A Remarkable Visible Light Effect on Atom-Transfer Radical Polymerization[†]

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Introduction

Living polymerizations offer the opportunity for better control on molecular weight, polydispersity, functional groups, and macromolecular architectures.[1] In principle, "living" radical polymerization is more practical than other types of living polymerizations because of the robust features of radical reactions. Though a true living radical polymerization (without termination and chain-transfer reaction) is difficult to achieve due to the high reactivity of free radicals, significant progress has been made in this area, and several controlled/"living" radical polymerization systems have been developed in recent years.[2−18] In all these systems, a reversible termination equilibrium is utilized to suppress radical termination reactions by reducing the stationary concentration of growing radicals. Stable organic radicals such as 2,2,6,6-tetramethylpiperidinyloxy (TEMPO)[3,5−8] and organometallic radicals such as cobalt−porphyrin complexes[9] have been used successfully to control radical polymerization of styrene and acrylate monomers, respectively. Living radical polymerization with reversible addition−fragmentation chain transfer (RAFT) can be achieved with the use of dithiocarbamate derivatives.[10] Recently, atom-transfer radical addition reaction (or Kharasch reaction) has been applied successfully to control radical polymerizations of a variety of vinyl monomers.[11−18]

Since the initial reports of atom-transfer radical polymerization (ATRP) in 1995,[11−16] ATRP has generated wide interest as a promising new class of controlled/"living" radical polymerization methods. ATRP has been applied to the polymerizations of various vinyl monomers to control their molecular weight and polydispersity.[11−18] *However, the current catalysts reported in the literature are generally not very active, and hence relatively large amounts of catalyst were used in the reported polymerizations*.[11−18] This not only increases the cost of the polymerization process but also requires postpolymerization catalyst removal. This problem becomes more serious in making low molar mass polymers. *Therefore, it is important to find a process in which the catalyst level can be significantly reduced*. It was reported recently that ATRP can be carried out in the presence of a relatively small amount of catalyst when either a large amount of initiator is used such as in self-condensing vinyl polymerization[19] or a zerovalent metal is added.[20] It was also reported that carboxylate salts can enhance the rate of some ATRP systems.[21] However, in general, the catalysts for ATRP were used stoichiometrically relative to the initiators.

We recently discovered that visible light significantly effects the ATRP of MMA.[22] At reduced catalyst concentration, the ATRP of MMA under irradiation of visible light is faster and reaches much higher final monomer conversion compared to the corresponding polymerization in the dark. Kinetic studies revealed that the living character (or control of the polymerization) of ATRP at reduced catalyst concentration was better for photoenhanced ATRP than dark ATRP.

Results and Discussion

The polymerization data are summarized in Table 1. Entries 1 and 2 were conducted under the same conditions (with the ratio of [MMA]/[RCl] = 100/1 and [CuCl]/[bipy]/[RCl] = 0.1/0.3/1) except that entry 2 was irradiated with visible light and entry 1 in the dark.[23] After polymerization at 80 °C for 16 h, the monomer conversion reached only 41% for ATRP in the dark.[24] Kinetic studies revealed that the polymerization in the dark actually stopped after 6 h (Figure 1), which is presumably due to deactivation of the catalyst. In contrast, the same polymerization irradiated with visible light reached 100% monomer conversion (entry 2, Table 1). Figure 1 demonstrates that visible light accelerates the polymerization significantly. In about 6 h, 80% of the monomer was polymerized under irradiation. The molecular weight data in Table 1 show that the photoenhanced ATRP is under good control. The number-average molecular weight is very close to the theoretical value, and the polydispersity is relatively narrow.

Control experiments were run with no initiator (entry 3) or no catalyst (entry 4). Without RCl initiator and/or CuCl/bipy catalyst, the polymerization was not controlled as evidenced by the very high molecular weight and the broad polydispersity of the resulting polymers. With the addition of a small amount of catalyst (at the ratio of CuCl/bipy/RX = 0.02/0.06/1) (entry 5), 75% monomer conversion was obtained in 16 h, and the molecular weight was controlled with relatively narrow polydispersity. Therefore, the photoeffect is through the enhancement of ATRP instead of simple photoinitiation.[25] The practical significance of the photoenhancement is that the catalyst level can be reduced by almost 2 orders of magnitude without sacrificing the rate and living character of the polymerization.

Figure 2 compares the first-order kinetic plots for ATRP in the dark and under irradiation of visible light. For polymerization under visible light, the linear relationship of $\ln([M]_0/[M])$ with time demonstrates the first-order kinetics for monomer consumption, and the concentration of radicals was constant throughout the polymerization, indicating a good living character of the polymerization. In contrast, the dark ATRP did not show good living character.[26] The good living character of light-enhanced ATRP was confirmed by the linear increase of molecular weight with monomer conversion and the narrow PDI (Figure 3).

