Chinese Journal of
POLYMER SCIENCE

ARTICLE

https://doi.org/10.1007/s10118-020-2441-7
Chinese J. Polym. Sci. **2020**, *38*, 1178–1184

Activation and Deactivation of Chain-transfer Agent in Controlled Radical Polymerization by Oxygen Initiation and Regulation

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Electronic Supplementary Information

Abstract The activation and deactivation of the chain-transfer agent were achieved by oxygen initiation and regulation with triethylborane under ambient temperature and atmosphere. The autoxidation of triethylborane overcame the oxygen inhibition and produced initiating radicals that selectively activate the chain-transfer agent for the chain growth or deactivate the active chain-end of polymer in controlled radical polymerization. Both activation and deactivation were highly efficient with broad scope for various polymers with different chain-transfer agents in both organic and aqueous systems. Oxygen molecule was particularly used as an external regulator to initiate and achieve the temporal control of both activation and deactivation by simply feeding the air.

Keywords RAFT; Oxygen; Borane

Citation: Lv, C. N.; Li, N.; Du, Y. X.; Li, J. H.; Pan, X. C. Activation and deactivation of chain-transfer agent in controlled radical polymerization by oxygen initiation and regulation. *Chinese J. Polym. Sci.* **2020**, *38*, 1178–1184.

INTRODUCTION

Controlled radical polymerization (CRP) was recognized as the most important breakthrough in macromolecular science during the last half-century that provided practical routes for synthesizing polymers with precisely defined molecular weights, molecular weight distributions, and architectures.[1−3] Atom transfer radical polymerization (ATRP)[4−6] and reversible addition-fragmentation chain transfer (RAFT)[7,8] polymerization were extensively investigated and commonly used CRP methods. Compared to the utilization of alkyl bromides or chlorides as ATRP initiators, chain-transfer agents (CTAs) were responsible for the controlled polymerization in RAFT process, such as dithioesters, trithiocarbonates, dithiocarbamates, and xanthates.[9,10] The sulfur-containing CTAs could be activated to generate initiating or propagating radicals by conventional radical initiators[11,12] and photoredox catalysts *via* photoinduced electron/energy transfer (PET) process.[13−18] However, sulfur-containing groups left in synthetic polymers were undesirable due to their heavy odor, color, toxicity, and reactivity, limiting the practical application and commercialization.[19] Additional methods such as deactivations or transformations of CTAs were required to solve these problems.[20−22]

Oxygen molecule was considered as a radical inhibitor in almost all the radical reactions including controlled radical polymerization at low temperature. To overcome this limitation, physical deoxygenations were required before conducting radical polymerization, including freeze-pump-thaw technique and deoxygenation with inert gas. Moreover, chemical deoxygenation methods were developed using specific transformations to convert oxygen into non-initiating byproducts.[23−27] Some strategies on oxygen-tolerant polymerizations were also reported.[28−30] We previously reported an alternative method called “oxygen initiation and regulation” using autoxidation of triethylborane (Et_3B) to convert oxygen to active radicals in CRP without any process of removing oxygen under ambient atmosphere and temperature.[31,32] The similar initiation mechanism using amine-alkylborane was reported in RAFT polymerization triggered by carboxylic acid to liberate the reactive trialkylborane.[33] As a rare example, oxygen was also adopted as an external regulator to have spatiotemporal control in CRP.[6,34,35]

In the presence of oxygen, Et_3B spontaneously generated ethyl radicals (Et•), boron peroxyl radical, and ethyl peroxyl radical.[36,37] The initiating Et• efficiently activated RAFT chain transfer agent and added to C=S moiety to form the intermediate that fragmented to another propagating radical (P_n•). Under proper conditions, the ethyl radicals could potentially deactivate CTAs *via* bimolecular radical terminations between Et• and P_n• in RAFT polymerization (Scheme 1a). Therefore, we proposed that either activation or deactivation of CTAs in RAFT polymerization could be initiated and regulated in both organic and aqueous systems by the same type of initiation mechanism (autoxidation of trialkylborane) but tuned by different amounts of Et_3B or oxygen.

