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Organocatalytic cationic degenerate chain transfer polymerization of vinyl ethers with excellent temporal control†

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An organocatalytic cationic degenerate chain transfer (DCT) polymerization of vinyl ethers with temporal control under visible light is reported. By using a bisphosphonium salt (BPS) as the photocatalyst and easily prepared thioacetal as the chain transfer agent, well-defined and colorless poly(vinyl ether)s with good molecular weight control and narrow molecular weight distributions can be obtained. The resulting polymers exhibited high chain-end fidelity, allowing further *in situ* chain extension and chain-end functionalization to synthesize block copolymers and end-functionalized polymers. Notably, the excellent stability and efficiency of BPS enables a strict temporal control over polymer chain growth at high monomer conversion for a long dark period.

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Introduction

Living/controlled polymerization represents a highly useful, effective, and widely applicable method for the synthesis of functional polymers with specific physical properties and well-defined structures.^{1,2} Recently, external stimuli^{3–5} (such as thermal,^{6,7} chemical,^{8–12} photo^{13–16} and electrochemical^{17–21}) regulated living polymerizations have attracted considerable research interests, due to the possibility to introduce additional control over the polymerization process. Among these external stimuli, visible light, as an unlimited source of renewable and clean energy from nature, has shown many appealing features, particularly, with the capability to impose a spatiotemporal control on the material construction.^{22–26}

Recently, photo-controlled cationic polymerization have received increasing attention, and several visible light-regulated polymerizations have been successfully developed, including cationic reversible addition–fragmentation chain transfer (RAFT)^{27–32} and degenerate chain transfer (DCT)^{33,34} polymerization, ring opening metathesis polymerization (ROMP),^{35–37} ring opening polymerization (ROP).^{38–40} You, Nicewicz and Perkowski reported the first photoredox-initiated

living cationic DCT polymerization of 4-methoxystyrene by using a pyrylium salt as the photo-initiator and MeOH as the chain-transfer agent (CTA).³³ Later on, the Fors group disclosed a photo-controlled cationic RAFT polymerization of vinyl ethers with methoxy-substituted pyrrlium salt as the photoredox catalyst,²⁷ and achieved much better temporal control later by using iridium complexes as the photocatalyst.^{29,30} Recently, Zhu and co-workers reported a visible light-induced cationic RAFT polymerization by employing commercially available iron or manganese complexes as a photocatalys.^{31,32} Very recently, Kamigaito *et al.* demonstrated that acridinium salts were also suitable photoredox organocatalysts for the visible light-mediated cationic RAFT polymerizations of vinyl ethers, and achieved substantial temporal control *via* catalyst structure-optimization (Fig. 1A).⁴¹

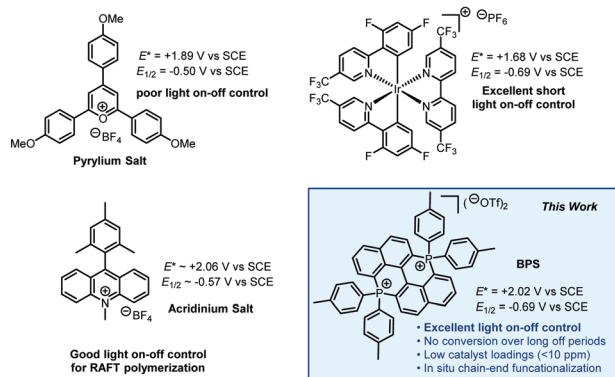
The capability of thioethers to mediate cationic degenerative chain transfer polymerization in the presence of triflic acid was first demonstrated by Kamigaito, which was proposed to proceed through reversibly interchanges between the growing carbocationic and the dormant sulfonium.^{42,43} Importantly, compared with thiocarbonylthio esters, thioethers can be easily prepared and could afford colorless polymer products. However, the corresponding photo-controlled cationic DCT polymerization with thioethers as the CTA has been proved to be more challenging to achieve a good temporal control.^{34,41} For example, pyrylium salts and iridium complexes showed excellent temporal control in the cationic RAFT polymerizations of vinyl ethers,²⁹ while in the corresponding degenerate chain-transfer cationic polymerization with thioacetals as the CTA, pyrylium salts almost lost the tem-

