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Photoinduced Organocatalyzed Atom Transfer Radical Polymerization Using Low ppm Catalyst Loading

Justin P. Cole, Celia R. Federico, Chern-Hooi Lim, and Garret M. Miyake*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, United States

Abstract

Photoinduced organocatalyzed atom-transfer radical polymerization (O-ATRP) is a controlled radical polymerization methodology that can be mediated by organic photoredox catalysts under the influence of light. However, typical O-ATRP systems require relatively high catalyst loadings (1000 ppm) to achieve control over the polymerization. Here, new core-extended diaryl dihydrophenazine photoredox catalysts were developed for O-ATRP and demonstrated to efficiently operate at low catalyst loadings of 5–50 ppm to produce polymers with excellent molecular weight control and low dispersity, while achieving near-quantitative initiator efficiency. Photophysical and electrochemical properties of the catalysts were computationally predicted and experimentally measured to correlate these properties with improved catalytic performance. Furthermore, these catalysts were utilized to synthesize materials with complex architectures, such as triblock copolymers and star polymers. To demonstrate their broad utility, polymerizations employing these catalysts were successfully scaled up to 5 g and revealed to efficiently operate under air.

Graphical Abstract

*Corresponding Author Garret.Miyake@colostate.edu.

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b02688.

Experimental and computational details; Figures S1–S106 (PDF)

X-ray crystallographic data for PC 1 (CIF)

X-ray crystallographic data for PC 2⁺⁺ (CIF)

X-ray crystallographic data for PC 3a (CIF)

INTRODUCTION

Atom-transfer radical polymerization (ATRP) has become the most well-studied controlled radical polymerization (CRP) method for the synthesis of polymers with controlled molecular weights (MWs) and low dispersity (M_w/M_n).^{1–3} An often-cited drawback to transition-metal-mediated ATRP is the presence of trace metal impurities in the final product, which can be difficult to remove.^{4,5} A substantial advancement in transition-metal-mediated ATRP has been the development of systems that operate using extremely low amounts of copper catalyst loading (i.e., 10–50 ppm of Cu).⁶ Polymerizations using these low loadings of catalysts often rely on exogenous redox agents,^{7–9} electrochemical modulation,^{10,11} or irradiation^{12,13} to control the oxidation state of the catalyst.

In 2012, a photoredox-catalyzed ATRP was first reported,¹⁴ allowing for well-controlled polymerizations to be performed using visible light as the driving force with 50 ppm of Ir(ppy)₃ (tris[2-phenylpyridinato-C2,N]iridium(III)) as the catalyst. This system utilized a low concentration of the Ir noble metal as well as employed a simple reaction setup requiring only catalyst, monomer, initiator, solvent, and white light. Several researchers have built on these findings, and many transition metal complexes have since been reported to efficiently catalyze ATRP using visible light.^{15,16}

More recently, organic photoredox catalysts¹⁷ (PCs) based on perylene,¹⁸ phenothiazine,¹⁹ dihydrophenazine,²⁰ and phenoxazine²¹ chromophore motifs have been developed to mediate organocatalyzed ATRP (O-ATRP) to produce polymers with controlled MW, high initiator efficiency ($F^* = \text{MW}_{\text{theo}}/\text{MW}_{\text{exp}}$), and low M_w/M_n (Figure 1) while avoiding the possibility for incorporating metal contamination into the polymer product.^{22,23} Since the seminal reports on O-ATRP, PC structural modifications,²⁴ photophysical characterizations,^{25–27} solvent effects,²⁸ light intensity modulations,²⁹ and synthesis of higher-order polymer architectures^{30–32} have been reported to advance the O-ATRP processes.

