Controlled Radical Polymerization of Acrylates Regulated by Visible Light

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Ⓢ *Supporting Information*

ABSTRACT: The controlled radical polymerization of a variety of acrylate monomers is reported using an Ir-catalyzed visible light mediated process leading to well-defined homo-, random, and block copolymers. The polymerizations could be efficiently activated and deactivated using light while maintaining a linear increase in molecular weight with conversion and first order kinetics. The robust nature of the *fac*-[Ir(ppy)$_3$] catalyst allows carboxylic acids to be directly introduced at the chain ends through functional initiators or along the backbone of random copolymers (controlled process up to 50 mol % acrylic acid incorporation). In contrast to traditional ATRP procedures, low polydispersity block copolymers, poly(acrylate)-*b*-(acrylate), poly(methacrylate)-*b*-(acrylate), and poly(acrylate)-*b*-(methacrylate), could be prepared with no monomer sequence requirements. These results illustrate the increasing generality and utility of light mediated Ir-catalyzed polymerization as a platform for polymer synthesis.
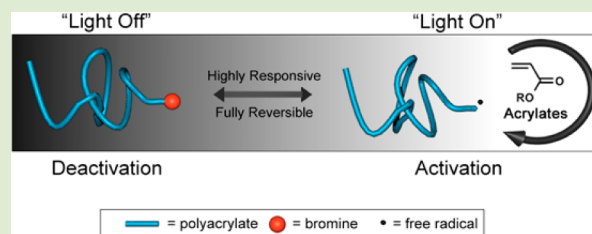
Controlled radical polymerizations (CRP), such as nitroxide-mediated polymerization (NMP),[1,2] reversible-addition–fragmentation chain transfer polymerization (RAFT),[3] and atom transfer radical polymerization (ATRP),[4] have revolutionized the field of polymer chemistry, allowing for the synthesis of well-defined macromolecular structures with excellent functional group tolerance. Perhaps of greater importance is the facile reaction conditions that allow nonexperts access to these materials, enabling significant advances across a number of fields. More recently, additional control over living radical polymerizations has been achieved through regulation of the chain growth process by an external stimulus.[5] For example, electrochemical ATRP has been used to pattern polymer brushes on surfaces,[6−8] as well as gain control over aqueous polymerizations.[9] While the employment of externally regulated polymerizations is in its infancy, the potential for further innovation is significant.

In considering the wide range of possible external stimuli, light offers many attractive features such as readily available light sources, tunability, and both spatial and temporal control. On this basis, significant work has been dedicated to the development of photoinitiated[10−17] and photoregulated radical polymerizations (i.e., photocontrolled RAFT,[18−20] ATRP,[21−24] organocatalytic,[25,26] cobalt-mediated,[27] and tellurium-mediated[28] methods). Recently, our group reported the controlled radical polymerization of methacrylates regulated by visible light and the photoredox catalyst, *fac*-[Ir(ppy)$_3$] (Scheme 1).[29] This approach uses a simple reaction setup with only ppm levels of Ir(ppy)$_3$ and enables efficient activation and

Scheme 1. Controlled Radical Polymerization Mediated by Light Employing *fac*-[Ir(ppy)$_3$] as the Catalyst
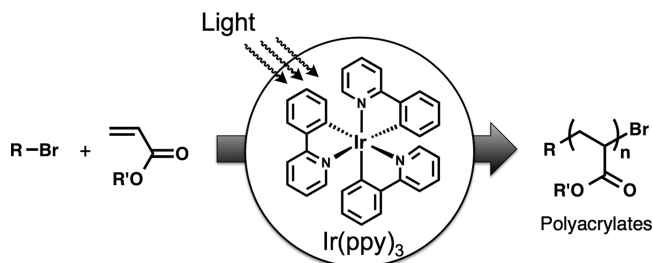
deactivation of polymerization leading to control over molecular weight and molecular weight distributions. A fundamental element of this process is that in the absence of irradiation, the chain end rests as the dormant alkyl bromide, protected from deleterious radical reactions but available for reactivation upon re-exposure to light. Moreover, the spatial and temporal control of Ir-catalyzed photomediated processes has been exploited for patterning polymer brushes on surfaces to give novel, 3-D nanostructures.[30]

