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Free Radical Polymerization Initiated and Controlled by Visible Light Photocatalysis at Ambient Temperature

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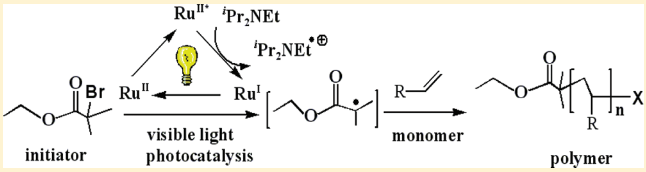
Supporting Information



ABSTRACT: A new method of free radical polymerization is developed on the basis of visible light photocatalysis using $Ru(bpy)_3Cl_2$ that initiates and controls the polymerization at ambient temperature. The α-haloester and benzylic halide act as radical initiators that can be activated through the $Ru(bpy)_3^+$ photoredox cycle under visible light irradiation. Successful free radical polymerizations of various methacrylates were realized using a Xe arc lamp as well as a household fluorescent lamp as light source. The polymerization is initiated with light on and immediately terminated upon turning the light off. In addition, the molecular weight of polymer can be varied by changing the ratio of monomer and initiator. The present photocatalytic method has merits of the mild reaction conditions with weak light irradiation, ambient temperature, and lower catalyst loading, which could be an alternative to the traditional thermal or photo-based free radical initiation methods. It is also advantageous over other photopolymerization methods in that the radical initiator is separated from the photosensitizer.

INTRODUCTION

The development of active and versatile initiating systems in radical polymerization has been intensively studied.[1] The radical polymerization reactions are conventionally initiated by thermal decomposition of azo-compounds (e.g., dialkyldiazenes, AIBN), peroxides (e.g., diaroyl peroxides), organometallic compounds (e.g., trialkyltin hydride), or their combination (Scheme 1). In contrast to thermochemical initiation, which usually requires elevated temperature, photochemical initiation enables the easy control of the polymerization under ambient temperature even for heat-sensitive or thermodegradable monomers.[2] The free radical initiators can be produced by UV-induced photolysis of aromatic carbonyl compounds (benzoin and its derivatives) through "α-cleavage" (type I) or aromatic ketones (benzophenone, quionones) through the bimolecular hydrogen abstraction in the presence of hydrogen atom donors (type II) (Scheme 1).[3]

Since UV light is less in the solar spectrum, potentially harmful, and costly in generation and maintenance, the use of visible light that is abundant in solar light, safe, less costly, less damaging to chemicals, and easy to use is more favored in synthetic applications. In addition, visible light initiated polymerization in many targeted applications such as dental filling materials, photoresists, and integrated circuits is very attractive and promising.[4] However, visible light initiation in free radical polymerization is rare and needs to be developed.[5,6] An example study is that Rose Bengal derivatives were employed as a photoinitiator (at 514 nm) for the photopolymerization of polyol acrylates.[7] The heterogeneous semiconductor (e.g., ZnO, CdS) photocatalysis can also be applied to the visible light induced initiation of polymerization.[8] However, the radicals produced by semiconductor photocatalysis are usually unstable and less efficient, which lead to lower degree of polymerization and higher polydispersity.[9]

On the other hand, dye molecules are often used as visible light sensitizers in many photochemical reaction systems. In particular, ruthenium(II)−polypyridine complexes (e.g., $Ru^{II}(bpy)_3$ and its derivatives) are extensively studied as photoredox catalysts because of their strong absorbance in the visible region (∼450 nm), chemical stabilities, long excited-state lifetimes, and the favorable redox potentials. Recently, the research groups of MacMillan,[10] Yoon,[11] and Stephenson[12] have demonstrated that the $Ru(bpy)_3^{2+}$ as a photoredox catalyst offers promising possibilities in a series of radical-mediated organic reactions such as the enantioselective alkylation of aldehydes, C−H functionalization, and [2 + 2] cycloaddition. $Ru(bpy)_3^{2+}$ is excited to $Ru^*(bpy)_3^{2+}$ upon absorbing a visible light photon, which is reductively quenched by a sacrificial electron donor (e.g., trialkylamines) to generate a powerful single-electron reductant, $Ru(bpy)_3^+$ ($E^0 \approx -1.09$ V_{NHE}[10]), which can dechlorinate organic halides to generate carbon-centered radical species. However, little information about the photonic efficiency in the photocatalytic production of radicals was reported in the previous studies.[10−12]

