

Photocontrolled Stereoselective Cationic Polymerization

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ABSTRACT: By virtue of noninvasive regulations by light, photocontrolled polymerizations have attracted considerable attention for the precision synthesis of macromolecules. However, a cationic polymerization with simultaneous photo-control and tacticity-regulation remains elusive and challenging to achieve. Herein, we introduce an asymmetric ion-pairing photoredox catalysis strategy, which allows for the development of a stereoselective cationic polymerization with light control for the first time. By employing a chiral ion pair photoredox catalyst ($PC^+/*A^-$) consisting of a photoredox active cationic part (PC^+) and a sterically confined chiral anion ($*A^-$) to deliver the stereochemical control, the stereoselective cationic polymerization of vinyl ethers with the assistance of photo control can be achieved with high isotactic selectivity (up to 91% *m*) at a remarkable low level of catalyst loading (50 ppm).

In the past two decades, the capability of external stimuli to regulate the polymerization process has attracted considerable interest from both academia and industry.¹⁻³ In particular, visible light, by virtue of its non-invasiveness, low energy, unique spatiotemporal control, etc., has been widely employed in polymer synthesis and material constructions, which has become a focus of extensive studies and pushed forward the precision in polymer synthesis to an unprecedented high level.⁴⁻¹² Accordingly, a number of polymerization methods with visible light regulation have been developed in the past years, including reversible deactivation radical polymerization (RDRP),¹³⁻¹⁷ living cationic polymerization (LCP),¹⁸⁻²² ring-opening metathesis polymerization (ROMP),²³⁻²⁵ and ring opening polymerization,²⁶⁻²⁸ etc., offering various approaches for the synthesis of polymers with well-defined structures and spatiotemporal control by light. However,

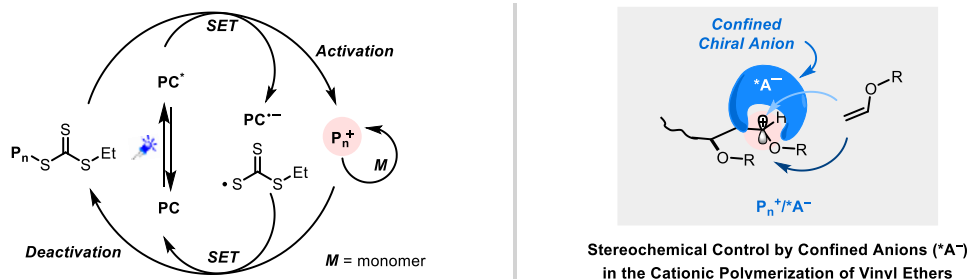
despite the above progress, few photo-controlled polymerizations could concurrently realize an effective stereochemical control in the chain growth to achieve regulation of tacticity.²⁹⁻³¹

The tacticity of vinyl polymers is a critical factor that determines the property of materials.³²⁻³⁴ As a well-known example, atactic, syndiotactic, and isotactic polypropylenes, differentiated by the orientation of the methyl groups on the backbone, could exhibit distinct thermomechanical properties.³² Poly(vinyl ether)s are an important class of polymeric materials, featuring abundant chemical feedstock, good biodegradability, and appealing and tunable properties,^{35,36} while the property of these polymers also highly depends on their tacticity. For example, commercial poly(isobutyl vinyl ether) (poly(IBVE)) products are commonly an amorphous viscoelastic fluid at room temperature because of low isotacticity.^{35,36} In contrast, increasing the content of *meso* diads to above 90% *m* could endow the polymers with a nature of semi-crystalline thermoplastics ($T_m > 110$ °C) and greatly enhanced mechanical properties.³⁶ In fact, considerable research efforts have been dedicated to the development of effective stereoselective polymerization methods to access isotactic vinyl ether polymers since the 1940s, and significant progress has been gained in the past two decades by employing Lewis acids (e.g. Ti complexes)³⁵⁻⁴⁵ or confined Brønsted acids (e.g. IDPi & PADI)⁴⁶⁻⁴⁹ as a catalyst. Whereas, as mentioned above, even though significant advance has been achieved in both photo-controlled cationic polymerization and stereoselective cationic polymerization of vinyl ethers, a photo-controlled cationic polymerization with a simultaneous tacticity regulation remains elusive. To achieve light regulation and stereochemical control at the same time in a radical polymerization, typically, a two-catalyst system comprising a photocatalyst to exert the control by light and a Lewis acid catalyst (unable to initiate radical polymerization) to mediate the stereochemistry was employed.²⁹ However, in the case of cationic polymerization, the Lewis or Brønsted acid catalysts used for stereocontrol could also initiate the polymerization, which would lead to a background reaction in the absence of light and thus result in the loss of control by light. Therefore, a simple combination of known photocatalysts and chiral (Lewis) acid catalysts^{18-22,35-49} is in principle unable to establish a cationic polymerization with photo- and stereo-control concurrently. Accordingly, a new strategy is required.

