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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Stereo-, Temporal and Chemical Control through Photoactivation of Living Radical Polymerization: Synthesis of Block and Gradient Copolymers

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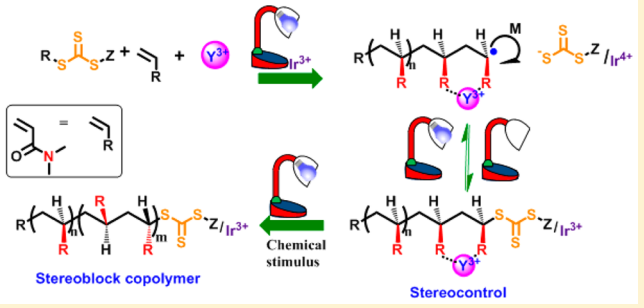
Supporting Information

ABSTRACT: Nature has developed efficient polymerization processes, which allow the synthesis of complex macromolecules with a perfect control of tacticity as well as molecular weight, in response to a specific stimulus. In this contribution, we report the synthesis of various stereopolymers by combining a photoactivated living polymerization, named photoinduced electron transfer−reversible addition−fragmentation chain transfer (PET-RAFT) with Lewis acid mediators. We initially investigated the tolerance of two different photoredox catalysts, i.e., $Ir(ppy)_3$ and $Ru(bpy)_3$, in the presence of a Lewis acid, i.e., $Y(OTf)_3$ and $Yb(OTf)_3$, to mediate the polymerization of *N*,*N*-dimethyl acrylamide (DMAA). An excellent control of tacticity as well as molecular weight and dispersity was observed when $Ir(ppy)_3$ and $Y(OTf)_3$ were employed in a methanol/toluene mixture, while no polymerization or poor control was observed with $Ru(bpy)_3$. In comparison to a thermal system, a lower amount of $Y(OTf)_3$ was required to achieve good control over the tacticity. Taking advantage of the temporal control inherent in our system, we were able to design complex macromolecular architectures, such as atactic *block*-isotactic and isotactic-*block*-atactic polymers in a one-pot polymerization approach. Furthermore, we discovered that we could modulate the degree of tacticity through a chemical stimulus, by varying $[DMSO]_0/[Y(OTf)_3]_0$ ratio from 0 to 30 during the polymerization. The stereochemical control afforded by the addition of a low amount of DMSO in conjunction with the inherent temporal control enabled the synthesis of stereogradient polymer consisting of five different stereoblocks in one-pot polymerization.



INTRODUCTION

Biological systems have evolved over several billion years to attain an extraordinary level of synthetic accuracy. Perhaps one of the most fascinating examples of precision synthesis, from the point of view of a polymer chemist, is the transcription of nuclear DNA into mRNA, followed by its translation into proteins in response to a specific external or internal stimulus, allowing biological systems to rapidly adapt and respond to their environments. Ribosomes play a central role in these biological processes, as they are capable of producing flawless functional macromolecules, with remarkable control of molecular weight (degree of polymerization), regiochemistry (sequence) and stereochemistry (tacticity). By controlling these three parameters, nature has perfected the synthesis of tertiary and quaternary polymeric structures with perfect sequence control affording key biological functions. Such macromolecular precision as well as temporal and spatial control remains unachievable even by our most recent living polymerization techniques,[1−6] and macromolecular engineering tools, such as click chemistry, as both techniques only provide statistical distribution of both chain length and sequence.[7−9] Although seminal works have demonstrated some degree of control in sequence[10−13] and tacticity,[14−19] which confers new properties to our synthetic polymers,[20−23] these synthetic methods pale in comparison to biological processes. Nevertheless, the development of polymerization techniques capable of controlling the stereochemistry of vinyl polymers has generated considerable interest in polymer science in the past 30 years. Isotactic and syndiotactic polymers present remarkable interactions and properties in comparison to atactic polymers as the stereoregularity significantly affects its physical and chemical properties.[24,25] Although good control over tacticity has been demonstrated by living ionic and coordination polymerization techniques due to the presence of counterion, control of stereochemistry in free radical polymerization is still challenging and remains a hot topic due to the numerous potential applications of syndiotactic and isotactic polymers in industry.[22,26]

Stereospecific radical polymerization has been achieved through several methods, which include polymerization in confined media, exploiting the inherent stereospecificity in

Received: June 8, 2015
Published: July 14, 2015

DOI: 10.1021/jacs.5b05903
J. Am. Chem. Soc. 2015, 137, 9988−9999

Table 1. Effects of Lewis Acid Mediators in PET-RAFT Polymerization of Poly(*N*,*N*-dimethylacrylamide) with $Ir(ppy)_3$ and $Ru(bpy)_3$ as Photoredox Catalysts[a]

entry	photoredox catalyst	$[DMAA]_0/[Y(OTf)_3]_0$	$[DMAA]_0/[Yb(OTf)_3]_0$	time (h)	α[b]	$M_{n,th}$ (g/mol)[c]	$M_{n,GPC}$ (g/mol)[d]	M_w/M_n	tacticity (m/r)[e]	tacticity (mm)[f]
1[g]	$Ir(ppy)_3$	0	0	5	0.73	8880	7650	1.08	0.48/0.52	0.24
2[h]	$Ru(bpy)_3$	0	0	3	0.92	11180	12100	1.08	0.50/0.50	–
3[g]	$Ir(ppy)_3$	0.05	0	1	0.88	10660	8690	1.25	0.83/0.17	0.70
4[h]	$Ru(bpy)_3$	0.05	0	22	0	–	–	–	–	–
5[g]	$Ir(ppy)_3$	0	0.05	18	0.23	2980	3220	1.36	0.74/0.26	–
6[h]	$Ru(bpy)_3$	0	0.05	22	0.47	5830	5770	1.19	0.76/0.24	–

[a]The reactions were performed in the absence of oxygen at room temperature in methanol or methanol/toluene mixture (1:1) under blue light irradiation (0.7 mW/cm^2, λ_{max} = 460 nm) with either $Ir(ppy)_3$ or $Ru(bpy)_3$ as the photoredox catalyst with molar of [DMAA]:[BTPA]:[$Ir(ppy)_3$ or $Ru(bpy)_3$]:[$Y(OTf)_3$ or $Yb(OTf)_3$] = 120:1:1.2 × 10^{-3}:5.75 at room temperature. [b]Monomer conversion was determined by using 300 MHz ^{1}H NMR spectroscopy. [c]Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_0/[RAFT]_0 \times MW^M \times \alpha + MW^{RAFT}$, where $[M]_0$, $[RAFT]_0$, MW^M, α, and MW^{RAFT} correspond to initial monomer concentration, initial RAFT concentration, molar mass of monomer, conversion determined by 300 MHz ^{1}H NMR, and molar mass of RAFT agent. [d]Molecular weight and dispersity were determined by GPC analysis with DMAC as eluent and calibrated to PMMA standards. [e]Determined by 300 or 600 MHz ^{1}H NMR. [f]Determined by 600 MHz ^{1}H NMR. [g]Methanol:toluene mixture of 1:1 was employed as the solvent. [h]Methanol was employed as the solvent.

monomer structure or via the addition of solvents or additives.[15] Polymerization in confined media induces stereoregulation via the confinement of the propagating radical and monomer, which leads to the suppression of free rotation and diffusion, and consequently results in highly stereospecific propagation. However, this approach can only be applied to a limited number of monomers in confined environments such as the crystalline solid state,[27−32] inclusion compounds,[33,34] porous materials[35,36] and templates.[37−40] Another method to obtain stereoregularity is by utilizing the inherent stereospecificity in monomer structure. In this approach, monomers with bulky substituents,[41−47] monomers with chiral auxiliary groups[48−50] and monomers with self-assembling groups[51−54] are often exploited to induce stereoregular control. In the case of stereoregular control by additives, many specific solvents[55−57] and Lewis acid mediators[49,58] afford stereospecific radical polymerizations by interacting with monomers through either hydrogen bonding, coordination or ionic bonding to change their inherent structures. Of these methods of inducing stereoregulation, control by solvents and additives is the most promising solution to engineer stereospecific polymers when taking into consideration the versatility and production cost.[15,55] The different means of stereospecific radical polymerization has now been extended into controlled/living radical polymerization, such as atom transfer radical polymerization (ATRP), single electron transfer−living radical polymerization (SET-LRP), reversible addition−fragmentation chain transfer polymerization (RAFT) and nitroxide mediated polymerization (NMP) to impose control over both molecular weight and tacticity.[15,59−61]