Our previous reports on photomediated radical polymerizations focused exclusively on methacrylates. In order to increase the scope and applicability of this strategy, extension to

other monomer families is required. Our attention was therefore drawn to acrylate-based polymers, as they offer broad opportunities in both academia and industry.[31,32] Despite this significance, controlled radical polymerization of acrylates represented a formidable challenge due to the increased propagation rate and difficulty in chain end reduction relative to methacrylate derivatives.[33]

Initial studies on methyl acrylate (MA) employed similar conditions to those developed for the polymerization of methacrylates: 0.005 mol % of Ir(ppy)$_3$ and benzyl α-bromoisobutyrate (**1**) as initiator in *N*,*N*-dimethylacetamide (DMA) with irradiation by either 380 nm LEDs or a 50 W fluorescent lamp for 4 h (see Supporting Information). Encouragingly, our initial conditions indicated moderate control, showing an approximate agreement between theoretical and experimental molecular weights with $Đ$ = 1.45 (Table 1,

**Table 1. Optimization of a Light-Mediated Polymerization of Methyl Acrylate Using Ir(ppy)$_3$[a]**

entry	Ir(ppy)$_3$ (mol %)	conversion (%)	M_n (exp; g/mol)	M_n (theo; g/mol)	M_w/M_n
1[b]	0.005	76	14400	15200	1.45
2	0.005	79	16000	15800	1.39
3	0.01	76	15200	15200	1.30
4	0.05	63	12500	12600	1.25
5	0.1	54	10900	10800	1.32
6[c]	0.05	0			
7	0	43	240000[d]	8600	1.76

[a]Reaction conditions: MA (1 equiv), Ir(ppy)$_3$ (0−0.1 mol %), **1** (0.004 equiv), DMA (3.5 M of MA) at room temperature with irradiation from 380 nm LEDs for 4 h (M_n = number-average molecular weight; M_w = weight-average molecular weight). $Đ$ or M_w/M_n, determined using size exclusion chromatography (SEC). M_n determined by NMR except where noted. [b]Reaction run at 2 M. [c]Reaction run in the dark. [d]M_n determined by SEC.

entry 1), where $Đ$ = M_w/M_n. However, the degree of control was inferior when compared to the polymerization of methacrylates. We hypothesized that increased control over these polymerizations could be achieved by varying the catalyst and monomer concentrations to account for the marked difference in k_p and k_t for acrylates versus methacrylates. Indeed, increasing the monomer concentration to 3.5 M narrowed the molecular weight distribution to 1.30 (Table 1, entry 2). Further, increasing the catalyst loading to 0.05 mol % provided additional improvement in polydispersity (Table 1, entries 3−5). It should be noted that even at Ir(ppy)$_3$ concentrations as high as 0.1 mol %, controlled polymerization was observed, whereas for methacrylates such high catalyst loadings resulted in uncontrolled polymerization.[29] This difference may be due to the known difficulty in acrylate chain end reduction compared to methacrylate systems. Control experiments without catalyst or in the absence of irradiation led to either uncontrolled or no polymerization, respectively (Table 1, entries 6 and 7).[34] These results clearly

indicate that control over polymerization arises from the Ir catalyst with light as an external stimuli mediating the polymerization.