According to a typical mechanism of photo-controlled cationic polymerizations of vinyl ethers (Figure 1A, left),⁵⁰ oxidation of the dormant chains by the excited photocatalyst (PC*) via single electron transfer (SET) is the key activation step to produce the active cationic species (P_n^+),

which will subsequently initiate the addition of vinyl ether monomer (M) to achieve chain growth. We conceived that the cationic nature of the propagating chains (P_n^+) in cationic polymerization makes it possible to “pair” with a suitable bulky anion (e.g. a sterically confined chiral anion, $^*A^-$),⁵¹⁻⁵³ which could then bias the addition of the incoming monomer to the planar carbocation, thus reaching a stereochemical control in the bond-forming step (Figure 1A, right).^{48,49} Based on this idea of bulky anion-control, we have successfully developed a highly stereoselective cationic polymerization of vinyl ethers by employing confined chiral Brønsted acids (like IDPi and PADI) as the catalyst.^{48,49} Inspired by this success, we considered if there is an appropriate and effective way to introduce the bulky anion $^*A^-$ “in time” to pair with the P_n^+ generated in photocontrolled cationic polymerizations (Figure 1, left), a cationic polymerization with simultaneous photo- and stereo-control might be possible. In the end, this idea led us to the ion-pair type of photocatalysts (PC^+X^-),⁵⁴⁻⁵⁶ in which the X^- is typically a small anion (e.g. TfO^- , BF_4^- , etc.) that is unable to shield one side of the planar carbocationic chain end of P_n^+ to exert an

A. Typical Mechanism of Photocontrolled Cationic RAFT Polymerization and Introduction of Stereocontrol by Confined Anion ($^*A^-$)



B. This Work: Development of Asymmetric Ion-Pairing Photoredox Catalysis for Photocontrolled Stereoselective Cationic Polymerization

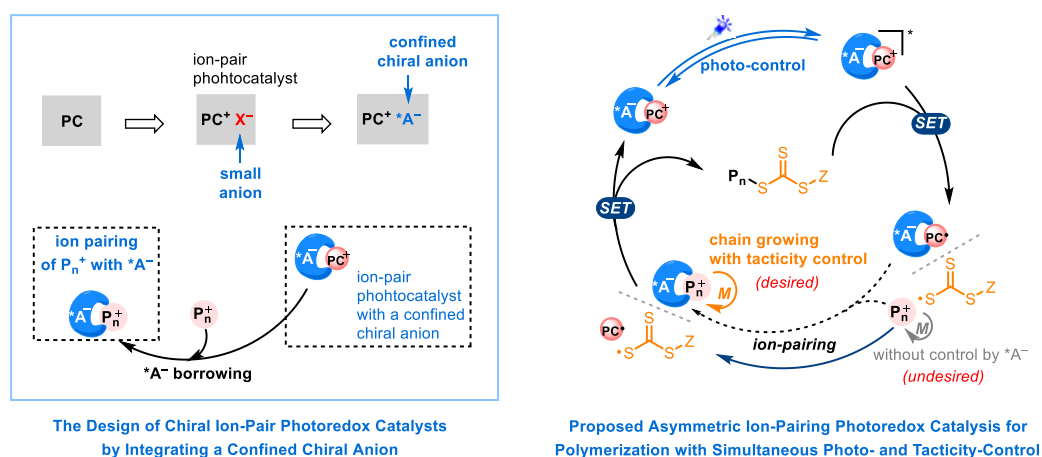


Fig. 1. The design of ion-pairing photoredox catalysts for the development of photo-controlled stereoselective cationic polymerization.

effective stereochemical control. We conceived replacing the non-photoredox active X^- with a bulky anion ($*A^-$) could generate a new ion pair photoredox catalyst ($PC^+/*A^-$), and the anion $*A^-$ can be borrowed by P_n^+ via an ion-pairing process in the polymerization (Figure 1B, left). If the transfer of anion $*A^-$ from the reduced photocatalyst ($PC^•/*A^-$) to the active P_n^+ via a cation/anion ion-pairing process is fast enough (Figure 1B, right), the desired chain growth with stereocontrol by the confined chiral anion $*A^-$ would become predominated. In this way, a cationic polymerization with both photo- and tacticity-control could become possible.

