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Dimanganese decacarbonyl/2-cyanoprop-2-yl 1-dithionaphthalate: toward sunlight induced RAFT polymerization of MMA

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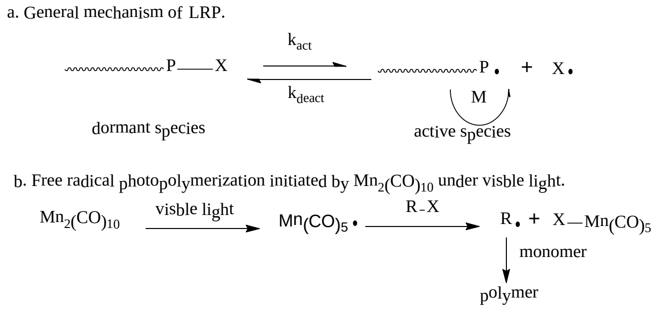
Well-controlled poly(methyl methacrylate) was synthesized by the mediating of dimanganese decacarbonyl [$Mn_2(CO)_{10}$]/2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) with photo-induced controlled radical polymerization of methyl methacrylate under visible (green LED with λ_{max} of 565 nm) or sunlight irradiation at moderate temperature. The manganese carbonyl [$Mn_2(CO)_{10}$] was acted as the light absorbing component, and 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) was acted as pseudo-alkyl halide initiator and mediating agent. The polymerization showed the characteristics behaviour of living polymerization, such as linear kinetics, the molecular weight of the polymers linearly increasing with monomer conversion, and the obtained polymers showed narrow molecular weight distribution, under the appropriate conditions. The obtained polymer showed high end functionality degree, which could be used for further chain extensions, using either through traditional thermal initiated RAFT polymerization or through light-irradiated LRP in the presence of [$Mn_2(CO)_{10}$]. The possibility of stopping and restarting the polymerization process was realized simply by turning off or on the LED light.

Introduction

For the endless pursuing in synthetic polymer chemistry, more and more attention has been paid on the so-called macromolecular engineering, namely, the synthesis of novel polymers with well-defined molecular parameters, such as narrow molecular weight distribution, controlled molecular weight, and pre-determined structure.[1] In such field, controlled/“living” radical polymerization (LRP)[2-13] was one of the most important strategies due to its moderate conditions, widely available monomer families, and simplicity. Nitroxide-mediated polymerization (NMP),[2, 14] atom transfer radical polymerization (ATRP),[5, 6] and reversible addition–fragmentation chain-transfer (RAFT)[10] polymerization were the most popular LRP techniques for the synthesis of polymers with precise tailor-made architectures.[15, 16] LRP was relied on the reversible generation of the active species from the dormant species (Scheme 1a).[4, 17] For the LRP’s general mechanism showed in Scheme 1a, k_{act} and k_{deact} were pseudo-first-order activation rate constant and deactivation rate constant, respectively. With different capping agent (X), the dormant species (P-X) can be activated by physical and/or chemical stimuli, such as heat, metal catalysts, and free-radical initiators.[9] All of these physical and chemical stimuli have been used to realize efficient activation/deactivation and control of the molecular weight and narrow molecular weight distribution.



Scheme 1. General mechanism.

Photochemistry has also been widely used in not only conventional radical polymerization, but also almost each specific method of LRPs.[14, 18-32] The motivations to utilize photochemistry were the activation of catalysts, generation of controlling agents, improving the polymer-end structure, and especially enable LRP to proceed under mild thermal conditions by activating the dormant species at relative low temperature, which would be helpful to minimize the uncontrolled side reactions. Moreover, the “on” and “off” of the polymerization process can be realized by using photochemistry as external stimuli.[20] Consequently, the scope of LRP can be vastly expanded via the photo-induced LRP.[29] Eri Yoshida reported the photo-induced NMP of MMA at room temperature.[33] By this photo-NMP, various supramolecules including not only block copolymers, but also micromolecules-sized vesicles have been prepared.[34] Recently, Hawker et al. reported the light-induced ATRP of methacrylates regulated by visible light using an iridium based photoredox catalyst.[32]

Among these photo-induced LRPs, photo-induced RAFT polymerization has been extensively studied because of the wide range of monomer families and moderate polymerization conditions.[21, 22, 24-26] Different photo-induced RAFT polymerization systems, namely generation free radicals directly from RAFT agents[21, 22] or photoinitiators under UV irradiation have been developed.[24] However, the non-selective decomposition of S-C bond in polymer chain ends and RAFT agent caused the accumulation of uncontrolled reaction during the polymerization, which finally resulted in the loss of control on high monomer conversion.[35] Cai and co-works proved that photolysis of some RAFT agents would occur under short-wavelength light, such as 365 nm, which might have a detrimental effect on the polymerization.[24] They have successfully realized well-controlled polymerization under long-wavelength UV (λ> 365 nm) irradiation in the presence of photoinitiators, like (2,4,6-trimethylbenzoyl) diphenylphosphine oxide (TPO).[36] Thus, the using of long-wavelength light to induce the polymerization in case of photo-induced RAFT polymerization was important for reducing the possibility of RAFT agent decomposition during the polymerization and improving the controllability for such method.