By analogy with the methacrylate system previously reported, the absence of reaction in the dark allows for temporal influence over the polymerization process. To demonstrate the capability to turn the polymerization "on" and "off" while maintaining control, methyl acrylate, initiator **1**, and Ir(ppy)$_3$ were combined and kept in the dark for 1 h, with no polymerization being observed. The reaction was then exposed to light, reaching 33% conversion after 1 h (Figure 1a). When
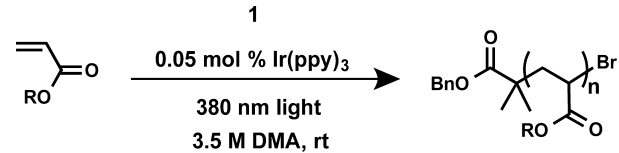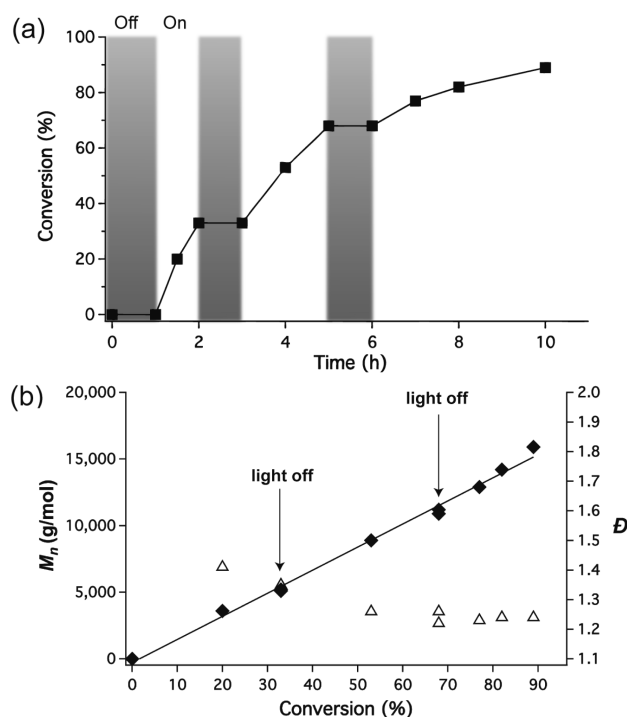

Figure 1. Polymerization of MA with Ir(ppy)$_3$ while cycling the reaction's exposure to light; (a) conversion vs time; (b) molecular weight (M_n) vs conversion (◆) and $Đ$ vs conversion (△; $Đ$ = M_w/M_n).

irradiation was subsequently removed from the system, the polymerization became dormant and no conversion was observed. On re-exposure to light, the polymerization process was reactivated and this cycle could be repeated multiple times with no conversion observed in the absence of irradiation. Significantly, a linear relationship between molecular weight and conversion was observed up to high (>90%) conversion even with multiple on/off cycles (Figure 1b). Finally, a linear relationship for $\ln([M]_0/[M]_t)$ versus time of light exposure indicated that a constant radical concentration exists throughout the polymerization (Figure S3) illustrating the stimuli-responsive and living nature of these Ir(ppy)$_3$-based acrylate polymerizations.

To further expand the range of polymerizable acrylate monomers and to demonstrate control of molecular weight for a variety of acrylate structures, the ratio of initiator to monomer was varied for methyl, *n*-butyl, and *t*-butyl acrylate, as shown in Table 2.[35−40]

In all cases, excellent agreement is observed between experimental and theoretical values for molecular weights of less than 1000 g/mol to greater than 100000 g/mol (Table 2,

Table 2. Molecular Weight Control of Alkyl-Substituted Acrylates[a]

entry	monomer	M_n (exp; g/mol)	M_n (theo; g/mol)	Đ
1	methyl acrylate	900	800	1.42
2		3000	2800	1.32
3		7900	8200	1.19
4		18400	18000	1.22
5		28900	29000	1.37
6	n-butyl acrylate	2400	2500	1.34
7		5100	4800	1.25
8		11300	10600	1.24
9		24800	27600	1.31
10		42600	38400	1.45
11	t-butyl acrylate	3900	3600	1.37
12		7000	7200	1.26
13		14300	14600	1.27
14		32300	28800	1.29
15		40600	40200	1.36
16		62700	60000	1.42
17		109000	108000	1.46
18		200000	193000	1.44

[a]Reaction conditions: methyl acrylate, n-butyl acrylate, t-butyl acrylate (1 equiv), $Ir(ppy)_3$ (0.05 mol %), **1** (0.00043–0.026 equiv), DMA (3.5 M of monomer) at room temperature with irradiation from 380 nm LEDs for 3–5 h (M_n = number-average molecular weight; M_w = weight-average molecular weight). Đ or M_w/M_n, determined using SEC. M_n determined by NMR and MALLS.

