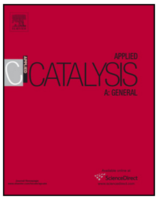
Applied Catalysis A: General 522 (2016) 1–12

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Cu^I-catalyzed aerobic oxidation of tertiary amines as chain initiation for radical polymerization of methyl methacrylate. Syndiotactic-rich alpha-amino PMMA via mono-centered initiation

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ARTICLE INFO

Article history:
Received 23 November 2015
Received in revised form 30 March 2016
Accepted 26 April 2016
Available online 27 April 2016

Keywords:
Cu^{II}-amine redox initiation
Catalytic aerobic oxidation
Radical polymerization
Tertiary amine
Methyl methacrylate
Catalytic efficiency

ABSTRACT

Cu^I-catalyzed aerobic oxidation of tertiary amines as the substrate involves active radicals as the oxidized intermediates, in which the reduced intermediates, Cu^I complexes, play a role of oxygen carriers to activate O_2 into the proton/electron/hydrogen-atom acceptor, while tertiary amines serve as the corresponding donor and afford alpha aminoalkyl carbon-centered radicals. Cu^I-catalyzed oxidation of various tertiary amines using aerobic O_2 diffused from air as the ultimate oxidant and air-stable Cu^{II} salts as the catalyst precursor was adopted as the chain initiation for radical polymerization of methyl methacrylate (MMA) in dimethylsulfoxide at 90 °C. The polymerization kinetics was monitored by gas chromatography, while the molecular weight and stereotacticity of PMMA were determined by gel-permeation chromatography and nuclear magnetic resonance spectroscopy. Triethylamine behaved as an efficient substrate while Cu^{II}/2,2′-bipyridine complexes displayed a higher catalytic activity. The polymerization proceeded in a conventional fashion at a comparable rate even using several micromol of Cu^{II}/2,2′-bipyridine complexes per liter, leading to syndiotactic-rich PMMA (syndiotacticity >55%) with an alpha-amino terminal moiety as the residue from the tertiary amine substrate, which was confirmed by UV-induced benzophenone-initiated radical polymerization using the so-obtained PMMA as the macro-sensitizer. The catalyst-performance analysis suggested that each molecule of Cu^{II}/2,2′-bipyridine complexes could generate 3×10^2 propagating $PMMA^{\bullet}$ radicals in 3 h under optimal conditions.

1. Introduction

Certain complexes of some transition metals in the lower oxidation state (*e.g.* Cu^I, Fe^{II}, Ni^{II}, Co^{II} etc) can bind molecular dioxygen (O_2) and form complexes with oxidative ligands (*e.g. superoxo*, *peroxo* or *oxo*) at a rapid rate, while the latter releases O_2 or its derivatives such as H_2O, OH^- etc under appropriate conditions [1]. Naturally occurring cases include metalloenzymes (*e.g.* Cu-based laccases and Fe-based horseradish peroxidases) and metalloproteins (*e.g.* Fe-based hemoglobins and hemerythrins, and Cu-based hemocyanins) [1]. In particular, O_2 could coordinate Cu^I, and form a diverse array of oxidative complexes with a different Cu^I:O_2 stoichiometric ratio and configuration [2].

These oxidative complexes offer superior advantages as an environment-friendly clean strategy in catalytically oxidizing organic substrates, since they directly utilize O_2 as the ultimate oxidant and result in H_2O_2 (two-electron reduction of O_2) or H_2O (four-electron reduction of O_2) as a byproduct. Cu-based complexes have been demonstrated to successfully catalyze oxidation of cyclohexadiene to benzene, benzene to phenol, phenolics to quinones, thioethers to sulfones, alkanes to alcohols or aldehydes, alcohols to aldehydes, tertiary amines to secondary amines, primary amines to aldehydes or nitriles, or oxidative coupling of alcohol-primary amine to imines, primary amine-primary amine to azo, etc using air or O_2 as the ultimate oxidant [3].