This study aimed to employ the $Ru(bpy)_3^{2+}$-based visible light photocatalysis as a new radical initiation method for the free radical polymerization reaction. The efficiency of radical generation through the visible light photocatalytic process was quantitatively investigated as well. Poly(methyl methacrylate) (PMMA),

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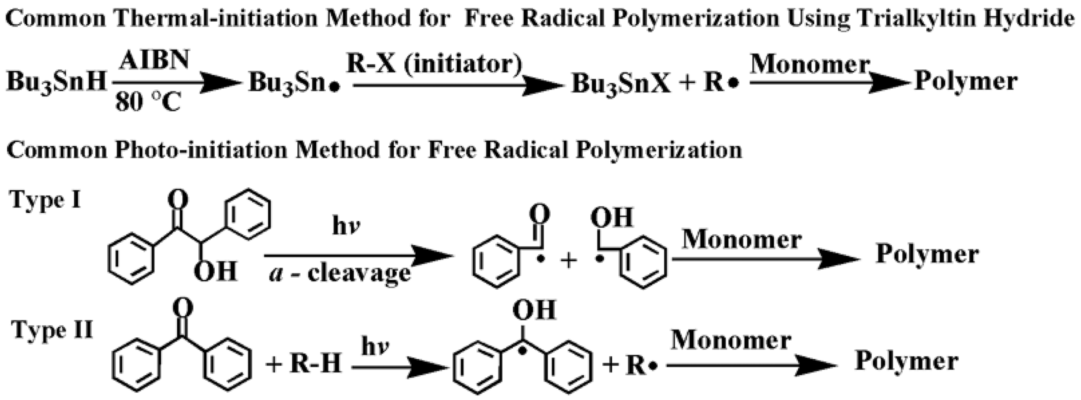
Scheme 1. Illustration of Commonly Used Thermal Initiation and Photoinitiation Methods for Free Radical Polymerization



the most common methacrylate polymer, is synthesized through the radical polymerization of its monomer methyl methacrylate (MMA). Although some visible light photopolymerization systems employing photosensitizers were reported, either the radicals of electron donors or photosensitizers served as the initiating radicals as well, which limits the practical application of the photopolymerization.[3b,7] Various α-haloesters and benzylic halides are particularly good initiators in the reaction of well-controlled radical polymerization.[13] We thus used α-bromoisobutyrate ($E^0 \approx -0.82$ V_{NHE} in DMF[13]) and benzyl bromide ($E^0 \approx -0.46$ V_{NHE} in DMF[14]) as radical initiators that can be activated through the $Ru(bpy)_3^+$ photocatalytic cycle under visible light irradiation. The present photocatalytic polymerization method has a clear merit in that the radical initiator is separated from the photosensitizer.

EXPERIMENTAL SECTION

Materials. Methyl methacrylate (MMA, 99% Aldrich), ethyl methacrylate (EMA, 99% Aldrich), butyl methacrylate (BMA, 99% Aldrich), *tert*-butyl methacrylate (TBMA, 98% Aldrich), isobutyl methacrylate (IBMA, 97% Aldrich), glycidyl methacrylate (GMA, 97%, Aldrich), and 2-ethoxyethyl methacrylate (EEMA, 99% Aldrich) were purified three times through a column filled with basic alumina oxides. The purified monomers were stored at −20 °C and purged with high-purity nitrogen prior to use. Ethyl 2-bromoisobutyrate (EBiB, 98%, Aldrich), benzyl bromide (BB, 98% Aldrich), *N*,*N*-diisopropylethylamine ($^i Pr_2NEt$, 98%, Aldrich), tris(bipyridine)ruthenium(II) dichloride hexahydrate ($Ru(bpy)_3Cl_2 \cdot 6H_2O$, Aldrich), and *N*,*N*-dimethylformamide (DMF, 99.5%, Aldrich) were used as received.

