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Solvent Effects and Side Reactions in Organocatalyzed Atom Transfer Radical Polymerization for Enabling the Controlled Polymerization of Acrylates Catalyzed by Diaryl Dihydrophenazines

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Abstract

Investigation of the effects of a solvent on the photophysical and redox properties of the photoredox catalyst (PC), *N,N*-di(2-naphthyl)-5,10-dihydrophenazine (PC **1**), revealed the opportunity to use tetrahydrofuran (THF) to modulate the reactivity of PC **1** toward achieving a controlled organocatalyzed atom transfer radical polymerization (O-ATRP) of acrylates. Compared with dimethylacetamide (DMAc), in tetrahydrofuran (THF), PC **1** exhibits a higher quantum yield of intersystem crossing ($\Phi_{ISC} = 0.02$ in DMAc, 0.30 in THF), a longer singlet excited-state lifetime ($\tau_{\text{Singlet}} = 3.81$ ns in DMAc, 21.5 ns in THF), and a longer triplet excited-state lifetime

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Supporting Information

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Materials for polymerization syntheses, instrumentation for compound characterization, organocatalyzed atom transfer radical polymerization (O-ATRP) procedures, previous attempts at the O-ATRP of *n*-BA catalyzed by phenazines, pseudo-first-order kinetic plots for the O-ATRP of *n*-BA in DMAc and THF, model reactions between PC **1** and DBMM, characterization of polymerization aliquots, and GPC traces from the o-atrpf of additional acrylates (PDF)

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($\tau_{\text{Triplet}} = 4.3 \mu\text{s}$ in DMAc, $15.2 \mu\text{s}$ in THF). Destabilization of 1^{*+} , the proposed polymerization deactivator, in THF leads to an increase in the oxidation potential of this species by 120 mV ($E_{1/2}^0 = 0.22 \text{ V}$ vs SCE in DMAc, 0.34 V vs SCE in THF). The O-ATRP of *n*-butyl acrylate (*n*-BA) catalyzed by PC **1** proceeds in a more controlled fashion in THF than in DMAc, producing P(*n*-BA) with low dispersity, ($\text{M}_w/\text{M}_n < 1.2$). Model reactions and spectroscopic experiments revealed that two initiator-derived alkyl radicals add to the core of PC **1** to form an alkyl-substituted photocatalyst (**2**) during the polymerization. PC **2** accesses a polar CT excited state that is $\sim 40 \text{ meV}$ higher in energy than PC **1** and forms a slightly more oxidizing radical cation ($E_{1/2}^0 = 0.22 \text{ V}$ for 1^{*+} and 0.25 V for 2^{*+} in DMAc). A new O-ATRP procedure was developed wherein PC **1** is converted to **2** *in situ*. The application of this method enabled the O-ATRP of a number of acrylates to proceed with moderate to good control ($\text{M}_w/\text{M}_n = 1.15\text{--}1.45$ and $P^* = 83\text{--}127\%$).

Graphical Abstract

INTRODUCTION

Reversible-deactivation radical polymerizations (RDRPs) have enabled the synthesis of polymers with tailored molecular weights, functionality, and architectures from a broad scope of vinyl monomers.¹ The use of external stimuli such as heat, light, and electricity to initiate and mediate RDRPs provides additional handles for controlling these processes and the properties of materials produced using these techniques.² Light is one attractive stimulus for achieving such control since it can easily be spatially and temporally manipulated and offers the opportunity to employ wavelength-selective chemistries.³ Interest in using light to control polymerizations has led to the development of a number of photoredox-catalyzed RDRPs^{3d,e} including organocatalyzed atom transfer radical polymerization (O-ATRP).⁴ In O-ATRP, light is used to excite an organic photoredox catalyst (PC), providing it with sufficient energy to reduce the alkyl halide bond of an initiator or polymer chain end to enable initiation and polymerization propagation. Since the initial reports of O-ATRP in 2014, a number of advances have been made, including the development and study of new families of O-ATRP PCs,⁵ improved understanding of the reaction mechanism,⁶ elucidation of the tolerance of these polymerizations to lighting conditions,⁷ reagent purification,⁸ and reactor design⁹ and the synthesis of polymers with varied composition and architecture.¹⁰ Researchers have capitalized on the unique features of O-ATRP to synthesize materials for advanced applications.^{10c,11} Despite the development of a number of PCs for O-ATRP, the monomer scope of this polymerization method remains limited, with the majority of studies focusing on the polymerization of methacrylates. While a few reports demonstrated the

controlled polymerization of other monomers,^{5c,12} continued work in this area is necessary to expand the utility of this polymerization method.

The mechanism of O-ATRP (Figure 1A, left) proceeds through the photoexcitation of a ground-state PC to access a singlet excited state ($^1\text{PC}^*$) that may react or undergo intersystem crossing (ISC) to form a triplet excited state ($^3\text{PC}^*$). The efficiency of ISC, excited-state lifetime (τ), and excited-state reduction potential (E^{0*}) of the $^1\text{PC}^*$ and $^3\text{PC}^*$ will dictate which state is operative. In either case, the PC^* must be sufficiently reducing to reduce the alkyl halide bond ($E^0 \sim -0.6$ to -0.8 V vs SCE) of the initiator (R-X) or polymer chain end ($\text{P}_n\text{-X}$) to yield an initiator-derived radical ($\text{R}^\bullet$) or active polymer chain ($\text{P}_n^\bullet$) as well as the halide anion (X^-) and oxidized PC ($^2\text{PC}^{*+}$). This reaction, termed the activation step, is required for initiation (addition of $\text{R}^\bullet$ to monomer) and propagation (addition of $\text{P}_n^\bullet$ to monomer) to occur. Pairing of the radical cation and halide anion forms $^2\text{PC}^{*+}\text{X}^-$, which must be sufficiently oxidizing to react with the propagating radical of polymer chain ends ($E^0 > -0.8$ V) to reinstall the alkyl halide group (deactivation step). To synthesize polymers of target molecular weights and narrow molecular weight distributions, initiation must be efficient and propagation must be controlled by rapid deactivation such that the concentration of radicals in solution remains low, suppressing bimolecular termination. Since the relative rates of activation and deactivation depend on the thermodynamics of electron transfer involving the PC, emphasis has been placed on developing families of O-ATRP PCs with tailored redox properties such that the rates of these reactions can be tuned to polymerize monomers that exhibit different rates of propagation in a controlled fashion.^{5a-j,13a,13}

