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Conjugated Cross-linked Phenothiazines as Green or Red Light Heterogeneous Photocatalysts for Copper-Catalyzed Atom Transfer Radical Polymerization

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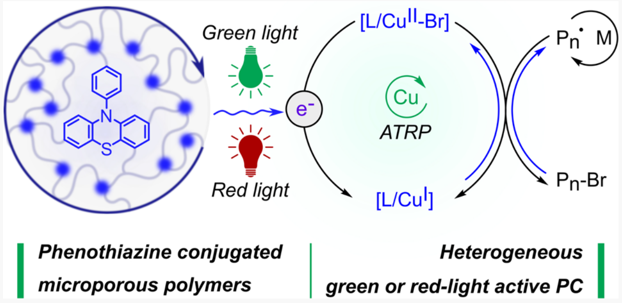
ABSTRACT: Using the power of light to drive controlled radical polymerizations has provided significant advances in synthesis of well-defined polymers. Photoinduced atom transfer radical polymerization (ATRP) systems often employ UV light to regenerate copper activator species to mediate the polymerization. Taking full advantage of long-wavelength visible light for ATRP would require developing appropriate photocatalytic systems that engage in photoinduced electron transfer processes with the ATRP components to generate activating species. Herein, we developed conjugated microporous polymers (CMP) as heterogeneous photocatalysts to exploit the power of visible light in promoting copper-catalyzed ATRP. The photocatalyst was designed by cross-linking phenothiazine (PTZ) as a photoactive core in the presence of dimethoxybenzene as a cross-linker via the Friedel−Crafts reaction. The resulting PTZ-CMP network showed photoactivity in the visible region due to the extended conjugation throughout the network because of the aromatic groups connecting the PTZ units. Therefore, photoinduced copper-catalyzed ATRP was performed with CMPs that regenerated activator species under green or red light irradiation to start the ATRP process. This resulted in efficient polymerization of acrylate and methacrylate monomers with high conversion and well-controlled molecular weight. The heterogeneous nature of the photocatalyst enabled easy separation and efficient reusability in subsequent polymerizations.



INTRODUCTION

Photochemistry is a powerful technique in the synthesis of well-defined polymers that offers spatiotemporal control over the growth of polymer chains and fabrication of advanced polymer materials. A multitude of photocatalytic or photosensitization approaches have been developed to convert the energy of light to promote new chemical reactivities that mediate the controlled synthesis of well-defined polymers.[1−6] One possibility for conducting photoinduced polymerizations is via direct activation of polymer chains by electron/energy transfer from the excited state photocatalysts, which can also mediate the deactivation and control the polymerization process. For example, organo-catalyzed atom transfer radical polymerization (ATRP)[7,8] or photoinduced electron/energy transfer radical or cationic reversible addition−fragmentation chain transfer (RAFT) polymerization systems[9,10] employ photocatalysts to mediate the activation/deactivation of polymer chains. Alternatively, dual catalytic systems use a catalyst to control the polymerization process in the ground state which can be activated by photoinduced electron/energy transfer reactions in the presence of a photocatalyst. We envisioned that use of visible-light-active photocatalysts for activating Cu complexes that offer excellent control in ATRP[11,12] would open new possibilities for modulating the catalytic reactivity and the polymerization process.

Although visible or near-infrared (NIR) light-active catalytic systems have been successfully applied in RAFT polymerizations,[13−18] the power of visible light in activating ATRP has not been fully explored. In photoinduced ATRP systems, UV light is used to generate L/Cu^I activator to start the polymerization.[19−24] Excitation of the Cu catalysts under UV light followed by a reductive quenching process in the presence of electron donors is suggested as a main pathway for generation of L/Cu^I activators. However, the use of UV light may not be desirable for special applications considering its high energy and low depth of penetration.

Using visible or NIR light in ATRP requires developing suitable photocatalysts or photosensitizers for generation of