General Procedure for Polymerization of MMA. A Schlenk flask was charged with DMF (2.1 mL, 50% v/v vs monomer) and $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (1.5 mg, 2 μmol). The flask was sealed with rubber septum and was purged with nitrogen for 20 min to remove the oxygen. The degassed monomer methyl methacrylate (2.1 mL, 20 mmol) was then added to the flask by using a syringe under protection of nitrogen. The flask was degassed by three vacuum/N_2 refilling cycles to remove the oxygen. Then, $^i Pr_2NEt$ (170 μL, 1 mmol) and EBiB (75 μL, 0.5 mmol) were added under protection of nitrogen. Then, the flask was irradiated by a 300 W Xe arc lamp (Oriel). Light beam passed through a 10 cm IR water filter, a UV-cutoff filter ($\lambda > 420$ nm), and a neutral density 1.0 filter to reduce the light intensity. The light irradiation area was about 2 cm^2, and the light intensity was measured about 25 mW/cm^2 in the range of 420−645 nm by using a calibrated Si photodiode. At time intervals, samples were collected from the flask with a syringe under protection of nitrogen. The temperature of the solution during irradiation was around 25 °C. Parts of the polymer solution were precipitated with large excess of methanol, filtered, and washed with methanol and then dried overnight to obtain powder samples.

The apparent quantum efficiency (QE) was determined from the polymerization of MMA under irradiation at 450 nm (fwhm 40 nm) by using combined band-pass filter and neutral density 1.0 filter. The light intensity was measured to be about 4 mW/cm^2 at 450 nm. The polymerization of MMA was also conducted with using a 27 W household fluorescent lamp as a light source.

Characterization. The gel permeation chromatography (GPC) measurement determined the molecular weights (M_n and M_w) of the polymers. The GPC column system was calibrated with polystyrene standards. The chloroform was used as the solvent to dissolve polymer powder. The yields of polymers were calculated gravimetrically. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL ECA 500 spectrometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). Chemical shifts for ^{1}H NMR were reported as δ, parts per million, relative to the signal of $CHCl_3$ at 7.26 ppm. Chemical shifts for ^{13}C NMR were reported as δ, parts per million, relative to the center line signal of the $CDCl_3$ triplet at 77.0 ppm. The abbreviations s, br s, d, br d, t, q, and m stand for the resonance multiplicity singlet, broad singlet, doublet, broad doublet, triplet, quartet, and multiplet, respectively.

Poly(methyl methacrylate) (PMMA)[15]. (Table 2, entry 1): [MMA]:[EBiB]:[$Ru(bpy)_3^{2+}$]:[$^i Pr_2NEt$] = 200:5:0.02:10, MMA:DMF = 1:1 (v/v), visible light irradiation 24 h, yield = 80%. ^{1}H NMR ($CDCl_3$, 500 MHz): 3.72 (br s, 3H), 1.94−2.04 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): 177.7, 54.4, 51.8, 45.0, 17.0.

Poly(ethyl methacrylate) (PEMA)[15]. (Table 2, entry 2): [EMA]:[EBiB]:[$Ru(bpy)_3^{2+}$]:[$^i Pr_2NEt$] = 200:5:0.02:10, MMA:DMF = 1:1 (v/v), visible light irradiation 24 h, yield = 75%. ^{1}H NMR ($CDCl_3$, 500 MHz): 4.0 (q, 2H), 1.94−2.04 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.0 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): 177.7, 60.7, 54.2, 45.1, 18.5, 13.8.

Poly(butyl methacrylate) (PBMA)[16]. (Table 2, entry 3): [BMA]:[EBiB]:[$Ru(bpy)_3^{2+}$]:[$^i Pr_2NEt$] = 200:5:0.02:10, MMA:DMF = 1:1 (v/v), visible light irradiation 24 h, yield = 74%. ^{1}H NMR ($CDCl_3$, 500 MHz): 3.96 (t, *J* = 5.8 Hz, 2H), 1.93−2.03 (m, 2H), 1.59−1.67 (m, 2H), 1.37−1.45 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.89−1.04 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): 177.5, 64.7, 54.2, 44.8, 30.2, 19.2, 16.5, 13.7.