To identify a suitable chiral ion pair photoredox catalyst ($PC^+/*A^-$) for the development of a photocontrolled stereoselective cationic polymerization of vinyl ethers, we commenced our study with the screening of photoredox cations (PC^+) in combination with the chiral anion (**a**) derived from PADI acid, which has shown its stereo-induction capability in the acid-catalyzed cationic RAFT polymerization of vinyl ethers.⁴⁹ As shown in Figure 2, two common oxidative photoredox catalysts, pyrylium and acridinium tetrafluoroborates, were first examined. The corresponding chiral ion pair photoredox catalyst (IPPC: $PC^+/*A^-$) **1a** & **2a** were prepared by replacing the small counteranions ($X^- = BF_4^-$) with confined chiral anion, PADI **a**, via anion exchange. Initially, the polymerizations were performed at $-20\text{ }^\circ\text{C}$ a ratio $[IBVE]_0/[CTA]_0/[IPPC]_0$ of 100/1/0.01. To our delight, the two ion pair photocatalysts (**1a** & **2a**) comprising a confined anion could well promote the cationic polymerization of IBVE under the irradiation of blue LED with 100 ppm catalyst only, and a significant stereochemical control ($>65\%$ *m*) exerted by the confined anion ($*A^-$) was observed in both cases. In contrast, the corresponding pyrylium and acridinium tetrafluoroborates (**1a**/ BF_4^- & **2a**/ BF_4^-) afforded much lower isotactic selectivity (Figure 2, step 1). Of note, similar to radical polymerizations,^{29-31,57} cationic polymerizations also experience a similar level of low reaction energy barrier, and the observed improvement in isotacticity control at $-20\text{ }^\circ\text{C}$ is quite significant. Importantly, these initial study suggests that the key ion pairing of the propagating carbocation P_n^+ with the chiral anion ($*A^-$) from the ion-pair catalyst ($PC^+/*A^-$) indeed happened during the polymerization, and it is possible to impose a stereochemical control on the photocontrolled cationic polymerization via this asymmetric ion-pairing photoredox catalysis strategy (Figure 1B). Encouraged by the initial proof of this concept, we further examined several phosphonium-type cations⁵⁴⁻⁵⁶ (**6-8**, for a detailed screening study, please see Table S1). Pleasingly, compared with **1a** and **2a**, these phosphonium ion-pair photocatalysts (**3a-5a**) could further improve the isotactic selectivity to a higher level, reaching 70% *m* and 71% *m* at $-20\text{ }^\circ\text{C}$ with **3a** and **5a** as the catalyst, respectively.

We next examined the effect of the different anions in combination with the photoredox active cation **5**, under the same polymerization conditions (Figure 2). A series of PADI anions (**b-g**) with variation on the aryl groups at the 3,3'-position were first examined. The PADI anion with a 3,3'-phenyl group (**5b**) or the ones with electron-withdrawing -CF₃ or donating methyl groups at the 3,5-positions of the phenyls (**5c** and **5d**) gave lower isotactic selectivity than that of **5a**. Nevertheless, the bulky anion PADI **e** with 2,4,6-trisopropyl-substituted phenyl groups could afford a similar stereoselectivity (**5e**, 70% *m*) to PADI **a**. Next, we turned to the sterically more confined IDPi anions, and an apparent influence of the variation of the aryl groups of IDPi anions was observed. **5j** with 3,5-dimethyl aryl groups on the BINOL scaffold provided the most effective stereochemical control in the polymerization and further improved the isotactic selectivity to 73% *m*, affording poly(IBVE) with controlled molecular weight ($M_{n,GPC}$ 10.1 kg/mol, $M_{n,theo}$ 10.2 kg/mol) and low dispersity (\bar{D} 1.54) after full monomer conversion in 6 hours.

