



Catalytic aerobic radical polymerization of methyl methacrylate in N,N-dimethylformamide: Stepwise in situ activation of dioxygen to peroxides and further to oxyl radicals



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ABSTRACT

The aerobic radical polymerization of methyl methacrylate (MMA) in N,N-dimethylformamide (DMF) catalyzed by ppm-level complexes of copper(II), cobalt(II), or iron(III), leading to high-molecular-weight polymer (PMMA), was investigated in detail. No active radicals were formed, although DMF could reduce these complexes into their intermediates in the low oxidation state. Oligo(MMA peroxide)s formed in situ as multifunctional initiators decomposed into oxyl radicals to initiate polymerization under catalysis of these complexes. It was further revealed that these complexes undertook two-step O₂ activation. They initially catalyzed the interpolymerization of MMA with O₂ to afford oligo(MMA peroxide)s and then reduced oligo(MMA peroxide)s into alkyloxyl radicals to initiate polymerization of MMA in DMF, which played a triple role as the O₂-rich solvent, the ligand, and the reducing agent.

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1. Introduction

N,N-dimethylformamide (DMF) is widely adopted in radical polymerization of vinylic monomers because of its excellent miscibility with other solvents, low hydrogen-atom transfer (HAT) tendency to carbon-centered radicals, and good dissolution capacity for a large variety of polyolefins substituted with heteroatoms or miscellaneous groups. There have been several reviews of its multidimensional participation in various chemical or catalytic reactions as more than just a common solvent [1–3]. Recently, ligand-free Fe^{II}-catalyzed atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) has been reported in DMF, leading to well-defined poly(methyl methacrylate) with a predictable average molecular weight (MW) and a polydispersity index (PDI) below 1.30, as DMF mediates reversible activation–deactivation equilibrium in ATRP by coordinating Fe^{II}/Fe^{III} complexes and adjusting their redox potentials [4,5]. However, some other behavior has scarcely been studied. For example, MMA could undertake thermally induced interpolymerization with molecular dioxygen (O₂) and afford oligo(MMA peroxide)s in DMF above 75 °C [6]. These oligo(MMA peroxide)s undergo thermally induced

decomposition into oxygen-centered primary radicals to initiate radical polymerization of MMA, which results in diblock copolymer oligo(MMA peroxide)-b-PMMA [6]. Thus, the induction (converting O₂ to peroxides) and polymerization (converting MMA to –MMA–) occur concurrently without any external chemical initiators or catalysts. On the other hand, Co^{II}-catalyzed epoxidation of styrene (St) and other alkenes using O₂ as the ultimate oxidant in DMF, which has a higher oxygen-dissolving capacity than other solvent, displays a good reactivity and selectivity [7–15]. Radical polymerization of St occurred on some occasions, leading to high-MW polystyrene, indicating that a radical mechanism is involved [7,11,12]. Although its HAT tendency to carbon-centered radicals is admitted to be negligible (the HAT constant of polystyrene propagating radicals to DMF, $k_{H,DMF}$, is about 1×10^{-4} at 40–100 °C) [16], DMF is a labile HAT donor to alkyloxyl radicals ($k_{H,DMF} \approx 10^6\text{--}10^7 \text{ L mol}^{-1} \text{ s}^{-1}$) [17,18] and nitroxyl stable radicals [19,20]. Further, DMF might be subject to catalytic oxidation into carbon-centered radicals by some oxidative complexes via a HAT or proton-coupled electron transfer (PCET) process [21]. Certainly, these carbon-centered radicals might propagate across vinylic monomers and initiate radical polymerization.