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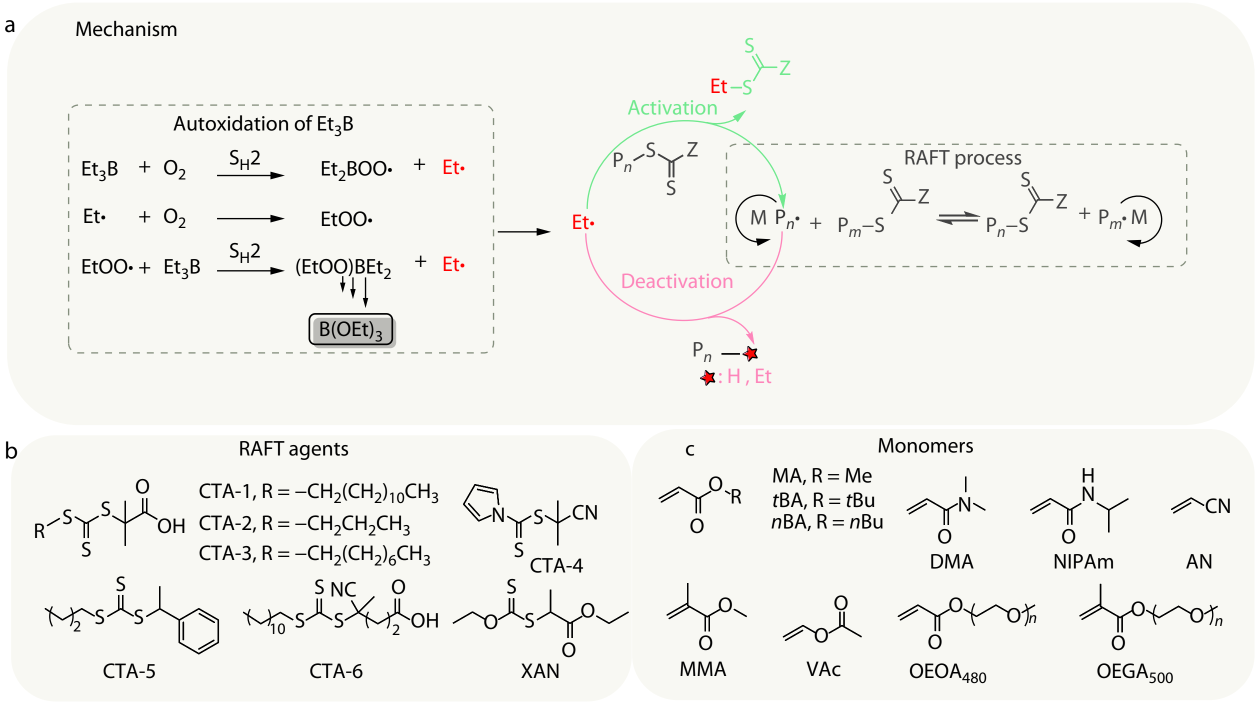
Received March 6, 2020; Accepted April 9, 2020; Published online June 5, 2020



Scheme 1 (a) Mechanism for activation and deactivation of the RAFT polymerization by oxygen initiation and regulation; (b) structures of chain-transfer agents (CTAs); (c) structures of monomers studied in this work.

EXPERIMENTAL

General Procedure for Deactivation of Polymers with Sulfur Chain Ends

For a typical deactivation experiment, a 25 mL vial equipped with a magnetic stirrer was charged with polymer-CTA (0.01 mmol) and solvent (3 mL). Then, triethylborane (0.05 mmol, 0.05 mL of 1 mol/L tetrahydrofuran solution) was added. Finally, the reaction mixture was stirred for 2 min in an open vessel. After the reaction, samples were directly taken out and analyzed using ^{1}H-NMR, UV-Vis, and GPC.

Scaled-up Deactivation Experiment

Methyl methacrylate (10.02 g, 100 mmol), CTA-6 (1.564 g, 4 mmol), and 5 mL of dimethyl sulfoxide were mixed in a 50 mL beaker flask. The mixture was stirred for 2 min. Then, triethylborane (4.0 mL of 1 mol/L THF solution, 4 mmol) was added. Finally, the mixture was stirred for 15 min at room temperature. After the reaction, samples were taken out and purified by water and dried at 35 °C. Finally, the yellow product was obtained as PMMA-CTA6. Next, for deactivation experiment (PMMA-H), PMMA-CTA6 (6 g, 2.6 mmol) and tetrahydrofuran (50 mL) were mixed in a beaker. Then, triethylborane (13 mL of 1 mol/L THF solution, 13 mmol) was added into the solution. After 2 min of stirring, the deactivation was completed.