Poly(tert-butyl methacrylate) (PTBMA)[17]. (Table 2, entry 4): [TBMA]:[EBiB]:[$Ru(bpy)_3^{2+}$]:[$^i Pr_2NEt$] = 200:5:0.02:10, MMA:DMF = 1:1 (v/v), visible light irradiation 24 h, yield = 65%. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.79−1.90 (m, 2H), 1.44 (br s, 9H), 1.03 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): 177.2, 80.9, 50.6, 46.4, 27.7, 17.8.

Poly(isobutyl methacrylate) (PIBMA)[15]. (Table 2, entry 5): [IBMA]:[EBiB]:[Ru(bpy)$_3^{2+}$]:[^{i}Pr$_2$NEt] = 200:5:0.02:10, MMA:DMF = 1:1 (v/v), visible light irradiation 24 h, yield = 70%. ^{1}H NMR (CDCl$_3$, 500 MHz): 3.72 (d, J = 6.8 Hz, 2H), 1.95−2.02 (m, 2H), 1.05 (br s, 1H), 0.98 (d, J = 6.8 Hz, 6H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz): 177.7, 71.1, 54.7, 45.1, 29.5, 19.3, 16.4.

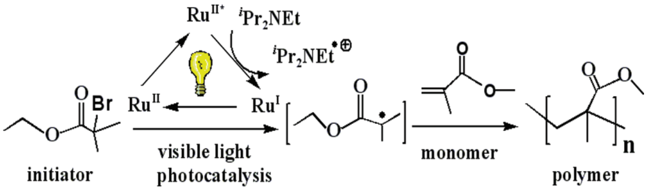
Poly(glycidyl methacrylate) (PGMA)[18]. (Table 2, entry 6): [GMA]:[EBiB]:[Ru(bpy)$_3^{2+}$]:[^{i}Pr$_2$NEt] = 200:5:0.02:10, MMA:DMF = 1:1 (v/v), visible light irradiation 12 h, yield = 86%. ^{1}H NMR (CDCl$_3$, 500 MHz): 3.80−4.30 (br d, J = 6.8 Hz, 2H), 3.18−3.24 (m, 1H), 2.61−2.84 (br d, 2H), 1.88−2.00 (m, 2H), 0.92−1.07 (t, J = 7.2 Hz, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz): 176.9, 126.1, 65.1, 50.5, 48.9, 44.6, 18.2.

Poly(2-ethoxyethyl methacrylate) (PEEMA)[19]. (Table 2, entry 7): [EEMA]:[EBiB]:[Ru(bpy)$_3^{2+}$]:[^{i}Pr$_2$NEt] = 200:5:0.02:10, MMA:DMF = 1:1 (v/v), visible light irradiation 12 h, yield = 83%. ^{1}H NMR (CDCl$_3$, 500 MHz): 4.09 (t, J = 5.8 Hz, 2H), 3.53 (t, J = 5.8 Hz, 2H), 3.50 (t, J = 5.8 Hz, 2H), 1.84−2.02 (m, 2H), 1.22 (t, 3H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz): 177.6, 67.7, 66.5, 63.9, 54.1, 17.3, 13.4.

■ RESULTS AND DISCUSSION

The polymerization of MMA was carried out at ambient temperature under visible light irradiation (Xe arc lamp with the light intensity of 25 mW/cm^2 in the range of 420−645 nm). The reactants typically consisted of [MMA]:[EBiB]:[Ru(bpy)$_3^{2+}$]:[^{i}Pr$_2$NEt] = 200:1:0.02:5 with MMA:solvent (DMF) = 1:1 (v/v). ^{i}Pr$_2$NEt was used as a sacrificial electron donor that reduces the excited state Ru*(bpy)$_3^{2+}$ to Ru(bpy)$_3^+$ as shown in Scheme 2. Several control experiments were carried out with removing an essential component one-by-one, and the results are shown in Table 1 (entries 1 and 2). First, the polymerization without light, initiator EBiB, ^{i}Pr$_2$NEt, or dye was completely absent, which confirms that each component is required for successful polymerization. The control test results support that the polymerization proceeds through the photocatalytic initiation mechanism that we have proposed in Scheme 2.