Complexes of transition metal cations have been widely explored in radical polymerization and play different roles. They may serve as nonregenerative oxidizing agents (e.g., complexes

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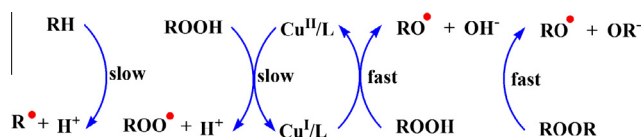
of Cu^{II}, Fe^{III} and Co^{III}) in conjugation with various hydrocarbons as the reducing substrates, leading to carbon-centered primary radicals, as presented in Scheme 1 [22]. Alternatively, they could serve as reducing agents (e.g., complexes of Cu^I, Fe^{II} and Co^{II}) in conjugation with peroxides, or a recyclable catalyst in conjugation with hydroperoxides, leading to oxygen-centered radicals via Fenton-type reactions, as also presented in Scheme 1 [22]. Some complexes of Cu^I/Cu^{II}, Fe^{II}/Fe^{III}, Co^{II}/Co^{III} pairs have been successfully exploited to mediate activation–deactivation equilibrium of ATRP via reversible inner-sphere electron-transfer (ISET) between the coordinated cations in the high oxidation state and their (pseudo)halido ligands [23,24]. In addition, some Cu^I and Co^{II} complexes could catalyze the interpolymerization of vinylic monomers with O₂, leading to in situ formation of oligoperoxides [25–29].

Taking the preceding factors into consideration, the synergistic effect of in situ formation of peroxides, decomposition of oligoperoxides, and oxidation of DMF would exert an intriguing effect on polymerization behavior of MMA in DMF, especially in the presence of some complexes as catalysts. In this work, we systematically investigated the aerobic radical polymerization of MMA in DMF catalyzed by complexes of Cu^{II}, Fe^{III} or Co^{II} at no higher than 70 °C in the absence of any thermal or chemical initiators. In this report, the initiation step is attributed solely to the stepwise in situ activation of aerobic O₂ into oligo(MMA peroxide)s and further into alkyloxyl radicals. As the first case, we report that these inexpensive complexes could consecutively activate O₂ to peroxides in situ as a reversible oxygen carrier and further to oxyl radicals to initiate polymerization of MMA in DMF.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA, ≥98.0%) was from Lingfeng Reagent Co., Ltd., and was washed three times with a 5 wt.% aqueous solution of NaOH and one time with deionized water, dried overnight over anhydrous CaCl₂, distilled under reduced pressure, and then stored in a refrigerator before use. N,N-dimethylformamide (DMF, AR) was from Chinasun (Ennox) Specialty Products Co., Ltd., Shanghai, China. Triphenylphosphine (PPh₃, CP), dimethylsulfoxide (DMSO, ≥99.0%), and tetrahydrofuran (THF, ≥99.0%) were purchased from Lingfeng Reagent Co., Ltd., Shanghai, China. CuSO₄·5H₂O, CuCl₂·2H₂O, and 2,2'-bipyridine (bPy, AR) were purchased from Shanghai Chemical Reagent Co., Ltd., Shanghai, China. FeCl₃·6H₂O and tert-butyl hydroperoxide (TBH, aqueous solution, concentration ca. 70 wt.%) were from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Cobaltous acetate (Co(OAc)₂, >99.5%) and 1,10-phenanthroline hydrate (Phen, >99.0%) were from Runjie Chemical Co., Ltd., Shanghai, China. N,N,N',N',N''-pentamethyl-diethylenetriamine (PMDETA, ≥98.0%) was from Jiangdian Chemical Co. Ltd., Changzhou, China. 2,2,6,6-Tetramethylpiperidinyl-1-oxyl (TEMPO, >98.5%) was purchased from Jiana Chemical Co., Ltd., Changzhou, China. 2,2'-Azobis(2-methylpropionitrile) (AIBN, CP) was from Shanghai No. 4 Reagent & H.V. Chemical Co., Ltd., Shanghai, China.



Scheme 1. Reduction of Cu^{II}/ligand complexes into Cu^I/ligand complexes by hydrocarbons or hydroperoxides and oxidation of Cu^I/ligand complexes into Cu^{II}/ligand complexes by hydroperoxides or dialkylperoxides in a radical mechanism.

N,N-dimethylacrylamide (DMAAm, >99.0%), from Volant Chemical Co., Ltd., Nantong, China, was purified by passing it through a column fitted with Na₂CO₃, nanosilica, and basic Al₂O₃ (from top to bottom) to remove inhibitors and then stored in a refrigerator before use.