Our group has investigated a number of organic molecules as PCs for O-ATRP, including dihydrophenazines,^{5a,h} phenoxazines,^{5b,g} and dimethylacridines⁵ⁱ (Figure 1A, right). Comparing between these PC families, the nature of the heterocyclic core largely dictates the range of redox properties accessed (E^{0*} and oxidation potential [$E_{1/2}^0$]).¹⁴ Within each family, installation of conjugated, electron-withdrawing, or electron-donating *N*-aryl and core substituents can be used to further tailor the redox properties of each PC. These advances in PC design have been critical for broadening the scope of monomers that can be polymerized using O-ATRP. For example, dimethyl-dihydroacridines were recently shown to catalyze the O-ATRP of acrylates,⁵ⁱ which have been challenging to polymerize in a controlled fashion using other PCs. The observed difficulty polymerizing acrylates has been attributed to the more reactive propagating radical and the more difficult-to-reduce dormant polymer chain end.^{4a,5a,b,h} The ability of dimethyl-dihydroacridines to efficiently mediate the O-ATRP of acrylates has been proposed to arise from the redox properties of this family of PCs, which exhibit more oxidizing $^2\text{PC}^{*+}$ s compared with dihydrophenazines and phenoxazines. While this report represents an advance in using PC design to broaden the monomer scope of O-ATRP, we wondered whether the properties of established PCs could be modulated using modified reaction conditions to achieve the same aim. Previous work has shown that the catalytic performance of dihydrophenazines is impacted by the polarity of the reaction media,^{5e,l,15} indicating that the solvent choice may be a useful tool for the intentional modification of PC properties. We envisioned that solvent polarity could be used to tailor the properties of dihydrophenazines allowing a single PC to be used for the

polymerization of multiple monomer families, circumventing challenges associated with the development of new classes of PCs and the synthesis of unique PCs for each monomer.

Dihydrophenazines efficiently mediate the O-ATRP of methacrylates and vinyl cyclopropanes through accessing strongly reducing excited states ($E^{0*} \sim -2.0$ V *vs* SCE) and forming sufficiently oxidizing $^2\text{PC}^{*+}$ s ($E_{1/2}^0 \sim 0.2$ V *vs* SCE).^{5a,13} The *N*-aryl substituents of dihydrophenazines influence the nature of the excited states, enabling access to intramolecular CT excited states involving the *N*-aryl substituent.¹⁴ Similar to CT states in other molecules where the donor and acceptor are nearly orthogonal, the $^1\text{PC}^*$ ($S_{1,\text{CT}}$) and $^3\text{PC}^*$ ($T_{1,\text{CT}}$) states of PC **1** are anticipated to be nearly degenerate.¹⁶

CT PC **1** was previously shown to maintain control over the O-ATRP of methyl methacrylate (MMA) in ethyl acetate (EtOAc), tetrahydrofuran (THF), and benzene, whereas the use of non-CT phenazines led to no monomer conversion or uncontrolled polymerization in these less polar solvents.^{5e} A structurally similar variant of PC **1** bearing *N*-(1-naphthyl) substituents demonstrated improved catalytic performance for the O-ATRP of MMA in mixed dimethylacetamide (DMAc)/THF solvent systems.¹⁴ In these prior works, it was postulated that the influence of solvent polarity on the catalytic performance of dihydrophenazines arises from a balance of the effects of altering the energy of the PC^* and changing the favorability of ion pairing between $^2\text{PC}^{*+}$ and X^- .

Despite the desirable performance of PC **1** for the O-ATRP of MMA, a system for the controlled polymerization of acrylates has not been achieved using this PC or other dihydrophenazines. Compared with poly(methacrylates), the alkyl halide chain end of poly(acrylates) is more challenging to reduce.^{6a,17} In addition, reduction of the poly(acrylate) alkyl halide chain end yields a secondary radical that is less stabilized than the tertiary radical formed in the case of poly(methacrylates), leading to an increased rate of polymerization propagation for acrylates compared with methacrylates.¹⁸ As such, the deactivator ($^2\text{PC}^{*+}\text{X}^-$) must be more oxidizing to maintain a low concentration of radicals in a solution for the polymerization of acrylates. To address these challenges, we hypothesized that less polar solvents could be used to simultaneously make PC **1** * more reducing and **1** $^{*+}$ more oxidizing. While it has been previously shown that less polar solvents destabilize the polar $^1\text{PC}^*$ ($S_{1,\text{CT}}$) of PC **1**,¹⁴ we anticipated that the polar **1** $^{*+}$ would be impacted similarly.

In this work, the impacts of solvent polarity on the photophysical and redox properties of PC **1** are elucidated and used to inform the use of solvents of varying polarity for the O-ATRP of acrylates. Through investigation of these polymerizations, a side reaction involving the addition of initiator-derived alkyl radicals to the core of PC **1** was identified that limits initiator efficiency (F^*) in the polymerization. As such, this reactivity was exploited to synthesize a core-substituted alkyl phenazine that prevented this undesirable side reaction and allowed the achievement of high F^* . Overall, the insights gained from the exploration of the influence of a solvent and side reactions on this polymerization were leveraged to develop a new O-ATRP procedure for the controlled polymerization acrylates.

RESULTS AND DISCUSSION

Part 1: Properties and Catalytic Performance of PC 1 in THF and DMAc.