An important challenge to address in O-ATRP is to lower the required PC loading while still producing well-defined polymers. Typically, comparatively high PC loadings (~1000 ppm of catalyst relative to monomer) have been required to achieve a well-controlled polymerization. Carbazole-based PCs were recently reported as O-ATRP catalysts using 5–40 ppm PC loading;³³ however, these systems exhibited poor control over polymer MW growth and resulted in polymers possessing broad molecular weight distributions ($\text{M}_w/\text{M}_n \sim 1.50$). Recently, 1,3,4,5-tetrakis(diphenylamino)-2,6-dicyanobenzene was demonstrated to catalyze O-ATRP at concentrations as low as 0.5 ppm.³⁴ Although an impressively low catalyst loading, this system exhibited poor control over MW ($F^* = 63\%$) only moderate control over polymer dispersity ($\text{M}_w/\text{M}_n \sim 1.37$) and was not shown to possess chain-end fidelity. As such, it remains a challenge for O-ATRP to match the performance of Cu-catalyzed ATRP at low ppm catalyst loading. Herein, we report highly efficient core-substituted diaryl dihydrophenazine PCs capable of operating a highly controlled polymerization, producing well-defined polymers ($\text{M}_w/\text{M}_n \sim 1.1$, $F^* \sim 100\%$) using only 5–50 ppm PC loadings in an O-ATRP process.

RESULTS AND DISCUSSION

Catalyst Synthesis.

Although 5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine (PC **1** (Figure 1)) was previously demonstrated as a successful organic PC for O-ATRP,^{20,32} the initiator efficiency typically only reached ~70%. We hypothesized that radical addition (from the activated initiator or propagating polymer chain) to the dihydrophenazine core of PC **1** may contribute to premature radical termination (thus resulting in nonquantitative initiator efficiency) and that functionalization at the dihydrophenazine core could eliminate such nonproductive radical addition and enable improved initiator efficiency. Additionally, core functionalization presents new avenues for photophysical and electrochemical tuning of dihydrophenazine PCs. Guided by these hypotheses, **1** was brominated using excess bromine to generate a tetrabrominated radical cation bromide salt **2**^{•+}Br[−] (Figure 2),³⁵ which was subsequently reduced using copper wire to afford compound **2**.

From tetrabrominated compound **2**, palladium-catalyzed Suzuki couplings³⁶ yielded a series of core-substituted dihydrophenazine derivatives possessing electron-withdrawing trifluoromethyl groups (**3a**), conjugation-extending biphenyl and 2-naphthyl groups (**3b** and **3c**, respectively), and electron-donating methoxyphenyl and *N,N*-dimethylaminophenyl (**3d** and **3e**, respectively) core substituents (Figure 2). This library of PCs allowed investigation into the various effects that these substitutions imparted on the photophysical and catalytic properties of the PCs (Table 1). For detailed synthetic procedures, see the Supporting Information. In the solid state all these catalysts proved to be stable in air and can be stored on the benchtop with no signs of degradation over the course of several weeks.

Photophysical and Electrochemical Properties of the Catalysts.

Core-modified PCs **2** and **3a–3e** all exhibited a red shift in λ_{max} of absorption and significantly higher ϵ_{max} compared to the parent catalyst **1** in *N,N*-dimethylacetamide (DMAc) (Table 1). In addition, PCs **3a–3e** possess a less redshifted maximum emission wavelength ($\lambda_{\text{em,max}}$) and thus smaller Stokes shifts than the parent catalyst **1** in DMAc. PC **2** was nonemissive presumably due to efficient intersystem crossing to a dark triplet state afforded by the heavy atom effect of Br.³⁷ The lowest singlet excited state energy ($E_{\text{S1,exp}}$) values were then obtained from their corresponding $\lambda_{\text{em,max}}$. Interestingly, fluorescence spectroscopy revealed that catalysts **1** and **3a–3e** form complexes at catalytically relevant concentrations that emit when excited at wavelengths much longer than their λ_{max} of absorption (see the Supporting Information).

