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Investigation of iron complexes in ATRP: Indications of different iron species in normal and reverse ATRP

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ABSTRACT

In an attempt to correlate the ATRP kinetics and the redox properties of the mediator, eight iron complexes with nitrogen, phosphorous and carboxylic acid containing ligands were investigated by electrochemical measurements and by using them as mediators in normal and reverse ATRP of MMA in DMF. The redox properties of the iron complexes in DMF, measured by cyclic voltammetry, did not differ significantly, which was reflected in the ATRP kinetics as the apparent rate constants were practically the same with all the complexing ligands. The degree of control over the polymerization was, however, much improved in reverse ATRP as compared to normal ATRP. In this ATRP system, the ligand type is not crucial for the redox or polymerization properties. Several observations indicate that the iron species in the two systems were not the same, the Fe(III) species resulting from oxidation of Fe(II) in normal ATRP is different from the starting Fe(III) species in reverse ATRP.

1. Introduction

Atom transfer radical polymerization (ATRP) is one of the most commonly employed techniques for controlled radical polymerization [1–3]. Control over molecular weight and a low degree of termination requires a low concentration of radicals. In ATRP, this is realized through an equilibrium between the dormant polymer chain (RX) and the corresponding polymer radical ($R^{\bullet}$), mediated by a transition metal complex (activator) (Scheme 1). The equilibrium should be shifted towards the dormant species to keep the radical concentration sufficiently low to minimize termination reactions. The reduction potentials of the alkyl halide (dormant polymer chain) and the transition metal complex, together with the halidophilicity (halogen affinity) of the oxidized transition metal complex, all being part of the equilibrium constant ($K_{ATRP} = k_{act}/k_{deact} = f(E_{RX}, E_{Mt}, K_x)$), are properties of the polymerization system which are crucial for the performance of the polymerization (i.e. the degree of control).

In normal ATRP, the polymerization starts from the initiator (alkyl halide) and the transition metal in its lower oxidation state. Alternatively, it can be started with a conventional radical initiator (e.g. AIBN) and the transition metal in its higher oxidation state, so called reverse ATRP [4]. The radicals arising from the (thermal) dissociation of the initiator are reversibly terminated by the transition metal, hence resulting in an alkyl halide and the reduced transition metal. A third technique is AGET (activators generated by electron transfer) ATRP, where the transition metal is added in its higher oxidation state and is reduced by e.g. ascorbic acid before it can activate the alkyl halide initiator [5].

The environmental aspects of ATRP have gained increased interest in recent years. Many of the employed transition metals (e.g. copper) and ligands are harmful and it is also desirable to reduce the use of hydrocarbon solvents. ARGET (activators regenerated by electron transfer) ATRP has emerged as one way to reduce the amount of copper [6]. Also, ionic liquids have been used in an effort to facilitate the removal of the mediator and as a means to reduce the amount of solvent (through reuse) [7]. The most commonly used transition metal so far is copper, but to use iron complexes as mediators in ATRP is an attractive route to less harmful ATRP systems. A recent review by Ouchi et al. [8] gave an overview of a large number of ATRP mediators, including both iron and copper complexes. Iron has been used in ATRP together with various ligands, e.g. triphenyl phosphine [9–14], diimines and diamines [15,16], imino- and aminopyridines [17,18], salicylaldiminato ligands [19], various organic acids [20–30], and derivatives of (di)picolinic acid [31].

For copper systems, a linear relationship between the reduction potential of the copper complex and the logarithm of the equilibrium constant or the logarithm of the apparent rate constant ($k_p^{app} = k_p[R^{\bullet}]$) has been shown [32–37]. A lower (more negative) reduction potential of the copper complex (i.e. a more active mediator) results in a higher equilibrium constant and apparent rate

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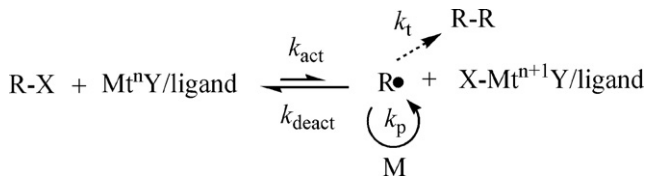

Scheme 1. General mechanism for ATRP.

constant for propagation. Although the reduction potentials of some iron complexes have been measured in acetonitrile and qualitative comparisons have been made between the potentials and the polymerization results [15–19], a quantitative correlation between the potential and the logarithm of the apparent rate constant, as for copper complexes, has not been reported for iron complexes.

Understanding the effect of different ligands on the ATRP system with iron is as important as it is for copper systems, not least in the search for more environmental friendly ligands. In this work we report on the investigation of the redox properties of some iron complexes and their behavior in normal and reverse ATRP of MMA in DMF. To avoid complications in the data interpretation due to heterogeneity, DMF was chosen as the solvent to ensure complete solubility of all the ligands and complexes used in this study in both electrochemical measurements and polymerizations.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA, 99%, Aldrich) was passed through a column of neutral alumina prior to polymerization. *N*,*N*-Dimethylformamide (DMF, ≥99%, VWR Int.), ethyl acetate (EtOAc, z.A., Merck), anhydrous $FeCl_2$ (99.5%, Alfa Aesar), $FeCl_3{\cdot}6H_2O$ (z.A., Merck), $CuBr_2$ (≥99%, Sigma–Aldrich), L-ascorbic acid (≥99%, Fluka), azobisisobutyronitrile (AIBN, ≥98%, Fluka), 2,2′-bipyridine (bipy, 99+%, Aldrich), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), triphenylphosphine (PPh_3, ≥98.5%, Fluka), isophthalic acid (IPA, ≥98%, Aldrich), iminodiacetic acid (IDA, ≥98%, Fluka), dipicolinic acid (PDA, 99%, Aldrich), oxalic acid (98%, Aldrich), 2-picolinic acid (PA, Nobel Chemicals), tetrabutylammonium tetrafluoroborate (Bu_4NBF_4, ≥98%, Fluka), ferrocene (98%, Alfa Aesar) and ethyl 2-bromoisobutyrate (EBiB, 98%, Sigma Aldrich) were used as received.