On the other hand, separate works in spatial and temporal control have recently emerged in polymer sciences, which allow the synthesis of functional polymers in response to a specific stimulus, such as light, electricity and others.[62,63] Because of its facile setup and its numerous industrial applications, such as photolithography, coatings, dental resins, etc., photoactivated polymerization has generated significant attention in the past 30 years. Under the impulsion of Hawker,[64−68] Matyjaszewski,[69−72] Haddleton,[73−75] Kamigaito,[76,77] Johnson,[78,79] and Yagci,[80−83] several types of photoactivated living polymerization techniques have emerged using UV or visible light as stimulus. In a seminal work, Hawker and co-workers,[64−68] proposed the use of photoredox catalysts for the activation of ATRP under blue light, while Matyjaszewski,[69−71,84] Yagci,[80−83] Haddleton,[74,85] Percec[6,74,86] and co-workers have employed copper complex to activate ATRP or SET-LRP under UV light (typically, λ = 365 nm). Our group has proposed a technique named photoinduced electron transfer−reversible addition−fragmentation chain transfer (PET-RAFT), which utilizes a photoredox catalyst for the activation of RAFT polymerization, via a photoinduced electron transfer (PET) from the photoredox catalyst to thiocarbonylthio compounds.[87−92] This process can be performed under various wavelengths (460−635 nm) as well as with a variety of photoredox catalysts, including metallo-,[87−90] organo-[91] and biologically derived catalysts.[92] However, all these works have never reported the control of the stereochemistry during the polymerization. The ability to control tacticity in combination with spatial and temporal control would bring us one step closer to emulating the synthetic capabilities of Nature.

In this contribution, we report for the first time a living radical polymerization technique capable of reversibly activating and deactivating under visible light in addition to the ability to control the polymer tacticity. We demonstrate stereo-, temporal and chemical control of living radical polymerization leading to the efficient synthesis of poly(*N*,*N*-dimethylacrylamide) (PDMAA) under visible light with dual control over molecular weight and tacticity. In this work, we successfully carried out efficient synthesis of stereoblock polymers comprised of segments with different tacticities, including atactic-*block*-isotactic and isotactic-*block*-atactic polymers. In addition, we introduced a novel technique for synthesizing pseudostereogradient polymers by manipulating the stereochemistry by discrete addition of dimethyl sulfoxide (DMSO) during the polymerization. We discovered that the addition of DMSO in the reaction mixture modified the tight complexation between $Y(OTf)_3$ and DMAA, resulting in the synthesis of a polymer with varying tacticity. By varying the $[DMSO]_0/[Y(OTf)_3]_0$ ratio from 0 to 30, we were able to gradually change the tacticity (m/r) from 0.83/0.17 to 0.47/0.53. The combination of our photoactivated living polymerization with a slow addition of DMSO gives us the capability to generate multiblock polymers containing 5 different stereoblocks.

RESULTS AND DISCUSSION

1. Mediating Tacticity Control with Different Lewis Acids and Photoredox Catalysts. Stereotacticity dictates important properties such as solubility, crystallinity, melting

DOI: 10.1021/jacs.5b05903
J. Am. Chem. Soc. 2015, 137, 9988−9999

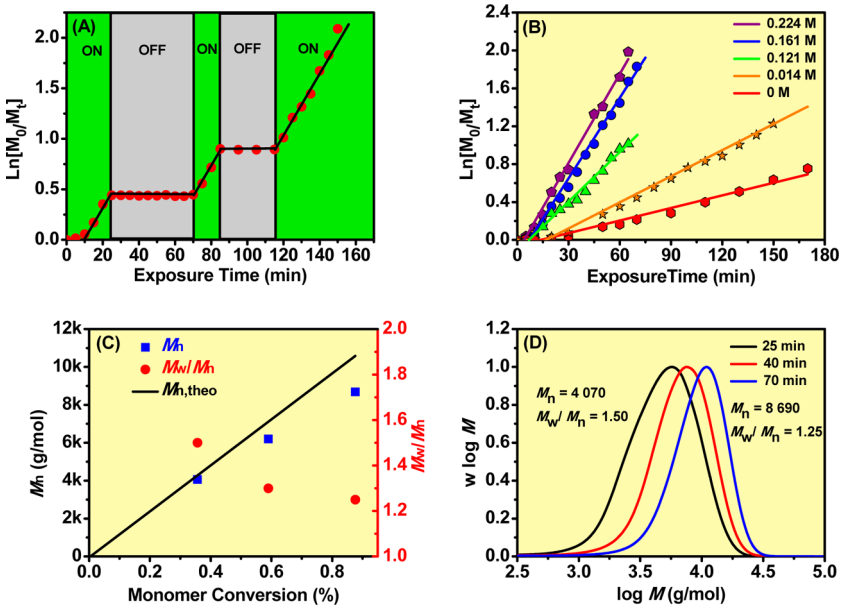


Figure 1. Online Fourier transform near-infrared (FTNIR) measurement for kinetic study of PET-RAFT polymerization of DMAA in the absence of oxygen at room temperature with $Ir(ppy)_3$ as photoredox catalyst under blue light irradiation with BTPA as the chain transfer agent and initiator, using molar ratio of [MA]:[BTPA]:[$Ir(ppy)_3$] = 120:1:1.2 × 10^{-3}. (A) "ON/OFF" online FTIR kinetics for molar ratio of [DMAA]:[BTPA]:[$Ir(ppy)_3$]:[$Y(OTf)_3$] = 120:1:1.2 × 10^{-3}:5.75]; (B) Plot of $\ln([M]_0/[M]_t)$ vs exposure time at different $Y(OTf)_3$ concentrations; (C) M_n vs conversion in the presence of 0.161 M $Y(OTf)_3$; and (D) molecular weight distributions at different time points in the presence of 0.161 M $Y(OTf)_3$.

point, glass transition temperature and mechanical strength of polymers. Although recent progress has been made to afford simultaneous control of both tacticity and molecular weights of polymer in controlled/living radical polymerization under thermal, there has not been any reported literature for tacticity and temporal control under visible light.[15,59] In this study, we successfully carried out polymerization of *N*,*N*-dimethylacrylamide (DMAA) to afford dual control over both molecular weight and tacticity under blue LED light irradiation (0.7 mW/cm^2, λ_{max} = 460 nm) in the presence of Lewis acid compounds as mediators at room temperature.

Inspired by the seminal works of Matyjaszewski,[14] Okamoto[18] and co-workers, we evaluated rare earth triflates, $Y(OTf)_3$ and $Yb(OTf)_3$, to determine their suitability for PET-RAFT polymerization with both $Ir(ppy)_3$ and $Ru(bpy)_3$ as photoredox catalyst (Table 1). Methanol was chosen as an ideal solvent for this investigation due to high solubility of $Y(OTf)_3$ and $Yb(OTf)_3$. Furthermore, previous studies have shown that the highest level of stereocontrol was obtained in methanol for both free radical and controlled/living radical polymerizations.[14,93] Unlike $Ru(bpy)_3$, $Ir(ppy)_3$ exhibited poor solubility in methanol and was therefore used in a mixture of toluene and methanol (methanol/toluene mixture = 2:1).[88,90] All the polymerizations were carried out in the presence of 2-(*n*-butyltrithiocarbonate)-propionic acid (BTPA) as thiocarbonylthio compound, which acts as both an initiator and chain transfer agent (iniferter) in our system. For these initial tests, the concentration of photoredox catalyst was fixed at 10 ppm relative to monomer. As control experiments, we have performed several polymerizations using the similar experimental conditions, i.e., in the presence of $Y(OTf)_3$ or $Yb(OTf)_3$, BTPA and DMAA, but in the absence of photoredox catalysts. For all these polymerizations, a very low monomer conversion (α < 10%, after 12 h) was observed in accord with our previous results (data not shown).[79,80] These results show that $Y(OTf)_3$ and $Yb(OTf)_3$ cannot initiate a polymerization under blue LED (λ = 460 nm).