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A. Photocatalysts for Cationic Degenerate Chain Transfer Polymerization of Vinyl Ethers



B. Mechanism for the Photo-controlled Degenerate Chain Transfer Cationic Polymerization

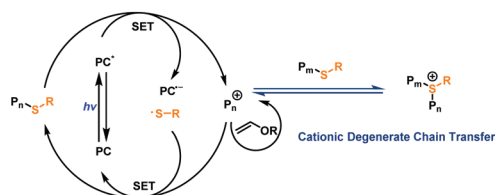


Fig. 1 Photo-controlled degenerate chain transfer cationic polymerization of vinyl ethers.

poral control.³⁴ Accordingly, the development of an organocatalytic cationic degenerate chain transfer polymerization with strict temporal control remains a challenge task.

Recently, by following a photocatalyst design logic based on heteroatom-doping of polycyclic arenes,^{44,45} we successfully identified bisphosphonium salts (BPS) as an effective type of organophotocatalysts for the cationic reversible addition-fragmentation chain transfer (RAFT) polymerizations of vinyl ethers.⁴⁶ Their highly oxidizing excited state potential and suitable ground state redox potential ($E^* > +2.00 \text{ V}$, $E_{1/2} < -0.60 \text{ V vs. SCE}$), as well as high stability, enabled the polymerization proceed at a low ppm level of catalyst loading with strict temporal control. We conceived BPS could also oxidize the DCT agents (e.g. thioacetals) upon excitation to generate the active carbocation, and the reduced BPS with thiol radical could recapture the cationic chain end to regenerate the DCT agent (or the dormant chains), thus establishing a light-regulated degenerative chain-transfer process (Fig. 1B). Here, we report our efforts toward this goal, and the development of an organocatalytic photo-controlled cationic degenerate chain-transfer polymerization of vinyl ethers with a thioacetal as the chain transfer agent with high chain-end fidelity and excellent temporal control.

Experimental methods

Materials and characterization

All monomers (isobutyl vinyl ether (99%, TCI), ethyl vinyl ether (99%, TCI), *n*-propyl vinyl ether (99%, TCI), *n*-butyl vinyl ether (98%, TCI), isopropyl vinyl ether (98%, Energy Chemical),

tert-butyl vinyl ether (98%, TCI), cyclohexyl vinyl ether (>95%, TCI), 2,3-dihydrofuran (99%, TCI), 2-chloroethyl vinyl ether (97%, TCI) and solvent (DCM (HPLC, J&K)) were dried over calcium hydride (CaH_2) for 24 h, collected under reduced pressure, deoxygenized by freeze-pump-thaw cycle three times and stored at -20°C in the glove box. Butyl(1-isobutoxyethyl) thioether (CTA) was synthesized according to literature.⁴² Other chemicals were purchased from Energy Chemical or Adamas-beta, and used without further purification. ^1H NMR was recorded on a Bruker AVIII 400 MHz spectrometer using TMS as the internal standard. Number-average molecular weight (M_n , GPC) and molecular weight distributions (D) were obtained by GPC (Waters 1515 series) in THF at 35°C , and equipped with two Styragel Column (HR3 and HR4, $7.8 \times 300 \text{ mm}$, flow rate = 1.0 mL min^{-1}) using Shodex Polystyrene standards (890 to $5.98 \times 10^5 \text{ g mol}^{-1}$).