Table 3. Random Copolymerizations of Acrylic Acid (AA) and Ethyl Acrylate (EA)[a]

entry	AA/EA	% AA incorp	M_n (exp; g/mol)	M_n (theo; g/mol)	M_w/M_n
1	0:100	0	7700	7600	1.28
2	5:95	2	12300	12400	1.28
3	10:90	8	9500	10600	1.38
4	10:90	8	17300	21600	1.44
5	10:90	7	38300	37200	1.45
6	20:80	15	13800	12200	1.38
7	30:70	21	13500	11100	1.51
8	40:60	36	16300	12100	1.65
9	50:50	46	20500	11500	1.90

[a]Reaction conditions: EA (1 equiv), AA (0–1 equiv), $Ir(ppy)_3$ (0.05 mol %), **1** (0.004 equiv), DMA (3.5 M of monomer) at room temperature with irradiation from 380 nm LEDs for 2–5 h (M_n = number-average molecular weight; M_w = weight-average molecular weight). % AA incorp = mol % acrylic acid incorporation. Đ or M_w/M_n, determined using SEC. M_n determined by NMR. For characterization of the acid functionalized copolymers, methylation with trimethylsilyldiazomethane was performed prior to analysis.
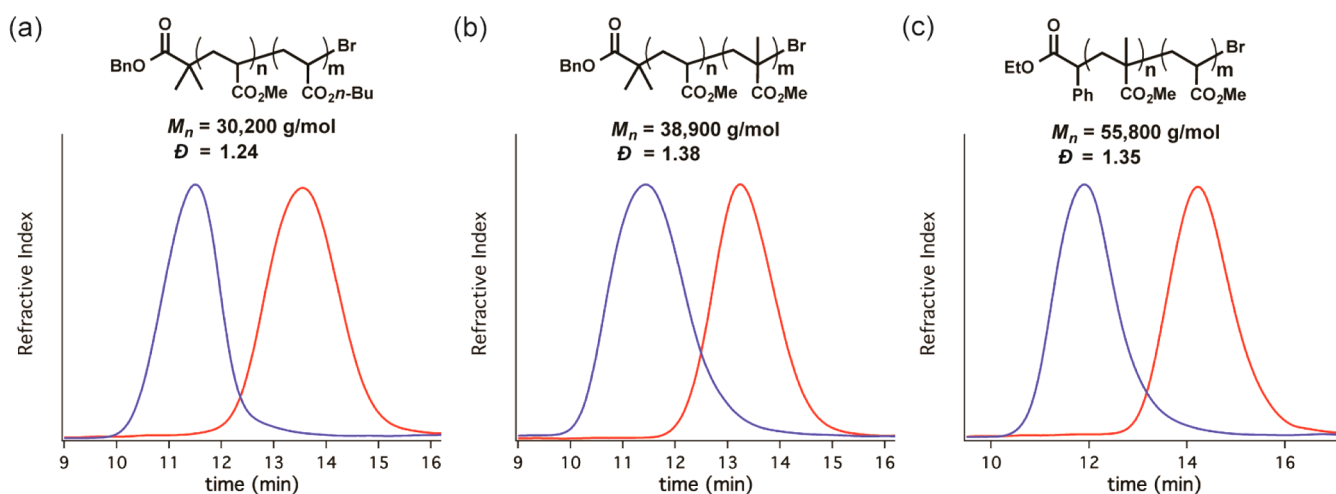
increasing to about 1.40–1.50. Only at higher incorporations of AA (30–50 mol %) was increased polydispersities observed.

This capacity to incorporate acrylic acid directly into acrylate backbones at moderate loading levels while retaining control over the polymerization process is significant and offers a wide range of opportunities in the design of functional macromolecules.

