

Controlled Radical Polymerization: from Oxygen Inhibition and Tolerance to Oxygen Initiation

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Abstract Molecular oxygen is a radical scavenger in both conventional and controlled radical polymerization (CRP), resulting in many time-consuming methods for physically removing oxygen before the polymerization. Different approaches have been developed to have oxygen tolerance by chemically consuming or converting molecular oxygen into non-initiating species to address this issue. Recently, we propose another approach called oxygen initiation that directly transforms molecular oxygen into the initiating carbon radical in CRP. This feature article summarizes our recent developments in this direction. Oxygen-initiated reversible addition-fragmentation transfer (RAFT) polymerization has been successfully conducted using oxygen and trialkylborane as co-initiators under the ambient conditions and atmosphere without any prior degassed procedures. This gas-triggered initiation provides the opportunity for spatiotemporal control of the polymerization by molecular oxygen or air. Rationally synthesized alkylborane compounds could derive the predesigned structure of the initiating alkyl radical to minimize the side reactions and free polymer chains, achieving the synthesis of ultra-high molecular weight polymers. The challenges and perspectives are also discussed in the end.

Keywords Oxygen; Radical polymerization; Controlled; Alkylborane; RAFT

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INTRODUCTION

Polymer materials have driven the rapid evolution of modern civilization, owing to the synthesis of significant and functional polymers, including synthetic rubbers, engineering plastics, and fibers.^[1–3] Since Staudinger came up with the macromolecule conception, chemists are committed to the precise synthesis of polymers with predetermined molecular weight, narrow molecular weight distribution, and complex architectures.^[4–7] In the last decades, controlled radical polymerization (CRP, also called “living” radical polymerization, LRP, or reversible-deactivation radical polymerization, RDRP suggested by IUPAC) has become one predominant method to synthesize well-defined polymers.^[8,9] The most widely used and investigated CRP techniques include atom transfer radical polymerization (ATRP),^[10–13] reversible addition-fragmentation transfer (RAFT) polymerization,^[14,15] and nitroxide-mediated polymerization (NMP).^[16,17]

CRP methods are compatible with various vinyl monomers and solvents including water; however, the polymerization still needs to be performed under an inert atmosphere. Oxygen molecules are undesired radical scavengers, and they directly react with active carbon radicals to yield peroxy radicals

that have the poor ability in propagating the polymer chain.^[18] Because this oxygen inhibition limits the scalable capability of industrialization and broad application of CRP, solving this drawback is extremely significant to drive the researching progress of polymer science. In this feature article, we will initially mention the conventional CRP methods with the physical oxygen-removal process and then briefly introduce several approaches with some degree of oxygen tolerance using chemical deoxygenation (Scheme 1). We recently propose another approach called oxygen initiation in CRP that converts the oxygen molecules to active radicals by the autoxidation reaction.^[19–22] We will mainly discuss the recent progress in this direction and point out the challenges and perspectives in the future in the end.

