

Electrochemically Mediated Atom Transfer Radical Polymerization

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Atom transfer radical polymerization (ATRP) is an important living radical polymerization method. It is widely used industrially to polymerize acrylates, styrenes, pyridines, methacrylates, and acrylonitriles [1]. ATRP can produce coatings, surfactants, foamers, and many other products in a variety of markets [2]. The “living” descriptor of ATRP indicates that the growing polymer chains are all growing at the same rate, leading to very narrow molecular weight dispersity. ATRP achieves this by reversibly terminating growing chains through transferring a halogen atom between the polymer chain and a catalytic metal complex. To activate polymerization, an activator molecule ($Mt^m L$) removes the halogen, creating a deactivator molecule ($Mt^{m+1} L$) and a radical on the polymer chain. After a short period of polymerization, the deactivator transfers the halogen back to the polymer chain and regenerates the activator molecule. ATRP controls polymer chain growth and limits radical termination through having a higher deactivation rate than activation rate. This leads to short spurts of growth with longer periods of deactivation [1–3]. Figure 1 show the overall mechanism for ATRP and the equation for polymerization rate.

ATRP is a well understood and widely used system. However, it does suffer from some issues. Whichever transition metal is used in the catalytic compound (usually copper) remains in the final polymer. Additives to control catalyst performance are often toxic and can cause undesired side effects, such as initiating or terminating chains independently. Finally, ATRP generally has

very poor performance in aqueous media [1, 3]. Electrochemically mediated ATRP (eATRP) overcomes many of these issues by eliminating the need for most additives, offering precise control over polymerization rate, completely removing the copper catalyst by plating it onto the electrode, and working in aqueous media [4].

eATRP functions in the same manner as ATRP, except that the applied potential determines the ratio of activator to deactivator rather than the equilibrium of the initial reaction mixture. In an ATRP mixture, the reaction starts once all the components have been added. In eATRP the starting mixture contains only monomer, solvent, alkyl halide initiator, supporting electrolyte, and deactivator ($XCu^{II}L$). The reaction will not start until the potential is applied and the deactivator is reduced to $XCu^I L$ on the cathode [4, 5]. The Nernst equation, $\frac{[XCu^I L]}{[XCu^{II} L]} = e^{\frac{F}{RT}(E_{app} - E_{1/2})}$, shows that the ratio of the deactivator to activator is a function of applied potential (E_{app}). $E_{1/2}$ (standard

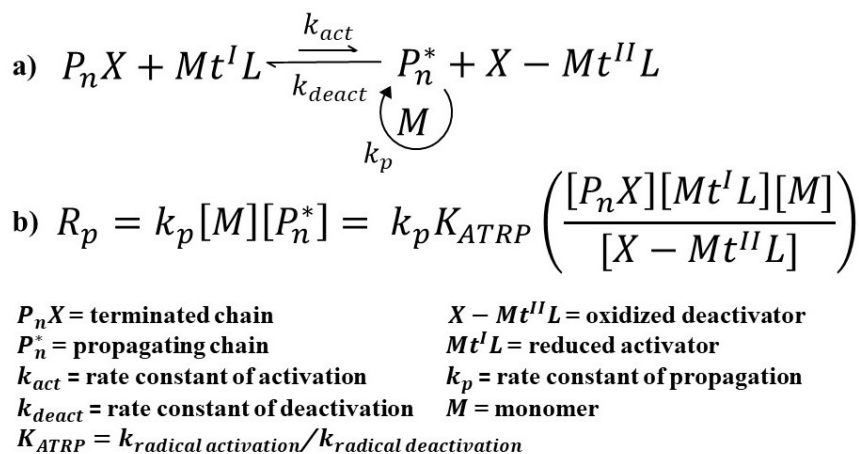


Figure 1: (a) ATRP mechanism (b) equation for rate of polymerization for ATRP [1–3]

reduction potential of the redox pair), R (gas constant), T (temperature), and F (Faraday constant) are fixed, therefore applying an increasingly negative potential drives an increase in activator concentration which leads to an increasing polymerization rate [6]. This relationship holds true until mass transport of the deactivator to the electrode is slower than charge transfer. To make sure that this mass transport limit does not affect most polymerizations, vigorous stirring is used to homogenize the reaction mixture [4,6]. By moving from a negative applied potential to a positive potential all of the activator is turned into deactivator, and the polymerization stops [7]. This can be done repeatedly with negligible effects on the polymer end product.