In the absence of any metal triflates, both $Ir(ppy)_3$ and $Ru(bpy)_3$ afforded controlled polymerization of DMAA via the PET-RAFT process in good agreement with our previous studies[87−92] under blue LED light (Table 1, entries 1 and 2), but led to the formation of atactic chains as determined by ^{1}H NMR spectroscopy (tacticity m/r around 0.5/0.5). The tacticity was determined by analyzing backbone methylene protons (Figure 1 and SI, Figure S6) from 1.7 to 0.9 ppm (2H) in the ^{1}H NMR spectrum; the meso (*m*) and racemic (*r*) content of the polymer chains can be determined to evaluate the degree of isotacticity of the chains.[14,18,94−98] For the meso dyads, the methylene proton peaks are not equivalent, and therefore, appear at 1.6 and 1.05 ppm. On the other hand, the racemic proton peaks are equivalent and appear at 1.4 ppm. As the proton peak at 1.05 ppm for meso dyads are well resolved, the meso content can be determined by finding the ratio of twice the integral at 1.05 ppm to the integral from 1.7 to 0.9 ppm ($m = 2I^{1.05\ ppm}/I^{1.7-0.9\ ppm}$). In addition, tacticity of the polymer chains can also be determined by analyzing the triad content of the cis and trans amido methyl protons (3.1−2.6 ppm, 6H).[14,98] The cis and trans methyl protons are not equivalent leading to a split to form three peaks (*mm*, *mr* and *rr*). In the broad region between 3.1 to 2.6 ppm, the integration from 3.1 to 2.9 ppm will constitute the determination of trans mm triad while the integration from 2.9 to 2.6 ppm will constitute to the determination of three cis triads (*mm* + *mr* + *rr*) and two trans triads (*mr* + *rr*). Therefore, the fraction of the isotactic triad in the polymer chains can be determined by finding the ratio of twice the integral at 3.1−2.9 ppm to the integral from 3.1 to 2.6 ppm ($mm = 2I^{3.1-2.9\ ppm}/I^{3.1-2.6\ ppm}$).

In the presence of $Y(OTf)_3$ using a DMAA/$Y(OTf)_3$ molar ratio of 0.05, only $Ir(ppy)_3$ (Table 1, entry 3) was able to successfully polymerize DMAA with good control over both the

DOI: 10.1021/jacs.5b05903
J. Am. Chem. Soc. 2015, 137, 9988−9999

Table 2. Polymerization Rate of DMAA with Different Concentrations of $Y(OTf)_3$[a]

#	$[Y(OTf)_3]_0/[DMAA]_0$	$Y(OTf)_3$ (M)	k_p^{app} (min^{-1})	yield (α)[b]	$M_{n,th}$ (g/mol)[c]	$M_{n,GPC}$ (g/mol)[d]	M_w/M_n	tacticity (m/r)[e] (±0.03)	tacticity (mm)[e] (±0.03)	end group fidelity (±0.05) (f)[f]
1	0.067	0.224	3.13×10^{-2}	86	10470	8600	1.33	0.84/0.16	0.71	0.90
2	0.048	0.161	2.74×10^{-2}	88	10710	8690	1.25	0.83/0.17	0.70	0.98
3	0.033	0.121	1.64×10^{-2}	86	10470	8390	1.20	0.83/0.17	0.68	0.97
4	0.004	0.014	0.83×10^{-2}	90	10930	9850	1.09	0.64/0.36	0.40	0.98
5	0	0	0.44×10^{-2}	73	8800	7970	1.09	0.48/0.52	0.24	0.92[e]

[a]The reactions were performed in the absence of oxygen at room temperature in methanol/toluene mixture (2:1) under blue light irradiation (0.7 mW/cm^2, λ_{max} = 460 nm) with either $Ir(ppy)_3$ as the photoredox catalyst with molar of [DMAA]:[BTPA]:[$Ir(ppy)_3$] = 120:1:1.2 × 10^{-3} with specified $[Y(OTf)_3]_0/[DMAA]_0$ ratios at room temperature. [b]Monomer conversion was determined by using FTNIR. [c]Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_0/[RAFT]_0 \times MW^M \times \alpha + MW^{RAFT}$, where $[M]_0$, $[RAFT]_0$, MW^M, α, and MW^{RAFT} correspond to initial monomer concentration, initial RAFT concentration, molar mass of monomer, conversion determined by online FTNIR, and molar mass of RAFT agent. [d]Molecular weight and dispersity were determined by GPC analysis with DMAc as eluent and calibrated to PMMA standards. [e]Determined by 600 MHz ^{1}H NMR. [f]Determined by UV−vis spectrometer using the following formula: $f = [A/(c \times l \times \varepsilon_{lit})]$ where A is the experimentally determined absorbance of the sample at 309 nm, c is the molar concentration of the polymer, l is the path length of the cell in cm, and ε_{lit} is molar absorptivity in L mol^{-1} cm^{-1} reported in the literature (~15 800 L mol^{-1} cm^{-1}).[109]

molecular weight and molecular weight distribution (M_w/M_n = 1.25). The molecular weight distribution is slightly higher than the values obtained in the absence of $Y(OTf)_3$ and was attributed to the complexation of $Y(OTf)_3$ with monomers. Interestingly, the tacticity in the presence of $Y(OTf)_3$ was controlled. The absence of polymerization in the presence of $Ru(bpy)_3$ may be related to the unfavorable interaction between bipyridine and the $Y(OTf)_3$ which has been observed for ATRP in the presence of Lewis acid compound.[14] However, in the presence of $Yb(OTf)_3$, both $Ir(ppy)_3$ (Table 1, entry 5) and $Ru(bpy)_3$ (Table 1, entry 6) resulted in extremely slow polymerization kinetics which suggests that deactivation of the photoredox catalysts may have been a dominant factor in these reactions. As $Ir(ppy)_3$ and $Y(OTf)_3$ allowed for excellent control over tacticity and molecular weight, similar to previously reported thermal reactions,[14,15,18,93,99−101] this combination was selected for further investigation.

2. Kinetic Studies on $Y(OTf)_3$ Induced Tacticity Control. One of the advantages of tacticity control with PET-RAFT is that no external initiator is needed to initiate the polymerization as the presence of photoredox catalyst enables the thiocarbonylthio compound to act as both an initiator and chain transfer agent (iniferter) under visible light at room temperature. Such system allows higher end group fidelity in comparison to conventional RAFT polymerization, which allows the synthesis of multiblock copolymer in one-pot polymerization.[88] In our previous studies on PET-RAFT,[87−92] we have demonstrated temporal control by repeated reactivation of the system by turning ON or OFF the light without any detriment to the livingness as demonstrated by the synthesis of decabock copolymers with a low dispersity (<1.30). In this study, temporal control of DMAA polymerization was demonstrated by "ON/OFF" experiments in the presence of $Y(OTf)_3$ (Figure 1A). In the absence of light ("OFF"), the system remained dormant with no polymerization taking place, while in the presence of light ("ON") the system was activated allowing polymerization to take place. Interestingly, in the presence of $Y(OTf)_3$, we observed faster polymerization kinetics in comparison to the polymerizations performed without this mediator. In order to understand the effects of concentration of $Y(OTf)_3$ on the polymerization kinetics of DMAA, kinetics studies were conducted using an online Fourier transform near-infrared (FTNIR) spectroscopy, according to a method reported in the literature, at different ratios of $[Y(OTf)_3]_0/[DMAA]_0$. Polymerization of DMAA showed first-order kinetics for $\ln([M]_0/[M]_t)$ against exposure time for the different $[Y(OTf)_3]_0/[DMAA]_0$ ratios.