Using cyclic voltammetry (CV), the oxidation potential ($E_{1/2}$, V vs SCE) values involving the $^2\text{PC}^{•+}/^1\text{PC}$ redox couple of **1–3e** were determined in DMAc (Table 1). Overall, we observed that functionalization at the dihydrophenazine core has a drastic effect on $E_{1/2}$. At 0.60 V, the radical cation ($^2\text{PC}^{•+}$) of the tetrabrominated PC **2** is significantly more oxidizing than the parent compound **1** (0.28 V). Generally, we also observed that aryl core substituents containing electronwithdrawing groups destabilize $^2\text{PC}^{•+}$ (0.45 V for **3a**) while electron-donating groups stabilize $^2\text{PC}^{•+}$ (0.15 V for **3e**). Oxidation potentials (E_{ox}^0) of the $^2\text{PC}^{•+}/$

¹PC redox couple were also predicted using density functional theory (DFT), and the computational results corroborated these values to within ~0.2 V of the experimental values.

The experimental singlet excited state reduction potential values were determined from $E^{0*}_{S1,exp} = E_{1/2} - E_{S1,exp}$ (Table 1). Ranging from -1.68 to -1.88 V vs SCE, the $E^{0*}_{S1,exp}$ values of **3a–3e** do not vary significantly from the -1.74 V value of the parent species **1**, and all of these values are significantly more negative than ~-0.7 V needed to reduce the alkyl bromide bond on the initiator or dormant polymer chain end to initiate an O-ATRP process.^{38,39} The redox potentials of excited state singlets and triplet charge transfer (CT) states are relatively isoenergetic (<0.2 eV).^{40,41} Using this assumption, the experimentally measured redox potentials from $E^{0*}_{S1,exp}$ are representative of the triplet excited state redox potentials.

Aryl substitution on the dihydrophenazine core also impacts photophysical processes, manifesting into effects on the catalytic performance of these compounds. Recently, our group showed that photoinduced intramolecular CT in the excited state is a characteristic of successful O-ATRP PCs. CT can facilitate intersystem crossing to long-lived triplet species.²⁶ In particular, it is observed that dihydrophenazine PCs access a photoinduced CT excited state when they contain an *N*-aryl substituent possessing an electron-withdrawing substituent or extended π -system.^{42,43} The CT excited state of PC **1** is evidenced from extensive solvatochromism (Figure 3A), where the emission is shifted from blue (in nonpolar 1-hexene solvent) to red (in polar DMF).⁴⁴

Computationally, the CT excited state of **1** is characterized by a charge-separated singly occupied molecular orbital (SOMO) of the ³PC* and the electrostatic potential (ESP)-mapped electron density diagram showing the localization of charge in the *N*-aryl substituent of ³PC* (Figure 3B). For the core-substituted **3c**, we similarly observed solvatochromism (Figure 3A) but with an overall lesser degree in red-shift in emission from green (1-hexene) to yellow (DMF). Computations revealed a qualitatively distinct CT process for **3c**, where the high-lying SOMO resides on the core-substituent of **3c** as opposed to the *N*-aryl substituent in **1**; the ESP diagram similarly indicated that charge is localized on the coresubstituent of the ³PC* of **3c** (Figure 3C). Similar trends were observed for PCs **3a** and **3b**. Interestingly, PCs **3d** and **3e** possessing electron-rich core substitutions exhibited a much larger red shift in emission, similar to PC **1** (see the Supporting Information), although computationally, the high-lying SOMO of the electron-rich derivatives (**3d** and **3e**) also resides on the dihydrophenazine core rather than the core substituent, which is also supported by the ESP diagram. It is worth noting that none of the core-extended PCs are predicted to exhibit CT to the *N*-aryl substituent in the ³PC* state. This distinct mode of CT leads to PCs **3a–3e** having much smaller changes in dipole moments (μ) between the ground state and triplet excited state when compared to PC **1** (Figure 3B,C).

Polymerization of Methyl Methacrylate.