Manganese carbonyl [$Mn_2(CO)_{10}$] was one of the widely used visible light sensitive agents, which produced highly reactive metal-centered radical [$\bullet Mn(CO)_5$] at a controlled concentration under appropriate light irradiation conditions.[37, 38] Although such radical lacked the activity for initiating the polymerization of normal vinyl monomer, it can abstract halide, like iodine or bromide, from alkyl halides and generate the corresponding carbon centered radicals (Scheme 1 b), which could initiate the polymerization. Since the reverse reaction between carbon centered radical (R•) and X-$Mn(CO)_5$ regenerating R-X and $\bullet Mn(CO)_5$ was less likely due to the strength of Mn-X bond, the radical polymerization can be realized.[26, 27, 39] Many radical polymerization examples induced by $Mn_2(CO)_{10}$ with alkyl halide compounds have been reported at moderate conditions under visible light irradiation since the radical polymerization were reported in 1960s and 1970s.[40] The application of $Mn_2(CO)_{10}$ in LRPs also has been realized in recent years. Yagci *et al.* reported the ATRP under light-induced activation of $Mn_2(CO)_{10}$, and even with the sunlight irradiation. Kamigaito *et al.* reported the degenerative iodine transfer polymerization using $Mn_2(CO)_{10}$ in conjunction with alkyl iodides.[27] Although the mechanism was still remained unclear, such system showed moderate controllability for the polymerization of not only conjugated monomers such as acrylate and styrene but also unconjugated monomers such as vinyl acetate. They further extended the $Mn_2(CO)_{10}$ to RAFT polymerization by using $Mn_2(CO)_{10}$ to abstract xanthane or dithiocarbonyl compounds to generate the carbon centered radicals using as the initiator, followed with the RAFT process, successfully realized the LRP. This system was applicable to both conjugated (acrylate) and unconjugated (vinyl acetate) monomers.[26]

In our preliminary work, we have successfully applied the dithiocarbonyl compounds as the ATRP initiator, which further confirmed the pseudo-halide property of dithiocarbonyl group.[41] By using 2-cyanoprop-2-yl1-dithionaphthalate (CPDN) as the initiator under the activation of iron based catalyst system, LRP of methacrylate was conducted. The so obtained polymer showed high end functionality of dithiocarbonyl group, which was considered as versatile functional group for the further modification, such as chain extension, thiol-ene, and thiol-yne click reactions.[42-44] In the current work, we further extended the LRP system based on CPDN under green-light (λ_{max} = 565 nm, Fig. 1S) and sunlight irradiation by using $Mn_2(CO)_{10}$ as the light absorbing component and CPDN as pseudo halide initiator and chain transfer agent at moderate temperature. The introducing of light may offer the new system not only with the simplicity of catalysis system, but also realize the on and off polymerization with on and off the light source, which would be beneficial for their practical application, especially in large scale.

Experimental

Materials

Monomers, methyl methacrylate (MMA) (>99%, Aldrich), methyl acrylate (MA) (>99%, Aldrich), and styrene (St) (>99%, Aldrich) were washed with an aqueous solution of sodium hydroxide (5 wt %) three times, followed by deionized water until the solution was neutralized and dried over anhydrous magnesium sulfate. Then these monomers were distilled under reduced pressure, and stored at -18℃. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) (>99%, Aldrich) was distilled under reduced pressure before use. 9-Vinylcarbazole (NVC) was recrystallized from petroleum ether before use. Manganese carbonyl ($Mn_2(CO)_{10}$) (>98%) was purchased from Sigma-Aldrich and used as received. 2-Cyanoprop-2-yl1-dithionaphthalate (CPDN) was synthesized according to the literature, achieving a purity greater than 98% (Waters 515 HPLC; ^{1}H NMR (CDCl3): 1.95 (s, 6H), 7.42 (m, 2H), 7.51 (m, 2H), 7.85 (m, 2H), and 8.10 (m, 1H)). 2,2'-Azobis(2-methylpropionitrile) (AIBN) was purchased from Shanghai Chemical Reagents Co. Ltd. China and purified by recrystallized three times from ethanol. Tetrahydrofuran (THF) was purchased from Shanghai Chemical Reagents Co. Ltd. China and distilled under reduced pressure. All other chemicals were obtained from Shanghai Chemical Reagents Co. Ltd. China and used as received unless mentioned.

Typical procedures for the polymerization of MMA under light irradiation in the presence of $Mn_2(CO)_{10}$ and CPDN

A typical polymerization procedure for the molar ratio of $[MMA]_0/[Mn_2(CO)_{10}]_0/[CPDN]_0$ = 200/0.2/1 was as follows: the solution was prepared by mixing $Mn_2(CO)_{10}$ (0.0278 mg, 0.071 mmol), CPDN (0.0960 mg, 0.354 mmol), MMA (7.5 mL, 70.8 mmol), and THF (7.5 mL) in a dried reaction bulb (25 mL) with a stir bar. The solution was deoxygenated with three standard freeze-pump-thaw cycles and placed in a stirring apparatus under green-light irradiation supplied by a LED lamp (Chemical Machine Co. Ltd. Shanghai, China) at 40°C. After the desired polymerization time, the solution contents were extracted from the reaction bulb and dissolved in 5 mL of THF, and then precipitated into 250 mL of methanol. The polymers were isolated by filtration and dried under vacuum until a constant weight at room temperature. The monomer conversion was determined gravimetrically.