To better understand the effects of solvent polarity on the performance of PC 1, its photophysical properties were characterized in DMAc (dielectric constant, ϵ , is 37), THF ($\epsilon = 7.6$), and toluene ($\epsilon = 2.4$) (Figure 2 and Table S2). We note that DMAc and THF were chosen for these studies since DMAc is commonly used as a solvent for O-ATRP and mixed DMAc/THF solvent systems were previously shown to improve the catalytic performance of phenazines for the O-ATRP of MMA.¹⁴ Changing from DMAc to THF does not appreciably affect the photoexcitation of PC 1, as indicated by the highly similar absorption profiles (Figure S50; $\lambda_{\text{abs}} = 343$ nm in DMAc and 342 nm in THF) and molar extinction coefficients ($\epsilon_{\text{abs}} = 5950$ cm⁻¹ M⁻¹ in DMAc and 6250 cm⁻¹ M⁻¹ in THF). Following photoexcitation, rapid relaxation of the Frank Condon excited state ($^1\text{PC}^*[\text{S}_m]$) yields $^1\text{PC}^*(\text{S}_{1,\text{CT}})$. As summarized in Figure 2A, this state decays primarily through nonradiative pathways to the ground state ($\Phi_{\text{em}} \sim 0.004$; $\Phi_{\text{nr}} = 0.98$) and has inefficient formation of the T₁ state in DMAc ($\Phi_{\text{ISC}} = 0.02$).

In THF, the yields (and rates) of radiative decay and intersystem crossing for PC 1 are larger ($\Phi_{\text{em}} \sim 0.03$, $\Phi_{\text{ISC}} = 0.30$) and, conversely, the yield and rate of nonradiative decay is lower ($\Phi_{\text{nr}} = 0.67$) than in DMAc. Furthermore, this trend of decreased Φ_{nr} and increased Φ_{ISC} continues when moving from THF to toluene ($\Phi_{\text{em}} \sim 0.03$, $\Phi_{\text{ISC}} = 0.52$, $\Phi_{\text{nr}} = 0.45$). We posit that decreased nonradiative decay in less polar solvents arises from destabilization of the polar $^1\text{PC}^*(\text{S}_{1,\text{CT}})$. For PC 1, the energy of the singlet state [E_{S_1}] is 2.48 eV in DMAc and 2.60 eV in THF. This effect is also observed when the CT states of analogous catalysts are destabilized through installation of *N*-aryl substituents with higher-lying π^* orbitals.¹⁹ We find it intriguing that the Φ_{ISC} can be modified so drastically by changing the solvent polarity (increasing from 0.02 to 0.52 in DMAc and toluene, respectively) and suspected that this outcome may influence the performance of PC 1 in O-ATRP.

Compared with DMAc, PC 1 exhibits a longer singlet and triplet excited-state lifetime in THF and toluene ($\tau_{\text{Singlet}} = 3.81$, 21.5, and 10.1 ns in DMAc, THF, and toluene, respectively; $\tau_{\text{Triplet}} = 4.3$, 15.2, and 17.8 μs in the same solvents). We note that while toluene was an ideal solvent for photophysical comparisons, the susceptibility of hydrogen atom abstraction at the benzylic position renders it a less desirable medium for the synthesis of well-defined polymers *via* radical polymerizations.

The effect of DMAc and THF on the E^{0*} and $E_{1/2}^0$ of PC 1 was explored since these properties will partially dictate the thermodynamic feasibility of activation and deactivation, respectively. To investigate the impacts of a solvent on the E^{0*} of PC 1, the energy of the excited state was derived from vibronic progression analysis of the emission profile of PC 1 in DMAc (Table S7). The $E_{1/2}^0$ of PC 1 was measured using cyclic voltammetry. Moving from DMAc to THF destabilizes the polar CT excited state of PC 1 by 120 meV (Figure 2B), and a similar destabilizing effect is observed for $\mathbf{1}^{*+}$ ($E_{1/2}^0 = 0.22$ and 0.34 V in DMAc and THF, respectively). The destabilization of PC $\mathbf{1}^*$ and $\mathbf{1}^{*+}$ leads this PC to exhibit the same E^{0*} in both solvents ($E^{0*} = -2.26$ V *vs* SCE) but exhibit an increased $E_{1/2}^0$ in THF. These changes in the redox properties of PC 1 indicate that this PC will exhibit similar

reactivity in the activation step of O-ATRP in both solvents, but the more oxidizing $\mathbf{1}^{++}$ may enable faster deactivation in THF. Thus, the previous observation that PC **1** maintains control over the O-ATRP of MMA in less polar solvents may be due to an increased rate of deactivation.

With an improved understanding of the photophysical and redox properties of PC **1** in THF, we posited that this solvent could be used to favorably modulate the properties of PC **1** for the O-ATRP of acrylates. The O-ATRP of butyl acrylate (*n*-BA) was previously attempted using several *N,N*-diaryl dihydrophenazines (including PC **1**) in DMac, but all PCs exhibited poor control over the polymerization as evidenced by the synthesis of P(*n*-BA) with unpredictable molecular weights and high dispersity, (~ 1.4 to 1.6) (Table S1). To determine whether a solvent can be used to improve catalytic performance, the O-ATRP of *n*-BA using diethyl 2-bromo-2-methylmalonate (DBMM) as the initiator was conducted in solvents of varying polarity (Table 1). In polar solvents like DMF and DMac (runs 1 and 2), the polymerization reaches moderate to high conversion in 2 h and produces P(*n*-BA) with high (~ 1.5). The high of the P(*n*-BA) produced under these conditions suggests that termination events are occurring due to inefficient mediation of the polymerization by PC **1**. In contrast, conducting the polymerization in less polar solvents (runs 3–5) results in slower conversion of monomer to polymer while enabling the synthesis of P(*n*-BA) with low to moderate (~ 1.1 – 1.2). In EtOAc and benzene, P(*n*-BA) with < 1.2 is produced, but the gel permeation chromatography (GPC) traces for these polymer samples exhibit high- and low-molecular-weight shoulders, indicating the presence of some termination events (Figures S8 and S10; see Figure S11 for comparison). Performing the polymerization in THF (run 4) leads to the synthesis of P(*n*-BA) with the highest F^* ($F^* = 78\%$, where $F^* = M_{n,theo}/M_n \times 100$; $M_{n,theo}$ is the theoretical number-average polymer molecular weight and M_n is the experimentally measured number-average polymer molecular weight measured using gel permeation chromatography [GPC] coupled with a light-scattering detector) and the lowest ($= 1.12$) of the conditions explored.