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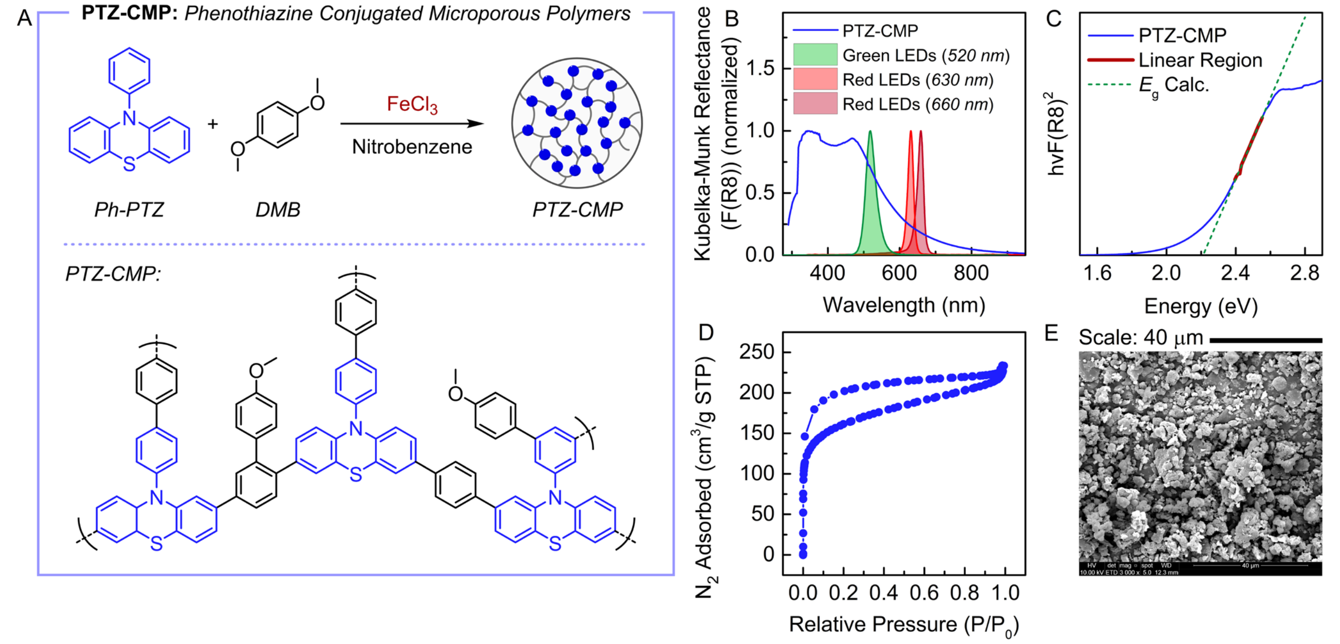


Figure 1. (A) Synthesis of phenothiazine-based conjugated microporous polymers (PTZ-CMP) by Friedel−Crafts alkylation between Ph-PTZ (1 equiv) and dimethoxybenzene (DMB, 8 equiv) as a cross-linker in the presence of $FeCl_3$ (24 equiv) in nitrobenzene. The reaction was heated at 80 °C for 4 h, and then the temperature was increased to 120 °C for 20 h. Bottom-left: an idealized, representative structure of the cross-linked network. (B) UV−vis diffuse reflectance spectra of the photocatalyst overlaid with the emission spectra of the light sources. (C) Tauc plot of transformed Kubelka−Munk reflectance as a function of the energy for PTZ-CMP. (D) Nitrogen sorption isotherms of BET surface area analysis of the PTZ-CMP polymers. (E) SEM image of the photocatalyst.

activating species. Under such dual catalytic systems, photoreduction of the $L/Cu^{II}-Br$ catalyst via electron transfer events from the excited state photocatalyst generates L/Cu^{I} activator species to start the ATRP process.[25−27] Furthermore, activation of the chain ends by the excited state photocatalyst can provide additional pathways for generation of initiating radicals where control over polymerization can be achieved by the Cu catalysts. Recently, sensitization of the Cu catalyst by up-conversion nanoparticles that absorb NIR light and emit UV light for the excitation of the Cu catalyst has been reported in ATRP.[28] Visible or NIR light active photocatalysts have diverse structures and photophysical properties, but the presence of photoactive species may lead to potentially undesired side reactions.

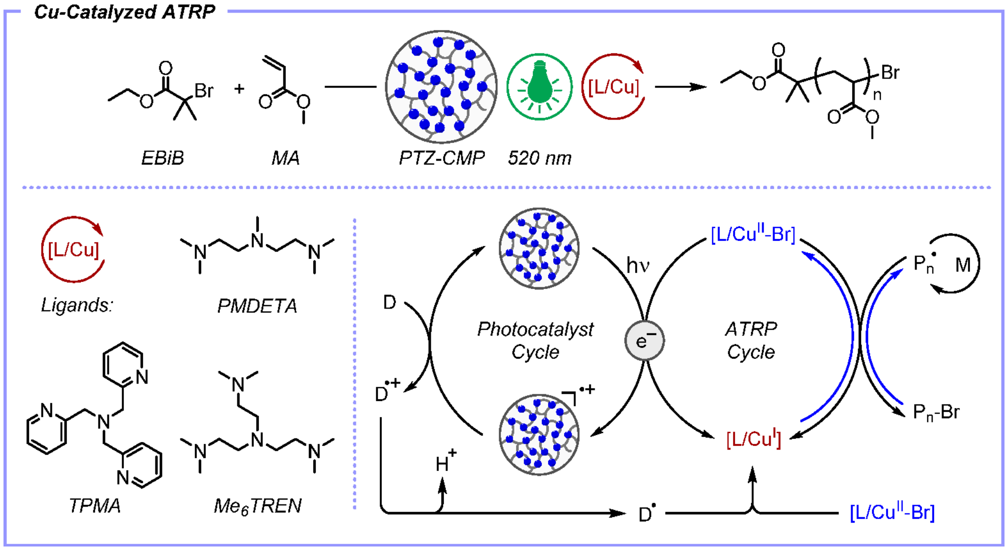
Moreover, removal of these soluble compounds can often be challenging. Therefore, developing heterogeneous systems would offer the possibility of easy purification of the final product as well as the photocatalyst recycling. Immobilization of photocatalysts onto a heterogeneous support or a gel network was employed to design heterogeneous photocatalytic systems for controlled radical polymerization techniques.[29−34] In contrast, using photocatalysts as building blocks for construction of frameworks or polymeric networks offers the additional opportunity for tuning the photophysical and structural properties of the heterogeneous photocatalysts.[35−39] For example, synthesis of the catalyst network by cross-linking of a photocatalytically active compound using linkages that extend conjugation throughout the network would alter the absorption profile of the network to longer wavelengths. Therefore, photocatalysis can be performed under longer wavelengths using conjugated microporous polymers (CMP) as photocatalysts.[40,41]