The precise mechanism of the visible light enhancement of ATRP is not clear. The mechanism of Kharasch type reactions or atom-transfer radical reactions is generally considered to be an electron-transfer reaction accompanied by a halogen atom transfer.[27,28] Photons promote electron-transfer processes in general.[29] A visible light induced halogen-transfer reaction was

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Table 1. Results of MMA Polymerization[a]

entry	MMA (mmol)	RCl (mmol)	CuCl (mmol)	conversion (%)	GPC $M_n \times 10^{-4}$ (PDI)	$M_n \times 10^{-4}$ (calcd)[b]
1[c]	47	0.47	0.050	41	0.48 (1.42)	0.41
2	47	0.47	0.050	100	1.05 (1.25)	1.00
3	94	0	0	19	59.2 (2.25)	N/A
4	94	0.94	0	87	3.58 (2.52)	0.87
5	94	0.94	0.020	75	1.23 (1.33)	0.75

[a] All polymerizations used 50 v/v % solution in toluene at 80 °C for 16 h.[16] In all polymerizations the ratio of [MMA]/[RCl] = 100, and [bipy]/[CuCl] = 3. The initiator RCl was 2,2-dichloroacetophenone. Polymerization entries 2−4 were carried out under irradiation of a 275 W sunlamp. [b] The theoretical M_n was calculated from M_n (calc) = MW([MMA]/[RCl])(conversion/100), where MW is the molecular weight of MMA. [c] This polymerization was carried out in the dark for comparison.

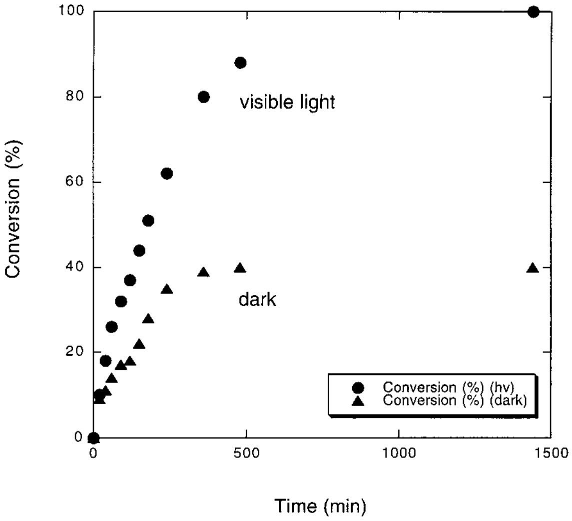


Figure 1. Conversion−time curves for both dark and photoenhanced ATRP of MMA.[22,23] The conditions for both polymerizations were identical except with or without visible light irradiation. Polymerization was conducted at 50 vol % MMA solution in toluene with 2,2′-dichloroacetophenone (RCl) as initiator and CuCl/2,2′-dipyridyl as catalyst with MMA/RCl/CuCl/Bipy = 100/1/0.1/0.3.

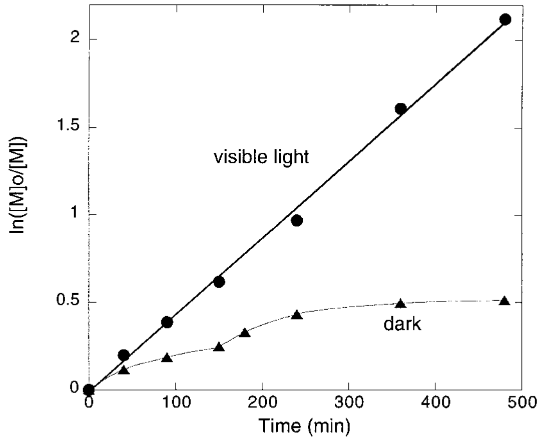


Figure 2. First-order kinetic plots for both dark and photoenhanced ATRP of MMA. The experimental conditions were identical to those in Figure 1.

reported many years ago in Taube's classical studies on atom-transfer reactions of inorganic species such as $Pt^{IV}Cl_6$.[30] Osborn et al. reported later that irradiation with visible light (436 nm) greatly accelerated oxidative addition of some organic halides on some Ir^I complexes via a radical mechanism.[31] The visible light effect was also observed in the oxidative addition of α-bromo esters to Rh^I complexes.[32] In this case, the photochemical effect was attributed to the activation of charge-transfer complexes formed between the α-bromo esters and the Rh^I complexes, [Rh^I, RBr].[32] In our ATRP under irradiation of visible light, the low-energy light source (sunlamp) is clearly insufficient to cause fission of RCl bond by a direct photolytic process.[33] The photochemical effect may be through the activation of the inner-sphere complex[28] between the catalyst and the alkyl chloride, [Cu^I, RCl], or through the activation of the catalyst alone. Since UV/vis spectra indicate that a charge-transfer complex forms between the catalyst and the initiator,[34] we tentatively propose that the mechanism for the photoenhancement on ATRP is through the photoactivation of the inner-sphere complex [Cu^I, RCl].