Increasing the concentration of $Y(OTf)_3$ not only increased the isotacticity of the polymer chains (m/r tacticity from 0.48/0.52 to 0.84/0.16) but also increased the apparent propagation rate constant (k_p^{app} from 4.4 × 10^{-3} to 3.13 × 10^{-2} min^{-1}) (Table 2, entries 1−5 and Figure 1B). Furthermore, we observed a significant decrease of the inhibition period from 15 min to a few minutes. This inhibition period has been observed in our PET-RAFT process[88] as well as in conventional RAFT polymerization.[4] The dramatic increase in the apparent propagation rate constants afforded by increasing the $[Y(OTf)_3]_0/[DMAA]_0$ ratio (Figure 1B) can be attributed to the complexation of $Y(OTf)_3$ to the monomer or around the growing polymer terminus. Such behavior has been previously observed in Lewis acid mediated radical polymerizations.[14,15,59,95,100,102,103] Studies[102,103] have shown that radical polymerization rate of monomers with ester carbonyl groups can be increased through the use of Lewis acids as complexing agents. Lewis acids such as $Y(OTf)_3$ and $Yb(OTf)_3$ are able to coordinate with ester carbonyl group on monomers resulting in reduced electron density in the conjugated C=C bond, and thereby, increasing the reactivity of the generated radical.[104,105] As the polymerization of DMAA with different concentrations of $Y(OTf)_3$ is well-controlled, it is highly likely that the presence of this Lewis acid increases the reactivity of the propagating radical rather than increasing the concentration of the propagating radical. In addition, in a control experiment with styrene, the presence of Lewis acid did not lead to any polymerization rate enhancement.[104] Therefore, it is most likely that the presence of Lewis acids such as $Y(OTf)_3$ leads to an increment in the reactivity of the propagating radical rather than concentration of the radical. As a result, increasing amounts of $Y(OTf)_3$ leads to higher dispersity (M_w/M_n) due to the increase in propagation rate constant. Nevertheless, it is also possible that unknown side reactions and slower rate of exchange within the dormant intermediate radical complexed to Lewis acid through the thiocarbonylthio group and the active propagating radical may lead to higher dispersity.[106] In addition, the increase of $Y(OTf)_3$ was accompanied by a slight widening of the molecular weight distribution from 1.08 to 1.33. This result is in good agreement with previous studies, that have suggested that a higher concentration of $Y(OTf)_3$ leads to a lower exchange rate of the trithiocarbonate, and therefore, results in higher molecular weight distribu-

DOI: 10.1021/jacs.5b05903
J. Am. Chem. Soc. 2015, 137, 9988−9999

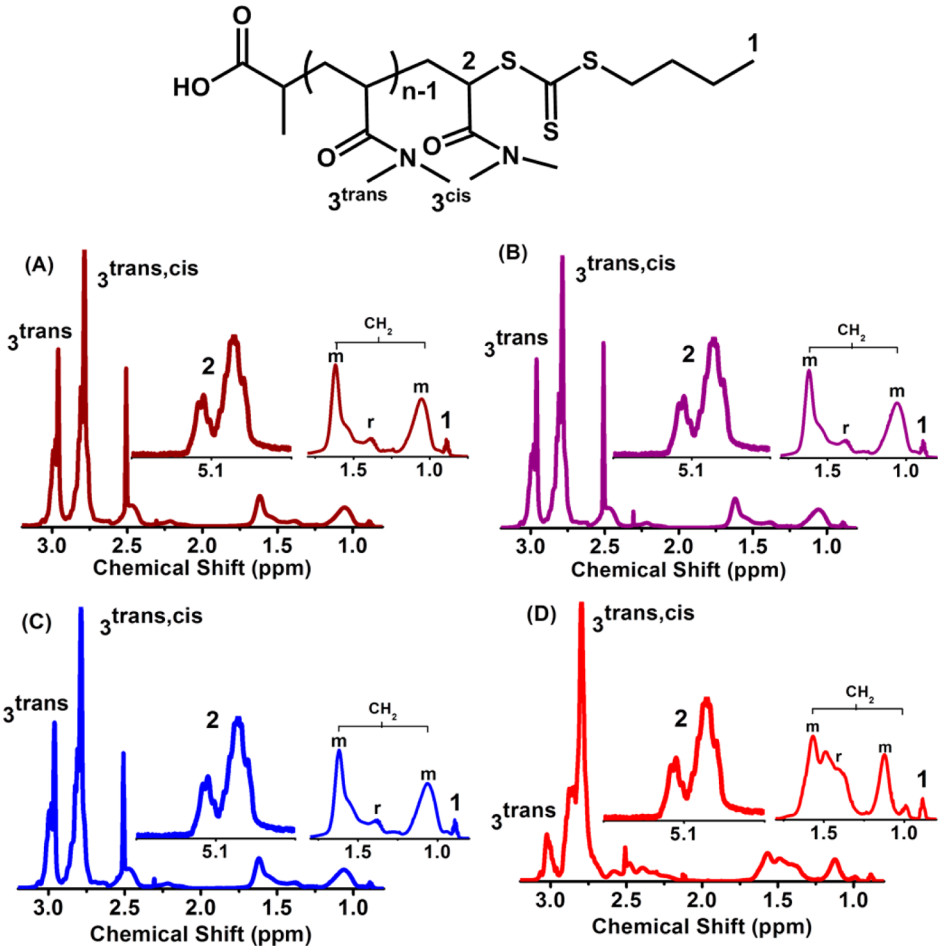
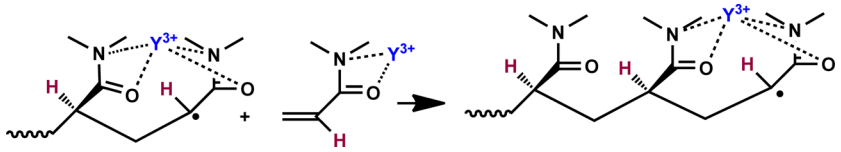


Figure 2. (Top) Structure of poly(*N*,*N*-dimethylacrylamide), and (Bottom) 600 MHz ^{1}H NMR spectrum of poly(*N*,*N*-dimethylacrylamide) in DMSO-d_6 at 28 °C in the presence of different concentrations of $Y(OTf)_3$: (A) 0.224 M, (B) 0.161 M, (C) 0.121 M and (D) 0 M.

Scheme 1. Coordination of $Y(OTf)_3$ to Amide Functionalities in the Propagating Radical and Incoming Monomer Unit



tions.[14,107,108] However, this behavior does not affect the control over the polymerization as demonstrated by an excellent agreement with the theoretical and experimental molecular weight values. Finally, the presence of thiocarbonylthiol end group was confirmed by the signal at 5.1 ppm attributed to CH-S(C═S) group as shown in Figure 2. In addition, using 600 MHz ^{1}H NMR spectroscopy and the following equation: $f^{\text{end-group}} = I^{5.1\text{ ppm}}/(I^{1.0\text{ ppm}}/3) \times 100$, where $I^{5.1\text{ ppm}}$ and $I^{1.0\text{ ppm}}$ correspond to the integration values of signals at 5.1 and 1.0 ppm respectively, the end-group fidelity was determined to be close to 100% (see for instance, Table 2, entry 5 and SI, Figures S5 and S6) for all the polymers made using $[Y(OTf)_3]_0/[DMAA]_0$ ratio between 0−0.048. Further verification with UV−vis spectroscopy confirmed high retention of RAFT end group ($f > 0.9$) (Table 2, entries 2 and 3 and SI, Figure S4) for $Y(OTf)_3$ concentrations from 0.224 to 0.121 M. A slight drop in end group fidelity was observed at 0.224 M (Table 2, entry 1) as compared to when lower concentration of $Y(OTf)_3$ was employed. As discussed above, with a higher concentration of $Y(OTf)_3$, the probability of coordination trithiocarbonate to $Y(OTf)_3$ also increases,[14,102,103] and therefore, results in reduction in rate of exchange between active and dormant chains leading to an increase in dispersity.