Typical procedures for chain extension of PMMA using PMMA as precursor

The PMMA sample ($M_{n,GPC}$ = 10200 g/mol, M_w/M_n = 1.14) obtained by $Mn_2(CO)_{10}$/CPDN mediated polymerization was used as the macro-mediator for the chain extension reaction. PMMA (0.2 g, 0.0196 mmol) was dissolved in fresh MMA (0.5 mL) in a 5 mL ampule. This solution was added by AIBN (0.52 mg, 0.00317 mmol) and deoxygenated by three standard freeze-pump-thaw cycles. Then the ampule was flame-sealed and placed in a stirred oil bath equipped with a thermostat in dark at 60℃. After 5.5 h, the ampule was opened and the contents were dissolved in 5 mL of THF. The rest of the procedure was identical to that described above. The monomer conversion was 41.6% by gravimetrical calculation. The Mn and Mw/Mn values were determined by GPC with PMMA standards ($M_{n,GPC}$ = 15400 g/mol, M_w/M_n = 1.11). The same solution was added by $Mn_2(CO)_{10}$ (1.22 mg, 0.00313 mmol) and placed under green-light irradiation at 40℃. The rest of the procedure was identical to that described above. The monomer conversion was 58.4%, $M_{n,GPC}$ = 17900 g/mol, M_w/M_n = 1.18).

Characterization

The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the resulting polymers were determined using a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive-index detector (Waters 2414), using HR 1, HR 2 and HR 4 (7.8 × 300 mm, 5 μm beads size) columns with molecular weights ranging from 10^2 to 5×10^5 g/mol. THF was used as the eluent at a flow rate of 1.0 mL/min at 30°C. GPC samples were injected using a Waters 717 plus autosampler and calibrated with poly(methyl methacrylate) (PMMA) and polystyrene (PSt) standards, which was purchased from Waters. PMMA was used as calibration standard for PMMA, PMA and PDMAEMA. PSt was used as standard for PNVC and PSt. The ^{1}H NMR spectrum of the polymer was recorded on an INOVA 400 MHz nuclear magnetic resonance instrument using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard.

Table 1 Solution polymerization of MMA at 40 °C, V_{MMA} = 1 mL, V_{THF} = 1 mL.

Entry	$[MMA]_0/[Mn_2(CO)_{10}]_0$ /$[CPDN]_0$	Time (h)	Conv. (%)	$M_{n, th}$[c] (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1[a]	200/0.2/0	48	0	--	--	--
2[a]	200/0/1	48	0	--	--	--
3[b]	200/0.2/1	48	0	--	--	--
4[a]	200/0.2/1	24	71.8	23900	23200	1.21

[a] Polymerization was conducted under green-light irradiation.

[b] Polymerization was conducted in dark.

[c] The value was calculated by $([MMA]_0/(0.6*[CPDN]_0))*M_{MMA}*$Conversion, where 0.6 was the residual ratio of the initial CPDN.

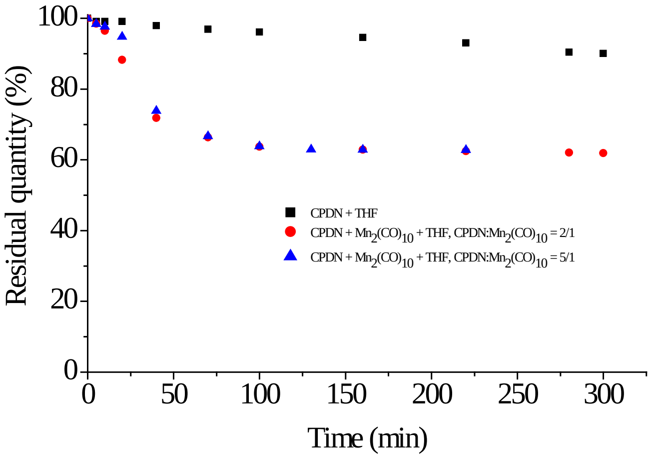


Fig. 1 Photolysis of CPDN with or without $Mn_2(CO)_{10}$ under green light irradiation at 40 °C. Condition: $[CPDN]_0$ = 0.2 mmol/L in THF.

Results and discussion

RAFT polymerization of MMA under the mediating of $Mn_2(CO)_{10}$/CPDN with or without green-light irradiation supplied by a LED lamp was investigated under different conditions. The results were summarized in Table 1.

It showed that no polymer was formed after 48 hours green-light irradiation at 40°C without CPDN or $Mn_2(CO)_{10}$ (Entries 1-2 in Table 1). It was known that the $Mn_2(CO)_{10}$ can be activated to form •$Mn(CO)_5$ under the visible light irradiation. However, the $Mn(CO)_5$ radical did not initiate the vinyl monomer. Thus, no polymer was found in Entry 1 after 48 h polymerization. The polymerization also didn't occur only with CPDN (Entry 2 in Table 1). Polymers with narrow molecular weight distribution was obtained in the mediating of $Mn_2(CO)_{10}$/CPDN under light irradiation(Entry 4 in Table 1). However, the polymerization didn't occur without the light (Entry 3 in Table 1).