2.2. Cyclic voltammetry

Cyclic voltammetry was performed with a PAR 263A potentiostat/galvanostat interfaced to a base PC using the EG&G Model 270 software package. The cell was a standard three-electrode setup using a 2 mm diameter glassy carbon working electrode, a platinum coil counter electrode and a saturated calomel reference electrode. Full IR compensation was employed in all measurements. All measurements were performed in DMF with 0.1 M Bu_4NBF_4 as supporting electrolyte. The half-wave potential ($E_{1/2}$) of ferrocene (1 mM) was 490 mV. The iron complexes were measured at 3 mM concentration, using a saturated calomel electrode (SCE) as reference electrode, and the scan rate was 1000 mV/s. All potentials are reported vs. SCE. In most cases, the iron:ligand ratio was 1:2, except for PMDETA where it was 1:1.

2.3. UV–vis spectroscopic analyses

UV–vis spectroscopy was used to analyze iron complexes in DMF and DMF + EtOAc (ethyl acetate) on a Jasco V-630 spectrophotometer. Samples of $FeCl_3$, $FeCl_3$/IPA, $FeCl_3$/PPh_3, $FeCl_2$/IPA and $FeCl_2$/PPh_3 (all 2 mM, Fe/ligand = 1/2) were prepared in DMF. The absorbance was measured between 270 and 1100 nm. The samples with $FeCl_2$/ligand were prepared under inert atmosphere and measured immediately. They were then exposed to air and the absorbance was measured again after oxidation (denoted "ox"). In addition, one sample was prepared to resemble a polymerization mixture. $FeCl_2$/IPA (25 mM) and the ATRP initiator EBiB (25 mM) were added to a 1:1 mixture of DMF and EtOAc (which was used instead of MMA, being similar in structure) under inert atmosphere in a glass vial. The sample was heated to 50 °C for 3 h. The color change from lightly yellow-brown to orange indicated that the iron complex had reacted with the initiator. The absorbance was measured after the reaction, both for a sample which was not exposed to air and one that was removed from the closed vial and exposed to air (which resulted in a color change to dark orange). For all samples measured, dilution was required due to the high absorbance below 450 nm.

2.4. General procedure for normal ATRP

In all polymerizations, the targeted DP was 200 and the amount of solvent (DMF) was 50% (w/w). $FeCl_2$ (0.25 mmol, 31.7 mg) was charged into a dry round-bottomed flask equipped with a magnetic stirring bar. The flask was sealed with a rubber septum and degassed by purging with argon for 20 min. A separately degassed solution of ligand (0.5 mmol (0.25 mmol for PMDETA)) in DMF (5 g) was added via a degassed syringe and the resulting solution was stirred until all $FeCl_2$ was dissolved. The initiator (EBiB, 0.25 mmol) was mixed with MMA (50 mmol, 5 g), the solution was purged with argon and then added to the round bottomed flask containing the DMF solution with the iron complex. The flask was placed in a thermostated oil bath at the desired temperature. Aliquots were withdrawn with a degassed syringe at timed intervals, diluted in toluene or ethyl acetate and passed through a small column of neutral alumina to remove the iron complex. Conversion was followed by ^{1}H NMR and the molecular weights were analyzed by SEC.

2.5. General procedure for reverse ATRP

The procedure for reverse ATRP was the same as for normal ATRP, except that the initiator, AIBN (0.125 mmol, 20.5 mg), was added to the round-bottomed flask together with $FeCl_3{\cdot}6\ H_2O$ (0.25 mmol, 67.6 mg).

2.6. General procedure for AGET ATRP

The procedure for AGET ATRP with iron chloride was the same as for normal ATRP in general. $FeCl_3{\cdot}6\ H_2O$ (0.25 mmol, 67.6 mg), PPh_3 (0.5 mmol, 131.1 mg) and DMF (3 g) were charged into a round bottomed flask and ascorbic acid (0.125 mmol, 22 mg) was dissolved separately in DMF (2 g) and added to the flask after degassing both solutions. EBiB (0.25 mmol, 48.8 mg) was used as initiator.

2.7. General procedure for chain extension with AGET ATRP from macroinitiator

The macroinitiator was PMMA-X (X = Cl or Br) prepared through normal or reverse ATRP with one of the iron complexes, precipitated into MeOH and dried. The targeted DP in the chain extensions was 500. A stock solution of $CuBr_2$ (6.3 mM) and PMDETA (6.3 mM) in DMF was prepared and degassed with argon, after which ascorbic acid (3.1 mM) was added to reduce the copper complex. The macroinitiator (0.03 mmol), DMF (0.4 g) and MMA (1.4 g) were charged into a round-bottomed flask, which was then sealed with a rubber septum, and stirred until the macroinitiator was completely