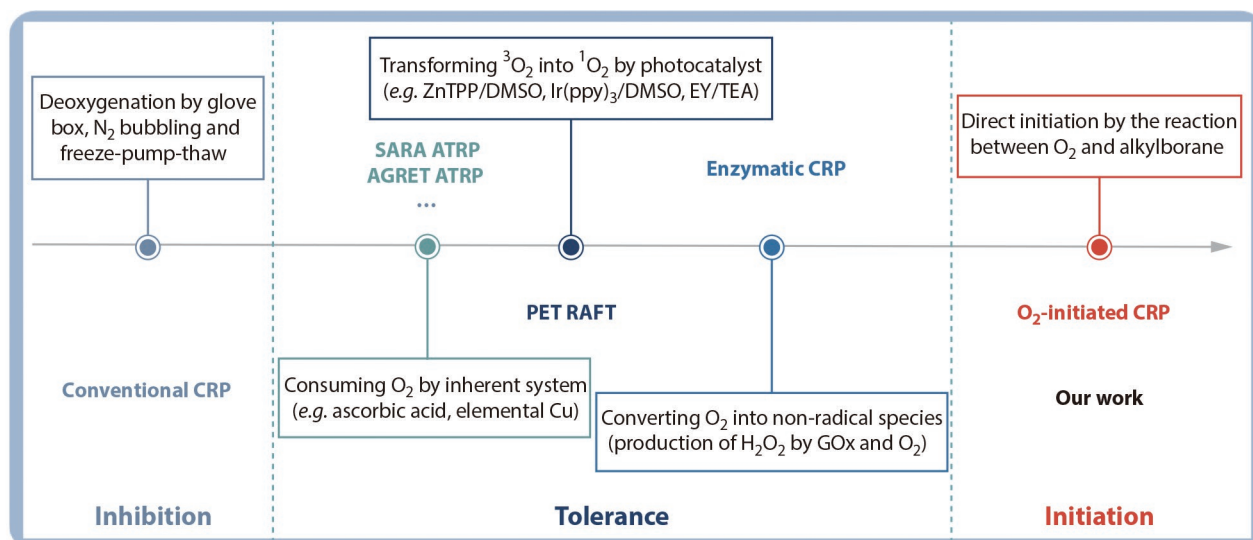
OXYGEN INHIBITION AND TOLERANCE

Physical deoxygenation was widely used to remove oxygen molecules in conventional CRP. For instance, the polymerization could be performed in the glove box to exclude any oxygen containment. The reaction mixture could also be treated with nitrogen bubbling or freeze-pump-thaw using liquid nitrogen. These methods are time-consuming and not user-friendly for non-experts, leading to the limitations of scalable synthesizing polymer materials. Herein, several approaches have recently been developed to have some oxygen tolerance by chemically consuming oxygen molecules. Since the oxygen tolerant CRP has been recently reviewed,^[11] we only highlight several typical

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Scheme 1 Controlled radical polymerization: from oxygen inhibition and tolerance to oxygen initiation.

strategies in this section.

In transition-metal catalyzed ATRP, oxygen inhibits the active radical species and could oxidize the low-valent metal (such as Cu^{I} and Fe^{II}), resulting in rapid deactivation and ultimately ceasing the polymerization.^[23,24] The chemical reduction can continuously reduce the deactivator complex and regenerate the reducing agent (low-valent metal) in ATRP. These ATRP techniques with activator regeneration have some degree of oxygen tolerance. Depending on the different types of reduction mechanisms, there could be chemical reduction in A(R)GET (activators (re)generated by electron transfer) ATRP,^[25–29] using elemental Cu in SARA (supplemental activators and reducing agent) ATRP,^[30] or photochemical reduction in photoATRP.^[11,31] All these techniques were reported for effective polymerizations in the presence of oxygen/air.^[32–35] Photoinduced electron/energy transfer RAFT (PET-RAFT) polymerization was a recently developed technique, showing some unusual oxygen tolerance.^[36–40] A higher degree of oxygen tolerance could be achieved using ZnTPP (zinc tetraphenylporphyrin) as a photoredox catalyst that could convert triplet oxygen into singlet oxygen (Fig. 1a).^[41] This singlet oxygen was consumed by the oxidation with DMSO, and the kinetic study showed that the induction period still existed due to the consumption of molecular oxygen.

It was also worth mentioning that the enzyme converting gave a biological pathway for scrubbing oxygen in CRP. Glucose oxidase (GOx) was one of the most acceptable enzymes since its stable performance and abundance. It could convert oxygen molecules and glucose to hydrogen peroxide (H_2O_2) and gluconolactone. In 2014, the first example of an enzyme (GOx) to deoxygenate CRP was reported by Stevens, showing a RAFT polymerization of 2-hydroxyethyl acrylate in the presence of VA-044 (2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride) as a thermal radical initiator without any prior deoxygenation (Fig. 1b).^[42,43] After GOx-scrubbing oxygen in aqueous ATRP conditions, Matyjaszewski observed that H_2O_2 would initiate new polymer chains under Freton's mechanism, so the combination of GOx and sodium pyruvate were

used to consume oxygen and intermediate product H_2O_2 .^[44,45] Keitz extended this concept and used microbial organisms (*Shewanella oneidensis*) to realize the aerobic CRP.^[46,47] An's group presented an elegant strategy based on generating initiating carbon radicals from the reaction between horseradish peroxidase (HRP) and acetylacetone in the presence of H_2O_2 .^[48] This approach can both deoxygenate and initiate the RAFT polymerization without any prior deoxygenation and other radical initiation. They also reported that pyranose oxidase (P2Ox) showed higher efficiency for oxygen scrubbing and was adopted in an oxygen-tolerant RAFT polymerization to synthesize well-defined polymers with ultra-high molecular weights (Fig. 1c).^[49–51]

OXYGEN INITIATION

In the approaches mentioned above, the oxygen molecule was consumed or converted into other non-initiating species by various methods for avoiding inhibition. We pointed out that the oxygen could be used as a co-initiator in the initiation step to provide the active initiating radical in a controllable manner.^[19] Then we could achieve CRP utilizing the concept of oxygen initiation. Oxygen initiation offered an opposite perspective for regulating the CRP process, which mechanistically introduced oxygen to the initiating step but did not simply consume oxygen before the polymerization. Because of the empty p-orbitals on boron atoms, alkylborane compounds as the Lewis acids readily reacted with oxygen to provide alkyl radicals in the autoxidation mechanism.^[21,52] The combination of alkylborane and oxygen was widely used as a radical initiating system in radical organic chemistry.