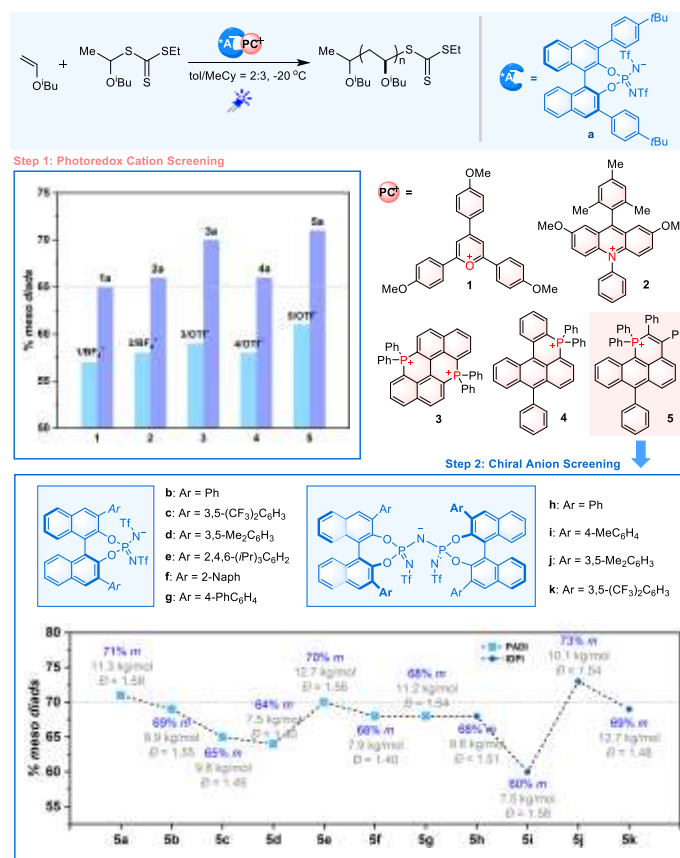


Fig. 2. Effect of photoredox cations and chiral anions on the photocontrolled stereoselective cationic RAFT polymerization of IBVE.

Isotactic poly(IBVE) with 90% *m* can be obtained by conducting the polymerization at -78 °C in toluene/MeCy by employing ion pair **5j** as the catalyst under the irradiation of blue LED (Table 1, entry 1). Notably, solid poly(IBVE) products became accessible at -60 °C via this photocontrolled stereoselective polymerization method (86% *m*, entry 2). Remarkably, the catalyst loading can be decreased to 50 ppm, while maintaining a high isotactic selectivity (entry 4). To the best of our knowledge, it is the first example that could achieve 90% *m* stereoselectivity in the cationic polymerization of IBVE at a catalyst loading below 100 ppm. As in the ion pairing process of P_n^+ with $^*A^-$, a rapid transfer of the bulky anion ($^*A^-$) from the reduced ion pair catalyst (after SET) to the propagating carbocationic chain end of P_n^+ is necessary to suppress the undesired chain growth without the mediation by the bulky anion $^*A^-$ (Figure 1B, right), in which the dissociation and re-pairing of ionic species could be influenced by the solvent polarity. We thus performed the polymerization with 50 ppm **5j** as the catalyst in different solvent combinations (entry 5 vs 6). Not unexpectedly, the addition of dichloromethane (DCM) slightly decreased

Table 1. Photocontrolled Stereoselective Cationic RAFT Polymerization of Vinyl Ethers ^a



Entry	[M]	[M]/[CTA]/[Cat]	$M_{n,GPC}$ (kg/mol) ^b	\bar{D} ^b	<i>m</i> ^c
1	IBVE	100:1:0.01	15.2	1.81	90%
2 ^d	IBVE	100:1:0.01	14.1	1.67	86%
3 ^e	IBVE	100:1:0.01	13.0	1.59	86%
4	IBVE	100:1:0.005	15.7	1.74	90%
5 ^f	IBVE	100:1:0.005	13.8	1.83	89%
6 ^g	IBVE	100:1:0.005	10.6	1.38	84%
7	IBVE	100:2:0.005	6.7	1.48	90%
8	IBVE	100:4:0.005	3.9	1.35	89%
9	IBVE	200:1:0.01	20.4	1.89	90%
10	BVE	100:1:0.005	14.3	1.71	90%
11	PVE	100:1:0.005	13.8	1.60	90%
12	HVE	100:1:0.005	14.7	1.66	91%

^a $[M]_0 = 0.4$ M, under blue LED irradiation, 6h; ^b Determined by GPC using polystyrene standards, kg/mol;