The decomposition of CPDN with and without the activation of $Mn_2(CO)_{10}$ under the light irradiation was monitored, which was showed in Figure 1. It showed that CPDN was reasonable stable under the green light (residual quantity is more than 92% after 5 hours irradiation) without $Mn_2(CO)_{10}$, while 40% of CPDN was consumed within 100 min in the presence of $Mn_2(CO)_{10}$. These results indicated that the reaction was occurred between CPDN and $Mn_2(CO)_{10}$ under green-light irradiation. The polymerization could be initiated by the products formed from the reaction between CPDN and

Mn$_2$(CO)$_{10}$, which may through the way similar as the results reported by Kamigaito *et al.*, e.g. the •Mn(CO)$_5$ abstracted dithiocarbonyl moiety from CPDN to form the carbon centred radical.[26] All of these results agreed with the results showed in Table 1, which implied that CPDN could be activated by Mn$_2$(CO)$_{10}$ under green-light irradiation to form the initiating radical followed with the RAFT polymerization under the mediating of CPDN. The reaction rate of these two components was low in the initial time, e.g. at the first 10-20 min, and followed with an acceleration, which was indicated by the slow decreasing of CPDN concentration followed with sharp decreasing of CPDN concentration in Figure 1. The initial period was increased with the decreasing of Mn$_2$CO$_{10}$. It was interesting that the residual quantity of CPDN was achieved almost constant value of 60% with different molar ratio between CPDN and Mn$_2$(CO)$_{10}$ after irradiation of 60 min. Such results indicated that about 60% of initial CPDN was remained as the mediating agent for the polymerization. The calculated molecular weight according to this value was close to the GPC determined molecular weight in the polymerization (Entry 4 in Table 1), which confirmed such result.

Effect of the temperature of this system

The light-induced polymerization could be conducted in relative low temperature, such as room temperature. For the current system, the effect of temperature on the polymerization was investigated. The kinetics of the light-induced polymerization of MMA was studied with the mediating of CPDN and Mn$_2$(CO)$_{10}$ under green-light irradiation at 20°C, 30°C, 40°C, and 50°C respectively. The results were summarized in Figure 2. It indicated that the polymerization showed an induction period of about 3h in all of the different temperatures. The induction period in this system may be caused by the time for decomposition of Mn$_2$(CO)$_{10}$ and followed with the reaction between •Mn(CO)$_5$ and CPDN to generate the real initiator, •C(CH$_3$)$_2$CN, which agreed with the results showed in Figure 1. After the induction period, the polymerization took place smoothly. The polymerization rate was slightly dropped after about 20 h at 20°C and 30°C. After increasing the temperature to 40°C and 50°C, linear relationship between ln([M]$_0$/[M]) and polymerization time was observed (Fig. 2) in the investigated time, which implied that a constant concentration of the propagating free radicals can be achieved in these conditions. As shown in Fig. 2, the polymerization rate was increased with the increasing of the temperature, which may due to the increase of equilibrium constant in RAFT polymerization after the increasing of the temperature.

The derivation of the molecular weight and molecular weight distribution with conversion were shown in Fig. 3. The molecular weights of the polymers were linearly increased with conversion till high conversion at 40°C and 50°C. All of the obtained polymers showed narrow molecular weight distributions (M_w/M_n < 1.2, Fig. 3) at all of the investigated temperatures. The GPC traces of all polymers were unimodal profiles with normal distribution which were showed in Fig. 2S.

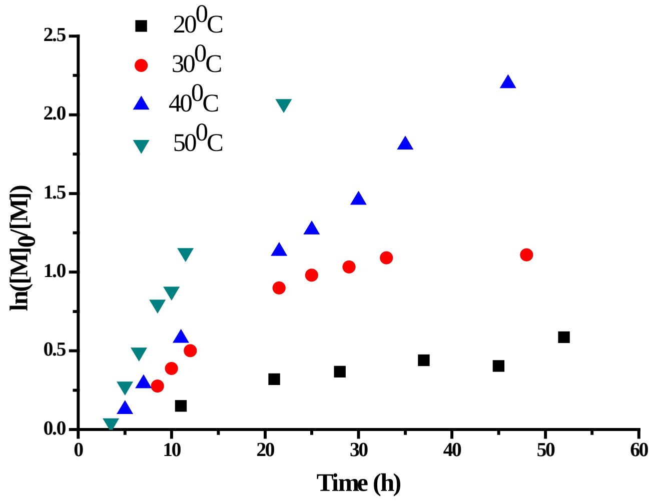


Fig. 2 Kinetic investigation (ln([M]$_0$/[M]) versus time) of the photo-induced RAFT solution polymerization of MMA in the presence of CPDN and Mn$_2$(CO)$_{10}$ at various temperature under green-light irradiation (λ_{max} = 565 nm), [MMA]$_0$/[Mn$_2$(CO)$_{10}$]$_0$/[CPDN]$_0$ = 200/0.2/1, V_{MMA} = V_{THF} = 7.5 mL.