In 2018, we reported the oxygen-initiated RAFT polymerization without any protocol of oxygen removal, initiating the RAFT process by ethyl radical from the reaction of triethylborane and oxygen (Fig. 2).^[19] The RAFT polymerization of methyl acrylate (MA) reached >95% monomer conversion in DMSO in 15 min, providing polymers with predetermined molecular weight and narrow molecular weight distribution. The control experiment under nitrogen atmosphere did not

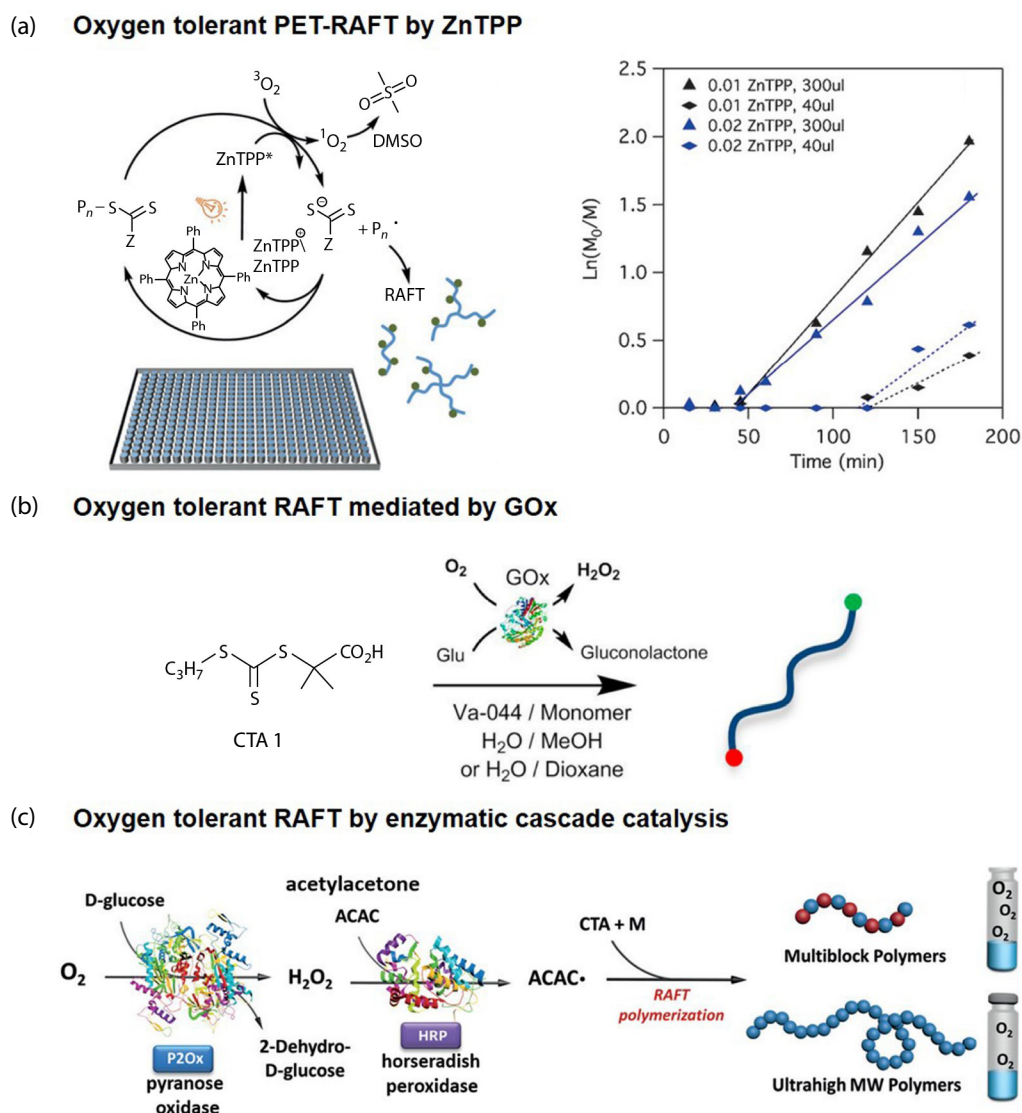


Fig. 1 Several typical examples for oxygen tolerant RAFT polymerizations. ((a) Reproduced with permission from Ref. [34]; Copyright (2018) Wiley; (b) Reproduced with permission from Ref. [35]; Copyright (2014) American Chemical Society; and (c) Reproduced with permission from Ref. [42]; Copyright (2017) Wiley.)

give any polymerization, showing the necessity of oxygen in the initiation step. These experiments indicated that the rate of autoxidation was faster than that of oxygen inhibition to ensure efficient initiation and rapid polymerization.