Oxidation of labile X-H moieties (X = C, N, O) into the corresponding radicals $X^{\bullet}$ followed by bimolecular coupling underlies stepwise polymerization of 2,6-dimethylphenol, anilines, aromatic diamines, diacetylenes, 1 thiophenes and other low-MW organic substrates containing activated X-H moieties, denoted as ***H**-FG-**H*** [4]. In common, substrates ***H**-FG-**H*** are oxidized to ***H**-FG*$^{\bullet}$ radicals by chemical oxidizing agents (such as Cu^{II}, Ce^{IV} and peroxysulfate) or oxidative complexes via a sequential proton-transfer followed by electron transfer (PT-ET), sequential electron-transfer followed by proton-transfer (ET-PT), hydrogen-atom transfer (HAT) or proton-coupled electron transfer (PCET) process [5], and bimolecular

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http://dx.doi.org/10.1016/j.apcata.2016.04.030
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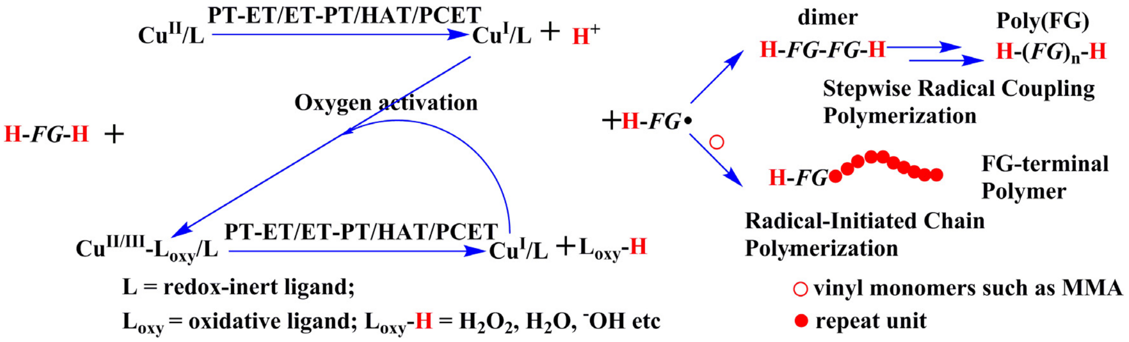
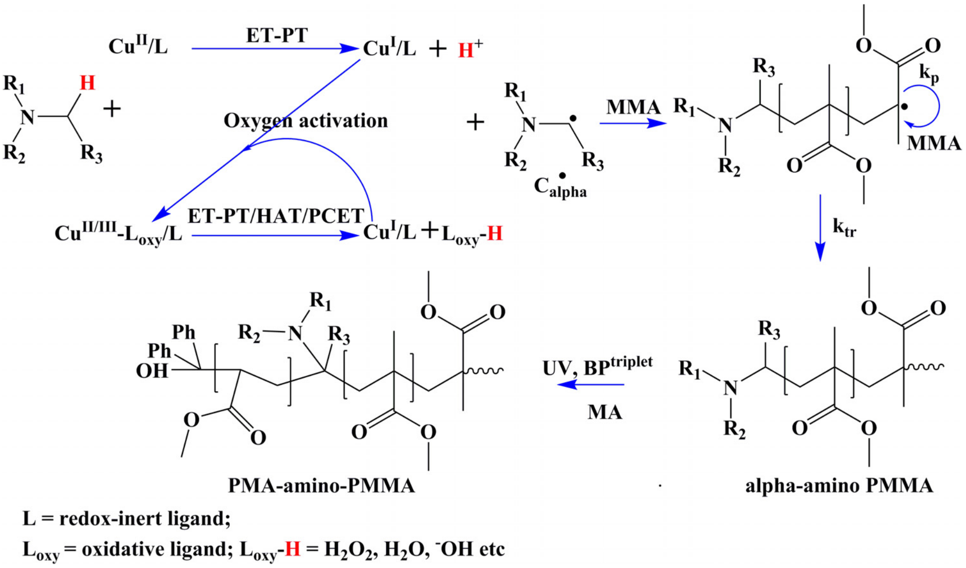


Scheme 1. Direct Oxidation by Cu^{II}/L Complexes and Catalytic Aerobic Oxidation by Cu$^{II/III}$-L$_{oxy}$/L Complexes of *H-FG-H* for Stepwise Radical Coupling Polymerization and Radical-initiated Chain Polymerization.



