Photo-Induced Living Radical Polymerization via Organic Catalysis

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Photo-controlled organocatalyzed living radical polymerization was developed. The polymerization was induced and controlled at desired wavelengths over a wide range of wavelengths (350-750 nm) by exploiting suitable catalysts. This polymerization was finely responsive to the irradiation power and wavelength. The polymer molecular weight and its distribution ($M_w/M_n = 1.1–1.4$) were well controlled for methacrylate monomers. The monomer scope encompassed various functional methacrylates, and their block copolymers were obtained. Applicability to a wide range of polymer designs is an advantage of this polymerization.

Keywords: Photolysis, living radical polymerization, organic catalysis, temporal control, wavelength responsiveness

1. Introduction

Living radical polymerization (LRP) has attracted increasing attention as an efficient tool for designing polymer architectures with predictable molecular weights and narrow molecular weight distributions [1,2]. Mechanistically, LRP is based on the reversible activation of a dormant species (Polymer-X) to a propagating radical (Polymer$^*$) (Scheme 1a). A sufficiently large number of activation-deactivation cycles are required to achieve low polydispersity. In addition to thermal heating, photo irradiation has been utilized to control several LRP systems [4-19]. A restriction of the current systems is that the feasible wavelength is nearly fixed in each system. Also, wavelengths longer than 600 nm have never been utilized in any systems. A wider range of the feasible wavelengths could be highly beneficial for increasing the scope of photo LRP.

We recently developed a new family of LRP, reversible complexation-mediated polymerization (RCMP) [20-23]. RCMP uses iodine as X (capping agent) and organic amines and organic salts as catalysts to drive the reversible activation (Scheme 1b). RCMP and our related LRP system [24-26] are the first LRP systems to use organic catalysts. An advantage of RCMP is that no special capping agents or metals are used. The catalysts are inexpensive, relatively non-toxic, easy to handle, and amenable to a variety of functional groups and monomers. Another useful feature is that RCMP can be controlled photochemically [22,23] as well as thermally [20,21].

(a) Reversible activation (general scheme)

(b) RCMP

In this review, we briefly summarize the concept, polymerization performance, and applications of this photo-controlled RCMP (photo RCMP) [22,23]. This system is an ideal on-off switchable system by an external photo stimulus and that the polymerization rate ($R_p$) is also finely tunable by the photo irradiation power. RCMP is unique in that organic molecules with generous structures...
can serve as catalysts. This aspect allows us to utilize various organic molecules with different absorption wavelengths as catalysts in photo RCMP. We can thus expand the range of feasible wavelengths to 350-750 nm, and can also selectively control the polymerization at desired wavelengths by exploiting suitable catalysts. The feasibility over the whole visible region was unprecedented.

2. Results and discussion

2.1. Concept

RCMP is based on a reaction of Polymer–I with a catalyst to reversibly generate Polymer

\[ \text{Polymer}^* \] (Scheme 1b). The catalyst initially coordinates with the iodine of Polymer–I to form a complex, and the C-I bond of the complex is subsequently thermally or photochemically dissociated. We propose a mechanism (Scheme 2) in which the catalyst operates as an antenna that absorbs the light and transfers the energy to cleave the C–I bond of the complex.

2.2. Absorption Spectra

Figure 1 shows the structures and abbreviations of the initiating dormant species (alkyl iodide), CP-I, and the four catalysts, TBA, C1-DCI, DHMI, and C3-DCI, studied in this work. Figure 1 also shows the absorption spectra of CP-I only and a mixture of CP-I and a catalyst. The spectrum of CP-I showed a peak at 280 nm that extended to approximately 400 nm (black line). A new shoulder peak appeared in the spectrum of the mixture of CP-I and TBA and ranged from 350 nm to 450 nm (blue line). This shoulder peak corresponds to a complex of CP-I and TBA. Thus, we can use a wavelength between 350 nm and 450 nm for the TBA system. The mixtures of CP-I with C1-DCI (green line), DHMI (orange line), and C3-DCI (red line) exhibited longer absorption wavelengths. The peak maxima for these three mixtures were located at 530, 600, and 720 nm, respectively. With these catalysts, we can use longer wavelengths to control the polymerization.