In the absence of Lewis acid, the propagating carbon radical has almost planar configuration leading to equal probability for both meso (m) and racemic (r) type addition of monomers. The addition of $Y(OTf)_3$ leads to coordination with the last two pendant amide groups of the propagating radical and incoming monomer unit, resulting in meso type addition and an increase in isotacticity as shown in Scheme 1.[14,95] The meso and racemic dyads and the isotactic triads for the different concentrations of $Y(OTf)_3$ used are shown in Table 2 with the fraction of the meso dyads and the fraction of isotactic triads agreeing very closely to Bernoullian statistics ($mm = m^2$). In the absence of the $Y(OTf)_3$ mediator, atactic chains are formed with low m and mm values (Table 2, entry 5). However, the introduction of $Y(OTf)_3$ leads to higher contents of isotactic

DOI: 10.1021/jacs.5b05903
J. Am. Chem. Soc. 2015, 137, 9988−9999

Table 3. Effects of Solvents on the Properties on Poly(*N*,*N*-dimethy1acrylamide)[a]

entry	solvent mixture (v/v)	solvent/DMAA (v/v)	time (h)	yield (α)[b]	$M_{n,th}$ (g/mol)[c]	$M_{n,GPC}$ (g/mol)[d]	M_w/M_n	tacticity (m/r)[e]	tacticity (mm)[e]
1	toluene/methanol (1:1)	1:2	18	0.50	6190	5390	1.60	0.82/0.18	0.67
2	toluene/methanol (1:2)	1:3	1	0.88	10660	8960	1.25	0.83/0.17	0.70
3	toluene/ethanol (1:2)	1:3	4	0.60	7400	9780	1.25	0.83/0.17	0.68
4	toluene/isopropanol (1:2)	1:3	4	0.25	3250	2180	1.64	0.79/0.21	0.64
5	toluene/*n*-butanol (1:2)	1:3	4	0.12	1620	1790	2.14	N.D.[f]	N.D.[f]

[a]The reactions were performed in the absence of oxygen at room temperature in alcohol/toluene mixture under blue light irradiation (0.7 mW/cm^2, λ_{max} = 460 nm) with Ir(ppy)$_3$ as the photoredox catalyst with molar ratio of [DMAA]:[BTPA]:[Ir(ppy)$_3$]:[Y(OTf)$_3$] = 120:1:1.2 × 10^{-3}:5.75 at room temperature. [b]Monomer conversion was determined by using 300 MHz ^{1}H NMR spectroscopy. [c]Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_0/[RAFT]_0 \times MW^M \times \alpha + MW^{RAFT}$, where $[M]_0$, $[RAFT]_0$, MW^M, α, and MW^{RAFT} correspond to initial monomer concentration, initial RAFT concentration, molar mass of monomer, conversion determined by 300 MHz ^{1}H NMR, and molar mass of RAFT agent. [d]Molecular weight and dispersity were determined by GPC analysis with DMAc as eluent and calibrated to PMMA standards. [e]Determined by 600 MHz ^{1}H NMR. [f]N.D. stands for data not determined.

dyads and triads (Table 2, entries 1−4) with apparent changes seen in both 3.1−2.6 ppm and 1.7−0.9 ppm regions in the ^{1}H NMR spectra (Figure 2).

Interestingly, the addition of the Lewis acid mediator did not affect the livingness previously demonstrated by the PET-RAFT process. The evolution of molecular weights to monomer conversion in the presence of Y(OTf)$_3$ exhibited linearity with good agreement with the theoretical molecular weights (Figure 1C; SI, Figures S2A and S3A) in addition to decreasing molecular weight distributions with exposure time, which is an accord with a living process. Furthermore, the molecular weight distributions measured by GPC shifted symmetrically from low to high molecular weights during the polymerization (Figure 1D, SI, Figures S2B and S3B).

Furthermore, another interesting aspect that was investigated was the influence of monomer conversion on the tacticity of PDMAA. In order to investigate the tacticity of PDMAA at different monomer conversions, polymerization with [Y(OTf)$_3$]$_0$/[DMAA]$_0$ of 0.048 was carried out (SI, Figure S1). A similar polymerization kinetics was observed as before (Table 1, entry 2). Interestingly, there is very little change to the isotacticity ($m \approx 0.84$) of PDMAA with increasing monomer conversion (SI, Figure S1). A similar observation was also made by Ray et al.[100,106] during the synthesis of isotactic poly(*N*-isopropylacrylamide) using thermal reaction in the presence of Y(OTf)$_3$, where the isotacticity of the polymer does not change with the increase in monomer conversion. Isobe et al.[105] carried out NMR studies that revealed that Lewis acids, such as Y(OTf)$_3$, form a stronger complex with one or more monomers than with the polymer. In addition, Thang and co-workers have also revealed through NMR studies that the interaction between metal triflates and trithiocarbonates is much weaker than the interaction between metal triflates and monomers with ester groups.[110] Although the Lewis acid may remain at the propagating end after the addition of the complexed monomer, it eventually be detached from the polymer and become available to be complexed by other monomers. Consequently, only a catalytic amount is required to induce stereoregulation.[104,105]

Previous attempts on tacticity control with Y(OTf)$_3$ required a ratio of Lewis acid to monomer between 0.05 and 0.1 to synthesize isotactic poly(*N*,*N*-dimethylacrylamide) chains with high content of isotactic dyads (m > 0.8) and triads (mm > 0.64).[14,18] In our investigation, we were able to achieve a similar feat with ratios of the Lewis acid to monomer, which were almost three times lower (from 0.05 to 0.017) (Table 2, entries 3 versus 2) with excellent control of molecular weight and tacticity. In order to demonstrate the dual control over both molecular weight and tacticity at high conversions (>90%), we performed studies to compare the characteristics of the polymerization at low (0.017) and high (0.033) Lewis acid to monomer ratios. Both 0.017 and 0.033 (SI, Figures S7 and S6) Lewis acid to monomer ratios afforded isotactic polymers with high end group fidelity (assessed by 600 MHz ^{1}H NMR spectroscopy), controlled molecular weights and narrow molecular weight distributions. In a control experiment (Table 2, entry 5, and SI, Figure S8) in the absence of the mediator, poor tacticity control was observed but the RAFT end group fidelity was retained with controlled molecular weights and molecular weight distributions (M_w/M_n < 1.30).

As we were able to reduce the catalytic amount of Lewis acid used for stereocontrol of PDMAA, we sought further optimizations as stereoregulation depended not only on the type of Lewis acid but also on solvent and temperature. In a previous study by Matyjaweski and co-workers,[14] solvent effects were found to be less explicit for RAFT polymerization even in the case of solvent mixtures (methanol/toluene). In our study, we discovered that solvents play an important role as only toluene/methanol and toluene/ethanol afforded dual control of both tacticity and molecular weight. In the presence of a 1:1 (Table 3, entry 1) toluene/methanol mixture, a low monomer conversion with broad molecular weight distributions was observed. However, increasing the amount of methanol, to a toluene/methanol mixture of 1:2 (Table 3, entry 2) led to a higher yield and a narrowing of the molecular weight distribution. This result was attributed to the higher solubility of Y(OTf)$_3$ in methanol as compared to toluene.