^c Determined by ¹³C NMR. ^d At -60 °C. ^e With **5a** as the catalyst. ^f In toluene/MeCy = 1:4. ^g In DCM/MeCy = 1:4.

the stereoselectivity, while a narrower molecular weight distribution was obtained (entry 6). Furthermore, the synthesis of isotactic polymers with different molecular weights (from 3.9 kg/mol to 20.4 kg/mol) was also demonstrated through this photocontrolled stereoselective method at 50 ppm catalyst loadings by varying the ratios of $[\text{IBVE}]_0/[\text{CTA}]_0$ (entries 7-9). Other simple vinyl ether monomers like *n*-butyl vinyl ether (NBVE), *n*-propyl vinyl ether (NPVE), and hex-5-enyl vinyl ether (HVE) also well polymerized with high isotactic selectivity (90-91% *m*, entries 10-12) via this asymmetric ion-pairing photoredox catalysis approach.

Of note, even though with a stereochemical mediation by the same chiral anion, higher stereoselectivity was observed in the photocontrolled stereoselective polymerization process when comparing with the corresponding chiral acid-catalyzed polymerization process that lacks a light control (Figure 3). The stereoselective cationic RAFT polymerization of IBVE with ion pair photocatalyst **5j** or chiral acid IDPi **j-H⁺** as a catalyst were performed under the same conditions ($[\text{IBVE}]_0/[\text{CTA}]_0/[\text{Cat}] = 100/1/0.02$, $[\text{IBVE}]_0 = 0.4 \text{ M}$) at different reaction temperature. As shown in Figure 3, the photocontrolled method afforded apparent higher stereoselectivity at all temperature (0, -20, -40, -60, and -78 °C). This interesting phenomenon may benefit from the controlled (lowered) polymerization rate by light, also suggesting a possible advantage of introducing photo-control into polymerization when seeking a tacticity regulation.

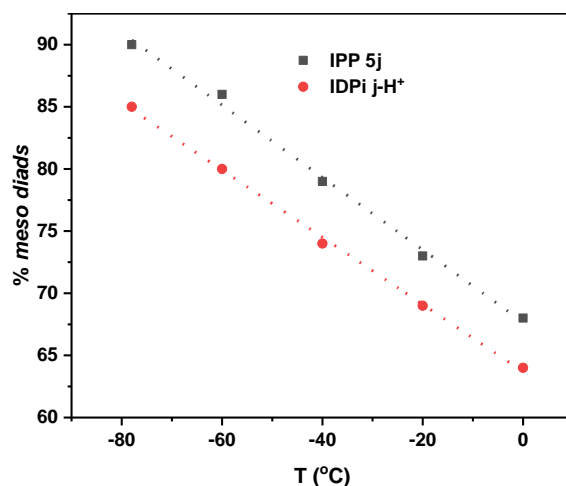


Fig. 3. A comparison of the temperature effect on the photocontrolled stereoselective cationic RAFT polymerization (with ion pair **5j**) of IBVE or the acid IDPi **j-H⁺** catalysed polymerization.

Moreover, the photophysical and electrochemical properties of the ion pair catalyst **5j** were examined, and the selected results are depicted in Figure 4. This ion pair catalyst exhibited a strong absorption in the blue band ($\lambda_{\max} = 441$ nm), with an ϵ_{\max} over $17.4 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ (Figure 4a). The absorption profile in the visible light region is similar to that of the **5-OTf**⁻, indicating the photocatalytic activity is from the cationic part of the ion pair **5j**. In addition, the cyclic voltammetry experiments showed that the ground-state redox power of **5j** ($E_{1/2} = -0.93$ V vs SCE) is similar to that of **5-OTf**⁻ ($E_{1/2} = -0.89$ V vs SCE), which is enough to recap the chain-end ($E_{1/2} < -0.5$ V vs SCE)⁵⁰ in the deactivation step (Figure 1). According to the above results, the good photoredox property of **5-OTf**⁻ was well retained after anion exchange (**5j** $E^*(\text{PC}^*/\text{PC}^{\cdot-}) = 1.66$ V, **5-OTf**⁻ $E^*(\text{PC}^*/\text{PC}^{\cdot-}) = 1.70$ V vs SCE).⁵⁶ The photoluminescence quenching experiments unveiled a strong quenching of **5j**^{*} by CTA, suggesting that **5j**^{*} prefers to oxidize the CTA. Further, by virtue of integrating a photoredox cation, besides tacticity control, the present stereoselective cationic polymerization could now proceed with the desired light-regulation. As shown in Figure 4d, the polymerization can be effectively controlled by light via “On/Off” operations. No significant background polymerization and chain growth were observed during the dark periods after the light was switched off, and the polymerization can restart again when the light was switched on, suggesting an effective activation-deactivation process was established with this chiral ion pair photocatalyst.