Based on these advantages, the technical combination of polymerization and high-throughput enabled the fast screening for the proper experimental conditions and the synthesis of a polymer library. Comparing with other solutions for consuming or converting oxygen in CRP, the oxygen-initiated CRP introduced the oxygen or air as a new type of external regulator to give excellent temporal and spatial control in the rapid polymerization (Fig. 3a). Additionally, a uniform film by RAFT process was formed regardless of removing oxygen, stemming from the similar precise M_n control and narrow molecular weight distribution in different regions (Fig. 3b).

As a novel regulating method, oxygen initiation contributed to a distinct perspective to conduct the CRP process, transforming the obstacle of inhibition into the initiation.^[53]

The oxygen inhibition was considered a competitive reaction in contrast to polymerization. The autoxidation of triethylborane overwhelmed the inhibition of oxygen in the polymerization, and it also provided the external radicals to initiate the RAFT polymerization directly. This gas-triggered initiation showed a more effective and flexible protocol to the CRP process, avoiding strict degassing manipulation.

In the following study, we found that while the suitable amount of triethylborane presented an activating pathway for initiating the RAFT polymerization, the excess amounts gave a deactivating pathway for removing the sulfur-containing chain-ends of synthesized polymers (Fig. 4).^[20] And this regulating process had universality in both aqueous and organic systems. In 2020, we reported this effective oxygen-initiated method for synthesizing the functional polymer, which incorporated *N*-methyliminodiacetic acid (MIDA) into the boronic acid for stabilizing the boron-containing polymers.^[54] The polymers of MIDA boronate structures were successfully