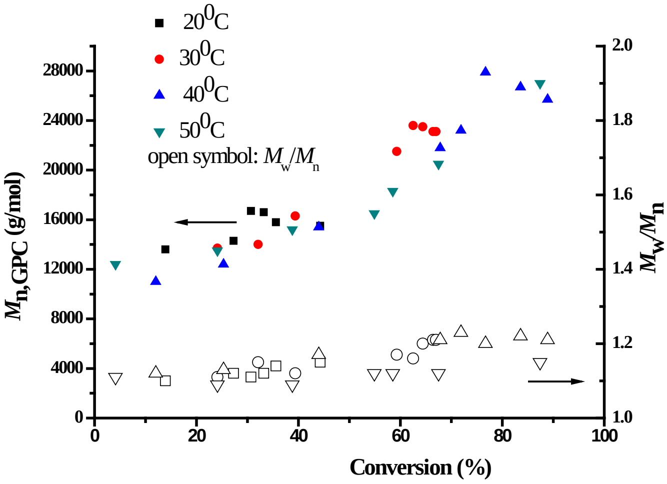


Fig. 3 Number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the PMMAs from the photo-induced RAFT solution polymerization, which were conducted in the presence of CPDN and Mn$_2$(CO)$_{10}$, versus the conversion at various temperature under green-light irradiation (λ_{max} = 565 nm), [MMA]$_0$/[Mn$_2$(CO)$_{10}$]$_0$/[CPDN]$_0$ = 200/0.2/1, V_{MMA} = V_{THF} = 7.5 mL.

All of these evidence indicated that the polymerization of MMA was well-controlled at moderate temperature (higher than 40°C) in the presence of CPDN and Mn$_2$(CO)$_{10}$ under green-light irradiation.

Effect of the feeding molar ratio

To further understand the polymerization behaviour, the kinetic of photo-induced RAFT polymerization of MMA was investigated with different feeding molar ratios of CPDN and Mn$_2$(CO)$_{10}$ under green-light irradiation at 40℃. As shown in Fig. 4, the polymerization showed induction period in all of the investigated feeding ratios. It was interesting that the duration of induction time can be reduced by increasing the amount of Mn$_2$(CO)$_{10}$. Such result indicated that the induction period may

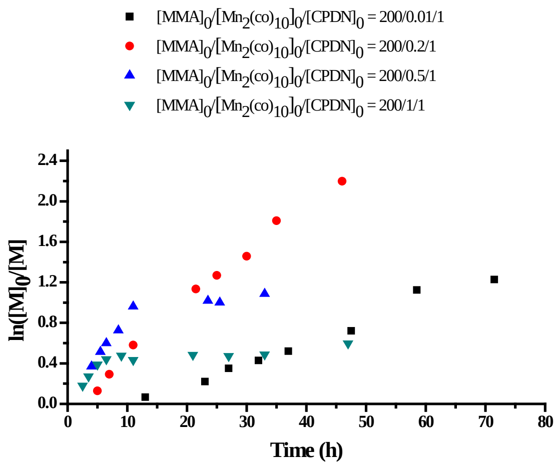


Fig. 4 Kinetic investigation (ln([M]$_0$/[M]) versus time) of the photo-induced RAFT solution polymerization of MMA in the presence of CPDN and $Mn_2(CO)_{10}$ at various [MMA]$_0$/[$Mn_2(CO)_{10}$]$_0$/[CPDN]$_0$ ratios under green-light irradiation (λ_{max} = 565 nm) at 40 °C, $V_{MMA} = V_{THF}$ = 7.5 mL.

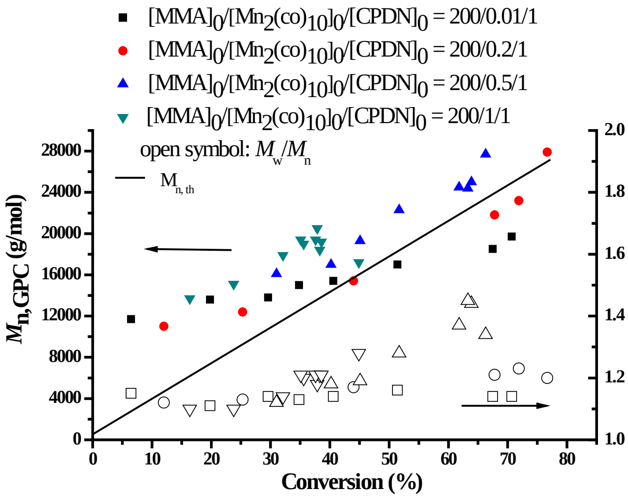


Fig. 5 Number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the PMMAs from the the photo-induced RAFT solution polymerization, which were conducted in the presence of CPDN and $Mn_2(CO)_{10}$, versus the conversion at various [MMA]$_0$/[$Mn_2(CO)_{10}$]$_0$/[CPDN]$_0$ ratios under green-light irradiation (λ_{max} = 565 nm) at 40℃, $V_{MMA} = V_{THF}$ = 7.5 mL.

be caused by the time consumed in the formation of real initiation radical between the reaction of $Mn_2(CO)_{10}$ and CPDN under the light irradiation. Increasing the molar ratio of $Mn_2(CO)_{10}$/CPDN would evidently speed up such reaction, which resulted in the decreasing of induction period. After the induction period, linear relationship between ln[M]$_0$/[M] and the polymerization time was observed in the cases of [MMA]$_0$/[$Mn_2(CO)_{10}$]$_0$/[CPDN]$_0$ = 200/0.01/1 and 200/0.2/1, while the ln[M]$_0$/[M] researched a constant value after 12 h and 7 h in the cases of [MMA]$_0$/[$Mn_2(CO)_{10}$]$_0$/[CPDN]$_0$ = 200/0.5/1 and 200/1/1 respectively. Furthermore, the highest conversion can be reached was decreased from 59.3% to 34.3% with the increasing of the molar ratio from [$Mn_2(CO)_{10}$]$_0$/[CPDN]$_0$ = 0.5/1 to 1/1. The increasing of molar ratio between [$Mn_2(CO)_{10}$]$_0$/[CPDN]$_0$ increasing the concentration of initial free radicals, which may cause the accumulation of uncontrolled transfer and termination reactions, and finally terminated the polymerization. At the same time, due to the increasing of initial free radical concentration, the polymerization rate was increased by increasing the molar ratio of [$Mn_2(CO)_{10}$]$_0$/[CPDN]$_0$.