To determine whether control over the polymerization could be achieved using other PCs that exhibit excellent performance for the polymerization of MMA, the O-ATRP of *n*-BA was performed using core modified phenoxazines and phenazines (Table S3). For both PC systems, the polymerization proceeds with less control compared with the reaction using PC **1** as evidenced by the production of P(*n*-BA) with high (~ 1.6 – 2.6), regardless of the solvent used.

To better understand the impact of solvent polarity on the performance of PC **1** for the polymerization of *n*-BA, the evolution of polymer molecular weight and dispersity was tracked over time. In DMac, the O-ATRP of *n*-BA using PC **1** exhibits 84% conversion after 2 h with a mostly linear correlation between polymer M_n and monomer conversion, but with measured M_n values that deviate from theoretical values (Figure 3A). The dispersity of the P(*n*-BA) synthesized remains high throughout the polymerization (~ 1.5), indicating the occurrence of termination reactions. The polymerization in THF (Figure 3B) proceeds more slowly (82% conversion in 7 h) and exhibits a linear correlation between polymer M_n and monomer conversion to produce P(*n*-BA) with measured M_n values that exhibit poor to moderate agreement with theoretical values ($F^* = 79\%$ at 82% conversion). Excitingly, the

dispersity of the P(*n*-BA) synthesized remains low throughout the polymerization (~ 1.1), indicating that termination events are suppressed due to more efficient mediation of the polymerization by PC **1**. Both reactions exhibit linear pseudo-first-order kinetic plots, albeit neither plot has a line of best fit with a y-intercept of zero (Figure S16).

To gain insight into whether the apparent improvement in polymerization control in THF is due to the hypothesized influence of a solvent on the catalytic performance of PC **1** or an alternative effect of a solvent on the reaction (i.e., suppression of background polymerization), a series of controls were performed omitting PC, initiator, light, or all three components (Table S5). These control experiments reveal that the background polymerization (free radical polymerization of *n*-BA in the absence of PC or initiator) occurs on a shorter timescale in THF than in DMAc (monomer conversion after 2 h is 0% in DMAc versus 19% in THF). Based on these data, we conclude that the improved polymerization outcomes observed in THF do not arise from the suppression of this background reactivity. The control reactions omitting light, PC, or initiator demonstrate that all three components are necessary for the polymerization to proceed in a controlled fashion (i.e., to synthesize P[*n*-BA] with P^* close to 100% and $\bar{M}_w/\bar{M}_n < 1.5$).

Part 2: In Situ Formation of Alkyl-Substituted PC.

While the degree of control achieved for the O-ATRP of *n*-BA using PC **1** in THF is a major advance over previous attempts to mediate this polymerization using phenazines and phenoxazines, we aimed to further improve this polymerization system through the identification of potential side reactions involving PC **1**. In particular, we considered whether the relatively low P^* observed for this polymerization ($P^* < 80\%$) is an inherent limitation of PC **1**, a result of inefficient activation, or due to side reactions involving the initiator. With regard to the latter, we hypothesized that the alkyl radical derived from the reduction of the initiator may react with $\mathbf{1}^{*+}$ leading to nonquantitative P^* .

To investigate whether this side reaction can occur, a solution of PC **1** and 2 equiv of DBMM in THF was irradiated using a white-light LED beaker (the same light source for O-ATRP) and aliquots were removed to track the reaction using proton NMR (Figure 4A; see the Supporting Information for more details). NMR spectra of the crude aliquots exhibited broad signals for protons on the core of PC **1**, indicating the presence of radical cation (Figure S20). As such, triethylamine (TEA) was added as a reductant of $\mathbf{2PC}^{*+}$ to each NMR sample to enable peak assignment. Formation of a mono-alkyl-substituted derivative of PC **1** was observed after 5 min of irradiation (Figure 4A, green trace) while 20 min of irradiation (blue trace) led to complete conversion to the di-alkyl-substituted derivative termed **2** (Figure 4A). An analogous reaction using 10 equiv of DBMM relative to PC **1** (the same ratio of [PC **1**]/[DBMM] used for the O-ATRP of *n*-BA in Figure 3) and irradiating for 24 h also led to complete conversion of PC **1** to **2** with no indication of further conversion to tri- or tetra-alkyl-substituted derivatives (Figure S21). Using conditions similar to these model reactions, ~ 0.5 g of **2** was synthesized, purified using column chromatography (67% yield), and characterized using proton and carbon NMR (Figures S4 and S5). Comparison of the proton NMR spectrum of isolated **2** with those of the model reaction aliquots confirmed that **2** is formed under these conditions.

After determining that initiator-derived alkyl radicals add to the PC core on a relatively short timescale (<20 min while the polymerization reaches high conversion in ~9 h), the potential for this side reaction to occur during the polymerization was investigated. To investigate this possibility, we first determined whether the spectroscopic signatures of PC **1** and **2** could be used to track the nature of the PC in the O-ATRP of *n*-BA. Comparison of UV-visible absorption spectra (Figure S22) revealed that **2** is red-shifted relative to PC **1** (λ_{abs} shifts from 343 nm for PC **1** to 348 nm for **2**).