Activation and Deactivation of Chain Transfer Agent of RAFT Polymerization in Organic and Aqueous Systems

Monomer, CTA-1/6, and methyl cyanide were mixed in a 25 mL vial. The mixture was stirred for 2 min. Then, triethylborane (0.2 mL of 1 mol/L THF solution, 2 equiv. molar ratio to CTA) was added. Finally, the reaction mixture was stirred for 15 min at room temperature. After the reaction, samples were taken out and purified by water and dried at 60 °C. The product was divided into two parts, one for chain extension and the other for deactivation of the chain-end group.

Part one for the deactivation of end group (P_n-H), P_n-CTA1/6 (0.01 mmol), 1.2 mL of methyl cyanide or water were mixed in a 25 mL vial. Then, triethylborane (0.05 mL, 0.05 mmol) was added into the mixture. After 2 min of stirring, the samples were taken out and analyzed using ^{1}H-NMR, UV-Vis and GPC.

Part two for the chain extension (P_n-*b*-P_m-CTA1/6), P_n-CTA1/6 (0.06 mmol), 1.2 mL of methyl cyanide or water, and another monomer were mixed in a 25 mL vial. Then, triethyborane (2 equiv. molar ratio to CTA) was added into the mixture. The reaction mixture was stirred for 15 min at room temperature, and then placed at room temperature for 15 min. After the reaction, samples were taken out, purified and analyzed using ^{1}H-NMR, UV-Vis, and GPC. Part of P_n-CTA1/6 (0.01 mmol) was taken out and dissolved in methyl cyanide or water, and triethylborane (5 equiv. molar ratio to CTA) was added into the mixture solution. After 2 min of stirring, the samples (P_n-*b*-P_m-H) were taken out and analyzed using UV-Vis, ^{1}H-NMR, and GPC.

Temporal Control of the Terminal Activity of the Polymer

The synthesis of PMA oligomer: CTA-1 (1.82 g, 5 mmol) and methyl acrylate (4.3 g, 50 mmol) were mixed in a 25 mL vial. The mixture solution was stirred for 2 min. Then, triethylborane (0.2 mL of 1 mol/L THF solution, 2 equiv. molar ratio to CTA) was added. Finally, the reaction mixture was stirred for 15 min at room temperature. After the reaction, samples were taken out and purified by water and dried by vacuum oven.

The oligomer of PMA-CTA1 ($M_{n,GPC}$ = 880) was dissolved in methyl cyanide in a 25 mL vial. The mixture solution was degassed by bubbling the nitrogen for 30 min. Then, triethylborane (0.2 mL of 1 mol/L THF solution, 15 equiv. molar ratio to CTA) was added into the reaction mixture. After that, the reaction mixture was left at room temperature. The first stage was completed in a nitrogen atmosphere. In the second stage, 0.9 mL of air (based on the mechanism of alkyl boron auto-oxidation, we assume that the ratio of O_2 to Et_3B = 1/2, then, the ratio of O_2 to CTA = 2.5/1, $V(O_2)$ = [0.01 mmol oligomer × (1 − 66%) × 2.5 mmol] × 22.4 L = 0.19 mL, V(Air) = 0.19 mL/21% = 0.9 mL) was added to deactivate the end group of PMA-CTA1. After 2 min, samples (PMA-CTA1, PMA-H) were taken out and analyzed using ^{1}H-NMR and GPC. The reaction mixture was then kept under nitrogen atmosphere. In the fourth stage, 100 equiv. of MA was added with adding 0.7 mL of air (assume the ratio of O_2 to Et_3B = 1/2, then, the ratio of O_2 to CTA = 2.5/1, $V(O_2)$ = [0.01 mmol oligomer × 66% × 1 mmol] × 22.4 L = 0.15 mL, V(Air) = 0.15 mL/21% = 0.7 mL) to activate the active end of the polymer to achieve chain growth for 15 min. These “off”, “on/activation”, and “on/deactivation” stages were repeated another cycle. Finally, three different compositions of polymers were obtained and characterized by SEC in THF. ^{1}H-NMR spectroscopy was used to determine the chain end functionality by using DMF as the internal standard.

