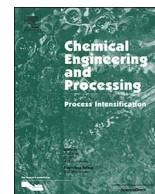




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Exemplification of catalyst design for microwave selective heating and its application to efficient *in situ* catalyst synthesis

Kaiyang Wang, Georgios Dimitrakis*, Derek J. Irvine*

Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, UK

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ABSTRACT

The use of dielectric property monitoring to develop an underpinning understanding of the molecular transformations involved in achieving the successful, rapid *in situ* synthesis of a catalytic chain transfer polymerisation (CCTP) catalyst using microwave heating is reported. The hypothesis behind the molecular design of this catalyst, such that it was tailored towards the application of microwave heating (MWH), is discussed, reviewed relative to the empirical results and compared to the performance of a benchmark pre-formed catalyst. The overall number/type of function group present in the catalyst, the degree of flexibility exhibited by its organic ligand system and level of solvation achieved are shown to be key factors affecting the interaction between the catalyst and the applied microwave energy. Use of microwave heating leads to fast, *in situ* formation of the catalyst (approximately 32 s) within the polymerisation mixture, rendering pre-preparation steps unnecessary and ensuring it is generated prior to the polymerisation reaction commencing. Thus potentially presenting an enormous opportunity to intensify current industrial processes.

1. Introduction

The last few decades have witnessed a significant increase in the number of methods and known mechanisms that can be used to control polymerisation reactions of all types. In the particular case of free radical chemistry, the control methods have been reported include: Nitroxide Mediated Polymerisation (NMP) [1], Atom Transfer Radical Polymerisation (ATRP) [2], Reversible Addition Fragmentation Polymerization (RAFT) [3], and Catalytic Chain Transfer Polymerisation (CCTP) [4]. The advent of these new control methodologies has allowed the polymer using community to gain access to many new polymer molecular structural types that were previously unobtainable.

Amongst these new materials, the ability to obtain oligomers, *i.e.* polymers with relative low molecular weight (*i.e.* $< 10,000 \text{ g mol}^{-1}$), has generated significant interest. The aim of developing these species is to provide novel materials that deliver specific improved application performance in fields such as: coatings, surfactants, dispersants, emulsifiers, *etc.* [5–9]. In the specific cases of free radically produced oligomers, the control method that is often most appropriate to use to synthesise such moieties is CCTP [4,10]. In a typical CCTP reaction, low spin cobalt (II) organometallic catalysts are utilised to control the molecular weight and the polydispersity (δ) of the polymer by acting as chain transfer agents (CTA). A CTA prematurely terminates the growth of one polymer chain (thus controlling its molecular weight), but keeps

the radical “alive” such that it can initiate the growth of new chain (hence ensuring a high yield). It is the catalytic nature of these CCTP control agents that enables the facile synthesis of very low molecular weight oligomers when using very low levels of CTA, typically parts per million (ppm).

Currently, the most frequently cited of these cobalt CTA's is bis-[(difluoroboryl) diphenylglyoximate] cobalt (II) (PhCoBF), because it exhibits the best balance between activity and stability. However, it is synthesised in a two-step process that is not highly atom efficient. The first step involves the reaction of two mole equivalents of the diphenylglyoxime (DPG) ligand with cobalt (II) acetylacetonate to form cobaloxime which contains 2 bidentate DPG ligands (See Fig. 1, structure (a)).

This procedure has also been reported with the dimethylglyoxime version of the ligand (DMG) and both of these products have been shown to be active CCTP catalysts in their own right. However, they are sensitive to being deactivated by oxidation and/or hydrolysis. The second step involves reacting this step 1 product with boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$) to generate a single tetradentate ligand as shown in Fig. 1, (structure (b)) [10–12]. This enhances the complexes' stability towards oxidation and hydrolysis and allows it to be handled readily in air in solid form. However, the yield from this second stage is typically only in the region of 40% and so requires purification stages to be added to the manufacturing process, increasing both the cost and the

* Corresponding authors.

E-mail addresses: georgios.dimitrakis@nottingham.ac.uk (G. Dimitrakis), derek.irvine@nottingham.ac.uk (D.J. Irvine).<http://dx.doi.org/10.1016/j.cep.2017.01.012>Received 27 July 2016; Accepted 27 January 2017
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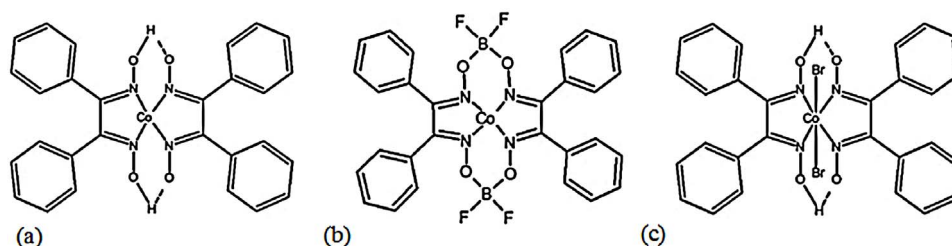


Fig. 1. Molecule structure of: (a) Cobaloxime, (b) PhCoBF and (c) $\text{CoBr}_2\text{DPG}_2$.

environmental footprint of the process [10].