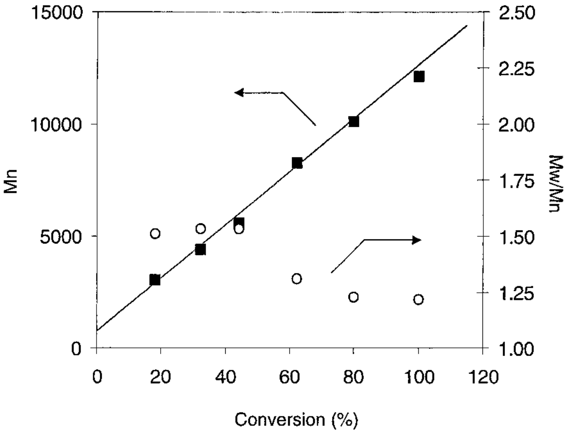
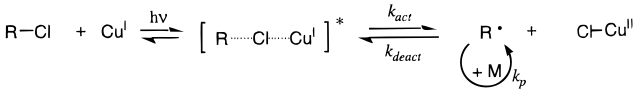


Figure 3. Dependence of M_n (EnDash○) and polydispersity (■) on conversion for photoenhanced ATRP of MMA. The experimental conditions were identical as described in Figure 1.



The photoexcitation of the inner-sphere complex accelerates the dynamic equilibrium of chlorine atom transfer and, hence, promotes the polymerization. Because of the faster dynamic equilibrium under irradiation, the catalyst level can be reduced to a lower level. Since the deactivation of the active propagating radical is a very fast process,[12−15] the polymerization is still under good control.

In summary, we have discovered a significant photochemical effect of visible light on ATRP of MMA. The irradiation of visible light on ATRP of MMA not only accelerates the polymerization but also improves the living character of the polymerization at low catalyst level. By using visible light, the catalyst level for ATRP can be significantly reduced. The reduction in catalyst concentration is important in order to apply ATRP practically.

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Supporting Information Available: Wavelength profile for the sunlamp used in the photopolymerizations and UV/vis spectra of CuCl/bipy and CuCl/bipy/2,2′-dichloroacetophenone in methylene chloride. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Typical experimental polymerization conditions: CuCl (5.0 mg, 0.050 mmol) and 2,2′-dipyridyl (24 mg, 0.15 mmol) were put into degassed toluene (5.0 mL). Purified MMA (5.0 mL, 0.047 mol) and 2,2′-dichloroacetophenone (66 μL, 0.48 mmol) were added. The solution was mixed well, sealed under nitrogen, and then immersed in an oil bath at 80 °C. Polymerization was continued at 80 °C under the irradiation of a 275 W sunlamp for 16 h. The solution was diluted with more toluene and then precipitated into methanol. Solid polymer was filtered, rinsed with methanol, and dried under vacuum (4.75 g of polymer, 100% conversion of MMA). The polymer was analyzed by GPC with THF as eluent and PMMA as standard. The number average molecular weight (M_n) was 10 500, and M_w/M_n was 1.25.

(24) The conversion of the polymerization at the same conditions under regular laboratory light (50%) is slightly higher than in total darkness (41%). The monomer conversions were followed by ^{1}H NMR. Each aliquot was extracted with EDTA solution to remove copper ions and then dissolved in $CDCl_3$ for ^{1}H NMR measurement. The monomer conversion was calculated from the integrals of MMA vinyl protons and the ester methyl protons of both MMA and PMMA.

(25) We have conducted two additional experiments to verify the photoeffect: (a) We used a less photoactive initiator (1,1,1-trichloroacetone) for ATRP and observed similar visible light effect (90% conversion for MMA polymerization with irradiation and 50% conversion for the same polymerization in dark). This supports that the observed photoeffect is not simply due to more supply of radicals by the photoreaction of 1,1′-dichloroacetophenone. (b) We have conducted a two-step ATRP of MMA with the initiation in dark for 1 h followed by irradiation of the 275 W sunlamp. We obtained exactly the same results (100% conversion in 16 h) as the polymerization done under irradiation all the time. This supports that the photoacceleration is linked to the propagation instead of the additional flux of radicals in the initiation step.

(26) From slopes of the plots, the apparent rate constants for the polymerizations (k_{app}) were calculated to be 7.28×10^{-5} s^{-1} for polymerization under irradiation and 3.03×10^{-5} s^{-1} for initial polymerization in the dark.

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(33) The light source contains very little amount of UV light with the majority of the light in the visible and infrared region (Supporting Information). The temperature of all polymerizations was controlled by a constant-temperature bath. The Pyrex glass of both the reaction flask and the constant temperature oil bath should filter off any small fraction of UV light from the light source. We also did ATRP polymerization with low-pressure mercury UV lamp as the light source, and the control of polymerization was poor. This provides strong evidence that the observed photoeffect is not due to simple photolysis of RCl initiator but, instead, is due to the enhancement of ATRP.

(34) The CuCl/bipy complex absorbs at two bands with λ_{max} at 335 and 443 nm. With the addition of the alkyl chloride initiator, the two bands are shifted to longer wavelength: one at 397 nm and the other broad band with λ_{max} at 722 nm (Supporting Information). This suggests the formation of a charge-transfer complex between the metal complex and the alkyl chloride.

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