For the preparation of each NMR samples, 50 μL of the reaction solution and 500 μL of the deuterated reagent were quantitatively taken out using a micro-syringe and added to the NMR tube. The entire operation was completed in a glove box.

RESULTS AND DISCUSSION

Deactivation of the Chain-transfer Agent in Organic and Aqueous Systems

To evaluate our hypothesis, RAFT polymerization of methyl acrylate (MA) was first conducted using chain-transfer agent (CTA-1) to synthesize trithiocarbonate-functionalized poly(methyl acrylate) (PMA, M_n = 6800, M_w/M_n = 1.06). Based on the color of polymer synthesized by RAFT method, UV-Vis spectroscopy was applied to analyze the polymer that showed a significant absorption around 309 nm (Fig. 1a). Under ambient temperature and atmosphere, various amounts of Et_3B were directly injected into the MeCN solution of PMA-CTA1 in the open vial. As the amount of alkylborane increased, the yellowish color of the reaction mixture gradually faded. In particular, when it increased to 5.0 equivalent or more, the absorbance peak around 309 nm completely disappeared compared to the absorption spectrum of the starting polymer, indicating a complete deactivation of trithiocarbonate moiety in RAFT polymer (entry 1, Table S1 in the electronic supplementary information, ESI). The complete deactivation process was also observed in DMF, THF, and DMSO (entries 2–4, Table S1 in ESI) by using the same ratio of Et_3B, showing excellent tolerance in different solvents.

The degrees of chain-end deactivation were calculated by the absorption of PMA-CTA1 at 309 nm, and molecular weights and molecular weight distributions were characterized by SEC. The molecular weights and molecular weight distributions of the obtained polymers showed no significant difference compared to the original polymers, and no shoulder peak was observed in the SEC traces (Fig. 1b), suggesting neither chain-chain coupling termination of the macromolecular radical nor cleavage of polymer chain during the deactivation of chain-end. Such deactivation of the chain-end was also characterized by ^{1}H-NMR spectroscopy (Fig. 1c), showing complete disappearance of the methylene signals ($-\underline{CH_2}-S-C(S)-S-$) attached to the thiocarbonyl ester.

Table 1 summarizes and presents deactivation reactions of different types of polymers with various chain transfer agents shown in Scheme 1. RAFT polymerizations of *tert*-butyl acrylate, *n*-butyl acrylate, *N*,*N*-dimethylacrylamide, *N*-isopropylacrylamide, and acrylonitrile with CTA-1 (Scheme 1) were conducted to obtain P*t*BA, P*n*BA, PDMA, PNIPAm, and PAN, respectively, with trithiocarbonate as chain-end fidelity (Figs. S1−S11 in ESI). Under ambient conditions and aerobic atmosphere, 5 equiv. of Et_3B deactivated the sulfur-containing chain end efficiently (entries 1–5, Table 1). PMA polymers with different chain-transfer agents (CTA-2, CTA-3, CTA-4, and CTA-5) were accordingly synthesized and deactivated to obtain the polymers without sulfur-containing chain end groups (entries 6–9, Table 1, Figs. S14−S25 in ESI).

CTA-6 with the cyano group adjacent to trithiocarbonate and XAN with xanthate group were used in RAFT polymerization of methyl methacrylate (MMA) and vinyl acetate (VAc), respectively. Chain end functionality in both PMMA-CTA6 and PVAc-XAN was deactivated using 5 equiv. of Et_3B in MeCN at ambient temperature and atmosphere (entries 10 and 11, Table 1, Figs. S26−S31 in ESI). This deactivation of chain-end fidelity in PVAc was also characterized by MALDI-TOF-MS spectroscopy (Figs. 1d−1g), which shows a series of mass signals for the hydrogen-atom terminated polymers ($n \times M_{VAc} + M_{Na^+} + M_H + M[H_2C(CH_3)COOCH_2CH_3]$, 2534.4, 2620.5 g/mol) obtained from MALDI-TOF-MS, and another end group of polymers was also detected, corresponding to PVAc-Et (2562.4, 2648.5 g/mol). No values were found for polymers with XAN as chain-end fidelity ($n \times M_{VAc} + M_{XAN} + M_{Na^+}$). This further confirmed that trithiocarbonate moiety was completely deactivated after reaction between the RAFT polymers with excess Et_3B.