To investigate the performance of these compounds as O-ATRP catalysts, PCs **1–3e** were employed in the polymerization of methyl methacrylate (MMA) (Table 2). The standard conditions used in this study were [100]:[1] ratio of [monomer]:[initiator] with 1000 ppm PC loading (relative to monomer). At this catalyst loading, PCs **3a–3e** all outperformed PC **1**

(lower $\bar{M}_n$, higher P^*), while PCs **3d** and **3e** exhibited less control over the polymerization than the other PCs. Surprisingly, the brominated compound **2** did not catalyze polymerization at all. Because of their higher ϵ_{max} , we hypothesized that PCs **3a–3c** may control O-ATRP at lower catalyst loadings. Indeed, PCs **3a–3c** outperformed PC **1** in every metric: the polymers produced possessed a lower $\bar{M}_n$ while achieving near-quantitative P^* , a significant increase in performance when compared to PC **1**. This excellent control was maintained with as low as 50 ppm catalyst loading (see Table S1), a 95% reduction in PC loading compared to previous examples of O-ATRP using dihydrophenazine PCs. Excitingly, PC **3c** even demonstrated excellent control over MW at 5 ppm catalyst loading ($P^* = 103\%$), although a polymer with higher $\bar{M}_n$ was produced ($\bar{M}_n = 1.42$). All polymerizations of MMA by PCs **3a–3c** exhibited linear first-order kinetic behavior and linear relationships between MW and monomer conversion to produce polymers possessing a low $\bar{M}_n$ and achieving high P^* (near quantitative) during polymerization (see the Supporting Information). Furthermore, varying the loading of the initiator allowed for predictable tuning of the MW of the polymers that were produced (Table 3).

To further investigate the control of these PCs in the polymerization of MMA, chain extension polymerizations and pulsed irradiation on–off experiments were performed with PCs **3a–3c** at 50 ppm catalyst loadings (Figure 4). The chain extension experiments utilized macroinitiators that had been polymerized to high conversion (~80%) by PCs **3a–3c**. The macroinitiators were then isolated, purified, and used to initiate further polymerization of MMA. For each catalyst, the chain-extended polymers still possessed low $\bar{M}_n$ and unimodal gel permeation chromatography (GPC) traces (Figure 4A; see the Supporting Information for details and results for PCs **3a** and **3b**). Control over the polymerization by irradiation was demonstrated using a pulsed-irradiation on–off experiment (Figure 4B). Notably, the pulsed irradiation on–off experiment showed that these PCs could remain dormant for a full 12 h before resuming polymerization in a controlled manner.⁴⁵ The chain-extension and pulsed-irradiation on–off experiments, as well as analysis of the polymer by MALDI-TOF (see the Supporting Information), all confirm high chain-end fidelity. Combined, these metrics for PCs **3a–3c**, at a low catalyst loading of 50 ppm, demonstrate the characteristics of a controlled radical polymerization.

Polymerization of Other Monomers.

O-ATRP has been successfully demonstrated on a variety of methacrylate-based monomers,²² but expanding the monomer scope to other vinyl monomers has proven challenging.⁴⁶ PCs **3a–3c** were applied to the polymerizations of other methacrylate-based monomers as well as butyl acrylate, acrylonitrile, 1-hexene, styrene, and vinyl acetate (Table 4; for full details and results see Table S4). No polymer was produced in the cases of 1-hexene and vinyl acetate. This new family of PCs was able to catalyze the polymerization of styrene, acrylonitrile, and butyl acrylate with moderate to good MW control, but poor control over the $\bar{M}_n$ of the resulting polymers was achieved. Interestingly, PC **3a** outperformed PC **3c** in the polymerization of styrene, whereas PC **3c** outperformed PC **3a** for the polymerization of all of the other monomers that were tested.