The derivation of the molecular weight and molecular weight distribution with conversion were shown in Fig. 5. The molecular weights of the polymers were linearly increased with the conversions. The GPC determined molecular weight was close to the value calculated by assuming 0.6 of initial CPDN remained after it reacted with Mn_2CO_{10}, especially at high conversions. As shown in Fig. 5, the obtained polymers showed narrow molecular weight distributions (M_w/M_n <1.22) in the case of [MMA]$_0$/[$Mn_2(CO)_{10}$]$_0$/[CPDN]$_0$ = 200/0.01/1 and 200/0.2/1. However, the polymers showed broad molecular weight distributions in other two cases at high conversion, which also indicated the accumulation of uncontrolled reaction was serious in cases of high molar ratio of [Mn_2CO_{10}]/[CPDN] due to the high concentration of initial radical. The GPC traces of the polymers were showed in Fig. 3S as unimodal profiles with normal distribution. All of these results showed that well-controlled photo-induced RAFT polymerization of MMA can be realized under green-light irradiation at mild temperature by choosing the appropriate conditions.

Effect of irradiation on the polymerization process

A surpassing advantage of the light-induced LRP was the possibility of stopping and restarting the polymerization proceed just via turning on or off the light.[20, 32] Here, the effect of green-light irradiation on the polymerization of MMA was investigated by employing a periodic light on–off process (Fig. 6). As shown in Fig. 6a, under the mediating of CPDN and $Mn_2(CO)_{10}$, the MMA polymerization only proceeded while the LED irradiation occurred. There was essentially no polymerization in the absence of green-light irradiation, instead, the molar weight (Fig. 6b) of the polymers and the conversion (Fig. 6 a) of MMA had slight decrease (about 300-500), which may attribute to the calculation error and/or the decay for the violent stir. The polymerization was “woke up” when the mixture was exposed to green-light irradiation again, which proceeded with the similar polymerization rate as that observed in the former light-on process. Even the reason was remained unknown, it implied that light irradiation not only controlled the initiation steps, but also availably impacted on the chain growth during the polymerization process. Furthermore, the polymers obtained from all of the polymerization process showed narrow molecular weight distributions (M_w/M_n < 1.20). The GPC traces of the polymers showed unimodal profiles (Fig. 4S).

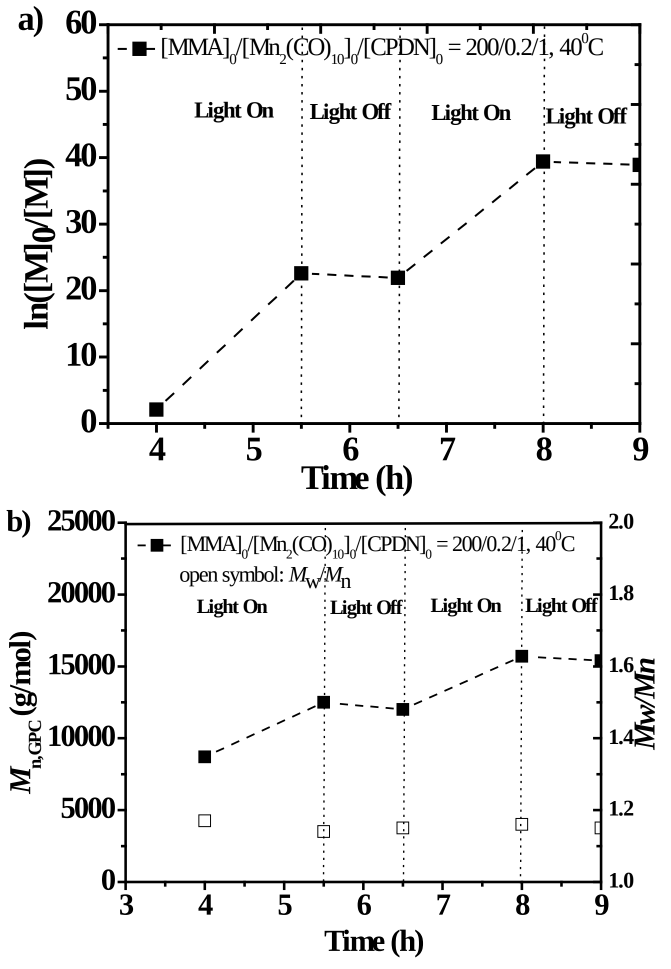


Fig. 6 a) Conversion, and b) number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) versus time of the bulk polymerization of MMA with light and dark (on and off) periods in the presence of CPDN and $Mn_2(CO)_{10}$ at 40 °C, $[MMA]_0/[Mn_2(CO)_{10}]_0/[CPDN]_0$ = 200/0.2/1, V_{MMA} = 10 mL.