A scaled-up reaction (50 mL) was conducted for the deactivation of trithiocarbonate group in RAFT synthesized PMMA. In an open beaker, 5 equiv. of Et_3B was directly injected into the solution, and it was easy to tell that the color was diminished in 1 min and completely disappeared in 2 min (Fig. S32 in ESI).

As Lewis acid Et_3B is able to make the complexation with Lewis base such as water,[38,39] Et_3B might be unstable to lose its reactivity in aqueous media. It was interesting to see that the deactivation of POEOMA-CTA1 and PNIPAm-CTA1 successfully provided the reduced polymers using 5 equiv. Et_3B in aqueous conditions (entries 12 and 13, Table 1).

Activation and Deactivation

Our previous work showed that RAFT polymerization could be carried out by activation of CTA using 2:1 ratio of Et_3B:CTA, and additional second monomers and Et_3B (2 equiv. molar ratio to

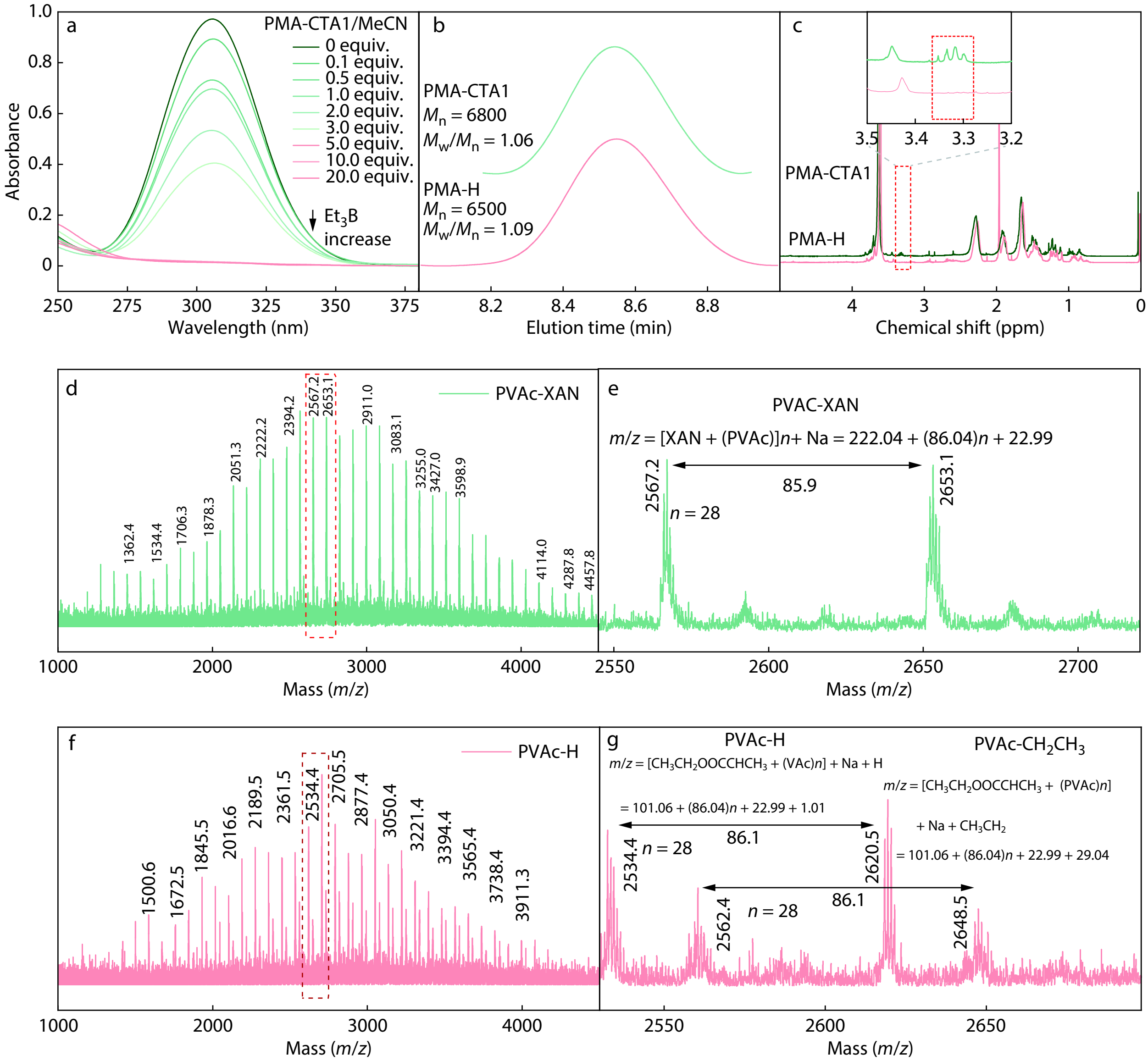


Fig. 1 (a) UV-Vis spectra for deactivation of PMA-CTA1 with various Et_3B in MeCN; (b) SEC traces of PMA-CTA1 and after treatment by 5 equiv. of Et_3B; (c) ^1H-NMR spectra of PMA-CTA1 and after treatment with 5 equiv. of Et_3B; (d) MALDI-TOF-MS spectra for PVAc-XAN; (e) chain-end group analysis; (f) MALDI-TOF-MS spectra of PVAc-XAN after treatment with 5 equiv. of Et_3B ($[\text{PVAc-XAN}]_0$:$[Et_3B]_0$ = 1:5); (g) chain-end group analysis after deactivation.

the chain-end group) were added to make the chain extension to provide block copolymers with active chain-end moiety.