In this paper, we developed a dual catalytic system comprising a CMP of phenothiazine (PTZ-CMP) as a heterogeneous photocatalyst and a Cu catalyst for mediating ATRP under green or red light irradiation. Phenothiazines have been previously used as homogeneous photocatalysts for organo-catalyzed ATRP to mediate the activation and deactivation processes during polymerization.[42−46] However, many PTZ compounds show photocatalytic activity under UV light and can provide moderate control over polymerization of a limited range of monomers such as methacrylates. Herein, we show that PTZ can be modified to form heterogeneous photocatalysts for ATRP of several acrylate and methacrylate monomers mediated by Cu complexes. The CMPs showed photocatalytic activity under green light irradiation. Cross-linking the PTZ units through aromatic linkages imparted extended conjugation within the network and therefore visible light activity. The ATRP activator species was generated by photoinduced redox reactions enabled by the heterogeneous photocatalyst to yield well-controlled polymerizations mediated by the ppm amounts of ATRP catalysts. Importantly, the heterogeneous nature of the photocatalyst provided easy separation and excellent reusability in further polymerizations without any decrease of photocatalytic efficiency.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of the Photocatalyst. Conjugated microporous polymers were synthesized using a Friedel−Crafts alkylation reaction between 10-phenylphenothiazine (Ph-PTZ) as a photocatalyst unit and dimethoxybenzene (DMB) as a cross-linker in the presence of iron(III) chloride to form a hyper-cross-linked network (Figure 1A and Figure S2 in Supporting Information).[47−49] In addition to yielding a heterogeneous photocatalyst, cross-linking through aromatic units provided extended conjugation throughout the network, therefore shifting its absorption profile to longer wavelengths. Solid-state diffuse reflectance UV−vis spectra of

Scheme 1. Photoinduced Copper-Catalyzed ATRP in the Presence of PTZ-CMP as a Heterogeneous Photocatalyst Used To Generate the L/Cu^I Activator Catalyst under Green Light Irradiation in the Presence of Amine Electron Donors (D); Bottom Left: Structure of the Ligands *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA), Tris(2-pyridylmethyl)amine (TPMA), and Tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN); Bottom-Right: Proposed Mechanism for Generation of ATRP Activators via Photoredox Reactions in the Presence of CMP-PTZ



PTZ-CMP showed absorption in the visible region extending to >600 nm, which overlaps with the emission spectra of the green LEDs used for polymerization (520 nm) (Figure 1B) The band gap energy of the photocatalyst was calculated to be E_g = 2.23 eV corresponding to ~556 nm (Figure 1C). Nitrogen sorption isotherms shown in Figure 1D revealed that the resulting PTZ-CMP possessed a high Brunauer−Emmett−Teller (BET) surface area of 526 m^2/g with an estimated pore size of 32.8 Å (Figure S3). The nitrogen adsorption−desorption isotherm showed a hysteresis loop at low relative pressures suggesting adsorption into mesopores.[50] Scanning electron microscopy (SEM) analysis revealed photocatalyst particles with micrometer dimensions and fused, mixed morphology (Figure 1E and Figure S4).

Cu-Catalyzed ATRP Using PTZ-CMP as a Photocatalyst. The viability of the synthesized CMPs as a photocatalyst for ATRP was examined in activating Cu-catalyzed ATRP under green light irradiation (Scheme 1). Excitation of the PTZ-CMP photocatalyst results in separation of electron−hole charge carriers that can generate activating species upon reacting with the Cu catalyst and electron donors, respectively. The ATRP activator, L/Cu^I, can be generated by an electron transfer from the photocatalyst reducing L/Cu^{II}−Br to L/Cu^I. Furthermore, transfer of holes to amine electron donors (D) forms amine radical cation (D$^{•+}$) species while also regenerating the initial ground state PTZ-CMP photocatalyst. Deprotonation of the amine radical cation may further proceed to generate α-aminoalkyl radicals (D$^•$) that can reduce L/Cu^{II}−Br and generate the activator L/Cu^I catalyst.[51] Therefore, activating/initiating species can be formed through different pathways in the presence of the photocatalyst to start the ATRP process.

Generation of L/Cu^I activator was confirmed by electrochemical analysis of the catalytic system. A solution of CuBr$_2$ with PMDETA was irradiated under green light in the presence of the PTZ-CMP photocatalyst. Linear sweep voltammetry of the Cu catalyst showed increasing currents as a function of irradiation time. This increase in the current at positive potentials corresponds to generation of Cu^I during the photoreduction process (Figure 2A). Kinetics of the photoreduction of L/CuBr$_2$ showed a linear semilogarithmic behavior with a reduction rate constant (k_{red}) of 4.11 × 10^{-5} s^{-1} (Figure 2B).