Scheme 2. Proposed Mechanism of Visible Light Photoredox Catalysis That Initiates Free Radical Polymerization of Methyl Methacrylate (MMA)



A series of polymerization reactions were carried out with changing the molar ratio of monomer/initiator/dye/electron donor (entries 3−7, Table 1). In all cases, the polydispersity index (PDI = M_w/M_n) is around 2.0, which indicates that the visible light induced radical polymerization yields a fairly good distribution of polymers. Compared with the reference condition of entry 3, increasing the concentration of the photocatalyst (dye) 5-fold (0.01 → 0.05 mol %) only slightly increased the yield of PMMA (entry 4), which indicates that even tiny amount of the dye catalyst is sufficient in initiating the polymerization reaction. Increasing the initiator (EBiB) concentration by 5 times raised the yield from 23 to 31% (entry 5). Furthermore, the concentration of electron donor (^{i}Pr$_2$NEt) has a significant effect on the polymerization yield (entries 6 and 7). From the reference condition (entry 3), lowering [^{i}Pr$_2$NEt] to a fifth markedly reduced the yield (entry 6: 2%), whereas doubling it enhanced the yield (entry 7: 30%). In addition, it is noted that the molecular weight of PMMA progressively decreases with increasing [^{i}Pr$_2$NEt] (entry 6 → 3 → 7); the results indicate that the tertiary amine should play a dual role of an electron donor and a hydrogen atom donor that terminates the polymerization reaction. Therefore, the termination of polymer chain radicals, which leads to reduced molecular weight, should be favored in the presence of excess ^{i}Pr$_2$NEt with reducing the molecular weight. Finally, we fixed the molar ratio at 200:5:0.02:10 as the optimized experimental condition. The yields of PMMA at this condition are 34% and 76% after 4 and 20 h reaction, respectively (entries 8 and 9).

We further conducted the polymerization of MMA using BB as an initiator under the optimized condition (entry 10, Table 1). Since the reduction potential of Ru^{2+}/Ru$^+$ is more negative than that of EBiB and BB, the reduction of EBiB and BB by Ru(bpy)$_3^+$ is thermodynamically feasible. The polymerization performed with EBiB initiator gave higher yield compared with that carried out with BB initiator (34% vs 12%), which indicates that EBiB is a more efficient initiator in this photocatalytic polymerization system. To quantify the quantum efficiency (QE) of the photocatalytic

Table 1. Photocatalytic Polymerization Performed with Varying the Ratio of Active Components and Conditions[a]

entry	component ratio [MMA]:[EBiB]:[Ru(bpy)$_3^{2+}$]:[^{i}Pr$_2$NEt]	M_n	M_w/M_n (PDI)	yield[b] (%)
1	control (no light, no EBiB, or no ^{i}Pr$_2$NEt)			0
2	control (no dye)			0
3	200:1:0.02:5	56 400	2.0	23
4	200:1:0.1:5	42 400	2.0	25
5	200:5:0.02:5	38 900	2.1	31
6	200:1:0.02:1	58 000	2.0	2
7	200:1:0.02:10	36 500	2.1	30
8	200:5:0.02:10	26 400	2.0	34
9[c]	200:5:0.02:10	25 900	2.0	76
10[d]	200:5:0.02:10	37 100	2.7	12
11[e]	200:5:0.02:10	33 500	2.0	16
12[f]	200:5:0.02:10	30 600	1.7	39

[a] Reactions carried out with 20 mmol of MMA, MMA/solvent (DMF) = 1:1 (v/v); visible light illuminated for 4 h (except entry 9). [b] The yield is the average of two experiments. [c] Illuminated for 20 h. [d] Using BB as an initiator. [e] Illuminated at 450 (±20) nm for 4 h (light intensity = 4 mW/cm^2). [f] Illuminated for 4 h by a 27 W fluorescent lamp (10 cm from the reactor).

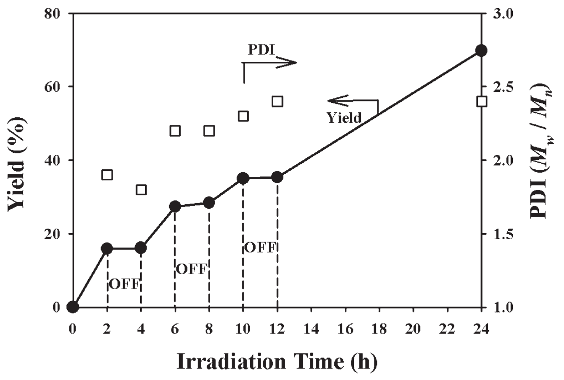


Figure 1. Effect of visible light irradiation on the yield and PDI value of the free radical polymerization of methyl methacrylate in 50% DMF at 25 °C. Reactions conducted with the molar ratio of [MMA]:[EBiB]:[$Ru(bpy)_3^{2+}$]:[$^i Pr_2NEt$] = 200:5:0.02:10.