To track the nature of the PC species during the O-ATRP of *n*-BA, aliquots were removed from the polymerization and analyzed using UV-visible absorption spectroscopy (Figure 4B). All absorption features within 300–800 nm were assumed to arise from ^1PC or $^2\text{PC}^{\bullet+}$ since the other reaction components (*n*-BA, P[*n*-BA], or DBMM) do not absorb in this region. The absorption profile of the PC in the polymerization mixture prior to introducing the reaction to light matches that of PC **1** in THF ($\lambda_{\text{abs}} = 343$ nm), but during the first 30 min of irradiation, the λ_{abs} of the PC red-shifts from 343 to 349 nm. We reasoned that this spectral change may arise due to the conversion of PC **1** to **2** (and $2^{\bullet+}$) or conversion of PC **1** to $1^{\bullet+}$. Comparison of the absorption profiles of these polymerization aliquots with the absorption profile of isolated **2** in THF ($\lambda_{\text{abs}} = 348$ nm) indicates that PC **1** is converted to **2** and $2^{\bullet+}$ after ~15 min of irradiation (Figure S23), consistent with the timescale of model reactions between PC **1** and DBMM (Figure 4A). To refute the alternative hypothesis that the PC absorption profile red-shifts due to conversion of PC **1** to $1^{\bullet+}$, an oxidizing potential was used to generate $1^{\bullet+}$ and its absorption profile was acquired (see Figure S24 and the Supporting Information for more details). During the electrochemical conversion of PC **1** to $1^{\bullet+}$, the peak at 343 nm is observed to broaden and the profile of $1^{\bullet+}$ does not overlay well with that of the polymerization aliquot (Figure S26), suggesting that the observed spectral changes are not due to the formation of $1^{\bullet+}$. Moreover, as the polymerization proceeds, the formation of $^2\text{PC}^{\bullet+}$ gives rise to a peak at 487 nm which overlays more closely with the spectrum of electrochemically generated $2^{\bullet+}$ ($\lambda_{\text{abs}} = 483$ nm, Figure S25) than $1^{\bullet+}$ ($\lambda_{\text{abs}} = 466$ nm), providing further evidence that **2** and $2^{\bullet+}$ are formed *in situ* (Figure S26).

To gain further support that PC **1** is converted to **2** during the polymerization, an aliquot was removed from the O-ATRP of *n*-BA after 1 h of irradiation and analyzed using proton NMR and electron paramagnetic resonance (EPR) spectroscopy. Half of this aliquot was concentrated in the dark and dissolved in deuterated benzene (C_6D_6) to acquire the crude proton NMR spectrum (Figure 4C, turquoise trace), while the other half of the aliquot was reserved for characterization using EPR. After 1 h, monomer conversion to polymer is sufficiently low such that removal of the volatile monomer (*n*-BA) from the crude aliquot allows for NMR signals corresponding to protons on the PC to be resolved. Furthermore, the model reactions and spectroscopic experiments (Figure 4A,B) also indicate that removing the aliquot after 1 h provides sufficient time for the conversion of PC **1** to **2**. Comparison of the NMR spectrum of the crude aliquot (Figure 4C, turquoise trace) to the spectra of PC **1** (black trace) and **2** (purple trace) demonstrate that proton resonances in this region are more similar to that of **2** than of PC **1**. However, the presence of **2** in this sample cannot be accurately determined due to the broad nature of the peaks, likely arising from the presence of $^2\text{PC}^{\bullet+}$. The addition of TEA as a sacrificial electron donor to the sample revealed the

presence of peaks with the same chemical shifts and splitting patterns as those for the core protons of **2** (Figure 4C, gold trace) as well as the presence of signals at 3.65–3.82 ppm corresponding to protons on the malonate groups of **2** (see Figure S27 for full spectrum). Despite the addition of increasing amounts of TEA, the NMR signals of the PC core protons remained relatively broad, likely due to the presence of residual radical cation. We note that the presence of $^2\text{PC}^{\bullet+}$ may be due to incomplete reaction of $^2\text{PC}^{\bullet+}$ with TEA or due to reaction of the PC with the alkyl halide capped polymer to form $^2\text{PC}^{\bullet+}$.

To determine whether the broadening of these NMR signals is due to the presence of $^2\text{PC}^{\bullet+}$, the other half of the polymerization aliquot was analyzed using EPR spectroscopy (Figure 4C, right, turquoise trace). The observance of a signal in the EPR spectrum confirmed the presence of a radical species that we assign to be $^2\text{PC}^{\bullet+}$ based on the shift and splitting pattern of this signal compared with those of analogous phenazine radical cations.²⁰ The presence of radical cation in this sample supports the assignment of **2** and $2^{\bullet+}$ in the NMR spectrum of this polymerization aliquot.

To gain insight into whether the observed EPR signal arises from the presence of $1^{\bullet+}$ or $2^{\bullet+}$, $2^{\bullet+}$ was generated chemically *via* reaction between PC **1** and 2 equiv of DBMM (see the Supporting Information for more details) and the EPR spectrum of this sample was acquired (Figure 4C, right, purple trace). The close overlay of these two EPR spectra supports the formation of $2^{\bullet+}$ during the polymerization. Together, these data from model reactions and spectroscopic experiments support the hypothesis that PC **1** reacts with 2 equiv of DBMM-derived alkyl radicals to form **2** and $2^{\bullet+}$ during the O-ATRP of *n*-BA.

With knowledge that initiator-derived radicals add to the core of PC **1** to generate **2** during the polymerization, we sought to better understand the repercussions of this side reaction on polymerization outcomes. As was noted earlier, the moderate to low $F^{\bullet}$ s ($F^{\bullet} < 80\%$) observed for the O-ATRP of *n*-BA catalyzed by PC **1** (Figure 3B) may arise from the loss of 2 equiv of DBMM during the conversion of PC **1** to **2**. To investigate this phenomenon, the O-ATRP of *n*-BA catalyzed by PC **1** was carried out using 12 equiv of DBMM instead of 10 equiv (Figure S28). By calculating the $F^{\bullet}$ assuming that 2 equiv of DBMM are lost during the formation of **2** (i.e., that the target degree of polymerization [DP] is 100), near-quantitative $F^{\bullet}$ s are obtained at high conversions, supporting the hypothesis that **2** is formed during the polymerization.