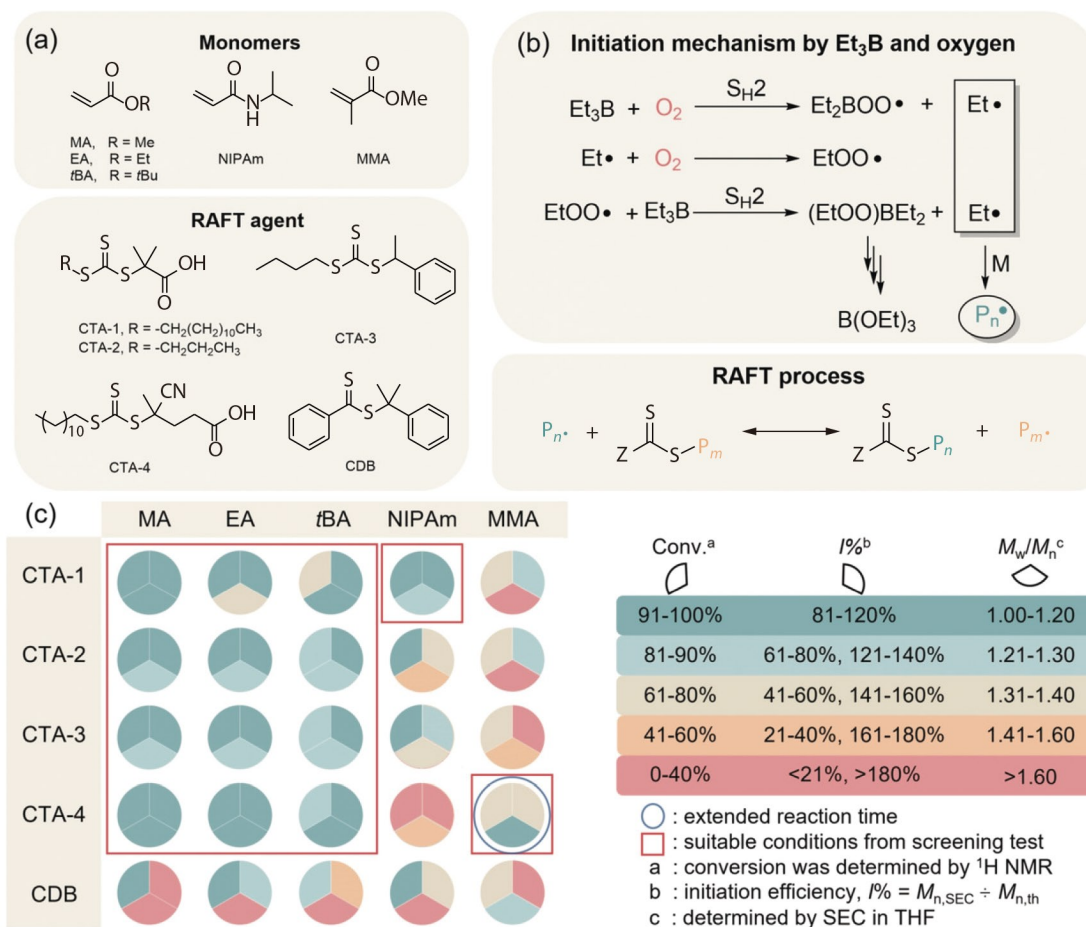


Fig. 2 Oxygen-initiated RAFT polymerization by triethylborane and oxygen: (a) structures of selected monomers and RAFT chain-transfer agents (CTA), (b) autoxidation mechanism of triethylborane, (c) high-throughput screening results under conditions ([Monomer]₀: [CTA]₀: [Et₃B]₀ = 400:1:2, [M]₀ = 8 mol/L in DMSO, ambient temperature and atmosphere); left pie segment: conversion; right segment: initiation efficiency; bottom segment: molecular weight distributions. (Reproduced with permission from Ref. [19]; Copyright (2018) Wiley.)

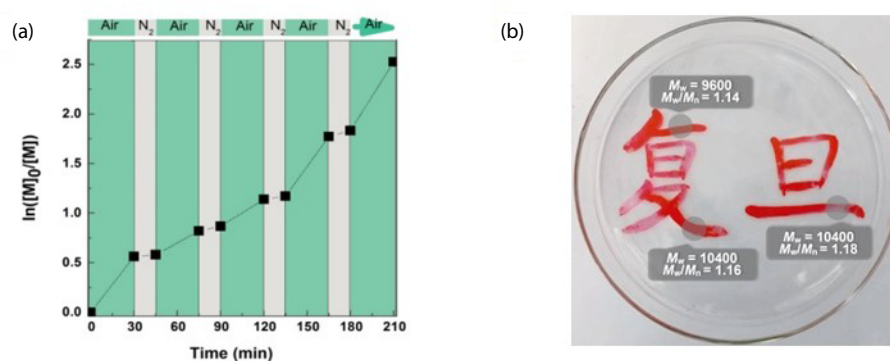


Fig. 3 (a) Temporal control process via injecting oxygen into the degassed reaction mixture under conditions [MA]₀: [CTA]₀: [Et₃B]₀ = 400:1:2, [MA]₀ = 8 mol/L in DMSO; (b) Painting on a surface using RAFT polymerization by oxygen initiation and the characterizations of polymer films. (Reproduced with permission from Ref. [19]; Copyright (2018) Wiley.)

synthesized, and excess amounts of triethylborane were used to remove the chain-end functionality to avoid sulfur effects in the palladium catalysts.^[55] After the Suzuki-Miyaura coupling, the polymers with MIDA groups can incorporate various functionalities.

Magenau's group reported an analogous initiating system

using alkylborane-amine complex, which released the corresponding alkylborane under the acid condition for consuming oxygen and providing the external radicals to the RAFT process.^[56] They also expanded this system to synthesize the star-like polymers by regulating the concentration of cross-linkers in one-pot.^[57] In the recent report from Feng's group,

the oxygen-initiated system using triethylborane also showed the efficient post-polymerization modification in removing thioester chain-end.^[58] By adding the excess triethylborane, this removing process without tedious operation was very time-saving (less than 1 min). Son reported a surface-initiating RAFT polymerization using oxygen and trialkylborane by grafting the chain-transfer agents onto a silicon wafer to polymerize different types of monomers, yielding anti-biofouling hydrophilic surfaces.^[59]

Although organoboranes such as triethylborane and tributylborane are commercially available compounds, they provide limited initiating structured radicals such as ethyl and butyl radicals in high radical flux.^[22,60] These energetic ethyl or butyl radicals would continuously initiate free polymer chains during the whole RAFT polymerization, leading to a “relatively” low molecular weight polymer (less than 60 kg/mol). We rationally designed and synthesized various *B*-alkylcatecholborane (RBCat) compounds (Fig. 5) with a single alkyl substituent at the boron center. The incorporation of two oxygen atoms from catechol also tuned the Lewis acidity and the autoxidation rate of the alkylborane. Notably,

the alkyl substituent could be tailored for providing suitable initiating radicals for effective CRP.