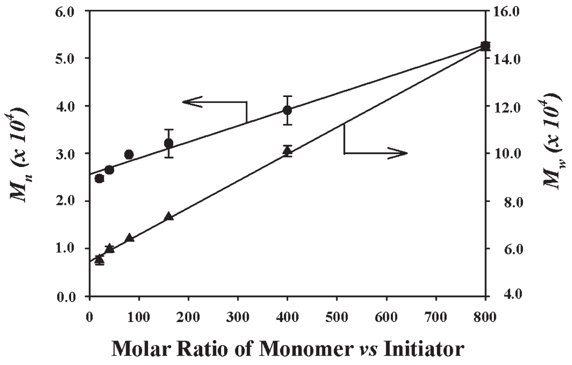


Figure 2. Effect of molar ratio of momomer vs initiator on the molecular weight (M_n and M_w) of PMMA.

polymerization, the photoreaction was carried out using monochromatic irradiation that was filtered by a band-pass filter (centered at 450 ± 20 nm, light intensity = 4 mW/cm^2) (entry 11 in Table 1). The monochromatic radiation coincides with the main absorption band of $Ru(bpy)_3^{2+}$. The fraction of the incident light (450 nm) absorbed by $Ru(bpy)_3^{2+}$ is about 31% under the present experimental condition ([dye] = 4.6 μM, ε_{450} = 11 500 M^{-1} cm^{-1}, light path length = 3 cm). The yields of PMMA obtained under the monochromatic radiation are 16% (entry 11, Table 1), which is much lower than those obtained under white radiation (420−700 nm) because the photon flux in the monochromatic radiation is far lower. The QE value for the photocatalytic polymerization was calculated using the following equation with assuming that all photogenerated free radicals could form new polymer chains:

$$
\begin{aligned}
&\text{QE } [\%] \text{ (at 450 nm)}\\
&= (\text{no. of initiated radicals})/(\text{no. of adsorbed photons by } \mathrm{Ru(bpy)_3}^{2+})\\
&\quad \times 100\\
&= (\text{no. of polymer chains})/(\text{no. of incident photons} \times 0.31) \times 100\\
&= (\text{polymer weight}/M_n)/(\text{no. of incident photons} \times 0.31) \times 100
\end{aligned}
$$

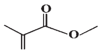
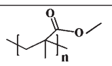
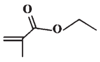
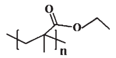
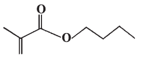
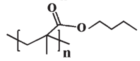
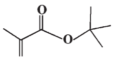
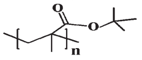
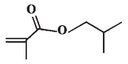
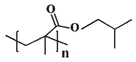
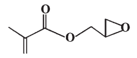
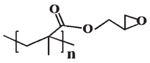
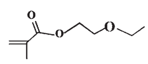
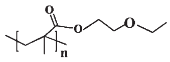
According to the above equation, QE in the photocatalytic polymerization of MMA during 4 h reaction is calculated to be about 7%. In other words, this implies that only a fraction (<10%) of the total number of excited $Ru(bpy)_3^{2+}$ can take part successfully in the initiation process. The factors that may contribute to QE are the fluorescence quenching of the excited sensitizers, the rate of reaction between $Ru(bpy)_3^{2+*}$, and $^i Pr_2NEt$ and the rate of the subsequent reaction between $Ru(bpy)_3^{+}$ and EBiB. We further demonstrated that the photocatalytic polymerization of MMA could be successfully carried out using a 27 W household fluorescent lamp as a light source as shown in Table 1 (entry 12). This indicates that the present photocatalytic polymerization method can be used even when the visible light illumination is as weak as the ambient light.