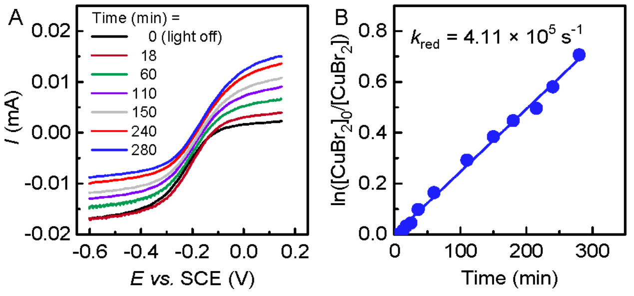


Figure 2. Photoreduction of the Cu catalyst monitored by linear sweep voltammetry (LSV) of CuBr$_2$ with PMDETA showing the generation of Cu^I species by photoreduction in the presence of PTZ-CMP (2 mg/mL) under green light irradiation (520 nm, 9 mW/cm^2) ([CuBr$_2$] = 1.1 mM, PMDETA/CuBr$_2$ = 5 in DMSO). The spectra were recorded on a rotating disk electrode (RDE) with a GC working electrode at ν = 0.01 V/s and ω = 2500 rpm.

Polymerization of methyl acrylate (MA) was initially conducted using CuBr$_2$/PMDETA as the ATRP catalyst in dimethyl sulfoxide (DMSO) solvent in the presence of PTZ-CMP as the photocatalyst under green light irradiation, with ethyl α-bromoisobutyrate (EBiB, 1 equiv) as the initiator (Scheme 1 and Table 1). An excess of amine electron donor (PMDETA) was needed to start the polymerization. No monomer conversion was observed without an excess of electron donor (i.e., CuBr$_2$/PMDETA = 1/1). However, increasing the concentration of the ligand from 1 to 3, 5, and 7 equiv (with respect to CuBr$_2$) resulted in increasing monomer conversion to near-quantitative values, yielding well-defined

Table 1. Results of ATRP of MA Using PTZ-CMP Photocatalyst in the Presence of Different Ligands under Green Light Irradiation[a]

entry	ligand	$CuBr_2$/L	PTZ-CMP (mg/mL)	solvent	conv (%)	$M_{n,th}$	M_n	$Đ$
1	PMDETA	1/1	2	DMSO	0	–	–	–
2	PMDETA	1/3	2	DMSO	50	8700	8300	1.09
3	PMDETA	1/5	2	DMSO	98	17 100	18 600	1.08
4	PMDETA	1/7	2	DMSO	99	17 300	18 500	1.09
5	PMDETA	1/5	1	DMSO	98	17 100	16 700	1.10
6	PMDETA	1/5	0.5	DMSO	98	17 100	17 800	1.09
7	PMDETA	1/5	2 − in dark	DMSO	0	–	–	–
8	PMDETA	1/5	0	DMSO	0	–	–	–
9[c]	TPMA	1/5[b]	2	DMSO	94	16 500	17 900	1.08
10[c]	TPMA	1/5[b]	0 − in dark	DMSO	0	–	–	–
11[c]	Me_6TREN	1/5	2	DMF	98	17 100	18 300	1.08
12[c]	Me_6TREN	1/5	0	DMF	0	–	–	–
13[c]	Me_6TREN	1/5	2	MeCN	94	16 400	18 000	1.07
14[c]	Me_6TREN	1/5	0	MeCN	0	–	–	–

[a] Reaction conditions: [MA]/[EBiB]/[$CuBr_2$]/[L] = 200/1/0.04/x (L = PMDETA, TPMA, or Me_6TREN; x = 1, 3, 5, or 7. [b] Triethanolamine (0.6 equiv relative to EBiB) was used as the electron donor in the presence of TPMA in different solvents (50 vol %) under green light irradiation (520 nm, 9 mW/cm^2) for 24 h. [c] Polymerizations run for 18 h.

polymers with low dispersity ($Đ$ < 1.1) and controlled molecular weights (entries 1−4, Table 1). The concentration of PTZ-CMP could be decreased from 2 to 1 and 0.5 mg/mL (corresponding to 0.4, 0.2, and 0.1 wt % with respect to the monomer, respectively) while still providing efficient and well-controlled polymerization of MA with near-quantitative monomer conversions and polymers with low dispersities in all cases (entries 5 and 6, Table 1) and narrow, monomodal molecular weight distributions (Figure S5). Importantly, no monomer conversion was obtained in the absence of PTZ-CMP or in the dark, signifying the importance of the photocatalyst for (re)generation of the activator species under green light irradiation (entries 7 and 8, Table 1).

To demonstrate the versatility of this system for a wider range of ATRP catalysts, polymerization of MA was successfully performed in the presence of TPMA and Me_6TREN ligands, in solvents including, *N*,*N*-dimethylformamide (DMF) or acetonitrile (MeCN). For example, in the presence of TPMA ligand, polymerization of MA reached 94% conversion within 18 h, yielding polymers with controlled molecular weights (M_n = 17,900, $Đ$ = 1.08; entry 9, Table 1). A control experiment in the absence of the PTZ-CMP photocatalyst or in the dark showed no monomer conversion proving the critical role of the photocatalyst in activating the ATRP process (entry 10, Table 1). Additionally, control experiments using Me_6TREN in the absence of PTZ-CMP showed no monomer conversion in DMF or MeCN under green light irradiation, indicating that no background reaction generated L/Cu^I activator to start the polymerization. However, polymerizations were successful in the presence of PTZ-CMP under green light irradiation reaching high monomer conversions and yielding polymers with low dispersity values ($Đ$ < 1.1) and controlled molecular weights (entries 11−14, Table 1). Size exclusion chromatography (SEC) analysis of the resultant polymers showed narrow, monomodal molecular weight distributions (Figure S6).