Typical DCT polymerization procedure

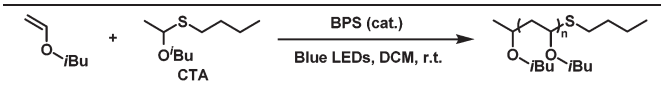
In glove box, 10 mL Schlenk tube equipped with a magnetic stir bar, with IBVE (300 mg, 3.0 mmol, 100 eq., 3.0 M), CTA (30.0 μmol , 1 eq.), BPS (0.03 μmol , 0.001 eq., 10 ppm) in DCM was used. The mixture was stirred under blue LEDs irradiation (6 W, $\lambda_{\text{max}} = 460 \text{ nm}$, 30 mW cm^{-2}) at room temperature. Following the desired amount of reaction time, benzene was added as an internal standard to measure the conversions by ^1H NMR. Later, the reaction was quenched by the addition of MeOH/ NET_3 (9 : 1, 1 mL) and the reaction mixture stirred at room temperature for another 0.5 h. The pure polymer was obtained by vacuo to remove the solvent, and analyzed by GPC to determine the number average molecular weights (M_n), and molecular weight distributions (M_w/M_n).

Typical chain-end functionalization procedure

In glove box, 10 mL Schlenk tube equipped with a magnetic stir bar, with IBVE (300 mg, 3.0 mmol, 100 eq., 3.0 M), CTA (30.0 μmol , 1 eq.), BPS (0.03 μmol , 0.001 eq.) in DCM was used. The mixture was stirred under blue LEDs irradiation (6 W, $\lambda_{\text{max}} = 460 \text{ nm}$, 30 mW cm^{-2}) at room temperature for 20 min. Upon completion, alcohol (90.0 μmol , 3 eq.), and 2,6-di-*tert*-butylpyridine (30.0 μmol , 1 eq.) were added, and then exposed to light again for 5 h. Later, the reaction was quenched by the addition of MeOH/ NET_3 (9 : 1, 1 mL) and the reaction mixture stirred at room temperature for another 0.5 h. The polymer was obtained by vacuo to remove the solvent, then precipitated from cold methanol, and dried *in vacuo* to afford pure polymer, and the polymer was analyzed by GPC and ^1H NMR.

Results and discussion

We commenced our study on the development of a degenerate chain transfer cationic polymerization of isobutyl vinyl ether by using butyl(1-isobutoxyethyl)thioether as the chain transfer agent and bisphosphonium salt (BPS) as the catalyst, under the irradiation of blue LEDs. To our delight, full monomer

Table 1 Photo-controlled degenerate chain transfer cationic polymerization of isobutyl vinyl ether^a


Entry	[M] ₀ /[CTA] ₀ /[BPS]	Conv. ^b (%)	<i>M</i> _{n,GPC} ^c (kg mol ⁻¹)	<i>D</i> ^c
1	100/1/0.01	>99	8.6	1.35
2	100/1/0.02	>99	8.1	1.46
3	100/1/0.005	>99	9.0	1.34
4	100/1/0.002	>99	9.2	1.33
5	100/1/0.001	>99	10.0	1.30
6 ^d	100/1/0.0005	>99	9.0	1.40
7 ^e	100/1/0.001	>99	9.1	1.34
8	100/1/—	—	—	—
9	100/—/0.001	95	20.2	2.0
10 ^f	100/1/0.001	—	—	—
11	35/1/0.001	>99	3.8	1.21
12	50/1/0.001	>99	5.1	1.20
13	200/1/0.001	98	17.5	1.38

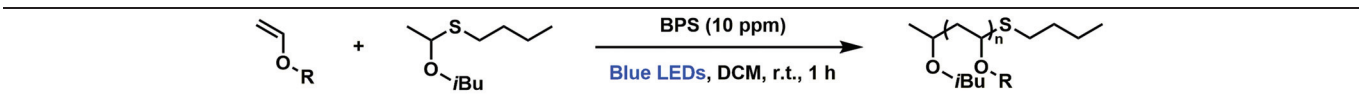
^a [M]₀/[CTA]₀/[BPS]₀ ratio as shown in the table, in DCM (3 M), 6 W Blue LEDs, 1 h. ^b Determined by ¹H NMR using benzene as an internal standard. ^c *M*_n and *D* were measured by GPC with polystyrene standards. ^d 6 W Blue LEDs for 3 h. ^e 2.0 M of IBVE was carried out. ^f Carried out in dark.