Both ethanol (Table 3, entry 3) and isopropanol (Table 3, entry 4) afforded isotactic polymer chains but with a lower monomer conversion compared to methanol. Interestingly, an increase of the molecular weight distribution (M_w/M_n) was observed when increasing the aliphatic chain of the alcohol; toluene/*n*-butanol, afforded low monomer conversion and poor tacticity control compared to the other alcoholic mediums with shorter aliphatic chains. The isotacticity decreases in the order: methanol > ethanol > isopropanol, which is consistent with previous study by Okamoto et al.[93]

3. Stereoblock Polymers. One of the main advantages of implementing stereochemical control in a living radical polymerization system is the ability to synthesize unique stereocontrolled polymers, such as stereoblock and stereo-gradient polymers, with good control over the chain architecture and microstructure.[14,15,59,99,106,111−114] Stereoblock polymers are synthesized by introducing abrupt changes at

DOI: 10.1021/jacs.5b05903
J. Am. Chem. Soc. 2015, 137, 9988−9999

Table 4. Synthesis of Atactic-*block*-Isotactic Stereoblock Polymer

entry	yield (α)[c]	$M_{n,th}$ (g/mol)[d]	$M_{n,GPC}$ (g/mol)[e]	M_w/M_n[e]	tacticity (m)[f]	tacticity (mm)[f]	DP	m_2[g]
1[a]	56	6080	6890	1.08	0.51 (m_1)	0.26	DP_1 = 67	–
2[b]	82	10000	12380	1.09	0.65 (m_2)	0.44	DP_2 = 31	0.90 (±0.05)

[a]The reactions were performed at room temperature in methanol/toluene mixture (2:1) under blue light irradiation (0.7 mW/cm^2, λ_{max} = 460 nm), with Ir(ppy)$_3$ as the photoredox catalyst with molar ratio of [DMAA]:[BTPA]:[Ir(ppy)$_3$] = 120:1:1.2 × 10^{-3} at room temperature for 4 h. [b]Addition of Y(OTf) with a molar ratio of $[Y(OTf)_3]_0/[DMAA]_0$ = 0.048. [c]Monomer conversion was determined via 300 MHz ^{1}H NMR spectroscopy. [d]Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_0/[RAFT]_0 \times MW^M \times \alpha + MW^{RAFT}$, where $[M]_0$, $[RAFT]_0$, MW^M, α, and MW^{RAFT} correspond to initial monomer concentration, initial RAFT concentration, molar mass of monomer, conversion determined by 300 MHz ^{1}H NMR, and molar mass of RAFT agent. [e]Molecular weight and dispersity (M_w/M_n) were determined by GPC analysis with DMAc as eluent and calibrated to PMMA standards. [f]Determined by 600 MHz ^{1}H NMR. [g]m_2 represents the fraction of isotacticity in the second block determined by the following formula: $m_2 = (mDP - m_1DP_1)/DP_2$ where m, m_1, m_2, DP, DP_1, and DP_2 are fraction of meso dyads in the polymer, meso dyads in the atactic segment, meso dyads in the isotactic segment of the block, overall degree of polymerization determined by monomer conversion, degree of polymerization of atactic segment determined by monomer conversion and degree of polymerization of isotactic segment determined by monomer conversion, respectively.

certain positions in the chain. On the other hand, stereogradient polymers are a rather novel concept where the instantaneous composition changes gradually along the polymer chain. In our study, we successfully carried out a one-pot synthesis of a stereoblock polymer consisting of atactic-*block*-isotactic polymer. The initial synthesis of the atactic block was started off in the absence Y(OTf)$_3$ mediator until a monomer conversion of 56% was reached after 4 h of irradiation under blue LED light. The initial segment displayed well controlled molecular weight and molecular weight distributions, but was atactic in nature due to the absence of Y(OTf)$_3$ as noted by the low meso content (Table 4, entry 1). For the formation of the isotactic segment, a degassed solution of Y(OTf)$_3$ dissolved in methanol/toluene mixture (2:1) was added into the reaction mixture to yield a ratio of $[Y(OTf)_3]_0/[DMAA]_0$ of 0.048. The reaction mixture was then irradiated for another 45 min before the polymerization was stopped (Table 4, entry 2) to reach a monomer conversion of 82%. As shown in Figure 3, a clear shift in molecular weight distribution

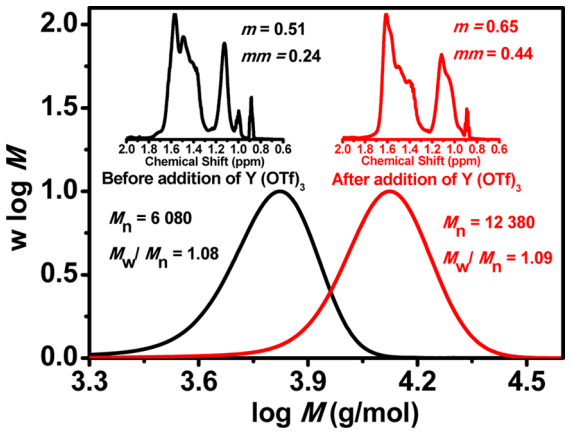


Figure 3. GPC traces of atactic block PDMAA (black line) and atactic-*b*-isotactic stereoblock PDMAA after addition of Y(OTf)$_3$ (red line) with insets showing 300 MHz ^{1}H NMR of backbone methylene protons before (black line) and after (red line) Y(OTf)$_3$ addition.

with good control of the molecular weight and dispersity (M_w/M_n) were observed. Furthermore, the addition of Y(OTf)$_3$ led to an increase in the isotactic regions as shown in the insets of Figure 3. The content of the meso dyads in the second block was estimated to be around 0.90 (±0.05).

4. Stereogradient Polymer. Stereogradient polymers can be a means toward discovering novel homopolymer-based materials as careful manipulation of tacticities along a polymer chain can bestow different properties in a controlled manner. However, synthesis of stereogradient polymers in living radical polymerization remains understudied and is restricted to three different methods: utilizing two monomers with different reactivities and stereospecificities,[115] utilizing rapid monomer conversion,[116] or manipulating monomer concentration through the use of bulky methacrylate.[117] In our study, we aimed to develop a novel method in the synthesis of stereogradient polymers via the utilization of Lewis acid−base complexation and the temporal control afforded by our PET-RAFT process. During this investigation, we discovered that DMSO (Lewis base) deactivated Y(OTf)$_3$ due to its tight complexation to the Lewis acid, which consequently leads to a loss of stereoregularity.[95] We utilized this property to gradually regulate the tacticity of PDMAA. The use of DMSO as a solvent for isotactic-specific polymerization has never been successful as tight coordination of DMSO to Y(OTf)$_3$ often prevents any interaction of the monomer with the Lewis acid resulting in atacticity.[95] By carefully titrating known concentrations of DMSO (or by varying $[DMSO]_0/[Y(OTf)_3]_0$ ratio) during the polymerization, we were able to gradually change the isotacticity of PDMAA polymer chains, enabling the synthesis of pseudogradient pentablock polymers with five segments of varying degrees of isotacticity. The property of PET-RAFT to provide reversible activation/deactivation without compromising end group fidelity affords the ability to precisely target the length of each chain and modulate the isotacticity. Additionally, as the trithiocarbonate acts as the initiator and chain transfer agent (iniferter), no additional external initiator was required and the reaction could be initiated and stopped with ease by turning OFF the light. These feats are quite difficult to achieve in a thermal reaction as simultaneous control of precise degree of polymerization and tacticity would not be possible due to the absence of reversible activation and deactivation of polymerization as seen in PET-RAFT.