Scheme 2. Direct oxidation by Cu^{II}/L complexes and catalytic aerobic oxidation by Cu$^{II/III}$-L$_{oxy}$/L complexes of tertiary amines to initiate radical polymerization of MMA to prepare alpha-amino PMMA, and subsequent BP-initiated UV-induced radical polymerization of MA using alpha-amino PMMA as the Macro-sensitizer to prepare Diblock copolymer PMA-b-PMMA.

coupling of ***H***-*FG*$^\bullet$ radicals leads to dimers ***H***-*FG-FG*-***H***. Further oxidation and radical coupling result in high-MW ***H***-*Poly(FG)*-***H***, as illustrated in Scheme 1 (top part). As each radical coupling corresponds to oxidation of two labile X-***H*** moieties to unity ***H***$_2$O or ***H***$_2$O$_2$, formation of high-MW ***H***-*Poly(FG)*-***H*** via multiple coupling necessitates a high loading of oxidizing agents or catalysts of a high activity.

There have been few reports on radical chain polymerization redox-initiated by pairs of oxidative complexes and proper substrates, as outlined in Scheme 1 (bottom part). When performing $CuSO_4$-hydrazine (N_2H_4) redox-initiated aerobic radical emulsion polymerization of MMA, Menon noticed that the polymerization proceeded at 30 °C even with an initial $CuSO_4$ concentration of 1.0×10^{-5} mol L^{-1}, and an initial N_2H_4 concentration of 8.0×10^{-2} mol L^{-1} [6]. Therefore, it was proposed that after the initial reduction of Cu^{II} by N_2H_4 via an ET-PT process, Cu^{I} formed superoxo complexes ([Cu^{II}-$^-$OO$^\bullet$]$^+$) with O_2 diffused from air, which oxidized another N_2H_4 and yielded a new $N_2H_3^\bullet$ radical [6]. Thus, each molecule of Cu^{II} cation generated multiple primary $N_2H_3^\bullet$ radicals and PMMA$^\bullet$ propagating radicals during the course of polymerization. After observing that a small amount of O_2 triggered the radical polymerization of methacrylates catalyzed by Cu^{I}X/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) (X = Cl$^-$ or Br$^-$) in the absence of any initiator, Mathias proposed that some Cu^{I}(O_2)X/PMDETA complexes were *in-situ* formed, and oxidized PMDETA to aminoalkyl radicals initiating reverse atom transfer radical polymerization regulated by Cu^{I}(O_2)X/PMDETA complexes [7].

On the other hand, radical polymerization redox-initiated by pairs of O_2/H_2O_2 and active substrates of labile C—H moieties (beta-diketones such as acetylacetone, ACAC, in most cases) under the catalysis of metalloenzymes, viz. laccase, horseradish peroxidase, manganese peroxidase has been widely reported during last two decades [8]. These metalloenzymes in the reduced state form high-activity oxidative complexes with O_2/H_2O_2, which oxidize beta-diketones into carbon-centered primary radicals to initiate polymerization of acrylic acid, acrylamide, sodium styrenic sufonate, MMA, styrene, and 2-vinyl naphthalene in homogenous (solution) or heterogeneous (emulsion or from silica surface) aqueous media [9]. Characteristic of enzymatic catalysis of a high activity, the polymerization proceeds at a rapid rate even at room temperature, so the so-prepared PMMA exhibits a syndiotactic-rich stereoregularity (rr ≈ 85%) and a glass transition temperature above 130 °C [9h].

Tertiary amines could be oxidized by complexes of transition metal cations in the super-normal (*e.g.* Cu^{III} in highly alkaline media) [10] or high oxidation state (*e.g.* Cu^{II} [11] and Ce^{IV} in acidic media [12]), peroxides (such as benzoyl peroxide, hydroperoxides, H_2O_2 and peroxysulfate) [13], arylketone under photo irradiation [14] to radicals. In most cases, tertiary amines are oxidized