[31] In the absence of monomers, the active chain-end moiety of synthesized RAFT polymers could be deactivated and removed using 5 equiv. of Et_3B (molar ratio to the chain-end group). Therefore, the sequence of added monomers and different amounts of Et_3B could be adjusted to activate or deactivate RAFT polymerization to synthesize homopolymers and block copolymers with either active chain-end group or hydrogen-termination. The synthetic route and the results are described in Table 2. Under ambient atmosphere in the open flask, RAFT polymerization of MA was conducted under conditions ($[\text{MA}]_0/[\text{CTA-1}]_0/[Et_3B]_0$ = 20/1/2.0), providing PMA-CTA1 with M_n = 1900 and M_w/M_n = 1.13. Both ^1H-NMR (characteristic signal disappears) and UV-Vis analyses confirmed the removal of active end groups. While 5 equiv. of Et_3B was subjected to the solution containing part of the synthesized polymers to give PMA-H, in the activation process, 2 equiv. of Et_3B, 50 equiv. of *n*BA or 200 equiv. of *t*BA was separately injected into the reaction mixture to provide PMA-*b*-P*n*BA-CTA1 or PMA-*b*-P*t*BA-CTA1 (M_n = 7700, M_w/M_n = 1.26, or $M_n = 2.9 \times 10^4$ and M_w/M_n = 1.27, entries 1 and 2, Table 2), respectively. The synthesized block copolymers with active trithiocarbonate group were further reacted with 5 equiv. of Et_3B to give hydrogen-terminated block copolymers (PMA-*b*-P*n*BA-H, M_n = 7900, M_w/M_n = 1.24, and PMA-*b*-P*t*BA-H, $M_n = 2.95 \times 10^4$, M_w/M_n = 1.30, entries 1 and 2, Table 2, Figs. S33–S39 in ESI).

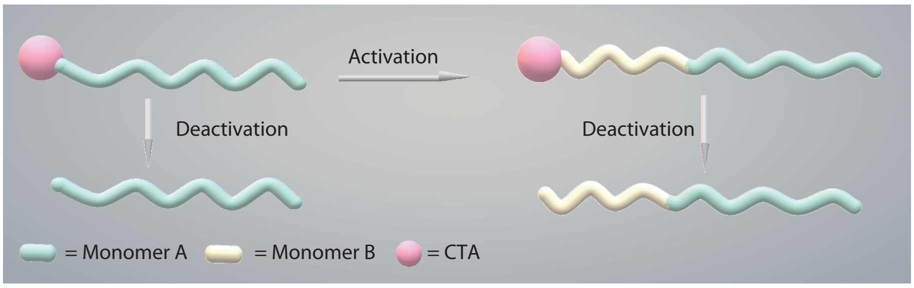
Similarly, the activation of PMMA-CTA6 was successful with MA, EA, *n*BA, and *t*BA to provide corresponding block copolymers that were further deactivated to hydrogen-terminated