A control experiment performed using a CMP composed of only the dimethoxybenzene cross-linker (DMB-CMP) (without PTZ) proved the importance of the PTZ as a photocatalyst that allowed ATRP under green light. Although ATRP of MA using PTZ-CMP afforded full monomer conversions, DMB-CMP resulted in 48% conversion (M_n = 7100, $Đ$ = 1.06) after 18 h of irradiation under green light. The conjugated nature of the DMB-CMP network may be responsible for initiating polymerization under green light.

ATRP under Red Light. The efficiency of the PTZ-CMP system was also studied in promoting ATRP under red light irradiation. Polymerization of MA was first conducted using PTZ-CMP under red light irradiation with PMDETA ligand in DMSO (Table S1 and Figure S7). The polymerizations were triggered to high conversions (84%) and well-controlled molecular weight properties only under strong red lights (660 nm, ∼40 mW/cm^2). Using red LEDs with relatively low light intensity (630 nm, 4 mW/cm^2) did not provide monomer conversion after 24 h.

Similar results were obtained in the presence of Me_6TREN where no polymerization of MA was observed under the weak red LEDs (630 nm, 4 mW/cm^2). Using the red lamps with high intensity (660 nm, ∼ 40 mW/cm^2), polymerization of MA gave 40% conversion with well-controlled molecular weight and low dispersity. Importantly, with Me_6TREN ligand no monomer conversion was observed in the absence of the photocatalyst, indicating no generation of the L/Cu^I activator was realized under the red light.

Kinetics and Temporal Control of Polymerization. Kinetics of the ATRP of MA in the presence of PMDETA ligand showed a short induction period <2 h, after which the polymerization progressed with the apparent rate constant of k_p = 0.21 h^{-1}, similar to that observed in the presence of Me_6TREN ligand (k_p = 0.22 h^{-1}) (Figure 3A). Molecular weights of the polymers increased as a function of monomer conversion in line with theoretical values, confirming high initiator efficiency and well-controlled polymerizations with low dispersity values (Figure 3B and Figure S8).

Moreover, the polymerizations showed temporal control behavior in response to switching the light on/off. Polymerizations proceeded in the presence of light irradiation. Only negligible monomer conversion was observed after light was switched off due to the presence of small amounts of residual L/Cu^I activator, which could continue activation of the polymer chains (Figure 3C).[24,52] However, the L/Cu^I activator can be consumed via radical termination to convert to the

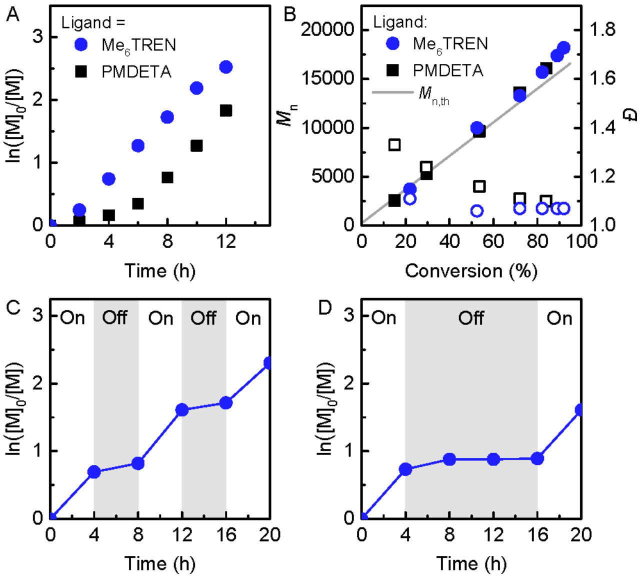


Figure 3. (A) Kinetics and (B) evolution of molecular weight (M_n, filled points) and dispersity ($Đ$, empty points) of the polymers as a function of monomer conversion in the ATRP of MA using PTZ-CMP photocatalyst with PMDETA or Me_6TREN ligands. (C and D) Temporal control in ATRP of MA upon intermittent switching green light on/off in the presence of Me_6TREN ligand. Reaction conditions: [MA]/[EBiB]/[$CuBr_2$]/[L] = 200/1/0.04/0.2, L = PMDETA or Me_6TREN in 50 vol % DMSO or MeCN, respectively, irradiated under green light LEDs (520 nm, 9 mW/cm^2).

deactivator L/Cu^{II}−Br. Consequently, polymerization stopped when the reaction was kept in the dark for 12 h consecutively (after initial 4 h of irradiation, Figure 3D). The resulting polymers showed well-controlled properties through temporal control of the polymerization (Figure S9).