Analysis of Chain End and Chain Extension

The structure of the polymer was analysed by ^{1}H NMR to show some information of the polymerization process. As shown in Fig. 7, the chain ends of the PMMA ($M_{n.GPC}$ = 15200 g/mol, M_w/M_n = 1.17), prepared in the presence of CPDN with $Mn_2(CO)_{10}$ under green-light irradiation at 40 °C, was determined by ^{1}H NMR spectroscopy. The chemical shifts at δ = 7.40 - 8.15 ppm (7H, integral value: $I_{8.15}$ = 0.30) were assigned to the aromatic protons of the naphthalene units in CPDN, which indicated that the dithiocarbonyl moieties of CPDN were successfully attached to the polymer chain ends (ω chain end). The signals at δ = 3.40 - 3.80 ppm in the ^{1}H NMR spectrum were corresponded to the protons of methoxy in PMMA repeat units (3H, integral value: $I_{3.60}$ = 20.19). Assuming that each polymer chain of PMMA was captured by one naphthyl moiety from CPDN, the molecular weight ($M_{n,NMR}$) of PMMA can be calculated from the integrals in ^{1}H NMR, according to the following formula (eq 1):

$$M_{n,NMR}\ (\mathrm{g/mol}) = (I_{3.60}/3) \times 100.1/(I_{8.15}/7) + 271.5 \qquad (\mathbf{1})$$

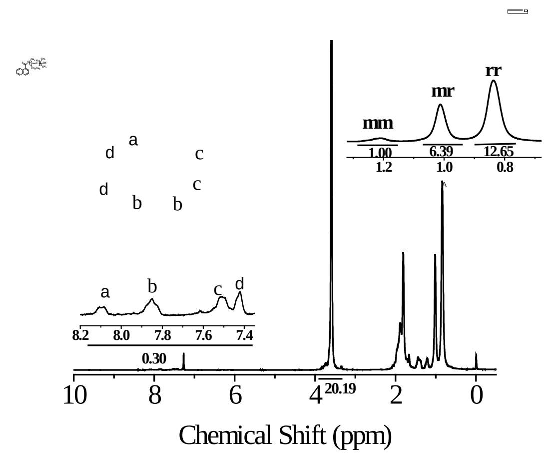


Fig. 7 ^{1}H NMR spectrum of poly(Methyl methacrylate) (PMMA, 37.5% conversion, $M_{n,GPC}$ = 15200 g/mol, M_w/M_n = 1.17) obtained from the photo-induced RAFT polymerization in the presence of CPDN and $Mn_2(CO)_{10}$ under green-light irradiation at 40 °C, $[MMA]_0/[Mn_2(CO)_{10}]_0/[CPDN]_0$ = 200/0.2/1. $CDCl_3$ was used as the solvent and Tetramethylsilane (TMS) as the internal standard.

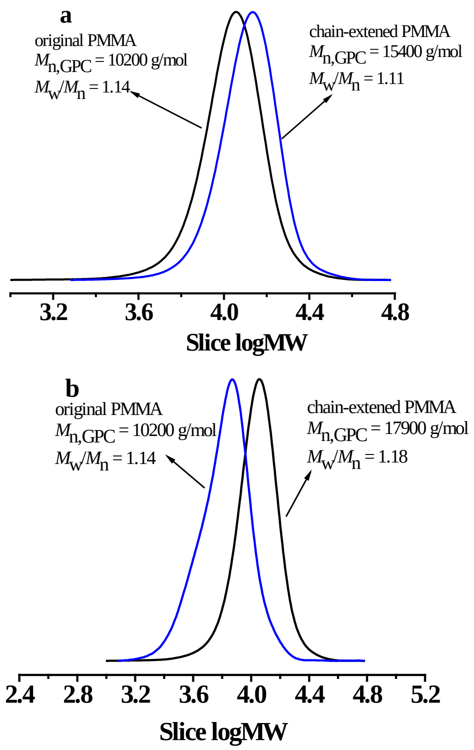


Fig. 8 GPC curves before and after chain extension with poly(Methyl methacrylate) (PMMA) as the macroinitiator/mediators: (a) $[MMA]_0/[PMMA]_0/[AIBN]_0$ = 240/1/0.2, V_{MMA} = 0.5 mol, in dark, T = 60℃, 5.5 h, 41.6% conversion; (b) $[MMA]_0/[PMMA]_0/[Mn_2(CO)_{10}]_0$ = 240/1/0.2, V_{MMA} = 0.5 mL, under green-light irradiation, T = 40 °C, 2.5 h, 58.4% conversion. The original PMMA was obtained from the photo-induced RAFT bulk polymerization of MMA under green-light irradiation in the presence of CPDN and $Mn_2(CO)_{10}$ at 40 °C.

where 271.5 and 100.1 were the molecular weights of CPDN and MMA, respectively. It was found that the molecular weights of PMMA calculated from the ^{1}H NMR spectrum ($M_{n,NMR}$) was 15990 g/mol, which was close to the GPC value, 15200 g/mol. These results indicated that the PMMA was end-capped by CPDN species with high fidelity. Moreover, the signals at about 0.81, 1.01 and 1.17 ppm (^{1}H NMR) were attributed to syndiotactic (rr), atactic (mr), and isotactic (mm) methyl groups, respectively. The tacticity of the obtained PMMA was calculated with 5.0% mm, 31.8% mr and 63.2% rr triads, which agreed with the tacticity distribution for common radical polymerization of MMA. Such result further confirmed that the polymerization was via a radical-mediated mechanism.