Table 1 Results for deactivation of chain-end fidelity of synthesized RAFT polymers. [a]

Entry	Polymer-CTA	Solvent	M_n, M_w/M_n [b]	M_n, M_w/M_n [c]	Degree of end group removal [e]
1	P*t*BA-CTA1	MeCN	5000, 1.31	5100, 1.30	Complete
2	P*n*BA-CTA1	MeCN	11600, 1.24	11800, 1.33	Complete
3 [d]	PDMA-CTA1	MeCN	1300, 1.07	1000, 1.25	Complete
4 [d]	PNIPAm-CTA1	MeCN	9100, 1.22	9900, 1.23	Complete
5 [d]	PAN-CTA1	DMF	3300, 1.09	2400, 1.06	Complete
6	PMA-CTA2	MeCN	5000, 1.34	3700, 1.50	Complete
7	PMA-CTA3	MeCN	3800, 1.13	4000, 1.10	Complete
8	PMA-CTA4	MeCN	1100, 1.13	1400, 1.17	Complete
9	PMA-CTA5	MeCN	5700, 1.28	6000, 1.31	Complete
10	PMMA-CTA6	MeCN	2300, 1.17	2900, 1.18	Complete
11	PVAc-XAN	MeCN	2700, 1.25	2600, 1.18	Complete
12 [d]	POEOMA-CTA1	H_2O	2700, 1.08	3100, 1.11	Complete
13 [d]	PNIPAm-CTA1	H_2O	7300, 1.15	8700, 1.16	Complete

[a] Reaction conditions: [polymer-CTA] = 3.3×10^{-3} mmol/L, [polymer-CTA]/[Et_3B] = 1/5, Et_3B injected at once, T = 25 °C. M_n and M_w/M_n were determined by SEC in THF, based on linear PMMA calibration standards; [b] Measured for polymer-CTA; [c] Measured for polymer-H after deactivation of polymer-CTA; [d] Determined by SEC in DMF, based on linear PMMA calibration standards; [e] Estimated by the absorption spectra comparison to the starting polymer.

Table 2 Activation and deactivation of RAFT polymerization with Et_3B/oxygen in both organic and aqueous conditions. [a]



Entry	P_n-CTA	P_n-H	P_n-*b*-P_m-CTA	P_n-*b*-P_m-H
1	PMA-CTA1 1900/1.13	PMA-H 1900/1.15	PMA-*b*-P*n*BA-CTA1 7700/1.26	PMA-*b*-P*n*BA-H 7900/1.24
2			PMA-*b*-P*t*BA-CTA1 2.9×10^4/1.27	PMA-*b*-P*t*BA-H 2.95×10^4/1.30
3	PMMA-CTA6 2300/1.26	PMMA-H 2200/1.22	PMMA-*b*-PMA-CTA6 2.64×10^4/1.22	PMMA-*b*-PMA-H 2.86×10^4/1.26
4			PMMA-*b*-PEA-CTA6 1.46×10^4/1.27	PMMA-*b*-PEA-H 1.51×10^4/1.29
5			PMMA-*b*-P*n*BA-CTA6 3.8×10^4/1.36	PMMA-*b*-P*n*BA-H 4.3×10^4/1.38
6			PMMA-*b*-P*t*BA-CTA6 4.4×10^4/1.36	PMMA-*b*-P*t*BA-H 4.42×10^4/1.35
7 [b]	PDMA-CTA1 1400/1.16	PDMA-H 1300/1.08	PDMA-*b*-PDMA-CTA1 7100/1.43	PDMA-*b*-PDMA-H 8200/1.34
8 [b]			PDMA-*b*-PNIPAm-CTA1 7600/1.39	PDMA-*b*-PNIPAm-H 8400/1.31
9 [b]			PDMA-*b*-POEOA-CTA1 4900/1.10	PDMA-*b*-POEOA-H 4600/1.13
10 [b]	POEOMA-CTA1 2700/1.08	POEOMA-H 3100/1.11	POEOMA-*b*-POEOMA-CTA1 5700/1.26	POEOMA-*b*-POEOMA-H 5700/1.19