The methacrylate monomers, diethylene glycol methyl ether methacrylate (DEGMA) and benzyl methacrylate (BnMA), were polymerized with good molecular weight control ($P^* = 118\%$ and 97.4% , respectively) and moderate to good control over dispersity ($\text{M}_w/\text{M}_n = 1.35$ and 1.25 , respectively). These results show that the thermodynamic and kinetic properties of PCs **3a–3c** are well-suited for the polymerization of methacrylate monomers.

Synthesis of Advanced Polymer Architecture.

With the knowledge that the PC **3c** could catalyze the polymerization of a variety of methacrylates with excellent chain-end fidelity at low catalyst loading, we set out to synthesize a triblock copolymer with blocks of MMA, BnMA, and DEGMA (Figure 5, top). Each block was polymerized to high conversion using only 50 ppm of catalyst, then isolated, and purified before polymerizing the next block. The resulting triblock copolymer possessed a unimodal GPC trace and an $M_w = 80.0$ kDa, $\text{M}_w/\text{M}_n = 1.54$, and a final P^* of 119% .

Previously, our group has used *N*-aryl phenoxazines to synthesize star polymers using a core-first approach.³⁰ This work required high loading of catalyst and only relatively low MW (<25 kDa) star polymers were synthesized. Using the new core-extended dihydrophenazine PC **3c** at 50 ppm, we were able to synthesize star polymers possessing 3, 6, and 8 arms with high MW, P^* near unity, and good control over M_w/M_n (Table 5). These results further demonstrate the versatility and excellent control over the polymerization of methacrylates by catalyst **3c**.

Oxygen Tolerance and Scalability.

Recently, a subset of core-extended phenoxazine PCs have been shown to control the O-ATRP of MMA in the presence of oxygen in contrast to non-core-substituted dihydrophenazines.⁴⁷ Excitingly, the core-extended *N,N*-diaryl dihydrophenazines **3a** and **3c** were also able to control the polymerization of MMA when the reaction was performed exposed to air using only 50 ppm catalyst loading. In these polymerizations, inhibitor was removed from the monomer by flashing through a plug of basic alumina, but neither monomer nor solvent was degassed and the polymerization was run on the benchtop. The resulting polymers possessed a $M_w = 6.99$, $\text{M}_w/\text{M}_n = 1.17$, and $P^* = 109\%$ for PC **3a** and $M_w = 6.13$, $\text{M}_w/\text{M}_n = 1.15$, and $P^* = 111\%$ for PC **3c** (see Table S3 for full details). This observation is impressive as it shows no significant loss of performance when the polymerization is performed exposed to air.

Lastly, to demonstrate scalability, a polymerization was run at 5 g scale of monomer using 50 ppm of catalyst loading (see the Supporting Information). The resulting polymer possessed an $M_w = 10.7$, $\text{M}_w/\text{M}_n = 1.19$, and $P^* = 104\%$, meaning that using these catalysts with only very minor variations in reaction setup, we can scale up polymerizations to multigram scale.

CONCLUSION

In summary, a family of new core-substituted *N,N*-diaryl dihydrophenazines were synthesized, characterized, and employed in O-ATRP. The core-substituted *N,N*-diaryl dihydrophenazine PCs reported here represent the most efficient O-ATRP systems yet

reported, rivaling the performance of Cu-catalyzed ATRP at ppm level of catalyst loading. Importantly, these PCs mediated the polymerization of MMA in a well-controlled fashion, maintaining excellent control over the polymerization, even with only 50 ppm loading (a 95% reduction of loading over previous O-ATRP reports). PC **3c** was successfully employed as a catalyst in the synthesis of star polymers and triblock copolymers, which demonstrates the versatility and control that this catalyst has over the O-ATRP catalytic cycle. Broad applicability was demonstrated by the scale-up of polymerization from 1 g of MMA to 5 g of MMA and the successful control of O-ATRP under air.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Top: general synthetic scheme for the polymerization of methyl methacrylate (MMA) using PCs. Bottom: structures of *N,N*-diaryl dihydrophenazine PCs used for O-ATRP.