The eATRP set up requires a working electrode (commonly platinum but glassy carbon, stainless steel, and other electrodes have been shown to work), a counter electrode separated from the solution (to prevent oxidation of the activator), a reference electrode (to measure and control the applied potential), vigorous stirring, and a supporting electrolyte (to make sure the mixture is sufficiently ionically conductive) [8]. A simplified approach (called seATRP) uses only a working electrode and a sacrificial aluminum counter electrode (the Al^{3+} ions formed do not interact with the polymerization), stirring, and a supporting electrolyte [9]. The seATRP set up is simpler, but without the reference electrode the reaction must be done under constant current (i.e. galvanostatic) conditions [4,9]. To determine how much current to apply, an eATRP run with a constant applied potential must be consulted. When a constant potential is applied to an eATRP mixture the current used to produce that potential can be recorded. Initially, a large amount of current is needed to convert deactivator to activator. Current decreases over time as the reaction reaches the equilibrium between activator and deactivator (Figure 2a) determined by the applied potential. An seATRP can match the results of an eATRP by applying current steps that match the current delivered over that time step [9] (Figure 2b).

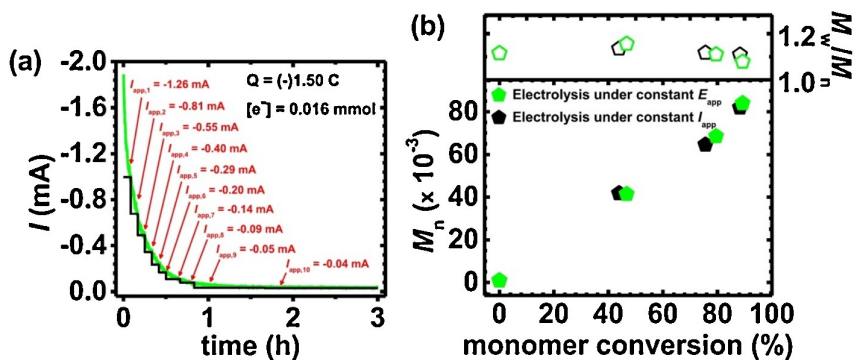


Figure 2: (a) Current vs. time for an eATRP with constant applied potential (green) and seATRP polymerization with stepped applied current (black). (b) Molecular weight and M_w/M_n vs. monomer conversion. Polymerization of 50% n-buty acrylate v/v in DMF and 0.2 M tetrabutylammonium perchlorate. [6]

and aqueous solutions [16]. While eATRP is not currently licensed by any companies, it could be an excellent industrial method due to lower cost (by way of lower amounts of metal catalyst) and easier purification than traditional ATRP (requires fewer additives, and can plate out the copper). Additionally, a seATRP set up would further reduce costs and increase ease of use [4].

Overall, eATRP is an innovative approach to ATRP that takes a broadly applicable method and provides greater control. It provides facile tuning of polymerization rates, stop/start control, is

eATRP is widely used in research to produce a variety of polymers and architectures. It can polymerize acrylates, methacrylates, acrylamides, and ethylene oxide [4]. It can create homopolymers, block copolymers [10], stars [11], graft polymers [12], and brushes [13]. eATRP works in solution, emulsion, mini-emulsion [14], and surface initiated methods [15], and in both organic solvents

more environmentally friendly than traditional ATRP, functions in a wide variety of methods, and can produce a variety of architectures.

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