conversion (>99%) can be achieved in 1 h, in the presence of 100 ppm of BPS only, affording poly(IBVE), 8.6 kg mol⁻¹ with a narrower *D* of 1.35 (Table 1, entry 1). Although a higher loading of BPS (200 ppm) resulted in a broader dispersity (*D* 1.46, entry 2), decreasing the catalyst loading to 10 ppm delivered even a better control, giving poly(IBVE) with good control of molecular weight and low dispersity (*D* 1.30, entry 5). Full monomer conversion and good control were also

achieved when decreasing the catalyst loading to 5 ppm (entry 6). Control experiments indicated that the photocatalyst, light irradiation, and CTA were all important to ensure the polymerization proceeding in a controlled manner (entries 8–10). Moreover, controlled molecular weights and narrow molecular weight distributions were observed with different ratio of [M]₀/[CTA]₀ (35/1 to 200/1, entries 11–13).

The BPS-mediated degenerative chain transfer cationic polymerization also worked well with other vinyl ether monomers, such as ethyl vinyl ether (EVE), *n*-propyl vinyl ether (NPVE), *n*-butyl vinyl ether (NBVE) and isopropyl vinyl ether (IPVE) (Table 2). In the presence of 10 ppm of BPS as the photocatalyst, high conversions were achieved after 1 hour of irradiation with blue LEDs at room temperature, affording the corresponding poly(vinyl ether)s with narrow molecular weight distribution, together with a good control over the molecular weight (entries 1–7). Bulky vinyl ethers, such as *tert*-butyl vinyl ether (TBVE) and cyclohexanyl vinyl ether (CyVE), could also polymerize under the standard conditions, albeit with relatively broader dispersity (entries 8 and 9). These results may indicate that increased steric hindrance could decrease the degenerative chain transfer rate. Further, the polymerization of 2,3-dihydrofuran (DHF) afforded poly(DHF) as white solids also with good control over molecular weight and dispersity. Moreover, 2-chloroethyl vinyl ether (Cl-EVE) could be polymerized with 50 ppm of BPS catalyst for 2 h, delivering the polymer product with a dispersity of 1.32 (entry 11).

Next, the progress of this cationic DCT polymerization at a ratio of [IBVE]₀/[CTA]₀/[BPS] = 100/1/0.001 was tracked. Under the standard conditions, 50% conversion of monomer was observed within 15 min, reaching 97% conversion after 60 min (Fig. 2A). A linear relationship between ln([IBVE]₀/[IBVE]_t) and

Table 2 Photo-controlled cationic degenerate chain transfer polymerization of various vinyl ethers^a


Entry	M	[M] ₀ /[CTA] ₀	Conv. ^a (%)	<i>M</i> _{n,theo} ^b (kg mol ⁻¹)	<i>M</i> _{n,GPC} ^c (kg/mol)	<i>D</i> ^c
1	EVE	50/1	93	3.6	3.2	1.20
2	EVE	100/1	94	6.9	6.3	1.16
3	NPVE	50/1	92	4.1	3.6	1.17
4	NPVE	100/1	94	8.3	7.2	1.19
5	NBVE	50/1	>99	5.2	4.6	1.20
6	NBVE	100/1	>99	10.2	9.8	1.30
7	IPVE	100/1	>99	8.8	6.9	1.34
8	TBVE	100/1	>99	10.2	9.0	1.41
9	CyVE	100/1	>99	12.8	8.3	1.63
10	DHF	100/1	94	6.8	6.8	1.38
11	Cl-EVE	100/1	72	7.9	12.3	1.32

^a Determined by ¹H NMR analysis with benzene as an internal standard. ^b Calculated as ([monomer]₀/[CTA]₀) × (*M*_w of monomer) × conversion + (*M*_w of CTA). ^c Determined by GPC in THF using polystyrene standards.