Consequently, the authors have investigated the synthesis of alternative catalysts that are more economically and atom efficient. In previous journal publications, the authors have reported a successful adaptation of the existing PhCoBF synthesis, which generates the cobalt halide/glyoxime catalyst of the type shown in Fig. 1 (structure (c)) [13]. The bromide member of this family has been shown to demonstrate levels of activity and stability similar to those of PhCoBF, but it is synthesised using a single step and without the need to be ring closed to achieve the greater level of stability. Thus, this catalyst is significantly more atom efficient, sustainable and potential industrial applicable than PhCoBF. Furthermore, adopting a single stage process potentially enables the use of *in situ* catalyst manufacture and continuous flow processing. To do so would further increase the sustainability and intensification of the process, because it reduces waste by; (a) removing the catalyst pre-preparation process from the overall manufacturing cycle, (b) eliminating catalyst deactivation during storage and (c) minimising inter-batch cleaning of the polymerisation *etc.*

However, to successfully achieve a free radical polymerisation process that utilises *in situ* catalyst synthesis, it must be ensured that the catalyst synthesis has been achieved within the polymerisation medium prior to the onset of initiation to produce the radicals. This is of particular importance when low concentrations of reagents are being used, such as in the case of catalytic CTA usage, because it must be ensured that diffusion issues do not retard generation of the control agent. The application of microwave (or dielectric) heating (MWH) methods is known to accelerate reaction processes by achieving either/both rapid/uniform and selective heating [14]. This is because with MWH methods, energy is transferred by directly coupling the dipoles within the target material with an applied alternating electromagnetic (EM) field. Therefore, the dielectric properties (ϵ' : dielectric constant and ϵ'' : dielectric loss) of a material determine the ability of a specific material to both; interact with/store energy from such an alternating field in the case of ϵ' , and then convert an amount of the stored energy into heat with regard to ϵ'' . When a mixture of several different materials is placed within an EM field, the material with the higher dielectric properties typically has a greater potential to couple with the alternating field, and thus undergo selective heating [15]. The existence of selective heating has already been reported on metal catalysts such as Fe [16,17], Sn [18,19], and Co [12].

Prior work by the authors has empirically demonstrated that applying MWH to the *in situ* CCTP process can accelerate the rate of the combined *in situ* catalyst generation and polymerisation process by utilising selective MWH [13,18]. This paper investigates the interactions between the metal complexes and ligands discussed above with an EM field. The aims are to assess how the selective heating changes as the ligands coordinated to the cobalt centre are modified, and so develop a fundamental understanding of how MWH of a complex can be influenced by its structure. This knowledge will hopefully enable the design of improved catalysts structures which maximise the benefits of MWH. This work would also prove that the catalysts have been synthesised prior to the polymerisation commencing and demonstrate that dielectric spectroscopy can be a facile tool to aid in defining mechanistic behaviour in complex mixtures.

2. Materials and methods

2.1. Materials

Cobalt (II) bromide (98%, Aldrich), PhCoBF (Dupont), dimethylglyoxime (98%, Aldrich), diphenylglyoxime (98%, Aldrich), and cyclohexanone (98%, Aldrich) were all used as supplied without further purification.

2.2. Synthesis of organic liganded catalysts $\text{Co}_2\text{Br}_2\text{DPG}_2$ and $\text{Co}_2\text{Br}_2\text{DMG}_2$

In a typical synthesis conducted following the methods described in previous publications [13,20], a stock solution of cobalt (II) bromide (104.9 mg, 0.48 mmol) and DPG (225.8 mg, 0.96 mmol) or DMG (111.5 mg, 0.96 mmol) (*i.e.* a mole ratio of 1:2) were added to cyclohexanone (40 mL, 386 mmol) with stirring at room temperature. A dark green ($\text{Co}_2\text{Br}_2\text{DPG}_2$) and light green ($\text{Co}_2\text{Br}_2\text{DMG}_2$) solution was obtained as the *in situ* catalyst was formed.

2.3. Dielectric property measurements

The dielectric properties of all samples were measured using the cavity perturbation technique. The equipment and methods used are detailed in prior publications [21,22]. In this study, the cavity resonated in the TM_{050} transverse magnetic mode at a frequency of 2470 MHz. The cavity perturbation technique is ideally suited in measuring accurately small quantities of materials because it centres on measuring small perturbations in the resonant characteristics of standing modes inside a hollow metal cavity of predetermined geometry and does require the elaborate calibration procedures to be conducted prior to measurement. Dielectric property measurements were conducted on cyclohexanone solutions of all premade organometallic complexes used in this study. Since the molecular concentrations of the organometallics in the solvent can potentially have an effect in the overall dielectric response of the solvent/organometallic solution. Care was taken to ensure that the molar concentration of each test sample in the solvent was maintained at a solvent to solute molar ratio of 800:1. Typically, a stock solution of each test sample was prepared by dissolving CoBr_2 (104.9 mg, 0.48 mmol), diphenyl glyoxime (DPG) (112.9 mg, 0.48 mmol), and PhCoBF (303.4 mg, 0.48 mmol) in cyclohexanone (40 mL, 386 mmol). Meanwhile a 0.48 mmol solution of $\text{CoBr}_2\text{DPG}_2$ was prepared following the method described in Section 2.2. A 30 min pre-stirring was applied to each sample mixture before the samples for dielectric property measurements were prepared. This involved mixing a 0.5 mL of each stock solution with 16 mL of cyclohexanone to make a 240 ppm test solution, which were then transferred into step tubes and set into the cavity perturbation equipment to allow the dielectric property measurements to be made.

2.4. Microwave heating trials

All heating experiments were conducted in a single mode Sairem Miniflow microwave reactor (maximum power 200 W). In order to ensure maximum transfer of microwave (MW) power into the sample,

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