Figure 2.

(A) Synthetic scheme for the synthesis of PCs **2–3e**; isolated yield (in %) were indicated. (B) Molecular structures of **1**, **2⁺ Br[−]**, and **3a** derived by single crystal X-ray diffraction. ORTEP plots with anisotropic displacement parameters set at 50% probability. Atoms are represented as the following colors: carbon, gray; nitrogen, blue; hydrogen, white; fluorine, green; bromine, beige. Solvent molecules have been omitted for clarity.

Figure 3.

(A) Photographs of catalysts **1** and **3c** in solvents of varying polarity irradiated using a hand-held UV lamp at 365 nm demonstrating the solvatochromic shift in emission. Solvent dielectric constants (ϵ) from left to right: 1-hexene (2.07), benzene (2.27), dioxane (2.21), tetrahydrofuran (7.43), pyridine (13.0), *N,N*-dimethylformamide (37.2). Computed molecular orbitals and electrostatic potential (ESP)-mapped electron density diagram of the ground state singlet and the lowest triplet states of (B) PC **1** and (C) PC **3c**. HOMO, highest occupied molecular orbital; SOMO, singly occupied molecular orbital. Computed dipole moments (μ) in units of debye (D).

Figure 4.

(A) Synthetic scheme, results, and GPC traces of the chain extension of poly(methyl methacrylate) (pMMA) using PC **3c** at 50 ppm catalyst loading. (B) Plots of the polymerization data from the pulsed irradiation on–off experiment using PC **3c** at 50 ppm loading. Left: conversion versus time. Right: M_n versus conversion (blue markers) and versus conversion (orange markers). Filled markers are data from aliquots taken directly after irradiation, and hollow markers are data from aliquots taken directly after a dark period. Conversion was measured by ^1H NMR. M_n and $\bar{D}$ were measured by GPC.

Figure 5.

Top: structure and results of pMMA-*b*-pBnMA-*b*-pDEGMA triblock copolymerization catalyzed by PC **3c** at 50 ppm catalyst loading. Bottom: GPC traces of pMMA macroinitiator (blue), pMMA-*b*-pBnMA macroinitiator (orange), and pMMA-*b*-pBnMA-*b*-pDEGMA triblock copolymer (green).

Photophysical and Electrochemical Properties of PCs 1-3e

Table 1.

PC	λ_{max} (nm)	ϵ_{max} ($\text{M}^{-1} \text{cm}^{-1}$)	$\lambda_{\text{em,max}}$ (nm)	$E_{\text{S1,exp}}$ (eV)	$E_{1/2}(\text{PC}^{+/0}\text{PC})^b$ (V vs SCE)	$E_{\text{ox}}^0(\text{PC}^{+/0}\text{PC})^c$ (V vs SCE)	$E_{\text{S1,exp}}^0(\text{PC}^{+/0}\text{PC})^d$ (V vs SCE)	$E_{\text{T1,computed}}^0(\text{PC}^{+/0}\text{PC})^e$ (V vs SCE)
1	367	5200	611	2.02	0.28	0.21 ^e	-1.74	-2.17 ^e
2	385	10800	N/A ^f	N/A ^f	0.60	0.50	N/A ^f	-1.73
3a	385	14400	582	2.13	0.45	0.26	-1.68	-1.63
3b	389	22200	562	2.20	0.34	0.11 ^g	-1.86	-1.81 ^g
3c	388	20000	557	2.22	0.38	0.17	-1.84	-1.79
3d	388	11400	597	2.08	0.27	0.07	-1.81	-2.12
3e	392	14600	610	2.03	0.15	-0.10	-1.88	-2.15

^a Measured in *N,N*-dimethylacetamide (DMAc). λ_{max} , maximum absorption wavelength; ϵ_{max} , molar absorptivity at λ_{max} ; λ_{em} , max, maximum emission wavelength; $E_{\text{S1,exp}}$, lowest singlet excited state energy determined from $\lambda_{\text{em,max}}$.