With evidence that **2** may be formed during this polymerization, we were prompted to explore the properties and catalytic activity of this compound. Compared to PC **1**, **2** accesses an excited state that is 37 meV higher in energy (Figure S22) and forms a slightly more oxidizing $^2\text{PC}^{\bullet+}$ ($E_{1/2}^0 = 0.22$ V for **1** and 0.25 V for **2** in DMAc). The emission peak of **2** is, like PC **1**, broad and featureless in DMAc (Figure S52) and exhibits a hypsochromic shift in less polar solvents (Figure S53). These data suggest that the introduction of alkyl substituents on PC **1** to form **2** does not significantly perturb the nature of the excited state. The effects of solvent polarity seen for PC **1** are also observed for **2**, with less polar solvents destabilizing 2^* (2^* is 170 meV higher in energy in THF than DMAc²¹) and $2^{\bullet+}$ ($2^{\bullet+}$ is 130 mV more oxidizing in THF than DMAc). Thus, 2^* is 40 mV more reducing when the solvent is changed from DMAc to THF ($E^{0*} = -2.27$ V in DMAc and -2.31 V in THF).

These impacts on the properties of **2** lead to a similar solvent effect for the O-ATRP of *n*-BA when **2** is discretely added as the PC compared to when PC **1** is added (Table S4). In particular, polymerizations using less polar solvents such as EtOAc, THF, and benzene proceed in a more controlled fashion (i.e., P(*n*-BA) with lower $\bar{M}_w/\bar{M}_n$ is produced) than polymerizations conducted in DMF or DMAc.

The addition of **2** as the PC for the O-ATRP of *n*-BA leads to distinct polymerization outcomes (Figure 5A) compared with the polymerization starting with PC **1** (Figure 3B). The polymerization catalyzed by PC **2** exhibits $\bar{M}_n$'s closer to 100% throughout the reaction, albeit with $\bar{M}_n$ values exceeding 100% at high monomer conversion (Figure 5A). While the use of PC **2** improves the $\bar{M}_n$, the P(*n*-BA) synthesized exhibits much higher $\bar{M}_w/\bar{M}_n$ early in the polymerization ($\bar{M}_w/\bar{M}_n = 1.73$ at 30% conversion) compared with the reaction catalyzed by PC **1** ($\bar{M}_w/\bar{M}_n = 1.17$ at 27% conversion). In the polymerization using PC **2**, the $\bar{M}_w/\bar{M}_n$ of the P(*n*-BA) produced lowers as the polymerization proceeds, but the final material still exhibits a broader molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.35$ at 91% conversion) compared with the material synthesized using PC **1** ($\bar{M}_w/\bar{M}_n = 1.14$ at 82% conversion). The higher $\bar{M}_w/\bar{M}_n$ of the P(*n*-BA) synthesized in the polymerization starting with PC **2** (Figure 5A) compared with that starting with PC **1** (Figure 3B) suggests that the conversion of PC **1** to PC **2** has additional impacts on the polymerization. While more studies are required to elucidate the mechanism of the reaction that converts PC **1** to PC **2**, one feature that is evident from our NMR and EPR studies is that $2^{•+}$ is formed (*vide supra*). A buildup of $2^{•+}$ early in the polymerization, from the conversion of PC **1** to $2^{•+}$, is expected to increase the rate of deactivation leading to suppression of termination reactions and the synthesis of P(*n*-BA) with lower $\bar{M}_w/\bar{M}_n$, as is seen when the polymerization is performed starting from PC **1** ($\bar{M}_w/\bar{M}_n = 1.12$ – 1.18) instead of **2** ($\bar{M}_w/\bar{M}_n = 1.35$ – 1.73). We note that the concept of starting the polymerization with both activator (**2**) and deactivator ($2^{•+}$) present is analogous to a number of copper-catalyzed RDRP approaches that intentionally skew the ratio of these species to synthesize polymeric material with low $\bar{M}_w/\bar{M}_n$ using lower catalyst loadings.²²

Part 3: Development of an Improved System for the O-ATRP of Acrylates.

With an improved understanding of the polymerizations using PC **1** and PC **2**, we aimed to develop a superior O-ATRP procedure that addresses both the low $\bar{M}_n$ observed in the reaction starting with PC **1** and the high $\bar{M}_w/\bar{M}_n$ of the polymer synthesized when starting with PC **2**. To address the drawbacks of these polymerizations, we developed a procedure to generate PC **2** and $2^{•+}$ *in situ* by irradiating a solution of PC **1** and two exogenous equivalents of DBMM for 20 min prior to adding monomer and initiator (Figure 5B). Through this approach, PC **2** is generated in an operationally simple manner starting with commercially available PC **1**. Excitingly, the O-ATRP of *n*-BA using *in situ* generation of PC **2** and $2^{•+}$ proceeds in a controlled fashion (Figure 5C) and merges the beneficial attributes of polymerizations starting with PC **1** or PC **2** to enable the synthesis of P(*n*-BA) with $\bar{M}_w/\bar{M}_n$ of 1.15 and $\bar{M}_n$ of 101%. In support of the hypothesis that DBMM adds to PC **1** twice, the reaction of PC **1** with one or three exogenous equivalents of DBMM during the initial irradiation step leads to the synthesis of P(*n*-BA) with similar dispersity, but $\bar{M}_n$ values below 100% in the polymerization using one exogenous equivalent and $\bar{M}_n$ values above 100% in the polymerization using three exogenous equivalents (Figure S37).

Through modulating the initiator and monomer loadings (not including the DBMM used for generation of PC **2**), P(*n*-BA) with a range of molecular weights ($M_n = 6.2$ –14 kDa) and low to moderate ($\bar{M}_w/\bar{M}_n = 1.13$ –1.35) is synthesized (Table 2). We note that a limitation of this system appears to be the synthesis of P(*n*-BA) with target DPs of 125–200 for which P^* values are observed to deviate appreciably from 100% ($P^* = 150$ –183). Application of this procedure for the O-ATRP of a number of other acrylates including those with bulky groups (i.e., *tert*-butyl, isobornyl, dicyclopentanyl), more polar side chains (i.e., ethylene glycidyl monomethyl ether acrylate), and less polar side chains (2-ethylhexyl acrylate) allows for the synthesis of polyacrylates with target molecular weights ($P^* = 83$ –127) and low to moderate ($\bar{M}_w/\bar{M}_n = 1.15$ –1.40). P(*t*-BA) synthesized using this method (run 21) was used as a macroinitiator for the O-ATRP of *n*-BA to synthesize a P(*t*-BA)-*b*-P(*n*-BA) block copolymer with $\bar{M}_w/\bar{M}_n = 1.45$ and $P^* = 136\%$. Proton NMR and GPC analysis of this block copolymer confirm chain extension of the macroinitiator, consistent with reinstallation of alkyl halide chain end groups during O-ATRP.