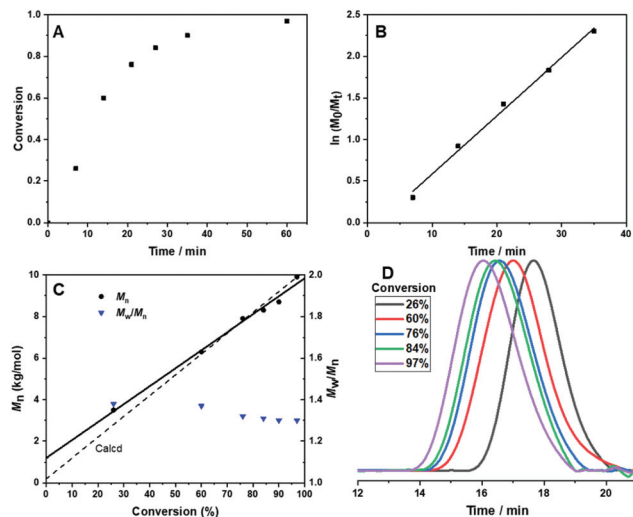


Fig. 2 Kinetic investigation of the cationic DCT polymerization. (A) Conversion vs. time; (B) $\ln([M]_0/[M])$ vs. time; (C) molecular weight (M_n) and molecular weight distribution (D) vs. conversion; (D) GPC traces of polymerization at different conversions.

time was also observed (Fig. 2B). Importantly, linearly increased molecular weight with monomer conversion was achieved (Fig. 2C), which is in line with a living/controlled chain growth. The molecular weight distributions (D) decreased upon the polymer chain extended, and the GPC traces also clearly showed an increased molecular weight over conversion (Fig. 2D). All these data suggested that the good living/controlled characteristics of this BPS-mediated cationic DCT polymerization.

Therefore, to assess the capability of the current catalytic system on temporal control over the chain growth, light on-off experiments with short and long off periods were carried out. Using 10 ppm of bisphosphonium salt with blue LEDs, monomer conversion reached 31% after the first “ON” cycle. Then, the reaction was placed in dark, and notably no conversion was observed during this light-off period. When the reaction was re-exposed to the irradiation of blue LEDs, the polymerization rate could recover. This light on-off operation can be repeated several times, showing uniformly strict temporal control (Fig. 3A). Further, a long dark period at a high monomer conversion (>60%) was also examined. As shown in Fig. 3B, no conversion was observed with the long dark period up to 3 h. This strict temporal control by light indicated an efficient activation-deactivation mechanism of this BPS-mediated cationic DCT polymerization under visible light.

The performance of this bisphosphonium salt in the cationic DCT polymerization was further examined in the one-pot chain extension and block copolymer synthesis with 10 ppm BPS as the catalyst (Fig. 4). The chain extension experiment was carried under the standard conditions, the pIBVE (4.3 kg mol^{-1}) was first synthesized. Then, 40 equiv. of IBVE was added to the Schlenk tube, the pIBVE-*b*-pIBVE was obtained with 7.8 kg mol^{-1} and D 1.35 after 2 h (full conversion). A

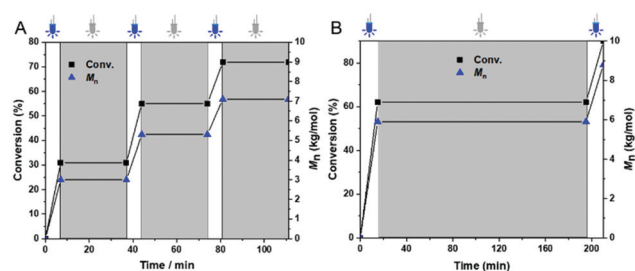


Fig. 3 (A) Time vs. monomer conversion and molecular weight (M_n) of the on/off experiment; (B) long dark period of the on/off experiment.