^b Measurements were performed in a three-compartment electrochemical cell with an Ag/AgNO₃ reference electrode in MeCN (0.01 M) and 0.10 M NBu₄PF₆ electrolyte solution. DMAc was used in the working electrode compartment, while platinum was used as the working and counter electrodes. $E(\text{V vs SCE}) = E(\text{V vs Ag/AgNO}_3 [0.01 \text{ M}]) + 0.298 \text{ V}$.

^c DFT calculations performed at the uM06/6-311+G**//uM06/6-31G** level of theory with CPCM-described aqueous solvation.

^d Singlet excited state reduction potentials were calculated as $E_{\text{S1,exp}}^0 = E_{1/2} - E_{\text{S1,exp}}$.

^e Values used from ref 28, computed at the uM06/6-311+G**//uM06/6-31+G** level of theory.

^f Not available due to nonemissive singlet excited state.

^g Frequency calculations were computed in the gas phase (see the Supporting Information).

Table 2.

Results of the O-ATRP of MMA Using Different Catalyst Loadings

PC	catalyst loading (ppm)	time (h)	conv ^a (%)	M_w^b (kDa)	$(M_w/M_n)^b$	I^* (%)
1	1000	8	72.0	15.4	1.30	79.5
1	50	12	66.9	14.1	1.66	82.1
3a	50	12	88.1	10.9	1.14	94.5
3b	50	12	93.0	10.1	1.13	107
3c	100	12	85.6	10.4	1.09	93.2
3c	50	8	79.8	8.84	1.14	106
3c	10	8	79.0	11.3	1.27	92.3
3c	5	8	74.9	10.7	1.42	103
3d	1000	12	44.8	6.03	1.34	105
3e	1000	12	13.6	13.6	1.82	129

^a Measured by ¹H NMR.^b Measured by gel GPC coupled with multiangle light scattering (see the Supporting Information for full experimental details and results).

Table 3.

Results of the O-ATRP of MMA by PC 3c Using Different Initiator Loadings

catalyst loading (ppm)	[monomer]: [Initiator]	conv ^a (%)	M_w^b (kDa)	$(M_w/M_n)^b$	I^* (%)
50	1000:10	79.8	8.84	1.14	106
50	1000:4	61.4	18.9	1.28	106
50	1000:2	63.9	32.7	1.25	98.6
50	1000:1	63.5	62.8	1.36	138

^a Measured by ¹H NMR.^b Measured by GPC coupled with multiangle light scattering (see the Supporting Information for full experimental details and results).

Table 4.

Results of the O-ATRP of Different Vinyl Monomers

PC	catalyst loading (ppm)	monomer	time (h)	conv ^a (%)	M_w^b (kDa)	$(M_w/M_n)^b$	P^* (%)
3a	500	styrene	25	52.8	13.2	2.41	105
3c	50	acrylonitrile	8	79.5	10.4	2.01	86.6
3c	500	n-butyl acrylate	2	82.7	24.9	2.34	104
3c	100	DEGMA	8	87.1	19.1	1.35	118
3c	100	BnMA	8	86.4	19.8	1.25	97.4

^a Measured by ¹H NMR.^b Measured by GPC coupled with multiangle light scattering (see the Supporting Information for full experimental details and results).

Table 5.

Results of the O-ATRP of MMA Star Polymers Using PC 3c

catalyst loading (ppm)	no. of arms	conv ^a (%)	M_w^b (kDa)	$(M_w/M_n)^b$	I^* (%)
50	3	65.8	22.3	1.13	103
50	6	72.5	55.0	1.28	104
50	8	73.3	82.8	1.42	104

^a Measured by ¹H NMR.^b Measured by GPC coupled with multiangle light scattering (see the Supporting Information for full experimental details and results).