[a] Activation conditions: [P_n-CTA] = 0.05 mmol/L, [monomer]/[P_n-CTA]/[Et_3B] = DP/1/2, Et_3B injected at once, T = 25 °C; deactivation conditions: [P_n-CTA] = 3×10^{-3} mmol/L, [P_n-CTA]/[Et_3B] = 1/5, Et_3B injected at once, T = 25 °C. M_n and M_w/M_n were determined by SEC in THF, based on linear PMMA calibration standards. [b] Determined by SEC in DMF, based on linear PMMA calibration standards.

block copolymers (entries 3–6, Table 2, Figs. S40–S51 in ESI). The activation of POEOMA and PDMA with monomers such as OEOMA, DMA, NIPAm, and OEOA using 2 equiv. of Et_3B and deactivation using 5 equiv. of Et_3B were both achieved in aqueous conditions (entries 7–10, Table 2, Figs. S52–S60 in ESI).

Oxygen Regulated Temporal Control

Based on the fact that different amounts of Et_3B were able to selectively activate or deactivate RAFT polymerization, similar behavior could be approached with excess Et_3B using air (oxygen) as an external regulator (Fig. 2). Under nitrogen atmosphere, treatment of methyl acrylate oligomer with CTA1 as chain-end group (M_n = 880, M_w/M_n = 1.16) with excess Et_3B (15 equiv.) did not provide any loss of chain-end functionality (CEF), while CEF dropped down to 66% when injecting air into the solution owing to the radical termination between macromolecular radical and ethyl radical in the deactivation stage. The mixture was under the nitrogen atmosphere

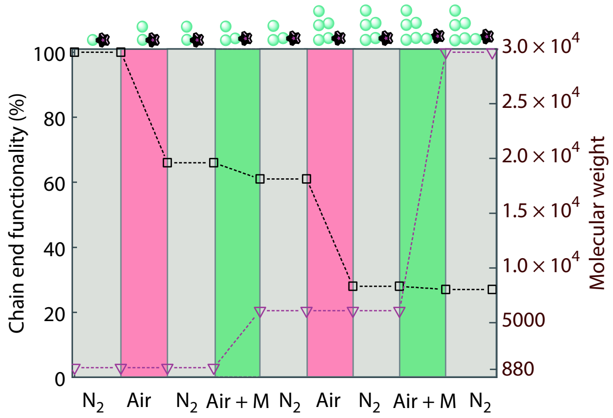


Fig. 2 Spatiotemporal control of the activation and deactivation of polymer chain-end based on oxygen regulation.

afterward to turn off the reaction. In the next activation stage, 100 equiv. of MA (ratio to CTA) and air were injected into the reaction mixture to obtain the polymers (M_n = 6100, M_w/M_n = 1.37; M_n = 880, M_w/M_n = 1.16), and slight loss of CEF was observed under this stage. These "off", "on/activation", and "on/deactivation" stages repeated another cycle to obtain three different compositions of polymers (34% H-terminated oligomer, M_n = 880; 73% H-terminated polymer, M_n = 6100, and 27% CTA-terminated diblock copolymers, M_n = 2.97 × 10⁴) (Figs. S63–S66 in ESI).

CONCLUSIONS

This work demonstrates that the chain-transfer agents in RAFT polymerization could be selectively activated and deactivated by different amounts of trialkylborane and oxygen based on our previous proposed "oxygen initiation and regulation" concept. This oxygen initiated and regulated method using autoxidation of trialkylborane mechanism was able to tolerate different RAFT chain transfer agents and different types of monomers such as acrylate, methacrylate, acrylonitrile, vinyl acetate, and acrylamide in both organic and aqueous conditions. In the presence of monomer and trialkylborane under aerobic conditions, the activation of chain transfer agents resulted in the RAFT polymerization, while the deactivation was realized using an excess of trialkylborane without monomers. Oxygen/nitrogen could be used as an external regulator to turn off the reaction and turn on the activation or deactivation depending on the presence of monomers or not. This concept and methodology with broad scope overcomes the inhibition of oxygen in controlled radical polymerization and provides more precise control of the reactivity to yield chain-end functionalized or hydrogen-terminated polymers with different molecular weights.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2441-7.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 21704017, 21871056, and 91956122).

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