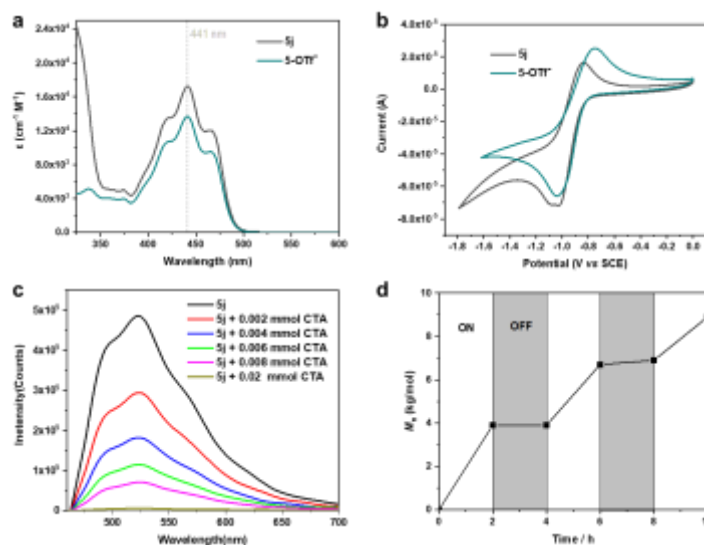


Fig. 4. Characterizations of **5j**. a) UV absorption spectrum of **5j** in DCM; b) The cyclic voltammogram of **5j** in MeCN using SCE (saturated calomel electrode) as reference electrode; c) Fluorescence quenching of **5j** by the addition of CTA; d) The photocontrol on the chain growth via light on/off operations.

Moreover, it is worth mentioning that poly(vinyl ether)s with high chain-end fidelity can be prepared with this photocontrolled stereoselective cationic polymerization method, which could thus allow for the synthesis of stereo-block copolymers by employing isotactic polymers as a macro-CTA in the subsequent chain extension. As demonstrated in Figure S1-4 with isotactic poly(IBVE), via mechanistic switching, e.g. to AIBN-initiated radical RAFT polymerization of vinyl acetate (Figure S3) or visible light-regulated PET-RAFT polymerization of pentafluorophenyl methacrylate (Figure S4), various stereo-block copolymers become accessible.

In summary, asymmetric ion-pairing photoredox catalysis has been demonstrated as an effective strategy for the development of photocontrolled stereoselective cationic polymerization. By employing a designed chiral ion pair photoredox catalyst ($PC^+/*A^-$) consisting of a photoredox active cationic part (PC^+) and a sterically confined chiral anion ($*A^-$), the photocontrolled cationic polymerization of vinyl ethers was successfully developed with simultaneous photo- and tacticity-control for the first time. A rapid ion-pairing process of the confined anion $*A^-$ with the propagating cationic chain ends generated from the photoredox catalytic cycle during the polymerization is conceived critical to the observed high stereoselectivity. Of note, besides the features of simultaneous spatiotemporal control by light and the tacticity-regulation, this photocontrolled stereoselective polymerization was found affording a better stereoselectivity than the corresponding chiral acid (H^*A)-mediated process, suggesting a possible beneficial effect of introducing photo-control to tacticity regulation. Further, high isotacticity (up to 90% *m*) can be achieved at a 50 ppm-level of catalyst loading, which, to the best of our known, represents the lowest catalyst loading so far in the stereoselective polymerization of vinyl ethers that could afford such a high stereoselectivity. With the first successful demonstration of asymmetric ion-pairing photoredox catalysis⁵⁸ in the development of a cationic polymerization of vinyl ethers with dual photo- and tacticity-control, further application of this strategy in the development of other photocontrolled stereoselective cationic polymerizations can be anticipated.

Supporting Information

Synthesis of monomer, experimental procedures, characterization data, copies of NMR spectra.

Notes

The authors declare no conflict of interests.

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