2.2. UV–vis online monitoring of the Cu^{II}/Fe^{III}–DMF redox process

A portion of 20 mL of DMF solution containing CuSO₄ (concentration = 10⁻³ mol L⁻¹) was prepared. A ligand such as bPy or PMDETA was added to promote the dissolution and to adjust the redox potentials. In this work, unless stated elsewhere, the stoichiometric ratio of bPy or Phen to Co^{II} or Cu^{II} was fixed at 2:1, with that of PMDETA to Cu^{II} at 1:1, that of bPy or Phen to Fe^{III} at 3:1, and that of PPh₃ to Fe^{III} at 6:1, respectively. About 5 mL of the solution was transferred to an Agilent Cary 100 UV–vis spectrophotometer, and the cell temperature was regulated at 30–70 °C using a Varian dual-cell Peltier accessory. The spectra were collected periodically. The Fe^{III}/bPy–DMF redox process was conducted with a DMF solution containing FeCl₃/bPy (concentration 10⁻⁴ mol L⁻¹) at 25 °C.

2.3. UV–vis online monitoring of TEMPO scavenging of carbon-centered radicals

For thermally induced AIBN-initiated radical scavenging by TEMPO, 5 mL of DMSO solution containing AIBN (concentration = 5.0 × 10⁻² mol L⁻¹) and TEMPO (concentration = 1.0 × 10⁻¹ mol L⁻¹) was transferred to an Agilent Cary 100 UV–vis spectrophotometer, and the cell temperature was regulated at 70 °C using a Varian dual-cell Peltier accessory. The spectra were collected periodically.

For Cu^{II}/Co^{II}-catalyzed TBH-initiated radical scavenging by TEMPO in DMSO, 20 mL of DMSO solution containing TBH (concentration = 4 × 10⁻² mol L⁻¹), DMAAm (concentration = 8 × 10⁻² mol L⁻¹), and TEMPO (concentration = 4 × 10⁻² mol L⁻¹) was prepared in advance. CuSO₄·5H₂O/bPy or Co(OAc)₂/bPy complexes were added to achieve a specific concentration of 10⁻⁴ mol L⁻¹. About 5 mL of the solution was transferred to an Agilent Cary 100 UV–vis spectrophotometer, and the cell temperature was regulated at 80 °C using a Varian dual-cell Peltier accessory. The spectra were collected periodically.

For Cu^{II}/Co^{II}-catalyzed TBH-initiated radical scavenging by TEMPO in DMF, 20 mL of DMF solution containing TBH (concentration 4 × 10⁻² mol L⁻¹), DMAAm (concentration = 8 × 10⁻² mol L⁻¹), and TEMPO (concentration = 4 × 10⁻² mol L⁻¹) was prepared in advance. CuSO₄·5H₂O or Co(OAc)₂ was added to achieve a specific concentration of 10⁻⁴ mol L⁻¹. About 5 mL of the solution was transferred to an Agilent Cary 100 UV–vis spectrophotometer, and the cell temperature was regulated at 70 or 80 °C using a Varian dual-cell Peltier accessory. The spectra were collected periodically.

For Cu^{II}/Co^{II}-catalyzed oligo(MMA peroxide)-initiated radical scavenging by TEMPO in DMF, 40 mL of MMA/DMF (V_{MMA}:V_{DMF} = 1:1) solution was heated at 70 °C for 5 h to incubate oligo (MMA peroxide)s in situ. A portion of 5 mL of the solution was collected, and TEMPO and CuSO₄·5H₂O/bPy (Co(OAc)₂/bPy or FeCl₃/bPy) complexes were added to achieve concentrations of 10⁻² and 10⁻⁴ mol L⁻¹, respectively. The solution was transferred to an Agilent Cary 100 UV–vis spectrophotometer, and the cell temperature was regulated at 70 or 80 °C using a Varian dual-cell Peltier accessory. The spectra were collected periodically.

2.4. Catalytic aerobic radical polymerization of MMA in DMF

Portions of 10 mL of freshly distilled MMA and 10 mL of DMF were added stepwise into a 50 mL flask. A predetermined amount

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