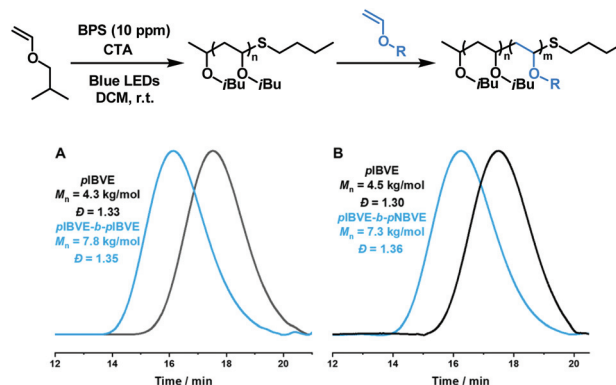


Fig. 4 (A) Poly(isobutyl vinyl ether) chain extension; (B) synthesis of poly(isobutyl vinyl ether)-*block*-poly(butyl vinyl ether).

diblock copolymer pIBVE-*b*-pNBVE was also successfully synthesized with 10 ppm of BPS, with GPC traces showing a significant shift to high molecular weight region (7.3 kg mol^{-1} vs. 4.5 kg mol^{-1}).

Encouraged by the above chain extension experiments, we conceived this polymerization with high chain-end fidelity may be used to synthesize polymers with a chain-end functionalization (Fig. 5). Oxidation of the thioacetal by BPS* in the polymer chain-end generates carbocations, which can be thus trapped by nucleophilic substrates. To test this proposal, we first synthesized pIBVE ($[M]_0/[CTA]_0 = 100:1$) by the cationic DCT polymerization. Then, 1.0 equiv of 2,6-di-*tert*-

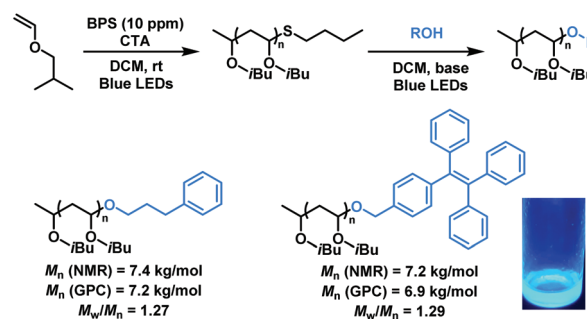


Fig. 5 Photo-controlled DCT polymerization followed by chain-end functionalization.

butylpyridine as the base and 3.0 equiv of alcohol as the nucleophilic substrates were added. After irradiation with 6 W Blue LEDs for 3 h at room temperature, the desired acetal polymers were obtained in high yields. The chemical structure of the chain-end groups in polymers were further confirmed by ^1H NMR analysis (for details, please see Fig. S6 and S7†). Interestingly, the tetraphenylethylene functionalized poly (IBVE) showed strong aggregation-induced emission (AIE) behavior with a charming azure color.^{47–49}

Conclusions

In summary, the bisphosphonium salt (BPS) has been identified as effective organophotocatalyst for the cationic degenerate chain transfer (DCT) polymerization, which allowed for the development of the metal-free cationic DCT polymerization of vinyl ethers with strict temporal control under visible light. Through this DCT polymerization system, colourless poly(vinyl ether)s can be synthesized with good molecular weight control and high chain-end fidelity at a low ppm level of catalyst loading (<10 ppm). Further application of this polymerization system to the one-pot synthesis of block copolymers and polymer chain-end functionalization was also demonstrated.

Conflicts of interest

There is no conflict of interest to report.

Acknowledgements

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