrenic derivatives in the presence of **4a**

Comonomer	Molar ratio of styrene/co-monomer	M_n (kg mol^{-1})	M_w/M_n
	50/50	15.4	1.32
	10/90	15.5	1.38
	0/100	14.7	1.34
	50/50	12.5	1.27
	10/90	13.0	1.27
	0/100	12.2	1.47
	50/50	21.3	1.24
	10/90	17.6	1.26
	0/100	19.3	1.26
	50/50	13.0	1.35
	10/90	15.0	1.43
	0/100	15.3	1.47

Reaction conditions: triazine unimolecular initiator **4a** (1.0 equiv.), monomer (200 equiv.), in bulk at 125 °C for 12 h (M_n = number-average molecular weight; M_w = weight-average molecular weight). M_n and M_w/M_n determined using size exclusion chromatography (SEC) relative to linear polystyrene standards.

Table 2 Dispersities and experimental molecular weights (M_n) for the bulk random copolymerizations of styrene and butyl acrylate or methyl methacrylate in the presence of **4a**

Comonomer	Molar ratio of styrene/co-monomer	M_n (kg mol^{-1})	M_w/M_n
	90/10	16.8	1.17
	80/20	14.8	1.18
	60/40	15.6	1.27
	50/50	14.8	1.32
	90/10	11.6	1.11
	60/40	16.4	1.16
	40/60	16.9	1.22
	20/80	14.4	1.27
	10/90	11.1	1.34

Reaction conditions: triazine unimolecular initiator **4a** (1.0 equiv.), 200 total monomer equiv., in bulk, at 125 °C for 8 h (M_n = number-average molecular weight; M_w = weight-average molecular weight). M_n and M_w/M_n determined using size exclusion chromatography (SEC).

showed controlled behavior. Subsequently, homopolymerization of the same functional monomers were examined, and again low dispersities were observed (Table 1), further demonstrating the robust nature of triazine-mediated polymerizations.

These initial results using functional styrene monomers encouraged us to explore the utility of triazine-based unimolecular initiators for polymerization of other monomer families. Consequently, a series of copolymerizations of styrene with butyl acrylate and methyl methacrylate were conducted. When butyl acrylate was copolymerized with styrene in bulk at 125 °C employing the unimolecular initiator **4a**, well-defined polymers with low dispersities were observed up to 50 mol% acrylate loadings (Table 2). Loadings of >50 mol% butyl acrylate dramatically reduced the rate of polymerization. Further work is needed to fully understand the mechanism behind this behavior. However, in contrast to the butyl acrylate system, copolymerizations of styrene with methyl methacrylate resulted in a controlled system at up to 90 mol% methyl methacrylate ($M_w/M_n = 1.1$ –1.34). In stark contrast to NMP, triazine-mediated polymerizations do not suffer from termination by disproportionation of chain ends, as indicated by an absence of peaks in the 5.50–6.20 ppm region of the ^1H NMR spectrum (Fig. S10†).^{35,36} Although homopolymerization of butyl acrylate and methyl methacrylate currently do not show controlled behavior, these initial results suggest that triazines may be further developed to control polymerization of these important monomer families.

Conclusions

Triazine-based stable radicals have been developed for controlled radical polymerization. A tunable synthesis allowed for the production of a variety of unimolecular initiators and their ability to mediate the polymerization of styrene was demonstrated with a linear increase in molecular weight with conversion and first order kinetics. A variety of functional styrenic

derivatives could be homopolymerized and the copolymerization of styrene with butyl acrylate or methyl methacrylate resulted in well-defined polymers. Control over chain ends was demonstrated *via* UV-vis, NMR, and block copolymerization experiments. These initial results demonstrate the utility of triazine derivatives as stable radicals for controlling the polymerization of vinyl monomers.

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