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New protocol to determine the equilibrium constant of atom transfer radical polymerization

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ABSTRACT

A new electrochemical procedure is described to determine the equilibrium constant of atom transfer radical polymerization, K_{ATRP}. A rotating disk electrode (RDE) was used to monitor the concentration of the catalyst, Cu^IL^+, during a reaction between the metal complex and an alkyl halide (RX) used as a polymerization initiator. K_{ATRP} values with errors in the range ±10% were measured. Conditions were defined to avoid undesired reactions such as catalytic radical termination and competition between RX and X^- for the reactive site of copper. The RDE technique was also used to determine the equilibrium constant for association of X^- to Cu^IL^+, K_X^I, a parameter hardly accessible by other methods. The RDE technique was applied to different ligands, initiators, solvent/monomer combinations, and reaction temperatures. Linear correlations between $\log K_{ATRP}$ and $\log k_{act}$ and $\log k_{deact}$ were found.

1. Introduction

Atom transfer radical polymerization (ATRP) is a leading technique to generate polymers with narrow molecular weight distributions and predetermined architectures [1,2]. The core of ATRP is the electron transfer (ET) between the active catalyst (mainly Cu^IL^+, where L is a polydentate amine ligand) and the initiator (RX) or the dormant macromolecular chain (P_nX). The ET, which proceeds by an inner sphere mechanism, is concerted with the transfer of a halogen atom [3], so that the deactivator species, $XCu^{II}L^+$, and an active radical, $R^\bullet$ or $P_n^\bullet$, are generated in a single step (Scheme 1a). Generated radicals add to a few monomer molecules, after which they are rapidly reverted to their dormant state. The activation/deactivation cycles extend the lifetime of the radicals.

The equilibrium constant, K_{ATRP}, of the ATRP reaction (Scheme 1a) depends on the combination of catalyst, initiator, solvent, and temperature. K_{ATRP} can be expressed as the ratio between the activation and deactivation rate constants, k_{act}/k_{deact}. It is the most important parameter to determine the reactivity of catalysts, with values varying from 10^{-12}, measured for less active catalysts in acetonitrile, to 10^{-1}, estimated for active catalysts in water [4–7]. Information on K_{ATRP} is used to select the appropriate catalyst-monomer combination, and to choose the best procedure to regenerate the active Cu^IL^+ catalyst.

K_{ATRP} has been traditionally determined by using UV–Visible spectroscopy or gas chromatography to follow the evolution of Cu^{II} or RX concentration during the reaction between a catalyst and an initiator [8–11]. These techniques often required large amounts of Cu^I and RX to obtain reliable signals. K_{ATRP} was derived from the rate of $X–Cu^{II}L^+$ formation or RX consumption due to activation and biradical termination, according to an equation originally proposed by Fischer and Fukuda [12,13] but later modified to be valid for faster systems [9].

No electrochemical tools are yet available to determine K_{ATRP}, despite the established use of electrochemical techniques to determine k_{act} values, in a broad range from 10^{-4} to 10^8 M^{-1} s^{-1} [7,14–17]. Among these electroanalytical techniques, the use of a rotating disk electrode (RDE) is a simple and reproducible method applicable to $k_{act} < 10^4$ $M^{-1}s^{-1}$ [14]. The procedure to determine k_{act} requires the use of a radical scavenger (generally the stable nitroxide radical TEMPO) to kinetically isolate the activation step, by rapidly trapping all generated radicals (Scheme 1b).

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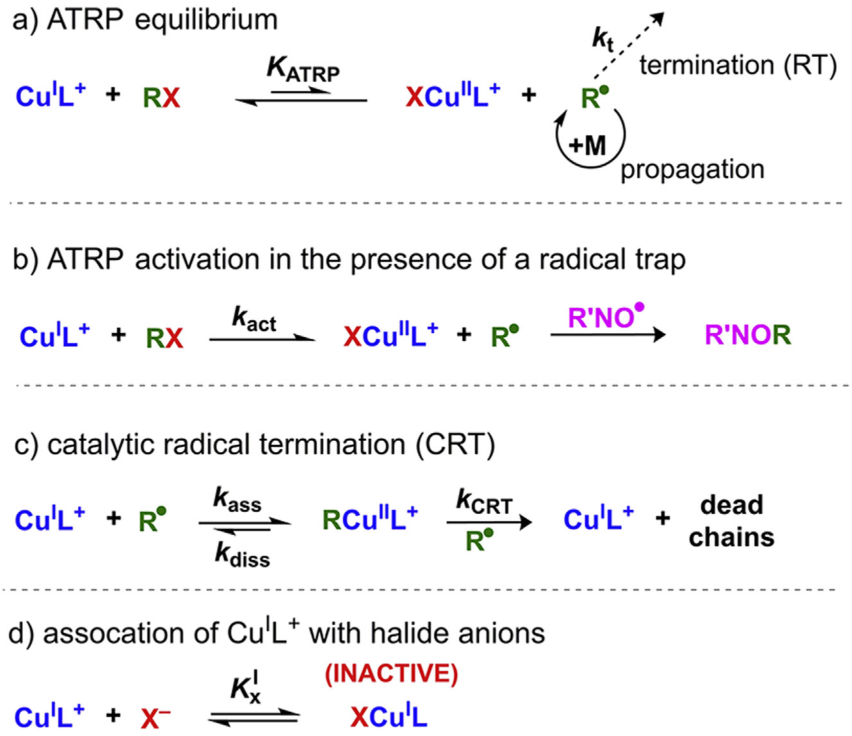