To further investigate the "living" characteristic, the PMMA ($M_{n,GPC}$ = 10200 g/mol, M_w/M_n = 1.14), prepared by photo-induced RAFT polymerization under green-light irradiation in the presence of CPDN and $Mn_2(CO)_{10}$, was used as predecessor in the chain-extension experiments with two different conditions. One part of the PMMA sample was dissolved in fresh MMA with AIBN, and conducted in dark at 60 °C, while another part of PMMA sample was dissolved in fresh MMA with $Mn_2(CO)_{10}$, and conducted under green-light irradiation at 40℃. As shown in Fig. 8a and 8b, there have clearly been peaks shift from the original PMMAs to the chain-extended PMMAs, which showed obvious larger molecular weights than the original PMMAs' with narrow molecular weight distributions, e.g. from the original of 10200 g/mol, M_w/M_n = 1.14 to 15400 g/mol, M_w/M_n = 1.11 and 17900 g/mol, M_w/M_n = 1.18, respectively. The GPC traces of the chain-extended PMMAs showed unimodal distribution. These results confirmed the features of the controlled/"living" polymerization of MMA under green-light irradiation in the presence of CPDN and $Mn_2(CO)_{10}$ at 40°C. The end dithiocarbonyl moiety not only could be acted as regular RAFT agent, but also could be further activated by $Mn_2(CO)_{10}$.

Furthermore, the residual quantity of manganese-metal in PMMA was characterized by ICP-AES as 2.36×10^{-3} mg Mn-metal of 1 g PMMA, which almost can be ignored in most of the cases. Such result was another evidence for the assuming that Mn_2CO_{10} and related $\bullet MnCO_5$ were just the activator for CPDN. They were excluded in the polymerization process.

Application of this system to other monomers

The green-light irradiation light-induced polymerization under the mediating of $Mn_2(CO)_{10}$/CPDN was also applied to several other monomers under the same conditions as the polymerization of MMA. Table 2 shows the polymerization results. As shown in the results, monomers, such as NVC (normally was considered as the unconjugated monomer, Entry 1, Table 2), MA (Entry 2, Table 2), St (Entry 3, Table 2), and DMAEMA (Entry 4, Table 2) could be polymerized under controlled manner. Polymers with narrow molecular weight distributions were obtained. Such results indicated the wide monomer application of the current system. However, the conversion in case of NVC was limited at about 15% due to the high activity of NVC radical.

Table 2 The polymerization of different monomers under green light irradiation in the presence of CPDN and $Mn_2(CO)_{10}$[a].

Entry	Monomer	Time (h)	Conv. (%)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	NVC[b]	72	10.1	2600	1.22
2	St[c]	144	31.3	11600	1.23
3	MA[c]	96	35.0	15900	1.10
4	DMAEMA[b]	3.5	60.0	19600	1.37
5	MMA[d]	6.5	63.1	17400	1.30

[a] $[Monomer]_0/[Mn_2(CO)_{10}]_0/[CPDN]_0$ = 200/0.2/1; $V_{St/MA/DMAEMA/MMA}$ = 2 mL, m_{NVC} = 0.7 g; Solution polymerization of NVC using 1,4-dioxane (1 mL) as solvent; St, MA, DMAEMA were polymerized in bulk.

[b] The polymerization was conducted at 40 °C.

[c] The polymerization was conducted at 50 °C.

[d] Bulk polymerization of MMA under sunlight irradiation at 40 °C.

Furthermore, the current polymerization system was also conducted under sunlight (Entry 5, Table 2). The PMMA was obtained with relative high molecular weight distribution (M_w/M_n = 1.30), which may due to that the sunlight covers a broad energy band including infrared, visible, and ultra-violet light, X-rays and gamma rays.[45] The light with short wavelength may cause the undesired decomposition of CPDN, which would evidently increase the possibility of the uncontrolled polymerization.[24] However, the GPC trace of the polymer still showed unimodal profiles (Fig. 5S).

Conclusions

The photo-induced RAFT polymerization of Methyl methacrylate was successfully carried out using manganese carbonyl [$Mn_2(CO)_{10}$] as photosensitizer, and 2-cyanoprop-2-yl1-dithionaphthalate (CPDN) as photoinitiator and regulator, under green-light irradiation (λ_{max} = 565 nm) at moderate temperature. Poly(methyl methacrylate) with narrow molecular weight distribution (M_w/M_n < 1.20) and controlled molecular weight was obtained. The remained Mn-metal was very few (ppm level), which almost can be ignored in most application cases. The current polymerization protocol can be successfully applied to unconjugated monomer (9-vinylcarbazole), some other common conjugated monomers (styrene and methyl acrylate), and the water-soluble monomer, 2-(dimethylamino)ethyl methacrylate. Furthermore, the polymerization process can be stopped and started simply by turning on or off the LED light. The present LED induced RAFT polymerization system can be used as an easy, convenient and inexpensive process to conduct the living radical polymerization of several kinds of monomers, which broaden the scope of light-induced LRP. Such polymerization system also can be activated by the sunlight, which increased the versatility of its application. Furthermore, the polymer synthesized by the current protocol containing similar dithiocarbonyl moiety as RAFT, which offered the potential modification for further applications.

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Notes and references

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Graphical Abstract

Dimanganese decacarbonyl/2-cyanoprop-2-yl 1-dithionaphthalate: toward sunlight induced RAFT polymerization of MMA

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