The polymerization depended on the structure of RBCat, and the most efficient polymerization was initiated by PhCH(Me)BCat compound, providing a carbon-centered phenethyl radical PhCH(Me)•.^[22] The releasing phenethyl radical selectively reacted with the RAFT agent and minimized the monomer addition to achieve almost quantitative initiating efficiency. Besides, the period of exposure to air has effectively influence polymerization. However, the reacting system with longer exposure to air presented a longer inhibition time before initiation, showing a faster rate in the following polymerization. Because of this unique feature, this oxygen-initiated strategy was successfully applied to various (meth)acrylate polymers, which also showed narrow molecular weight distributions ($M_w/M_n=1.10-1.20$) and ultrahigh molecular weight (UHMW) >1000 kg/mol (Figs. 6a and 6b). For verifying the fidelities of RAFT agent chain-ends, several chain extension experiments were conducted, especially a typical example from poly(methyl acrylate) (PMA, $M_w=1.445$ kg/mol, $M_w/M_n=1.20$) to poly(methyl acrylate)-*b*-poly(ethyl acrylate)

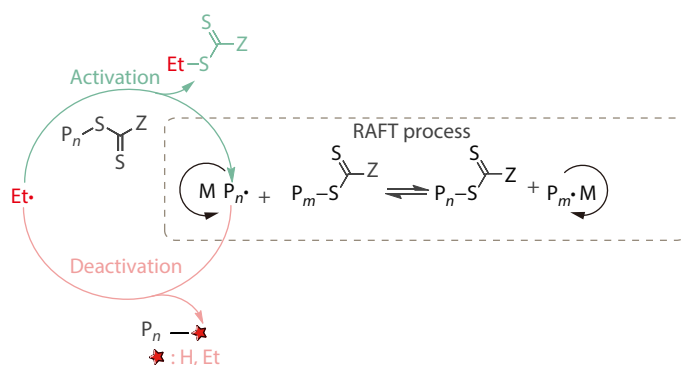


Fig. 4 The mechanism of activation and deactivation of CTA by ethyl radical from the reaction between oxygen and different amounts of triethylborane. (Reproduced with permission from Ref. [20]; Copyright (2020) Springer.)

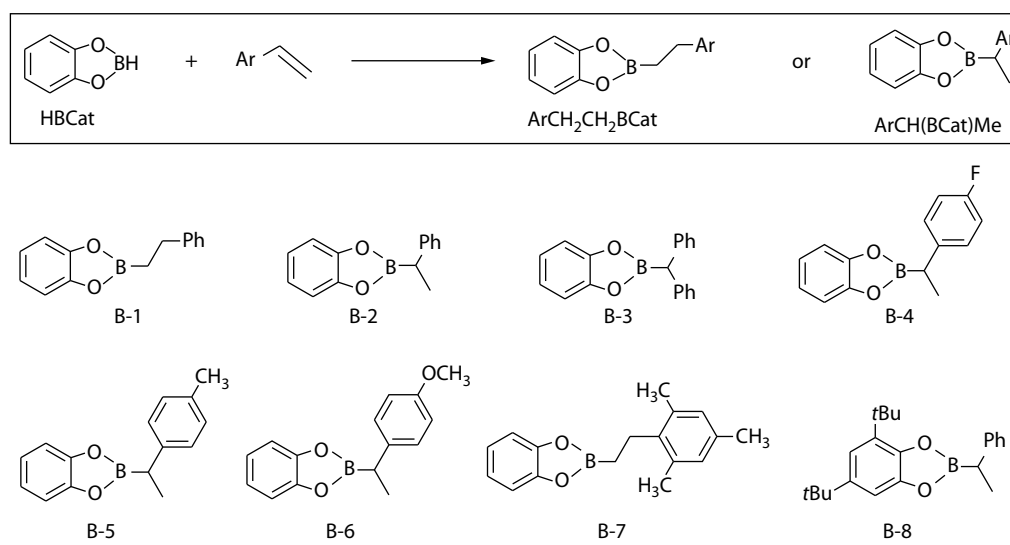


Fig. 5 The synthetic scheme and structures of *B*-alkylcatecholboranes. (Reproduced with permission from Ref. [22]; Copyright (2020) Elsevier.)

(PMA-*b*-PEA, $M_w=3.036$ kg/mol, $M_w/M_n=1.23$, Fig. 6c).