Scheme 1. Mechanism of (a) ATRP equilibrium, (b) ATRP in the presence of the radical scavenger TEMPO (R'NO•), (c) catalytic radical termination, and (d) association of Cu^I complexes to halide ions, forming inactive XCu^IL.

Following the recent progress on the study of the reactivity of copper catalysts by electrochemical methods, a protocol is presented here to accurately determine K_{ATRP} while avoiding undesired side reactions. In fact, accurate determination of K_{ATRP} by the proposed method requires that radicals terminate only by conventional biradical termination (RT, Scheme 1a). However, Cu^I species may be also involved in a catalytic radical termination (CRT, Scheme 1c) [18], which should be minimized by using an excess of RX, thus favoring RT over CRT [19,20].

Cu^IL^+ is also involved in another reaction, the reversible association with halide ions to form the inactive complexes XCu^IL (Scheme 1d), $Cu^IX_2^-$, and other species [21,22], causing to underestimate kinetic and thermodynamic parameters [8–10,22,23]. X^- is often introduced in ATRP systems from Cu^IBr or Cu^ICl employed as a source of copper for the catalyst, because they are inexpensive, non-hygroscopic, and quite air-stable. In contrast, the use of Cu^I salts with non-complexing ions such as trifluoromethanesulfonate (OTf) allows to avoid this issue. Therefore, in this work, $Cu^I(OTf)$ was used as a source of Cu^I.

Cu^{II} is also involved in speciation equilibria, but the oxidized species $XCu^{II}L^+$ generated by atom transfer is highly stable in organic solvents [21]. It is the main Cu^{II} species present because X^- binds much more strongly to $Cu^{II}L^{2+}$ than to Cu^IL^+ [21,24].

Herein, we report the use of RDE to measure K_{ATRP}, by following the disappearance of Cu^IL^+ during its reaction with RX. This method requires that the contribution of reactions such as CRT and formation of inactive XCu^IL (Scheme 1c–d) are minimized. The accuracy of the RDE technique, as well as its applicability to different ligands, solvents, and temperatures, were evaluated. Reported values agree with previous reports if side reactions in Scheme 1c–d are taken into account. A method to evaluate the association constant between Cu^IL^+ and X^-, K_X^I, is also proposed, by exploiting the decrease in measured K_{ATRP}^{app} in the presence of different amounts of X^-.

2. Experimental

2.1. Materials

Acetonitrile (MeCN, Sigma-Aldrich, ≥99.9%), *N,N*-dimethylformamide (DMF, VWR, 99.9%), tris [2-(dimethylamino)ethyl] amine (Me_6TREN, VWR, 99+%), tris(2-pyridylmethyl)amine (TPMA, Sigma-Aldrich, 98%), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, Sigma-Aldrich, 98%), methyl 2-bromopropionate (MBP, Sigma-Aldrich, 98%), and ethyl 2-chloropropionate (ECP, Sigma-Aldrich, 97%) were used as received. Tetraethylammonium tetrafluoroborate (Et_4NBF_4, Alfa Aesar, 99%), used as supporting electrolyte, was recrystallized from ethanol and dried in a vacuum oven at 70 °C for 24 h. Tetraethylammonium bromide (Et_4NBr, Sigma-Aldrich, 98%) and tetraethylammonium chloride (Et_4NCl, Sigma-Aldrich, ≥98%) were recrystallized from ethanol and from a mixture of ethanol/diethyl ether, respectively, and dried in a vacuum oven at 70 °C for 24 h. *n*-Butyl acrylate (BA, Sigma-Aldrich, ≥99%) was purified by passing through a column filled with basic Al_2O_3 to remove the polymerization inhibitor. A stock solution of Cu^I in MeCN was prepared by comproportionation between Cu^{II} trifluoromethanesulfonate ($Cu^{II}(OTf)_2$, Alfa Aesar, 99%) and a Cu wire, previously activated by washing in MeOH/HCl 3/1 and rinsed with water and acetone. The exact concentration of $Cu^I(OTf)$ was determined by spectrophotometric titration, using 2,9-dimethyl-1,10-phenanthroline as a specific ligand ($\varepsilon = 8458\ M^{-1}\ cm^{-1}$) in a 3-fold excess with respect to the metal [25].

2.2. Instrumentation

All electrochemical measurements were carried out in a three-electrode cell connected to an Autolab PGSTAT302N potentiostat/galvanostat, run by a PC with NOVA 2.1 software (Metrohm AG, Switzerland). The working electrode was a 3 mm GC disk, polished

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