CONCLUSIONS

Investigation of the photophysical properties of PC **1** in solvents of varying polarity revealed that changing the solvent from DMAc to THF leads to longer singlet and triplet excited-state lifetimes and an increased Φ_{ISC} ($\Phi_{ISC} = 0.02$ in DMAc, 0.30 in THF). Moreover, destabilization of PC **1**^{*} and **1**^{•+} in THF leads to retention of a strongly reducing excited state coupled with an increased $E_{1/2}^0$. Guided by these characterization data, the use of THF as a solvent for the O-ATRP of *n*-BA catalyzed by PC **1** enabled the polymerization to proceed in a controlled fashion with a linear correlation between polymer M_n and monomer conversion and the production of P(*n*-BA) with $\bar{M}_w/\bar{M}_n < 1.2$. Despite this progress, the polymerization exhibited low to moderate P^* s, which prompted us to investigate the occurrence of side reactions during the polymerization. Through a combination of spectroscopic experiments and model or polymerization reactions, we uncovered that two initiator-derived alkyl radicals add to PC **1** during the polymerization to yield alkyl-substituted PC **2**. Leveraging our understanding of this side reaction, an improved O-ATRP procedure was developed that enabled the polymerization of *n*-BA to proceed in a more controlled fashion ($\bar{M}_w/\bar{M}_n < 1.2$, $P^* \sim 100\%$). Moreover, this method was used to polymerize a number of other acrylate monomers to produce polyacrylates with $\bar{M}_w/\bar{M}_n = 1.15$ –1.40 and $P^* = 83$ –127%.

We believe that the conversion of PC **1** to PC **2** under these polymerization conditions has broader implications for the use of dihydrophenazines as PCs for O-ATRP and small-molecule reactions. Other current work is focused on exploring the mechanism and scope of radical addition to the core of dihydrophenazines including the relevance of the electronics and sterics of the radical. We anticipate that an improved understanding of this side reaction can inform the application of dihydrophenazines as PCs and advance the application of alkyl core-substituted PC families.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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A. Mechanism of O-ATRP and PC Structures

B. Polar CT Excited State of PC 1

Figure 1.

(A) Mechanism of organocatalyzed atom transfer radical polymerization (O-ATRP) using alkyl halide initiators (left) and structures of organic photocatalysts (PCs) used by our group (right). (B) Figure adapted from ref 14. Previous work demonstrated that *N,N*-dinaphthyl dihydrophenazines such as PC 1 (far left) access charge transfer (CT) excited states. Electrostatic potential (ESP) mapped electron density of PC 1 in the ground state ($^1PC[S_0]$) and triplet excited state ($^3PC^*[T_{1,CT}]$) enables visualization of the shift of electron density ("red" indicates electron-rich regions, while "blue" indicates electron-poor regions) from the phenazine core in the ground state to one *N*-naphthyl substituent in the CT excited state (middle). Numbers indicate the computed partial charge (δ , in units of e) using the ESP CHELPG formalism. The polar CT excited state of PC 1 is destabilized in less polar solvents leading to a blue shift in the wavelength of emission of PC 1*. This solvatochromic

phenomenon is displayed in the photograph (right), wherein a UV-light is being used to irradiate solutions of PC **1** in solvents of increasing polarity (from left to right: 1-hexene, benzene, dioxane, tetrahydrofuran (THF), pyridine, and *N,N*-dimethylformamide (DMF)).

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A. Photophysical Properties of 1

DMAc	THF
$\lambda_{\text{abs}} = 343 \text{ nm}$	$\lambda_{\text{abs}} = 342 \text{ nm}$
$\epsilon = 5,950 \text{ cm}^{-1}\text{M}^{-1}$	$\epsilon = 6,250 \text{ cm}^{-1}\text{M}^{-1}$
$\Phi_{\text{em}} = 0.004$	$\Phi_{\text{em}} = 0.03$
$\Phi_{\text{nr}} = 0.98$	$\Phi_{\text{nr}} = 0.67$
$\Phi_{\text{ISC}} = 0.02$	$\Phi_{\text{ISC}} = 0.30$
$\tau_{\text{S1}} = 3.81 \text{ ns}$	$\tau_{\text{S1}} = 21.5 \text{ ns}$
$\tau_{\text{T1}} = 4.3 \text{ }\mu\text{s}$	$\tau_{\text{T1}} = 15.2 \text{ }\mu\text{s}$

B. Redox Properties of 1

Figure 2.

Effects of a solvent on the photophysical and redox properties of PC **1**. (A) Jablonski diagram representing the energetic states of PC **1** (black lines) and the photophysical processes PC **1** engages in (arrows). For results using toluene, see the Supporting Information. (B) Plot of the excited-state reduction potential (E^{0*}) and oxidation potential ($E_{1/2}^0$) of PC **1** in DMAc and THF. E^{0*} was calculated using the equation $E^{0*} = E_{1/2}^0 - E_{\text{S1}}$, where $E_{1/2}^0$ was measured using cyclic voltammetry, and E_{S1} was determined by fitting a vibronic progression to the emission profile of PC **1** (see the Supporting Information for more details). E^{0*} and $E_{1/2}^0$ are expected to affect catalytic performance in the activation and deactivation steps of the polymerization, respectively.

A. O-ATRP of *n*-BA in DMAc

B. O-ATRP of *n*-BA in THF

Figure 3.