2.3. Polymerization of MMA and Temporal Control

We carried out a bulk polymerization of methyl methacrylate (MMA) (100 eq) with CP-I (1 eq) and TBA (0.25 eq) irradiated at 350-450 nm at ambient temperature. The light source was a xenon lamp, equipped with band-pass optical mirror and filter. Figure 2 demonstrates temporal control of
the polymerization. The lamp was turned on and off at every 30 min in four cycles. When the lamp was turned on, the system was switched “on” and the polymerization smoothly proceeded in all cycles. When the lamp was turned off, the system was immediately switched “off” and perfectly no polymerization occurred in the dark. This system is an ideal photo on-off switchable system. Also importantly, $R_p$ was finely tuned by the lamp power. At the studied 30, 60, 30, and 120 W lamp powers in the four cycles, the incremental monomer conversion was 5, 12, 5, and 25 %, respectively, in each 30 min polymerization. Thus, $R_p$ was finely tunable according to the lamp power. The $M_n$ and polydispersity were also well controlled after the very initial stage of polymerization.

2.4. Polymerization over a Wide Range of Wavelengths

We then expanded the feasible wavelength. We studied polymerizations of MMA (100 equiv) containing CP-I (1 equiv), and TBA (0.25 equiv), C1-DCI (0.125 equiv), DHMI (0.5 equiv), or C3-DCI (0.25 equiv) as a catalyst. Because the absorption wavelength was complementary among the four catalysts (Figure 1), we were able to select suitable catalysts to desired wavelengths. Figure 3 and Table 1 present controlled polymerizations at 400 ($\pm$ 10) nm (TBA), 500 ($\pm$ 10) nm (C1-DCI), 600 ($\pm$ 10) nm (DHMI), and 700 ($\pm$ 50) nm (C3-DCI).

![Figure 3](image-url)

Figure 3. Plots of (a) $\ln([M]_0/[M])$ vs time $t$ and (b) $M_n$ and $M_w/M_n$ vs conversion for the MMA/CP-I/catalyst systems (ambient temperature). For experimental conditions, see Table 1. The symbols are indicated in the figure.

| Table 1. Polymerizations of MMA. |
|----------------------------------|
| entry | catalyst | wavelength (nm) | lamp electric power (W) $^a$ | light intensity at the solution (W/cm²)$^b$ | [MMA]₀/[CP-I]₀/[catalyst]₀ (mM) | $t$ (h) | conv (%) | $M_n$ ($M_n$ theo) | $M_w/M_n$ |
|-------|----------|-----------------|-----------------------------|---------------------------------|---------------------------------|--------|---------|-----------------|-----------|
| 1     | TBA      | 350-600         | 60                          | 0.19                            | 8000/80/20                      | 5      | 79      | 8200 (7900)    | 1.36      |
| 2     | C1-DCI   | 550-750         | 150                         | 0.23                            | 8000/80/10                      | 24     | 65      | 7800 (6500)    | 1.23      |
| 3     | DHMI     | 550-750         | 150                         | 0.23                            | 8000/80/40                      | 6      | 81      | 7800 (8100)    | 1.17      |
| 4     | C3-DCI   | 550-750         | 150                         | 0.23                            | 8000/80/20                      | 24     | 80      | 7900 (8000)    | 1.13      |

$^a$ Input electricity power of xenon lamp. $^b$ Actual light intensity (at the position of the reaction solution) experimentally measured by a power meter. The actual light intensity depends on the range of studied wavelength and the input electricity power. $^c$ Diluted with 25 wt% diglyme (MMA/diglyme = 75/25 wt%).