To further investigate the effect of visible light irradiation on the photocatalytic polymerization of MMA, the light was turned on and off intermittently during the reaction (light off at 2−4, 6−8, and 10−12 h in Figure 1). Figure 1 shows the yield of PMMA and PDI as a function of time at ambient temperature. M_w increased to 71 200 and 93 600 with the irradiation time of 2 and 18 h, respectively, whereas M_n remained relatively constant in the range of 37 100−39 500 during 2−18 h irradiation period. The gradual increase of the yield with the irradiation time clearly indicates that the polymerization is driven by light. The polymer yield increased only under the visible light irradiation while the polymerization stopped in the light-off period. This indicates that the generation and termination of active radicals can be controlled by a simple light on−off operation. In the successive polymerization periods through the light on−off cycles, the polymerization rate was somewhat decelerated in the later periods, but the polymerization steadily continued as long as light was irradiated. The periodic on−off process of polymerization demonstrates that the visible light irradiation have a good control over the free radical polymerization process. The polymerization is initiated with light on and immediately terminated upon turning the light off. This is clearly contrasted with the thermally initiated polymerization in which the termination of radical chain reaction cannot be controlled. This is because the initiators are activated sequentially by the photocatalytic process that is limited by the photon flux whereas they are all activated simultaneously in the thermal initiation process. On the other hand, it is notable that the repeated on−off cycles were accompanied by the gradual increase in PDI (from 1.9 to 2.4). This indicates that the repeated cycles of polymerization broadens the distribution of the molecular weight, which is due to the buildup of shorter chain polymers from the previous "on−off" experiment.

The molecular weight of polymers could be also controlled by adjusting the molar ratio of monomer/initiator (MMA/EBiB). As shown in Figure 2, M_n and M_w of PMMA linearly increase with increasing [monomer]/[initiator]. This indicates that lower concentration of initiators generate fewer radicals, which favors the formation of longer polymer chains with the given amount of monomers.

The photocatalytic polymerization was carried out for not only MMA but also other methacrylates with different functional groups, and the results are summarized in Table 2. In all cases, 0.01 mol % of the Ru photocatalyst was sufficient for successful radical polymerization (yield: 60−90%). Methacrylates containing electron-withdrawing substituents (entries 6 and 7, Table 2) were polymerized faster than those containing electron-donating substituents (entries 1−5, Table 2). These results illustrate the generality of the present photocatalytic free radical polymerization to a variety of methacrylates. This photocatalytic method was also tested for the polymerization of styrene and acrylate monomers. However, the polymerization efficiency was relatively

Table 2. Photocatalytic Radical Polymerization of Various Methacrylates[a]

Entry	Substrate	product	*t* (h)	M_n	PDI (M_w/M_n)	Yield[a]
1			24	25100	2.0	80%
2			24	31300	2.0	75%
3			24	80200	1.7	74%
4			24	34200	2.1	65%
5			24	55600	1.8	70%
6			12	41700	3.8	86%
7			12	42300	3.5	83%

[a] Reaction conditions: 10 mmol of substrates, $Ru(bpy)_3^{2+}$ = 0.01 mol %, DMF = 50% (v/v), visible light (420−700 nm). Yield was estimated by precipitating the sample in methanol.

lower compared with methacrylate monomers. The higher efficiency in methacrylates polymerization can be ascribed to the stability of the propagating tertiary radical centers.

CONCLUSIONS

In summary, a new method of photoinitiated and photocontrolled free radical polymerization was developed by employing visible light photocatalysis under ambient temperature. Successful polymerization of methyl methacrylate using α-bromoisobutyrate as an initiator was realized, with achieving the quantum efficiency of about 7% within 4 h visible light illumination. The polymerization process can be easily controlled by light on and off, and the molecular weight of polymer can be varied by changing the ratio of monomer and initiator. It is noteworthy that even a household fluorescent lamp can be used as a light source to induce the polymerization reaction. The present photoinitiated radical polymerization is also adapted to a series of methacrylates with different functional groups. The present photocatalytic polymerization can be used as an easy, convenient, and inexpensive process as an alternative to the traditional thermal or photo-based free radical initiation methods.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Characterization of synthetic polymers, including GPC traces as well as ^{1}H NMR and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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