Effect of the Cu Catalyst. Control experiments conducted in the absence of the Cu catalysts showed its importance in providing controlled polymerizations. No conversion of MA was observed in the presence of only monomer or monomer with the EBiB initiator (both run in the absence of $CuBr_2$ and PMDETA), indicating that under these conditions the excited state photocatalyst was unable to generate initiating radicals from the monomer/initiator (entries 1 and 2, Table S2). However, in the presence of PMDETA (without additional $CuBr_2$), fast and uncontrolled polymerization of MA was observed under free radical polymerization conditions because of the formation of initiating radicals from PMDETA (entry 3, Table S2). Conversely, polymerizations were successful and controlled only in the presence of both excess electron donor and the Cu catalyst to facilitate photocatalysis and control the growth of polymer chains (entries 4 and 5, Table S2). These results indicate the importance of all polymerization components, including the photocatalyst, electron donors, and the Cu catalyst in initiating and affording well-controlled ATRP under green light.

To further examine the effect of the Cu catalyst, ATRP of MA was performed by decreasing the concentration of $CuBr_2$ (Table 2). In the presence of 0.005 equiv (with respect to initiator or 25 ppm with respect to monomer) of initially added $CuBr_2$ with 0.2 equiv of PMDETA, fast polymerization of MA was observed that gave 94% monomer conversion in <4 h showing a high dispersity of 2.06 (entry 1, Table 2). Increasing concentration of $CuBr_2$ resulted in a decrease in the rate of polymerization but afforded well-controlled polymers with low dispersity values. For example, in the presence of 0.01 or 0.02 equiv (50 or 100 ppm, respectively) of $CuBr_2$, the resultant polymers showed a moderate dispersity of 1.34 and 1.13, respectively (entries 2 and 3, Table 2). Further increasing the catalyst concentration to 200 ppm provided even better control with a lower dispersity of 1.08 (entry 4, Table 2). SEC traces of the resulting polymers showed monomodal distribution of molecular weights, broadened as the concentration of the $CuBr_2$/PMDETA catalyst was decreased from 200 to 25 ppm (Figure S10).

Because of the low activity of the Cu catalyst in the presence of PMDETA, not enough L/Cu^{II}−Br deactivator is present to ensure efficient deactivation of polymer chains at low catalyst concentrations.[53,54] However, increasing the activity of the Cu catalyst by changing the ligand from PMDETA to Me_6TREN results in a higher concentration of the deactivator. Therefore, well-controlled polymerizations can be achieved even at lower ppm concentration of the Cu catalyst. For example, good control over the polymerization of MA was achieved with 25 ppm of $CuBr_2$/Me_6TREN yielding a PMA with a low dispersity of 1.11 (entries 5−8, Table 2).

Heterogeneous and Visible-Light Photocatalytic Activity of PTZ-CMP. The conjugated nature of the heterogeneous network was important for enabling photocatalysis under green light irradiation for activating Cu-catalyzed ATRP. Additional control experiments conducted using the filtrates of the dispersion of PTZ-CMP in various solvents proved the heterogeneous nature of the photocatalytic process and the importance of the conjugated network to

Table 2. Polymerization of MA Using Heterogeneous PTZ-CMP Photocatalyst in the Presence of Low Concentrations of the Cu Catalyst[a]

entry	$CuBr_2$ (equiv)	ligand	solvent	time (h)	conv (%)	$M_{n,th}$	M_n	$Đ$
1	0.005	PMDETA	DMSO	4	94	16 400	20 200	2.06
2	0.01	PMDETA	DMSO	4	89	15 800	17 600	1.34
3	0.02	PMDETA	DMSO	24	99	17 300	18 600	1.13
4	0.04	PMDETA	DMSO	24	98	17 100	18 600	1.08
5	0.005	Me_6TREN	MeCN	18	98	17 100	20 700	1.11
6	0.01	Me_6TREN	MeCN	18	97	17 000	18 800	1.09
7	0.02	Me_6TREN	MeCN	18	97	17 000	20 300	1.08
8	0.04	Me_6TREN	MeCN	18	94	16 400	18 000	1.07

[a] Reaction conditions: [MA]/[EBiB]/[$CuBr_2$]/[L] = 200/1/x/0.2 (L = PMDETA or Me_6TREN and x = 0.04, 0.02, 0.01, and 0.005 equiv with respect to initiator corresponding to 200, 100, 50, and 25 ppm with respect to monomer) in 50 vol % solvent under green light irradiation (520 nm, 9 mW/cm^2).

enable photocatalysis under green light irradiation. To confirm this feature, a dispersion of PTZ-CMP in solvents such as DMSO, DMF, or MeCN (2 mg/mL of PTZ-CMP) was stirred for 24 h and then filtered through syringe filters to remove the heterogeneous parts. The transparent filtrate solutions were analyzed by UV−vis spectroscopy that showed absorption in the UV region <400 nm (Figure S11). These absorption peaks may be due to the presence of monomeric/oligomeric photocatalyst units that can dissolve in the solvents. The soluble parts were estimated to account for about <0.5 wt % of the total network. Moreover, the filtrates were used as solvents to examine the activity of the species dissolved from the network in ATRP under green light irradiation in the presence of Cu catalysts with PMDETA or Me_6TREN ligands. However, no polymerization of MA was observed after 24 h of irradiation in all solutions and regardless of the ligand. These results indicate that the small amount of soluble parts present in the filtrates did not promote photocatalysis to start the ATRP process (Table S3). Considering the very low concentration of the soluble parts and their absorption in the UV region, the conjugated nature of the heterogeneous photocatalyst sheets was essential for inducing photocatalysis under green light irradiation and well-controlled polymerizations.