In our preliminary experiments, we titrated known concentration of DMSO in the presence of a Lewis acid to monomer ratio of 0.048 for different polymerizations. We were able to successfully tune the stereoregularity of the polymer chains as shown in SI, Table S1. Interestingly, the isotacticity exponentially decreases with increasing ratio of $[DMSO]_0/[Y(OTf)_3]_0$ (Figure 4). The analysis of backbone methylene protons from 1.7 to 0.9 ppm using 300 MHz ^{1}H NMR spectroscopy in Figure 4 shows a clear transition toward higher racemic content due to the increase in the intensity of the peak

DOI: 10.1021/jacs.5b05903
J. Am. Chem. Soc. 2015, 137, 9988−9999

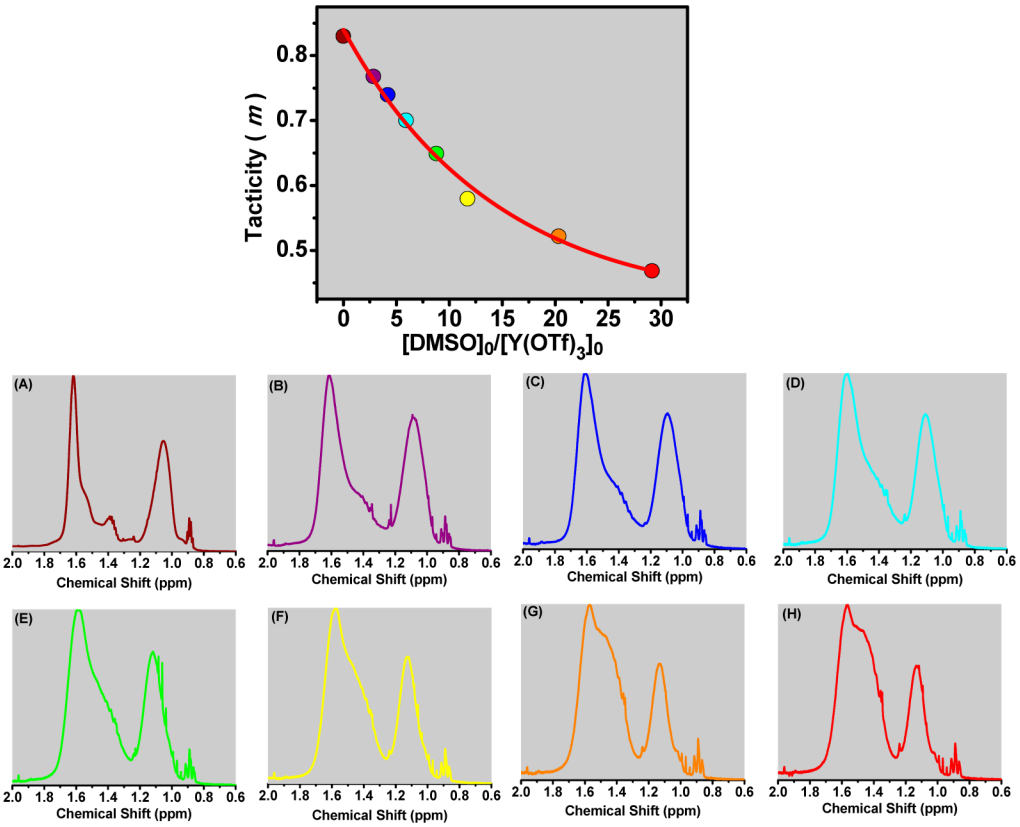


Figure 4. (Top) Stereoregulation in the presence of different ratios of $[DMSO]_0/[Y(OTf)_3]_0$; (Bottom) 300 MHz ^{1}H NMR spectra highlighting the changes in the meso- and racemic- regions at specified ratios of $[DMSO]_0/[Y(OTf)_3]_0$.

at 1.4 ppm. A $[DMSO]_0/[Y(OTf)_3]_0$ ratio of 1:29.10 results in the synthesis of atactic polymer (Figure 4H).

To further demonstrate the ability of DMSO to suppress tacticity at specific segments of a polymer chain, we synthesized a PDMAA stereoblock consisting of isotactic-*block*-atactic segments. The polymerization was initially started with a $[Y(OTf)_3]_0/[DMAA]_0$ ratio of 0.048 in the absence of DMSO. The reaction was allowed to proceed for 1 h to reach a conversion of 46%. This was followed by the addition of DMSO with the ratio of $[DMSO]_0/[Y(OTf)_3]_0$ being 1:29.10 to induce the formation of a completely atactic segment. Upon irradiation under blue light, further extension of the polymer was made possible with a drop of cumulative isotacticity (Table 5). As shown in Figure 5, a clear shift in molecular weight is shown by the GPC curves before and after the addition of DMSO. In addition, the ^{1}H NMR shows an increase in racemic content with an increase in the peak at 1.4 ppm after addition of DMSO. Further chain extension after the addition of DMSO led to a completely atactic segment leading to the synthesis of a stereoblock polymer consisting of $PDMAA_{isotactic(55)}$-*block*-$PDMAA_{atactic(18)}$.

As the addition of DMSO before and during the polymerization resulted in polymers with lower isotacticity, we expanded our work further into exploring the possibility of building a pseudogradient of different isotacticities during the course of polymerization through in situ addition of discrete volumes of DMSO. In our work, we were able to build a polymer chain with five different segments of varying isotacticity. In order to do this, we exploited the temporal control provided by PET-RAFT to precisely target the degree of polymerization for each varying isotactic segments. The polymerization was initially started in the absence of DMSO with a $[Y(OTf)_3]_0/[DMAA]_0$ ratio of 0.048. Upon reaching the

Table 5. Synthesis of Isotactic-*block*-Atactic Stereoblock

entry	yield (α)[c]	$M_{n,th}$ (g/mol)[d]	$M_{n,GPC}$ (g/mol)[e]	M_w/M_n[e]	tacticity (m)[f]	DP	m_2[g]
1[a]	46	5710	5810	1.36	0.83 (m_1)	DP_1 = 55	–
2[b]	61	7500	6990	1.30	0.76 (m_2)	DP_2 = 18	0.55

[a]The reaction was performed in the absence of oxygen at room temperature in methanol/toluene mixture (2:1) under blue light irradiation (0.7 mW/cm^2, λ_{max} = 460 nm) with $Ir(ppy)_3$ as the photoredox catalyst with molar ratio of [DMAA]:[BTPA]:$[Ir(ppy)_3]$:$[Y(OTf)_3]$ = 120:1:1.2 × 10^{-3}:5.75 at room temperature for 1 h. [b]Addition of DMSO to yield a molar ratio of $[DMSO]_0/[Y(OTf)_3]_0$ = 29.10. [c]Monomer conversion was determined by using 300 MHz ^{1}H NMR spectroscopy. [d]Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_0/[RAFT]_0 \times MW^M \times \alpha + MW^{RAFT}$, where $[M]_0$, $[RAFT]_0$, MW^M, α, and MW^{RAFT} correspond to initial monomer concentration, initial RAFT concentration, molar mass of monomer, conversion determined by ^{1}H NMR, and molar mass of RAFT agent. [e]Molecular weight and dispersity were determined by GPC analysis with DMAc as eluent and calibrated to PMMA standards. [f]Determined by 300 MHz ^{1}H NMR. [g]m_2 represents the fraction of isotacticity in the second block determined by the following formula:[14] $m_2 = (mDP - m_1DP_1)/DP_2$ where m, m_1, m_2, DP, DP_1, and DP_2 are fraction of meso dyads in the polymer, meso dyads in the isotactic segment, meso dyads in the atactic segment of the block, overall degree of polymerization determined by monomer conversion, degree of polymerization of isotactic segment determined by monomer conversion and degree of polymerization of atactic segment determined by monomer conversion, respectively.

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J. Am. Chem. Soc. 2015, 137, 9988−9999

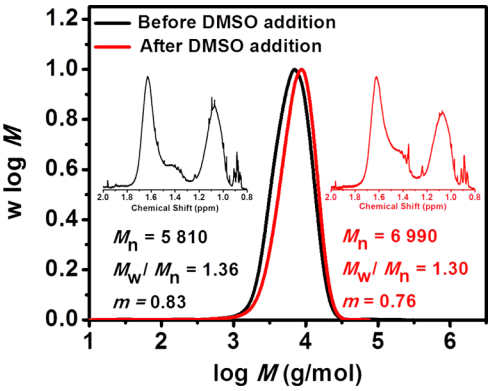

Figure 5. GPC curves of PDMAA stereoblock consisting of isotactic-*block*-atactic segments with 300 MHz ^{1}H NMR insets highlighting the changes in the meso and racemic regions before and after the addition of DMSO.