The ability to polymerize acrylates coupled with the prior demonstration of the controlled polymerization of methacrylates prompted an investigation into the utility of Ir-catalyzed polymerizations for producing block copolymers. Initially, simple reinitiation was studied by the chain extension of a methyl acrylate homopolymer (M_n = 7600 g/mol; Đ = 1.31) with n-butyl acrylate to yield a block copolymer (M_n = 30200 g/mol; Đ = 1.24). Size exclusion chromatography (SEC) shows minimal residual homopolymer after chain-extension, indicating excellent fidelity and reactivation of the alkyl bromide chain-end (Figure 2a).

For the more complex, acrylate-methacrylate diblock copolymer systems, the sequence of monomer polymerization can have a dramatic influence on the fidelity of the process. In traditional ATRP, the use of comonomers[41] or halogen exchange[42] is necessary when chain extending polyacrylate macroinitiators with methacrylates. In this case, a PMA homopolymer was synthesized and used as a macroinitiator to polymerize methyl methacrylate under the conditions previously reported[27] to yield a PMA-b-PMMA block copolymer with a polydispersity of 1.38 and little tailing in the homopolymer regime of the SEC trace (Figure 2b). For the reverse case, a poly(methyl methacrylate) homopolymer was synthesized under our photocontrolled conditions and chain extended with methyl acrylate to yield the inverse block copolymer with accurate control over molecular weight and polydispersity (Figure 2c). This high level of control in both cases further illustrates the robust nature and simplicity of this catalyst system and the absence of a required monomer sequence is a potential advantage over traditional ATRP systems.

In conclusion, we have demonstrated the light-mediated, controlled radical polymerization of a variety of acrylate monomers using an Ir-based photoredox catalyst. Linear

entries 1, 17, and 18). These results clearly demonstrate that molecular weight can be controlled by adjusting initiator to monomer ratio and, importantly, that the optimized conditions lead to low polydispersities for a variety of acrylate monomers.

With the successful polymerization of a variety of acrylate monomers, we next addressed the challenge of incorporating functional initiators or monomers directly into the polymer backbone. As a test case, carboxylic acid units were examined as they are traditionally difficult to control under standard ATRP conditions. This difficulty is due to the Cu catalysts for ATRP being formed in situ through coordination chemistry which is in direct contrast to the covalent nature of fac-$[Ir(ppy)_3]$. The stability of fac-$[Ir(ppy)_3]$ should therefore result in a more robust system with an increased tolerance to acidic groups. To demonstrate this, the synthesis of chain end functionalized poly(n-butyl acrylate) from 3-bromopropionic acid as an initiator was examined. Over a wide range of initiator/monomer ratios, accurate control over molecular weight and narrow polydispersities were obtained (Supporting Information).

Synthetically more demanding is the copolymerization of acrylic acid (AA) and ethyl acrylate (EA), which was examined at feed ratios of up to 50 mol % acrylic acid (Table 3).

For feed ratios of 5–20 mol %, excellent agreement between experimental and theoretical molecular weights is observed with low polydispersities between 1.25 and 1.40. Increasing the molecular weight for 10 mol % feed ratios resulted in a similar level of molecular weight control with the polydispersity

Figure 2. Block copolymer synthesis and corresponding SEC traces (red trace = homopolymer, blue trace = block copolymer): (a) PMA-*b*-*n*-PBA; (b) PMA-*b*-PMMA; (c) PMMA-*b*-PMA.

increases in molecular weight with conversion and first order reaction rates for a wide range of molecular weights demonstrates a well-behaved system with efficient chain capping and reinitiation in response to light. The robust nature of this polymerization system was illustrated by tolerance to acidic functional groups and the ability to control the copolymerization of acrylic acid. An added advantage of the Ir-based photoredox system is the lack of specific monomer order for block copolymer formation with well-defined materials being formed from both MA-MMA and MMA-MA sequences. This work demonstrates an expanding range of compatible monomers for Ir-based photoredox polymerizations and the significant potential that externally regulated systems offer.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Experimental conditions and supplementary data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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