The heterogeneous CMP photocatalysts were synthesized using Ph-PTZ, which shows an absorption profile below 400 nm in the monomeric form. To further confirm the important role of the CMPs as visible light active photocatalysts, ATRP of MA was attempted using the monomeric Ph-PTZ photocatalyst under green light irradiation. However, no polymerization of MA was observed in the presence of $CuBr_2$ and PMDETA, indicating a lack of photocatalytic activity of Ph-PTZ under green light irradiation as it absorbs in the UV region (Figure S12). Therefore, the conjugated nature of the catalyst is key for altering the photophysical properties of the photocatalyst to extend its absorption profile to longer wavelengths. As a result of this photocatalytic activity under green light irradiation, CMPs can be used to generate activating species for ATRP.

Reusability. An important feature of the heterogeneous PTZ-CMP photocatalyst was the ability to be easily separated from the reaction mixture and reused in multiple ATRP cycles while retaining its high photocatalytic efficiency. Recycling the PTZ-CMP photocatalyst enabled successive ATRP of MA conducted in the presence of $CuBr_2/Me_6TREN$ catalyst in MeCN. After each polymerization cycle, the photocatalyst was separated by centrifugation and washed with MeCN multiple times and dried before using in the next cycle. Near-quantitative monomer conversions and polymers with well-controlled molecular weights and low dispersity values were obtained over six cycles with no decrease in the photocatalyst's performance (Figure 4 and Figure S13).

Monomer Scope and Copolymerization. Polymerization of a variety of acrylate monomers was successfully initiated and controlled in the presence of PTZ-CMP and $CuBr_2/Me_6TREN$ as the catalyst under green light irradiation. Monomers such as *n*-butyl acrylate (BA), (2-methoxyethyl) acrylate (MEA), and 2,2,2-trifluoroethyl acrylate (TFEA) were polymerized to high conversions, yielding polymers with controlled molecular weight and dispersity values <1.1 (Figure 5A). Furthermore, chain extension experiments revealed the high chain end fidelity of the resulting polymers to enable synthesis of diblock copolymers. A poly(*n*-butyl acrylate) (PBA) macroinitiator was initially synthesized with controlled molecular weight and a low dispersity of 1.08 (M_n = 7400, monomer conversion >90%). The second monomer, MEA, was added *in situ* to generate the second block. SEC traces of the block copolymer showed a clear shift of the molecular weight distribution to higher values (M_n = 29100 and $Đ$ = 1.11), indicating the high retention of chain end fidelity of the polymers (Figure 5B).

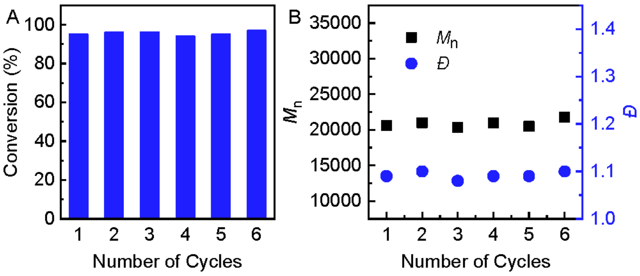


Figure 4. Recycling PTZ-CMP as a photocatalyst in ATRP of MA showing retention of photocatalytic activity over multiple cycles. (A) Monomer conversion and (B) molecular weight (M_n, squares) and dispersity ($Đ$, circles) of the resulting polymers in recycling experiments. Reaction conditions: $[MA]/[EBiB]/[CuBr_2]/[Me_6TREN]$ = 200/1/0.04/0.2 in MeCN (50 vol %) under green light irradiation (520 nm, 9 mW/cm^2), PTZ-CMP = 2 mg/mL.

Additionally, polymerization of methyl methacrylate (MMA) was conducted in the presence and absence of the Cu catalyst to study whether PTZ-CMP has similar effects on the control of the ATRP of a methacrylate monomer (Figure 6). In the presence of $CuBr_2$/PMDETA and ethyl α-bromophenylacetate (EBPA) as the initiator, the ATRP of MMA afforded polymers with controlled molecular weights and low dispersity values (Figure 6A and B and Figure S14). The rate of the polymerization increased as the concentration of the electron donor (excess PMDETA) was increased (Figure 6A). However, no monomer conversion was observed in the absence of the Cu catalyst and the ligand. These results indicate that, under low energy green light irradiation, the PTZ-CMP acted as a photocatalyst to selectively reduce $L/Cu^{II}-Br$ as opposed to activation of the EBPA initiator, which has a more negative reduction potential than the Cu catalyst. Therefore, no supplemental activation was feasible with the heterogeneous photocatalyst when irradiated under green light. Using a Cu catalyst that can engage with the photocatalyst to generate activating/deactivating species can afford well-controlled polymerization of methacrylate monomers with high efficiency.