desired degree of polymerization, the reaction was removed from light and sampling was carried out to characterize the first isotactic block. ^{1}H NMR confirmed the formation of an isotactic segment with a high composition of meso dyads, while GPC showed the formation of polymers with controlled molecular weight and dispersity. This was followed by the addition of DMSO with a $[DMSO]_0/[Y(OTf)_3]_0$ ratio of 2.328. The reaction mixture was then placed back under blue light irradiation for further chain extension. Upon reaching the desired degree of polymerization, irradiation was stopped followed by sampling and characterization by NMR and GPC. These steps were repeated for each segment of the pseudogradient polymer leading to an "ON/OFF" period as shown in Figure 6A. An interesting fact to note is that the apparent propagation rate constant (k_p^{app}) (Table 6) was the highest in the absence of DMSO and drops upon addition of DMSO due to the dilution factor and the decomplexation of $Y(OTf)_3$ with trithiocarbonate. By analyzing the aliquots obtained during sampling via 400 MHz ^{1}H NMR, tacticity at different DMSO concentrations were obtained. As the amido methyl protons (3.1−2.6 ppm, 6H) were much stronger in intensity, they were used to determine the cumulative meso content at different degrees of polymerization. As expected, gradual increase of DMSO concentration led to the formation of polymer segments of lower tacticity (Table 6 and Figure 6B) with very little compositional drift in the cumulative tacticity but much higher compositional drift in the instantaneous tacticity of each segment. We managed to vary the gradient composition of each polymer chain starting with a highly isotactic segment (Table 6, Block 1) leading to an almost atactic final segment (Table 6, Block 5). The overall polymerization kinetics showed living behavior with the evolution of molecular weights to monomer conversion showing a linear plot in close agreement to theoretical molecular weights (Figure 6C). Dispersity (M_w/M_n) measured by GPC decreased with exposure time (i.e., monomer conversion), while molecular weight distributions gradually shifted from low to high molecular weights (Figure 6C,D). End group fidelity was also determined to be higher than 95% (±5%) by NMR and UV−vis.

CONCLUSION

In this article, we report a simple method for the tacticity and temporal control of polymerization of poly(*N*,*N*′-dimethylacrylamide) by combining Lewis Acid ($Y(OTf)_3$) in the presence of photoredox catalysts. Although a poor control and low monomer conversion was observed when $Ru(bpy)_3$ was employed as photoredox catalyst, successful polymerizations were achieved in the presence of $Ir(ppy)_3$. Optimal

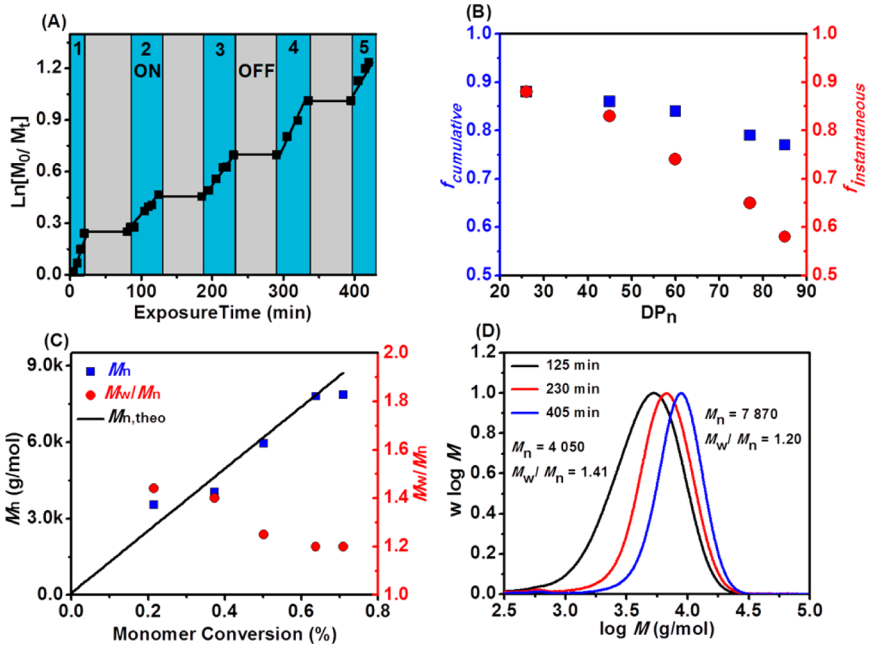

Figure 6. DMSO titration studies for building pseudostereogradient PDMAA polymer chains with five segments of decreasing isotacticity. (A) "ON/OFF" online FTIR kinetics for molar ratio of [DMAA]:[BTPA]:$[Ir(ppy)_3]$:$[Y(OTf)_3]$ = 120:1:1.2 × 10^{-3}: 5.75 with the blue areas representing the polymerization of different isotactic segments ("ON" periods), while the gray areas represent the "OFF" periods and periods of sampling; (B) Plot of cumulative and instantaneous tacticity for the five segments; (C) M_n vs monomer conversion; and (D) typical molecular weight distributions at three different time points.

DOI: 10.1021/jacs.5b05903
J. Am. Chem. Soc. 2015, 137, 9988−9999

Table 6. Stereogradient Control via Addition of DMSO[a]

blocks	$[DMSO]_0/[Y(OTf)_3]_0$	$M_{n,th}$ (g/mol)[b]	DP_n (cum)[c]	k_p^{app} (min^{-1})	$M_{n,GPC}$ (g/mol)[d]	M_w/M_n[d]	f_{cum}[e]	$f_{instant}$[f]
1	0	2800	26	1.49×10^{-2}	3540	1.44	0.88	0.88
2	2.328	4680	45	4.6×10^{-3}	4040	1.40	0.86	0.84
3	1.164	6190	60	5.5×10^{-3}	5970	1.25	0.84	0.78
4	2.328	7850	77	9.7×10^{-3}	7804	1.20	0.79	0.60
5	3.493	8690	85	6.8×10^{-3}	870	1.20	0.77	0.58

[a]The reactions were performed at room temperature in methanol/toluene mixture (2:1) under blue light irradiation (0.7 mW/cm^2, λ_{max} = 460 nm) with $Ir(ppy)_3$ as the photoredox catalyst with molar ratio of [DMAA]:[BTPA]:$[Ir(ppy)_3]$:$[Y(OTf)_3]$ = 120:1:1.2 × 10^{-3}:5.75. [b]Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_0/[RAFT]_0 \times MW^M \times \alpha + MW^{RAFT}$, where $[M]_0$, $[RAFT]_0$, MW^M, α, and MW^{RAFT} correspond to initial monomer concentration, initial RAFT concentration, molar mass of monomer, conversion determined by online FTNIR, and molar mass of RAFT agent. [c]Degree of polymerization (DP_n) was determined using online FTNIR. [d]Molecular weight and dispersity were determined by GPC analysis with DMAc as eluent and calibrated to PMMA standards. [e]Determined by 400 MHz ^{1}H NMR by analyzing amido methyl protons (3.1−2.6 ppm, 6H). [f]$f_{instant}$ represents the fraction of isotacticity in each block determined by 400 MHz ^{1}H NMR.

reaction conditions were observed when the reaction was carried out in methanol/toluene or ethanol/toluene mixture of 2:1 (v/v). By switching ON or OFF the blue LED light, we were able to activate or deactivate the polymerization with good control over the molecular weight and dispersity. Taking advantage of the temporal control of our photoactivated living polymerization (PET-RAFT) and varying the concentration of Lewis Acid, we were able to build complex structures, such as block polymers containing segments with various degrees of tacticity. In addition, we discovered that we could manipulate the tacticity by adding small amount of DMSO in the polymerization mixture. The synthesis of pseudostereogradient polymers were achieved by combining dual temporal and chemical control. Both methods, i.e., addition of discrete amount of $Y(OTf)_3$ or DMSO, result in a good control of molecular weight and a low dispersity (M_w/M_n < 1.25). Such approach can be employed for the polymerization of other acrylamides and methacrylamides. Finally, these stereoblock and gradient copolymers present remarkable physical and chemical properties and are currently being investigated. This will be reported in further studies.

■ ASSOCIATED CONTENT

Supporting Information

Experimental part, UV−vis, NMR spectra and GPC traces (Figures S1−S8 and Table S1). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05903.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

CB acknowledges Australian Research Council (ARC) for his Future Fellowship (F1200096) and thanks UNSW (DVCR Prof. Les Field) for internal funding (SPF01).

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