Plots of growth of the polymer M_n as a function of monomer conversion (left graphs, black squares) with $M_{n,theo}$ values represented by the gray dashed line for the O-ATRP of *n*-BA mediated by PC **1** in DMAc (A) and THF (B). Dispersity values for each P(*n*-BA) sample are shown (blue squares, secondary y -axis). Plots of the normalized differential refractive index (dRI) signal as a function of retention time for GPC traces of each aliquot from the polymerizations (C). See the Supporting Information for more details.

A. Tracking the Reaction between PC 1 and DBMM by ^1H NMR

B. Tracking the Formation of 2 in O-ATRP using Absorption Spectroscopy

C. ^1H NMR and EPR Spectra of O-ATRP Aliquots

Figure 4.

(A) Crude ^1H NMR spectra of aliquots removed from the reaction of PC 1 with 2 equiv of DBMM in THF (left). NMR samples were prepared by concentrating each aliquot, dissolving the crude material in C_6D_6 , and adding the sacrificial electron donor, triethylamine (TEA), to the solution. Circles represent peaks corresponding to the phenazine core protons as indicated on the structures of PC 1 and 2 (right). (B) Normalized UV-visible absorption spectra of aliquots from the O-ATRP of *n*-BA before irradiation (black dashed line, 0 min; absorption profile of PC 1), after irradiation (blue traces), synthesized and isolated 2 (purple trace), and electrochemically generated 2^{*+} (green trace; residual 2 is present). Magnification of the spectral region near the maximum wavelength of absorption (λ_{abs}) for PC 1 (right). (C) ^1H NMR spectra of aliquots from the O-ATRP of *n*-BA before

(turquoise trace) and after (orange trace) the addition of TEA (left). For comparison, the ^1H NMR spectra of isolated PC **1** (black trace) and **2** (purple trace) are shown. Electron paramagnetic resonance (EPR) spectra (right) of an aliquot from the O-ATRP of *n*-BA (turquoise trace) and $\mathbf{2}^{\bullet+}$ (purple trace). For the latter spectrum, $\mathbf{2}^{\bullet+}$ was generated *via* reaction of PC **1** with 2.0 equiv of DBMM. See the Supporting Information for more details.

A. O-ATRP of *n*-BA in THF Catalyzed by **2** B. Procedure for *in situ* Generation of **2** from Commercially-Available **1** C. O-ATRP of *n*-BA via *in situ* Generation of **2** **Figure 5.**

(A) Plot of growth of polymer M_n as a function of monomer conversion (left graph, black squares) with theoretical values (gray dashed line) for the O-ATRP of *n*-BA mediated by PC **2** (**2** was introduced to the reaction in a discrete fashion after synthesis and isolation). Dispersity values for each P(*n*-BA) sample are shown (purple squares, secondary *y*-axis). Plot of the normalized differential refractive index (dRI) signal as a function of retention time for the GPC traces of each aliquot from the polymerization (right graph). (B) Schematic for the procedure developed to generate PC **2** *in situ* starting from PC **1**. (C) Plots analogous to those shown in (A) for the O-ATRP of *n*-BA catalyzed by **2** using the procedure for *in situ* generation of **2** as described in (B).

Table 1.

Results of the O-ATRP of *n*-BA in the Solvents of Decreasing Polarity^a

O-ATRP of <i>n</i> -BA

run	solvent	time (h)	conv. (%) ^b	<i>M_n</i> (kDa) ^c	<i>M_w</i> (kDa) ^c	(<i>M_w</i> / <i>M_n</i>)	<i>I</i> [*] (%) ^d
1	DMF	2	63	18.8	28.8	1.53	44
2	DMAc	2	84	15.0	22.3	1.49	74
3	EtOAc	11.5	91	16.8	19.0	1.13	71
4	THF	7	85	14.2	15.9	1.12	78
5	benzene	9	60	14.5	17.1	1.18	55

^aStructure of PC 1 and reaction scheme for the O-ATRP of *n*-BA catalyzed by **1** (top). O-ATRP was performed targeting a degree of polymerization of 100 using a [1000]:[10]:[1] ratio of [*n*-BA]/[diethyl 2-bromo-2-methylmalonate (DBMM)]/[PC 1] using a 1:1 ratio of solvent/*n*-BA (v/v) and 1.00 mL of *n*-BA. A white-light light-emitting diode (LED) beaker was used as the light source (see the Supporting Information for more details).

^bConversion of monomer to polymer was determined using ¹H NMR.

^cValues were measured using gel permeation chromatography (GPC).

^dInitiator efficiency (*I*^{*}) was calculated using the equation $I^* = M_{n,theo}/M_n \times 100$, where *M_{n,theo}* is the theoretical number-average polymer molecular weight and *M_n* is the experimentally measured number-average polymer molecular weight measured using gel permeation chromatography [GPC] coupled with a light-scattering detector.

Results of the O-ATRP of Acrylates Catalyzed by *in situ* Generated PC 2.^a

[illegible]

run	M ^b	[M]/[DBMM] ^c /[I]	target DP ^d	time (h)	conv. (%) ^e	M _n (kDa) ^f	M _w (kDa) ^f	D (M _w /M _n)	I* (%) ^g
21	t-BA	[1000]; [2 + 12]:[1]	83	7	65	8.8	11.0	1.25	81
22	n-BA	[1000]; [2 + 10] ^h : [1]	100	13.5	93	15.3	22.2	1.45	136

^a Reaction scheme for the O-ATRP of acrylates catalyzed by PC 2 targeting a degree of polymerization of 100 (top). PC 2 is generated *in situ* from reaction of PC 1 with 2 equiv of DBMM (see Figure 4B and the Supporting Information for more details).

^b M = monomer.

^c [DBMM] is written as [2 + X], where the first 2.0 equiv are used to generate PC 2 *in situ* from PC 1 and X is the loading of initiator used to achieve the target degree of polymerization (DP).

^d Target DP = degree of polymerization targeted with the reaction stoichiometry.

^e Conversion of monomer to polymer was determined by ¹H NMR.

^f Values were measured using GPC.

^g Initiator efficiency (*f*^g) was calculated using the equation *f*^g = M_{n,theo}/M_n × 100.

^h P(t-BA) synthesized in run 21 is used as a macroinitiator.