■ CONCLUSIONS

In summary, we developed conjugated microporous polymers of phenothiazine as a heterogeneous photocatalyst to activate Cu-catalyzed ATRP. The conjugated nature of the heterogeneous photocatalyst enabled photocatalysis under green- or red-light irradiation. The activator species for ATRP was generated by photoredox reactions of the photocatalyst with the Cu complexes and electron donors. The use of a Cu catalyst enabled controlling polymerizations of acrylate and methacrylate monomers with high efficiency to yield near-quantitative monomer conversions and polymers with controlled molecular weights and low dispersity values. The heterogeneous nature of the photocatalyst allowed easy separation and reuse in multiple cycles with retention of

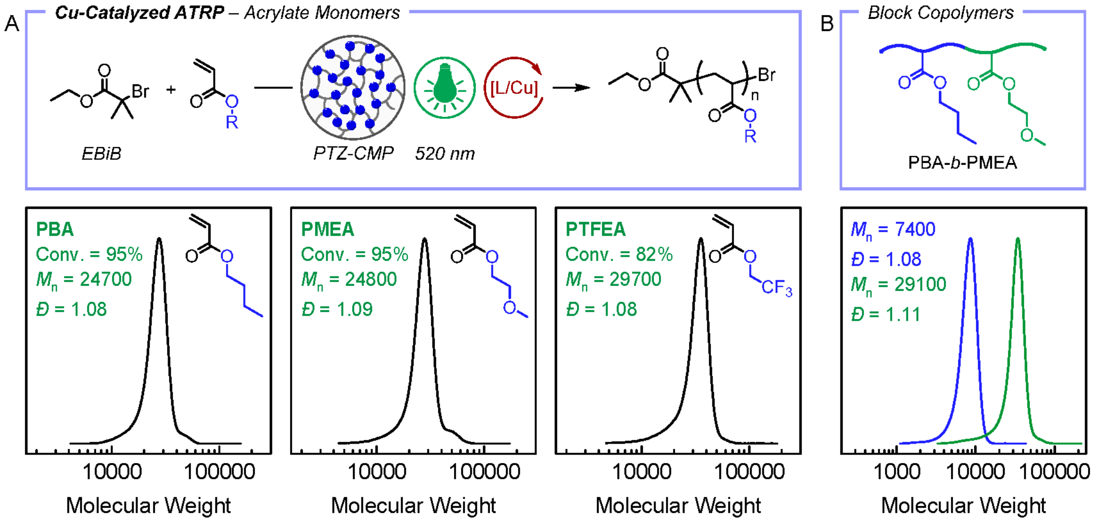


Figure 5. (A) Results of ATRP of acrylate monomers (BA, MEA, and TFEA) and (B) *in situ* block copolymerization experiments using PTZ-CMP photocatalyst. Reaction conditions: [M]/[EBiB]/[$CuBr_2$]/[Me_6TREN] = 200/1/0.04/0.2 in MeCN (50 vol %) under green light irradiation (520 nm, 9 mW/cm^2), PTZ-CMP = 2 mg/mL. (B) SEC traces of PBA macroinitiator (in blue) and PBA-*b*-PMEA block copolymer (in green) upon *in situ* chain extension showing high chain-end fidelity and successful chain extension.

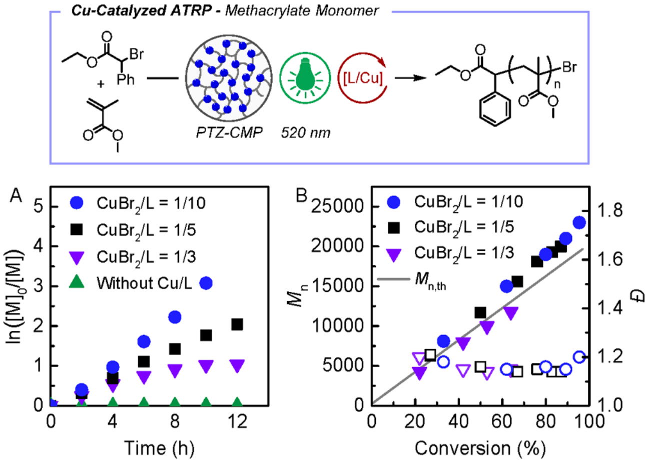


Figure 6. ATRP of methyl methacrylate (MMA) using PTZ-CMP as a photocatalyst in the presence or absence of the Cu catalyst using different concentrations of excess PMDETA ligand as electron donor: (A) kinetics of polymerization and (B) molecular weight (M_n, solid points) and dispersity ($Đ$, empty points) of the resulting polymers as a function of monomer conversion. Reaction conditions: [MMA]/[EBPA]/[$CuBr_2$]/[PMDETA] = 200/1/0.04/x (x = 0.12, 0.2, or 0.4) in DMSO (50 vol %) under green light irradiation (520 nm, 9 mW/cm^2), PTZ-CMP = 2 mg/mL.

high photocatalytic efficiency. As presented in this paper, designing new photocatalytic systems to promote ATRP under visible or NIR light irradiation provides new opportunities in advancing photoinduced ATRP systems. Regarding heterogeneous photocatalysis, developing strategies to further control the physical, structural, and photochemical properties of the photocatalyst networks would enable efficient photocatalysis applicable for a wide range of controlled polymerization systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c04428.

Details of experimental procedures and additional control experiments and polymerization results (PDF)

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Notes

The authors declare no competing financial interest.

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