| Table 2. Block Copolymerizations of Functional Methacrylates from PMMA-I Macrorinitiator ($M_n = 3100$, PDI = 1.13). |
|---------------------------------------------------------------|
| entry | monomer | catalyst | wavelength (nm) | lamp electric power (W) | light intensity at the solution (W/cm²)$^a$ | $[\text{monomer}]_0/[\text{PMMA-I}]_0$ | $t$ (h) | conv (%) | $M_n$ ($M_n$ theo) | $M_w/M_n$ |
|-------|---------|----------|-----------------|--------------------------|---------------------------------|-----------------|--------|-----------------|-----------|
| 1     | HEMA    | DHMI     | 550 ± 10        | 280                      | 0.016                           | 8000/80/10$^a$  | 10     | 98      | 15000 (16000)   | 1.34      |
| 2     | GMA     | C1-DCI   | 500 ± 10        | 300                      | 0.017                           | 8000/80/20$^a$  | 20     | 69      | 12000 (13000)   | 1.26      |
| 3     | PEGMA$^d$ | DHMI  | 550 ± 10        | 300                      | 0.017                           | 8000/80/10      | 2      | 64      | 11000 (22000)   | 1.22      |
| 4     | DMAEMA  | C3-DCI   | 700 ± 50        | 300                      | 0.28                            | 8000/80/20      | 5      | 67      | 16000 (14000)   | 1.40      |

$^a$ Determined by GPC with a PMMA calibration (eluent = THF in all cases). $^b$ Diluted with 40 wt% ethanol. $^c$ Diluted with 25 wt% diglyme (MMA/diglyme = 75/25 wt%). $^d$ Molecular weight of monomer = 300.
2.5. Rate Control by Wavelength

Figure 4 demonstrate the control of $R_p$ by the irradiation wavelength. In this C1-DCI system, the irradiation wavelength was altered every 3 h from 700 nm to, 600 nm, 500 nm, and 400 nm. Perfectly no polymerization occurred during the first 3 h because no light was absorbed at 700 nm. When the wavelength was altered to 600 nm, the system was switched “on”, and the polymerization smoothly proceeded. The $R_p$ responded to the irradiation wavelength. At 600, 500, and 400 nm, the incremental conversion was 10, 17, and 8%, respectively, during each 3 h polymerization, according to the absorption intensity at each wavelength. A similar rate control was achieved using other catalysts.

2.6. Functional Monomers and Block Copolymerization

An advantage of the utilized organic catalysts is their good compatibility with functional monomers. Hydrophobic and hydrophilic polymers were thus successfully obtained. Another advantage of this polymerization is its good livingness, enabling the preparation of well-defined block copolymers. We used a macroinitiator, poly(methyl methacrylate)-iodide (PMMA-I) ($M_n = 3100$ and $M_w/M_n = 1.13$), in the polymerizations of hydroxyethyl (HEMA), glycidyl (GMA), poly(ethylene glycol) (PEGMMA), and dimethylaminoethyl (DMAEMA) methacrylates, and obtained the desired block copolymers (Table 2). The GPC chromatograms showed that only a small amount of the starting macroinitiator was present in the products (Figure 5), indicating efficient block copolymer formation.

2.7. Selective Control of Two Different Polymerizations by Wavelength

Selective control of multiple reactions by the irradiation wavelength is a unique application of photo reactions. An example described here of photo RCMP is a “one-pot” synthesis of a block copolymer of MMA and δ-valerolactone (VL) (Scheme 3). RCMP and ring-opening polymerization (ROP) were selectively regulated in one pot by simply altering the irradiation wavelength. We utilized a dual initiator, PhEOH-I (Scheme 3), which possesses both iodine to initiate RCMP and a hydroxyl group to initiate ROP. The mixture of MMA (25 equiv), VL (25 equiv), PhEOH-I (1 equiv), DHMI (0.06 equiv), an ROP catalyst (a photo acid generator, TSPF$_6$ (Scheme 3)) (0.002 equiv) [27], and a solvent (propylene carbonate) was subjected to polymerization. The
wavelengths of 550-750 nm (absorbed by DHMI) and 350-380 nm (absorbed by TSPF 6) were feasible for selectively inducing RCMP and ROP, respectively (Figure 6), and successfully affording the desired block copolymer.

3. Conclusions

Photo RCMP was developed as a new photo LRP. The polymerization was induced and controlled at desired wavelengths over a wide range of wavelengths by exploiting suitable catalysts. This polymerization was an ideal photo switchable system responding both irradiation power and wavelength. This polymerization was compatible with various functional monomers, and their block copolymers were obtained. A block copolymer of MMA and VL was obtained in one pot via selective RCMP and ROP by altering the irradiation wavelength. An advantage of this system is that no special capping agents or metals are used; in addition, the catalysts are commercially available. The facile operation, fine response to wavelength, and applicability to a large variety of polymer designs may be greatly beneficial in various applications.

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