This RBCat-mediated polymerization provided a powerful tool to synthesize the ultra-high molecular weight polymer based on slowly supplying the external radicals and keeping

low radical concentrations, avoiding the chain coupling even in the extremely low concentrations of CTA and a high ratio of monomer to CTA.^[22] In the proposed mechanism, the molecular oxygen was embodied by RB-Cat to form the corres-

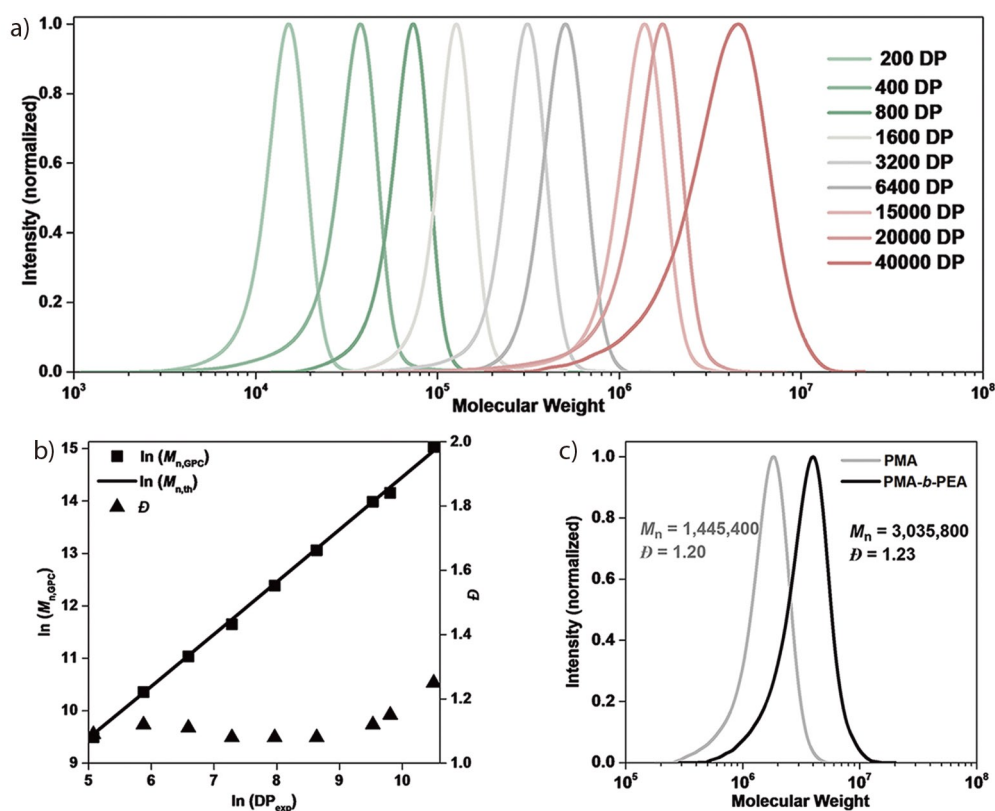


Fig. 6 Characterizations of UHMW polymers by *B*-alkylcatecholboranes: (a) molecular weight distribution traces of PMA with various degrees of polymerizations (DP), (b) plots of molecular weights for polymerization of MA at various targeted DP, (c) molecular weight distribution traces of block UHMW copolymers PMA-*b*-PEA from PMA. (Reproduced with permission Ref. [22]; Copyright (2020) Elsevier.)

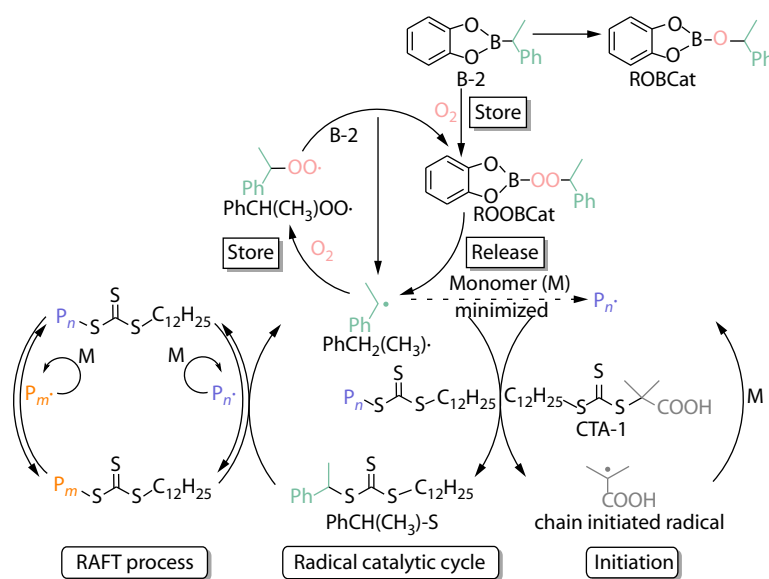


Fig. 7 The proposed oxygen storage and initiation mechanism of RBCat-mediated CRP. (Reproduced with permission from Ref. [22]; Copyright (2020) Elsevier.)

ponding alkyl-O-O-catecholborane (ROOB-Cat) compound (Fig. 7). Then, the oxidized boron adducts ROOB-Cat slowly released alkyl radical (*i.e.*, phenethyl radical) to initiate the RAFT process. The phenethyl radical could be oxidized by molecular oxygen, providing the phenethyl peroxy radical that was incapable of efficiently initiating the polymerization. The unoxidized RBCat could react with peroxy radicals to generate ROOB-Cat and the initiating phenethyl radicals, efficiently reducing the amount of side reactions and the concentration of oxygen molecules.

CONCLUSIONS AND PERSPECTIVE

In the most conventional CRP methods, due to the oxygen intolerance of free radicals, physical deoxygenation methods are often required. However, these physical methods use special experimental instruments and glassware equipment, as well as personnel training to conduct these reactions in a reliable way to obtain reproducible results. These reasons have greatly restricted the further development of these reactions, especially for researchers in other fields who are not experts in synthetic chemistry. With the continuous development of oxygen tolerance CRP methods, researchers now can carry out these polymerizations without strict physical deoxygenation conditions. Most methods are to chemically consume oxygen molecules to achieve oxygen tolerance in the polymerization. The oxygen initiation mainly discussed in this feature article uses another concept that it directly uses some autoxidation reactions not only to consume oxygen molecules through chemical reactions but also to generate active free radicals, thereby initiating and driving CRP reaction.

In this feature article, we have summarized our recent advances in CRP by oxygen initiation. The rapid oxygen-initiated and -regulated RAFT polymerization has been successfully carried out using triethylborane and oxygen as the initiation system under ambient conditions and atmosphere without any prior degassed procedures. Comparing with other conventional initiated pathways, this pathway provides a totally different initiation mechanisms for radical polymerization. This gas-triggered initiation provides the opportunity for spatiotemporal control of the polymerization by molecular oxygen as well as air. Different amounts of triethylborane also provided different routes for initiation/activation or deactivation of the polymerization, achieving an efficient chain-end removal process for RAFT synthesized polymers. By rationally designed the alkylborane, we can control the structure of the initiating alkyl radical to minimize the side reactions and free polymer chains, achieving the UHMW polymer synthesis. During the same period or after our related concept report, the combination of oxygen and trialkylborane has been also applied to synthesize sophisticated polymeric materials including star-like polymers and inorganic-organic hybrids.

For this oxygen initiation strategy, the challenge is to control the autoxidation and to avoid the effects of molecular oxygen in radical polymerization. This is the reason that only alkylborane compounds have been reported for this strategy since their autoxidation is much faster than oxygen inhibition of radicals. The control of the autoxidation mainly depends on the amount of alkylborane used and molecular oxygen left in the reaction system. If in the open system, the precise con-

trol will be affected by the diffusion capability of oxygen molecules and the oxygen solubility. Therefore, optimization is still necessary to achieve the best control based on the reaction setup with different oxygen levels.

There is no doubt that this oxygen initiation strategy is still under development and can be used to synthesize polymer materials with predetermined molecular weights, narrow distribution, and predesigned structures. In particular, it can make a difference in the surface initiation system under the air environment to realize the grafting polymer on the inorganic surface, or the combination with biological macromolecules to realize the protein-polymer and DNA-polymer hybrids. From a prospective aspect, the compound with autoxidation capability could be investigated such as organozinc or other non-metal-containing organic molecules. Except for RAFT polymerization, other CRP methods are still unexplored such as ATRP, cobalt-mediated, or iodine-mediated CRPs. We hope that this article could attract more researchers to join in this direction, and we believe that our proposed oxygen initiation can break the barriers of previous CRP methods so that more non-synthetic researchers can use CRP to synthesize functional polymers for wide ranges of applications.

BIOGRAPHY

Xiang-Cheng Pan is an associate professor and principal investigator in the State Key Laboratory of Molecular Engineering of Polymers and the Department of Macromolecular Science at Fudan University. In 2014, he obtained his Ph.D. in organic chemistry from the University of Pittsburgh under the guidance of Prof. Dennis P. Curran. He then spent three years of postdoctoral research at the group of Krzysztof Matyjaszewski at Carnegie Mellon University. In 2017, he returned to China and joined Fudan University. The research interest of his group focuses on the development of novel polymerization methods and sustainable polymers.

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